THE UNIVERSITY OF HULL

Frustration and Chirality in Anisotropic Fluids.

being a Thesis submitted for the Degree of Doctor of Philosophy

in the University of Hull

by

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I would like to dedicate this work to my mother,

and to the memory of my father who passed away before it was complete.

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1. INTRODUCTION TO MOLECULAR CHIRALITY.

1.1 Symmetry and Molecular Structure.

The shape and form that a molecule takes often has a major influence not only on its physical and chemical properties, but also on any biological processes in which it may be involved[1]. In order to define the shape and structure of a molecule four aspects need to be considered. Namely, its *constitution, configuration, chirality* and *conformation.* The constitution of a compound specifies the atoms that are present in a molecule, and the types of bonds used for direct interatomic bonding. Configuration can be described by two terms, relative and absolute. *Relative configuration* specifies the relative spatial arrangements of the various bonds and atoms that constitute the molecule, without regard to the multiplicity of spatial arrangements that may occur on rotation about single bonds. *Absolute configuration* specifies the actual spatial arrangement of atoms and bonds within a given structure. The conformations that a molecule may possess describe the different spatial arrangements of atoms that may arise by rotation about single bonds within the structure. Chirality, which will be discussed more extensively in section 1.2, is a property associated with three-dimensional forms that are not superimposable with respect to their mirror images.

Constitution, configuration and chirality are static properties which specify the shape of a molecule in three-dimensional space; however, it must be remembered that the dynamics of molecular movement can have a major influence on the structure with many conformations being possible. The various more energetically stable conformations defining the conformational structure of the molecule. This will be expanded upon in the results and discussion section of this thesis.

1.2 Chirality.

In the early nineteenth century the French physicist, Jean Baptiste Biot, discovered that certain substances of biological origin caused a rotation of plane polarized light, that is to say they were optically active[2]. At this time the origin of such behaviour could not be defined in chemical terms because the shape, structure and physical properties of molecules themselves were still somewhat of a mystery. Biot's discovery raised two important questions, firstly, what was the physical nature of light, which makes the phenomenon of optical activity possible, and secondly, why do some molecules display this property whereas others do not?

In 1822 Augustin Fresnel put forward a transverse wave theory of light that accounted for several of the phenomena associated with plane polarized light[3]. In particular Fresnel showed mathematically that linearly polarized light could be resolved into two circularly polarized components that rotate in opposite directions (a right-circularly polarized and left-circularly polarized ray), and that the direction of linear polarization rotates if the two circularly-polarized rays travel through a medium at different velocities. Fresnel therefore suggested that the concept of optical rotation of plane polarized light was equivalent to "circular double refraction", a theory which to this day forms the basis of more complex understandings of this effect. Fresnel later reasoned that certain substances are optically active due to a particular constitution of the refracting medium or of its constituent molecules. He suggested that a helical arrangement of the molecules in a medium, could present contrasting properties for opposing helical twist senses[4]. This concept was, at the time, foreign to chemistry as nothing was particularly known about the geometrical arrangement of molecules in matter, even though helices were recognised to exist in nature, e.g., snails' shells and whirlpools. However, in the case of quartz crystals Fresnel's idea turned out to be correct, but this shed little light on the concept of molecular optical activity (in the liquid or gaseous phases).

The first step in our understanding of optical activity in discrete molecules was taken when Louis Pasteur discovered that for a number of substances, the occurrence of dissymmetric crystals was correlated with the existence of optical rotatory power in solution[5]. Further experimentation with sodium ammonium tartrate[6] led him to the discovery that two crystal forms occur which are mirror images of each other. When the two forms were separated and dissolved in a suitable solvent, each gave a rotation of plane polarized light, but in opposite directions. From this discovery Pasteur concluded that the similarity of the two crystal forms implied a similarity of the constituent molecules. The opposite rotations of plane polarized light observed, when each form was dissolved in a suitable solvent, indicated that the molecules were not identical, but were mirror images of one another. The constituent molecules were therefore termed asymmetric, or more latterly chiral, a term first used to describe a lack of symmetry by the physicist Lord Kelvin[7] in a series of lectures conducted at John Hopkins University, Baltimore.

The next step in our understanding of optical activity in organic materials came in 1874 when Jacobus H. van't Hoff, and Joseph A. Le Bel, both published papers proposing a tetrahedral arrangement of atoms bonded to carbon as the basis for molecular chirality[8, 9]. They argued that such a structure would be asymmetric if the four atoms attached to carbon were different, and would be symmetric if any two were identical. This theory, although giving an exact correlation with the observed optical activity data available at the time, was not immediately accepted, and indeed became the subject of some ridicule, with a particularly scathing attack coming from Hermann Kolbe, who at the time held the Chair of chemistry at the University of Leipzig. In this attack he stated that there was a fundamental lack of general and fundamental chemical knowledge which led to, quote "the spread of the weed of the apparently scholarly and clever, but actually trivial and stupid, natural philosophy, which was displaced fifty years ago by exact natural science, but which is now brought forth again, out of the store-room harbouring the errors of the human mind,

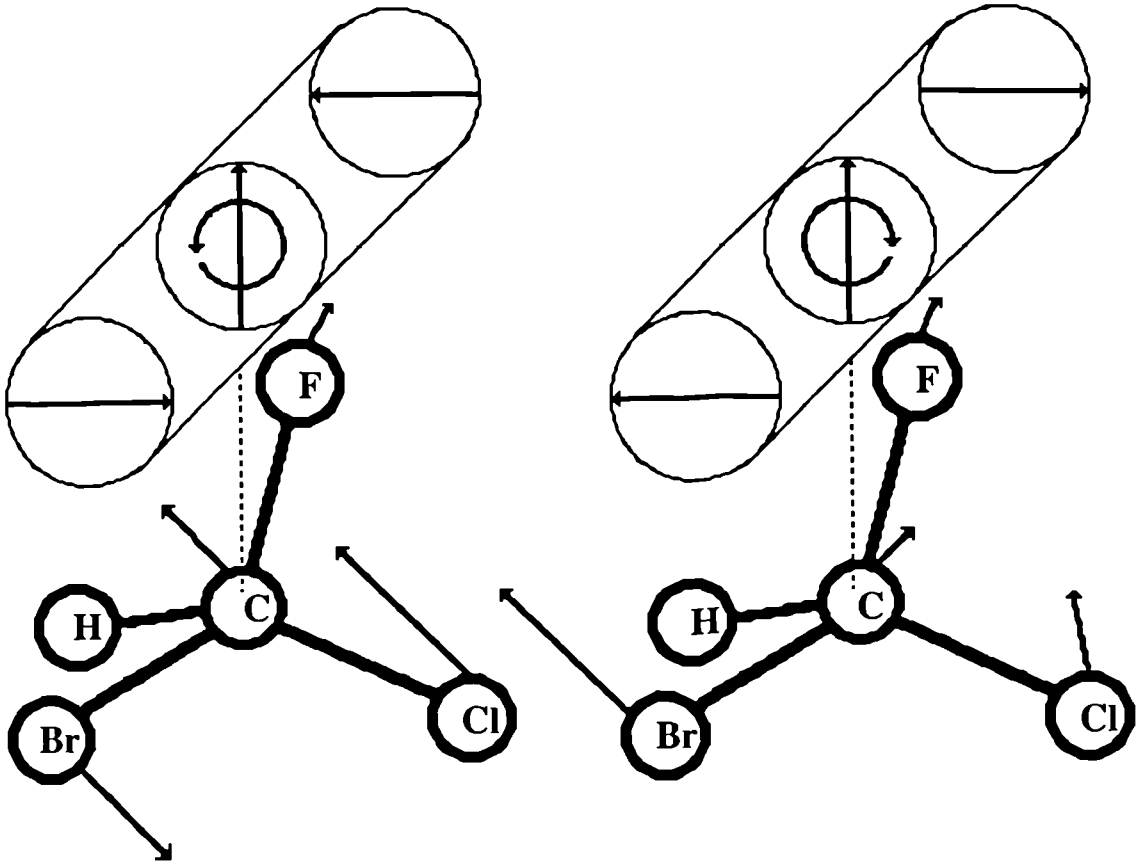
by pseudo scientists who try to smuggle it, like a fashionably dressed and freshly rouged prostitute, into good society, where it does not belong"[10]. In 1878, van't Hoff, however, was appointed Professor of Chemistry, Mineralogy, and Geology at the University of Amsterdam, and in 1901 was the recipient of the first Nobel prize for his work on the structure of carbon containing compounds.

A greater understanding of the exact mechanism of the optical rotatory power of chiral organic molecules was now being sought by a number of scientists. The reasons why an asymmetric tetrahedral molecule should be optically active required a mathematical treatment of an extremely complex physical problem, namely the interaction of four different atoms at the corners of a tetrahedron with a beam of incident light. The theories[11, 12, 13] of Max Born, Carl Wilhelm Oseen, and Frank Gray suggested that the rotations of plane polarized light given by molecules that were mirror images of one another would be equal, but opposite, and that the rotation would be zero if the molecule was symmetric. The theories were based on the idea that the sum of the induced dipoles in asymmetric molecules, in the presence of circularly polarized light, were dependent on the polarization direction, and this would be the case even after the induced dipoles are averaged over all random orientations of the molecules in the liquid or gas phases. This is illustrated in figure 1, for one of the simplest optically active organic materials, bromochlorofluoro-methane. In figure 1 the molecule is imagined to be located inside each of the circularly polarized light beams shown above it. The atoms are polarized at some instant in time by the electric field of the light wave, shown by the arrows in each beam. The arrows on the atoms show the direction and strength of the induced dipoles associated with each individual atom (assuming C-H is zero). The total induced dipole associated with the whole molecule is different for each polarization direction (of the light wave), as shown by the calculated values that are given in units of 10^{-6} debyes, for a field strength of 1 electrostatic unit[14]. The resulting difference in the refractive index of the two waves produces optical rotation.

An important discovery by the French physicist Aime Cotton in 1895 found that optically active compounds of tartaric acid that contained copper and chromium (which gave them colour) showed an unequal absorption of right- and left-circularly polarized light in the wavelength region where the absorption occurred[15]. This effect, which came to be known as "circular dichroism", was soon understood to arise in a similar manner to the optical rotation of plane polarized light given by some asymmetric materials. Absorption occurs when the induced molecular dipole oscillates out of phase with the incident light wave. If the induced dipoles exhibit a phase shift, then the inequality of the induced moments in the two waves results in a difference in absorption intensities. This difference (left- minus right-circularly polarized rays) acts as a measure of circular dichroism. Due to their common origins, circular dichroism and optical rotatory power offer similar information about the structure of a material. Circular dichroism, however, is concentrated more on the light absorbing entities within a molecular structure.

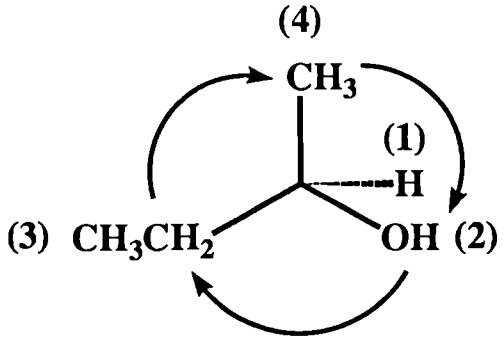
The classification of molecules that are optically active needs a number of terms. Firstly, any molecule that possesses a tetrahedral carbon atom with four different groups attached to it is said to be asymmetric, or chiral in nature. The two-mirror image forms that may exist are known as enantiomers, with each one giving an equal, but opposite rotation of plane polarized light. A 50 %/50 % mixture of the two enantiomers is known as a racemic mixture and is optically inactive. If, however, one enantiomer is in excess then the mixture will be optically active. Each enantiomer is usually labelled according to the absolute configuration of its asymmetric centre. The labelling system most commonly used (accepted by IUPAC) was first introduced by Cahn, Ingold, and Prelog in the 1950's[16, 17]. The system operates by first prioritising each atom (or group) in terms of atomic number (oxidation number), that is attached to the asymmetric carbon atom (priority rule). The tetrahedron is then viewed with the lowest priority group (or atom) set to the rear. A path is then traced between the remaining three groups (or atoms) from the highest to the lowest priority (sequence

rule). If a clockwise direction is transcribed then the chiral centre is classified as *Rectus* or Right *(R)*. If, however, an anticlockwise path is taken then the chiral centre is classified as being *Sinister* or Left *(S)*. This is illustrated in figure 2 for butan-2-ol.



Total dipole moment = 5.32 **Total dipole moment = 4.98**

Figure 1. The induced Dipoles that Occur in an Asymmetric Molecule on the Interaction with Electromagnetic Radiation[14].



Rotation is clockwise, therefore molecule is Rectus *(R)*

Hydrogen facing back into the page is given the lowest priority

Figure 2. The Cahn, Ingold and Prelog Priority Labelling System for Asymmetric Molecules[16, 17].

The directions of rotations of plane polarized light given by either enantiomer is classified as being either positive (+) in the case of a clockwise rotation, or negative (-) in the case of an anticlockwise rotation. No obvious correlation, however, exists between the configurations of enantiomers, or between the *(R)* and *(S)* designation and the direction of rotation (+) or (-).

If a molecule has two or more chiral centres, then the material may be diastereometric. This is illustrated in figure 3, giving an aldotetrose as an example.

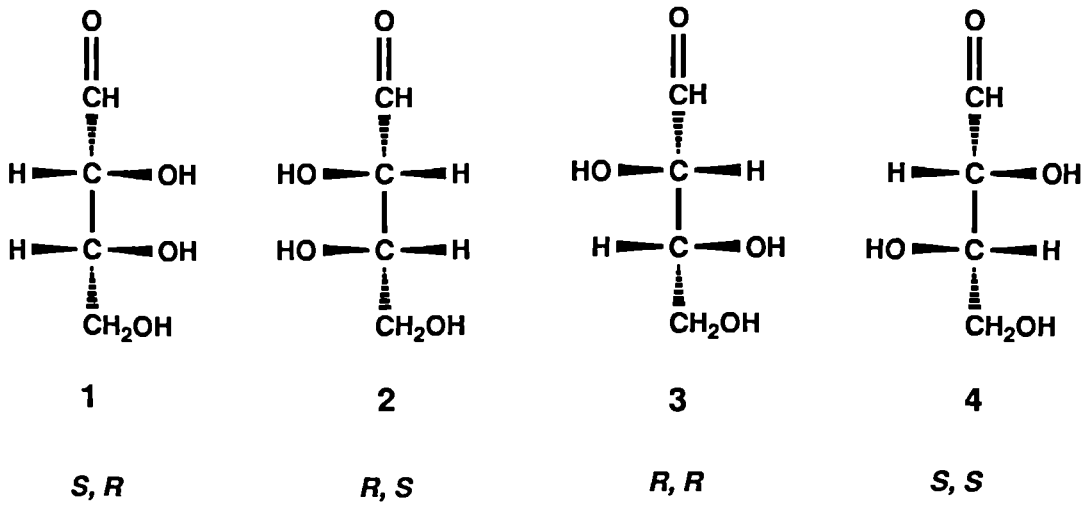


Figure 3. Diastereoisomers in a Simple Sugar.

A molecule which has two asymmetric centres that have an *(R,S)* configuration, i.e., one chiral centre is labelled as *(S)*, whereas the other is *(R)*, is the diastereoisomer of a molecule that has an *(R,R)* configuration. Similarly a molecule with an *(S,S)* configuration is the diastereoisomer of a molecule with an *(R,S)* configuration. A molecule with an *(R,S)* configuration, however, is the enantiomer of another with an *(S,R)* configuration, this relationship also holding true for molecules with *(S,S)* and and *(R,R)* configurations. Classical theory dictates that the physical properties of enantiomers are the same, whereas those of diastereoisomers may differ[18]. This will, however, be expanded on later (see chapter 8).

Molecules that have mirror symmetry and contain two identical, but oppositely labelled asymmetric centres are themselves non-chiral. They are termed meso compounds. They possess an additional plane of symmetry and are found to be optically inactive. An example of a meso compound (meso-2,3-butanediol) is illustrated in figure 4.

Another interesting situation arises when a molecule that does not possess an asymmetric carbon atom is optically active. An example of this is helicene in which all carbon atoms are sp^2 hybridised (distortion of the molecular orbitals due to the gross structure of the molecule may cause slight asymmetry, leading to some orbitals having a reduced symmetry) and therefore possess a necessary mirror plane to classify them as symmetric. The material is, however, optically active because of its helical structure and does not have a superimposable mirror image (the rings are twisted out of plane giving rise to a left- or right-handed helical structure). The structure of helicene is illustrated in figure 5.

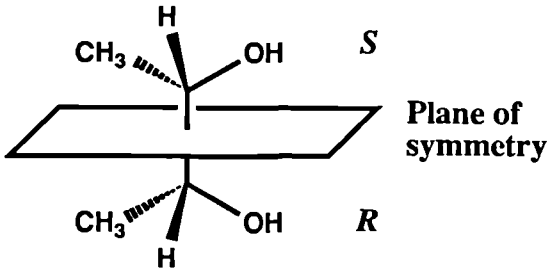


Figure 4. A Meso Compound (Meso-2,3-butanediol).

Helicene has an extra symmetry element in comparison to an asymmetric carbon atom, a simple two-fold axis of rotation, and so is considered as dissymmetric and not asymmetric. Both asymmetric and dissymmetric molecules are, however, considered chiral in most instances. The maximum symmetry element allowable for chirality is then a rotational axis; if, however, mirror symmetry is introduced then the system becomes achiral.

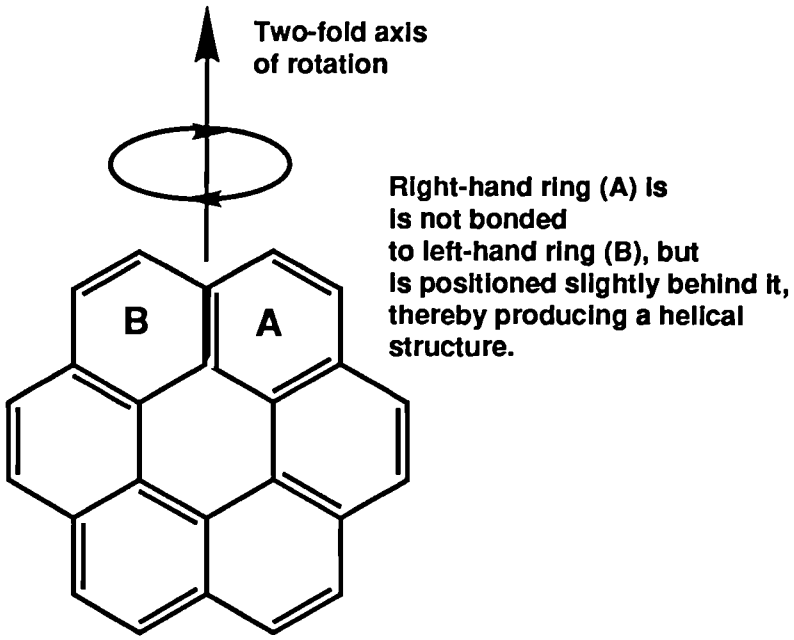


Figure 5. Helicene, a Dissymmetric Molecule.

At this stage it should be mentioned that carbon is not the only atom that is associated with optical activity. Silicon and germanium, from the same group in the periodic table, also form tetrahedral compounds and therefore have the ability to display optical activity[19]. In certain instances a chiral nitrogen or sulphur atom may also be used, with a lone pair of electrons taking the place of an atom or group in the asymmetric structure[20].

2. INTRODUCTION TO ANISOTROPIC MEDIA.

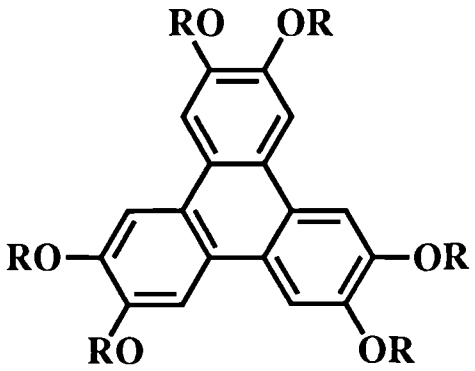
2.1 Anisotropic Fluids.

An anisotropic fluid or liquid crystal, is a substance that is fluid in nature, yet retains some degree of order. Liquid-crystalline materials can be divided into two main classes, lyotropic systems that are formed by surfactant/solvent mixtures[21] and thermotropic systems where the various mesophases are formed on heating or cooling.

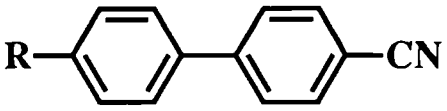
Thermotropic liquid crystals usually[22] fall into two main classes, discotics, which are made up of disc-shaped molecules, and calamitics, where the molecules have extended rod-like structures, with a large length to breadth ratio. Another class of liquid crystals is that of polymeric materials, where either disc- or rod-like molecules are attached to (side-chain) or incorporated in (main-chain) a polymer in such a way that mesophases may be formed[23]. The phases formed in polymeric materials are structurally analogous to those formed by monomeric materials. Examples of the types of materials that form liquid-crystalline phases are illustrated in figure 6.

Possibly the best understood of all classes of liquid crystals are the calamitics. They were the first thermotropic liquid crystals to be reported[24], and since that time many advances have been made in terms of our understanding of their structures, phase morphologies and potential uses[25]. Calamitics can be divided into three main classes, nematic, that possess only orientational order (of the molecules within the phase), smectics, that posses orientational order and limited positional order, and disordered crystals that possess orientational order and a high degree of positional order. It should be noted that a material may exhibit multiple phases, each phase being a thermodynamically stable entity at a given temperature and pressure. Boundary and surface effects can, however, have a marked influence on phase formation and transition temperatures in some materials[26].

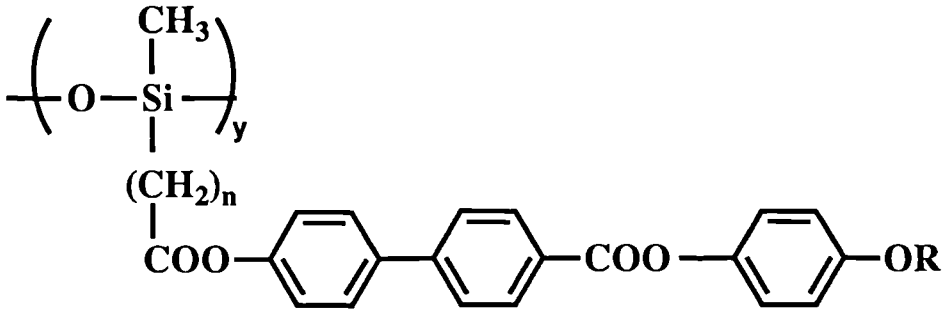
Another important aspect to consider is the fact that the types of molecules that constitute liquid-crystalline phases are invariably, or at least in part, organic in nature. Organic molecules, if their structure allows, have the ability to be optically active, that is they may contain an asymmetric carbon atom (see chapter 1). This asymmetry of the molecules can lead in some instances to mesophases that are themselves optically active. Molecular chirality and its effect on phase formation and the physical properties displayed by mesogenic materials form the basis of the research carried out in this thesis, and therefore this phenomenon and its effects are discussed extensively in the next section (2.2).



Discotic liquid crystal



Calamitic liquid crystal



Calamitic polymer liquid crystal

where R is alkyl, n and y are integers

Figure 6. Some Examples of Materials that Exhibit Liquid-Crystalline Behaviour.

2.2 Chirality in Anisotopic Media.

The types of molecules that form calamitic liquid-crystalline phases usually possess an extended rod-like structure. Chirality can be built into the mesogenic system by the inclusion of a functionality containing an asymmetric carbon atom. This functionality may be incorporated into any part of the molecule, but because of synthetic considerations it is most often placed in either one, or both of the terminal aliphatic chains that are often part of the molecular structure. The effects of chirality in mesogenic systems will be discussed in greater detail later in this section and in chapter 3, however, chiral properties can usually be quantified in terms of the pitch length of optically active phases (see section 2.3), the thermal stability of liquid-crystalline phases that are known to depend on a high degree of molecular chirality for their existence, e.g., blue phases (see chapter 3), and the value of the spontaneous polarization in ferroelectric phases (see section 2.5.2).

In order to induce a high level of chirality into the system the enantiomeric excess (e.e.) must be high, that is to say that the minority enantiomer must be present only in very small amounts. This can be accomplished using synthetic routes and reagents to specifically achieve this purpose[27], or by utilising optically pure biological materials[28]. The position of the chiral centre within the molecular structure in relation to the core of the mesogen also has a major effect on the degree of chirality induced into the system, as do substituents located at the chiral centre itself. This topic forms a large area of the research conducted in this project and so will be mentioned briefly here, and then discussed more extensively in the results and discussion section (see chapter 8).

Firstly, the dipoles associated with, and the size and steric shape of the substituents located at the chiral centre, can have large effects on the chirality of the system. Usually, a large resultant dipole enhances the chirality[29], as does a bulky group associated with the asymmetric centre. The second effect is thought to be due to a

restriction in rotational freedom of the optically active centre about the long axis, thereby increasing polarity and steric interactive effects. This effect can also be observed if the chiral group is placed very close to the core structure[30], or in some instances when lateral substituents located at the core structure are extended in length. In at least one example the linking group associated with the chiral moiety was selected so that it would hydrogen bond with a lateral group attached to the core, thereby reducing the rotational freedom of the chiral centre completely (see figure 7)[31].

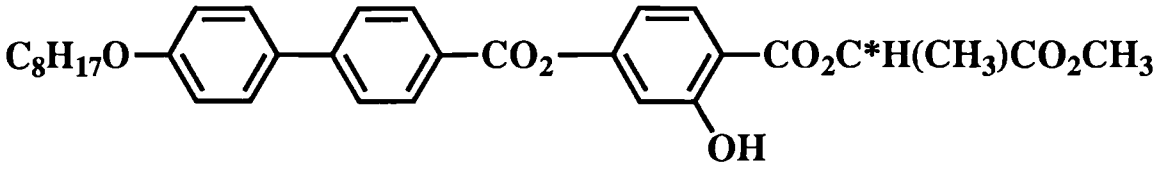


Figure 7. Lateral Substitution can Cause an Increase in Chirality.

Rotational freedom can also be reduced by extending the terminal aliphatic chain on the peripheral side of the chiral centre[32], although it must be remembered that this may also cause a dilution effect (of the dipole) as well. These points are summarised in figure 8.

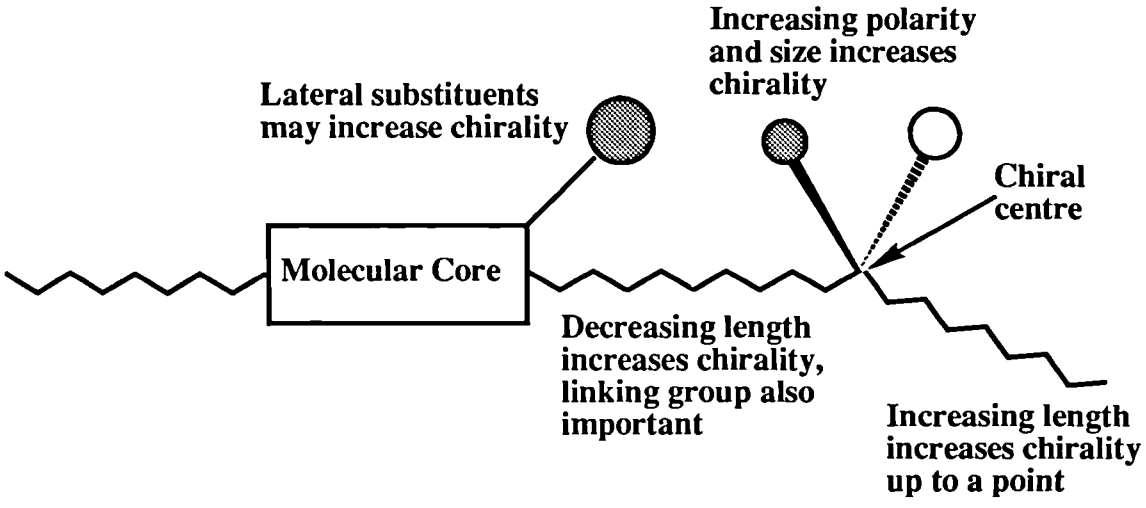


Figure 8. Chirality in Calamitic Liquid Crystal Molecules.

The number of mesophases formed by optically active materials are many; these are illustrated in figure 9 which shows the variety of mesophases that may be formed by optically active calamitic materials.

<table>
<tr><td>Disordered Crystal</td><td colspan="3">Liquid Crystal</td></tr>
<tr><td>Layer Structures</td><td colspan="2">Smectic</td><td>Nematic</td></tr>
<tr><td rowspan="2">Orthogonal. E* B*</td><td>Based on weakly coupled ordered layers 'two-dimensional' systems.</td><td>Based on one-dimensional density wave (liquid-layers).</td><td rowspan="3">N* (Ch)</td></tr>
<tr><td>SmB*</td><td>SmA*
SmA* (TGB)</td></tr>
<tr><td>Tilted. H* G*
K* J*</td><td>SmF*
SmI*</td><td>SmC*
(ferri- and anti-phases)</td></tr>
<tr><td colspan="4">Cubic Structures</td></tr>
<tr><td colspan="4">BP I, II, III</td></tr>
</table>

Figure 9. The Phases formed by Optically Active Calamitic Materials.

It can be seen from figure 9, that smectics and disordered crystals can be further subdivided into orthogonal and tilted phases. Whether a phase is tilted or not depends on the time-averaged direction that the director (the unit vector describing the average direction of the long-molecular axes) points with respect to the layer-planes. Tilted phases when composed of, or 'doped' with, optically active material[33] may themselves display a helical ordering of the molecules, that is they may become dissymmetric and exhibit, *form* optical activity. The helical ordering can transcribe either a left-handed or a right-handed helix, the convention for labelling helices being described by Cahn, Ingold and Prelog[34]. This helical ordering, however, may be suppressed in some of the more crystalline tilted modifications. For example, X-ray studies have failed to find any helical ordering in the crystal J*, G*, H* or K* phases[35].

The orthogonal phases do not display *form* optical activity under normal circumstances, and indeed special cases also exist, where tilted smectic phases that contain chiral molecules do not have this particular property. These will be discussed

later in the results and discussion section of this thesis (see chapter 8). Suffice it to say, optical activity has become a very important focus for research into mesogenic materials and leads to some of their most useful properties.

2.3 Optically Active Mesophases.

The majority of work contained in this thesis is centred on the liquid-crystalline phases that display *form* optical activity. A brief resume of chiral mesophases will therefore now be given.

2.3.1 *The Cholesteric Phase*

The cholesteric phase is closely related to the nematic phase in that the molecules possess only orientational order, lacking any degree of positional order. In the nematic phase intermolecular forces tend to align the molecules parallel with one another. In the cholesteric phase the molecules tend to align laterally at a slight angle to one another, the director prescribing a macroscopic helix, thereby imparting *form* optical activity to the phase. A simple model of the cholesteric phase is one where it is composed of a series of layers or sheets, each sheet displaying a slightly different director orientation in comparison to neighbouring sheets. It must, however, be emphasised that this is only a model used to represent the phase and that in reality the concept of layers or sheets is not applicable to the cholesteric phase. This type of schematic representation of the cholesteric phase can be seen in figure 10.

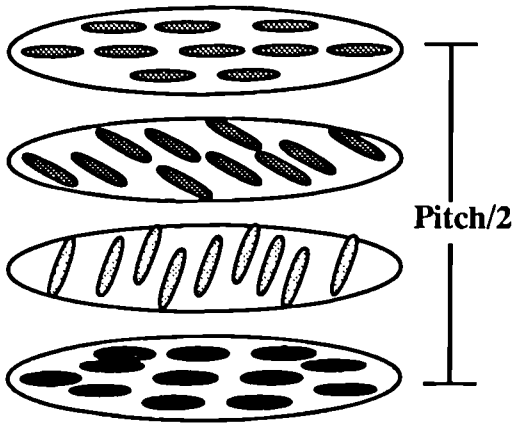


Figure 10. A Schematic Representation of the Cholesteric Mesophase.

As a succession of layers is traversed, the director turns through 360°; this is known as the pitch of the helix. In the figure only one-half pitch is illustrated, that is p/2. The pitch is found to be temperature dependent and in most instances is found to increase on cooling from the isotropic or blue phases, until it reaches infinity at the transition to a smectic A phase, for example. This type of variation in cholesteric pitch with respect to temperature, however, is not always the case and instances when this does not occur will be elaborated on further in the results and discussion section of this thesis (see chapter 8). It should also be noted that the helix of the cholesteric phase can be right- or left-handed, the twist sense depending on the nature and position of the chiral centre. Gray and McDonnell[36] showed that for the cholesteric mesophase a simple relationship exists between the absolute spatial configuration, and parity (odd or even atom count from the core structure) of the chiral centre and the helical twist sense. The rules they obtained are illustrated in table 1, and although not infallible, turned out to be a useful guide for most materials.

Abs. Spatial Configuration	Parity of the Chiral Centre	Helical Twist Sense
S	even (e)	dextro (*d*)
S	odd (o)	laevo (*l*)
R	even (e)	laevo (*l*)
R	odd (o)	dextro (*d*)

Table 1. The Helical Twist Sense in the Cholesteric Mesophase.

The cholesteric phase commonly displays one of two optical textures when viewed in the polarizing microscope. The first texture is commonly called the focal-conic or natural texture of the cholesteric phase. It is formed on cooling from the isotropic or blue phases and occurs when the packing of the cholesteric helices transcribe an ellipse and a hyperbola. The structure provides a rapidly changing orientation of the optic axis and so has the property of scattering light, thereby appearing opaque in nature. Plate 1 shows a photomicrograph of the natural texture of the cholesteric phase.

The second optical texture displayed by the cholesteric phase occurs when the material is momentarily subjected to mechanical stress causing flow alignment of the cholesteric helices perpendicular to the substrate. This texture is known variously as the Grandjean plane texture[37] or the 'oily-streak texture'. The 'oily streaks' that can be clearly seen in plate 2, are edge dislocations and can be seen to freely move through the fluid structure of the cholesteric phase.

Recently, the cholesteric phase has received much interest for use in both temperature, and to a lesser degree pressure sensors[38]. The applications ranging from medical thermography and stress testing of metals, to more trivial marketing gimmicks.

2.3.2 *The Chiral Smectic C* Phase*

The chiral smectic C* phase is the optically active variant of a normal smectic C phase. In a normal smectic C mesophase the molecules are arranged in diffuse layers, with their long-molecular axes tilted at a temperature dependent angle (θ) with respect to the layer normal. The positional ordering within a layer is of a hexagonal nature, but is extremely short range (15 Å), leading to what is essentially a random packing arrangement. The tilt direction, however, remains reasonably constant for a monodomain sample and so the phase can be said to possess tilt-orientational order.

When the phase is composed of optically active material, a macroscopic helical arrangement of the molecules occurs. The helix is created by a precession of the tilt (of the molecules) about an axis perpendicular to the layer planes, as shown in figure 11. The tilt direction of the molecules is rotated through an azimuthal angle (ψ) on moving from one layer to the next. This rotation being in a constant direction, leads to the formation of a helix, either left-handed or right-handed. The helical twist sense, as with the cholesteric phase, being determined by the nature and position of the chiral centre. Rules to determine the twist sense of the chiral smectic C* phase,

were based on Gray and McDonnell's rules for the cholesteric phase, but were later modified by Goodby and Leslie[39] to take into account the inductive effect at the chiral centre. This was necessary as some anomalies were found, but even now the rules should be taken as a guide and not as absolute. Table 2 illustrates the relationship between absolute spatial configuration, parity, and inductive effect at the chiral centre with the helical twist sense of the smectic C* phase.

One 360° rotation (of the molecules) in the helix for the smectic C* phase usually extends over hundreds of layers as the azimuthal angle is generally found to be of the order of 0.1-0.01 of a degree.

The smectic C phase and smectic C* phase commonly exhibit two types of texture. The first of these is the broken focal-conic texture, which is similar to the analogous texture seen for the normal smectic A phase[40]. As with the smectic A focal-conic texture the layers form around two singularities that have a confocal relationship, but due to the inherent tilt of the molecules, the fans that are seen appear broken, or cracked when viewed in the polarizing microscope. Due to the fluidity of the system and the ability of the molecules to fill space this cannot be the case, the dark "cracks", in fact representing places in the texture where the molecules are aligned with one or other of the two polarizers. In the case of the optically active smectic C* phase periodic lines may be seen on the backs of the observed fans, these are in some instances due to the pitch of the helix. Care, however, must be taken when endeavouring to measure pitch from these lines as certain defect structures tend to show lines that are due to one-half of the pitch length[41]. The broken focal-conic fan texture of the smectic C* phase is shown in plate 3.

The other common texture associated with the smectic C* phase is the *schlieren* texture, which is similar to that seen for the nematic phase. In the case of the smectic C* phase, however, defects with strength $S = \pm 1/2$ are not observed, except for in

special cases such as in the antiferroelectric phase.[42] A typical *schlieren* texture for a smectic C* phase is shown in plate 4.

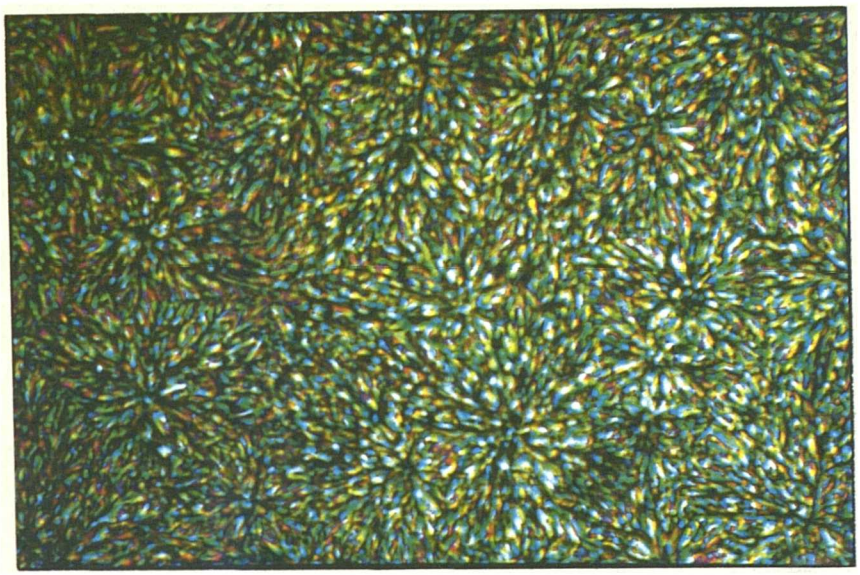


Plate 1. The Natural Texture of the Cholesteric Phase Displayed by *(S)*-2-Chloro-4-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate.

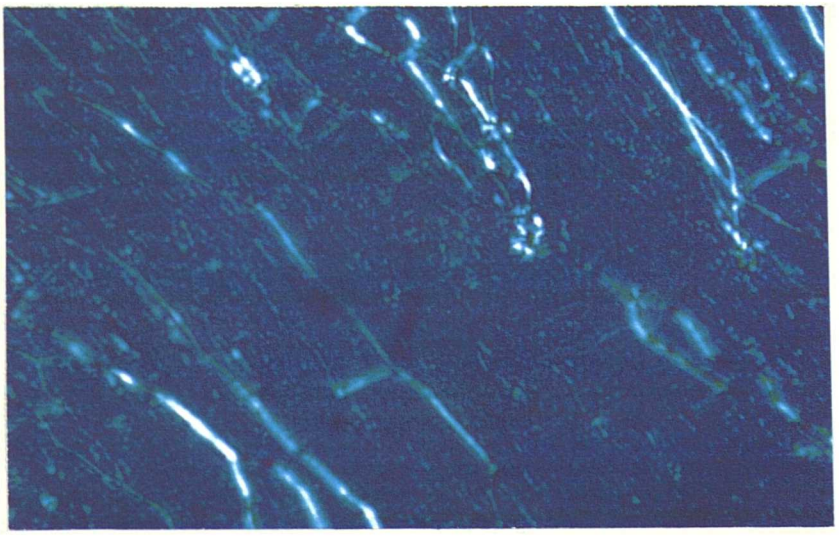


Plate 2. The Grandjean-Plane (Oily Streak) Texture of the Cholesteric Phase Displayed by *(S)*-2-Chloro-4-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate.

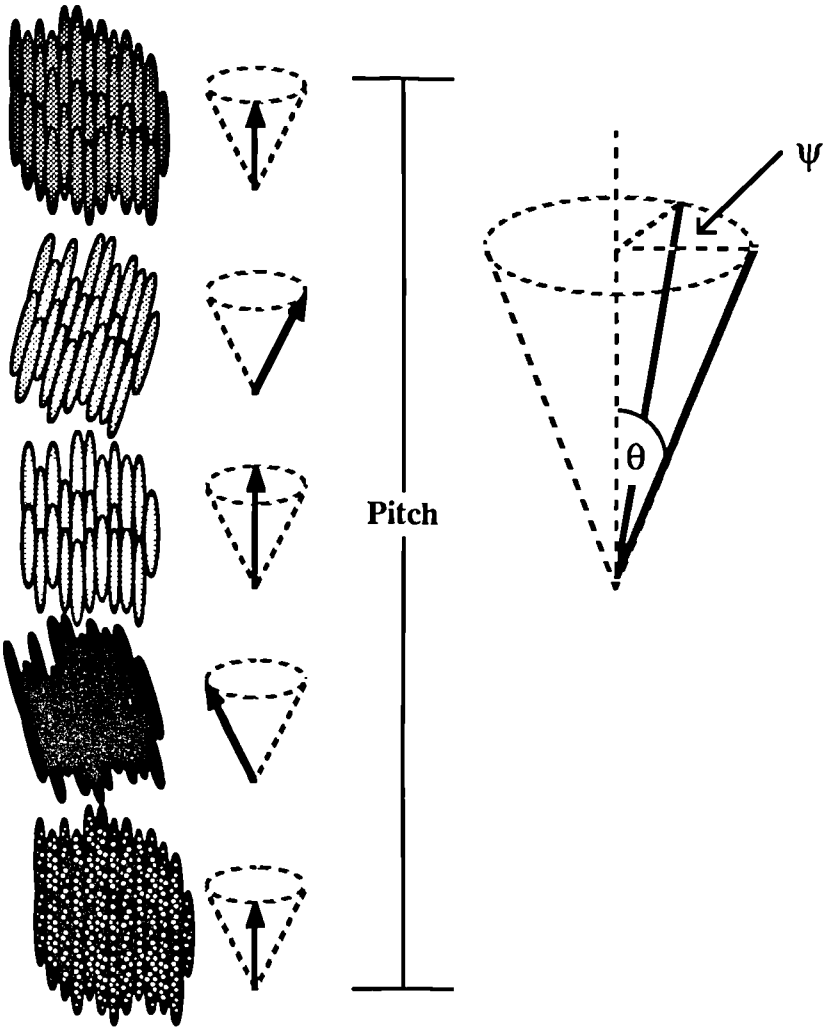


Figure 11. A Schematic Illustration of The Chiral Smectic C* Phase (the tilt of the molecules processes around the surface of a cone).

Abs. Spatial Configuration	Parity of the Chiral Centre	Helical Twist Sense	Inductive Effect at the Chiral Centre
S	e	*d*	+I
S	o	*L*	+I
R	e	*L*	+I
R	o	*d*	+I
S	e	*L*	-I
S	o	*d*	-I
R	e	*d*	-I
R	o	*L*	-I

Table 2. The Helical Twist Sense in the Chiral Smectic C* Mesophase.

The smectic C* has recently received much attention due to it's ferroelectric properties (see section 2.5.2) and it's potential uses therefore, in fast switching display devices, the best known of these being the surface-stabilised ferroelectric display device proposed by Clark and Lagerwall[43].

2.3.3 *Higher Ordered Phases*

In the smectic I and F phases the molecules have a similar arrangement to that found in the smectic C phase, except that the ordering within an individual layer is far more extensive. The hexagonal packing of the molecules is still short range in nature (150-600 Å), but considerably greater than that seen in the smectic C phase. The hexagonal packing order is seen to remain in the same orientation over long distances in three dimensions, thereby giving long range bond orientational order. The tilt orientation as with the smectic C phase also appears to be constant over many layers. The smectic I and smectic F phase differ by virtue of the fact that in the I phase the tilt in the molecules is directed towards the apex of the hexagonal packing net, whereas in the F phase the tilt is directed towards the edge of the packing net.

When either the I or F phases are composed of optically active material the generation of a helix occurs in an analogous fashion to that in the chiral smectic C* phase. The pitch, however, is usually seen to be longer than that in the smectic C* phase[44], because the additional order is thought to restrict the size of the azimuthal angle. The textures shown by the I and F phases are shown in plates 5 through to 10.

Plate 3. The Broken Focal-Conic Texture of the Smectic C* Phase Displayed by *(S)*-2-Chloro-4-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate.

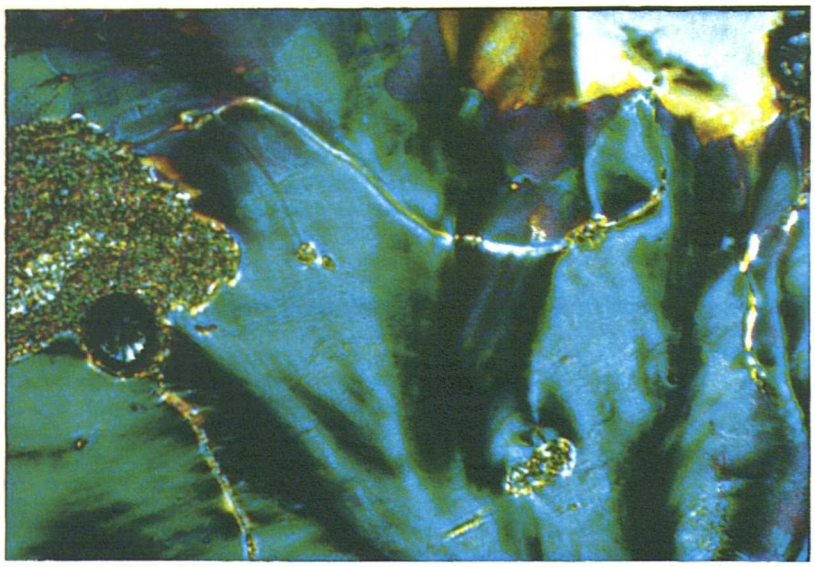


Plate 4. The *Schlieren* Texture of the Smectic C* Phase Displayed by *(S)*-2-Chloro-4-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate.

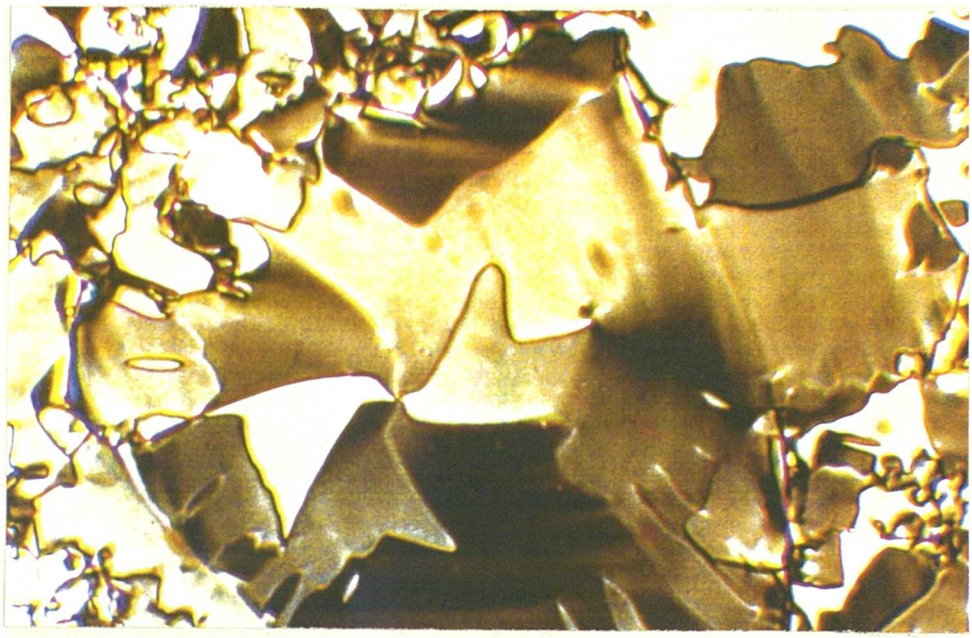


Plate 5. The Natural Texture of the Smectic I Phase Displayed by 4',4-bis-(n-Octadecylamino)biphenyl.

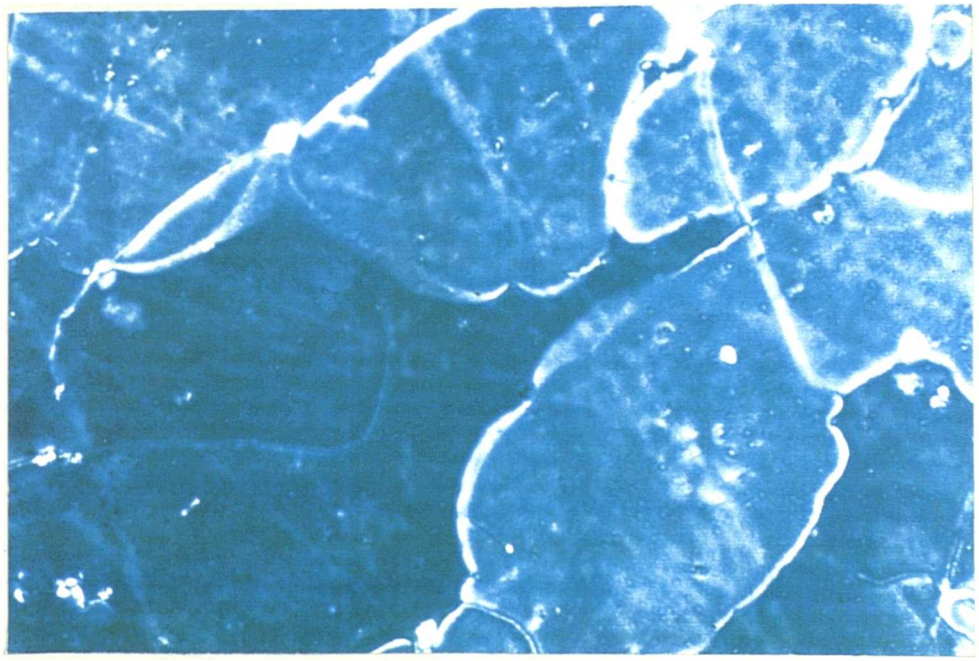


Plate 6. The Plane (Bubble) Texture of the Smectic I* Phase Displayed by (+)-4-(2'-Methylbutyl)phenyl 4'-n-Octyloxybiphenyl-4-carboxylate.

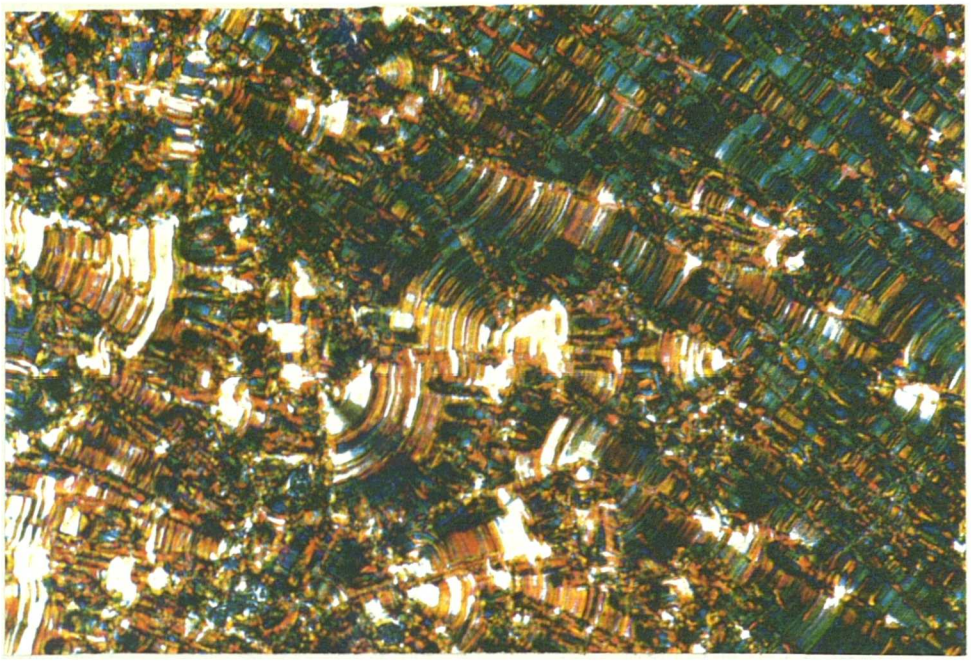


Plate 7. The Focal-Conic Texture of the Smectic I* Phase Displayed by (+)-4-(2'-Methylbutyl)phenyl 4'-n-octyloxybiphenyl-4-carboxylate.

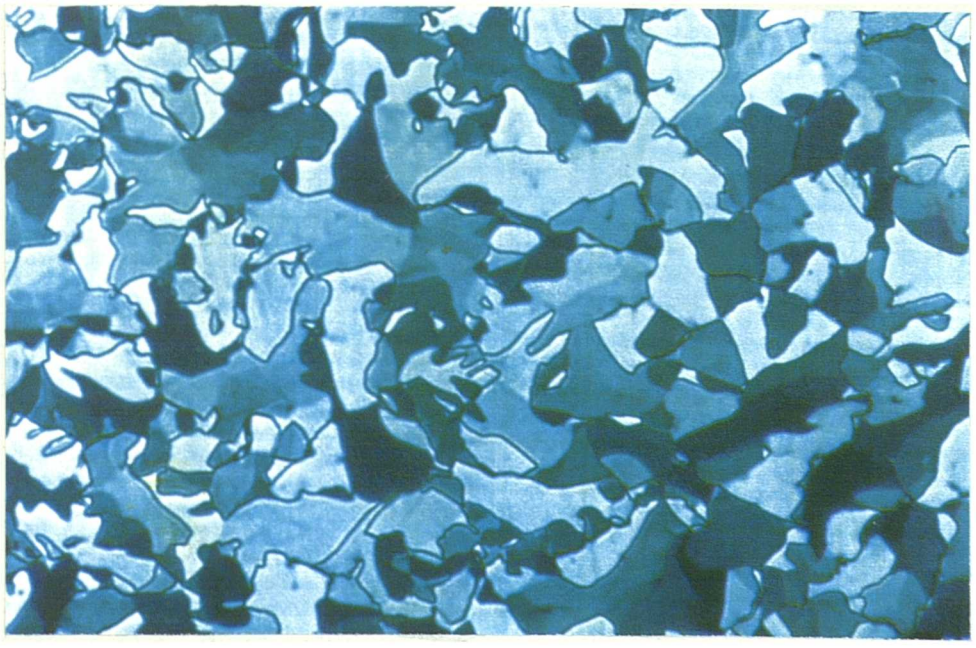


Plate 8. The Natural Mosaic Texture of the Smectic F Phase Displayed by n-(4'-Nonyloxybenzylidene)-4-n-butylaniline.

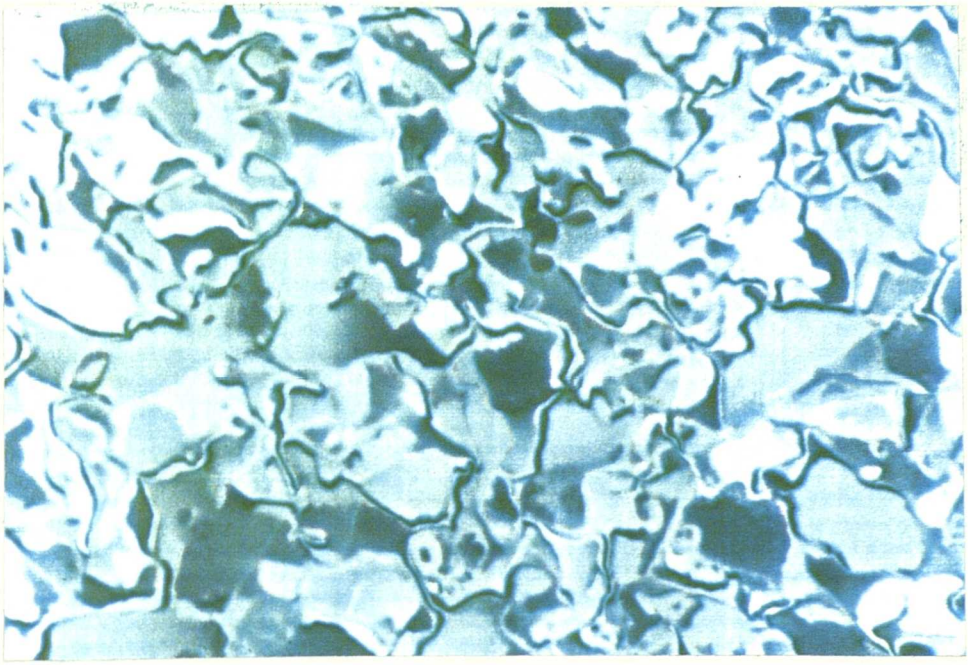


Plate 9. The *Schlieren* Texture of the Smectic F* Phase Displayed by (+)-4-(2''-Chlorobutanoyloxy)-4'-n-octyloxybiphenyl.

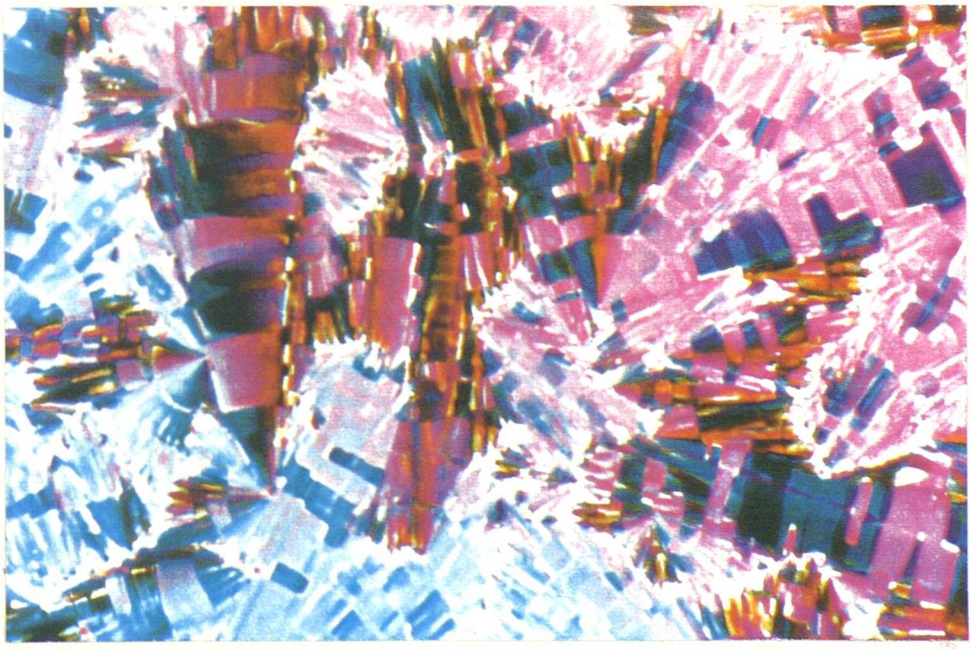


Plate 10. The Broken Focal-Conic Texture of the Smectic F* Phase Displayed by (+)-4-(2''-Chlorobutanoyloxy)-4'-n-octyloxybiphenyl.

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2.4 Properties: of Mesogenic Materials in General.

2.4.1 *Optical Anisotropy*

Optically isotropic materials, such as liquids, amorphous solids and crystals or mesophases with cubic symmetry are found to be optically isotropic, that is they possess one value for the refractive index at any given frequency. Most mesophases and certain crystalline modifications[45], however, can be termed optically anisotropic as the refractive index depends on the propagation direction of incident light. Incident light, on passing through an anisotropic material, is resolved into two waves, the electric vectors of which, vibrate perpendicular to one another. The wave that has it's electric vector vibrating perpendicular to the optic axis, is termed the ordinary ray (o-ray) and travels through the medium at a velocity that is independent of propagation direction. The other ray with an electric vector that lies parallel to the optic axis, has a speed that is determined by the propagation direction, and is termed the extraordinary ray (e-ray). In a uniaxial material, there is one direction only that both rays travel at an identical speed, this is termed the optic axis. Huygens described this effect in terms of the propagation of light in all directions from a point source inside a crystal[45]. The ordinary ray behaves as in an isotropic media, and has a spherical wave front, whilst the extraordinary ray has a wave front that forms an ellipsoid which touches the sphere at two points only (the line joining these two points is the optic axis). The ellipsoid may lie inside or outside the sphere depending on the relative velocities of the ordinary and extraordinary rays. If the extraordinary ray passes through the medium with a greater velocity (except along the optic axis), the material is said to be negatively uniaxial. If the ordinary ray has a greater velocity then the material is positively uniaxial. Figure 12 illustrates in two-dimensions the wave fronts associated with a negative and positive uniaxial material.

Biaxial materials possess two optic axes which closely relate to the optic axis found in uniaxial materials. In general, a ray of light entering a biaxial material is split into two rays that have electric vectors which vibrate in directions perpendicular to one

another, but neither ray obeys the ordinary laws of refraction, i.e., two extraordinary rays are formed. Passing through any point in the material, however, there are three planes at 90° to one another, each of which is characterised by the fact that one of the two rays, in that plane alone, behaves as an ordinary ray. That is, one of the rays travels at the same velocity in any direction within the plane. The three planes are defined by three mutually perpendicular axes, each axis being associated with a different value of the refractive index. This is illustrated in figure 13, along with the three principal sections of biaxial wave surfaces.

Consider rays travelling in the XOY plane through O (see figure 13). In any direction two rays may travel, one vibrating along OZ (normal to the plane) and having a constant refractive index γ, whilst the other vibrates in the plane with its refractive index being dependent on direction. When the ray travels along OY, it vibration direction lies along OX and the refractive index is α. When the ray travels along OX, its vibration direction lies along OY, its refractive index being β. For all other directions the ray has a refractive index that has a value somewhere between that of α and that of β. The behaviour of rays passing through the other two planes is exactly analogous to the behaviour just described. In each of the three planes then, is one ray that behaves as an ordinary ray, its wave front in the plane describing a circle. The corresponding wave surface for the other ray is an ellipse, the semi-axes of which coincide with the two axes defining the plane (OY and OX in the case of plane XOY). In figure 13, the wave surfaces associated with the three principal sections are illustrated, with OA, OB and OC corresponding to the velocities of rays travelling along the three axes (OA > OB > OC). In the section made by the plane XOY, the circle lies entirely inside the ellipse, because the ray that travels with constant velocity is the slowest. OC is the radius of the circle, with OB and OA being the minor and major semi-axes of the ellipse respectively. OA is the ray direction with refractive index α, and corresponds to OY, with OB corresponding to OX.

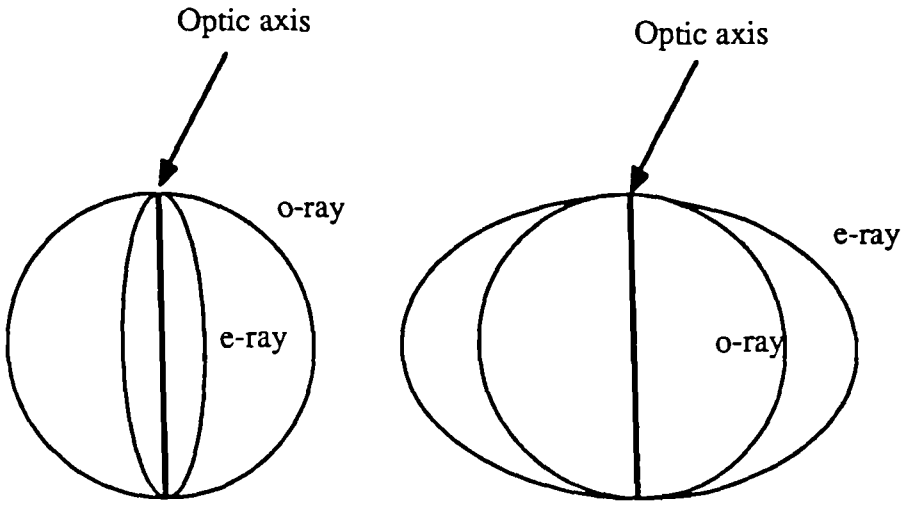


Figure 12. The Wave Fronts Associated with Uniaxial Materials.

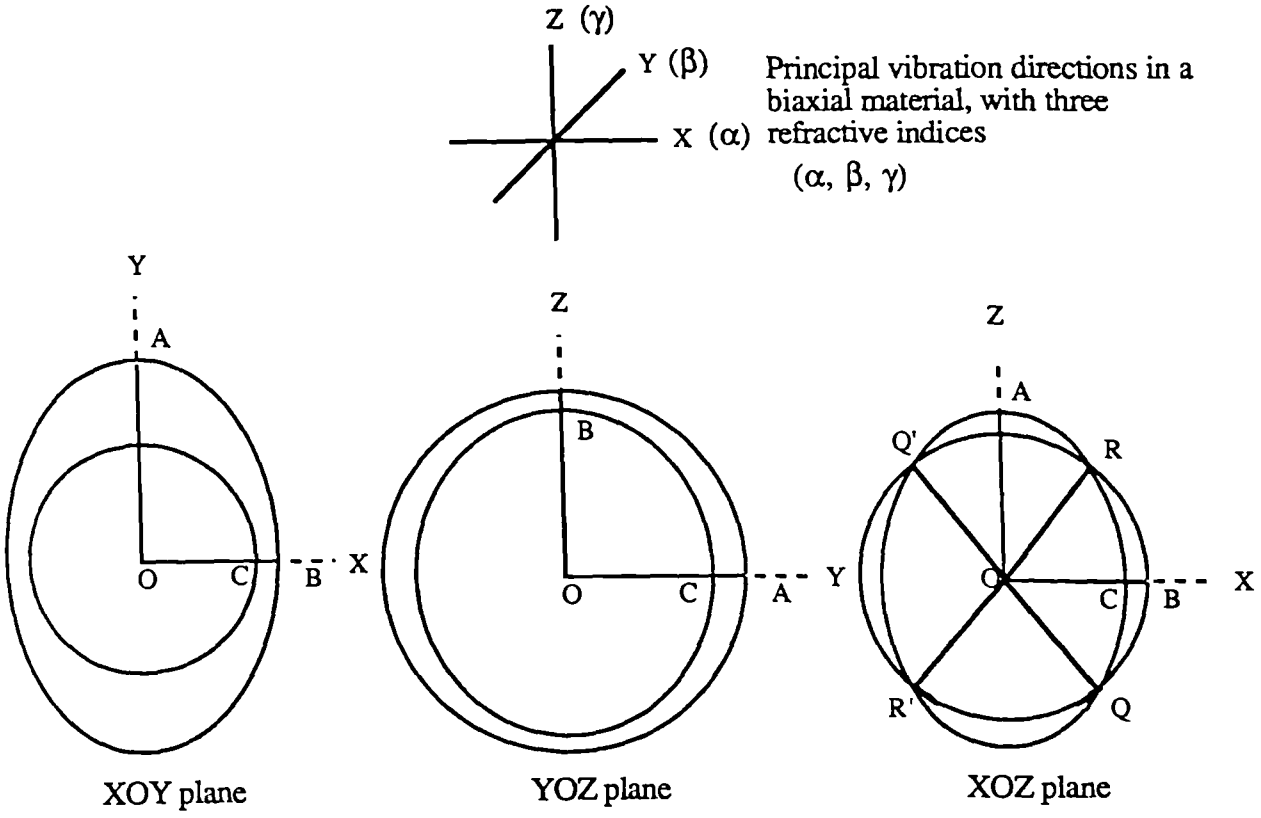


Figure 13. Principal Vibration Directions and Sections of Wave Surfaces of a Biaxial Material.

The YOZ plane can be treated in an analogous manner to the XOY plane. The XOZ plane, however, is more complex as the circle and the ellipse interact at four points. This is due to the fact that the ray of constant velocity has the intermediate value of

refractive index and therefore velocity. The other ray changes velocity from maximum γ to minimum α. Rays which travel from O through any points in the intersection (OR, OR', OQ, OQ'), have the same velocity whether they have wave fronts corresponding to the circle or the ellipse. ROR' and QOQ' form two straight lines through which all rays travel with the same velocity. They correspond to the optic axes in uniaxial materials and are known variously as secondary optic axes, lines of single ray velocity or optic biradials.

In the field of liquid crystals the D phase is optically isotropic[46], whilst most nematics are uniaxial in nature. An example of a biaxial phase would be crystal E, with the smectic C phase being weakly biaxial[47].

2.4.2 *Dielectric Anisotropy*

The dielectric permttivity (ε) of a liquid-crystalline material can be discussed in a similar way to that for the optical anisotropy. The dielectric permittivity can be defined as the relationship of the capacitance (C) of a capacitor, with the material acting as a dielectric, to the corresponding capacitance of a vacuum (C_o), obtained using an identical experimental arrangement. The capacitance (C) is given by the equation

$$C = \varepsilon.C_o$$

where ε is a dimensionless, material specific, permittivity constant (as is the case of the refractive index) and is found to be anisotropic for liquid-crystalline media. The corresponding values, for a dielectrically uniaxial material, are termed $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, and are strongly dependent on the spatial structure of the molecules as well as the degree of order within the phase. The values of the two permittivities depend on both permanent and induced dipoles in the molecular structure, as well as other contributions from the presence of ionic impurities and inhomogenicity of the sample. The difference between $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, $\Delta\varepsilon$, can have a negative or positive value and is highly dependent on the frequency of the applied a.c. field at which the permittivities

are measured[48]. At higher frequencies dielectric loss is seen to occur with a corresponding measured reduction in the permittivity. The value of $\Delta\varepsilon$ is also reduced as the liquid crystal phase approaches its clearing point. As in the case of optical anisotropy, not all materials and liquid crystal phases are uniaxial in terms of their dielectric properties, some have been found to be biaxial in nature[47].

2.4.3 *Visco-elastic Properties*

Solid bodies are usually subjected to restoring forces when moved from their equilibrium state, if their elastic limit is not exceeded. These forces can be described in terms of elasticity, torsion and compression[49]. In an isotropic liquid, however, there is only the isotropic displacement force reacting to a displacement of the molecules. In mesogenic materials one may expect restoring forces related to, but not the same as the restoring forces associated with a solid. These forces are correspondingly smaller in liquid crystals, the elasto-mechanical behaviour being governed by elastic constants. A generalised theory of elasticity in mesogenic materials has not been realised at this point in time. Oseen, however, described the three basic mechanical deformation patterns associated with the nematic phase[50], that were later formalised by Frank[51]. These are illustrated in figure 14, and are known as splay, twist and bend.

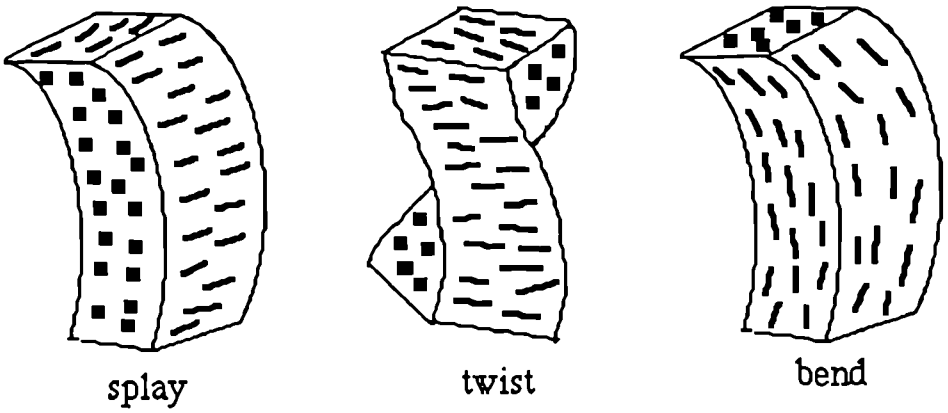


Figure 14. The Elastic Deformations Associated with the Nematic Phase.

It is worthy to note at this point that, as with most crystals, liquid crystals are not usually perfect in their natural state. Most crystals possess defects and this is also true for mesophases[52]. The defects that are found range from dislocations (twist and edge) and grain boundaries found in the more ordered modifications, to huge changes in director field found in the less structured phases, the latter being known as disclinations. Distortions in the director field give rise to *schlieren* when viewed in the polarizing microscope, the type of defect being classified by an S number (S = number of *schlieren* /4)[53]. The textures displayed by different mesophases depend on the type of defects present and so aid in the identification of phases. It should be noted, however, that some defects are common to more than one phase and texture, and that combinations of defects may occur which can be extremely complex in nature[54]. Discontinuities in a fluid structure, such as a liquid crystal are also seen to move quite freely, and in some instances annihilation may take place[54]. Some common defects are illustrated in figure 15.

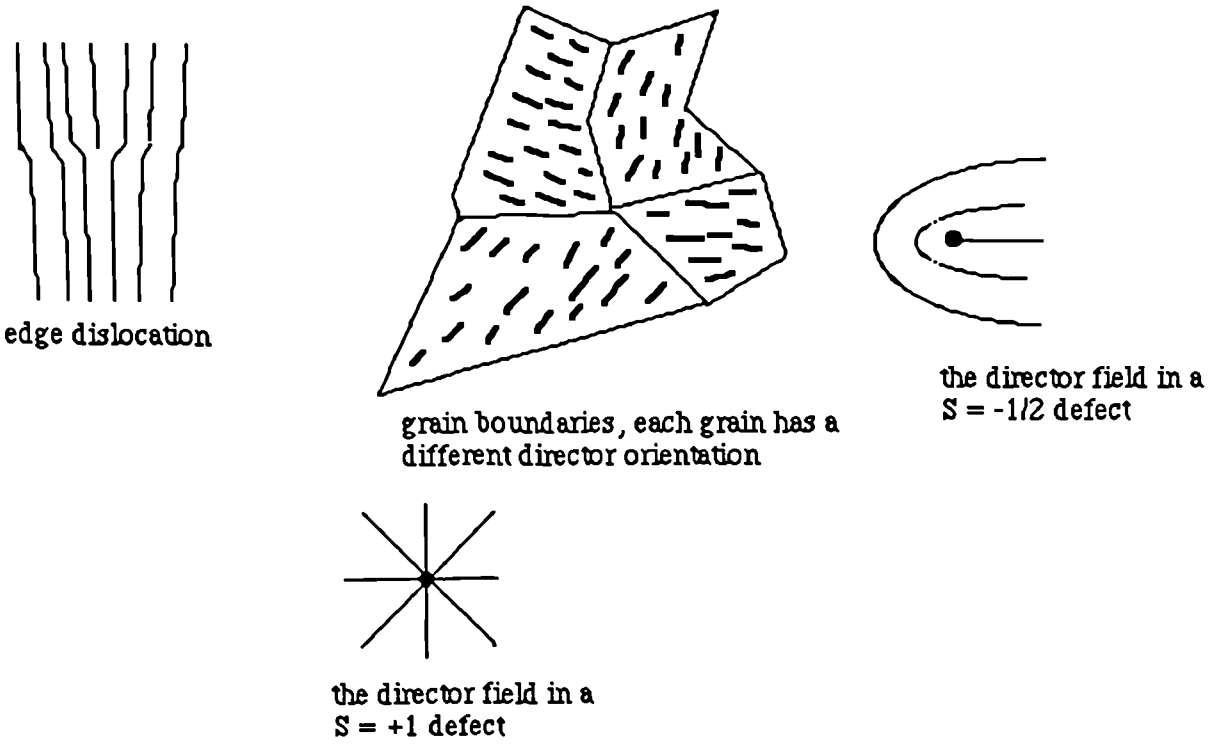


Figure 15. Some Common Defects found in Liquid Crystal Systems.

The textures associated with liquid-crystalline phases are paramorphotic, that is they depend on the nature of the preceding phase. In some special cases, that will be discussed in greater detail in chapter 3, the existence of the mesophase depends on the inclusion of defects in its structure. As a liquid crystal is an elastic medium, the presence of defects depends on a stabilisation by external forces or by an entropy rise which reduces the free energy of the system[52]. In all cases the restoring forces associated with the elastic constants need to be overcome. The elastic constants are a very important criteria in device formulation[55].

Another property that has a major effect on device suitability is the viscosity. The viscosity depends on the order parameters of the system and the fluid motion relative to the ordering. Once again, no generalised theory of viscosity in mesogenic compounds has been realised, research being conducted at a heuristic level[56], the nematic phase being the best understood[57].

2.5 Properties: of Optically Active Mesogenic Materials

Optically active liquid-crystalline phases possess some additional properties to those seen for achiral phases. These will now be discussed.

2.5.1 *Optical Properties*

Helical phases made up of chiral compounds or achiral materials doped with an optically active substance possess properties that are quite different from their achiral counterparts. In the cholesteric phase, for example, the director is not constant, but rotates about an axis in a helical fashion. If we assume the rotation takes place about the Z-axis, then the director rotates uniformly in the XY plane, a 360° rotation corresponding to the pitch of the cholesteric helix. The rotation of the director is illustrated in figure 16.

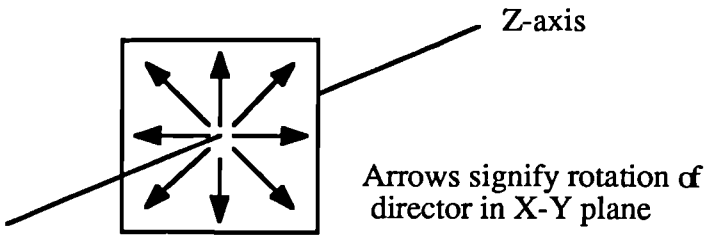


Figure 16. The Rotation of the Director in the Cholesteric Phase.

Consider light that is linearly polarized along the X-axis and that is propagating along the Z-axis. The ray must interact with the director at all angles with respect to the vibration direction. An analogous situation is found for light that is polarized along the Y-axis, and any axis described in the X-Y plane. This means that plane polarized light will propagate along the Z-axis at a rate that is independent of it's polarization direction. This is an entirely different situation than that encountered with the nematic phase where phase changes usually occur due to the anisotropy of the director orientation. Thus, in the cholesteric phase the ordinary and extraordinary rays travel at the same velocity along the Z-axis, i.e., there is no difference in refractive index for linearly polarized light ($\Delta n = 0$). This, however, is not the case for light that is circularly polarized. The value of the refractive index for left-handed circularly polarized light is different to that for right-handed circularly polarized light. Each value depends on whether the phase itself exhibits a right-handed or left-handed helix and also on the wavelength of the incident light. Helical phases can be said to exhibit circular birefringence[58]. This means that one of the polarizations will advance through the medium at a greater velocity than the other, so creating a phase difference. If light, linearly polarized along the Y-axis enters a cholesteric liquid crystal the electric fields for the right-handed and left-handed components continue to rotate, but because they travel at different velocities, one advances ahead of the other. If it is assumed that the left-handed component is the slowest, at any time after entering the medium the right-handed component will be ahead, that is the vector field will be at a more advanced angle. On adding the two fields, what emerges is linearly polarized light at an angle to that at which it entered the material. This is

illustrated in figure 17. The degree to which the light is turned is known as the optical activity of the phase; typically values can be as high as 300° mm^{-1}.

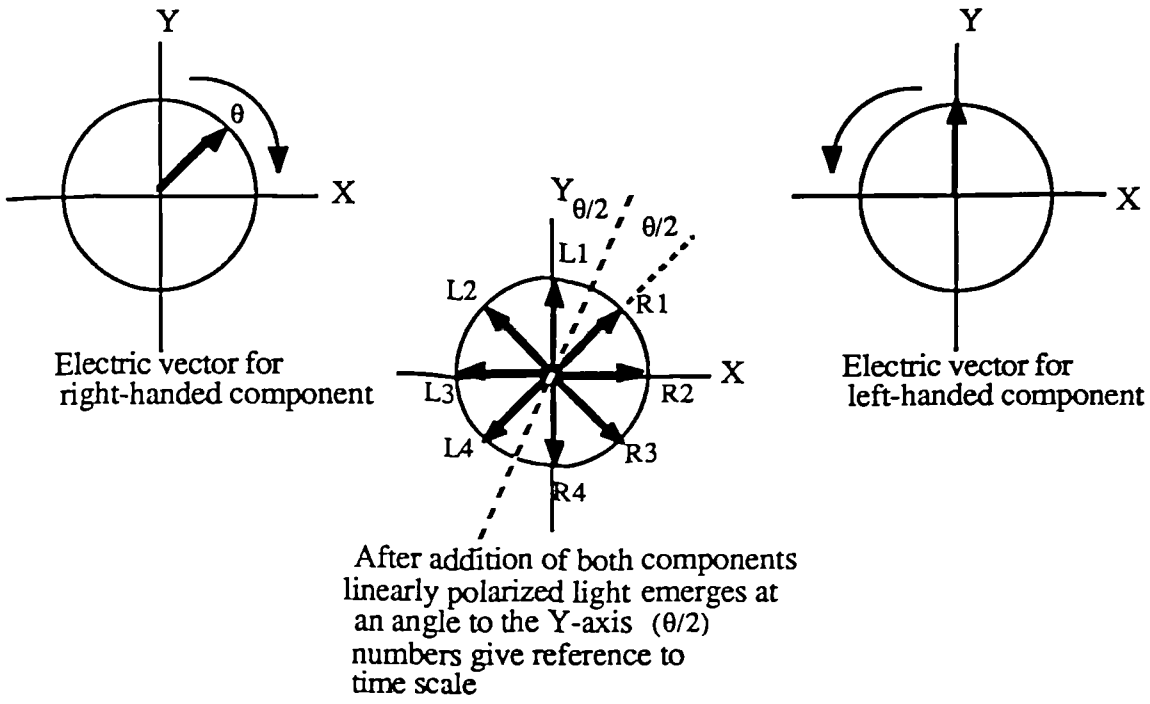


Figure 17. Circularly Polarized Light and Helical Phases.

Another property of helical phases is that of selective reflection of light. If the pitch of the material is equal to half the wavelength of the incident light, then constructive interference occurs where a large proportion of reflected rays are in phase. If white light is incident on the material, then most of it will be transmitted, except for a small wavelength range that is approximately equal to the pitch length. If this wavelength falls in the visible region then the material will appear coloured. When the reflected ray is analysed it is found to be either left- or right-handed circularly polarized monochromatic light, indicating that only one polarization is reflected depending on the helical twist sense of the material. The wavelength of the reflected light is specific for a given pitch. The fact that the pitch of the material can be extremely sensitive to temperature leads to a property known as thermochromism that has been utilised in liquid crystal devices[59]. The fact that only one polarization is reflected can have a dramatic effect on the optical activity of the sample. For thick samples and a suitable wavelength of light, one polarization is totally reflected whilst the other

passes through the material. For wavelengths near this value, however, the refractive index for the polarization that is reflected changes abruptly from a value much smaller than the index associated with the other polarization to one much larger. Since the sign of the optical activity depends on which index is larger, it inverts quite abruptly at this wavelength. Also the size of the optical activity is dependent on the difference between the values of each index, causing a very large change in the optical activity at a specified wavelength, values of 10,000° mm^{-1} are not uncommon. This effect, which is analogous to the Cotton effect for chiral molecules[14], is represented in figure 18, and is said to occur when the Mauguin limit[60] is reached.

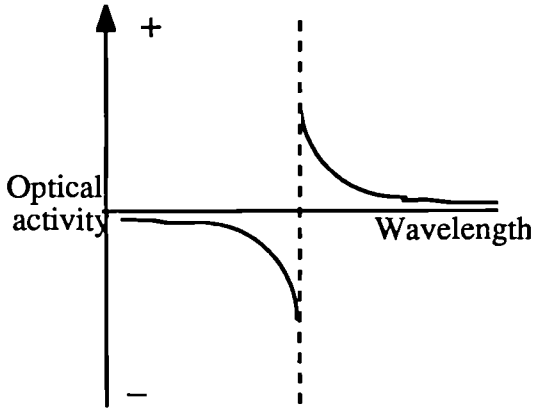


Figure 18. Sign Reversal at the Mauguin Limit in a Cholesteric Phase.

When a nematic liquid crystal is viewed between crossed polarizers the sample appears bright as the linearly polarized ray is converted into elliptically polarized light on passing through the sample, hence, some light will be transmitted by the analyser. The linear birefringence is somewhat wavelength dependent and so colours from one end of the spectrum may appear preferentially to others. Linearly polarized light passing through a sample of cholesteric material has the polarization axis rotated to some degree. The larger the rotation the brighter the sample will appear. As mentioned earlier wavelengths that approximate to the pitch of the material are rotated the most; thus the light that passes through the analyser is of a specific colour. Constructive interference is also found when light propagates at an angle to the helical axis of the material, the light must satisfy the Bragg condition to be reflected,

however, and this will occur at different wavelengths for different incident angles. The colour of the material is therefore found to be very dependent on viewing angle[61].

Bragg scattering of electromagnetic radiation that has a much shorter wavelength, i.e., x-rays, is used in structure determination experiments both in the solid state, and for liquid-crystalline materials. X-rays, however, are not reflected by the helical pitch of a cholesteric or chiral smectic C* material as the pitch is invariably much greater than the wavelength of the incident radiation. In smectic materials, however, the layer spacings are approximately equal to a molecular length and so scattering occurs, as this distance approximates to the desired wavelength.

One final optical property associated with the more fluid liquid crystal phases is the fact that they scatter light. This is due to variations in director field caused by molecular vibrations. A ray of light entering the medium will interact with a constantly shifting electronic field and so refraction and reflection may occur in all directions.

2.5.2 *The Ferroelectric Effect*

The ferroelectric effect is associated with all tilted phases that are composed of or doped with optically active material. Since this effect was first noted in the solid state, it's discovery and occurrence in crystalline materials will be reviewed in the first instance.

2.5.2.1 *Ferroelectricity in the Solid State*

The polarization of a normal dielectric material by the application of an applied field is found to be proportional to the magnitude of the applied field. Anderson, however, found a marked departure from this behaviour in his studies of the dielectric properties of Rochelle salt[62]. Valasek on further investigation of the phenomenon, noted that a hysteresis was observed when he plotted some experimental results on

how the unit charge varied with applied field, when Rochelle salt was used as the dielectric material in a condenser[63]. He proposed that the hysteresis observed was analogous to the hysteresis found in ferromagnetism. The curves associated with the hysteresis loop were displaced from zero on the charge axis owing to a natural polarization of the material.

Rochelle salt was found to display this unusual behaviour, which was later to be called ferroelectricity, only within a defined temperature range (-18 to 24 °C). Investigations into how the crystal structure of Rochelle salt varied with temperature revealed that a transition from orthorhombic to monoclinic symmetry occurred at -18 °C, the crystal structure reverting to orthorhombic symmetry again at 24 °C. Thus, ferroelectricity was linked to a reduction in space symmetry in a similar manner to the origin of the piezoelectric and electroclinic effects[64, 65]. In the piezoelectric effect, changes in the symmetry in the parent crystal are achieved through mechanical stress. In a ferroelectric material the reduction in symmetry results because of a phase transition or indeed may drive the phase transition in the case of intrinsic ferroelectrics, such as Rochelle salt.

If the symmetry elements of an orthorhombic and monoclinic crystal are now considered it becomes evident that on moving from an orthorhombic to a monoclinic environment the symmetry elements are reduced from a centre of symmetry, three mirror planes of symmetry and three two-fold axes of symmetry (symmetry class D_{∞}) to a centre of symmetry, a single mirror plane and a single two-fold axis of rotation (symmetry class C_{2h}). The symmetry elements are further reduced to a single two-fold axis of rotation (symmetry class C_2) if a structural element is introduced which breaks the symmetry further, i.e., removes the mirror symmetry. The introduction of a chiral centre or the superimposition of a dipole, where the dipole lies along the C_2 axis, could have this effect. Figure 19 details the symmetry elements associated with both orthorhombic and monoclinic unit cells. The material will therefore possess a

polarization as the dipole associated with the C_2 axis is not cancelled out with equal and opposite dipoles, as would be expected in an environment of higher symmetry.

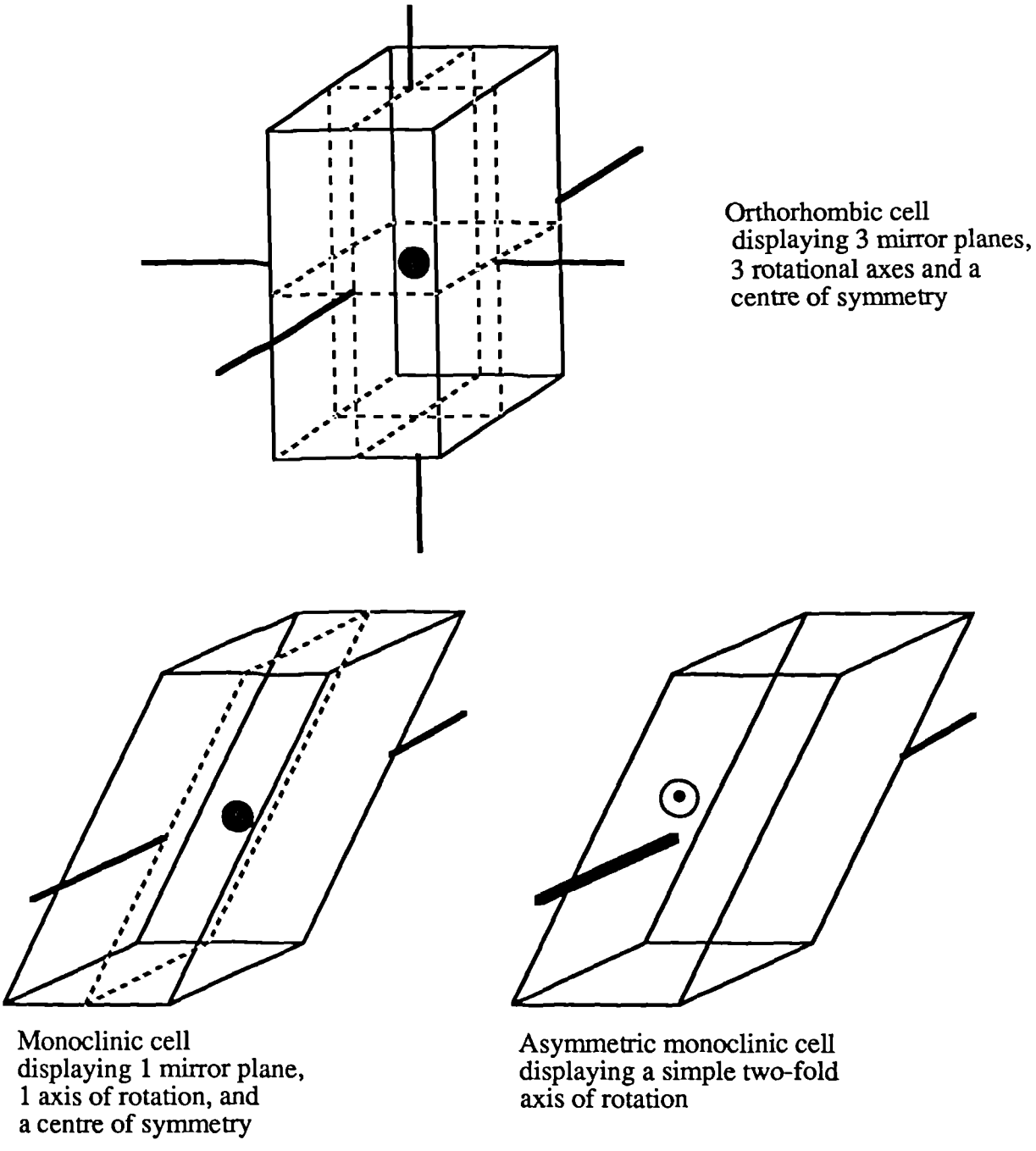


Figure 19. The Symmetry Elements Associated with Orthorhombic, Monoclinic and Asymmetric Monoclinic Unit Cells.

The hysteresis observed in the dielectric properties of Rochelle salt will be considered in the first instance for a polydomain sample where alignment of domains is not

present, so that in the bulk sample the polarization is effectively zero. This is detailed in figure 20.

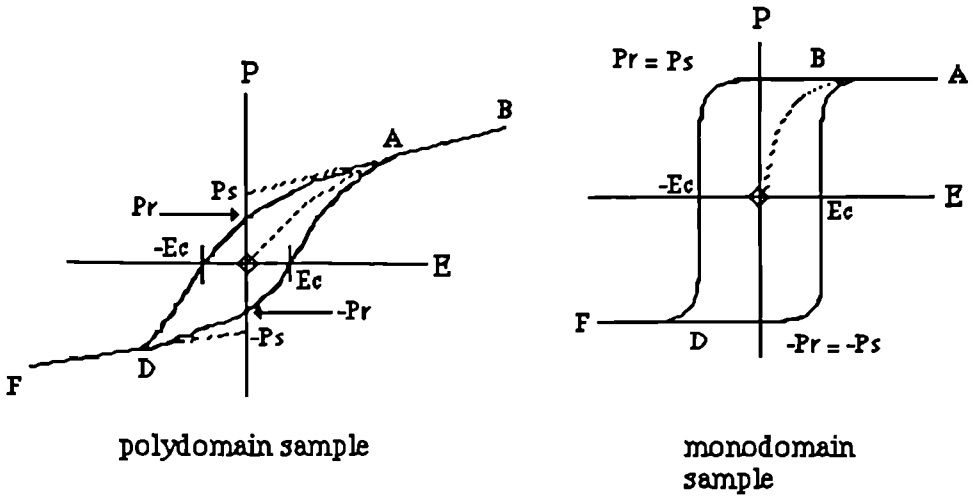


Figure 20. Hysteresis Loops for a Polydomain and Monodomain Ferroelectric.

When an electric field is applied to a polydomain ferroelectric material that has unaligned domains, the polarization of the sample increases along O-A (see figure 20). The polarization in the domains that are already aligned with the field will enlarge, whereas the domains where the polarization opposes the field will tend to reverse their polarization. When A is reached, further polarization is due to the normal dielectric properties, and at this point the polarization rises linearly with applied field. When the applied field is removed the polarization drops due to domain relaxation, some polarization, however, remains and this is known as the residual polarization (Pr)[66]. The residual polarization is equal to the spontaneous polarization in the absence of relaxation processes.

As the applied field is reversed, the domains begin to align as before, but in the opposite direction; the polarization being reduced until it becomes zero at a certain field strength (Ec)[66], which is termed the coercive field. Increasing the field in the negative sense leads to point D that is analogous to point A for a positive field. Removal of the field leads to decay, until the value of the residual polarization is reached (-Pr). For a ferroelectric material that carries no natural charge the residual polarizations in both negative and positive directions are equal, and the extrapolation

of D-F gives the value of the residual polarization in a negative direction (-Ps). Increasing the field in the positive sense leads to the coercive field strength (Ec) and a further increase completes the loop at point A.

For a single domain sample or an aligned multi-domain sample the loop becomes almost rectangular, as domain relaxation does not occur and Pr reaches it's limiting value, Ps. Both polarization states should be equally stable and so bistability is achieved[43].

2.5.2.2 *Ferroelectricity in Liquid Crystals*

Meyer[67] was the first person to compare the environmental space symmetry arguments for chiral and non-chiral tilted smectic phases leading to his prediction that the optically active variants would show ferroelectric properties. In order to present his arguments the chiral smectic C* phase will be used as an example. Previously it was noted that ferroelectricity was brought about by a reduction in space symmetry, the monoclinic structure of Rochelle salt being used as an example. The local structure of the smectic C phase in one layer can also be regarded as being monoclinic in nature. Therefore, Meyer argued that in a non-chiral smectic C phase the symmetry elements would be, a mirror plane perpendicular to the layers in which the molecules lie; a two-fold axis of rotation normal to the mirror plane and parallel to the layers and a centre of symmetry, for the ensemble average. The symmetry construction for an achiral smectic C phase is therefore the same as for a monoclinic cell, C_{2h}. If the phase is composed of or doped with optically active material, the symmetry elements are reduced to a single two-fold axis of rotation as with the asymmetric monoclinic environment, hence, the symmetry classification is C_2. Figure 21 shows a schematic representation of this situation where the asymmetric molecules are depicted as fish[44]. At the eye of each fish a dipole points along the Y-axis, and as the fish prefer to be oriented as shown, a polar two-fold axis results. The

tilt angle of the molecules with respect to the layer planes is given by θ, the director by n.

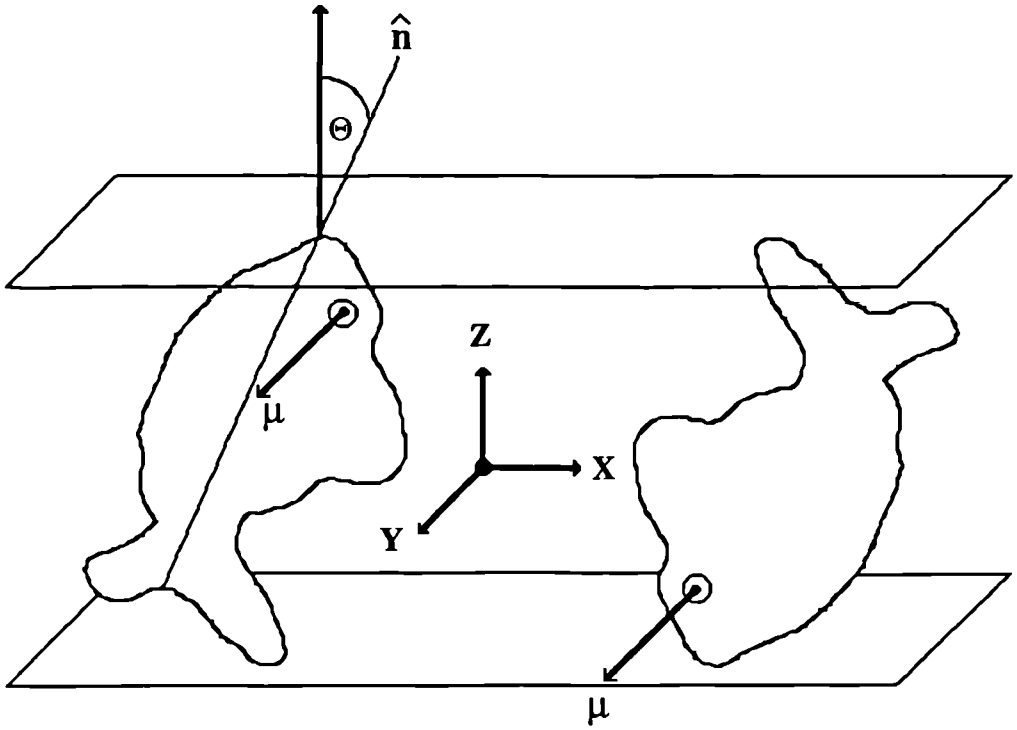


Figure 21. The Origin of the Ferroelectric Effect.

Therefore, for a bulk specimen of a ferroelectric liquid crystal we find a spontaneous polarization produced along the C_2 axis of the phase. Furthermore, for a molecule tilted back into the page as is shown in figure 22, lateral dipoles can be oriented in one of two ways relative to the C_2 axis, in an unpoled state. This in effect makes the C_2 axis polar. Consequently, a material may have one of two directions associated with the polarization, i.e., it can have either a negative or a positive spontaneous polarization. An illustration of this is given in figure 22.

For a molecule which is tilted back into the page, when the negative end of the lateral dipole lies to the right of the vertical plane containing the tilt axis, the material is said to have a positive spontaneous polarization (Ps+). For the reverse situation it is said to have a negative spontaneous polarization (Ps-)[68]. This polarization in a bulk sample, however, is normally zero due to the gradual spiralling tilt of the molecules on going from layer to layer. Therefore the phase is in a sense helielectric[67] and not a

true ferroelectric. This helical arrangement can, however, be suppressed by surface stabilisation techniques[69], the application of an electric or magnetic field[70], or by shear alignment[71]. The surface stabilisation method is utilised in the surface stabilised ferroelectric liquid crystal display device (SSFLCD)[43].

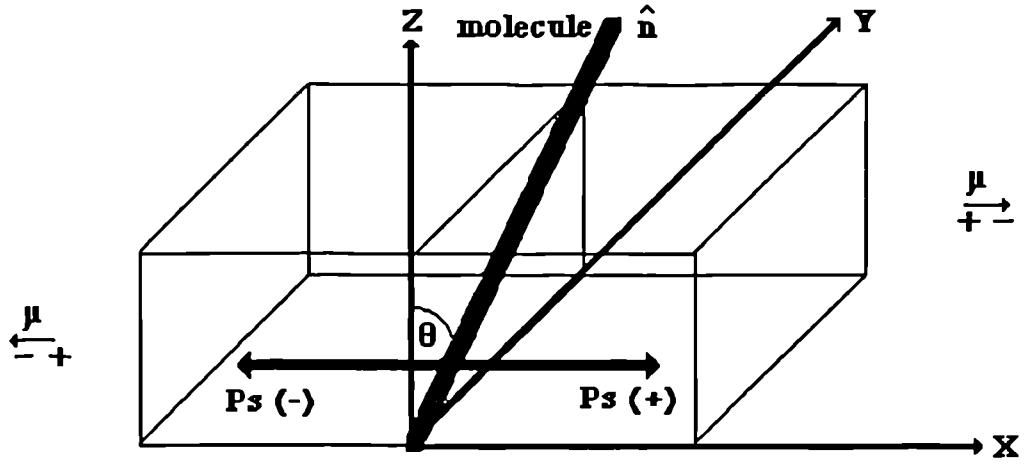


Figure 22. The Polarization Direction in the Ferroelectric Smectic C* Phase.

The magnitude of the polarization is found to vary across the chiral smectic C* phase, initially rising quite steeply on cooling from a higher phase and then either saturating or continuing to rise, but with a reduced steepness. On cooling molecular rotations and fluctuations will be reduced and this along with the increase in tilt angle that the molecules experience is thought to contribute to the increased polarization. There are, however, exceptions to this where the polarization is seen to initially increase and then decrease rapidly, passing through the point of zero polarization and then increasing again, but with the opposite sign[72].

Meyer indicated that two effects influenced the magnitude of the spontaneous polarization, firstly, the ability of the molecule to couple to it's monoclinic environment and, secondly, the coupling of the chiral centre of the molecule to lateral dipoles within the molecule.

In order to explain the first effect a model of the chiral smectic C* phase must be considered in which the molecules are free to rotate, yet some rotational states will be preferred, that is of lower energy[73]. Experiments suggest that either a high or low tilt configuration of the aromatic core within the layer structure usually occurs[74], depending on whether the smectic C* phase was formed from an overlying cholesteric phase (which usually gives a high tilt configuration), or smectic A phase (which usually gives a low tilt configuration). Figure 23 depicts the high and low tilt states that the molecules may adopt in the smectic C or smectic C* layer.

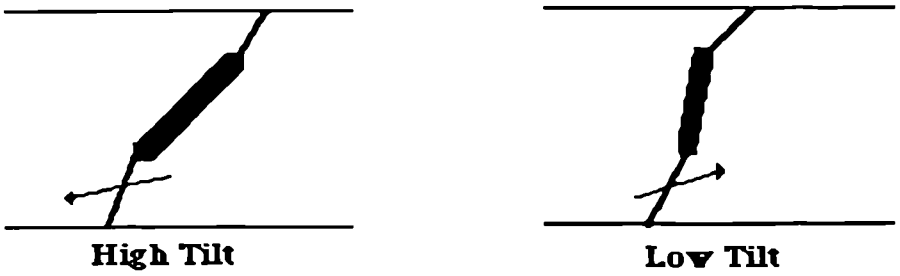


Figure 23. High and Low Tilt States of the Molecules in a Smectic C or Smectic C* Phase.

The predominant conformation of the alkyl chains associated with the molecule is in most instances thought to be all *trans*[75]. Thus, the orientation of the lateral dipole associated with the chiral centre is essentially fixed, with respect to the long-molecular axis, and this dipole is thought to be the major contributor to the spontaneous polarization. Rotation of the molecules about their long-molecular axes will, however, lead to a polarization of opposite sign, as may a conversion between the two tilt states. The direction and value of the spontaneous polarization will therefore depend on the relative stability of all rotational species (rotamers), and the energy barrier between rotations. It is usually found that the high tilt state restricts rotation to a greater degree than the low tilt state, and so materials that adopt this configuration tend to have higher spontaneous polarization values. The shape of the energy curve associated with molecular rotations will, of course, be temperature

dependent and therefore the degree of rotation of the molecules and, hence, the bulk polarization of the sample will also depend on temperature. Meyer termed this effect the coupling of the molecule to the molecular environment.

The second effect is the coupling of the chiral centre to the lateral dipole of the molecule. The lateral dipole in many liquid crystal molecules is an ester group, and the chiral moieties used are numerous, but for the sake of discussion let's say that a lateral methyl group is located at the chiral centre. If the coupling between the methyl group and the ester linkage is strong, which is usually the case when the two groups are in close proximity, then the value for the spontaneous polarization will be large. This effect is illustrated when the values of the spontaneous polarization for the two esters illustrated in figure 24 are evaluated[76].

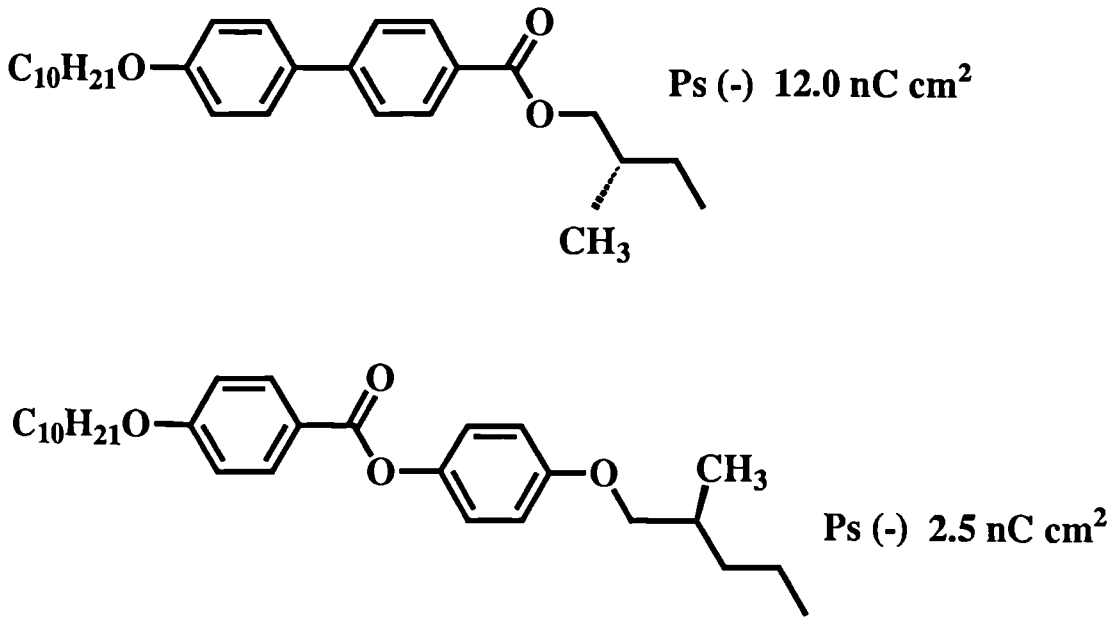


Figure 24. The Effect of Lateral Dipole/Chiral Centre Coupling on the Spontaneous Polarization in the Smectic C* Phase.

2.5.3 *The Electroclinic Effect*

The electroclinic effect[65] is related to the ferroelectric effect in that it also occurs as a result of a reduction in symmetry. The electroclinic effect, however, is generally found in orthogonal smectic phases and in certain circumstances, the nematic phase[77].

In order to obtain electroclinic switching a conducting cell is filled with material which is then cooled into an orthogonal phase, usually a smectic A phase just above the transition to a smectic C* phase, and a field is applied parallel to the smectic layers. The electric field breaks the symmetry of the phase and causes a tilting of the molecules relative to the layer normal.

The electroclinic phenomenon in liquid crystals was first investigated by Meyer and Garoff[65], who presented the following symmetry argument. In the smectic A phase the molecules are arranged in layers with their long molecular axes on average lying perpendicular to the layer planes. There are two symmetry axes of rotation perpendicular to the molecules, one parallel, 3 mirror planes and a centre of symmetry, which gives an orthorhombic unit cell as described in section 2.5.2. When an electric field is applied parallel to the smectic layers, however, the symmetry is reduced, giving a monoclinic environment. If the molecules that constitute the phase are achiral then the symmetry elements that still persist are a single 2-fold axis of rotation parallel to the applied field, a mirror plane that lies parallel to the applied field and the director, and a centre of symmetry, giving a symmetric monoclinic environment. If chiral molecules are present, however, a single 2-fold axis of rotation remains giving an asymmetric monoclinic environment and an induced molecular tilt occurs. The magnitude of this induced tilt is seen to vary linearly with the applied electric field, but is most prominent at a temperature just above the smectic A to smectic C* transition. At higher temperatures a much larger voltage is required to produce a measurable effect[78].

Furthermore, the polarization induced by the applied electric field in the electroclinic effect can be connected by two possible directions in the angular deflection of the molecular axis. If the deflection which is regarded as a vector (right-hand rule) has the same sign as the applied field then the electroclinic effect is said to be positive. If the signs are opposite than the electroclinic effect is said to be negative[79].

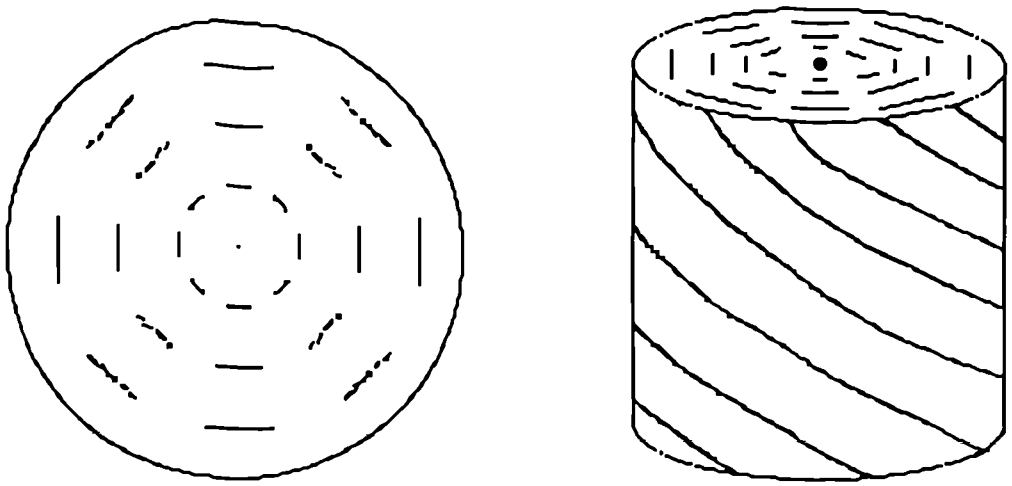
3. INTRODUCTION TO FRUSTRATED MEDIA AND DISLOCATION PHASES.

3.1 Dislocation Phases.

Dislocation phases are so called because their very existence depends on the inclusion of defects in the structure of the mesophase. As previously mentioned (see section 2.4.3), defects occur in most bulk samples of crystalline and liquid-crystalline materials; however, under normal circumstances the defects seen depend on how the phase was formed, and are stable due to a reduction in the free energy associated with the system; but are not a prerequisite to phase formation. In dislocation phases, which are an example of frustrated media[80], defects must be present to relieve competition that is generated between local interactions which produce an inhomogeneous structure, on a scale much larger than the molecular length.

3.1.1 *Blue Phases*

Blue phases (there are three types labelled BPI, BPII and BPIII), named after their visual appearance, often appear in a narrow temperature range between the cholesteric phase and the isotropic liquid, in materials that have a cholesteric phase with a relatively short pitch (0.3 μm). Unlike in the cholesteric phase where the director transcribes a single helix, the blue phases possess ordering that is often referred to as a 'double twist' structure. In this structure the director rotates about every axis perpendicular to a line drawn through the centre of a tube. This is depicted in figure 25 (25a shows a cross-sectional view of a 'double twist' cylinder, in the centre the director is parallel to the cylinder axis. On moving outwards from the centre of the cylinder the director is twisted. Figure 25b shows a perspective view of a 'double twist' cylinder where the director has rotated by 45° on moving from the centre to the outside edge).



a) A 'double twist' cylinder (plan view)

b) A 'double twist' cylinder

Figure 25. The Blue Phase 'Double Twist' Cylinder.

This 'double twist' structure in fact, is a more stable arrangement of the molecules than that which occurs for single twist, but only in cylinders below a certain size. Since the size of the cylinder depends on the pitch of the material, only compounds with short pitches exhibit blue phases. Furthermore, on cooling from the isotropic liquid, the transition from blue phase to cholesteric phase readily occurs as the pitch length increases.

The 'double twist' cylinders, because of their small radii, are found to fill space very efficiently when packed together. The structure shown in figure 25b being far more stable than an equal volume of single twist cholesteric phase. A macroscopic structure can therefore be built up from 'double twist' cylinders, but only if defects are incorporated at regular points between the cylinders. Defects, which in two of the blue phases (BPI and BPII) form a regular cubic array, occur at every point where different director fields meet. The defects tend to destabilise the structure, but not to the extent that a single twist cholesteric would be more energy profitable. The defects are therefore arranged in a cubic lattice, but unlike a regular crystal lattice the molecules are free to move, and the lattice points are occupied by disclinations. As with regular crystals, however, blue phase single crystals can be grown and have

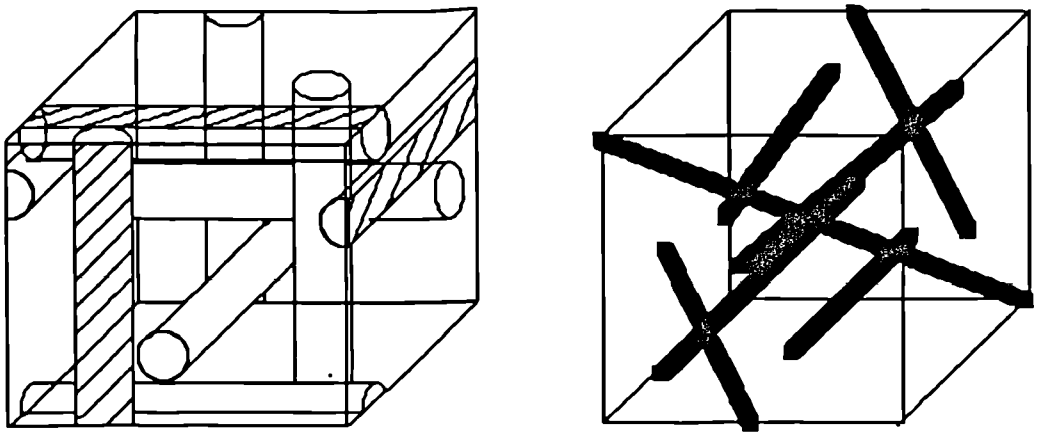
provided much structural information[81]. On transition between blue phases defects can occur in the lattice, similar to those that occur for crystal to crystal transitions, these defects being additional to the ones stabilising the structure. The blue phases, due to their lattice parameters, are also found to give Bragg-like scattering of light in the same way that a crystal interacts with electromagnetic radiation in the X-ray region, this giving rise to their distinctive colours (which unlike the name suggests is not always blue).

As previously mentioned there are three blue phases that are well documented, a fourth has been reported recently[82]. The first two blue phases, BPI and BPII, differ in the way that the 'double twist' cylinders are packed together, and therefore in the structure of the lattice that is formed by the array of defects. The defects associated with BPI form a body centred cubic lattice (O^{8-} symmetry), whereas the defects associated with BPII form a simple cubic lattice (O^2 symmetry). These structures are illustrated in figure 26. The orientation of the director is the same for both cylinders at the point where two double-twist cylinders touch. Defects are only present in regions where three cylinders meet.

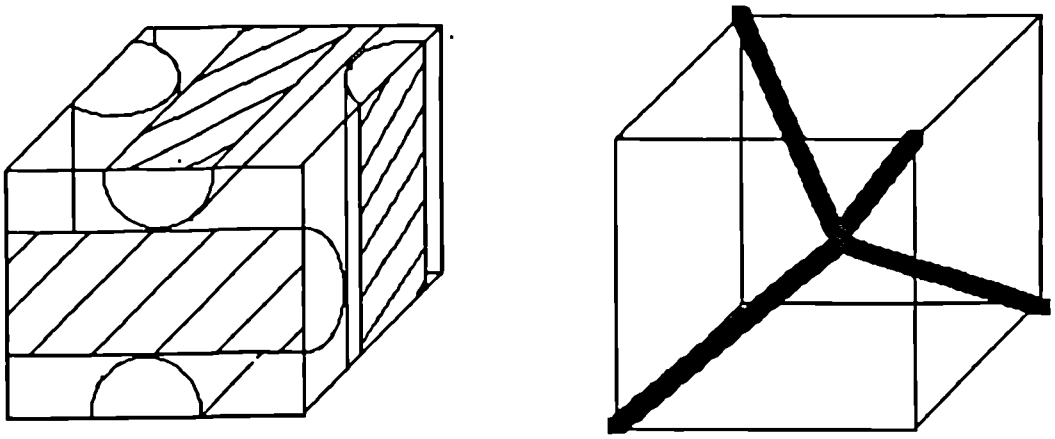
The textures of BPI and BPII are similar in nature, both phases appearing as platelets when viewed in the polarizing microscope. The cubic symmetry is evident in some instances in the shape of platelets. BPI, however, differs from BPII in that the platelets are cross-hatched, the striations occurring at the transition from BPII to BPI. The texture associated with BPII is shown in plate 11, whilst that of BP I is depicted in plate 12.

The third, and most enigmatic, blue phase (BPIII) is the least understood, its structure being unclear at this point in time. BPIII does not appear to have the same regular cubic lattice of defects as seen in BPI or BPII, although some of it's properties are similar to those observed for the other two blue phases. It appears in the polarizing

microscope as a very faint, amorphous bluey-gray phase, and because of this it is also known as the blue fog or fog phase.



26a) The arrangement of 'double twist' tubes (left), and disclination lines (right) for a unit cell of BPI (the local directors are shown as lines for some tubes).



26b) The arrangement of 'double twist' tubes (left), and disclination lines (right) for a unit cell of BPII (the local directors are shown as lines for some tubes).

Figure 26. The Arrangement of "Double Twist' Tubes and Disclination Lines in BPI and BPII.

Optically, blue phase III selectively reflects circularly polarized light, with a broader peak at a different wavelength than the other two blue phases[83]. It's rotatory power is intermediate between that of the other blue phases, and the isotropic liquid. Thermodynamically, blue phase III is closer to blue phase II, as the latent heat of transition between the two blue phases is much smaller than that obtained for the

clearing point[84], yet the texture it exhibits appears to be much closer to that of the isotropic liquid.

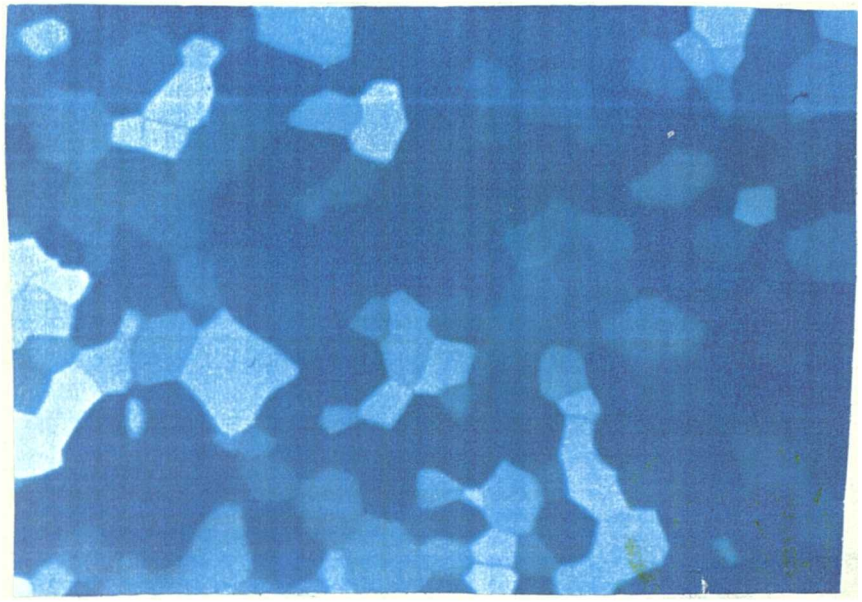


Plate 11. The Platelet Texture of the Blue Phase II Displayed by (+)-4'-n-Hexyloxy-4-biphenylyl 4-(2'-methylbutyl)benzoate.

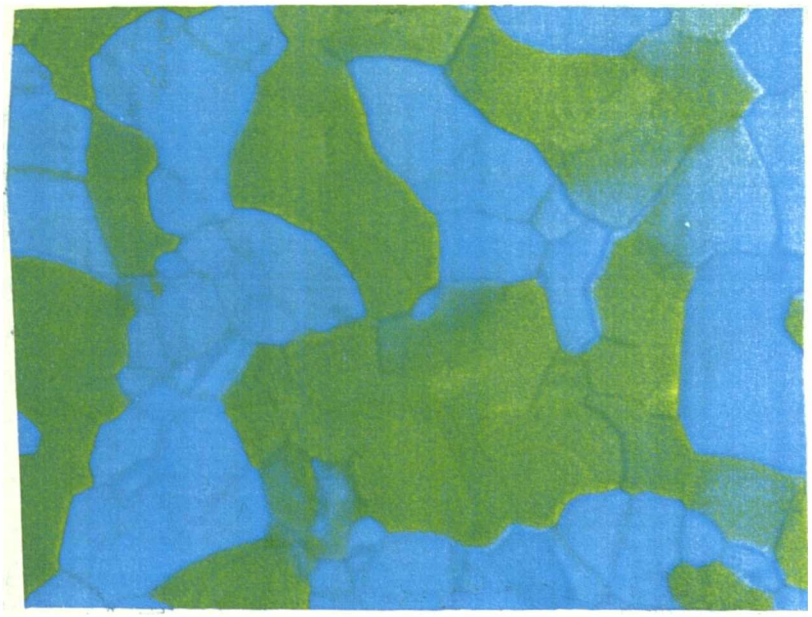


Plate 12. The Cross-Hatched Platelet Texture of the Blue Phase I Displayed by (+)-4'-n-Hexyloxy-4-biphenylyl 4-(2'-methylbutyl)benzoate.

Several models for the structure of blue phase III have been suggested. The first, as depicted in figure 27, is a spaghetti-like tangle of 'double twist' tubes, the ordering of the molecules decreasing to zero at the extremity of each tube. Theoretical calculations have shown this structure, which is the analogue of an amorphous solid with a random dispersion of lattice points, to be stable[85].

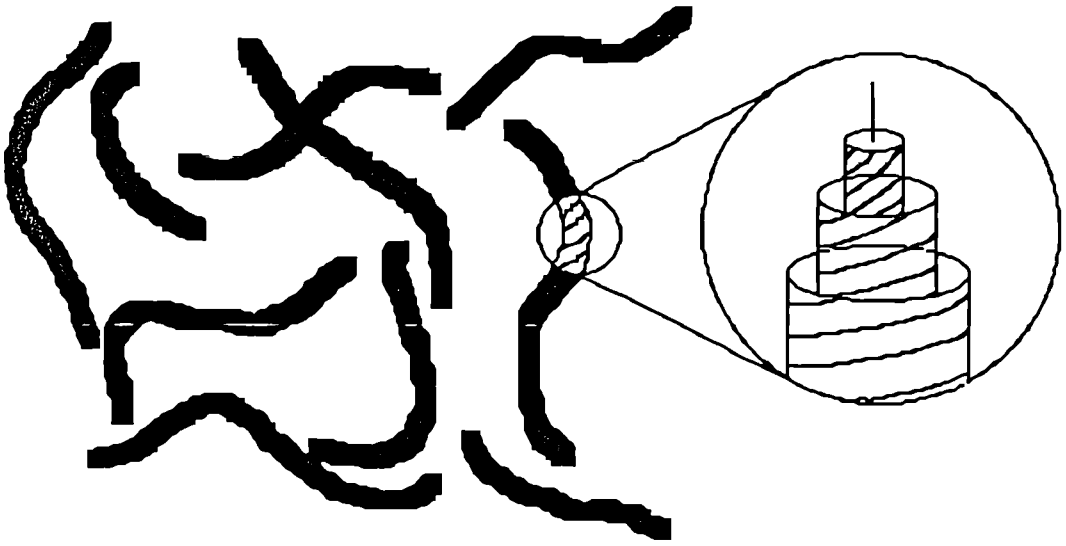


Figure 27. The Double Twist Model of Blue Phase III.

The second model is termed the cubic domain model[86] and consists of small, randomly oriented regions having cubic symmetry, similar to that observed for blue phase I and blue phase II. Both simple cubic and body-centred cubic structures have been suggested, with the domain size (correlated region) having a diameter of the order of a few pitch lengths This model is depicted in figure 28.

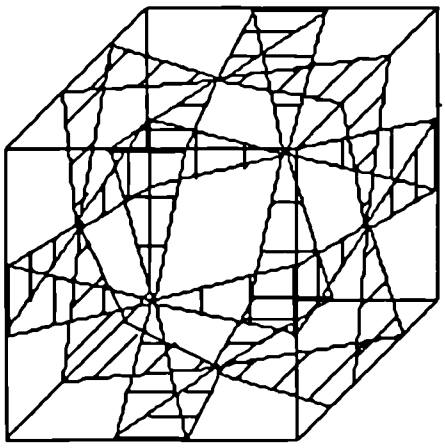


Figure 28. The Cubic Domain Model of Blue Phase III.

The third and last model of blue phase III is termed the quasicrystal model[87]. Here the structure has long range quasicrystalline order, with reciprocal lattice vectors that form a regular icosahedron, as shown in figure 29.

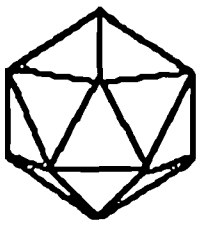


Figure 29. The Possible Icosahedral Symmetry of Blue Phase III.

All of the proposed models can be used to explain the principle features of blue phase III, but further experimentation remains necessary. Firstly, it is expected that for the cubic domain and quasicrystal models, the selective reflections from higher order Bragg planes would be observed. Experimentally, however, this is not the case[88]. Electrical studies, with materials that have a negative dielectric anisotropy, have revealed a sharpening of the reflection band associated with the phase. This is interpreted as a thickening of the aligned sample boundary, data being consistent only with the 'double twist' model[89].

Our understanding of blue phase III, therefore, is far from complete. A tentative picture being one of small domains possessing some degree of correlation. Further work, however, is necessary.

3.1.2 *The Twisted Smectic A* Phase (TGB A*)*

The twisted smectic A* or twist grain boundary phase (TGB) is another example of a frustrated liquid crystal medium. The twisted smectic A* (which shall henceforth be termed the TGB A* phase) was theoretically predicted by Renn and Lubensky[90] to occur at the transition from the cholesteric to the smectic A phase, where the helical cholesteric phase is transformed into the non-helical layered smectic A phase. The TGB state was predicted to mediate this transition under certain circumstances. The

structure of the TGB A* phase is one where the helical ordering associated with the cholesteric phase (helical axis normal to the long molecular axes), competes with the desire of the molecules to form a lamellar configuration. These two structures are incompatible and cannot co-exist, without the inclusion of defects. The structure of the TGB A* phase is therefore one where blocks of normal A phase are rotated with respect to one another, thereby producing a macroscopic helix in the plane of the layers. In between the blocks of A phase are screw dislocations or isotropic-like regions, which allow two individual blocks to be set at a slight angle to one another. The dislocations themselves are periodic in nature, Renn and Lubensky predicted the formation of a lattice of grain boundaries; hence, they called the phase a twist grain boundary (TGB) phase. The structure of the TGB A* phase is illustrated in figure 30.

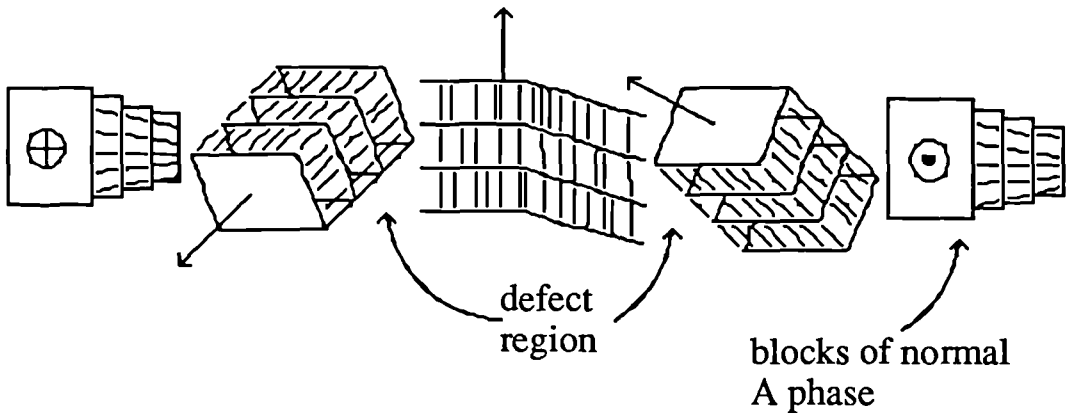
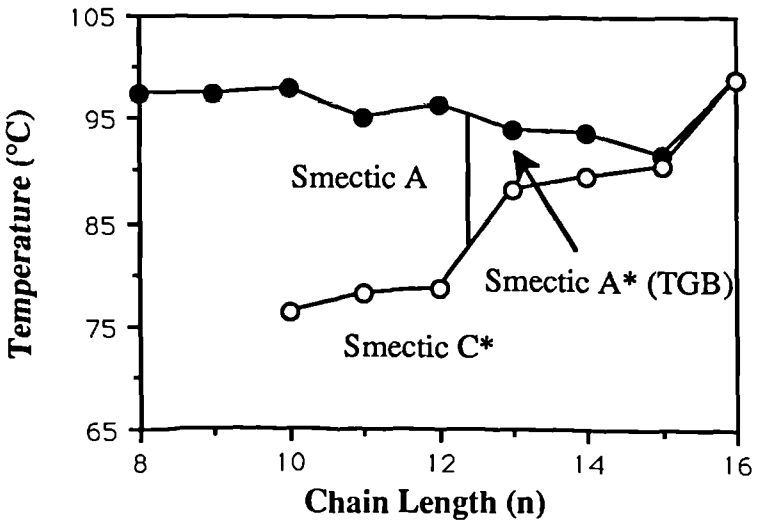


Figure 30. A Schematic Representation of the TGB A* Phase.

The first example of this novel liquid-crystalline phase was found in certain members of a series of propiolate esters, that possessed a high degree of molecular chirality[91]. The phase was observed on cooling from the isotropic liquid, further cooling yielding transitions to a smectic C* phase, followed by ferrielectric[92] and antiferroelectric phases[93]. The transition temperatures for these materials close to the clearing point are illustrated in figure 31, along with their molecular structure.

The helical pitch in the TGB A* phase for the propiolate esters, was determined by optical studies to be approximately 0.38 to 0.63 μm, leading to the selective reflection

of light. X-ray studies suggested that the smectic block size (in the plane of the layers) is about 185 Å. At present the exact nature of the defects between the blocks remains somewhat uncertain, as high resolution X-ray studies have been unsuccessful at elucidating the exact structure. Recent, freeze-fracture and light-scattering studies, however, do suggest strongly that a lattice of defects (screw-dislocations) is present[94].



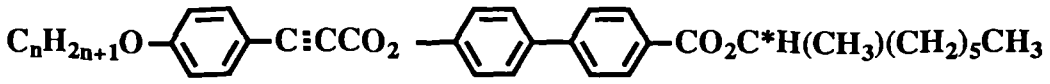


Figure 31. The Structure and Clearing Point Transitions of the First Series of Materials to be Reported as Exhibiting a Smectic A* (TGB) Phase.

Prior to Renn and Lubensky's work, de Gennes[95] had predicted that dislocation phases may occur at the nematic to smectic A transition, when he attempted to unify the theory of phase transitions in superconducting materials and in liquid crystals. The superconductor analogy will be dealt with fully in the next section (3.2), but essentially de Gennes predicted that in a similar way to how magnetic flux penetrates a type II superconductor *via* a lattice of vortices, twist and bend distortions could be incorporated into a layered smectic A structure, *via* the presence of an array of screw or edge dislocations. Thus de Gennes suggested the TGB A* phase, as it is now called, is one liquid-crystalline analogue of the Abrikosov flux phase[96]. It is thought that TGB A* phases are also present in polymeric materials[97], and mixtures[98]. The

theorists are also predicting the presence of TGB phases in the smectic C and chiral smectic C* phases[99], but this has yet to be experimentally proven[100].

3.2 The Superconductor Analogy.

De Gennes[95] was the first person to recognise the physical analogy between transitions that occur in superconducting materials, and those which are seen in liquid-crystalline systems. In order to explain the de Gennes analogy, a brief introduction to some aspects of both type I (soft), and type II (hard) superconductors will now be given.

A superconducting material can carry an electrical current with a zero energy loss (due to resistance), provided that the current density does not exceed a critical value (Jc)[101]. The value of Jc is found to be dependent on both the material, and the temperature at which the experiment is carried out. This type of behaviour is seen for a number of pure metals, mixtures and ceramics, but is only usually observed at very low temperatures. Another critical factor in determining the behaviour of a superconductor is the presence of impurities in the material. Non-magnetic impurities are seen to have little effect, but the presence of magnetic impurities can totally destroy the superconducting state. The same can be said for the application of a magnetic field, and it is with respect to this point that type I and type II superconductors can be differentiated.

When a superconductor is placed in a magnetic field the lines of magnetic flux are totally excluded (the superconductor acts as a perfectly diamagnetic material), until a critical value of field strength is reached. This is known as the Meissner effect, and is frequently demonstrated by the floating magnet experiment. The behaviour of a type I superconductor in a magnetic field is, however, quite different to that of a type II superconductor, even though the mechanism by which superconductivity occurs[102], and the thermal properties at the superconducting to normal metal transition are the

same. A type I superconductor is seen to exclude magnetic flux completely, until a threshold value (Hc) is reached. At this point superconductivity is suppressed, and the magnetic field penetrates the material completely as with a normal metal. A type II superconductor excludes a magnetic field completely, up to a point (Hc1) (see figure 32). At greater field strengths, however, the field is only partially excluded, but the specimen remains electrically superconducting. At a much higher field strength (Hc2) there is total penetration, and the superconductivity vanishes (an outer surface of the material can sometimes remain superconducting up to a higher field strength (Hc3)). This type of behaviour is illustrated in figure 32, where a plot of magnetization of the material versus the applied magnetic field is shown for typical type I and type II superconductors.

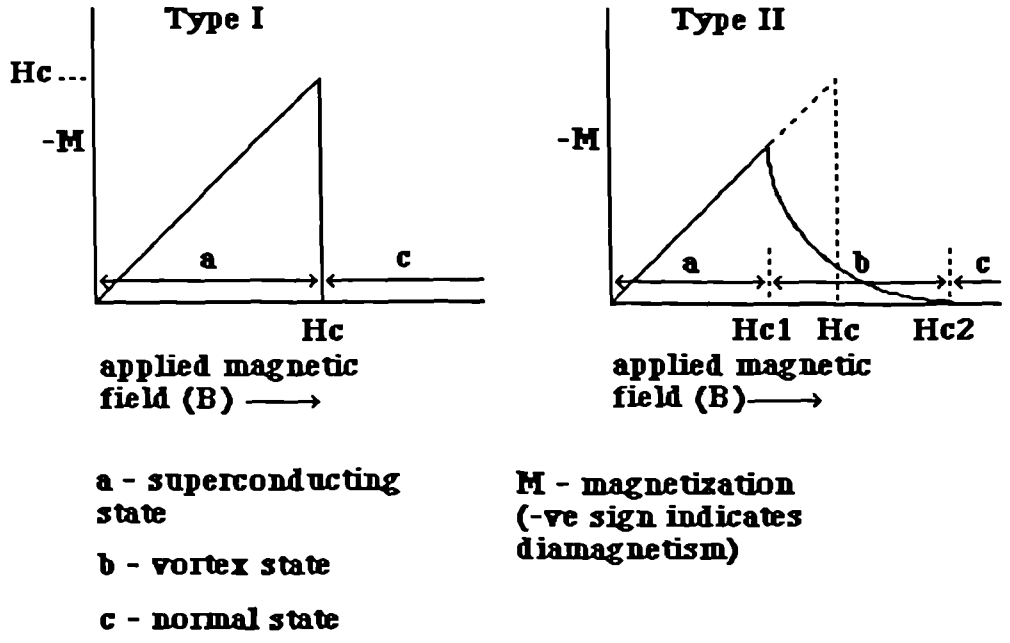


Figure 32. Magnetization versus Applied Magnetic Field for Type I and Type II Superconductors (Bulk Sample).

The type of superconductor (I or II) can be characterised by a ratio known as the Ginsburg parameter (κ)[103], where κ is λ/ε. λ is the London penetration depth, and is a measure of how far a magnetic field will penetrate a superconductor (whether type I, or II), whilst ε is the coherence length, and is a measure of the distance within

which the gap parameter cannot change drastically within a spatially varying magnetic field (a measure of the spatial extent of a transition layer between superconducting and normal metal phases). If κ is found to have a value $< 1\sqrt{2}$, then the material will show type I behaviour, but if κ has a value $> 1\sqrt{2}$, then type II behaviour will be observed. A plot of the variation of the energy gap parameter (ψ), in an applied magnetic field at the normal metal/superconducting metal interface is illustrated in figure 33.

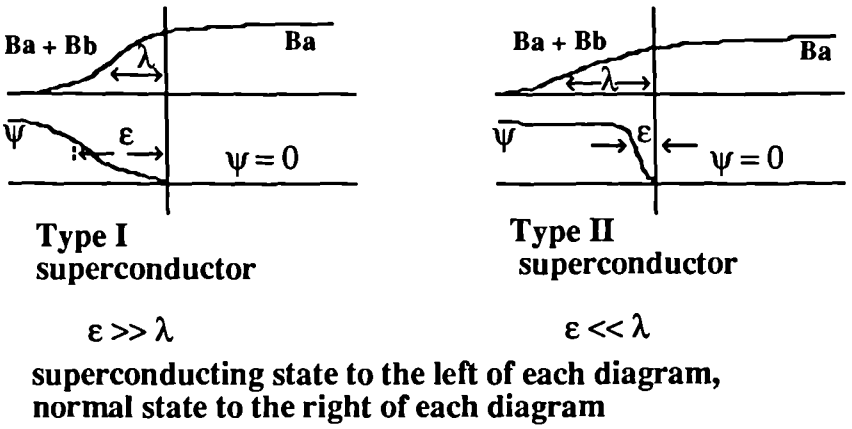


Figure 33. A Plot of Energy Gap Parameter versus Applied Magnetic Field for Type I and II Superconductors.

Due to the fact that type I superconductors are usually pure metals, and type II superconductors are usually alloys, it is sometimes possible to convert a type I to a type II by the addition of other elements to an otherwise pure element[104]. For type II behaviour to occur, however, the energetics of the system must be favourable. At the interface between normal and superconducting metal the surface energy is decreased on the application of a magnetic field, whereas the bulk energy is increased. A thin film superconductor can be penetrated quite easily, but the energy of the film will increase only slowly with increasing field strength. A large field is therefore necessary to destroy superconductivity in thin films (Hc3), but the energy gap and properties remain unchanged and are wholly independent of sample thickness. A thin film therefore may not be a type II superconductor, but does illustrate that superconductivity can occur at high temperatures. The properties of thin films imply

that it may be possible to have a stable superconducting configuration in high magnetic fields. A configuration of thin rods of metal in the normal state, surrounded by superconducting metal, was first proposed by Landau in 1937[105], and later developed by Ginsburg[103] and Abrikosov[96] in the 1950's. In this state an applied magnetic field would penetrate uniformly the thin normal metal regions, with a degree of penetration occurring also in the superconducting areas. The circulation of superconductive currents in vortices throughout the specimen, led to this being described as the vortex state, or flux lattice phase. The state is stable due to a reduction of the surface free energy, at the normal metal to superconducting metal interface. The stability of the vortex state is related to λ an ε in the following manner, $Hc1 = 1/\lambda^2$, and $Hc2 = 1/\varepsilon^2$.

The analogy between the transitions that occur in liquid crystals and those observed in superconductors (in an applied magnetic field) is based on a number of physical similarities. It should be noted that the analogy refers to the smectic A to nematic transition. Both the superconducting state and smectics are examples of ordered phases characterised by an order parameter which in the case of a superconductor is the Cooper pair amplitude (ψ)[102], and in the case of a smectic is the density wave amplitude (ψ')[106]. The Frank director (n) in smectics plays the role of the vector potential (A) in superconductors, and the coupling between ψ' and δn in smectics is identical to the coupling between the gap function and the vector potential in a superconductor. So the nematic phase is seen to correspond to a normal metal, the smectic A phase corresponds to the superconducting state, and a smectic A structure with twist or bend distortions incorporated *via* the presence of an array of screw or edge dislocations, corresponds to the Meissner phase (vortex state). De Gennes predicted that for a second order nematic to smectic A transition, that the transition temperature would be lowered if twist and bend distortions were imposed, and that the Frank coefficients K_{22} and K_{33} would show strong anomalies in the pre-transitional region. He defined two characteristic lengths, the coherence length

(smectic correlation length), ε', which is equivalent to the coherence length in superconductors, and the penetration depth (twist or bend), λ', which is equivalent to the London penetration depth in superconductors. The ratio of these two quantities, the Landau-Ginsburg parameter (κ), is exactly analogous to the situation found in superconductors, with dislocation phases only occurring when $\kappa > 1/\sqrt{2}$, in a similar manner to the flux penetration occurring in type II superconducting materials. The de Gennes analogy was later expanded by Renn and Lubensky to include the cholesteric to smectic A phase transition, leading to the prediction of a lattice of screw dislocations (TGB phase) occurring at the transition point[90].

4. NOMENCLATURE IN OPTICALLY ACTIVE MESOPHASES.

4.1 Nomenclature.

The nomenclature of liquid-crystalline phase types has developed somewhat chronologically; for example, as a new smectic, or crystal mesophase (which were formerly labelled as being smectics) was discovered and characterised it was assigned a label that was essentially the next letter available in the alphabet (e.g., the smectic A phase was discovered before the smectic B phase). However, some of the labels denoting different phases are more descriptive in nature; an example of this being the blue phases which are so called because of their visual appearance being labelled as BP[107], or the cholesteric phase which is called after the parent compound, of the derivative, in which it was first discovered, being labelled Ch (the cholesteric phase is also known as the chiral nematic and can be labelled N*).

Changes over the years have been made to the labelling system in order to improve its technical correctness, for example what was formerly called the smectic E phase (S_E) is now called crystal E or simply the E phase (E), as its degree of order classifies it as being more crystalline than smectoid in nature. The hexatic B phase has also been renamed as smectic B (S_B), as the confusion of having two B phases has now been resolved, as the formerly named smectic B is now classified as crystal B (which in some instances has been referred to as smectic L)[108].

Chirality in mesogenic systems has always been denoted by an asterisk being placed after the label. So, for example, a smectic C phase (S_C) becomes a smectic C* phase (S_C*), when composed of optically active material.

Nomenclature within such a field has, and probably will always cause problems as new modifications and effects are continually being discovered. The potential problems associated with the nomenclature of mesogenic phase types will now be

addressed, with special attention being devoted to the naming of phases that contain optically active material, and in the light of recent discoveries.

4.2 Complications with the Present System.

As previously mentioned, when a liquid crystal phase is composed of, or doped with optically active material an asterisk is added to the label in order to convey this point. So for example a smectic A phase, composed of achiral material is labelled as S_A, whilst the phase containing optically active compound is labelled as S_A*. For the smectic C phase the labels are S_C and S_C* respectively. There is, however, an important difference between these two examples. The chiral smectic C* is itself optically active, with the molecules forming a macroscopic helical structure. The asterisk can, therefore, be used to denote not only the optical activity associated with the molecules, but with the macroscopic structure of the mesophase itself. This, however, is not the case with a smectic A* phase composed of chiral material, as no macroscopic helix is observed. The asterisk, therefore, denotes only the optical activity associated with the constituent molecules. This system works well for the majority of phase types, but becomes more complicated if one considers the twist grain boundary A* phase, which is composed of chiral material and itself exhibits optical activity in the form of a macroscopic helical arrangement of the molecules (see chapter 3). If the TGB phase is simply labelled as A*, then confusion arises as to which type of A phase is being referred to, for example the A phase that displays molecular and *form* optical activity, or the A phase that displays only molecular optical activity. One solution would be to denote the TGB phase with a double asterisk so becoming S_A**. TGB phases, however, are now being predicted to occur in the achiral and chiral smectic C phases, which would necessitate the labelling to be S_C** for the former (molecular and macroscopic chirality), and S_C*** for the latter (molecular and macroscopic chirality, which occurs in both parrallel and perpendicular directions to the layer planes). The addition of the number of asterisks

necessary to describe some phases therefore becomes very cumbersome and confusing.

Another problem of nomenclature arises even if one were to accept the asterisk as denoting optical activity associated with the mesophase, and not with the constituent molecules. The label applied does not give any hint as to the direction of the macroscopic helix whether it be right- or left-handed. This does not cause any major problems unless the helix is seen to invert with temperature, a phenomenon which is known to occur in a number of materials (see results and discussion section, chapter 8). In order to invert, the helix passes through an infinite pitch region where the phase can no longer be considered chiral, which raises the question as to whether the material should be described as having a S_C or S_C* phase or both (in terms of labelling). If the asterisk refers simply to the chiral molecules from which the phase is composed then the label S_C* should be applied, but this gives no indication whatsoever of the unusual phase behaviour that is occurring.

In terms of the design of ferroelectric mixtures for device use, or indeed scientific investigation it may be profitable to label chiral phases in such a way, that the twist sense of the macroscopic helix is immediately obvious. From the chemists point of view, it would also make sense to have an indication of the absolute spatial configuration of the constituent molecules, in the labelling system, as the helical twist sense and absolute spatial configuration can sometimes be related to one another.

At this point the author would like to suggest a labelling system that although not foolproof, would overcome some of the inherent problems of the present system. In smectic phases the lettered labelling system is so widespread and well known that it would be foolhardy to even attempt to suggest a better system to assign to each phase. Modifications could, however, be made to this system in order to clarify a number of

points. All of the modifications would utilise the Cahn, Ingold and Prelog system of labelling optically active materials[16,17].

Firstly, the asterisk which at the moment is most often taken to imply the presence of optically active material, could be replaced with a letter denoting the absolute spatial configuration of the chiral centre of the molecules. The letter, however, would be moved infront of the phase type designation, and would always refer to molecular optical activity (If two or more optically active centres are present, each designation would have to appear, the first being taken as referring to the chiral centre closest to the core structure, but if no chiral centres are present than the space would be left blank).

Secondly, the type of helicity the phase possesses could be noted, immediately after the phase type label. This would require the use of the letters *M* and *P* (*M*, Minus, left-handed; *P*, Plus, right-handed), after Cahn, Ingold and Prelog[34]. If the helix inverted at any time during the temperature range of the phase, this could then be noted by using both labels, quoting the twist sense of the higher temperature helix first.

The third modification would involve the indication of the presence of TGB phases. Once again the same helical designation would need to be used as mentioned previously (*M* and *P*), but this time could be added in brackets after the designation of any primary helix present.

So in labelling a chiral smectic C* phase with a left-handed helix composed of molecules whose absolute spatial configuration is *R*, the label would be as below

$$^{R}S_{C}{}^{M}$$

If a TGB S_C* phase was present instead and the helical twist sense could be determined (as *P* for example), the label would be as follows

$$^{R}S_{C}{}^{M(P)}$$

An alternative label being

$$^{R}TGB_{C}{}^{M(P)}$$

where TGB becomes accepted nomenclature.

If the handedness of the helix, either the primary helix or the TGB helix direction, could not be determined then an asterisk would simply be used to indicate the chirality. If the phase was in both a molecular and a macromolecular sense achiral then the usual S_C label would be used, and a chiral smectic C* phase with infinite pitch would have an ∞, after the phase type label to denote that no helix was present, to give, for example.

$$^{R}Sc^{\infty}$$

Another example would be a material with two chiral centres, one *S* and closest to the core, and one *R*. If it is also documented that this material undergoes an inversion in the smectic C* phase from a left to a right-handed helix, the label would be

$$^{S,R}Sc^{M,P}$$

Obvious shortfalls in this system can be seen almost immediately, but I mention it only to illustrate the possibilities; better alternatives will doubtlessly be developed to cope with developments in the field.

5. EVALUATION OF MESOGENIC MATERIALS.

5.1 Evaluation of Mesogenic Materials.

Many diverse methods are used to evaluate the physical properties associated with mesogenic materials. Section 5.1, however, will be restricted to methods that were used in the evaluation of the materials reported in this thesis.

5.1.1 *Optical Microscopy*

Mesogenic materials, when viewed in the polarizing microscope, exhibit textures that arise, at least in part, because of defects that are characteristic of a particular phase. If the possible defect structures are known for a particular phase and the sample can be aligned in certain orientations, then it is possible that a phase can be identified by optical microscopy alone. Alignment of materials can be achieved using various methods[69, 71]. The techniques used to align materials will not be discussed for reasons of brevity.

5.1.2 *Differential Scanning Calorimetry (DSC)*

Differential scanning calorimetry is widely used to determine not only phase transition temperatures, but also the enthalpies associated with such transitions. Conclusive phase identification, however, is not possible using thermal techniques alone and so they are used in most instances to complement optical microscopy. The thermogram obtained from the DSC, however, can disclose whether a transition is first-order (the first derivatives of the chemical potential, $(d\mu/dT)_P$ and $(d\mu/dP)_T$, are discontinuous across the transition), or second-order (where the first derivatives are continuous and the second derivatives are discontinuous). A first-order transition is characterised by a divergent heat capacity at the phase transition point, whereas, in the case of a second-order transition no enthalpy or latent heat is observed, the heat capacity may, however, change on going through the transition. Most mesophase-

mesophase, mesophase-crystal, mesophase-liquid transitions are either strongly or weakly first order.

5.1.3 *Helical Twist Sense (in Chiral Smectics)*

The helical twist sense of chiral smectics can be determined by two different, but complementary methods. The first method is based on polarimetry techniques for chiral materials, and a pseudo-homeotropic alignment of the material in the helical phase is necessary. This can be achieved between glass plates using a suitable aligning agent, or by preparing a free-standing film of the sample to be tested[44]. The aligned sample is then placed between crossed polarizers, and the top polarizer (analyser) is rotated with respect to the bottom one which is held stationary. In one direction the film appears more coloured than if the analyser is rotated in the other direction. A clockwise rotation to produce a greater coloration indicates a dextro or left-handed helix, an anti-clockwise rotation thereby indicating a laevo or right-handed helix. The coloration that is observed is thought to be due to an unequal rotation of the various wavelengths of white light as it passes through the film. The exact physical mechanism of this technique, however, is not fully understood and so confirmation of the twist sense of a material may be required, and can be obtained using a second technique known as the contact method[44].

When using the contact method to determine helical twist sense, a standard material of known helix direction is necessary, as this is a comparative method. The two materials, test and standard are allowed to make a sharp contact in the isotropic phase, and then rapidly cooled into their helical smectic phases. At this point dechiralization lines appear in the focal-conic textures of both materials. If the lines, when observed in the polarizing microscope, are seen to be continuous across the contact region then the test and standard materials have the same twist sense. If, however, there is a discontinuity in the observed lines then the materials have opposite twist senses, the pitch diverging in the contact region. This method relies on the accurate assessment

of the helical twist sense in a standard material, which in some tightly twisted materials may be difficult, and also does not take into account anomalous behaviour which is sometimes observed in binary mixtures which possess strong molecular associations when mixed. The contact method, however, is a good indication of the twist sense and one that can also be used to determine the twist sense in cholesteric materials.

5.1.4 *Pitch Measurements (in Chiral Smectics)*

The pitch length of the helix in a chiral smectic phase can also be determined optically by measuring the distance between successive pitch bands in the focal-conic texture of the mesophase[44]. This distance can be measured using a special eyepiece (Filar) with processor for digital readout, which can be calibrated against a standard scale. Care, however, must be taken when measurements are taken as some defect structures can produce results which correspond to the half-pitch[41].

5.1.5 *Polarization Direction and Tilt Angle (in Chiral Smectic Phases)*

The direction of the spontaneous polarization in relation to the direction of the tilt axis of the molecules can be determined directly from electric field studies. The material to be tested is placed in a cell (usually by capillary action in the isotropic phase) that is constructed of two pieces of glass that have been coated with indium-tin oxide on their inner surfaces. The cell spacing (distance between top and bottom glass plates) is dependent on spacers that are placed between the plates and is usually of the order of 2-30 μm. Once the cell is filled, electrical contacts are made with the upper and lower glass plates and a d.c. voltage supply connected. The material is then cooled into the smectic A phase (or other orthogonal smectic phase), in the absence of an electric field, and the sample is rotated on the stage until the aligned focal-conic or planar homogeneous domains become extinct. On further cooling into a ferroelectric phase some degree of extinction is maintained due to the inherent helicity of the structure. The sample is then subjected to a d.c. voltage of known

polarity and the helical structure unwinds, the material becoming uniformly poled with it's spontaneous polarization coupling to the applied field. The extinction direction is now altered relative to the reference axis and the stage is rotated through a minimum angle to regain extinction. The direction of rotation determines the polarization direction, clockwise for Ps(-), and anti-clockwise for Ps(+) assuming a positively poled top glass plate.

The angle through which the sample is rotated to regain extinction corresponds to the optical tilt angle of the phase, which enables temperature versus tilt angle data to be easily obtained. The applied electric field, however, must be large enough to achieve complete switching of the material if results are to be valid and so large fields (30-70 V per 3 μm cell spacing) are usually used.

5.1.6 *Polarization Value (in Smectic C* Phases)*

The magnitude of the spontaneous polarization is determined using a modified Diamant Bridge[109]. The material is placed in a cell, that is constructed as described in section 5.1.5, with a cell spacing of approximately 2-5 μm. The small cell spacing ensures good alignment of the liquid crystal and reduces the possibility of misalignment or twisted states, which is important if a correct value for the spontaneous polarization is to be obtained. The cell is connected to an a.c. frequency generator (30-60 Hz, 30 V peak to peak), which is also connected to the x-plate of a dual trace oscilloscope. The cell forms one arm of a capacitance bridge, which is illustrated schematically in figure 34.

Hysteresis in the liquid crystal sample causes a lag in the response to the a.c. field, causing a slight imbalance across the bridge. This imbalance is fed to the y-plate of the oscilloscope, *via* the amplifier, and a loop is obtained. The loop is balanced using the variable resistance and capacitance controls to yield a value for the polarization which can be read digitally from the instrument. Since the value of the spontaneous

polarization is dependent on the active area of the cell, this must also be taken account of with values usually quoted in nC cm^2.

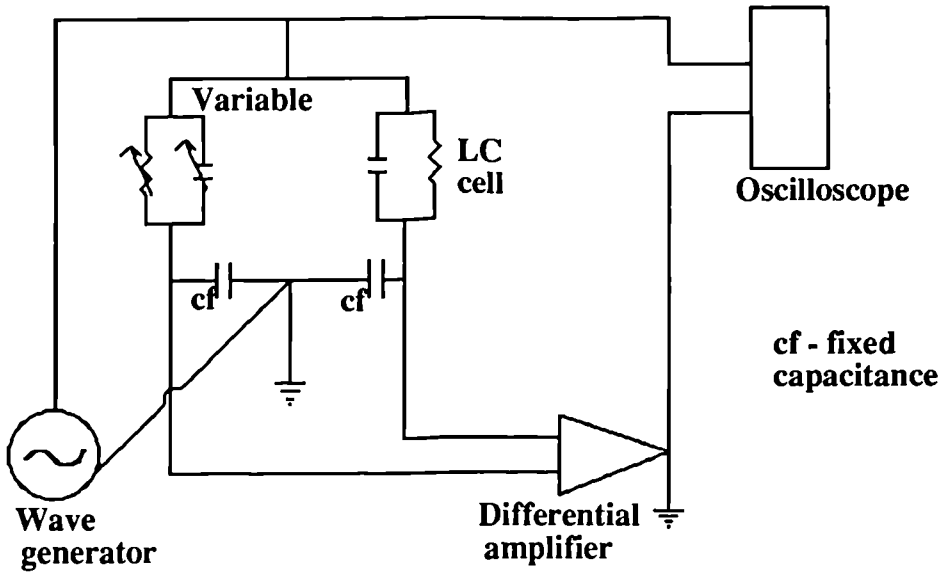


Figure 34. The Diamant Bridge Set-Up used for Spontaneous Polarisation Measurements.

5.1.7 *Electroclinic Response*

The electroclinic response of a material is measured in a similar way to how the tilt angle is measured in a ferroelectric phase[110]. The material is placed in a conducting cell and aligned in the A phase, the stage being rotated until extinction is achieved. The sample is then cooled to just above the smectic A to smectic C* transition point. A d.c. field is then applied across the sample causing switching to occur; the extinction direction changing at this point. The stage is then rotated until extinction is regained, the size of the rotation needed giving some measure of the electroclinic response. Throughout the measurement the magnitude of the applied electric field must be constant as the response is voltage dependent. It should also be remembered that the angles obtained for most materials are quite small even when measurements are taken close to the smectic A to smectic C* transition.

6. AIMS OF RESEARCH.

The aims of this research fall into two categories, those that deal with chiral materials and those for achiral systems. The general aims were as follows:

1. To synthesise novel chiral and achiral materials.
2. To study the effect of "molecular chirality" on chirality dependent properties such as helicity, polarization, pitch and tilt angle in smectic C* phases.
3. To elucidate the effect of molecular chirality on the formation of structurally frustrated mesophases (TGB and BPs).
4. To develop routes to asymmetric substrates.
5. To look for structurally frustrated phases in achiral systems (edge dislocation phase, EGB) through the synthesis of materials that have bent molecular structures.

Thus, the majority of the work reported in this thesis is centred on optically active materials. The aims of the research programme therefore were principally as follows. Firstly, to investigate the effects of altering various structural parameters on the ferroelectric and chiral dependent properties of the smectic C* phase, and secondly to develop structure/property correlations for structurally frustrated phases, in particular the recently discovered TGB A* phase[91].

A particular objective was to quantify the effects produced by various steric and dipolar factors relating to the chiral centre of the material, and their effect on the physical properties of the system. These studies would enable us to evaluate a material in terms of the degree of "chirality" of the system as a whole. This form of analysis was found to be important in many instances; for example, the thermal stability of frustrated phases was found to be dependent on the degree of chirality of the liquid crystal system as a whole. Similarly, this is clearly apparent when the

thermal stability of the blue phases is related to the helical pitch in the cholesteric phase and then to the molecular structure[111]. It is found that materials with a helical pitch in excess of 5000 Å do not exhibit blue phases, and bearing this in mind a number of structural changes can be made at the chiral centre in order to increase the degree of "molecular chirality" and hence improve the chances of finding materials that exhibit blue phases.

Two particular molecular templates were investigated as shown in figure 35. A variety of peripheral alkyl (R) groups were also evaluated, both normal and branched chain, in order to examine if the free rotation of the chiral centre with respect to the core could be reduced, thereby increasing the chirality of the system[32]. For example, positioning of the chiral centre adjacent to the rigid core (template 2), and then locating a branched aliphatic chain adjacent to the asymmetric atom on the peripheral side to the core, would be expected to trap the free rotation of the chiral centre, thereby enhancing the chirality dependent properties. Some examples of the types of peripheral alkyl group used are given in figure 36.

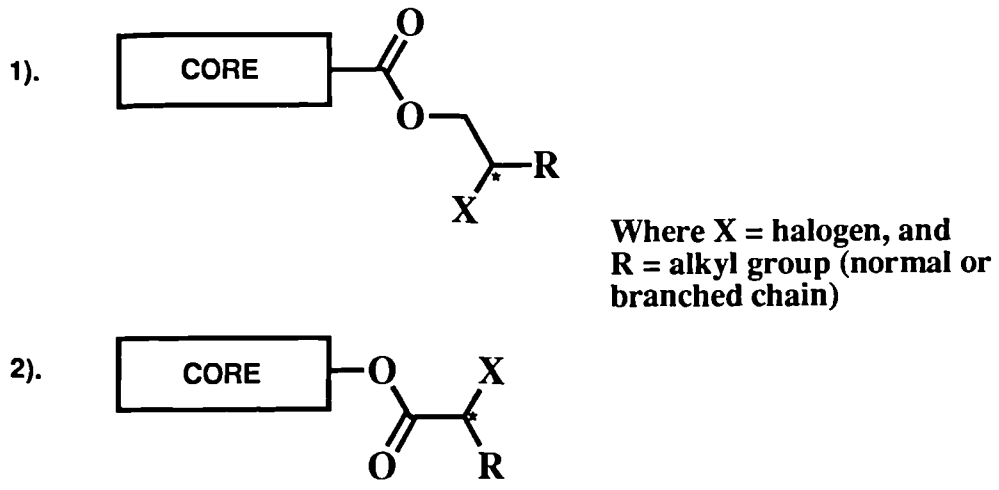


Figure 35. The Types of Chiral Entity Studied.

R GROUPS

$-CH_3$

$-CH(CH_3)_2$

$-C^*H(CH_3)CH_2CH_3$

$-CH_2CH(CH_3)_2$

Figure 36.

It can be seen from figure 36 that one of the groups also possesses a chiral centre in its structure, thereby giving the possibility of having two chiral centres in the molecule positioned in one of the terminal alkyl chains. The chiral centre in this case can have either an *S* or an *R* absolute spatial configuration, enabling the study of the effect that sequential chiral centres, and their relative stereochemical structures, has on chirality dependent properties.

The laterally positioned atoms (X) at the chiral centre were the halogens (fluorine, chlorine, and bromine). These atoms were selected for study because the results were expected to give a comparison of the strength of the effective dipole at the chiral centre and how it would influence the material properties. It is clear, however, that the comparisons made have to be tempered by the fact that as there is an increase in the effective dipole on moving from bromine through chlorine to fluorine, there is also a marked decrease in size of atom. Thus the property/structure correlations developed may not have been purely reliant on the strength of the dipole in this case, but may also be dependent on atom size.

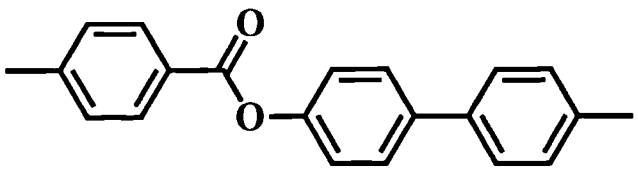
The final modification made that directly affected the chiral centre involved the linking group, which in most cases was kept constant as an ester function. The direction of the ester was, however, reversed (see figure 35) in some materials. This had the effect of moving the carbonyl function further from the core and adjacent to the chiral centre. It was hoped that by positioning the chiral centre adjacent to the carbonyl moiety of the linking group, the chirality of the system would be increased

due to an increased coupling between the carbonyl function and the lateral dipole associated with the chiral centre.

In order to ascertain how optical purity affects certain properties and structures of chiral liquid crystals, the racemic versions of some of the materials were prepared and utilised as components in binary mixtures in order to vary the enantiomeric excess. This exercise allowed for the investigation of phase diagrams as a function of optical purity and hence, the degree of molecular chirality.

A variety of core structures were utilised in this project in order to generate families of liquid crystals for study. The most prevalent cores used are illustrated in figure 37.

3).



4).

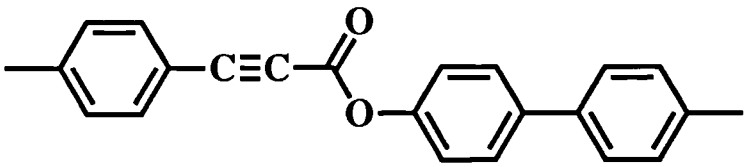


Figure 37. Two of the Core Structures Utilised.

The first point to notice is that two different central linking groups were used in these core templates. In the first case (3) a simple ester was used to link two aromatic regions together, and in the second example, template 4, a propiolate linking group was employed in the core. In comparison to template 3, the introduction of a triple bond in template 4 lengthens the core of the molecule and extends the region of delocalised electrons. In addition, the presence of a triple bond in this case allows for an increase in the freedom of rotation of the phenyl entity with respect to the biphenyl group, thereby producing a more rotationally disordered core structure.

As well as variations made to the linking group within the core, the structure of each core sub-unit was also varied. For example, the phenyl unit was replaced by variously substituted naphthalene moieties, and in one instance a cyclohexane unit. This approach was directed towards broadening the molecular architecture in the case of the naphthalene units, or making it less rigid in the case of the cyclohexane unit. In both cases the objective was to reduce the relative transition temperatures, and also decrease the layer strength of any lamellar phases formed. The reduction in layer strength was sought in order to allow for the easier formation of TGB A* phases[95]. In addition, the biphenyl unit was also replaced by naphthalene, with the same objectives in mind as previously mentioned.

In these studies the final variable to be altered was the length of alkoxy chain situated at the opposite end of the molecular structure from the chiral centre. This template (5) is illustrated in figure 38. The alkyl chain length (R) was varied in order to produce a number of homologous series and to investigate the properties across a series. In particular, increasing the length of the aliphatic chain (R) has the effect of stabilising tilted phases, and hence, ferroelectric properties in chiral compounds. Thus, the effect of the length of this chain on chirality dependent properties was also investigated.

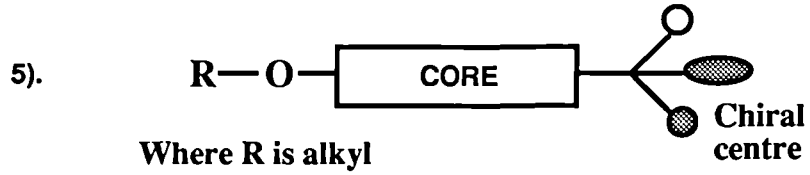


Figure 38. The Alkoxy Chain was Varied in Length in Some Materials.

In addition to the work on production of novel liquid crystals, the research project also involved the preparation of novel chiral intermediates that were suitable for incorporation in mesogenic materials. This involved the development of a variety of synthetic methodologies in order to generate chiral substrates that had high optical purities.

The final, and somewhat disconnected, piece of work involved the investigation into non-chiral dimeric materials. However, the aim of this section of the work was in fact, to try and prepare materials that would produce a dislocation stabilised phase based on bend rather than twist distortions (as is the TGB A* phase), at the nematic to smectic A transition point[95]. The majority of the work contained in this thesis on frustrated phases is based on the competition between twist deformations and layer ordering. De Gennes original theory for the stabilisation of such structures, however, was primarily based on the incorporation of bend deformations in the smectic A phase leading to an edge-dislocation phase[95]. Thus, the later part of this work reports on the search for this phase through the examination of the liquid-crystalline properties of molecules that had bent gross shapes, which might stabilise the formation of edge dislocations. Consequently, a number of the dimeric materials were produced and in some cases chiral centres were also incorporated into their structures in order to explore the possibility of producing the extraordinary phase having both twist and bend distortions. The types of dimeric template targeted for synthesis are illustrated schematically in figure 39.

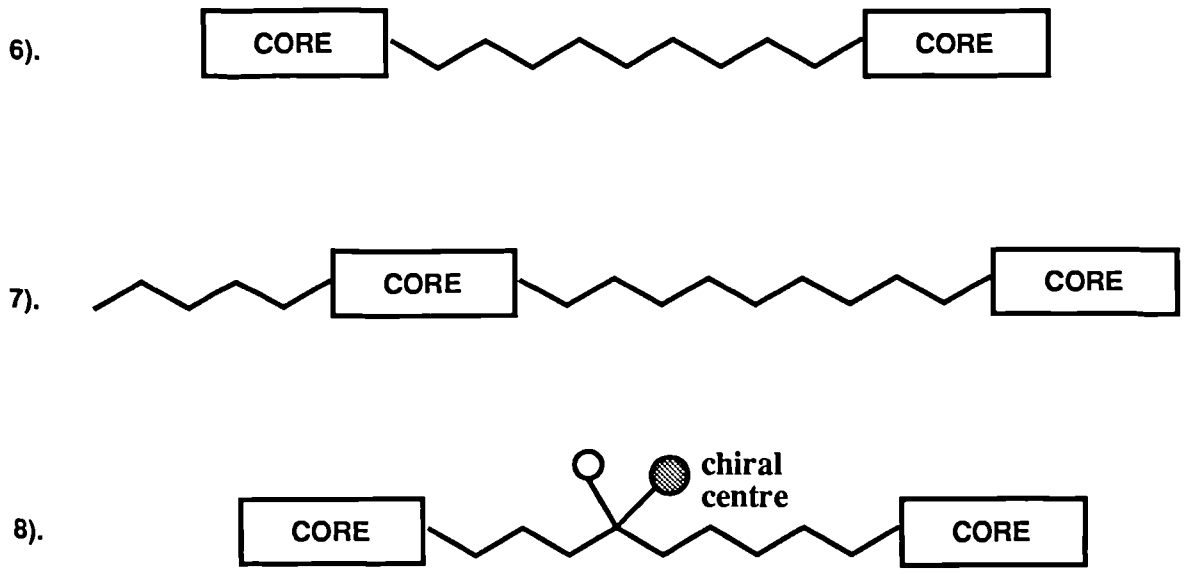


Figure 39. A Schematic Diagram of the Structures of the Dimeric Molecules Prepared.

7. EXPERIMENTAL.

7.1 General Notes.

7.1a *Purity of Materials Synthesized*

i). The purities of all of the compounds produced (intermediates and final products) were checked by thin layer chromatography (tlc). The plates used were Kieselgel 60 F_{254} (Merck, Darmstadt). The eluant most commonly used was dichloromethane, although mixtures involving petroleum spirit (b.p. 40-60°)/dichloromethane and tetrahydrofuran/ dichloromethane were used in some instances when the polarity of the compound dictated that this was necessary. Detection of spots was achieved by ultra-violet fluorescence (254 and 365 nm), and where necessary by contact with iodine vapour.

ii). Flash column chromatography was carried out over Sorbsil Silica Gel C60-H (40-60 μm). Gravity column chromatography was carried out over Fisons Silica Gel 60-120 mesh (0.125-0.250 mm).

iii). The purities of all final compounds were investigated further by both normal and reverse-phase high-pressure liquid chromatography (hplc). Normal-phase chromatography was carried out over silica gel (5 μm pore size, 25 x 0.46 cm, Dynamax Scout column) using acetonitrile as the eluant. Reverse-phase chromatography was performed over octadecylsiloxane (5 μm pore size, 25 x 0.46 cm, ODS Microsorb Dynamax 18 column) using acetonitrile as eluant. Detection of the eluting products was achieved using a Spectroflow 757 UV-VIS detector (λ = 254 nm).

iv). Melting points were determined using a Gallenkamp melting point apparatus.

7.1b *Transition Temperatures and Enthalpies of Transition*

i). Transition temperatures (+/- 0.1°) and initial phase assignments were determined by thermal optical microscopy using a Zeiss Universal polarizing light microscope equipped with a Mettler FP52 micro-furnace and FP5 control unit. A heating and cooling rate of 2° min^{-1} was used where practical.

ii). Temperatures and heats of transition were determined by differential scanning calorimetry using a Perkin-Elmer DSC-7 calorimeter in conjunction with a thermal analysis data station (TADS). As a check of instrumental accuracy an indium standard was run at 10 °C min^{-1}, at frequent intervals. The measured latent heat was found to be within 0.5 % of the expected value of 28.45 J g^{-1}, on every occasion.

7.1c *Spectroscopic and Optical Data*

i). Infra-red spectroscopy was carried out using a Perkin-Elmer 783 infrared spectrophotometer.

ii). Proton nuclear magnetic resonance spectroscopy was carried out using a JEOL JNM-GX270 FT nuclear magnetic resonance spectrometer.

iii). Mass spectrometry was carried out using a Finnigan MAT 1020 automated GC/ MS.

iv). Optical rotations were determined using a Bendix-NPL automated polarimeter, with a Bendix ETL-NPL control unit. Values were taken at the sodium D-line (589 nm), at ambient temperature (see experimental details, section 7.3).

7.1d *Electrical and Alignment Studies*

Electrical and alignment studies were carried out in glass cells (of varying cell spacing) the inner surfaces of which had been coated with polyimide and unidirectionally buffed.

7.1e *Drying and Purification of Solvents*

i). Benzene and diethyl ether were both dried over sodium wire.

ii). Hexane and dichloromethane were purified by distillation over phosphorous pentoxide.

iii). Tetrahydrofuran was purified by distillation over sodium and benzophenone.

iv). Super-dry ethanol was prepared in the following manner. Clean, dry magnesium turnings (5 g), iodine (0.5 g), and ethanol (50-75 ml) were stirred and warmed until the iodine was seen to disappear (if evolution of hydrogen did not occur a further 0.5 g of iodine was added). Heating was then continued until the magnesium was seen to disappear, at which point the ethanolic solution was heated under reflux.

v). Super-dry methanol was obtained in an analogous manner to super-dry ethanol.

7.1f *Abbreviations in Reporting Experimental Details and Procedures*

i). In reporting nmr data, the following abbreviations have been used: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; quin, quintet; sext, sextet; oct, octet; m, multiplet; br, broad.

ii). In reporting infrared data vs has been used to identify a very strong absorbtion band.

iii). In reporting transition temperatures t.t. has been used as an abbreviation, whilst melting point has been abbreviated to m.p., and boiling point to b.p..

iv). In reporting experimental procedures m and h have been used as abbreviations for minutes and hours respectively.

v). In reporting mass spectral data, for reasons of brevity, no attempt has been made to differentiate between fragment ions and radicals.

7.1g *Nomenclature*

The IUPAC nomenclature has been used throughout, except when for reasons of clarity an alternative was considered more suitable.

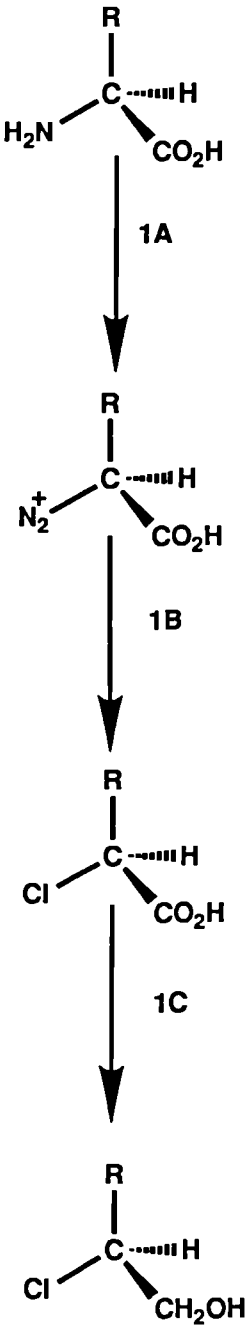
7.1h *General Preparations*

The experimental section has been set out in the following manner.

Reaction Schemes (7.2); Procedure followed, data collected and notes (7.3); Discussion of Schemes (7.4).

7.2 Reaction Schemes.

Reaction Scheme 1



1, R = CH_3
2, R = $CH(CH_3)_2$
3, R = $C^*H(CH_3)CH_2CH_3$ *(S,S)*
4, R = $C^*H(CH_3)CH_2CH_3$ *(S,R)*
5, R = $CH_2CH(CH_3)_2$
6, R = $CH_2CH(CH_3)_2$ *(+/-)*
7, R = $CH_2CH_2SCH_3$
8, R = $CH_2CH_2CH_3$
9, R = $CH_2CH_2CH_2CH_3$

10, R = CH_3
11, R = $CH(CH_3)_2$
12, R = $C^*H(CH_3)CH_2CH_3$ *(S,S)*
13, R = $C^*H(CH_3)CH_2CH_3$ *(S,R)*
14, R = $CH_2CH(CH_3)_2$
15, R = $CH_2CH(CH_3)_2$ *(+/-)*
16, R = $CH_2CH_2SCH_3$
17, R = $CH_2CH_2CH_3$
18, R = $CH_2CH_2CH_2CH_3$

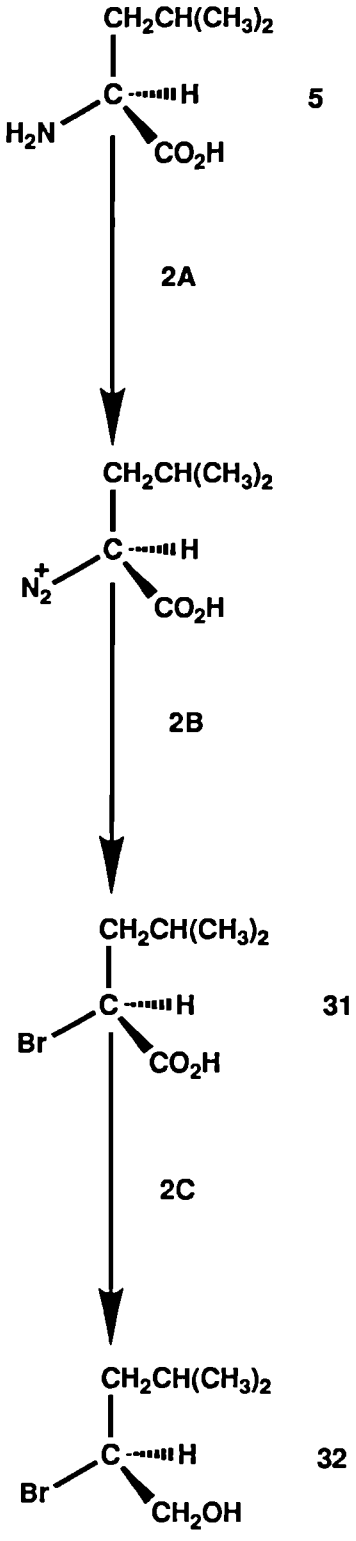
19, R = CH_3
20, R = $CH(CH_3)_2$
21, R = $C^*H(CH_3)CH_2CH_3$ *(S,S)*
22, R = $C^*H(CH_3)CH_2CH_3$ *(S,R)*
23, R = $CH_2CH(CH_3)_2$
24, R = $CH_2CH(CH_3)_2$ *(+/-)*
25, R = $CH_2CH_2SCH_3$
26, R = $CH_2CH_2CH_3$
27, R = $CH_2CH_2CH_2CH_3$

Commercially available alcohols used:

28, R = $(CH_2)_5CH_3$
29, R = $(CH2)_7CH_3$
30, R = $(CH2)_9CH_3$

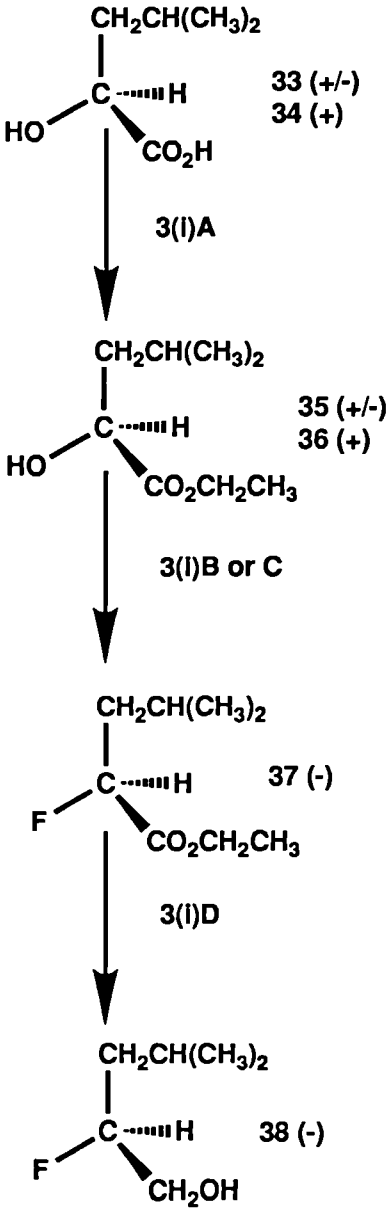
1A/1B $NaNO_2$, 5N HCl
1C $LiAlH_4$, $(CH_3CH_2)_2O$

Reaction Scheme 2



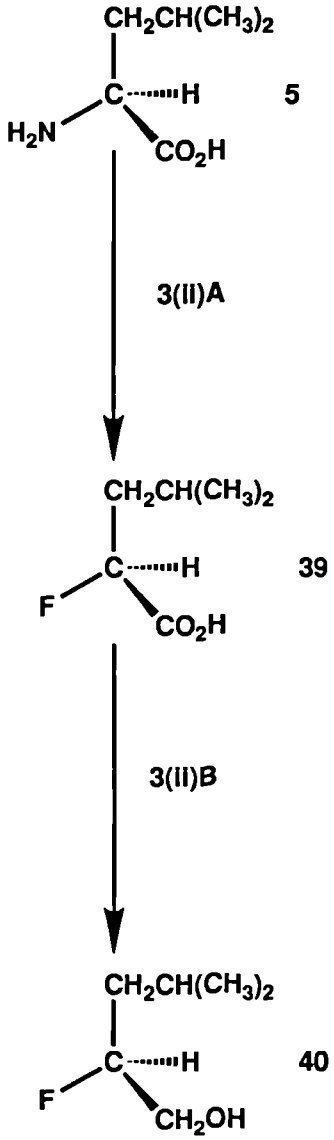
2A/2B $NaNO_2$, 5N HBr
2C $LiAlH_4$, $(CH_3CH_2)_2O$

Reaction Scheme 3 (i)



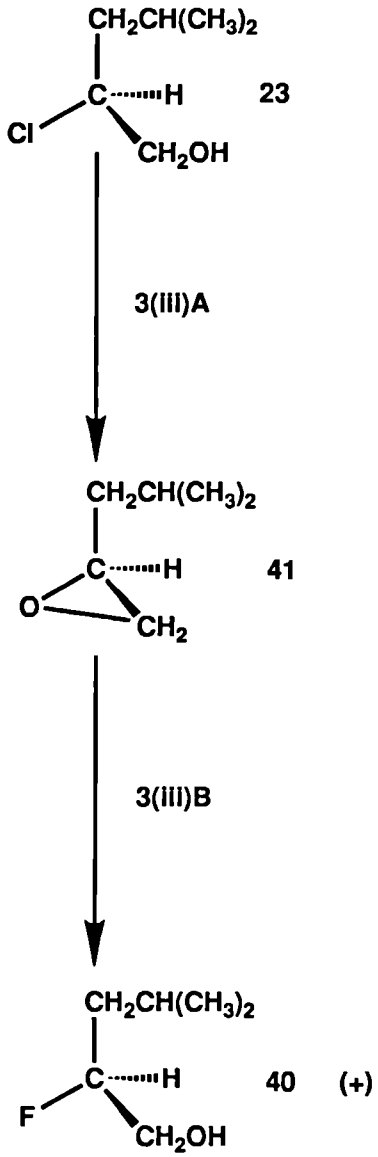
3(I)A H_2SO_4, CH_3CH_2OH
3(I)B HF/C_5H_5N
3(I)C $(CH_3CH_2)_2NSF_3$, CH_2Cl_2
3(I)D $LiAlH_4$, $(CH_3CH_2)_2O$

Reaction Scheme 3 (ii)



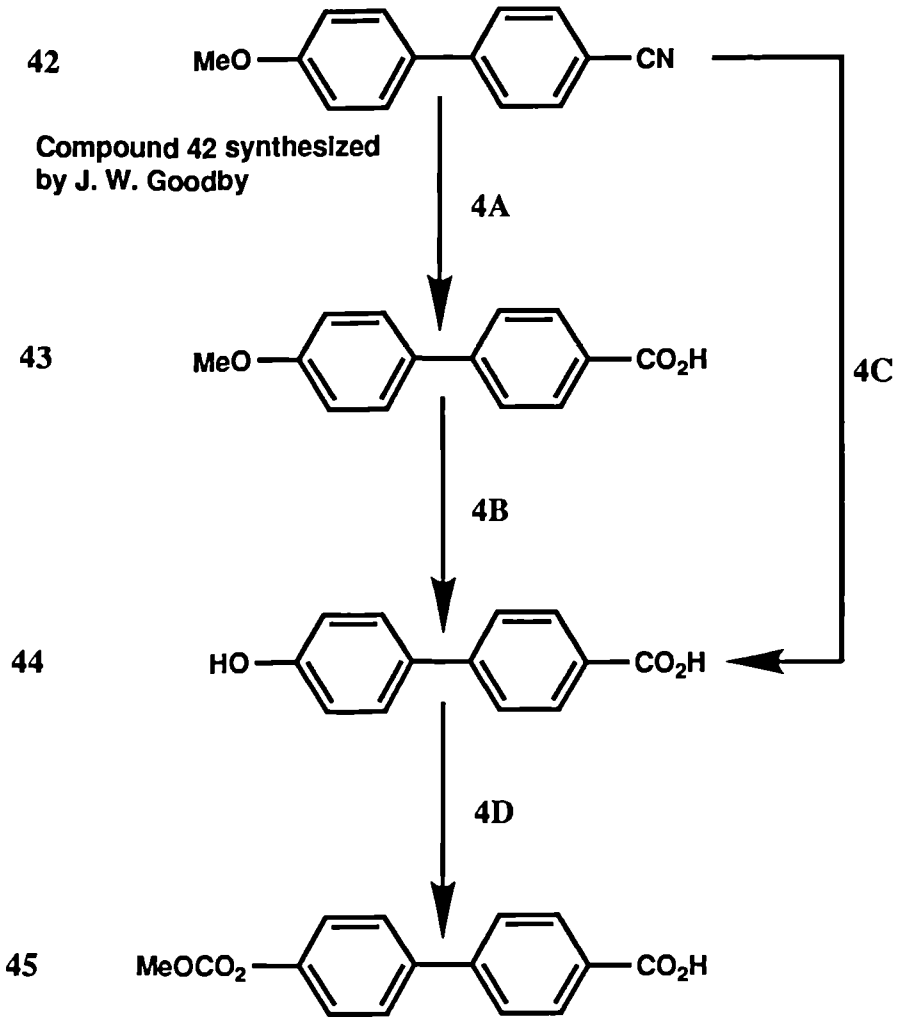
3(II)A $NaNO_2$, HF/C_5H_5N
3(II)B $LiAlH_4$, $(CH_3CH_2)_2O$

Reaction Scheme 3 (iii)



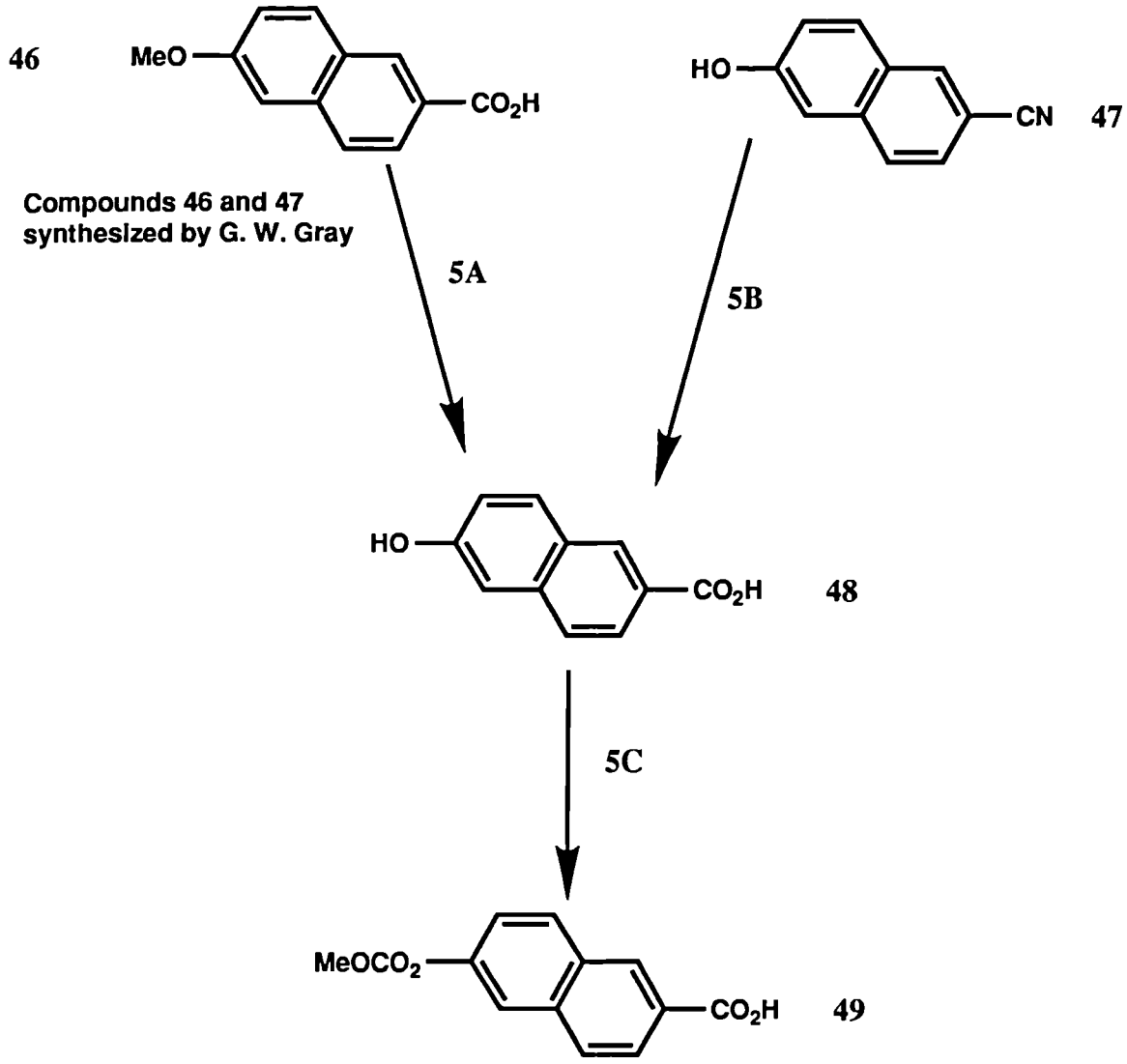
3(iii)A KOH
3(iii)B HF/C_5H_5N

Reaction Scheme 4



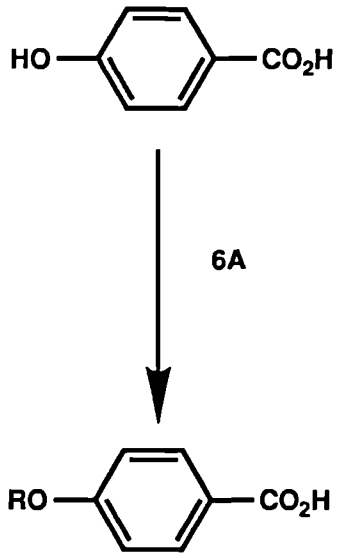
4A H_2SO_4, CH_3CO_2H, H_2O
4B/4C HBr, CH_3CO_2H
4D a).CH_3OCOCl, NaOH, H_2O
b). HCl

Reaction Scheme 5



5A BBr_3, CH_2Cl_2
5B H_2SO_4, CH_3CO_2H, H_2O
5C a).CH_3OCOCl, NaOH, H_2O
b).HCl

Reaction Scheme 6



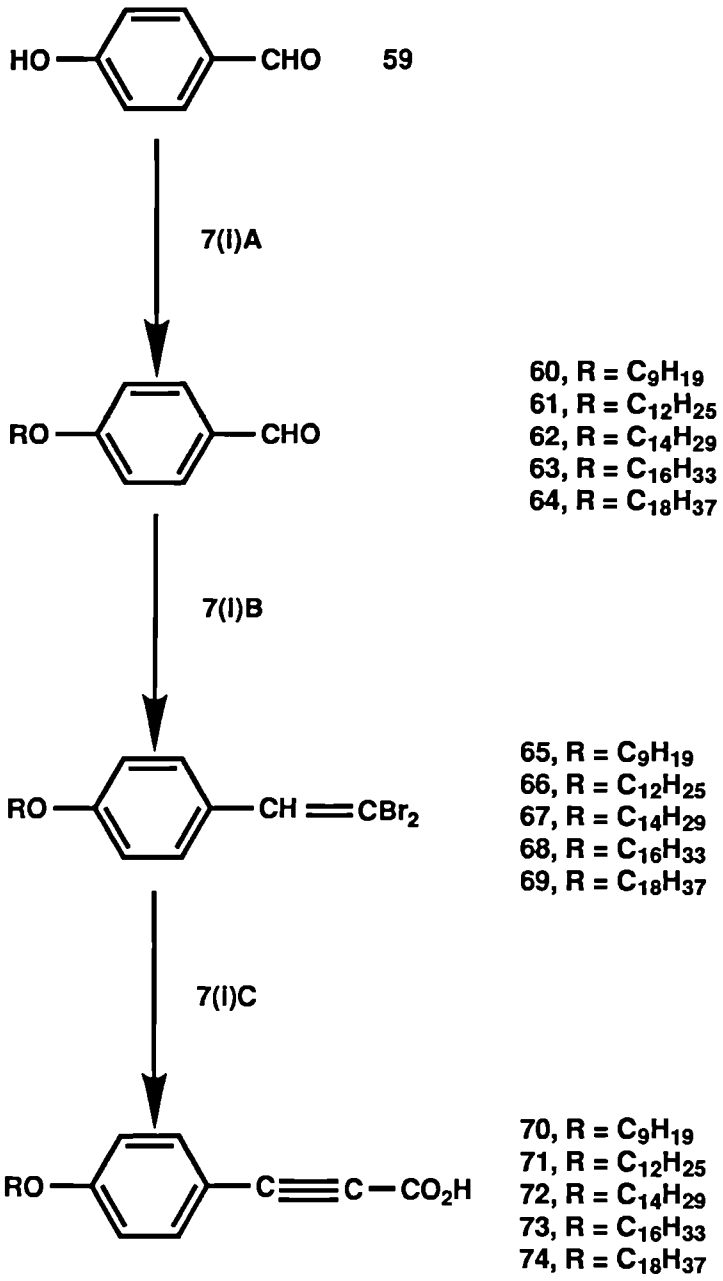
51, R = C_9H_{19}
52, R = $C_{10}H_{21}$
53, R = $C_{11}H_{23}$
54, R = $C_{12}H_{25}$

Other 4-alkoxybenzoic acids used; synthesized by J. W. Goodby

55, R = C_7H_{15}
56, R = C_8H_{17}
57, R = $C_{13}H_{27}$
58, R = $C_{14}H_{29}$

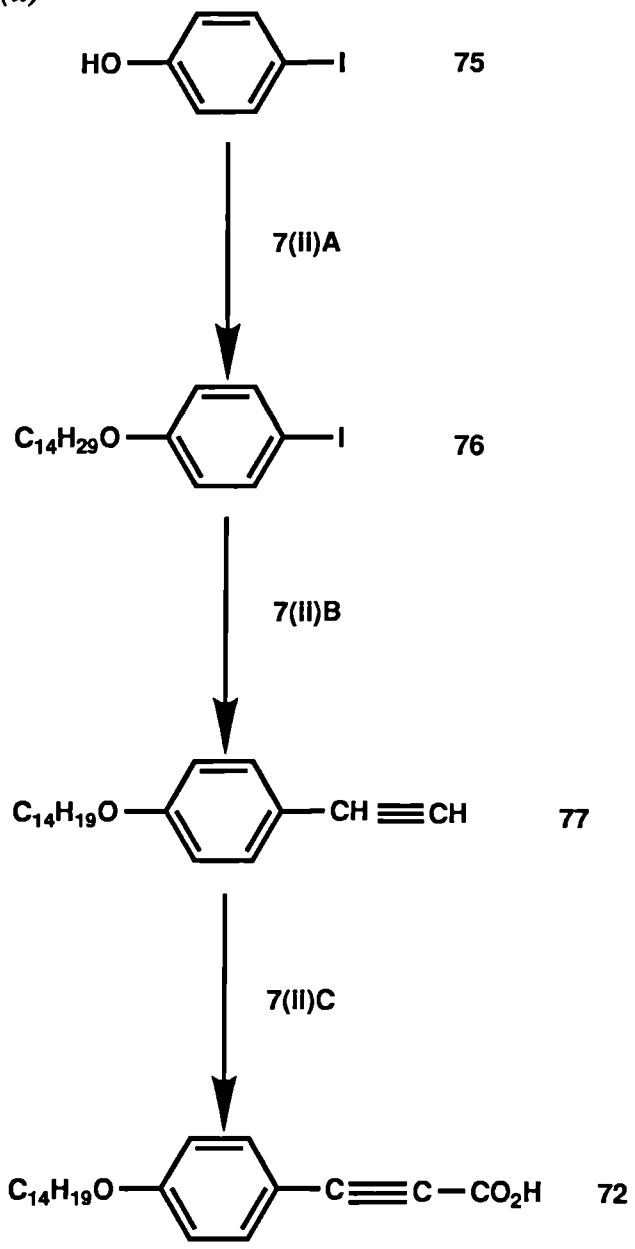
6A KOH, RBr, CH_3CH_2OH, H_2O

Reaction Scheme 7 (i)



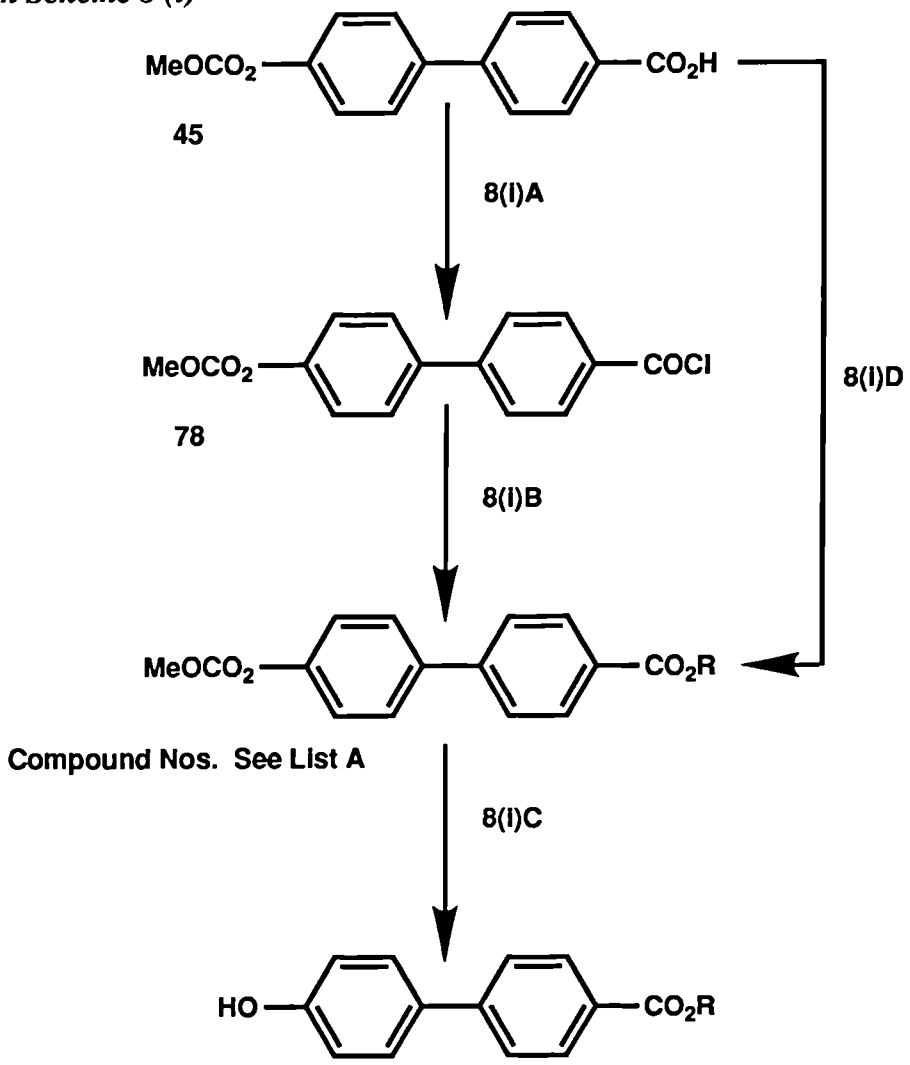
7(I)A RBr, K_2CO_3, $(CH_3)_2CO$
7(I)B $(C_6H_5)_3P$, CBr_4, Zn, CH_2Cl_2
7(I)C a). C_4H_9LI, C_4H_8O (THF) b). CO_2 c). dil. HCl

Reaction Scheme 7 (ii)



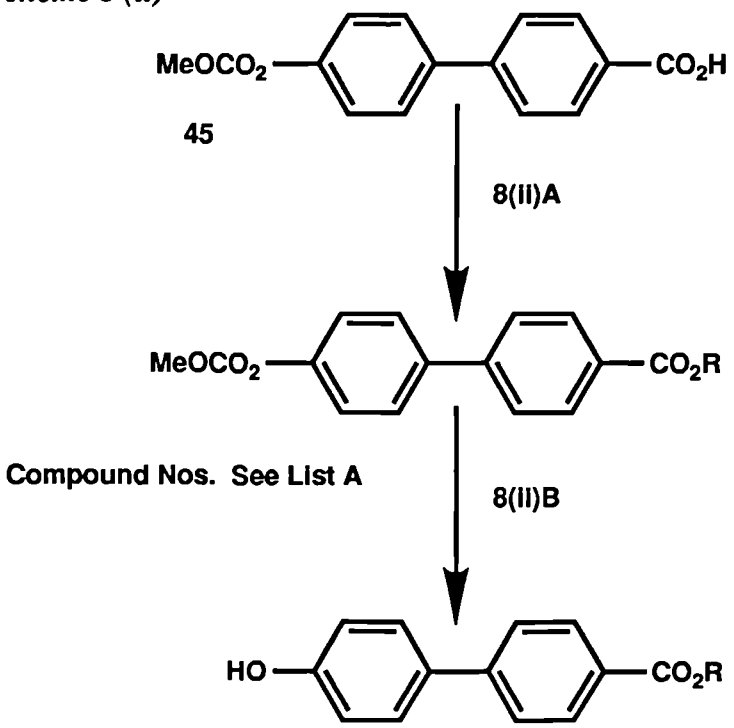
7(II)A $C_{14}H_{29}Br$, K_2CO_3, C_4H_8O (THF)
7(II)B $ZnCl_2$, $Pd(PPh_3)_4$, $HCCLI.H_2N(CH_2)_2NH_2$, C_4H_8O (THF)
7(II)C a). C_4H_9LI, C_4H_8O (THF) b). CO_2 c). dil. HCl

Reaction Scheme 8 (i)



8(I)A $SOCl_2$
8(I)B ROH, C_6H_6, C_4H_8O (THF), C_5H_5N
8(I)C NH_3(aq), CH_3CH_2OH
8(I)D $(C_6H_{11}N)_2C$ (DCC), $(CH_3)_2NC_5H_4N$ (DMAP), $(CH_3CH_2)O$, ROH

Reaction Scheme 8 (ii)



Compound Nos. See List B

8(II)A $(C_2H_5O_2CN)_2$ (DEAD), $(C_6H_5)_3P$, ROH, C_4H_8O (THF)
8(II)B NH_3(aq), CH_3CH_2OH

Reaction Schemes 8 (i) and (ii) - Compound Numbers

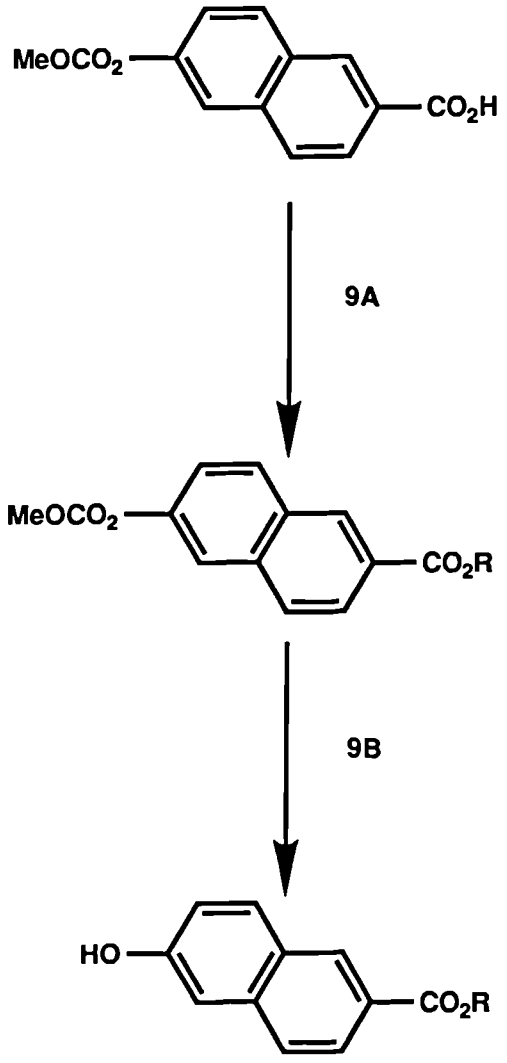
List A

79, R = $CH_2C^*H(Cl)CH_3$
80, R = $CH_2C^*H(Cl)CH(CH_3)_2$
81, R = $CH_2C^*H(Cl)C^*H(CH_3)CH_2CH_3$ *(S,S)*
82, R = $CH_2C^*H(Cl)C^*H(CH_3)CH_2CH_3$ *(S, R)*
83, R = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$
84, R = $CH_2CH(Cl)CH_2CH(CH_3)_2$ *(+/-)*
85, R = $CH_2C^*H(Cl)CH_2CH_2CH_3$
86, R = $CH_2C^*H(Cl)CH_2CH_2CH_2CH_3$
87, R = $CH_2C^*H(Cl)(CH_2)_5CH_3$
88, R = $CH_2C^*H(Cl)(CH_2)_7CH_3$
89, R = $CH_2C^*H(Cl)(CH_2)_9CH_3$
90, R = $CH_2C^*H(Br)CH_2CH(CH_3)_2$
91, R = $CH_2C^*H(F)CH_2CH(CH_3)_2$
92, R = $C^*H(Me)(CH_2)_5CH_3$

List B

93, R = $CH_2C^*H(Cl)CH_3$
94, R = $CH_2C^*H(Cl)CH(CH_3)_2$
95, R = $CH_2C^*H(Cl)C^*H(CH_3)CH_2CH_3$ *(S,S)*
96, R = $CH_2C^*H(Cl)C^*H(CH_3)CH_2CH_3$ *(S, R)*
97, R = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$
98, R = $CH_2CH(Cl)CH_2CH(CH_3)_2$ *(+/-)*
99, R = $CH_2C^*H(Cl)CH_2CH_2CH_3$
100, R = $CH_2C^*H(Cl)CH_2CH_2CH_2CH_3$
101, R = $CH_2C^*H(Cl)(CH_2)_5CH_3$
102, R = $CH_2C^*H(Cl)(CH_2)_7CH_3$
103, R = $CH_2C^*H(Cl)(CH_2)_9CH_3$
104, R = $CH_2C^*H(Br)CH_2CH(CH_3)_2$
105, R = $CH_2C^*H(F)CH_2CH(CH_3)_2$
106, R = $C^*H(Me)(CH_2)_5CH_3$

Reaction Scheme 9

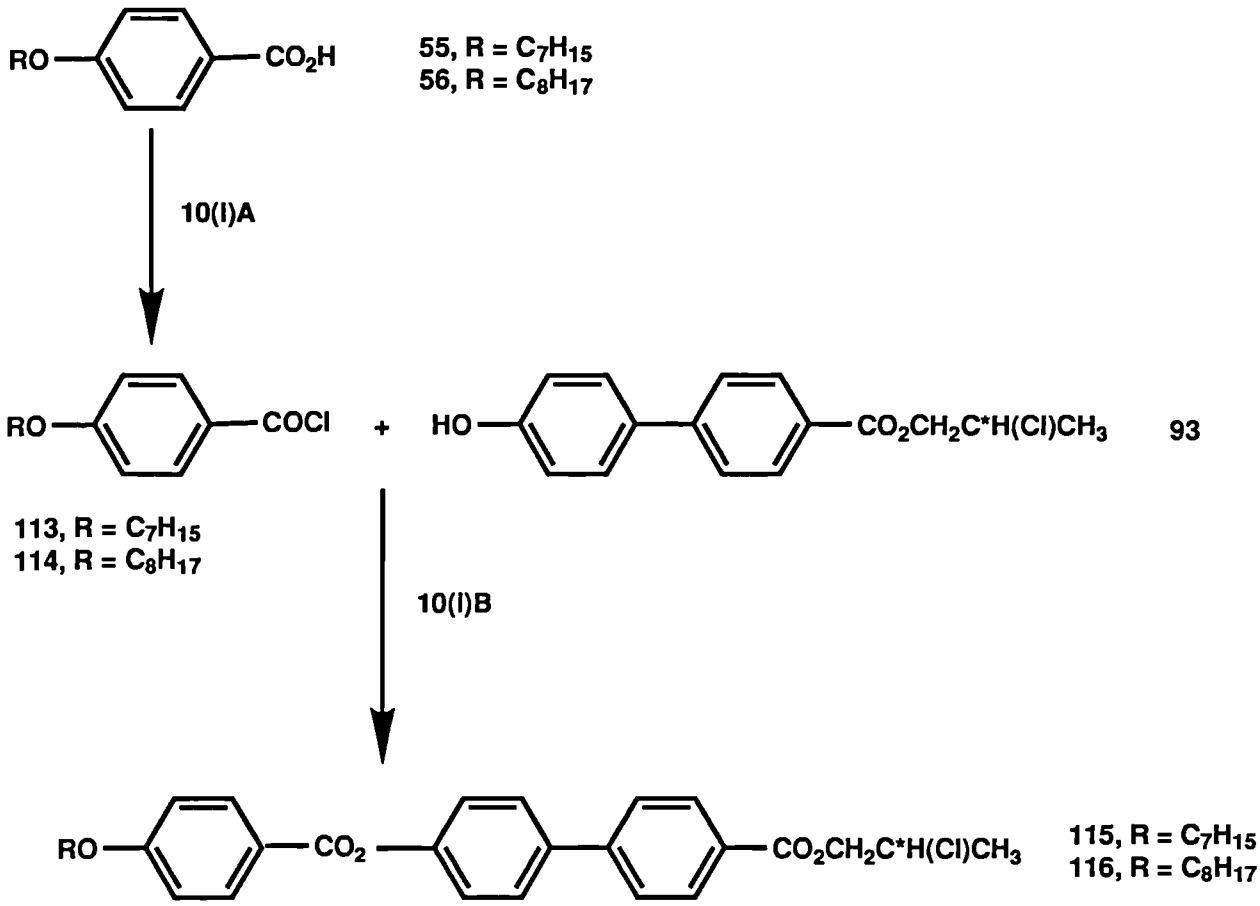


107, R = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$
108, R = $CH_2CH(Cl)CH_2CH(CH_3)_2$ (+/-)
109, R = $C^*H(CH_3)(CH_2)_5CH_3$

110, R = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$
111, R = $CH_2CH(Cl)CH_2CH(CH_3)_2$ (+/-)
112, R = $C^*H(CH_3)(CH_2)_5CH_3$

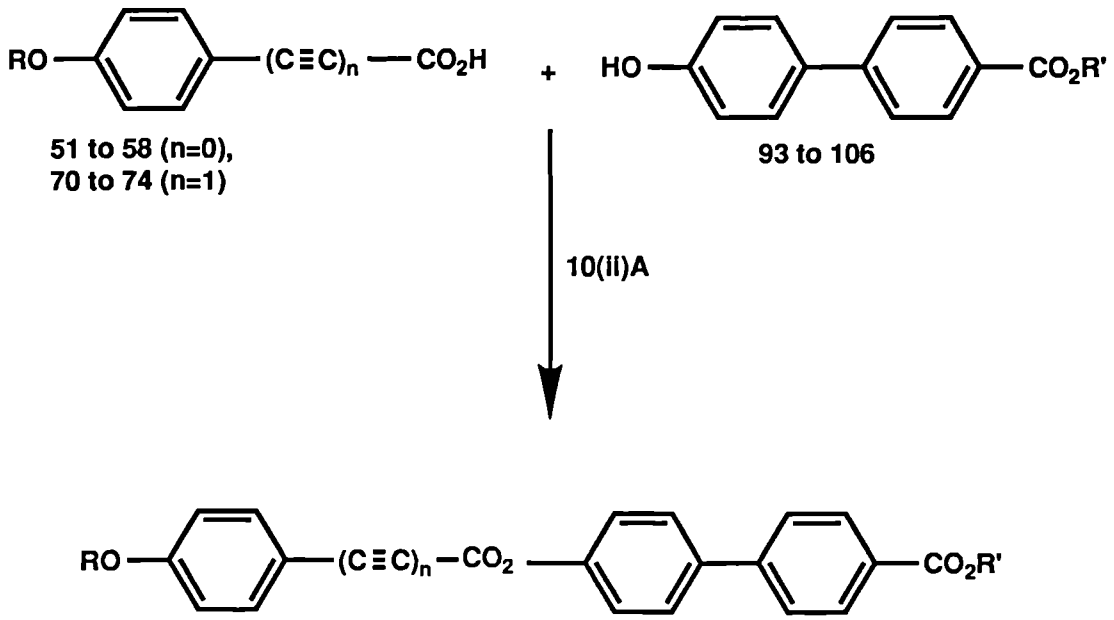
9A $(C_2H_5O_2CN)_2$ (DEAD), $(C_6H_5)_3P$, ROH, C_4H_8O (THF)
9B NH_3(aq), CH_3CH_2OH

Reaction Scheme 10 (i)



10(I)A $SOCl_2$
10(I)B C_6H_6, C_5H_5N

Reaction Scheme 10 (ii)



Compound Nos. See List

10(II)A $(C_6H_{11}N)_2C$ (DCC), $(CH_3)_2NC_5H_4N$ (DMAP), $(CH_3CH_2)_2O$

Scheme 10 (ii) - Compound Numbers

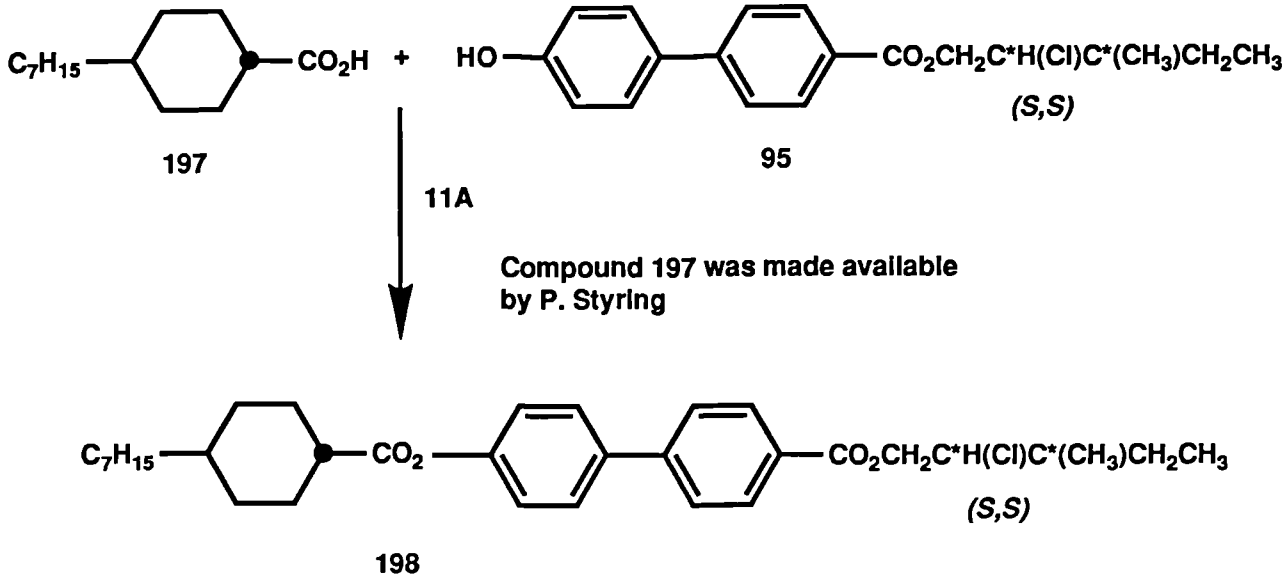
No.	R	n	R'
117	C_9H_{19}	0	$CH_2C^*H(Cl)CH_3$
123	"	1	"
118	$C_{10}H_{21}$	0	"
119	$C_{11}H_{23}$	"	"
120	$C_{12}H_{25}$	"	"
124	"	1	"
121	$C_{13}H_{27}$	0	"
122	$C_{14}H_{29}$	"	"

No.	R	n	R'
125	"	1	"
126	$C_{16}H_{33}$	"	"
127	$C_{18}H_{37}$	"	"
128	C_7H_{15}	0	$CH_2C^*H(Cl)CH(CH_3)_2$
129	C_8H_{17}	"	"
130	C_9H_{19}	"	"
136	"	1	"
131	$C_{10}H_{21}$	0	"
132	$C_{11}H_{23}$	"	"
133	$C_{12}H_{25}$	"	"
137	"	1	"
134	$C_{13}H_{27}$	0	"
135	$C_{14}H_{29}$	"	"
138	"	1	"
139	$C_{16}H_{33}$	"	"
140	$C_{18}H_{37}$	"	"
141	C_7H_{15}	0	$CH_2C^*H(Cl)C^*H(CH_3)CH_2CH_3$ (S,S)
142	C_8H_{17}	"	"
143	C_9H_{19}	"	"
149	"	1	"
144	$C_{10}H_{21}$	0	"
145	$C_{11}H_{23}$	"	"
146	$C_{12}H_{25}$	"	"
150	"	1	"
147	$C_{13}H_{27}$	0	"
148	$C_{14}H_{29}$	"	"

No.	R	n	R'
151	"	1	"
152	$C_{16}H_{33}$	"	"
153	$C_{18}H_{37}$	"	"
154	C_9H_{19}	0	$CH_2C^*H(Cl)C^*H(CH_3)CH_2CH_3$ (S,R)
155	"	1	"
156	C_7H_{15}	0	$CH_2C^*H(Cl)CH_2CH(CH_3)_2$
157	C_8H_{17}	"	"
158	C_9H_{19}	"	"
164	"	1	"
159	$C_{10}H_{21}$	0	"
160	$C_{11}H_{23}$	"	"
161	$C_{12}H_{25}$	"	"
165	"	1	"
162	$C_{13}H_{27}$	0	"
163	$C_{14}H_{29}$	"	"
166	"	1	"
167	$C_{16}H_{33}$	"	"
168	$C_{18}H_{37}$	"	"
169	C_9H_{19}	0	$CH_2CH(Cl)CH_2CH(CH_3)_2$ (+/-)
170	C_9H_{19}	0	$CH_2C^*H(Cl)(CH_2)_2CH_3$
171	"	1	"
172	C_9H_{19}	0	$CH_2C^*H(Cl)(CH_2)_3CH_3$
173	"	1	"
174	C_7H_{15}	0	$CH_2C^*H(Cl)(CH_2)_5CH_3$
175	C_8H_{17}	"	"
176	C_9H_{19}	"	"

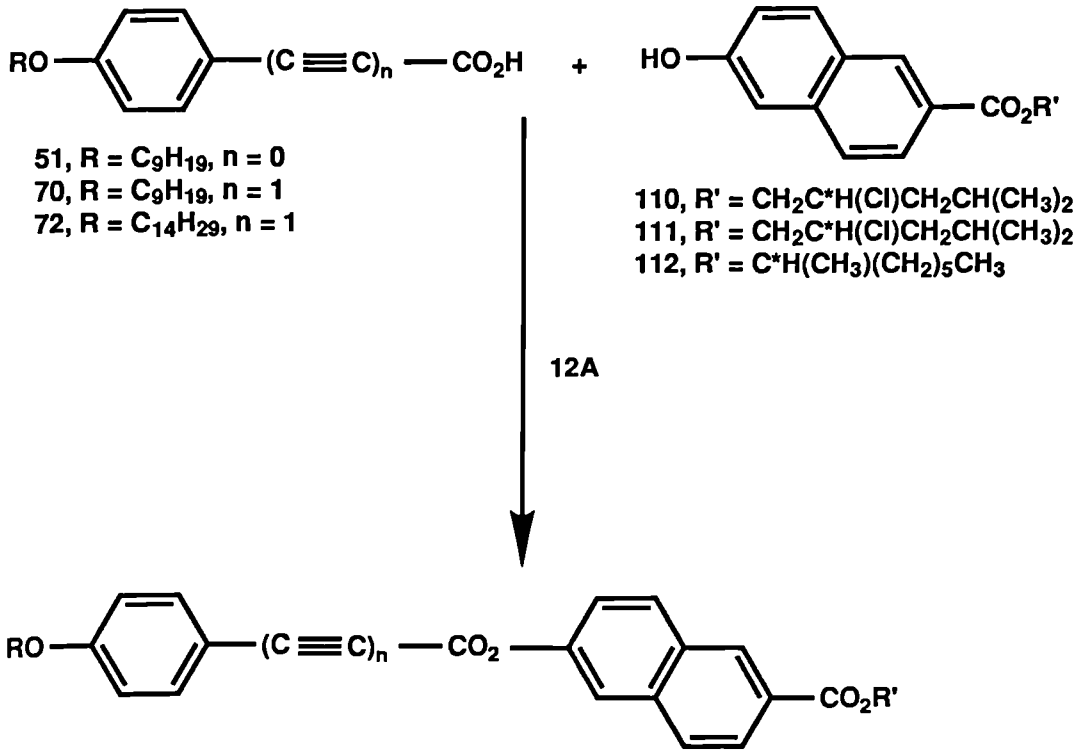
No.	R	n	R'
178	"	1	"
177	$C_{10}H_{21}$	0	"
179	C_7H_{15}	0	$CH_2C^*H(Cl)(CH_2)_7CH_3$
180	C_8H_{17}	"	"
181	C_9H_{19}	"	"
183	"	1	"
182	$C_{10}H_{21}$	0	"
184	C_7H_{15}	0	$CH_2C^*H(Cl)(CH_2)_9CH_3$
185	C_8H_{17}	"	"
186	C_9H_{19}	"	"
188	"	1	"
187	$C_{10}H_{21}$	0	"
189	C_7H_{15}	0	$CH_2C^*H(Br)CH_2CH(CH_3)_2$
190	C_8H_{17}	"	"
191	C_9H_{19}	"	"
193	"	1	"
192	$C_{10}H_{21}$	0	"
194	C_9H_{19}	0	$CH_2C^*H(F)CH_2CH(CH_3)_2$
195	"	1	"
196	$C_{14}H_{29}$	1	$C^*H(CH_3)(CH_2)_5CH_3$

Reaction Scheme 11



11A $(C_6H_{11}N)_2C$ (DCC), $(CH_3)_2NC_5H_4N$ (DMAP), $(CH_3CH_2)_2O$

Reaction Scheme 12



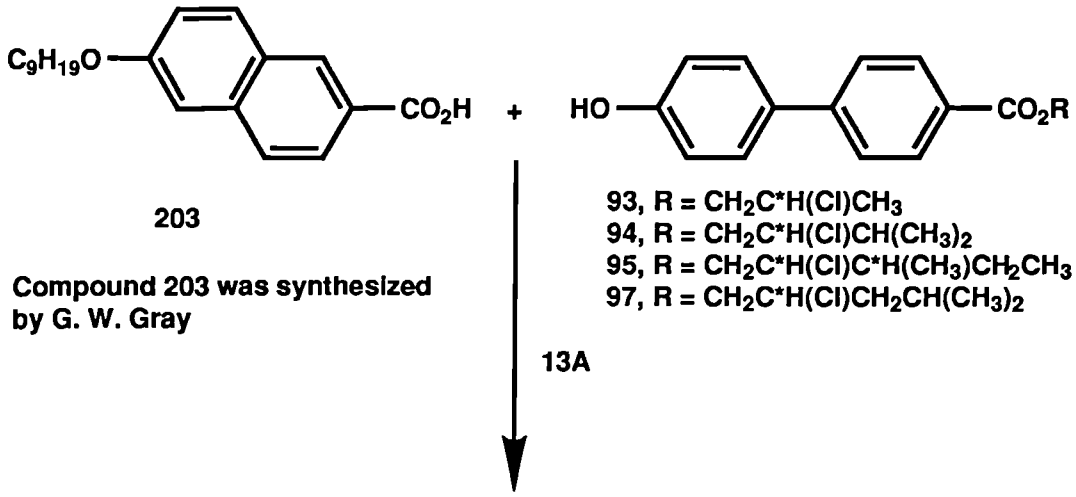
51, R = C_9H_{19}, n = 0
70, R = C_9H_{19}, n = 1
72, R = $C_{14}H_{29}$, n = 1

110, R' = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$
111, R' = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$ (+/-)
112, R' = $C^*H(CH_3)(CH_2)_5CH_3$

199, R = C_9H_{19}, n = 0, R' = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$
200, R = C_9H_{19}, n = 1, R' = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$
201, R = C_9H_{19}, n = 1, R' = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$ (+/-)
202, R = $C_{14}H_{29}$, n = 1, R' = $C^*H(CH_3)(CH_2)_5CH_3$

12A $(C_6H_{11}N)_2C$(DCC), $(CH_3)_2NC_5H_4N$ (DMAP),$(CH_3CH_2)_2O$

Reaction Scheme 13

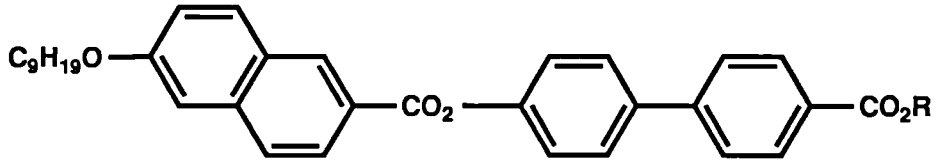


203

Compound 203 was synthesized by G. W. Gray

93, R = $CH_2C^*H(Cl)CH_3$
94, R = $CH_2C^*H(Cl)CH(CH_3)_2$
95, R = $CH_2C^*H(Cl)C^*H(CH_3)CH_2CH_3$ *(S,S)*
97, R = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$

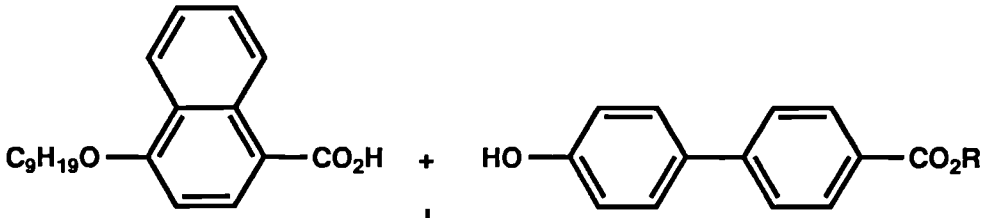
13A



204, R = $CH_2C^*H(Cl)CH_3$
205, R = $CH_2C^*H(Cl)CH(CH_3)_2$
206, R = $CH_2C^*H(Cl)C^*H(CH_3)CH_2CH_3$ *(S,S)*
207, R = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$

13A $(C_6H_{11}N)_2C$(DCC), $(CH_3)_2NC_5H_4N$ (DMAP), $(CH_3CH_2)_2O$

Reaction Scheme 14

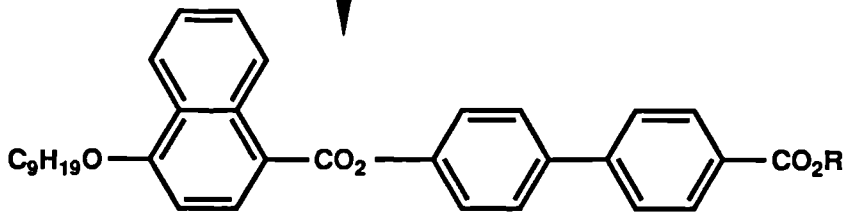


208

Compound 208 was synthesized by G. W. Gray

93, R = $CH_2C^*H(Cl)CH_3$
94, R = $CH_2C^*H(Cl)CH(CH_3)_2$
95, R = $CH_2C^*H(Cl)C^*H(CH_3)CH_2CH_3$ *(S,S)*
97, R = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$

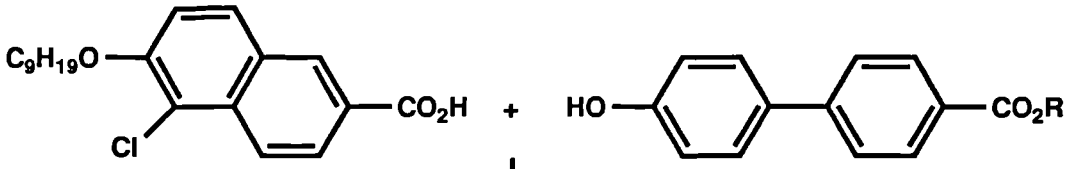
14A



209, R = $CH_2C^*H(Cl)CH_3$
210, R = $CH_2C^*H(Cl)CH(CH_3)_2$
211, R = $CH_2C^*H(Cl)C^*H(CH_3)CH_2CH_3$ *(S,S)*
212, R = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$

14A $(C_6H_{11}N)_2C$ (DCC), $(CH_3)_2NC_5H_4N$ (DMAP), $(CH_3CH_2)_2O$

Reaction Scheme 15

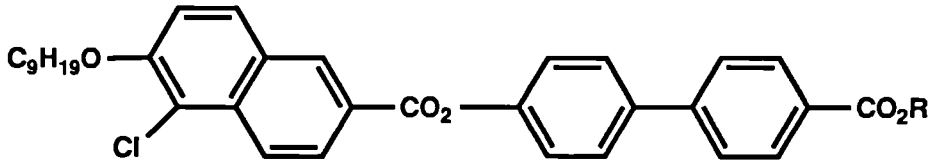


213

Compound 213 was synthesized by G. W. Gray

93, R = $CH_2C^*H(Cl)CH_3$
94, R = $CH_2C^*H(Cl)CH(CH_3)_2$
95, R = $CH_2C^*H(Cl)C^*H(CH_3)CH_2CH_3$ *(S,S)*
97, R = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$

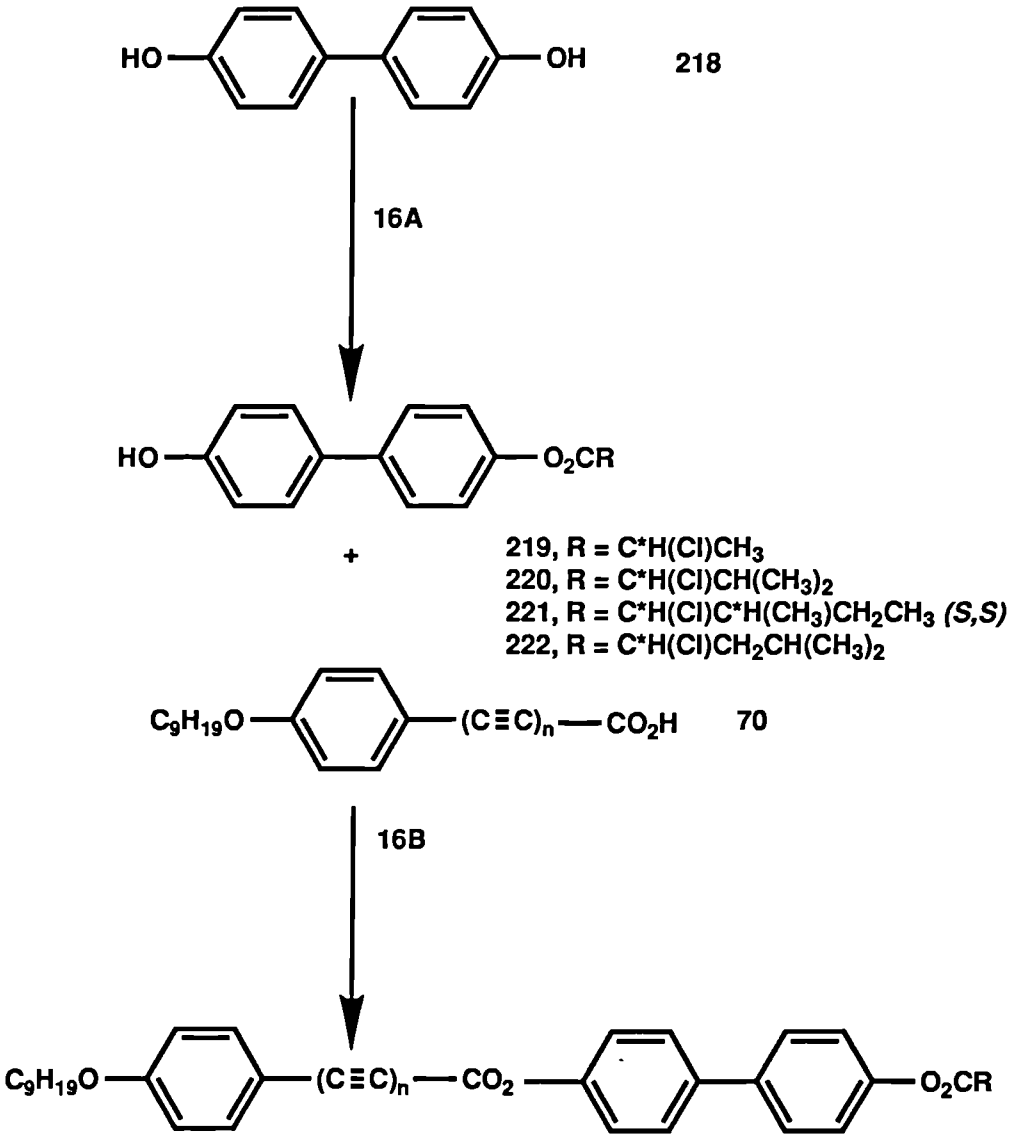
15A



214, R = $CH_2C^*H(Cl)CH_3$
215, R = $CH_2C^*H(Cl)CH(CH_3)_2$
216, R = $CH_2C^*H(Cl)C^*H(CH_3)CH_2CH_3$ *(S,S)*
217, R = $CH_2C^*H(Cl)CH_2CH(CH_3)_2$

15A $(C_6H_{11}N)_2C$ (DCC), $(CH_3)_2NC_5H_4N$ (DMAP), $(CH_3CH_2)_2O$

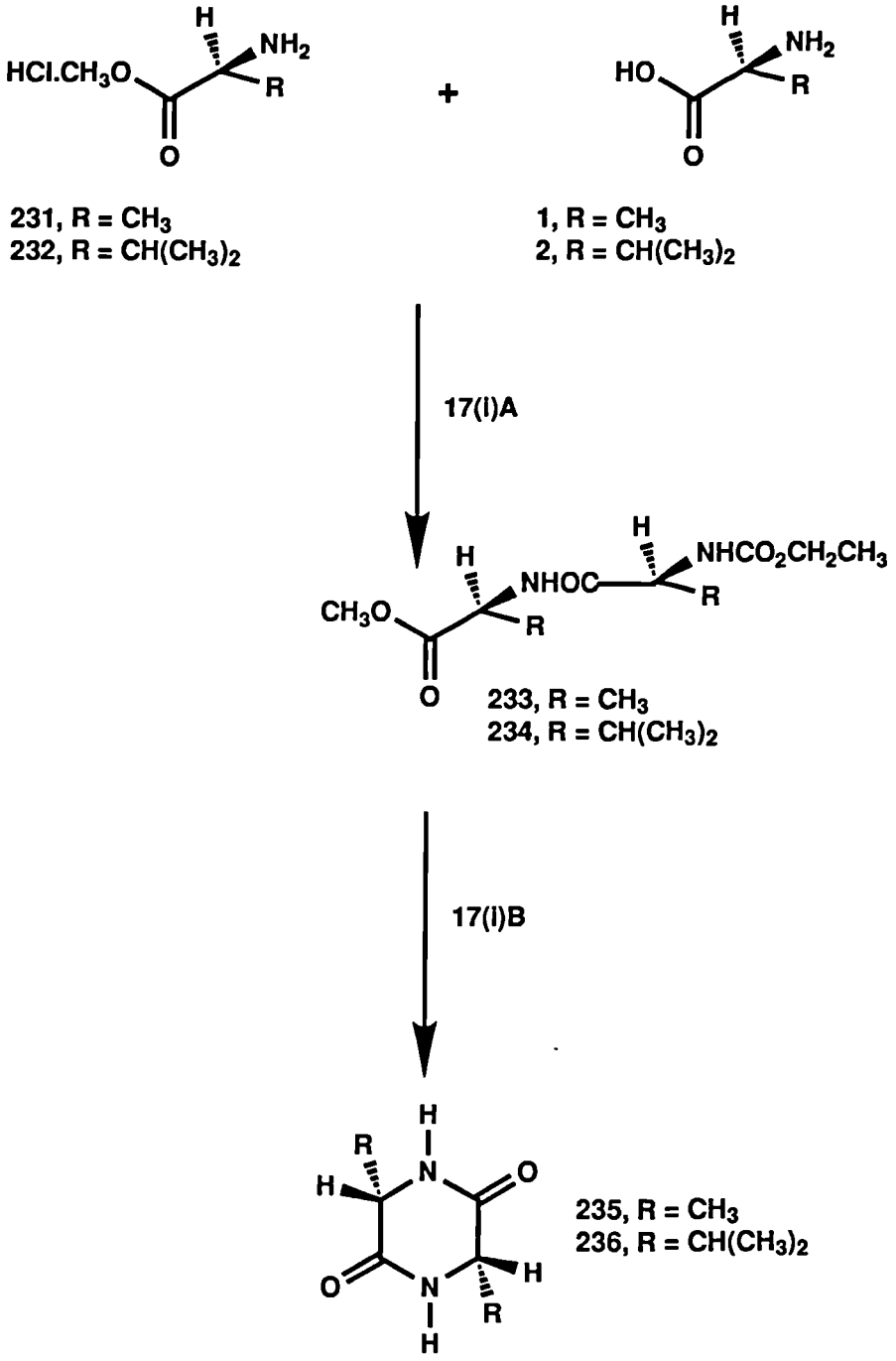
Reaction Scheme 16



223, n = 0, R = C*H(Cl)CH3
224, n = 0, R = C*H(Cl)CH(CH3)2
225, n = 0, R = C*H(Cl)C*H(CH3)CH2CH3 *(S,S)*
226, n = 0, R = C*H(Cl)CH2CH(CH3)2
227, n = 1, R = C*H(Cl)CH3
228, n = 1, R = C*H(Cl)CH(CH3)2
229, n = 1, R = C*H(Cl)C*H(CH3)CH2CH3 *(S,S)*
230, n = 1, R = C*H(Cl)CH2CH(CH3)2

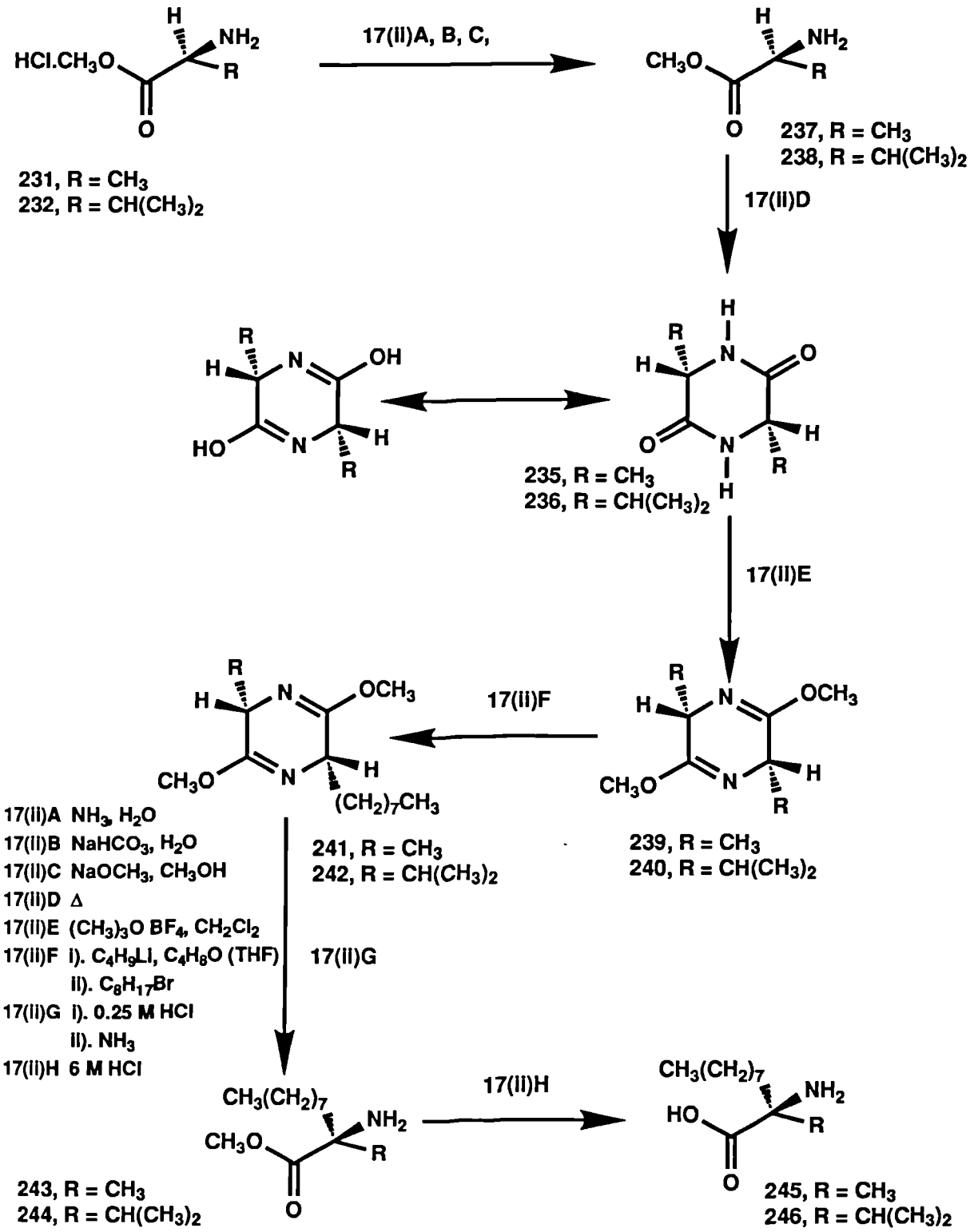
16A $(C_6H_{11}N)_2C$ (DCC), $(CH_3)_2NC_5H_4N$ (DMAP), C_4H_8O (THF)
16B $(C_6H_{11}N)_2C$ (DCC), $(CH_3)_2NC_5H_4N$ (DMAP), $(CH_3CH_2)_2O$

Reaction Scheme 17 (i)

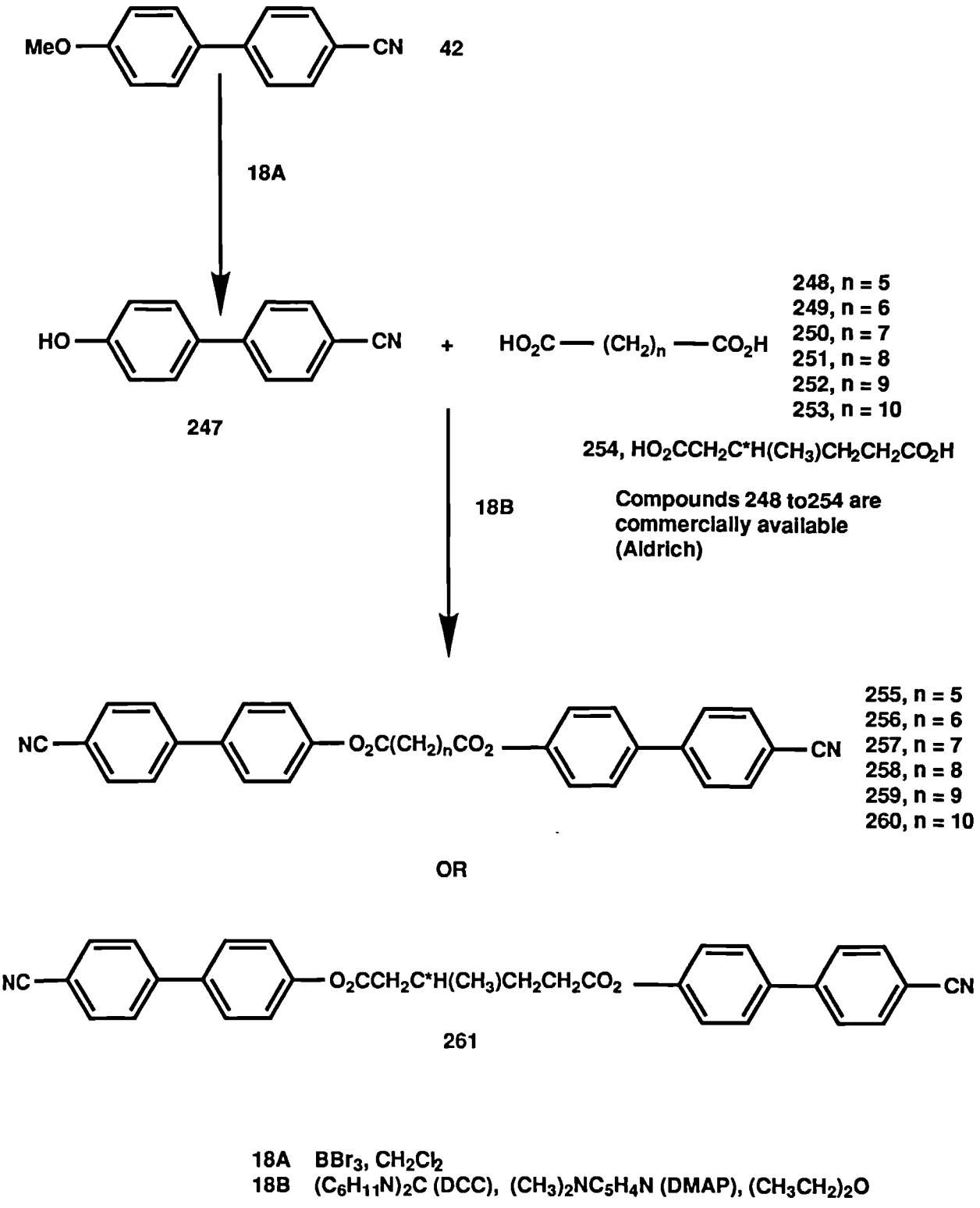


17(I)A I). CH_3CH_2COCl, C_4H_8O (THF)
II). $CH_3NC_4H_8O$, $(CH_3)_2NCO$
17(I)B I).10 % Pd/C, CH_3OH

Reaction Scheme 17 (ii)

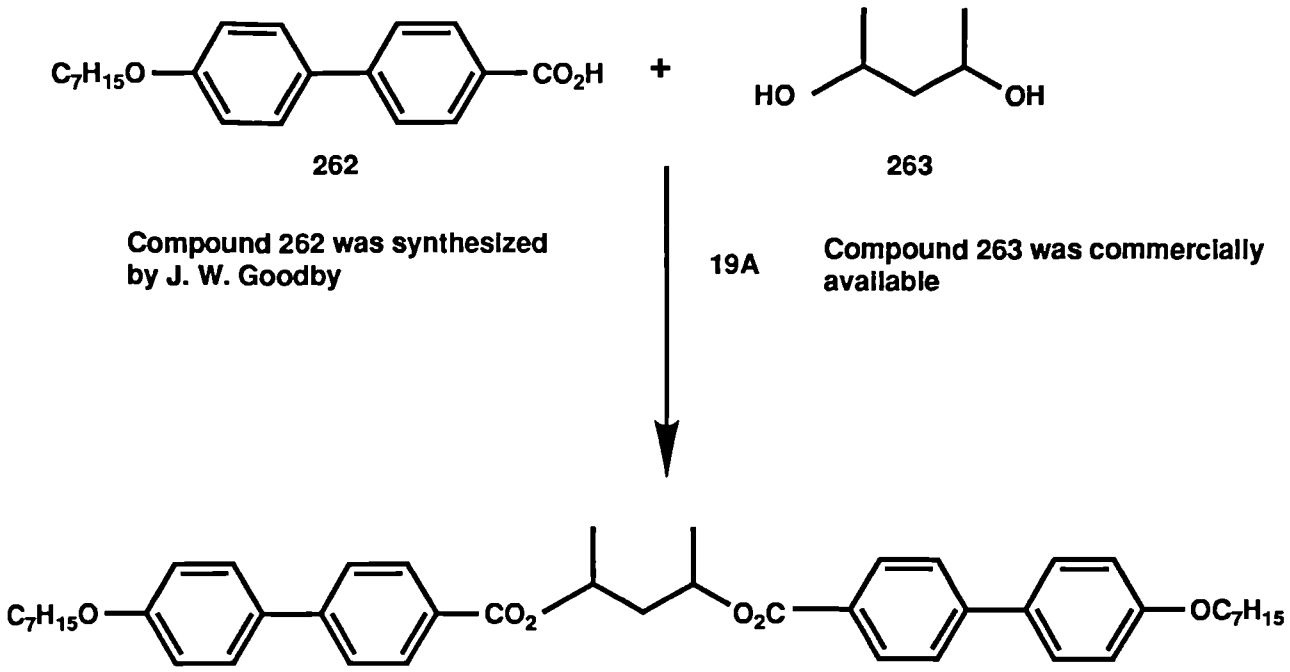


Reaction Scheme 18



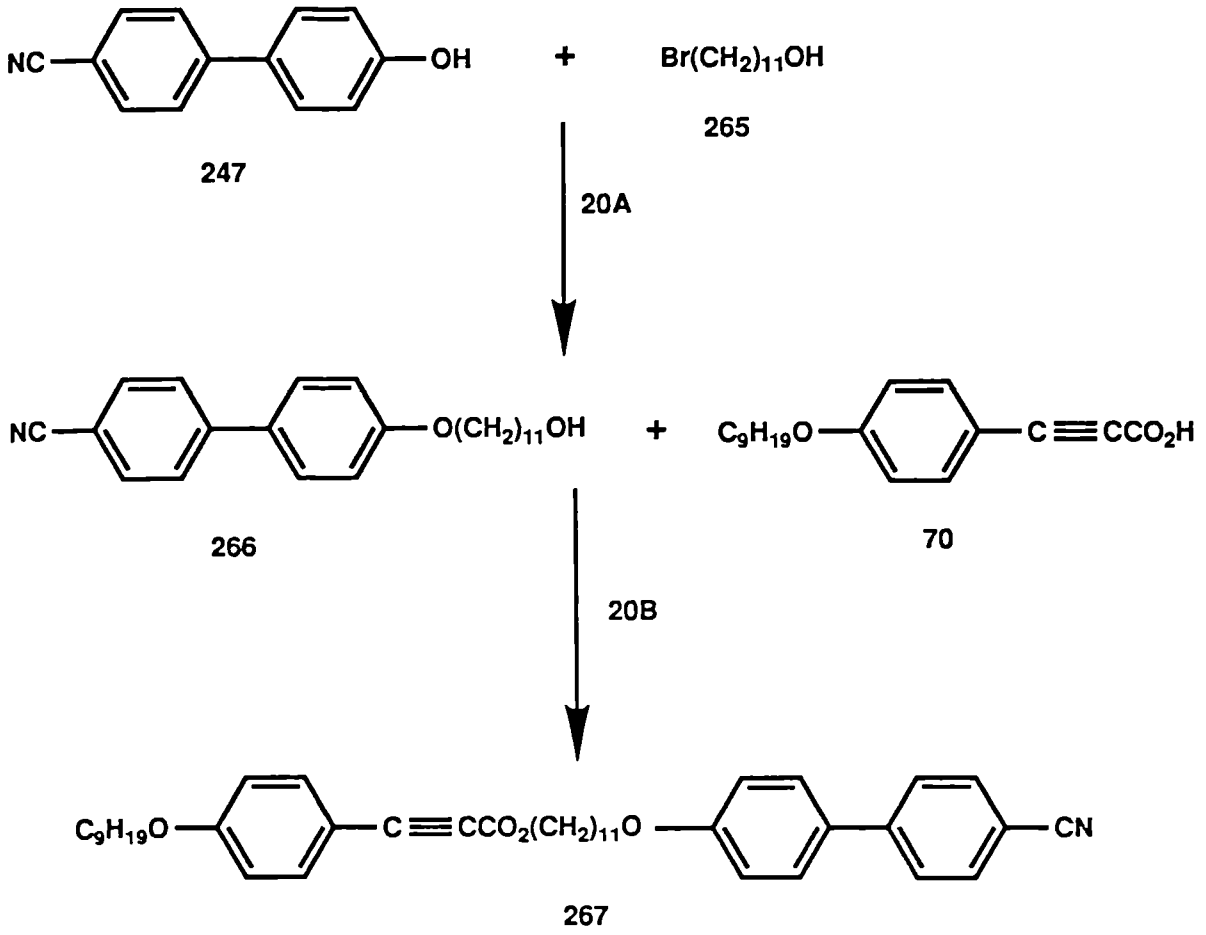
18A BBr_3, CH_2Cl_2
18B $(C_6H_{11}N)_2C$ (DCC), $(CH_3)_2NC_5H_4N$ (DMAP), $(CH_3CH_2)_2O$

Reaction Scheme 19



19A $(C_2H_5O_2CN)_2$ (DEAD, $(C_6H_5)_3P$, C_4H_8O (THF)

Reaction Scheme 20



20A K_2CO_3, C_4H_8O
20B $(C_6H_{11}N)_2C$ (DCC), $(CH_3)_2NC_5H_4N$ (DMAP), $(CH_3CH_2)_2O$

7.3 Experimental Procedures and Spectroscopic Data.

7.3.1 Reaction Scheme 1.

Preparation of (S)-2-Chloroalkanoic Acids

All *(S)*-2-chloroalkanoic acids were prepared using similar methods. The example given below illustrates the general method used; changes for specific acids are noted later.

***(S)-2-Chloropropanoic acid* 10**

To a stirred solution of *(S)*-alanine (**1**) (50 g, 0.6 mol) dissolved in 5 N hydrochloric acid (720 ml) and maintained at 0-5°, a cooled solution of sodium nitrite (62 g, 0.9 mol) dissolved in water (400 ml) was added dropwise. The mixture was stirred for a further 5 h at 0-5° and then allowed to warm to room temperature overnight. Stirring was continued for a further 3 h while the mixture was subjected to a partial pressure of approximately 20 mmHg, in order to remove nitrous oxide fumes. Solid sodium carbonate (56 g, 0.56 mol) was added, slowly, and the product extracted into diethyl ether (4 x 300 ml). The combined extracts were reduced in volume to approximately 500 ml by evaporation under reduced pressure and washed with brine. The combined ethereal extracts were dried over anhydrous calcium chloride for 8 h. After filtration the diethyl ether was then removed by evaporation under reduced pressure and the liquid residue purified by distillation. The fraction boiling between 48-54° at 0.1 mmHg was collected, to yield an almost colourless oil (**10**), (32.0 g, 53 %), (lit.[112] b.p. 75-77° at 10.0 mmHg). $[\alpha]_D^{25}$ -18.9° (79.4 mg cm^{-3} in $CHCl_3$), (lit.[112] -14.0°); $\nu_{max.}$ (thin film) 3700-2300 (O-H stretch), 1730 (C=O stretch), 1455 and 1440-1355 (C-H deformation), 1355-1115 (C-OH stretch or O-H deformation), 1080, 990 (O-H deformation, dimeric), 855, 720, 680; δ_H (270 MHz, $CDCl_3$) 11.95 (1 H, s, -$CO_2\underline{H}$), 4.47 (1 H, q, J 7.0 Hz, -$C\underline{H}$(Cl)-), 1.74 (3 H, d, J 7.0 Hz, $C\underline{H}_3$-); m/z 110, 108 (1:3) [M^+], 91 [M-(-OH)], 72 [M-(HCl)], 63 [M-(-CO_2H)], 58 [M-(CH_3Cl)], 45 [M-(CH_3CH(Cl)-)].

(S)-2-Chloro-3-methylbutanoic acid **11**

Quantity of acid (**2**) used in reaction (52.8 g, 0.45 mol), yield (36.1 g, 59 %), b.p. (66-74° at 0.3 mmHg), (lit.[112] b.p. 103-105° at 10.0 mmHg). $[\alpha]_D^{24}$ -4.5° (74.8 mg cm^{-3} in $CHCl_3$), (lit.[112] -1.4°); $\nu_{max.}$ (thin film) 3700-2300 (O-H stretch), 1725 (C=O stretch), 1470-1360 (C-H deformation), 1350-1130 (C-OH stretch or O-H deformation), 1000-880 (O-H deformation, dimeric), 850, 800, 700; δ_H (270 MHz, $CDCl_3$) 9.65 (1 H, s, -CO_2H), 4.20 (1 H, d, J 6.0 Hz, -CH(Cl)-), 2.36 (1 H, oct, J 6.5 Hz, -CH(CH_3)$_2$), 1.09 (3 H, d, J 7.0 Hz, -CH(CH_3)CH_3), 1.07 (3 H, d, J 7.0 Hz, -CH(CH_3)CH_3); m/z 137 [M^+], 101 [M-(HCl)], 96, 94 (1:3)[M-(-CH(CH_3)$_2$)], 78, 76 (1:3), 55, 45 [(M-(-CH(Cl)CH(CH_3)$_2$)].

(S,S)-2-Chloro-3-methylpentanoic acid **12**

Quantity of acid (**3**) used in reaction (100 g, 0.76 mol), yield (61.6 g, 54 %), b.p. (60-62° at 0.1 mmHg), (lit.[112] b.p. 111-112° at 10.0 mmHg). $[\alpha]_D^{25}$ -4.8° (155.3 mg cm^{-3} in $CHCl_3$), (lit.[112] -4.8°); $\nu_{max.}$ (thin film) 3700-2200 (O-H stretch), 1730 (C=O stretch), 1510-1380 (C-H deformation), 1290 and 1205 (C-OH stretch or O-H deformation), 1090, 970-860 (O-H deformation, dimeric), 840, 690; δ_H (270 MHz, $CDCl_3$) 9.70 (1 H, br s, -CO_2H), 4.23 (1 H, d, J 6.5 Hz, -CH(Cl)-), 2.11 (1 H, m, -CH(CH_3)CH(H)CH_3), 1.66 (1 H, m, -CH(CH_3)CH(H)CH_3), 1.35 (1 H, m, -CH(CH_3)CH_2CH_3), 1.06 (3 H, d, J 6.5 Hz, -CH(CH_3)CH_2CH_3), 0.94 (3H, t, J 7.0 Hz, -CH(CH_3)CH_2CH_3); m/z 150 [M^+], 115 [M-(-Cl)], 96, 94 (1:3) [M-(-C(CH_3)CH_2CH_3)], 78, 76 (1:3), 57, 45 [M-(-CH(Cl)CH(CH_3)CH_2CH_3)].

(S,R)-2-Chloro-3-methylpentanoic acid **13**

Quantity of acid (**4**) used in reaction (5 g, 0.38 mol), yield (2.8 g, 50 %), b.p. (58-68° at 0.1 mmHg). $[\alpha]_D$ (insufficient sample); $\nu_{max.}$ (thin film) 3720-2200 (O-H stretch), 1725 (C=O stretch), 1500-1390 (C-H deformation), 1290 and 1210 (C-OH stretch or O-H

deformation), 1090, 960-860 (O-H deformation, dimeric), 860, 700; δ_H (270 MHz, $CDCl_3$) 9.70 (1 H, br s, -CO_2H), 4.24 (1 H, d, J 6.5 Hz, -CH(Cl)-), 2.10 (1 H, m, -CH(CH_3)CH(H)CH_3), 1.66 (1 H, m, -CH(CH_3)CH(H)CH_3), 1.34 (1 H, m, -CH(CH_3)CH_2CH_3), 1.07 (3 H, d, J 6.5 Hz, -CH(CH_3)CH_2CH_3), 0.95 (3H, t, J 7.0 Hz, -CH(CH_3)CH_2CH_3); m/z 150 [M^+], 115 [M-(-Cl)], 96, 94 (1:3) [M-(-C(CH_3)CH_2CH_3)], 85, 76, 68, 45 [M-(-CH(Cl)CH(CH_3)CH_2CH_3)].

(S)-2-Chloro-4-methylpentanoic acid **14**

Quantity of acid (**5**) used in reaction (50.2 g, 0.38 mol), yield (35 g, 61 %), b.p. (72-78° at 0.1 mmHg), (lit.[112] b.p. 113-115° at 10.0 mmHg). $[\alpha]_D^{24}$ -34.2° (67.6 mg cm^{-3} in $CHCl_3$), (lit.[112] -31.7°); $\nu_{max.}$ (thin film) 3700-2100 (O-H stretch), 1725 (C=O stretch), 1525-1355 (C-H deformation), 1290 and 1210 (C-OH stretch or O-H deformation), 1120, 1030, 1005-780 (O-H deformation, dimeric), 685; δ_H (270 MHz, $CDCl_3$) 11.35 (1 H, s, -CO_2H), 4.36 (1 H, br t, J 7.0 Hz, -CH(Cl)-), 1.88 (3 H, m, -CH_2CH(CH_3)$_2$), 0.99 (3 H, d, J 6.5 Hz, -CH_2CH(CH_3)CH_3), 0.95 (3 H, d, J 6.5 Hz, -CH_2CH(CH_3)CH_3); m/z 152, 150 (1:3) [M^+], 114 [M-(HCl)], 96, 94 (1:3) [M-(-CHCH(CH_3)$_2$)], 73, 68, 59, 57 (1:3), 45 [M-(-CH(Cl)CH(CH_3)$_2$)].

(+/-)-2-Chloro-4-methylpentanoic acid **15**

Quantity of acid (**6**) used in reaction (50.2 g, 0.38 mol), yield (42.8 g, 75 %), b.p. (70-78° at 0.1 mmHg). $[\alpha]_D^{25}$ 0° (neat); $\nu_{max.}$ (thin film) 3600-2300 (O-H stretch), 1725 (C=O stretch), 1490-1350 (C-H deformation), 1290 and 1210 (C-OH stretch or O-H deformation), 1120, 1030, 1005-775 (O-H deformation, dimeric), 690; δ_H (270 MHz, $CDCl_3$) 11.95 (1 H, s, -CO_2H), 4.35 (1 H, br t, J 7.0 Hz, -CH(Cl)-), 1.88 (3 H, m, -CH_2CH(CH_3)$_2$), 0.99 (3 H, d, J 6.5 Hz, -CH_2CH(CH_3)CH_3), 0.95 (3 H, d, J 6.5 Hz, -CH_2CH(CH_3)CH_3); m/z 152, 150 (1:3) [M^+], 115 [M-(-Cl)], 96, 94 (1:3) [M-

(-$CHCH(CH_3)_2$)], 73, 68, 58, 56 (1:3) [M-(-$CH_2(Cl)CH(CH_3)_2$)], 45 [M-(-$CH(Cl)CH(CH_3)_2$)].

(S)-2-Chloro-4-thiopentanoic acid **16**

Reaction failed, no data collected for product.

(S)-2-Chloropentanoic acid **17**

Quantity of acid (**8**) used in reaction (5.29 g, 45.2 mmol), yield (3.69 g, 60 %), b.p. (76-78° at 0.1 mmHg). $[\alpha]_D^{21}$ -16.7° (42.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 3740-2200 (O-H stretch), 1730 (C=O stretch), 1510-1350 (C-H deformation), 1350-1160 (C-OH stretch or O-H deformation), 1140, 970-810 (O-H deformation, dimeric), 690; δ_H (270 MHz, $CDCl_3$) 10.50 (1 H, s, -$CO_2\underline{H}$), 4.35 (1 H, dd, J 8.0 Hz, -C$\underline{H}$(Cl)-), 1.98 (2 H, m, -CH(Cl)C$\underline{H_2}$-), 1.52 (2 H, m, -$CH(Cl)CH_2C\underline{H_2}$-), 0.97 (3 H, br t, J 7.0 Hz, -$CH(Cl)(CH_2)_2C\underline{H_3}$); m/z 137 [$M^+$], 101 [M-(HCl)], 96, 94 (1:3) [M-(-$(CH_2)_2CH_3$)], 76, 73, 58, 55, 45 [M-(-$CH(Cl)(CH_2)_2CH_3$)].

(S)-2-Chlorohexanoic acid **18**

Quantity of acid (**9**) used in reaction (5.67 g, 43.2 mmol), yield (3.58 g, 55 %), b.p. (70-72° at 0.1 mmHg). $[\alpha]_D^{21.5}$ -15.7° (58.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 3700-2300 (O-H stretch), 1720 (C=O stretch), 1500-1350 (C-H deformation), 1350-1145 (C-OH stretch or O-H deformation), 1140, 1080, 990-870 (O-H deformation, dimeric), 680; δ_H (270 MHz, $CDCl_3$) 10.16 (1 H, br s, -$CO_2\underline{H}$), 4.32 (1 H, dd, J 8.0 Hz, -C$\underline{H}$(Cl)-), 1.97 (2 H, m, -CH(Cl)C$\underline{H_2}$-), 1.42 (4 H, m, -$CH(Cl)CH_2(C\underline{H_2})_2$-), 0.93 (3 H, br t, J 7.0 Hz, -$CH(Cl)(CH_2)_3C\underline{H_3}$); m/z 150 [$M^+$], 115 [M-(HCl)], 96, 94 (1:3) [M-(-$CH(CH_2)_2CH_3$)], 87, 76, 73, 69, 57, 45 [M-(-$CH(Cl)(CH_2)_3CH_3$)].

Preparation of (S)-2-Chloroalkanols

All *(S)*-2-chloroalcohols were prepared using similar methods. The example given below illustrates the general method used; changes for specific alcohols are noted later.

(S)-2-chloropropan-1-ol **19**

A solution of *(S)*-2-chloropropanoic acid (**10**) (27.5 g, 0.3 mol) in dry diethyl ether (200 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (10.7 g, 0.3 mol) in dry diethyl ether (400 ml), which had been precooled to between 0-5°, over a period of approximately 10 m. The reaction was carried out under an atmosphere of dry nitrogen. The temperature of the reaction mixture was maintained with stirring for 15 m, and water (15 ml) was added slowly. The precipitate produced was dissolved in 2 N sulphuric acid (750 ml), and the ethereal and aqueous layers separated. The aqueous layer was extracted with diethyl ether (2 x 300 ml), the combined extracts and the original ether layer then being combined. The combined ethereal solution was washed successively with water (50 ml), saturated sodium carbonate solution (50 ml) and saturated sodium bicarbonate solution (50 ml). The ethereal solution was dried over sodium sulphate for 8 h, and then concentrated by evaporation of solvent to yield an oily residue which was purified by distillation. The fraction boiling between 38-43° at 20 mmHg was collected, to yield an almost colourless oil (**19**) (10.0 g, 44 %), (lit.[113] b.p. 131° at 725 mmHg). $[\alpha]_D^{22.5}$ +20.9° (21.0 mg cm^{-3} in $CHCl_3$), (lit.[113] +17.8°); $\nu_{max.}$ (thin film) 3740-3040 (O-H stretch), 3040-2720 (C-H stretch), 1460 and 1380 (C-H deformation), 1315-1240 and 1215 (C-OH stretch or O-H deformation), 1095, 1085-995 (C-OH stretch or O-H deformation), 985, 700, 620, 580, 500; δ_H (270 MHz, $CDCl_3$) 4.90 (1 H, s, -$CH_2O\underline{H}$), 4.03 (1 H, sext, J 6.5 Hz, -$C\underline{H}$(Cl)-), 3.61 (2 H, AB m, J_{gem} 11.5 Hz, -$C\underline{H_2}$OH), 1.46 (3 H, d, J 7.0 Hz, $C\underline{H_3}CH(Cl)$-); m/z 94 [M^+], 79 [M-(-CH_3)], 77 [M-(-OH)], 76 [M-(H_2O)], 65, 62, 58 [M-(HCl)].

(S)-2-Chloro-3-methylbutan-1-ol **20**

Quantity of acid (**11**) used in reaction (30 g, 0.2 mol), yield (13.9 g, 55 %), b.p. (28-34° at 0.1 mmHg), (lit.[113] b.p. 91° at 50 mmHg). $[\alpha]_D^{24}$ +7.3° (21 mg cm^{-3} in $CHCl_3$), (lit.[113] +3.6°); $\nu_{max.}$ (thin film) 3740-3100 (O-H stretch), 3060-2720 (C-H stretch), 1470 and 1390-1370 (C-H deformation), 1290 and 1200 (C-OH stretch or O-H deformation), 1120, 1075-1025 (C-OH stretch or O-H deformation), 800, 670; δ_H (270 MHz, $CDCl_3$) 3.93 (1 H, m, -C<u>H</u>(Cl)-), 3.78 (2 H, m, -C<u>H</u>$_2$OH), 3.58 (1 H, s, -CH$_2$O<u>H</u>), 2.21 (1 H, m, -C<u>H</u>$(CH_3)_2$), 1.04 (3 H, d, J 6.5 Hz, -CH(C<u>H</u>$_3$)CH$_3$), 1.01 (3 H, d, J 6.5 Hz, -CH(CH$_3$)C<u>H</u>$_3$); m/z 122 [M^+], 105 [M-(-OH)], 104 [M-(H_2O)], 86 [M-(HCl)], 69, 58, 54.

(S,S)-2-Chloro-3-methylpentan-1-ol **21**

Quantity of acid (**12**) used in reaction (38.8 g, 0.3 mol), yield (11.8 g, 35 %), b.p. (78-86° at 18 mmHg), (lit.[113] b.p. 75° at 10 mmHg). $[\alpha]_D^{25}$ -7.5° (106.9 mg cm^{-3} in $CHCl_3$), (lit.[113] -7.6°); $\nu_{max.}$ (thin film) 3720-3080 (O-H stretch), 3080-2680 (C-H stretch), 1460 and 1385 (C-H deformation), 1275 and 1190 (C-OH stretch or O-H deformation), 1120, 1075 and 1030 (C-OH stretch or O-H deformation), 835, 820, 775, 740, 705, 670, 605; δ_H (270 MHz, $CDCl_3$) 3.98 (1 H, m, -C<u>H</u>(Cl)-), 3.79 (2 H, m, -C<u>H</u>$_2$OH), 2.95 (1 H, s, -CH$_2$O<u>H</u>), 1.83 (1 H, m, -CH(Cl)C<u>H</u>(CH_3)-), 1.60 (1 H, m, -CH(CH_3)C(<u>H</u>)H-), 1.31 (1 H, m, -CH(CH_3)C(H)<u>H</u>-), 1.01 (3 H, d, J 6.5 Hz, -CH(Cl)CH(C<u>H</u>$_3$)-), 0.92 (3 H, t, J 7.0 Hz, -CH(CH_3)CH$_2$C<u>H</u>$_3$; m/z 136 [M^+], 135 [M-(-H)], 119 [M-(-OH)], 103 [M-(-CH_3), and (H_2O)], 101 [M-(-Cl)], 100 [M-(HCl)], 83, 79 [M-(-CH(CH_3)CH$_2$CH$_3$)], 69, 55, 54.

(S,R)-2-Chloro-3-methylpentan-1-ol **22**

Quantity of acid (**13**) used in reaction (2.53 g, 16.9 mmol), crude yield (1.2 g, 52 %). $[\alpha]_D$ (insufficient sample); $\nu_{max.}$ (insufficient sample); δ_H (270 MHz, $CDCl_3$) 3.96 (1 H,

m, -C<u>H</u>(Cl)-), 3.80 (2 H, m, -C<u>H</u>$_2$OH), 2.95 (1 H, s, -CH$_2$O<u>H</u>), 1.85 (1 H, m, -CH(Cl)C<u>H</u>(CH$_3$)-), 1.60 (1 H, m, -CH(CH$_3$)C(<u>H</u>)H-), 1.30 (1 H, m, -CH(CH$_3$) C(H)<u>H</u>-), 1.00 (3 H, d, J 6.5 Hz, -CH(Cl)CH(C<u>H</u>$_3$)-), 0.90 (3 H, t, J 7.0 Hz, -CH(CH$_3$)CH$_2$C<u>H</u>$_3$; m/z (Insufficient sample).

(S)-2-Chloro-4-methylpentan-1-ol **23**

Quantity of acid (**14**) used in reaction (28.4 g, 0.19 mol), yield (15.2 g, 59 %), b.p. (40-44° at 0.05 mmHg), (lit.[113] b.p. 92° at 30 mmHg). $[\alpha]_D^{26}$ -45.9° (50.1 mg cm^{-3} in $CHCl_3$), (lit.[113] -48.8°); $\nu_{max.}$ (thin film) 3740-3040 (O-H stretch), 3040-2720 (C-H stretch), 1470 and 1390 (C-H deformation), 1320-1245 and 1210 (C-OH stretch or O-H deformation), 1120-990 (C-OH stretch or O-H deformation), 890, 690, 620; δ_H (270 MHz, $CDCl_3$) 4.08 (1 H, m, -C<u>H</u>(Cl)-), 3.71 (2 H, m, -C<u>H</u>$_2$OH), 3.05 (1 H, s, -CH$_2$O<u>H</u>), 1.90 (1 H, m, -CH$_2$C<u>H</u>(CH$_3$)$_2$), 1.67 (1 H, m, -C(<u>H</u>)HCH(CH$_3$)$_2$), 1.49 (1 H, m, -C(H)<u>H</u>CH(CH$_3$)$_2$), 0.95 (3 H, d, J 6.5 Hz, -CH(C<u>H</u>$_3$)CH$_3$), 0.92 (3 H, d, J 6.5 Hz, -CH(CH$_3$)C<u>H</u>$_3$); m/z 136 [M$^+$], 119 [M-(-OH)], 103 [M-(-CH$_3$), and (H$_2$O)], 101 [M-(-Cl)], 100 [M-(HCl)], 83, 79 [M-(-CH$_2$CH(CH$_3$)$_2$)], 69, 55.

(+/-)-2-Chloro-4-methylpentan-1-ol **24**

Quantity of acid (**15**) used in reaction (25.0 g, 0.17 mol), yield (15 g, 65 %), b.p. (46-50° at 0.2 mmHg). $[\alpha]_D^{25}$ 0° (neat); $\nu_{max.}$ (thin film) 3720-3040 (O-H stretch), 3040-2690 (C-H stretch), 1470 and 1390 (C-H deformation), 1325-1240 and 1210 (C-OH stretch or O-H deformation), 1110-980 (C-OH stretch or O-H deformation), 900, 700, 610; δ_H (270 MHz, $CDCl_3$) 4.08 (1 H, m, -C<u>H</u>(Cl)-), 3.71 (2 H, m, -C<u>H</u>$_2$OH), 2.95 (1 H, s, -CH$_2$O<u>H</u>), 1.90 (1 H, m, -CH$_2$C<u>H</u>(CH$_3$)$_2$), 1.67 (1 H, m, -C(<u>H</u>)HCH(CH$_3$)$_2$), 1.49 (1 H, m, -C(H)<u>H</u>CH(CH$_3$)$_2$), 0.96 (3 H, d, J 6.5 Hz, -CH(C<u>H</u>$_3$)CH$_3$), 0.92 (3 H, d, J 6.5 Hz, -CH(CH$_3$)C<u>H</u>$_3$); m/z 136 [M$^+$], 119 [M-(-OH)], 103 [M-(-CH$_3$), and (H$_2$O)], 101 [M-(-Cl)], 100 [M-(HCl)], 83, 79 [M-(-CH$_2$CH(CH$_3$)$_2$)], 69, 55.

(S)-2-Chloro-4-thiopentan-1-ol acid **25**

Synthetic scheme failed at previous stage (Steps 1A and 1B).

(S)-2-Chloropentan-1-ol **26**

Quantity of acid (**17**) used in reaction (1.32 g, 9.7 mmol), crude yield (0.92 g, 77 %). $[\alpha]_D$ (insufficient sample); $\nu_{max.}$ (insufficient sample); δ_H (270 MHz, $CDCl_3$) 4.04 (1 H, m, -C<u>H</u>(Cl)-), 3.73 (2 H, m, -C<u>H</u>$_2$OH), 2.35 (1 H, br s, -CH$_2$O<u>H</u>), 1.73 (2 H, m, -C<u>H</u>$_2$CH(Cl)CH$_2$OH), 1.52 (2 H, m, CH$_3$C<u>H</u>$_2$-), 0.95 (3 H, br t, J 7.0 Hz C<u>H</u>$_3$(CH$_2$)$_2$-); m/z 121 [M-(-H)], 104 [M-(H_2O)], 90 [M-(CH_3OH)], 85, 79 [M-($CH_3(CH_2)_2$-)], 68, 57, 55.

(S)-2-Chlorohexan-1-ol **27**

Quantity of acid (**18**) used in reaction (3.24 g, 21.5 mmol), crude yield (2.1 g, 71 %). $[\alpha]_D$ (insufficient sample); $\nu_{max.}$ (insufficient sample); δ_H (270 MHz, $CDCl_3$) 4.02 (1 H, m, -C<u>H</u>(Cl)-), 3.73 (2 H, m, -C<u>H</u>$_2$OH), 2.25 (1 H, br s, -CH$_2$O<u>H</u>), 1.72 (2 H, m, -C<u>H</u>$_2$CH(Cl)CH$_2$OH), 1.36 (4 H, m, CH$_3$C<u>H</u>$_2$C<u>H</u>$_2$-), 0.92 (3 H, br t, J 7.0 Hz, C<u>H</u>$_3$CH$_2$-); m/z 135 [M-(-H)], 119 [M-(-OH)], 104 [M-(CH_3OH)], 100 [M-(HCl)], 87, 79 [M-($CH_3(CH_2)_3$-)], 69, 67, 57, 55.

Notes:

1. The example given, for the conversion of an α-amino acid to the corresponding α-chloro acid, describes the method used when *(S)*-alanine is the parent acid. For the less soluble amino acids, that is all others (**2** to **9**), the quantity of 5 N hydrochloric acid used was increased by a factor of 1.8. The amount of sodium carbonate used to buffer the solution on completion of reaction was adjusted accordingly. (Steps 1A and 1B)

2. The example given, for the reduction of an α-chloro acid to the corresponding alcohol, involves *(S)*-2-chloropropanoic acid as the starting material. The reaction time, in this

case, was 15 m. The reaction time for more sterically hindered acids, that is, all others (**11** to **18**) was increased to 30 m. (Step 1C)

3. *(S)*-2-Chlorohexan-1-ol (**28**), *(S)*-2-chlorodecan-1-ol (**29**), and *(S)*-2-chlorododecan-1-ol (**30**) were all commercially available[114].

7.3.2 Reaction Scheme 2.

(S)-2-Bromo-4-methylpentanoic acid **31**

To a stirred solution of *(S)*-leucine (**5**) (50 g, 0.42 mol) dissolved in 5 N hydrobromic acid (350 ml) and maintained at 0 - 5°, a cooled solution of sodium nitrite (29.1 g, 0.42 mol) dissolved in water (200 ml) was added dropwise. The mixture was stirred for a further 5 h at 0 - 5° and then allowed to warm to room temperature overnight. Stirring was continued for a further 3 h while the mixture was subjected to a partial pressure of approximately 20 mmHg, in order to remove nitrous oxide fumes. Sodium carbonate (27.2 g, 0.26 mol) was added, slowly, as a solid and the product extracted into diethyl ether (4 x 300 ml). The combined extracts were reduced in volume to approximately 500 ml by evaporation under reduced pressure and washed with brine. The combined ethereal extracts were dried over anhydrous calcium chloride for 8 h. After filtration the diethyl ether was then removed by evaporation under reduced pressure and the liquid residue purified by distillation. The fraction boiling between 190-200° at 0.1 mmHg was collected, to yield an almost colourless oil (**31**), (54.8 g, 67 %). $[\alpha]_D^{23.5}$ -2° (29.1 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 3720-2200 (O-H stretch), 1720 (C=O stretch), 1495-1360 (C-H deformation), 1280 and 1175 (C-OH stretch or O-H deformation), 1120, 1020, 990-890 (O-H deformation, dimeric), 680; δ_H (270 MHz, $CDCl_3$) 10.45 (1 H, s, -CO_2<u>H</u>), 4.30 (1 H, t, J 7.5 Hz, -C<u>H</u>(Br)-), 1.92 (3 H, m, -C<u>H</u>$_2$C<u>H</u>$(CH_3)_2$), 0.98 (3 H, d, J 6.5 Hz, -CH_2CH(C<u>H</u>$_3$)CH_3), 0.94 (3 H, d, J 6.5 Hz, -CH_2CH(CH_3)C<u>H</u>$_3$); m/z 196,

194 (1:1) [M^+], 179, 177 (1:1) [M-(-OH)], 168, 166 (1:1) [M-(-Br)], 140, 138 (1:1) [M-(-$CHCH(CH_3)_2$)], 97, 73, 69, 58, 45 [M-(-$BrCH_2CH(CH_3)_2$)].

(S)-2-Bromo-4-methylpentan-1-ol **32**

A solution of *(S)*-2-bromopropanoic acid (**31**), (40 g, 0.21 mol) in dry diethyl ether (100 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (7.8 g, 0.21 mol) in dry diethyl ether (400 ml), which had been precooled to between 0-5°, over a period of approximately 10 m. The reaction was carried out under an atmosphere of dry nitrogen. The temperature of the reaction mixture was maintained with stirring for 30 m, after which water (15 ml) was added slowly. The precipitate produced was dissolved in 2 N sulphuric acid (500 ml), and the ethereal and aqueous layers separated. The aqueous layer was extracted with diethyl ether (2 x 300 ml), the combined extracts and the original ether layer then being combined. The combined ethereal solution was washed successively with water (50 ml), saturated sodium carbonate solution (50 ml) and saturated sodium bicarbonate solution (50 ml). The ethereal solution was dried over sodium sulphate for 8 h and then concentrated by evaporation of solvent to yield an oily residue which was purified by distillation. The fraction boiling between 38-45° at 0.1 mmHg was collected, to yield an almost colourless oil (**32**), (20.5 g 55 %). $[\alpha]_D^{24}$ -1.1° (227.1 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 3720-3050 (O-H stretch), 3050-2740 (C-H stretch), 1500-1350 (C-H deformation), 1260 and 1110-985 (C-OH stretch or O-H deformation), 1180, 880, 640, 545; δ_H (270 MHz, $CDCl_3$) 4.21 (1 H, m, -C<u>H</u>(Br)-), 3.78 (2 H, m, -C<u>H</u>$_2$OH), 2.33 (1 H, s, -CH_2O<u>H</u>), 1.87 (1 H, m, -CH_2C<u>H</u>$(CH_3)_2$), 1.81 (1 H, m, -CH(Br)C(<u>H</u>)H$(CH_3)_2$), 1.56 (1 H, m, -CH(Br)C(H)<u>H</u>$(CH_3)_2$), 0.96 (3 H, d, J 6.5 Hz, -CH(C<u>H</u>$_3$)CH_3), 0.91 (3 H, d, J 6.5 Hz, -$CH(CH_3)$C<u>H</u>$_3$); m/z 180 [M^+], 179 [M-(-H)], 164, 162 (1:1) [M-(H_2O)], 137 [M-(-$CH(CH_3)_2$)], 99 [M-(HBr)], 82, 69, 67, 55.

7.3.3.1 Reaction Scheme 3 (i).

Preparation of the Ethyl Esters of 2-Hydroxyisocaproic Acid (Optically Active and Racemic Variants)

Both racemic and optically active hydroxy esters were prepared using an identical method. The example given below, for the optically active variant, illustrates the method used.

***(S)-Ethyl 2-hydroxy-4-methylpentanoate* 36**

(S)-2-Hydroxy-4-methylpentanoic acid (**34**) (13 g, 98.3 mmol), ethanol (500 ml) and fuming sulphuric acid (1 ml) were stirred under reflux for 24 h, during which time the reaction was monitored by glc. It appeared that 100 % conversion had been achieved. The ethanol was removed by evaporation under reduced pressure, and the oily residue was purified by distillation. The fraction boiling between 97-99° at 20 mmHg was collected, to yield an almost colourless oil (**36**), (8.2 g 47 %). $[\alpha]_D^{24}$ -7.7° (60.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 3740-3100 (O-H stretch), 3100-2650 (C-H stretch), 1745 (C=O stretch), 1475, 1375 (C-H deformation), 1275 and 1215 (C-OH stretch or O-H deformation), 1150 (C-OH stretch or O-H deformation), 1095, 1040, 940, 870, 755; δ_H (270 MHz, $CDCl_3$) 4.36 (2 H, q, J 7.0 Hz, $CH_3C\underline{H}_2O$-), 4.33 (1 H, dd, -C<u>H</u>(OH)-), 3.86 (1 H, s, -O<u>H</u>), 2.03 (1 H, m, $-CH_2C\underline{H}(CH_3)_2$), 1.69 (2 H, dd, $-CH(OH)C\underline{H}_2CH(CH_3)_2$), 1.43 (3 H, t, J 7.0 Hz, $C\underline{H}_3CH_2O$-), 1.09 (3 H, d, J 6.5 Hz, $-CH(C\underline{H}_3)CH_3$), 1.08 (3 H, d, J 6.5 Hz, $-CH(CH_3)C\underline{H}_3$); m/z 258, 229, 215, 173 [M-(-H), and + ($-CH_3$)], 161, 144 [M-($-CH_3$)], 116 [M-($-CH(CH_3)_2$)], 87, 73 [87-($-CH_3$), and + (-H)], 69, 55.

***(+/-)-Ethyl 2-hydroxy-4-methylpentanoate* 35**

Quantity of acid (**33**) used in reaction (5 g, 17.7 mmol), yield (2.8 g, 47 %), b.p. (98° at 20 mmHg). $[\alpha]_D^{24}$ 0° (84.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 3740-3080 (O-H stretch), 3080-2700 (C-H stretch), 1735 (C=O stretch), 1470, 1370 (C-H deformation), 1270 and 1210 (C-OH stretch or O-H deformation), 1140 (C-OH stretch or O-H

deformation), 1090, 1030, 930, 860, 740; δ_H (270 MHz, $CDCl_3$) 4.14 (2 H, q, J 7.0 Hz, $CH_3C\underline{H}_2O$-), 4.10 (1 H, t, J 7.0 Hz, -C<u>H</u>(OH)-), 3.62 (1 H, s, -O<u>H</u>), 1.80 (1 H, m, $-CH_2C\underline{H}(CH_3)_2$), 1.47 (2 H, t, J 7.0 Hz, $-CH(OH)C\underline{H}_2CH(CH_3)_2$), 1.21 (3 H, t, J 7.0 Hz, $C\underline{H}_3CH_2O$-), 0.86 (3 H, d, J 6.5 Hz, $-CH(C\underline{H}_3)CH_3$), 0.85 (3 H, d, J 6.5 Hz, $-CH(CH_3)C\underline{H}_3$); m/z 258, 229, 215, 173 [M-(-H), and + ($-CH_3$)], 161, 144 [M-($-CH_3$)], 116 [M-($-CH(CH_3)_2$)], 87, 73 [87-($-CH_3$), and + (-H)], 69, 55.

Fluorination of the (S)-Ethyl 2-hydroxy-4-methylpentanoate

Fluorination was attempted on the optically active hydroxy-ester only. See note later.

***(R)-2-Fluoro-4-methylpentanoic acid ethyl ester* 37**

(S)-Ethyl 2-hydroxy-4-methylpentanoate (**36**), (1.35 g, 8.4 mmol) was dissolved in dry dichloromethane (10 ml). The mixture was cooled to 0-5°, and a solution of mopholinoaminosulphur trifluoride (morpho-DAST) (2.2 g, 12.6 mmol) in dry dichloromethane (10 ml) was added dropwise, with stirring. Stirring was continued as the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was kept under nitrogen throughout. The solvent was then removed by evaporation under reduced pressure, to leave a light brown residue. Purification was attempted by bulb to bulb distillation, but proved unsuccessful.

Notes:

1. The fluorination was attempted on the optically active compound (**36**), using step 3(i)C. Step 3(ii)D was not used in this instance, due to problems with this type of synthetic scheme[115].

7.3.3.2 Reaction Scheme 3 (ii).

(S)-2-Fluoro-4-methylpentanoic acid **39**

Solid *(S)*-leucine (**5**) (5.25 g, 0.04 mol) was added, with stirring, to a mixture of sodium nitrite (4.14 g, 0.06 mol) and pyridinium-polyhydrogen fluoride (100 g), that had been previously cooled to between 0-5°. The reaction mixture was stirred at this temperature for a further 4 h before being allowed to warm to room temperature overnight. The reaction mixture was kept under nitrogen throughout. The mixture was extracted with dichloromethane (2 x 300 ml), the dichloromethane layers being washed with water (100 ml), and saturated sodium carbonate solution (100 ml). The solvent was removed by evaporation under reduced pressure after first being dried over anhydrous sodium sulphate for 8 h. The residue was purified by distillation. The fraction boiling between 56-62° at 0.7 mmHg was collected to yield a colourless oil (**39**) that became increasingly turbid on standing (1.5 g 30 %). $[\alpha]_D^{26}$ -4.1° (98.4 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 3700-1990 (O-H stretch), 1850-1500 (C=O stretch), 1500-1310 (C-H deformation), 1290 (C-OH stretch or O-H deformation), 1120 (C-OH stretch or O-H deformation), 1060, 960-790 (O-H deformation, dimeric), 620, 530; δ_H (270 MHz, $CDCl_3$) 8.41 (1 H, br s, -$CO_2\underline{H}$), 4.99 (1 H, m, J_{HF} 50.0 Hz, -C<u>H</u>(F)-), 2.66 (1 H, t, J 8.0 Hz, -C<u>H</u>(H)$CH(CH_3)_2$), 2.07 (1 H, t, J 8.0 Hz, -CH(<u>H</u>)$CH(CH_3)_2$), 1.84 (1 H, m, -C<u>H</u>$(CH_3)_2$), 0.99 (6 H, d, J 6.5 Hz, -$CH(C\underline{H}_3)_2$); m/z 114 [M-(HF)], 99 [M-(HF), and -($-CH_3$)], 92, 78, 70, 59 [M-(-$FCHCH(CH_3)_2$)], 58 [M-(-$FCH_2CH(CH_3)_2$)], 57, 55, 45 [M-(-$FCHCH_2CH(CH_3)_2$)].

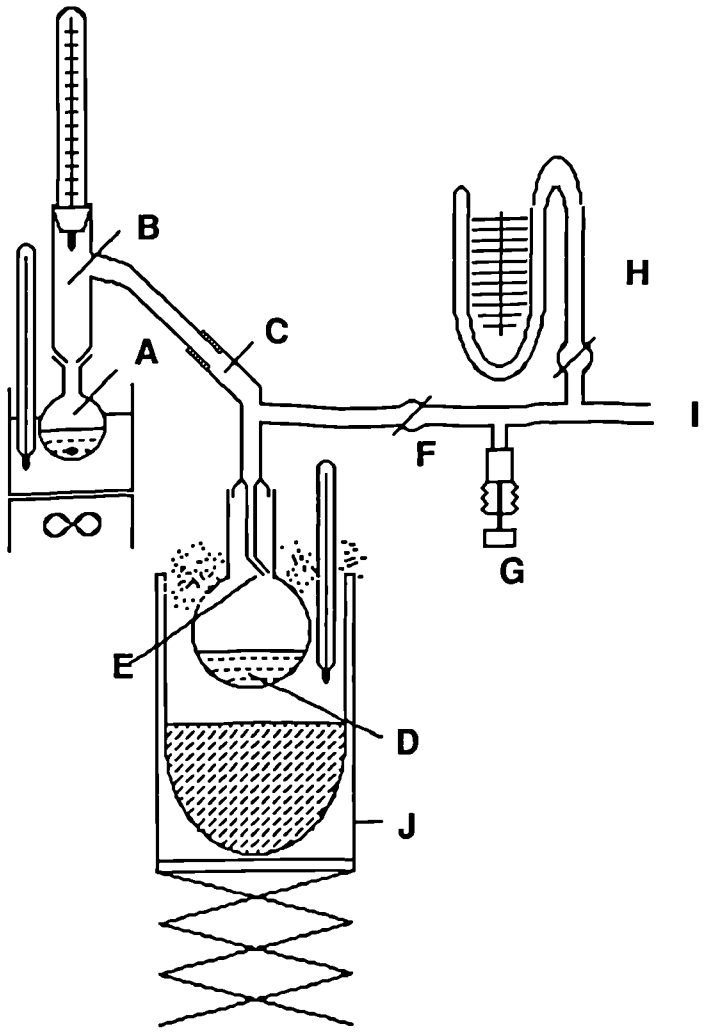
Notes:

1. Although the reaction was partially successful, a better alternative was sought.

7.3.1.3 Reaction Scheme 3 (iii).

(R)-1,2-Epoxy-4-methylpentane **41**

The reaction was carried out in a specially designed apparatus, in order to minimise loss of volatile oxirane[113]. The apparatus used for this reaction is illustrated in figure 40. The collecting flask (D) was cooled to approximately -80°, and a partial pressure of 100 mmHg obtained, whilst inlet valve (F) was kept closed. A solution of potassium hydroxide (9.45 g, 0.17 mol), in water (10 ml) was placed in vessel (A) which was then cooled to 0 °C. *(S)*-2-chloro-4-methylpentanol (**23**) (13.01 g, 0.01 mol) was added in one lot to the alkaline solution, and stillhead (B) fitted. The reaction mixture was kept at 0 °C, whilst being vigorously stirred. The pressure in the system was reduced to, and kept at 100 mmHg by sporadically opening valve (F). After 10 m the temperature of the reaction mixture was increased to 20°, a white precpitate of potassium chloride being formed as the cyclisation proceeded. The reaction mixture was then slowly heated, in order to generate a gentle boiling of the oxirane as it was formed, the product being collected in flask (D) as it distilled. On completion the apparatus was returned to atmospheric pressure, flask (D) being allowed to warm to room temperature. Water (lower layer) was removed from the product, which was then purified by distillation from calcium hydride, in the apparatus just described.



(A)-reaction vessel equipped with magnetic stirrer, (B)-Claisen stillhead, (C)-receiver adaptor with vacuum connection, (D)-collecting flask, (E)-inlet pipe, (F)-outlet valve, (G)-needle valve, to adjust pressure, (H)-mercury manometer, (I)-connected to water aspirator, (J)-Dewar, partially filled with liquid nitrogen and sealed with cotton wool.

Figure 40. The Experimental Set-Up for the Preparation of the Chiral Epoxide (40).

The fraction boiling between 108-112° at 710 mmHg was collected, to yield a colourless oil (**41**), (7.2 g, 75 %), (lit.[113] b.p. 108° at 730 mmHg). $[\alpha]_D^{24}$ +12.9° (48.9 mg cm^{-3} in $CHCl_3$), (lit.[113] +20.5°); $\nu_{max.}$ (thin film) 3050, 3015-2760 (C-H stretch), 1470 and 1385 (C-H deformation), 1370, 1260 (C-O stretch), 1190-1110, 920, 840, 810 (C-H stretch),

755; δ_H (270 MHz, $CDCl_3$) 2.93 (1 H, m, -C<u>H</u>CH_2-O-), 2.76 (1 H, dd, J_{cis} 4.0 Hz, J_{gem} 5.0 Hz, -CHC<u>H</u>(H)-O-), 2.44 (1 H, dd, J_{trans} 2.5 Hz, J_{gem} 5.0 Hz, -CHCH(<u>H</u>)-O-), 1.84 (1 H, m, -C<u>H</u>$(CH_3)_2$), 1.41 (2 H, m, -CHC<u>H</u>$_2$CH$(CH_3)_2$), 0.99 (3 H, d, J 6.5 Hz, -CHC<u>H</u>$_3$$(CH_3)$), 0.98 (3 H, d, J 6.5 Hz, -CHC$H_3$$(C$<u>H</u>$_3)$); m/z 100 [$M^+$], 85 [M-($CH_3$-)], 69, 67, 57, 55.

(S)-2-Fluoro-4-methylpentanol 40

(R)-1,2-Epoxy-4-methylpentane (**41**) (4 g, 0.04 mol) in dry diethyl ether (20 ml) was added slowly, with stirring, to pyridinium-polyhydrogen fluoride (12 ml) that had been previously cooled to 0-5°. The reaction mixture was stirred for 45 m under an atmosphere of dry nitrogen. Water (40 ml) was then added and the mixture extracted with diethyl ether (3 x 50 ml). The ether layer was then washed with saturated sodium carbonate solution (100 ml) and dried over anhydrous magnesium sulphate for 24 h. After removal of solvent the crude product was purified by distillation. The fraction boiling between 90-105° at 80 mmHg was collected, to yield an almost colourless oil (**38**) (1.95 g, 41 %). After examination of spectroscopic results a further distillation was carried out. The fraction boiling between 95-103° at 80 mmHg was collected, yield (1 g, 21 %). $[\alpha]_D^{25}$ (insufficient sample); $\nu_{max.}$ (insufficient sample); δ_H (270 MHz, $CDCl_3$) 4.66 (1 H, m, J_{HF} 50.0 Hz, -C<u>H</u>(F)-), 3.68 (2 H, m, -C<u>H</u>$_2$OH), 2.52 (1 H, br s, -CH_2O<u>H</u>), 1.72 (1 H, m, -C<u>H</u>$(CH_3)_2$), 1.36 (1 H, m, -C<u>H</u>(H)CH$(CH_3)_2$), 1.23 (1 H, m, -CH(<u>H</u>)CH$(CH_3)_2$), 0.95 (6 H, d, J 6.5 Hz, -CH(C<u>H</u>$_3)_2$); m/z (insufficient sample).

7.3.4 Reaction Scheme 4.

4'-Methoxy-4-biphenylcarboxylic acid 43

A mixture of 4-cyano-4'-methoxybiphenyl (**42**) (10.3 g, 0.05 mol), concentrated sulphuric acid (20 ml), water (20 ml) and glacial acetic acid (200 ml) was heated under reflux for 8 h.

The resultant hot mixture was poured into an ice and water mixture (500 ml), whereupon a white solid precipitated out. The mixture was left to cool to room temperature, the solid was filtered off and recrystallized from glacial acetic acid, to yield a white powder (**43**), (8.5 g, 82 %), (m.p. 252°, t.t. I 290.6 N 234.4 K), (lit.[116] t.t. K 258.0 N 300.0 I). $\nu_{max.}$ (KCl disc) 3300-2400 (O-H stretch), 1680 (C=O stretch), 1600 and 1530 (arom. C=C stretch), 1325-1220 (C-OH stretch or O-H deformation), 1200 (C-O stretch), 1030, 970-870 (O-H deformation, dimeric), 830 (1,4-disub. ring), 780, 710, 550; δ_H (270 MHz, $CDCl_3$) 8.00 (2 H, AA'XX', J_{AX} 7.6 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.65 (2 H, AA'XX', J_{AX} 7.6 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.60 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 6.91 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 3.75 (3 H, s, $C\underline{H}_3O$-); m/z 228 (M^+), 213 [M-(-CH_3)], 197 [M-(-OCH_3)], 185 [M-(-CH_2 (phenol)), and - (-CHO)], 168, 152, 139, 77 [M-($CH_3OC_6H_4$-), and -(CO_2)], 51 [77-(-C_2H_2)].

4'-Hydroxy-4-biphenylcarboxylic acid **44 (Step 4B)**

A mixture of 4'-methoxy-4-biphenylcarboxylic acid (**43**) (8 g, 0.05 mol), 48 % hydrobromic acid (100 ml) and glacial acetic acid (150 ml) was heated under reflux for 16 h. Water (100 ml) and a small amount of charcoal were added and the mixture was again heated under reflux momentarily. The solution was filtered hot, the filtrate was then allowed to cool to room temperature, where by the product precipitated out. This was filtered off and recrystallised fom glacial acetic acid, to yield a white powder (**44**), (6.9 g, 92 %), (m.p. approx. 300°). $\nu_{max.}$ (KCl disc) 3700-2140 (O-H stretch), 3700-2500 (vs O-H stretch), 1680 (C=O stretch), 1605 and 1535 (arom. C=C stretch), 1595, 1300-1200 (C-OH stretch or O-H deformation), 975-885 (O-H deformation, dimeric), 830 (1,4-disub. ring), 775, 720, 555; δ_H (270 MHz, $CDCl_3$) 9.33 (1 H, br s, -O$\underline{H}$ or -$CO_2\underline{H}$), 8.03 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.60 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.49 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 0.9 Hz, biphenyl), 6.91 (2 H,

AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 0.9 Hz, biphenyl); m/z 214 [M^+], 197 [M-(-OH)], 185 [M-(-CHO)], 169 [M-(-CO_2H)], 139, 115.

4'-Hydroxy-4-biphenylcarboxylic acid **44 (Step 4C)**

A mixture of 4-cyano-4'-methoxybiphenyl (**42**) (20 g, 0.09 mol), 48 % hydrobromic acid (150 ml) and glacial acetic acid (200 ml) was heated under reflux for 8 h. Water (100 ml) and a small amount of animal charcoal was added and the mixture heated under reflux momentarily. The solution was filtered hot, the filtrate was allowed to cool to room temperature, whereby the product precipitated out. The white solid was filtered off and recrystallized from glacial acetic acid, to yield a white powder (**44**), (18.8 g, 91 %), (m.p. approx. 300°). $\nu_{max.}$ (thin film) 3700-2140 (O-H stretch), 3700-2500 (vs O-H stretch), 1680 (C=O stretch), 1605 and 1535 (arom. C=C stretch), 1595, 1300-1200 (C-OH stretch or O-H deformation), 975-885 (O-H deformation, dimeric), 830 (1,4-disub. ring), 775, 720, 555; δ_H (270 MHz, $CDCl_3$) 9.33 (1 H, br s, -O<u>H</u> or -CO_2<u>H</u>), 8.03 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.60 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.49 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 0.9 Hz, biphenyl), 6.91 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 0.9 Hz, biphenyl); m/z 214 [M^+], 197 [M-(-OH)], 185 [M-(-CHO)], 169 [M-(-CO_2H)], 139, 115.

4'-Methoxycarbonyloxy-4-biphenylcarboxylic acid **45**

To a solution of sodium hydroxide (10.4 g, 0.26 mol) in water (300 ml), which had been precooled to -5°, 4'-hydroxy-4-biphenylcarboxylic acid (**34**) (19 g, 0.09 mol) was added. The reaction mixture was stirred vigorously and methyl chloroformate (14.2 g, 0.15 mol) was added slowly to the resulting suspension. The reaction mixture was stirred at 0° for 4 h and then brought to pH 5 by the dropwise addition of 5 N hydrochloric acid. The voluminous, white precipitate produced was filtered off and dried. The solid was recrystallized from glacial acetic acid and washed with water, to yield a white powder (**45**),

(21.5 g, 89 %), (t.t. K 233-235 N >300 I). $\nu_{max.}$ (KCl disc) 3300-3200 (O-H stretch), 1680 (C=O stretch), 1600 and 1530 (arom. C=C stretch), 1585, 1565, 1420, 1325-1220 (C-OH stretch or O-H deformation), 1200, 1130 (C-O stretch), 1035, 975-875 (O-H deformation, dimeric), 830 (1,4-disub. ring), 780, 710, 550, 500; δ_H (270 MHz, $CDCl_3$) 8.08 (2 H, AA'XX', biphenyl), 7.69 (2 H, AA'XX', biphenyl), 7.67 (2 H, AA'XX', biphenyl), 7.29 (2 H, AA'XX', J_{AX} 8.9 Hz, $J_{AX'}$ 0.6 Hz, biphenyl), 3.90 (3 H, s, $C\underline{H}_3OCO_2C_6H_4$-), m/z 272 [$M^+$], 228 [M-(-$CO_2$)], 213 [M-($CH_3OCO$-)], 197 [M-($CH_3OCO_2$-)], 185 (M-($CO_2$), and -(-$CH_2$(phenol), and -(-CHO)], 168, 157, 139, 59.

7.3.5 Reaction Scheme 5.

6-Hydroxy-2-naphthoic acid **48 (Step 5A)**

A solution of boron tribromide (9.1 g, 36.4 mmol) in dry dichloromethane (50 ml) was added dropwise, with stirring, to a solution of 6-methoxy-2-naphthoic acid (**46**) (3.67 g, 18.2 mmol) in dry dichloromethane (300 ml) that had been pre-cooled to -70°. The mixture was allowed to warm to room temperature overnight, whilst being kept under an atmosphere of dry nitrogen. The mixture was tipped into water (200 ml), and then the organic products were extracted into diethyl ether (2 x 500 ml). The ethereal layers were dried over magnesium sulphate for 8 h, and then removed by evaporation under reduced pressure, to yield a yellow powder (**48**), (3.02 g, 88 %), (m.p. 247°). $\nu_{max.}$ (KCl disc) 3500-3190 (vs O-H stretch), 3500-1750 (O-H stretch), 1670 (C=O stretch), 1620 and 1520 (arom. C=C stretch), 1480, 1290 and 1180 (C-OH stretch or O-H deformation), 860 (O-H deformation, dimeric), 830, 815, 765, 640, 530, 465; δ_H (270 MHz, $CDCl_3$) 9.59 (1 H, s, -O$\underline{H}$ or -$CO_2\underline{H}$), 8.47 (1 H, s, naphthalene), 7.94 (1 H, dd, J_o 8.5 Hz, J_m 1.5 Hz, biphenyl), 7.79 (1 H, d, J_o 9.5 Hz, naphthalene), 7.65 (1 H, d, J_o 8.5 Hz, naphthalene), 7.17 (1 H, s, naphthalene), 7.16 (1 H, dd, J_m 2.0 Hz, naphthalene); m/z 188 [M^+], 171 [M-(-OH)], 159 [M-(-CHO)], 143 [M-(-CO_2H)], 115, 80.

***6-Hydroxy-2-naphthoic acid* 48 (Step 5B)**

A mixture of 2-cyano-6-hydroxynaphthalene, (**47**) (5.2 g, 0.03 mol), concentrated sulpuric acid (20 ml), water (20 ml), and glacial acetic acid (200 ml) was heated under reflux for 16 h. The resultant hot mixture was poured into an ice/water mixture (400 ml), whereupon a white solid precipitated out. The mixture was left to cool to room temperature, the solid filtered off, and recrystallized from glacial acetic acid, to yield a brownish white powder (**48**), (3.7 g, 66 %), (m.p. 246-247°). $\nu_{max.}$ (KCl disc) 3500-3190 (vs O-H stretch), 3500-1750 (O-H stretch), 1670 (C=O stretch), 1620 and 1520 (arom. C=C stretch), 1480, 1290 and 1180 (C-OH stretch or O-H deformation), 860 (O-H deformation, dimeric), 830, 815, 765, 640, 530, 465; δ_H (270 MHz, $CDCl_3$) 9.59 (1 H, s, -O<u>H</u> or -CO_2<u>H</u>), 8.47 (1 H, s, naphthalene), 7.94 (1 H, dd, J_o 8.5 Hz, Jm_o 1.5 Hz, biphenyl), 7.79 (1 H, d, J_o 9.5 Hz, naphthalene), 7.65 (1 H, d, J_o 8.5 Hz, naphthalene), 7.17 (1 H, s, naphthalene), 7.16 (1 H, dd, J_m 2.0 Hz, naphthalene); m/z 188 [M^+], 171 [M-(-OH)], 159 [M-(-CHO)], 143 [M-(-CO_2H)], 115, 80.

***2-Methoxycarbonyloxynaphthyl-6-carboxylic acid* 49**

To a solution of sodium hydroxide (2.4 g, 0.06 mol) in water (150 ml), which had been precooled to -5°, 6-hydroxy-2-naphthoic acid (**48**) (3.7 g, 0.02 mol) was added. The reaction mixture was stirred vigorously, and methyl chloroformate (3.3 g, 0.04 mol) was added slowly to the resulting suspension. The reaction mixture was stirred at 0° for 4 h, and then brought to pH 5 by the dropwise addition of 5 N hydrochloric acid. The voluminous white precipitate produced was filtered off and dried. The dry solid then being recrystallized from glacial acetic acid and washed with water to yield an off-white powder (**49**), (5.1 g, 100 %), (m.p. 216-218°). $\nu_{max.}$ (KCl disc) 3270-2000 (O-H stretch), 1780 (CH_3)OC=O stretch), 1690 (C=O stretch), 1630 and 1540 (arom. C=C stretch), 1480, 1340, 1330 and 1220 (C-OH stretch or O-H deformation), 1210, 1160, 1130 (C-O stretch), 970, 945, 875, 810, 770, 605, 475; δ_H (270 MHz, $CDCl_3$) 9.66 (1 H, br s,

-$CO_2\underline{H}$), 8.62 (1 H, s, naphthalene), 8.09 (1 H, dd, J_o 8.5 Hz, J_m 1.5 Hz, naphthalene), 8.00 (1 H, d, J_o 9.0 Hz, naphthalene), 7.87 (1 H, d, J_o 8.5 Hz, naphthalene), 7.70 (1 H, d, J_m 2.0 Hz, naphthalene), 7.38 (1 H, dd, J_m 2.0 Hz, J_o 9.0 Hz, naphthalene), 3.95 (3 H, t, $C\underline{H}_3O(C{=}O)O$; m/z 246 ($M^+$), 202 [M-(-$CO_2$)], 185, 171 [M-($CH_3OCO_2$-)], 159, 142, 131, 114, 103, 77.

7.3.6 Reaction Scheme 6.

Preparation of 4-Alkoxybenzoic Acids

All 4-n-alkoxybenzoic acids were prepared using the same synthetic method. The example given below illustrates this method.

4-Nonyloxybenzoic acid **51**

4-Hydroxybenzoic acid (**50**) (13.8 g, 0.1 mol) was added slowly to a stirred solution of potassium hydroxide (11.2 g, 0.2 mol) in a mixture of ethanol (200 ml) and water (20 ml). To the resulting clear solution 1-bromononane (24.8 g, 0.12 mol) was added. The mixture was heated under reflux, with stirring for 16 h. To the mixture 10 % potassium hydroxide solution (10 ml) was added and the mixture was again heated under reflux for a further 2 h. The resulting solution was cooled to room temperature and poured into water (500 ml). The mixture was acidified with concentrated hydrochloric acid, causing the precipitation of a white solid. The solid was filtered off and recrystallized from ethanol, to yield white crystals (**51**), (13.2 g, 50 %), (t.t. K 94 S_C 119 N 145 I), (lit.[117] t.t. K 94 S_C 117 N 143 I). $\nu_{max.}$ (KCl disc) 3320-2000 (O-H stretch), 1690 (C=O stretch), 1610 and 1515 (arom. C=C stretch), 1580, 1465, 1370-1185 (C-OH stretch or O-H deformation), 1170 (C-O stretch), 1130, 1065, 1020, 980-900 (O-H deformation, dimeric), 845 (1,4-disub. ring), 770, 720, 695, 650, 550, 505; δ_H (270 MHz, $CDCl_3$) 8.05 (2 H, AA'XX', J_{AX} 9.3 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 6.93 (2 H, AA'XX', J_{AX} 9.3 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 4.03 (2 H, t, J 6.5 Hz, -$C\underline{H}_2$O-), 1.81 (2 H, m, -$C\underline{H}_2CH_2$O-), 1.47 (see 1.28, m, alkyl chain), 1.28

(12 H, br s, alkyl chain), 0.89 (3 H, br t, J 6.5 Hz, C<u>H</u>$_3$-chain); m/z 264 [M^+], 247 [M-(-OH)], 138 [M-(C_9H_{18}-)], 121 [138-(-OH)], 77, 55.

4-Decyloxybenzoic acid **52**

Quantity of acid (**50**) used in reaction (15.8 g, 0.11 mol), yield (16.7 g, 55 %), (t.t. K 94 S_C 120 N 140 I), (lit.[117] t.t. K 97 S_C 122 N 142 I). $\nu_{max.}$ (KCl disc) 3350-2000 (O-H stretch), 1690 (C=O stretch), 1610 and 1515 (arom. C=C stretch), 1580, 1470, 1360-1190 (C-OH stretch or O-H deformation), 1170 (C-O stretch), 1105, 1065, 1020, 940 (O-H deformation, dimeric), 845 (1,4-disub. ring), 770, 720, 695, 650, 550, 505; δ_H (270 MHz, $CDCl_3$) 8.05 (2 H, AA'XX', phenyl), 6.93 (2 H, AA'XX', phenyl), 4.03 (2 H, t, -C<u>H</u>$_2$O-), 1.78 (2 H, m, -C<u>H</u>$_2$$CH_2$O-), 1.46 (see 1.28, m, alkyl chain), 1.28 (14 H, br s, alkyl chain), 0.88 (3 H, br t, C<u>H</u>$_3$-chain); m/z 278 [M^+], 261 [M-(-OH)], 138 [M-($C_{10}H_{20}$-)], 121 [138-(-OH)], 83, 69.

4-Undecyloxybenzoic acid **53**

Quantity of acid (**50**) used in reaction (13.8 g, 0.1 mol), yield (14.1 g, 47 %), (t.t. K 84 S_C 127.5 N 140 I), (lit.[117] t.t. K 84.5 S_C 128 N 139.5 I). $\nu_{max.}$ (KCl disc) 3250-1990 (O-H stretch), 1690 (C=O stretch), 1610 and 1515 (arom. C=C stretch), 1580, 1470, 1365-1185 (C-OH stretch or O-H deformation), 1170 (C-O stretch), 1065, 1030, 985, 950 (O-H deformation, dimeric), 845 (1,4-disub. ring), 770, 720, 695, 650, 550, 505; δ_H (270 MHz, $CDCl_3$) 8.05 (2 H, AA'XX', phenyl), 6.93 (2 H, AA'XX', phenyl), 4.02 (2 H, t, -C<u>H</u>$_2$O-), 1.81 (2 H, m, -C<u>H</u>$_2$$CH_2$O-), 1.46 (see 1.27, m, alkyl chain), 1.27 (16 H, br s, alkyl chain), 0.88 (3 H, br t, C<u>H</u>$_3$-chain); m/z 292 [M^+], 275 [M-(-OH)], 138 [M-($C_{11}H_{22}$-)], 121 [138-(-OH)], 83, 69.

4-Dodecyloxybenzoic acid **54**

Quantity of acid (**50**) used in reaction (13.8 g, 0.1 mol), yield (13.3 g, 48 %), (t.t. K 95 S_C 131 N 139 I), (lit.[117] t.t. K 95 S_C 129 N 137 I). $\nu_{max.}$ (KCl disc) 3300-2000 (O-H stretch), 1690 (C=O stretch), 1610 and 1515 (arom. C=C stretch), 1580, 1470, 1360-1185 (C-OH stretch or O-H deformation), 1170 (C-O stretch), 1130, 1065, 995, 980-900 (O-H deformation, dimeric), 845 (1,4-disub. ring), 770, 720, 695, 650, 550, 505; δ_H (270 MHz, $CDCl_3$) 8.05 (2 H, AA'XX', phenyl), 6.93 (2 H, AA'XX', phenyl), 4.02 (2 H, t, -C<u>H</u>$_2$O-), 1.81 (2 H, m, -C<u>H</u>$_2$CH$_2$O-), 1.47 (see 1.30, m, alkyl chain), 1.30 (18 H, br s, alkyl chain), 0.87 (3 H, br t, C<u>H</u>$_3$-chain); m/z 306 [M^+], 289 [M-(-OH)], 138 [M-($C_{12}H_{24}$-)], 121 [138-(-OH)], 111.

Notes:

1. 4-Heptyloxybenzoic acid (**55**), 4-octyloxybenzoic acid (**56**), 4-tridecyloxybenzoic acid (**57**) and 4-tetradecyloxybenzoic acid (**58**) had previously been synthesized and were readily available.[118]

7.3.7.1 Reaction Scheme 7 (i).

Preparation of 4-Alkoxybenzaldehydes

All 4-alkoxybenzaldehydes were prepared using similar methods. The example given below illustrates the general method used. Any changes to this specific method for certain homologues are noted later.

4-Dodecyloxybenzaldehyde **61**

A mixture of 4-hydroxybenzaldehyde (**59**) (48.4 g, 0.4 mol), 1-bromododecane (100 g, 0.4 mol), potassium carbonate (110.6 g, 0.8 mol) and acetone (400 ml) was heated under reflux, with stirring for 72 h. The mixture was cooled to room temperature and added to water (1 l), which was then extracted with dichloromethane (2 x 400 ml). The yellow solid

produced after removal of solvent, by evaporation under reduced pressure, was recrystallized from ethanol, to yield a yellow powder (**61**), (101 g, 88 %), (m.p. 32-34°). $\nu_{max.}$ (KCl disc) 3140-2640 (C-H stretch), 1700 (C=O stretch), 1605 and 1515 (arom. C=C stretch), 1580, 1430, 1395, 1310, 1260 and 1110 (C-O stretch), 1160, 1120, 1020, 835 (1,4-disub. ring), 720, 650, 620, 515; δ_H (270 MHz, $CDCl_3$) 9.87 (1 H, s, -C<u>H</u>O), 7.83 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.6 Hz, phenyl), 7.00 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.6 Hz, phenyl), 4.07 (2 H, t, J 6.5 Hz, -C<u>H</u>$_2$O-), 1.80 (2 H, m, -C<u>H</u>$_2$CH$_2$O-), 1.46 (see 1.30, m, alkyl chain), 1.30 (18 H, br s, alkyl chain), 0.90 (3 H, br t, J 6.5 Hz, C<u>H</u>$_3$-chain); m/z 290 [M^+], 261 [M-(-CHO)], 140, 123 [M-($C_{12}H_{23}$-)], 105, 97 [M-(-$C_5H_{10}OC_6H_4CHO$), and -(2H)], 83 [M-(-$C_6H_{12}OC_6H_4CHO$), and -(2H)], 77, 69 [M-(-$C_7H_{14}OC_6H_4CHO$), and -(2H)].

4-Nonyloxybenzaldehyde **60**

Quantity of aldehyde (**59**) used in reaction (50.1 g, 0.41 mol), quantity of bromide used in reaction (85.4 g, 0.41 mol), yield (85 g, 84 %), b.p. (150-160° at 0.1 mmHg). $\nu_{max.}$ (KCl disc) 3040-2870 (C-H stretch), 1700 (C=O stretch), 1610 and 1505 (arom. C=C stretch), 1570, 1390, 1315, 1260 and 1110 (C-O stretch), 1160, 1015, 835 (1,4-disub. ring), 720, 655, 620, 525; δ_H (270 MHz, $CDCl_3$) 9.85 (1 H, s, -C<u>H</u>O), 7.80 (2 H, AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.05 (2 H, t, -C<u>H</u>$_2$O-), 1.80 (2 H, m, -C<u>H</u>$_2$CH$_2$O-), 1.45 (see 1.30, m, alkyl chain), 1.30 (12 H, br s, alkyl chain), 0.90 (3 H, br t, C<u>H</u>$_3$-chain); m/z 248 [M^+], 219 [M-(-CHO)], 163, 140, 123 [M-(C_9H_{17}-)], 105, 97 [M-(-$CH_2OC_6H_4CHO$), and -(2H)], 83 [M-(-$C_2H_4OC_6H_4CHO$), and -(2H)], 77, 69 [M-(-$C_3H_6OC_6H_4CHO$), and -(2H)].

4-Tetradecyloxybenzaldehyde **62**

Quantity of aldehyde (**59**) used in reaction (27 g, 0.22 mol), quantity of bromide used in reaction (61 g, 0.22 mol), yield (52 g, 90 %), (m.p. 36.5-37.5°). $\nu_{max.}$ (KCl disc) 3050-

2770 (C-H stretch), 1695 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1580, 1400, 1315, 1260 and 1110 (C-O stretch), 1160, 1020, 835 (1,4-disub. ring), 725, 655, 620, 520; δ_H (270 MHz, $CDCl_3$) 9.88 (1 H, s, -C<u>H</u>O), 7.84 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.03 (2 H, t, -C<u>H</u>$_2$O-), 1.79 (2 H, m, -C<u>H</u>$_2$CH$_2$O-), 1.46 (see 1.29, m, alkyl chain), 1.29 (22 H, br s, alkyl chain), 0.89 (3 H, br t, C<u>H</u>$_3$-chain); m/z 318 [M^+], 300, 289 [M-(-CHO)], 163, 135, 123 [M-($C_{14}H_{27}$-)], 111 [M-(-$C_6H_{12}C_6H_4CHO$)], 108, 105, 97 [M-(-$C_7H_{14}OC_6H_4CHO$), and -(2H)], 83 [M-(-$C_8H_{16}OC_6H_4CHO$), and -(2H)], 77, 69 [M-(-$C_9H_{18}OC_6H_4CHO$), and -(2H)].

4-Hexadecyloxybenzaldehyde **63**

Quantity of aldehyde (**59**) used in reaction (36.6 g, 0.3 mol), quantity of bromide used in reaction (100 g, 0.3 mol), yield (96.3 g, 86 %), (m.p. 42-44°). $\nu_{max.}$ (KCl disc) 3005-2680 (C-H stretch), 1690 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1580, 1400, 1310, 1255 and 1110 (C-O stretch), 1170, 1050, 1035, 1015, 835 (1,4-disub. ring), 720, 655, 620, 520; δ_H (270 MHz, $CDCl_3$) 9.89 (1 H, s, -C<u>H</u>O), 7.84 (2 H, AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.03 (2 H, t, -C<u>H</u>$_2$O-), 1.80 (2 H, m, -C<u>H</u>$_2$CH$_2$O-), 1.45 (see 1.29, m, alkyl chain), 1.29 (26 H, br s, alkyl chain), 0.88 (3 H, br t, C<u>H</u>$_3$-chain); m/z 346 [M^+], 328, 317 [M-(-CHO)], 163, 135, 123 [M-($C_{16}H_{31}$-)], 111 [M-(-$C_8H_{16}C_6H_4CHO$)], 108, 97 [M-(-$C_9H_{18}OC_6H_4CHO$), and -(2H)], 83 [M-(-$C_{10}H_{20}OC_6H_4CHO$), and -(2H)], 77, 69 [M-(-$C_{11}H_{22}OC_6H_4CHO$), and -(2H)].

4-Octadecyloxybenzaldehyde **64**

Quantity of aldehyde (**59**) used in reaction (36.6 g, 0.3 mol), quantity of bromide used in reaction (100 g, 0.3 mol), yield (102.2 g, 91 %), (m.p. 44.5-45.5°). $\nu_{max.}$ (KCl disc) 3000-2600 (C-H stretch), 1690 (C=O stretch), 1600 and 1510 (arom. C=C stretch), 1580, 1400, 1310, 1270 and 1110 (C-O stretch), 1170, 1035, 1035, 1010, 835 (1,4-disub. ring), 720, 655, 620, 520; δ_H (270 MHz, $CDCl_3$) 9.87 (1 H, s, -C<u>H</u>O), 7.84 (2 H,

AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.04 (2 H, t, -C<u>H</u>$_2$O-), 1.83 (2 H, m, -C<u>H</u>$_2$CH$_2$O-), 1.49 (see 1.31, m, alkyl chain), 1.31 (30 H, br s, alkyl chain), 0.90 (3 H, br t, C<u>H</u>$_3$-chain); m/z 374 [M$^+$], 356, 345 [M-(-CHO)], 163, 135, 123 [M-($C_{18}H_{35}$-)], 111 [M-(-$C_{10}H_{20}C_6H_4$CHO)], 108, 97 [M-(-$C_{11}H_{22}OC_6H_4$CHO), and -(2H)], 83 [M-(-$C_{12}H_{24}OC_6H_4$CHO), and -(2H)], 77, 69 [M-(-$C_{13}H_{26}OC_6H_4$CHO), and -(2H)].

Preparation of 4-n-Alkoxy-β,β-dibromostyrenes

All 4-n-alkoxy-β,β-dibromostyrenes were prepared using similar synthetic procedures. The example given below illustrates the general method used.

***4-Dodecyloxy-β,β-dibromostyrene* 66**

A solution of carbon tetrabromide (22.5 g, 0.07 mol) in dry dichloromethane (100 ml) was added dropwise, with stirring, to a mixture containing triphenylphosphine (17.8 g, 0.07 mol), zinc powder (4.5 g, 0.07 mol) and dry dichloromethane (100 ml). The resulting mixture was stirred at room temperature, under dry conditions, for 24 h. A solution containing 4-n-dodecyloxybenzaldehyde (**61**) (10 g, 0.03 mol) in dry dichloromethane (50 ml) was then added slowly, and stirring continued for a further 8 h. The resulting mixture was poured into hexane (600 ml), and the slurry was filtered through hyflo filter aid. After removal of solvent by evaporation under reduced pressure, the concentrate was purified by flash chromatography over silica gel using a mixture of hexane-diethyl ether (99:1) as the eluant to yield a yellow solid (**66**), (12.6 g, 82 %), (m.p. 39-39.5°). $\nu_{max.}$ (KCl disc) 3000-2550 (C-H stretch), 1725, 1610 and 1510 (arom. C=C stretch), 1425, 1395, 1310, 1285, 1255 and 1120 (C-O stretch), 1185, 1030, 1005, 870 (C-H deformation), 845-775 (1,4-disub. ring), 690, 665, 630; δ_H (270 MHz, $CDCl_3$) 7.49 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 7.39 (1 H, s, -C<u>H</u>=CBr_2), 6.87 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 3.96 (2 H, t, J 7.0 Hz, -C<u>H</u>$_2$O-), 1.80 (2 H, quin, -C<u>H</u>$_2$CH$_2$O-), 1.44 (see 1.27, m, alkyl chain), 1.27 (18 H, br s, alkyl chain), 0.86 (3 H, br t, J 7.0 Hz,

C<u>H</u>$_3$-chain); m/z 448, 446, 444 (1:2:1) [M^+], 366 [M-(HBr)], 304, 280, 278, 276 (1:2:1) [M-($C_{12}H_{25}$-)], 261 [M-($C_{12}H_{25}O$-)], 197, 118, 89, 69.

***4-Nonyloxy-β,β-dibromostyrene* 65**

Quantity of aldehyde (**60**) used in reaction (42.1 g, 0.17 mol), yield (90 g, 77 %), (m.p. 35.4°). $\nu_{max.}$ (KCl disc) 3010-2560 (C-H stretch), 1730, 1610 and 1510 (arom. C=C stretch), 1425, 1390, 1310, 1290, 1250 and 1120 (C-O stretch), 1185, 1030, 1010, 870 (C-H deformation), 830 (1,4-disub. ring), 690, 670, 630; δ_H (270 MHz, $CDCl_3$) 7.49 (2 H, AA'XX', phenyl), 7.40 (1 H, s, -C<u>H</u>=CBr_2), 6.87 (2 H, AA'XX', phenyl), 3.95 (2 H, t, -C<u>H</u>$_2$O-), 1.79 (2 H, quin, -C<u>H</u>$_2$CH_2O-), 1.45 (see 1.28, m, alkyl chain), 1.28 (12 H, br s, alkyl chain), 0.87 (3 H, br t, C<u>H</u>$_3$-chain); m/z 406, 404, 402 (1:2:1) [M^+], 324 [M-(HBr)], 304, 280, 278, 276 (1:2:1) [M-(C_9H_{19}-)], 261 [M-($C_9H_{19}O$-)], 197, 118, 83, 69.

***4-Tetradecyloxy-β,β-dibromostyrene* 67**

Quantity of aldehyde (**62**) used in reaction (47.7 g, 0.15 mol), yield (48.5 g, 68 %), (m.p. 44.2°). $\nu_{max.}$ (KCl disc) 3000-2740 (C-H stretch), 1610 and 1510 (arom. C=C stretch), 1570, 1460, 1305, 1260 and 1115 (C-O stretch), 1180, 1025, 870 (C-H deformation), 820 (1,4-disub. ring), 755, 720, 580, 530; δ_H (270 MHz, $CDCl_3$) 7.49 (2 H, AA'XX', phenyl), 7.40 (1 H, s, -C<u>H</u>=CBr_2), 6.87 (2 H, AA'XX', phenyl), 3.96 (2 H, t, -C<u>H</u>$_2$O-), 1.78 (2 H, quin, -C<u>H</u>$_2$CH_2O-), 1.45 (see 1.27, m, alkyl chain), 1.27 (22 H, br s, alkyl chain), 0.88 (3 H, br t, C<u>H</u>$_3$-chain); m/z 476, 474, 472 (1:2:1) [M^+], 394 [M-(HBr)], 303, 280, 278, 276 (1:2:1) [M-($C_{14}H_{29}$-)], 261 [M-($C_{14}H_{29}O$-)], 197, 152, 135, 118, 83, 69.

***4-Hexadecyloxy-β,β-dibromostyrene* 68**

Quantity of aldehyde (**63**) used in reaction (34.6 g, 0.1 mol), yield (40.1 g, 80 %), (m.p. 51-51.5°). $\nu_{max.}$ (KCl disc) 3020-2740 (C-H stretch), 1610 and 1510 (arom. C=C stretch), 1570, 1465, 1310, 1260 and 1115 (C-O stretch), 1180, 1025, 870 (C-H deformation), 855, 820 (1,4-disub. ring), 755, 730, 720, 580, 530; δ_H (270 MHz, $CDCl_3$) 7.50 (2 H, AA'XX', phenyl), 7.40 (1 H, s, -C<u>H</u>=CBr_2), 6.88 (2 H, AA'XX', phenyl), 3.96 (2 H, t, -C<u>H</u>$_2$O-), 1.78 (2 H, quin, -C<u>H</u>$_2$$CH_2$O-), 1.45 (see 1.27, m, alkyl chain), 1.27 (26 H, br s, alkyl chain), 0.88 (3 H, br t, C<u>H</u>$_3$-chain); m/z 504, 502, 500 (1:2:1) [M^+], 422 [M-(HBr)], 280, 278, 276, 276 (1:2:1) [M-($C_{16}H_{33}$-)], 261 [M-($C_{16}H_{33}$O-)], 197, 182, 135, 118, 97, 83, 69.

***4-Octadecyloxy-β,β-dibromostyrene* 69**

Quantity of aldehyde (**64**) used in reaction (34.9 g, 0.1 mol), yield (37.4 g, 66 %), (m.p. 56.5°). $\nu_{max.}$ (KCl disc) 3000-2740 (C-H stretch), 1610 and 1515 (arom. C=C stretch), 1570, 1465, 1305, 1250 and 1115 (C-O stretch), 1175, 1020, 870 (C-H deformation), 855, 820 (1,4-disub. ring), 755, 730, 720, 560, 530; δ_H (270 MHz, $CDCl_3$) 7.49 (2 H, AA'XX', phenyl), 7.40 (1 H, s, -C<u>H</u>=CBr_2), 6.87 (2 H, AA'XX', phenyl), 3.96 (2 H, t, -C<u>H</u>$_2$O-), 1.78 (2 H, quin, -C<u>H</u>$_2$$CH_2$O-), 1.45 (see 1.28, m, alkyl chain), 1.28 (30 H, br s, alkyl chain), 0.87 (3 H, br t, C<u>H</u>$_3$-chain); m/z 532, 530, 528 (1:2:1) [M^+], 450 [M-(HBr)], 280, 278, 276, 276 (1:2:1) [M-($C_{18}H_{37}$-)], 261 [M-($C_{18}H_{37}$O-)], 197, 118, 97, 83, 69.

Preparation of 4-Alkoxyphenylpropiolic acids

All 4-n-alkoxyphenylpropiolic acids were prepared using similar synthetic procedures. The example given below illustrates the general method used.

***4-Dodecyloxyphenylpropiolic acid* 71**

Butyllithium (1.6 m) (18 ml, 0.028 mol) was added dropwise, with stirring, to a solution of 4-dodecyloxy-β,β-dibromostyrene (**66**) (5.6 g, 0.013 mol) in dry tetrahydrofuran (100 ml), which had been precooled to -78°. Stirring was continued at this temperature for a further 2 h. The mixture was then added to an excess of solid carbon dioxide, and the whole allowed to warm to room temperature overnight. The reaction mixture was poured into water (300 ml), and then extracted into hexane (100 ml) in order to remove by-products. The hexane layer was separated off and the aqueous layer acidified (pH 4 to 5) with dilute hydrochloric acid (0.1 N). The aqueous layer was further extracted with diethyl ether (2 x 200 ml), in order to separate out the acid product. The ethereal extracts were combined and dried over magnesium sulphate for 8 h. After removal of the diethyl ether by evaporation under reduced pressure, the crude yellow solid obtained was recrystallized from a water-methanol mixture to obtain white needles (**71**), (2 g, 46 %), (t.t. K 104 N 117 I), (lit.[119] t.t. K 106 N 118 I). $\nu_{max.}$ (KCl disc) 3300-2730 (C-H stretch), 2200 (C≡C stretch), 1690 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1420, 1390, 1315, 1295, 1260 and 1110 (C-O stretch), 1220, 1170, 1065, 1030, 990, 955, 910, 830 (1,4-disub. ring), 745, 720, 610, 540; δ_H (270 MHz, $CDCl_3$) 7.57 (2 H, AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 6.87 (2 H, AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 4.00 (2 H, t, J 6.0 Hz, -C<u>H</u>$_2$O-), 1.81 (2 H, quin, -C<u>H</u>$_2$CH$_2$O-), 1.47 (see 1.33, m, alkyl chain), 1.33 (18 H, br s, alkyl chain), 0.89 (3 H, br t, J 7.0 Hz, C<u>H</u>$_3$-chain); m/z 330 [M^+], 320, 286 [M-(CO_2)], 162 [M-($C_{12}H_{24}$-)], 148, 118 [M-($C_{12}H_{24}$-), and -(CO_2)], 69, 55, 45 [M-($C_{12}H_{25}OC_6H_4C{\equiv}C$-)].

***4-Nonyloxyphenylpropiolic acid* 70**

Quantity of dibromostyrene (**65**) used in reaction (30 g, 0.074 mol), yield (11.4 g, 54 %), (t.t. K 94 N 113 I), (lit.[119] t.t. K 94 N 113 I). $\nu_{max.}$ (KCl disc) 3200-2640 (C-H stretch), 2200 (C≡C stretch), 1695 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1420,

1395, 1320, 1295, 1255 and 1110 (C-O stretch), 1230, 1170, 1065, 1020, 970, 925, 830 (1,4-disub. ring), 750, 725, 610, 540; δ_H (270 MHz, $CDCl_3$) 7.55 (2 H, AA'XX', phenyl), 6.88 (2 H, AA'XX', phenyl), 3.98 (2 H, t, -C<u>H</u>$_2$O-), 1.79 (2 H, quin, -C<u>H</u>$_2$CH$_2$O-), 1.45 (see 1.28, m, alkyl chain), 1.28 (12 H, br s, alkyl chain), 0.88 (3 H, br t, C<u>H</u>$_3$-chain); m/z 288 [M^+], 278, 244 [M-(CO_2)], 162 [M-(C_9H_{18}-)], 138, 118 [M-(C_9H_{18}-), and -(CO_2)], 69, 55, 45 [M-($C_9H_{19}OC_6H_4C{\equiv}C$-)].

***4-Tetradecyloxyphenylpropiolic acid* 72**

Quantity of dibromostyrene (**67**) used in reaction (15.2 g, 0.032 mol), yield (7.3 g, 64 %). $\nu_{max.}$ (KCl disc) 3200-2740 (C-H stretch), 2200 (C≡C stretch), 1670 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1415, 1290, 1255 and 1105 (C-O stretch), 1210, 1170, 1010, 925, 840 (1,4-disub. ring), 720, 610, 540; δ_H (270 MHz, $CDCl_3$) 7.55 (2 H, AA'XX', phenyl), 6.88 (2 H, AA'XX', phenyl), 3.98 (2 H, t, -C<u>H</u>$_2$O-), 1.79 (2 H, quin, -C<u>H</u>$_2$CH$_2$O-), 1.45 (see 1.27, m, alkyl chain), 1.27 (22 H, br s, alkyl chain), 0.88 (3 H, br t, C<u>H</u>$_3$-chain); m/z 358 [M^+], 314 [M-(CO_2)], 162 [M-($C_{14}H_{28}$-)], 148, 118 [M-($C_{14}H_{28}$-), and -(CO_2)], 69, 55, 45 [M-($C_{14}H_{29}OC_6H_4C{\equiv}C$-)].

***4-Hexadecyloxyphenylpropiolic acid* 73**

Quantity of dibromostyrene (**68**) used in reaction (10 g, 0.02 mol), yield (3.6 g, 47 %). $\nu_{max.}$ (KCl disc) 3120-2720 (C-H stretch), 2200 (C≡C stretch), 1680 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1420, 1355, 1290, 1260 and 1110 (C-O stretch), 1210, 1170, 1025, 920, 840 (1,4-disub. ring), 720, 610, 590, 540; δ_H (270 MHz, $CDCl_3$) 7.55 (2 H, AA'XX', phenyl), 6.88 (2 H, AA'XX', phenyl), 3.98 (2 H, t, -C<u>H</u>$_2$O-), 1.79 (2 H, quin, -C<u>H</u>$_2$CH$_2$O-), 1.45 (see 1.27, m, alkyl chain), 1.27 (26 H, br s, alkyl chain), 0.88 (3 H, br t, C<u>H</u>$_3$-chain); m/z 386 [M^+], 376, 342 [M-(CO_2)], 162 [M-($C_{16}H_{32}$-)], 147, 118 [M-($C_{16}H_{32}$-), and (CO_2)], 69, 55, 45 [M-($C_{16}H_{33}OC_6H_4C{\equiv}C$-)].

4-Octadecyloxyphenylpropiolic acid **74**

Quantity of dibromostyrene (**69**) used in reaction (25.1 g, 0.047 mol), yield (9.8 g, 50 %). $\nu_{max.}$ (KCl disc) 3200-2720 (C-H stretch), 2200 (C≡C stretch), 1670 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1415, 1290, 1255 and 1110 (C-O stretch), 1215, 1170, 1015, 925, 835 (1,4-disub. ring), 720, 610, 590, 545; δ_H (270 MHz, $CDCl_3$) 7.55 (2 H, AA'XX', phenyl), 6.89 (2 H, AA'XX', phenyl), 4.00 (2 H, t, -C$\underline{H_2}$O-), 1.81 (2 H, quin, -C$\underline{H_2}$CH_2O-), 1.43 (see 1.28, m, alkyl chain), 1.28 (30 H, br s, alkyl chain), 0.88 (3 H, br t, C$\underline{H_3}$-chain); m/z 414 [M^+], 404, 370 [M-(CO_2)], 162 [M-($C_{18}H_{36}$-)], 147, 118 [M-($C_{18}H_{36}$-), and -(CO_2)], 69, 57, 45 [M-($C_{18}H_{37}OC_6H_4C{\equiv}C$-)].

Notes:

1. 4-Nonyloxybenzaldehyde (**60**) was purified by reduced pressure distillation rather than recrystallization from ethanol, as it was an oil at room temperature.

7.3.7.2 Reaction Scheme 7 (ii).

1-Iodo-4-tetradecyloxybenzene **76**

A mixture of 4-iodophenol (**75**) (16.5 g, 0.075 mol), 1-bromotetradecane (20.8 g, 0.075 mol), potassium carbonate (31.1 g, 0.023 mol) and dry butanone (400 ml) was heated under reflux for 24 h. The mixture was allowed to cool to room temperature and the suspended solid was removed by filtration. The solvent was removed from the filtrate by evaporation under reduced pressure, leaving an oil that crystallized on standing. The crude product was recrystallized from 90 % aqueous ethanol, to yield a white waxy solid (**76**), (29.1 g, 93 %), (m.p. 48.3°). $\nu_{max.}$ (KCl disc) 3040-2660 (C-H stretch), 1590 and 1490 (arom. C=C stretch), 1570, 1390, 1285, 1250 and 1100 (C-O stretch), 1175, 1030, 1000, 830 (1,4-disub. ring), 815, 730, 720, 630, 510; δ_H (270 MHz, $CDCl_3$) 7.53 (2 H, AA'XX', J_{AB} 8.6 Hz, $J_{AB'}$ 0.9 Hz, phenyl), 6.66 (2 H, AA'XX', J_{AB} 8.6 Hz, $J_{AB'}$ 0.9

Hz, phenyl), 3.90 (2 H, t, J 6.5 Hz, -C<u>H</u>$_2$O-), 1.76 (2 H, quin, -C<u>H</u>$_2$CH$_2$O-), 1.43 (see 1.26, m, alkyl chain), 1.26 (22 H, br s, alkyl chain), 0.88 (3 H, br t, J 6.5 Hz, C<u>H</u>$_3$-chain); m/z 416 [M$^+$], 220 [M-($C_{14}H_{28}$-)], 203 [M-($C_{14}H_{29}O$-)], 94, 69.

4-Tetradecyloxyphenylacetylene **77**

A solution of anhydrous zinc chloride (14.6 g, 107.2 mmol) in dry tetrahydrofuran (200 ml) was added dropwise to a suspension of tetrakis-triphenylphosphine-palladium complex ($Pd(PPh_3)_4$) (12.51 g, 13.4 mmol) in dry tetrahydrofuran (150 ml) that had been pre-cooled to 0°. The resulting mixture was allowed to warm to room temperature and then stirred for a further 30 m, during which time the mixture took on a chocolate brown colour. The mixture was again cooled to 0° and a solution of 4-n-tetradecyloxy-4'-iodobenzene (**76**) in dry tetrahydrofuran (200 ml) was added, slowly. Stirring was continued for 10 m and lithium acetylide ethylene-diamine complex was added in one portion. The reaction mixture was stirred at room temperature for 1 h, and then quenched with 2 M hydrochloric acid (100 ml). Petroleum spirit (100 ml) was added and the resulting mixture stirred. The two layers were separated, and the aqueous layer was extracted with diethyl ether (2 x 200 ml). The combined organic layers were washed with saturated sodium bicarbonate solution (100 ml) and dried over anhydrous magnesium sulphate. After removal of the solvent, the residue was purified by flash chromatography over silica gel using a mixture of petroleum spirit-diethyl ether (20:1) as the eluant, to yield a colourless oil that crystallized on standing to give a white solid (**76**) (1.4 g, 4 %), (m.p. oil at room temperature). $\nu_{max.}$ (KCl disc) 3310 (C≡C-H, C-H stretch), 3020-2760 (C-H stretch), 2100 (C≡C stretch), 1610 and 1510 (arom. C=C stretch), 1570, 1380, 1290, 1250 and 1100 (C-O stretch), 1170, 1040, 830 (1,4-disub. ring), 720, 640, 590, 535; δ_H (270 MHz, $CDCl_3$) 7.41 (2 H, AA'XX', J_{AB} 8.2 Hz, $J_{AB'}$ 0.8 Hz, phenyl), 6.82 (2 H, AA'XX', J_{AB} 8.2 Hz, $J_{AB'}$ 0.8 Hz, phenyl), 3.94 (2 H, t, J 6.5 Hz, -C<u>H</u>$_2$O-), 2.99 (1 H, s, -C≡C<u>H</u>), 1.78 (2 H, quin, -C<u>H</u>$_2$CH$_2$O-),

1.45 (see 1.26, m, alkyl chain), 1.26 (22 H, br s, alkyl chain), 0.90 (3 H, br t, J 7.0 Hz, $C\underline{H}_3$-chain); m/z 304 [M^+], 303 [M-(-H)], 118 [M-($C_{14}H_{28}$-)], 69, 55.

***4-Tetradecyloxyphenylpropiolic acid* 72**

Butyllithium (1.6 m) (3 ml, 4.80 mmol) was added dropwise, with stirring, to a solution of 4-tetradecyloxyphenylacetylene (**77**) (1.3 g, 4.8 mmol) in dry tetrahydrofuran (30 ml), which had been precooled to -5°. Stirring was continued at this temperature for a further 30 m. The mixture was then added to an excess of solid carbon dioxide (100 g), and allowed to warm to room temperature over a period of 1 h. The reaction mixture was poured into water (200 ml), and then extracted into hexane (100 ml) in order to remove by-products. The hexane layer was separated off and the aqueous layer made acidic (pH 4 to 5) with dilute hydrochloric acid. The aqueous layer was further extracted with diethyl ether (2 x 200 ml), in order to separate out the acid product. The ethereal extracts were combined and dried over magnesium sulphate for 8 h. After removal of the diethyl ether by evaporation under reduced pressure, the crude yellow solid obtained was recrystallized from a water-methanol mixture to obtain white needles (**72**), (0.2 g, 12 %), (t.t. insufficient sample). $\nu_{max.}$ (KCl disc) 3200-2740 (C-H stretch), 2200 (C≡C stretch), 1670 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1415, 1290, 1255 and 1105 (C-O stretch), 1210, 1170, 1010, 925, 840 (1,4-disub. ring), 720, 610, 540; δ_H (270 MHz, $CDCl_3$) 7.55 (2 H, AA'XX', phenyl), 6.88 (2 H, AA'XX', phenyl), 3.98 (2 H, t, -$C\underline{H}_2$O-), 1.79 (2 H, quin, -$C\underline{H}_2CH_2$O-), 1.45 (see 1.27, m, alkyl chain), 1.27 (22 H, br s, alkyl chain), 0.88 (3 H, br t, $C\underline{H}_3$-chain); m/z 358 [M^+], 314 [M-(CO_2)], 162 [M-($C_{14}H_{28}$-)], 148, 118 [M-($C_{14}H_{28}$-), and -(CO_2)], 69, 55, 45 [M-($C_{14}H_{29}OC_6H_4C{\equiv}C$-)].

7.3.8.1 Reaction Scheme 8 (i).

Preparation of Alkyl 4'-Methoxycarbonyloxy-4-biphenylcarboxylates

All alkyl 4'-methoxycarbonyloxy-4-biphenylcarboxylates in this scheme were prepared using similar synthetic procedures. The example given below illustrates the general method used.

***(S)-2-Bromo-4-methylpentyl 4'-methoxycarbonyloxy-4-biphenyl carboxylate* 90**

A mixture of 4'-methoxycarbonyloxy-4-biphenylcarboxylic acid (**45**) (1 g, 3.67 mmol) and thionyl chloride (30 ml) was stirred overnight, under dry conditions and at room temperature. The thionyl chloride was removed by evaporation under reduced pressure, to leave an off-white solid (**78**), [$\nu_{max.}$ (KCl disc) 1770 (-COCl, C-O stretch)]. The solid was partially dissolved in benzene (50 ml), the solvent then being removed by evaporation under reduced pressure, in order to remove any residual thionyl chloride. To the white solid was added *(S)*-2-bromo-4-methylpentan-1-ol (**32**) (0.6 g, 3.7 mmol), benzene (20 ml), and dry tetrahydrofuran (20 ml). This mixture was stirred at room temperature for 10 m, followed by the addition of pyridine (5 ml), with further stirring, and heating under reflux conditions for 10 h. The solvents were removed by evaporation under reduced pressure, the black residue being purified by flash chromatography over silica gel using dichloromethane as the eluant, to yield white crystals (**90**), (0.63 g, 40 %), (m.p. 58°). $[\alpha]_D^{24.5}$ -0.6° (10.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3060-2760 (C-H stretch), 1770 ((MeO)C=O stretch), 1720 (C=O stretch), 1615 and 1530 (arom. C=C stretch), 1440, 1400, 1370, 1360-1150 and 1115 (C-OH stretch or O-H deformation), 1075, 1010, 835 (1,4-disub. ring), 775, 740, 705; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', J_{AX} 7.9 Hz, $J_{AX'}$ 0.2 Hz, biphenyl), 7.65 (2 H, AA'XX', biphenyl), 7.63 (2 H, AA'XX', biphenyl), 7.29 (2 H, AA'XX', J_{AX} 7.9 Hz, $J_{AX'}$ 0.2 Hz, biphenyl), 4.57 (2 H, d, J 7.0 Hz, -$CO_2C\underline{H}_2CH(Br)$-), 4.33 (1 H, m, -$CO_2CH_2C\underline{H}(Br)$-), 3.94 (3 H, s, $C\underline{H}_3OCO_2$-),

1.93 (1 H, m, -C<u>H</u>(H)CH$(CH_3)_2$), 1.88 (1 H, m, -CH(<u>H</u>)CH$(CH_3)_2$), 1.69 (1 H, m, $CH_2C\underline{H}(CH_3)_2$), 1.00 (3 H, d, J 6.5 Hz, -$CH_2CH(C\underline{H}_3)CH_3$), 0.94 (3 H, d, J 6.5 Hz, -$CH_2CH(CH_3)C\underline{H}_3$); m/z 436, 434 (1:1) [$M^+$], 375 [M-($CH_3OCO$-)], 272 [M-(-$CHCH(Br)CH_2CH(CH_3)_2$)], 255 [M-(-$OCH_2CH(Br)CH_2CH(CH_3)_2$)], 228 [M-(-$CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$), and +(-H)], 213, 211 (1:1), 196 [M-(-$OCH_2CH(Br)CH_2CH(CH_3)_2$), and -($CH_3OCO$)], 185, 168, 151, 139, 59.

***(S)-1-Methylhepyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate* 92**

Quantity of acid (**78**) used in reaction (5 g, 18.4 mmmol), quantity of *(S)*-2-octanol used in reaction (2.4 g, 18.4 mmol), yield (4.1 g, 58 %), (m.p. 43-44°). $[\alpha]_D^{21.5}$ +43.0 (16.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3180-2760 (C-H stretch), 1770 ((MeO)C=O stretch), 1720 (C=O stretch), 1615 and 1530 (arom. C=C stretch), 1400, 1340-1160 and 1115 (C-OH stretch or O-H deformation), 1070, 1010, 940, 840 (1,4-disub. ring), 780, 750; δ_H (270 MHz, $CDCl_3$) 8.11 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.3 Hz, biphenyl), 7.62 (4 H, AA'XX', biphenyl), 7.28 (2 H, AA'XX', J_{AX} 8.4 Hz, $J_{AX'}$ 0.6 Hz, biphenyl), 5.18 (1 H, m, -$CO_2C\underline{H}(CH_3)(CH_2)_5CH_3$), 3.93 (3 H, s, $C\underline{H}_3OCO_2$-), 1.76 (1 H, m, -$CO_2CH(CH_3)C\underline{H}(H)(CH_2)_4CH_3$), 1.62 (1 H, m, -$CO_2CH(CH_3)CH(\underline{H})(CH_2)_4CH_3$), 1.35 (3 H, m, -$CO_2CH(C\underline{H}_3)(CH_2)_5CH_3$), 1.28 (8 H, br s, -$CO_2CH(CH_3)(CH_2)(\underline{CH}_2)_4CH_3$), 0.85 (3 H, br t, J 6.5 Hz, -$CO_2CH(CH_3)(CH_2)_5\underline{CH}_3$); m/z 384 [$M^+$], 368 [M-(-$CH_3$), and -(-H)], 355 [M-(-$CH_2CH_3$)], 325 [M-($CH_3OCO$-)], 299 [M-(-$(CH_2)_5CH_3$)], 309 [M-($CH_3OCO_2$-)], 272 [M-(-$C(CH_3)(CH_2)_5CH_3$)], 255 [M-(-$OCH(CH_3)(CH_2)_5CH_3$)], 228 [M-(-$CO_2CH(CH_3)(CH_2)_5CH_3$), and +(-H)], 196 [M-(-$OCH(CH_3)(CH_2)_5CH_3$), and -($CH_3OCO$-)], 185, 152, 139, 129, 69, 59, 55.

NOTES:

1. Step 8(i)C is identical to step 8(ii)B and is therefore not illustrated in this scheme. An example of the synthetic procedure used, as well as the spectral data from the compounds prepared, can be seen in reaction scheme 8(ii).

2. Step 8(i)D was not pursued due to solubility problems.

7.3.8.2 Reaction Scheme 8 (ii).

Preparation of Alkyl 4'-Methoxycarbonyloxy-4-biphenylcarboxylates

All alkyl 4'-methoxycarbonyloxy-4-biphenylcarboxylates were prepared using similar synthetic procedures. The example given below illustrates the general method used.

***(S)-2-Chloropropyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate* 79**

Triphenylphosphine (2.89 g, 11 mmol) was added, in one portion, to a mixture of 4'-methoxycarbonyloxy-4-biphenylcarboxylic acid (**45**) (3 g, 11 mmol), *(S)*-2-chloropropan-1-ol (**19**) (1.05 g, 11.1 mmol), diethylazodicarboxylate (DEAD) (1.92 g, 11 mmol) and dry tetrahydrofuran (300 ml). The reaction was kept moisture-free throughout. On addition of triphenylphosphine a colourless, clear solution was formed (the mixture was originally turbid). The reaction was allowed to stir at room temperature for 8 h, and the solvent was then removed by evaporation under reduced pressure. The crude material was purified by flash chromatography over silica gel using dichloromethane as eluant, the product being isolated as a white powder (**79**), (2.78 g, 73 %), (m.p. 80- 81°). $[\alpha]_D^{24}$ +15.2° (39.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3100-2800 (C-H stretch), 1770 ((MeO)C=O stretch), 1720 (C=O stretch), 1610 and 1500 (arom. C=C stretch), 1385, 1360-1160 and 1110 (C-OH stretch or O-H deformation), 1010, 940, 835 (1,4-disub. ring), 775, 705; δ_H (270 MHz, $CDCl_3$) 8.13 (2 H, AA'XX', J_{AX} 7.8 Hz, $J_{AX'}$ 0.2 Hz, biphenyl), 7.65 (2 H, AA'XX', biphenyl), 7.63 (2 H, AA'XX', biphenyl), 7.29 (2 H, AA'XX', J_{AX} 7.8 Hz, $J_{AX'}$ 0.2 Hz, biphenyl), 4.50 (2 H, d, J 5.5 Hz,

-$CO_2C\underline{H}_2CH(Cl)$-), 4.34 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 3.93 (3 H, s, $C\underline{H}_3OCO_2$-), 1.62 (3 H, d, J 5.5 Hz, -$CH(Cl)C\underline{H}_3$); m/z 350, 348 (1:3) [M^+], 304, 291, 289 (1:3) [M-(CH_3OCO-)], 274, 272 (1:3) [M-(CH_3OCO_2-)], 255 [M-(-$OCH_2CH(Cl)CH_3$)], 228 [M-(-$CO_2CH_2CH(Cl)CH_3$), and + (-H)], 211, 196 [M-(-$OCH_2CH(Cl)CH_3$), and -(CH_3OCO-)] , 185, 168, 152, 139, 76 [M-($CH_3OCO_2C_6H_4C_6H_4CO_2$-), and -(-H)], 59.

***(S)-2-Chloro-3-methylbutyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate* 80**

Quantity of acid (**45**) used in reaction (4.1 g, 15 mmol), quantity of alcohol (**20**) used in reaction (1.84 g, 15 mmol), yield (2.93 g, 51 %), (m.p. 75.5-76°). $[\alpha]_D^{24}$ +17° (52.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3060-2840 (C-H stretch), 1770 ((MeO)C=O stretch), 1725 (C=O stretch), 1610 and 1500 (arom. C=C stretch), 1395, 1365-1140 and 1115 (C-OH stretch or O-H deformation), 1010, 940, 835 (1,4-disub. ring), 775, 670; δ_H (270 MHz, $CDCl_3$) 8.13 (2 H, AA'XX', J_{AX} 7.8 Hz, $J_{AX'}$ 0.3 Hz, biphenyl), 7.64 (2 H, AA'XX', biphenyl), 7.63 (2 H, AA'XX', biphenyl), 7.28 (2 H, AA'XX', J_{AX} 7.8 Hz, $J_{AX'}$ 0.3 Hz, biphenyl), 4.54 (2 H, sept, -$CO_2C\underline{H}_2CH(Cl)$-), 4.17 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 3.94 (3 H, s, $C\underline{H}_3OCO_2$-), 2.19 (1 H, m, -$CH(Cl)C\underline{H}(CH_3)_2$), 1.11 (3 H, d, J 6.5 Hz, -$CH(Cl)CH(C\underline{H}_3)CH_3$), 1.08 (3 H, d, J 6.5 Hz, -$CH(Cl)CH(CH_3)C\underline{H}_3$); m/z 378, 376 (1:3) [$M^+$], 361 [M-($CH_3$-)], 332 [M-(-$CH_2(CH_3)_2$)], 317 [M-($CH_3OCO$-)], 301 [M-($CH_3OCO_2$-)], 272 [M-(-CHCH(Cl)$CH(CH_3)_2$)], 255 [M-(-OCHCH(Cl)$CH(CH_3)_2$)], 228 [M-(-$CO_2CH_2CH(Cl)CH(CH_3)_2$), and + (-H)], 211, 196 [M-(-$OCH_2CH(Cl)CH(CH_3)_2$), and -(CH_3OCO-)], 185, 168, 152, 139, 69.

***(S,S)-2-Chloro-3-methylpentyl 4'-methoxycarbonyloxy-4-biphenyl carboxylate* 81**

Quantity of acid (**45**) used in reaction (3 g, 11 mmol), quantity of alcohol (**21**) used in reaction (2.9 g, 11 mmol), yield (4 g, 94 %), (m.p. 74-75°). $[\alpha]_D^{24}$ +13.4° (26.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3080-2800 (C-H stretch), 1770 ((MeO)C=O stretch), 1720 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1395, 1360-1150 and 1120 (C-OH stretch or O-H deformation), 1010, 940, 830 (1,4-disub. ring), 775, 655; δ_H (270 MHz, $CDCl_3$) 8.13 (2 H, AA'XX', J_{AX} 7.4 Hz, $J_{AX'}$ 0.1 Hz, biphenyl), 7.64 (2 H, AA'XX', biphenyl), 7.63 (2 H, AA'XX', biphenyl), 7.29 (2 H, AA'XX', J_{AX} 8.3 Hz, $J_{AX'}$ 0.2 Hz, biphenyl), 4.55 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.21 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 3.94 (3 H, s, $C\underline{H}_3OCO_2-$), 1.95 (1 H, m, $-CH(Cl)C\underline{H}(CH_3)-$), 1.65 (1 H, m, $-CH(Cl)CH(CH_3)C\underline{H}(H)CH_3$), 1.40 (1 H, m, $-CH(Cl)CH(CH_3)CH(\underline{H})CH_3$), 1.10 (3 H, d, J 6.5 Hz, $-CH(Cl)CH(C\underline{H}_3)-$), 0.97 (3 H, t, J 7.5 Hz, $-CH(Cl)CH(CH_3)CH_2C\underline{H}_3$); m/z 392, 390 (1:3) [$M^+$], 361 [M-($CH_3CH_2-$)], 346, 331 [M-($CH_3OCO-$)], 315 [M-($CH_3OCO_2-$)], 297, 272 [M-(-CHCH(Cl)$CH(CH_3)CH_2CH_3$)], 255 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 228 [M-(-$CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$), and +(-H)], 211, 196 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$), and -($CH_3OCO-$)], 185, 168, 152, 139, 55.

***(S,R)-2-Chloro-3-methylpentyl 4'-methoxycarbonyloxy-4-biphenyl carboxylate* 82**

Quantity of acid (**45**) used in reaction (1.77 g, 6.5 mmol), quantity of alcohol (**22**) used in reaction (0.89 g, 6.5 mmol), yield (1.57 g, 62 %), (m.p. 36.5-37°). $[\alpha]_D^{22}$ -18.3° (38.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3240-2700 (C-H stretch), 1765 ((MeO)C=O stretch), 1680 (C=O stretch), 1610 and 1520 (arom. C=C stretch), 1565, 1390, 1340-1155 and 1110 (C-OH stretch or O-H deformation), 1010, 940, 835 (1,4-disub. ring), 770, 740, 700, 670, 545, 495; δ_H (270 MHz, $CDCl_3$) 8.13 (2 H, AA'XX', J_{AX} 8.0 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.64 (2 H, AA'XX', biphenyl), 7.63 (2 H, AA'XX', biphenyl), 7.29

(2 H, AA'XX', J_{AX} 8.3 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 4.53 (2 H, d, J 6.5 Hz, -$CO_2C\underline{H}_2CH(Cl)$-), 4.32 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 3.94 (3 H, s, $C\underline{H}_3OCO_2$-), 1.89 (1 H, m, -$CH(Cl)C\underline{H}(CH_3)$-), 1.58 (1 H, m, -$CH(Cl)CH(CH_3)C\underline{H}(H)CH_3$), 1.40 (1 H, m, -$CH(Cl)CH(CH_3)CH(\underline{H})CH_3$), 1.04 (3 H, d, J 6.5 Hz, -$CH(Cl)CH(C\underline{H}_3)$-), 0.96 (3 H, d, J 7.0 Hz, -$CH(Cl)CH(CH_3)CH_2C\underline{H}_3$); m/z 392, 390 (1:3) [$M^+$], 331 [M-($CH_3OCO$-)], 315 [M-($CH_3OCO_2$-)], 272 [M-(-CHCH(Cl)$CH(CH_3)CH_2CH_3$)], 255 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 228 [M-(-$CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$), and +(-H)], 211, 196 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$), and ($CH_3OCO$-)], 185, 168, 152, 139, 83, 59, 55.

***(S)-2-Chloro-4-methylpentyl 4'-methoxycarbonyloxy-4-biphenyl carboxylate* 83**

Quantity of acid (**45**) used in reaction (5 g, 18.4 mmol), quantity of alcohol (**23**) used in reaction (2.5 g, 18.4 mmol), yield (6.2 g, 87 %), (m.p. 62°). $[\alpha]_D^{23}$ -6.7° (39.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3150-2600 (C-H stretch), 1760 ((MeO)C=O stretch), 1625 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1395, 1370, 1355-1205 and 1115 (C-OH stretch or O-H deformation), 1190, 1065, 1010, 940, 835 (1,4-disub. ring), 775, 735, 690, 495, 400; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', J_{AX} 7.8 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 7.65 (2 H, AA'XX', biphenyl), 7.64 (2 H, AA'XX', biphenyl), 7.29 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 4.48 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.27 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 3.94 (3 H, s, $C\underline{H}_3OCO_2$-), 1.98 (1 H, m, -$CH_2C\underline{H}(CH_3)_2$), 1.78 (1 H, m, -$C\underline{H}(H)CH(CH_3)_2$), 1.62 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 0.99 (3 H, d, J 6.5 Hz, -$CH_2CH(C\underline{H}_3)CH_3$), 0.95 (3 H, d, J 6.5 Hz, -$CH_2CH(CH_3)C\underline{H}_3$); m/z 392, 390 (1:3) [$M^+$], 331 [M-($CH_3OCO$-)], 315 [M-($CH_3OCO_2$-)], 272 [M-(-CHCH(Cl)$CH_2$ $CH(CH_3)_2$)], 255 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 228 [M-(-$CO_2CH_2CH(Cl)CH_2$ $CH(CH_3)_2$), and + (-H)], 211, 196 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$), and ($CH_3OCO$-)], 185, 168, 152, 139, 83, 58, 55.

***(+/-)-2-Chloro-4-methylpentyl 4'-methoxycarbonyloxy-4-biphenyl carboxylate* 84**

Quantity of acid (**45**) used in reaction (3 g, 11 mmol), quantity of alcohol (**24**) used in reaction (2.9 g, 11 mmol), yield (4 g, 94 %), (m.p. 61.5-62.5°). $[\alpha]_D^{23}$ 0° (51.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3200-2700 (C-H stretch), 1760 ((MeO)C=O stretch), 1635 (C=O stretch), 1610 and 1520 (arom. C=C stretch), 1400, 1375, 1360-1215 and 1110 (C-OH stretch or O-H deformation), 1180, 1065, 1010, 940, 840 (1,4-disub. ring), 770, 735, 690, 495; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', J_{AX} 7.7 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 7.65 (2 H, AA'XX', biphenyl), 7.64 (2 H, AA'XX', biphenyl), 7.30 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 4.47 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.27 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 3.93 (3 H, s, $C\underline{H}_3OCO_2-$), 1.99 (1 H, m, $-CH_2C\underline{H}(CH_3)_2$), 1.79 (1 H, m, $-C\underline{H}(H)CH(CH_3)_2$), 1.63 (1 H, m, $-CH(\underline{H})CH(CH_3)_2$), 0.99 (3 H, d, J 6.5 Hz, $-CH_2CH(C\underline{H}_3)CH_3$), 0.96 (3 H, d, J 6.5 Hz, $-CH_2CH(CH_3)C\underline{H}_3$); m/z 392, 390 (1:3) [$M^+$], 331 [M-($CH_3OCO-$)], 315 [M-($CH_3OCO_2-$)], 272 [M-(-$CHCH(Cl)CH_2CH(CH_3)_2$)], 255 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 228 [M-(-$CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$), and +(-H)], 211, 196 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$), and -($CH_3OCO-$)], 185, 168, 152, 139, 83, 58, 57.

***(S)-2-Chloropentyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate* 85**

Quantity of acid (**45**) used in reaction (1.66 g, 6.1 mmol), quantity of alcohol (**26**) used in reaction (0.83 g, 6.8 mmol), yield (1.68 g, 74 %), (m.p. 87°). $[\alpha]_D^{23}$ +1.0 (48.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3100-2700 (C-H stretch), 1760 ((MeO)C=O stretch), 1610 (C=O stretch), 1605 and 1520 (arom. C=C stretch), 1400, 1355-1140 and 1115 (C-OH stretch or O-H deformation), 1170, 1010, 940, 840 (1,4-disub. ring), 775, 740, 710, 510; δ_H (270 MHz, $CDCl_3$) 8.13 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.65 (2 H, AA'XX', biphenyl), 7.63 (2 H, AA'XX', biphenyl), 7.29 (2 H, AA'XX', J_{AX} 9.1 Hz, $J_{AX'}$ 0.9 Hz, biphenyl), 4.50 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.23 (1 H, m,

-$CO_2CH_2C\underline{H}(Cl)$-), 3.94 (3 H, s, $C\underline{H}_3OCO_2$-), 1.83 (2 H, m, -$CH(Cl)C\underline{H}_2CH_2CH_3$), 1.59 (2 H, m, -$CH(Cl)CH_2C\underline{H}_2CH_3$), 0.98 (3 H, t, J 7.0 Hz, -$CH(Cl)CH_2CH_2C\underline{H}_3$); m/z 378, 376 (1:3) [$M^+$], 332, 317 [M-($CH_3OCO$-)], 301 [M-($CH_3OCO_2$-)], 272 [M-(-$CHCH(Cl)(CH_2)_2CH_3$)], 255 [M-(-$OCH_2CH(Cl)(CH_2)_2CH_3$)], 228 [M-(-$CO_2CH_2$ $CH(Cl)(CH_2)_2CH_3$), and +(-H)], 211, 196 [M-(-$OCH_2CH(Cl)(CH_2)_2CH_3$), and -(CH_3OCO-)], 185, 168, 152, 139, 139.

***(S)-2-Chlorohexyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate* 86**

Quantity of acid (**45**) used in reaction (3.65 g, 13.4 mmol), quantity of alcohol (**27**) used in reaction (2 g, 14.8 mmol), yield (2.93 g, 56 %), (m.p. 40°). $[\alpha]_D^{23}$ +0.6 (41.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3160-2740 (C-H stretch), 1770 ((MeO)C=O stretch), 1725 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1565, 1395, 1355-1155 and 1110 (C-OH stretch or O-H deformation), 1065, 1010, 940, 835 (1,4-disub. ring), 775, 740, 700; δ_H (270 MHz, $CDCl_3$) 8.13 (2 H, AA'XX', J_{AX} 8.0 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.65 (2 H, AA'XX', biphenyl), 7.63 (2 H, AA'XX', biphenyl), 7.29 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.21 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 3.94 (3 H, s, $C\underline{H}_3OCO_2$-), 1.86 (2 H, m, -$CH(Cl)C\underline{H}_2(CH_2)_2CH_3$), 1.57 (4 H, m, -$CH(Cl)CH_2(C\underline{H}_2)_2CH_3$), 0.94 (3 H, t, J 6.5 Hz, -$CH(Cl)CH_2(CH_2)_2C\underline{H}_3$); m/z 392, 390 (1:3) [$M^+$], 331 [M-($CH_3OCO$-)], 279, 272 [M-(-$CHCH(Cl)(CH_2)_3CH_3$)], 255 [M-(-$OCH_2CH(Cl)(CH_2)_3CH_3$)], 228 [M-(-$CO_2CH_2$ $CH(Cl)(CH_2)_3CH_3$), and +(-H)], 211, 196 [M-(-$OCH_2CH(Cl)(CH_2)_3CH_3$), and -(CH_3OCO-)], 185, 167, 148, 139, 113.

***(S)-2-Chloro-octyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate* 87**

Quantity of acid (**45**) used in reaction (4 g, 14.7 mmol), quantity of alcohol (**28**) used in reaction (2.42 g, 14.7 mmol), yield (6.15 g, 100 %), (m.p. 35-36°). $[\alpha]_D^{24}$ -1.8 (18.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3160-2780 (C-H stretch), 1770 ((MeO)C=O stretch),

1725 (C=O stretch), 1615 and 1525 (arom. C=C stretch), 1400, 1365-1160 and 1120 (C-OH stretch or O-H deformation), 1070, 1010, 940, 835 (1,4-disub. ring), 775, 700; δ_H (270 MHz, $CDCl_3$) 8.13 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.64 (2 H, AA'XX', biphenyl), 7.62 (2 H, AA'XX', biphenyl), 7.28 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.3 Hz, biphenyl), 4.49 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.21 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 3.92 (3 H, s, $C\underline{H}_3OCO_2-$), 1.83 (2 H, m, $-CH(Cl)C\underline{H}_2(CH_2)_4CH_3$), 1.59 (see 1.30, m, $-CH(Cl)CH_2(C\underline{H}_2)_4CH_3$), 1.49 (see 1.30, m, $-CH(Cl)CH_2(C\underline{H}_2)_4CH_3$), 1.30 (8 H, br s, $-CH(Cl)CH_2(C\underline{H}_2)_4CH_3$), 0.89 (3 H, br t, J 7.0 Hz, $-CH(Cl)(CH_2)_5C\underline{H}_3$); m/z 420, 418 (1:3) [$M^+$], 359 [M-($CH_3OCO-$)], 279, 277 (1:3), 272 [M-(-CHCH(Cl)$(CH_2)_5CH_3$)], 255 [M-(-$OCH_2CH(Cl)(CH_2)_5CH_3$)], 228 [M-(-$CO_2CH_2CH(Cl)(CH_2)_5CH_3$), and +(-H)], 211, 185, 168, 152, 139, 108, 77.

(S)-2-Chlorodecyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate **88**

Quantity of acid (**45**) used in reaction (4 g, 14.7 mmol), quantity of alcohol (**29**) used in reaction (2.83 g, 14.7 mmol), yield (5.07 g, 77 %), (m.p. 36.5-37.5°). $[\alpha]_D^{21.5}$ -2.6 (36.5 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2800 (C-H stretch), 1770 ((MeO)C=O stretch), 1725 (C=O stretch), 1615 and 1530 (arom. C=C stretch), 1440, 1420-1360, 1360-1205 and 1115 (C-OH stretch or O-H deformation), 1190, 1070, 1010, 940, 840 (1,4-disub. ring), 775, 700; δ_H (270 MHz, $CDCl_3$) 8.13 (2 H, AA'XX', J_{AX} 8.3 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 7.64 (2 H, AA'XX', biphenyl), 7.62 (2 H, AA'XX', biphenyl), 7.28 (2 H, AA'XX', J_{AX} 8.3 Hz, $J_{AX'}$ 0.2 Hz, biphenyl), 4.49 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.21 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 3.93 (3 H, s, $C\underline{H}_3OCO_2-$), 1.84 (2 H, m, $-CH(Cl)C\underline{H}_2(CH_2)_6CH_3$), 1.60 (see 1.28, m, $-CH(Cl)CH_2(C\underline{H}_2)_6CH_3$), 1.47 (see 1.28, m, $-CH(Cl)CH_2(C\underline{H}_2)_6CH_3$), 1.28 (12 H, br s, $-CH(Cl)CH_2(C\underline{H}_2)_6CH_3$), 0.88 (3 H, br t, J 7.0 Hz, $-CH(Cl)(CH_2)_7C\underline{H}_3$); m/z 448, 446 (1:3) [$M^+$], 387 [M-($CH_3OCO-$)], 274, 272 (1:3) [M-(-CHCH(Cl)$(CH_2)_7CH_3$)], 255 [M-(-$OCH_2CH(Cl)(CH_2)_7CH_3$)], 228 [M-

(-$CO_2CH_2CH(Cl)(CH_2)_7CH_3$), and +(-H)], 211, 196 [M-(-$OCH_2CH(Cl)(CH_2)_7CH_3$), and -(CH_3OCO-)], 185, 168, 152, 139, 69.

***(S)-2-Chlorododecyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate* 89.**

Quantity of acid (**45**) used in reaction (4 g, 14.7 mmol), quantity of alcohol (**29**) used in reaction (3.25 g, 14.7 mmol), yield (6.6 g, 95 %), (m.p. 49°). $[\alpha]_D^{22}$ -1.5 (38.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2800 (C-H stretch), 1765 ((MeO)C=O stretch), 1720 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1445, 1360-1195 and 1115 (C-OH stretch or O-H deformation), 1185, 1070, 1010, 940, 840 (1,4-disub. ring), 775, 705; δ_H (270 MHz, $CDCl_3$) 8.13 (2 H, AA'XX', J_{AX} 7.9 Hz, $J_{AX'}$ 0.6 Hz, biphenyl), 7.65 (2 H, AA'XX', biphenyl), 7.63 (2 H, AA'XX', biphenyl), 7.29 (2 H, AA'XX', J_{AX} 8.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.21 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 3.94 (3 H, s, $C\underline{H}_3OCO_2$-), 1.84 (2 H, m, -$CH(Cl)C\underline{H}_2(CH_2)_8CH_3$), 1.60 (see 1.30, m, -$CH(Cl)CH_2(C\underline{H}_2)_8CH_3$), 1.48 (see 1.30, m, -$CH(Cl)CH_2(C\underline{H}_2)_8CH_3$), 1.30 (16 H, br s, -$CH(Cl)CH_2(C\underline{H}_2)_6CH_3$), 0.88 (3 H, br t, J 6.5 Hz, -$CH(Cl)(CH_2)_9C\underline{H}_3$); m/z 476, 474 (1:3) [$M^+$], 415 [M-($CH_3OCO$-)], 274, 272 (1:3) [M-(-$CHCH(Cl)(CH_2)_9CH_3$)], 255 [M-(-$OCH_2CH(Cl)(CH_2)_9CH_3$)], 228 [M-(-$CO_2CH_2CH(Cl)(CH_2)_9CH_3$), and +(-H)], 211, 196 [M-(-$OCH_2CH(Cl)(CH_2)_9CH_3$), and -(CH_3OCO-)], 185, 168, 152, 139, 69.

***(S)-2-Bromo-4-methylpentyl 4'-methoxycarbonyloxy-4-biphenyl carboxylate* 90**

Quantity of acid (**45**) used in reaction (4 g, 14.7 mmol), quantity of alcohol (**32**) used in reaction (2.7 g, 14.9 mmol), yield (6 g, 94 %), (m.p. 58°). $[\alpha]_D^{23}$ slight negative deflection (49.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3060-2760 (C-H stretch), 1770 ((MeO)C=O stretch), 1720 (C=O stretch), 1615 and 1530 (arom. C=C stretch), 1440, 1400, 1370, 1360-1150 and 1115 (C-OH stretch or O-H deformation), 1075, 1010, 835

(1,4-disub. ring), 775, 740, 705; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', J_{AX} 7.9 Hz, $J_{AX'}$ 0.2 Hz, biphenyl), 7.65 (2 H, AA'XX', biphenyl), 7.63 (2 H, AA'XX', biphenyl), 7.29 (2 H, AA'XX', J_{AX} 7.9 Hz, $J_{AX'}$ 0.2 Hz, biphenyl), 4.57 (2 H, d, J 7.0 Hz, -$CO_2C\underline{H}_2CH(Br)$-), 4.33 (1 H, m, -$CO_2CH_2C\underline{H}(Br)$-), 3.94 (3 H, s, $C\underline{H}_3OCO_2$-), 1.93 (1 H, m, -$C\underline{H}(H)CH(CH_3)_2$), 1.88 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.69 (1 H, m, $CH_2C\underline{H}(CH_3)_2$), 1.00 (3 H, d, J 6.5 Hz, -$CH_2CH(C\underline{H}_3)CH_3$), 0.94 (3 H, d, J 6.5 Hz, -$CH_2CH(CH_3)C\underline{H}_3$); m/z 436, 434 (1:1) [$M^+$], 375 [M-($CH_3OCO$-)], 272 [M-(-$CHCH(Br)CH_2CH(CH_3)_2$)], 255 [M-(-$OCH_2CH(Br)CH_2CH(CH_3)_2$)], 228 [M-(-$CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$), and +(-H)], 213, 211 (1:1), 196 [M-(-$OCH_2CH(Br)CH_2CH(CH_3)_2$), and -($CH_3OCO$-)], 185, 168, 151, 139, 59.

(R)-2-Fluoro-4-methylpentyl 4'-methoxycarbonyloxy-4-biphenyl carboxylate **91**

Quantity of acid (**45**) used in reaction (2.15 g, 7.9 mmol), quantity of alcohol (**41**) used in reaction (0.95 g, 7.9 mmol), yield (2.4 g, 81 %), (m.p. 63-64°). $[\alpha]_D^{25}$ -1.5 (31.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3060-2760 (C-H stretch), 1755 ((MeO)C=O stretch), 1715 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1440, 1400, 1370, 1355-1135 and 1110 (C-OH stretch or O-H deformation), 1070, 1005, 935, 835 (1,4-disub. ring), 770, 740, 705; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', J_{AX} 8.0 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.64 (2 H, AA'XX', biphenyl), 7.63 (2 H, AA'XX', biphenyl), 7.28 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 4.92 (1 H, m, $J_{gem(F)}$ 39.0 Hz, -$CO_2CH_2C\underline{H}(F)$-), 4.44 (2 H, m, -$CO_2C\underline{H}_2CH(F)$-), 3.93 (3 H, s, $C\underline{H}_3OCO_2$-), 1.89 (1 H, m, -$C\underline{H}(H)CH(CH_3)_2$), 1.75 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.42 (1 H, m, $CH_2C\underline{H}(CH_3)_2$), 1.00 (3 H, d, J 6.5 Hz, -$CH_2CH(C\underline{H}_3)CH_3$), 0.99 (3 H, d, J 6.5 Hz, -$CH_2CH(CH_3)C\underline{H}_3$); m/z 374 [$M^+$], 315 [M-($CH_3OCO$-)], 299 [M-($CH_3OCO_2$-)], 272 [M-(-$CHCH(F)CH_2CH(CH_3)_2$)], 255 [M-(-$OCH_2CH(F)CH_2CH(CH_3)_2$)], 228 [M-(-$CO_2CH_2CH(F)CH_2CH(CH_3)_2$), and +(-H)], 211, 185, 168, 151, 139, 123, 111, 95.

***(S)-1-Methylhepyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate* 92**

Quantity of acid (**45**) used in reaction (5 g, 18.4 mmol), quantity of *(S)*-2-octanol used in reaction (2.4 g, 18.4 mmol), yield (5.2 g, 73 %), (m.p. 42-44°). $[\alpha]_D^{21.5}$ +31 (16.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3180-2760 (C-H stretch), 1770 ((MeO)C=O stretch), 1720 (C=O stretch), 1615 and 1530 (arom. C=C stretch), 1400, 1340-1160 and 1115 (C-OH stretch or O-H deformation), 1070, 1010, 940, 840 (1,4-disub. ring), 780, 750; δ_H (270 MHz, $CDCl_3$) 8.11 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.3 Hz, biphenyl), 7.62 (4 H, AA'XX', biphenyl), 7.28 (2 H, AA'XX', J_{AX} 8.4 Hz, $J_{AX'}$ 0.6 Hz, biphenyl), 5.18 (1 H, m, $-CO_2C\underline{H}(CH_3)(CH_2)_5CH_3$), 3.93 (3 H, s, $C\underline{H_3}OCO_2-$), 1.76 (1 H, m, $-CO_2CH(CH_3)C\underline{H}(H)(CH_2)_4CH_3$), 1.62 (1 H, m, $-CO_2CH(CH_3)CH(\underline{H})(CH_2)_4CH_3$), 1.35 (3 H, m, $-CO_2CH(C\underline{H_3})(CH_2)_5CH_3$), 1.28 (8 H, br s, $-CO_2CH(CH_3)CH_2(\underline{CH_2})_4CH_3$), 0.85 (3 H, br t, J 6.5 Hz, $-CO_2CH(CH_3)(CH_2)_5\underline{CH_3}$); m/z 384 [$M^+$], 368 [M-(-$CH_3$), and -(-H)], 355 [M-(-$CH_2CH_3$)], 325 [M-($CH_3OCO$-)], 299 [M-(-$(CH_2)_5CH_3$)], 309 [M-($CH_3OCO_2$-)], 272 [M-(-$C(CH_3)(CH_2)_5CH_3$)], 255 [M-(-$OCH(CH_3)(CH_2)_5CH_3$)], 228 [M-(-$CO_2CH(CH_3)(CH_2)_5CH_3$), and +(-H)], 196 [M-(-$OCH(CH_3)(CH_2)_5CH_3$), and ($CH_3OCO$-), 185, 152, 139, 129, 69, 59, 55.

Preparation of Alkyl 4'-Hydroxy-4-biphenylcarboxylates

All alkyl 4'-hydroxy-4-biphenylcarboxylates were prepared using similar synthetic procedures. The example given below illustrates the general method used.

***(S)-2-Chloropropyl 4'-hydroxy-4-biphenylcarboxylate* 93**

To a mixture of *(S)*-2-chloropropyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate (**79**) (3.94 g, 11.3 mmol) and ethanol (200 ml), concentrated ammonia solution was added, dropwise, with stirring. The reaction was monitored by tlc over silica using dichloromethane as the eluant. On complete reaction, the solvent was removed by evaporation under reduced pressure, the crude product then being taken up into diethyl

ether (200 ml) and washed with water (100 ml). The ethereal solution was then dried over anhydrous magnesium sulphate for 8 h. After removal of drying agent by filtration, the solvent was once again removed, to yield a white solid (**93**), (3.21 g, 97 %), (m.p. 154°). $[\alpha]_D^{22.5}$ +18° (23.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3580-3160 (O-H stretch), 3040-2840 (C-H stretch), 1700 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1595, 1380 and 1340-1240 (C-OH stretch or O-H deformation), 1215, 1185, 1115 (C-O stretch), 840 (1,4-disub. ring), 775, 730, 630; δ_H (270 MHz, $CDCl_3$) 8.11 (2 H, AA'XX', J_{AX} 8.4 Hz, $J_{AX'}$ 0.6 Hz, biphenyl), 7.62 (2 H, AA'XX', J_{AX} 8.4 Hz, $J_{AX'}$ 0.6 Hz, biphenyl), 7.53 (2 H, AA'XX', J_{AX} 8.4 Hz, $J_{AX'}$ 0.6 Hz, biphenyl), 6.94 (2 H, AA'XX', J_{AX} 8.4 Hz, $J_{AX'}$ 0.6 Hz, biphenyl), 4.45 (2 H, d, J 5.5 Hz, $-CO_2C\underline{H}_2CH(Cl)-$), 4.34 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 1.62 (3 H, d, J 6.5 Hz, $-CH(Cl)C\underline{H}_3$); m/z 292, 290 (1:3) [M^+], 255 [M-(-Cl)], 214 [M-(-$CH(Cl)CH_3$)], 197 [M-(-$OCH_2CH(Cl)CH_3$)], 185, 168, 151, 139, 115, 99, 84, 58.

***(S)-2-Chloro-3-methylbutyl 4'-hydroxy-4-biphenylcarboxylate* 94**

Quantity of protected phenol used in reaction (**80**) (2.5 g, 6.6 mmol), yield (2.1 g, 100 %), (m.p. 122.7°). $[\alpha]_D^{22.5}$ +22.6° (39.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 3540-3060 (O-H stretch), 3060-2800 (C-H stretch), 1680 (C=O stretch), 1605 and 1535 (arom. C=C stretch), 1590, 1375 and 1345-1235 (C-OH stretch or O-H deformation), 1210, 1190, 1125 (C-O stretch), 1020, 835 (1,4-disub. ring), 775, 720, 650; δ_H (270 MHz, $CDCl_3$) 8.10 (2 H, AA'XX', J_{AX} 8.0 Hz, $J_{AX'}$ 0.6 Hz, biphenyl), 7.62 (2 H, AA'XX', J_{AX} 8.0 Hz, $J_{AX'}$ 0.6 Hz, biphenyl); 7.52 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 1.0 Hz, biphenyl), 6.95 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 1.0 Hz, biphenyl), 4.53 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.17 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 2.19 (1 H, m, $-CH(Cl)C\underline{H}(CH_3)_2$), 1.10 (3 H, d, J 6.4 Hz, $-CH(Cl)CH(C\underline{H}_3)CH_3$), 1.07 (3 H, d, J 6.4 Hz, $-CH(Cl)CH(CH_3)C\underline{H}_3$); m/z 320, 318 (1:3) [$M^+$], 283 [M-(-Cl)], 214 [M-(-CH $CH(Cl)CH(CH_3)_2$)], 197 [M-(-$OCH_2CH(Cl)CH(CH_3)_2$)], 185, 168, 151, 139, 115.

***(S,S)-2-Chloro-3-methylpentyl 4'-hydroxy-4-biphenylcarboxylate* 95**

Quantity of protected phenol (**81**) used in reaction (3.5 g, 8.9 mmol), yield (2.91 g, 98 %), (m.p. 124°). $[\alpha]_D^{25}$ +19.3° (18.1 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3600-3100 (O-H stretch), 3040-2810 (C-H stretch), 1695 (C=O stretch), 1605 and 1530 (arom. C=C stretch), 1590, 1420-1370 and 1330-1230 (C-OH stretch or O-H deformation), 1370-1330, 1190, 1120 (C-O stretch), 990, 835 (1,4-disub. ring), 780, 725, 670; δ_H (270 MHz, $CDCl_3$) 8.09 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 7.63 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 7.52 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 6.94 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 3.99 (2 H, m, -CO_2CH_2CH(Cl)-), 3.78 (1 H, m, -CO_2CH_2CH(Cl)-), 1.84 (1 H, m, -CH(Cl)CH(CH_3)-), 1.60 (1 H, m, -CH(Cl)CH(CH_3)CH(H)CH_3), 1.34 (1 H, m, -CH(Cl)CH(CH_3)CH(H)CH_3), 1.02 (3 H, d, J 6.5 Hz, -CH(Cl)CH(CH_3)-), 0.94 (3 H, t, J 6.5 Hz, -CH(Cl)CH(CH_3)CH_2CH_3); m/z 334, 332 (1:3) [M^+], 298, 214 [M-(-CH CH(Cl)CH(CH_3)CH_2CH_3)], 197 [M-(-OCH_2CH(Cl)CH(CH_3)CH_2CH_3)], 185, 168, 151, 141, 115.

***(S,R)-2-Chloro-3-methylpentyl 4'-hydroxy-4-biphenylcarboxylate* 96**

Quantity of protected phenol (**82**) used in reaction (1.31 g, 3.3 mmol), yield (1.1 g, 100 %), (m.p. 100-101.5°). $[\alpha]_D^{26}$ -5.6° (42 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3620-3050 (O-H stretch), 3020-2760 (C-H stretch), 1685 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1590, 1405, 1380, 1355, 1335-1200 (C-OH stretch or O-H deformation), 1190, 1130 (C-O stretch), 1015, 970, 860, 830 (1,4-disub. ring), 770, 730, 695, 630, 525, 490; δ_H (270 MHz, $CDCl_3$) 8.10 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.62 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.52 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 6.94 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 5.46 (1 H, s, -OH), 4.52 (2 H, m, -CO_2CH_2CH(Cl)-), 4.32 (1 H, m, -CO_2CH_2CH(Cl)-), 1.89 (1 H, m, -CH(Cl)CH(CH_3)-), 1.57 (1 H, m,

-CH(Cl)CH(CH_3)C<u>H</u>(H)CH_3), 1.37 (1 H, m, -CH(Cl)CH(CH_3)CH(<u>H</u>)CH_3), 1.03 (3 H, d, J 6.5 Hz, -CH(Cl)CH(C<u>H</u>$_3$)-), 0.95 (3 H, t, J 7.5 Hz, -CH(Cl)CH(CH_3)CH_2C<u>H</u>$_3$); m/z 334, 332 (1:3) [M^+], 279, 242, 214 [M-(-CHCH(Cl)CH(CH_3)CH_2CH_3)], 197 [M-(-OCH_2CH(Cl)CH(CH_3)CH_2CH_3)], 185, 168, 139, 115, 83, 69.

***(S)-2-Chloro-4-methylpentyl 4'-hydroxy-4-biphenylcarboxylate* 97**

Quantity of protected phenol (**83**) used in reaction (5.29 g, 13.5 mmol), yield (3.87 g, 86 %), (m.p. 48.3). $[\alpha]_D^{22}$ -10.9° (8.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3700-3100 (O-H stretch), 3020-2760 (C-H stretch), 1705 (C=O stretch), 1605 and 1530 (arom. C=C stretch), 1570, 1425-1330 and 1330-1155 (C-OH stretch or O-H deformation), 1155-1060 (C-O stretch), 1020, 865, 835 (1,4-disub. ring), 725, 700, 630; δ_H (270 MHz, $CDCl_3$) 8.11 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.63 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.53 (2 H, AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 1.3 Hz, biphenyl), 6.94 (2 H, AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 1.3 Hz, biphenyl), 4.49 (2 H, m, -CO_2C<u>H</u>$_2$CH(Cl)-), 4.27 (1 H, m, -CO_2CH_2C<u>H</u>(Cl)-), 1.98 (1 H, m, -CH_2C<u>H</u>(CH_3)$_2$), 1.77 (1 H, m, -C<u>H</u>(H)CH(CH_3)$_2$), 1.63 (1 H, m, -CH(<u>H</u>)CH(CH_3)$_2$), 0.99 (3 H, d, J 6.5 Hz, -CH_2CH(C<u>H</u>$_3$)CH_3), 0.95 (3 H, t, J 6.5 Hz, -CH_2CH(CH_3)C<u>H</u>$_3$); m/z 334, 332 (1:3) [M^+], 298, 214 [M-(-CHCH(Cl)CH_2CH(CH_3)$_2$)], 197 [M-(-OCH_2CH(Cl)CH_2 CH(CH_3)$_2$)], 185, 168, 151, 139, 115.

***(+/-)-2-Chloro-4-methylpentyl 4'-hydroxy-4-biphenylcarboxylate* 98**

Quantity of protected phenol (**84**) used in reaction (2.5 g, 6.4 mmol), yield (2.1 g, 99 %), (m.p. 47-49°). $[\alpha]_D^{22}$ 0° (115.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3705-3080 (O-H stretch), 3010-2740 (C-H stretch), 1705 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1570, 1410-1330 and 1320-1155 (C-OH stretch or O-H deformation), 1155-1040 (C-O stretch), 1020, 865, 840 (1,4-disub. ring), 720, 705, 630; δ_H (270 MHz, $CDCl_3$) 8.10 (2 H, AA'XX', J_{AX} 7.4 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.63 (2 H, AA'XX', J_{AX} 7.4

Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.52 (2 H, AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 1.3 Hz, biphenyl), 6.94 (2 H, AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 1.3 Hz, biphenyl), 4.49 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.28 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 1.98 (1 H, m, -$CH_2C\underline{H}(CH_3)_2$), 1.76 (1 H, m, -$C\underline{H}(H)CH(CH_3)_2$), 1.63 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.00 (3 H, d, J 6.5 Hz, -$CH_2CH(C\underline{H}_3)CH_3$), 0.96 (3 H, t, J 6.5 Hz, -$CH_2CH(CH_3)C\underline{H}_3$); m/z 334,332 (1:3) [$M^+$], 298, 214 [M-(-$CHCH(Cl)CH_2CH(CH_3)_2$)], 197 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 185, 168, 151, 139, 115.

***(S)-2-Chloropentyl 4'-hydroxy-4-biphenylcarboxylate* 99**

Quantity of protected phenol (**85**) used in reaction (1.55 g, 4.1 mmol), yield (1.22 g, 93 %), (m.p. 86.5). $[\alpha]_D^{25}$ 0.8° (59.5 mg cm^{-3} in C_2H_5OH); $\nu_{max.}$ (KCl disc) 3700-3060 (O-H stretch), 3020-2640 (C-H stretch), 1685 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1595, 1375 and 1270 (C-OH stretch or O-H deformation), 1195, 1105 (C-O stretch), 1020, 830 (1,4-disub. ring), 770, 725, 620; δ_H (270 MHz, $CDCl_3$) 8.10 (2 H, AA'XX', J_{AX} 10.0 Hz, $J_{AX'}$ 1.0 Hz, biphenyl), 7.62 (2 H, AA'XX', J_{AX} 10.0 Hz, $J_{AX'}$ 1.0 Hz, biphenyl), 7.51 (2 H, AA'XX', J_{AX} 9.1 Hz, $J_{AX'}$ 0.4 Hz, biphenyl), 6.94 (2 H, AA'XX', J_{AX} 9.1 Hz, $J_{AX'}$ 0.4 Hz, biphenyl), 5.44 (1 H, br s, $\underline{H}O$-); 4.49 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.22 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 1.82 (2 H, m, -$CO_2CH_2CH(Cl)C\underline{H}_2CH_2CH_3$), 1.64 (2 H, m, -$CO_2CH_2CH(Cl)CH_2C\underline{H}_2CH_3$), 0.97 (3 H, t, J 7.0 Hz, -$CO_2CH_2CH(Cl)CH_2CH_2C\underline{H}_3$); m/z 320, 318 (1:3) [$M^+$], 283 [M-(-Cl)], 242, 214 [M-(-$CHCH(Cl)(CH_2)_2CH_3$)], 197 [M-(-$OCH_2CH(Cl)(CH_2)_2CH_3$)], 185, 168, 149, 139, 115, 84, 58.

***(S)-2-Chlorohexyl 4'-hydroxy-4-biphenylcarboxylate* 100**

Quantity of protected phenol (**86**) used in reaction (2.6 g, 6.7 mmol), yield (1.82 g, 82 %), (m.p. 108.6°). $[\alpha]_D^{25}$ -1.4° (33.0 mg cm^{-3} in C_2H_5OH); $\nu_{max.}$ (KCl disc) 3640-3080 (O-H stretch), 3040-2780 (C-H stretch), 1685 (C=O stretch), 1610 and 1530 (arom.

C=C stretch), 1595, 1370 and 1270 (C-OH stretch or O-H deformation), 1230, 1195, 1110 (C-O stretch), 1020, 835 (1,4-disub. ring), 775, 725, 620, 500; δ_H (270 MHz, $CDCl_3$) 8.09 (2 H, AA'XX', J_{AX} 8.9 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 7.61 (2 H, AA'XX', J_{AX} 8.9 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 7.51 (2 H, AA'XX', J_{AX} 8.3 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 6.96 (2 H, AA'XX', J_{AX} 8.3 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 6.70 (1 H, br s, HO-); 4.49 (2 H, m, -CO_2CH_2CH(Cl)-), 4.21 (1 H, m, -CO_2CH_2CH(Cl)-), 1.84 (2 H, m, -$CO_2CH_2CH(Cl)CH_2(CH_2)_2CH_3$), 1.58 (see 1.39, m, -$CO_2CH_2CH(Cl)CH_2$ $(CH_2)_2CH_3$), 1.39 (4 H, m, -$CO_2CH_2CH(Cl)CH_2(CH_2)_2CH_3$), 0.93 (3 H, t, J 7.0 Hz, -$CO_2CH_2CH(Cl)CH_2(CH_2)_2CH_3$); m/z 334, 332 (1:3) [$M^+$], 279, 242, 214 [M-(-CH CH(Cl)$(CH_2)_3CH_3$)], 197 [M-(-$OCH_2CH(Cl)(CH_2)_3CH_3$)], 185, 168, 148, 139, 114, 83, 69.

(S)-2-Chloro-octyl 4'-hydroxy-4-biphenylcarboxylate **101**

Quantity of protected phenol (**87**) used in reaction (5.43 g, 13 mmol), yield (4.7 g, 100 %), (m.p. 108-109°). $[\alpha]_D^{21}$ -4.8° (44.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3700-3050 (O-H stretch), 3050-2770 (C-H stretch), 1695 (C=O stretch), 1615 and 1530 (arom. C=C stretch), 1570, 1410 and 1350-1250 (C-OH stretch or O-H deformation), 1230, 1190, 1120 (C-O stretch), 845 (1,4-disub. ring), 775, 730, 705, 655; δ_H (270 MHz, $CDCl_3$) 8.11 (2 H, AA'XX', J_{AX} 7.8 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 7.62 (2 H, AA'XX', J_{AX} 7.8 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 7.52 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 1.0 Hz, biphenyl), 6.95 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 1.0 Hz, biphenyl), 4.50 (2 H, m, -CO_2CH_2CH(Cl)-), 4.21 (1 H, m, -CO_2CH_2CH(Cl)-), 3.53 (1 H, s, HO-), 1.84 (see 1.30, m, -$CO_2CH_2CH(Cl)(CH_2)_5CH_3$), 1.66 (see 1.30, m, -$CO_2CH_2CH(Cl)$ $(CH_2)_5CH_3$), 1.48 (see 1.30, m, -$CO_2CH_2CH(Cl)(CH_2)_5CH_3$), 1.30 (10 H, br s, -$CO_2CH_2CH(Cl)(CH_2)_5CH_3$), 0.88 (3 H, br t, J 6.5 Hz, -$CO_2CH_2CH(Cl)(CH_2)_5CH_3$); m/z 362, 360 (1:3) [$M^+$], 325 [M-(-Cl)], 214 [M-(-CHCH(Cl)$(CH_2)_5CH_3$)], 197 [M-(-$OCH_2CH(Cl)(CH_2)_5CH_3$)], 185, 168, 151, 139, 115.

(S)-2-Chlorodecyl 4'-hydroxy-4-biphenylcarboxylate **102**

Quantity of protected phenol (**88**) used in reaction (4.46 g, 10 mmol), yield (3.15 g, 81 %), (m.p. 70.4°). $[\alpha]_D^{21}$ -4° (17.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3700-3040 (O-H stretch), 3020-2780 (C-H stretch), 1700 (C=O stretch), 1610 and 1500 (arom. C=C stretch), 1595, 1450, 1400 and 1360-1250 (C-OH stretch or O-H deformation), 1225, 1200, 1130 (C-O stretch), 1020, 990, 830 (1,4-disub. ring), 770, 720, 660; δ_H (270 MHz, $CDCl_3$) 8.10 (2 H, AA'XX', J_{AX} 7.4 Hz, $J_{AX'}$ 0.6 Hz, biphenyl), 7.62 (2 H, AA'XX', J_{AX} 7.4 Hz, $J_{AX'}$ 0.6 Hz, biphenyl), 7.53 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 6.94 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 4.49 (2 H, m, $-CO_2CH_2CH(Cl)-$), 4.21 (1 H, m, $-CO_2CH_2CH(Cl)-$), 1.83 (2 H, m, $-CO_2CH_2CH(Cl)CH_2(CH_2)_6CH_3$), 1.59 (see 1.28, m, $-CO_2CH_2CH(Cl)CH_2(CH_2)_6CH_3$), 1.48 (see 1.28, m, $-CO_2CH_2CH(Cl)CH_2(CH_2)_6CH_3$), 1.28 (12 H, br s, $-CO_2CH_2CH(Cl)CH_2(CH_2)_6CH_3$), 0.88 (3 H, br t, J 7.0 Hz, $-CO_2CH_2CH(Cl)CH_2(CH_2)_6CH_3$); m/z 390, 388 (1:3) [$M^+$], 214 [M-(-CHCH(Cl)$(CH_2)_7CH_3$)], 197 [M-(-$OCH_2$CH(Cl)$(CH_2)_7CH_3$)], 185, 168, 151, 141, 115, 94.

(S)-2-Chlorododecyl 4'-hydroxy-4-biphenylcarboxylate **103**

Quantity of protected phenol (**89**) used in reaction (6.24 g, 13.1 mmol), yield (5.46 g, 100 %), (m.p. 76.9°). $[\alpha]_D^{21}$ -1.1° (42.4 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3700-3100 (O-H stretch), 3020-2760 (C-H stretch), 1690 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1595, 1445, 1400 and 1350-1240 (C-OH stretch or O-H deformation), 1220, 1190, 1140 (C-O stretch), 1040, 830 (1,4-disub. ring), 775, 725, 635; δ_H (270 MHz, $CDCl_3$) 8.10 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.62 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.52 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 6.95 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 4.49 (2 H, m, $-CO_2CH_2CH(Cl)-$), 4.21 (1 H, m, $-CO_2CH_2CH(Cl)-$), 3.71 (1 H, s, HO-), 1.84 (2 H, m, $-CO_2CH_2CH(Cl)CH_2(CH_2)_8CH_3$), 1.58 (see 1.29, m, $-CO_2CH_2CH(Cl)CH_2$

($C\underline{H}_2)_8CH_3$), 1.48 (see 1.29, m, $-CO_2CH_2CH(Cl)CH_2$ ($C\underline{H}_2)_8CH_3$), 1.29 (16 H, br s, $-CO_2CH_2$ $CH(Cl)CH_2(C\underline{H}_2)_8CH_3$), 0.89 (3 H, br t, J 7.0 Hz, $-CO_2CH_2CH(Cl)$ $(CH_2)_9C\underline{H}_3$); m/z 418, 416 (1:3) [M^+], 348, 227, 213 [M-(-$CH_2CH(Cl)(CH_2)_9CH_3$)], 197 [M-(-OCH_2 $CH(Cl)(CH_2)_9CH_3$)], 185, 168, 151, 139, 114.

(S)-2-Bromo-4-methylpentyl 4'-hydroxy-4-biphenylcarboxylate **104**

Quantity of protected phenol (**90**) used in reaction (5.31 g, 12.3 mmol), yield (4.34 g, 94 %), (m.p. 43-45°). $[\alpha]_D^{21}$ +4.4° (45.1 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3700-3100 (O-H stretch), 3020-2820 (C-H stretch), 1690 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1595, 1450, 1400 and 1350-1240 (C-OH stretch or O-H deformation), 1220, 1190, 1150-1100 (C-O stretch), 840 (1,4-disub. ring), 770, 730, 705; δ_H (270 MHz, $CDCl_3$) 8.11 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.3 Hz, biphenyl), 7.62 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.3 Hz, biphenyl), 7.52 (2 H, AA'XX', J_{AX} 9.1 Hz, $J_{AX'}$ 1.0 Hz, biphenyl), 6.95 (2 H, AA'XX', J_{AX} 9.1 Hz, $J_{AX'}$ 1.0 Hz, biphenyl), 4.57 (2 H, d, J 7.0 Hz, $-CO_2C\underline{H}_2CH(Br)$-), 4.32 (1 H, m, $-CO_2CH_2C\underline{H}(Br)$-), 3.71 (1 H, s, $\underline{H}O$-), 1.94 (1 H, m, $-CH_2C\underline{H}(CH_3)_2$), 1.88 (1 H, m, $-C\underline{H}(H)CH(CH_3)_2$), 1.68 (1 H, m, $-CH(\underline{H})CH(CH_3)_2$), 1.00 (3 H, d, J 6.5 Hz, $-CH_2CH(C\underline{H}_3)CH_3$), 0.94 (3 H, t, J 6.5 Hz, $-CH_2CH(CH_3)C\underline{H}_3$); m/z 378, 376 (1:1) [$M^+$], 214 [M-(-$CHCH(Br)CH_2CH(CH_3)_2$)], 197 [M-(-$OCH_2CH(Br)CH_2CH(CH_3)_2$)], 185, 168, 152, 139, 115, 94.

(R)-2-Fluoro-4-methylpentyl 4'-hydroxy-4-biphenylcarboxylate **105**

Quantity of protected phenol (**91**) used in reaction (1.81 g, 4.8 mmol), yield (1.51 g, 100 %), (m.p. 135.4). $[\alpha]_D^{21}$ 8.8° (88.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3720-3100 (O-H stretch), 3040-2790 (C-H stretch), 1695 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1590, 1435, 1395 and 1350-1235 (C-OH stretch or O-H deformation), 1220, 1195, 1140-1110 (C-O stretch), 840 (1, 4-disub. ring), 775, 730, 705; δ_H (270 MHz, $CDCl_3$) 8.11 (2 H, AA'XX', J_{AB} 8.2 Hz, $J_{AB'}$ 0.3 Hz, biphenyl), 7.62 (2 H, AA'XX',

J_{AB} 8.2 Hz, $J_{AB'}$ 0.3 Hz, biphenyl), 7.52 (2 H, AA'XX', J_{AB} 9.1 Hz, $J_{AB'}$ 1.0 Hz, biphenyl), 6.95 (2 H, AA'XX', J_{AB} 9.1 Hz, $J_{AB'}$ 1.0 Hz, biphenyl); 4.57 (2 H, d, J 7.0 Hz, -$CO_2C\underline{H}_2CH(F)$-), 4.32 (1 H, m, -$CO_2CH_2C\underline{H}(F)$-), 3,71 (1 H, s, $\underline{H}O$-), 1.94 (1 H, m, -$CH_2C\underline{H}(CH_3)_2$), 1.88 (1 H, m, -$C\underline{H}(H)CH(CH_3)_2$), 1.68 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.00 (3 H, d, J 6.5 Hz, -$CH_2CH(C\underline{H}_3)CH_3$), 0.94 (3 H, t, J 6.5 Hz, -$CH_2CH(CH_3)C\underline{H}_3$); m/z 315 [$M^+$], 214 [M-(-$CHCH(F)CH_2CH(CH_3)_2$)], 197 [M-(-O $CH_2CH(F)CH_2CH(CH_3)_2$)], 185, 168, 152, 139, 115, 94.

(S)-1-Methylhepyl 4'-hydroxy-4-biphenylcarboxylate **106**

Quantity of protected phenol (**92**) used in reaction (5.4 g, 14.1 mmol), yield (4.6 g, 100 %), (m.p. 114-116). $[\alpha]_D^{23}$ +47.8° (35.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3600-3100 (O-H stretch), 3020-2780 (C-H stretch), 1690 (C=O stretch), 1605 and 1535 (arom. C=C stretch), 1590, 1570, 1410, 1370 and 1340-1250 (C-OH stretch or O-H deformation), 1200, 1120 (C-O stretch), 840 (1,4-disub. ring), 780, 730; δ_H (270 MHz, $CDCl_3$) 8.10 (2 H, AA'XX', J_{AX} 7.3 Hz, $J_{AX'}$ 0.4 Hz, biphenyl), 7.63 (2 H, AA'XX', J_{AX} 7.3 Hz, $J_{AX'}$ 0.4 Hz, biphenyl), 7.52 (2 H, AA'XX', J_{AX} 8.3 Hz, $J_{AX'}$ 0.9 Hz, biphenyl), 6.94 (2 H, AA'XX', J_{AX} 8.3 Hz, $J_{AX'}$ 0.9 Hz, biphenyl), 5.19 (1 H, m, -$CO_2C\underline{H}(CH_3)(CH_2)_5CH_3$), 1.76 (1 H, m, -$CO_2CH(CH_3)C\underline{H}(H)(CH_2)_4CH_3$), 1.62 (1 H, m, -$CO_2CH(CH_3)CH(\underline{H})(CH_2)_4CH_3$), 1.35 (3 H, m, -$CO_2CH(C\underline{H}_3)(CH_2)_5CH_3$), 1.29 (8 H, br s, -$CO_2CH(CH_3)CH_2$ ($\underline{CH}_2)_4CH_3$), 0.84 (3 H, br t, J 6.5 Hz, -$CO_2CH(CH_3)(CH_2)_5C\underline{H}_3$); m/z 326 [$M^+$], 241 [M-(-$(CH_2)_5CH_3$)], 214 [M-(-$C(CH_3)(CH_2)_5CH_3$)], 197 [M-(-$OCH(CH_3)(CH_2)_5CH_3$)], 185, 168, 151, 139, 115, 69, 55.

7.3.9 Reaction Scheme 9.

Preparation of Alkyl 6-Methoxycarbonyloxy-2-naphthoates

All alkyl 6-methoxycarbonyloxy-2-naphthoates were prepared using similar methods to the biphenyl analogues (Step 8(ii)A).

(S)-2-Chloro-4-methylpentyl 6-methoxycarbonyloxy-2-naphthoate **107**

Quantity of acid (**49**) used in reaction (5 g, 20.6 mmol), quantity of alcohol (**23**) used in reaction (2.9 g, 21.6 mmol), yield (3.2 g, 43 %), (m.p. colourless oil-did not crystallise on standing). $[\alpha]_D^{24}$ -6.2° (16.1 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3140-2800 (C-H stretch), 1770 ((MeO)C=O stretch), 1725 (C=O stretch), 1635 and 1510 (arom. C=C stretch), 1440, 1395, 1340, 1330-1145 and 1105 (C-OH stretch or O-H deformation), 1130, 1065, 945, 885, 815, 770, 625, 485; δ_H (270 MHz, $CDCl_3$) 8.64 (1 H, br s, naphthalene), 8.10 (1 H, dd, J_o 8.5 Hz, J_m 1.5 Hz, naphthalene), 8.00 (1 H, d, J_o 9.0 Hz, naphthalene), 7.87 (1 H, d, J_o 8.5 Hz, naphthalene), 7.71 (1 H, d, J_m 2.0 Hz, naphthalene), 7.39 (1 H, dd, J_o 9.0 Hz, J_m 2.0 Hz, naphthalene), 4.52 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.31 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 3.95 (3 H, s, $C\underline{H}_3OCO_2-$), 2.00 (1 H, m, $-CH_2C\underline{H}(CH_3)_2$), 1.80 (1 H, m, $-C\underline{H}(H)CH(CH_3)_2$), 1.63 (1 H, m, $-CH(\underline{H})CH(CH_3)_2$), 1.00 (3 H, d, J 6.5 Hz, $-CH_2CH(C\underline{H}_3)CH_3$), 0.96 (3 H, d, J 6.5 Hz, $-CH_2CH(CH_3)C\underline{H}_3$); m/z 366, 364 (1:3) [$M^+$], 349 [M-(-$CH_3$], 328 [M-(HCl)], 305 [M-(CH_3OCO-)], 289 [M-(CH_3OCO_2-)], 246 [M-(-$CHCH(Cl)CH_2CH(CH_3)_2$)], 229 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 212, 202 [M-(-$CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$), and +(-H)], 187 [M-(-$CHCH(Cl)CH_2CH(CH_3)_2$), and -($CH_3OCO-$)], 170 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$), and -($CH_3OCO-$)], 159, 142, 126, 114.

***(+/-)-2-Chloro-4-methylpentyl 6-methoxycarbonyloxy-2-naphthoate* 108**

Quantity of acid (**49**) used in reaction (1 g, 4.1 mmol), quantity of alcohol (**24**) used in reaction (0.56 g, 4.1 mmol), yield (0.92 g, 61 %), (m.p. colourless oil-did not crystallise on standing). $[\alpha]_D^{20}$ 0° (10.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3200-2760 (C-H stretch), 1775 ((MeO)C=O stretch), 1730 (C=O stretch), 1630 and 1510 (arom. C=C stretch), 1440, 1390, 1340, 1330-1140 and 1110 (C-OH stretch or O-H deformation), 1120, 1065, 945, 885, 815, 770, 625, 490; δ_H (270 MHz, $CDCl_3$) 8.63 (1 H, br s, naphthalene), 8.10 (1 H, dd, J_o 8.6 Hz, J_m 1.5 Hz, naphthalene), 8.01 (1 H, d, J_o 9.0 Hz, naphthalene), 7.87 (1 H, d, J_o 8.6 Hz, naphthalene), 7.70 (1 H, d, J_m 2.1 Hz, naphthalene), 7.40 (1 H, dd, J_o 9.0 Hz, J_m 2.1 Hz, naphthalene), 4.53 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.32 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 3.95 (3 H, s, $C\underline{H}_3OCO_2-$), 2.00 (1 H, m, $-CH_2C\underline{H}(CH_3)_2$), 1.81 (1 H, m, $-C\underline{H}(H)CH(CH_3)_2$), 1.62 (1 H, m, $-CH(\underline{H})CH(CH_3)_2$), 1.01 (3 H, d, J 6.5 Hz, $-CH_2CH(C\underline{H}_3)CH_3$), 0.95 (3 H, d, J 6.5 Hz, $-CH_2CH(CH_3)C\underline{H}_3$); m/z 366, 364 (1:3) [$M^+$], 349 [M-(-$CH_3$)], 328 [M-(HCl)], 305 [M-(CH_3OCO-)], 289 [M-(CH_3OCO_2-)], 246 [M-(-$CHCH(Cl)CH_2CH(CH_3)_2$)], 229 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 212, 202 [M-(-$CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$), and +(-H)], 187 [M-(-$CHCH(Cl)CH_2CH(CH_3)_2$), and -($CH_3OCO-$)], 170 [M-(-$OCH_2$ $CH(Cl)CH_2CH(CH_3)_2$), and -(CH_3OCO-)], 159, 142, 126, 114.

***(S)-1-Methylheptyl 6-methoxycarbonyloxy-2-naphthoate* 109**

Quantity of acid (**49**) used in reaction (1 g, 4.1 mmol), quantity of *(R)*-2-octanol used in reaction (0.56 g, 4.1 mmol), yield (0.56 g, 39 %), (m.p. colourless oil-did not crystallise on standing). $[\alpha]_D^{20}$ -0.1° (2.5 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3150-2740 (C-H stretch), 1770 ((MeO)C=O stretch), 1720 (C=O stretch), 1620 and 1510 (arom. C=C stretch), 1440, 1390, 1330, 1320-1120 and 1110 (C-OH stretch or O-H deformation), 1060, 945, 885, 810, 770, 635, 470; δ_H (270 MHz, $CDCl_3$) 8.62 (1 H, br s, naphthalene), 8.12 (1 H, dd, J_o 8.5 Hz, J_m 1.2 Hz, naphthalene), 8.00 (1 H, d, J_o 9.0

Hz, naphthalene), 7.85 (1 H, d, J_o 8.5 Hz, naphthalene), 7.72 (1 H, d, J_m 1.5 Hz, naphthalene), 7.41 (1 H, dd, J_o 9.0 Hz, J_m 2.5 Hz, naphthalene), 5.25 (1 H, m, $-CO_2C\underline{H}(CH_3)(CH_2)_5CH_3$), 3.99 (3 H, s, $C\underline{H}_3OCO_2-$), 1.78 (1 H, m, $-CO_2CH(CH_3)C\underline{H}(H)(CH_2)_4CH_3$), 1.65 (1 H, m, $-CO_2CH(CH_3)CH(\underline{H})(CH_2)_4CH_3$), 1.37 (3 H, m, $-CO_2CH(C\underline{H}_3)(CH_2)_5CH_3$), 1.29 (8 H, br s, $-CO_2CH(CH_3)CH_2(\underline{CH_2})_4CH_3$), 0.87 (3 H, br t, J 6.5 Hz, $-CO_2CH(CH_3)(CH_2)_5\underline{CH_3}$); m/z 358 [$M^+$], 299 [M-($CH_3OCO-$)], 273 [M-(-$(CH_2)_5CH_3$)], 246 [M-(-$C(CH_3)(CH_2)_5CH_3$), and +(-H)], 229 [M-(-$OCH(CH_3)(CH_2)_5CH_3$)], 202 [M-(-$CO_2CH(CH_3)(CH_2)_5CH_3$), and +(-H)], 185, 170 [M-(-$OCH(CH_3)(CH_2)_5CH_3$), and -(CH_3OCO-)], 159, 142, 127, 114.

Preparation of Alkyl 6-Hydroxy-2-naphthoates

All alkyl 6-hydroxy-2-naphthoates were prepared using similar methods to those used for the biphenyl analogues (8(ii)B).

(S)-2-Chloro-4-methylpentyl 6-hydroxy-2-naphthoate **110**

Quantity of protected phenol (**107**) used in reaction (3.17 g, 8.7 mmol), yield (2.6 g, 100 %), (m.p. 35.7°). $[\alpha]_D^{25}$ -8° (5.1 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3600-3090 (O-H stretch), 3020-2780 (C-H stretch), 1695 (C=O stretch), 1620 and 1520 (arom. C=C stretch), 1435, 1395 and 1280 (C-OH stretch or O-H deformation), 1200, 1110 (C-O stretch), 1090, 860, 825, 750, 690, 620, 475; δ_H (270 MHz, $CDCl_3$) 8.56 (1 H, br s, naphthalene), 8.03 (1 H, dd, J_o 8.5 Hz, J_m 1.5 Hz, naphthalene), 7.89 (1 H, d, J_o 9.0 Hz, naphthalene), 7.72 (1 H, d, J_o 8.5 Hz, naphthalene), 7.19 (1 H, s, naphthalene), 7.17 (1 H, dd, J_m 2.0 Hz, naphthalene), 5.49 (1 H, s, $\underline{H}O-$), 4.51 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.30 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 1.99 (1 H, m, $-CH_2C\underline{H}(CH_3)_2$), 1.79 (1 H, m, $-C\underline{H}(H)CH(CH_3)_2$), 1.63 (1 H, m, $-CH(\underline{H})CH(CH_3)_2$), 1.00 (3 H, d, J 6.5 Hz, $-CH_2CH(C\underline{H}_3)CH_3$), 0.95 (3 H, d, J 6.5 Hz, $-CH_2CH(CH_3)C\underline{H}_3$); m/z 308, 306

(1:3) [M^+], 291 [M-(-CH_3)], 372 [M-(-Cl), and +(-H)], 216, 188 [M-(-CHCH(Cl) $CH_2CH(CH_3)_2$)], 171 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 159, 143, 115.

(+/-)-2-Chloro-4-methylpentyl 6-hydroxy-2-naphthoate **111**

Quantity of protected phenol (**108**) used in reaction (0.88 g, 2.4 mmol), yield (0.61 g, 83 %), (m.p. 34-35°). $[\alpha]_D^{24.5}$ 0° (115.1 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3660-3095 (O-H stretch), 3040-2760 (C-H stretch), 1690 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1435, 1400 and 1290 (C-OH stretch or O-H deformation), 1200, 1110 (C-O stretch), 1090, 865, 825, 750, 690, 620, 480; δ_H (270 MHz, $CDCl_3$) 8.56 (1 H, br s, naphthalene), 8.02 (1 H, dd, J_o 8.5 Hz, J_m 1.5 Hz, naphthalene), 7.90 (1 H, d, J_o 9.0 Hz, naphthalene), 7.72 (1 H, d, J_o 8.5 Hz, naphthalene), 7.20 (1 H, s, naphthalene), 7.18 (1 H, dd, J_m 2.0 Hz, naphthalene), 5.69 (1 H, s, HO-), 4.52 (2 H, m, -CO_2CH_2CH(Cl)-), 4.30 (1 H, m, -CO_2CH_2CH(Cl)-), 1.99 (1 H, m, -$CH_2CH(CH_3)_2$), 1.80 (1 H, m, -CH(H)$CH(CH_3)_2$), 1.65 (1 H, m, -CH(H)$CH(CH_3)_2$), 1.02 (3 H, d, J 6.5 Hz, -$CH_2CH(CH_3)CH_3$), 0.96 (3 H, d, J 6.5 Hz, -$CH_2CH(CH_3)CH_3$); m/z 308, 306 (1:3) [M^+], 291 [M-(-CH_3)], 372 [M-(-Cl), and +(-H)], 216, 188 [M-(-CHCH(Cl) $CH_2CH(CH_3)_2$)], 171 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 159, 143, 115.

(S)-1-Methylheptyl 6-hydroxy-2-naphthoate **112**

Quantity of protected phenol (**109**) used in reaction (0.46 g, 1.3 mmol), yield (0.4 g, 100 %), (m.p. insufficient sample). $[\alpha]_D$ (insufficient sample); $\nu_{max.}$ (KCl disc) 3700-3090 (O-H stretch), 3020-2780 (C-H stretch), 1685 (C=O stretch), 1630 and 1510 (arom. C=C stretch), 1440, 1395 and 1285 (C-OH stretch or O-H deformation), 1205, 1100 (C-O stretch), 1030, 940, 865, 810, 770, 750; δ_H (270 MHz, $CDCl_3$) 8.52 (1 H, br s, naphthalene), 8.02 (1 H, dd, J_o 8.5 Hz, J_m 1.5 Hz, naphthalene), 7.87 (1 H, d, J_o 8.5 Hz, naphthalene), 7.69 (1 H, d, J_o 8.5 Hz, naphthalene), 7.19 (1 H, s, naphthalene), 7.16 (1 H, dd, J_m 2.5 Hz, naphthalene), 5.51 (1 H, s, HO-), 5.21 (1 H, sext, J 6.5 Hz,

-$CO_2C\underline{H}(CH_3)(CH_2)_5CH_3$), 1.79 (see 1.65, m, -$CO_2CH(CH_3)(C\underline{H}_2)_2(CH_2)_3CH_3$), 1.65 (4 H, m, -$CO_2CH(CH_3)(C\underline{H}_2)_2(CH_2)_3CH_3$), 1.38 (3 H, d, J 6.5 Hz, -$CO_2CH(C\underline{H}_3)(CH_2)_5CH_3$), 1.34 (see 1.28, m, -$CO_2CH(CH_3)(CH_2)_2(C\underline{H}_2)_3CH_3$), 1.28 (6 H, br s, -$CO_2CH(CH_3)(CH_2)_2(C\underline{H}_2)_3CH_3$), 0.87 (3 H, br t, J 6.5 Hz, -$CO_2CH(CH_3)(CH_2)_5C\underline{H}_3$); m/z 300 [$M^+$], 215 [M-(-$(CH_2)_5CH_3$)], 188 [M-(-$C(CH_3)(CH_2)_5CH_3$), and +(-H)], 171 [M-(-$OCH(CH_3)(CH_2)_5CH_3$)], 159, 143 [M-(-$CO_2CH(CH_3)(CH_2)_5CH_3$)], 143, 115, 55.

7.3.10.1 Reaction Scheme 10 (i).

The two materials prepared using this synthetic route were both prepared in a similar manner. The example given below illustrates the general method used.

***(S)-2-Chloropropyl 4'-(4-heptyloxybenzoyloxy)-4-biphenylcarboxylate* 115**

A mixture of 4-n-heptyloxybenzoic acid (**55**) (0.19 g, 0.76 mmol) and thionyl chloride (20 ml) was heated under reflux for 3h, under dry conditions. The thionyl chloride was removed by evaporation under reduced pressure and dry benzene (100 ml) was added. The benzene was then removed by evaporation under reduced pressure to yield a brown liquid (**113**), [$\nu_{max.}$ (KCl disc) 1775 (-COCl, C-O stretch)]. This liquid was dissolved in a mixture of dry benzene (50 ml) and dry tetrahydrofuran (50 ml) and *(S)*-2-chloropropyl 4'-hydroxy-4-biphenylcarboxylate was added (**93**) (0.23 g, 0.79 mmol). The mixture was stirred at room temperature for 10 m, and then pyridine (10 ml) was added and the reactants were heated under reflux for 4 h. The solvents were removed by evaporation under reduced pressure to yield a brown solid that was purified, in the first instance, by flash chromatography over silica gel using dichloromethane as the eluant, and then recrystallization from acetonitrile to eventually give white crystals (**115**), (0.14 g, 36 %). The purity of this compound was tested by hplc, over both silica [method 1 (M1)] and

octadecylsilane columns [method 2 (M2)], using acetonitrile as the eluant. The purity of this compound, determined by each method, was found to be (M1 100 %, M2 99.9 %). (t.t. see results and discussion section). $[\alpha]_D^{24}$ +5.3° (6.5 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2810 (C-H stretch), 1735 and 1715 (C=O stretch), 1605 and 1525 (arom. C=C stretch), 1300-1220 and 1115 (C-O stretch), 1210, 1190, 1170, 1070, 1010, 850 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 6.97 (2 H, AA'XX', J_{AX} 9.3 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 4.46 (2 H, d, J 6.0 Hz, -$CO_2C\underline{H}_2CH(Cl)$-), 4.35 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.85 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.63 (3 H, d, J 6.5 Hz, -$CH(Cl)C\underline{H}_3$), 1.51 (see 1.33, m, alkyl chain), 1.33 (8 H, br s, alkyl chain), 0.91 (3 H, br t, J 6.5 Hz, $C\underline{H}_3CH_2$-); m/z 508 [M^+], 415 [M-(-$OCH_2CH(Cl)CH_3$)], 219 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)], 197, 139, 121 [M-($C_7H_{14}$-), and -($OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)].

(S)-2-Chloropropyl 4'-(4-octyloxybenzoyloxy)-4-biphenylcarboxylate **116**

Quantity of acid (**56**) used in reaction (0.5 g, 2.4 mmol), quantity of phenol (**93**) used in reaction (0.7 g, 2.4 mmol), yield (0.4 g, 29 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ +16.7° (10.4 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2800 (C-H stretch), 1730 and 1720 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1305-1240 and 1120 (C-O stretch), 1320, 1190, 1170, 1070, 1010, 850 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.66 (2 H, AA'XX', phenyl), 7.34 (2 H, AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.47 (2 H, d, -$CO_2C\underline{H}_2CH(Cl)$-), 4.36 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, -$C\underline{H}_2O$-), 1.85 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.66 (3 H, d, -$CH(Cl)C\underline{H}_3$), 1.49 (see 1.36, m, alkyl chain), 1.36 (10 H, br s, alkyl chain), 0.93 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 522 [M^+], 429 [M-(-$OCH_2CH(Cl)CH_3$)], 233

[M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)], 197, 139, 121 [M-($C_8H_{16}$-), and -($OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)].

7.3.10.2 Reaction Scheme 10 (ii).

The materials prepared using this synthetic route were prepared in a similar manner. The example given below illustrates the general method used.

(S)-2-Chloropropyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate **117**

Dicyclohexylcabodiimide (DCC) (0.21 g, 1.03 mmol) and dimethylaminopyridine (DMAP) (0.01 g, 0.12 mmol) were added, with stirring, in one portion to a mixture containing 4-nonyloxybenzoic acid (**51**) (0.27 g, 1.03 mmol), *(S)*-2-chloropropyl 4'-hydroxy-4-biphenylcarboxylate (**93**) (0.30 g, 1.03 mmol) and dry diethyl ether (100 ml). The mixture was stirred at room temperature, under dry conditions for 24 h. The solution was filtered in order to remove precipitated dicyclohexylurea (DCU), washed with water and dried over anhydrous magnesium sulphate for 8 h. After removal of the drying agent by filtration, the solvent was removed by evaporation under reduced pressure. The residue was purified by flash chromatography over silica gel using dichloromethane as the eluant, and then recrystallization from acetonitrile, to eventually give white crystals (**117**), (0.3 g, 54 %). The purity of this compound was tested by hplc, on both silica [method 1 (M1)] and octadecylsilane columns [method 2 (M2)], using acetonitrile as eluant. The purity determined by each method was found to be as follows (M1 99.0 %, M2 100 %). (t.t. see results and discussion section). $[\alpha]_D^{30}$ +11° (1.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2800 (C-H stretch), 1735 and 1720 (C=O stretch), 1615 and 1530 (arom. C=C stretch), 1395, 1305-1240 and 1125 (C-O stretch), 1320, 1225, 1195, 1175, 1075, 1010, 850 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.19 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.69 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.33 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.46 (2 H, d,

-$CO_2C\underline{H}_2CH(Cl)$-), 4.36 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 1.84 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.65 (3 H, d, -$CH(Cl)C\underline{H}_3$), 1.48 (see 1.32, m, alkyl chain), 1.32 (12 H, br s, alkyl chain), 0.91 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 536 [M^+], 443 [M-(-$OCH_2CH(Cl)CH_3$)], 247 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)], 197, 139, 121 [M-($C_9H_{18}$-), and -($OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)].

(S)-2-Chloropropyl 4'-(4-decyloxybenzoyloxy)-4-biphenylcarboxylate **118**

Quantity of acid (**52**) used in reaction (0.47 g, 1.73 mmol), quantity of phenol (**93**) used in reaction (0.5 g, 1.71 mmol), yield (0.38 g, 40 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{30}$ -33° (0.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2700 (C-H stretch), 1730 and 1720 (C=O stretch), 1610 and 1520 (arom. C=C stretch), 1385, 1310-1240 and 1125 (C-O stretch), 1220, 1175, 1075, 1010, 850 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.18 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.66 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.46 (2 H, d, -$CO_2C\underline{H}_2CH(Cl)$-), 4.34 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, -$C\underline{H}_2O$-), 1.84 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.64 (3 H, d, -$CH(Cl)C\underline{H}_3$), 1.49 (see 1.32, m, alkyl chain), 1.32 (14 H, br s, alkyl chain), 0.91 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 550 [M^+], 457 [M-(-$OCH_2CH(Cl)CH_3$)], 261 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)], 197, 139, 121 [M-($C_{10}H_{20}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)].

(S)-2-Chloropropyl 4'-(4-undecyloxybenzoyloxy)-4-biphenylcarboxylate **119**

Quantity of acid (**53**) used in reaction (0.5 g, 1.71 mmol), quantity of phenol (**93**) used in reaction (0.5 g, 1.71 mmol), yield (0.35 g, 36 %), (purity, M1 99.6 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{31}$ +8.4° (16.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2700 (C-H stretch), 1730 (C=O stretch), 1610 and 1525 (arom. C=C stretch),

1400, 1305-1240 and 1115 (C-O stretch), 1320, 1220, 1190, 1170, 1080, 1010, 850 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.70 (2 H, AA'XX', phenyl), 7.69 (2 H, AA'XX', phenyl), 7.33 (2 H, AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.47 (2 H, d, -$CO_2C\underline{H}_2CH(Cl)$-), 4.35 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.07 (2 H, t, -$C\underline{H}_2O$-), 1.84 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.65 (3 H, d, -$CH(Cl)C\underline{H}_3$), 1.50 (see 1.29, m, alkyl chain), 1.29 (16 H, br s, alkyl chain), 0.89 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 564 [M^+], 471 [M-(-$OCH_2CH(Cl)CH_3$], 275 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)], 196, 139, 121 [M-($C_{11}H_{22}$-), and -(-$OC_6H_4$ $C_6H_4CO_2CH_2CH(Cl)CH_3$)].

***(S)-2-Chloropropyl 4'-(4-dodecyloxybenzoyloxy)-4-biphenylcarboxylate* 120**

Quantity of acid (**54**) used in reaction (0.51 g, 1.70 mmol), quantity of phenol (**93**) used in reaction (0.5 g, 1.71 mmol), yield (0.41 g, 42 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{33}$ +11.3° (5.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2650 (C-H stretch), 1725 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1400, 1305-1245 and 1110 (C-O stretch), 1325, 1230, 1190, 1170, 1080, 1005, 835 (1,4-disub. ring), 770, 695; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.66 (2 H, AA'XX', phenyl), 7.30 (2 H, AA'XX', phenyl), 6.97 (2 H, AA'XX', phenyl), 4.47 (2 H, d, -$CO_2C\underline{H}_2CH(Cl)$-), 4.34 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 1.82 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.64 (3 H, d, -$CH(Cl)C\underline{H}_3$), 1.48 (see 1.26, m, alkyl chain), 1.26 (18 H, br s, alkyl chain), 0.87 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 578 [M^+], 485 [M-(-$OCH_2CH(Cl)CH_3$)], 289 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)], 196, 139, 121 [M-($C_{12}H_{24}$-), and -(-$OC_6H_4$ $C_6H_4CO_2CH_2CH(Cl)CH_3$)].

***(S)-2-Chloropropyl 4'-(4-tridecyloxybenzoyloxy)-4-biphenylcarboxylate* 121**

Quantity of acid (**57**) used in reaction (0.38 g, 1.2 mmol), quantity of phenol (**93**) used in reaction (0.34 g, 1.2 mmol), yield (0.25 g, 33 %), (purity, M1 99.8 %, M2 99.5 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ slight positive deflection (8.1 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2700 (C-H stretch), 1735 and 1720 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1400, 1310-1200 and 1110 (C-O stretch), 1290, 1190, 1170, 1075, 1085, 1005, 840 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.66 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.46 (2 H, d, -$CO_2C\underline{H}_2CH(Cl)$-), 4.35 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, -$C\underline{H}_2O$-), 1.83 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.64 (3 H, d, -$CH(Cl)C\underline{H}_3$), 1.47 (see 1.26, m, alkyl chain), 1.26 (20 H, br s, alkyl chain), 0.88 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 592 [M^+], 499 [M-(-$OCH_2CH(Cl)CH_3$)], 303 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)], 197, 139, 121 [M-($C_{13}H_{26}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)].

***(S)-2-Chloropropyl 4'-(4-tetradecyloxybenzoyloxy)-4-biphenylcarboxylate* 122**

Quantity of acid (**58**) used in reaction (0.43 g, 1.29 mmol), quantity of phenol (**93**) used in reaction (0.38 g, 1.3 mmol), yield (0.1 g, 12 %), (purity, M1 100 %, M2 99.6 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ +24° (5.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2700 (C-H stretch), 1735 and 1715 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1390, 1310-1225 and 1120 (C-O stretch), 1320, 1190, 1175, 1080, 1010, 850 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 8.12 (2 H, AA'XX', phenyl), 7.71 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.48 (2 H, d, -$CO_2C\underline{H}_2CH(Cl)$-), 4.37 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.07 (2 H, t, -$C\underline{H}_2O$-), 1.84 (2 H, m, -$C\underline{H}_2CH_2O$-),

1.65 (3 H, d, -CH(Cl)C<u>H</u>$_3$), 1.50 (see 1.30, m, alkyl chain), 1.30 (22 H, br s, alkyl chain), 0.90 (3 H, br t, C<u>H</u>$_3$CH$_2$-); m/z 606 [M$^+$], 513 [M-(-OCH$_2$CH(Cl)CH$_3$)], 317 [M-(-OC$_6$H$_4$C$_6$H$_4$CO$_2$CH$_2$CH(Cl)CH$_3$)], 197, 139, 121 [M-(C$_{14}$H$_{28}$-), and -(-OC$_6$H$_4$ C$_6$H$_4$CO$_2$CH$_2$CH(Cl)CH$_3$)].

(S)-2-Chloropropyl 4'-(4-nonoyloxyphenylpropioloyloxy)-4-biphenyl carboxylate **123**

Quantity of acid (**70**) used in reaction (0.26 g, 0.9 mmol), quantity of phenol (**93**) used in reaction (0.25 g, 0.86 mmol), yield (0.25 g, 56 %), (purity, M1 99.6 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ +4.7° (5.1 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2780 (C-H stretch), 2200 (C≡C stretch), 1725 (C=O stretch), 1605 and 1530 (arom. C=C stretch), 1565, 1395, 1475, 1400, 1275 and 1140 (C-O stretch), 1210, 1185, 1170, 1110, 1010, 935, 840 (1,4-disub. ring), 775, 695, 600, 545; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', J_{AX} 7.9 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 7.66 (4 H, AA'XX', phenyl), 7.58 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 7.30 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 6.90 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 4.46 (2 H, d, J 6.5 Hz, -CO$_2$C<u>H</u>$_2$CH(Cl)-), 4.34 (1 H, m, -CO$_2$CH$_2$C<u>H</u>(Cl)-), 4.00 (2 H, t, J 6.5 Hz, -C<u>H</u>$_2$O-), 1.80 (2 H, m, -C<u>H</u>$_2$CH$_2$O-), 1.63 (3 H, d, J 6.5 Hz, -CH(Cl)C<u>H</u>$_3$), 1.46 (see 1.28, m, alkyl chain), 1.28 (12 H, br s, alkyl chain), 0.89 (3 H, br t, C<u>H</u>$_3$CH$_2$-); m/z 560 [M$^+$], 483 [M-(-CH$_2$CH(Cl)CH$_3$)], 467 [M-(-OCH$_2$ CH(Cl)CH$_3$)], 385, 271 [M-(-OC$_6$H$_4$C$_6$H$_4$CO$_2$CH$_2$CH(Cl)CH$_3$)], 255, 228, 197, 139, 145 [M-(C$_9$H$_{18}$-), and -(-OC$_6$H$_4$C$_6$H$_4$CO$_2$CH$_2$CH(Cl)CH$_3$)].

(S)-2-Chloropropyl 4'-(4-dodecyloxyphenylpropioloyloxy)-4-biphenyl carboxylate **124**

Quantity of acid (**71**) used in reaction (0.29 g, 0.9 mmol), quantity of phenol (**93**) used in reaction (0.26 g, 0.9 mmol), yield (0.26 g, 44 %), (purity, M1 100 %, M2 99.8 %), (t.t.

see results and discussion section). $[\alpha]_D^{25}$ +7.5° (25.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3050-2740 (C-H stretch), 2200 (C≡C stretch), 1720 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1570, 1495, 1400, 1275 and 1120 (C-O stretch), 1190, 1170, 1105, 1005, 940, 830 (1,4-disub. ring), 770, 730, 630, 605, 540; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', phenyl), 7.65 (4 H, AA'XX', phenyl), 7.59 (2 H, AA'XX', phenyl), 7.28 (2 H, AA'XX', phenyl), 6.90 (2 H, AA'XX', phenyl), 4.45 (2 H, d, -$CO_2C\underline{H}_2CH(Cl)$-), 4.35 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 3.99 (2 H, t, -$C\underline{H}_2O$-), 1.79 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.64 (3 H, d, -$CH(Cl)C\underline{H}_3$), 1.47 (see 1.26, m, alkyl chain), 1.26 (18 H, br s, alkyl chain), 0.88 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 602 [M^+], 525, 509 [M-(-$OCH_2CH(Cl)CH_3$)], 330, 313 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)], 290, 213, 197, 144 [M-($C_{12}H_{25}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)], 115, 68, 57.

***(S)-2-Chloropropyl 4'-(4-etradecyloxyphenylpropioloyloxy)-4-biphenyl carboxylate* 125**

Quantity of acid (**72**) used in reaction (0.38 g, 1.1 mmol), quantity of phenol (**93**) used in reaction (0.32 g, 1.1 mmol), yield (0.2 g, 27 %), (purity, M1 100 %, M2 99.6 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ +7.2° (13.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2720 (C-H stretch), 2200 (C≡C stretch), 1720 (C=O stretch), 1605 and 1530 (arom. C=C stretch), 1570, 1495, 1400, 1275 and 1145 (C-O stretch), 1210, 1185, 1170, 1110, 1010, 935, 835 (1,4-disub. ring), 770, 720, 695, 605, 545; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 7.65 (4 H, AA'XX', phenyl), 7.60 (2 H, AA'XX', phenyl), 7.29 (2 H, AA'XX', phenyl), 6.91 (2 H, AA'XX', phenyl), 4.45 (2 H, d, -$CO_2C\underline{H}_2CH(Cl)$-), 4.35 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, -$C\underline{H}_2O$-), 1.79 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.60 (3 H, d, -$CH(Cl)C\underline{H}_3$), 1.44 (see 1.27, m, alkyl chain), 1.27 (22 H, br s, alkyl chain), 0.89 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 630 [M^+], 554 [M-(-$CH CH(Cl)CH_3$)], 537 [M-(-$OCH_2CH(Cl)CH_3$)], 341 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)], 313, 290, 196, 144 [M-$C_{14}H_{29}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)], 54.

***(S)-2-Chloropropyl 4'-(4-hexadecyloxyphenylpropioloyloxy)-4-biphenyl carboxylate* 126**

Quantity of acid (**73**) used in reaction (0.33 g, 0.9 mmol), quantity of phenol (**93**) used in reaction (0.25 g, 0.9 mmol), yield (0.25 g, 44 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ +6.1° (7.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2720 (C-H stretch), 2200 (C≡C stretch), 1720 (C=O stretch), 1605 and 1505 (arom. C=C stretch), 1570, 1495, 1400, 1275 and 1140 (C-O stretch), 1210, 1185, 1170, 1110, 1010, 935, 840 (1,4-disub. ring), 770, 720, 695, 605, 540; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 7.68 (4 H, AA'XX', phenyl), 7.60 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 6.92 (2 H, AA'XX', phenyl), 4.46 (2 H, d, $-CO_2C\underline{H}_2CH(Cl)-$), 4.36 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 4.01 (2 H, t, $-C\underline{H}_2O-$), 1.80 (2 H, m, $-C\underline{H}_2CH_2O-$), 1.63 (3 H, d, $-CH(Cl)C\underline{H}_3$), 1.46 (see 1.26, m, alkyl chain), 1.26 (26 H, br s, alkyl chain), 0.88 (3 H, br t, $C\underline{H}_3CH_2-$); m/z 658 [M^+], 566 [M-(-OCH_2 $CH(Cl)CH_3$), and +(-H)], 369 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)], 290, 214, 197, 145 [M-($C_{16}H_{32}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_3$)], 139, 114, 85, 69.

***(S)-2-Chloropropyl 4'-(4-octadecyloxyphenylpropioloyloxy)-4-biphenyl carboxylate* 127.**

Quantity of acid (**74**) used in reaction (0.28 g, 0.68 mmol), quantity of phenol (**93**) used in reaction (0.2 g, 0.69 mmol), yield (0.14 g, 29 %), (purity, M1 100 %, M2 99.6 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ +8.2° (32 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3060-2740 (C-H stretch), 2200 (C≡C stretch), 1720 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1570, 1495, 1400, 1275 and 1145 (C-O stretch), 1210, 1185, 1170, 1110, 1010, 930, 840 (1,4-disub. ring), 770, 720, 695, 605, 540; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 7.65 (4 H, AA'XX', phenyl), 7.59 (2 H, AA'XX', phenyl), 7.30 (2 H, AA'XX', phenyl), 6.91 (2 H, AA'XX', phenyl), 4.46 (2 H, d, $-CO_2C\underline{H}_2CH(Cl)-$), 4.35 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 3.99 (2 H, t, $-C\underline{H}_2O-$), 1.80 (2 H,

m, -C<u>H</u>$_2$CH$_2$O-), 1.63 (3 H, d, -CH(Cl)C<u>H</u>$_3$), 1.47 (see 1.25, m, alkyl chain), 1.25 (30 H, br s, alkyl chain), 0.88 (3 H, br t, C<u>H</u>$_3$CH$_2$-); m/z 686 [M$^+$], 609 [M-(-CH$_2$CH(Cl)CH$_3$)], 594 [M-(-OCH$_2$CH(Cl)CH$_3$), and +(-H)], 397 [M-(-OC$_6$H$_4$C$_6$H$_4$CO$_2$CH$_2$CH(Cl)CH$_3$)], 341, 213, 289, 213, 196, 145 [M-(C$_{18}$H$_{36}$-), and -(-OC$_6$H$_4$C$_6$H$_4$CO$_2$CH$_2$CH(Cl)CH$_3$)], 139, 114.

(S)-2-Chloro-3-methylbutyl 4'-(4-heptyloxybenzoyloxy)-4-biphenyl carboxylate **128**

Quantity of acid (**55**) used in reaction (0.19 g, 0.81 mmol), quantity of phenol (**94**) used in reaction (0.25 g, 0.78 mmol), yield (0.15 g, 36 %), (purity, M1 99.3 %, M2 99.7 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -11.3° (22 mg cm^{-3} in CHCl$_3$); $\nu_{max.}$ (KCl disc) 3040-2710 (C-H stretch), 1735 and 1720 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1400, 1310-1200 and 1115 (C-O stretch), 1290, 1190, 1170, 1075, 1085, 1005, 840 (1,4-disub. ring), 770, 690; δ_H (270 MHz, CDCl$_3$) 8.16 (2 H, AA'XX', phenyl), 8.13 (2 H, AA'XX', phenyl), 7.68 (4 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', J_{AX} 7.7 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 6.99 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 1.0 Hz, phenyl), 4.54 (2 H, m, -CO$_2$C<u>H</u>$_2$CH(Cl)-), 4.17 (1 H, m, -CO$_2$CH$_2$C<u>H</u>(Cl)-), 4.06 (2 H, t, J 6.5 Hz, -C<u>H</u>$_2$O-), 2.20 (1 H, m, -C<u>H</u>(CH$_3$)$_2$), 1.84 (2 H, m, -C<u>H</u>$_2$CH$_2$O-), 1.49 (see 1.33, m, alkyl chain), 1.33 (8 H, br s, alkyl chain), 1.12 (3 H, d, J 6.5 Hz, -CH(C<u>H</u>$_3$)CH$_3$), 1.08 (3 H, d, J 6.5 Hz, -CH(CH$_3$)C<u>H</u>$_3$), 0.91 (3 H, br t, J 7.0 Hz, C<u>H</u>$_3$CH$_2$-); m/z 536 [M$^+$], 415 [M-(-OCH$_2$CH(Cl)CH(CH$_3$)$_2$)], 219 [M-(-OC$_6$H$_4$C$_6$H$_4$CO$_2$CH$_2$CH(Cl)CH(CH$_3$)$_2$)], 196, 121 [M-(C$_7$H$_{14}$-), and -(-OC$_6$H$_4$C$_6$H$_4$CO$_2$CH$_2$CH(Cl)CH(CH$_3$)$_2$)].

***(S)-2-Chloro-3-methylbutyl 4'-(4-octyloxybenzoyloxy)-4-biphenyl carboxylate* 129**

Quantity of acid (**56**) used in reaction (0.2 g, 0.80 mmol), quantity of phenol (**94**) used in reaction (0.25 g, 0.78 mmol), yield (0.23 g, 54 %), (purity, M1 99.7 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -12.4° (89.1 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2700 (C-H stretch), 1730 and 1720 (C=O stretch), 1605 and 1530 (arom. C=C stretch), 1400, 1310-1200 and 1115 (C-O stretch), 1290, 1190, 1160, 1070, 1085, 1005, 840 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 8.13 (2 H, AA'XX', phenyl), 7.67 (4 H, AA'XX', phenyl), 7.66 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.53 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.17 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 4.05 (2 H, t, $-C\underline{H}_2O-$), 2.20 (1 H, m, $-C\underline{H}(CH_3)_2$), 1.84 (2 H, m, $-C\underline{H}_2CH_2O-$), 1.49 (see 1.32, m, alkyl chain), 1.32 (10 H, br s, alkyl chain), 1.12 (3 H, d, $-CH(C\underline{H}_3)CH_3$), 1.06 (3 H, d, $-CH(CH_3)C\underline{H}_3$), 0.91 (3 H, br t, $C\underline{H}_3CH_2-$); m/z 550 [M^+], 429 [M-(-$OCH_2CH(Cl)CH(CH_3)_2$)], 233 [M-(-O $C_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 196, 121 [M-($C_8H_{16}$-), and -(-$OC_6H_4C_6H_4CO_2$ $CH_2CH(Cl)CH(CH_3)_2$)].

***(S)-2-Chloro-3-methylbutyl 4'-(4-nonyloxybenzoyloxy)-4-biphenyl carboxylate* 130**

Quantity of acid (**51**) used in reaction (0.22 g, 0.83 mmol), quantity of phenol (**94**) used in reaction (0.25 g, 0.78 mmol), yield (0.17 g, 39 %), (purity, M1 99 %, M2 99.4 %), (t.t. see results section and discussion section). $[\alpha]_D^{24}$ -1.8° (13.4 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2700 (C-H stretch), 1730 and 1720 (C=O stretch), 1605 and 1530 (arom. C=C stretch), 1400, 1310-1200 and 1115 (C-O stretch), 1290, 1190, 1160, 1070, 1085, 1005, 840 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.68 (4 H, AA'XX', phenyl), 7.66 (2 H, AA'XX', phenyl), 7.33 (2 H, AA'XX', phenyl), 7.01 (2 H, AA'XX', phenyl), 4.54

(2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.17 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 2.20 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.84 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.49 (see 1.33, m, alkyl chain), 1.33 (12 H, br s, alkyl chain), 1.12 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 1.05 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 564 [M^+], 443 [M-(-$OCH_2CH(Cl)CH(CH_3)_2$)], 247 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 196, 121 [M-($C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)].

(S)-2-Chloro-3-methylbutyl 4'-(4-decyloxybenzoyloxy)-4-biphenyl carboxylate **131**

Quantity of acid (**52**) used in reaction (0.3 g, 1.14 mmol), quantity of phenol (**94**) used in reaction (0.31 g, 1.09 mmol), yield (0.05 g, 9 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -2.1° (15.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2700 (C-H stretch), 1730 and 1720 (C=O stretch), 1605 and 1530 (arom. C=C stretch), 1400, 1310-1200 and 1115 (C-O stretch), 1290, 1190, 1160, 1070, 1085, 1005, 840 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.67 (4 H, AA'XX', phenyl), 7.66 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.54 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.17 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.04 (2 H, t, -$C\underline{H}_2O$-), 2.20 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.85 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.49 (see 1.33, m, alkyl chain), 1.33 (14 H, br s, alkyl chain), 1.11 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 1.04 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 578 [M^+], 457 [M-(-$OCH_2CH(Cl)CH(CH_3)_2$)], 261 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 196, 121 [M-$C_{10}H_{20}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)].

***(S)-2-Chloro-3-methylbutyl 4'-(4-undecyloxybenzoyloxy)-4-biphenyl carboxylate* 132**

Quantity of acid (**53**) used in reaction (0.3 g, 1.09 mmol), quantity of phenol (**94**) used in reaction (0.31 g, 1.09 mmol), yield (0.2 g, 34 %), (purity, M1 100 %, M2 99.7 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ +15.1° (22.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3010-2700 (C-H stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1410, 1320-1200 and 1115 (C-O stretch), 1290, 1190, 1165, 1070, 1085, 1005, 840 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.67 (4 H, AA'XX', phenyl), 7.65 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 7.02 (2 H, AA'XX', phenyl), 4.53 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.17 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.04 (2 H, t, -$C\underline{H}_2O$-), 2.22 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.86 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.49 (see 1.34, m, alkyl chain), 1.34 (16 H, br s, alkyl chain), 1.11 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 1.04 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 592 [M^+], 471 [M-(-$OCH_2CH(Cl)CH(CH_3)_2$)], 275 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 196, 121 [M-($C_{11}H_{22}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)].

***(S)-2-Chloro-3-methylbutyl 4'-(4-dodecyloxybenzoyloxy)-4-biphenyl carboxylate* 133**

Quantity of acid (**54**) used in reaction (0.32 g, 1.1 mmol), quantity of phenol (**94**) used in reaction (0.31 g, 1.09 mmol), yield (0.2 g, 33 %), (purity, M1 100 %, M2 99.9 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ +1.9° (5.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2680 (C-H stretch), 1735 (C=O stretch), 1600 and 1525 (arom. C=C stretch), 1400, 1325-1195 and 1110 (C-O stretch), 1290, 1190, 1165, 1070, 1085, 1005, 840 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.66 (4 H, AA'XX', phenyl), 7.65 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.54 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-),

4.17 (1 H, m, -$CO_2CH_2C\underline{H}$(Cl)-), 4.04 (2 H, t, -$C\underline{H_2}O$-), 2.22 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.86 (2 H, m, -$C\underline{H_2}CH_2O$-), 1.49 (see 1.33, m, alkyl chain), 1.33 (18 H, br s, alkyl chain), 1.10 (3 H, d, -$CH(C\underline{H_3})CH_3$), 1.03 (3 H, d, -$CH(CH_3)C\underline{H_3}$), 0.91 (3 H, br t, $C\underline{H_3}CH_2$-); m/z 606 [M^+], 485 [M-(-$OCH_2CH(Cl)CH(CH_3)_2$)], 289 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 196, 121 [M-($C_{12}H_{24}$-), and -($OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)].

***(S)-2-Chloro-3-methylbutyl 4'-(4-tridecyloxybenzoyloxy)-4-biphenyl carboxylate* 134**

Quantity of acid (**57**) used in reaction (0.35 g, 1.09 mmol), quantity of phenol (**94**) used in reaction (0.31 g, 1.09 mmol), yield (0.15 g, 24 %), (purity, M1 99.9 %, M2 99.9 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ +9.3° (38.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2680 (C-H stretch), 1725 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1400, 1325-1195 and 1110 (C-O stretch), 1290, 1190, 1165, 1070, 1085, 1010, 840 (1,4-disub. ring), 770; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.67 (4 H, AA'XX', phenyl), 7.65 (2 H, AA'XX', phenyl), 7.30 (2 H, AA'XX', phenyl), 7.02 (2 H, AA'XX', phenyl), 4.53 (2 H, m, -$CO_2C\underline{H_2}CH$(Cl)-), 4.17 (1 H, m, -$CO_2CH_2C\underline{H}$(Cl)-), 4.04 (2 H, t, -$C\underline{H_2}O$-), 2.22 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.86 (2 H, m, -$C\underline{H_2}CH_2O$-), 1.50 (see 1.33, m, alkyl chain), 1.33 (20 H, br s, alkyl chain), 1.08 (3 H, d, -$CH(C\underline{H_3})CH_3$), 1.00 (3 H, d, -$CH(CH_3)C\underline{H_3}$), 0.90 (3 H, br t, $C\underline{H_3}CH_2$-); m/z 620 [M^+], 499 [M-(-$OCH_2CH(Cl)CH(CH_3)_2$)], 303 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 196, 121 [M-($C_{13}H_{26}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)].

***(S)-2-Chloro-3-methylbutyl 4'-(4-tetradecyloxybenzoyloxy)-4-biphenyl carboxylate* 135**

Quantity of acid (**58**) used in reaction (0.37 g, 1.11 mmol), quantity of phenol (**94**) used in reaction (0.31 g, 1.09 mmol), yield (0.10 g, 16 %), (purity, M1 99.8 %, M2 99.1 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ +5.6° (30.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2660 (C-H stretch), 1730 (C=O stretch), 1605 and 1525 (arom. C=C stretch), 1400, 1325-1195 and 1110 (C-O stretch), 1290, 1190, 1165, 1070, 1085, 1010, 840 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.65 (4 H, AA'XX', phenyl), 7.64 (2 H, AA'XX', phenyl), 7.30 (2 H, AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.52 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.17 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.04 (2 H, t, -$C\underline{H}_2O$-), 2.20 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.85 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.50 (see 1.31, m, alkyl chain), 1.31 (22 H, br s, alkyl chain), 1.06 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.98 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.88 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 634 [M^+], 513 [M-(-$OCH_2CH(Cl)CH(CH_3)_2$)], 317 [M-(-O $C_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 196, 121 [M-($C_{14}H_{28}$-), and -(-$OC_6H_4C_6H_4$ $CO_2CH_2CH(Cl)CH(CH_3)_2$)].

***(S)-2-Chloro-3-methylbutyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate* 136**

Quantity of acid (**70**) used in reaction (0.18 g, 0.62 mmol), quantity of phenol (**94**) used in reaction (0.2 g, 0.63 mmol), yield (0.31 g, 86 %), (purity, M1 99.2 %, M2 99.1 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ +11.4° (11.4 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2760 (C-H stretch), 2200 (C≡C stretch), 1710 (C=O stretch), 1605 and 1530 (arom. C=C stretch), 1565, 1495, 1395, 1400, 1270 and 1150 (C-O stretch), 1255, 1185, 1160, 1120, 1010, 935, 840 (1,4-disub. ring), 770, 735, 605, 545; δ_H (270 MHz, $CDCl_3$) 8.13 (2 H, AA'XX', J_{AX} 7.9 Hz, $J_{AX'}$ 0.6 Hz, phenyl), 7.66 (4 H, AA'XX', phenyl), 7.58 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 7.30 (2 H, AA'XX',

J_{AX} 9.1 Hz, $J_{AX'}$ 0.4 Hz, phenyl), 6.90 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 4.54 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.17 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 2.20 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.80 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.46 (see 1.28, m, alkyl chain), 1.28 (12 H, br s, alkyl chain), 1.11 (3 H, d, J 6.5 Hz, -$CH(C\underline{H}_3)CH_3$), 1.08 (3 H, d, J 6.5 Hz, -$CH(CH_3)C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 588 [M^+], 483 [M-(-$CH_2CH(Cl)CH(CH_3)_2$)], 467 [M-(-$OCH_2CH(Cl)CH(CH_3)_2$)], 397, 271 [M-(-O $C_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 196, 139, 145 [M-($C_9H_{18}$-), and -(-$OC_6H_4$ $C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 138, 115.

(S)-2-Chloro-3-methylbutyl 4'-(4-dodecloxyphenylpropioloyloxy)-4-biphenylcarboxylate **137**

Quantity of acid (**71**) used in reaction (0.43 g, 1.3 mmol), quantity of phenol (**94**) used in reaction (0.41 g, 1.29 mmol), yield (0.39 g, 46 %), (purity, M1 100 %, M2 99.8 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ +12.7° (31.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2720 (C-H stretch), 2200 (C≡C stretch), 1710 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1565, 1495, 1400, 1270 and 1150 (C-O stretch), 1190, 1170, 1110, 1020, 1005, 940, 830 (1,4-disub. ring), 770, 730, 605, 540; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 7.68 (4 H, AA'XX', phenyl), 7.60 (2 H, AA'XX', phenyl), 7.30 (2 H, AA'XX', phenyl), 6.90 (2 H, AA'XX', phenyl), 4.54 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.17 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, -$C\underline{H}_2O$-), 2.19 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.79 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.44 (see 1.25, m, alkyl chain), 1.25 (18 H, br s, alkyl chain), 1.11 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 1.06 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 630 [M^+], 615 [M-(-CH_3)], 587 [M-(-$CH(CH_3)_2$)], 509 [M-(-$OCH_2CH(Cl)CH(CH_3)_2$)], 313 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 289, 271, 214, 196, 145 [M-($C_{12}H_{24}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 128, 114.

***(S)-2-Chloro-3-methylbutyl 4'-(4-tetradecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate* 138**

Quantity of acid (**72**) used in reaction (0.26 g, 0.7 mmol), quantity of phenol (**94**) used in reaction (0.23 g, 0.7 mmol), yield (0.2 g, 43 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{21}$ +13° (16.4 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2660 (C-H stretch), 2200 (C≡C stretch), 1710 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1565, 1495, 1400, 1265 and 1150 (C-O stretch), 1190, 1170, 1110, 1005, 940, 830 (1,4-disub. ring), 770, 730, 605, 540; δ_H (270 MHz, $CDCl_3$) 8.13 (2 H, AA'XX', phenyl), 7.66 (4 H, AA'XX', phenyl), 7.57 (2 H, AA'XX', phenyl), 7.29 (2 H, AA'XX', phenyl), 6.91 (2 H, AA'XX', phenyl), 4.53 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.17 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.01 (2 H, t, -$C\underline{H}_2O$-), 2.20 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.80 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.44 (see 1.27, m, alkyl chain), 1.27 (22 H, br s, alkyl chain), 1.14 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 1.09 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 658 [M^+], 643 [M-(-CH_3)], 615 [M-(-$CH(CH_3)_2$)], 537 [M-(-O $CH_2CH(Cl)CH(CH_3)_2$)], 341 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 313, 214, 196, 168, 145 [M-$C_{14}H_{28}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 139, 88, 68.

***(S)-2-Chloro-3-methylbutyl 4'-(4-hexadecloxyphenylpropioloyloxy)-4-biphenylcarboxylate* 139**

Quantity of acid (**73**) used in reaction (0.43 g, 1.11 mmol), quantity of phenol (**94**) used in reaction (0.34 g, 1.07 mmol), yield (0.14 g, 18 %), (purity, M1 100 %, M2 99.9 %), (t.t. see results and discussion section). $[\alpha]_D^{21}$ +10.7° (24.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2680 (C-H stretch), 2200 (C≡C stretch), 1720 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1570, 1495, 1390, 1285 and 1150 (C-O stretch), 1185, 1170, 1110, 1010, 930, 835 (1,4-disub. ring), 775, 760, 730, 600, 540; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 7.65 (4 H, AA'XX', phenyl), 7.56 (2 H, AA'XX',

phenyl), 7.30 (2 H, AA'XX', phenyl), 6.90 (2 H, AA'XX', phenyl), 4.54 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.17 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, -$C\underline{H}_2O$-), 2.19 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.81 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.44 (see 1.24, m, alkyl chain), 1.24 (26 H, br s, alkyl chain), 1.12 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 1.07 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.88 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 686 [M^+], 643 [M-(-$CH(CH_3)_2$)], 565 [M-(-$OCH_2CH(Cl)CH(CH_3)_2$)], 369 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 341, 313,271, 214, 196, 168, 156, 145 [M-($C_{16}H_{32}$-), and - (-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 139, 115, 96.

(S)-2-Chloro-3-methylbutyl 4'-(4-octadecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate **140**

Quantity of acid (**74**) used in reaction (0.3 g, 0.72 mmol), quantity of phenol (**94**) used in reaction (0.23 g, 0.72 mmol), yield (0.1 g, 14 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{21}$ +11° (17.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2660 (C-H stretch), 2220 (C≡C stretch), 1730 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1570, 1495, 1395, 1270 and 1140 (C-O stretch), 1190, 1170, 1110, 1010, 930, 855, 835 (1,4-disub. ring), 775, 760, 720, 600, 540; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 7.67 (4 H, AA'XX', phenyl), 7.60 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 6.90 (2 H, AA'XX', phenyl), 4.53 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.17 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, -$C\underline{H}_2O$-), 2.20 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.82 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.46 (see 1.27, m, alkyl chain), 1.27 (30 H, br s, alkyl chain), 1.12 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 1.07 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 714 [M^+], 699 [M-(-CH_3)], 593 [M-(-$OCH_2CH(Cl)CH(CH_3)_2$)], 397 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$), and + (-H)], 369, 341, 317, 213, 197, 185, 168, 157, 145 [M-($C_{18}H_{36}$-), and - (-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)_2$)], 139, 128, 110.

***(S,S)-2-Chloro-3-methylpentyl 4'-(4-heptyloxybenzoyloxy)-4-biphenyl carboxylate* 141**

Quantity of acid (**55**) used in reaction (0.18 g, 0.75 mmol), quantity of phenol (**95**) used in reaction (0.25 g, 0.75 mmol), yield (0.15 g, 36 %), (purity, M1 99.7 %, M2 99 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ +28° (7.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2760 (C-H stretch), 1745 and 1720 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1490, 1400, 1320, 1310-1225 and 1120 (C-O stretch), 1220, 1190, 1170, 1075, 1010, 850, 830 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', J_{AX} 7.8 Hz, $J_{AX'}$ 0.2 Hz, phenyl), 6.99 (2 H, AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 4.56 (2 H, m, -$CO_2C\underline{H}_2$CH(Cl)-), 4.21 (1 H, m, -$CO_2CH_2C\underline{H}$(Cl)-), 4.06 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.96 (1 H, m, -$C\underline{H}(CH_3)$-), 1.89 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.69 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.50 (see 1.32, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.32 (9 H, br s, alkyl chain), 1.11 (3 H, d, J 6.5 Hz, -$CH(C\underline{H}_3)CH_2CH_3$), 0.98 (3 H, t, J 6.5 Hz, -$CH(CH_3)CH_2C\underline{H}_3$), 0.90 (3 H, br t, J 7.0 Hz, $C\underline{H}_3CH_2$-); m/z 550 [M^+], 415 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 196, 121 [M-($C_7H_{14}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)].

***(S,S)-2-Chloro-3-methylpentyl 4'-(4-octyloxybenzoyloxy)-4-biphenyl carboxylate* 142**

Quantity of acid (**56**) used in reaction (0.19 g, 0.75 mmol), quantity of phenol (**95**) used in reaction (0.25 g, 0.75 mmol), yield (0.1 g, 24 %), (purity, M1 99.2 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ +19.5° (4.1 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2780 (C-H stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1400, 1370-1205 and 1125 (C-O stretch), 1190, 1170, 1075, 1010, 850, 820 (1,4-disub. ring), 690; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.69 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.32 (2

H, AA'XX', phenyl), 6.98 (2 H, AA'XX', phenyl), 4.56 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.21 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.96 (1 H, m, -$C\underline{H}(CH_3)$-), 1.89 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.69 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.50 (see 1.32, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.32 (11 H, br s, alkyl chain), 1.11 (3 H, d, -$CH(C\underline{H}_3)CH_2CH_3$), 0.98 (3 H, t, -$CH(CH_3)CH_2C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 564 [M^+], 429 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 196, 121 [M-($C_8H_{16}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)].

(S,S)-2-Chloro-3-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenyl carboxylate **143**

Quantity of acid (**51**) used in reaction (0.2 g, 0.75 mmol), quantity of phenol (**95**) used in reaction (0.25 g, 0.75 mmol), yield (0.2 g, 46 %), (purity, M1 99.2 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ slight positive deflection (1.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2800 (C-H stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1430, 1400, 1280 and 1120 (C-O stretch), 1220, 1175, 1075, 1010, 850, 830 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.12 (2 H, AA'XX', phenyl), 7.69 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.30 (2 H, AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.56 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.21 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 1.95 (1 H, m, -$C\underline{H}(CH_3)$-), 1.84 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.65 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.48 (see 1.32, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.32 (13 H, br s, alkyl chain), 1.10 (3 H, d, -$CH(C\underline{H}_3)CH_2CH_3$), 0.98 (3 H, t, -$CH(CH_3)CH_2C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 578 [M^+], 443 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 247 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 196, 121 [M-($C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)].

***(S,S)-2-Chloro-3-methylpentyl 4'-(4-decyloxybenzoyloxy)-4-biphenyl carboxylate* 144**

Quantity of acid (**52**) used in reaction (0.21 g, 0.75 mmol), quantity of phenol (**95**) used in reaction (0.25 g, 0.75 mmol), yield (0.2 g, 45 %), (purity, M1 100 %, M2 99 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ +11° (7.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2800 (C-H stretch), 1740-1720 (C=O stretch), 1615 and 1530 (arom. C=C stretch), 1495, 1400, 1320, 1305-1240 and 1125 (C-O stretch), 1230, 1190, 1175, 1080, 1010, 850, 830 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.70 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.34 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.56 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.22 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.04 (2 H, t, -$C\underline{H}_2O$-), 1.96 (1 H, m, -$C\underline{H}(CH_3)$-), 1.84 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.65 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.48 (see 1.29, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.29 (15 H, br s, alkyl chain), 1.10 (3 H, d, -$CH(C\underline{H}_3)CH_2CH_3$), 0.96 (3 H, t, -$CH(CH_3)CH_2C\underline{H}_3$), 0.87 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 592 [M^+], 457 [M-(-O $CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 261 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)$ CH_2CH_3)], 196, 121 [M-($C_{10}H_{20}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)$ CH_2CH_3)].

***(S,S)-2-Chloro-3-methylpentyl 4'-(4-undecyloxybenzoyloxy)-4-biphenyl carboxylate* 145**

Quantity of acid (**53**) used in reaction (0.22 g, 0.75 mmol), quantity of phenol (**95**) used in reaction (0.25 g, 0.75 mmol), yield (0.15 g, 33 %), (purity, M1 99.9 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{23.5}$ +12.3° (17.5 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2805 (C-H stretch), 1730 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1490, 1400, 1320, 1310-1240 and 1125 (C-O stretch), 1225, 1190, 1175, 1080, 1010, 850, 830 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX',

phenyl), 8.14 (2 H, AA'XX', phenyl), 7.70 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.34 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.56 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.22 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.04 (2 H, t, -$C\underline{H}_2O$-), 1.96 (1 H, m, -$C\underline{H}(CH_3)$-), 1.84 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.65 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.48 (see 1.29, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.29 (17 H, br s, alkyl chain), 1.10 (3 H, d, -$CH(C\underline{H}_3)CH_2CH_3$), 0.96 (3 H, t, -$CH(CH_3)CH_2C\underline{H}_3$), 0.87 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 606 [M^+], 471 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 275 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 196, 121 [M-($C_{11}H_{22}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)].

***(S,S)-2-Chloro-3-methylpentyl 4'-(4-dodecyloxybenzoyloxy)-4-biphenyl carboxylate* 146**

Quantity of acid (**54**) used in reaction (0.23 g, 0.75 mmol), quantity of phenol (**95**) used in reaction (0.25 g, 0.75 mmol), yield (0.15 g, 32 %), (purity, M1 99.9 %, M2 99.8 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -10° (4.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2750 (C-H stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1495, 1430, 1365-1205 and 1120 (C-O stretch), 1190, 1175, 1085, 1010, 850, 830 (1,4-disub. ring), 770, 730, 690, 665; δ_H (270 MHz, $CDCl_3$) 8.19 (2 H, AA'XX', phenyl), 8.16 (2 H, AA'XX', phenyl), 7.70 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.34 (2 H, AA'XX', phenyl), 7.10 (2 H, AA'XX', phenyl), 4.56 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.22 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 1.94 (1 H, m, -$C\underline{H}(CH_3)$-), 1.82 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.66 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.47 (see 1.26, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.26 (19 H, br s, alkyl chain), 1.11 (3 H, d, -$CH(C\underline{H}_3)CH_2CH_3$), 0.98 (3 H, t, -$CH(CH_3)CH_2C\underline{H}_3$), 0.87 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 620 [M^+], 485 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 289 [M-(-O

$C_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3)]$, 196, 121 [M-($C_{12}H_{24}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3)$].

(S,S)-2-Chloro-3-methylpentyl 4'-(4-tridecyloxybenzoyloxy)-4-biphenyl carboxylate **147**

Quantity of acid (**57**) used in reaction (0.24 g, 0.75 mmol), quantity of phenol (**95**) used in reaction (0.25 g, 0.75 mmol), yield (0.15 g, 31 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{24.5}$ +3.5° (2.5 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2750 (C-H stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1495, 1430, 1365-1205 and 1120 (C-O stretch), 1190, 1175, 1085, 1010, 850, 830 (1,4-disub. ring), 770, 730, 690, 665; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.15 (2 H, AA'XX', phenyl), 7.70 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.34 (2 H, AA'XX', phenyl), 7.09 (2 H, AA'XX', phenyl), 4.56 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.22 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 1.95 (1 H, m, -$C\underline{H}(CH_3)$-), 1.81 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.66 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.46 (see 1.30, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.30 (21 H, br s, alkyl chain), 1.10 (3 H, d, -$CH(C\underline{H}_3)CH_2CH_3$), 0.97 (3 H, t, -$CH(CH_3)CH_2C\underline{H}_3$), 0.86 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 634 [M^+], 499 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 303 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 196, 121 [M-($C_{13}H_{26}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)].

(S,S)-2-Chloro-3-methylpentyl 4'-(4-tetradecyloxybenzoyloxy)-4-biphenyl carboxylate **148**

Quantity of acid (**58**) used in reaction (0.25 g, 0.75 mmol), quantity of phenol (**95**) used in reaction (0.25 g, 0.75 mmol), yield (0.2 g, 41 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ +5.6° (6.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl

disc) 3050-2750 (C-H stretch), 1720 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1480, 1430, 1365-1205 and 1120 (C-O stretch), 1190, 1175, 1085, 1010, 850, 830 (1,4-disub. ring), 770, 730, 690, 660; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.70 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.34 (2 H, AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.55 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.22 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 1.95 (1 H, m, -$C\underline{H}(CH_3)$-), 1.80 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.65 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.50 (see 1.29, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.29 (23 H, br s, alkyl chain), 1.10 (3 H, d, -$CH(C\underline{H}_3)CH_2CH_3$), 0.97 (3 H, t, -$CH(CH_3)CH_2C\underline{H}_3$), 0.87 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 648 [M^+], 513 [M-(-OCH_2 $CH(Cl)CH(CH_3)CH_2CH_3$)], 317 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2$ CH_3)], 196, 121 [M-$C_{14}H_{28}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)].

(S,S)-2-Chloro-3-methylpentyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate **149**

Quantity of acid (**70**) used in reaction (0.23 g, 0.8 mmol), quantity of phenol (**95**) used in reaction (0.25 g, 0.75 mmol), yield (0.2 g, 49 %), (purity, M1 100 %, M2 99.2 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ 0° (25 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3010-2720 (C-H stretch), 2210 (C≡C stretch), 1720 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1495, 1470, 1405, 1320-1230 and 1110 (C-O stretch), 1220, 1190, 1170, 1070, 1010, 845 (1,4-disub. ring), 770, 695; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.9 Hz, phenyl), 7.66 (4 H, AA'XX', phenyl), 7.59 (2 H, AA'XX', J_{AX} 7.7 Hz, $J_{AX'}$ 0.2 Hz, phenyl), 7.30 (2 H, AA'XX', J_{AX} 7.7 Hz, $J_{AX'}$ 0.2 Hz, phenyl), 6.91 (2 H, AA'XX', J_{AX} 7.7 Hz, $J_{AX'}$ 0.2 Hz, phenyl), 4.55 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.21 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.95 (1 H, m, -$C\underline{H}(CH_3)$-), 1.80 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.66 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.45 (see 1.29, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.29

(13 H, br s, alkyl chain), 1.10 (3 H, d, J 6.5 Hz, -CH(C<u>H</u>$_3$)CH$_2$CH$_3$), 0.97 (3 H, t, J 6.5 Hz, -CH(CH$_3$)CH$_2$C<u>H</u>$_3$), 0.89 (3 H, br t, J 7 Hz, C<u>H</u>$_3$CH$_2$-); m/z 602 [M$^+$], 467 [M-(-OCH$_2$CH(Cl)CH(CH$_3$)CH$_2$CH$_3$)], 271 [M-(-OC$_6$H$_4$C$_6$H$_4$CO$_2$CH$_2$CH(Cl)CH(CH$_3$)CH$_2$CH$_3$)], 197, 145 [M-(C$_9$H$_{18}$-), and -(-OC$_6$H$_4$C$_6$H$_4$CO$_2$CH$_2$CH(Cl)CH(CH$_3$)CH$_2$CH$_3$)].

(S,S)-2-Chloro-3-methylpentyl 4'-(4-dodecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate **150**

Quantity of acid (**71**) used in reaction (0.3 g, 0.91 mmol), quantity of phenol (**95**) used in reaction (0.3 g, 0.90 mmol), yield (0.25 g, 43 %), (purity, M1 100 %, M2 99.3 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -21.1° (30 mg cm^{-3} in CHCl$_3$); $\nu_{max.}$ (KCl disc) 3010-2710 (C-H stretch), 2200 (C≡C stretch), 1720 (C=O stretch), 1610 and 1535 (arom. C=C stretch), 1495, 1470, 1405, 1320-1230 and 1110 (C-O stretch), 1220, 1190, 1170, 1080, 1010, 845 (1,4-disub. ring), 770, 695; δ_H (270 MHz, CDCl$_3$) 8.14 (2 H, AA'XX', phenyl), 7.66 (4 H, AA'XX', phenyl), 7.60 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', phenyl), 6.90 (2 H, AA'XX', phenyl), 4.55 (2 H, m, -CO$_2$C<u>H</u>$_2$CH(Cl)-), 4.21 (1 H, m, -CO$_2$CH$_2$C<u>H</u>(Cl)-), 4.00 (2 H, t, -C<u>H</u>$_2$O-), 1.95 (1 H, m, -C<u>H</u>(CH$_3$)-), 1.80 (2 H, m, -C<u>H</u>$_2$CH$_2$O-), 1.66 (1 H, m, -CH(CH$_3$)C<u>H</u>(H)CH$_3$), 1.45 (see 1.30, m, -CH(CH$_3$)CH(<u>H</u>)CH$_3$ and alkyl chain), 1.30 (19 H, br s, alkyl chain), 1.10 (3 H, d, -CH(C<u>H</u>$_3$)CH$_2$CH$_3$), 0.97 (3 H, t, -CH(CH$_3$)CH$_2$C<u>H</u>$_3$), 0.90 (3 H, br t, C<u>H</u>$_3$CH$_2$-); m/z 644 [M$^+$], 509 [M-(-OCH$_2$CH(Cl)CH(CH$_3$)CH$_2$CH$_3$)], 313 [M-(-OC$_6$H$_4$C$_6$H$_4$CO$_2$CH$_2$CH(Cl)CH(CH$_3$)CH$_2$CH$_3$)], 197, 145 [M-(C$_{12}$H$_{24}$-), and -(-OC$_6$H$_4$C$_6$H$_4$CO$_2$CH$_2$CH(Cl)CH(CH$_3$)CH$_2$CH$_3$)].

***(S,S)-2-Chloro-3-methylpentyl 4'-(4-tetradecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate* 151**

Quantity of acid (**72**) used in reaction (0.32 g, 0.9 mmol), quantity of phenol (**95**) used in reaction (0.3 g, 0.9 mmol), yield (0.33 g, 53 %), (purity, M1 99.9 %, M2 99.8 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -10.2° (42.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3010-2710 (C-H stretch), 2200 (C≡C stretch), 1720 (C=O stretch), 1610 and 1535 (arom. C=C stretch), 1495, 1470, 1405, 1320-1230 and 1110 (C-O stretch), 1220, 1190, 1170, 1080, 1010, 845 (1,4-disub. ring), 770, 695; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 7.66 (4 H, AA'XX', phenyl), 7.60 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', phenyl), 6.90 (2 H, AA'XX', phenyl), 4.55 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.21 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, -$C\underline{H}_2O$-), 1.96 (1 H, m, -$C\underline{H}(CH_3)$-), 1.81 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.66 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.45 (see 1.30, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.30 (23 H, br s, alkyl chain), 1.10 (3 H, d, -$CH(C\underline{H}_3)CH_2CH_3$), 0.97 (3 H, t, -$CH(CH_3)CH_2C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 672 [M^+], 537 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 341 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 197, 145 [M-($C_{14}H_{28}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)].

***(S,S)-2-Chloro-3-methylpentyl 4'-(4-hexadecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate* 152**

Quantity of acid (**73**) used in reaction (0.29 g, 0.75 mmol), quantity of phenol (**95**) used in reaction (0.25 g, 0.75 mmol), yield (0.35 g, 67 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -12° (103.5 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2710 (C-H stretch), 2210 (C≡C stretch), 1720 (C=O stretch), 1605 and 1530 (arom. C=C stretch), 1495, 1470, 1405, 1320-1230 and 1110 (C-O stretch), 1220, 1190, 1170, 1080, 1010, 850 (1,4-disub. ring), 770, 695; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', phenyl), 7.67 (4 H, AA'XX', phenyl), 7.60 (2 H, AA'XX', phenyl), 7.31

(2 H, AA'XX', phenyl), 6.89 (2 H, AA'XX', phenyl), 4.55 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.20 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, -$C\underline{H}_2O$-), 1.96 (1 H, m, -$C\underline{H}(CH_3)$-), 1.81 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.66 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.46 (see 1.30, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.30 (27 H, br s, alkyl chain), 1.10 (3 H, d, -$CH(C\underline{H}_3)CH_2CH_3$), 0.97 (3 H, t, -$CH(CH_3)CH_2C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 700 [M^+], 565 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 369 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 197, 145 [M-($C_{16}H_{32}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)].

(S,S)-2-Chloro-3-methylpentyl 4'-(4-octadecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate **153**

Quantity of acid (**74**) used in reaction (0.37 g, 0.9 mmol), quantity of phenol (**95**) used in reaction (0.3 g, 0.9 mmol), yield (0.41 g, 59 %), (purity, M1 100 %, M2 99.7 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -6.8° (25.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2690 (C-H stretch), 2215 (C≡C stretch), 1720 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1495, 1470, 1410, 1320-1230 and 1110 (C-O stretch), 1220, 1190, 1170, 1080, 1000, 850 (1,4-disub. ring), 770, 695; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 7.67 (4 H, AA'XX', phenyl), 7.60 (2 H, AA'XX', phenyl), 7.29 (2 H, AA'XX', phenyl), 6.90 (2 H, AA'XX', phenyl), 4.54 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.20 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, -$C\underline{H}_2O$-), 1.96 (1 H, m, -$C\underline{H}(CH_3)$-), 1.81 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.66 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.45 (see 1.28, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.28 (30 H, br s, alkyl chain), 1.10 (3 H, d, -$CH(C\underline{H}_3)CH_2CH_3$), 0.97 (3 H, t, -$CH(CH_3)CH_2C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 728 [M^+], 593 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 397 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 197, 145 [M-($C_{18}H_{36}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)].

***(S,R)-2-Chloro-3-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenyl carboxylate* 154**

Quantity of acid (**51**) used in reaction (0.32 g, 1.21 mmol), quantity of phenol (**96**) used in reaction (0.4 g, 1.2 mmol), yield (0.25 g, 36 %), (purity, M1 100 %, M2 99.8 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -12.7° (18.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2800 (C-H stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1430, 1400, 1280 and 1120 (C-O stretch), 1220, 1175, 1075, 1010, 850, 830 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.13 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 6.99 (2 H, AA'XX', J_{AX} 8.5 Hz, $J_{AX'}$ 0.5 Hz, phenyl), 4.53 (2 H, d, J 6.5 Hz, $-CO_2C\underline{H}_2CH(Cl)-$), 4.33 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 4.05 (2 H, t, J 6.5 Hz, $-C\underline{H}_2O-$), 1.83 (3 H, m, $-C\underline{H}(CH_3)-$ and $-C\underline{H}_2CH_2O-$), 1.55 (see 1.29, m, alkyl chain and $-CH(CH_3)C\underline{H}_2CH_3$), 1.29 (17 H, br s, alkyl chain), 1.04 (3 H, d, J 6.5 Hz, $-CH(C\underline{H}_3)CH_2CH_3$), 0.96 (3 H, t, J 7.0 Hz, $-CH(CH_3)CH_2C\underline{H}_3$), 0.89 (3 H, br t, J 7.0 Hz, $C\underline{H}_3CH_2-$); m/z 578 [M^+], 443 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 247 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 196, 121 [M-($C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)].

***(S,R)-2-Chloro-3-methylpentyl 4'-(4-nonyloxypropioyloxy)-4-biphenyl carboxylate* 155**

Quantity of acid (**70**) used in reaction (0.29 g, 1.01 mmol), quantity of phenol (**96**) used in reaction (0.33 g, 0.99 mmol), yield (0.49 g, 82 %), (purity, M1 99 %, M2 99.1 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -3.8° (30.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3010-2720 (C-H stretch), 2200 (C≡C stretch), 1725 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1495, 1470, 1405, 1320-1220 and 1120 (C-O stretch), 1220, 1190, 1170, 1070, 1010, 845 (1,4-disub. ring), 770, 695; δ_H (270 MHz, $CDCl_3$) 8.14 (2

H, AA'XX', J_{AX} 7.9 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 7.66 (4 H, AA'XX', phenyl), 7.59 (2 H, AA'XX', J_{AX} 7.6 Hz, $J_{AX'}$ 0.2 Hz, phenyl), 7.30 (2 H, AA'XX', J_{AX} 7.6 Hz, $J_{AX'}$ 0.2 Hz, phenyl), 6.91 (2 H, AA'XX', J_{AX} 7.6 Hz, $J_{AX'}$ 0.2 Hz, phenyl), 4.55 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.21 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.95 (1 H, m, -$C\underline{H}(CH_3)$-), 1.80 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.66 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.45 (see 1.30, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.30 (13 H, br s, alkyl chain), 1.10 (3 H, d, J 6.5 Hz, -$CH(C\underline{H}_3)CH_2CH_3$), 0.97 (3 H, t, J 6.5 Hz, -$CH(CH_3)CH_2C\underline{H}_3$), 0.89 (3 H, br t, J 7 Hz, $C\underline{H}_3CH_2$-); m/z 602 [M^+], 467 [M-(-O$CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 271 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2$ CH_3)], 197, 145 [M-(C_9H_{18}-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)].

***(S)-2-Chloro-4-methylpentyl 4'-(4-heptyloxybenzoyloxy)-4-biphenyl carboxylate* 156**

Quantity of acid (**55**) used in reaction (0.33 g, 1.41 mmol), quantity of phenol (**97**) used in reaction (0.47 g, 1.41 mmol), yield (0.24 g, 31 %), (purity, M1 99.3 %, M2 99.3 %), (t.t. see results and discussion section). $[\alpha]_D^{23}$ -5.6° (8.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3010-2800 (C-H stretch), 1745 and 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1470, 1400, 1370, 1310-1230 and 1115 (C-O stretch), 1320, 1190, 1175, 1070, 1010, 850 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 1.4 Hz, phenyl), 6.99 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 4.49 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.28 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.96 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.85 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.68 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.46 (see 1.34, m, alkyl chain), 1.34 (8 H, br s, alkyl chain), 1.13 (3 H, d, J 6.0 Hz, -$CH(C\underline{H}_3)CH_3$), 1.00 (3 H, d, J 6.0 Hz, -$CH(CH_3)C\underline{H}_3$), 0.92 (3 H, br t, J 6.5 Hz, $C\underline{H}_3CH_2$-); m/z 550 [M^+], 415 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 219 [M-(-$OC_6H_4$

$C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2)]$, 196, 121 [M-($C_7H_{14}$-), and -(-$OC_6H_4C_6H_4CO_2$ $CH_2CH(Cl)CH_2CH(CH_3)_2)$].

(S)-2-Chloro-4-methylpentyl 4'-(4-octyloxybenzoyloxy)-4-biphenyl carboxylate **157**

Quantity of acid (**56**) used in reaction (0.3 g, 1.2 mmol), quantity of phenol (**97**) used in reaction (0.4 g, 1.2 mmol), yield (0.28 g, 42 %), (purity, M1 100 %, M2 99.6 %), (t.t. see results and discussion section). $[\alpha]_D^{20}$ -7.1° (2.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2700 (C-H stretch), 1725 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1470, 1370, 1350-1230 and 1110 (C-O stretch), 1215, 1175, 1075, 1010, 890, 850 (1,4-disub. ring), 820, 770, 690; δ_H (270 MHz, $CDCl_3$) 8.20 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.65 (2 H, AA'XX', phenyl), 7.34 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.30 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 1.98 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.84 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.65 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.50 (see 1.34, m, alkyl chain), 1.34 (10 H, br s, alkyl chain), 0.96 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.93 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.85 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 564 [M^+], 429 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 233 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)$ $CH_2CH(CH_3)_2$)], 196, 121 [M-(C_8H_{16}-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2$ $CH(CH_3)_2$)].

(S)-2-Chloro-4-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenyl carboxylate **158**

Quantity of acid (**51**) used in reaction (0.32 g, 1.21 mmol), quantity of phenol (**97**) used in reaction (0.4 g, 1.2 mmol), yield (0.27 g, 39 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{20}$ -14.8° (2.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2740 (C-H stretch), 1730 (C=O stretch), 1610 and 1515 (arom. C=C stretch),

1475, 1400, 1370, 1345-1235 and 1120 (C-O stretch), 1220, 1175, 1075, 1010, 850 (1,4-disub. ring), 775, 695; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.15 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.49 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.28 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, -$C\underline{H}_2O$-), 1.98 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.81 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.63 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.49 (see 1.29, m, alkyl chain), 1.29 (12 H, br s, alkyl chain), 1.00 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.97 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 578 [M^+], 443 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 247 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 196, 121 [M-($C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)].

***(S)-2-Chloro-4-methylpentyl 4'-(4-decyloxybenzoyloxy)-4-biphenyl carboxylate* 159**

Quantity of acid (**52**) used in reaction (0.42 g, 1.54 mmol), quantity of phenol (**97**) used in reaction (0.5 g, 1.49 mmol), yield (0.35 g, 39 %), (purity, M1 100 %, M2 99.6 %), (t.t. see results and discussion section). $[\alpha]_D^{22}$ -25° (0.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2750 (C-H stretch), 1735 and 1725 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1470, 1300-1230 and 1115 (C-O stretch), 1220, 1190, 1170, 1080, 1010, 850 (1,4-disub. ring), 775, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.13 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.30 (2 H, AA'XX', phenyl), 6.98 (2 H, AA'XX', phenyl), 4.49 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.28 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, -$C\underline{H}_2O$-), 1.99 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.80 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.62 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.47 (see 1.29, m, alkyl chain), 1.29 (14 H, br s, alkyl chain), 0.97 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.94 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.88 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 592 [M^+], 457 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 261 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)$

$CH_2CH(CH_3)_2)]$, 196, 121 [M-($C_{10}H_{20}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2$ $CH(CH_3)_2)$].

(S)-2-Chloro-4-methylpentyl 4'-(4-undecyloxybenzoyloxy)-4-biphenyl carboxylate **160**

Quantity of acid (**53**) used in reaction (0.44 g, 1.53 mmol), quantity of phenol (**97**) used in reaction (0.5 g, 1.49 mmol), yield (0.4 g, 44 %), (purity, M1 100 %, M2 99.6 %), (t.t. see results and discussion section). $[\alpha]_D^{22}$ -16.7° (17.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2750 (C-H stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1470, 1400, 1300-1230 and 1115 (C-O stretch), 1220, 1190, 1170, 1080, 1010, 845 (1,4-disub. ring), 775, 690; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.29 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.28 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, -$C\underline{H}_2O$-), 1.99 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.80 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.62 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.47 (see 1.30, m, alkyl chain), 1.30 (16 H, br s, alkyl chain), 0.97 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.94 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 606 [M^+], 471 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 275 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)$ $CH_2CH(CH_3)_2$)], 196, 121 [M-($C_{11}H_{22}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2$ $CH(CH_3)_2$)].

(S)-2-Chloro-4-methylpentyl 4'-(4-dodecyloxybenzoyloxy)-4-biphenyl carboxylate **161**

Quantity of acid (**54**) used in reaction (0.61 g, 2 mmol), quantity of phenol (**97**) used in reaction (0.67 g, 2 mmol), yield (0.25 g, 20 %), (purity, M1 100 %, M2 99.2 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -12.4° (1.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2700 (C-H stretch), 1730 (C=O stretch), 1615 and 1525 (arom. C=C stretch), 1470,

1400, 1320, 1305-1240 and 1120 (C-O stretch), 1230, 1190, 1175, 1085, 1010, 850 (1,4-disub. ring), 830, 770, 690; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.69 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.30 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.28 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, -$C\underline{H}_2O$-), 1.99 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.80 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.62 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.47 (see 1.27, m, alkyl chain), 1.27 (18 H, br s, alkyl chain), 0.97 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.94 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.87 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 620 [M^+], 485 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 289 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 196, 121 [M-($C_{12}H_{24}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)].

***(S)-2-Chloro-4-methylpentyl 4'-(4-tridecyloxybenzoyloxy)-4-biphenyl carboxylate* 162**

Quantity of acid (**57**) used in reaction (0.75 g, 2.34 mmol), quantity of phenol (**97**) used in reaction (0.78 g, 2.34 mmol), yield (0.35 g, 24 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -42° (1.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2700 (C-H stretch), 1735 and 1720 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1470, 1400, 1320, 1305-1230 and 1115 (C-O stretch), 1220, 1190, 1170, 1080, 1010, 850 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.15 (2 H, AA'XX', phenyl), 7.69 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.49 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.28 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, -$C\underline{H}_2O$-), 1.98 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.81 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.63 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.51 (see 1.26, m, alkyl chain), 1.26 (20 H, br s, alkyl chain), 1.00 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.96 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 634 [M^+], 499 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 303 [M-(-O

$C_6H_4C_6H_4CO_2CH_2$ $CH(Cl)CH_2CH(CH_3)_2)]$, 197, 121 [M-($C_{13}H_{26}$-), and -(-OC_6H_4 $C_6H_4CO_2CH_2CH(Cl)$ $CH_2CH(CH_3)_2)]$.

(S)-2-Chloro-4-methylpentyl 4'-(4-tetradecyloxybenzoyloxy)-4-biphenyl carboxylate **163**

Quantity of acid (**58**) used in reaction (0.75 g, 2.24 mmol), quantity of phenol (**97**) used in reaction (0.74 g, 2.23 mmol), yield (0.41 g, 28 %), (purity, M1 100 %, M2 99.6 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -8.6° (5.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2700 (C-H stretch), 1735 and 1720 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1470, 1400, 1330, 1300-1230 and 1115 (C-O stretch), 1220, 1190, 1170, 1080, 1010, 855 (1,4-disub. ring), 775, 695; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.12 (2 H, AA'XX', phenyl), 7.69 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.30 (2 H, AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.52 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.30 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.07 (2 H, t, -$C\underline{H}_2O$-), 2.00 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.80 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.65 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.50 (see 1.26, m, alkyl chain), 1.26 (22 H, br s, alkyl chain), 1.00 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.95 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3$ CH_2-); m/z 648 [M^+], 513 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 317 [M-(-O C_6H_4 $C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 197, 121 [M-($C_{14}H_{28}$-), and -(-$OC_6H_4$ $C_6H_4CO_2CH_2CH(Cl)$ $CH_2CH(CH_3)_2$)].

(S)-2-Chloro-4-methylpentyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate **164**

Quantity of acid (**70**) used in reaction (0.43 g, 1.5 mmol), quantity of phenol (**97**) used in reaction (0.5 g, 1.5 mmol), yield (0.56 g, 60 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -16.8° (36.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3010-2700 (C-H stretch), 2200 (C≡C stretch), 1710 (C=O stretch), 1605 and 1530 (arom.

C=C stretch), 1495, 1470, 1400, 1310, 1300-1230 and 1110 (C-O stretch), 1220, 1190, 1170, 1070, 1010, 830 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', J_{AX} 8.1 Hz, $J_{AX'}$ 0.9 Hz, phenyl), 7.66 (4 H, AA'XX', phenyl), 7.58 (2 H, AA'XX', J_{AX} 7.7 Hz, $J_{AX'}$ 0.3 Hz, phenyl), 7.30 (2 H, AA'XX', J_{AX} 7.7 Hz, $J_{AX'}$ 0.3 Hz, phenyl), 6.90 (2 H, AA'XX', J_{AX} 7.7 Hz, $J_{AX'}$ 0.3 Hz, phenyl), 4.49 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.29 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 2.02 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.80 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.62 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.46 (see 1.30, m, alkyl chain), 1.30 (12 H, br s, alkyl chain), 1.00 (3 H, d, J 6.5 Hz, -$CH(C\underline{H}_3)CH_3$), 0.96 (3 H, d, J 6.5 Hz, -$CH(CH_3)C\underline{H}_3$), 0.89 (3 H, br t, J 6.5 Hz, $C\underline{H}_3CH_2$-); m/z 602 [M^+], 467 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 271 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 197, 145 [M-($C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)].

***(S)-2-Chloro-4-methylpentyl 4'-(4-dodecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate* 165**

Quantity of acid (**71**) used in reaction (0.25 g, 0.76 mmol), quantity of phenol (**97**) used in reaction (0.25 g, 0.75 mmol), yield (0.39 g, 80 %), (purity, M1 99.8 %, M2 99.2 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -13.7° (49 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3010-2720 (C-H stretch), 2210 (C≡C stretch), 1720 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1495, 1470, 1405, 1320-1230 and 1110 (C-O stretch), 1220, 1190, 1170, 1070, 1010, 845 (1,4-disub. ring), 770, 695; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 7.66 (4 H, AA'XX', phenyl), 7.59 (2 H, AA'XX', phenyl), 7.29 (2 H, AA'XX', phenyl), 6.91 (2 H, AA'XX', phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.30 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.01 (2 H, t, -$C\underline{H}_2O$-), 2.00 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.80 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.63 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.46 (see 1.30, m, alkyl chain), 1.30 (18 H, br s, alkyl chain), 1.00 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.97 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 644

[M^+], 509 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 313 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 197, 145 [M-($C_{12}H_{24}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)].

***(S)-2-Chloro-4-methylpentyl 4'-(4-tetradecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate* 166**

Quantity of acid (**72**) used in reaction (0.4 g, 1.26 mmol), quantity of phenol (**97**) used in reaction (0.42 g, 1.26 mmol), yield (0.5 g, 58 %), (purity, M1 99.8 %, M2 99.6 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -6.2° (26.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2700 (C-H stretch), 2200 (C≡C stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1495, 1470, 1400, 1320-1230 and 1120 (C-O stretch), 1220, 1190, 1170, 1070, 1010, 835 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 7.66 (4 H, AA'XX', phenyl), 7.58 (2 H, AA'XX', phenyl), 7.30 (2 H, AA'XX', phenyl), 6.90 (2 H, AA'XX', phenyl), 4.49 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.29 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.04 (2 H, t, -$C\underline{H}_2O$-), 2.01 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.80 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.63 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.45 (see 1.28, m, alkyl chain), 1.28 (22 H, br s, alkyl chain), 0.99 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.96 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.87 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 672 [M^+], 537 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 341 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 196, 145 [M-($C_{14}H_{28}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)].

***(S)-2-Chloro-4-methylpentyl 4'-(4-hexadecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate* 167**

Quantity of acid (**73**) used in reaction (0.29 g, 0.75 mmol), quantity of phenol (**97**) used in reaction (0.25 g, 0.75 mmol), yield (0.1 g, 13 %), (purity, M1 99.6 %, M2 98.6 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -12° (102.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$

(KCl disc) 3020-2800 (C-H stretch), 2200 (C≡C stretch), 1730 (C=O stretch), 1605 and 1525 (arom. C=C stretch), 1490, 1475, 1400, 1340, 1320-1230 and 1120 (C-O stretch), 1220, 1190, 1170, 1070, 1010, 840 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 7.64 (4 H, AA'XX', phenyl), 7.56 (2 H, AA'XX', phenyl), 7.28 (2 H, AA'XX', phenyl), 6.88 (2 H, AA'XX', phenyl), 4.49 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.29 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, -$C\underline{H}_2O$-), 2.01 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.80 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.63 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.45 (see 1.29, m, alkyl chain), 1.29 (26 H, br s, alkyl chain), 0.99 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.96 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 700 [M^+], 565 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 369 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 196, 145 [M-($C_{16}H_{32}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)].

(S)-2-Chloro-4-methylpentyl 4'-(4-octadecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate **168**

Quantity of acid (**74**) used in reaction (0.19 g, 0.46 mmol), quantity of phenol (**97**) used in reaction (0.15 g, 0.45 mmol), yield (0.15 g, 40 %), (purity, M1 100 %, M2 99.5 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -17.2° (29.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2800 (C-H stretch), 2200 (C≡C stretch), 1730 (C=O stretch), 1605 and 1525 (arom. C=C stretch), 1490, 1470, 1400, 1340, 1300 and 1120 (C-O stretch), 1220, 1190, 1170, 1070, 1010, 845 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', phenyl), 7.63 (4 H, AA'XX', phenyl), 7.55 (2 H, AA'XX', phenyl), 7.28 (2 H, AA'XX', phenyl), 6.88 (2 H, AA'XX', phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.30 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.04 (2 H, t, -$C\underline{H}_2O$-), 2.00 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.81 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.62 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.44 (see 1.30, m, alkyl chain), 1.30 (30 H, br s, alkyl chain), 0.97 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.94 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.86 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 728

[M^+], 593 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 397 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 196, 145 [M-($C_{18}H_{36}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)].

(+/-)-2-Chloro-4-methylpentyl 4'-(4-nonyloxybenzoloyloxy)-4-biphenyl carboxylate **169**

Quantity of acid (**51**) used in reaction (0.5 g, 1.89 mmol), quantity of phenol (**98**) used in reaction (0.63 g, 1.9 mmol), yield (0.52 g, 48 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ 0° (52.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2740 (C-H stretch), 1730 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1475, 1405, 1370, 1350-1235 and 1110 (C-O stretch), 1220, 1175, 1075, 1010, 850 (1,4-disub. ring), 775, 695; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.69 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.49 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.28 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, -$C\underline{H}_2O$-), 1.98 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.81 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.63 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.49 (see 1.30, m, alkyl chain), 1.30 (12 H, br s, alkyl chain), 1.00 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.98 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 578 [M^+], 443 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 247 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 197, 121 [M-($C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)].

(S)-2-Chloropentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate **170**

Quantity of acid (**51**) used in reaction (0.19 g, 0.72 mmol), quantity of phenol (**99**) used in reaction (0.23 g, 0.73 mmol), yield (0.18 g, 44 %), (purity, M1 100 %, M2 98.7 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ -0.8° (30 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2740 (C-H stretch), 1725 (C=O stretch), 1610 and 1530 (arom. C=C stretch),

1495, 1400, 1275 and 1120 (C-O stretch), 1190, 1170, 1075, 1005, 845 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', J_{AX} 8.5 Hz, $J_{AX'}$ 0.5 Hz, phenyl), 6.99 (2 H, AA'XX', J_{AX} 9.3 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.23 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.83 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2CH_2CH_3$), 1.65 (2 H, m, -$CH_2C\underline{H}_2CH_3$), 1.49 (see 1.29, m, alkyl chain), 1.29 (12 H, br s, alkyl chain), 0.98 (3 H, t, J 7.0 Hz, -$CH_2CH_2C\underline{H}_3$), 0.89 (3 H, br t, J 7.0 Hz, $C\underline{H}_3CH_2$-); m/z 564 [M^+], 443 [M-(-$OCH_2CH(Cl)CH_2CH_2CH_3$)], 247 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH_2CH_3$)], 196, 121 [M-($C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH_2CH_3$)].

***(S)-2-Chloropentyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenyl carboxylate* 171**

Quantity of acid (**70**) used in reaction (0.21 g, 0.73 mmol), quantity of phenol (**99**) used in reaction (0.23 g, 0.73 mmol), yield (0.2 g, 47 %), (purity, M1 100 %, M2 99.2 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -2.5° (9.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3015-2680 (C-H stretch), 2210 (C≡C stretch), 1720 (C=O stretch), 1610 and 1515 (arom. C=C stretch), 1565, 1495, 1395, 1355-1230 and 1125 (C-O stretch), 1210, 1155, 1010, 840 (1,4-disub. ring), 820, 770, 700, 600, 540; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', phenyl), 7.66 (4 H, AA'XX', phenyl), 7.58 (2 H, AA'XX', phenyl), 7.30 (2 H, AA'XX', phenyl), 6.90 (2 H, AA'XX', phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.23 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 3.99 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.80 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2CH_2CH_3$), 1.65 (2 H, m, -$CH_2C\underline{H}_2CH_3$), 1.46 (see 1.29, m, alkyl chain), 1.29 (12 H, br s, alkyl chain), 0.98 (3 H, t, J 7.0 Hz, -$CH_2CH_2C\underline{H}_3$), 0.89 (3 H, br t, J 7.0 Hz, $C\underline{H}_3CH_2$-); m/z 588 [M^+], 545 [M-(-$CH_2CH_2CH_3$)], 484 [M-(-CH CH(Cl)$CH_2CH_2CH_3$)], 467 [M-(-$OCH_2CH(Cl)CH_2CH_2CH_3$), and +(-H)], 271 [M-(-O

$C_6H_4C_6H_4CO_2CH_2CH(Cl)CH_2CH_2CH_3)]$, 213, 196, 145 [M-($C_9H_{18}$-), and -(-$OC_6H_4$ $C_6H_4CO_2CH_2CH(Cl)CH_2CH_2CH_3)$].

(S)-2-Chlorohexyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate **172**

Quantity of acid (**51**) used in reaction (0.25 g, 0.95 mmol), quantity of phenol (**100**) used in reaction (0.31 g, 0.94 mmol), yield (0.25 g, 46 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ -1.3° (17.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2740 (C-H stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1495, 1400, 1280 and 1120 (C-O stretch), 1190, 1170, 1080, 1005, 845 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', J_{AX} 9.3 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 6.98 (2 H, AA'XX', J_{AX} 9.1 Hz, $J_{AX'}$ 0.9 Hz, phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.22 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.83 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2(CH_2)_2CH_3$), 1.59 (2 H, m, -$C\underline{H}_2CH_2CH_3$), 1.48 (see 1.29, m, -$(CH_2)_2C\underline{H}_2CH_3$ and alkyl chain), 1.29 (14 H, br s, alkyl chain), 0.94 (3 H, t, J 7.0 Hz, -$(CH_2)_3C\underline{H}_3$), 0.89 (3 H, br t, J 7.0 Hz, $C\underline{H}_3CH_2$-); m/z 578 [M^+], 443 [M-(-$OCH_2CH(Cl)(CH_2)_3CH_3$)], 247 [M-(-OC_6H_4 $C_6H_4CO_2CH_2CH(Cl)(CH_2)_3CH_3$)], 196, 121 [M-($C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2$ $CH(Cl)(CH_2)_3CH_3$)].

(S)-2-Chlorohexyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenyl carboxylate **173**

Quantity of acid (**70**) used in reaction (0.27 g, 0.94 mmol), quantity of phenol (**100**) used in reaction (0.31 g, 0.94 mmol), yield (0.2 g, 35 %), (purity, M1 99.7 %, M2 99.5 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -1.6° (14.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3025-2700 (C-H stretch), 2205 (C≡C stretch), 1720 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1565, 1385, 1350-1225 and 1190-1100 (C-O stretch), 1210,

1010, 930, 840 (1,4-disub. ring), 820, 770, 730, 700, 600, 540; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', J_{AX} 8.0 Hz, $J_{AX'}$ 0.5 Hz, phenyl), 7.66 (4 H, AA'XX', phenyl), 7.58 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.6 Hz, phenyl), 7.30 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.6 Hz, phenyl), 6.91 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.6 Hz, phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.21 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 3.99 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.80 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2(CH_2)_2CH_3$), 1.57 (see 1.28, m, -$CH_2(C\underline{H}_2)_2CH_3$ and alkyl chain), 1.43 (see 1.28, m, alkyl chain), 1.28 (16 H, br s, alkyl chain), 0.91 (3 H, t, J 7.0 Hz, -$(CH_2)_3C\underline{H}_3$), 0.89 (3 H, br t, J 7.0 Hz, $C\underline{H}_3CH_2$-); m/z 602 [M^+], 587 [M-(-CH_3)], 559 [M-(-$(CH_2)_2CH_3$)], 271 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_3CH_3$)], 213, 196, 145 [M-($C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_3CH_3$)], 128, 116, 55.

(S)-2-Chloro-octyl 4'-(4-heptyloxybenzoyloxy)-4-biphenylcarboxylate **174**

Quantity of acid (**55**) used in reaction (0.33 g, 1.4 mmol), quantity of phenol (**101**) used in reaction (0.5 g, 1.39 mmol), yield (0.36 g, 45 %), (purity, M1 99.4 %, M2 99.6 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ -3.7° (6.5 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2680 (C-H stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1495, 1425, 1400, 1275 and 1120 (C-O stretch), 1075, 1005, 880, 850 (1,4-disub. ring), 800, 770, 690, 510; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 6.99 (2 H, AA'XX', J_{AX} 8.4 Hz, $J_{AX'}$ 1.1 Hz, phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.22 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.83 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2(CH_2)_4CH_3$), 1.59 (see 1.32, m, alkyl chain), 1.49 (see 1.32, m, alkyl chain), 1.32 (16 H, br s, alkyl chain), 0.89 (3 H, t, -$(CH_2)_5C\underline{H}_3$), 0.88 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 578 [M^+], 415 [M-(-$OCH_2CH(Cl)(CH_2)_5CH_3$)], 219 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_5CH_3$)], 196, 121 [M-($C_7H_{14}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_5CH_3$)], 57.

***(S)-2-Chloro-octyl 4'-(4-octyloxybenzoyloxy)-4-biphenylcarboxylate* 175**

Quantity of acid (**56**) used in reaction (0.35 g, 1.4 mmol), quantity of phenol (**101**) used in reaction (0.5 g, 1.39 mmol), yield (0.56 g, 68 %), (purity, M1 100 %, M2 99.2 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ -4.2° (3.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2680 (C-H stretch), 1725 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1495, 1425, 1395, 1275 and 1120 (C-O stretch), 1190, 1170, 1070, 1020, 1005, 880, 845 (1,4-disub. ring), 770, 725, 690, 660; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 8.13 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.65 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', phenyl), 6.97 (2 H, AA'XX', phenyl), 4.50 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.21 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 4.05 (2 H, t, $-C\underline{H}_2O-$), 1.81 (4 H, m, $-C\underline{H}_2CH_2O-$ and $-C\underline{H}_2(CH_2)_4CH_3$), 1.58 (see 1.32, m, alkyl chain), 1.47 (see 1.32, m, alkyl chain), 1.32 (18 H, br s, alkyl chain), 0.91 (3 H, t, $-(CH_2)_5C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3CH_2-$); m/z 592 [M^+], 429 [M-(-$OCH_2CH(Cl)(CH_2)_5CH_3$)], 233 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_5CH_3$)], 196, 121 [M-($C_8H_{16}$-), and -(-$OC_6H_4$ $C_6H_4CO_2CH_2CH(Cl)(CH_2)_5CH_3$)], 92, 69, 55.

***(S)-2-Chloro-octyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate* 176**

Quantity of acid (**51**) used in reaction (0.37 g, 1.4 mmol), quantity of phenol (**101**) used in reaction (0.5 g, 1.39 mmol), yield (0.55 g, 66 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{26.5}$ -4.9° (4.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2760 (C-H stretch), 1730 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1400, 1395, 1270 and 1120 (C-O stretch), 1190, 1170, 1075, 1005, 845 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.66 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.51 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.23 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 4.07 (2 H, t, $-C\underline{H}_2O-$), 1.84 (4 H, m, $-C\underline{H}_2CH_2O-$ and $-C\underline{H}_2(CH_2)_4CH_3$), 1.60 (see 1.34, m, alkyl chain), 1.48 (see 1.34, m, alkyl chain), 1.34

(20 H, br s, alkyl chain), 0.93 (3 H, t, -$(CH_2)_5C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 606 [M^+], 443 [M-(-$OCH_2CH(Cl)(CH_2)_5CH_3$)], 247 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_5CH_3$)], 196, 121 [M-($C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_5CH_3$)].

(S)-2-Chloro-octyl 4'-(4-decyloxybenzoyloxy)-4-biphenylcarboxylate **177**

Quantity of acid (**52**) used in reaction (0.39 g, 1.4 mmol), quantity of phenol (**101**) used in reaction (0.5 g, 1.39 mmol), yield (0.47 g, 54.7 %), (purity, M1 100 %, M2 99.6 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ -5.3° (6.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2700 (C-H stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1395, 1270 and 1115 (C-O stretch), 1190, 1170, 1075, 1020, 1005, 850 (1,4-disub. ring), 770, 730, 690; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 8.11 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.66 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.23 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.07 (2 H, t, -$C\underline{H}_2O$-), 1.85 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2(CH_2)_4CH_3$), 1.60 (see 1.33, m, alkyl chain), 1.50 (see 1.33, m, alkyl chain), 1.33 (22 H, br s, alkyl chain), 0.94 (3 H, t, -$(CH_2)_5C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 620 [M^+], 457 [M-(-$OCH_2CH(Cl)(CH_2)_5CH_3$)], 261 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_5CH_3$)], 196, 121 [M-($C_{10}H_{20}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_5CH_3$)].

(S)-2-Chloro-octyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenyl carboxylate **178**

Quantity of acid (**70**) used in reaction (0.4 g, 1.39 mmol), quantity of phenol (**101**) used in reaction (0.5 g, 1.39 mmol), yield (0.52 g, 60 %), (purity, M1 99.8 %, M2 99.5 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -1.3° (35.5 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3025-2720 (C-H stretch), 2200 (C≡C stretch), 1720 (C=O stretch), 1610 and

1530 (arom. C=C stretch), 1565, 1400, 1350-1210 and 1110 (C-O stretch), 1190, 1170, 1150, 1005, 940, 830 (1,4-disub. ring), 770, 730, 695, 605, 540; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', J_{AX} 7.7 Hz, $J_{AX'}$ 0.3 Hz, phenyl), 7.66 (4 H, AA'XX', phenyl), 7.58 (2 H, AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 7.30 (2 H, AA'XX', J_{AX} 7.8 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 6.90 (2 H, AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 4.50 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.22 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 4.00 (2 H, t, J 6.5 Hz, $-C\underline{H}_2O-$), 1.80 (4 H, m, $-C\underline{H}_2CH_2O-$ and $-C\underline{H}_2(CH_2)_4CH_3$), 1.60 (see 1.30, m, alkyl chain), 1.45 (see 1.30, m, alkyl chain), 1.30 (20 H, br s, alkyl chain), 0.92 (3 H, t, J 7.0 Hz, $-(CH_2)_5C\underline{H}_3$), 0.88 (3 H, br t, J 7.0 Hz, $C\underline{H}_3CH_2-$); m/z 630 [M^+], 467 [M-(-$OCH_2CH(Cl)(CH_2)_5CH_3$), and +(-H)], 271 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_5CH_3$)], 213, 196, 145 [M-($C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_5CH_3$)].

(S)-2-Chlorodecyl 4'-(4-hepyloxybenzoyloxy)-4-biphenylcarboxylate **179**

Quantity of acid (**55**) used in reaction (0.24 g, 1.02 mmol), quantity of phenol (**102**) used in reaction (0.4 g, 1.03 mmol), yield (0.51 g, 82 %), (purity, M1 100 %, M2 98.2 %), (t.t. see results and discussion section). $[\alpha]_D^{21}$ +3.3° (7.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2800 (C-H stretch), 1735 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1585, 1495, 1400, 1275 and 1120 (C-O stretch), 1190, 1170, 1070, 1020, 1005, 850 (1,4-disub. ring), 765, 685; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', J_{AX} 10.0 Hz, $J_{AX'}$ 0.6 Hz, phenyl), 6.99 (2 H, AA'XX', J_{AX} 9.5 Hz, $J_{AX'}$ 0.4 Hz, phenyl), 4.49 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.22 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 4.05 (2 H, t, J 6.5 Hz, $-C\underline{H}_2O-$), 1.83 (4 H, m, $-C\underline{H}_2CH_2O-$ and $-C\underline{H}_2(CH_2)_6CH_3$), 1.59 (see 1.29, m, alkyl chain), 1.49 (see 1.29, m, alkyl chain), 1.29 (20 H, br s, alkyl chain), 0.91 (3 H, t, $-(CH_2)_7C\underline{H}_3$), 0.88 (3 H, br t, $C\underline{H}_3CH_2-$); m/z 606 [M^+], 415 [M-(-$OCH_2CH(Cl)(CH_2)_7CH_3$)], 219 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)$

$(CH_2)_7CH_3)]$, 196, 121 [M-(C_7H_{14}-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_7CH_3)$], 57.

(S)-2-Chlorodecyl 4'-(4-octyloxybenzoyloxy)-4-biphenylcarboxylate **180**

Quantity of acid (**56**) used in reaction (0.25 g, 1 mmol), quantity of phenol (**102**) used in reaction (0.4 g, 1.03 mmol), yield (0.43 g, 69 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{21}$ -5.9° (4 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2720 (C-H stretch), 1730 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1580, 1495, 1420, 1395, 1275 and 1120 (C-O stretch), 1190, 1170, 1075, 1005, 845 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.13 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.66 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.49 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.21 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 1.84 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2(CH_2)_6CH_3$), 1.56 (see 1.30, m, alkyl chain), 1.48 (see 1.30, m, alkyl chain), 1.30 (22 H, br s, alkyl chain), 0.86 (3 H, t, -$(CH_2)_7C\underline{H}_3$), 0.84 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 620 [M^+], 429 [M-(-$OCH_2CH(Cl)(CH_2)_7CH_3)$], 233 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_7CH_3)$], 196, 121 [M-($C_8H_{16}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_7CH_3)$], 93, 64, 55.

(S)-2-Chlorodecyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate **181**

Quantity of acid (**51**) used in reaction (0.2 g, 0.76 mmol), quantity of phenol (**102**) used in reaction (0.3 g, 0.77 mmol), yield (0.22 g, 46 %), (purity, M1 100 %, M2 99 %), (t.t. see results and discussion section). $[\alpha]_D^{21}$ -3.4° (10.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2660 (C-H stretch), 1725 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1580, 1490, 1420, 1395, 1275 and 1120 (C-O stretch), 1190, 1170, 1075, 1005, 850 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.13 (2 H, AA'XX', phenyl), 7.66 (2 H, AA'XX', phenyl), 7.64 (2 H, AA'XX',

phenyl), 7.30 (2 H, AA'XX', phenyl), 6.97 (2 H, AA'XX', phenyl), 4.49 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.21 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.04 (2 H, t, -$C\underline{H}_2O$-), 1.82 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2(CH_2)_6CH_3$), 1.55 (see 1.28, m, alkyl chain), 1.47 (see 1.28, m, alkyl chain), 1.28 (24 H, br s, alkyl chain), 0.89 (3 H, t, -$(CH_2)_7C\underline{H}_3$), 0.87 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 634 [M^+], 444 [M-(-$OCH_2CH(Cl)(CH_2)_7CH_3$), and +(-H)], 247 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_7CH_3$)], 196, 121 [M-$C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_7CH_3$)], 69, 55.

(S)-2-Chlorodecyl 4'-(4-decyloxybenzoyloxy)-4-biphenylcarboxylate **182**

Quantity of acid (**52**) used in reaction (0.33 g, 1.19 mmol), quantity of phenol (**102**) used in reaction (0.47 g, 1.21 mmol), yield (0.51 g, 66 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -6° (8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2640 (C-H stretch), 1720 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1580, 1495, 1420, 1395, 1270 and 1120 (C-O stretch), 1190, 1170, 1075, 1020, 1005, 880, 850 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.13 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.65 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', phenyl), 6.98 (2 H, AA'XX', phenyl), 4.51 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.22 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 1.82 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2(CH_2)_6CH_3$), 1.57 (see 1.28, m, alkyl chain), 1.46 (see 1.28, m, alkyl chain), 1.28 (26 H, br s, alkyl chain), 0.87 (3 H, t, -$(CH_2)_7C\underline{H}_3$), 0.85 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 648 [M^+], 457 [M-(-$OCH_2CH(Cl)(CH_2)_7CH_3$)], 261 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_7CH_3$)], 196, 121 [M-($C_{10}H_{20}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_7CH_3$)], 92, 55.

***(S)-2-Chlorodecyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenyl carboxylate* 183**

Quantity of acid (**70**) used in reaction (0.3 g, 1.04 mmol), quantity of phenol (**102**) used in reaction (0.4 g, 1.03 mmol), yield (0.62 g, 60 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{23}$ -1.4° (34.1 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3035-2740 (C-H stretch), 2200 (C≡C stretch), 1720 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1495, 1400, 1340-1200 and 1110 (C-O stretch), 1190, 1170, 1150, 1000, 935, 830 (1,4-disub. ring), 770, 730, 540; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', J_{AX} 7.2 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 7.66 (4 H, AA'XX', phenyl), 7.58 (2 H, AA'XX', J_{AX} 8.5 Hz, $J_{AX'}$ 1.0 Hz, phenyl), 7.30 (2 H, AA'XX', J_{AX} 8.5 Hz, $J_{AX'}$ 1.0 Hz, phenyl), 6.91 (2 H, AA'XX', J_{AX} 8.5 Hz, $J_{AX'}$ 1.0 Hz, phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.22 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.80 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2(CH_2)_6CH_3$), 1.60 (see 1.28, m, alkyl chain), 1.46 (see 1.28, m, alkyl chain), 1.28 (24 H, br s, alkyl chain), 0.89 (3 H, t, J 7.0 Hz, -$(CH_2)_7C\underline{H}_3$), 0.88 (3 H, br t, J 7.0 Hz, $C\underline{H}_3CH_2$-); m/z 658 [M+], 466 [M-(-O $CH_2CH(Cl)(CH_2)_7CH_3$)], 271 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_7CH_3$)], 213, 197, 145 [M-($C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_7CH_3$)].

***(S)-2-Chlorododecyl 4'-(4-heptyloxybenzoyloxy)-4-biphenylcarboxylate* 184**

Quantity of acid (**55**) used in reaction (0.28 g, 1.19 mmol), quantity of phenol (**103**) used in reaction (0.5 g, 1.20 mmol), yield (0.38 g, 50 %), (purity, M1 100 %, M2 99.1 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ -2.1° (11.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2740 (C-H stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1495, 1400, 1280 and 1120 (C-O stretch), 1190, 1170, 1070, 1010, 850 (1,4-disub. ring), 770, 685; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.31 (2

H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 6.99 (2 H, AA'XX', J_{AX} 9.3 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.22 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.83 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2(CH_2)_8CH_3$), 1.49 (see 1.27, m, alkyl chain), 1.32 (see 1.27, m, alkyl chain), 1.27 (24 H, br s, alkyl chain), 0.91 (3 H, t, -$(CH_2)_9C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 635 [M^+], 431 [M-(-$CH_2CH(Cl)(CH_2)_9CH_3$)-, and +(-H)], 415 [M-(-$OCH_2CH(Cl)(CH_2)_9CH_3$)], 219 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_9CH_3$)], 196, 121 [M-($C_7H_{14}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_9CH_3$)].

***(S)-2-Chlorododecyl 4'-(4-octyloxybenzoyloxy)-4-biphenylcarboxylate* 185**

Quantity of acid (**56**) used in reaction (0.3 g, 1.2 mmol), quantity of phenol (**103**) used in reaction (0.5 g, 1.2 mmol), yield (0.23 g, 29 %), (purity, M1 100 %, M2 99 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ -6.8° (7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2740 (C-H stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1495, 1395, 1280 and 1120 (C-O stretch), 1190, 1175, 1075, 1005, 845 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.19 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.69 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.34 (2 H, AA'XX', phenyl), 7.00 (2 H, AA'XX', phenyl), 4.51 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.24 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.06 (2 H, t, -$C\underline{H}_2O$-), 1.82 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2(CH_2)_8CH_3$), 1.59 (see 1.28, m, alkyl chain), 1.48 (see 1.28, m, alkyl chain), 1.28 (26 H, br s, alkyl chain), 0.86 (3 H, t, -$(CH_2)_9C\underline{H}_3$), 0.84 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 649 [M^+], 447 [M-(-$CH_2CH(Cl)(CH_2)_9CH_3$), and +(-H)], 431 [M-(-$OCH_2CH(Cl)(CH_2)_9CH_3$)], 219 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_9CH_3$)], 196, 121 [M-($C_8H_{16}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_9CH_3$)].

***(S)-2-Chlorododecyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate* 186**

Quantity of acid (**51**) used in reaction (0.32 g, 1.21 mmol), quantity of phenol (**103**) used in reaction (0.5 g, 1.2 mmol), yield (0.3 g, 38 %), (purity, M1 100 %, M2 99.3 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ -4.3° (7.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2760 (C-H stretch), 1730 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1455, 1395, 1270 and 1115 (C-O stretch), 1190, 1170, 1075, 1005, 850 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.11 (2 H, AA'XX', phenyl), 7.66 (2 H, AA'XX', phenyl), 7.64 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.50 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.20 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 4.05 (2 H, t, $-C\underline{H}_2O-$), 1.81 (4 H, m, $-C\underline{H}_2CH_2O-$ and $-C\underline{H}_2(CH_2)_8CH_3$), 1.60 (see 1.30, m, alkyl chain), 1.46 (see 1.30, m, alkyl chain), 1.30 (28 H, br s, alkyl chain), 0.87 (3 H, t, $-(CH_2)_9C\underline{H}_3$), 0.85 (3 H, br t, $C\underline{H}_3CH_2-$); m/z 663 [M^+], 461 [$M-(-CH_2CH(Cl)(CH_2)_9CH_3)$], 445 [$M-(-OCH_2CH(Cl)(CH_2)_9CH_3)$], 247 [$M-(-OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_9CH_3)$], 214, 196, 121 [$M-(C_9H_{18}-)$, and $-(-OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_9CH_3)$].

***(S)-2-Chlorododecyl 4'-(4-decyloxybenzoyloxy)-4-biphenylcarboxylate* 187**

Quantity of acid (**52**) used in reaction (0.33 g, 1.2 mmol), quantity of phenol (**103**) used in reaction (0.5 g, 1.2 mmol), yield (0.38 g, 47 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{26}$ -1.4° (17.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2760 (C-H stretch), 1730 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1460, 1395, 1270 and 1115 (C-O stretch), 1215, 1185, 1170, 1080, 1005, 845 (1,4-disub. ring), 770, 695; δ_H (270 MHz, $CDCl_3$) 8.18 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl), 7.69 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', phenyl), 6.98 (2 H, AA'XX', phenyl), 4.47 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$),

4.21 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 1.83 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2(CH_2)_8CH_3$), 1.60 (see 1.30, m, alkyl chain), 1.46 (see 1.30, m, alkyl chain), 1.30 (30 H, br s, alkyl chain), 0.90 (3 H, t, -$(CH_2)_9C\underline{H}_3$), 0.87 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 677 [M^+], 475 [M-(-$CH_2CH(Cl)(CH_2)_9CH_3$), and +(-H)], 459 [M-(-$OCH_2CH(Cl)(CH_2)_9CH_3$)], 261 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_9CH_3$)], 214, 196, 121 [M-($C_{10}H_{20}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_9CH_3$)].

(S)-2-Chlorododecyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenyl carboxylate **188**

Quantity of acid (**70**) used in reaction (0.35 g, 1.21 mmol), quantity of phenol (**103**) used in reaction (0.5 g, 1.2 mmol), yield (0.56 g, 68 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -3° (7.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2740 (C-H stretch), 2200 (C≡C stretch), 1715 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1495, 1400, 1345-1205 and 1115 (C-O stretch), 1190, 1170, 1150, 1005, 940, 830 (1,4-disub. ring), 770, 730, 690, 625, 600, 540; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 7.64 (4 H, AA'XX', phenyl), 7.58 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 6.91 (2 H, AA'XX', phenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.22 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, -$C\underline{H}_2O$-), 1.80 (4 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2(CH_2)_8CH_3$), 1.61 (see 1.27, m, alkyl chain), 1.46 (see 1.27, m, alkyl chain), 1.27 (28 H, br s, alkyl chain), 0.87 (3 H, t, -$(CH_2)_9C\underline{H}_3$), 0.86 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 686 [M^+], 466 [M-(-$OCH_2CH(Cl)(CH_2)_9CH_3$)], 271 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_9CH_3$)], 213, 197, 145 [M-(-$C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Cl)(CH_2)_9CH_3$)].

***(S)-2-Bromo-4-methylpentyl 4'-(4-heptyloxybenzoyloxy)-4-biphenyl carboxylate* 189**

Quantity of acid (**55**) used in reaction (0.16 g, 0.69 mmol), quantity of phenol (**104**) used in reaction (0.26 g, 0.69 mmol), yield (0.12 g, 29 %), (purity, M1 99.9 %, M2 99.5 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -2.1° (11.4 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2740 (C-H stretch), 1725 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1420, 1395, 1270 and 1115 (C-O stretch), 1190, 1175, 1075, 1005, 835 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.15 (2 H, AA'XX', phenyl), 7.69 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 0.9 Hz, phenyl), 6.99 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 0.9 Hz, phenyl), 4.57 (2 H, d, J 6.5 Hz, $-CO_2C\underline{H}_2CH(Br)-$), 4.33 (1 H, m, $-CO_2CH_2C\underline{H}(Br)-$), 4.05 (2 H, t, J 6.5 Hz, $-C\underline{H}_2O-$), 1.98 (1 H, m, $-C\underline{H}(CH_3)_2$), 1.84 (3 H, m, $-C\underline{H}_2CH_2O-$ and $-C\underline{H}(H)CH(CH_3)_2$), 1.69 (1 H, m, $-CH(\underline{H})CH(CH_3)_2$), 1.49 (see 1.34, m, alkyl chain), 1.34 (8 H, br s, alkyl chain), 1.00 (3 H, d, J 6.0 Hz, $-CH(C\underline{H}_3)CH_3$), 0.95 (3 H, d, J 6.0 Hz, $-CH(CH_3)C\underline{H}_3$), 0.91 (3 H, br t, J 6.5 Hz, $C\underline{H}_3CH_2-$); m/z 596, 594 (1:1) $[M^+]$, 515 [M-(-Br)], 415 [M-(-OCH_2 $CH(Br)CH_2CH(CH_3)_2$)], 219 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Br)CH_2$ $CH(CH_3)_2$)], 196, 121 [M-(C_7H_{14}-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Br)CH_2$ $CH(CH_3)_2$)], 93, 57.

***(S)-2-Bromo-4-methylpentyl 4'-(4-octyloxybenzoyloxy)-4-biphenyl carboxylate* 190**

Quantity of acid (**56**) used in reaction (0.33 g, 1.32 mmol), quantity of phenol (**104**) used in reaction (0.5 g, 1.33 mmol), yield (0.47 g, 58 %), (purity, M1 100 %, M2 98.4 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -7.2° (3.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2760 (C-H stretch), 1730 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1425, 1380, 1270 and 1110 (C-O stretch), 1170, 1075, 1010, 840 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.17 (2 H, AA'XX', phenyl), 8.14 (2 H, AA'XX', phenyl),

7.69 (2 H, AA'XX', phenyl), 7.67 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', phenyl), 4.57 (2 H, d, -$CO_2C\underline{H}_2CH(Br)$-), 4.34 (1 H, m, -$CO_2CH_2C\underline{H}(Br)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 1.94 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.81 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.70 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.49 (see 1.30, m, alkyl chain), 1.30 (10 H, br s, alkyl chain), 1.00 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.95 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 610, 608 (1:1) [M^+], 530 [M-(-Br), and +(-H)], 429 [M-(-$OCH_2CH(Br)CH_2CH(CH_3)_2$)], 233 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Br)CH_2CH(CH_3)_2$)], 196, 121 [M-($C_8H_{16}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Br)CH_2CH(CH_3)_2$)], 92, 65.

(S)-2-Bromo-4-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenyl carboxylate **191**

Quantity of acid (**51**) used in reaction (0.35 g, 1.32 mmol), quantity of phenol (**104**) used in reaction (0.5 g, 1.33 mmol), yield (0.31 g, 38 %), (purity, M1 99.9 %, M2 98.3 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -12.5° (6.4 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2760 (C-H stretch), 1745 and 1725 (C=O stretch), 1610 and 1515 (arom. C=C stretch), 1400, 1360-1235 and 1110 (C-O stretch), 1195, 1175, 1080, 1010, 850 (1,4-disub. ring), 770, 695; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.13 (2 H, AA'XX', phenyl), 7.59 (2 H, AA'XX', phenyl), 7.57 (2 H, AA'XX', phenyl), 7.32 (2 H, AA'XX', phenyl), 6.98 (2 H, AA'XX', phenyl), 4.56 (2 H, d, -$CO_2C\underline{H}_2CH(Br)$-), 4.32 (1 H, m, -$CO_2CH_2C\underline{H}(Br)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 1.95 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.83 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.70 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.48 (see 1.31, m, alkyl chain), 1.31 (12 H, br s, alkyl chain), 0.99 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.94 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 624, 622 (1:1) [M^+], 543 [M-(-Br)], 443 [M-(-$OCH_2CH(Br)CH_2CH(CH_3)_2$)], 247 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Br)CH_2CH(CH_3)_2$)], 196, 121 [M-($C_9H_{18}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Br)CH_2CH(CH_3)_2$)], 77, 55.

(S)-2-Bromo-4-methylpentyl 4'-(4-decyloxybenzoyloxy)-4-biphenyl carboxylate **192**

Quantity of acid (**52**) used in reaction (0.36 g, 1.32 mmol), quantity of phenol (**104**) used in reaction (0.5 g, 1.33 mmol), yield (0.45 g, 54 %), (purity, M1 100 %, M2 98.3 %), (t.t. see results and discussion section). $[\alpha]_D^{21}$ -4.4° (5.4 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2750 (C-H stretch), 1740 and 1720 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1395, 1270 and 1105 (C-O stretch), 1190, 1170, 1075, 1020, 1005, 845 (1,4-disub. ring), 770, 690; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.13 (2 H, AA'XX', phenyl), 7.68 (2 H, AA'XX', phenyl), 7.66 (2 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', phenyl), 6.98 (2 H, AA'XX', phenyl), 4.56 (2 H, d, -$CO_2C\underline{H}_2CH(Br)$-), 4.34 (1 H, m, -$CO_2CH_2C\underline{H}(Br)$-), 4.05 (2 H, t, -$C\underline{H}_2O$-), 1.95 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.84 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.70 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.48 (see 1.30, m, alkyl chain), 1.30 (14 H, br s, alkyl chain), 1.00 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 0.94 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 638, 636 (1:1) [M^+], 557 [M-(-Br)], 261 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(Br)CH_2CH(CH_3)_2$)], 196, 121 [M-($C_{10}H_{20}$-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(Br)CH_2CH(CH_3)_2$)], 93, 55.

(S)-2-Bromo-4-methylpentyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate **193**

Quantity of acid (**70**) used in reaction (0.37 g, 1.28 mmol), quantity of phenol (**104**) used in reaction (0.5 g, 1.33 mmol), yield (0.69 g, 84 %), (purity, M1 100 %, M2 99.6 %), (t.t. see results and discussion section). $[\alpha]_D^{21}$ -0.8° (30.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2660 (C-H stretch), 2200 (C≡C stretch), 1720 (C=O stretch), 1600 and 1510 (arom. C=C stretch), 1560, 1380, 1260 and 1100 (C-O stretch), 1200, 1160, 1010, 840 (1,4-disub. ring), 770, 730, 600, 540; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, phenyl), 7.66 (2 H, AA'XX', phenyl), 7.65 (2 H, AA'XX', phenyl), 7.58 (2 H, AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 0.3 Hz, phenyl), 7.30 (2 H, AA'XX',

J_{AX} 8.5 Hz, $J_{AX'}$ 1.0 Hz, phenyl), 6.90 (2 H, AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 0.3 Hz, phenyl), 4.57 (2 H, d, J 5.5 Hz, -$CO_2C\underline{H}_2CH(Br)$-), 4.33 (1 H, m, -$CO_2CH_2C\underline{H}(Br)$-), 3.99 (2 H, t, J 6.0 Hz, -$C\underline{H}_2O$-), 1.94 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.80 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.71 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.46 (see 1.29, m, alkyl chain), 1.29 (12 H, br s, alkyl chain), 1.00 (3 H, d, J 6.0 Hz, -$CH(C\underline{H}_3)CH_3$), 0.94 (3 H, d, J 6.0 Hz, -$CH(CH_3)C\underline{H}_3$), 0.89 (3 H, br t, J 6.0 Hz, $C\underline{H}_3CH_2$-); m/z 648, 646 (1:1) [M^+], 467 [M-(-$OCH_2CH(Br)CH_2CH(CH_3)_2$)], 271 [M-(-$OC_6H_4C_6H_4CO_2$ $CH_2CH(Br)CH_2$ $CH(CH_3)_2$)], 197, 145 [M-(C_9H_{18}-), and -(-$OC_6H_4C_6H_4CO_2CH_2$ $CH(Br)CH_2CH(CH_3)_2$)], 69, 57.

***(S)-2-Fluoro-4-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenyl carboxylate* 194**

Quantity of acid (**51**) used in reaction (0.29 g, 1.1 mmol), quantity of phenol (**105**) used in reaction (0.36 g, 1.1 mmol), yield (0.2 g, 36 %), (purity, M1 100 %, M2 98.5 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ -2.6° (9.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2760 (C-H stretch), 1730 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1490, 1400, 1350-1200 and 1110 (C-O stretch), 1190, 1170, 1070, 1005, 840 (1,4-disub. ring), 770, 690, 500; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 8.15 (2 H, AA'XX', phenyl), 7.67 (4 H, AA'XX', phenyl), 7.31 (2 H, AA'XX', phenyl), 6.98 (2 H, AA'XX', phenyl), 4.91 (1 H, m, $J_{gem(F)}$ 50.0 Hz, -$CO_2CH_2C\underline{H}(F)$-), 4.44 (2 H, m, -$CO_2C\underline{H}_2CH(F)$-), 4.05 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.83 (5 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}_2C\underline{H}(CH_3)_2$), 1.48 (see 1.29, m, alkyl chain), 1.29 (12 H, br s, alkyl chain), 1.00 (6 H, d, J 6.5 Hz, -$CH(C\underline{H}_3)_2$), 0.90 (3 H, br t, J 6.5 Hz, $C\underline{H}_3CH_2$-); m/z 562 [M^+], 443 [M-(-$OCH_2CH(F)CH_2CH(CH_3)_2$)], 247 [M-(-$OC_6H_4C_6H_4CO_2CH_2CH(F)CH_2$ $CH(CH_3)_2$)], 196, 121 [M-(C_9H_{18}-), and -(-$OC_6H_4C_6H_4CO_2CH_2CH(F)CH_2$ $CH(CH_3)_2$)], 77, 56.

***(S)-2-Fluoro-4-methylpentyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate* 195**

Quantity of acid (**70**) used in reaction (0.26 g, 0.9 mmol), quantity of phenol (**105**) used in reaction (0.27 g, 0.9 mmol), yield (0.35 g, 67 %), (purity, M1 99.5 %, M2 99 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ 0° (17.4 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2720 (C-H stretch), 2200 (C≡C stretch), 1715 (C=O stretch), 1605 and 1525 (arom. C=C stretch), 1495, 1400, 1345-1205 and 1110 (C-O stretch), 1190, 1170, 1150, 1005, 840 (1,4-disub. ring), 770, 730, 600, 540; δ_H (270 MHz, $CDCl_3$) 8.14 (2 H, AA'XX', J_{AX} 7.9 Hz, $J_{AX'}$ 0.6 Hz, phenyl), 7.66 (4 H, AA'XX', phenyl), 7.58 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, phenyl), 7.30 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, phenyl), 6.90 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, phenyl), 4.91 (1 H, m, $J_{gem(F)}$ 50.0 Hz, $-CO_2CH_2C\underline{H}(F)-$), 4.44 (2 H, m, $-CO_2C\underline{H_2}CH(F)-$), 4.00 (2 H, t, J 6.5 Hz, $-C\underline{H_2}O-$), 1.80 (4 H, m, $-C\underline{H_2}CH_2O-$ and $-C\underline{H_2}CH(CH_3)_2$), 1.46 (see 1.28, m, alkyl chain), 1.28 (16 H, br s, alkyl chain), 1.01 (3 H, d, J 6.5 Hz, $-CH(C\underline{H_3})CH_3$), 1.00 (3 H, d, J 6.5 Hz, $-CH(CH_3)C\underline{H_3}$), 0.89 (3 H, br t, J 7.0 Hz, $C\underline{H_3}CH_2-$); m/z 586, 467 [M-($-OCH_2CH(F)CH_2CH(CH_3)_2$)], 271 [M-($-OC_6H_4C_6H_4CO_2CH_2CH(F)CH_2CH(CH_3)_2$)], 197, 145 [M-($C_9H_{18}-$), and $-(-OC_6H_4C_6H_4CO_2CH_2CH(F)CH_2CH(CH_3)_2)$], 67, 58.

***(S)-1-Methylheptyl 4'-(4-tetradecyloxyphenylpropioloyloxy)-4-biphenyl carboxylate* 196**

Quantity of acid (**72**) used in reaction (2 g, 5.6 mmol), quantity of phenol (**106**) used in reaction (1.79 g, 5.5 mmol), yield (1.55 g, 42 %), (purity, M1 100 %, M2 99.9 %), (t.t. see results and discussion section). $[\alpha]_D^{23}$ +22.1° (30 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2740 (C-H stretch), 2240 (C≡C stretch), 1725 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1490, 1395, 1280 and 1110 (C-O stretch), 1190, 1150, 1005, 930, 850, 830 (1,4-disub. ring), 770, 735, 700, 600, 540, 490; δ_H (270 MHz, $CDCl_3$) 8.11 (2 H, AA'XX', J_{AX} 7.3 Hz, $J_{AX'}$ 0.2 Hz, phenyl), 7.64 (4 H, AA'XX', phenyl), 7.58 (2 H,

AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 0.3 Hz, phenyl), 7.29 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, phenyl), 6.90 (2 H, AA'XX', J_{AX} 8.7 Hz, $J_{AX'}$ 0.3 Hz, phenyl), 5.18 (1 H, m, -$CO_2C\underline{H}(CH_3)(CH_2)_6CH_3$), 3.99 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.80 (2 H, m, -$C\underline{H}_2CH_2$ O-), 1.66 (see 1.26, m, alkyl chain), 1.44 (see 1.26, m, alkyl chain), 1.36 (3 H, d, J 6.0 Hz, -$CO_2CH(C\underline{H}_3)(CH_2)_6CH_3$), 1.26 (32 H, br s, alkyl chain), 0.88 (6 H, t, J 6.5 Hz, -$CO_2CH(CH_3)(CH_2)_6C\underline{H}_3$ and $C\underline{H}_3CH_2$); m/z 666 [M^+], 578, 341 [M-(-$OC_6H_4C_6H_4$ $CO_2CH(CH_3)(CH_2)_5CH_3$)], 271, 197, 145 [M-($C_{14}H_{28}$-), and -(-$OC_6H_4C_6H_4CO_2$ $CH(CH_3)(CH_2)_5CH_3$)].

7.3.11 Reaction Scheme 11.

The material in this scheme was prepared using a similar method to the one used to prepare the materials in reaction scheme 10(ii).

***(S,S)-2-Chloro-3-methylpentyl 4'-(trans-4-n-heptylcyclohexyl carbonyloxy)-4-biphenylcarboxylate* 198**

Quantity of acid (**197**) used in reaction (0.21 g, 0.9 mmol), quantity of phenol (**95**) used in reaction (0.3 g, 0.9 mmol), yield (0.22 g, 45 %), (purity, M1 98.9 %, M2 98.7 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ +8.2° (8.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2720 (C-H stretch), 1710 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1490, 1380, 1270 and 1115 (C-O stretch), 1190, 1170, 1005, 875, 840 (1,4-disub. ring), 770, 695; δ_H (270 MHz, $CDCl_3$) 8.12 (2 H, AA'XX', J_{AX} 8.0 Hz, $J_{AX'}$ 0.6 Hz, phenyl), 7.65 (2 H, AA'XX', phenyl), 7.61 (2 H, AA'XX', phenyl), 7.17 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 0.5 Hz, phenyl), 4.55 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.21 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 2.51 (1 H, m, cyclohexane), 2.15 (2 H, m, cyclohexane), 1.92 (3 H, m, cyclohexane and -$C\underline{H}(CH_3)$-), 1.89 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.65 (1 H, m, -$CH(CH_3)C\underline{H}(H)CH_3$), 1.60 (2 H, m, cyclohexane), 1.54 (see 1.28, m, -$CH(CH_3)CH(\underline{H})CH_3$ and alkyl chain), 1.28 (9 H, br s, alkyl chain), 1.11 (3 H, d, J 6.5

Hz, -CH(C<u>H</u>$_3$)CH$_2$CH$_3$), 0.97 (3 H, t, J 6.5 Hz, -CH(CH$_3$)CH$_2$C<u>H</u>$_3$), 0.89 (3 H, br t, J 7.0 Hz, C<u>H</u>$_3$CH$_2$-); m/z 556 [M$^+$], 421 [M-(-OCH$_2$CH(Cl)CH(CH$_3$)CH$_2$CH$_3$)], 58.

7.3.12 Reaction Scheme 12.

The materials in this scheme were prepared using a similar method to the one used to prepare the materials in reaction scheme 10(ii).

(S)-2-Chloro-4-methylpentyl 6-(4-nonyloxybenzoyloxy)-2-naphthoate **199**

Quantity of acid (**51**) used in reaction (0.43 g, 1.63 mmol), quantity of phenol (**110**) used in reaction (0.5 g, 1.63 mmol), yield (0.3 g, 33 %), (purity, M1 99.7 %, M2 99.4 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -31° (7.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2700 (C-H stretch), 1720 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1390, 1255 and 1100 (C-O stretch), 1195, 1170, 1150, 1070, 1010, 850 (1,4-disub. ring), 795, 720, 485; δ_H (270 MHz, $CDCl_3$) 8.66 (1 H, br s, naphthalene), 8.19 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 1.0 Hz, phenyl), 8.10 (1 H, dd, J_o 8.5 Hz, J_m 1.5 Hz, naphthalene), 8.04 (1 H, d, J_o 9.0 Hz, naphthalene), 7.88 (1 H, d, J_o 8.5 Hz, naphthalene), 7.74 (1 H, d, J_m 2.0 Hz, naphthalene), 7.44 (1 H, dd, J_o 9.0 Hz, J_m 2.0 Hz, naphthalene), 7.00 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 1.0 Hz, phenyl), 4.53 (2 H, m, -CO$_2$C<u>H</u>$_2$CH(Cl)-), 4.32 (1 H, m, -CO$_2$CH$_2$C<u>H</u>(Cl)-), 4.06 (2 H, t, J 6.5 Hz, -C<u>H</u>$_2$O-), 1.99 (1 H, m, -C<u>H</u>(CH$_3$)$_2$), 1.82 (3 H, m, -C<u>H</u>$_2$CH$_2$O- and -C<u>H</u>(H)CH(CH$_3$)$_2$), 1.64 (1 H, m, -CH(<u>H</u>)CH(CH$_3$)$_2$), 1.49 (see 1.30, m, alkyl chain), 1.30 (12 H, br s, alkyl chain), 1.00 (3 H, d, J 6.5 Hz, -CH(C<u>H</u>$_3$)CH$_3$), 0.96 (3 H, d, J 6.5 Hz, -CH(CH$_3$)C<u>H</u>$_3$), 0.90 (3 H, br t, J 6.5 Hz, C<u>H</u>$_3$CH$_2$-); m/z 552 [M$^+$], 417 [M-(-OCH$_2$CH(Cl)CH$_2$ CH(CH$_3$)$_2$)], 247 [M-(-OC$_{10}$H$_6$CO$_2$CH$_2$CH(Cl)CH$_2$CH(CH$_3$)$_2$)], 219, 121 [M-(C$_9$H$_{18}$-), and -(-OC$_{10}$H$_6$CO$_2$CH$_2$CH(Cl)CH$_2$CH(CH$_3$)$_2$).

***(S)-2-Chloro-4-methylpentyl 6-(4-nonyloxyphenylpropioloyloxy) naphthoate* 200**

Quantity of acid (**70**) used in reaction (0.37 g, 1.3 mmol), quantity of phenol (**110**) used in reaction (0.4 g, 1.3 mmol), yield (0.4 g, 54 %), (purity, M1 99.9 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{23}$ -1.6° (15.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2700 (C-H stretch), 2200 (C≡C stretch), 1720 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1390, 1345-1205 and 1140 (C-O stretch), 1195, 1010, 965, 875, 835 (1,4-disub. ring), 775, 720, 605; δ_H (270 MHz, $CDCl_3$) 8.66 (1 H, br s, naphthalene), 8.09 (1 H, dd, J_o 8.5 Hz, J_m 1.5 Hz, naphthalene), 8.05 (1 H, d, J_o 9.0 Hz, naphthalene), 7.88 (1 H, d, J_o 8.5 Hz, naphthalene), 7.74 (1 H, d, J_m 2.0 Hz, naphthalene), 7.60 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 1.0 Hz, phenyl), 7.43 (1 H, dd, J_o 9.0 Hz, J_m 2.0 Hz, naphthalene), 6.92 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 1.0 Hz, phenyl), 4.54 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.31 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 4.01 (2 H, t, J 6.5 Hz, $-C\underline{H}_2O-$), 2.00 (1 H, m, $-C\underline{H}(CH_3)_2$), 1.82 (3 H, m, $-C\underline{H}_2CH_2O-$ and $-C\underline{H}(H)CH(CH_3)_2$), 1.64 (1 H, m, $-CH(\underline{H})CH(CH_3)_2$), 1.49 (see 1.30, m, alkyl chain), 1.30 (12 H, br s, alkyl chain), 0.99 (3 H, d, J 6.5 Hz, $-CH(C\underline{H}_3)CH_3$), 0.96 (3 H, d, J 6.5 Hz, $-CH(CH_3)C\underline{H}_3$), 0.90 (3 H, br t, J 6.5 Hz, $C\underline{H}_3CH_2-$); m/z 576 [M^+], 441 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 271 [M-(-$OC_{10}H_6CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 197, 145 [M-($C_9H_{18}$-), and -(-$OC_{10}H_6CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)].

***(+/-)-2-Chloro-4-methylpentyl 6-(4-nonyloxyphenylpropioloyloxy)-2-naphthoate* 201**

Quantity of acid (**70**) used in reaction (0.46 g, 1.6 mmol), quantity of phenol (**111**) used in reaction (0.48 g, 1.56 mmol), yield (0.5 g, 56 %), (purity, M1 99.8 %, M2 99.3 %), (t.t. see results and discussion section). $[\alpha]_D^{27}$ 0° (27.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2700 (C-H stretch), 2200 (C≡C stretch), 1715 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1390, 1345-1205 and 1150 (C-O stretch), 1190, 1150, 1010, 835

(1,4-disub. ring), 770, 730, 600; δ_H (270 MHz, $CDCl_3$) 8.65 (1 H, br s, naphthalene), 8.11 (1 H, dd, J_o 8.5 Hz, J_m 1.5 Hz, naphthalene), 8.03 (1 H, d, J_o 9.0 Hz, naphthalene), 7.89 (1 H, d, J_o 8.5 Hz, naphthalene), 7.73 (1 H, d, J_m 2.0 Hz, naphthalene), 7.59 (2 H, AA'XX', J_{AX} 9.3 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 7.41 (1 H, dd, J_o 9.0 Hz, J_m 2.0 Hz, naphthalene), 6.90 (2 H, AA'XX', J_{AX} 9.3 Hz, $J_{AX'}$ 0.8 Hz, phenyl), 4.53 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.31 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.00 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 2.00 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.80 (3 H, m, -$C\underline{H}_2CH_2O$- and -$C\underline{H}(H)CH(CH_3)_2$), 1.64 (1 H, m, -$CH(\underline{H})CH(CH_3)_2$), 1.46 (see 1.28, m, alkyl chain), 1.28 (12 H, br s, alkyl chain), 1.00 (3 H, d, J 6.5 Hz, -$CH(C\underline{H}_3)CH_3$), 0.96 (3 H, d, J 6.5 Hz, -$CH(CH_3)C\underline{H}_3$), 0.89 (3 H, br t, J 7.0 Hz, $C\underline{H}_3CH_2$-); m/z 576 [M^+], 441 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 271 [M-(-$OC_{10}H_6CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 197, 145 [M-($C_9H_{18}$-), and -(-$OC_{10}H_6CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)].

(S)-1-Methylheptyl 6-(4-nonyloxyphenylpropioloyloxy)-2-napthoate **202**

Quantity of acid (**72**) used in reaction (0.37 g, 1.28 mmol), quantity of phenol (**112**) used in reaction (0.4 g, 1.33 mmol), yield (0.4 g, 55 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{23}$ -1.6° (15.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2700 (C-H stretch), 2220 (C≡C stretch), 1725 (C=O stretch), 1630 and 1510 (arom. C=C stretch), 1385, 1270 and 1125 (C-O stretch), 1190, 1170, 1090, 1065, 950, 835 (1,4-disub. ring), 770, 745, 540, 480; δ_H (270 MHz, $CDCl_3$) 8.60 (1 H, br s, naphthalene), 8.10 (1 H, dd, J_o 8.5 Hz, J_m 1.5 Hz, naphthalene), 8.01 (1 H, d, J_o 9.0 Hz, naphthalene), 7.86 (1 H, d, J_o 8.5 Hz, naphthalene), 7.71 (1 H, d, J_m 2.0 Hz, naphthalene), 7.59 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, phenyl), 7.39 (1 H, dd, J_o 9.0 Hz, J_m 2.0 Hz, naphthalene), 6.90 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, phenyl), 5.22 (1 H, m, -$CO_2C\underline{H}(CH_3)CH_2$-), 4.00 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.80 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.66 (see 1.28, m, alkyl chain), 1.43 (see 1.28, m, alkyl chain), 1.36 (see 1.28, d, J 6.5 Hz, -$CO_2CH(C\underline{H}_3)CH_2$-), 1.28 (35 H, br s, alkyl chain), 0.89 (3 H, br t,

-$CO_2CH(CH_3)(CH_2)_5C\underline{H}_3$), 0.87 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 640 [M^+], 341 [M-(-O $C_6H_4C_6H_4CO_2CH(CH_3)(CH_2)_5CH_3$)], 197, 145 [M-($C_{14}H_{28}$-), and -(-$OC_6H_4C_6H_4CO_2$ $CH(CH_3)(CH_2)_5CH_3$)].

7.3.13 Reaction Scheme 13.

The materials in this scheme were prepared using a similar method to the one used to prepare the materials in reaction scheme 10(ii).

***(S)-2-Chloropropyl 4'-(6-nonyloxy-2-naphthoyloxy)-4-biphenylcarboxylate* 204**

Quantity of acid (**203**) used in reaction (0.16 g, 0.51 mmol), quantity of phenol (**93**) used in reaction (0.15 g, 0.52 mmol), yield (0.1 g, 33 %), (purity, M1 100 %, M2 99.4 %), (t.t. see results and discussion section). $[\alpha]_D^{22}$ +9.5° (16.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2760 (C-H stretch), 1735 and 1720 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1585, 1390, 1320-1140 and 1110 (C-O stretch), 1010, 895, 855 (1,4-disub. ring), 765, 700, 580; δ_H (270 MHz, $CDCl_3$) 8.67 (1 H, m, J_o 8.0 Hz, naphthalene), 8.58 (1 H, d, J_o 8.0 Hz, naphthalene), 8.50 (1 H, m, J_o 8.0 Hz, J_m 1.5 Hz, naphthalene), 8.16 (2 H, AA'XX', J_{AX} 7.7 Hz, $J_{AX'}$ 0.3 Hz, biphenyl), 7.72 (2 H, AA'XX', biphenyl), 7.70 (2 H, AA'XX', biphenyl), 7.59 (1 H, t, J 8.0 Hz, naphthalene), 7.52 (1 H, t, J 8.0 Hz, naphthalene), 7.40 (2 H, AA'XX', J_{AX} 7.1 Hz, $J_{AX'}$ 0.9 Hz, biphenyl), 6.90 (1 H, d, J_o 8.0 Hz, naphthalene), 4.46 (2 H, d, J 5.0 Hz, -$CO_2C\underline{H}_2CH(Cl)CH_3$), 4.35 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)CH_3$), 4.17 (2 H, t, J 6.0 Hz, -$C\underline{H}_2O$-), 1.96 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.63 (3 H, d, -$CO_2CH_2CH(Cl)C\underline{H}_3$), 1.58 (see 1.30, m, alkyl chain), 1.30 (12 H, br s, alkyl chain), 0.90 (3 H, br t, J 6.5 Hz, $C\underline{H}_3CH_2$-); m/z 586 [M^+], 552 [M-(-Cl), and + (-H)], 494 [M-(-CHCH(Cl)CH_3)], 460 [M-(C_9H_{18}-)], 383, 366, 297 [M-(-$OC_{10}H_6$ $CO_2CH_2CH(Cl)CH_3$)], 197, 171 [M-(C_9H_{17}-), and -(-$OC_{10}H_6CO_2CH_2CH(Cl)CH_3$)], 143 [M-$C_9H_{17}$-), and -(-$CO_2C_{10}H_6CO_2CH_2CH(Cl)CH_3$), 115, 69, 55.

***(S)-2-Chloro-3-methylbutyl 4'-(6-nonyloxy-2-naphthoyloxy)-4-biphenylcarboxylate* 205**

Quantity of acid (**203**) used in reaction (0.35 g, 1.11 mmol), quantity of phenol (**94**) used in reaction (0.3 g, 1.06 mmol), yield (0.2 g, 31 %), (purity, M1 100 %, M2 99.4 %), (t.t. see results and discussion section). $[\alpha]_D^{20}$ +1.2° (7.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2750 (C-H stretch), 1740 and 1720 (C=O stretch), 1605 and 1530 (arom. C=C stretch), 1585, 1420, 1390, 1335-1135 and 1100 (C-O stretch), 1005, 895, 855 (1,4-disub. ring), 795, 765, 700, 630, 580; δ_H (270 MHz, $CDCl_3$) 8.66 (1 H, m, naphthalene), 8.57 (1 H, d, naphthalene), 8.50 (1 H, m, naphthalene), 8.15 (2 H, AA'XX', biphenyl), 7.72 (2 H, AA'XX', biphenyl), 7.70 (2 H, AA'XX', biphenyl), 7.57 (1 H, t, naphthalene), 7.54 (1 H, t, naphthalene), 7.40 (2 H, AA'XX', biphenyl), 6.90 (1 H, d, naphthalene), 4.54 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.18 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)CH-$), 4.17 (2 H, t, $-C\underline{H}_2O-$), 2.20 (1 H, m, $-C\underline{H}(CH_3)_2$), 1.96 (2 H, m, $-C\underline{H}_2CH_2O-$), 1.60 (see 1.30, m, alkyl chain), 1.30 (12 H, br s, alkyl chain), 1.12 (3 H, d, $-CH(C\underline{H}_3)CH_3$), 1.08 (3 H, d, $-CH(CH_3)C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2-$); m/z 614 [M^+], 586, 493 [M-(-CHCH(Cl)$CH(CH_3)_2$)], 459, 383, 366, 297 [M-(-$OC_{10}H_6$ $CO_2CH_2CH(Cl)CH(CH_3)_2$)], 197, 171 [M-(C_9H_{17}-), and -(-$OC_{10}H_6CO_2CH_2$ $CH(Cl)CH(CH_3)_2$)], 143 [M-(C_9H_{17}-), and -(-$CO_2C_{10}H_6CO_2CH_2CH(Cl)CH(CH_3)_2$)], 115, 69, 55.

***(S,S)-2-Chloro-3-methylpentyl 4'-(6-nonyloxy-2-naphthoyloxy)-4-biphenylcarboxylate* 206**

Quantity of acid (**203**) used in reaction (0.35 g, 1.11 mmol), quantity of phenol (**95**) used in reaction (0.36 g, 1.08 mmol), yield (0.17 g, 25 %), (purity, M1 100 %, M2 99.2 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ +10.1° (18.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2760 (C-H stretch), 1725 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1430, 1390, 1270 and 1105 (C-O stretch), 1195, 1175, 1150, 1070, 1010, 900,

850 (1,4-disub. ring), 760, 480; δ_H (270 MHz, $CDCl_3$) 8.65 (1 H, m, naphthalene), 8.57 (1 H, d, naphthalene), 8.50 (1 H, m, naphthalene), 8.16 (2 H, AA'XX', biphenyl), 7.71 (2 H, AA'XX', biphenyl), 7.69 (2 H, AA'XX', biphenyl), 7.58 (1 H, t, naphthalene), 7.54 (1 H, t, naphthalene), 7.41 (2 H, AA'XX', biphenyl), 6.90 (1 H, d, naphthalene), 4.56 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.24 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)CH$-), 4.17 (2 H, t, -$C\underline{H}_2O$-), 1.96 (3 H, m, -$C\underline{H}_2CH_2O$- and -$CH(Cl)C\underline{H}(CH_3)CH_2CH_3$), 1.59 (see 1.30, m, alkyl chain and -$CH(Cl)CH(CH_3)C\underline{H}_2CH_3$), 1.30 (14 H, br s, alkyl chain), 1.10 (3 H, d, -$CH(Cl)CH(C\underline{H}_3)CH_2CH_3$), 0.96 (3 H, t, -$CH(Cl)CH(CH_3)CH_2C\underline{H}_3$ and +H), 0.88 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 628 [M^+], 494 [M-(-$CHCH(Cl)CH(CH_3)CH_2CH_3$), and +(-H)], 479, 366, 338, 297 [M-(-$OC_{10}H_6CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 197, 171 [M-($C_9H_{17}$-), and -(-$OC_{10}H_6CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 143 [M-($C_9H_{17}$-), and -(-$CO_2C_{10}H_6CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 113, 69, 55.

(S)-2-Chloro-4-methylpentyl 4'-(6-nonyloxy-2-naphthoyloxy)-4-biphenylcarboxylate **207**

Quantity of acid (**203**) used in reaction (0.28 g, 0.9 mmol), quantity of phenol (**97**) used in reaction (0.29 g, 0.9 mmol), yield (0.05 g, 11 %), (purity, M1 100 %, M2 99.1 %), (t.t. see results and discussion section). $[\alpha]_D^{23.5}$ -5.2° (21.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2750 (C-H stretch), 1740 and 1720 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1580, 1390, 1365, 1350-1135 and 1100 (C-O stretch), 1005, 890, 855 (1,4-disub. ring), 795, 765; δ_H (270 MHz, $CDCl_3$) 8.65 (1 H, m, naphthalene), 8.56 (1 H, d, naphthalene), 8.50 (1 H, m, naphthalene), 8.15 (2 H, AA'XX', biphenyl), 7.74 (2 H, AA'XX', biphenyl), 7.68 (2 H, AA'XX', biphenyl), 7.57 (1 H, t, naphthalene), 7.53 (1 H, t, naphthalene), 7.40 (2 H, AA'XX', biphenyl), 6.90 (1 H, d, naphthalene), 4.51 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.30 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.17 (2 H, t, -$C\underline{H}_2O$-), 1.96 (3 H, m, -$C\underline{H}_2CH_2O$- and -$CH(Cl)CH_2C\underline{H}(CH_3)_2$), 1.76 (1 H, m, -$CH(Cl)C\underline{H}(H)CH(CH_3)_2$), 1.62 (see 1.32, m, alkyl chain and -$CH(Cl)CH(\underline{H})CH(CH_3)_2$), 1.32

(13 H, br s, alkyl chain), 1.00 (3 H, d, -CH(Cl)CH_2CH($C\underline{H}_3$)CH_3), , 0.95 (3 H, t, -CH(Cl)CH_2CH(CH_3)$C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 628 [M^+], 585 [M-(-CH(CH_3)$_2$)], 493 [M-(-CHCH(Cl)CH_2CH(CH_3)$_2$)], 383, 366, 297 [M-(-$OC_{10}H_6CO_2CH_2$CH(Cl)CH_2CH(CH_3)$_2$)], 197, 171 [M-(C_9H_{17}-), and -(-$OC_{10}H_6CO_2CH_2$CH(Cl)CH_2CH(CH_3)$_2$)], 143 [M-(C_9H_{17}-), and -(-$CO_2C_{10}H_6CO_2CH_2$CH(Cl)CH_2CH(CH_3)$_2$)], 115, 69, 58.

7.3.14 Reaction Scheme 14.

The materials in this scheme were prepared using a similar method to the one used to prepare the materials in reaction scheme 10(ii).

(S)-2-Chloropropyl 4'-(4-nonyloxy-1-naphthoyloxy)-4-biphenylcarboxylate **209**

Quantity of acid (**208**) used in reaction (0.16 g, 0.51 mmol), quantity of phenol (**93**) used in reaction (0.15 g, 0.52 mmol), yield (0.12 g, 39 %), (purity, M1 100 %, M2 99.3 %), (t.t. see results and discussion section). $[\alpha]_D^{22}$ +9.5° (16.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2760 (C-H stretch), 1720 (C=O stretch), 1610 and 1515 (arom. C=C stretch), 1570, 1495, 1430, 1385, 1350-1145 and 1125 (C-O stretch), 1090, 995, 860 (1,4-disub. ring), 770, 700; δ_H (270 MHz, $CDCl_3$) 9.14 (1 H, m, J_o 8.0 Hz, naphthalene), 8.55 (1 H, d, J_o 8.0 Hz, naphthalene), 8.40 (1 H, m, J_o 8.0 Hz, J_m 1.5 Hz, J_p 0.5 Hz, naphthalene), 8.16 (2 H, AA'XX', J_{AX} 7.8 Hz, $J_{AX'}$ 0.3 Hz, biphenyl), 7.71 (2 H, AA'XX', biphenyl), 7.70 (2 H, AA'XX', biphenyl), 7.67 (1 H, m, naphthalene), 7.56 (1 H, m, naphthalene), 7.38 (2 H, AA'XX', J_{AX} 8.5 Hz, $J_{AX'}$ 0.6 Hz, biphenyl), 6.88 (1 H, d, J_o 8.0 Hz, naphthalene), 4.47 (2 H, d, J 5.5 Hz, -$CO_2C\underline{H}_2$CH(Cl)CH_3), 4.36 (1 H, m, -$CO_2CH_2C\underline{H}$(Cl)CH_3), 4.26 (2 H, t, J 6.0 Hz, -$C\underline{H}_2O$-), 1.99 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.63 (3 H, d, -CO_2CH_2CH(Cl)$C\underline{H}_3$), 1.60 (see 1.30, m, alkyl chain), 1.30 (12 H, br s, alkyl chain), 0.90 (3 H, br t, J 6.5 Hz, $C\underline{H}_3CH_2$-); m/z 586 [M^+], 493 [M-(-CH_2CH(Cl)

CH_3)], 297 [M-(-$OC_{10}H_6CO_2CH_2CH(Cl)CH_3$)], 197, 171 [M-(-$C_9H_{17}$-), and -(-$OC_{10}H_6CO_2CH_2CH(Cl)CH_3$), 143 [M-($C_9H_{17}$-), and -(-$CO_2C_{10}H_6CO_2CH_2CH(Cl)CH_3$), 115, 69, 57, 45.

(S)-2-Chloro-3-methylbutyl 4'-(4-nonyloxy-1-naphthoyloxy)-4-biphenyl carboxylate **210**

Quantity of acid (**208**) used in reaction (0.35 g, 1.11 mmol), quantity of phenol (**94**) used in reaction (0.3 g, 1.06 mmol), yield (0.35 g, 11 %), (purity, M1 100 %, M2 99 %), (t.t. see results and discussion section). $[\alpha]_D^{24}$ +10.2° (4.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2750 (C-H stretch), 1730 (C=O stretch), 1610 and 1520 (arom. C=C stretch), 1580, 1490, 1430, 1380, 1345-1145 and 1120 (C-O stretch), 1090, 995, 860 (1,4-disub. ring), 770, 700, 560; δ_H (270 MHz, $CDCl_3$) 9.14 (1 H, m, naphthalene), 8.55 (1 H, d, naphthalene), 8.40 (1 H, m, naphthalene), 8.15 (2 H, AA'XX', biphenyl), 7.71 (2 H, AA'XX', biphenyl), 7.70 (2 H, AA'XX', biphenyl), 7.66 (1 H, m, naphthalene), 7.55 (1 H, m, naphthalene), 7.38 (2 H, AA'XX', biphenyl), 6.88 (1 H, d, naphthalene), 4.54 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.25 (2 H, t, -$C\underline{H}_2O$-), 4.18 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)CH$-), 2.20 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.98 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.58 (see 1.32, m, alkyl chain), 1.32 (12 H, br s, alkyl chain), 1.12 (3 H, d, -$CH(C\underline{H}_3)CH_3$), 1.08 (3 H, d, -$CH(CH_3)C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 614 [M^+], 493 [M-(-CH CH(Cl)$CH(CH_3)_2$)], 297 [M-(-$OC_{10}H_6CO_2CH_2CH(Cl)CH(CH_3)_2$)], 214, 197, 171 [M-($C_9H_{17}$-), and -(-$OC_{10}H_6CO_2CH_2CH(Cl)CH(CH_3)_2$)], 143 [M-($C_9H_{17}$-), and -(-$CO_2$ $C_{10}H_6CO_2CH_2CH(Cl)CH(CH_3)_2$)], 115, 69, 55.

(S,S)-2-Chloro-3-methylpentyl 4'-(4-nonyloxy-1-naphthoyloxy)-4-biphenylcarboxylate **211**

Quantity of acid (**208**) used in reaction (0.35 g, 1.11 mmol), quantity of phenol (**95**) used in reaction (0.36 g, 1.08 mmol), yield (0.15 g, 22 %), (purity, M1 99.7 %, M2 99.6 %),

(t.t. see results and discussion section). $[\alpha]_D^{25}$ +9.7° (8.5 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2720 (C-H stretch), 1720 (C=O stretch), 1610 and 1515 (arom. C=C stretch), 1580, 1490, 1430, 1390, 1320-1140 and 1120 (C-O stretch), 1090, 1010, 855 (1,4-disub. ring), 770, 655; δ_H (270 MHz, $CDCl_3$) 9.14 (1 H, m, naphthalene), 8.55 (1 H, d, naphthalene), 8.40 (1 H, m, naphthalene), 8.14 (2 H, AA'XX', biphenyl), 7.70 (2 H, AA'XX', biphenyl), 7.68 (2 H, AA'XX', biphenyl), 7.64 (1 H, m, naphthalene), 7.55 (1 H, m, naphthalene), 7.35 (2 H, AA'XX', biphenyl), 6.87 (1 H, d, naphthalene), 4.56 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.23 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.25 (2 H, t, -$C\underline{H}_2O$-), 1.99 (3 H, m, -$C\underline{H}_2CH_2O$- and -$CH(Cl)C\underline{H}(CH_3)CH_2CH_3$), 1.61 (4 H, m, $CH(Cl)CH(CH_3)C\underline{H}_2CH_3$ and alkyl chain), 1.34 (10 H, br s, alkyl chain), 1.10 (3 H, d, -$CH(Cl)CH(C\underline{H}_3)CH_2CH_3$), 0.98 (3 H, t, -$CH(Cl)CH(CH_3)CH_2C\underline{H}_3$), 0.90 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 628 [M^+], 494 [M-(-$CHCH(Cl)CH(CH_3)CH_2CH_3$), and +(-H)], 367, 338, 297 [M-(-$OC_{10}H_6CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 171 [M-($C_9H_{17}$-), and -(-O $C_{10}H_6CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 143 [M-($C_9H_{17}$-), and -(-$CO_2C_{10}H_6CO_2$ $CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 113, 69, 55, 45.

(S)-2-Chloro-4-methylpentyl 4'-(4-nonyloxy-1-naphthoyloxy)-4-biphenyl carboxylate **212**

Quantity of acid (**208**) used in reaction (0.28 g, 0.9 mmol), quantity of phenol (**97**) used in reaction (0.29 g, 0.9 mmol), yield (0.2 g, 33 %), (purity, M1 100 %, M2 99.1 %), (t.t. see results and discussion section). $[\alpha]_D^{20}$ -4.8° (5 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3025-2740 (C-H stretch), 1720 (C=O stretch), 1610 and 1515 (arom. C=C stretch), 1580, 1490, 1430, 1385, 1330, 1300, 1280, 1240 and 1120 (C-O stretch), 1185, 1010, 980, 860 (1,4-disub. ring), 770, 625; δ_H (270 MHz, $CDCl_3$) 9.14 (1 H, m, naphthalene), 8.55 (1 H, d, naphthalene), 8.41 (1 H, m, naphthalene), 8.16 (2 H, AA'XX', biphenyl), 7.72 (2 H, AA'XX', biphenyl), 7.71 (2 H, AA'XX', biphenyl), 7.67 (1 H, m, naphthalene), 7.56 (1 H, m, naphthalene), 7.38 (2 H, AA'XX', biphenyl), 6.88 (1 H, d, naphthalene),

4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.29 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.25 (2 H, t, -$C\underline{H}_2O$-), 1.98 (3 H, m, -$C\underline{H}_2CH_2O$- and -$CH(Cl)CH_2C\underline{H}(CH_3)_2$), 1.79 (1 H, m, -$CH(Cl)C\underline{H}(H)CH(CH_3)_2$), 1.63 (see 1.34, m, alkyl chain and -$CH(Cl)CH(\underline{H})CH(CH_3)_2$), 1.34 (12 H, br s, alkyl chain), 1.02 (3 H, d, -$CH(Cl)CH_2CH(C\underline{H}_3)CH_3$), , 0.96 (3 H, t, -$CH(Cl)CH_2CH(CH_3)C\underline{H}_3$), 0.91 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 628 [M^+], 494 [M-(-$CHCH(Cl)CH_2CH(CH_3)_2$), and +(-H)], 368, 297 [M-(-$OC_{10}H_6CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 214, 197, 171 [M-($C_9H_{17}$-), and -(-O $C_{10}H_6CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 143 [M-($C_9H_{17}$-), and -(-$CO_2C_{10}H_6CO_2CH_2$ $CH(Cl)CH_2CH(CH_3)_2$)], 113, 69, 55.

7.3.15 Reaction Scheme 15.

The materials in this scheme were prepared using a similar method to the one used to prepare the materials in reaction scheme 10(ii).

(S)-2-Chloropropyl 4'-(6-nonyloxy-5-chloro-2-naphthoyloxy)-4-biphenyl carboxylate **214**

Quantity of acid (**213**) used in reaction (0.17 g, 0.49 mmol), quantity of phenol (**93**) used in reaction (0.15 g, 0.52 mmol), yield (0.22 g, 74 %), (purity, M1 99.9 %, M2 98.7 %), (t.t. see results and discussion section). $[\alpha]_D^{21}$ +13.1° (26.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2800 (C-H stretch), 1730 (C=O stretch), 1620 and 1525 (arom. C=C stretch), 1495, 1385, 1345, 1285 and 1115 (C-O stretch), 1185, 1090, 860 (1,4-disub. ring), 810, 770, 700; δ_H (270 MHz, $CDCl_3$) 8.76 (1 H, d, J_m 2.0 Hz, naphthalene), 8.34 (1 H, d, J_o 9.0 Hz, naphthalene), 8.27 (1 H, m, J_o 9.0 Hz, J_m 2.0 Hz, naphthalene), 8.17 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.94 (1 H, d, J_o 9.0 Hz, naphthalene), 7.72 (2 H, AA'XX', biphenyl), 7.70 (2 H, AA'XX', biphenyl), 7.39 (1 H, d, J_o 9.0 Hz, naphthalene), 7.38 (2 H, AA'XX', biphenyl), 4.47 (2 H, d, J 5.0 Hz, -$CO_2C\underline{H}_2CH(Cl)CH_3$), 4.36 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)CH_3$), 4.24 (2 H, t, J 6.0 Hz,

-C<u>H</u>$_2$O-), 1.93 (2 H, m, -C<u>H</u>$_2$CH$_2$O-), 1.63 (3 H, d, J 6.5 Hz, -CO$_2$CH$_2$CH(Cl)C<u>H</u>$_3$), 1.58 (see 1.29, m, alkyl chain), 1.29 (12 H, br s, alkyl chain), 0.89 (3 H, br t, J 6.5 Hz, C<u>H</u>$_3$CH$_2$-); m/z 620 [M$^+$], 527 [M-(-OCH$_2$CH(Cl)CH$_3$)], 365, 331 [M-(-OC$_{10}$H$_6$ CO$_2$CH$_2$CH(Cl)CH$_3$)], 297, 205 [M-(C$_9$H$_{18}$-), and -(-OC$_{10}$H$_6$CO$_2$CH$_2$CH(Cl)CH$_3$)], 197, 177, 171, 141, 113, 83, 69, 58, 45.

(S)-2-Chloro-3-methylbutyl 4'-(6-nonyloxy-5-chloro-2-naphthoyloxy)-4-biphenylcarboxylate **215**

Quantity of acid (**213**) used in reaction (0.3 g, 0.86 mmol), quantity of phenol (**94**) used in reaction (0.26 g, 0.78 mmol), yield (0.15 g, 30 %), (purity, M1 100 %, M2 99 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ +13.1° (10.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2750 (C-H stretch), 1720 (C=O stretch), 1625 and 1525 (arom. C=C stretch), 1485, 1355, 1340, 1285 and 1120 (C-O stretch), 1185, 1010, 855 (1,4-disub. ring), 815, 770, 525; δ_H (270 MHz, $CDCl_3$) 8.75 (1 H, d, naphthalene), 8.33 (1 H, d, naphthalene), 8.27 (1 H, m, naphthalene), 8.15 (2 H, AA'XX', biphenyl), 7.94 (1 H, d, naphthalene), 7.71 (2 H, AA'XX', biphenyl), 7.70 (2 H, AA'XX', biphenyl), 7.38 (1 H, d, naphthalene), 7.37 (2 H, AA'XX', biphenyl), 4.54 (2 H, m, -CO$_2$C<u>H</u>$_2$CH(Cl)-), 4.24 (2 H, t, -C<u>H</u>$_2$O-), 4.18 (1 H, m, -CO$_2$CH$_2$C<u>H</u>(Cl)CH-), 2.20 (1 H, m, -C<u>H</u>(CH$_3$)$_2$), 1.92 (2 H, m, -C<u>H</u>$_2$CH$_2$O-), 1.58 (see 1.29, m, alkyl chain), 1.29 (12 H, br s, alkyl chain), 1.12 (3 H, d, -CH(C<u>H</u>$_3$)CH$_3$), 1.09 (3 H, d, -CH(CH$_3$)C<u>H</u>$_3$), 0.89 (3 H, br t,C<u>H</u>$_3$CH$_2$-); m/z 648 [M$^+$], 527 [M-(-OCH$_2$CH(Cl)CH(CH$_3$)$_2$)], 493, 419, 365, 331 [M-(-OC$_{10}$H$_6$ CO$_2$CH$_2$CH(Cl)CH(CH$_3$)$_2$)], 297, 205 [M-(C$_9$H$_{18}$-), and -(-OC$_{10}$H$_6$CO$_2$CH$_2$CH(Cl) CH(CH$_3$)$_2$)], 197, 177, 171, 141, 113, 69, 55.

***(S)-2-Chloro-3-methylpentyl 4'-(6-nonyloxy-5-chloro-2-naphthoyloxy)-4-biphenylcarboxylate* 216**

Quantity of acid (**213**) used in reaction (0.3 g, 0.86 mmol), quantity of phenol (**95**) used in reaction (0.3 g, 0.9 mmol), yield (0.1 g, 17 %), (purity, M1 100 %, M2 100 %), (t.t. see results and discussion section). $[\alpha]_D^{24.5}$ +3.7° (2.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3040-2800 (C-H stretch), 1720 (C=O stretch), 1625 and 1525 (arom. C=C stretch), 1485, 1365, 1285 and 1120 (C-O stretch), 1185, 1090, 1010, 855 (1,4-disub. ring), 815, 775; δ_H (270 MHz, $CDCl_3$) 8.74 (1 H, d, naphthalene), 8.33 (1 H, d, naphthalene), 8.27 (1 H, m, naphthalene), 8.15 (2 H, AA'XX', biphenyl), 7.94 (1 H, d, naphthalene), 7.71 (2 H, AA'XX', biphenyl), 7.70 (2 H, AA'XX', biphenyl), 7.39 (1 H, d, naphthalene), 7.38 (2 H, AA'XX', biphenyl), 4.56 (2 H, m, $-CO_2C\underline{H}_2CH(Cl)-$), 4.25 (1 H, m, $-CO_2CH_2C\underline{H}(Cl)-$), 4.22 (2 H, t, $-C\underline{H}_2O-$), 1.92 (3 H, m, $-C\underline{H}_2CH_2O-$ and $-CH(Cl)C\underline{H}(CH_3)CH_2CH_3$), 1.58 (4 H, m, $CH(Cl)CH(CH_3)C\underline{H}_2CH_3$ and alkyl chain), 1.30 (10 H, br s, alkyl chain), 1.11 (3 H, d, $-CH(Cl)CH(C\underline{H}_3)CH_2CH_3$), 0.98 (3 H, t, $-CH(Cl)CH(CH_3)CH_2C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3CH_2-$); m/z 662 [M^+], 527 [M-(-$OCH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 493, 419, 366, 331 [M-(-$OC_{10}H_6CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 297, 214, 205 [M-($C_9H_{18}$-), and -(-$OC_{10}H_6CO_2CH_2CH(Cl)CH(CH_3)CH_2CH_3$)], 197, 171, 141, 113, 69, 55.

***(S)-2-Chloro-4-methylpentyl 4'-(6-nonyloxy-5-chloro-2-naphthoyloxy)-4-biphenylcarboxylate* 217**

Quantity of acid (**213**) used in reaction (0.28 g, 0.8 mmol), quantity of phenol (**97**) used in reaction (0.26 g, 0.8 mmol), yield (0.3 g, 63 %), (purity, M1 99.7 %, M2 99.2 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -2° (11.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3030-2760 (C-H stretch), 1730 and 1720 (C=O stretch), 1620 and 1525 (arom. C=C stretch), 1495, 1390, 1350, 1285 and 1120 (C-O stretch), 1245, 1185, 1090, 1055, 855 (1,4-disub. ring), 810, 770; δ_H (270 MHz, $CDCl_3$) 8.75 (1 H, d, naphthalene), 8.34 (1

H, d, naphthalene), 8.27 (1 H, m, naphthalene), 8.16 (2 H, AA'XX', biphenyl), 7.94 (1 H, d, naphthalene), 7.71 (2 H, AA'XX', biphenyl), 7.70 (2 H, AA'XX', biphenyl), 7.39 (1 H, d, naphthalene), 7.38 (2 H, AA'XX', biphenyl), 4.50 (2 H, m, -$CO_2C\underline{H}_2CH(Cl)$-), 4.28 (1 H, m, -$CO_2CH_2C\underline{H}(Cl)$-), 4.24 (2 H, t, -$C\underline{H}_2O$-), 1.92 (3 H, m, -$C\underline{H}_2CH_2O$- and -$CH(Cl)CH_2C\underline{H}(CH_3)_2$), 1.78 (1 H, m, -$CH(Cl)C\underline{H}(H)CH(CH_3)_2$), 1.58 (see 1.28, m, alkyl chain and -$CH(Cl)CH(\underline{H})CH(CH_3)_2$), 1.28 (12 H, br s, alkyl chain), 1.00 (3 H, d, -$CH(Cl)CH_2CH(C\underline{H}_3)CH_3$), 0.96 (3 H, t, -$CH(Cl)CH_2CH(CH_3)C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3CH_2$-); m/z 662 [M^+], 527 [M-(-$OCH_2CH(Cl)CH_2CH(CH_3)_2$)], 493, 419, 366, 331 [M-(-$OC_{10}H_6CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 297, 214, 205 [M-($C_9H_{18}$-), and -(-$OC_{10}H_6CO_2CH_2CH(Cl)CH_2CH(CH_3)_2$)], 197, 171, 141, 113, 69, 55.

7.3.16 Reaction Scheme 16.

Preparation of (S)-4'-Hydroxybiphenyl-4-yl Alkanoates

All 4'-hydroxybiphenyl-4-yl alkanoates were prepared using similar synthetic procedures. The example given below illustrates the general method used.

***(S)-4'-Hydroxybiphenyl-4-yl 2-chloropropanoate* 219**

To a mixture of 4,4'-dihydroxybiphenyl (**218**) (4 g, 21.5 mmol), 2-chloropropanoic acid (**10**) (1.16 g, 10.7 mmol) and dry tetrahydrofuran (200 ml) were added, with stirring. N,N-Dicyclohexylcarbodiimide (DCC) (2.21 g, 10.7 mmol) and N,N-dimethylaminopyridine (DMAP) (0.15 g, 1.2 mmol) was then added to the mixture, in one portion. The reaction was stirred at room temperature, under dry conditions for 24 h, the solvent then being removed by evaporation under reduced pressure. The residual solid was taken up, as far as possible, in chloroform and filtered through a short column of silica gel using chloroform as the eluant. The solvent was once again removed, the product being purified by flash chromatography over silica gel using dichloromethane as the eluant, to yield a white powder (**219**), (1.93 g, 65 %), (m.p. 154°). $[\alpha]_D^{23}$ -36.7° (3.9 mg cm^{-3} in

$CHCl_3$); $\nu_{max.}$ (KCl disc) 3660-3060 (O-H stretch), 3060-2840 (C-H stretch), 1780, 1760 (C=O stretch), 1610 and 1500 (arom. C=C stretch), 1600, 1380, 1340, 1310, 1230 and 1095 (C-OH stretch or O-H deformation), 1190, 1170, 1070, 1010, 1005, 900, 840 (1,4-disub. ring), 810, 750, 660, 510; δ_H (270 MHz, $CDCl_3$) 7.55 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 0.9 Hz, biphenyl), 7.45 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 0.9 Hz, biphenyl), 7.17 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 0.9 Hz, biphenyl), 6.90 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 0.9 Hz, biphenyl), 4.77 (1 H, s, HO-), 4.65 (1 H, q, J 7.0 Hz, $-O_2CCH(Cl)CH_3$), 1.85 (3 H, d, J 7.0 Hz, $-O_2CCH(Cl)CH_3$); m/z 278, 276 (1:3) [M^+], 214 [M-(-CH(Cl)CH_3), and +(-H)], 186 [M-(-OCCH(Cl)CH_3), and +(-H)], 169 [M-(-O_2CCH(Cl)CH_3), and +(-H)], 157, 128, 77, 63, 58, 51.

(S)-4'-Hydroxybiphenyl-4-yl 2-chloro-3-methylbutanoate **220**

Quantity of biphenyl (**218**) used in reaction (5 g, 26.9 mmol), quantity of acid (**11**) used in reaction (1.85 g, 13.5 mmol), yield (2.19 g, 53 %), (m.p. 108.5°). $[\alpha]_D^{25}$ +21.4° (13.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3670-3110 (O-H stretch), 3110-2730 (C-H stretch), 1740, 1710 (C=O stretch), 1610 and 1495 (arom. C=C stretch), 1595, 1390 and 1320-1175 (C-OH stretch or O-H deformation), 1165, 1110 (C-O stretch), 1075, 865, 830 (1,4-disub. ring), 700, 640, 575, 510; δ_H (270 MHz, $CDCl_3$) 7.54 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 7.44 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 7.16 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 6.90 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 5.02 (1 H, s, -OH), 4.35 (1 H, d, J 6.5 Hz, $-O_2CCH(Cl)CH(CH_3)_2$), 2.49 (1 H, m, $-O_2CCH(Cl)CH(CH_3)_2$), 1.11 (3 H, d, J 6.5 Hz, $-O_2CCH(Cl)CH(CH_3)CH_3$), 0.96 (3 H, d, J 6.5 Hz, $-O_2CCH(Cl)CH(CH_3)CH_3$); m/z 304 [M^+], 261 [M-(-$CH(CH_3)_2$)], 186 [M-(-OCCH(Cl)$CH(CH_3)_2$)], 169 [M-(-O_2CCH(Cl)$CH(CH_3)_2$)], 157, 128, 83, 55.

***(S,S)-4'-Hydroxybiphenyl-4-yl 2-chloro-3-methylpentanoate* 221**

Quantity of biphenyl (**218**) used in reaction (4.95 g, 26.6 mmol), quantity of acid (**12**) used in reaction (2 g, 13.3 mmol), yield (1.4 g, 33 %), (m.p. 118.8°). $[\alpha]_D^{25}$ +3° (21.1 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3680-3100 (O-H stretch), 3100-2720 (C-H stretch), 1750, 1710 (C=O stretch), 1605 and 1505 (arom. C=C stretch), 1590, 1390 and 1320-1175 (C-OH stretch or O-H deformation), 1160, 1105 (C-O stretch), 1075, 865, 835 (1,4-disub. ring), 700, 640, 575, 520; δ_H (270 MHz, $CDCl_3$) 7.56 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.46 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.18 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 6.92 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 5.00 (1 H, s, -O<u>H</u>), 4.21 (1 H, d, J 6.5 Hz, $-O_2CC\underline{H}(Cl)CH(CH_3)CH_2CH_3$), 1.90 (1 H, m, $-O_2CCH(Cl)C\underline{H}(CH_3)CH_2CH_3$), 1.83 (1 H, m, $-O_2CCH(Cl)CH(CH_3)C(\underline{H})HCH_3$), 1.62 (1 H, m, $-O_2CCH(Cl)CH(CH_3)C(H)\underline{H}CH_3$), 1.05 (1 H, m, $-O_2CCH(Cl)CH(C\underline{H}_3)CH_2CH_3$), 0.96 (3 H, t, J 6.5 Hz, $-O_2CCH(Cl)CH(CH_3)CH_2C\underline{H}_3$); m/z 318 [$M^+$], 186 [M-(-OCCH(Cl)CH($CH_3$)$CH_2$ CH_3), and +(-H)], 169 [M-(-O_2CCH(Cl)CH(CH_3)CH_2CH_3)], 157, 128, 83, 69.

***(S)-4'-Hydroxybiphenyl-4-yl 2-chloro-4-methylpentanoate* 222**

Quantity of biphenyl (**218**) used in reaction (4.95 g, 26.6 mmol), quantity of acid (**13**) used in reaction (2 g, 13.3 mmol), yield (2.81 g, 66 %), (m.p. 131.8°). $[\alpha]_D^{25}$ -21.1° (21.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3510 (O-H stretch), 3020-2780 (C-H stretch), 1740 (C=O stretch), 1610 and 1500 (arom. C=C stretch), 1440, 1285 (C-OH stretch or O-H deformation), 1235, 1215, 1170, 1120 (C-O stretch), 930, 830 (1,4-disub. ring), 810, 660; δ_H (270 MHz, $CDCl_3$) 7.53 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 7.43 (2 H, AA'XX', J_{AX} 8.8 Hz, $J_{AX'}$ 0.7 Hz, biphenyl), 7.16 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 6.88 (2 H, AA'XX', J_{AX} 8.2 Hz, $J_{AX'}$ 0.8 Hz, biphenyl), 5.00 (1 H, s, -O<u>H</u>), 4.56 (1 H, t, J 7.0 Hz, $-O_2CC\underline{H}(Cl)CH_2CH(CH_3)_2$), 1.98 (3 H, m, $-O_2CCH(Cl)C\underline{H}_2C\underline{H}(CH_3)_2$), 1.04 (3 H, d, J 6.5 Hz, $-O_2CCH(Cl)CH_2CH(C\underline{H}_3)CH_3$),

1.01 (3 H, d, J 6.5 Hz, -$O_2CCH(Cl)CH_2$ $CH(CH_3)C\underline{H}_3$); m/z 318 [M^+], 303 [M-(-CH_3)], 186 [M-(-$OCCH(Cl)CH_2CH(CH_3)_2$), and +(-H)], 169 [M-(-$O_2CCH(Cl)CH_2CH(CH_3)_2$)], 157, 128, 115, 69, 55.

Preparation of (S)-4'-(4-Nonyloxybenzoyloxy)biphenyl-4-yl Alkanoates

All *(S)*-4'-(4-nonyloxybenzoyloxy)biphenyl-4-yl alkanoates (**223-230**) were prepared using the DCC/DMAP esterification process as described for *(S)*-2-chloropropyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (**117**), in reaction scheme 10 (ii).

***(S)-4'-(4-Nonyloxybenzoyloxy)biphenyl-4-yl 2-chloropropanoate* 223**

Quantity of acid (**51**) used in reaction (0.23 g, 0.9 mmol), quantity of phenol (**219**) used in reaction (0.24 g, 0.9 mmol), yield (0.2 g, 44 %), (purity, M1 100 %, M2 99.2 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -14.5° (41 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2740 (C-H stretch), 1750 and 1735 (C=O stretch), 1610 and 1520 (arom. C=C stretch), 1490, 1475, 1345-1225 and 1115 (C-O stretch), 1200, 1140, 1075, 1005, 975, 850 (1,4-disub. ring), 800, 760, 690, 515; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', J_{AX} 8.5 Hz, $J_{AX'}$ 0.6 Hz, phenyl), 7.61 (4 H, AA'XX', phenyl), 7.28 (2 H, AA'XX', phenyl), 7.21 (2 H, AA'XX', phenyl), 6.98 (2 H, AA'XX', J_{AX} 8.5 Hz, $J_{AX'}$ 0.6 Hz, phenyl), 4.66 (1 H, q, J 7 Hz, -$O_2CC\underline{H}(Cl)CH_3$), 4.06 (2 H, t, J 6.5 Hz, -$C\underline{H}_2O$-), 1.86 (3 H, d, J 7 Hz, -$O_2CCH(Cl)C\underline{H}_3$), 1.82 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.47 (see 1.30, m, alkyl chain), 1.30 (12 H, br s, alkyl chain), 0.90 (3 H, br t, $C\underline{H}_3CH_2$); m/z 523 [M^+], 508 [M-(-CH_3)], 396 [M-(C_9H_{19}-)], 380 [M-($C_9H_{19}O$-)], 247 [M-($C_9H_{19}OC_6H_4CO_2$-), and -(-CH_3), and +(-H)], 185, 121.

***(S)-4'-(4-Nonyloxybenzoyloxy)biphenyl-4-yl 2-chloro-3-methylbutanoate* 224**

Quantity of acid (**51**) used in reaction (0.39 g, 1.5 mmol), quantity of phenol (**220**) used in reaction (0.44 g, 1.5 mmol), yield (0.32 g, 40 %), (purity, M1 100 %, M2 99.5 %), (t.t. see results and discussion section). $[\alpha]_D^{23}$ -1.2° (19.4 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3010-2740 (C-H stretch), 1760 and 1730 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1495, 1470, 1340-1220 and 1115 (C-O stretch), 1200, 1150, 1075, 1005, 975, 850 (1,4-disub. ring), 800, 760, 690, 515; δ_H (270 MHz, $CDCl_3$) 8.16 (2 H, AA'XX', phenyl), 7.60 (4 H, AA'XX', phenyl), 7.28 (2 H, AA'XX', phenyl), 7.20 (2 H, AA'XX', phenyl), 6.98 (2 H, AA'XX', phenyl), 4.36 (1 H, d, $-O_2CC\underline{H}(Cl)CH(CH_3)_2$), 4.05 (2 H, t, $-C\underline{H}_2O-$), 2.49 (1 H, m, $-O_2CCH(Cl)C\underline{H}(CH_3)_2$), 1.83 (2 H, m, $-C\underline{H}_2CH_2O-$), 1.48 (see 1.29, m, alkyl chain), 1.29 (12 H, br s, alkyl chain), 1.18 (6 H, d, $-O_2CCH(Cl)CH(C\underline{H}_3)_2$), 0.89 (3 H, br t, $C\underline{H}_3CH_2$); m/z 551 [M^+], 550 [M-(-H)], 508 [M-(-$CH(CH_3)_2$)], 424 [M-(C_9H_{19}-)], 408 [M-($C_9H_{19}O$-)], 247 [M-($C_9H_{19}OC_6H_4CO_2$-), and -(-$CH(CH_3)_2$), and +(-H)], 185, 121.

***(S,S)-4'-(4-Nonyloxybenzoyloxy)biphenyl-4-yl 2-chloro-3-methyl pentanoate* 225**

Quantity of acid (**51**) used in reaction (0.45 g, 1.7 mmol), quantity of phenol (**221**) used in reaction (0.53 g, 1.7 mmol), yield (0.34 g, 35 %), (purity, M1 99.9 %, M2 99.8 %), (t.t. see results and discussion section). $[\alpha]_D^{23}$ -0.8° (15.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2760 (C-H stretch), 1760 and 1730 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1500, 1470, 1400, 1320, 1270 and 1120 (C-O stretch), 1205, 1170, 1140, 1075, 1010, 840 (1,4-disub. ring), 800, 760, 690, 515; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 7.59 (4 H, AA'XX', phenyl), 7.27 (2 H, AA'XX', phenyl), 7.19 (2 H, AA'XX', phenyl), 6.97 (2 H, AA'XX', phenyl), 4.40 (1 H, d, $-O_2CC\underline{H}(Cl)CH(CH_3)CH_2CH_3$), 4.04 (2 H, t, $-C\underline{H}_2O-$), 2.23 (1 H, m, $-O_2CCH(Cl)C\underline{H}(CH_3)$

CH_2CH_3), 1.82 (3 H, m, -$C\underline{H}_2CH_2O$- and -$O_2CCH(Cl)CH(CH_3)C\underline{H}(H)CH_3$), 1.45 (see 1.28, m, alkyl chain and -$O_2CCH(Cl)CH(CH_3)CH(\underline{H})CH_3$), 1.28 (13 H, br s, alkyl chain), 1.14 (3 H, d, -$O_2CCH(Cl)CH(C\underline{H}_3)CH_2CH_3$), 1.00 (3 H, t, -$O_2CCH(Cl)CH(CH_3)CH_2C\underline{H}_3$), 0.88 (3 H, br t, $C\underline{H}_3CH_2$); m/z 565 [M^+], 564 [M-(-H)], 508 [M-(-$CH(CH_3)CH_2CH_3$)], 422 [M-($C_9H_{19}O$-)], 247 [M-($C_9H_{19}OC_6H_4CO_2$-), and -(-$CH(CH_3)CH_2CH_3$), and +(-H)], 185, 121.

(S)-4'-(4-Nonyloxybenzoyloxy)biphenyl-4-yl 2-chloro-4-methyl pentanoate **226**

Quantity of acid (**51**) used in reaction (0.4 g, 1.5 mmol), quantity of phenol (**222**) used in reaction (0.49 g, 1.5 mmol), yield (0.4 g, 47 %), (purity, M1 100 %, M2 99.5 %), (t.t. see results and discussion section). $[\alpha]_D^{23}$ -13.3° (14.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (KCl disc) 3020-2780 (C-H stretch), 1775 and 1730 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1500, 1470, 1350-1220 and 1125 (C-O stretch), 1205, 1170, 1075, 1005, 840 (1,4-disub. ring), 760, 690, 515; δ_H (270 MHz, $CDCl_3$) 8.15 (2 H, AA'XX', phenyl), 7.60 (4 H, AA'XX', phenyl), 7.28 (2 H, AA'XX', phenyl), 7.21 (2 H, AA'XX', phenyl), 6.98 (2 H, AA'XX', phenyl), 4.56 (1 H, t, -$O_2CC\underline{H}(Cl)CH_2CH(CH_3)_2$), 4.05 (2 H, t, -$C\underline{H}_2O$-), 2.00 (3 H, m, -$O_2CCH(Cl)C\underline{H}_2C\underline{H}(CH_3)_2$), 1.83 (2 H, m, -$C\underline{H}_2CH_2O$-), 1.48 (see 1.29, m, alkyl chain), 1.29 (12 H, br s, alkyl chain), 1.05 (3 H, d, -$O_2CCH(Cl)CH_2CH(C\underline{H}_3)CH_3$), 1.01 (3 H, t, $O_2CCH(Cl)CH_2CH(CH_3)C\underline{H}_3$), 0.89 (3 H, br t, $C\underline{H}_3CH_2$); m/z 565 [M^+], 564 [M-(-H)], 549 [M-(-CH_3)], 247 [M-($C_9H_{19}OC_6H_4CO_2$-), and -(-$CH_2CH(CH_3)_2$), and +(-H)], 184, 121.

(S)-4'-(4-Nonyloxypropioloyloxy)biphenyl-4-yl 2-chloropropanoate **227**

Quantity of acid (**70**) used in reaction (0.2 g, 0.7 mmol), quantity of phenol (**219**) used in reaction (0.18 g, 0.7 mmol), yield (0.35 g, 86 %), (purity, M1 100 %, M2 99.6 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -10.6° (26.7 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin

film) 3020-2780 (C-H stretch), 2200 (C≡C stretch), 1770 and 1720 (C=O stretch), 1605 and 1510 (arom. C=C stretch), 1490, 1470, 1395, 1340-1225 and 1125 (C-O stretch), 1200, 1005, 850 (1,4-disub. ring), 605, 540, 510; δ_H (270 MHz, $CDCl_3$) 7.59 (6 H, AA'XX', phenyl), 7.30 (2 H, AA'XX', phenyl), 7.20 (2 H, AA'XX', phenyl), 6.89 (2 H, AA'XX', phenyl), 4.66 (1 H, q, J 7 Hz, $-O_2CC\underline{H}(Cl)CH_3$), 4.00 (2 H, t, J 6.5 Hz, $-C\underline{H}_2O-$), 1.81 (3 H, d, J 7 Hz, $-O_2CCH(Cl)C\underline{H}_3$), 1.82 (2 H, m, $-C\underline{H}_2CH_2O-$), 1.47 (see 1.30, m, alkyl chain), 1.30 (12 H, br s, alkyl chain), 0.90 (3 H, br t, $C\underline{H}_3CH_2$); m/z 546 [M^+], 531 [M-(-CH_3)], 483 [M-(-$CH(Cl)CH_3$)], 271 [M-(-$OC_6H_4C_6H_4O_2CCH(Cl)CH_3$)], 144, 116, 55.

***(S)-4'-(4-Nonyloxypropioloyloxy)biphenyl-4-yl 2-chloro-3-methyl butanoate* 228**

Quantity of acid (**70**) used in reaction (0.43 g, 1.5 mmol), quantity of phenol (**220**) used in reaction (0.47 g, 1.6 mmol), yield (0.32 g, 40 %), (purity, M1 99.8 %, M2 99.8 %), (t.t. see results and discussion section). $[\alpha]_D^{23}$ -7.4° (32.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 3030-2760 (C-H stretch), 2200 (C≡C stretch), 1775 and 1715 (C=O stretch), 1600 and 1510 (arom. C=C stretch), 1490, 1470, 1390, 1340-1230 and 1130 (C-O stretch), 1200, 1005, 830 (1,4-disub. ring), 605, 540, 510; δ_H (270 MHz, $CDCl_3$) 7.58 (6 H, AA'XX', phenyl), 7.29 (2 H, AA'XX', phenyl), 7.20 (2 H, AA'XX', phenyl), 6.90 (2 H, AA'XX', phenyl), 4.36 (1 H, d, $-O_2CC\underline{H}(Cl)CH(CH_3)_2$), 3.99 (2 H, t, $-C\underline{H}_2O-$), 2.49 (1 H, m, $-O_2CCH(Cl)C\underline{H}(CH_3)_2$), 1.80 (2 H, m, $-C\underline{H}_2CH_2O-$), 1.46 (see 1.29, m, alkyl chain), 1.29 (12 H, br s, alkyl chain), 1.18 (6 H, d, $-O_2CCH(Cl)CH(C\underline{H}_3)_2$), 0.89 (3 H, br t, $C\underline{H}_3CH_2$); m/z 574 [M^+], 559 [M-(-CH_3)], 483 [M-(-$CH(Cl)CH(CH_3)_2$)], 271 [M-(-$OC_6H_4C_6H_4O_2CCH(Cl)CH(CH_3)_2$)], 247, 185, 144 [271-($C_9H_{19}$-)], 128, 116, 55.

***(S,S)-4'-(4-Nonyloxypropioloyloxy)biphenyl-4-yl 2-chloro-3-methylpentanoate* 229**

Quantity of acid (**70**) used in reaction (0.43 g, 1.5 mmol), quantity of phenol (**221**) used in reaction (0.49 g, 1.5 mmol), yield (0.36 g, 40 %), (purity, M1 99.2 %, M2 99.5 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -3.8° (30.9 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 3040-2760 (C-H stretch), 2205 (C≡C stretch), 1770 and 1710 (C=O stretch), 1610 and 1520 (arom. C=C stretch), 1490, 1470, 1390, 1340-1230 and 1130 (C-O stretch), 1205, 1005, 830 (1,4-disub. ring), 605, 540, 520; δ_H (270 MHz, $CDCl_3$) 7.60 (6 H, AA'XX', phenyl), 7.30 (2 H, AA'XX', phenyl), 7.21 (2 H, AA'XX', phenyl), 6.90 (2 H, AA'XX', phenyl), 4.40 (1 H, d, $-O_2CC\underline{H}(Cl)CH(CH_3)CH_2CH_3$), 4.00 (2 H, t, $-C\underline{H}_2O-$), 2.23 (1 H, m, $-O_2CCH(Cl)C\underline{H}(CH_3)\ CH_2CH_3$), 1.81 (3 H, m, $-C\underline{H}_2CH_2O-$ and $-O_2CCH(Cl)CH(CH_3)C\underline{H}(H)CH_3$), 1.45 (see 1.28, m, alkyl chain and $-O_2CCH(Cl)CH(CH_3)CH(\underline{H})CH_3$), 1.28 (13 H, br s, alkyl chain), 1.14 (3 H, d, $-O_2CCH(Cl)CH(C\underline{H}_3)CH_2CH_3$), 1.00 (3 H, t, $-O_2CCH(Cl)CH(CH_3)CH_2C\underline{H}_3$), 0.88 (3 H, br t, $C\underline{H}_3CH_2$); m/z 588 [M^+], 483 [M-(-$CH(Cl)CH(CH_3)CH_2CH_3$)], 271 [M-(-$OC_6H_4C_6H_4O_2CCH(Cl)CH(CH_3)CH_2CH_3$)], 116, 55.

***(S)-4'-(4-Nonyloxypropioloyloxy)biphenyl-4-yl 2-chloro-4-methyl pentanoate* 230**

Quantity of acid (**70**) used in reaction (0.36 g, 1.3 mmol), quantity of phenol (**222**) used in reaction (0.48 g, 1.5 mmol), yield (0.33 g, 46.2%), (purity, M1 99.8 %, M2 99.8 %), (t.t. see results and discussion section). $[\alpha]_D^{25}$ -19.9° (23.8 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 3030-2740 (C-H stretch), 2200 (C≡C stretch), 1770 and 1705 (C=O stretch), 1610 and 1510 (arom. C=C stretch), 1485, 1475, 1395, 1360-1220 and 1130 (C-O stretch), 1205, 1005, 830 (1,4-disub. ring), 605, 560, 520; δ_H (270 MHz, $CDCl_3$) 7.58 (6 H, AA'XX', phenyl), 7.29 (2 H, AA'XX', phenyl), 7.22 (2 H, AA'XX', phenyl), 6.90 (2 H, AA'XX', phenyl), 4.56 (1 H, t, $-O_2CC\underline{H}(Cl)CH_2CH(CH_3)_2$), 4.02 (2 H, t,

-C$\underline{H}_2$O-), 2.00 (3 H, m, -O_2CCH(Cl)C$\underline{H}_2$C$\underline{H}$(CH_3)$_2$), 1.80 (2 H, m, -C$\underline{H}_2$$CH_2$O-), 1.48 (see 1.30, m, alkyl chain), 1.30 (12 H, br s, alkyl chain), 1.05 (3 H, d, -O_2CCH(Cl)CH_2CH(C$\underline{H}_3$)CH_3), 1.01 (3 H, t, O_2CCH(Cl)CH_2CH(CH_3)C$\underline{H}_3$), 0.89 (3 H, br t, C$\underline{H}_3$$CH_2$); m/z 588 [$M^+$], 483 [M-(-CH(Cl)$CH_2$CH($CH_3$)$_2$)], 271 [M-(-$OC_6H_4$ $C_6H_4O_2$CCH(Cl)CH_2CH(CH_3)$_2$)], 116, 55.

7.3.17.1 Reaction Scheme 17 (i).

Preparation of (S)-Amino Acid Methyl Esters

This scheme illustrates one of the methods used in an attempt to prepare the cyclic compounds (**235 and 236**), *via* the formation of the dipeptide methyl esters (**233** and **234**). In the first instance the reaction was attempted to produce cyclo[*(S)*-alanine, *(S)*-alanine] (**235**).

(S)-Alanine dipeptide methyl ester **233**

Ethyl chloroformate (3.9 g, 36.2 mmol) was added dropwise to a solution of *(S)*-alanine (**1**) (3.43 g, 38.5 mmol) in dry tetrahydrofuran (50 ml), which had been cooled to -5°. This mixture was stirred at -5° for a further 15 m, before *(S)*-alanine methyl ester hydrochloride (5 g, 35.8 mmol) in N,N-dimethylformamide (40 ml) and N-methyl morpholine (4.5 g, 51.9 mmol) were added. The reaction mixture was allowed to warm to room temperature and then stirred for 4 h. The reaction mixture was filtered, the solvent then being removed by evaporation under reduced pressure to leave a solid residue that was taken up in ethyl acetate (1 l). This solution was washed successively with 20 % citric acid solution (2 x 20 ml), 7 % sodium hydrogen carbonate solution (30 ml) and water (30 ml). After drying over anhydrous sodium sulphate, the solvent was removed by distillation under reduced pressure to yield a solid residue. No evidence was found to suggest the presence of the desired product within this residue, although purification was attempted by recrystallization from various mixtures of ethyl acetate/hexane.

NOTES:

1. The reaction scheme was not attempted for cyclo[*(S)*-valine, *(S)*-valine], compound **236**, and a new synthetic route was sought at this point.

7.3.17.2 Reaction Scheme 17 (ii).

Preparation of (S)-Amino Acid Methyl Esters

The examples given below illustrate methods that were tried in an attempt to discover the most productive route to compound **237**. Both amino acid methyl esters (**237** and **238**) were eventually desired to complete the synthesis outlined in reaction scheme 17(ii).

***(S)-Alanine methyl ester* 237 (Step 17(ii)A)**

(S)-Alanine methyl ester hydrochloride (**231**) (10 g, 71.6 mmol) was dissolved in a minimum amount of water, and 35 % aqueous ammonia solution (4 ml) was added with stirring. Stirring was continued for 15 m, the solution then being extracted with diethyl ether (3 x 100 ml). The ether layers were dried over anhydrous magnesium sulphate, the drying agent and solvent then being removed, by filtration and evaporation under reduced pressure respectively. On evaporation of solvent, no final product was isolated from the ethereal layer, nor could the product or starting material be recovered from the aqueous layer. This method was therefore abandoned.

***(S)-Alanine methyl ester* 237 (Step 17(ii)B)**

(S)-Alanine methyl ester hydrochloride (**231**) (5 g, 35.8 mmol) was suspended in diethyl ether (100 ml). The ether layer was washed with saturated sodium bicarbonate solution (20 ml), whereby, the solid suspension dissolved. The organic and aqueous layers were separated, the organic layer being dried over anhydrous sodium sulphate. After removal of drying agent, the solvent was removed by evaporation under reduced pressure to yield a colourless oil, with a strong odour (**233**), (0.1 g, 2 %). $[\alpha]_D$ (insufficient sample); $\nu_{max.}$

(insufficient sample); δ_H (270 MHz, $CDCl_3$) 4.18 (1 H, q, J 7.0 Hz, $CH_3C\underline{H}(NH_2)CO_2CH_3$), 3.73 (3 H, s, $CH_3CH(NH_2)CO_2C\underline{H}_3$), 1.59 (2 H, s, $CH_3CH(N\underline{H}_2)CO_2CH_3$), 1.34 (3 H, d, J 7.0 Hz, $C\underline{H}_3CH(NH_2)CO_2CH_3$); m/z (insufficient sample).

***(S)-Alanine methyl ester* 237 (Step 17(ii)C)**

A 2 % sodium methoxide (164 ml, 0.143 mol) solution was added to a solution of *(S)*-alanine methyl ester hydrochloride (**231**) (20 g, 0.143 mol) in dry methanol (100 ml). The two solutions were mixed well, before dry diethyl ether (372 ml) was added and the mixture cooled in an ice/salt bath for 30 m. The resulting precipitate of sodium chloride was filtered off, the solvent then being removed by evaporation under reduced pressure to yield a colourless oil with a strong odour (**233**), (1.2 g, 8 %). $[\alpha]_D^{25}$ +4.2° (32.5 mg cm^{-3} in $CHCl_3$); (lit.,[120] +4.4°); $\nu_{max.}$ (thin film) 3380 (N-H symmetrical stretch), 3000 (N-H unsymmetrical stretch), 2980 (C-H stretch), 1740 (C=O stretch), 1610 (N-H bend); δ_H (270 MHz, $CDCl_3$) 4.17 (1 H, q, J 7.0 Hz, $CH_3C\underline{H}(NH_2)CO_2CH_3$), 3.73 (3 H, s, $CH_3CH(NH_2)CO_2C\underline{H}_3$), 1.59 (2 H, s, $CH_3CH(N\underline{H}_2)CO_2CH_3$), 1.34 (3 H, d, J 7.0 Hz, $C\underline{H}_3CH(NH_2)CO_2CH_3$); m/z 103 [$M^+$], 84, 58, 55.

***(S)-Valine methyl ester* 238 (Step 17(ii)C)**

Quantity of hydrochloride (**232**) used in reaction (28 g, 167.6 mmol), yield (1.1 g, 5 %). $[\alpha]_D^{25}$ +36.4°(14.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 3400 (N-H symmetrical stretch), 3330 (N-H unsymmetrical stretch), 2960 (C-H stretch), 1735 (C=O stretch), 1610 (N-H bend); δ_H (270 MHz, $CDCl_3$) 3.72 (3 H, s, $(CH_3)_2CHCH(NH_2)CO_2C\underline{H}_3$), 3.30 (1 H, d, J 5.0 Hz, $(CH_3)_2CHC\underline{H}(NH_2)CO_2CH_3$), 2.02 (1 H, m, $(CH_3)_2C\underline{H}CH(NH_2)CO_2CH_3$), 1.43 (2 H, s, $(CH_3)_2CHCH(N\underline{H}_2)CO_2CH_3$), 0.97 (3 H, d, J 7.0 Hz, $(C\underline{H}_3)CH_3CHCH(NH_2)CO_2CH_3$), 0.91 (3 H, d, J 7.0 Hz, $(CH_3)C\underline{H}_3C\,H\,CH(NH_2)CO_2CH_3$); m/z 131 [$M^+$], 112, 88 [M-(-$CH(CH_3)_2$)], 72, 58, 55.

NOTES:

1. Step 17(ii)C was eventually choosen as the most productive synthetic pathway.

Preparation of (3S,6S)-3,6-Dialkyl-1,4-diazinan-2,5-diones

Both *(3S,6S)*-3,6-dialkyl-1,4-diazinan-2,5-diones (**235** and **236**) were prepared using a similar synthetic procedure. The example given below illustrates the method used.

(3S,6S)-3,6-Dimethyl-1,4-diazinan-2,5-dione **235**

(S)-Alanine methyl ester (**237**) (1.15 g, 11 mmol) was heated at 100-110° for 24 h, under dry nitrogen. The temperature was reduced to 0° and, the solid that had formed was washed with diethyl ether. The product was purified by successive recrystallizations from water, to yield off-white crystals (**235**), (0.96 g, 62 %); (m.p. 294.7°), (lit.[121] m.p. 291°). $[\alpha]_D$ (insufficient sample); $\nu_{max.}$ (thin film) 3200 (N-H stretch), 1690 (C=O stretch), 1460 and 1380 (C-H deformation); δ_H (270 MHz, $CDCl_3$) 8.10 (2 H, s, 2 x -N<u>H</u> (or -O<u>H</u>)), 3.90 (2 H, q, J 7.0 Hz, 2 x -C(O)C<u>H</u>(CH_3)NH-), 1.26 (6 H, d, J 7.0 Hz, 2 x -C(O)CH(C<u>H</u>$_3$)NH-); m/z 142 [M^+], 114, 99, 71, 58, 56.

(3S,6S)-3,6-Diisopropyl-1,4-diazinan-2,5-dione **236**

Quantity of methyl ester (**238**) used in reaction (1.24 g, 7 mmol), yield (0.77 g, 41 %); (m.p. insufficient sample). $[\alpha]_D$ (insufficient sample); $\nu_{max.}$ (thin film) 3200 (N-H stretch), 1660 (C=O stretch), 1450 and 1350 (C-H deformation); δ_H (270 MHz, $CDCl_3$) 7.77 (2 H, s, 2 x -N<u>H</u> (or -O<u>H</u>)), 3.74 (2 H, m, 2 x -C(O)C<u>H</u>CH(CH_3)$_2$NH-), 2.31 (2 H, m, 2 x -C(O)CHC<u>H</u>(CH_3)$_2$NH-), 1.04 (6 H, d, J 7.0 Hz, 2 x -C(O)CHCH(C<u>H</u>$_3$)CH_3 NH-), 0.92 (6 H, d, J 7.0 Hz, 2 x -C(O)CHCH(CH_3)C<u>H</u>$_3$NH-); m/z 156, 127, 113, 85, 72, 55.

Preparation of (3S,6S)-3,6-Dialkyl-2,5-dimethoxy-1,4-diazinans

Both *(3S,6S)*-3,6-dialkyl-2,5-dimethoxy-1,4-diazinans (**239** and **240**) were prepared using a similar synthetic procedure. The example given below illustrates the general method used.

***(3S,6S)-3,6-Dimethyl-2,5-dimethoxy-1,4-diazinan* 239**

A mixture of *(3S,6S)*-3,6-dimethyl-1,4-diazinan-2,5-dione (**235**) (0.96 g, 6.8 mmol), trimethyloxonium tetrafluoroborate (3.2 g, 20 mmol) and dry dichloromethane (150 ml) was vigorously stirred at room temperature for 40 h. The mixture was cooled in an ice/salt bath and a buffer solution consisting of NaH_2PO_4 (3.18 g, 26.5 mmol), Na_2HPO_4 (7.72 g, 54.4 mmol) and water (100 ml) was added. After stirring for 10 m the layers were separated, and the aqueous layer was extracted with dichloromethane (3x100 ml). The combined organic layers were dried over anhydrous magnesium sulphate, the drying agent and solvent then being removed to yield an off white solid (**239**), (0.98 g, 86 %); (m.p. insufficient sample). $[\alpha]_D^{25}$ +31.4° (7.5 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 2980 (C-H stretch), 1690 (C=N stretch), 1240 (C-O stretch); δ_H (270 MHz, $CDCl_3$) 4.08 (2 H, m, 2 x -C(OCH_3)C<u>H</u>(CH_3)N-), 3.71 (3 H, s, -C(OC<u>H</u>$_3$)CH(CH_3)N-), 3.68 (3 H, s, -C(OC<u>H</u>$_3$)CH(CH_3)N-), 1.38 (6 H, d, J 7.0 Hz, 2 x -C(OCH_3)CH(C<u>H</u>$_3$)N-); m/z 170 [M^+], 155, 141, 112, 97, 82, 69.

***(3S,6S)-3,6-di-isopropyl-2,5-dimethoxy-1,4-diazinan* 240**

Quantity of diamide used (**236**) used in reaction (0.76 g, 3.84 mmol), yield (0.55 g, 63 %); (m.p. insufficient sample). $[\alpha]_D^{25}$ +68° (4.6 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 2980 (C-H stretch), 1690 (C=N stretch), 1230 (C-O stretch); δ_H (270 MHz, $CDCl_3$) 3.89 (2 H, m, 2 x -C(OCH_3)C<u>H</u>CH(CH_3)$_2$N-), 3.67 (6 H, s, 2 x -C(OC<u>H</u>$_3$)CHCH(CH_3)$_2$N-), 2.29 (2 H, m, 2 x -C(OCH_3)CHC<u>H</u>(CH_3)$_2$N-), 1.09 (6 H, d, J 7.0 Hz, 2 x

-C(OCH_3)CHCH(C$\underline{H_3}$)CH_3N-), 0.71 (6 H, d, J 7.0 Hz, 2 x -C(OCH_3)CHCH(CH_3)C$\underline{H_3}$ N-); m/z 226 [M^+], 183, 169, 152, 140, 127, 96.

Preparation of (3R,6S)-3,6-Dialkyl-3-octyl-2,5-dimethoxy-1,4-diazinans

Both *(3R,6S)*-3,6-dialkyl-3-octyl-2,5-dimethoxy-1,4-diazinans were prepared using similar synthetic procedures. The example given below illustrates the general method used.

***(3R,6S)-3,6-Dimethyl-3-octyl-2,5-dimethoxy-1,4-diazinan* 241**

Butyllithium (1.55 M) (4.7 ml, 7.2 mmol) was added dropwise to a stirred, cooled solution of *(3S,6S)*-3,6-dimethyl-2,5-dimethoxy-1,4-diazinan (**239**) (0.98 g, 5.76 mmol), in dry tetrahydrofuran (40 ml), under an atmosphere of dry nitrogen. After stirring for 20 m, n-octyl bromide (1.11 g, 5.7 mmol) in dry tetrahydrofuran (40 ml) was added and the reaction mixture left to warm to room temperature overnight. The solvent was removed by evaporation under reduced pressure, and water (10 ml) was added to the residue. This residue was then extracted with diethyl ether (3 x 10 ml), and the ether layers were dried over magnesium sulphate. Following the removal of drying agent and solvent, the residue was purified by distillation. The fraction boiling between 84-86° at 0.2 mmHg was collected, to yield an oil (**241**), (1.03 g, 64 %); (lit.,[121] b.p. 75-77° at 10 mmHg). $[\alpha]_D$ (insufficient sample); $\nu_{max.}$ (thin film) 2920 (C-H stretch), 1690 (C=N stretch), 1240 (C-O stretch); δ_H (270 MHz, $CDCl_3$) 3.68 (3 H, s, -C(OCH_3)C(CH_2)$_7$$CH_3$(C$\underline{H_3}$)N-), 3.48 (1 H, q, J 7.0 Hz, -C(OCH_3)C$\underline{H}$(CH_3)N-), 3.40 (6 H, s, 2 x -C(OC$\underline{H_3}$)CH(CH_3)N-), 1.86 (2 H, m, -C(OCH_3)CC$\underline{H_2}$(CH_2)$_6$$CH_3$($CH_3$)N-), 1.37 (3 H, d, J 7.0 Hz, -C(OCH_3)CH(C$\underline{H_3}$)N-), 1.28 (12 H, m, -C(OCH_3)CCH$_2$(C$\underline{H_2}$)$_6$$CH_3$($CH_3$)N-), 1.21 (3 H, t, J 7.0 Hz, -C(OCH_3)CCH$_2$(CH_2)$_6$C$\underline{H_3}$(CH_3)N-); m/z 155, 135, 113, 98, 83, 69.

***(3R,6S)-3,6-Di-isopropyl-3-octyl-2,5-dimethoxy-1,4-diazinan* 242**

Quantity of diazinan used (**240**) used in reaction (0.63 g, 2.43 mmol), crude yield (0.46 g, 56 %), (m.p. oil at room temperature). $[\alpha]_D$ (insufficient sample); $\nu_{max.}$ (thin film) 2960 (C-H stretch), 1690 (C=N stretch), 1240 (C-O stretch); δ_H (270 MHz, $CDCl_3$) 3.66 (3 H, s, -C(OC$\underline{H}_3$)C$(CH_2)_7CH_3(CH(CH_3)_2)$N-), 3.64 (3 H, s, -C(OC$\underline{H}_3$)C$(CH_2)_7CH_3$ $(CH(CH_3)_2)$N-), 2.35 (1 H, m, -C(OCH_3)C$\underline{H}(CH(CH_3)_2)$N-), 2.10 (2 H, m, -C$\underline{H}(CH_3)_2$-), 1.62 (2 H, t, -C$(OCH_3)CC\underline{H}_2(CH_2)_6CH_3(CH(CH_3)_2)$N-), 1.22 (12 H, m, -C$(OCH_3)CCH_2(C\underline{H}_2)_6CH_3(CH(CH_3)_2)$N-), 1.16 (3 H, t, J 7.0 Hz, -C$(OCH_3)C(CH_2)_7$ $C\underline{H}_3(CH(CH_3)_2)$N-), 1.10 (3 H, d, J 7.0 Hz, -C$(OCH_3)C(CH_2)_7CH_3(CH(C\underline{H}_3)CH_3)$ N-), 0.96 (3 H, d, J 7.0 Hz, -C$(OCH_3)C(CH_2)_7CH_3(CH(CH_3)C\underline{H}_3)$N-), 0.68 (3 H, d, J 7.0 Hz, -C$(OCH_3)C(CH_2)_7CH_3(CH(C\underline{H}_3)CH_3)$N-), 0.28 (3 H, d, J 7.0 Hz, -C(OCH_3) $C(CH_2)_7CH_3(CH(CH_3)C\underline{H}_3)$N-); m/z 338 $[M^+]$, 295, 253, 225, 183.

Preparation of (2R)-Methyl (2-Amino-2-alkyldecanoates)

Both *(2R)*-methyl (2-amino-2-alkyldecanoates) were prepared using similar methods. The example given below illustrates the general method used.

***(2R)-Methyl (2-amino-2-methyldecanoate)* 243.**

A suspension of *(3R,6S)*-3,6-dimethyl-3-octyl-2,5-dimethoxy-1,4-diazine (**241**) (1.03 g, 3.7 mmol) in 0.25 N hydrochloric acid, was stirred at room temperature for 1 h. The mixture was concentrated by evaporation under reduced pressure, the residue being taken up in water (10 ml), covered with diethyl ether (30 ml) and finally treated with concentrated ammonia solution (3.5 ml). After separation of organic and aqueous layers, the aqueous phase was extracted with diethyl ether (3 x 10 ml), the combined ether layers then being dried over anhydrous magnesium sulphate. The drying agent and solvent were then removed to yield a residue that was purified by distillation. The fraction boiling at 95° at 0.6 mmHg was collected to give (**243**), (0.37 g, 47 %). $[\alpha]_D^{25}$ +12 (3.2 mg cm^{-3} in

$CHCl_3$); $\nu_{max.}$ (thin film) 2920 (C-H stretch), 1470, 1240 (C-O stretch); δ_H (270 MHz, $CDCl_3$) 3.41 (3 H, t, J 7.0 Hz, -$C(OCH_3)CC\underline{H}_2(CH_2)_6CH_3(CH_3)N$-), 1.28 (12 H, m, -$C(OCH_3)CCH_2(C\underline{H}_2)_6CH_3(CH_3)N$-), 0.89 (3 H, t, J 7.0 Hz, -$C(OCH_3)C(CH_2)_7C\underline{H}_3(CH_3)N$-); m/z 215 [$M^+$], 213, 196.

(2R)-methyl (2-amino-2-isopropyldecanoate) **244**

Quantity of diazine used (**242**) used in reaction (0.88 g, 2.6 mmol), crude yield (0.36 g, 92 %), (b.p. insufficient sample). $[\alpha]_D$ (insufficient sample); $\nu_{max.}$ (thin film) 2960 (C-H stretch), 1690 (C=O stretch), 1240 (C-O stretch); δ_H (270 MHz, $CDCl_3$) 3.66 (3 H, S, $C\underline{H}_3O_2$-), 2.35 (1 H, m, -$C\underline{H}(CH_3)_2$), 1.22 (12 H, m, -$C(OCH_3)CCH_2(C\underline{H}_2)_6CH_3(CH(CH_3)_3)N$-), 0.96 (3 H, t, J 7.0 Hz, -$C(OCH_3)C(CH_2)_7C\underline{H}_3(CH(CH_3)_3)N$-), 0.68 (3 H, d, J 7.0 Hz, -$C(OCH_3)C(CH_2)_7CH_3(CH(C\underline{H}_3)CH_3)N$-), 0.62 (3 H, d, J 7.0 Hz, -$C(OCH_3)C(CH_2)_7CH_3(CH(CH_3)C\underline{H}_3)N$-); m/z 385 [$M^+$], 295, 253, 225, 183.

Notes.

1. A full interpretation of the proton nmr spectra was not possible for these materials due to the presence of impurities.

Preparation of (2R)-Amino-2-alkyldecanoic acids

Both *(2R)*-amino-2-alkyldecanoic acids were prepared using a similar method. The example given below illustrates the general method used. Any changes are noted later.

(2R)-Amino-2-methyldecanoic acid **245**

A solution of *(2R)*-methyl (2-amino-2-methyldecanoate) (**243**) (0.37 g, 1.7 mmol) in 6 N hydrochloric acid (15 ml) was heated under reflux for 1 h. The mixture was concentrated, ethanol (5 ml) and propylene oxide (2 ml) were then added. The resulting solution was heated for 10 m, until boiling, and then left to cool to room temperature. On cooling a

slight precipitation of solid occurred. This precipitate was filtered off and washed successively with ethanol and diethyl ether. Unfortunately, after drying, however, the yield was too small even for spectroscopic data to be collected.

***(2R)-amino-2-isopropyldecanoic acid* 246**

Quantity of methyl ester used (**244**) used in reaction (0.3 g, 1.68 mmol), yield (0.22 g, 65 %), (m.p. insufficient sample). $[\alpha]_D^{25}$ -50° (3.2 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (insufficient sample); δ_H (270 MHz, $CDCl_3$) 2.28 (2 H, t, J 7.0 Hz, -$C(OCH_3)CC\underline{H}_2(CH_2)_6CH_3(CH(CH_3)_3)N$-), 1.24 (12 H, m, -$C(OCH_3)CCH_2(C\underline{H}_2)_6CH_3(CH(CH_3)_3)N$-), 0.93 (3 H, d, J 7.0 Hz, -$C(OCH_3)C(CH_2)_7CH_3(CH(C\underline{H}_3)CH_3)N$-), 0.91 (3 H, d, J 7.0 Hz, -$C(OCH_3)C(CH_2)_7CH_3(CH(CH_3)C\underline{H}_3)N$-), 0.86 (3 H, t, J 7.0 Hz, -$C(OCH_3)C(CH_2)_7C\underline{H}_3(CH(CH_3)_3)N$-); m/z 267, 239, 201 [$M^+$], 197, 169.

Notes.

1. A full interpretation of the proton nmr spectra was not possible for compound **246** due to the presence of impurities.

7.3.18 Reaction Scheme 18.

4-Cyano-4'-hydroxybiphenyl 247

A solution of boron tribromide (8.8 g, 35.2 mmol) in dry dichloromethane (50 ml) was added dropwise, with stirring, to a solution of 4-cyano-4'-methoxybiphenyl (3.68 g, 76 mmol) in dry dichloromethane (300 ml) that had been pre-cooled to -70°. The mixture was allowed to warm to room temperature overnight, whilst being kept under an atmosphere of dry nitrogen. The mixture was poured into water (200 ml), and the organic products extrated into diethyl ether (2 x 500 ml). The ethereal layers were dried over magnesium sulphate for 8 h, and then the diethyl ether was removed by evaporation under

reduced pressure, to yield a yellow powder (**247**), (3.02 g, 88 %), (m.p. 199°). $\nu_{max.}$ (thin film) 3650-3050 (O-H stretch), 2235 (aryl C-N stretch), 1610 and 1520 (arom. C=C stretch), 830 (1,4-disub. ring); δ_H (270 MHz, $CDCl_3$) 8.03 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.60 (2 H, AA'XX', J_{AX} 7.5 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.49 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 0.9 Hz, biphenyl), 6.91 (2 H, AA'XX', J_{AX} 8.6 Hz, $J_{AX'}$ 0.9 Hz, biphenyl); m/z 195 [M^+], 178 [M-(-OH)].

Preparation of Bis (α,w)-di-(4'-cyanobiphenyl-4-yl)alkandioates

All members of this series of compounds were prepared using a similar method. The example given below illustrates the general method used. Any changes are noted later.

***Bis (1,7)-di-(4'-cyanobiphenyl-4-yl)heptandioate* 255**

N,N-Dicyclohexylcarbodiimide (DCC) (1.16 g, 5.6 mmol) and N,N-dimethylaminopyridine (0.05 g, 0.57 mmol) were added in one portion to a well stirred mixture of 4-cyano-4'-hydroxybiphenyl (**247**) (1 g, 5.1 mmol), pimelic acid (**248**) (0.41 g, 2.6 mmol) and dry diethyl ether (100 ml). The resulting mixture was stirred under dry conditions, and at room temperature for 24 h. The solvent was then removed from the reaction mixture by evaporation under reduced pressure, the residue being purified, in the first instance, by flash chromatography over silica gel using chloroform as the eluant, and then recrystallization from acetonitrile to eventually give a white powder (**255**) (0.75 g, 56 %). The purity of this compound was tested by hplc, over both silica [method 1 (M1)] and octadecylsilane columns [method 2 (M2)], using acetonitrile as the eluant. The purity was found to be (M1 100 %, M2 100 %). (t.t. see results section and discussion section). $\nu_{max.}$ (thin film) 2230 (aryl C-N stretch), 1755 (C=O stretch), 1610 and 1525 (arom. C=C stretch), 1175 and 1135 (C-O stretch), 830 (1,4-disub. ring); δ_H (270 MHz, $CDCl_3$) 7.69 (8 H, AA'XX', biphenyl), 7.59 (4 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 5.4 Hz, biphenyl), 7.20 (4 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 5.4 Hz, biphenyl), 2.59 (4 H, t, J 6.5 Hz,

-$CO_2C\underline{H}_2(CH_2)_3C\underline{H}_2O_2C$-), 1.78 (4 H, m, -$CO_2CH_2C\underline{H}_2CH_2C\underline{H}_2CH_2O_2C$-), 1.36 (2 H, m, -$CO_2(CH_2)_2C\underline{H}_2(CH_2)_2O_2C$-); m/z 514 [$M^+$].

***Bis (1,8)-di-(4'-cyanobiphenyl-4-yl)octandioate* 256**

Quantity of acid (**249**) used in reaction (0.45 g, 2.6 mmol), quantity of phenol (**247**) used in reaction (1 g, 5.1 mmol), yield (0.7 g, 51 %), (purity, M1 99.9 %, M2 99.8 %), (t.t. see results section and discussion section). $\nu_{max.}$ (thin film) 2230 (aryl C-N stretch), 1760 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1175 and 1130 (C-O stretch), 830 (1,4-disub. ring); δ_H (270 MHz, $CDCl_3$) 7.69 (8 H, AA'XX', biphenyl), 7.60 (4 H, AA'XX', biphenyl), 7.20 (4 H, AA'XX', biphenyl), 2.59 (4 H, t, -$CO_2C\underline{H}_2(CH_2)_4C\underline{H}_2O_2C$-), 1.78 (4 H, m, -$CO_2CH_2C\underline{H}_2(CH_2)_2C\underline{H}_2CH_2O_2C$-), 1.35 (4 H, m, -$CO_2(CH_2)_2(C\underline{H}_2)_2(CH_2)_2O_2C$-); m/z 528 [$M^+$].

***Bis (1,9)-di-(4'-cyanobiphenyl-4-yl)nonandioate* 257**

Quantity of acid (**250**) used in reaction (0.49 g, 2.6 mmol), quantity of phenol (**247**) used in reaction (1 g, 5.1 mmol), yield (0.79 g, 56 %), (purity, M1 100 %, M2 100 %), (t.t. see results section and discussion section). $\nu_{max.}$ (thin film) 2225 (aryl C-N stretch), 1755 (C=O stretch), 1615 and 1525 (arom. C=C stretch), 1170 and 1130 (C-O stretch), 835 (1,4-disub. ring); δ_H (270 MHz, $CDCl_3$) 7.68 (8 H, AA'XX', biphenyl), 7.59 (4 H, AA'XX', biphenyl), 7.21 (4 H, AA'XX', biphenyl), 2.58 (4 H, t, -$CO_2C\underline{H}_2(CH_2)_5C\underline{H}_2O_2C$-), 1.76 (4 H, m, -$CO_2CH_2C\underline{H}_2(CH_2)_3C\underline{H}_2CH_2O_2C$-), 1.32 (6 H, br s, -$CO_2(CH_2)_2(C\underline{H}_2)_3(CH_2)_2O_2C$-); m/z 542 [$M^+$].

***Bis (1,10)-di-(4'-cyanobiphenyl-4-yl)decandioate* 258**

Quantity of acid (**251**) used in reaction (0.52 g, 2.6 mmol), quantity of phenol (**247**) used in reaction (1 g, 5.1 mmol), yield (0.83 g, 57 %), (purity, M1 99.2 %, M2 99.5 %), (t.t. see results section and discussion section). $\nu_{max.}$ (thin film) 2230 (aryl C-N stretch), 1755

(C=O stretch), 1615 and 1530 (arom. C=C stretch), 1175 and 1135 (C-O stretch), 830 (1,4-disub. ring); δ_H (270 MHz, $CDCl_3$) 7.69 (8 H, AA'XX', biphenyl), 7.59 (4 H, AA'XX', biphenyl), 7.20 (4 H, AA'XX', biphenyl), 2.58 (4 H, t, $-CO_2C\underline{H}_2(CH_2)_6C\underline{H}_2O_2C-$), 1.76 (4 H, m,$-CO_2CH_2C\underline{H}_2(CH_2)_4C\underline{H}_2CH_2O_2C-$), 1.33 (8 H, br s, $-CO_2(CH_2)_2(C\underline{H}_2)_4(CH_2)_2O_2C-$); m/z 556 [$M^+$].

***Bis (1,11)-di-(4'-cyanobiphenyl-4-yl)undecandioate* 259**

Quantity of acid (**252**) used in reaction (0.56 g, 2.6 mmol), quantity of phenol (**247**) used in reaction (1 g, 5.1 mmol), yield (0.55 g, 37 %), (purity, M1 99.5 %, M2 99.5 %), (t.t. see results section and discussion section). $\nu_{max.}$ (thin film) 2230 (aryl C-N stretch), 1760 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1170 and 1130 (C-O stretch), 830 (1,4-disub. ring); δ_H (270 MHz, $CDCl_3$) 7.68 (8 H, AA'XX', biphenyl), 7.60 (4 H, AA'XX', biphenyl), 7.19 (4 H, AA'XX', biphenyl), 2.56 (4 H, t, $-CO_2C\underline{H}_2(CH_2)_7C\underline{H}_2O_2C-$), 1.74 (4 H, m,$-CO_2CH_2C\underline{H}_2(CH_2)_5C\underline{H}_2CH_2O_2C-$), 1.31 (10 H, br s, $-CO_2(CH_2)_2(C\underline{H}_2)_5(CH_2)_2O_2C-$); m/z 570 [$M^+$].

***Bis (1,12)-di-(4'-cyanobiphenyl-4-yl)dodecandioate* 260**

Quantity of acid (**253**) used in reaction (0.6 g, 2.6 mmol), quantity of phenol (**247**) used in reaction (1 g, 5.1 mmol), yield (0.78 g, 51 %), (purity, M1 100 %, M2 100 %), (t.t. see results section and discussion section). $\nu_{max.}$ (thin film) 2230 (aryl C-N stretch), 1755 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1175 and 1135 (C-O stretch), 830 (1,4-disub. ring); δ_H (270 MHz, $CDCl_3$) 7.69 (8 H, AA'XX', biphenyl), 7.59 (4 H, AA'XX', biphenyl), 7.20 (4 H, AA'XX', biphenyl), 2.59 (4 H, t, $-CO_2C\underline{H}_2(CH_2)_8C\underline{H}_2O_2C-$), 1.78 (4 H, m,$-CO_2CH_2C\underline{H}_2(CH_2)_6C\underline{H}_2CH_2O_2C-$), 1.36 (12 H, br s, $-CO_2(CH_2)_2(C\underline{H}_2)_6(CH_2)_2O_2C-$); m/z 584 [$M^+$].

***(R)-Bis (1,6)-di-(4'-cyanobiphenyl-4-yl)3-methylhexandioatedioate* 261**

Quantity of acid (**254**) used in reaction (0.42 g, 2.6 mmol), quantity of phenol (**247**) used in reaction (1 g, 5.1 mmol), yield (0.45 g, 34 %), (purity, M1 99 %, M2 99.1 %), (t.t. see results section and discussion section). $[\alpha]_D^{23}$ -1.7° (17.3 mg cm^{-3} in $CHCl_3$); $\nu_{max.}$ (thin film) 2230 (aryl C-N stretch), 1755 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1205 and 1120 (C-O stretch), 830 (1,4-disub. ring); δ_H (270 MHz, $CDCl_3$) 7.70 (8 H, AA'XX', biphenyl), 7.60 (4 H, AA'XX', biphenyl), 7.22 (4 H, AA'XX', biphenyl), 3.20 (4 H, m, $-CO_2C\underline{H}_2CH(CH_3)CH_2C\underline{H}_2O_2C-$), 2.32 (6 H, m, $-CO_2CH_2C\underline{H}(C\underline{H}_3)C\underline{H}_2CH_2O_2C-$); m/z 514 $[M^+]$.

7.3.19 Reaction Scheme 19.

***(R,R)-2,4-Di-(4'-heptyloxy-4-biphenylcarbonyloxy)pentane* 264**

Triphenylphosphine (1 g, 3.8 mmol) was added in one portion, to a mixture of diethyl azodicarboxylate (DEAD) (0.67 g, 3.8 mmol), *(R,R)*-2,4-pentanediol (**263**) (0.2 g, 1.9 mmol), 4-heptyloxy-4-biphenylcarboxylic acid (**262**) (1.2 g, 3.8 mmol) and dry tetrahydrofuran (30 ml). The reaction mixture was stirred at room temperature, under an atmosphere of dry nitrogen for a period of 24 h. The solvent was removed from the resulting mixture by evaporation under reduced pressure, the residue was purified, in the first instance, by flash chromatography over silica gel using dichloromethane as the eluant, and then recrystallization from acetonitrile to eventually give a white powder (**264**) (0.05 g, 4 %). The purity of this compound was tested by hplc, over both silica [Method 1 (M1)] and octadecylsilane columns [Method 2 (M2)], using acetonitrile as eluant. The purity was found to be (M1 100 %, M2 100 %). (t.t. see results section and discussion section). $[\alpha]_D$ (insufficient sample); $\nu_{max.}$ (thin film) 1770 (C=O stretch), 1610 and 1530 (arom. C=C stretch), 1170 and 1120 (C-O stretch), 860 (1,4-disub. ring); δ_H (270 MHz, $CDCl_3$) 7.55 (4 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 7.50 (8 H, AA'XX',

biphenyl), 6.94 (4 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 5.37 (2 H, m, 2x-OC<u>H</u>(CH_3)-), 4.00 (4 H, t, J 6.5 Hz, 2x$CH_3(CH_2)_5C\underline{H}_2O$-), 2.13 (2 H, t, J 6.5 Hz, -OCH(CH_3)C<u>H</u>$_2$CH(CH_3)O-), 1.82 (4 H, m, 2x$CH_3(CH_2)_4C\underline{H}_2CH_2O$-), 1.40 (22 H, m, alkyl chain and -OCH(C<u>H</u>$_3$)CH_2CH(C<u>H</u>$_3$)O-), 0.90 (6 H, t, J 6.5 Hz, 2x$C\underline{H}_3(CH_2)_6O$-); m/z 692 [$M^+$].

7.3.20 Reaction Scheme 20.

4'-(11-Hydroxyundecyloxy)-4-cyanobiphenyl **266**

11-bromo-1-undecanol (**265**) (10.23 g, 40 mmol) was added to a well-stirred mixture of 4-cyano-4'-hydroxybiphenyl (**247**) (7 g, 40 mmol), potassium carbonate (21.35 g, 0.24 mol) and dry butanone (400 ml). The mixture was stirred under reflux for 12 h, whilst being protected from moisture. After cooling to room temperature, the potassium carbonate was filtered off and washed well with acetone and ethyl acetate, the filtrate then being dried over anhydrous sodium sulphate. After removal of drying agent and solvent the residue was purified by recrystallization from ethanol to eventually give a white powder (**266**) (6.1 g, 42 %). The purity of this compound was tested by hplc, over an octadecylsilane column [Method 2 (M2)], using acetonitrile as eluant. The purity was found to be (M2 100 %). $\nu_{max.}$ (thin film) 3300 (O-H stretch), 2220 (arom. C≡N stretch), 830 (1,4-disub. ring); δ_H (270 MHz, $CDCl_3$) 7.67 (4 H, AA'XX', biphenyl), 7.53 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 6.99 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, biphenyl), 4.00 (2 H, t, J 6.5 Hz, HOC<u>H</u>$_2(CH_2)_{10}$O-), 3.64 (2 H, t, J 6.5 Hz, HO$(CH_2)_{10}C\underline{H}_2$O-), 1.81 (2 H, m, $HOCH_2C\underline{H}_2(CH_2)_9$O-), 1.60-1.25 (16 H, m, alkyl chain); m/z 365 [M^+].

11-(4'-cyanobiphenyl-4-yl)oxyundecanyl 4-nonyloxyphenylpropiolate **267**

N,N-Dicyclohexylcarbodiimide (DCC) (0.31 g, 1.5 mmol) and N,N-dimethylaminopyridine (DMAP) (0.02 g, 0.17 mmol) were added in one lot to a well

stirred mixture of 4-n-nonyloxyphenylpropiolic acid (**70**) (0.43 g, 1.5 mmol), 4'-(11-hydroxyundecyloxy)-4-cyanobiphenyl (**266**) (0.55 g, 1.5 mmol) and dry diethyl ether (100 ml). The resulting mixture was stirred under dry conditions, and at room temperature for 24 h. The solvent was then removed from the reaction mixture by evaporation under reduced pressure, the residue being purified, in the first instance, by flash chromatography over silica gel with chloroform as eluant, and then recrystallization from acetonitrile to eventually give a white powder (**267**) (0.45 g, 48 %). The purity of this compound was tested by hplc., over both silica [Method 1 (M1)] and octadecylsilane columns [Method 2 (M2)], using acetonitrile as eluant. The purity was found to be (M1 100 %, M2 100 %). (t.t. see results section and discussion section). $\nu_{max.}$ (thin film) 2220 (arom. C≡N and C≡C stretch), 1700 (C=O stretch), 1610 (C=C stretch), 1250 (C-O stretch), 825 (1,4-disub. ring); δ_H (270 MHz, $CDCl_3$) 7.66 (4 H, AA'XX', phenyl), 7.52 (4 H, AA'XX', phenyl), 6.99 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, phenyl), 6.86 (2 H, AA'XX', J_{AX} 9.0 Hz, $J_{AX'}$ 0.5 Hz, phenyl), 4.22 (2 H, t, J 7.0 Hz, -$CO_2C\underline{H}_2(CH_2)_{10}O$-), 3.98 (4 H, m, $CH_3(CH_2)_7C\underline{H}_2O$-$CO_2(CH_2)_{10}C\underline{H}_2O$-), 1.77 (6 H, m, -$CO_2CH_2C\underline{H}_2(CH_2)_7C\underline{H}_2CH_2O$- and $CH_3(CH_2)_6C\underline{H}_2CH_2O$-), 1.33 (26 H, m, alkyl chain), 0.89 (3 H, t, J 7.0 Hz, $C\underline{H}_3(CH_2)_8O$-); m/z 619 [$M^+$].

7.4 Discussion of Experimental Procedures.

Reaction Scheme 1 (compounds 1 - 30)

Reaction scheme 1 illustrates the procedure used for the preparation of a number of 2-chloro-alcohols, from naturally occurring α-amino acids. The method[112] used, initially, involves a diazotization reaction to produce the 2-chloroalkanoic acid, which is then reduced to give the desired alcohol.

The first step (1A) in the reaction sequence involves the formation of a diazonium salt, which is achieved in the presence of a sodium nitrite/hydrochloric acid mixture. This salt is not isolated, and readily undergoes further reaction to produce an unstable α-lactone. The lactone itself then breaks down, with the substitution of a chlorine atom at the chiral centre (1B). The reaction was seen to occur with overall retention of configuration at the optically active centre, this latter point becoming immediately obvious when certain liquid-crystalline properties of the final target molecules were explored[122]. Retention of configuration at the chiral centre occurs, as this reaction has a "neighbouring-group" mechanism, which essentially consists of two S_N2 substitutions, each of which causes an inversion, thereby leading to overall retention of configuration[123]. In order for this type of mechanism to occur, a group must be present (usually in the β-position) that has an unshared pair of electrons. In this instance the oxygen atom, associated with the hydroxyl group of the acid function, has the necessary lone-pair. Attack occurs as the electrons interact with the 'backside' of the carbon atom undergoing substitution, thereby displacing nitrogen and causing an inversion of configuration at the chiral centre. The external nucleophile, in this case a chloride ion, is now restricted to attack from the 'frontside', causing a second inversion of configuration, which gives overall retention. The mechanism of this reaction is detailed in figure 41.

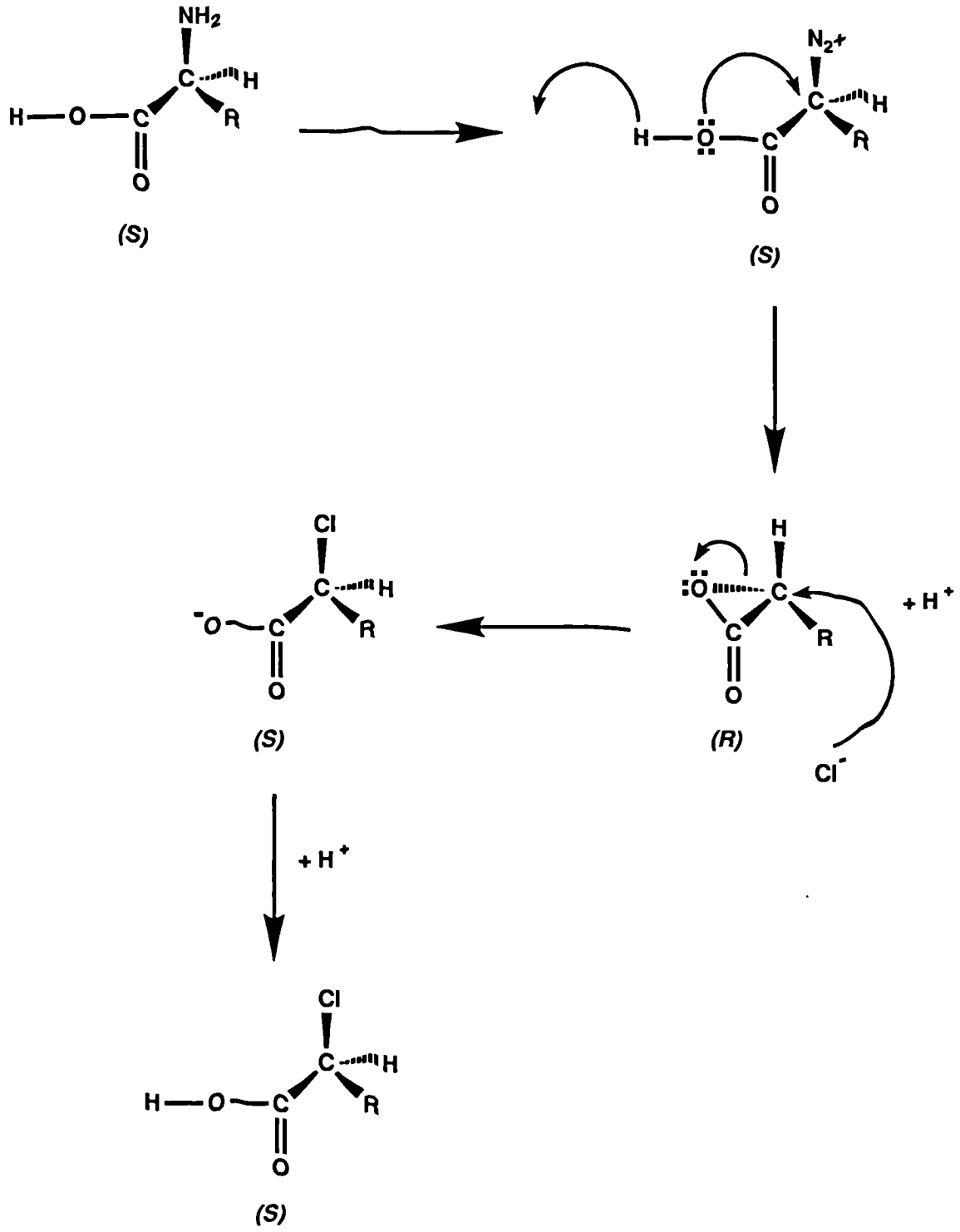


Figure 41. The "Neighbouring Group" Mechanism that Occurs in Synthetic Procedure 1B.

Yields of the desired 2-chloroalkanoic acids were generally good, ranging from 50 to 75 %, with one exception, compound **16**. The starting material in this instance was *(S)*-methionine (**7**), which contains a thio-ether linkage within its structure. In this case the desired product could not be isolated from the reaction mixture. Proton nmr spectroscopy, however, performed on the residue obtained from the process, indicated that a complex mixture of products had been obtained, one of which may have been the result of a dimerization process involving the two sulphur atoms. This could be facilitated only if the carbon-sulphur bonds in the molecule were broken. In view of the relatively harsh reaction conditions used this was thought to be quite reasonable. Another possibility is that the sulphur itself acted as the "neighbouring group", in the previously described mechanism, rather than the more electronegative oxygen atom, associated with the acid function. On hydrolysis this could lead to two products, as shown in figure 42, rather than just the one expected material[124].

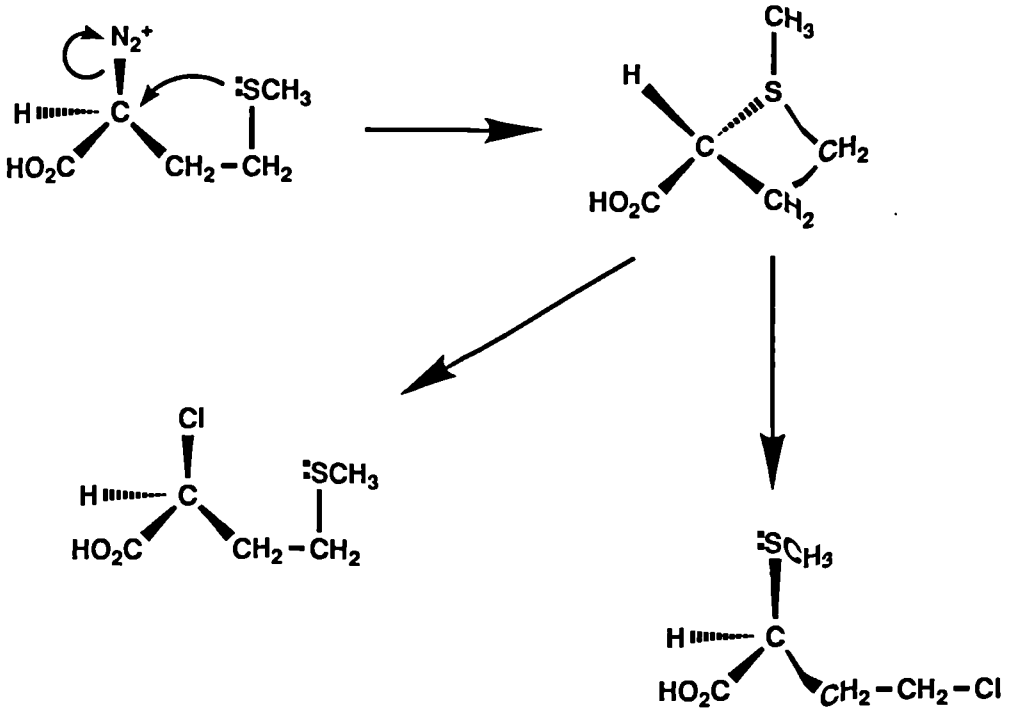


Figure 42. Sulphur as the "Neighbouring Group" in the Diazotisation of 7.

At this stage it was decided not to pursue the synthesis of compound **16** further.

The next step (1C) in the reaction sequence was to reduce the acids that had been prepared to the corresponding alcohols. This was achieved using lithium aluminium hydride, which, with careful monitoring of reaction time, avoids hydrogenolysis of the carbon-chlorine bond present in the molecule[125]. Yields for this stage of the reaction sequence were variable, but satisfactory, ranging from 33 to 77 %.

In addition to the alcohols that were synthetically prepared, three further materials were obtained from commercial sources (**28** to **30**)[114].

Reaction Scheme 2 (compounds 5 , 31 and 32)

The procedure described in reaction scheme 2 is analogous to the one used in reaction scheme 1, except that the desired product (**32**) is a β-bromo alcohol in this case, which is obtained *via* reduction of the corresponding α-bromo-acid (**31**). In order to substitute a bromine atom rather than a chlorine atom at the chiral centre, 5 N hydrobromic acid was used in this instance. The mechanistic details of the reaction, however, are thought to be identical to those described in reaction scheme 1.

A good yield of the desired bromo-acid was obtained (67 %), the optical purity of which, however, was called in to question at a later stage, when the liquid-crystalline properties of the final target molecules were examined. The materials (**189 -193**) that had a bromine atom attached to the chiral centre appeared to display a much reduced degree of chirality, when their mesogenic properties were compared with the analogous chlorine containing compounds (**156 - 159** and **164**)[126]. The values of the optical rotations, taken in solution (chloroform), for both the bromo-acid and at a later stage the bromo-alcohol, were also seen to be low compared to the analogous chlorine containing compounds. This fact also

suggests a reduction in the optical purity of the materials, although it by no means is an absolute confirmation of this. If indeed some degree of racemisation is taking place, then the reaction must proceed with more S_N2 character and a reduced degree of "neighbouring group" participation, compared to when a chlorine atom is substituted. Why this should occur is not immediately obvious, but is likely to be a result of two effects. Firstly, the increased size of the bromine atom may cause steric factors to influence the reaction profile, as might the relative strengths of the carbon-halogen bonds seen for both reaction schemes 1 and 2. Another possibility is that the intermediary α-lactone is not formed, and that the relevant species is a transient zwitterion (see figure 43), that allows a greater degree of 'frontside attack'.

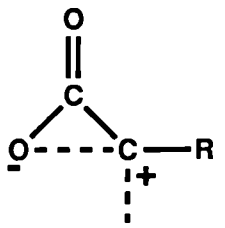


Figure 43. A Zwitterion and not an α-Lactone may be formed.

As with the chloro-acids in reaction scheme 1, the next stage of the synthetic procedure involved a reduction of the acid function using lithium aluminium hydride. Once again care was taken with reaction time in order to avoid hydrogenolysis of the carbon-halogen bond. A satisfactory yield (55 %) of compound **32** was obtained from this step of the reaction sequence.

Reaction Scheme 3 (compounds 5 and 33-41)

Reaction scheme 3 is divided into three sections (3(i)-3(iii)), each one detailing a route used in the attempted preparation of one of two optically active β-fluoroalcohols (**38** and **40**).

In reaction scheme 3(i) the fluorination step is carried out on an optically active alcohol (**37**) using morpholino-aminosulphurtrifluoride (Morpho-DAST)[127]. The first step (3(i)A), however, involved the preparation of the ethyl esters (**35** and **36**) of two readily available hydroxy-acids (**33** and **34**), the racemic variant (**33**) being used as a test reaction. The preparation of the ester, rather than carrying out a direct fluorination of the hydroxy-acid, was found to be a necessity, as the acid function was known to undergo conversion to the amide under the conditions stated[128]. The preparation of both the racemic and optically active hydroxy-esters was achieved by refluxing in an excess of ethanol, using fuming sulphuric acid as a catalyst. The yields for the conversion were found to be 47 % in both cases.

The next stage of the reaction sequence (3(i)C), 3(i)B was not attempted, was carried out on the optically active material only, using the mild fluorinating agent morpho-DAST, which would leave the ester function intact. The mechanism of this step was expected to give an inversion of absolute configuration at the chiral centre, as it was of the S_N2 type. Unfortunately, on completion of the synthetic procedure a light-brown residue remained, the components of which could not be separated, and so the scheme was abandoned at this point in favour of a different route (3(ii)).

In reaction scheme 3(ii) a direct fluorination of the optically active α-amino acid *(S)*-leucine (**5**) was attempted using pyridinium poly(hydrogen fluoride)[129]. The fluorination step, as with the chlorination and bromination steps (1B and 2B) in previous reaction schemes, was expected to proceed with retention of absolute configuration of the chiral centre, for reasons described in the discussion of reaction scheme 1. The final stage in the scheme (3(ii)B) being a reduction of the acid function using lithium aluminium hydride, to produce the desired alcohol (**40**). The reaction to produce the α-fluoro-acid proceeded to produce a colourless oil, which became increasingly turbid on standing.

Spectroscopic evidence indicated that even after purification by distillation the product contained a substantial amount of impurity. The proton nmr indicated that the desired material was present, but contained many additional methyl doublets, indicating a number of very similar impurities. At this point the reaction scheme was pursued no further and another route (3(iii)) was attempted in order to optimise yields and produce a higher purity material.

In the final reaction scheme the first step involved the preparation of a chiral epoxide (**41**), by alkoxy-dehalogenation of the previously prepared β-chloroalcohol (**23**)[113]. The reaction is base catalysed, the base, in this case potassium hydroxide, serves to remove a proton from the hydroxy function, enabling an internal S_N2 reaction to occur. This procedure leads to an inversion of configuration of the chiral centre which would be reversed in the following step (3(iii)B). Due to the extreme volatility of the epoxide the reaction was carried out in a closed system, as described in the experimental section. After purification a good yield of 75 % of the epoxide was obtained.

The next step involved the fluorination of the epoxide using pyridinium poly(hydrogen fluoride), the reaction yielding 21 % of material after two distillations.

The use of either pyridinium poly(hydrogen fluoride) or morpho-DAST as fluorinating agents in all of the three previous reaction schemes (3(i)-3(iii)) was called for as hydrogen fluoride itself is not always an effective fluorinating agent. The handling difficulties with hydrogen fluoride gas were also deemed unnecessarily hazardous.

Reaction Scheme 4 (compounds 42-45)

Reaction scheme 4 illustrates the procedure used to prepare protected 4'-hydroxy-4-biphenylcarboxylic acid (**45**). The starting material used in the synthetic route was 4-

cyano-4'-methoxybiphenyl (**42**), which in the first instance had to be converted to the hydroxy acid (**44**) itself. This stage of the reaction sequence could be accomplished by using either a one step or a two step process. The one step process (4C) was used to begin with and involved reaction of the starting material with a hydrobromic acid/acetic acid mixture. The reagents and conditions used were not only suitable to cleave the methyl ether and generate the desired phenol, but would also hydrolyse the nitrile in order to generate an acid function. In practice a very satisfactory yield of 91 % was obtained for this reaction. Some impurities, however, were detected which could not be removed even on multiple recrystallizations from glacial acetic acid. Assuming that the halo-dealkoxylation process had gone to completion to give the phenol, then it is possible that the impurity present may have been an amide that was generated by only partial hydrolysis of the nitrile.

It was decided at this stage to try and effect a cleaner reaction using the two step process (4A and 4B). The first step involved hydrolysis of the nitrile using a concentrated sulphuric acid/glacial acetic acid/water mixture, which gave a yield of 82 %. This was followed by the dealkoxylation step (4B) which used identical reagents and conditions to the one step route (4C). The yield for this later step was 92 %, and after recrystallization the product quality was found to be of a much higher standard. The two step process was therefore accepted as the more favourable synthetic route.

The final step in the reaction sequence (4D) involved the protection of the hydroxy function using methyl chloroformate in an alkaline, aqueous solution to produce a methyl carbonate[130]. The protecting group was necessary to prevent undesirable side reactions at a later stage in the synthesis of the final target molecules. The carbonate protecting group was selected as it was stable under the necessary conditions, but could easily be removed when desired, and under mild basic conditions. The yield for the protection step

was 89 %, purification being affected by recrystallization from glacial acetic acid. Care, however, was taken to wash the product with water after recrystallization in order to remove any acetic acid residues. This was necessary as the protecting group is acid labile on prolonged exposure.

The final product of this scheme (**45**) although high melting was found to possess a nematic phase. Decomposition, however, did occur at the elevated temperatures in which the compound was in its phase.

Reaction Scheme 5 (compounds 46- 49)

Reaction scheme 5 illustrates the procedure used to obtain an analogous material to that prepared in reaction scheme 4, this time based on naphthalene. Two starting materials were available, 6-methoxy-2-naphthoic acid (**46**), and 2-cyano-6-hydroxynaphthalene (**47**).

The dealkylation of compound **46**, was this time affected using the Lewis acid, boron tribromide, at a reduced temperature (-70 °C). A quantitative yield (100 %) was obtained with further purification after work-up was deemed unnecessary.

Hydrolysis of the nitrile function associated with compound **47**, was carried out using the sulphuric acid mixture, as described in reaction scheme 4 (4A). The yield for this reaction after purification was 66 %, the material being recrystallized from glacial acetic acid.

The protection step (5C) was achieved using an identical procedure to that described in reaction scheme 4 (4D). In this case a quantitative yield (100 %) was obtained, the product being purified in an analogous manner to the substituted biphenyl (**45**).

Reaction Scheme 6 (compounds 50- 58)

Reaction scheme 6 illustrates the procedure used to prepare a number of 4-alkoxybenzoic acids from 4-hydroxybenzoic acid (**50**). A Williamson ether synthesis[131] was employed using a variety of alkyl bromides as the substrates. The base used in this procedure, potassium hydroxide, served a double purpose, firstly to generate the desired aroxide ion, and secondly to saponify any unwanted ester formed by esterification of the acid moiety (with alcohol produced from side reactions of the alkyl bromide) . Yields were found to be much improved by the addition of a small quantity of potassium iodide, in some instances the reaction failed to work at all if this salt was not present. The improvement in yields was thought to be due to a halogen exchange (Finkelstein)[132] reaction that produced the alkyl iodide from the bromide, thereby forming a much more reactive substrate. All of the reactions carried out in this synthetic scheme had yields in the 50 % region, which produced reasonable quantities of four of the substituted benzoic acids (**51-54**). The other acids (**55-58**) were already available.

The materials prepared in this series (**51-58**) were found to be liquid-crystalline in nature, as expected. The reason for this is the ability of the compounds to dimerise by virtue of hydrogen-bonding of their acid functions, thereby producing a more elongated molecule. This has been well-documented previously[133] and so will not be expanded on further here.

Reaction Scheme 7(i) (compounds 59- 74)

Reaction scheme 7(i) details the synthetic procedure employed to prepare a series of 4-alkoxyphenylpropiolic acids. The first step in the reaction sequence involved the alkylation of 4-hydroxybenzaldehyde with a variety of alkyl bromides to produce a series of 4-alkoxybenzaldehydes (**60-64**). The base used to produce the desired aroxide ion in this instance was potassium carbonate. A stronger base, such as potassium hydroxide,

was not necessary because ester formation could not occur (compare with scheme 6). Nor was such a strong base desirable as the aldehyde could undergo what is known as the Cannizzaro reaction where one molecule of aldehyde oxidises another to the acid, itself being reduced to the primary alcohol. A strong base would also leave the aldehyde function open to hydrolysis. Yields for the alkylation step were good, being consistently over 80 %, and it was found that the reaction proceeded smoothly even without the addition of potassium iodide.

The next two steps (7(i)B, and 7(i)C) in the reaction sequence were, in methodology, analogous to the Wittig olefin synthesis[134], involving a chain extension reaction to the desired acetylenic moiety *via* the dehydrohalogenation and lithiation of a β,β-dibromostyrene[135]. Step 7(i)B first involved the formation of a phosphorus ylide by reaction of triphenylphosphine with carbon tetrabromide in the presence of zinc dust. The mechanism for the formation of the phosphorus ylide is illustrated in figure 44, where zinc plays the role of reducing triphenylphosphine dibromide formed in the reaction, back to triphenylphosphine. This enables a 50 % reduction in the quantity of triphenylphosphine needed to complete the process. Then to a solution of the ylide in dry dichloromethane the aldehyde prepared previously was added slowly. The reaction to produce the β,β-dibromostyrene proceeds *via* a betaine and an oxaphosphetane ring system, the mechanism for this being illustrated in figure 45.

Problems were not encountered if the reaction was carried out on a small scale (< 50 g), with yields being consistently over 60 %. If, however, the procedure was attempted on a large scale, the filtration through hyflo supercel became almost impossible to perform effectively. Triphenylphosphine oxide, produced as a by-product of the reaction, formed a viscous glue-like layer on the filter pad making filtration intolerably slow and seemed to be resistant to washing with both water and hexane.

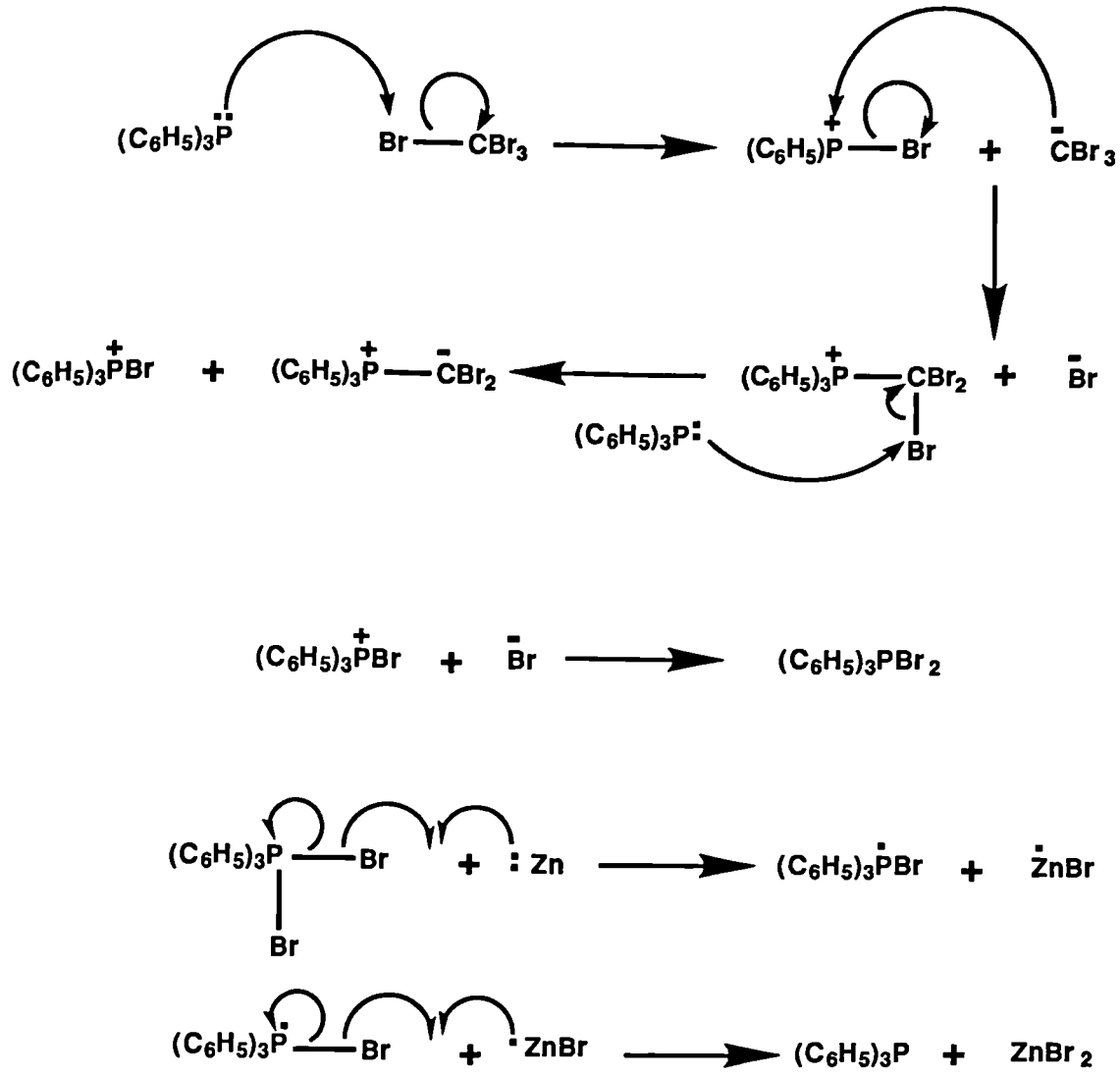


Figure 44. The Formation of a Phosphorus Ylide.

The last step (7(i)C) in the synthetic route involved the conversion of the β,β-dibromostyrene produced to the desired phenylpropiolic acid. This was facilitated by the preparation of a lithium acetylide, which could be further reacted to produce the desired acid by pouring the reaction mixture on to solid carbon dioxide, or the substituted acetylene by addition of the mixture to water. The lithium acetylide was produced by treatment of the β,β-dibromostyrene with 2 molar equivalents of n-butyllithium, at a reduced temperature. The reaction is thought to proceed in two stages, the first a dehydrohalogenation to yield an alkynyl bromide, the second a halogen-metal exchange

to give the desired salt. The mechanism for these two steps is illustrated in figure 46. The lithium salt then undergoes a carbonation reaction on contact with solid carbon dioxide to give the desired phenylpropiolic acid. Yields for this final step varied between 46 % and 64 %, with problems being encountered in some instances with the work-up and purification procedure. At the point where the product is extracted into ether, an emulsion often forms which is difficult to break up even on the addition of salt. This problem could, however, be overcome by leaving the mixture to stand for lengthy periods of time, whilst the aqueous and ethereal layers partitioned.

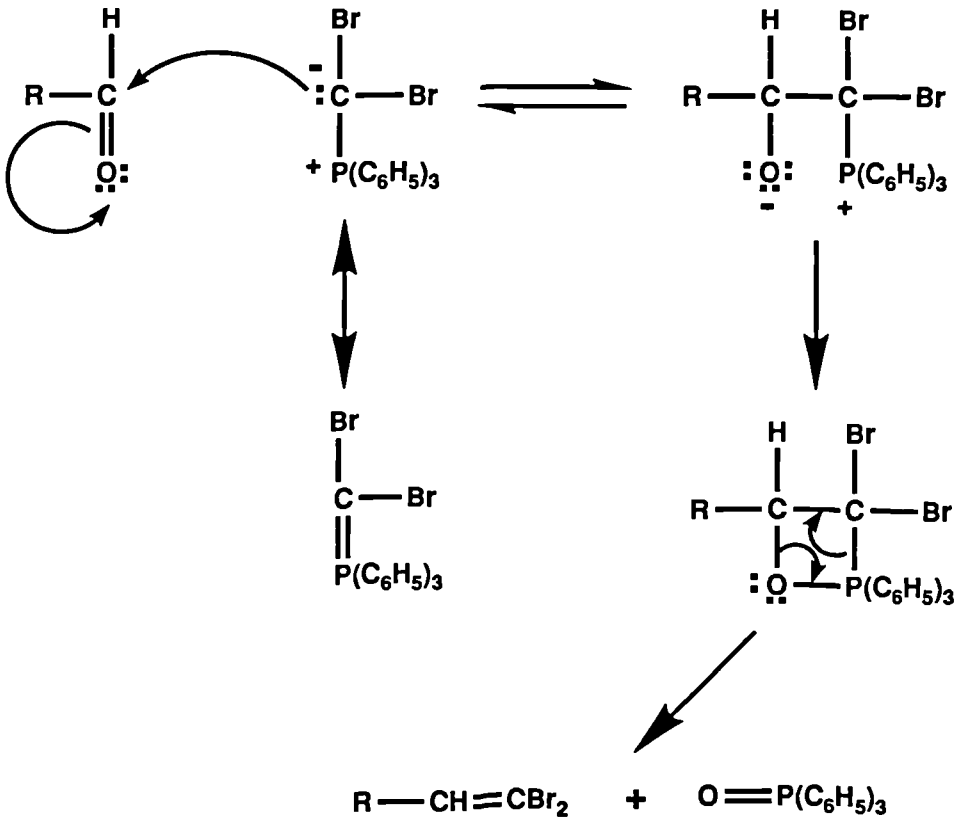


Figure 45. The Corey-Fuchs Chain Extension Reaction[135].

The second problem was encountered with the recrystallization procedure, the product coming out of solution as an oil which then coagulated at the bottom of the flask. A variety of solvents were tried, as well as an excess of the selected system (methanol/water mixture) in order to overcome this, but usually resulted in solubility problems or a loss of

material. Finally, quick cooling, using a carbon dioxide/acetone bath, in order to crystallize any oil that came out of solution, was implemented. This procedure worked extremely well, although the purity of the products themselves might have been reduced to some extent.

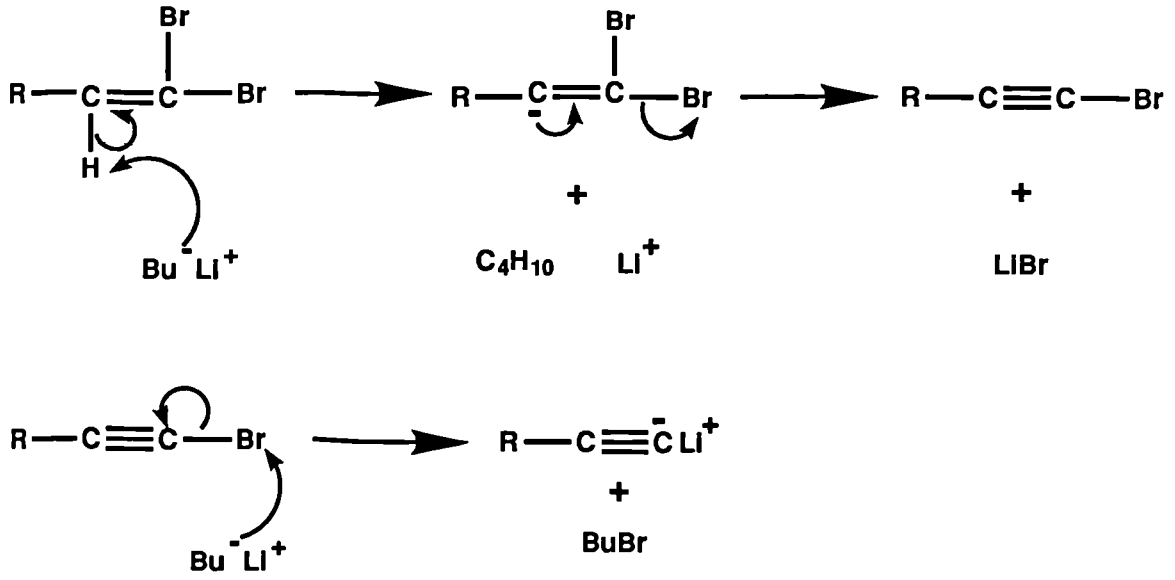


Figure 46. The Preparation of a Lithium Acetylide.

The acids in this series (**70-74**) when investigated by optical polarizing microscopy, were found to be liquid-crystalline in nature, this property being due to their ability to dimerise in a similar manner to that observed with the 4-alkoxybenzoic acids described for reaction scheme 6.

Reaction Scheme 7(ii) (compounds 75-77 and 72)

This reaction scheme illustrates an alternative procedure used in an attempt to prepare one of the desired phenylpropiolic acids (**72**).

The first step involved the alkylation of 4-iodophenol, using an analogous method to that described for 7(i)A. In this instance, however, the higher boiling solvent butanone was

used rather than acetone, with a corresponding reduction in reaction time. The product was produced in 93 % yield, and took the form of a waxy solid.

The next step 7(i)B involved the formation of the substituted acetylenic precursor[136] (**77**) which would then be lithiated and carbonated to give the desired product (**72**). The method used to obtain the desired precursor involved the coupling of the previously produced iodide (**76**) with lithium acetylide ethylene-diamine complex, using tetrakis-triphenylphosphinepalladium(0) as the catalyst. The yield for this reaction was exceptionally poor. The reason for this being put down to the age and condition of the catalyst, which was used in a very large excess to try and overcome its possible inactivity. The excess catalyst, however, appeared to make little difference.

The final step in the reaction scheme involved a hydrogen-lithium exchange reaction on the terminal acetylene (77), followed by the carbonation of the salt produced. The yield for this step was again found to be very poor (12 %), the reasons for this are not clear. If a comparison is made between this step and 7(i)C, which involves a halogen-lithium exchange, it can only be assumed that the better yields obtained for the latter are a result of the halogen being a better leaving group than the acetylenic proton.

At this stage it was decided that reaction scheme 7(i) was a more appropriate synthetic route and so was used to produce phenylpropiolic acids in every case thereafter.

Reaction Scheme 8(i) (compounds 45, 78 and 79-106)

Reaction scheme 8(i) illustrates two synthetic routes utilised in an attempt to prepare a number of substituted phenols (**93-106**).

Step 8(i)A involved the preparation of an acyl chloride[137] (**78**) from the substituted biphenylcarboxylic acid (**45**). This was achieved by stirring the acid in thionyl chloride, the reaction being proven to occur from the infra-red spectrum of the residue remaining after removal of excess reagent. Benzene was added and then distilled off in an attempt to break up and separate the residue, thereby removing the final traces of thionyl chloride. The next step (8(i)B) involved the reaction of the acyl halide with the desired alcohol[138]. This procedure was carried out in a mixed solvent consisting of 50 % benzene and 50 % tetrahydrofuran in order to aid in the solubility of the reactants. After stirring the reaction mixture briefly, pyridine was added to combine with the hydrogen chloride produced. The residue obtained after removal of solvent was purified by flash chromatography to give yields of 40 % and 58 % respectively for the two materials prepared by this method (**90** and **92**).

The next step (8(i)C) in the synthetic procedure involved the deprotection of the hydroxy function of the molecule. This reaction involved stirring in an ethanolic ammonia solution and is analogous to reaction 8(ii)B and so is discussed later.

Reaction 8(i)D in this scheme illustrates a one step process to obtain the desired protected esters. This method involves the catalytic dehydration of the alcohol and acid using N,N-dicyclohexylcarbodiimide (DCC) and N,N-dimethylaminopyridine (DMAP)[139]. Unfortunately, the method failed as the acid (**45**) proved to be insoluble in all suitable solvents, and the reaction would not proceed without the starting materials first being in solution.

Reaction Scheme 8(ii) (compounds 45 and 79-106)

Reaction scheme 8(ii) illustrates another route used to prepare the desired substituted phenols (**93-106**). Step 8(ii)A is a one step process involving the acid (**45**), the desired

alcohol, diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP)[140]. This process which is an example of a redox reaction in which the triphenylphosphine is oxidised and the diethyl azodicarboxylate is reduced, is often referred to as the Mitsonubu reaction. The mechanism is believed to be as shown in figure 47. In the first instance the DEAD and TPP combine to produce a quarternary ammonium salt. This salt is then protonated, the relative stabilities of the alkoxide and carboxylate ions dictating that the proton is abstracted from the acid function. This is followed by the formation of an alkoxyphosphonium salt and the final S_N2 displacement by the carboxylate ion. The advantages of using this route over that described in reaction scheme 8(i)A was its efficiency, yields were always in excess of 50 % and in most cases exceeded 80 %. The reaction was also very quick and clean, occurring almost instantaneously, and producing only two major by-products, triphenylphosphine oxide (TPPO) and diethyl hydrazinedicarboxylate (DEAD-H_2) both of which could easily be removed by flash chromatography. It was also apparent that the methylcarbonate protecting group associated with the molecule was stable under the reaction conditions utilised. The solubility of reactants caused little problem, and in fact turned out to be an efficient guide to when the reaction had gone to completeness. The protected acid (**45**) would typically form a suspension in tetrahydrofuran, taking on an yellow colour on addition of DEAD (which is deep orange in colour). On addition of TPP the reaction proceeded exothermically, rendering the reaction mixture clear and colourless in the case of a successful reaction. The ester product was usually soluble in tetrahydrofuran, with DEAD-H_2 also appearing colourless when dissolved in the solvent.

In the case of compound **92**, *(R)*-2-octanol, rather than *(S)*-2-octanol was used as the starting material. This is because an inversion of the absolute configuration of the chiral centre was expected to occur at the S_N2 substitution stage of the reaction. This was

confirmed when the optical rotation measurements (in solution) of compound **92** prepared by this route and the acid chloride/pyridine route 8(i), were compared.

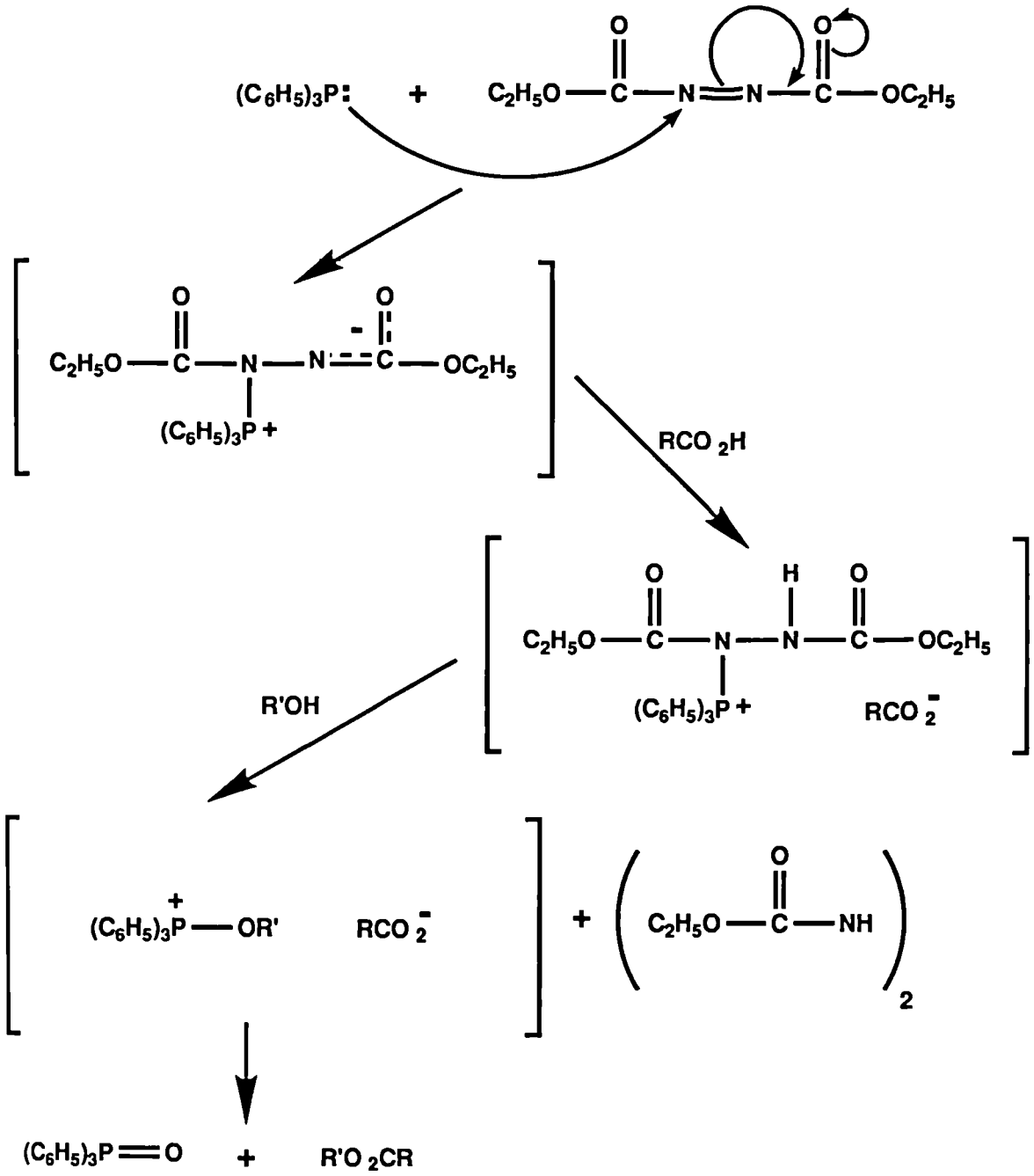


Figure 47. The Mechanism of the Mitsonubu Esterification.

In both cases a positive deflection was found, and since the acyl chloride route does not give inversion and the reaction was carried out on *(S)*-2-octanol, an inversion must occur

with DEAD/TPP. This of course is only the case if the hydroxy function to be reacted is attached directly to the chiral centre of the molecule. It was interesting to note that the value of the optical rotation of compound **92** prepared by the DEAD/TPP route was less (+31°) than that prepared by the acyl chloride route (+43°). This tends to suggest that in the case of the DEAD/TPP reaction a total inversion of configuration is not seen, leading to some degree of racemisation.

The final stage of this synthetic procedure was to remove the methoxycarbonyl protecting group, to thereby produce a phenol. The procedure for this simply involved stirring the reactant in ethanol, with the gradual addition of aqueous ammonia. The reaction was monitored by tlc and usually took place over a period of 24 h. The yields in this instance were exceptionally good, being almost quantitative in every case.

Reaction Scheme 9 (compounds 49 and 107-112)

Reaction scheme 9 illustrates an analogous procedure to that described in reaction scheme 8(ii), except that the core structure of the molecule to be reacted is based on naphthalene in this case.

Reaction Scheme 10(i) (compounds 55, 56, 89 and 113-116)

Reaction scheme 10(i) details the procedure used in an attempt to prepare two of the final liquid-crystalline di-esters. The esterification process is analogous to that used in reaction scheme 8(i). Firstly, the acyl chloride was prepared, this was then reacted with a phenol (rather than an alcohol) to produce the desired ester linkage. The acyl chloride was prepared this time by refluxing in thionyl chloride for 3 h, the harsher conditions being possible as no sensitive groups were present in the molecule (compare 8(i)A), a reduction in reaction time therefore being possible. The presence of an acyl chloride was

confirmed by infrared spectroscopy, the subsequent methods used were then analogous to those in reaction scheme 8(i)B.

Purification was achieved by flash chromatography, but in this instance the compounds were also recrystallized successively from acetonitrile, until hplc data dictated an acceptable level of purity (>99 % in most instances). Thus, the final yields for this scheme were moderate (approximately 30-35 %).

Reaction Scheme 10(ii) (compounds 51-58, 70-74, 93-106 and 117-196)

Reaction scheme 10(ii) illustrates the procedure used to prepare a large number of final target molecules. In this scheme a variety of 4-alkoxybenzoic and 4-phenylpropiolic acids were treated with the phenols (prepared as shown in schemes 8(i) and 8(ii)), in the presence of N,N-dicyclohexylcarbodiimide (DCC). The reaction is base catalysed, hence the use of N,N-dimethylaminopyridine (DMAP) in a catalytic amount. The mechanism is similar to that encountered in nucleophilic catalysis[141], in that the acid is converted to a compound with a much better leaving group. The full mechanism of the DCC/DMAP reaction is illustrated in figures 48 (a and b) . The process followed involved both the relevant acid and phenol in dry diethyl ether, and adding the two reagents (DCC and DMAP) in one portion. The reason for this was to avoid the formation of undesirable side-products such as N-acylureas, which are known to cause problems under certain circumstances. After completion of reaction, the urea formed (DCU) was removed by washing with water, purification being effected by flash chromatography and recrystallization in a similar manner to that described in reaction scheme 10(i). This route was especially useful in the preparation of the phenylpropiolate based esters as the acid chloride method was expected to lead to the unwanted addition of hydrogen chloride across the triple bond (in the target molecule), and the separation of the desired products and by-products was expected to be extremely difficult using the DEAD/TPP route.

Yields were found to be extremely variable, ranging from 86 %, down to 9 %, with the phenylpropiolate based materials tending to react quicker and with a better yield of product.

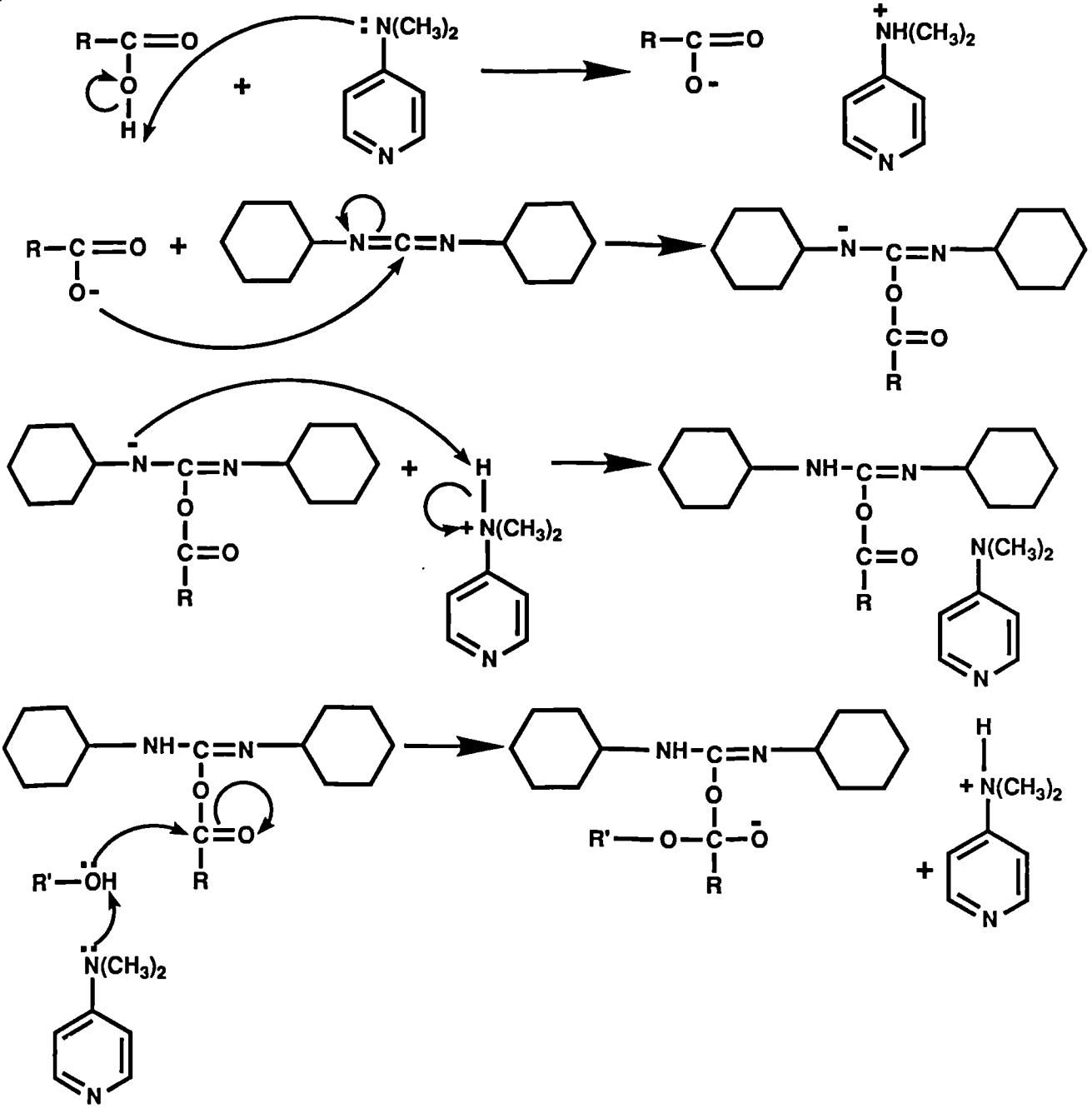


Figure 48 a. The Mechanism of the DCC/DMAP Esterification.

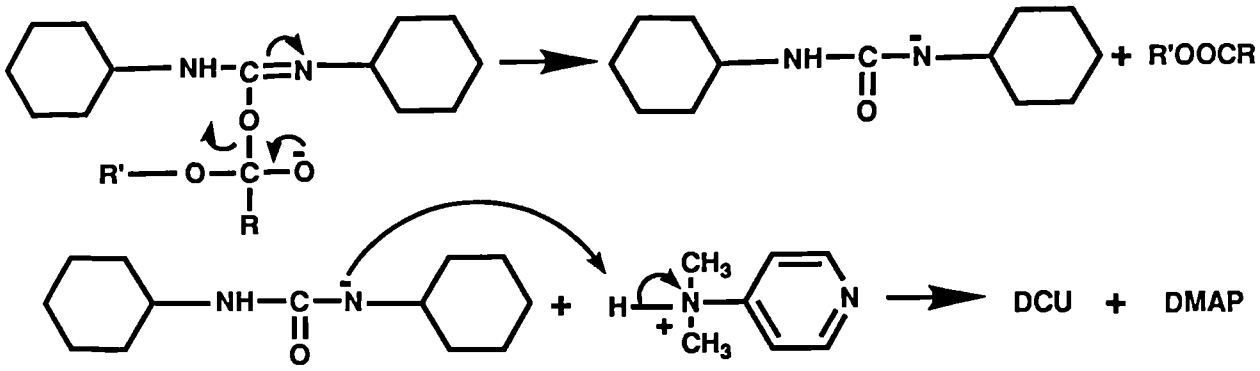


Figure 48 b. The Mechanism of the DCC/DMAP Esterification.

The reason for the enhanced reactivity of the phenylpropiolates was probably due to the increased lability of the acidic hydrogen. Thus, overall yields were mainly in the 20 % to 50 % region.

Reaction Schemes 11, 12, 13, 14, and 15 (compounds 51, 70, 72, 93-96, 110-112, and 197-217)

The materials produced *via* these reaction schemes employed the DCC/DMAP esterification process described for reaction scheme 10(ii). The materials differed from those in the previous scheme by virtue of their core structures. In reaction scheme 11 an alicyclic acid (**197**) was used as the starting material rather than an aromatic acid. The biphenyl part of the core was replaced by a naphthalene system in scheme 12. In schemes 13, 14 and 15 the phenyl group associated with the core of the molecule was replaced by a variety of substituted naphthalenes. Thus, all of the experimental procedures used to produce these materials were identical to those described in reaction scheme 10(ii).

Reaction Scheme 16 (compounds 218 - 230)

In reaction scheme 16 the DCC/DMAP esterification process was used in the first step (16A) to prepare a mono-esterified biphenol derivative, which was then further esterified in the second step (16B) to produce the final target molecules. This procedure achieves

the objective of the reversal of one of the ester groups compared to the materials produced in reaction scheme 10(ii).

Due to the fact that the starting material, 4,4'-dihydroxybiphenyl (**218**) contains two active sites (two hydroxy functions), an excess of this material was used in order to promote mono-substitution. The reaction solvent used for the first esterification in this scheme was tetrahydrofuran, as the solubility of 4,4'-dihydroxybiphenyl in diethyl ether was found to be quite low. Yields were found to be reasonable for all of the phenols prepared (**219-222**), ranging from almost quantitative to 33 %.

The next step (16B) in the reaction sequence was analogous to the DCC/DMAP esterifications carried out in reaction schemes 10(ii), 11, 12, 13, 14 and 15. Yields were mainly in the 30 to 50 % range, although an exceptionally good yield of 86 % was obtained for one of the materials (**227**).

Reaction Scheme 17(i) (compounds 231 - 236)

Reaction scheme 17(i) illustrates one procedure used in an attempt to prepare cyclo [*(S)*-ala, *(S)*-ala)] (**235**) and cyclo [*(S)*-val, *(S)*-val)] (**236**)[142]. The first step 17A involved the protection of the amino function of *(S)*-alanine (**1**), as a carbamate, using ethyl chloroformate. The protected species was then converted to the protected dipeptide (**233**) by reaction with *(S)*-alanine methyl ester hydrochloride (**231**). The next stage (17(i)B) of the procedure involved a deprotection reaction followed by a cyclization step, in order to generate the desired intermediate. Unfortunately, the product could not be isolated after the first synthetic procedure (17(i)A) had been carried out and so a new more convenient route was sought.

Reaction Scheme 17(ii) (compounds 231 - 246)

In reaction scheme 17(ii) three different methods were used in an attempt to prepare *(S)*-alanine methyl ester (**233**). The first method (17(ii)A) involved dissolving the hydrochloride salt (**231**) in water, adding concentrated ammonia solution, and extracting the mixture with diethyl ether. It was hoped that the free-base would have a greater solubility in ether than in water, and could be recovered from the ethereal solution. After removal of solvent, however, none of the desired product was obtained, the failure was thought to be due to the high solubility of the free-base in water, or hydrolysis of the unstable methyl ester.

The second method attempted (17(ii)B) was similar to the first except the base used in this instance was sodium bicarbonate. Once again the method proved unsatisfactory with only a 2 % yield of the desired product being obtained.

The third method[120] (17(ii)C) involved reaction of the hydrochloride (**231**) with a calculated amount of 2 % sodium methoxide solution (in methanol), This method had the advantage that the product would not have to be extracted from aqueous solution and so the yields were expected to be substantially improved. Diethyl ether was used to precipitate sodium chloride formed during the reaction, which could then be filtered off. After removal of solvent an improved, but nevertheless low yield of 8 % was obtained. As this was the most successful attempt at producing the desired free-base, this method was also used to prepare *(S)*-valine methyl ester (**234**), giving a yield of 5 %.

The next stage in the synthetic procedure (17(ii)D)[121] involved a cyclization reaction. Basically the reaction was a condensation between the acid and amine functions in the molecule, which because each molecule was bifunctional caused the formation of a cyclic diamide. The cyclization occurred spontaneously on the addition of heat, with no solvent

or catalyst being required. As the cyclization reaction proceeded a solid began to form in the reaction vessel (both methyl esters were originally liquids), this solid was purified by washing with ether and recrystallization from water. Yields for this step were reasonably good, being 62 % in the case of compound **235**, and 41 % in the case of compound **236**. The two diamides (**235** and **236**) were known to exist in two tautomeric forms (see reaction scheme). Step 17(ii)E was designed to trap the molecule in its enol form, by methylation of the hydroxy functions. This was achieved by stirring with a suspension of trimethyloxonium tetrafluoroborate in dichloromethane, for an extended period of time. The long reaction time was necessary due to the relative insolubility of the cyclic reactants in the specified solvent. During the course of the reaction a fine precipitate formed in the flask and large lumps of starting material appeared to dissolve. The mixture was then treated with a phosphate buffer solution to avoid hydrolysis of the ring system. Yields for this step were good, being over 60 % in both cases.

The next step (17(ii)F) involved the removal of an acidic proton (α to one of the nitrogen atoms) in a hydrogen-lithium exchange reaction, using butyllithium. On addition of alkyl bromide, nucleophilic displacement of the bromine would then occur to give the desired alkylated products (**239** and **240**). Although each cyclic system has two equivalent labile protons which could be displaced, only one is removed. The reason for this is that the removal of both protons would lead to an unstable anti-aromatic 8-π electron system. The reaction is thought to give a high degree of asymmetric induction for the following reason, which is illustrated in figure 49 (X and Y). The angular methyl at C-3 encumbers the bottom face of the molecule sufficiently to direct the approach of the alkylating agent from the top (X). This also places the bulky R group in a favourable *trans* position to the methyl at C-3 (Y). Another possibility, however, is that on removal of a proton using butyllithium the anion produced has a relatively localised negative charge and that the stereochemistry at C-6 is retained. For example the methyl group would remain pointing

downwards, leading to the substitution reaction occurring predominantly on the upper face of the molecule. This mechanism is illustrated in figure 50. The lactim ether is therefore a very effective way for inducing asymmetry in alkylation reactions, as well as providing a respectable induction of chirality in carbonyl compounds if desired.

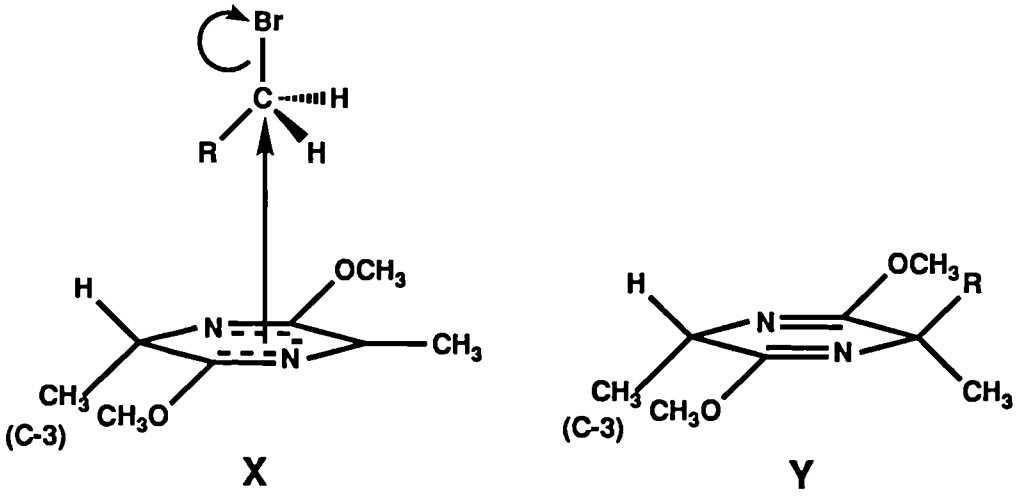


Figure 49. The High Asymmetric Induction Caused by the Formation of a Cyclic Lactim.

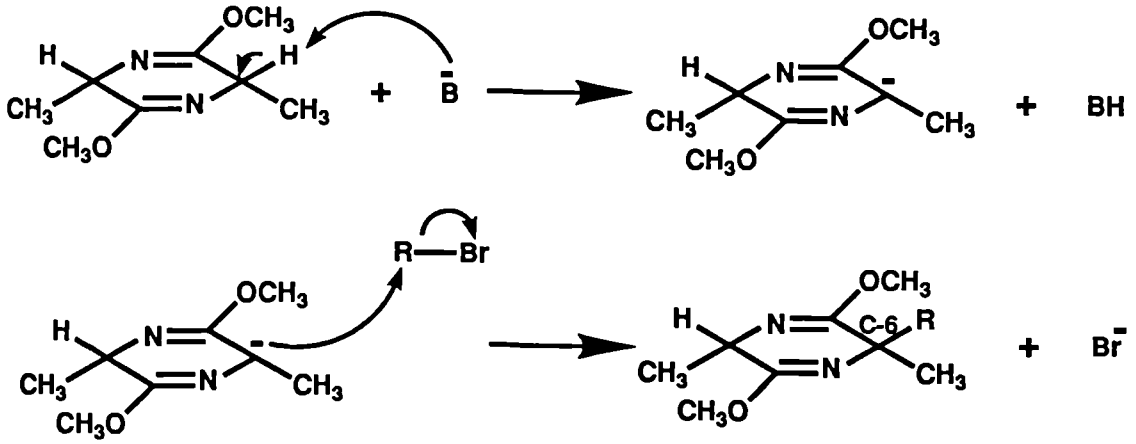


Figure 50. An Alternative Argument for the High Asymmetric Induction Seen in Compounds 239 and 240.

The yields for this step were 64 % in the case of compound **239**, and 54 % in the case of compound **240**. When spectroscopic analysis was carried out on the materials both infrared spectroscopy and proton nmr spectroscopy gave results consistent with the

expected structures. Mass spectral analysis, however, failed to detect a mass ion for compound **239**.

Step 17(ii)G involved the hydrolytic cleavage of the ring system of compounds **239** and **240** to produce the substituted methyl ethers (**241** and **242**). This was accomplished by stirring in 0.25 N hydrochloric acid at room temperature. The solution was then neutralised and extracted with diethyl ether, the products being very soluble in the organic solvent because of the long alkyl chains (compare compounds **233** and **234**). Mass spectrometry and infrared spectroscopy gave results that were consistent with the desired structures. The proton nmr spectra of both materials, however, proved rather messy, even though purification by distillation had been attempted. A number of peaks in the spectrum of each compound did, in fact, indicate the presence of desired functional groups. In both materials the octyl chain could be identified, and in the case of compound **242**, the isopropyl group was also clearly present.

The last step in this reaction scheme involved hydrolysis of the methyl ester, to produce the desired substituted amino acids (**243** and **244**). In this reaction 6 N hydrochloric acid was employed to hydrolyse the material, at an elevated temperature. In the case of compound **243** the yield was too small for any spectroscopic data to be collected. The yield for compound **244**, however, was 65 % with mass spectral analysis and proton nmr spectroscopy confirming the expected structure to some degree.

Unfortunately, the yields obtained at the end of this synthetic procedure were too small to be of any use. If greater quantities of the α-amino acids (**243** and **244**) had been obtained then they would have been employed in reactions analogous to those in scheme 1. At this point, however, the pathway was abandoned, although if initial problems with the first two steps (17(ii)C and 17(ii)D) could be overcome it shows great promise.

Reaction Scheme 18 (compounds 41 and 247 - 261)

Reaction scheme 18 illustrates the procedure used to prepare a number of dimeric liquid-crystalline materials (**255-261**). The first step (18A) in the reaction scheme involved the preparation of 4-cyano-4'-hydroxybiphenyl (**247**), by demethylation of 4-cyano-4'-methoxybiphenyl (**41**). The demethylation step was carried out using boron tribromide as described for the naphthalene based compound (**48**) in reaction scheme 5. The last step (18B) involved the DCC/DMAP esterification of a variety of aliphatic di-acids with the previously prepared phenol (**247**), to produce the desired dimeric materials. The procedure used for this esterification was similar to those described in other schemes in this thesis, except that two molar equivalents of phenol were used as the acids were bi-functional in nature.

Reaction Scheme 19 (compounds 262 - 264)

In this reaction scheme the DEAD/TPP esterification procedure was utilised to prepare another dimeric mesogenic material (**262**). The reaction, in fact, consisted of the formation of a di-ester from the chiral alcohol (**261**) and the biphenyl acid (**260**). The yield for this reaction was found to be extremely low (4 %), the reason for this probably being due to steric factors.

Reaction Scheme 20 (compounds 70, 247, and 265 - 267)

Reaction scheme 20 illustrates the procedure used to prepare a final dimeric material (**267**). The first step in the reaction scheme (20A) involved the alkylation of the phenol (**247**) with 11-bromoundecan-1-ol (**265**) to produce the alcohol (**266**). The reaction was carried out using a Williamson ether synthesis as described previously in reaction scheme 7. The second step (20B) involved a DCC/DMAP esterification to produce the target dimer.

8. RESULTS AND DISCUSSION (MATERIAL PROPERTIES).

8.1 Abbreviations Used in Tables and Graphs in Chapter 8.

i). Abbreviations used to define liquid-crystalline phases are as follows:
Iso or I refers to the isotropic liquid, BP refers to the blue phases, Ch refers to the cholesteric phase, TGB or TGB A* refers to the twist grain boundary smectic A* phase, SmA or S_A refers to a smectic A phase, SmC* or S_C* refers to a chiral smectic C* phase, SmI* or S_I* refers to a smectic I* phase, J* refers to a crystal J phase, and N refers to nematic phase.

ii). In reporting phase transitions Mpt. is used to indicate the melting point and Rec. refers to the recrystallization temperature.

iii). In reporting the properties of the smectic C* phase the following abbreviations have been used: n refers to the number of carbons in the alkoxy chain associated with the molecule, A.S.C. is the absolute spatial configuration of the chiral centre associated with the molecule, e or o represent an even or odd parity (corresponding to the odd or even atom count that the chiral centre is removed from the core), Rot. of PPL indicates the rotation of plane polarized light through the sample, which is either $\mathcal{L}$ (laevorotatory) or d (dextrorotatory), RH and LH signify either a right- or left-handed helix as defined by Cahn, Ingold and Prelog[16,17], Ind. Effect refers to the inductive effect at the chiral centre relative to the lateral group with respect to the long axis of the molecules, and Ps. Dir. refers to the direction of the spontaneous polarization.

8.2 Esters Based on the 2-Chloropropyl Chiral Moiety (Series I and II).

The first two series of materials (I and II) to be discussed are the di-esters, based on the 2-chloropropyl chiral moiety (**115-127**). Two mesogenic core structures were used which differed only in whether a triple bond had been incorporated into the molecule or not (compounds **123-127** included a triple bond in their structure). At the opposite end of the molecule from where the chiral centre was positioned, a normal alkoxy chain was located. This chain was varied in length, 7 to 14 carbon atoms for the alkoxybenzoic acid derivatives (series I), and 9, 12, 14, 16, or 18 carbon atoms for the alkoxyphenylpropiolic acid derivatives (series II). The general structures of these compounds are illustrated in figure 51.

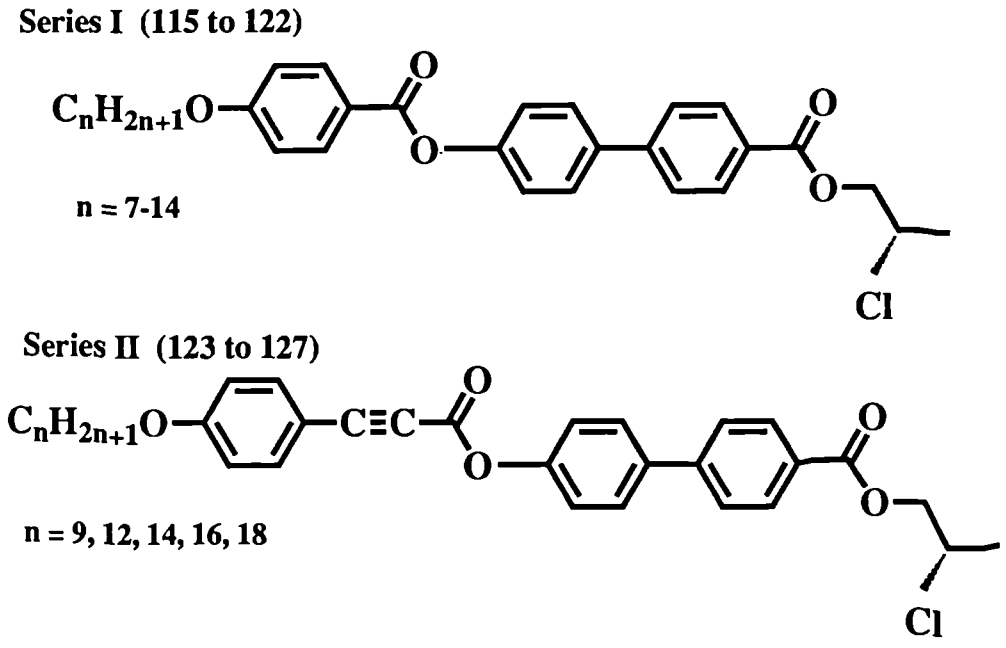


Figure 51. The Structures of the Di-Esters Based on a 2-Chloropropyl Chiral Moiety.

Due to the size of the alkyl chain attached to the peripheral side of the chiral centre (a methyl group), the freedom of rotation associated with the chiral centre with respect to the core structure is likely to be quite large. This would, in effect, "smear out" the dipole associated with the optically active centre (as the chiral centre rotates rapidly about the

C1-C2 bond), and therefore reduce the chirality of the system[143]. The consequences of this will become apparent when the properties of the materials are discussed, along with the effect of having a relatively short alkyl chain at one side of the core structure.

The materials (**115-122**) that did not possess a triple bond in their structure, i.e., those from series I will be considered first. Table 3 shows the transition temperatures associated with these materials (obtained by optical microscopy), whereas they are represented graphically in figure 52.

No.	n	Mpt.	I-Ch	I-S_A	Ch-S_A	S_A-S_{C^*}	Rec.
115	7	102.2	194.5		186.4	79.0	65.5
116	8	94.6	193.0		190.1	72.7	55.7
117	9	90.2		191.6		67.7	65.5
118	10	82.9		191.6		58.4	43.6
119	11	82.3		190.3		49.7	55.2
120	12	76.1		188.3			53.6
121	13	70.2		186.4			48.5
122	14	85.5		185.4			55.1

Table 3. The Transition Temperatures (°C) for the *(S)*-2-Chloropropyl 4'-(4-alkoxybenzoyloxy)-4-biphenylcarboxylates (115-122).

It can be seen from table 3 and figure 52, that the members of series I with a shorter alkoxy chain (associated with the side of the molecule opposite to where the chiral centre is located), exhibit an isotropic to cholesteric to smectic A to smectic C* phase sequence (**115** and **116**). As the chain length was increased the cholesteric phase and the smectic C* phase were found to disappear, the cholesteric phase no longer being evident in the nonyloxy member of this series (**117**), and the smectic C* phase only just being observed in the undecyloxy homologue (**119**) (despite crystallization occurring). In all of the materials the smectic C* phase was found to be monotropic, the temperature of the

transition from smectic A to the smectic C* phase falling off rapidly with increasing chain length. The smectic A phase temperature range in these compounds was found to be extremely large (in excess of 100 °C in some instances), due to the high clearing points, small cholesteric temperature range (in **115** and **116**), and low thermal stability of the underlying smectic C* phase. The reason why both the cholesteric phase and the smectic C* phase were relatively unstable in these compounds is thought to be due to the short alkyl chain attached to the side of the molecule containing the chiral centre. This type of behaviour has been well documented in the past and so for reasons of brevity will not be discussed here[144].

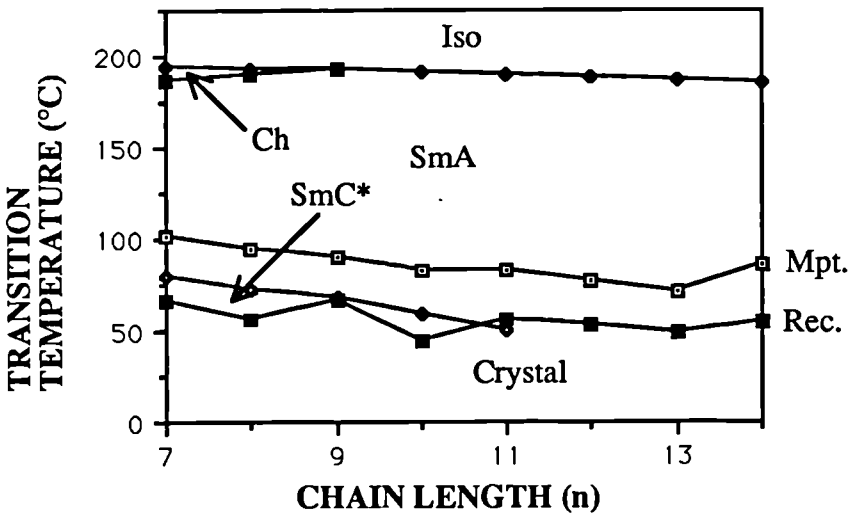


Figure 52. Transition Temperatures Versus Alkoxy Chain Length for Materials (115-122).

At the clearing points careful attention was paid to whether these materials displayed blue phases or not, as this could give some guide to the degree of chirality of the system. None were observed in either microscopic or thermal studies. The DSC trace for the heptyloxy homologue (**115**) showing just two peaks at the clearing point, corresponding to the transitions between smectic A and cholesteric, and cholesteric and isotropic phases. It was therefore concluded, that the pitch in the cholesteric phase was just too long to support the formation of blue phases. This may, as was suspected, suggest that the type

of chiral centre present did not possess the desired properties to produce a high level of chirality in the system.

The twist sense of the smectic C* helix in the materials exhibiting this phase, was determined directly by polarimetry using polarized light microscopy (see chapter 5 of this thesis) on free-standing films of the compounds. The results obtained are listed in table 4.

No.	n	A.S.C.	Parity	Rot. of PPL	Helix Dir.
115	7	S	e	$\mathcal{L}$	RH
116	8	S	e	$\mathcal{L}$	RH
117	9	S	e	$\mathcal{L}$	RH
118	10	S	e	$\mathcal{L}$	RH
119	11	S	e	$\mathcal{L}$	RH

Table 4. Helical Twist Sense of Materials in Series I (115-119).

It can be seen from the table that all of the materials possess a chiral centre which is designated as being *S*, by the Cahn, Ingold and Prelog system[16,17]. In each case the parity is even, and the rotation of plane polarized light through the sample was found to be laevo, thereby classifying the helix as being right-handed in all cases. This result is in agreement with the hypothesis mentioned earlier in chapter 2 of this thesis[39].

Measurement of the direction or value of the spontaneous polarization, in the ferroelectric smectic C* phase, for these compounds was not attempted, partly because of crystallization occurring.

The materials in series II that contain a triple bond in their structure (**123-127**) are now discussed. Prior to this study, the effect that the inclusion of a triple bond next to one of the ester linkages has on phase formation and physical properties was not known for

these materials. It was appreciated that the inclusion of a triple bond would not only extend the length of the core (and the molecule as a whole), and increase the number density of polarizable electrons; but would also make the core less rotationally rigid. This is because the biphenyl and phenyl sections of the core structure are now separated by four atoms rather than just two, as is the case for the materials in series I (**115-122**). This enables the two parts of the core to rotate rapidly relative to one another with a reduced degree of steric hindrance.

The transition temperatures for the materials are illustrated in table 5, and depicted graphically in figure 53.

No.	n	Mpt.	I-Ch	I-S_A	Ch-S_A	Rec.
123	9	102.6	166.0		137.0	62.0
124	12	76.9	157.4		149.0	65.1
125	14	69.9	150.1		149.2	44.4
126	16	87.7		150.8		41.8
127	18	91.6		149.5		47.5

Table 5. The Transition Temperatures (°C) for the *(S)*-2-Chloropropyl 4'-(4-alkoxyphenylpropioloyloxy)-4-biphenylcarboxylates (123 - 127).

It can be seen from table 4 and figure 53 that all of the compounds in series II possess a smectic A phase, the first two compounds (**123** and **124**) also exhibit a cholesteric phase. The temperature of the transition from either cholesteric or isotropic liquid phases to smectic A was seen to rise rapidly with increasing alkoxy chain length, before peaking and then gradually beginning to fall again (at about the dodecyloxy chain length, compound **124**). It is noticeable that a smectic C* phase was not observed in these materials; one possible reason for this is that the increase in core size (compared with compounds **115** to **122**) relative to the terminal aliphatic chains, decreases the smectic C* tendency of the materials[144].

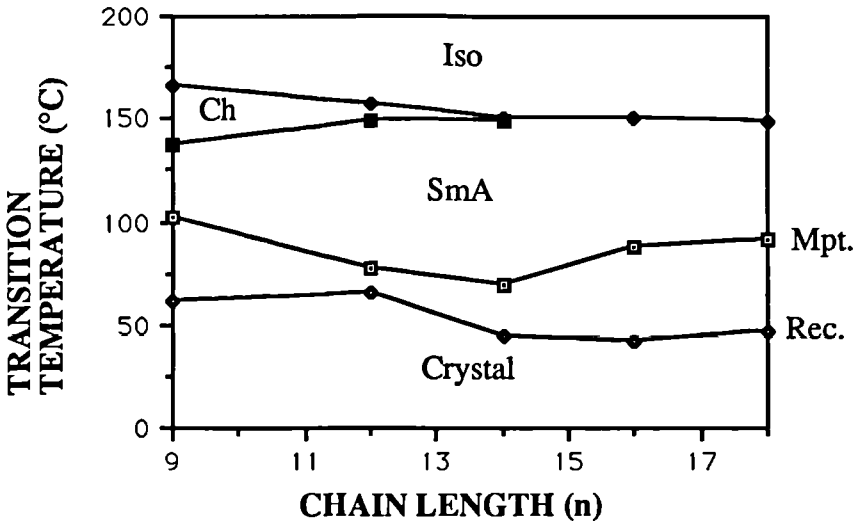


Figure 53. Transition Temperatures Versus Alkoxy Chain Length for Materials (123-127).

If a comparison is made between the nonyloxy homologue of series II (**123**) and the analogous compound from series I (**117**), a number of points are noted (see figure 54)

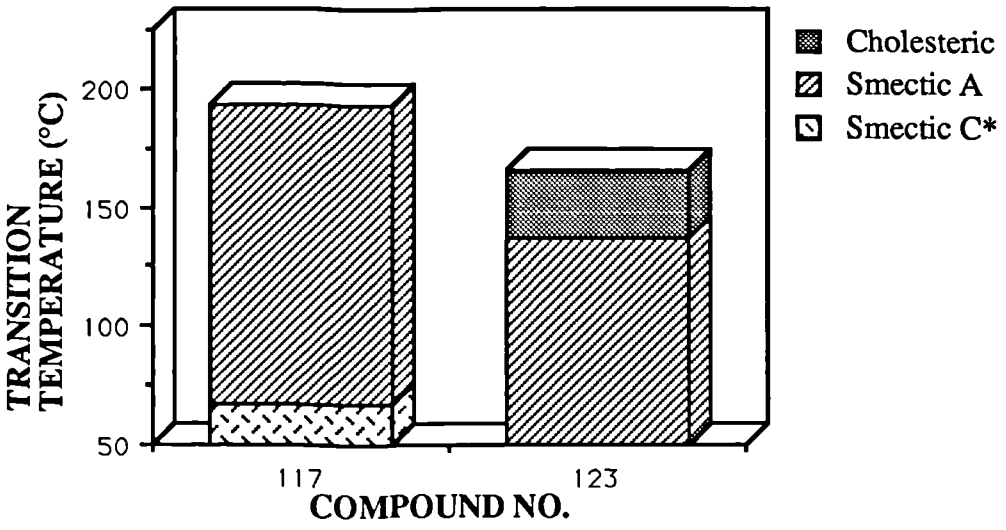
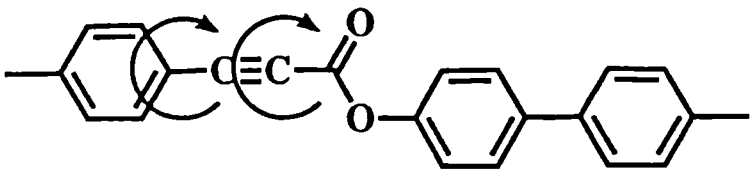


Figure 54. A Comparison of the Phase Behaviour of Compounds 117 and 123 (the Nonyloxy Homologues of Series I and II).

Firstly, the presence of a triple bond reduces the clearing point, and also increases the nematogenic tendency quite considerably (**117** does not possess a cholesteric phase,

whereas **123** has a cholesteric phase with almost a 30 °C temperature range). The chirality appears not to be enhanced by the presence of a triple bond, in this instance, as compound **123** does not display blue phases, nor is there any suggestion of the presence of a TGB A* phase. Compound **123** also, as previously mentioned, does not exhibit a smectic C* phase, whereas compound **117** does, albeit a monotropic one.

The reason why the nematogenic tendency is enhanced on the inclusion of a triple bond in the molecule may be related to the improved freedom of rotation associated with the biphenyl and phenyl ring systems in the core structure (see figure 55). This rotation may disturb the packing ability of the molecules, thereby reducing the tendency to form a lamellar arrangement, and weakening the layer ordering if one is formed. Equally, the nematogenic tendency may be enhanced, in the materials that constitute series II, because of the relative increase in core length with respect to alkyl chain length, thereby reducing the smectogenic tendency. Alternatively, an increase in the number of polarizable electrons, in the materials that contain a triple bond, may cause repulsion between individual molecules and reduce the probability of obtaining a lamellar structure. As a weak layer structure is one of the desired properties that aid in the formation of the smectic A* (TGB) phase, it may be asked why these materials did not show that phase. The reason is almost certainly due to the optically active centre present in these materials not imparting a sufficient degree of chirality in order to produce the necessary fluctuations at the cholesteric to smectic A transition[90].



triple bond allows for greater freedom of rotation

Figure 55. The Enhanced Freedom of Rotation About a Triple Bond.

Another interesting effect that concerns two of the materials (**123** and **124**) was the helix direction in the cholesteric phase. On cooling, or heating through the cholesteric temperature range an inversion in helical twist sense was seen to occur, *via* an infinite pitch cholesteric (nematic) phase. Taking **123** as an example, on cooling the material between untreated glass slides the cholesteric phase formed from the isotropic liquid to give a characteristic fingerprint texture. As the temperature was reduced the pitch of the cholesteric phase began to increase. This was clearly seen as the fingerprints associated with the pitch of the phase increased in breadth. At about 150 °C, regions of pseudo-homeotropic texture became apparent as the cholesteric phase split up into fingers, which then gradually reduced in size. This is illustrated in plate 13, where the cholesteric fingers can be clearly seen along with the pseudo-homeotropic texture of the ensuing nematic phase. On further cooling the whole texture of the cholesteric phase disappeared giving way to the homeotropic texture of a nematic phase. This texture was found to "flash", when subjected to mechanical stress, in a way characteristic of the nematic phase. In areas where the material was pinned to the side of the glass plates, or around air bubbles, a normal *schlieren* texture was observed. The sample was further cooled and at approximately 141 °C, a cholesteric phase formed, which was determined by rotation of the polars to have the opposite twist sense to the higher temperature cholesteric phase. The formation of this lower temperature cholesteric phase was promptly followed by a normal transition to the smectic A phase at 137 °C. On further cooling to 62 °C, the material recrystallized.

In order to conclusively establish that the two cholesteric phases observed did indeed have opposite twist senses, a contact preparation was made between compound **123**, and a standard material of known twist sense. The standard material selected for this study was *(S)*-4'-decyloxybiphenyl-4-yl 4-(2-methylbutyl)benzoate[145], which exhibits a cholesteric phase between 153 °C and 118 °C. The absolute spatial configuration of this material is designated as *S*, the parity is even, and the rotation of plane polarised light through the sample was found to be dextrorotatory (*d*). This classifies the helix for the standard material as being left-handed. On cooling slowly from the isotropic liquid (2 °C min^{-1}) to just below the clearing point of the standard material (152 °C), the boundary between the standard and compound **123** was found to show a continuous change in pitch across the contact region, but at no point did the pitch diverge, see plate 14. This means that the helix directions in the cholesteric phases of both compounds have the same twist senses, i.e., they are both left-handed. On further cooling to the temperature range in which the nematic phase of the test (**123**) material occurs (145 °C), the test material became non-helical with an infinite pitch. The contact appeared as a pseudo-hometropic region adjacent to the cholesteric texture of the test material, as shown in plate 15. Upon further cooling, to 141 °C, the cholesteric texture of the test material returned, but this time the boundary between the test material and the standard material showed a sharp discontinuity where the pitch became infinite, as illustrated in plate 16. From these studies it is reasonable to conclude that the lower temperature cholesteric phase of compound **123** has a twist sense that is opposite to that of the

standard material. Thus on cooling from the isotropic liquid, the cholesteric phase has a left-handed helical structure that inverts *via* an infinite pitch region to a right-hand helix.

Compound **123** was then investigated by differential scanning calorimetry, in order to ascertain if a measurable enthalpy was associated with the helix inversion in the cholesteric phase. At the clearing point a single peak was observed corresponding to the cholesteric to isotropic liquid transition. No evidence was found to suggest the presence of blue phases, and the temperatures of transition on both heating and cooling runs were in good agreement with those determined by optical microscopy. At 137 °C, the smectic A to cholesteric transition was clearly seen, but at the point at which the cholesteric helix was found to invert by optical microscopy, no associated enthalpy of transition was

observed. Figure 56 shows the heating scan of compound **123**, near the helix inversion point (2 °C min^{-1}).

The next step in investigating this inversion, was to measure the pitch of the cholesteric helix as a function of temperature. This was achieved by determining the distance between dechiralisation lines for the fingerprint texture of the mesophase using a Filar eyepiece (see chapter 5). The material was confined between a cover-slip and a microscope slide for these studies, and therefore the specimen thickness varied from approximately 70 to 100 μm. The value of the pitch as a function of temperature is shown in figure 57, and the reciprocal value of the pitch as a function of temperature is shown in figure 58 (slight variations in the collected data were found and attributed to thermal decomposition of the material and surface pinning, thus the data was collected using a number of specimen samples).

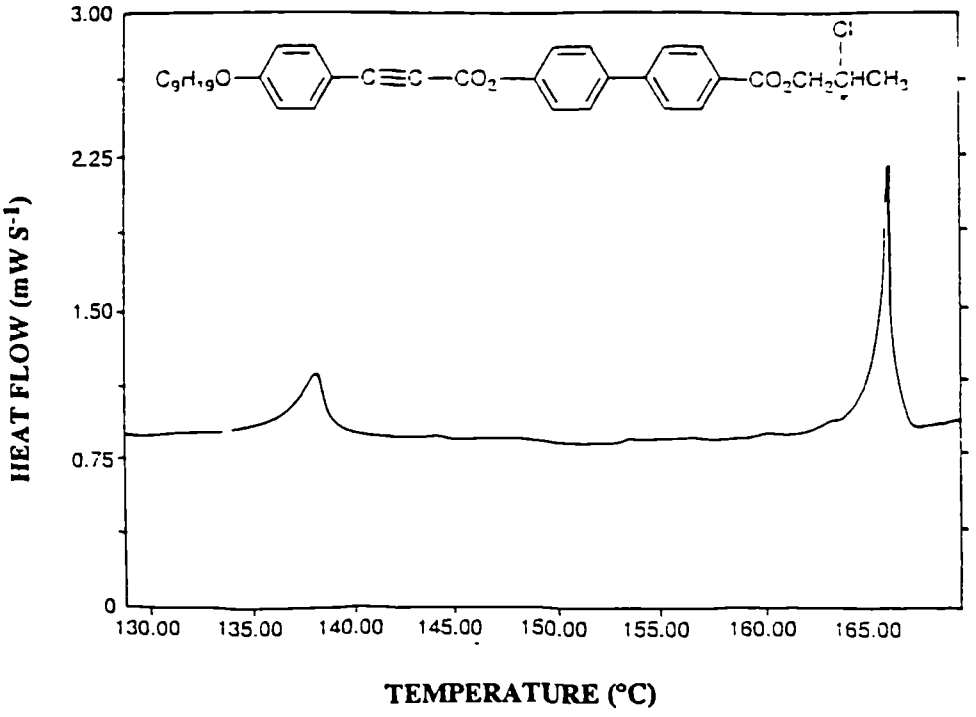


Figure 56. The Heating Cycle of *(S)*-2-Chloropropyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (123).

Plate 13. The Texture Observed at the Point of Inversion of Helical Twist Sense in Cholesteric Phase of (S)-2-Chloropropyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate, Compound 123 (150 °C).

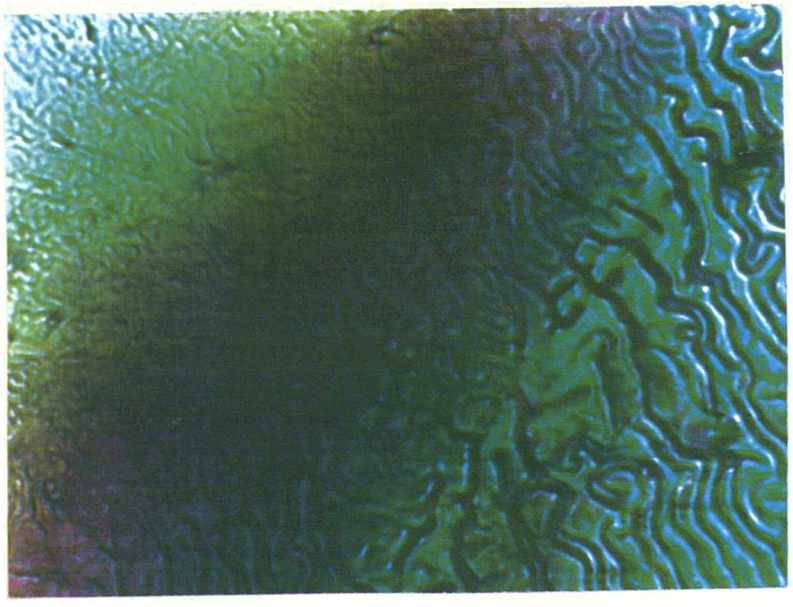


Plate 14. The Contact Region Observed Between *(S)*-4'-Decyloxybiphenyl-4-yl 4-(2-methylbutyl)benzoate and Compound 123 (152 °C).

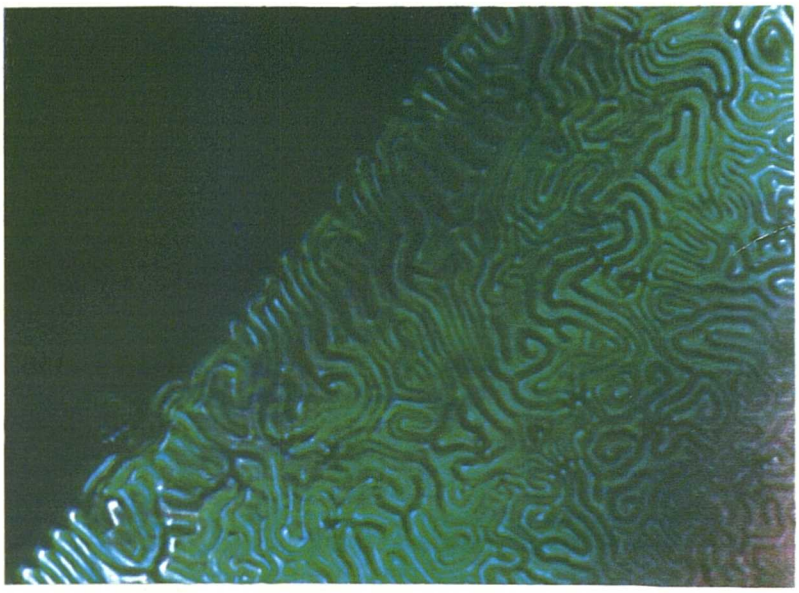


Plate 15. The Contact Region Observed Between *(S)*-4'-Decyloxybiphenyl-4-yl 4-(2-methylbutyl)benzoate and Compound 123 (145 °C).

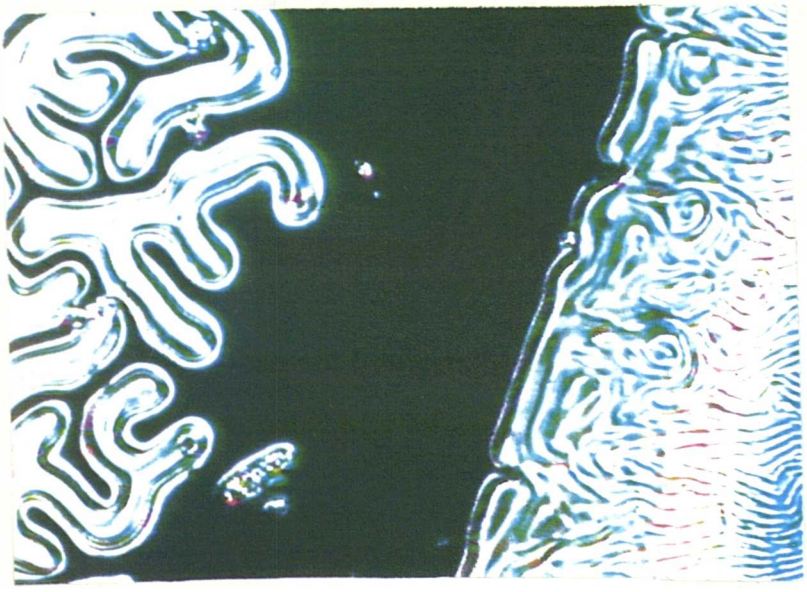


Plate 16. The Contact Region Observed Between *(S)*-4'-Decyloxybiphenyl-4-yl 4-(2-methylbutyl)benzoate and Compound 123 (141 °C).

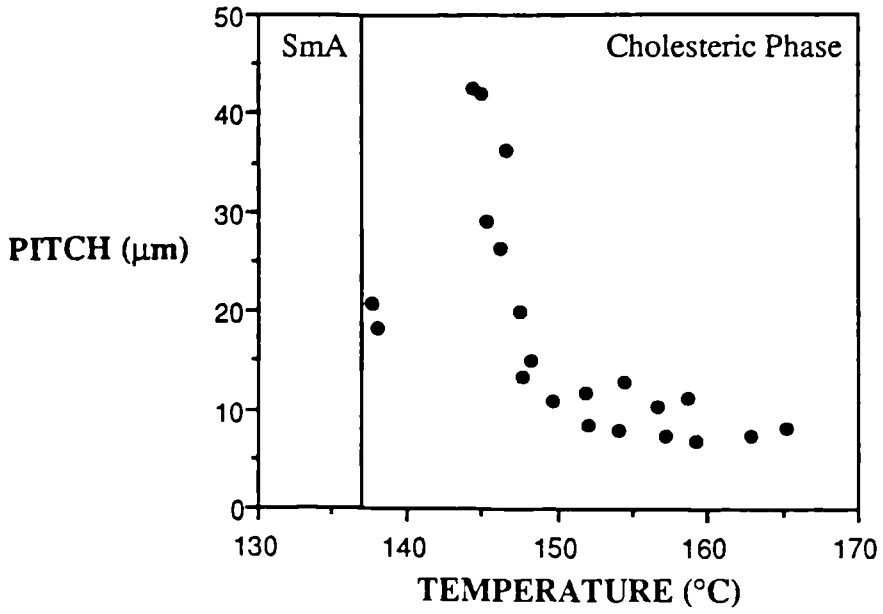


Figure 57. Pitch Length as a Function of Temperature in the Cholesteric Phase of Compound 123.

From figure 57 it can be seen that the pitch diverges in the temperature range of 140 to 145 °C. The reciprocal plot shows this value is approximately 141 to 142 °C, which is in agreement with textural observations made on the mesophase.

It is clear that compound **123** exhibits an inversion of helical twist sense in its cholesteric phase. Although this is not the only material reported in the literature[77] that exhibits this unusual phenomenon, it is possibly the first to show this behaviour when the molecule itself contains a single chiral centre in its structure. For instance, a previously reported material 4-(*2(S),3(S)*-epoxyhexyloxy)phenyl 4-decyloxybenzoate, which has two sequential chiral centres, also shows a helix inversion in the cholesteric phase[77]. The structure of this material is such that the two chiral centres form part of an oxirane ring, which may be considered as a single chiral unit. The structure of this material is shown in figure 59, where it can be seen that both chiral centres associated with the epoxy residue have an absolute spatial configuration that can be designated as *(S)*.

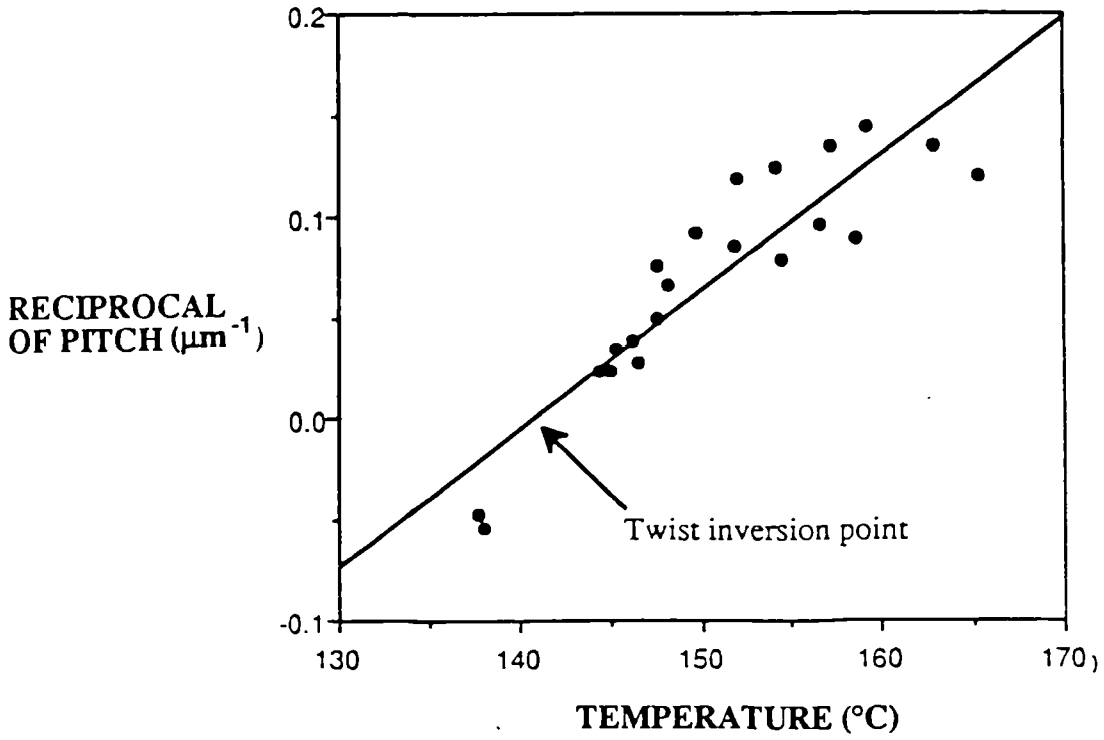


Figure 58. Reciprocal of Pitch as a Function of Temperature in Compound 123.

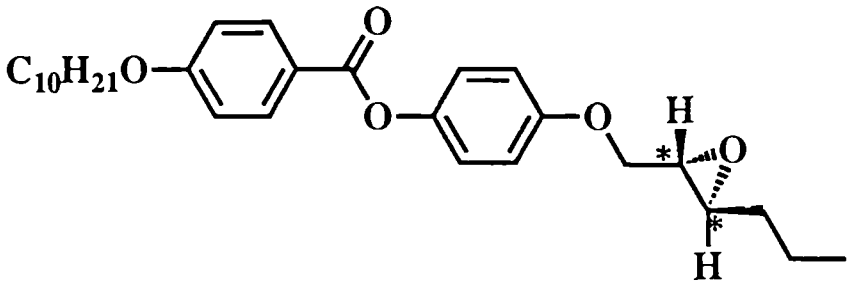


Figure 59. An Epoxide That Undergoes a Helix Inversion in its Cholesteric Phase.

As noted earlier, a simple rule exists that relates the absolute spatial configuration, the helical twist sense, and the parity, for cholesteric phases[36]. These relationships are as follows:

Rod ReL

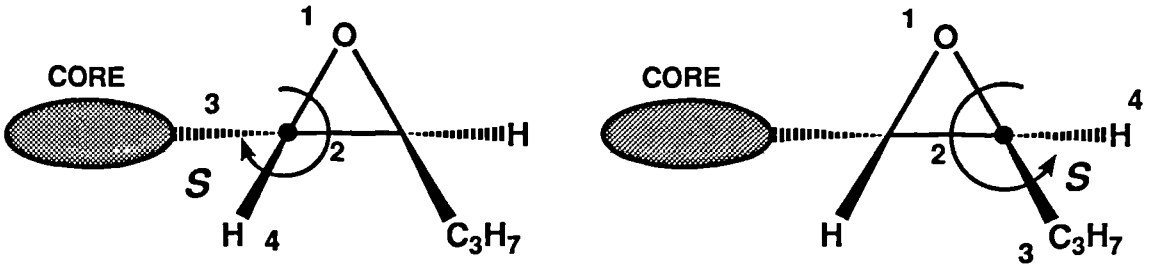
SoL Sed

In the light of this property-structure correlation, the properties of the epoxide can now be examined. For the chiral centre closest to the core, the absolute spatial configuration is *(S)*, the parity is odd (o), and so the helical twist sense for this chiral centre should be laevorotatory (*ℒ*), leading to a right-handed helix. When assessing the second chiral centre the situation is found to change. The absolute spatial configuration is still *(S)*, but this time the parity is even (e), leading to a twist sense that is dextrorotatory (*𝒹*), and consequently a left-handed helix. Therefore the chiral centres in the epoxide when treated individually should have opposed twist senses. The situation, however, is further complicated in the case of an epoxide because both of the chiral centres are connected by an oxygen bridge in the three-membered oxirane ring. This ties the chiral centres together and means they effectively act as one unit.

If the Cahn, Ingold and Prelog[16,17] labelling system for chiral centres is now considered, priority is given to the ring structure that contains the asymmetric atoms. This causes a shift in the priority ordering of the mesogenic core (priority 3 to 2) relative to the off-axis oxirane oxygen atom for the two sequential chiral atoms of the oxirane structure, as shown in figure 60. As a consequence of this shift in priority, in accordance with Gray and McDonnell's rules[36], this epoxide unit should be considered as equivalent to an *RS* system if the molecular core and terminal chains are designated as priorities 1 and 2 respectively. This would then give classifications of the chiral centres as *Ro𝒹*, *Se𝒹* on moving down the terminal chain, hence, the twist senses of the two centres should be additive. This analysis serves to emphasise the problems associated with the labelling of atoms in the Gray and McDonnell twist correlation, and that care should be taken when using the rules to predict the properties of materials.

Furthermore, it should be remembered that the labelling system used to define the spatial configuration is, however, dependent solely on oxidation number and not on polarity or

steric shape. In the case of the epoxide, if just the steric shape and the off axis location of the oxirane oxygen atom relative to the core is examined, it is clear that the two chiral centres will have additive polar and steric properties. Hence, they should not compete with one another to produce a twist inversion.



Priority of the core changes from 3 to 2 on sequential labelling of the two chiral centres

Figure 60. The Absolute Spatial Configurations (Priority Labelling) of the Asymmetric Atoms in a Chiral Oxirane Ring of a Liquid Crystal System.

Alternatively it may be possible to rationalise the twist inversion by examination of the steric effects. For example, the molecules in the cholesteric and certain smectic phases are known to be in dynamic motion such that they are rotating rapidly about their long axes on a time scale of 10^{11} sec^{-1}. However, because of the bulky size of the oxirane ring it is plausible that the rotational motion of this unit (and possibly of the molecule as a whole) about the long axis is not totally free, and therefore the molecules spend slightly more time in various preferred conformations and orientations. Thus, the time averaged picture of the mesophase may be one where there are a number of slightly more stable rotational species. However, as the molecules are in dynamic motion, the species will be expected to be interconvertable *via* relatively small energy barriers. Consequently, the concentrations, and hence the number densities, of the various species will be temperature dependent. Now if a situation is considered where two competing classes of species exist which have opposite helical twist senses and "twisting powers"; as the temperature of the

sample is altered the relative populations of each species could change, and in the process the helical driving forces of the two classes may be internally compensated for by one another. At the compensation point the pitch of the mesophase diverges, and the helix will change sign.

Conformational models of this type were first used by Patel and Goodby to explain polarization sign reversals in the *(S)*-2-methylbutyl 4'-alkanoyloxy-4-biphenylcarboxylate ferroelectric liquid crystals[72,146], and later adapted by Komitov *et al* to explain a sign reversal of the electrooptic coefficient in the smectic B* phase of certain epoxides[77]. Thus in the related phenylpropiolates, we can define three extreme conformational structures produced by rotations about the C1 - C2 bond (labelled A , B and C in figure 61) for which there will be differing dipole directions and different steric structures.

In conformer C, the sizes of the chloro and methyl substituents are rather similar and they are positioned on equivalent, but opposite sides, of the long axis. Thus, it might be expected that the steric effects of the two off-axis substituents in this conformer could compensate for one another. However, this is not the case for conformers A and B where either the chloro or the methyl substituent is located on the long axis of the molecule. In these two situations, therefore, it is quite possible that the extreme conformers A and B could produce opposing helical twist senses, based on steric effects. For example, if the Newman projections of the two species are compared it can be seen that in conformer A where the terminal methyl group is included in the long axis of the molecule, chlorine points off to the right-hand side, whereas for the reversed situation, conformer B, with chlorine in the long axis the methyl group now points on the opposite, left-hand, side of the long axis. If the helix direction is sterically driven then its twist sense will be dependant on the relative concentrations of such conformers in the pure material, and as noted above it is expected that the twist senses of conformers A and B will oppose one

another causing a twist inversion. However, the point at which the pitch of the cholesteric helix diverges would not necessarily occur at a 50:50 concentration of the two species A and B, as the two conformers will have different "twisting powers". For example, if conformer A induces a very short pitch whereas conformer B induces a very long pitch, the inversion point will occur at a concentration of conformer A that is much less than 50 %.

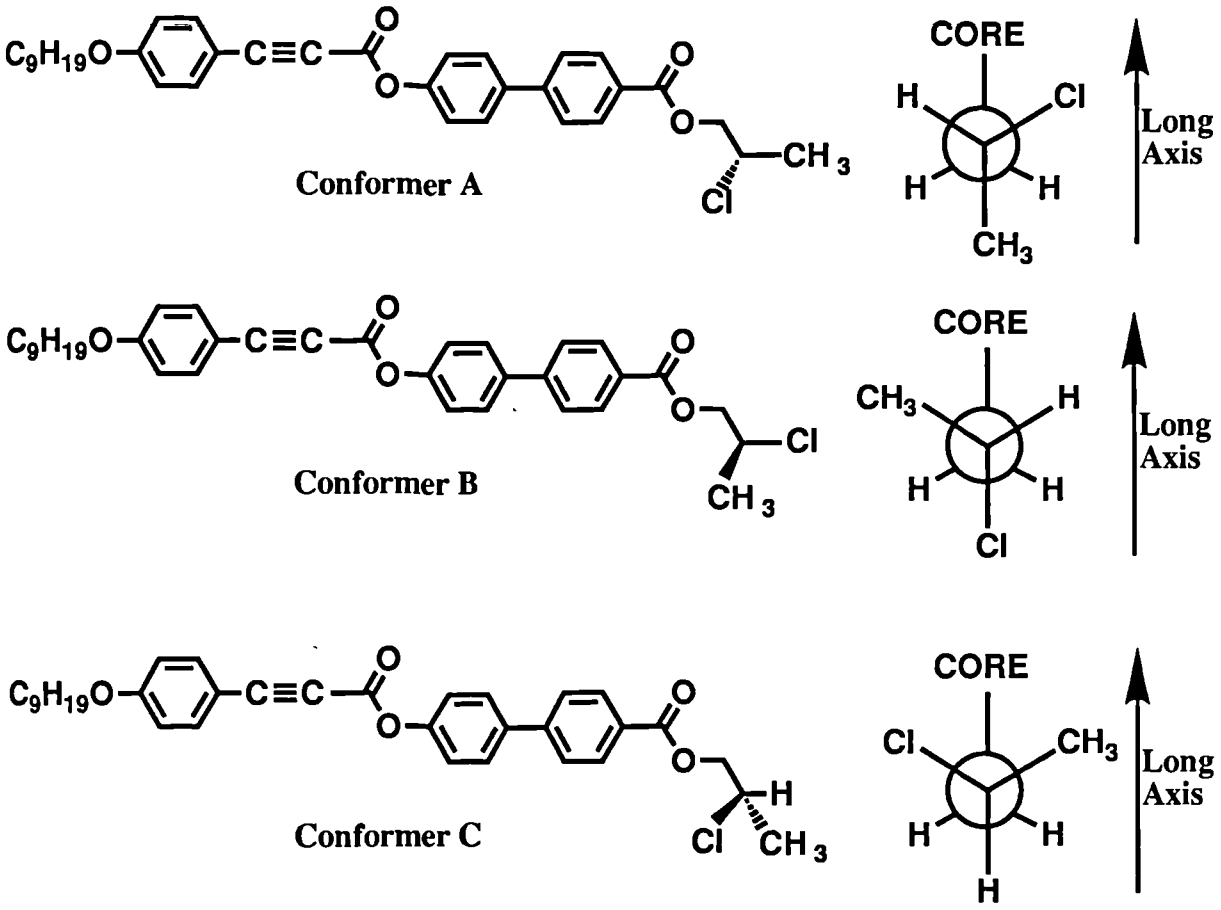
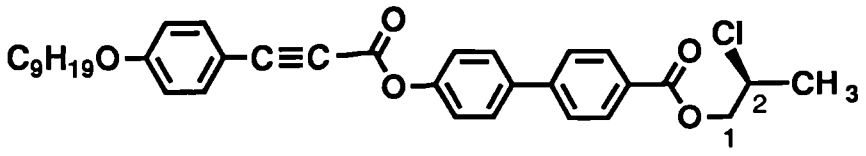


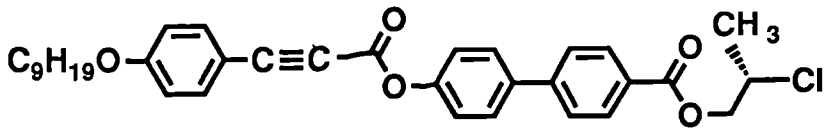
Figure 61. Three Extreme Conformer Species of the Chiral Phenylpropiolate System.

This argument can be extended further to include conformational structures for rotations about the C1 - O bond adjacent to the ester linking group. In this analysis the rotational isomers about the C1 - C2 bond must also be considered for each minimum energy position for rotations about the C1 - O bond. For example, figure 62 shows the three

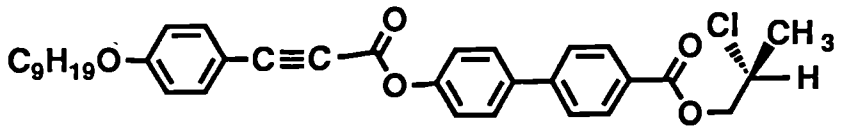
minimum energy conformers for one particular rotation about the C1 - O bond. Each conformer illustrated in figure 62 will have the opposite dipole and steric orientation relative to its corresponding "ground state" all *trans* isomer shown in figure 61. Thus, a competition between conformers exists for the secondary structures in a way similar to that obtained for the primary all *trans* conformers. However, it should be noted that such secondary structures will have substantially higher energies because of the increased steric hindrance.



Conformer A'



Conformer B'



Conformer C'

Figure 62. Three Extreme Conformer Species of the Chiral Phenylpropiolate System for One Particular Rotation About the C1 - O Bond.

A similar effect was found for the polarization inversion point in ferroelectric liquid crystals. In the *(S)*-2-methylbutyl esters of the 4'-n-alkanoyloxy-4-biphenylcarboxylic acids polarization inversions were found to occur, which were ascribed to conformational changes in structure, as shown in figure 63[72,146].

Again two extreme interconvertible conformational species were assumed to be present that have opposite polarization directions, and therefore the P_S was found to fall to zero when the two species compensated for each other. The temperature dependence of the concentration of the two species was assumed to affect the magnitude and direction of the polarization in the following way;

$$P_S = [P_A e^{-\Delta E/kT} + P_B(1- e^{-\Delta E/kT})] (T_C-T)^{\alpha}$$

where P_A and P_B are the intrinsic polarizations of conformers A and B, ΔE is the activation energy barrier for the transformation from A to B, T_C is the A to C* transition temperature and α is an exponent which has a theoretical value of 0.5. The term (T_C-T) reflects the temperature dependence of the polarization, which is dependent to some degree on the tilt angle of the phase.

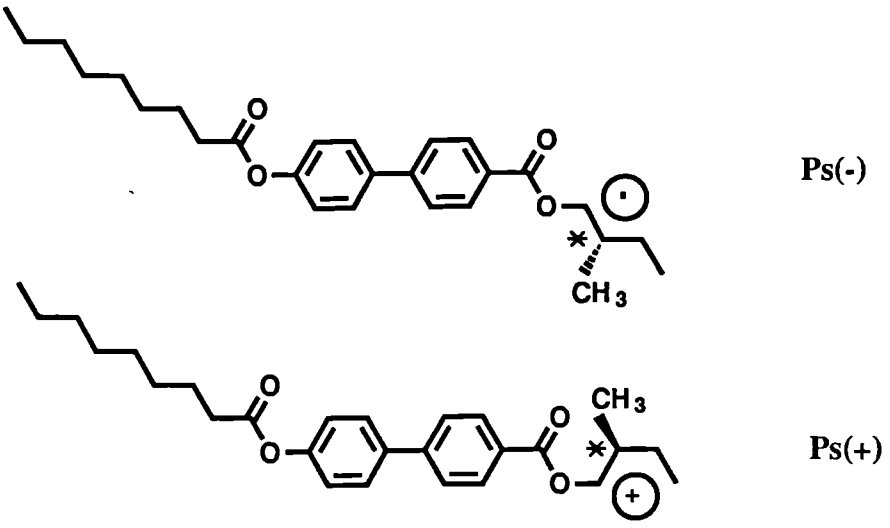


Figure 63. Postulated Reversal of the Polarization Sign in a Ferroelectric Liquid Crystal Caused by Competition Between Conformers of Differing Polarization Directions.

An equation similar to the one which was originally used to describe polarization inversions in the ferroelectric smectic C* phase may be analogously developed for use in

helix inversions. Computer modelling techniques can be used to develop this further and are currently being used to describe the properties of materials[147].

At this point it is interesting to note that on extending the terminal alkyl chain associated with the chiral centre no inversions are seen in the cholesteric phase (see later in this chapter). This suggests that in order for this phenomenon to occur the chiral centre must be free to rotate to give different conformers. Also, it must be remembered that a time averaged picture is being presented and that there are many interconverting species (conformers). Thus, using a model involving two conformers may prove in fact to be over simplified.

In the case of compound **124** (dodecyloxy homologue) a helix inversion in the cholesteric phase was also seen to occur, but the upper cholesteric phase had a very narrow temperature range (the clearing point is lower than in compound **123**). The material, therefore, quickly progressed to the nematic on cooling from the isotropic liquid, and on further cooling a cholesteric texture was once again found. The twist sense of this lower helical phase was shown to have the same twist sense as the lower cholesteric in compound **123**. This was noted by direct polarimetry, and then confirmed by contact studies.

8.3 Esters Based on the 2-Chloro-3-methylbutyl Chiral Moiety (Series III and IV).

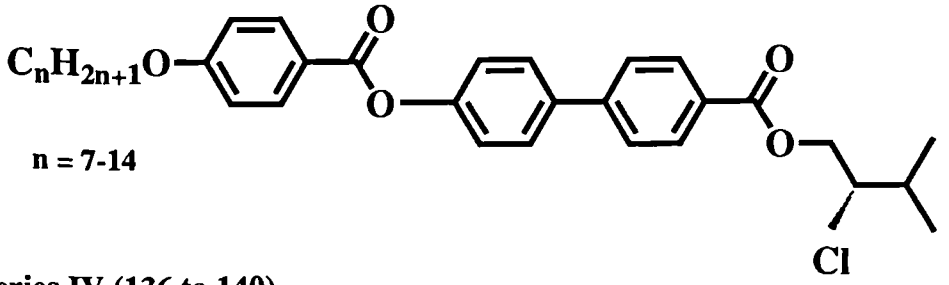
The second series of materials to be discussed are the di-esters, based on the 2-chloro-3-methylbutyl chiral moiety (**128-140**). Once again two mesogenic core structures were used which differed only in the inclusion or not of a triple bond in the structure (the materials in series IV, compounds **136-140**, included a triple bond in their structure). At the opposite end of the molecule from where the chiral centre was located, as with the materials in series I and II (**115-127**), a normal alkoxy chain was located. This chain was

varied in length, 7-14 carbon atoms for the alkoxybenzoic acid derivatives (series III), and 9, 12, 14, 16, or 18 carbon atoms for the alkoxyphenylpropiolic acid derivatives (series IV). The general structures of these compounds are illustrated in figure 64.

The structure of these materials, in comparison with the previous compounds based on a 2-chloropropyl chiral moiety, differ for two reasons. Firstly, the alkyl chain attached to the peripheral side of the chiral centre (an isopropyl group) is one carbon longer, and secondly it contains one branching position (a methyl group). The freedom of rotation associated with the chiral centre is likely therefore, to be more restricted in comparison with the previously discussed materials from series I and II. The time averaged dipole associated with the optically active centre, and with the molecule as a whole is likely to be larger, thereby enhancing the chirality of the system. As the degree of chirality in the system is increased, a number of factors may occur. Firstly, the helical pitch observed in any phases that display *form* chirality should be shorter, which in the case of the cholesteric phase would possibly lead to the presence of blue phases at the transition from the isotropic liquid. And secondly, there should be an increased possibility of seeing a TGB A* phase, mediating the transition from the cholesteric phase to the smectic A phase, assuming that the layer strength is still sufficiently weak to support such a phenomenon.

Firstly, the benzoate esters will be considered (**128-135**). Table 6 shows the transition temperatures associated with these materials (obtained by optical microscopy), and figure 65 depicts the transitions temperatures as a function of alkoxy chain length graphically. It can be seen from table 6 and figure 65 that the first three materials (**128-130**) in series III possess an isotropic to cholesteric to smectic A to smectic C* phase sequence, whereas, the compounds with longer alkoxy moieties (**131-135**) have an isotropic to smectic A to smectic C* phase sequence.

Series III (128 to 135)



Series IV (136 to 140)

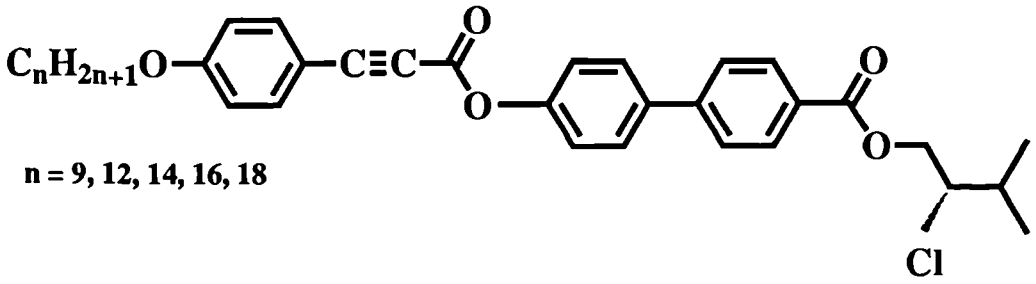


Figure 64. The Structures of the Di-Esters Based on a 2-Chloro-3-methylbutyl Chiral Moiety.

No.	n	Mpt.	I-BPIII	BPIII-BPII	BPII-BPI	BPI-Ch	Ch-TGB	TGB-S_A	I-S_A	S_A-S_C*	Rec.
128	7	94.7	164.6	164.4	164.0	159.5	158.5	158.5		123.8	51.5
129	8	97.0	164.1	163.9	163.6	160.7	160.2	160.2		125.5	67.7
130	9	98.5	161.3	161.1	160.8	160.0	159.7	159.7		128.7	71.0
131	10	77.1							159.0	125.7	48.6
132	11	64.2							159.1	126.7	40.7
133	12	63.8							157.1	126.9	46.3
134	13	73.5							156.1	125.9	48.5
135	14	68.7							149.9	117.9	48.1

Table 6. The Transition Temperatures (°C) for the *(S)*-2-Chloro-3-methylbutyl 4'-(4-alkoxybenzoyloxy)-4-biphenylcarboxylates (128 - 135).

In the materials that exhibited a cholesteric phase, the transition from the isotropic liquid was mediated by blue phases. This in itself is an indication of an enhanced degree of chirality in the system, and a shortening of the cholesteric pitch (< 5000 Å), with respect to the materials in series I (**115-122**). At the transition from the cholesteric phase to the smectic A phase, for compounds **128** to **130** a transitory TGB A* phase was also observed. This phase was instantly recognisable from its *vermis* or filamentary texture[148]. The presence of this phase suggests that the chirality of the system is increased relative to the previous series of analogous materials (series I), and also that the layer strength is relatively weak. The cholesteric phase is seen to persist in this series until the alkoxy chain length reaches nine carbon atoms, which is one greater than that observed for the analogous materials based on a 2-chloropropyl chiral moiety (**115-122**). On further cooling a smectic C* phase is formed in all of the materials, but this time it is enantiotropic in nature. The helical properties of the smectic C* phase proved to be extremely interesting and so will be discussed in depth later. Firstly, a comparison of the nonyloxy member of this series of compounds (**130**) with the analogous compound from series I (**117**) will be made, and is shown in figure 66.

It can be seen from figure 66 that as the chain length and degree of branching is increased on the peripheral side of the chiral centre, the clearing point is seen to drop quite markedly, as does the temperature range of the smectic A phase. The temperature range of the chiral smectic C* phase, however, is substantially increased, as expected. The enhanced chirality in compound **130** also leads to the formation of blue phases above the cholesteric phase, and of a TGB A* phase at the cholesteric to smectic A transition. As the TGB A* phase was of particular interest the clearing point transitions were studied extensively using thermal techniques (DSC). The results of these studies will be discussed later in this chapter when a comparison is made between selected materials taken from the first five series of benzoate esters (see section 8.6).

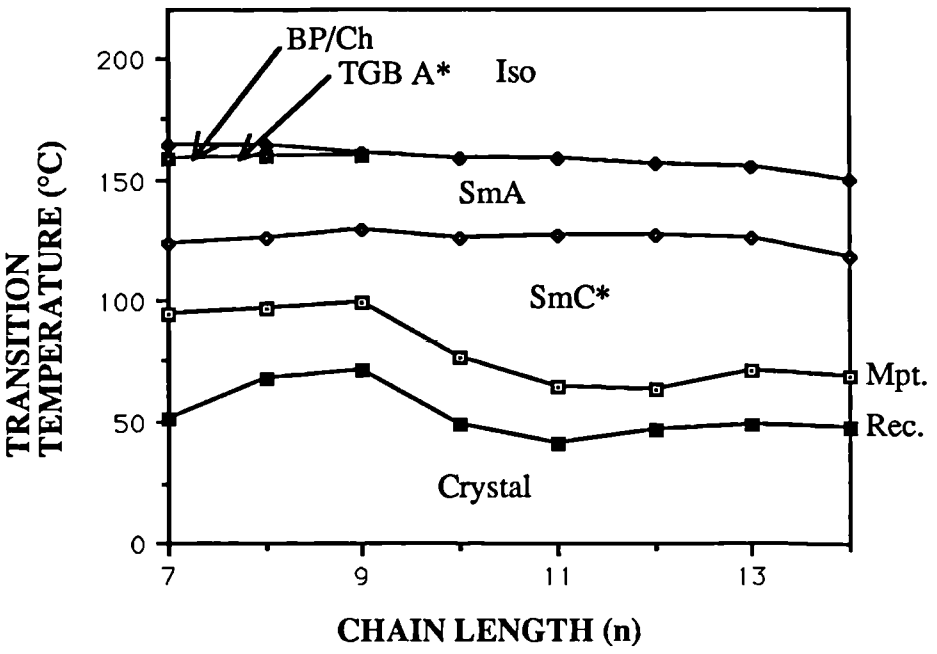


Figure 65. Transition Temperatures Versus Alkoxy Chain Length for Materials (128-135).

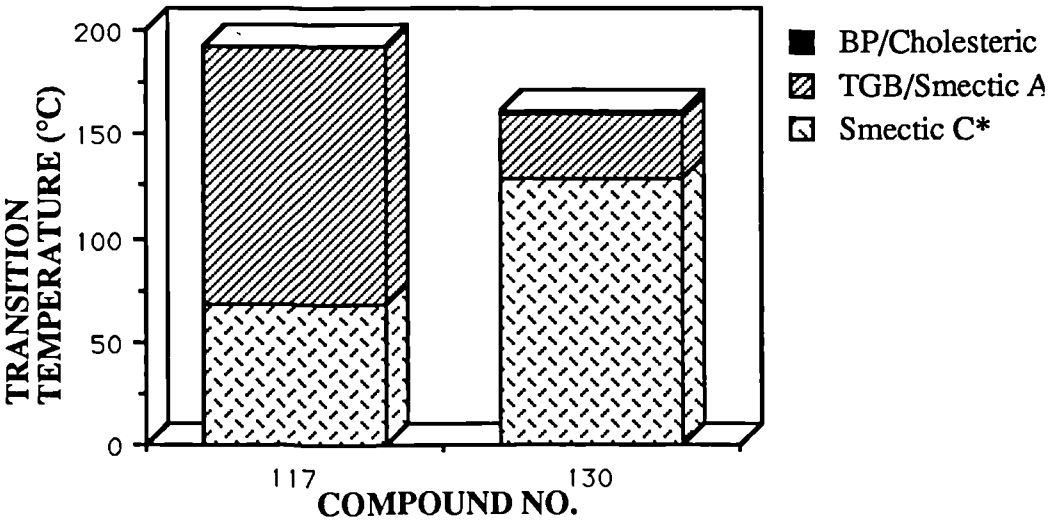


Figure 66. A Comparison of the Phase Behaviour in Compounds 117 and 130 (the Nonyloxy Homologues of Series I and III).

The helix direction in the chiral smectic C* phase of the materials in series III proved especially interesting. The results, which were obtained by direct polarimetry of free standing films for the materials are detailed in table 7, along with the direction of the spontaneous polarization for some materials, determined according to the method described in chapter 5.

It appears therefore that the general trend in these materials is one where the helical twist sense, in the chiral smectic C* phase, alternates from being left- to right-handed, as the alkoxy chain alternates from odd to even numbers when the series is ascended. Compound **130** seems to be the exception to this rule, where the helix in the C* phase actually appears to invert on cooling the material (and reverts back on heating). It was noticed that in some of the other materials studied the texture was also very mobile just below the transition from the smectic A phase with a deep coloration being apparent, indicating that the same type of helix inversion may be occurring for other compounds, but very close to the smectic A to smectic C* transition. The helix direction in the smectic C* phase was exceptionally hard to evaluate by polarimetry, particularly close to the A to C* transition. An attempt to measure the pitch as a function of temperature in compound **130**, by determining the distance between the dechiralization lines, unfortunately failed as a suitable texture could not be achieved.

In order to confirm that the helix direction was indeed alternating from left- to right-handed, a contact between compounds **131** and **132** (the decyloxy and undecyloxy members of series III) was made in the form of a free-standing film. On cooling into the smectic C* phase a characteristic pseudo-homeotropic texture formed. Unfortunately, defects along the boundary between the two materials were formed, and despite numerous attempts to 'pull' a defect free film, they always seemed to be present.

No.	n	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
128	7	S	e	*L*	RH	-ve	
129	8	S	e	*d*	LH	-ve	
130	9	S	e	*d**	LH*	-ve	+@
131	10	S	e	*d*	LH	-ve	
132	11	S	e	*L*	RH	-ve	+
133	12	S	e	*d*	LH	-ve	+
134	13	S	e	*L*	RH	-ve	
135	14	S	e	*d*	LH	-ve	

* The helix direction in this material was initially determined as being left-handed in the smectic C* phase, by direct polarimetry of the sample as a free-standing film. At approximately 126 °C, the bluish texture of the phase became very mobile, and seemed to wash continuously across the field of view. This was accompanied by an intense change in the birefringent colour of the sample, before the texture once again reverted to a blue colour. The textures of the higher and lower temperature modifications were found to be similar. When the helical twist sense was again determined, however, (below 126 °C) it appeared to have inverted relative to the higher temperature determination, and the phase was found to have a right-handed helix at the lower temperature.

@ direction determined at 127 °C and at 65 °C in order to confirm that the polarization had not inverted along with the helical twist sense (the direction was positive in each case).

Table 7. Chiral Properties Associated with the Smectic C* Phase of the Materials in Series III (128-135).

There was therefore little chance of observing the inversion phenomena at the boundary in order to confirm that the sign of the helix had changed. Polarimetry of the 'contact' of free standing films once again suggested that the materials were of opposite twist senses.

The experiment was then repeated between glass slides, but difficulties were again encountered in obtaining suitable textures. Polarimetry studies proved yet again that the helical twist senses were opposite in compounds **131** and **132** (the decyloxy and undecyloxy homologues of the materials in series III).

In order to determine if the tilt angle was reduced to zero at the helix reversal point in compound **130**, the tilt angle was measured as a function of temperature. The cell spacing used was 5 μm, and the switching voltage was 10 V dc. The results of this study are illustrated in figure 67 from which it can be seen that the plot of tilt angle versus temperature shows normal behaviour, with the tilt angle rising quite steeply as the temperature is reduced and then saturating. It can be assumed therefore that a radical change in tilt angle does not play a part in the helix reversal in this material.

For this series it appears that there is an odd/even effect with respect to the helix direction in the smectic C* phase. The reasons for this phenomenon are not clear at the moment, but may be linked to how easily the odd and even members can pack within a discrete layer, possibly in a similar manner as to how the polarization direction in the ferroelectric C* phase can be somewhat dependent on whether the molecules in the layers have a high or low tilt configuration[66]. It should be noted, however, that this system is somewhat different as the polarization direction appears to remain constant in these materials. The direction of the spontaneous polarization obeys rules suggested by Goodby and Leslie[39] that relate the polarization direction to the absolute spatial configuration of the chiral centre, the parity, and the inductive effect at the chiral centre.

The twist inversion in the smectic C* phase of compound **130** can be rationalised in a similar manner to how the twist inversion in the cholesteric phase of compound **123** (the nonyloxy member of series II) was analysed, i.e., by using a model based on the relative

thermal stability of a number of different conformers. In the case of compound **130**, however, the model is slightly more complex as there are more possible structural variations to consider.

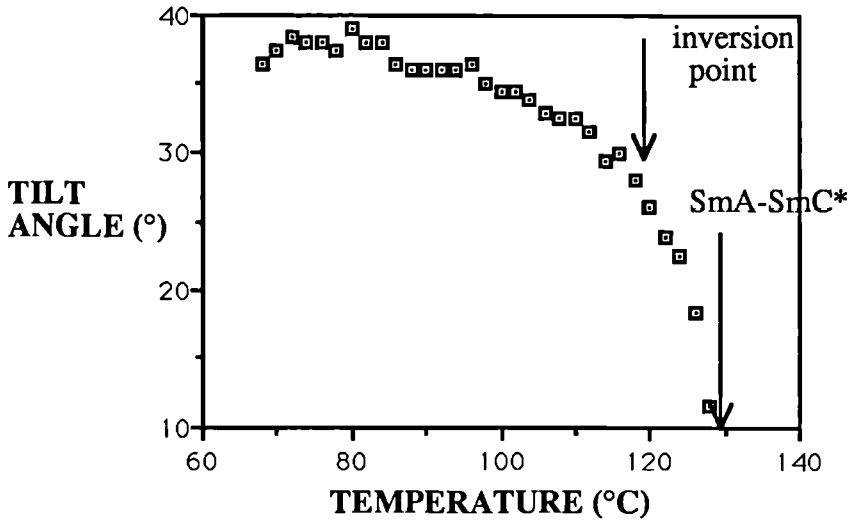


Figure 67. A Plot of Tilt Angle Versus Temperature in Compound 130 (the Nonyloxy Homologue of Series III).

Figure 68 shows the possible principle conformers that may be formed by rotation about the C1 - C2 bond, these giving a desirable all *trans* configuration and so being the most stable. As well as rotation about the C1 - C2 bond, rotation about the O - C1 bond may also occur leading to three possible secondary conformers. The secondary conformers will, however, be less energetically stable as they all have gauche configurations. In addition there may be tertiary conformers associated with the position of the isopropyl group with respect to the long molecular axis which can be associated with either the primary or secondary structures. This gives rise rise to twenty-seven possibilities in all, nine for each primary structure. Some of the secondary and tertiary structures are illustrated in figures 69 and 70 respectively. The situation therefore, in this series of molecules, is extremely complex. On the one hand the helix direction is seen to be highly dependent on an odd/even effect of the terminal alkoxy chain associated with the opposite end of the molecule to where the chiral centre is situated, yet compound **130** is seen to

undergo an inversion in helical twist sense which can be rationalised using different conformations for the chiral entity. It must also be remembered that the system is not static and many interconverting structural species may exist, and so a complete picture is very difficult to reach.

The polarization direction is constant for all of the materials tested, and does not change when the helix inverts in compound **130**. This indicates that if the conformational model is used to explain the helix inversion, then the two or more competing conformations which cause a twist inversion must have the same polarization direction, or that one particular species must dominate the polarization direction, even at small concentrations. For example, conformer A" from figure 70 and conformer C" from figure 70 are likely to have the same polarization direction as the dipole associated with the chlorine atom points in the same direction in each case. The steric interactions, however, are somewhat different in each conformer leading to the possibility of an inversion in twist sense. The polarization direction may be predominantly dipolar driven, whereas the helix direction in the chiral smectic C* phase may rely more heavily on steric factors. As the polarization direction is the same for both compounds **132** and **133** (the undecyloxy and dodecyloxy members of series III), which conversely have opposing twist senses, a model involving high and low tilt arrangements of the molecules within the layers (which had previously been used to explain different polarization directions in certain materials[66]), may be used, but needs to be modified. Infact, the situation becomes impossible to reconcile unless one considers that the chiral end group and high/low tilt conformational effects occur at the same time, thereby leading to an extremely complex situation in which there are a number of competing conformational species within a given layer and that the positions of the molecules within the layers may also change depending on the relative concentrations of the different conformations of the molecules.

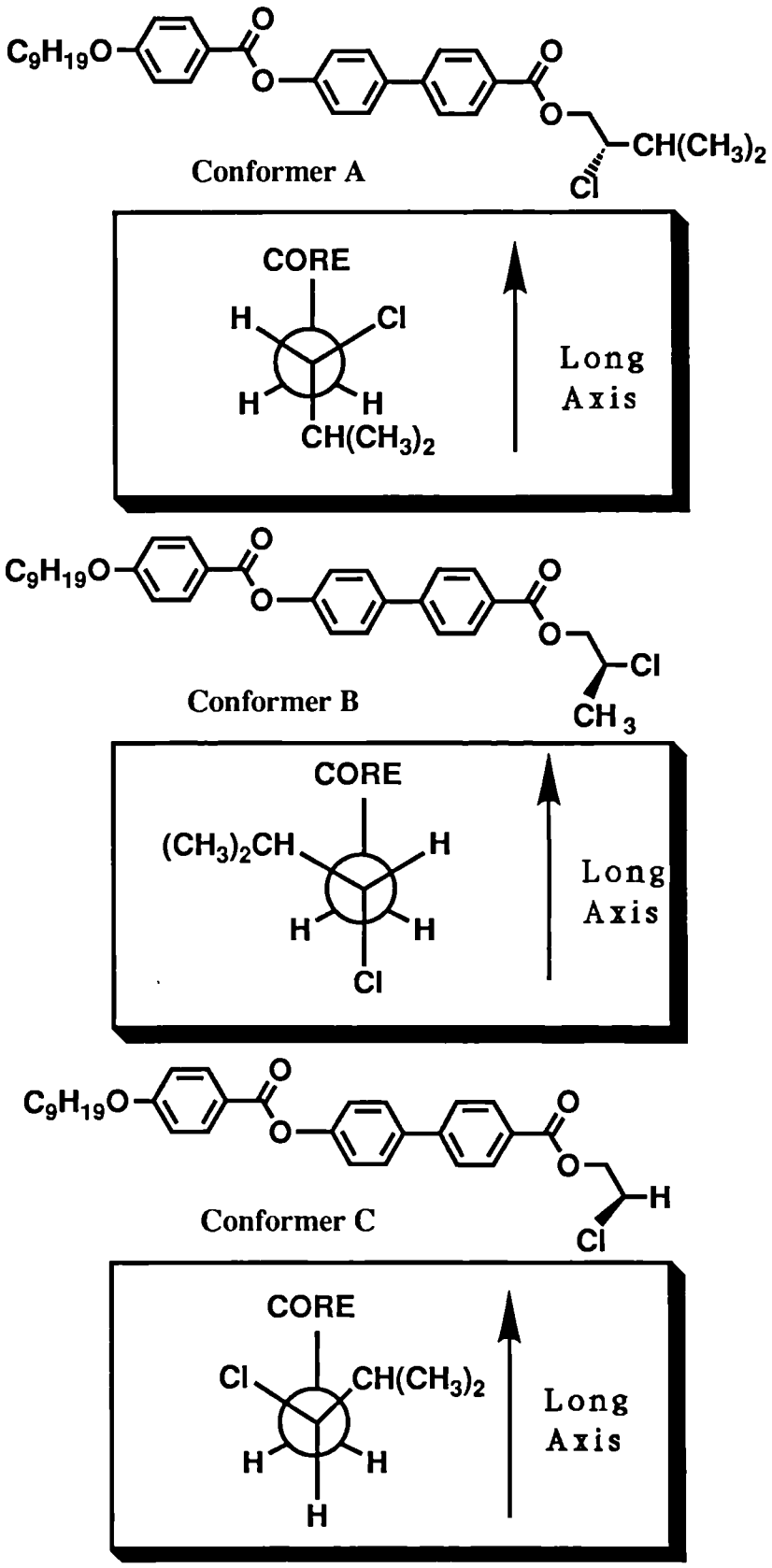
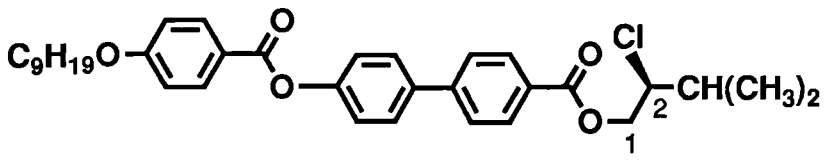
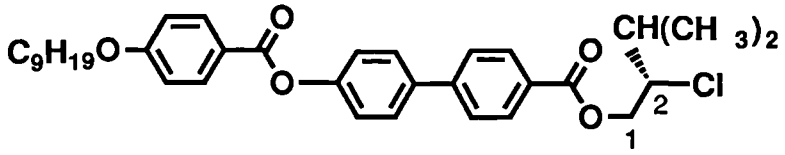


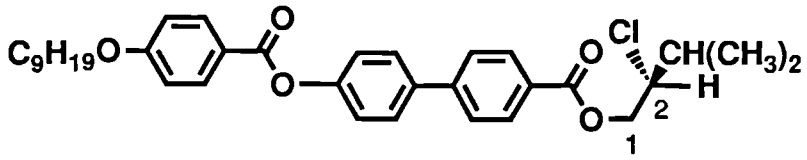
Figure 68. The Possible Primary Conformations Associated with Compound 130.



Conformer A'

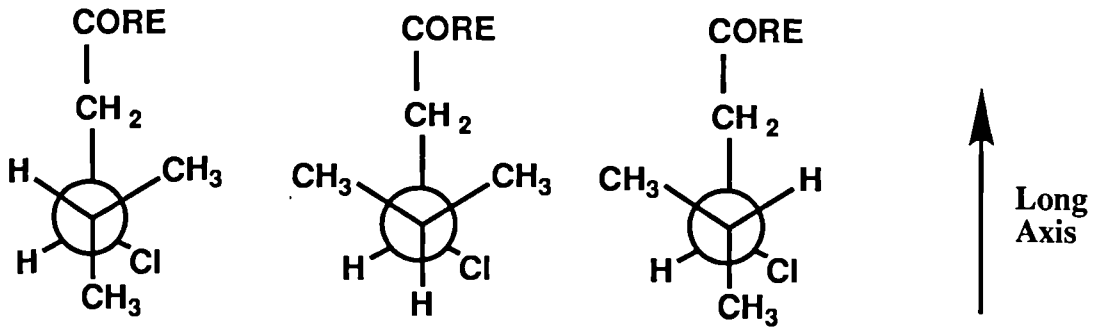


Conformer B'



Conformer C'

Figure 69. The Possible Secondary Conformations Associated with Compound 130.



Conformer A'' Conformer B'' Conformer C''

Figure 70. The Possible Tertiary Conformations Associated with Compound 130.

The materials that possess a triple bond within the core structure are now discussed (**136-140**). The phase transitions for these materials are shown in table 8, and figure 71, where it can be seen that the materials in series IV with a shorter alkoxy chain (**136-138**) possess an isotropic liquid to blue phase to cholesteric to TGB A* to smectic A to smectic C* phase sequence, whereas the two materials that possess relatively longer alkoxy chains (**139** and **140**) have a simple isotropic to smectic A to smectic C* phase sequence. The temperature range of the TGB A* phase in these materials is still quite short and was found to decrease slightly with increasing alkoxy chain

length. The blue phase/cholesteric temperature range is also seen to decrease with increasing alkoxy chain length. The temperature of the A to C* transition initially rises, reaching a maximum value of 125.8 °C in compound **139** (the hexadecyloxy homologue), and then falls slightly for the octadecyloxy homologue (**140**).

No.	n	Mpt.	I-BPIII	BPIII-BPII	BPII-BPI	BPI-Ch	Ch-TGB	TGB-S_A	I-S_A	S_A-S_C*	Rec.
136	9	81.5	135.1	134.9	134.5	134.1	111.6	110.5		82.5	69.8
137	12	86.2	130.6	130.5	130.3	128.6	122.1	121.5		94.5	73.4
138	14	71.6	127.2	127.2	126.8	124.9	124.2	123.7		97.7	53.1
139	16	62.1							125.3	98.5	44.8
140	18	63.5							123.6	98.1	57.6

Table 8. The Transition Temperatures (°C) for the *(S)*-2-Chloro-3-methylbutyl 4'-(4-alkoxyphenylpropioloyloxy)-4-biphenylcarboxylates (136 - 140).

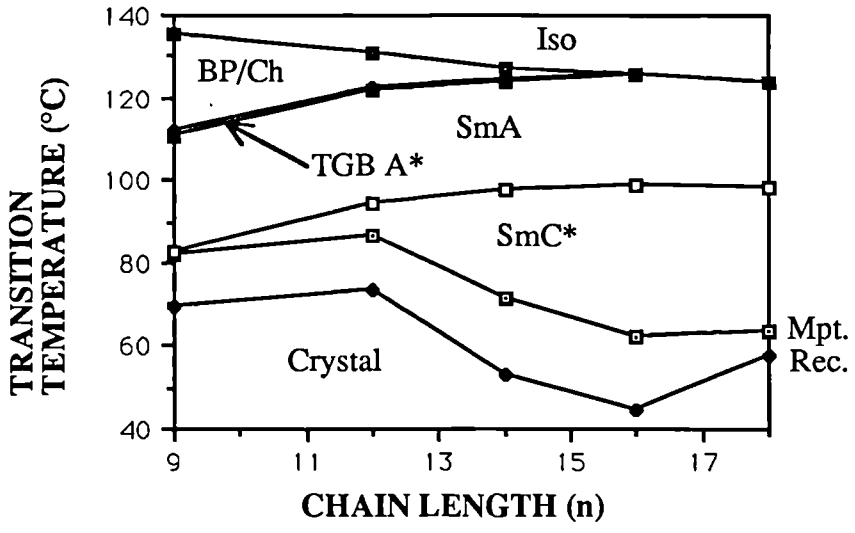


Figure 71. Transition Temperatures Versus Alkoxy Chain Length for Materials (136-140).

The thermal studies carried out on selected benzoate materials will be discussed later in this chapter. The results, however, were in general agreement with microscopic observations.

If a comparison is made between the nonyloxy member of this series (**136**), and the analogous compound from series III (**130**), a number of interesting features are found, and these are represented in figure 72.

Firstly, the clearing point and subsequent transitions to TGB A* or smectic A, and smectic C* are much reduced for the propiolate over the benzoic esters. The blue phase/cholesteric range is seen to increase quite considerably as does the TGB A* temperature range. The increase in the TGB A* temperature range is probably due to a reduction in layer stability rather than an increase in chirality, i.e., the chiral moieties are identical. This idea is supported by the fact that the blue phase temperature ranges in both compounds are of the same order (1.3 °C in the case of compound **130**, and 2.0 °C in the case of compound **136**). There is also a slight increase in the thermal stability of the A phase, and a corresponding decrease in the thermal stability of the smectic C* phase for compound **136** in relation to compound **130**. The reduction in the temperature range of the smectic C* phase may be due to the increased core length, which means that the terminal aliphatic chains can be considered as being relatively shorter for compound **136**. For example it is known that certain chain lengths favour the formation of tilted phases (with regard to the core size)[149]. The increased nematogenicity of compound **136** is possibly due to an increase in rotational freedom associated with the molecular core which tends to hinder the packing of the molecules into a lamellar structure. This of course is supported by the increase of the TGB A* temperature range, which relies on the presence of a weak layer ordering.

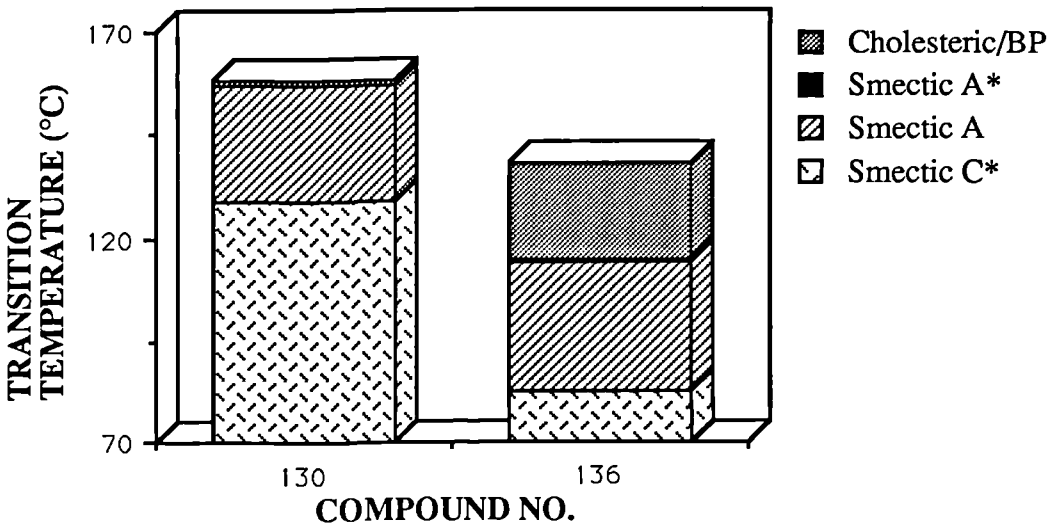


Figure 72. A Comparison of the Phase Behaviour of Compounds 130 and 136 the Nonyloxy Homologues of Series III and IV).

When the properties of the smectic C* phases of these materials were investigated (see table 9) it was found that each material could be classified as,

S e $\mathcal{L}$ RH Ps (+).

No.	n	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
136	9	S	e	$\mathcal{L}$	RH	-ve	+
137	12	S	e	$\mathcal{L}$	RH	-ve	
138	14	S	e	$\mathcal{L}$	RH	-ve	
139	16	S	e	$\mathcal{L}$	RH	-ve	
140	18	S	e	$\mathcal{L}$	RH	-ve	

Table 9. Chiral Properties Associated with the Smectic C* Phase of the Materials in Series IV (128-135).

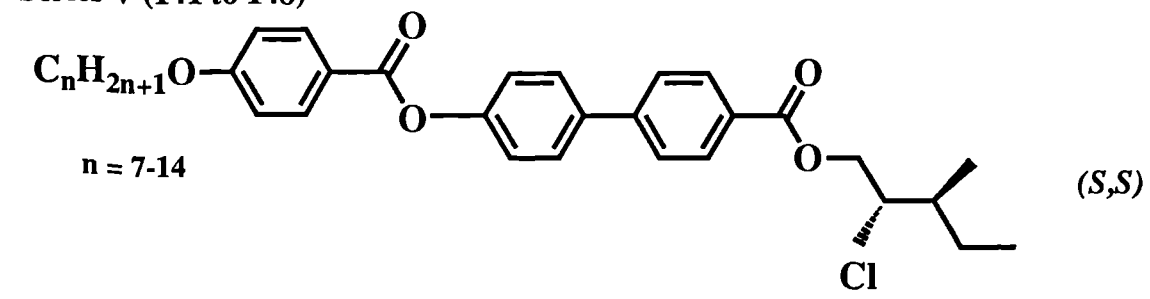
It is assumed that all the materials in this series have the same polarization direction that was determined for compound **136**, this direction being in agreement with predictions[39]. No anomalies were found in terms of twist inversions in any of the materials. The measurement of the spontaneous polarization for compound **136** with respect to temperature gave a value of 48 nC cm^{-2} at 10 °C below the Curie Point. A more detailed account of the polarization studies performed will be given later in this discussion, when the results obtained for selected materials will be expanded upon.

5.4 Esters Based on a 2-Chloro-3-methylpentyl Chiral Moiety (Series V, VI, VII, VIII).

The next four series of materials to be discussed (V to VIII) are based on a chiral moiety with two sequential chiral centres, in series V and VI the materials had chiral centres with an *(S,S)* configuration (**141-153**), whereas in series VII and VIII the materials had chiral centres with an *(S,R)* configuration (**154** and **155**). As with the compounds discussed earlier, materials were synthesized with and without a triple bond contained within the core structure. The general structures of the materials are shown in figure 73 for series V and VI, and figure 74 for series VII and VIII.

As the peripheral alkyl chain associated with the chiral centre is longer for these materials it was predicted that these compounds would exhibit a higher degree of chirality than that observed for the previous four series of materials (**115-140**). This would mean a shorter pitch for phases that possessed *form* optical activity, an increased blue phase temperature range, and a strong possibility for the enhancement of the TGB A* temperature range.

Series V (141 to 148)



Series VI (149 to 153)

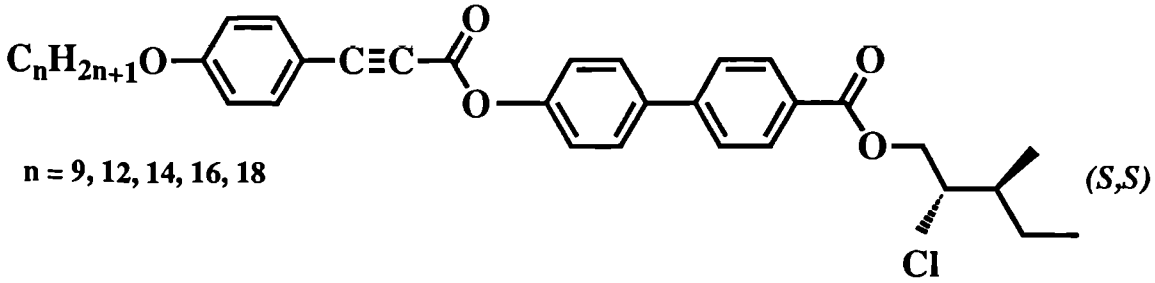
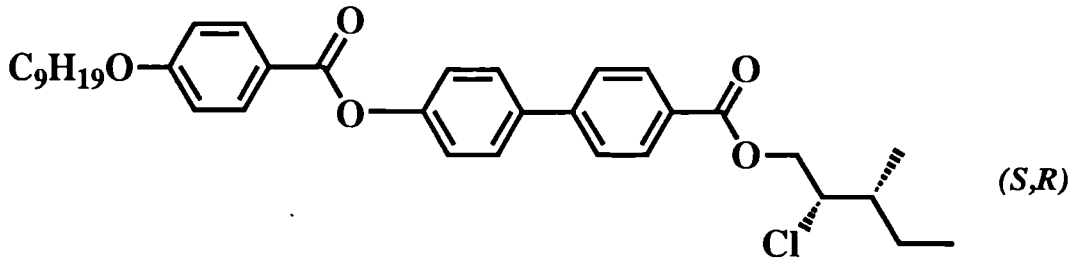


Figure 73. The Structures of the Di-Esters Based on an *(S,S)*-2-Chloro-3-methylpentyl Chiral Moiety.

Series VII (154)



Series VIII (155)

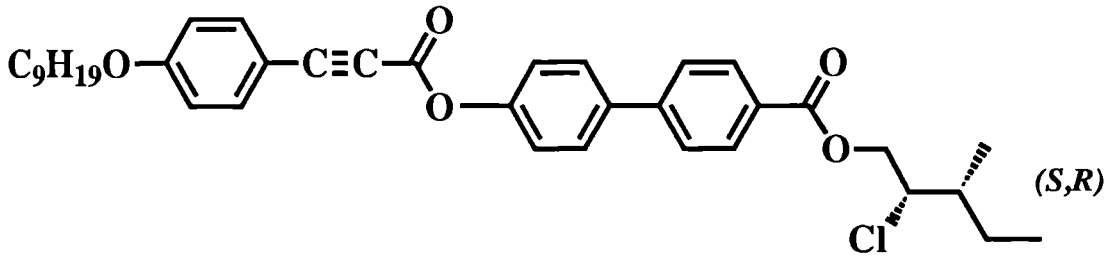


Figure 74. The Structures of the Di-Esters Based on an *(S,R)*-2-Chloro-3-methylpentyl Chiral Moiety.

It was not immediately obvious, however, what effect an additional chiral centre would have on the material properties. If the dipole associated with the first chiral centre is enhanced by the second chiral centre than one might expect the chirality to be increased.

It could, however, be possible that the two centres may oppose each other (in dipolar terms), and the effective chirality of the system may therefore be reduced. This argument is illustrated in figure 75 where the first structure shown (A), is one where the two chiral groups have additive dipolar properties, but opposing steric effects, i.e., the inductive effects of the methyl group and the chlorine atom add. This situation is not the case with the second structure illustrated (B), where the dipoles associated with the methyl group and the chlorine atom oppose each other, but the steric effects are additive. This situation of course does not take into account the fact that the system is not static, nor does it include any reference to a coupling of the lateral dipole of the chiral centre to the ester linkage, and if the second optically active centre (positioned furthest from the core) will affect this in any way. It does, however, illustrate how differences in properties may be explained in terms of the dipoles associated with two sequential chiral centres.

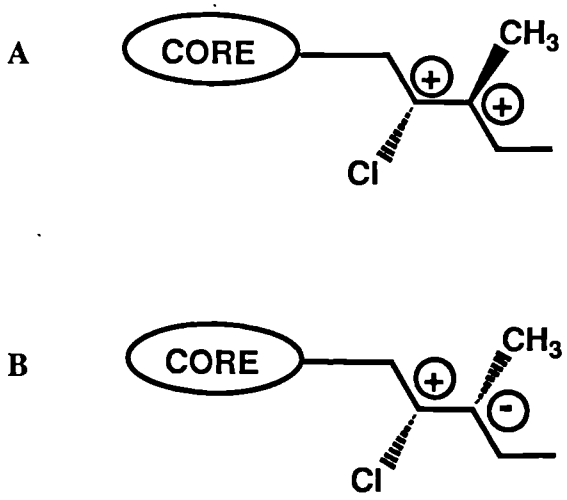


Figure 75. A Schematic Representation of the Dipoles Associated with *S,S* (Template A) and *S,R* (Template B) Chiral Centres.

In the first instance the benzoates with an *(S,S)* configuration of the two chiral centres will be considered (series V). The transition temperatures for these materials are illustrated in figure 76, and table 10.

No.	n	Mpt.	I-BPIII	BPIII-BPII	BPII-BPI	BPI-Ch	Ch-TGB	TGB-S_A	I-S_A	BPIII-S_A	BPI-S_A	S_A-S_C*	Rec.
141	7	80.8	157.6	157.3	156.7	147.2	145.8	145.1				107.2	53.3
142	8	91.5	158.4	158.1	157.6	152.1	150.9	150.3				118.1	63.5
143	9	89.6	155.8	155.3	153.8	151.5	150.4	150.1				123.9	54.7
144	10	63.8	154.5	154.2	153.9	151.6	151.3	150.9				124.7	43.4
145	11	62.5	151.8	151.3	150.9						150.5	125.3	45.2
146	12	61.0	150.7							150.6		126.1	45.6
147	13	64.2							148.6			125.2	47.3
148	14	64.2							148.0			125.2	44.5

Table 10. The Transition Temperatures (°C) for the *(S,S)*-2-Chloro-3-methylpentyl 4'-(-4-alkoxybenzoyloxy)-4-biphenylcarboxylates (141-148).

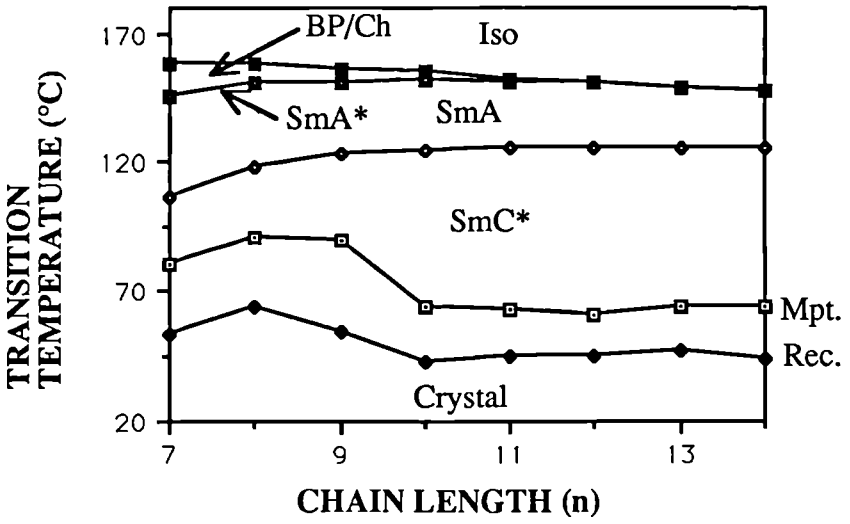


Figure 76. Transition Temperatures Versus Alkoxy Chain Length for Materials (141-148).

It can be seen from figure 76, and table 10 that the materials in series V with an alkoxy chain length of up to ten carbon atoms (**141-144**) possess an isotropic to blue phase to

cholesteric to smectic A to TGB A* to smectic C* phase sequence. Compounds **145** and **146**, which have slightly longer alkoxy moieties show interesting behaviour in that they also exhibit blue phases on cooling from the isotropic liquid; but on further cooling a direct transition to a smectic A phase is seen, with no indication of the presence of a cholesteric phase or a TGB A* phase. The reason for this can almost certainly be put down to supercooling of the blue phase transition, which may be somewhat due to surface pinning effects. Recent studies, however, showed the presence of a new metastable blue phase (BPS-blue phase supercooled) in at least one of these materials (**142**)[150]. The last two materials in series V (**147** and **148**) have direct isotropic liquid to smectic A transitions. The temperature range of the TGB A* phase in these materials, is seen to be short range and reasonably constant for every homologue that exhibits this phase. It must be remembered, however, that ascertaining the exact temperature range of the TGB A* phase is not always easy, as it is sometimes extremely difficult to determine when the transition from the cholesteric phase occurs. The smectic A to smectic C* transition temperatures for these materials are seen to initially rise quite steeply for the heptyl to nonyl homologues (**141** to **143**) and then dip slightly, before levelling off at an alkoxy chain length of thirteen carbons (**147**). Once again the clearing points and transitions from the cholesteric to smectic A phases were particularly important in these materials due to the presence of the TGB A* phase, and so were studied extensively by thermal analysis. The results will be reported later in this chapter.

All of the materials in this series (V) had a smectic C* phase, underlying the A phase, results obtained from some physical property studies are illustrated in table 11, where it can be seen that the materials are classified as

***S,S* e,o *d*LH Ps (+)**

(if the polarization direction is assumed to be consistent for all of the materials in relation to the result obtained for compound **146**). The result for helix direction deviates from Goodby and Leslie's rules[39].

No.	n	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
141	7	*S,S*	e, o	*d*	LH	-ve, +ve	
142	8	*S,S*	e, o	*d*	LH	-ve, +ve	
143	9	*S,S*	e, o	*d*	LH	-ve, +ve	
144	10	*S,S*	e, o	*d*	LH	-ve, +ve	
145	11	*S,S*	e, o	*d*	LH	-ve, +ve	
146	12	*S,S*	e, o	*d*	LH	-ve, +ve	+
147	13	*S,S*	e, o	*d*	LH	-ve, +ve	
148	14	*S,S*	e, o	*d*	LH	-ve, +ve	

Where the chiral centre closest to the core is the first designated.

Table 11. Chiral Properties Associated with the Smectic C* Phase of the Materials in Series V (141-148).

The chiral centre closest to the core is predicted to give an *Se*$\mathcal{L}$ result, whereas the second chiral centre is predicted as giving an *So*$\mathcal{L}$ relationship. Thus, the effects should in fact reinforce one another to give a right-handed, and not a left-handed helix. It appears therefore that the materials in this series are one of the exceptions to the proposed rule. The polarization direction, is, however, in agreement with earlier predictions if the helix direction is ignored, that is if only the absolute spatial configuration of the chiral centre, its parity, and inductive effect are taken into account. This agreement with predictions of the rule also applies when both chiral centres are taken into account. No evidence to suggest the presence of an inversion in helical pitch is noted in these compounds, and so it is assumed that the rotational freedom of the material to exist in a number of stable conformations which give opposite helix directions is limited, or alternatively the second

chiral centre negates this happening in some way. An investigation into the temperature dependence of the optical tilt angle for compound **143** will be discussed later, however, a maximum value for the tilt angle of approximately 27° was found, classifying these materials as having a reasonably high-tilt configuration. In order to assess the magnitude of the spontaneous polarization for this series of materials a study was carried out on one compound (**146**), see figure 77.

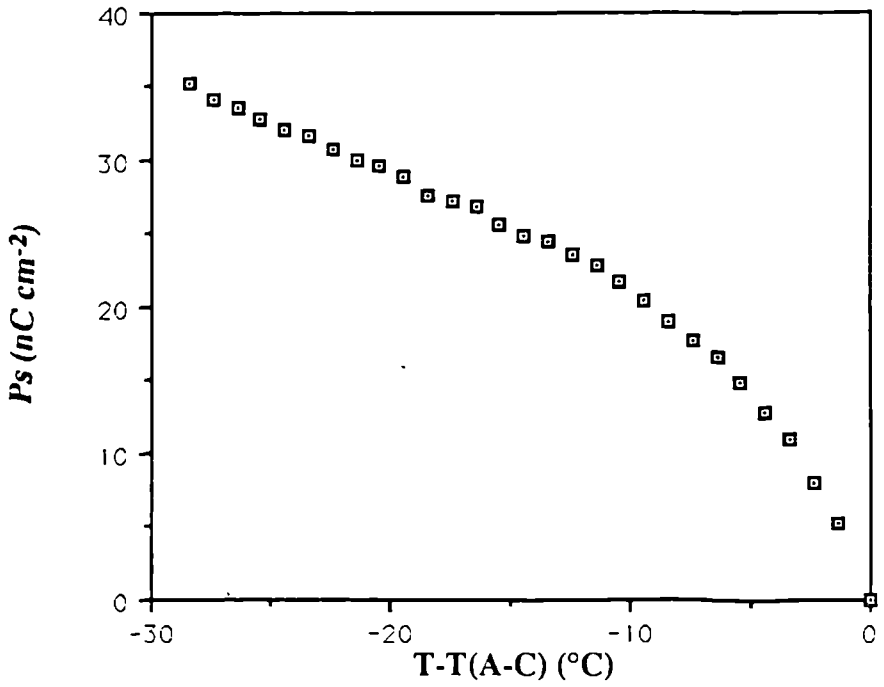


Figure 77. The Spontaneous Polarization in the Smectic C* Phase as a Function of Reduced Temperature for Compound 146.

A moderate value of approximately 20 nC cm^{-2} was measured at 10 °C below the smectic A to smectic C* transition point (at an applied field of 30 V peak to peak, 60 Hz). The pitch length, and tilt angle were measured for compounds **143** (the nonyloxy member of series V) with respect to temperature. The results will be discussed later when a comparison is made with the analogous member of series IX (materials based on the 2-chloro-4-methylpentyl moiety).

When the phase behaviour of the nonyloxy member of this series (**143**) is compared with the equivalent member of the series III, (**130**), a number of points can be made. The phase behaviour of the two materials is compared in figure 78.

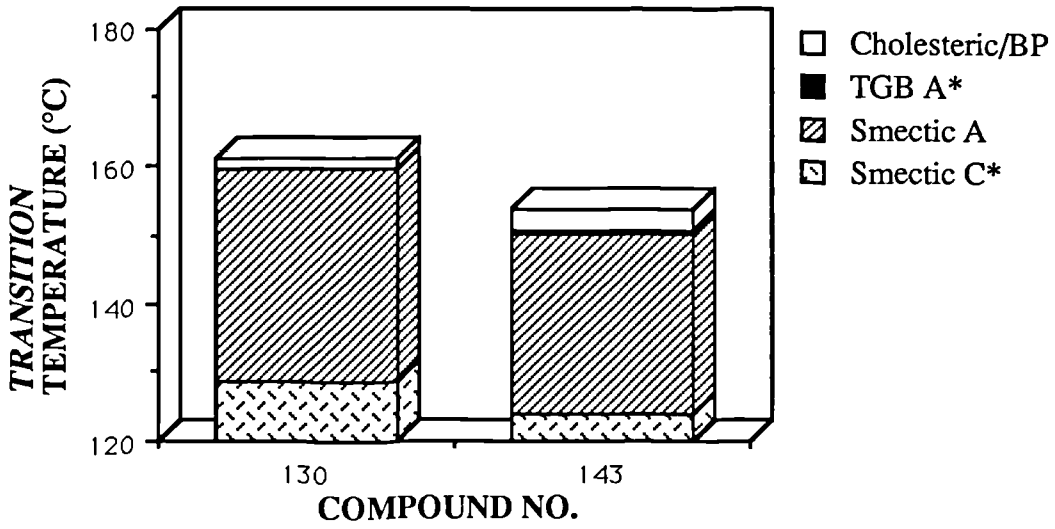


Figure 78. A Comparison of the Phase Behaviour in Compounds 130 and 143 (the Nonyloxy Homologues of Series III and V).

Firstly, the clearing point and subsequent transition temperatures to TGB A*, A and C* phases are lower for compound **143** with respect to compound **130**. The blue phase and TGB A* temperature ranges were found to increase, which is an expected result as the chirality of the system is likely to be larger by virtue of the reduced degree of rotational freedom associated with the chiral centre. It is also possible to speculate that the chirality of the molecule, in this instance, is not reduced to any great extent by any opposing dipolar effects of the chiral centres. The cholesteric temperature range in compound **143** is larger, indicating a more nematogenic tendency, with the smectic A stability being slightly smaller than that observed for compound **130**. A comparison of the results obtained for the heating cycle of compound **143** by differential calorimetry will be discussed later, along with the results obtained for compound **158** (the nonyloxy member of series IX).

The transition temperatures for material **154** (series VII) with an *(S,R)* configuration of the chiral centres is now discussed. The transition temperatures for compound **154** are given in table 12. Figure 79 shows a comparison between the results for compound **154** and compound **143** (which has an *(S,S)* configuration of the chiral centres)

No	Mpt.	I-BPIII	BPIII-BPII	BPII-BPI	BPI-Ch	Ch-S_A	S_A-S_C*	Rec.
154	94.5	149.4	149.2	148.9	148.8	148.5	123.9	65.0

Table 12. The Transition Temperatures (°C) for the *(S,R)*-2-Chloro-3-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylates (154).

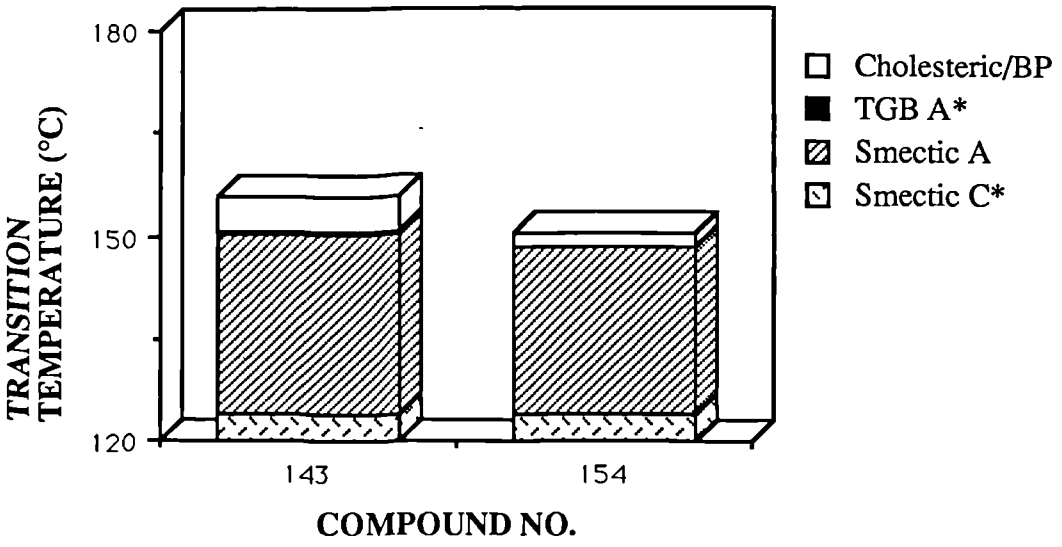


Figure 79. A Comparison of the Phase Behaviour in Compounds 143 and 154 (the Nonyloxy Homologues of Series V and VII).

The first noticeable point is that compound **154** *(with an (S,R)* configuration of optically active centres) does not possess a TGB A* phase, mediating the transition from the cholesteric to the smectic A phase. This would tend to suggest that there has been a reduction in the chirality of the system on moving from an *(S,S)* configuration to an *(S,R)* configuration of the chiral centres, assuming that the layer strength is the same for both compounds. The reason for a reduced degree of chirality may be due to the dipoles

associated with each chiral centre being subtractive, in terms of overall molecular dipole strength. This invariably depends on the most stable conformations that the molecules adopt. The possible primary conformers associated with each system are illustrated in figure 80.

Assuming that the most stable conformation is one where the ethyl group points down in an all *trans* conformation (conformer C in the *(S,S)* system, and conformer A in the *(S,R)* system) then for the *(S,S)* system the dipoles associated with the methyl group and the chlorine atom tend to be additive. In the *(S,R)* system, however, this is not the case as the dipoles oppose one another to some degree. This probably results in a reduction of the lateral dipole, and consequently a reduction in chirality.

The blue phase temperature range is also substantially reduced in the case of compound **154**. The reduction in the blue phase temperature range suggests a reduction in the chirality of the system, and not a strengthening of the layer ordering is responsible for the absence of a TGB A* in compound **154**. The stability of the A phase is also reduced, but the temperature of the transition to the smectic C* phase is found to be the same for each material. As these materials are diastereoisomers, and therefore may have unrelated phase behaviour the latter point cannot be considered unusual.

When the properties of the smectic C* phase of compound **154** were investigated, a marked difference was found in relation to the results obtained for compound **143** (the analogous material from series V). The results obtained for compounds **143** and **154** are compared in table 13.

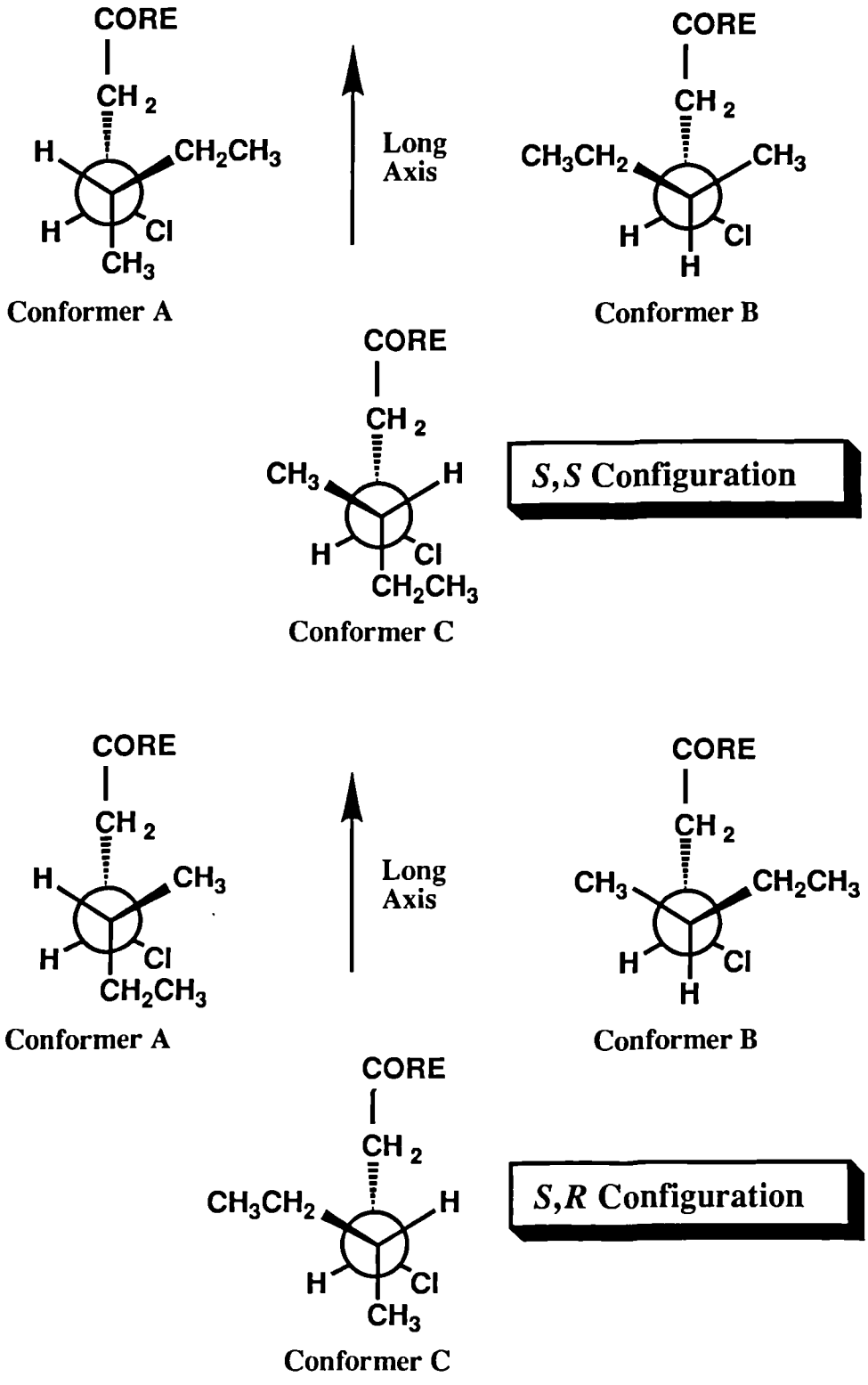


Figure 80. The Possible Primary Conformers Associated with the *(S,S)* and *(S,R)* Configurations.

No.	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
143	*S,S*	e, o	*d*	LH	-ve, +ve	*
154	*S,R*	e, o	*L*	RH	-ve, +ve	-

* although not determined for this particular compound, it is assumed to be positive as for compound **146** from the same series.

Table 13. A Comparison of the Chiral Properties Associated with the Smectic C* Phase of Materials 143 and 154 (the Nonyloxy Homologues of Series V and VII).

It can be seen quite clearly that the second chiral centre has a major impact on the properties of the smectic C* phase. Firstly, the helix directions in the materials are opposite, the result for one being left-handed (**143**), the other right-handed (**154**). As mentioned previously, compound **143** does not agree with the Goodby and Leslie hypothesis[39]. In the case of compound **154**, it is evident that the first chiral centre can be classified as *S* e *L* RH which agrees with the hypothesis, but the second chiral centre opposes this result and is classified as *R* o *L* RH. It is possible then that there may be a competition between twisting directions of the two chiral centres for this material, with the first chiral centre dominating. The competition between the optically active centres when resolved into steric and dipolar factors may also give an indication as to why the overall chirality of this material is thought to be reduced compared to compound **143**. The polarization direction in compound **154**, is also in agreement with the previous hypothesis for the first chiral centre, but opposes for the second. This result may not be totally unexpected as the strong dipole associated with the chlorine atom is likely to play a larger role in determining the polarization direction than the weaker methyl dipole associated with the second chiral centre. If one assumes that compound **143** has a positive spontaneous polarization (compound **146** was the only material tested from the series and was found to be positive), then the configurations of the two sequential chiral centres are also found to be important in determining polarization direction.

The phenylpropiolates with an *(S,S)* configuration (series VI) will now be considered. The transition temperatures for these compounds are illustrated in table 14 and figure 81, where it can be seen that all of the materials in series VII possess an isotropic to blue phase to cholesteric to TGB A* to smectic A to smectic C* phase sequence. The clearing points are seen to drop slightly for members of the series that have longer alkoxy chain lengths.

No.	n	Mpt.	I-BPIII	BPIII-BPII	BPII-BPI	BPIII-BPI	BPI-Ch	Ch-TGB	TGB-S_A	S_A-S_C*	Rec.
149	9	74.9	127.8	127.7	127.4		126.5	96.4	93.4	72.3	64.9
150	12	72.9	127.3	127.2	127.0		126.8	112.1	111.4	94.1	63.8
151	14	68.9	123.2	122.8	122.7		122.4	114.6	113.9	98.6	58.2
152	16	62.3	121.8	121.6	121.2		120.0	117.3	116.3	102.5	44.5
153	18	68.4	120.8			120.7	120.3	119.5	118.9	102.3	56.1

Table 14. The Transition Temperatures (°C) for the *(S,S)*-2-Chloro-3-methylpentyl 4'-(4-alkoxyphenylpropioloyloxy)-4-biphenylcarboxylates (149 - 153).

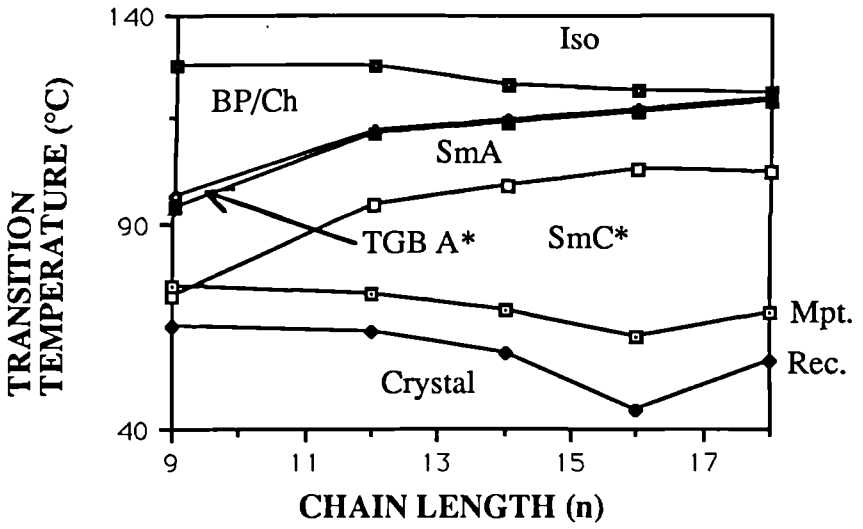


Figure 81. Transition Temperatures Versus Alkoxy Chain Length for Materials (149-153).

Similarly the blue phase/cholesteric phase temperature ranges are seen to markedly decrease as the series is ascended. This is partly due to a fall in clearing point, and also to an increase in the cholesteric to A*/A transition temperature. The temperature range of the TGB A* phase is seen to decrease for the members with longer alkoxy chain lengths, indicating that either the chirality of the system is becoming weaker, or that the layer ordering is getting stronger. It is also believed that the underlying smectic C* phase causes local perturbations which aid in the formation of the TGB A* phase. If the smectic C* phase is in closer proximety to the TGB A* to smectic A transition then an increased TGB A* phase temperature range is expected. In this series of materials the temperature range of the smectic A phase is of the same order of magnitude for all homologues, and so it would be expected that the effects caused by the presence of the smectic C* phase will be similar in all cases. It can be speculated that if the TGB A* to smectic A transition is close to the temperature at which the material goes to the isotropic liquid then the local perturbations will be large, hence increasing the TGB A* temperature range. If this is so it would be expected that the materials with a short blue phase/cholesteric temperature range would yield the largest TGB A* temperature range. In this series of materials this is found not to be the case, which suggests that the temperature range of the cholesteric phase itself may have some bearing on the TGB A* temperature range.

The transition from the smectic A phase to the smectic C* phase is seen to initially rise in this family of materials (series VI), and then begin to fall again as the octadecyloxy homologue is reached (**153**), with this effect influencing the thermal stability of the overlying A phase to some degree.

A comparison between the nonyloxypropiolate member of this series (**149**), and the analogous benzoate material from series V (**143**) is shown in figure 82, where it can be

seen that the clearing point is considerably reduced on the insertion of a triple bond into the core of the molecule, and that the nematogenic tendency is greatly increased. The temperature range of the TGB A* phase is found to be an order of magnitude larger for compound **149** in comparison to **143**, which tends to suggest that the layer ordering is much weaker. The temperature range of the smectic A phase is slightly larger in compound **143** relative to **149**, and the transition to smectic C* occurs at a higher temperature.

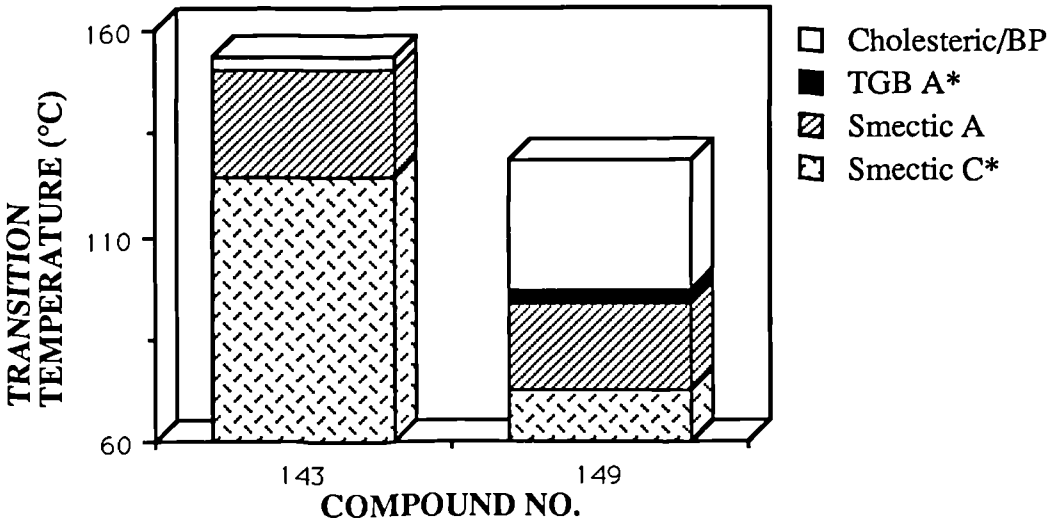


Figure 82. A Comparison of the Phase Behaviour of Compounds 143 and 149 (the Nonyloxy Homologues of Series V and VI).

The properties of the smectic C* phase in compounds **149** to **153** (series VI) are now discussed. The results obtained for the chirality related properties are summarised in table 15, where it can be seen that the results acquired for this series of materials are similar to those obtained for their benzoate counterparts (**141-148**). For example, the helix direction is determined as being left-handed and the direction of spontaneous polarization is positive. This classifies the materials as being

***S,S* e,o *d*LH Ps (+)**

(assuming the polarization direction is the same for all other members of the series as that determined for compound **149**) which once again deviates from earlier predictions[39] in

terms of the helix direction, but not in terms of the polarization direction. The magnitude of the spontaneous polarization was found to be 48 nC cm^{-2}, at 10 °C below the A to C* transition, an identical value to that found for *(S)*-2-Chloro-3-methylbutyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (**136**) from series IV, an observation that will be discussed later.

No.	n	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
149	9	*S,S*	e, o	*d*	LH	-ve, +ve	+
150	12	*S,S*	e, o	*d*	LH	-ve, +ve	
151	14	*S,S*	e, o	*d*	LH	-ve, +ve	
152	16	*S,S*	e, o	*d*	LH	-ve, +ve	
153	18	*S,S*	e, o	*d*	LH	-ve, +ve	

Table 15. Chiral Properties Associated with the Smectic C* Phase of the Materials in Series VI (149-153).

There was no evidence to suggest that the helix in the smectic C* phase inverted in this series of materials, a result that is probably related to a reduced rotational freedom of the system as noted earlier.

The next series that will be discussed (series VIII) constitutes one material (**155**) which is analogous to compound **149** except that its chiral centres have an *(S,R)* configuration. The transition temperatures, and phase behaviour for this material are given in table 16, and a comparison between this material and compound **149** is shown in figure 83.

No	Mpt.	I-BPIII	BPIII-BPII	BPII-BPI	BPI-Ch	Ch-TGB	TGB-S_A	S_A-S_C*	Rec.
155	82.4	130.8	130.5	129.9	128.6	102.9	99.3	82.4	68.1

Table 16. The Transition Temperatures (°C) for *(S)*-2-Chloro-3-methyl pentyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (155).

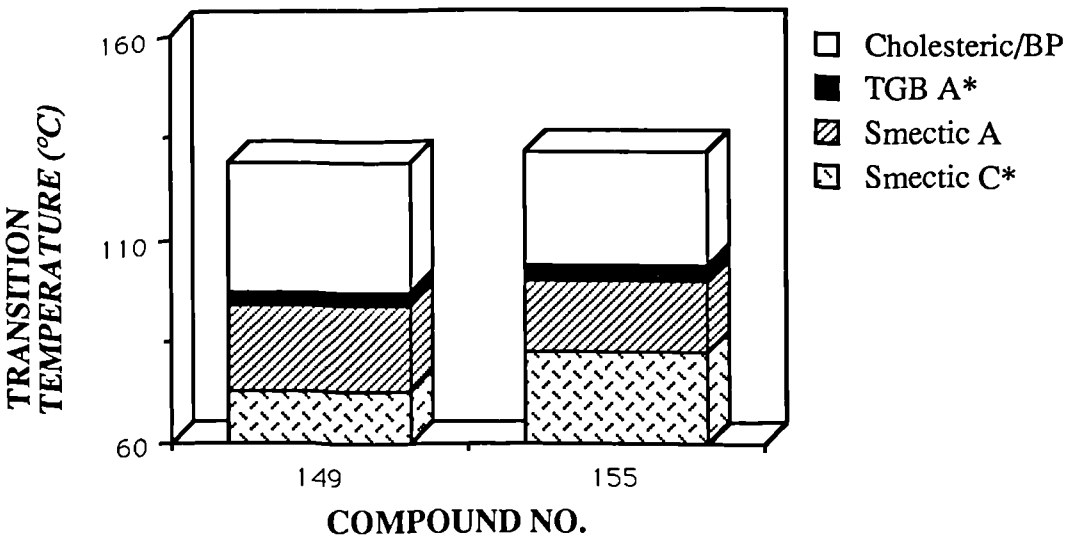


Figure 83. A Comparison of the Phase Behaviour of Compounds 149 and 155 (the Nonyloxy Homologues of Series VI and VIII).

From figure 83 it can be seen that the clearing point and subsequent transitions occur at a slightly higher temperature for compound **155** (that has an *(S,R)* configuration of chiral centres) in comparison to compound **149**. The blue phase/cholesteric temperature range is slightly shorter, whereas the TGB A* temperature range is slightly broader for compound **155**. The smectic A temperature range is broader in compound **149**, due to an increased thermal stability of the smectic C* phase in compound **155**, which reduces the smectic A thermal stability in that material. The greater TGB A* temperature range suggests that the chirality is higher, or that the layer ordering is much weaker in compound **155**. When these results are compared with those for the analogous benzoates, **143** and **154**, a number of interesting points are found. Firstly, the nematogenicity is found to decrease on moving from an *(S,S)* configuration to an *(S,R)* configuration in compounds **143** and **154** (the benzoates), as was the temperature range of the A phase. Compound **154** did not possess a TGB A* phase, but compound **143** did, and the transition to the smectic C* phase occurred at the same temperature in both compounds. The major point of interest is why the propiolate linkage should seem to reverse the

effects of the sequential chiral centres, in terms of the formation of the TGB A* phase, when it is situated in a position that is so far removed from the optically active centres. It is proposed that the triple bond in the first instance weakens the layer ordering, but this would lead to simply a greater TGB A* range in both **149** and **155**, with the phase stability still being greater in the material with an *(S,S)* configuration (**149**). If it is assumed that the triple bond can in no way effect the chirality of the materials, as it is too far removed from the optically active sites of the molecule, then another explanation must be sought. It must be remembered that these materials are diastereoisomers and that they can therefore have differing physical properties, such as melting point and phase behaviour (some phase thermal stabilities are, however, dependent on molecular chirality as has been previously indicated). Compound **155** has a reduced cholesteric phase temperature range, but a closer underlying smectic C* phase. It has already been mentioned that fluctuations from the smectic C* phase may effect the thermal stability of the TGB A* phase, and it is plausible that this may cause a slightly larger A* temperature range in compound **155**, relative to compound **149**.

When the properties of the smectic C* phase of both compound **149** and **155** are examined (see table 17), a number of issues ensue. Firstly, as with compounds **143** and **154** (the benzoates), the helix and polarization directions for compounds **149** and **155** are opposite to one another. It is therefore possible to say that in the smectic C* phase there is no fundamental difference in the behaviour, between the materials with and without a triple bond in their core structures.

No.	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
149	*S,S*	e, o	*d*	LH	-ve, +ve	+
155	*S,R*	e, o	*L*	RH	-ve, +ve	-

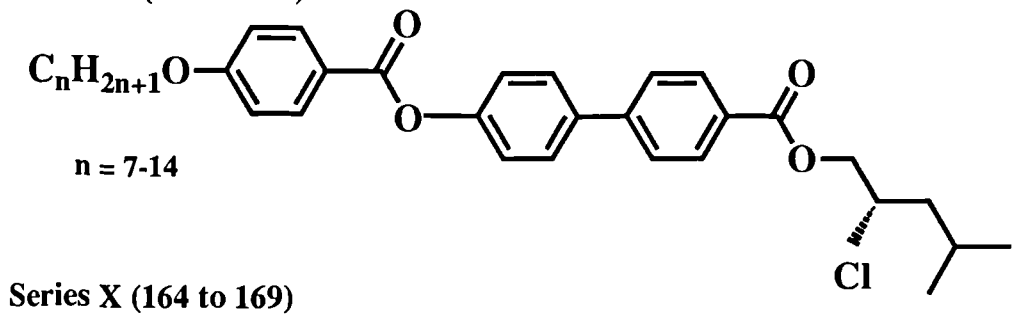
Table 17. A Comparison of the Chiral Properties Associated with the Smectic C* Phase of Compounds 149 and 155 (the Nonyloxy Homologues of Series VI and VIII).

The reasons why the materials give opposing properties in the C* phase were discussed earlier for compounds **143** and **154**, and so will not be elaborated on here. The magnitude of the spontaneous polarization as a function of temperature was determined for material **155**, the value being 62 nC cm^{-2} at 10 °C below the smectic A to smectic C* transition. A comparison of the values obtained for the spontaneous polarization in the smectic C* phase of selected compounds is given later.

8.5.1 Esters Based on a 2-Chloro-4-methylpentyl Moiety.

The next two series of materials to be discussed (compounds **156-169**) were materials with the general structures illustrated in figure 84; the terminal chiral moiety employed was a 2-chloro-4-methylpentyl group, which has only one optically active centre. In these materials the branching point is no longer next to the chiral centre and so the freedom of rotation of the chiral centre is expected to increase relative to the preceding four systems (series V to VIII). This is expected to lead to an overall reduction of chirality. The benzoate materials which do not have a triple bond incorporated in their core structures (**156-163**) are discussed first. The transition temperatures for this first series are listed in table 18, and illustrated in figure 85.

Series IX (156 to 163)



Series X (164 to 169)

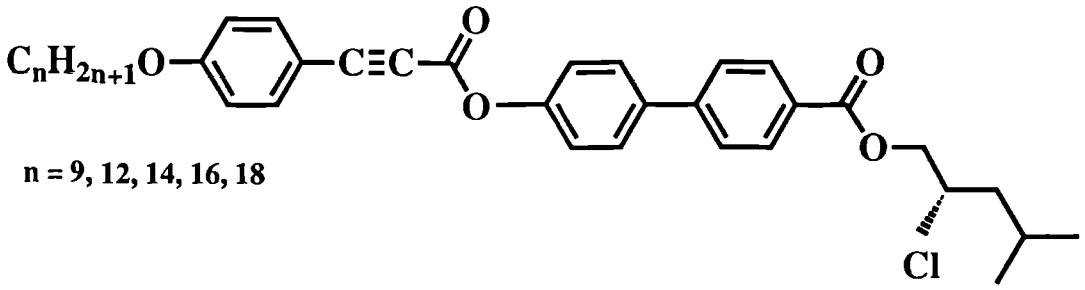


Figure 84. The Structures of the Di-Esters Based on a 2-Chloro-4-methyl Chiral Moiety.

No.	n	Mpt.	I-BPIII	BPIII-BPII	BPII-BPI	BPI-Ch	Ch-TGB	TGB-S_A	I-S_A	S_A-S_C*	Rec.
156	7	73.4	156.1	155.4	154.9	153.2	144.9	144.2		111.9	40.9
157	8	75.0	155.4	154.9	154.5	148.3	146.8	146.0		115.1	53.7
158	9	74.9	150.2	149.9	148.6	145.5	145.4	144.6		121.0	41.8
159	10	64.4	149.7	149.5	148.8	146.8	145.6	144.8		121.9	34.0
160	11	69.4	148.1	148.0	147.4	146.8	145.8	145.0		124.2	57.5
161	12	68.8	145.6	145.6	145.4	145.0	144.8	144.1		122.0	49.8
162	13	73.5							142.5	121.7	50.2
163	14	76.7							142.0	121.4	53.0

Table 18. The Transition Temperatures (°C) for the *(S)*-2-Chloro-4-methylpentyl 4'-(4-alkoxybenzoyloxy)-4-biphenylcarboxylates (156-163).

It can be seen from table 18 and figure 85 that the materials in this series of compounds exhibit an isotropic to blue phase to cholesteric to TGB A* to smectic A to smectic C* phase sequence, from the heptyloxy homologue up to the dodecyloxy member of the

series (**156-161**). At longer chain lengths than dodecyloxy, i.e., **162** and **163**, a simple isotropic to smectic A to smectic C* phase sequence is observed. As expected the blue phase/cholesteric temperature range is seen to decrease with increasing alkoxy chain length, the TGB A* temperature range, however, remains reasonably constant for all of the materials that exhibited this phase only decreasing slightly for the longer chain lengths. The temperature range of the smectic A phase was found to be reasonably constant across the series. The A to C* transition temperatures are seen to initially rise with increasing alkoxy chain length, peaking for compound **160** (the undecyloxy homologue, and then falling again. The TGB A* temperature range for these materials was slightly larger than that found for the analogous materials based on a 2-chloro-3-methylpentyl, or a 2-chloro-3-methylbutyl chiral moiety. This was not expected as the branching point is removed one carbon away from the chiral centre, unlike the situation in the previously mentioned materials where it is located adjacent to the first chiral centre. The rotational hindrance is therefore expected to be less in this series relative to the materials from series III, V, and VII, leading to a reduced chirality and smaller TGB A* temperature range, assuming that the layer strength is constant throughout all of the series.

As the temperature range of the TGB A* is actually larger in these materials (series IX) it must be assumed that the second optically active centre (in the 2-chloro-3-methylpentyl series) does not contribute to the chirality of the system; but actually subtracts from it in some way, in comparison, and that the shorter alkyl chain (in the 2-chloro-3-methylbutyl series) reduces the chirality of the system more than the relative position of the branch point increases it. It must be remembered, however, that the position of other optically active mesophases relative to the cholesteric to smectic A transition can have a major influence on whether TGB A* phases are observed, and it should be noted that the blue

phase/cholesteric temperature range is similar in the compounds from both series V and IX that are based on a chiral pentyl chain.

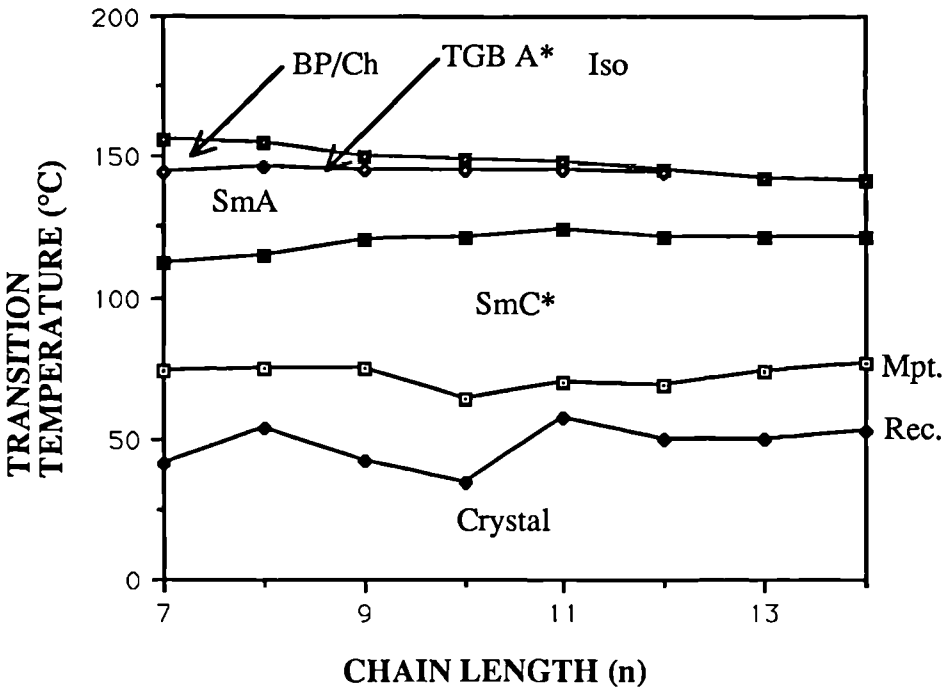


Figure 85. Transition Temperatures Versus Alkoxy Chain Length for Materials (156-163).

8.5.2 Calorimetric Analysis and Miscibility Studies Performed on Selected Benzoate Materials.

The results of thermal analysis (DSC) studies obtained from a number of materials in the previous five series of benzoate materials proved especially interesting. The nonyloxy members of series III, V, VII, and IX , that is compounds **130, 143, 154, 158,** are selected as examples and so are reported in this section. Figures 86, 87, 88 and 89 show the heating traces obtained by DSC for these materials. Only the transitions that occur near the clearing points are considered. The heating rate was 2 °C min^{-1} in all cases.

For *(S)*-2-Chloro-3-methylbutyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate, i.e., compound **130**, (figure 86) only two peaks were observed, which were so close together that they partially overlapped. These peaks correspond to the smectic A to cholesteric and cholesteric to isotropic liquid transitions. A small shoulder on the left hand side of the lower temperature peak may be due to a TGB A* to smectic A transition, for a TGB A* phase that only occurs over a very short temperature range (< 0.1 °C). The blue phase transitions are not resolved at all, probably because of their very short temperature range and/or low enthalpy values.

When the heating cycle of *(S,S)*-2-Chloro-3-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (**143**) was investigated near the clearing point four peaks were found which correspond to the smectic A to TGB A*, TGB A* to cholesteric, cholesteric to blue phase, and blue phase to isotropic liquid transitions (see figure 87). The phase changes between the individual blue phases were not resolved for this compound.

(S,R)-2-Chloro-3-methylbutyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (**154**) exhibits two peaks on clearing which correspond to the isotropic liquid to cholesteric and cholesteric to smectic A phase changes. A TGB A* phase was not observed for this material. The higher temperature peak does, however, show a small shoulder which may correspond to one of the blue phase transitions (see figure 88).

The resolution of the phase transitions was found to be better for *(S)*-2-Chloro-4-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (**158**), which has the largest TGB A* temperature range of all of the materials reported in this section. Five peaks can be clearly seen which correspond to the smectic A to TGB A*, TGB A* to cholesteric, cholesteric to blue phase I, blue phase I to blue phase II, and blue phase II to

isotropic liquid transitions (see figure 89). The transition for blue phase II to blue phase III could not be detected by calorimetry.

The cooling cycles for these materials were in good agreement with the heating cycles, except for the resolution between blue phase transitions and the transitions to and from the TGB A* phase. Peaks associated with the enthalpies of these transitions were not as clearly defined in comparison to the results obtained for the heating cycles. Most of the peaks were seen to supercool to some degree, the most striking example of this is the result obtained for compound **158** (the nonyloxy homologue of series IX) where the transition from blue phase I to cholesteric phase supercooled far enough for the blue phase I to the cholesteric peak to become amalgamated with the cholesteric to TGB A* peak. This is illustrated in figure 90, for the cooling cycle of compound **158** (cooling rate 2 °C min^{-1}).

In order to ascertain what effect molecular chirality had on the formation of the TGB A* phases, in terms of optical purity, the racemic variant of compound **158** was prepared (compound **169**). The transition temperatures for this material, are compared with those of the chiral variant, in table 19 and illustrated graphically in figure 91.

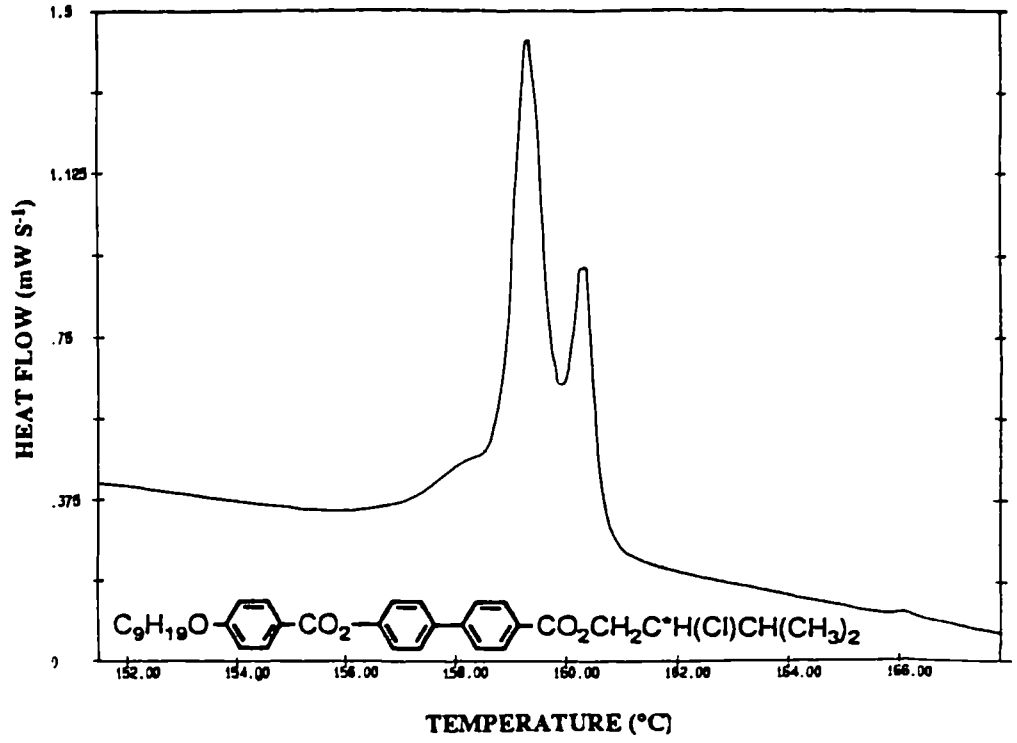


Figure 86. The Heating Cycle Close to the Clearing Point for *(S)*-2-Chioro-3-methylbutyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (130).

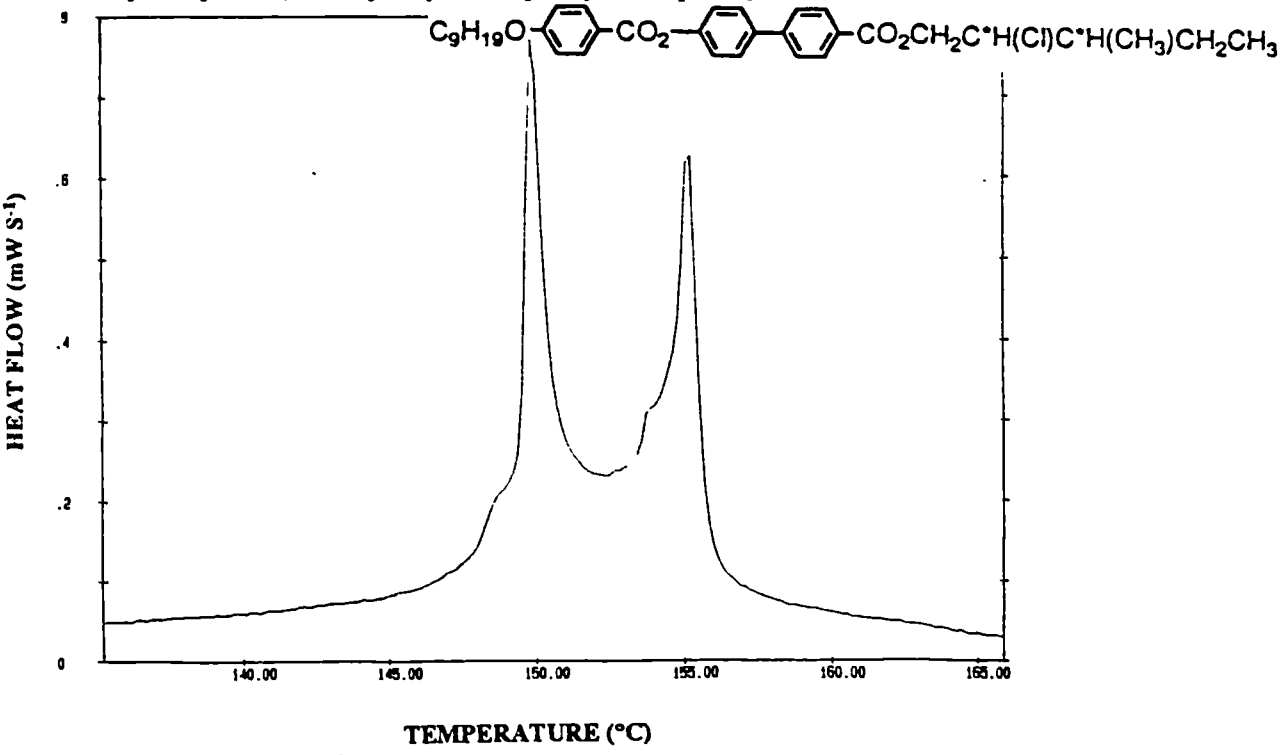


Figure 87. The Heating Cycle Close to the Clearing Point for *(S,S)*-2-Chloro-3-methylpenyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (143).

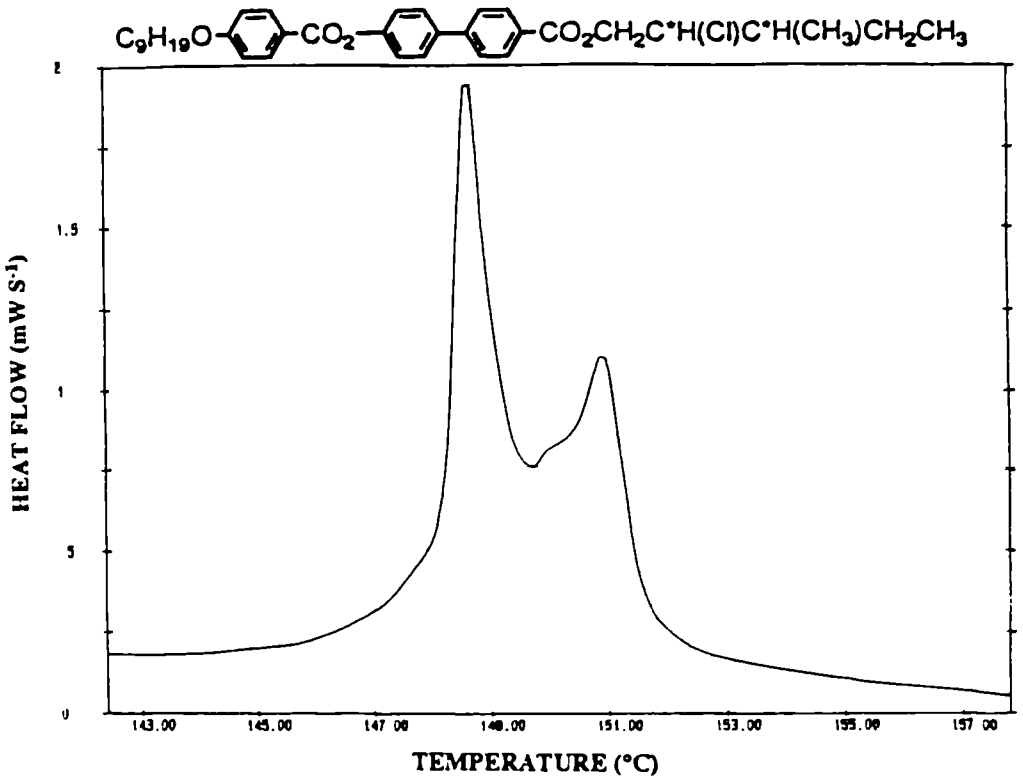


Figure 88. The Heating Cycle Close to the Clearing Point for *(S,R)*-2-Chloro-3-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (154).

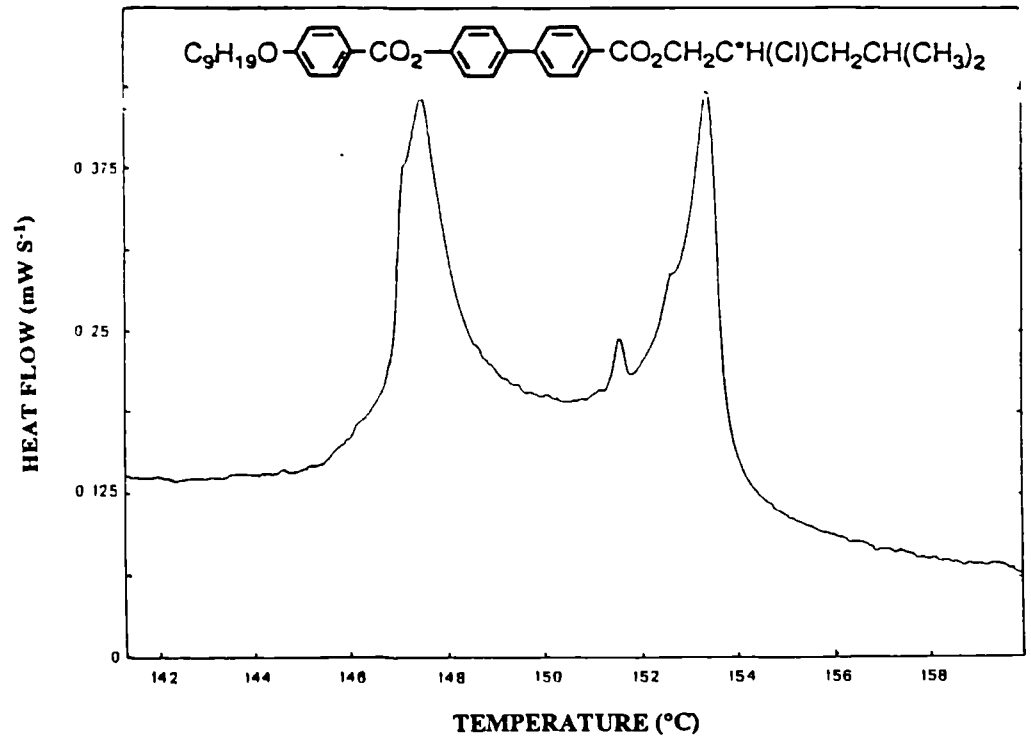


Figure 89. The Heating Cycle Close to the Clearing Point for *(S)*-2-Chloro-4-methylpenyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (158).

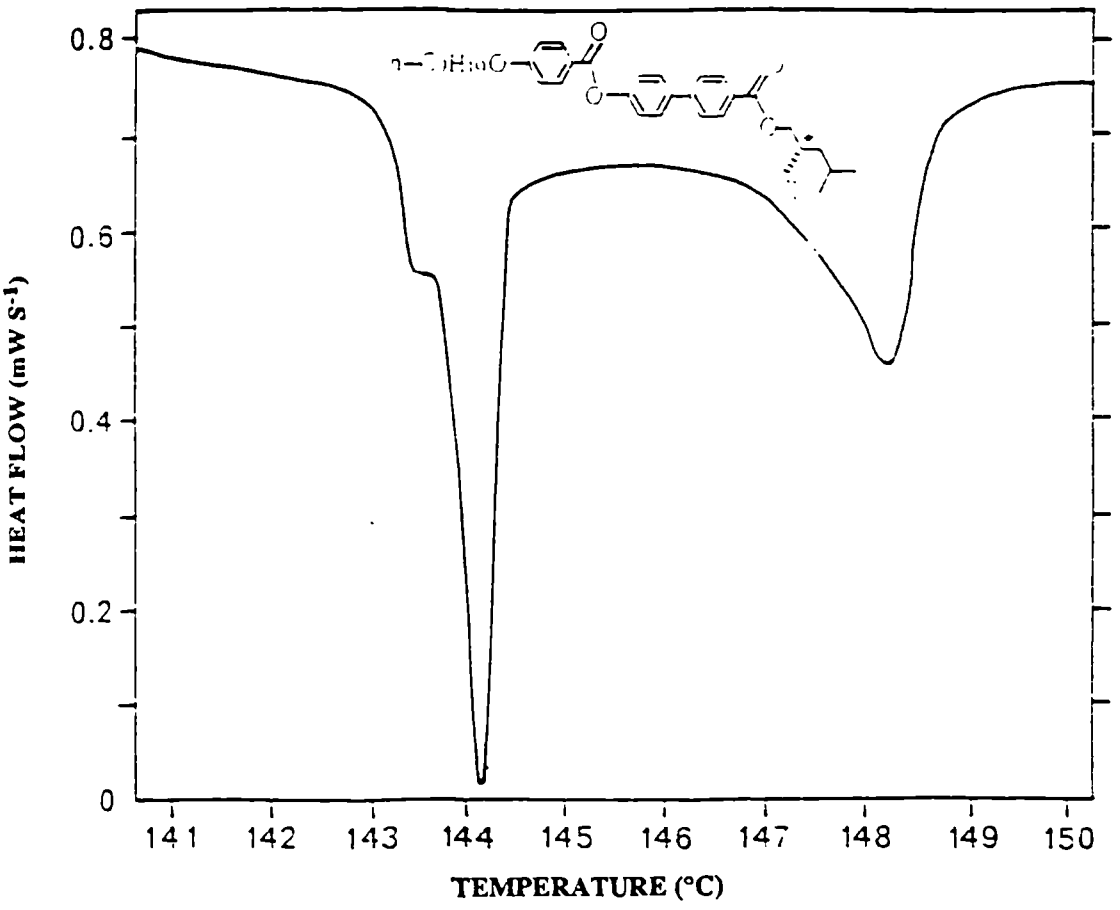


Figure 90. The Cooling Cycle Close to the Clearing Point for *(S)*-2-Chloro-4-methylpenyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (158).

No	ASC	I -BP/Ch	I-N	Ch-TGB	TGB-SA	N-S_A	S_A-S_C/ S_C*	S_C/S_C*-K
158	*S*	150.2		145.4	144.6		121.0	41.8
169	Racemic		153.1			147.5	121.4	50.3

Table 19. The Transition Temperatures (°C) for the Chiral and Racemic Modifications of 2-Chloro-4-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (158 and 169).

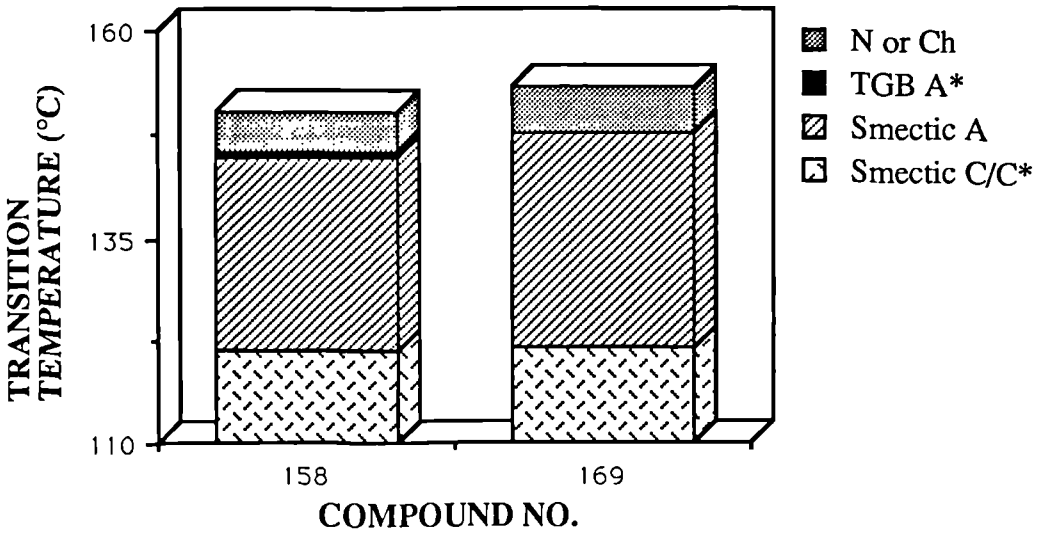


Figure 91. A Comparison of the Phase Behaviour of Compounds 158 and 169 (the Chiral and Racemic Modifications of 2-Chloro-4-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate).

The first thing that is noticeable from table 19, and figure 91 is that the racemic variant (**169**) does not possess a TGB A* phase or blue phases, indicating that optical activity is an important factor in the formation of these phases. The racemate possesses only three phases, nematic , smectic A, and smectic C. The clearing point for the racemic form (**169**) was found to be considerably higher (2.5 °C) than that for the chiral material (**158**), as was the transition from nematic (or cholesteric) to smectic A or TGB A* (2.1 °C). The

transition from smectic A to smectic C or smectic C*, however, was found to be only 0.4 °C higher in the racemate. These results are in agreement with the physical theory which suggests that anomalies will be found in the phase behaviour when strong distortions are applied to the system (in this case chirality)[90,95]. Thermal analysis confirmed the results obtained by optical microscopy. Only two peaks were found near the clearing point for the racemic variant, these corresponded to the transitions from smectic A to nematic, and nematic to isotropic liquid. The heating thermogram for the racemate (**169**), is shown in figure 92 (heating rate 2 °C min^{-1}).

In order to expand upon this last point a phase diagram was constructed by studying the phase transitions in various mixtures of compounds **158** and **169**. The miscibility phase diagram of these two compounds is illustrated in figure 93, where mixtures of *(S)*-isomer (**158**), and racemate (**169**) have been reflected across the phase diagram for the *(R)*-isomer in order to produce a complete miscibility figure over the full optical purity range. As expected the temperature ranges of the TGB A* phase and the various blue phases were found to decrease with decreasing optical purity. At values of 15 % and below of the chiral component in the binary mixtures, no TGB A* phase or blue phases were observed and an isotropic to cholesteric to smectic A phase sequence was obtained. As the 100 % level of the chiral component in the mixture was approached the cholesteric temperature range decreased, as the temperature of the transition from blue phase I to the cholesteric phase drops quite markedly, thereby increasing the temperature range of the blue phases, and decreasing that of the cholesteric phase. Furthermore, it was noted that, in the region of 100 % racemate to approximately 40 % of the chiral variant in the binary mixtures, the clearing points fell and then levelled off. A similar trend was observed for the cholesteric to TGB A* or smectic A transition. This unusual trend was not, however, particularly pronounced for the smectic A to smectic C* transition. This suggests therefore that the clearing point and cholesteric to smectic A/TGB A* transitions are

being markedly influenced by the degree of molecular chirality, whereas the smectic A to smectic C* transition is relatively unaffected. The fact that both the blue phase and TGB A* phase temperature ranges are affected by the degree of molecular chirality, tends to suggest that they may have some physical similarities.

Another miscibility study that was carried out using binary mixtures of compound **158**, and a standard material, *(S)*-1-methylheptyl 4'-(4-heptadecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (**15P1M7**)[91] was performed in order to confirm that the TGB A* phase seen in the compounds under investigation was the same phase that had been previously reported. The phase diagram obtained, along with the structure of **15P1M7** is illustrated in figure 94.

It can be seen from figure 94 that the smectic C* phases of both materials are continuously miscible across the phase diagram, thus confirming the presence of a smectic C* phase with a right-handed helix in the test material (**158**). The cholesteric phase was found to be present across half of the composition range. The temperature range of the cholesteric phase decreased as the amount of the standard material (**15P1M7**) was increased. At the lower temperature boundary, of the cholesteric phase, filaments that are characteristic of the TGB A* phase were formed at the transition to the smectic A phase. The temperature range for which the filaments were seen to occur was small, and found to be independent of the concentrations of the two components in the binary mixture. This latter point suggesting that this is not an impurity effect. Once the concentration of the standard material had reached a level of more than 50 % by weight in the binary mixtures, the cholesteric phase was no longer observed.

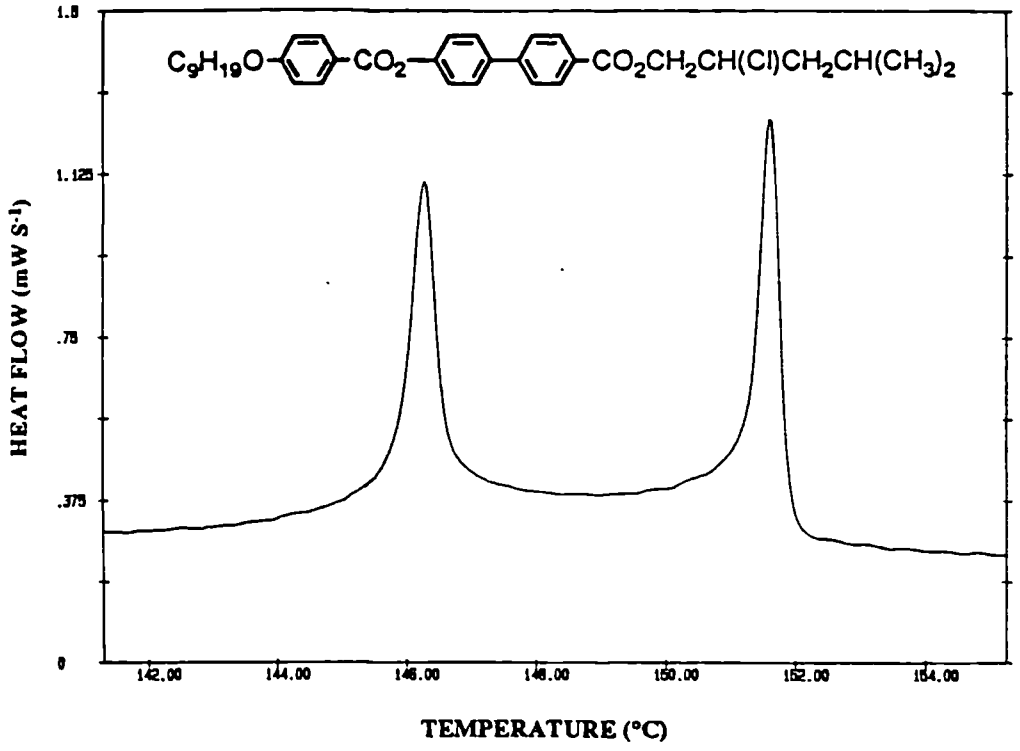


Figure 92. The Heating Cycle Close to the Clearing Point for Racemic-2-Chloro-4-methylpenyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (169).

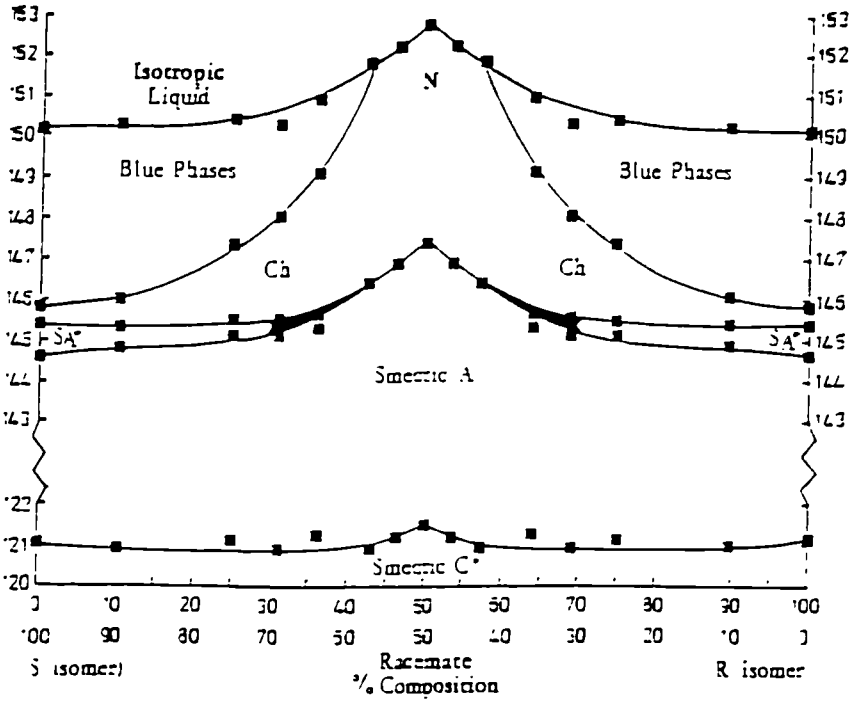


Figure 93. The Miscibility Phase Diagram for Binary Mixtures of Racemic and Optically Active 2-Chloro-4-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (158 and 169).

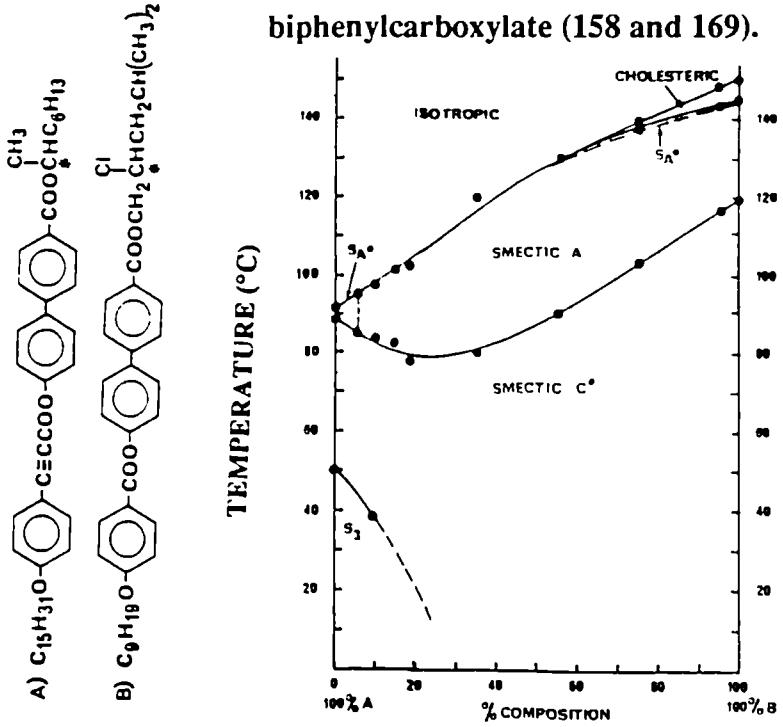


Figure 94. The Miscibility Phase Diagram for Binary Mixtures of 2-Chloro-4-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (158) and a Standard Material (15P1M7).

Furthermore, the filaments associated with the TGB A* phase also disappeared and the transition from isotropic liquid to smectic A (5-50 % by weight of **158** region of the phase diagram) took place in a normal fashion with the formation of typical focal-conic defects. In the region of 95-100 % of the standard material (**15P1M7**), the TGB A* phase was once again found. On cooling a direct transition to the smectic C* phase occurred, without the formation of an intermediary A phase. The phase diagram exemplifies a number of points. Firstly, the TGB A* phase is only seen accompanying a cholesteric to smectic A phase change, or in close proximity to a chiral smectic C* phase. Secondly, the filaments associated with the TGB A* phase are clearly not due to phase separation caused by impurities, as seen in other systems[151]. Thirdly, the TGB A* to smectic C* transition temperatures are depressed on adding the test material to the standard. Consequently, the TGB A* phase abruptly disappears, suggesting that the TGB A* phase is stabilised by the adjacent C* phase, as mentioned previously. Thus, continuous miscibility of the TGB A* phase across the phase diagram for the two materials is probably not practical for these two types of material. This is due to the fact that in the centre of the figure there is no cholesteric phase, and the C* phase is depressed too much to affect the cholesteric to smectic A transition.

8.5.3 Chiral Properties Associated with the Benzoate Materials in Series IX.

When the properties of the smectic C* phase found in the benzoate esters based on a 2-chloro-4-methylpentyl chiral moiety (**156** to **163**) were investigated, strange behaviour was once again noticed for a number of materials (see table 20).

Compounds **156** to **158** (the heptyloxy to nonyloxy homologues) were found to have a right-handed helical structure classifying them as being ***S*** **e** $\angle$ **RH**, whereas compounds **159** and **163** were classified as ***S*** **e** $\measuredangle$ **LH**, with a left-handed helical structure. The remaining three materials appeared to have an inversion in their helical structures on

cooling from the smectic A phase. Initially, on cooling from the smectic A phase they had a left-handed helix, and then the structure inverted to give a right-handed helix. A similar sort of texture change was seen at the inversion point as was described previously for compound **130** (the nonyloxy member of series III). Once again "contact-type" free-standing films were prepared in order to prove that an inversion was indeed taking place in these materials, the standard in this instance being compound **156** (the heptyloxy member of this series). As with previous experiments of this type a defect was seen to form at the boundary of the two materials. The occurrence of an inversion was, however, proved by polarimetry, with the standard retaining its helical twist sense throughout the temperature range, and the test material appearing to invert its direction. Contact studies using free-standing films were also utilised to prove that the twist sense in the homologues with shorter alkoxy chains (**156-158**) was indeed the opposite to that seen in compound **163**.

In order to determine if the inversion in helical twist sense, in compounds **160-162**, was accompanied by a measurable enthalpy, DSC studies were carried out. No enthalpy, however, could be measured at the inversion point. The cooling thermogram (5 °C min^{-1}) for compound **161** (the dodecyloxy member of series IX) is shown in figure 95.

The reason why the twist is found to be right-handed in some materials, left-handed in others, and to invert in some materials in this series may well related to the stability of various conformational species. It appears that the materials which have shorter alkoxy chains tend to form right-handed helices, whereas materials that have a longer alkoxy chain prefer a left-handed helix. Why this should be is an extremely complicated matter, especially when one begins to analyse the number of conformational species that may be formed by the chiral end group of the molecule .

No.	n	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
156	7	*S*	e	*L*	RH	-ve	
157	8	*S*	e	*L*	RH	-ve	
158	9	*S*	e	*L*	RH	-ve	+
159	10	*S*	e	*d*	LH	-ve	+!
160	11	*S*	e	*d*@	LH @	-ve	+!
161	12	*S*	e	*d*£	LH £	-ve	
162	13	*S*	e	*d*$	LH $	-ve	
163	14	*S*	e	*d*	LH	-ve	

@ the helical twist sense appeared to invert between 115 and 110 °C, £ the helical twist sense began to invert between 50 and 45 °C, $ the helical twist sense appeared to invert between 105 and 100 °C, ! evaluated every 10 °C throughout the smectic C* temperature range.

Table 20. Chiral Properties Associated with the Smectic C* Phase of the Materials in Series IX (156-163).

A full interpretation of the behaviour of these molecules will therefore not be attempted, but it does seem worthy of note that all the materials, which exhibited twist inversions in the chiral smectic C*, possess an isopropyl group attached to the peripheral side of the chiral centre. This group appears to have greater free rotation in the present series of materials (**156** to **163**), than the earlier series based on a 2-chloro-3-methylbutyl moiety (**128** to **135**). The possible conformers, however, are similar and are illustrated for the present series, IX, in figure 96, where out of the three proposed conformers, B is the only one that is symmetrical in terms of having a methyl group sticking out on either side of the long molecular axis. Conformers A and B are unsymmetrical as both of them have a methyl group that is placed along the direction of the molecular core, but the lateral methyl groups are positioned on opposite sides of the core. This may have some

influence on the helix direction, but the chiral centre must, in any comprehensive argument, also be taken into full account. It was interesting to note that the polarization direction remained constant throughout the temperature range of the smectic C* phase when ascertained for compound **159** (the decyloxy member of the series), indicating that the helix direction and polarization direction are not always linked. This suggests that as the chiral centre with its large dipole is invariably involved in determining the polarization direction, which remains constant, then the outer part of the molecule (beyond the chiral centre) plays a bigger role in determining the helix direction, in this case.

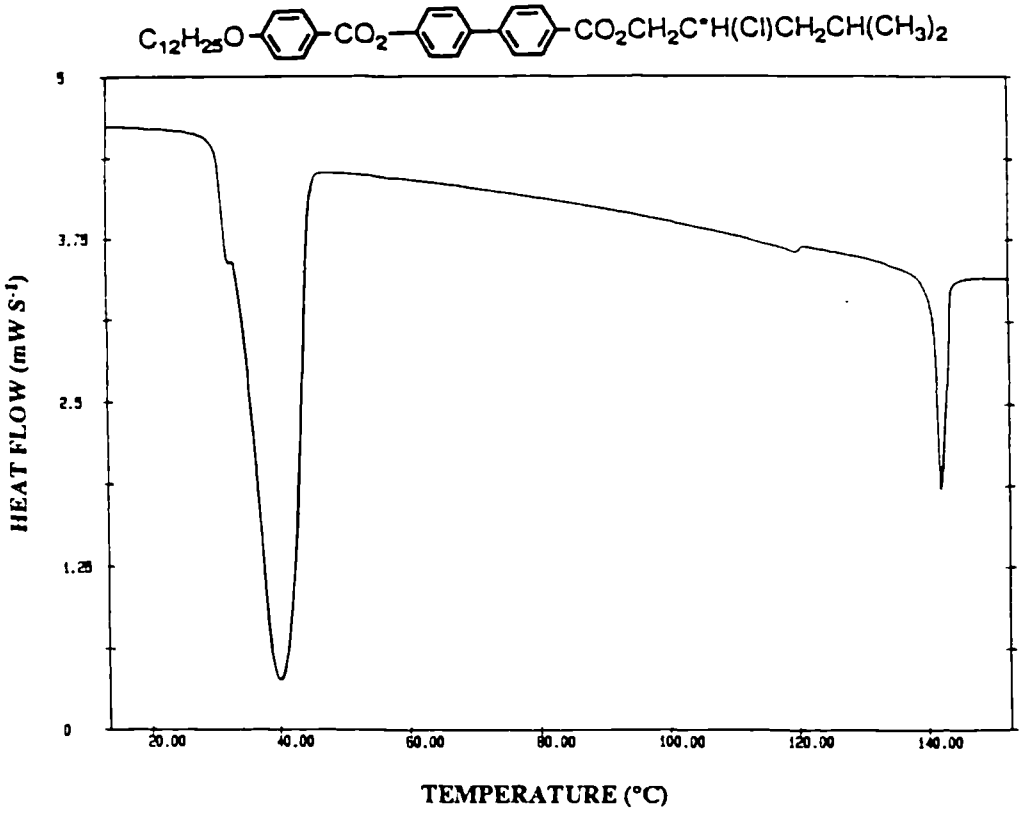


Figure 95. The Cooling Cycle for *(S)*-2-Chloro-4-methylpenyl 4'-(4-dodecyloxybenzoyloxy)-4-biphenylcarboxylate (161).

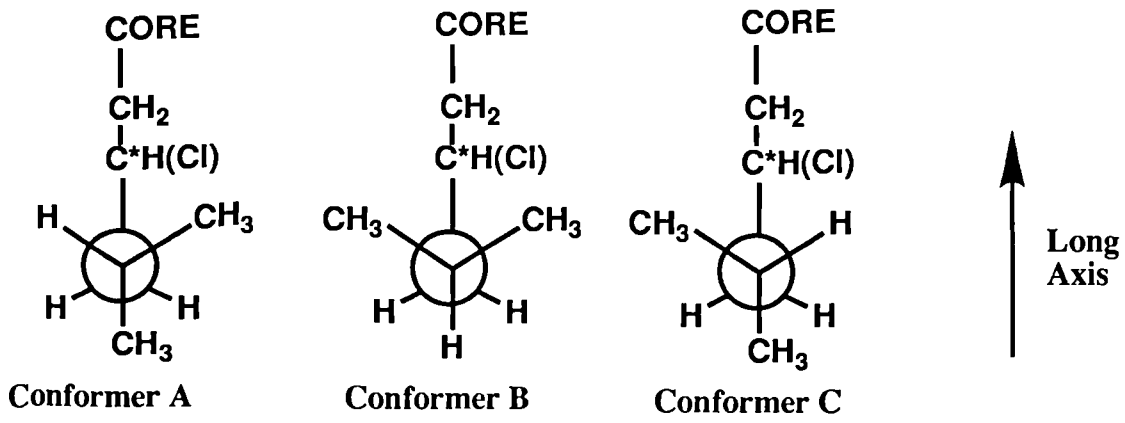


Figure 96. The Possible Conformers Associated with the End-Group in Compounds 156 to 163 (the Benzoate Materials Based on a 2-Chloro-4-methylpentyl Chiral Moiety).

The variation of both pitch and tilt angle with respect to temperature for compound **158** (the nonyloxy member of series IX) was determined, and compared with the results obtained for compound **143** (the nonyloxy member of series V). The reason for doing this was to try and determine which material exhibited the largest degree of chirality in the smectic C* phase and to try and relate this to the temperature range of the TGB A* phase. The results obtained for both compounds are shown in figures 97 and 98.

It can be seen from figure 97 that the tilt angle for compound **158** saturates at approximately 35°, whereas the tilt angle for compound **143** saturates at the lower value of 27°. Assuming the azimuthal angle is similar in both compounds, this suggests that compound **158** has a greater degree of chirality than that of compound **143**, in the smectic C* phase. This was investigated further when pitch measurements were taken (see figure 98). It can be seen from figure 98 that the pitch of compound **143** (based on a 2-chloro-3-methylpentyl chiral moiety) is considerably longer than that measured for compound **158** (based on a 2-chloro-4-methylpentyl chiral moiety).

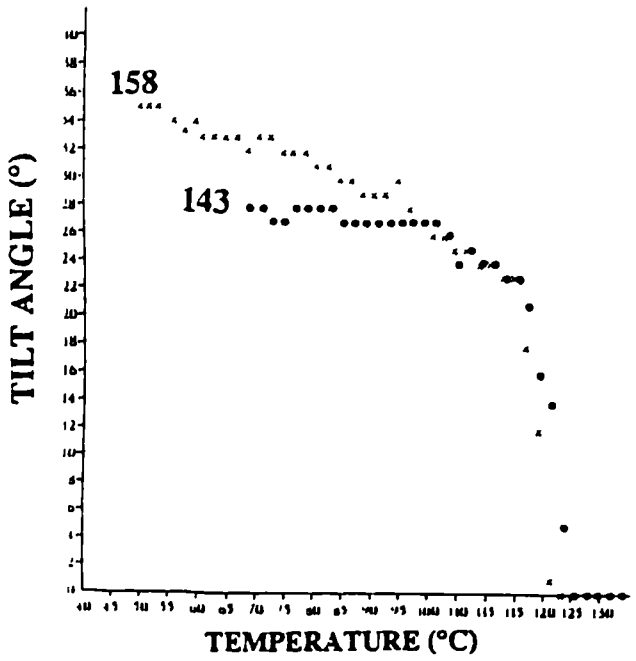


Figure 97. The Variation in Tilt Angle as a Function of Temperature in the Smectic C* Phases of Compounds 143 and 158 (the Nonyloxy Members of Series V and IX).

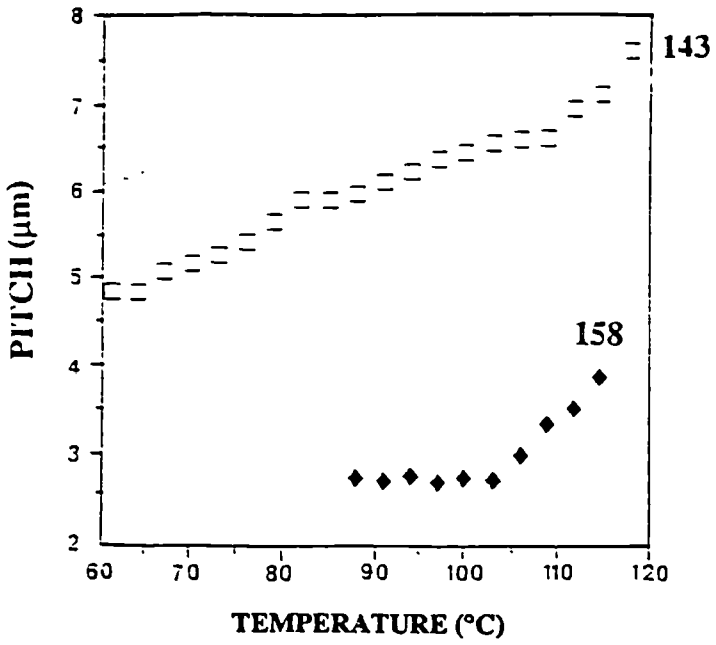


Figure 98. The Variation in Helical Pitch as a Function of Temperature in the Smectic C* Phases of Compounds 143 and 158 (the Nonyloxy Members of Series V and IX).

Furthermore, the pitch for compound **143** appears to vary linearly with respect to temperature. The pitch of compound **158** was more difficult to determine accurately because of its much shorter length. As a general trend, however, the pitch was seen to decrease quite sharply with decreasing temperature and then to saturate at a relatively constant value. The results therefore tend to suggest that compound **158** has a greater degree of chirality in the smectic C* phase. This may, however, not be the case throughout the whole phase sequence that the materials display, as inter- and intra-molecular interactions could differ in different phases. The fact that compound **158** has the greatest TGB A* phase range out of the two materials, tends, however, to confirm the hypothesis.

8.5.4 The Propiolate Materials (Series X).

The propiolate equivalent materials (**164-168**) will now be discussed, the phase transitions and behaviour of these compounds are illustrated in table 21, and figure 99.

It can be seen from table 21 and figure 99 that as the length of the alkoxy chain is increased the clearing points fall, as does the temperature range of the cholesteric/blue phase region. The width of the TGB A* phase was also reduced at longer alkoxy chain lengths, but the temperature of the transition from cholesteric phase to TGB A* phase increased. The transition from smectic A to smectic C* was seen to increase in temperature with increasing alkoxy chain length, but then began to fall again in the material with an octadecyloxy chain (**168**). The blue phase ranges in these materials were found to be quite short, with all three blue phases not being evident in all of the compounds. A short blue phase range tends to suggest a reduced chirality, but the TGB A* phase range was large. This can be accounted for if it is assumed that the layer strength is quite weak, thereby reducing the level of chirality needed to produce the dislocated TGB A* phase.

No.	n	Mpt.	I-BPIII	I-BPI	BPIII-BPII	BPIII-BPI	BPII-BPI	BPI-Ch	Ch-TGB	TGB-S_A	S_A-S_C*	Rec.
164	9	67.8	129.4		128.9		128.6	128.3	100.4	96.8	79.9	32.6
165	12	73.3		122.7				122.5	108.1	106.8	93.2	50.7
166	14	68.5	119.9		119.7		118.8	116.4	110.9	109.7	98.1	38.7
167	16	59.9	117.5			116.8		116.3	114.6	113.6	101.2	31.4
168	18	56.1		115.4				114.9	114.2	113.4	99.9	43.3

Table 21. The Transition Temperatures (°C) for the *(S)*-2-Chloro-4-methylpentyl 4'-(4-alkoxyphenylpropioloyloxy)-4-biphenylcarboxylates (164-168).

The smectic A to cholesteric transitions for these materials and the ones found for all the previous series were extensively studied by thermal techniques (DSC). The heating trace (scanning rate 5 °C min^{-1}) for the higher temperature transitions is shown in figure 100, for compound **165** (the dodecyloxy homologue of series X). Three peaks can be clearly seen corresponding to the isotropic liquid to cholesteric, cholesteric to smectic A/TGB A*, and smectic A/TGB A* to smectic C* phase transitions. The peak corresponding to the clearing point has a slight shoulder, which may correspond to one of the blue phase transitions, but the cholesteric to TGB A* and TGB A* to smectic A transitions are not resolved at all. This is quite surprising as the temperature range of the TGB A* phase is much larger in this material than in a previous material studied (**158**), but the resolution of the transitions is much better in compound **158** (the nonyloxy member of series IX, the benzoate equivalents) when studied by DSC. The peak corresponding to the transition associated with the TGB A* phase in compound **165** is, however, quite broad, indicating that more than one transition may be occurring.

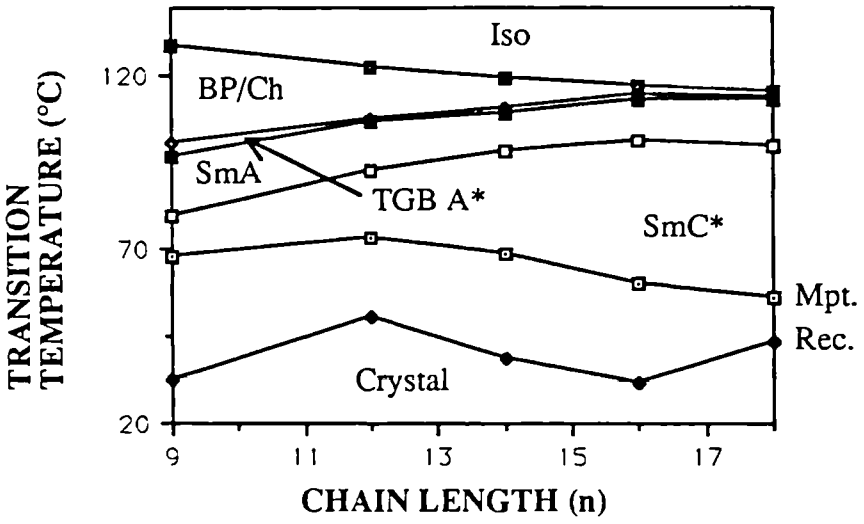


Figure 99. Transition Temperatures Versus Alkoxy Chain Length for Materials (164-168).

When the phase behaviour of the nonyloxy member of this series (**164**) is compared with the analogous benzoate material (**158**), a number of points can be noted. The phase behaviour of these two compounds is illustrated in figure 101.

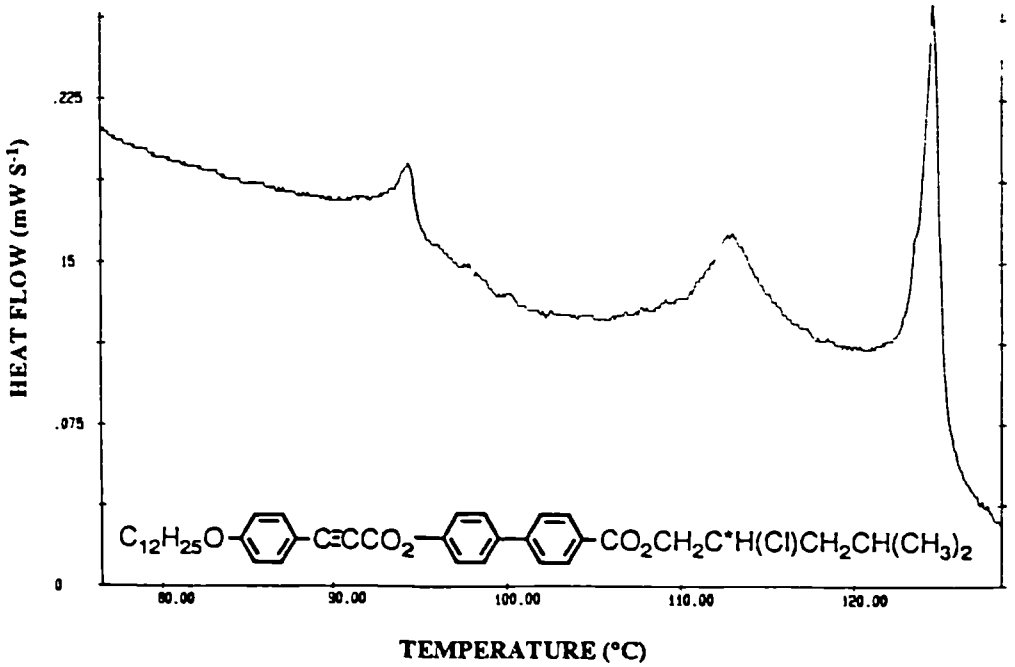


Figure 100. The Heating Cycle Close to the Clearing Point for *(S)*-2-Chloro-4-methylpentyl 4'-(4-dodecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (165).

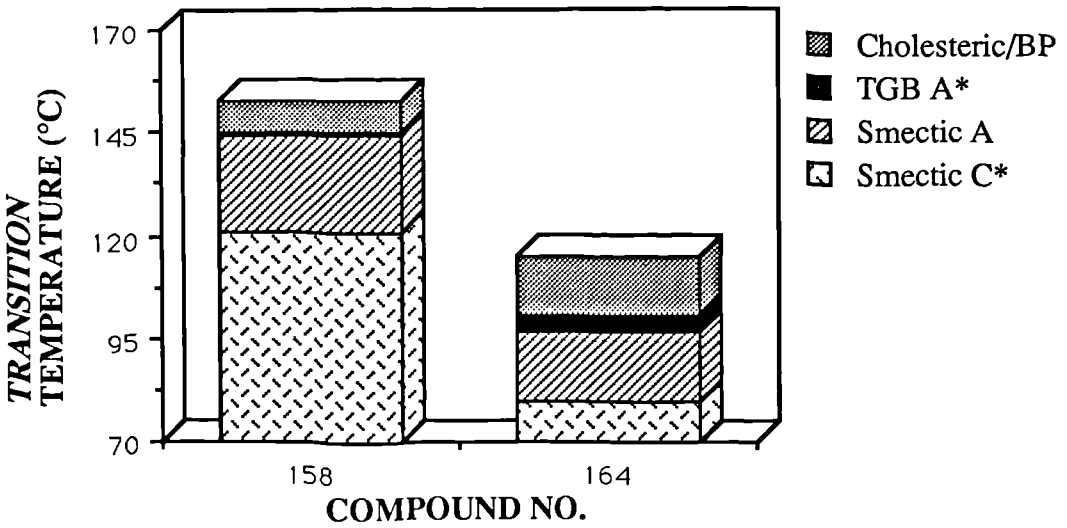


Figure 101. A Comparison of the Phase Behaviour of Compounds 158 and 164. (the Nonyloxy Homologues of Series IX and X).

Firstly, the TGB A* temperature range is much larger in the propiolate compound (**164**), than in benzoate material (**158**), even though the blue phase range is shorter, the later point suggesting a decrease in the chirality of the system on insertion of a triple bond into the core structure. This increase in the TGB A* temperature range can be explained in two ways, firstly the range of the smectic A phase is shorter for compound **164**, which brings the smectic C* phase closer to the cholesteric to smectic A transition, thereby increasing molecular fluctuations that will influence the transition. Secondly, it appears that the materials which possess a triple bond in their molecular structure display a weaker layer ordering, this is illustrated by the greater degree of nematogenicity found for these materials. The weak layer ordering aids in the formation of the TGB A* phase. The apparent reduction in chirality noted on addition of the triple bond may occur for two reasons, firstly as stated earlier the core structure is longer and so the net molecular chirality is diluted somewhat, and secondly, the degree of freedom of rotation of the core structure is increased thereby reducing the net molecular dipole.

As the cholesteric phase has a much larger temperature range for compound **164**, than that observed for compound **158** (the equivalent benzoate), it was decided to attempt a miscibility study, similar to the one carried out using compound **158**, with a standard material, *(S)*-1-methylheptyl 4'-(4-tetradecyloxyphenylpropioloyloxy)-4-biphenyl carboxylate (**14P1M7**), that showed a TGB A* phase. Once again miscibility of the TGB A* phase across the complete phase diagram was the desired result. Figure 102, however, illustrates the results obtained.

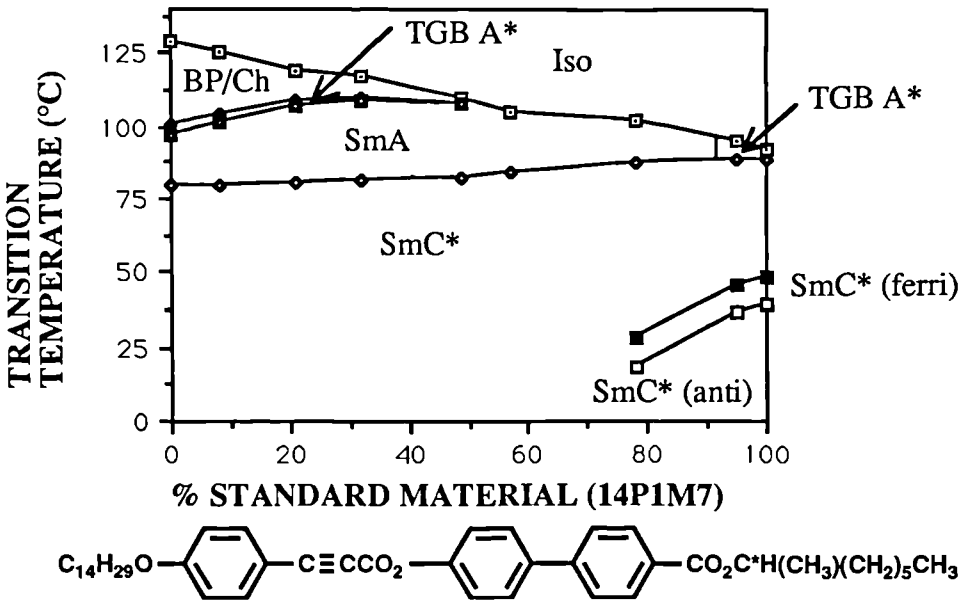


Figure 102. The Phase Miscibility Diagram Obtained for Binary Mixtures of Compound 164 (the Nonyloxy Member of Series X) and a Standard Material (14P1M7), and the Structure of 14P1M7.

It can be seen from figure 102 that miscibility of the TGB A* phase was not achieved across the whole composition range of the phase diagram. A similar picture to that observed for the previous miscibility study occurred (**158** and **15P1M7**). Firstly, the clearing points and cholesteric phase temperature range were seen to drop as the percentage of the standard material (**14P1M7**) was increased. The TGB A* phase was only present when it underpinned a cholesteric phase, and disappeared once the cholesteric phase vanished. The smectic A to smectic C* transition temperature

gradually rose as the percentage of standard increased, and at high concentrations of **14P1M7** (> 75 %), an underlying ferrielectric phase and antiferroelectric phase were observed. The TGB A* phase was seen in mixtures that were predominantly composed of the standard material (> 90 %) or the test material (> 50 %), but were not at all evident in the middle of the phase diagram (50 to 90 % test material). The miscibility serves to reinforce the points that were noted earlier, that is for the TGB A* phase to exist, the fluctuations occurring at the transition point must be large (whether this be an isotropic liquid to smectic A, or cholesteric to smectic A transition). This is only achieved if an overlying cholesteric or an underlying smectic C* phase is in close proximity to the transition.

When the properties of the smectic C* phase were investigated for the propiolate materials in series X (compounds **164** to **168**), a number of interesting effects were once again noted. The results obtained are illustrated in table 22.

No.	n	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
164	9	*S*	e	*d*@	LH @	-ve	+!
165	12	*S*	e	*d*@	LH @	-ve	
166	14	*S*	e	*d*@	LH @	-ve	
167	16	*S*	e	*d*£	LH £	-ve	
168	18	*S*	e	*d*@	LH @	-ve	

@ the helical twist sense appeared to begin to invert just prior to crystallisation, £ the helical twist sense appeared to invert at approximately 49-43 °C, ! the polarization direction was determined every 10 °C throughout the smectic C* temperature range.

Table 22. Chiral Properties Associated with the Smectic C* Phase of the Materials in Series X (164-168).

It can be seen from table 22 that the helix direction in every compound in this series appeared to invert. At the smectic A to smectic C* transition the sample was momentarily stressed in order to give a reasonable planar alignment. The texture was blue in colour and appeared quite iridescent. In the case of compound **167** (the hexadecyloxy member of series X) the texture is shown in plate 17, the helix direction was determined by polarimetry to be left-handed for this material. As the sample was cooled further the texture became very mobile, with an increasing degree of coloration as illustrated in plate 18. Further cooling resulted in the blue texture returning, the helix was, however, determined as right-handed. On occasions, where the material was pinned to the surface, the helix was seen to retain its original structure at a temperature below the inversion point.

In order to prove conclusively that the helix in compound **167** had in fact inverted, a contact study with a material of known twist sense was performed. The material selected was *(S)*-2-chloro-octyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate, compound **178**, which was found to have a left-handed helix in the smectic C* phase throughout its temperature range. Once the contact had been established between the two materials slow cooling was effected (2 °C min^{-1}). On cooling slowly from the smectic A phase, to a temperature just below the transition to the smectic C* phase for both materials, the boundary between the standard (**178**) and compound **167** was found to show a continuous change in pitch across the contact region, but at no point did the pitch diverge, see plate 19.

This means that the helices in the smectic C* phases of both compounds have the same twist senses, i.e., they are both left-handed. On further cooling to the temperature range in which the texture of the smectic C* phase of the test material (**167**) becomes mobile and highly coloured (approximately 46 °C), the test material appeared to become non-

helical with an infinite pitch. The contact appeared as a dark pseudo-homeotropic region adjacent to the smectic C* texture of the test material, as shown in plate 20.

Upon further cooling (approximately 35 °C) the pale blue planar texture of the test material returned, but this time the boundary between the test material and the standard material showed a sharp discontinuity where the *schlieren* texture of a non-helical smectic C phase was observed, as illustrated in plate 21.

From these studies it is reasonable to conclude that the lower temperature smectic C* phase of compound **167** has a twist sense that is opposite to that of the standard material, i.e., right-handed. Thus on cooling from the smectic A phase, the smectic C* phase has a left-handed helical structure that inverts *via* an infinite pitch region to a right-hand helix.

Thermal studies indicated that the inversion of helical twist sense in the smectic C* phase did not have a measurable enthalpy. The DSC cooling thermogram for compound **167** is shown in figure 103.

The reasons why this strange behaviour is encountered may once again be tied to conformational changes for the molecules that constitute the phase. Two possible mechanisms to describe how the inversion takes place are possible. The first involves a change in tilt angle, that is to say on cooling from the smectic A phase the tilt angle increases, until the material begins to invert when the tilt rapidly decreases again to give a smectic A phase, the tilt then increasing again to give a smectic C* phase with the opposite twist sense. In order to do this, however, the sign of the azimuthal angle must also change at the inversion point.

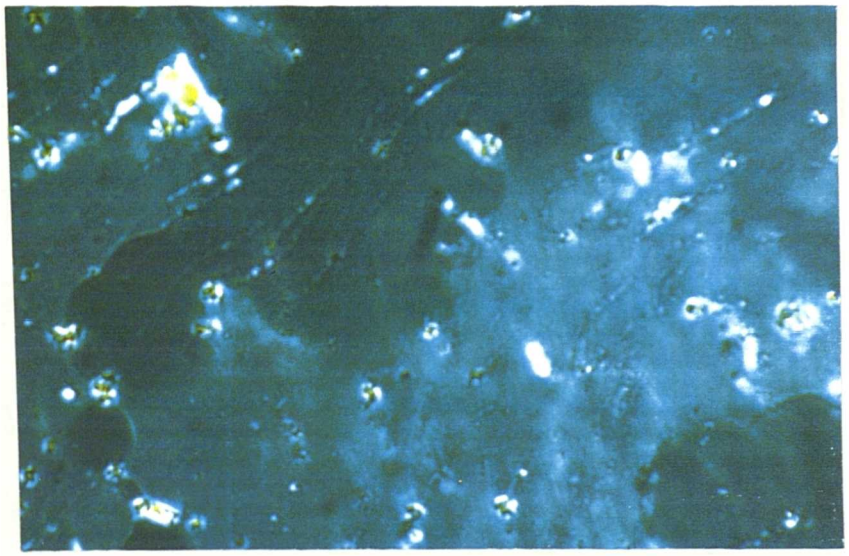


Plate 17. The Texture Observed for the Smectic C* Phase of *(S)*-2-Chloro-4-methylpentyl 4'-(4-hexadecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (167) at a Temperature above the Helix Inversion Inversion Point.

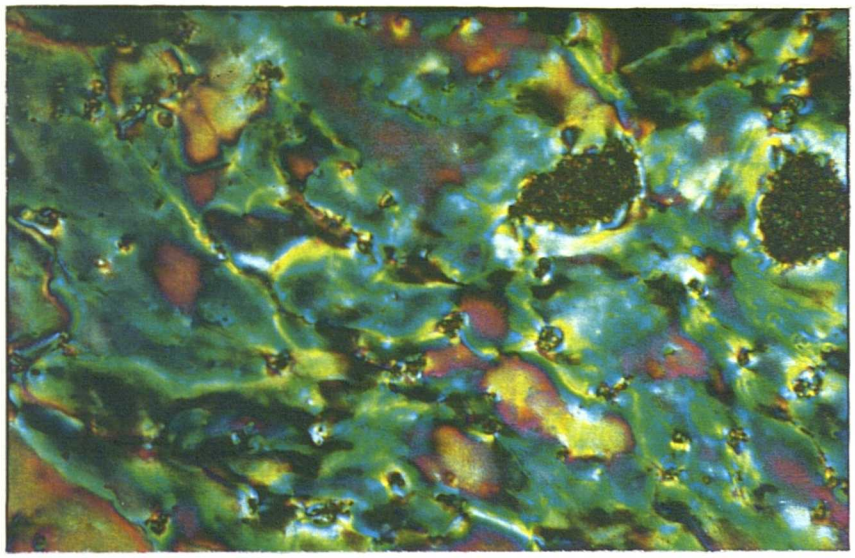


Plate 18. The Texture Observed for the Smectic C* Phase of *(S)*-2-Chloro-4-methylpentyl 4'-(4-hexadecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (167) at the Temperature of the Helix Inversion Inversion Point.

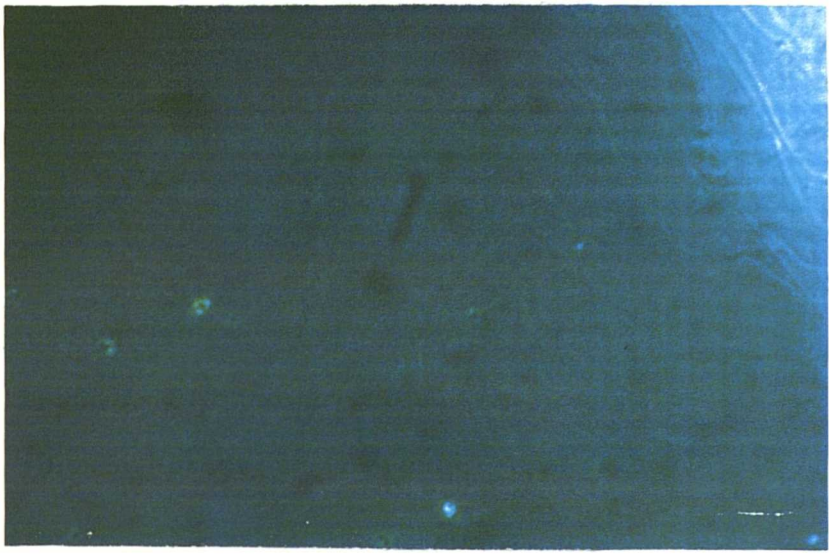


Plate 19. The Contact Region in the Smectic C* Phase Observed Between Compound 123 and *(S)*-2-Chloro-octyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (178) (approximately 65 °C).

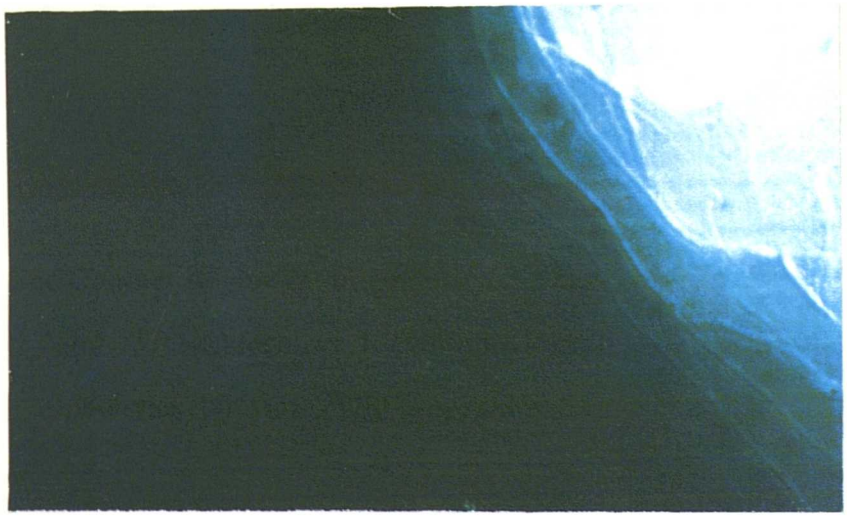


Plate 20. The Contact Region in the Smectic C* Phase Observed Between Compound 123 and *(S)*-2-Chloro-octyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (178) (approximately 46 °C).

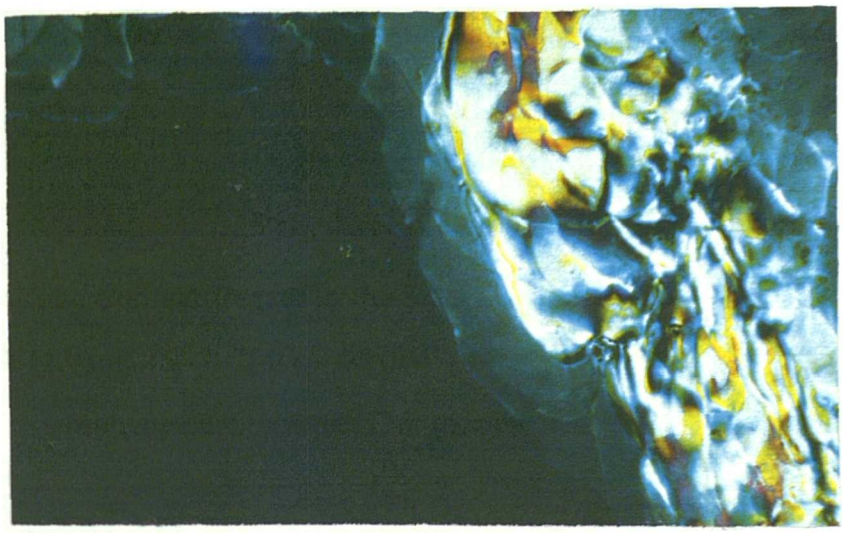


Plate 21. The Contact Region in the Smectic C* Phase Observed Between Compound 123 and *(S)*-2-Chloro-octyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (178) (approximately 35 °C).

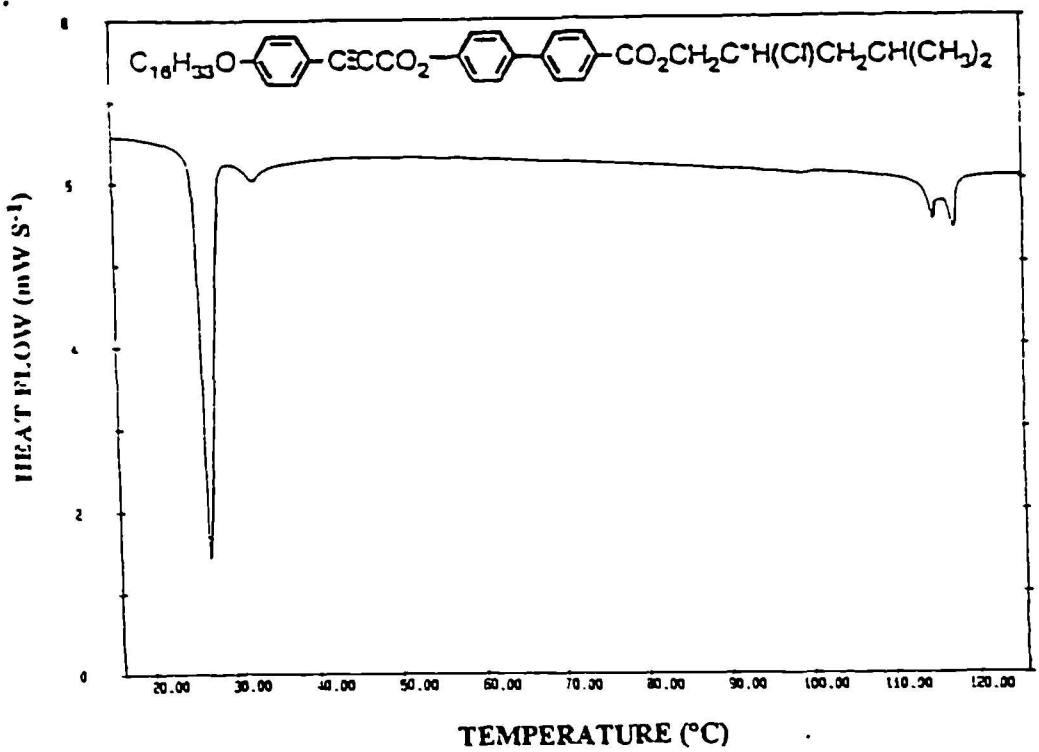


Figure 103. The Cooling Thermogram Obtained for *(S)*-2-Chloro-4-methylpentyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (167).

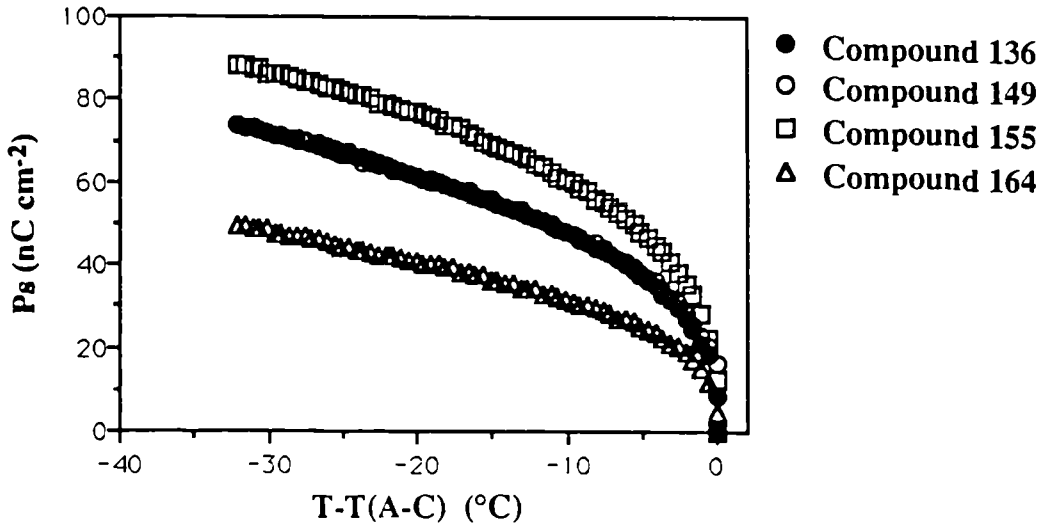
Textural studies suggest that a smectic A phase is not formed at the inversion point, and one may argue that the energy cost to the system would be too high in this case. The second possible mechanism involves a gradual reduction of the azimuthal angle on approaching the inversion point, thereby leading to a smectic C* phase of infinite pitch. As the material passes through its inversion point the azimuthal angle will once again increase gradually to form a helical modification. The precession of the molecules would, however, form a helix of differing twist sense to the previous one. The second mechanism does seem more plausible, and textural studies would suggest that this could be the appropriate one. This subject will be expanded upon later in this chapter.

When the polarization direction was studied the result was found to be positive in all of the cases measured, and on no occasion was it seen to invert along with the helix direction. The polarization was measured as a function of temperature, for compound **164** (the nonyloxy homologue) giving a value of 32 nC cm^2 at 10 °C (30 V pp, 60 Hz) below the smectic A to smectic C* phase transition.

8.5.5 Studies Concerning the Spontaneous Polarization in the Smectic C* Phase in Selected Propiolate Materials.

In order to compare the effects of the chiral end group on the magnitude and temperature dependence of the spontaneous polarization, the nonyloxy member of each phenylpropiolate series of materials, compounds **136**, **149**, **155** and **164**, (**123** did not possess a smectic C* phase), was assessed. The results obtained are shown in figure 104, where it can be seen that compound **164** (series X) has the lowest value of the spontaneous polarization in comparison to the other three materials tested. The branching point in this material is two atoms removed from the chiral centre, as opposed to one in the other materials. The greater separation of the chiral centre from the branching point is thought to reduce the value of the spontaneous polarization by allowing for an increase in

the rotational freedom of the chiral centre. In effect the chirality of the system in the smectic C* phase is reduced. The reduction in chirality is also borne out by the small blue phase temperature range observed at the clearing point for this material.



where **136** has a *(S)*-2-chloro-3-methylbutyl chiral moiety, **149** has a *(S,S)*-2-chloro-3-methylpentyl chiral moiety, **149** has a *(S,R)*-2-chloro-3-methylpentyl chiral moiety, and **149** has a *(S)*-2-chloro-4-methylpentyl chiral moiety.

Figure 104. The Effect of Chiral End Group on the Value of the Spontaneous Polarisation for Compounds 136, 149, 155, 164 (the Nonyloxy Homologues of Series IV, VII, VIII, and X).

Compounds **136** and **149** have the same value and temperature dependence of the spontaneous polarization, the values for which are intermediate compared to the other materials studied. Each material has a branching point on the atom located adjacent to the chiral centre, in the case of compound **136**, the branch is achiral, whereas in compound **149**, the branching point is chiral with the same absolute spatial configuration as the first optically active centre (both chiral centres are *S*). The terminal aliphatic chain on the peripheral side of the chiral centre is also longer in the case of compound **149**. The lengthening of the peripheral alkyl chain and the chirality associated with the branch point, in compound **149**, do not, however, affect the value of the spontaneous polarization

in this instance. Compound **155** (*S,R* configuration of chiral centres) has the largest value of the spontaneous polarisation of all the materials studied. Its structure is identical to that of compound **149** except that the configuration of the branch point and second chiral centre is *R*. This indicates that the configurations of sequential chiral centres are important in determining the value, and as previously mentioned the direction of the spontaneous polarization in the ferroelectric smectic C* phase.

8.6 A Summary of the Properties of the Materials in Series I to X.

In order to summarise the properties of the materials from the first ten series of compounds under discussion, figure 105 illustrates the phase behaviour of the nonyloxy member of each family, whilst table 23 illustrates the properties associated with the smectic C* phase of the same compounds.

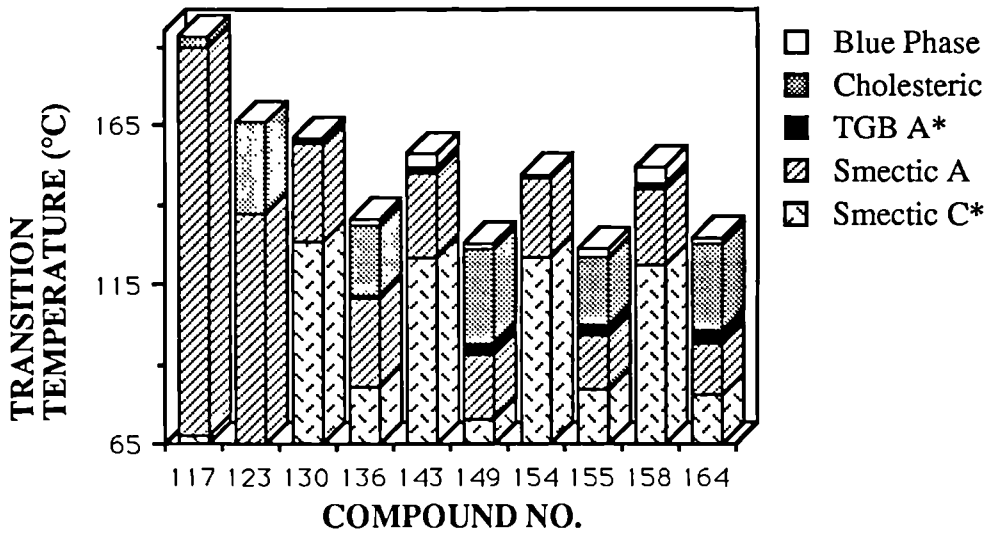


Figure 105. The Phase Behaviour Observed for the Nonyloxy Members of the First Ten Series of Compounds.

When analysing the results shown in figure 105 and table 23 it must be remembered that there were a number of variations some expected and some very unusual within each series, i.e., the length of alkoxy chain caused some very large effects. The comparisons here are meant to give a general impression of the effects that each chiral end group

imparts to the system. A number of points can be noted from the figures. Firstly, the insertion of a triple bond increases the nematogenic tendency of the materials, as well as lowering the clearing points.

No.	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.	End Group
117	*S*	e	*L*	RH	-ve		2Cl3
123	No S_C*	phase	in this	material	-ve		2Cl3
130	*S*	e	*L*@	RH @	-ve		2Cl3M4
136	*S*	e	*L*	RH	-ve	+	2Cl3M4
143	*S,S*	e, o	*d*	LH	-ve, +ve		2Cl3M5
149	*S,S*	e, o	*d*	LH	-ve, +ve	+	2Cl3M5
154	*S,R*	e, o	*L*	RH	-ve, +ve	-	2Cl3M5
155	*S,R*	e, o	*L*	RH	-ve, +ve	-	2Cl3M5
158	*S*	e	*L*	RH	-ve	+	2Cl4M5
155	*S*	e	*d*@	LH @	-ve	+	2Cl4M5

where @ signifies that the helical twist sense appeared to invert in the smectic C* phase of this material, and 2Cl3 refers to 2-chloropropyl, 2Cl3M4 refers to 2-chloro-3-methylbutyl, 2Cl3M5 refers to 2-chloro-3-methylpentyl, 2Cl4M5 refers to 2-chloro-4-methylpentyl.

Table 23. Chiral Properties Associated with the Smectic C* Phase of the Nonyloxy Homologues of Series I to X.

The blue phase temperature range, however, is decreased in the materials that have a triple bond in their structure. The decrease in blue phase thermal stability may be due to a reduction in chirality that is a result of a greater freedom of rotation of the mesogenic core and/or a dilution effect on lengthening the molecule. The greater rotational freedom of the core is probably responsible for the increased nematogenic tendency, as the layer ordering associated with smectics becomes less viable. Secondly, the TGB A* thermal

stability is greater in the materials that possess a triple bond. As the chirality of these materials is thought to be weaker, this means that either the layer ordering is not as strong (hence, a greater nematogenic tendency) or the phase sequences involved facilitate the formation of this entity. In every material that exhibits a TGB A* phase, the insertion of a triple bond reduces the smectic A temperature range, which effectively brings the cholesteric to smectic A transition closer to the smectic A to smectic C* transition, thereby increasing the effect of molecular fluctuations felt in the smectic A phase.

The effects of the various chiral end groups will now be discussed. The two materials *(S)*-2-chloropropyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate and *(S)*-2-chloropropyl 4'-(4-nonyloxypropioloyloxy)-4-biphenylcarboxylate (**117** and **123**) which possess the shortest terminal aliphatic chain associated with the chiral centre have the highest clearing points (relative to the analogous materials with longer chains), they do not display blue phases, and in the case of compound **123** a smectic C* phase was not observed. Neither material was seen to exhibit a TGB A* phase, but compound **123** did show interesting behaviour in the cholesteric phase, as the helical twist sense was seen to invert. This type of inversion in the cholesteric phase was not seen in any of the other materials in this comparison. The two materials with a slightly longer terminal chain, i.e., possessing a 2-chloro-3-methylpentyl chiral moiety, (**130** and **136**) had reduced clearing points, possessed blue phases, a TGB A* phase, albeit a very transitory one in compound **130**, and had a smectic C* phase. The presence of blue phases suggests that the chirality of the system has increased, this probably being due to the reduced freedom of rotation of the chiral centre. Compounds **143**, **149**, and **155** had a similar phase sequence, but with lower clearing points, a longer blue phase and TGB A* temperature range, and a reduced smectic A thermal stability. Compound **154** exhibited analogous phase behaviour, except that a TGB A* phase was not observed. The presence and temperature range of the TGB A* phase and blue phases suggests that a second chiral centre plays an important role in

determining the phase behaviour. The TGB A* thermal stability can, however, be enhanced or removed completely on moving from an *(S,S)* configuration to an *(S,R)* configuration depending on whether the material has a triple bond in its core structure or not. This suggests that no firm predictions can be made on how a second chiral centre will affect phase stability, as the effects may well be sensitive to the type of core, and therefore different in every case. If, however, more materials are prepared with these types of configuration some patterns of phase behaviour may well arise. Compounds **155** and **164**, had the highest TGB A* thermal stability, but a reduced blue phase temperature range in the case of compound **164** when compared to compounds **143** and **155**. This suggests that the layer ordering may be weaker, or the proximity of other helical modifications are important in determining the nature of the cholesteric to smectic A transition (**155** and **164** had the shortest smectic A temperature range, thereby bringing the smectic C* phase closer to the cholesteric to smectic A transition point and as a consequence increasing the pretransitional fluctuations).

When the properties of the smectic C* phase are evaluated for the materials in the first ten series, it is found that all of the materials except for compounds **130**, **143**, **149** and **155** can be classified as having a right-handed helix. Compounds **143** and **149** are based on a 2-chloro-3-methylpentyl chiral moiety with an *(S,S)* configuration of the sequential chiral centres contained in their structures, and compounds **155** (the propiolate material based on a 2-chloro-4-methylpentyl chiral moiety) and **130** (the benzoate material based on a 2-chloro-3-methylbutyl chiral group) have helices in their smectic C* phase that appear to invert with respect to temperature. It appears that inversions of the helix in the smectic C* phase occur in the materials that possess a terminal isopropyl moiety. The polarization direction was determined as being positive in every material, except the two compounds that were based on a 2-chloro-3-methylpentyl chiral moiety with an *(S,R)* configuration of chiral centres (**154** and **155**) in which it was found to be negative. The

direction of the spontaneous polarization remained unchanged even after the helix in certain materials had inverted. The latter point demonstrating that the polarization direction is not necessarily linked to the helical twist sense of the smectic C* phase.

8.7 Esters Based on the 2-Chloropentyl and 2-Chlorohexyl Chiral Moieties.

Four materials were prepared in these two series (XI and XII) with the general structures illustrated in figure 106.

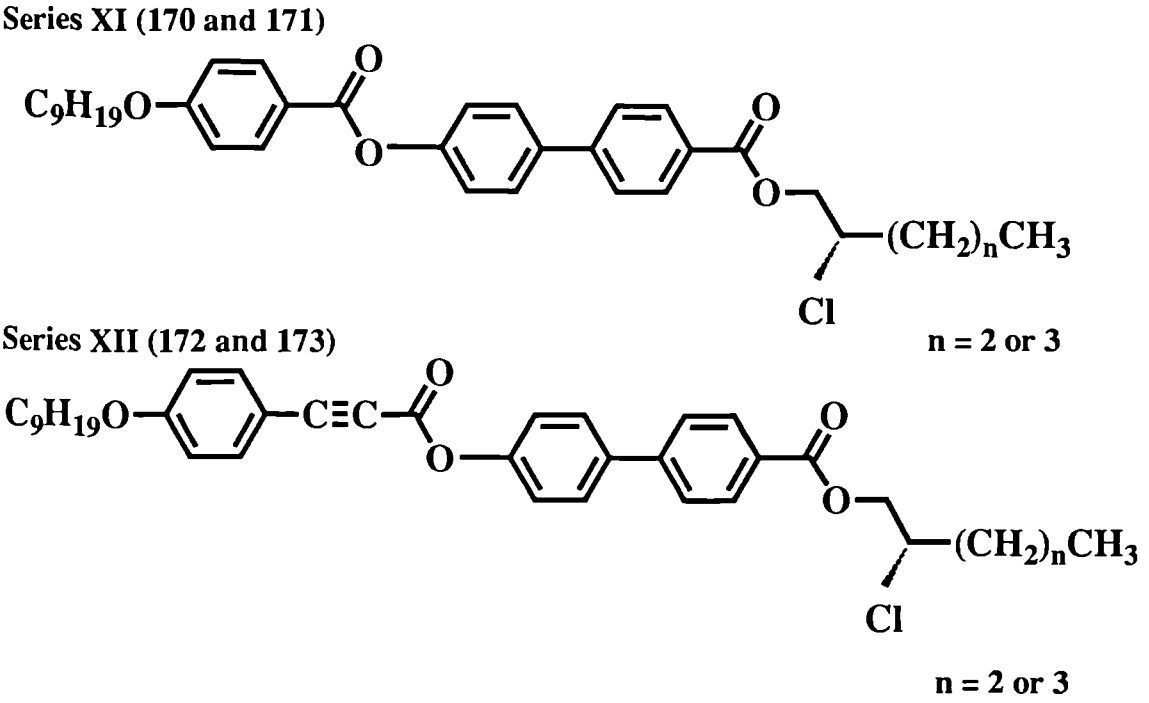


Figure 106. The Structures of the Materials Based on a 2-Chloropentyl and a 2-Chlorohexyl Chiral Moiety.

Although not possessing a n-alkyl branching point adjacent to or near to the chiral centre, the degree of chirality associated with the materials in this series was still anticipated as being quite high. The reason for this being that the terminal aliphatic chains associated with the peripheral side of the chiral centre were quite long, thereby causing a possible increase in the rotational damping of the chiral centre[32].

The phase behaviour for these materials is shown in table 24, and figure 107, where it is seen that all of the materials in this compilation of compounds possess an isotropic to blue phase to cholesteric to TGB A* to smectic A to smectic C* phase sequence. Comparison of the two benzoate materials (**170** and **172**) yields a number of points. Firstly, the clearing point for compound **172** is reduced compared with that of **170**, and the blue phase/cholesteric temperature range is slightly shorter, indicating an increase in the smectogenic tendency.

No.	n	Mpt.	I- BPIII	BPIII -BPII	BPII- BPI	BPI- Ch	Ch- TGB	TGB- S_A	S_A- S_C*	Rec.
170	2	90.9	163.9	163.6	163.2	158.5	157.6	157.3	117.5	59.9
171	2	68.2	141.7	141.6	141.3	140.6	105.4	103.8	67.4	46.3
172	3	89.5	158.7	158.3	157.8	154.4	154.2	153.9	121.0	62.5
173	3	67.5	136.2	136.0	135.7	135.1	105.7	104.0	76.2	59.6

Table 24. The Transition Temperatures (°C) for the *(S)*-2-Chloropentyl and 2-Chlorohexyl 4'-(4-alkoxybenzoyloxy) and phenylpropioloyloxy)-4-biphenylcarboxylates (170-174).

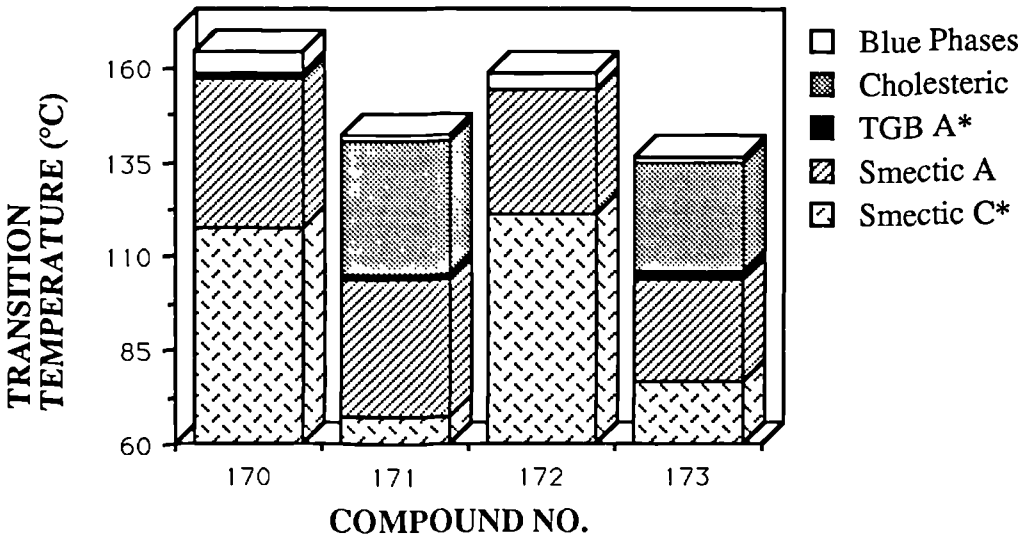


Figure 107. A Comparison of the Phase Behaviour of Compounds 170 to 173 (the Materials Based on a 2-Chloropentyl and 2-Chlorohexyl Chiral Moiety).

Each compound has a short temperature range TGB A* phase, the thermal stability of which appears to be identical for both compounds. This suggests that the layer ordering and chirality in these materials may be quite similar, which is not such an unexpected result as the structures differ only in the addition of one methylene unit to the terminal aliphatic chain. Finally, the smectic A to smectic C* transition is seen to occur at a slightly higher temperature in compound **172**, when compared with **170**.

Comparison of the propiolates (**171** and **173**) yields a similar picture. The clearing point decreases on increasing chain length (**171** to **173**), as does the temperature range of the nematic phase. The blue phase and TGB A* ranges are almost identical in both compounds, but the smectic A range is reduced in compound **173** as the transition from smectic A to smectic C* occurs at a higher temperature.

The transitions observed in these materials were studied by differential calorimetry, the results obtained being in general agreement with the data obtained by optical microscopy. Figures 108 and 109 show the heating traces for the cholesteric to smectic A* transition in compounds **171** and **173** respectively.

The thermogram in figure 108 (**171**) shows two peaks, the higher temperature one corresponding to the transition from cholesteric to TGB A* and TGB A* to smectic A, whereas the lower temperature peak corresponds to the transition from the smectic A to smectic C* phase. The higher temperature peak appears quite broad with a slight shoulder suggesting that two transitions may be present. A similar situation is seen for compound **173** (figure 109) where the higher temperature peak corresponds to the clearing point and the lower temperature peak to the transition to and from the TGB A* phase. The shoulder observed on the lower temperature peak is quite well defined in this instance.

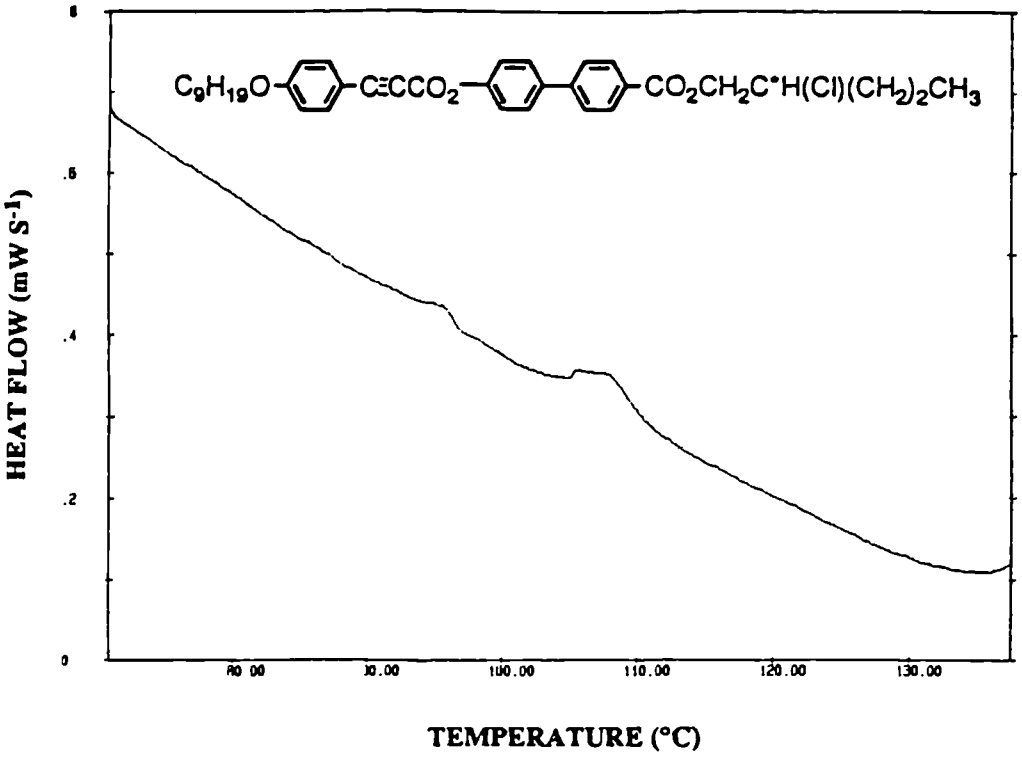


Figure 108. The Heating Cycle Close to the Cholesteric to Smectic A Transition for *(S)*-2-Chloropentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (171).

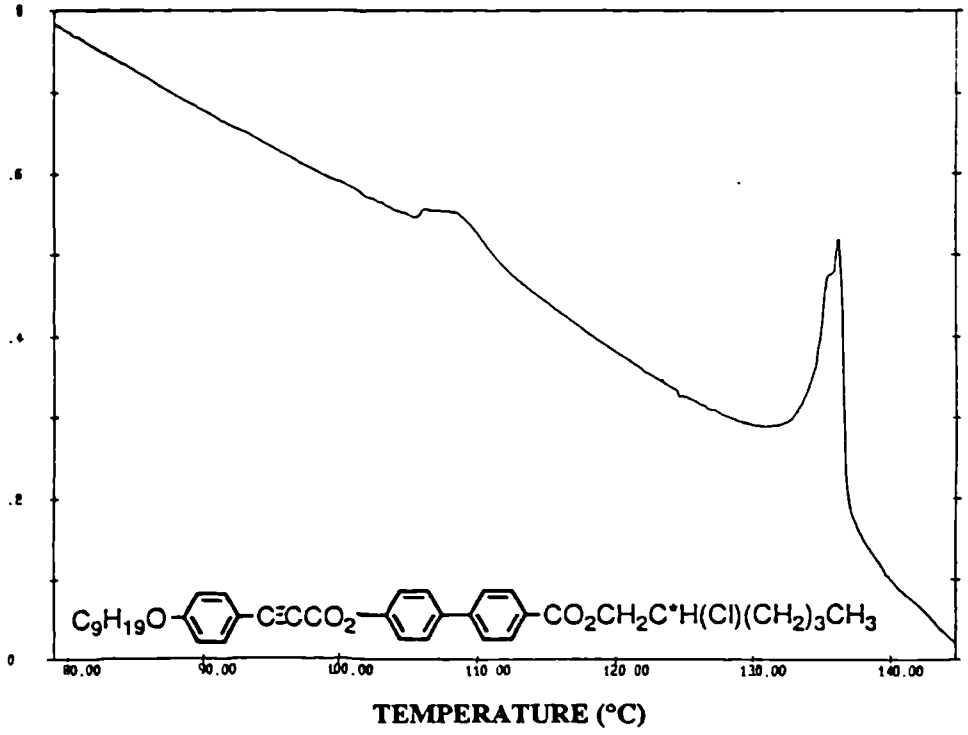


Figure 109. The Heating Cycle Close to the Cholesteric to Smectic A Transition for *(S)*-2-Chlorohexyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (173).

If a comparison is now made between the benzoate compound (**170**), and the propiolate compound (**171**) it is found that the clearing point and blue phase temperature range are much reduced for compound **171**. The latter point suggests a reduction in chirality (the cholesteric phase in this material is much larger than in **170**). The TGB A* phase, however, has an increased thermal stability in **171** compared with **170**. If the chirality in the system is reduced by the presence of the triple bond in the core of the molecule, then the increase in the TGB A* temperature range must, as with previous systems, be due to a weakening of the layer ordering and/or an increase in the fluctuations caused by the adjacent helical modifications, i.e., the smectic C* phase. The smectic A phase temperature range is reduced in **171**, and the transition to the smectic C* phase occurs at a much lower temperature.

If a comparison is now made between compound **171** and compound **164** (the analogous material containing a 2-chloro-4-methylpentyl chiral moiety), the effect of the branching point in the vicinity of the chiral centre can be established. The results of this comparison are illustrated in figure 110.

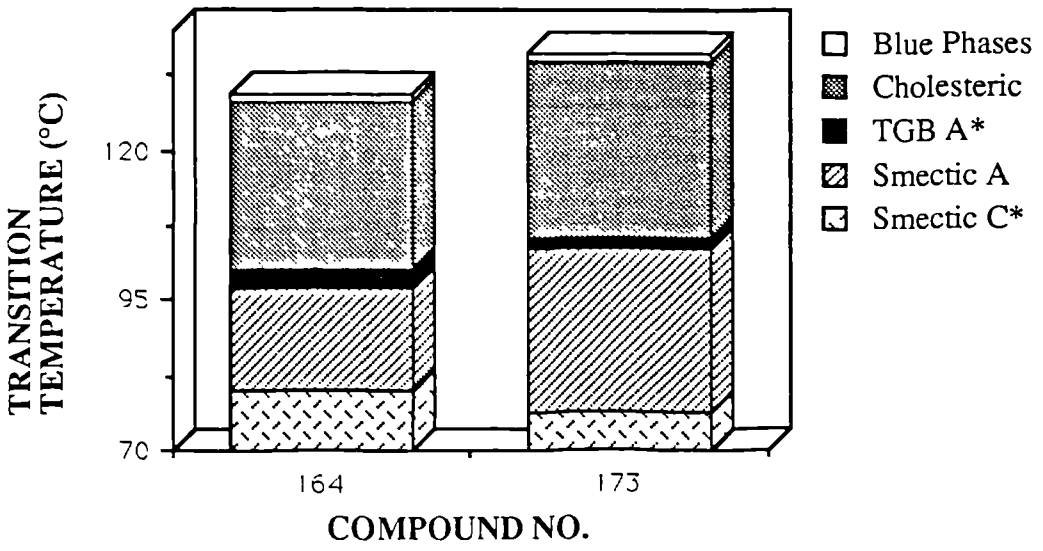


Figure 110. A Comparison of the Phase Behaviour in Compounds 164 (the Nonyloxy Member of Series X) and 173 (the Nonyloxy Homologue of Series XII).

It can be seen from figure 110 that, even though the only difference between these two materials is the positioning of a branching point (in **164**), and the subsequent removal of a methylene unit from the terminal alkyl chain (in **173**), i.e., the compounds have the same number of atoms, that the phase behaviour is somewhat different. Firstly, as expected the clearing point is lower in the material that possesses a branching point (**164**). The blue phase temperature range in each material is approximately the same, as is the cholesteric temperature range, the former suggesting that both materials have approximately the same degree of molecular chirality (in the mesophase). The TGB A* temperature range is, however, considerably larger in compound **164**, which may be explained by the closer proximity of the smectic A to smectic C* transition, to the cholesteric to TGB A* transition (the A phase is considerably shorter in **173**) causing a greater degree of molecular fluctuations and pretransitional effects at the cholesteric to smectic A transition.

When the properties of the smectic C* phase in materials **170-173** were investigated, the following results were obtained (see table 25).

No.	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
170	*S*	e	*d*	LH	-ve	
171	*S*	e	*d*	LH	-ve	+
172	*S*	e	*d*	LH	-ve	
173	*S*	e	*d*	LH	-ve	+

Table 25. Chiral Properties Associated with the Smectic C* Phase of the Materials in Series XI and XII (170-173).

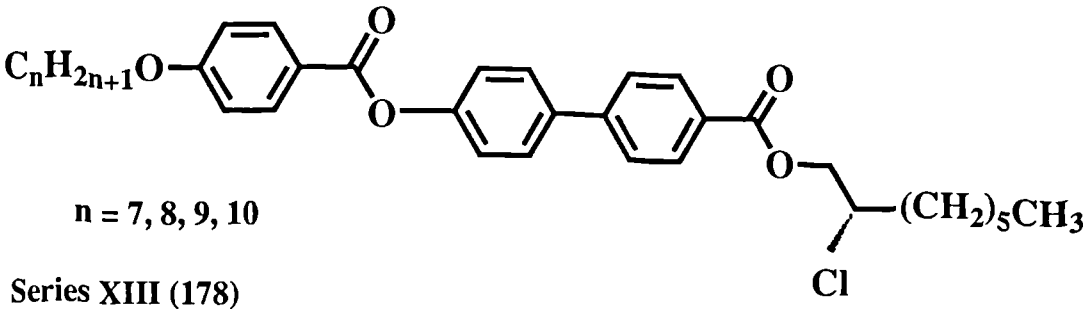
All of the materials were found to give a dextrorotation of plane polarised light and therefore possess a left-handed helix. This classifies them as being ***S*, e, *d*, LH**. This classification disagrees with the Goodby and Leslie hypothesis[39] in terms of helix

direction. The two phenylpropiolates, **171** and **173**, were also investigated to ascertain the direction and temperature dependence of the spontaneous polarization in the smectic C* phase. In each case the direction of the spontaneous polarization was found to be positive, the values at 10 °C below the A to C* transition being determined as 29 nC cm^{-2} for **171**, and 34 nC cm^{-2} for compound **173**. The result for the polarization direction is in agreement with the hypothesis, if the helix direction ignored. This therefore is another illustration of the fact that predictions cannot always be made which conclusively link the helix direction and the direction of the spontaneous polarization in the smectic C* phase. More will be said about the value of the spontaneous polarization in the smectic C* phase later in this discussion, with particular attention being paid to the effects of the length of the terminal alkyl chain situated on the external side of the chiral centre. The electroclinic effect associated with the smectic A phase will also be described for some materials.

8.8 Esters Based on a 2-Chloro-octyl Chiral Moiety.

The next series of materials (XIII) was based on a 2-chloro-octyl chiral moiety. Four benzoate materials were prepared (**174-177**), and one analogous phenylpropiolate was produced with a nonyloxy chain incorporated in its structure (**178**). The general structures of the materials in this series are illustrated in figure 111.

Series XIII (174-177)



n = 7, 8, 9, 10

Series XIII (178)

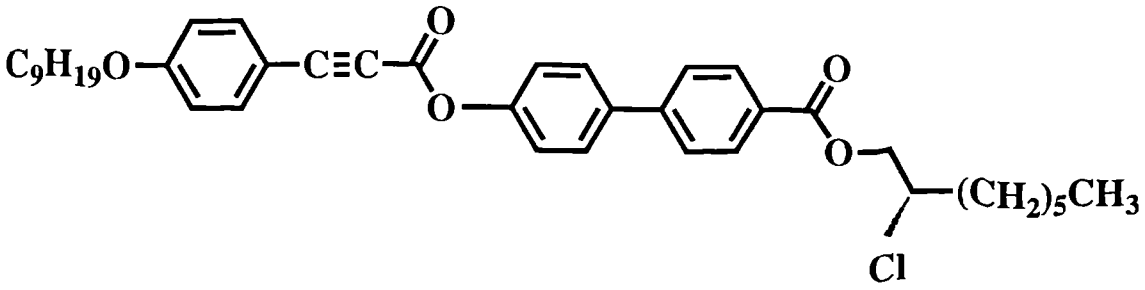


Figure 111. The Structures of the Di-Esters Based on a 2-Chloro-octyl Chiral Moiety.

The properties of these materials in terms of molecular chirality were very hard to predict, the reason being the length of the alkyl chain situated on the external side of the chiral centre. It was expected that the rotational damping, caused by the chiral centre in these molecules being situated deeper in the molecular architecture, would be quite high. The chirality, however, may to some extent be diluted because of the large size of the molecules caused by the long alkyl chain. It was also expected that the nematogenic tendency may be reduced to some extent, as is seen in other systems, when the chain at the opposite side of the molecule to where the chiral centre is situated is increased[152].

The phase behaviour for these materials is shown in table 26, and figure 112 where it can be seen that the materials in this series exhibit blue phases on cooling from the isotropic liquid. In the two benzoate materials, **174** and **175**, that have shorter alkoxy chains (attached to the opposite side of the molecule to where the chiral centre is located), the phase sequence on cooling is seen to be isotropic liquid to blue phase to cholesteric to TGB A* to smectic A to smectic C*. This is also found to be the case with the propiolate

material (**178**). In compounds **176** and **177**, however, the blue phase to cholesteric transition is seen to supercool to such an extent that a direct blue phase to smectic A transition is observed.

No.	n	Mpt.	I- BPIII	BPIII -BPII	BPII- BPI	BPI- Ch	BPI- S_A	Ch- TGB	TGB- S_A	S_A- S_C*	Rec.
174	7	85.2	154.0	153.3	152.6	147.7		146.2	145.7	99.0	57.8
175	8	86.4	154.8	154.4	154.0	150.8		150.5	150.1	110.0	57.7
176	9	84.6	152.1	151.6	150.6		149.3			121.1	59.9
177	10	74.5	151.1	151.0	150.7		149.9			125.5	58.6
178	9	69.3	131.1	130.9	130.6	129.8		107.9	106.5	80.7	58.6

Table 26. The Transition Temperatures (°C) for the Materials Based on the*(S)*-2-Chloro-octyl Chiral Moiety (174-178).

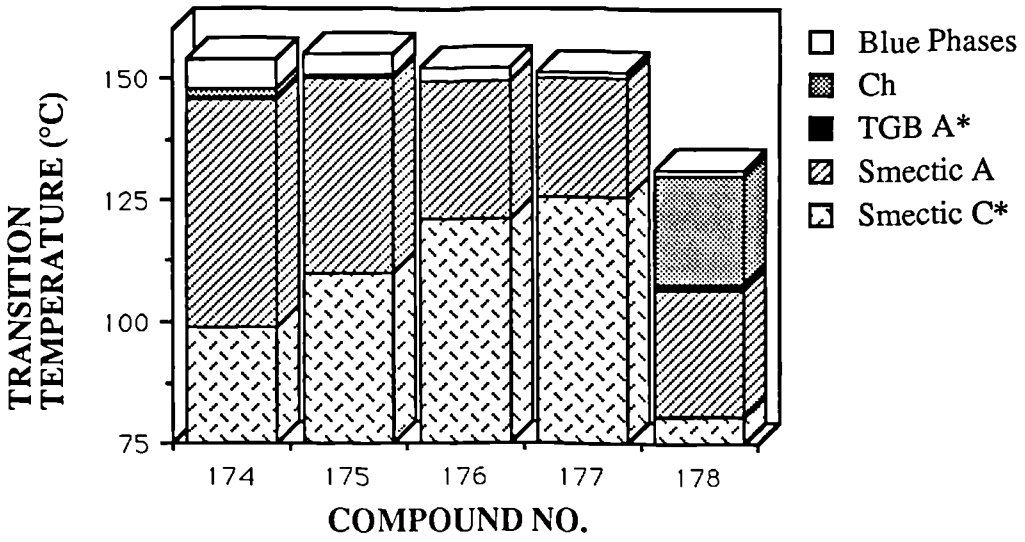


Figure 112. The Phase Behaviour the Materials Based on a 2-Chloro-octyl Chiral Moiety (Series XIII).

On cooling these materials through their mesomorphic states there is no evidence to suggest the presence of a TGB A* phase. On heating, however, this phase is observed over a fraction of a degree. Another point noted for the benzoates **174** to **177** was that, on increasing alkoxy chain length, the blue phase, and TGB A* phase temperature ranges

were reduced. The nematogenic tendency decreased, as did the temperature range of the smectic A phase, the latter being due to quite a steep rise in the A to C* transition temperature on ascending the series.

Thermal studies did not confirm the presence of a TGB A* phase in any of the materials. The heating traces of the clearing point transitions for compounds **174** and **177** being shown in figures 113 and 114 respectively. Figure 113 shows two major peaks corresponding to the isotropic to cholesteric and cholesteric to TGB A*/A transitions. The clearing point peak has two shoulders associated with it which correspond to transitions to and from the blue phases. In figure 114 it can be seen that the two peaks that correspond to the isotropic liquid to cholesteric and cholesteric to smectic A transitions have now become amalgamated, for compound **177** (**177** has a smaller cholesteric phase temperature range than **174**). Due to the close proximity of the peaks there is no resolution of the blue phase transitions.

On insertion of a triple bond into the core a more predictable pattern was found. The clearing point drops, the blue phase stability is reduced, whereas the cholesteric and TGB A* phase stabilities are increased.

Thermal studies carried out on the propiolate material (**178**) produced a similar pattern to that found for compounds **171** and **173** (the propiolate materials in series XI and XII). Figure 115 shows the heating trace for the transitions from smectic C* to smectic A and smectic A to TGB A*/cholesteric. The transition from smectic A to TGB A*, and TGB A* to cholesteric are once again amalgamated and appear as a broad peak.

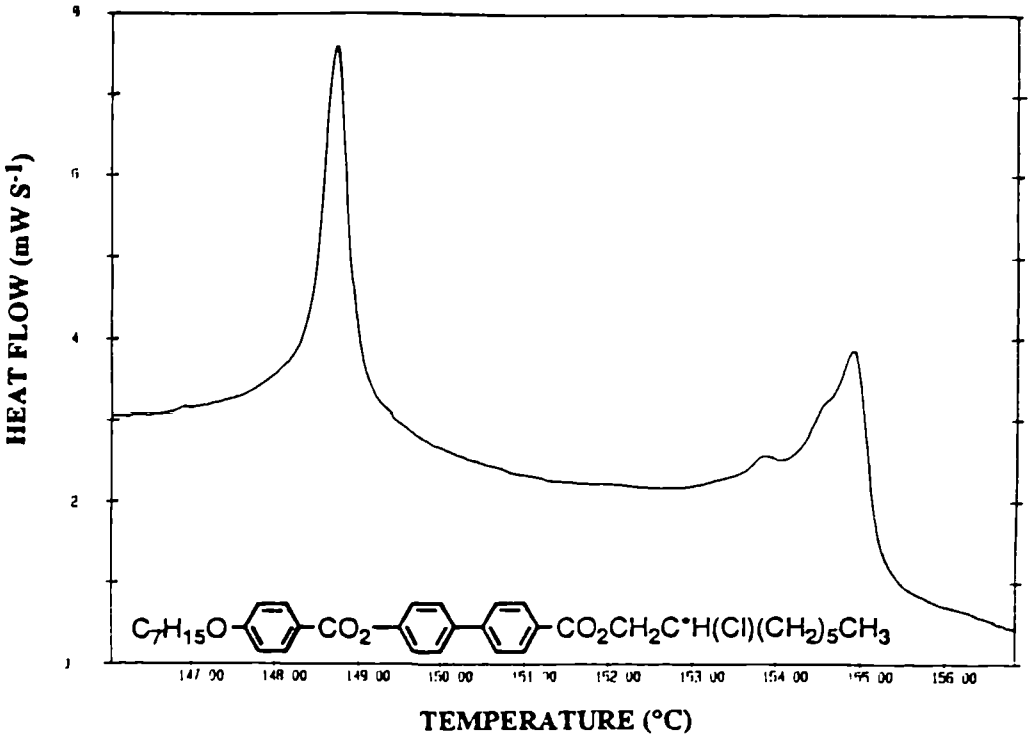


Figure 113. The Heating Cycle Close to the Cholesteric to Smectic A Transition for *(S)*-2-Chloro-octyl 4'-(4-heptyloxybenzoyloxy)-4-biphenylcarboxylate (174).

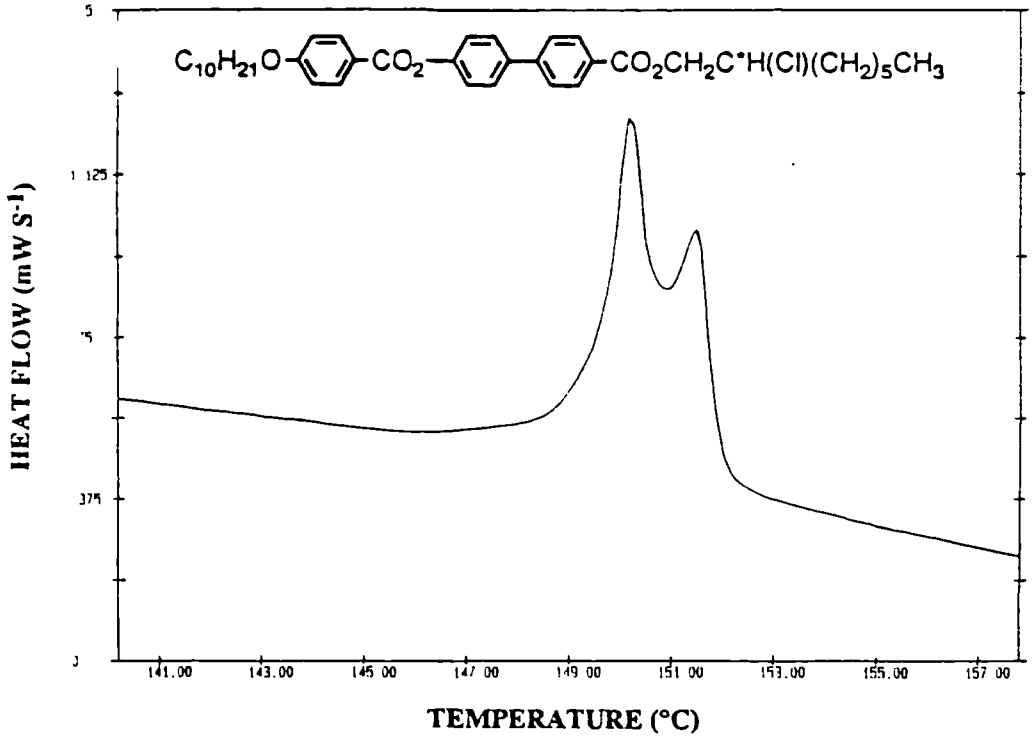


Figure 114. The Heating Cycle Close to the Cholesteric to Smectic A Transition for *(S)*-2-Chloro-octyl 4'-(4-decyloxybenzoyloxy)-4-biphenylcarboxylate (177).

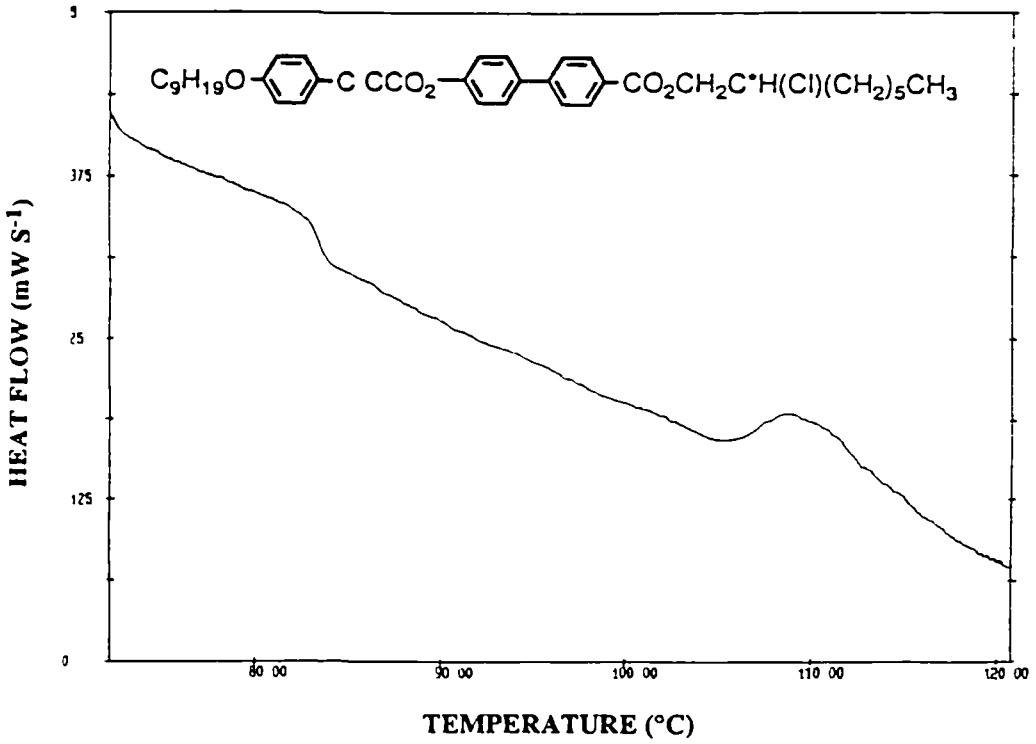


Figure 115. The Heating Cycle Close to the Cholesteric to Smectic A Transition for *(S)*-2-Chloro-octyl 4'-(4-nonyloxypropioyloxy)-4-biphenylcarboxylate (178).

Thus, it appears that the smectogenicity of these materials is greater than that found for the materials which possess a shorter terminal chain attached to the chiral centre, and that the overall chirality may be reduced slightly, due to dilution effects. A full comparison of the materials will be made later.

When the properties of the smectic C* phases were investigated for these materials the following results were obtained (see table 27).

No.	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
174	*S*	e	*d*	LH	-ve	
175	*S*	e	*d*	LH	-ve	+
176	*S*	e	*d*	LH	-ve	
177	*S*	e	*d*	LH	-ve	
178	*S*	e	*d*	LH	-ve	+

Table 27. Chiral Properties Associated with the Smectic C* Phase of the Materials in Series XIII (174-178).

It can be seen from table 27 that all of the materials in this series are classified as being ***S*, e, *d*, LH**, in a similar manner to compounds **170** to **173**. The pitch in the smectic C* phase appeared to be longer than for the previous materials (**170-173**), when the plane texture was viewed in the polarizing microscope. Attempts were made to obtain a suitable texture that would enable quantitative measurements of the pitch, but these were thwarted as the molecules preferred to be oriented in a pseudo-homeotropic alignment. This was probably due to surface anchorings that were quite strong, making alignment extremely difficult. As with the materials in series XI and XII (**170-174**) the direction and temperature dependence of the spontaneous polarization in the smectic C* phase were determined for the propiolate material (**178**). The spontaneous polarization direction was found to be positive, with a value determined at 10 °C below the A to C*

transition of 32 nC cm^{-2}. The direction was determined for the benzoate compound (**175**) and was also found to be positive. Once again a lengthy discussion of the polarization in the smectic C* phase will be made later, as will some investigations into the electroclinic effects noted for compound **178**.

8.9 Esters Based on a 2-Chlorodecyl Chiral Moiety (Series XIV).

The next series of materials are based on the 2-chlorodecyl chiral moiety. Four benzoates were produced(**179-182**), and one propiolate (**183**). The general structures of the materials in this series (XIV) are illustrated in figure 116.

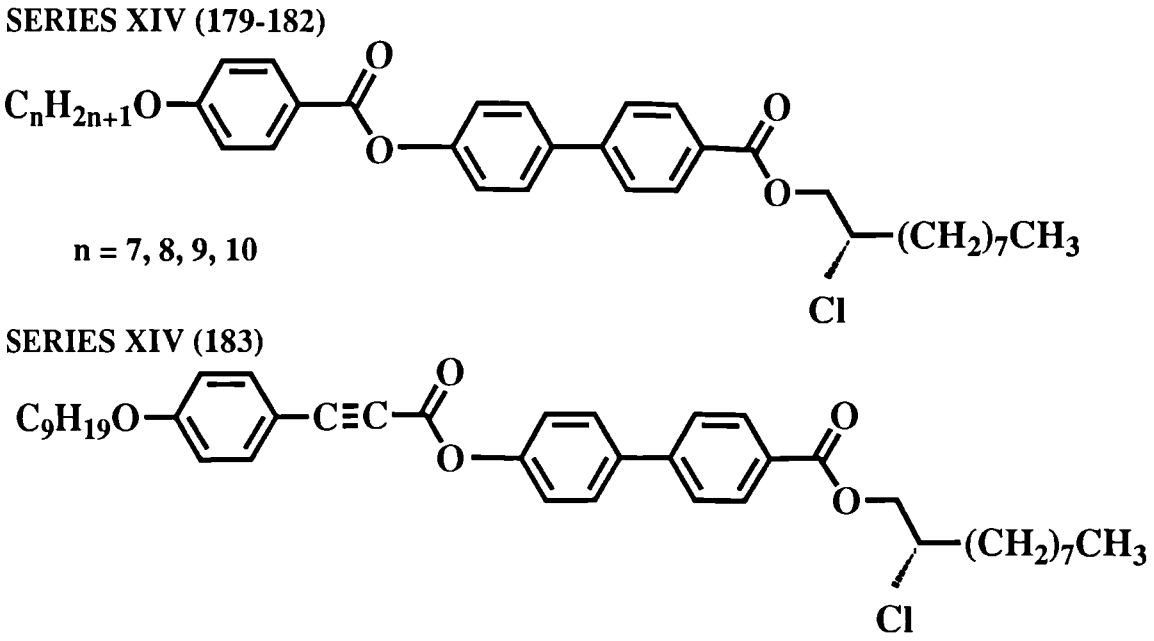


Figure 116. The Structures of the Di-Esters Based on the 2-Chlorodecyl Chiral Moiety (179-183).

It was believed that a reduction in chirality had already taken place on moving from a chiral moiety containing six carbon atoms (**172** and **173**) to one containing eight (**176** and **178**), the reason being a dilution in the overall molecular chirality caused by lengthening of the molecular structure. Whether this in fact is the case or not could be proved to some

extent by examination of this present series of materials (compounds **179-183**), as the chain length associated with the chiral moiety was now ten carbon atoms long (in total).

The phase transition temperatures for this series are illustrated in table 28, and in figure 117.

No.	n	Mpt.	I-BPIII	BPIII-BPII	BPII-BPI	BPI-Ch	Ch-TGB	TGB-SA	I-S_A	BPI-S_A	S_A-S_C*	Rec.
179	7	82.8	150.2	149.9	149.4					146.6	92.7	53.5
180	8	87.3	150.6	150.3	149.8					148.5	101.6	56.8
181	9	84.2	148.6	148.3	148.1					148.0	117.8	58.8
182	10	74.5							147.2		123.5	54.9
183	9	70.2	126.8	126.5	126.2	125.1	111.9	110.7			82.2	60.7

Table 28. The Transition Temperatures (°C) for the Materials Based on a *(S)*-2-Chlorodecyl Chiral Moiety (179-183).

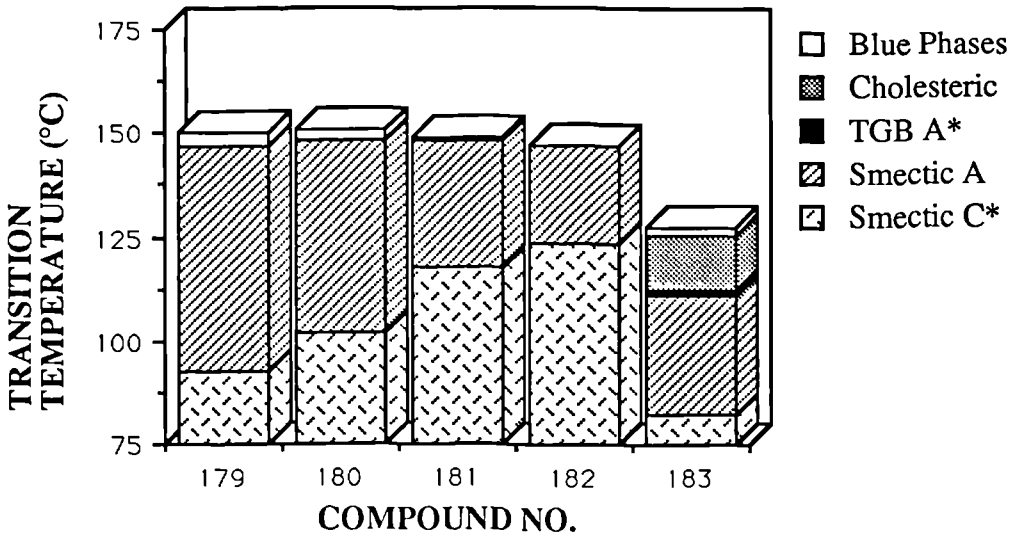


Figure 117. The Phase Transitions for the Materials Based on a 2-Chlorodecyl Chiral Moiety (179 to 183).

It can be seen from table 28 and figure 117 that three of the four benzoate materials in this series (**179** to **181**), displayed an isotropic to blue phase to smectic A to smectic C* phase sequence, on cooling. On heating a cholesteric phase, and an extremely short temperature range TGB A* phase was observed. The reason why the cholesteric phase was not observed on cooling was because the blue phase to cholesteric transition supercooled below the cholesteric to smectic A/TGB A* transition. It may be possible that the new BPS^{150} phase is also present in these materials. Compound **182** (the dodecyloxy material) displayed a simple isotropic to smectic A to smectic C* phase sequence. As the alkoxy chain associated with these materials was lengthened, the clearing points fell slightly and the smectic A to smectic C* phase transition temperature increased, thereby reducing the temperature range of the smectic A phase. The propiolate material (**183**) possesses an isotropic to blue phase to cholesteric to TGB A* to smectic A to smectic C* phase sequence, with a lower clearing point, and as expected an increase in nematogenicity relative to its benzoate analogue (**181**). The presence of an TGB A* phase on cooling indicates that the chirality associated with the material was still strong enough to support this behaviour.

Calorimetric studies were carried out and gave good general agreement with optical studies. Figure 118 illustrates the heating trace for the high temperature transitions for compound **179** (the heptyloxy member of the benzoate series), where only two peaks can be seen which correspond to the transitions from smectic A to cholesteric/blue phase and the cholesteric/blue phase to isotropic liquid. An analogous trace (see figure 119) for compound **183** (the propiolate) shows a peak for the clearing point, and a broad peak corresponding to the transition from the cholesteric to TGB A* phase and TGB A* phase to smectic A phase.

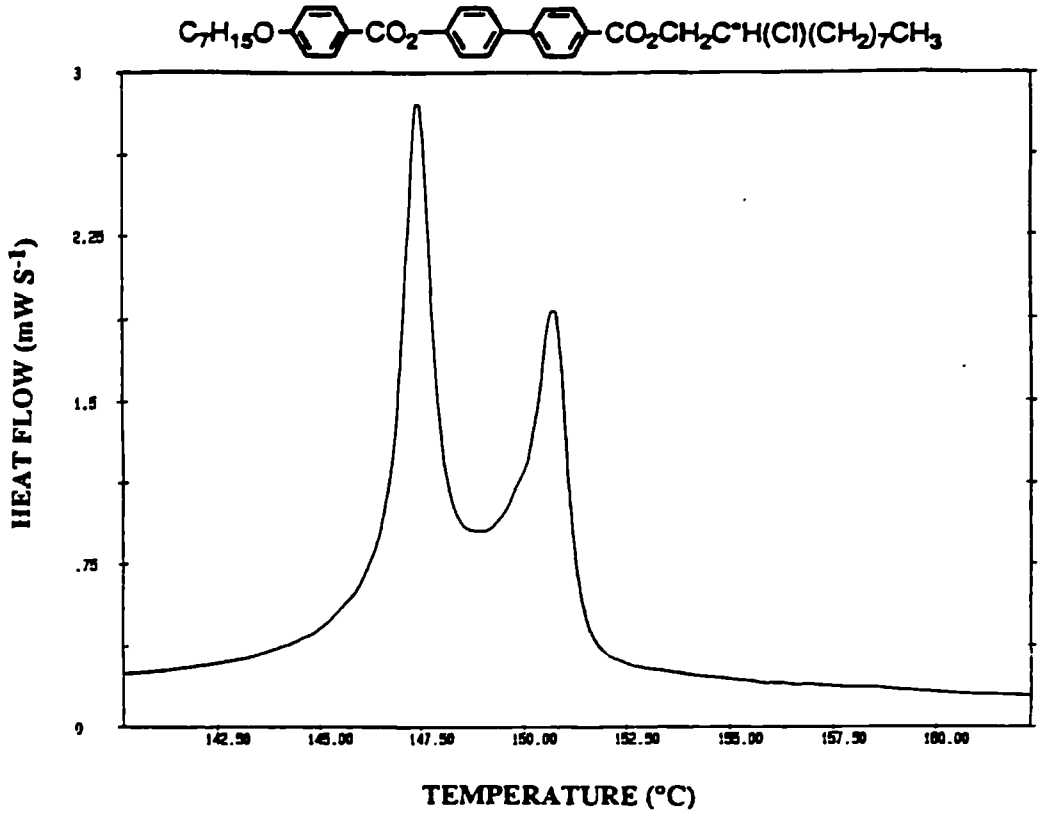


Figure 118. The Heating Cycle Close to the Cholesteric to Smectic A Transition for (*S*)-2-Chlorodecyl 4'-(4-heptyloxybenzoyloxy)-4-biphenylcarboxylate (179).

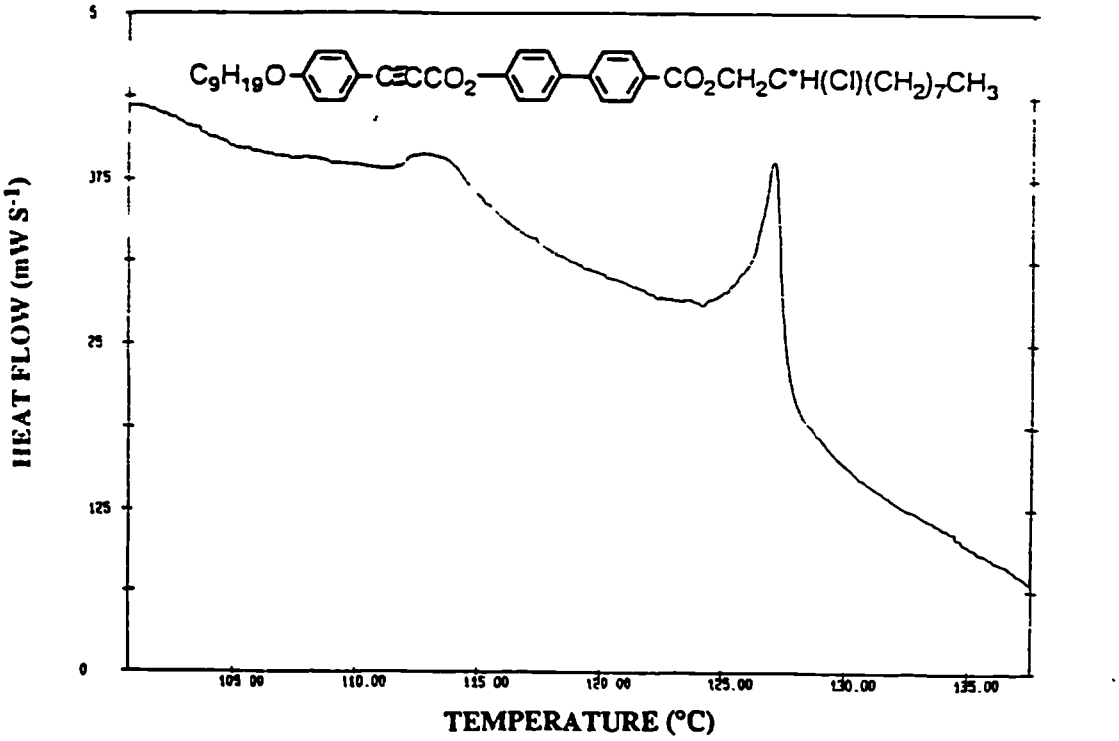


Figure 119. The Heating Cycle Close to the Cholesteric to Smectic A Transition for (*S*)-2-Chlorodecyl **4'-(4-nonyloxybenzoyloxy)**-4-biphenylcarboxylate (183).

When the properties of the smectic C* phase were investigated the following results were obtained (see table 29). As with the previous series of materials with an octyl chain associated with the chiral centre (XIII), the pitch in these materials appeared to be quite long, and a pseudo-homeotropic texture was preferred when samples were placed between glass plates. The helical twist sense was determined as being dextrorotatory, which classifies the helix in these materials as being left-handed. The polarization direction was determined as being positive for two materials **181** and **183** (the nonyloxy homologue of both the benzoate and propiolate materials). The value of the spontaneous polarization for **183** (the propiolate) was found to be 30 nC cm^{-2} at 10 °C below the Curie Point. The polarization studies, along with some experiments into electroclinic switching in this material will be discussed later.

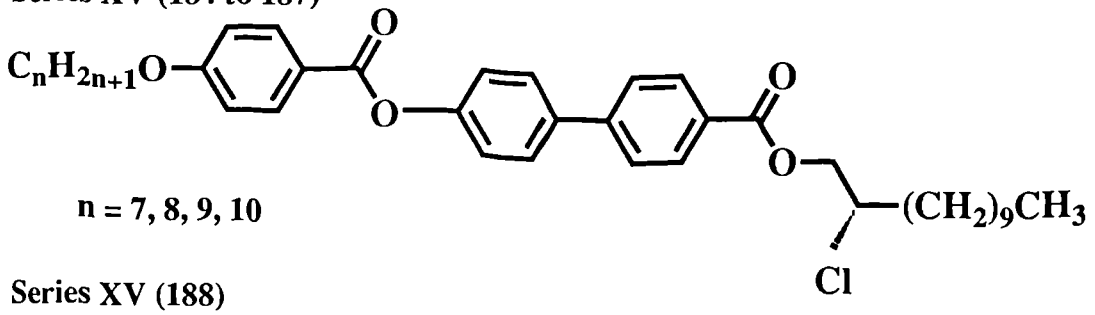
No.	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
179	*S*	e	*d*	LH	-ve	
180	*S*	e	*d*	LH	-ve	
181	*S*	e	*d*	LH	-ve	+
182	*S*	e	*d*	LH	-ve	
183	*S*	e	*d*	LH	-ve	+

Table 29. Chiral Properties Associated with the Smectic C* Phase of the Materials in Series XIV (179-183).

8.10 Esters Based on the 2-Chlorododecyl Chiral Moiety (Series XV).

The next series of materials were based on the 2-chlorododecyl chiral moiety. Four benzoate materials were once again produced (**184-187**), whereas one propiolate was prepared (**188**). The general structures of the materials in this series are illustrated in figure 120.

Series XV (184 to 187)



n = 7, 8, 9, 10

Series XV (188)

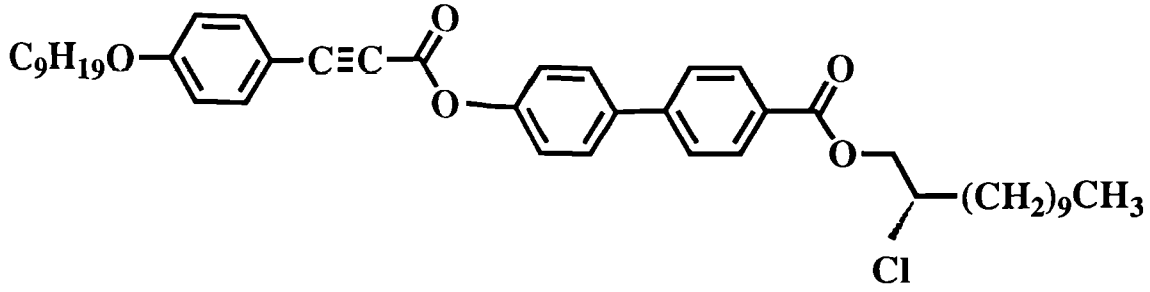


Figure 120. The Structures of the Di-Esters Based on the 2-Chlorododecyl Chiral Moiety (184-188).

As these materials (**184** to **187**) had the longest terminal alkyl chain attached to the external side of the chiral centre it was expected that the reduction in chirality due to a dilution effect would be the greatest out of all the materials with an n-alkyl chain studied. The nematogenic tendency was also expected to be reduced relative to the earlier materials (series XI to XIV). A decrease in the blue phase, cholesteric and TGB A* temperature ranges could therefore be predicted.

The phase transition temperatures for this series are listed in table 30, and illustrated in figure 121, where it can be seen that three (**185** to **187**) out of the four benzoates (**185** to **188**) have a simple isotropic to smectic A to smectic C* phase sequence. The material with the shortest alkoxy chain (**184**) was found to exhibit blue phases between the isotropic liquid and the smectic A phase, as was the case with the materials in the previous series (**179-181**). The nematogenic tendency of these materials is therefore not particularly strong, with the long chiral dodecyl chain promoting smectogenicity. On increasing alkoxy chain length the clearing points fall slightly, whereas the temperature

of the transition from smectic A to smectic C* increases, thereby reducing the smectic A temperature range.

No.	n	Mpt.	I-BPIII	BPIII-BPII	BPII-BPI	BPI-Ch	Ch-TGB	TGB-S_A	I-S_A	BPI-S_A	S_A-S_C*	Rec.
184	7	74.0	146.8	146.4	146.0					145.7	84.3	52.5
185	8	76.5							146.9		91.5	53.9
186	9	76.0							145.6		111.7	53.6
187	10	74.6							143.6		118.2	48.7
188	9	73.4	124.4	124.2	123.9	122.8	114.9	114.1			81.9	66.0

Table 30. The Transition Temperatures (°C) for the Materials Based on the *(S)*-2-Chlorododecyl Chiral Moiety (184-188).

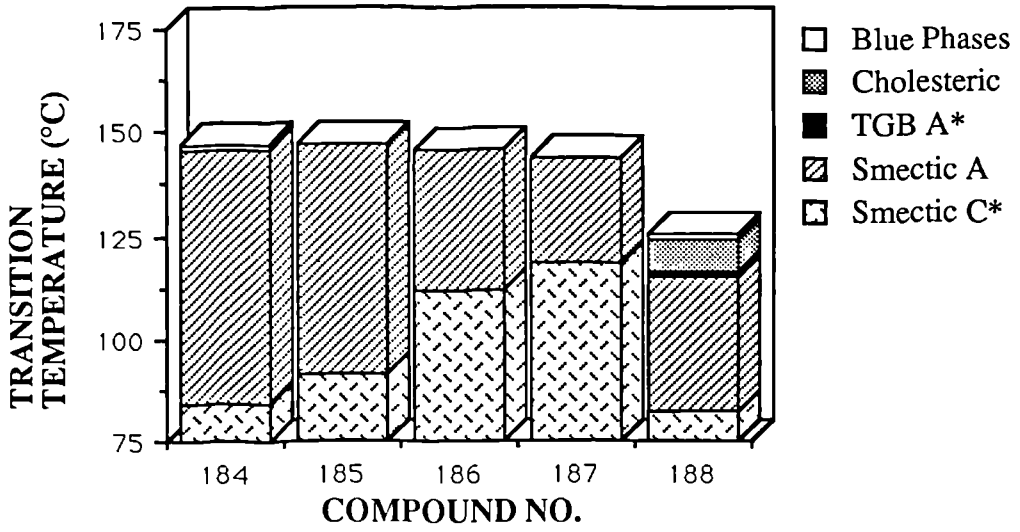


Figure 121. The Phase Transitions Associated with the Materials Based on the 2-Chlorododecyl Chiral Moiety (184 to 188).

The phenylpropiolate (**188**), as expected from previous results, showed a much reduced clearing point and a greater nematogenic tendency. Thus, compound **188** exhibited an isotropic to blue phase to cholesteric to TGB A* to smectic A to smectic C* phase sequence.

Calorimetric studies were found to be consistent with results obtained from thermal optical microscopy. Figure 122 shows the heating trace of compound **184**, at and around the clearing point. Two peaks are observed that are very close together which correspond to the smectic A to cholesteric/blue phase, and the clearing point transitions. Resolution of the transitions between blue phases is not observed because the temperature ranges of the blue phases are very short in this material.

The pitch in the smectic C* phase, as with the materials based on the octyl and the decyl chiral alkyl chains (series XII and XIV) appeared to be relatively long, and so determination of the helical twist sense was not very easy. The results obtained, however, related to the properties of the smectic C* phase in these materials are shown in table 31.

No.	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
184	*S*	e	*d*	LH	-ve	
185	*S*	e	*d*	LH	-ve	
186	*S*	e	*d*	LH	-ve	+
187	*S*	e	*d*	LH	-ve	
188	*S*	e	*d*	LH	-ve	+

Table 31. Chiral Properties Associated with the Smectic C* Phase of the Materials in Series XV (184-188).

The helix direction was classified as left-handed in these materials, the direction of the spontaneous polarization being positive when determined for compounds **186** and **188** (the nonyloxy homologues of the benzoate and propiolate materials). The value of the spontaneous polarization for compound **188** at 10 °C below the Curie point was determined as being 25 nC cm^{-2}. More will be said about the polarization associated with

the smectic C* phase in compound **188** later, along with a large electroclinic response that was found for with this material in the smectic A phase.

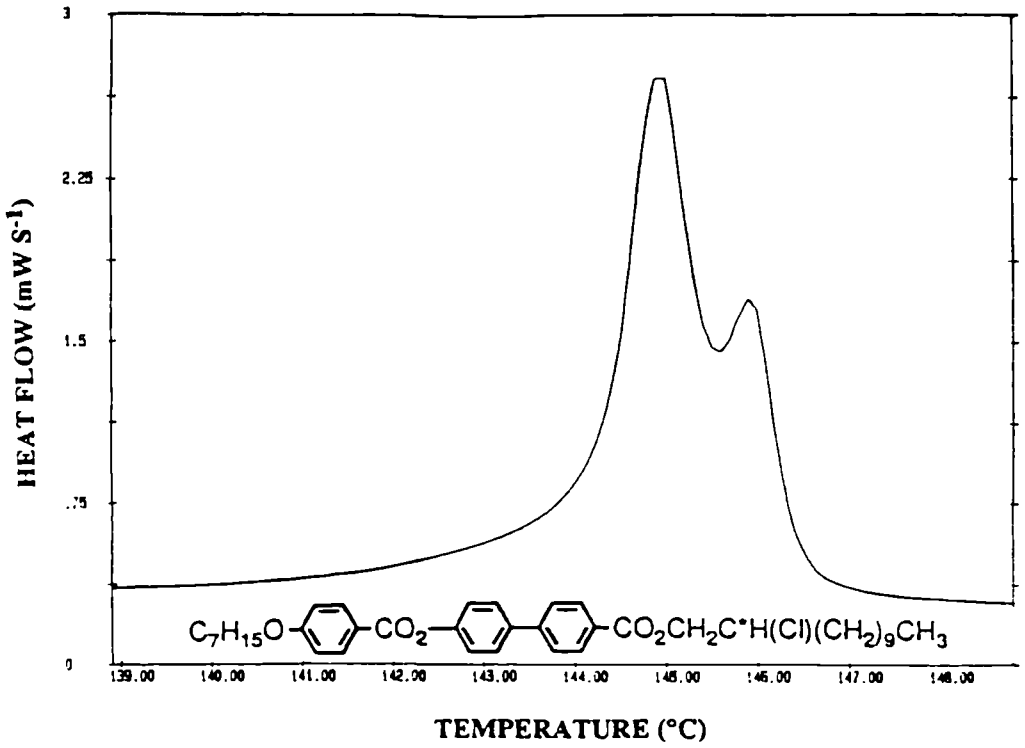
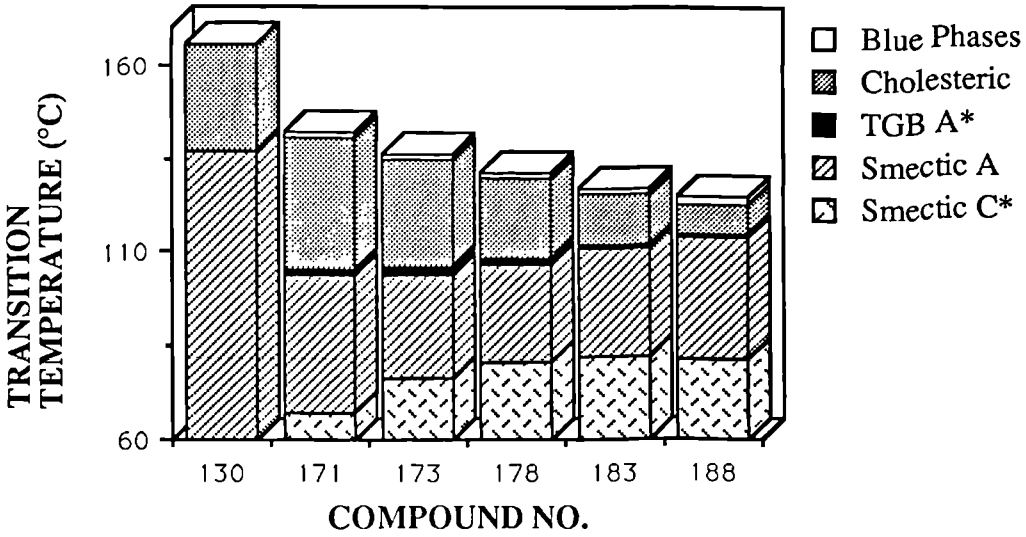


Figure 122. The Heating Cycle Close to the Blue Phase to Smectic A Transition for *(S)*-2-Chlorodecyl 4'-(4-heptyloxybenzoyloxy)-4-biphenylcarboxylate (184).

8.11 Summary of the Effects Caused by a Variation in Length of the Peripheral Alkyl Chain Attached to the External Side of the Chiral Centre.

At this point, a comparison can be made in order to evaluate the effect that increasing the terminal alkyl chain length situated on the external side of the chiral centre has on the phase transitions, and other mesogenic properties. Thus, the properties of the *(S)*-2-Chloro-n-alkyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylates will be compared (compounds **130, 171, 173, 178, 183, 188**). Figure 123 illustrates the phase transitions given by these materials.



Where **130** has a 2-chloropropyl chiral moiety, **171** has a 2-chloropentyl chiral moiety, **173** has a 2-chlorohexyl chiral moiety, **178** has a 2-chloro-octyl chiral moiety, **183** has a 2-chlorodecyl chiral moiety, and **188** has a 2-chlorododecyl chiral moiety.

Figure 123. A Comparison of the Phase Behaviour of the *(S)*-2-Chloroalkyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylates (130, 171, 173, 178, 183, and 188).

It can be seen from figure 123 that smooth trends in the transition temperatures were observed in the materials where the total chiral alkyl chain length ranges from five carbons to twelve carbons. The blue phase temperature range is approximately the same for all of the materials, but the cholesteric phase temperature range drops and the clearing points fall as the series is ascended. The temperature of the smectic A to smectic C* transition is seen to gradually increase in compounds **171** to **183** and then begin to fall again for the material with the longest chiral alkyl chain (**188**). The temperature range of the TGB A* phase is found to be at a maximum for compounds **171** and **173**. The range gradually decreasing for the longer chain lengths. It is thought that this trend occurs because of a dilution in the chirality as the chain length is extended, which offsets any increase in rotational damping that the chiral centre experiences as the alkyl chain is

lengthened. It may therefore be postulated that there is a balance that has to be struck between these two effects if a material is to display a maximum degree of 'molecular chirality' in its phase. Since there is little variation in the blue phase temperature range in these materials it is, however, possible that the variation in chirality is small and that layer strength plays a more important role in determining the TGB A* phase behaviour associated with these materials. The material with the shortest alkyl chain associated with the chiral centre displays behaviour that does not fit the trend that is observed for the other five compounds. Firstly, compound **130** does not display blue phases at its clearing point, nor is there any evidence to suggest the presence of a TGB A* phase at the cholesteric to smectic A transition. The clearing point is considerably higher in this material, but the cholesteric temperature range is shortened with respect to compound **171** (the compound with a 2-chloropentyl chiral moiety), as the cholesteric to smectic A transition temperature occurs at a much higher temperature. Compound **130** does not possess a smectic C* phase, probably because crystallization occurs at a relatively high temperature. The unusual behaviour associated with the cholesteric phase in compound **130** was discussed earlier. This type of inversion of helical twist sense in the cholesteric phase was not seen in any of the other materials in this comparison, nor was any inversion of helix direction noted in the smectic C* phase for any of these materials, as it had been earlier for some of the materials that contain a branching point in the terminal aliphatic chain e.g., compound **160** (from series X). The reasons why inversions may occur were discussed in terms of conformational species which may induce opposite twist senses in a material. When a long alkyl chain is attached to the peripheral side of the chiral centre, the interconversion between and the various species may become less likely due to unstable structures and high activation energies. The possible primary species for compound **183** (the chiral decyl chain) are depicted in figure 124.

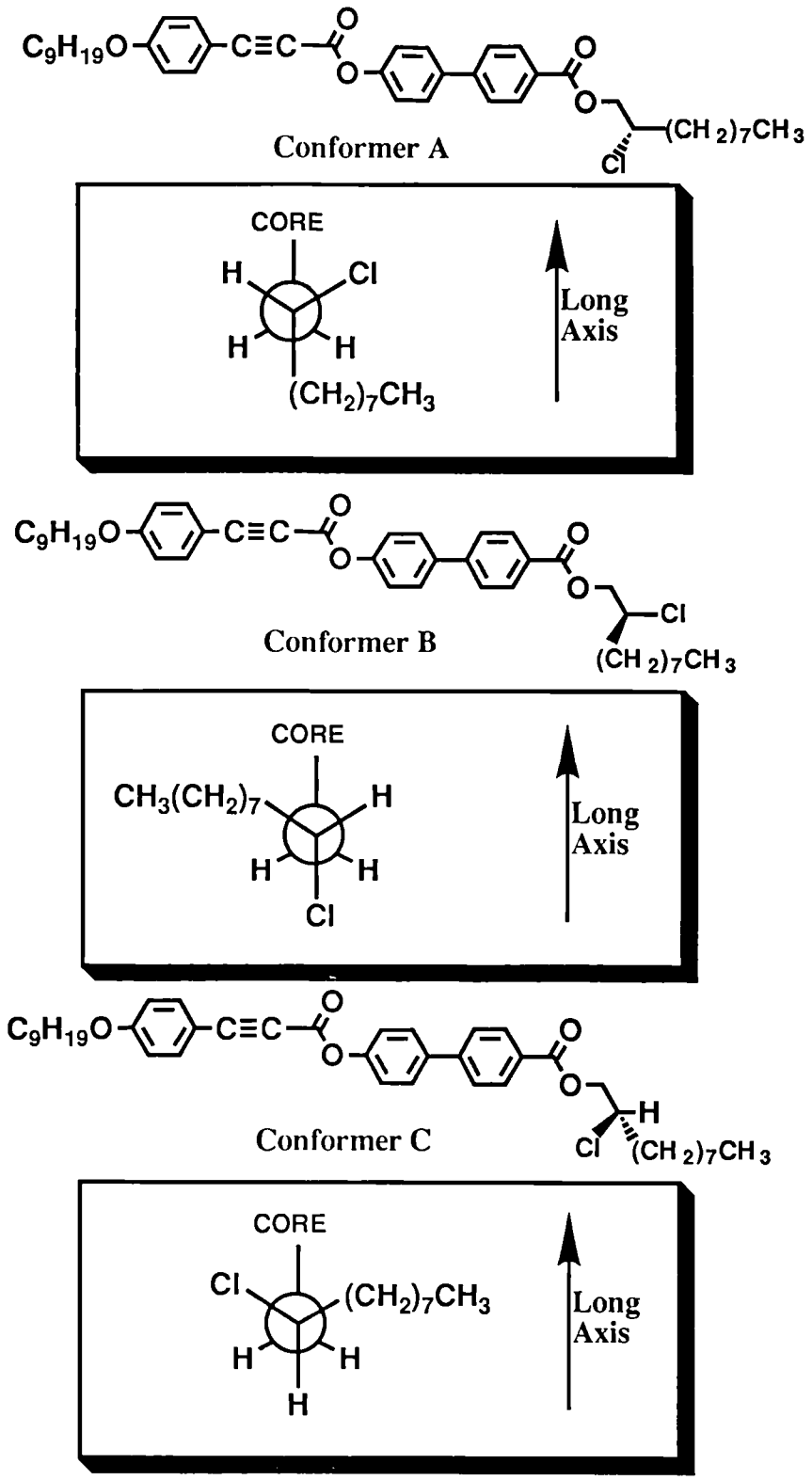


Figure 124. Some of the Possible Primary Conformers Associated with Compound 183.

It can be seen from figure 124 that there are three primary conformers that need to be considered. Out of these, two of them are likely to be relatively unstable as the long alkyl moiety points out to the side (conformers B and C) creating a bent molecular shape, rather than pointing along the long molecular axis. This would reduce the liquid-crystallinity of the system and probably increase the internal energy. If it is assumed therefore that conformer A is the most stable, then a single helix direction will be found throughout the temperature range of the chiral phase.

As noted earlier, studies of the value of the spontaneous polarization with respect to temperature were carried out for the chiral smectic C* phase of a number of materials. The following propiolates were evaluated **171**, **173**, **178**, **183**, and **188** in order to examine the effect on the polarization caused by lengthening the terminal aliphatic chain. The results for the value of the spontaneous polarization as a function of temperature are shown in figure 125 for the compounds.

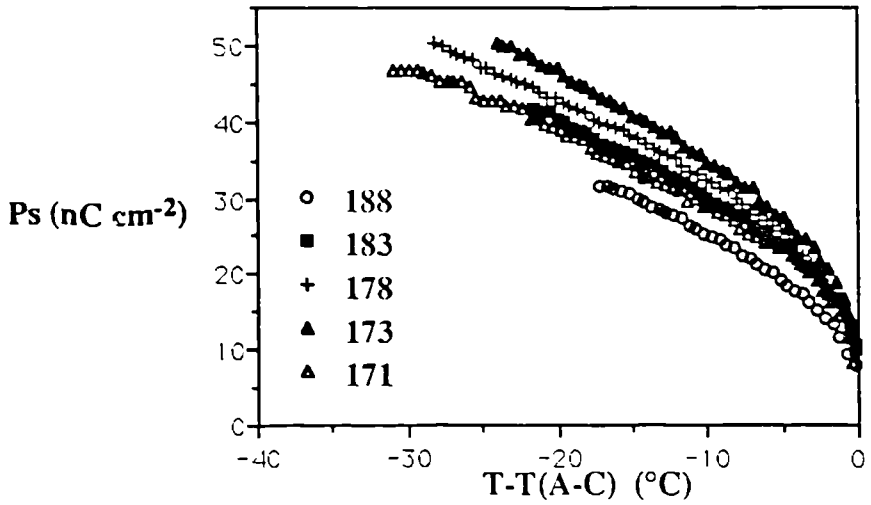


Figure 125. The Value of the Spontaneous Polarization in the Smectic C* Phase as a Function of Temperature for the Propiolate Materials with a 2-Chloroalkyl Chiral Moiety (171, 173, 178, 183, and 188).

It can be seen from figure 125 that the value of the spontaneous polarization in each of these materials rises quite steeply on cooling from the Curie point, the gradient of the curve gradually falling, but at no point levelling off for any of the materials. When a comparison is made of the values obtained for the materials, then it is found that the medium length chain gives the highest relative value, in this case compound **173** (with a 2-chlorohexyl chiral moiety). In fact, the material with the smallest polarization is compound **188** which has the longest alkyl chain associated with the chiral centre, whereas compounds **171**, **178** and **183** have intermediate values. Since the polarization value is tied somewhat to the degree of molecular chirality then it must be assumed that the maximum degree of molecular chirality is reached at some intermediate chain length, after which it begins to drop off due to dilution effects. The situation in terms of polarization value for these materials can be compared with their TGB A* temperature range. In both cases the maximum polarization, and TGB A* temperature range occur for compound **173**, that has a total alkyl chain length of six carbon atoms.

In the next study, the induced tilt angle (produced by electroclinic switching) relative to the magnitude of the applied field was measured at 5 °C above the smectic A to smectic C* transition. The results obtained in both a 1.6 μm and a 3.6 μm cell are shown in figure 126, and figure 127 respectively, where it can be seen that the induced tilt angles were found to be almost proportional to the applied field. The magnitude of the induced tilt was found to be quite large, especially in compound **188** (that had the longest alkyl chain associated with the chiral centre). This in itself is not unusual, except that the induced tilt (electroclinic effect) is thought to be somewhat related to the value of the spontaneous polarization in the smectic C* phase. The values obtained for the spontaneous polarization in the materials under study were at best moderate, whereas the values for the induced tilt were similar to those reported for 4-(3-methyl-2-chlorobutanoyloxy)-4'-heptyloxybiphenyl[42], which has a large spontaneous polarization

value in the range of 80 to 150 nC cm^{-2}. The results can be explained by taking into account the fact that deformation of the smectic layers is thought to play an important role in the occurrence of the molecular tilt induced by the electroclinic effect, because tilting effectively reduces the layer thickness.

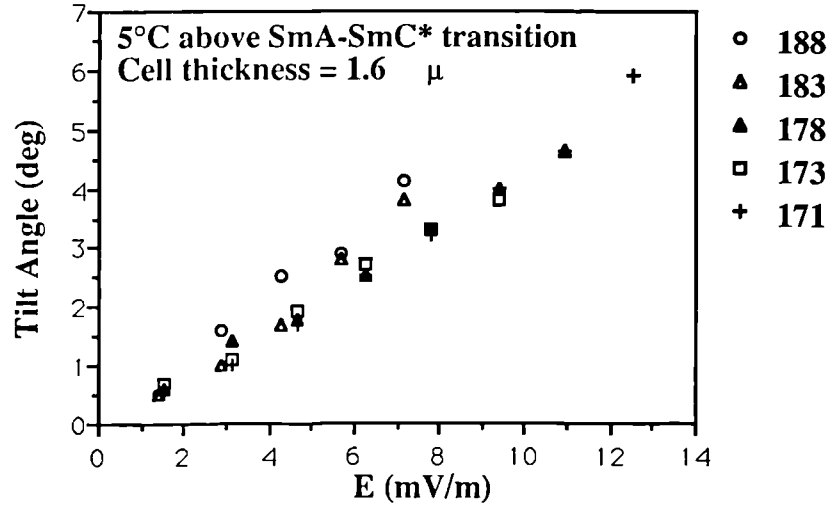


Figure 126. The Electroclinic Effect in the Propiolate Materials with the 2-Chloroalkyl Chiral Moiety (1.6 μm Cell).

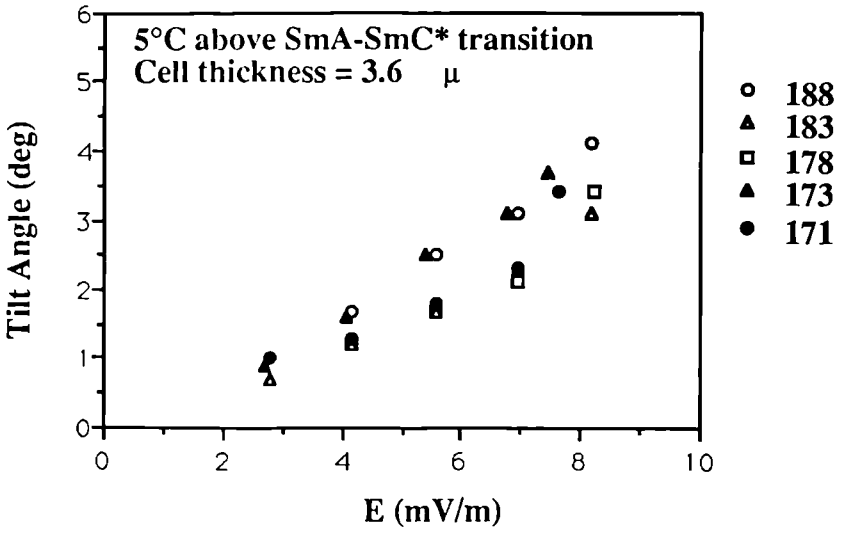


Figure 127. The Electroclinic Effect in the Propiolate Materials with the 2-Chloroalkyl Chiral Moiety (3.6 μm Cell).

The materials that were studied all exhibit TGB A* phases, which as already noted relies on a relatively weak layer ordering. The materials also contain a triple bond which seems to weaken the layer structure. It is no surprise then that the layer formation in these materials is relatively weak and so allows layer deformation and thereby large electroclinic effects to occur. It is not clear how the layers actually deform on switching, but neither zig-zag defects nor striped shaped domains, which are due to the formation of a chevron structure and an undulation of the smectic layer were observed in the field experiments[153].

In all of the materials, the striped shaped domains do, however, appear in the smectic C* phase on the application of a d.c. electric field. The striped shaped domains appear along a direction normal to the smectic layering, the region exhibiting these domains increases in size with increasing d.c. voltage. Plate 22 shows the appearance of the domains in the smectic C* phase of compound **188**. The appearance of the domains is similar to those reported for the smectic C* phase of 4-(2-methyloctanoyl)phenyl 4'-octyloxy-4-biphenylcarboxylate (MOPBIC)[154]. The chevron layer structure of this material was found to be converted into a bookshelf layer structure, on the application of a d.c. voltage, by X-ray diffraction measurements[155]. A layer undulation was also generated that could be observed by optical polarizing microscopy. In the chevron structure the spontaneous polarization is not perpendicular to the substrate plates (because of its characteristic direction), hence, an electric field applied perpendicular to the plates exerts a force on the smectic layer so that the bookshelf geometry is adopted. As MOPBIC has a large spontaneous polarization (112 nC cm^{-2} at 10 °C below the A to C* transition), this force, applied to the smectic layers may be strong. In the case of the compounds under study (especially **188**), the value of the spontaneous polarization was found to be moderate, thereby indicating a weak layer structure.

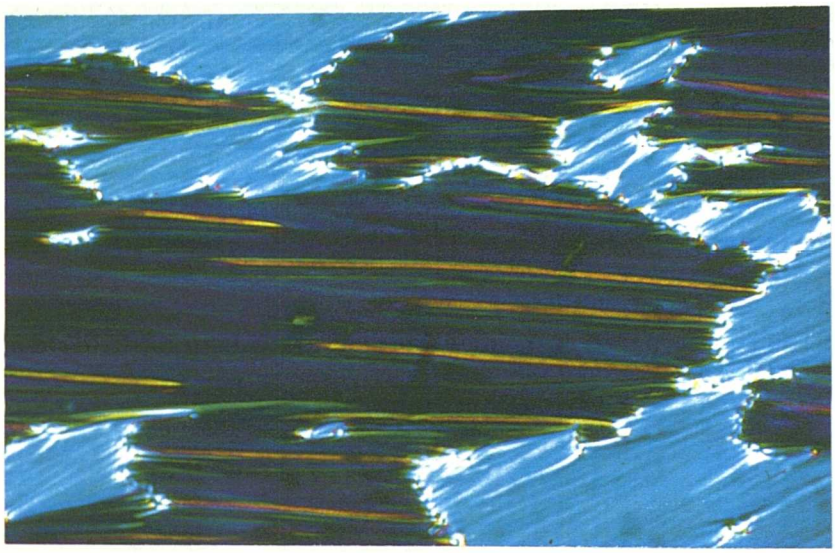
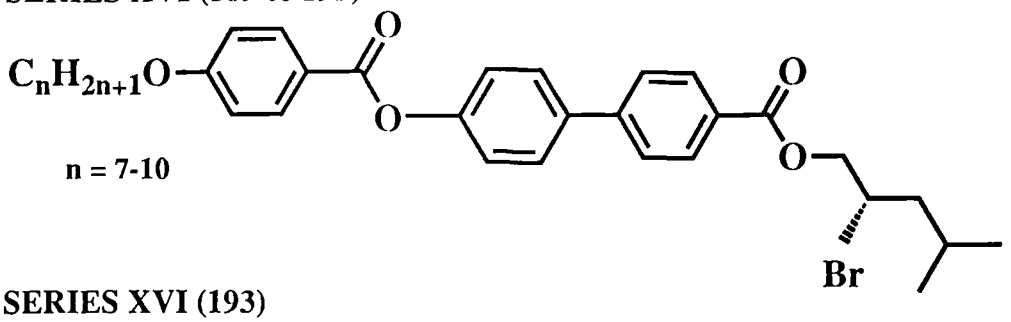


Plate 22. The Striped Shaped Domains that Appear in the Smectic C* Phase of *(S)*-2-Chlorododecyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (188) on Application of a d.c. Field.

8.12 Esters Based on a 2-Bromo-4-methylpentyl Chiral Moiety (Series XVI).

The materials in this series of compounds (**189** to **193**) were prepared in order to try and evaluate the effect of atom size at the chiral centre on mesomorphic properties. It was expected that by increasing the size of the atom, although in this case causing a reduction in the dipole at the optically active centre, that the rotation of the chiral centre might be restricted which may possibly extend the TGB A* temperature range. The chiral moiety selected for study was the 2-bromo-4-methylpentyl group, as the chloro analogues (**156-169**) had shown the widest TGB A* temperature range up to date. Once again, four benzoate materials were prepared (**189** to **192**), along with one propiolate material (**193**), the general structures of which are illustrated in figure 128.

SERIES XVI (189 to 192)



SERIES XVI (193)

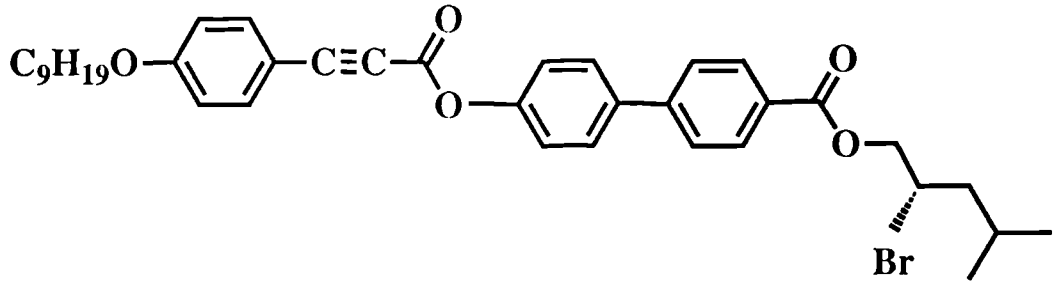


Figure 128. The Structures of the Di-Esters Based on a 2-Bromo-4-methylpentyl Chiral Moiety.

It was hoped that these materials would exhibit a large TGB A* temperature range due to the presence of the bromine atom at the chiral centre and the restricted rotation this would cause with respect to the core structure. The results obtained, however, were quite surprising, and are illustrated in table 32 and in figure 129.

No.	n	Mpt.	I-Ch	Ch-S_A	S_A-S_C*	Rec.
189	7	76.8	142.8	132.5	97.4	53.8
190	8	83.2	144.6	136.0	102.3	62.7
191	9	75.9	141.2	133.1	98.1	48.8
192	10	58.3	139.9	137.1	110.1	31.9
193	9	72.1	123.6	99.4	72.3	37.8

Table 32. The Transition Temperatures (°C) for the Materials Based on an *(S)*-2-Bromo-4-methylpentyl Chiral Moiety (189-193).

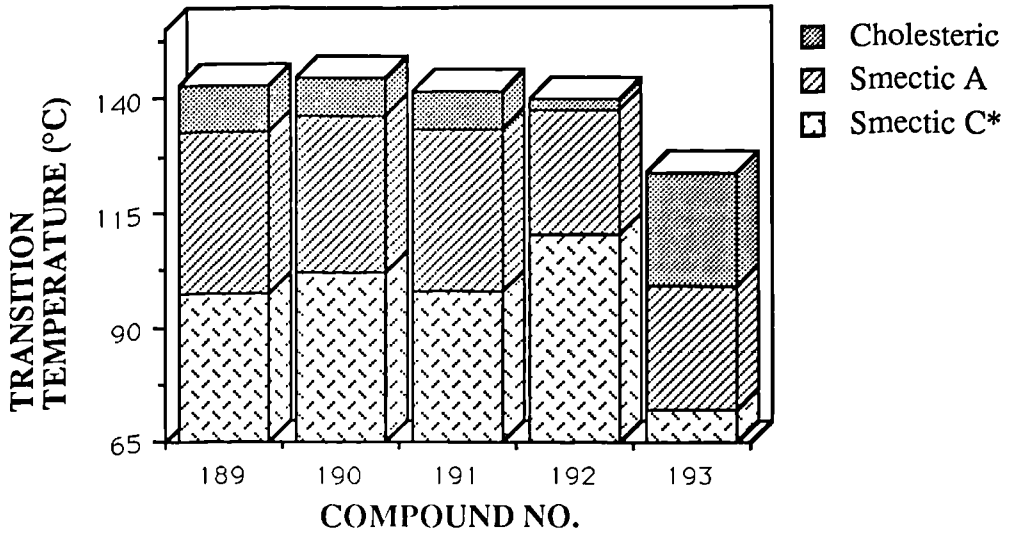


Figure 129. The Phase Behaviour Associated with the Materials Based on an *(S)*-2-Bromo-4-methylpentyl Chiral Moiety (189-193).

It can be seen from table 32 and figure 129 that all of the materials in series XVI have an isotropic to cholesteric to smectic A to smectic C* phase sequence. There is no evidence to suggest the presence of blue phases at the clearing point in any of the materials, nor do any of the compounds exhibit TGB A* phases at the transition from the smectic A phase to the smectic C* phase. It was also noted that the pitch in the cholesteric phase appeared to be much longer than in the analogous chlorine containing materials (series IX and X). It seems, therefore, that there may have been a reduction in chirality on moving from a chlorine to a bromine atom at the chiral centre. Two reasons, one of which is synthetic in nature, can be used to explain why this is so. Firstly, the synthetic procedure used to prepare the bromo compounds was similar to that used to prepare the analogous chloro compounds. The enantiomeric excess (ee) in the bromo compounds is, however, believed to be much lower than in the case of the chloro compounds because of synthetic reasons (see experimental section). If this is the case, then a reduction in chirality, leading to the absence of blue phases and a TGB A* phase, may ensue. The second possibility is tied to the size of the bromine atom and its effect on steric factors. Usually, the overall

polarization associated with the molecule is believed to be partly due to a coupling between the linking group that connects the core of the molecule (in this instance an ester moiety), and the substituent at the chiral centre (in this case a halogen). If the size of the bromine atom is large enough to distort the preferred conformation, so as to break the coupling with the linking group, then the polarization and therefore the overall chirality may be reduced. An illustration of this is shown in figure 130.

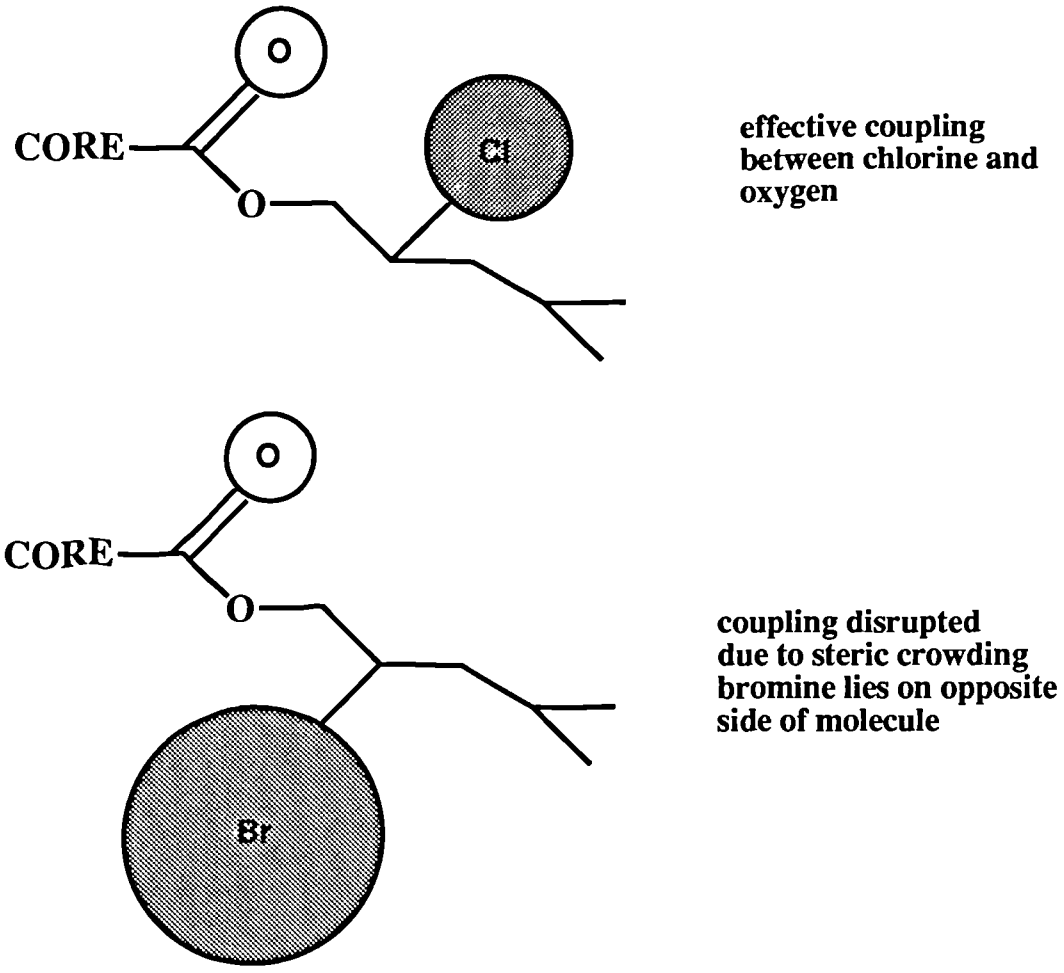


Figure 130. Linking Group and Chiral Centre Coupling in Optically Active Mesogens.

Another interesting point about the phase diagram for the benzoate materials in series XVI (**189** to **192**) is the effect of odd/even alternations in alkoxy chain length on the transition temperatures. This effect is usually pronounced for the clearing point

transitions in some systems[156], but can also be found for other phase transitions. In the system under discussion the odd/even effect is pronounced for the clearing points and the transition from cholesteric to smectic A. It is observed to a greater extent, however, for the smectic A to smectic C* transitions. This behaviour may support the fact that the molecules in this series are distorted in some way due to the large bromine atom positioned at the chiral centre. It should be noted that this type of effect was not seen in the analogous chlorine containing materials (series IX and X).

The propiolate **193**, was found to have a reduced clearing point over the benzoate equivalent (**191**), a much larger nematogenic tendency, and a lower temperature transition from the smectic A to the smectic C* phase. This type of behaviour is by now typical for the introduction of a triple bond into the molecular core in these systems.

Calorimetric studies carried out on these materials confirmed the results obtained by thermal optical microscopy. There was no indication of the presence of blue phases or TGB A* phases.

The properties of the smectic C* phases for compounds **189** to **193** (series XVI) were also investigated, the results obtained are summarised in table 33 where it can be seen that all of the materials in this series can be classified as ***S***, **e**, ***d***, and that in compounds **189** and **193** (the nonyloxy homologues) the direction of the spontaneous polarization was found to be positive. The helical twist sense in these materials therefore agrees with the previously stated hypothesis[39]. The polarization direction is also consistent with predicted patterns. An attempt was made to measure the value of the spontaneous polarization with respect to temperature for compound **193** (the propiolate material). The result of this study, however, indicates that the value of the spontaneous polarization in this material is very small, and could not be effectively measured.

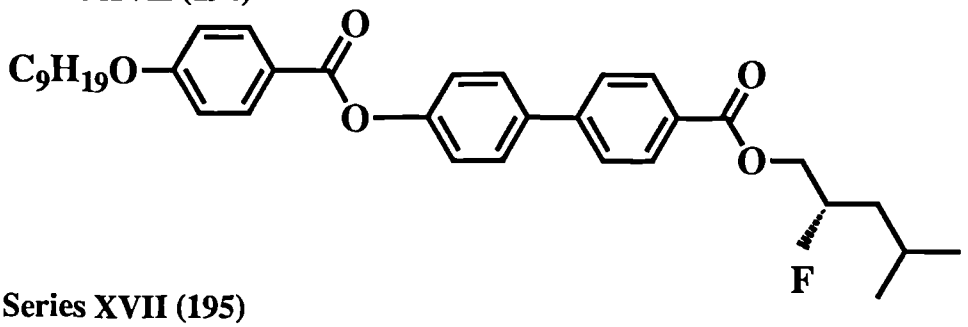
No.	n	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
189	7	*S*	e	*d*	LH	-ve	+
190	8	*S*	e	*d*	LH	-ve	
191	9	*S*	e	*d*	LH	-ve	
192	10	*S*	e	*d*	LH	-ve	
193	9	*S*	e	*d*	LH	-ve	+

Table 33. Chiral Properties Associated with the Smectic C* Phase of the Materials in Series XVI (189-193).

8.13 Esters Based on a 2-Fluoro-4-methylpentyl Chiral Moiety (Series XVII).

The next stage in the evaluation of how the size of atom associated with the chiral centre affects the material properties, was to substitute a fluorine atom in the position that was occupied by a bromine atom in the previous series (XVI). Two materials (**194** and **195**) were prepared, one benzoate and one propiolate (see figure 131).

Series XVII (194)



Series XVII (195)

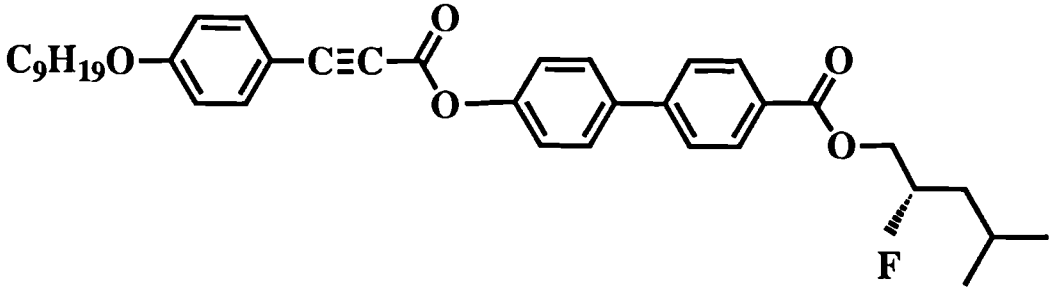


Figure 131. The Structures of the Fluorine Based Di-Esters (194 and 195).

The transitions associated with the two materials are illustrated in table 34, and also depicted in figure 132.

No.	Mpt.	I-BPIII	BPIII-BPII	BPII-BPI	BPI-Ch	Ch-TGB	TGB-S_A	S_A-S_C*	S_C*-S_I*	Rec.
194	69.9	167.9	167.8	167.2	166.1	166.1	166.1	140.5	54.6	52.6
195	68.4	142.0	141.7	141.3	141.0	113.4	111.3	94.4		54.5

Table 34. The Transition Temperatures (°C) for the Materials Based on an *(S)*-2-Fluoro-4-methylpentyl Chiral Moiety (194-195).

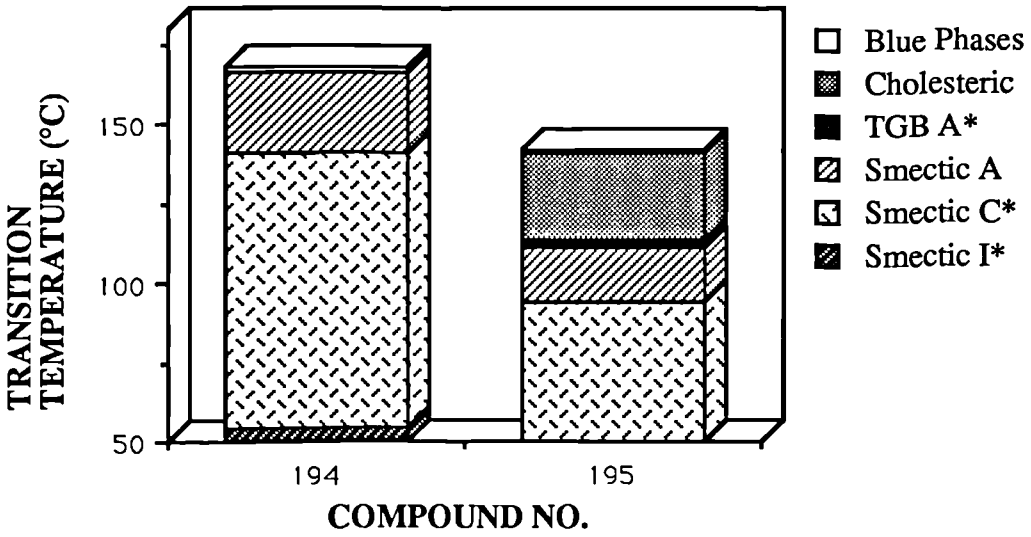


Figure 132. The Phase Behaviour Associated with the Materials Based on a 2-Fluoro-4-methylpentyl Chiral Moiety (194 and 195).

It can be seen from table 34 and figure 132 that the phase sequence exhibited on cooling by both materials was isotropic liquid to blue phases to cholesteric to TGB A* to smectic A to smectic C*. The cholesteric phase and the TGB A* phase observed by optical microscopy in compound **194** (the benzoate analogue) were only transitory in nature. The clearing point, as well as the blue phase temperature range was reduced in compound **195**, compared with **194**, but the cholesteric and TGB A* thermal stabilities were increased. A trend observed in many of the previous materials that were discussed

earlier. The transition to the smectic C* phase from the smectic A phase was seen to occur at a much higher temperature for compound **194**. Below the smectic C* phase in compound **194** (the benzoate material), a smectic I* phase was also observed.

As with a number of compounds, calorimetric studies failed to conclusively show the presence of blue phases or a TGB A* phase. The results obtained were, however, generally consistent with those found by optical microscopy.

When the properties of the smectic C* phase, in both the fluorine analogues, were evaluated more interesting results were obtained, and these are summarised in table 35.

No.	n	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
194	9	*S*	e	*d*@	LH @	-ve	+
195	9	*S*	e	*d*	LH	-ve	+

@ the helical twist sense was seen to invert from left- to right-handed at approximately 90-85 °C in this material.

Table 35. Chiral Properties Associated with the Smectic C* Phase of the Materials in Series XVII (194 and 195).

From table 35 it can be seen that the two materials can be classified as ***S*, e, *d*, LH**, at a temperature just below the smectic A to smectic C* transition. On further cooling, however, the helix associated with the smectic C* phase of compound **194** is seen to invert, in a similar way to how the smectic C* helix in a number of the chloro analogues inverts. It appears that for this phenomenon to occur it is favourable to have an isopropyl group present at the end of the chiral alkyl chain. The polarization direction in both materials was determined to be positive, and did not invert with temperature in compound **194**. The value of the spontaneous polarization was determined for compound **195**, with

respect to temperature giving 39.8 nC cm^{-2} at 10 °C below the Curie Point. This will be expanded upon later.

8.14 A Comparison of the Effects Observed on Varying the Halogeno Substituent Located at the Chiral Centre.

A comparison that was made between materials that vary in structure only by the type of halogen present at the chiral centre will now be discussed. Figure 133 illustrates the phase behaviour observed in the three propiolate materials (**164, 193, 195**).

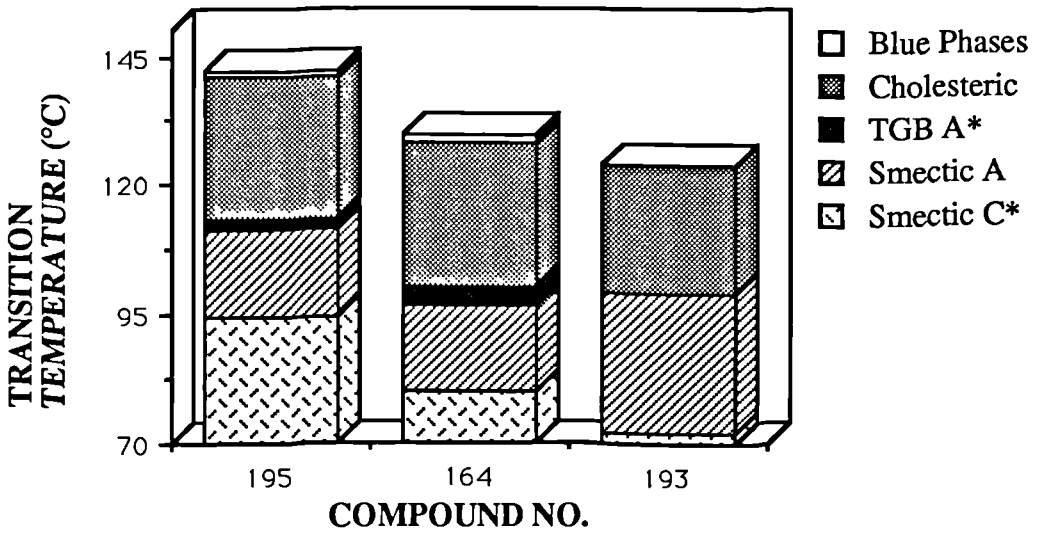


Figure 133. The Phase Behaviour of Compounds 195, 164, and 193 (the Fluoro, Chloro, and Bromo Propiolate Based Materials).

From figure 133 it is seen that compounds **164** and **195** exhibit an isotropic to blue phase to cholesteric to TGB A* to smectic A to smectic C* phase sequence. Compound **193** has an isotropic to cholesteric to smectic A to smectic C* phase sequence. The reasons why **193** (the bromo analogue) does not exhibit blue phases or a TGB A* phase have been discussed earlier. When a comparison is made between compounds **164** and **195**, which do exhibit these phases it is found that both the blue phase and the TGB A* temperature range is greater in the material with a chlorine atom situated at the chiral centre. The cholesteric and smectic A phases are approximately equal in terms of thermal

stability, and so the greater TGB A* temperature range in compound **164** can only be due to either weaker layer ordering or an increase in molecular chirality tied into the larger size of the chlorine atom. This may be due to a greater degree of rotational hindrance associated with the chiral centre. It must be remembered that this effect has to off-set the larger effective dipole that may be associated with the carbon-fluorine bond in **195**. The smectic A to smectic C* transition temperature is seen to rise with decreasing size of halogen, as do the clearing points.

When the properties of the smectic C* phase in these materials are compared a number of points are noted. Table 36 summarises the results obtained.

No.	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.	Halogen
164	*S*	e	*d*@	LH @	-ve	+	Cl
193	*S*	e	*d*	LH	-ve	+	Br
195	*S*	e	*d*	LH	-ve	+	F

@ the helical twist sense was seen to invert.

Table 36. Chiral Properties Associated with the Smectic C* Phase of Compounds 164, 193 and 195.

From table 36 it can be seen that all of the materials were classified as ***S*, e, *d*, LH,** with a positive direction of the spontaneous polarization at a temperature just below the smectic A to smectic C* transition. On further cooling the helix in the smectic C* phase of compound **164** (the chloro analogue) inverted. One may speculate that the helix in compound **193** (the bromo analogue) does not invert because the large size of the bromine atom does not allow for an interconversion between conformational species that would cause a helix inversion, and that for compound **195** (the fluoro analogue) conformational changes, due to the small size of the fluorine atom, are relatively easy and so different species are always interconverting. This leaves the intermediary sized

chlorine atom as the most perfectly sized substituent for inversions to occur. It is, however, worth noting that an inversion does take place in the smectic C* phase of compound **194** (the benzoate analogue of **195**).

The direction of the spontaneous polarization is the same in all of the materials, and does not invert with the helix inversion in compound **194**. The value of the spontaneous polarization was too small to measure in compound **193** (the bromo analogue), but is illustrated with respect to temperature for the other two materials in figure 134.

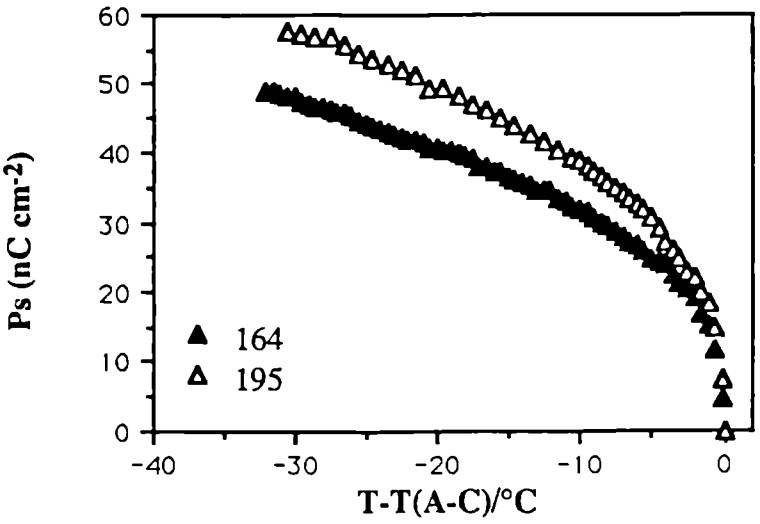


Figure 134. The Value of the Spontaneous Polarisation with Respect to Temperature in the Smectic C* Phase of Compounds 164 and 195.

The value of the spontaneous polarization is seen to rise steadily in both compounds **164** and **195** (see figure 134). At lower temperatures, however, the gradient of the slope and therefore the value of the polarization in the fluorine containing compound (**195**) is greater. This can be attributed to the larger effective dipole associated with carbon-fluorine bond situated at the chiral centre in this material.

8.15 An Ester Based on the 1-Methylheptyl Chiral Moiety (Series XVIII).

The first material[91] to exhibit the TGB A* phase was a compound based on a 1-methylheptyl chiral substituent. The structure of this material (**196**), which is also known as **14P1M7** is illustrated in figure 135.

Series XVIII (196)

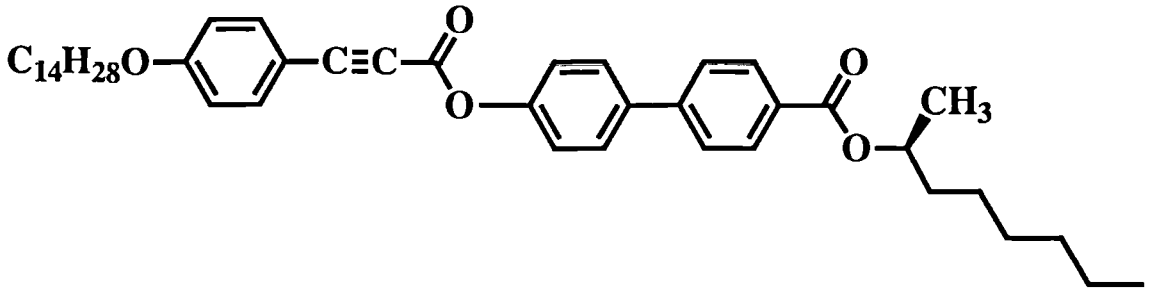


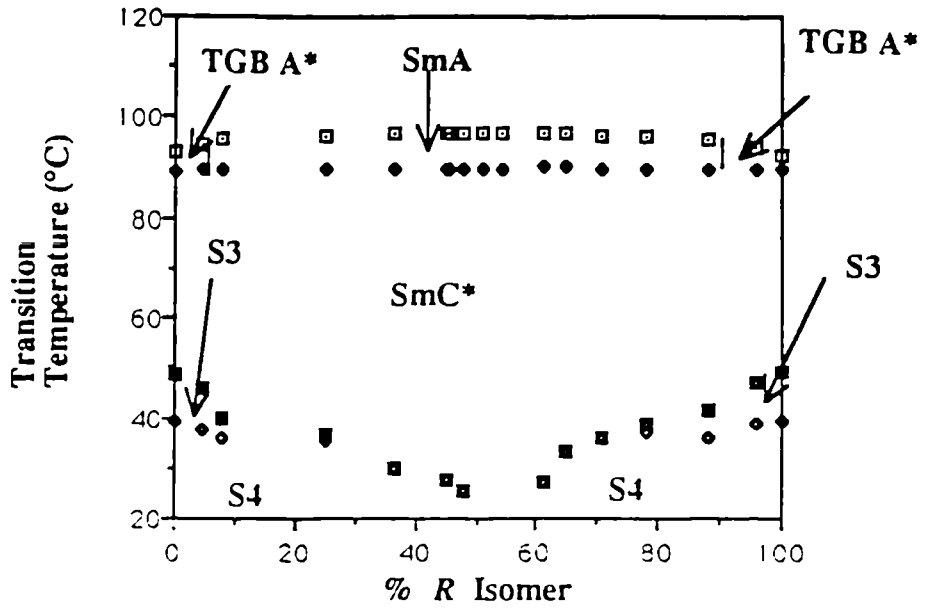
Figure 135. The Structure of (S)-1-Methylheptyl 4'-(4-tetradecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate, 14P1M7 (196).

This material was synthesized not only to allow a number of miscibility studies to take place with selected chlorine containing materials, described previously in this chapter, but also to enable a study to be carried out on the effects of optical purity on the formation of the TGB A* phase. Compound **196** was known to have two additional smectic C* modifications occurring at lower temperature, which are believed to be a ferrielectric and an antiferroelectric smectic C* phase. Whether chirality is needed to produce these phases was an important consideration. As one optical isomer was available *(R)*, the *(S)* isomer was synthesised. The transitions associated with this material are shown in table 37.

No.	n	Mpt.	I-TGB	TGB-S_C*	S_C*-S3	S3-S4	Rec.
196	14	89.7	94.0	90.0	53.6	43.8	<30

Table 37. The Transition Temperatures (°C) for *(S)*-1-Methylheptyl 4'-(4-tetradecyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (196).

On making binary mixtures of both the *(S)* and *(R)* isomers, the following results were obtained (see figure 136).



S3 is believed to be a ferrielectric C* phase, S4 is believed to be an antiferroelectric C* phase.

Figure 136. The Effect of Optical Purity on TGB A* Phase Formation in 14P1M7 (196).

It can be seen from figure 136 that the TGB A* phase is only stable at levels of optical purity that exceed 95 % of either enantiomer; in the middle of the phase diagram a transition from the isotropic liquid to the smectic A phase is observed. Another interesting point is the reduction in the clearing point temperature as the optical purity is increased; this effect was predicted to occur by de Gennes[95]. The thermal stabilities of the S3 and S4 phases are also markedly affected by optical purity. The smectic C* to S3 and S3 to S4 transition temperatures rise as the enantiomeric excess is increased. In the middle of the phase diagram the transition from smectic C* to S3, and subsequently to S4 occurs over a very narrow temperature range, making the identification of an S3 phase very difficult. It is expected that in the racemic mixture both the S3 and the S4 phase will

completely disappear. In this phase diagram an exact 50/50 mixture of optical isomers was not produced, and so it can only be concluded that these sub-phases are suppressed with a reduction in chirality.

8.16 Esters Based on Alternative Core Systems (Series XIX, XX, XXI, XXII, XXIII).

In order to try and clarify what effect changing the core structure would have on the liquid-crystalline behaviour of some of the materials that were previously discussed, a number of groups were substituted for the phenyl and biphenyl moieties that had been used earlier.

The first compound to be discussed (**198**), has a structure in which the phenyl ring present in compound **141** was replaced by a cyclohexyl group that had a *trans* configuration. The structure of this material is illustrated in figure 137.

Series XIX (198)

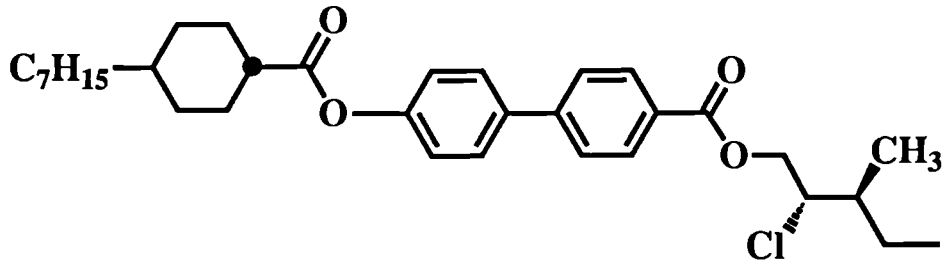


Figure 137. The Di-Ester with a Cyclohexyl Core Sub-Unit (198).

The incorporation of the cyclohexyl group reduces the rigidity of the material, as well as its polarizability. The group was expected to give a reduction in viscosity and melting point. The transition temperatures associated with this material, and a comparison between it and its benzoate analogue are given in table 37 and figure 138.

No.	n	Mpt.	I-BPIII	BPIII-BPII	BPII-S_A	S_A-S_B	Rec.
198	7	59.7	149.2	148.7	148.5	80.6	42.7

Table 37. The Transition Temperatures (°C) for *(S,S)*-2-Chloro-3-methylpentyl 4'(4-heptylcyclohexylcarbonyloxy)-4-biphenylcarboxylate 198.

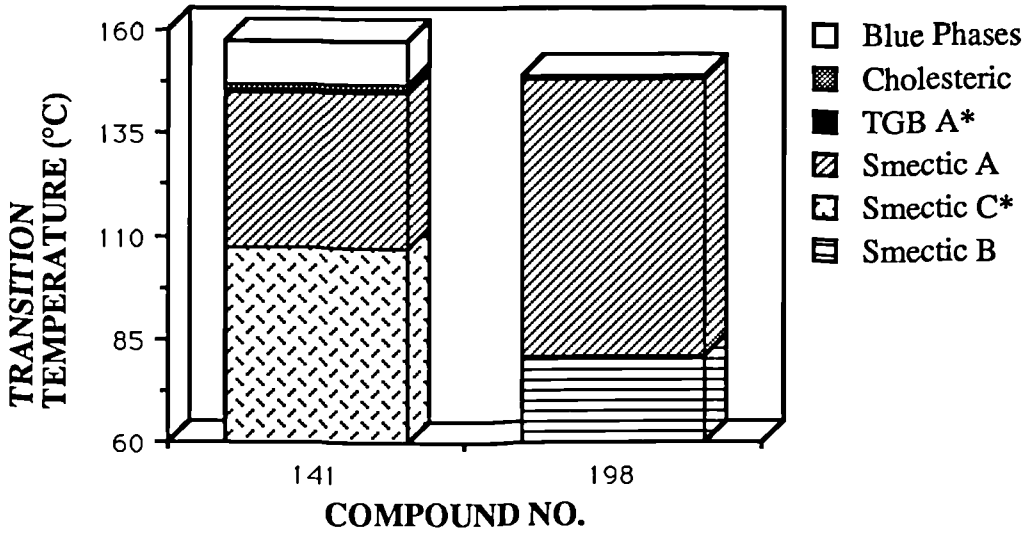


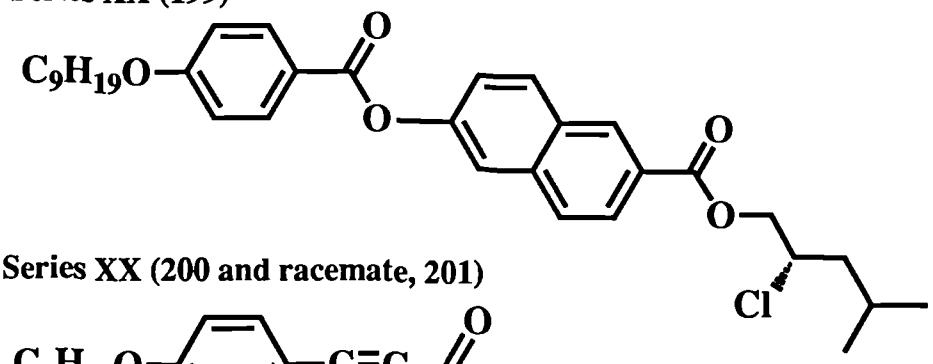
Figure 138. A Comparison of the Phase Behaviour of Compounds 141 and 198 (the Phenyl and Cyclohexyl Analogues with a 2-Chloro-3-methylpentyl Chiral Moiety).

It can be seen from table 37 that compound **198** shows an isotropic to blue phase to smectic A to smectic B phase sequence. The transition from blue phase to smectic A was easily seen, but the subsequent transition to smectic B was very difficult to detect indeed, occurring as a slight undulation in the focal-conic texture at the transition point (the transition was, however, confirmed by DSC). In comparison with its benzoate analogue, **141**, compound **198** does not exhibit a cholesteric phase, nor a TGB A* phase or a smectic C* phase. The clearing point in the cyclohexanecarboxylate ester was lower, than in the benzoate. The fact that **198** does not have a TGB A* phase is probably because of the absence of an underlying smectic C* phase. The reduction in the smectic

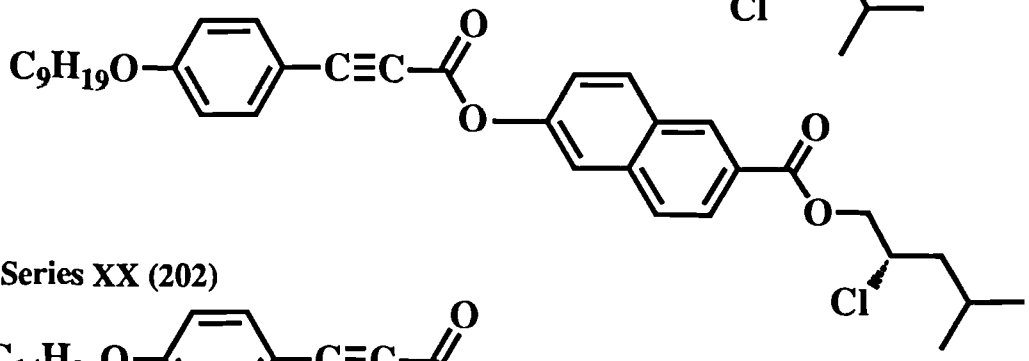
C* phase stability, and the appearance of the more ordered orthogonal B phase, although not predicted in this system, has been known to occur for other systems[157].

The next series of materials (XX) were based on compounds in which the biphenyl core, described in the earlier part of this discussion was replaced with a naphthalene moiety. The reason for doing this was two-fold, firstly to try and weaken the layer ordering in order to generate a TGB A* phase with a wide temperature range, and secondly to try and reduce the clearing point temperature so that the TGB A* phase may occur at a lower temperature than in some of the previous materials. Two chiral groups were selected to attach to the core system, the first being the 2-chloro-4-methylpentyl moiety, the second being the 1-methylheptyl moiety, both of which were known to give wide TGB A* temperature ranges in materials discussed earlier . In one instance a racemate (**201**) was prepared in order to make a comparison with the chiral analogue (**200**). The structures of the materials in series XX are illustrated in figure 139.

Series XX (199)



Series XX (200 and racemate, 201)



Series XX (202)

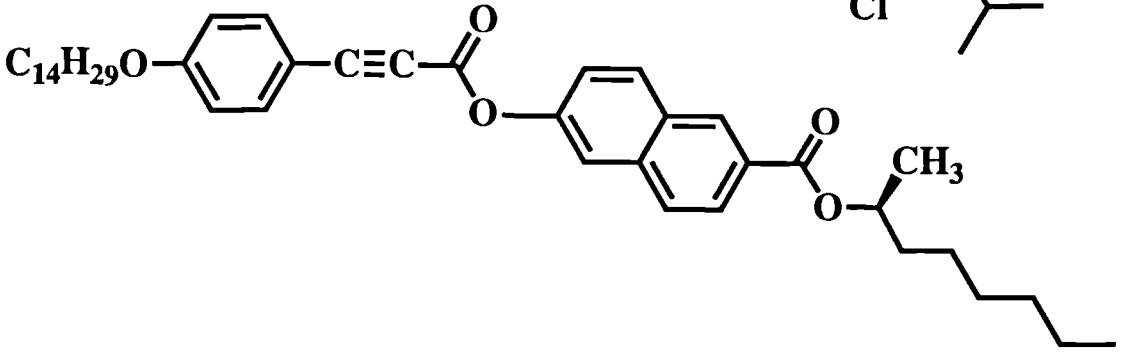


Figure 139. The Structures of the Di-Esters Based on a 2,6-Disubstituted Naphthalene Core Unit (199 to 202).

The phase sequences of the four materials in this series are shown in table 38, and figure 140.

No.	Mpt.	I-BPIII	I-N	I-S_A	BPIII-BPII	BPII-BPI	BPIII-BPI	BPI-Ch	Ch-TGB	TGB-S_A	N-S_A	S_A-S_C*	Rec.
199	70.3	86.1			85.7	85.3		84.2	84.2	84.2		53.7	<30
200	52.4	67.7					67.0	65.7	50.0	47.9			<30
201	53.7		68.3								53.2		52.5
202	55.4			39.6									<30

Table 38. The Transition Temperatures (°C) for the Materials in Alkyl 6-(4-alkoxybenzoyloxy and phenylpropioyloxy)-2-napthoates (199 to 202).

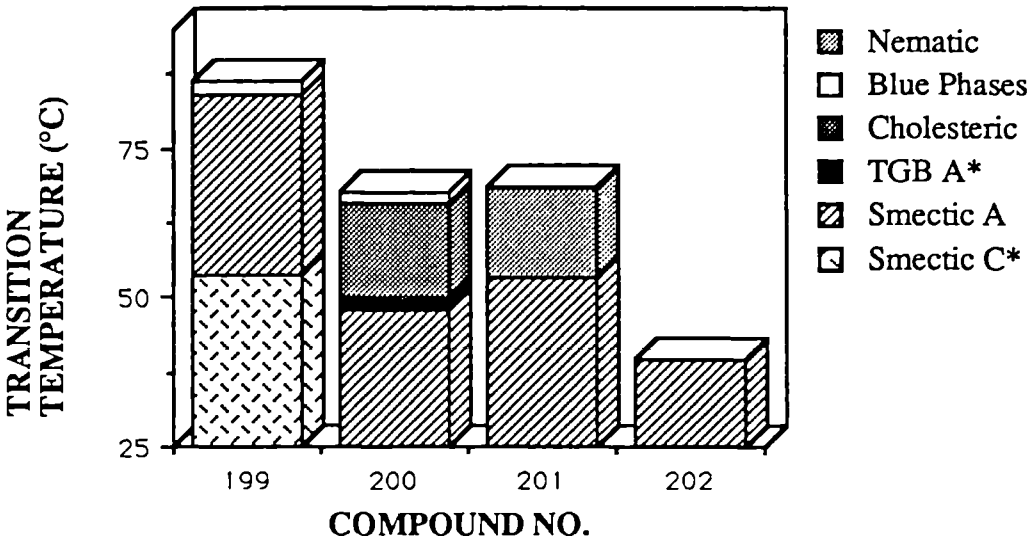


Figure 140. The Comparison of the Phase Behaviour for the Materials in Series XX (199 to 202).

From table 38 and figure 140 it can be seen that compound **199** (the benzoate material) exhibits an isotropic to blue phase to cholesteric to TGB A* to smectic A to smectic C* phase sequence. The TGB A* and cholesteric phases in this material are, however, only transitory as the blue phase to cholesteric transition is seen to supercool quite considerably (figure 141 shows the heating trace obtained by DSC at the clearing point).

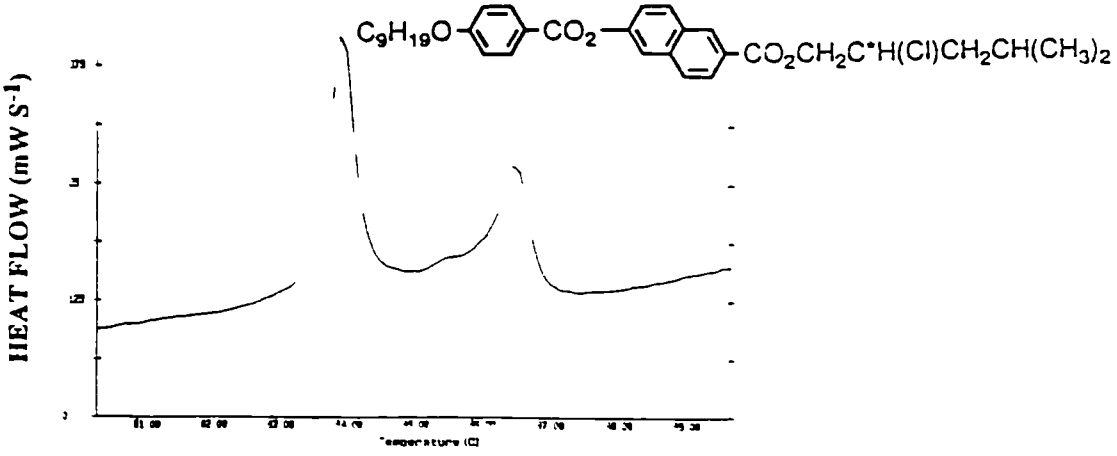


Figure 86. The Heating Cycle Close to the Clearing Point for *(S)*-2-Chloro-4-methylpentyl 6-(4-nonyloxybenzoyloxy)-2-napthoate (199).

When compared to the equivalent material that has a biphenyl core unit (**158**) a number of differences are noted (see figure 141).

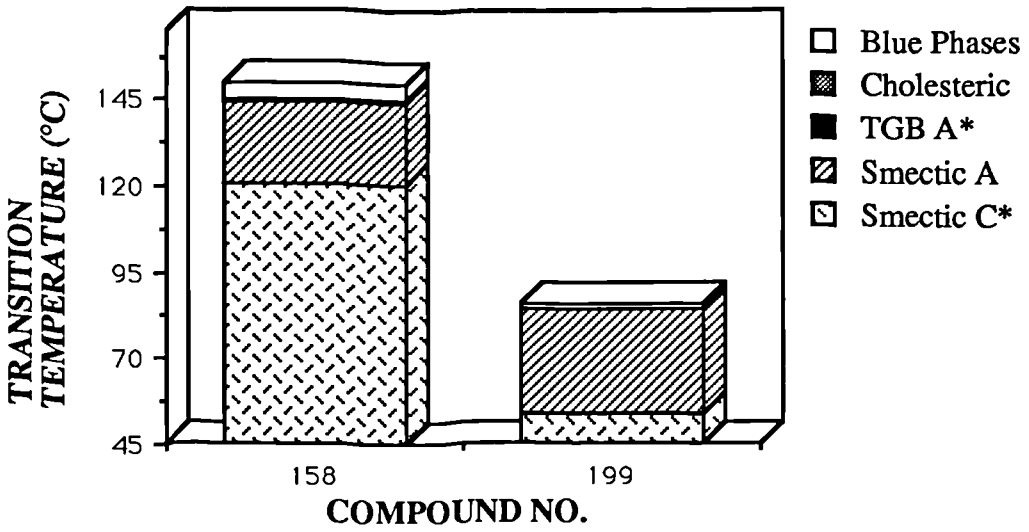


Figure 141. A Comparison of the Phase Behaviour of Compounds 158 and 199.

It can be seen from figure 141 that compound **158**, based on the biphenyl core structure, has a significantly higher clearing point than the naphthyl compound **199**. Compound **158** also has a much greater nematogenic tendency, and a greater TGB A* phase thermal stability. It is well documented that a naphthalene core unit can suppress clearing points, but it does not appear in this instance to weaken the layer structure in order to give a large TGB A* temperature range. In fact the nematogenicity of the material is greatly reduced in comparison with its biphenyl analogue. When the helical twist sense in compound **199** was examined it was found that the material could be classified as being ***S*, e, *L*, RH**, which is an analogous situation to when the core structure was based on a biphenyl moiety as in compound **158**.

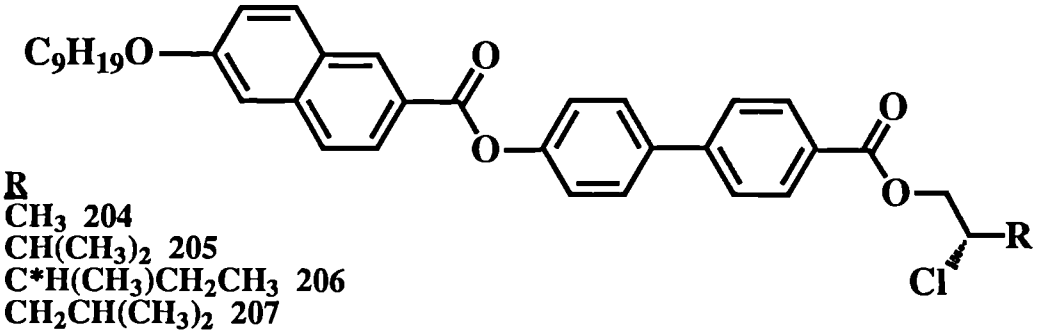
When a triple bond is added to the core structure of the material, as is the case with compound **200**, it is found that in comparison to compound **199**, the clearing point falls, but the TGB A* and cholesteric temperature ranges increase considerably. It is

interesting to note that a smectic C* phase was not observed in compound **200**. When compound **200** was compared with its racemic variant, compound **201**, which showed an isotropic to nematic to smectic A phase sequence, it was noticeable that the clearing point and to a greater degree the transition to smectic A was suppressed in the optically active material. This suppression of the nematic to smectic A transition was initially predicted to occur by de Gennes[95].

Compound **202** which was based on a 1-methylheptyl chiral moiety exhibited a simple isotropic to smectic A phase sequence. The clearing point was found to be considerably lower than that observed for the other materials in this series, thus, the liquid-crystallinity was substantially suppressed. It is also thought that on exchanging a naphthalene core for a biphenyl core that the chirality is in some way suppressed. Compound **202** has a smectic A and not a TGB A* phase, and the TGB A* temperature range is reduced in all materials where the biphenyl core was exchanged for a naphthalene moiety.

The next three series of materials involve compounds where the phenyl entity that is observed in a number of the earlier materials is replaced by a variety of naphthalene moieties. Once again the reason for this study was to try and weaken the layer ordering and so induce a wider TGB A* temperature range. The first series involves a 2,6-substituted naphthalene unit in the core to replace the previously used phenyl ring system. The general structure of the materials produced is illustrated in figure 142. A number of chiral groups were used the results for which are listed in table 39, with figure 143 illustrating these results graphically.

Series XXI



R
CH_3 204
$CH(CH_3)_2$ 205
$C^*H(CH_3)CH_2CH_3$ 206
$CH_2CH(CH_3)_2$ 207

Figure 142. The Structure of the 2,6-Disubstituted Naphthalenes in Series XXI (204-207).

No.	Mpt.	I-Ch	I-BPIII	BPIII-BPII	BPII-BPI	BPI-Ch	Ch-S_A	Ch-TGB	TGB-S_A	Rec.
204	114.9	160.9					132.4			100.4
205	113.1		129.4	129.4	126.3	126.2		113.9	113.9	89.3
206	106.8		126.8	126.5	126.0	125.1		101.9	100.9	85.5
207	97.7		122.6	122.4	121.9	120.6		98.5	97.0	85.9

Table 39. The Transition Temperatures (°C) for the Alkyl 4'-(6-nonyloxy-2-napthoyloxy)-4-biphenylcarboxylates (204-207).

It can be seen from table 39 and figure 143 that the first material (**204**) in series XXI has an isotropic to cholesteric to smectic A phase sequence, whilst the other three materials (**205** to **207**) have an isotropic to blue phase to cholesteric to TGB A* to smectic A phase sequence. The melting point and recrystallization temperatures in these materials were higher than in the analogous materials with a phenyl moiety in the core, which is to be expected as the naphthalene based materials essentially contain an additional aromatic ring. The higher recrystallization temperatures may well explain why a smectic C* phase is not observed, although it is also obvious that tilted phases are suppressed in these materials. Due to the reduced clearing points, the liquid-crystallinity as a whole has also been suppressed to some extent.

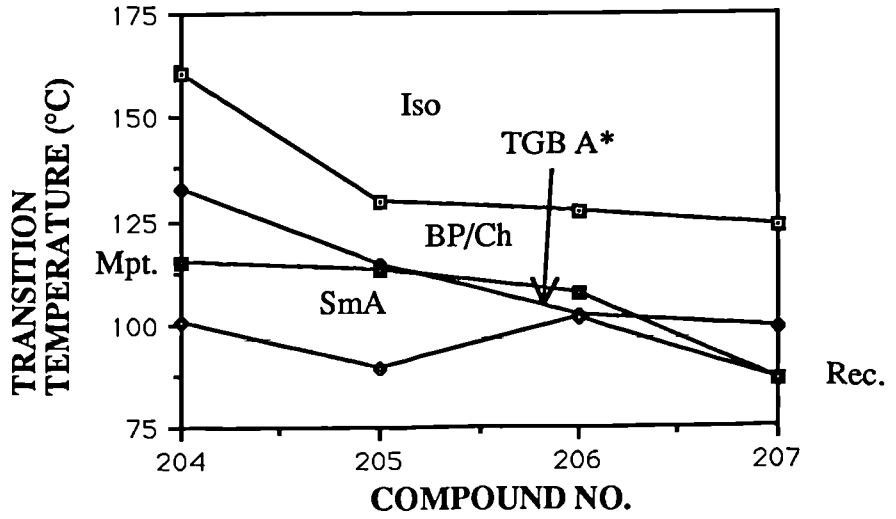


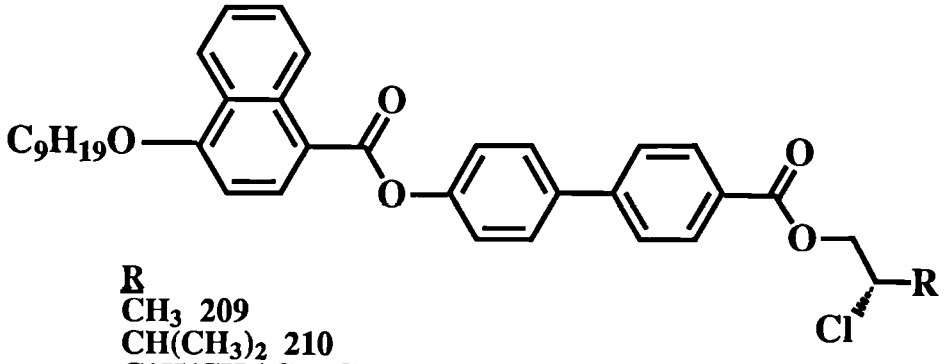
Figure 143. Transition Temperature Versus Chiral End Group for Materials (204 to 207).

When the effects of chiral end group are considered a similar pattern emerges to that previously found with a shorter alkyl chain attached to the chiral centre not producing frustrated phases (blue phases and TGB A*), but with the TGB A* phase and blue phases appearing in the other three materials (**205** to **207**). The TGB A* temperature range was again found to be largest in the two materials with longer alkyl chains appended to the chiral centre (**206** and **207**). Unusually, however, the blue phase temperature range is widest for the intermediary compound (**205**). It appears that this anomaly may be due to supercooling. Another point of interest is the widening of the cholesteric temperature range in comparison to the analogous phenyl containing compounds. It appears therefore that the naphthalene structure does weaken layer formation in these materials. This is supported by the slight enhancement in the TGB A* temperature range.

The next series of materials to be examined, series XXII, was also based on materials containing a naphthalene core structure, but this time a 1,4-disubstituted naphthalene unit was employed. This effectively shortens the molecular lengths slightly, but also

increases their widths substantially. The same four chiral end groups were used as for the previous series (XXI), the structures of the materials being illustrated in figure 144.

Series XXII



R
CH_3 209
$CH(CH_3)_2$ 210
$C^*H(CH_3)CH_2CH_3$ 211
$CH_2CH(CH_3)_2$ 212

Figure 144. The Structure of the 1,4-Disubstituted Naphthalenes in Series XXII (209-212).

The phase behaviour and transition temperatures for the materials are listed in table 40, and shown in figure 145.

No.	Mpt.	I-Ch	Ch-S_A	I-BPIII	Rec.
209	113.6	121.2	107.0		55.9
210	115.9			95.6	95.1
211	110.0				100.9
212	105.5				96.5

Table 40. The Transition Temperatures (°C) for the Alkyl 4'-(4-nonyloxy-1-napthoyloxy)-4-biphenylcarboxylates (209-212).

From table 40 and figure 145 it can be seen that compared with the previous series (XXI) the liquid crystallinity in this series is much reduced. Compound **209** (based on a 2-chloropropyl chiral end group) shows an isotropic to cholesteric to smectic A phase sequence, but on moving across the series the recrystallization temperature rises

drastically, even though the melting point is seen to drop slightly. As a consequence of this, liquid crystal phases are not observed for these three materials (**210** to **212**).

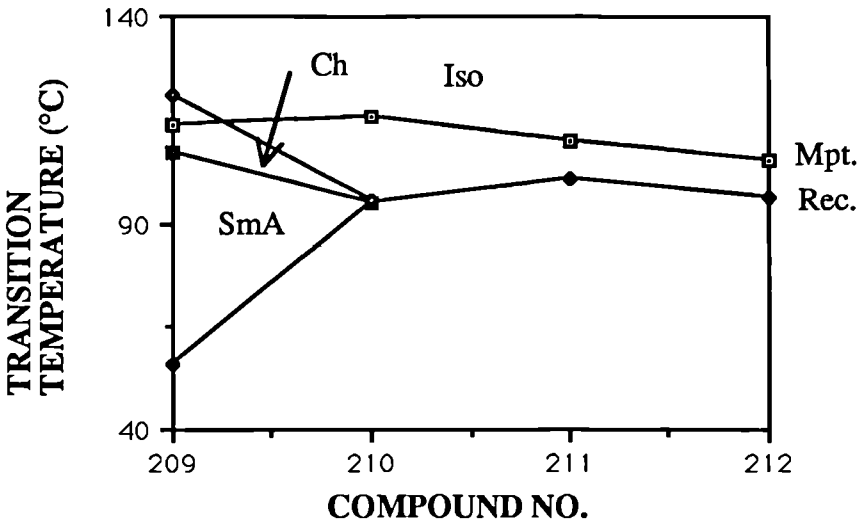
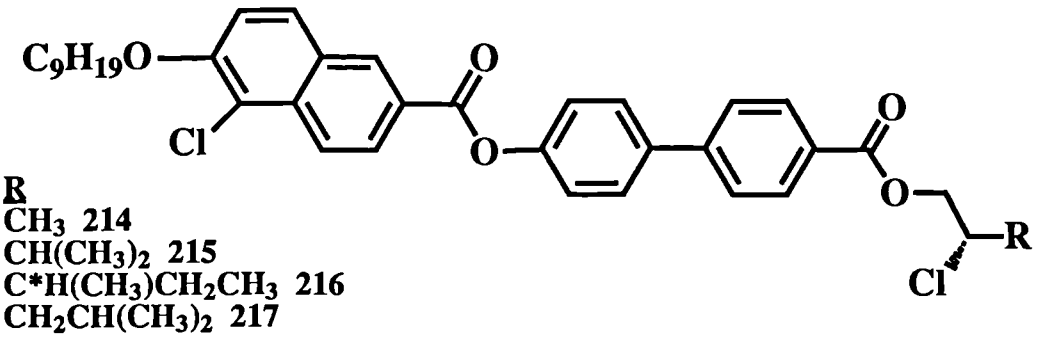


Figure 145. Transition Temperature Versus Chiral End Group for Materials (209 to 212).

The final series of materials that employed a naphthalene core unit, series XXIII, were based on the standard four chiral entities used in the previous two series. The general structure of the materials is shown in figure 146.

The effect of this naphthalene core unit was to widen the molecular core. This core was again used in an attempt to break up the layer ordering. The effect was expected to be intermediate between that of the 2,6-substituted (series XXI) and that of the 1,4-substituted (series XXII) systems. The results obtained for the phase behaviour of these materials are listed in table 41, and depicted in figure 147.

Series XXIII



R
CH_3 214
$CH(CH_3)_2$ 215
$C^*H(CH_3)CH_2CH_3$ 216
$CH_2CH(CH_3)_2$ 217

Figure 146. The Structure of the 1,2,6-Trisubstituted Naphthalenes in Series XXIII (214-217).

No.	Mpt.	I-S_A	S_A-S_C*	Rec.
214	152.9	238.9		144.0
215	141.7	220.2	175.2	127.6
216	128.4	210.3	164.3	111.7
217	128.6	209.4	172.8	111.3

Table 41. The Transition Temperatures (°C) for the Alkyl 4'-(7-chloro-6-nonyloxy-2-napthoyloxy)-4-biphenylcarboxylates (214-217).

It can be seen from table 41, that any nematogenic tendency in the materials in this series is completely suppressed. All of the materials possess a smectic A phase, and in the case of compounds **215** to **217** (with longer chiral alkyl chains) an underlying smectic C* phase is also present. The reason why the smectogenic tendency is increased may well be a consequence of the increased polarity of the core and polarizability of the molecules due to the presence of the chlorine atom in the core structure.

When the chloro substituted compound **217**, and the related non-chloro substituted material **207**, are compared (see figure 148), it is found that a smectic C* phase with an extremely wide temperature range is present for **217**. The smectic A temperature range is much reduced, and the nematogenic tendency is completely suppressed. In these two

related materials therefore, the presence of a chlorine moiety in a lateral position in the core has increased the desire for the compounds to form smectic phases, and in particular tilted phases. The clearing point is also much reduced in compound **207** in comparison to compound **217.**

When the smectic C* phase of compounds **215** to **217** were investigated the materials were found to have a helical twist sense that was dextrorotatory. The results for the three materials are shown in table 42, where it can be seen that the materials in this series can be classified as being **S, e, L, RH,** which agrees with the Goodby and Leslie hypothesis[39].

Thermal investigations of the materials in the previous three series gave results that were generally consistent with those obtained by microscopy.

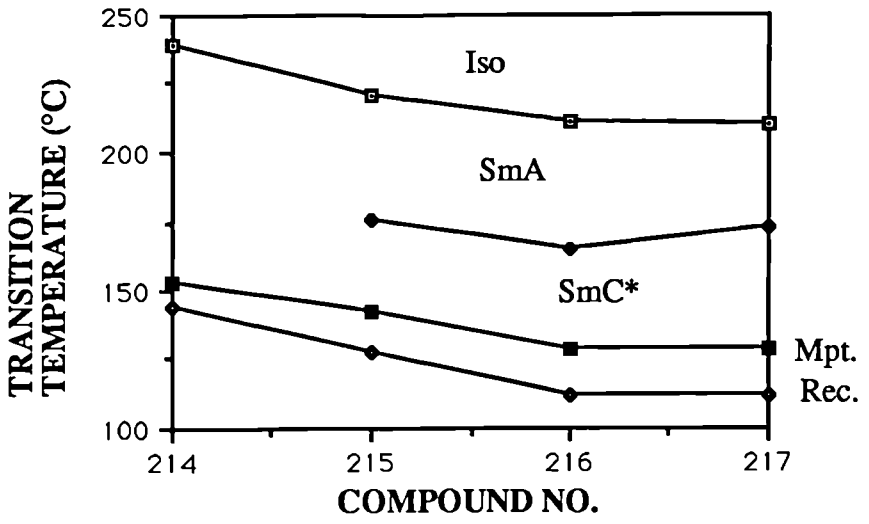


Figure 147. Transition Temperature Versus Chiral End Group for Materials (214 to 217).

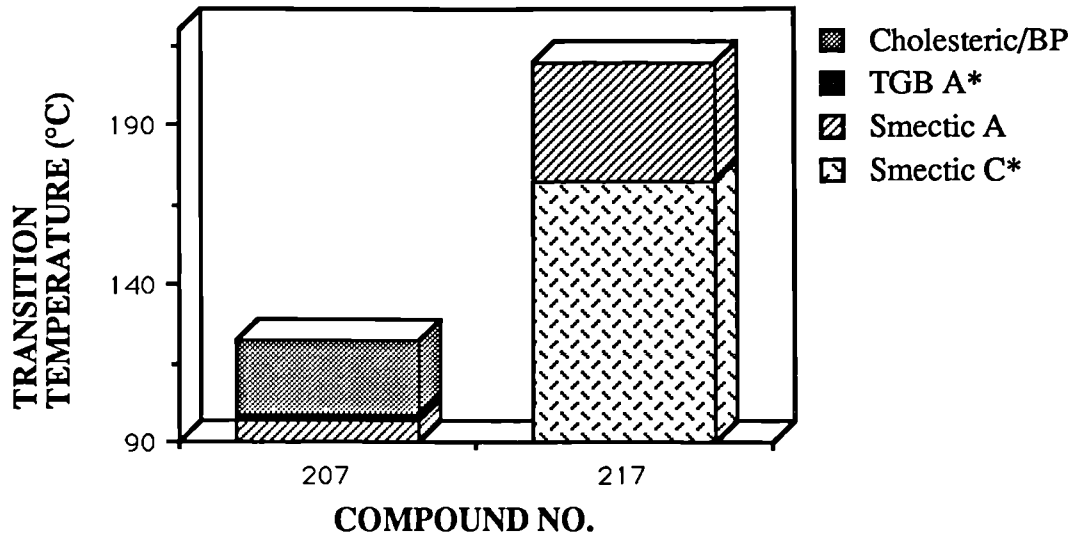


Figure 148. A Comparison of the Phase Behaviour for the Materials With and Without a Chlorinated Core Structure (217 and 207).

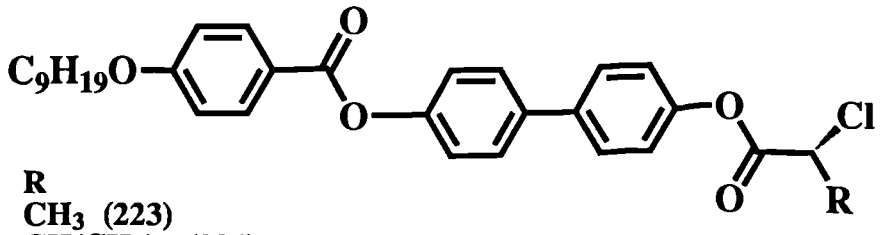
No.	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect
215	*S*	e	*L*	RH	-ve
216	*S*	e	*L*	RH	-ve
217	*S*	e	*L*	RH	-ve

Figure 42. Chiral Properties Associated with the Smectic C* Phase in Compounds 215 to 217.

8.17 Reverse Esters Based on Selected Chiral Moieties (Series XXIV and XXV).

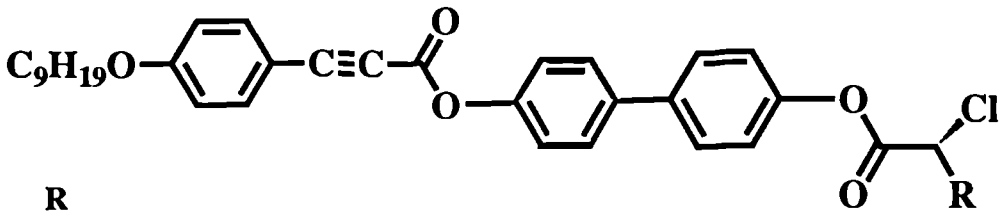
In order to determine what effect the reversal of one of the ester groups has on the liquid-crystalline properties in these systems, the nonyloxy analogues of certain materials, both propiolate and benzoate esters, from the first ten series of materials that were discussed, were prepared and evaluated. The general structures of the materials in these two series are illustrated in figure 149.

Series XXIV



R
CH_3 (223)
$CH(CH_3)_2$ (224)
$C^*H(CH_3)CH_2CH_3$ (225)
$CH_2CH(CH_3)_2$ (226)

Series XXV



R
CH_3 (227)
$CH(CH_3)_2$ (228)
$C^*H(CH_3)CH_2CH_3$ (229)
$CH_2CH(CH_3)_2$ (230)

Figure 149. The Structures of the Reverse Esters in Series XXIV and XXV (223-230).

The reversal of the ester group effectively brings the chiral centre closer to the core structure, and the carbonyl moiety of the linking group. On this basis alone an increase in the chirality of the system might be expected. It must be remembered, however, that the reversal of the group means that the carbonyl function is removed further from the core which may in fact have a large effect on the phase behaviour. These points of course ignore totally how the reversal may cause vastly different interactions between molecules in the phase, and so property/structure predictions are hard to make.

The phase behaviour of the benzoate materials (**223-226**) that constitute series XXIV are discussed first. The transition temperatures and phase behaviour for these compounds are illustrated in table 43, and figure 150.

No.	Mpt.	I-BPIII	I-BPII	I-Ch	BPIII-BPII	BPII-BPI	BPI-Ch	Ch-TGB	TGB-S_A	S_A-S_C*	TGB-S_C*	S_C*-S_I*	S_C*-J*	S_I*-J*	Rec.
223	119.8			207.8				188.2	188.2	182.4		119.2		109.7	104.6
224	89.1		178.1			177.4	175.4	155.1			155.1		74.0		73.8
225	84.0	161.0			161.0	160.7	156.8	140.9			140.9				50.7
226	103.2			150.8				150.3	150.3	136.7					77.9

Table 43. The Transition Temperatures (°C) for the (S)-4'-(4-Nonyloxybenzoyloxy)biphenyl-4-yl 2-chloroalkanoates (223-226).

It can be seen from table 43 and figure 150 that the materials in this series of compounds have very strong smectogenic properties. Compound **223** has an isotropic to cholesteric to smectic A to smectic C* to smectic I* to crystal J* phase sequence, with a transitory TGB A* phase appearing at the cholesteric to smectic A transition point.

The chirality in the material with the shortest chiral alkyl chain (**223**) is believed to be reasonably low due to the length of the chain attached to the external side of the chiral centre, which may explain the absence of blue phases. The smectic A phase range in this material is also very short, because of the relatively high smectic A to smectic C* transition temperature. Underlying this phase a smectic I*, and a crystal J* phase are present. These results indicate that tilted phases are preferred. It is interesting to note that compound **223** is the only material found so far in this research to exhibit a TGB A* phase when the chiral end group is relatively small, i.e., 1-chloroethyl. Compound **224** (the 1-chloro-2-methylpropyl member) does exhibit blue phases leading to the assumption that chirality is enhanced in this compound (relative to **223**). Underlying the blue phases, a cholesteric to smectic C* to crystal J* phase sequence is observed which suggests that the desire to form orthogonal phases has been suppressed altogether for this

material. There also appears to be a transitory TGB A* phase (or possibly a TGB C* phase) at the transition from the cholesteric to the smectic C* phase.

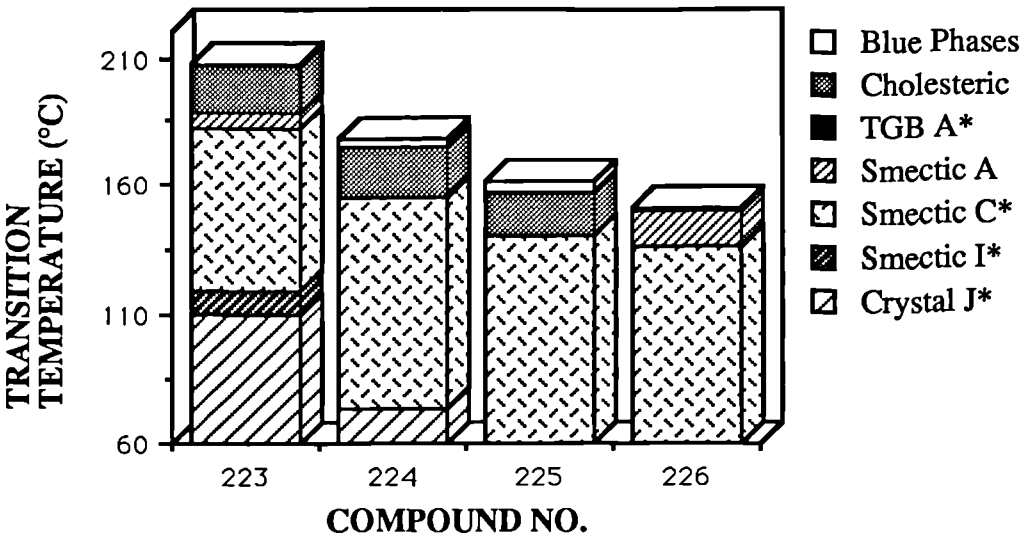


Figure 150. Transition Temperatures Versus Chiral End Group for Materials 223 to 226.

Compound **225** (the 1-chloro-2-methylbutyl homologue) possesses an isotropic to blue phase to cholesteric to smectic C* phase sequence, with once again a transitory TGB A* or TGB C* phase appearing at the cholesteric to smectic C* transition. There are, however, no higher order smectic modifications observed below the smectic C* phase on cooling for this material. Compound **226** (the 1-chloro-3-methylbutyl member) possesses a cholesteric to smectic A to smectic C* phase sequence, with a transitory TGB A* phase appearing at the cholesteric to smectic A transition. There are, however, no blue phases observed above the cholesteric phase in this material tending to suggest a reduced chirality. This is quite surprising as the alkyl chain attached to the external side of the chiral centre is in fact longer than for compound **224** (with a shorter chiral alkyl chain) which is found to exhibit blue phases. The branching point in compound **226** is, however, moved along one position from the chiral centre in comparison with compounds **224** and **225** which may explain the reduced chirality. It is expected that this act will reduce the rotational hindrance associated with the chiral centre. This effect does,

however, contrast with the materials in which the ester group is not reversed (see earlier discussions with regard to series I to X).

Calorimetric studies were found to be consistent with results obtained by thermal optical microscopy. Figures 151, 152, 153, and 154 show the DSC cooling traces of compounds **223**, **224**, **225**, and **226** respectively.

In figure 151 peaks corresponding to the clearing point, cholesteric to TGB A*/A, TGB A*/A to smectic C*, smectic C* to smectic I*, smectic I* to crystal J*, and recrystallization can be clearly seen for compound **223** (1-chloroethyl chiral moiety). The transitions at, or near, the clearing point (on heating) are shown in figure 155 for compound **223**, with three peaks being evident. These correspond to smectic C* to smectic A/TGB A*, smectic A/TGB A* to cholesteric, and the clearing transition to the isotropic liquid.

Figure 152 shows the transitions that occur for compound **224**. The clearing point is evident with the lower temperature transitions that occur in this material, namely cholesteric to TGB A*/C*, smectic C* to crystal J*, and recrystallization, also being evident. The transition to crystal J* appears as a double peak, indicating that a further phase change may be present that was not identified by microscopy.

Figure 153 illustrates the cooling trace obtained for compound **225**. In this thermogram the isotropization point is clearly seen, as is the subsequent transition to the smectic C* phase. Both peaks, however, possess shoulders that may indicate the presence of blue phases and a TGB A* phase. It is interesting to note the first order character associated with the transition from the cholesteric to the smectic C* phase in this compound. At lower temperatures three further peaks are seen, one of which is thought to correspond to

recrystallization. These lower temperature phase changes were not observed by microscopy as recrystallization was nucleated at a higher temperature.

Figure 155 shows the cooling trace of the final material (**226**) which has peaks that correspond to the clearing point and subsequent transition to smectic C*, and two further peaks at lower temperature. Once again only recrystallization was seen to occur by microscopy, with no other higher order phases being evident.

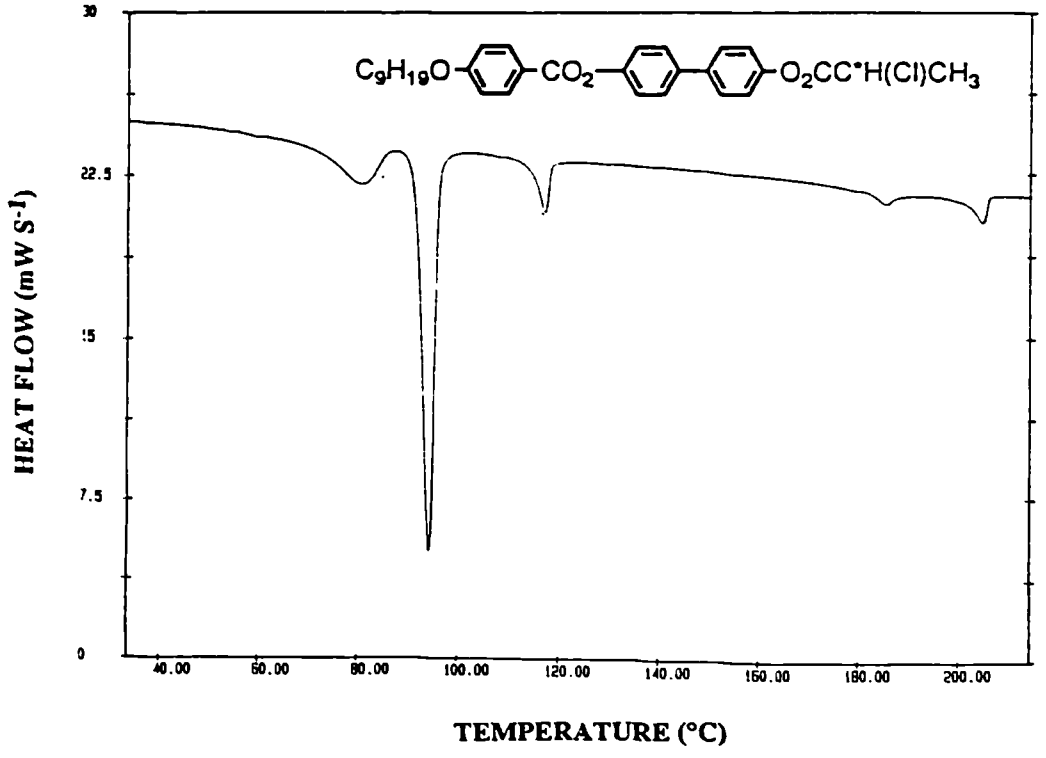


Figure 151. The Cooling Cycle for *(S)*-4'(4-Nonyloxybenzoyloxy)biphenyl-4-yl 2-chloropropanoate (223).

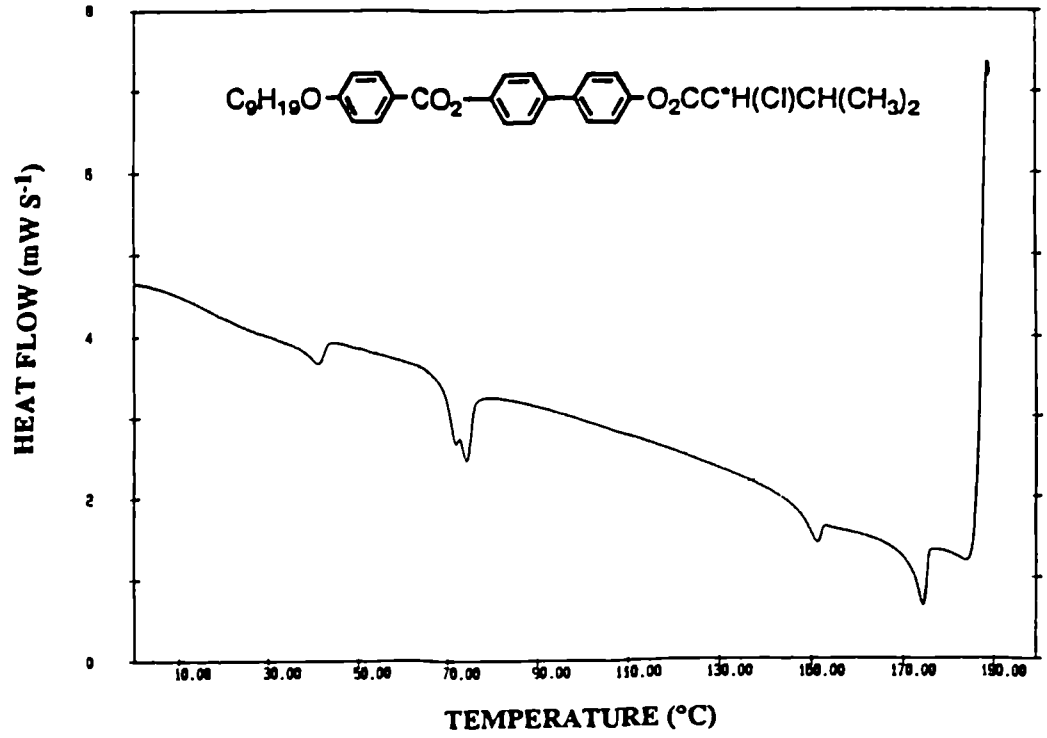


Figure 152. The Cooling Cycle for *(S)*-4'(4-Nonyloxybenzoyloxy)biphenyl-4-yl 2-chloro-3-methylbutanoate (224).

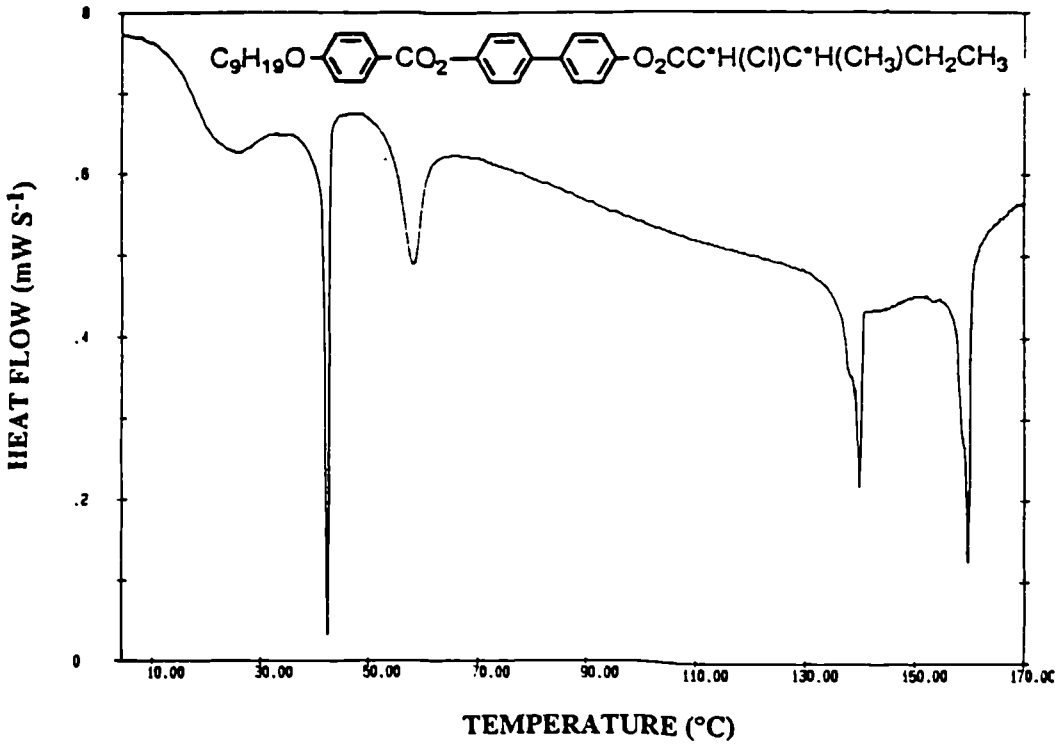


Figure 153. The Cycle for *(S)*-4'(4-Nonyloxybenzoyloxy)biphenyl-4-yl 2-chloro-3-methylpenanoate (225).

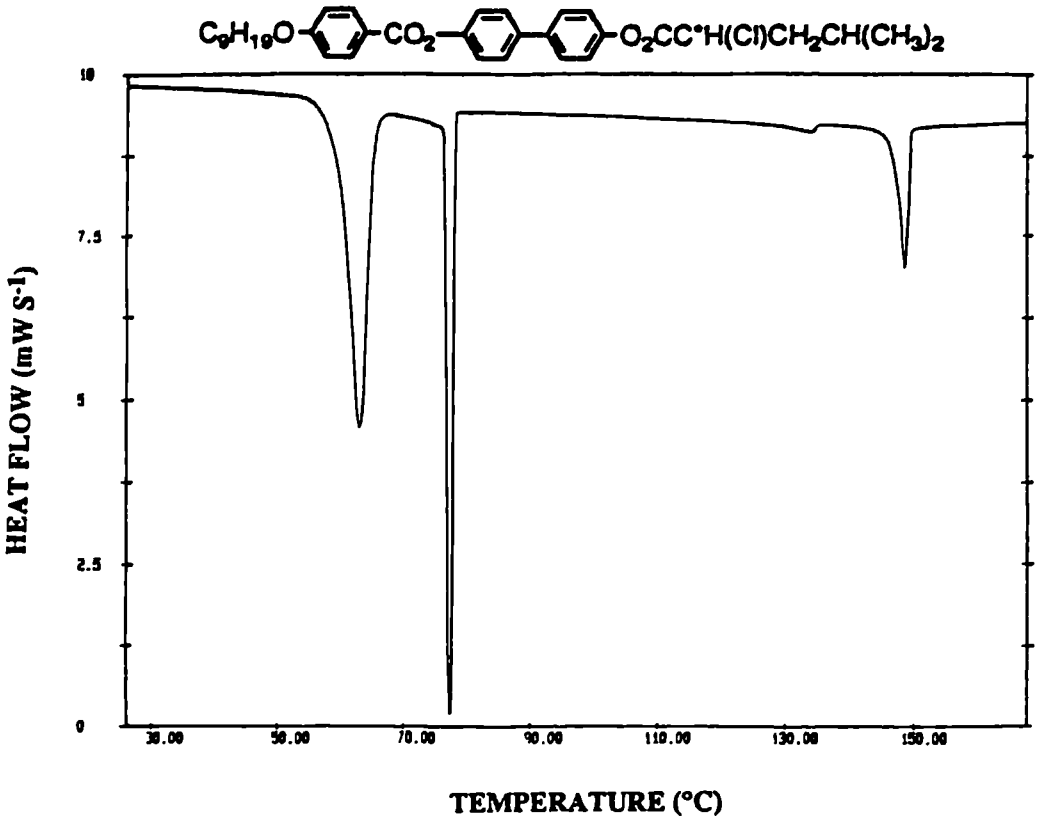


Figure 154. The Cooling Cycle for *(S)*-4'(4-Nonyloxybenzoyloxy)biphenyl-4-yl 2-chloro-4-methylbutanoate (226).

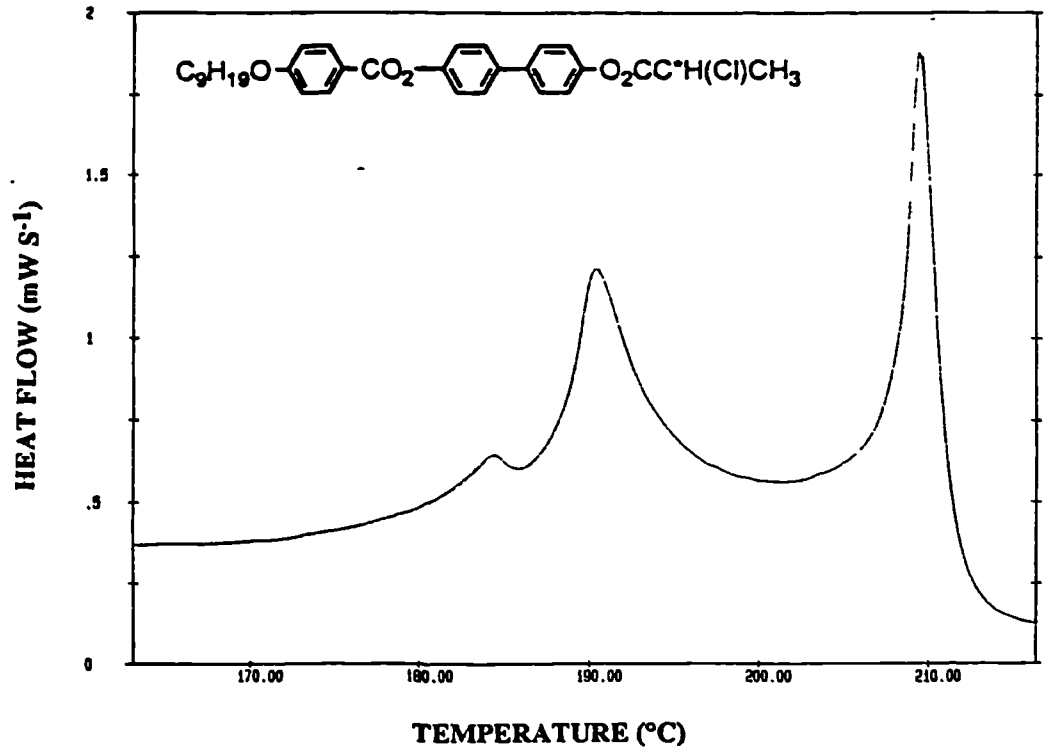


Figure 155. The Heating Cycle Close to the Clearing Point for *(S)*-4'(4-Nonyloxybenzoyloxy)biphenyl-4-yl 2-chloropropanoate (223).

When the properties of the smectic C* phase in these materials was examined, unusual behaviour was again found with respect to helical twist sense. A summary of the properties associated with the smectic C* phase in these materials is shown in table 44.

No.	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
223	*S*	o	*d*	LH	-ve	
224	*S*	o	*d*@	LH @	-ve	
225	*S,S*	o, e	*d*£	LH £	-ve, +ve	-$
226	*S*	o	*d*	LH	-ve	-

@ the pitch in the smectic C* phase becomes infinite at a temperature just above the transition to crystal J*, with the texture becoming very mobile just before the transition.

£ the helix in the smectic C* phase was found to invert between 80 and 69 °C.

$ the direction of the spontaneous polarization was measured above (130 °C), at (74 °C), and below (55 °C) the smectic C* helix inversion point, but was found to be negative in every case.

Table 44. Chiral Properties Associated with the Smectic C* Phase in Compounds 223 to 226.

It is evident from table 44 that the helix direction in these materials just below the transition to smectic C* could be classified as ***S*, o, *d*, LH** which is in agreement with the Goodby/Leslie hypothesis[39]. Compound **225** (based on a 1-chloro-3-methylbutyl chiral moiety) can also be classified as ***S*, e, *d*, LH** because of its second chiral centre, which is also in agreement with the hypothesis. On cooling through the smectic C* temperature range in compounds **224** and **225**, however, the texture became very mobile and reminiscent of that produced by an achiral smectic C phase. In compound **224**, this was followed by a transition to a phase that was assigned as crystal J*, before the helical twist could fully invert. In compound **225** the helix direction was seen to fully invert, this

being initially evident by polarimetry of free standing films (no peak was evident by DSC). Confirmation of the presence of a helix inversion was gained when the material was cooled between glass slides. In one part the texture was focal-conic in nature, and on cooling into the smectic C* phase displayed pitch bands. On cooling towards the inversion point these bands could be visibly seen to grow further apart and then disappear completely as the *schlieren* texture of a non-chiral smectic C phase was formed on another part of the slide. Further cooling led to the formation once again of a helical modification, and the pitch bands were seen to slowly return.

In order to understand further the mechanism of the inversions in the smectic C* phase of the materials studied, and in particular compound **225**, a study of the tilt angle with respect to temperature was undertaken, in a similar manner to that carried out for compound **130**. For the smectic C* helix to invert, either the tilt and the azimuthal angle associated with the molecules may decrease and pass through zero and then increase again in the opposite sense. If some variation in tilt angle occurs then this implies that the inversion occurs *via* a non-helical smectic A modification. If, however, it is the azimuthal angle alone that changes sign then the inversion occurs *via* a non-helical smectic C phase. Textural studies strongly suggest it is the latter mechanism that is the case and the inversion proceeds *via* changes in the azimuthal angle (as for compound **130**). This was confirmed by measuring the dependence of the optical tilt angle on temperature for compound **225** (see figure 156). The cell spacing for this experiment was 4.3 μm, with a switching voltage of 10 V d.c., which was increased to 20 V d.c. on moving through the phase transition (possibly to S_I*).

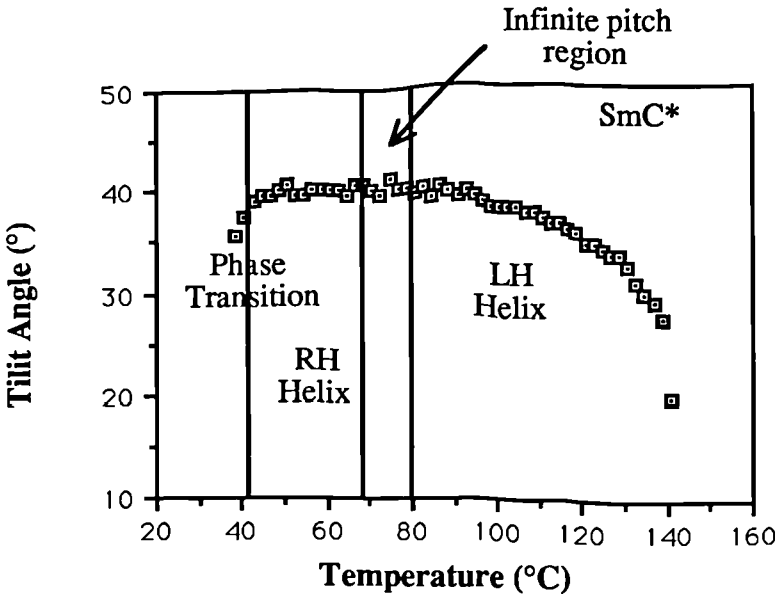


Figure 156. Tilt Angle as a Function of Temperature in the Smectic C* Phase of Compound 225.

It can be seen from figure 156 that the tilt angle rises quite steeply and then begins to level off as the temperature is reduced from the Curie point, but at no time does it return to zero and then increase in a negative sense. This indicates that the tilt angle is not appreciably effected as the helix in the phase inverts, which suggests very strongly that it is only the azimuthal angle that changes. Unfortunately, the azimuthal angle is not easy to measure and so this hypothesis could not be conclusively confirmed. It can also be seen from figure 156 that a phase transition that was not observed by conventional thermal microscopy, was observed in the cell used for this study because the recrystallization process was suppressed. The transition became apparent when the switching became very slow, and an increase in voltage was required. The measured tilt angle was also seen to decrease slightly. As switching did occur, the lower phase was thought to be non-crystalline in nature, possibly being a higher ordered tilted smectic. This, however, was not confirmed, as the transition was rapidly followed by recrystallization. This transition was, however, detected by calorimetric techniques.

It was noted that the spontaneous polarization in compound **225** (1-chloro-2-methylpentyl member of series XXIV) was determined as having a negative direction, and did not invert as the helical twist sense inverted. When the magnitude of the polarization was assessed it was determined to be 82.8 nC cm^{-2}, at 10 °C below the smectic A to smectic C* transition. More will be said about the spontaneous polarization in the smectic C* phase of compound **225** later in this discussion.

The analogous phenylpropiolates (**227-230**) will now be discussed. If the result of placing a triple bond in the core structure has a similar effect to that seen in the diesters discussed in the first part of this chapter, then it may be expected that the chirality would be reduced slightly, whilst the layer disordering and so the nematogenic tendency would increase. It was expected that an increase in the TGB A* temperature range may ensue. The phase behaviour for the four materials in series XXV as well as the accompanying transition temperatures are listed in table 45, and illustrated in figure 157.

No.	Mpt.	I-BPII	I-Ch	BPII-BPI	BPI-Ch	Ch-S_C*	Rec.
227	89.3		158.6			83.2	71.5
228	79.2		155.9			80.6	67.4
229	70.7	143.4		143.4	142.6	79.8	57.2
230	67.0		127.9			83.8	44.0

Table 45. The Transition Temperatures (°C) for the *(S)*-4'-(4-Nonyloxyphenylpropioloyloxy)biphenyl-4-yl 2-chloroalkanoates (227-230).

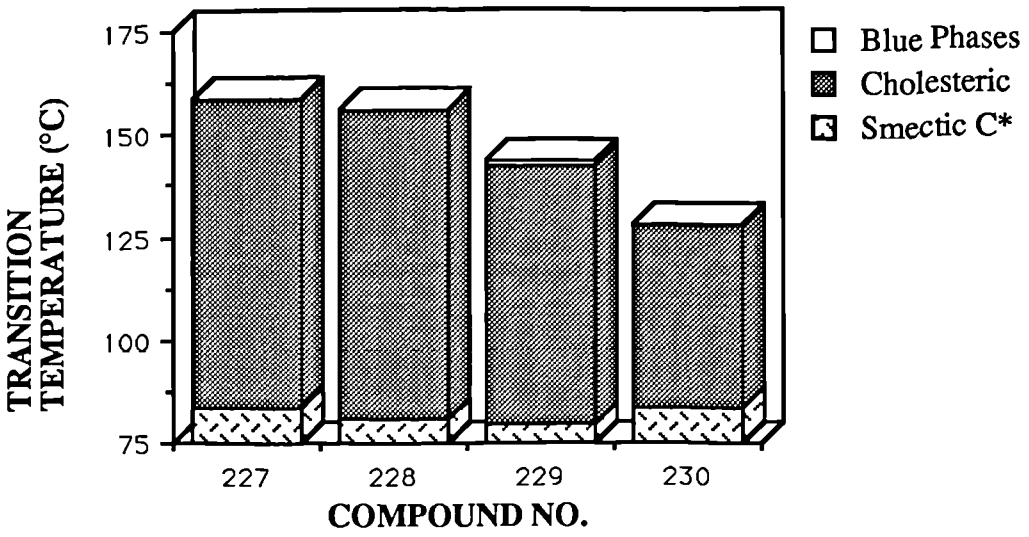


Figure 157. Transition Temperatures Versus Chiral End Group for Materials 227 to 230.

In can be seen from table 45 and figure 157 that compounds **227**, **228** and **230** possess an isotropic to cholesteric to smectic C* phase sequence. Compound **229** (with a 1-chloro-2-methylbutyl chiral end group) has the same phase sequence, but in addition displays blue phases at the clearing point. The clearing points are found to fall as the series is ascended, accompanied by a corresponding decrease in the cholesteric phase temperature range. The transition to the smectic C* phase occurs within a few degrees of each other for every compound. It is obvious that the nematogenic tendency is very great in these materials, and that any smectogenicity is directed towards tilted phases.

One interesting point associated with the cholesteric phase in compound **229** (the 1-chloro-2-methylpentyl member of the series) is that on cooling through its cholesteric temperature range the twist sense is seen to invert *via* a non-helical nematic phase in a similar manner to that seen for compound **130**. On cooling from the isotropic liquid a cholesteric phase forms which was determined by polarimetry to have a right-handed helix. On further cooling to approximately 107°C the colour associated with the

cholesteric phase began to disappear eventually leaving the homeotropic texture of a nematic phase. At approximately 91 °C the cholesteric texture returned, the helical twist sense being determined as left-handed. After further cooling a normal transition to the smectic C* phase occurred.

Calorimetric studies were consistent with the results obtained by thermal optical microscopy for all of the materials in this series. The helix inversion in compound **229**, did, however, not produce a measurable enthalpy. A result that is consistent with earlier observations on other materials.

When the properties of the smectic C* phase in these materials were examined the following results were obtained (see table 46).

No.	A.S.C.	Parity	Rot. of PPL	Helix Dir.	Ind. Effect	Ps Dir.
227	*S*	o	*d*	LH	-ve	
228	*S*	o	*d*	LH	-ve	
229	*S,S*	o, e	*d*	LH	-ve, +ve	-
230	*S*	o	*d*	LH	-ve	-

Table 46. Chiral Properties Associated with the Smectic C* Phase in Compounds 227 to 230.

It can be seen from table 46 that in terms of helical twist sense these materials can all be classified as ***S*, o, *d*, LH,** which is in agreement with the Goodby/Leslie hypothesis[39]. Compound **229** can also be classified as being ***S*, e, *d*, LH** when the second chiral centre is taken into account and this is also in agreement with the hypothesis. The polarization direction was found to be negative, with a magnitude of 112.4 nC cm^{-2}, at 10 °C below the cholesteric to smectic C* transition.

When compound **230** (the propiolate based material with a 1-chloro-3-methylbutyl chiral end group) and the analogous benzoate (**226**) are compared the following results are found (see figure 158).

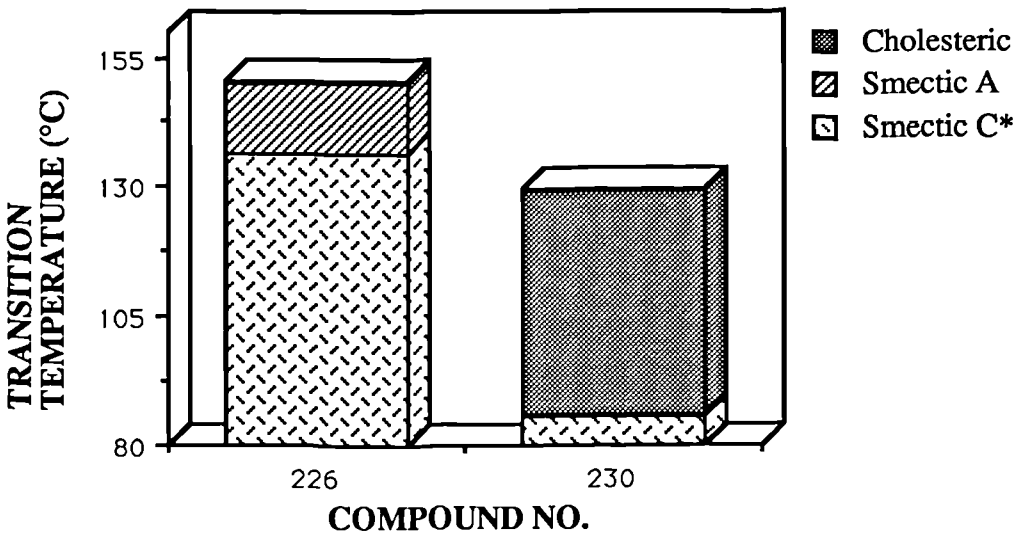


Figure 158. A Comparison of the Phase Behaviour Associated with Compounds 226 and 230 (the Members of Series XXIV and XXV with a 1-Chloro-3-methylbutyl Chiral End Group).

It can be seen from figure 158 that the propiolate has a lower clearing point, whereas the temperature range of the cholesteric phase is increased substantially. Compound **226** is also found to exhibit a smectic A phase (that is not present in the other members of the series), and a transitory TGB A* phase, which suggests that the tendency to form orthogonal smectic phases is greater in the benzoate. It should be noted that blue phases could not be detected in either **226** or **230**, which suggests relatively low chiralities for both systems.

When **230** is compared with the analogous material that does not have a reversed ester linkage, i.e., compound **164** from series X the following points can be made (see figure 159).

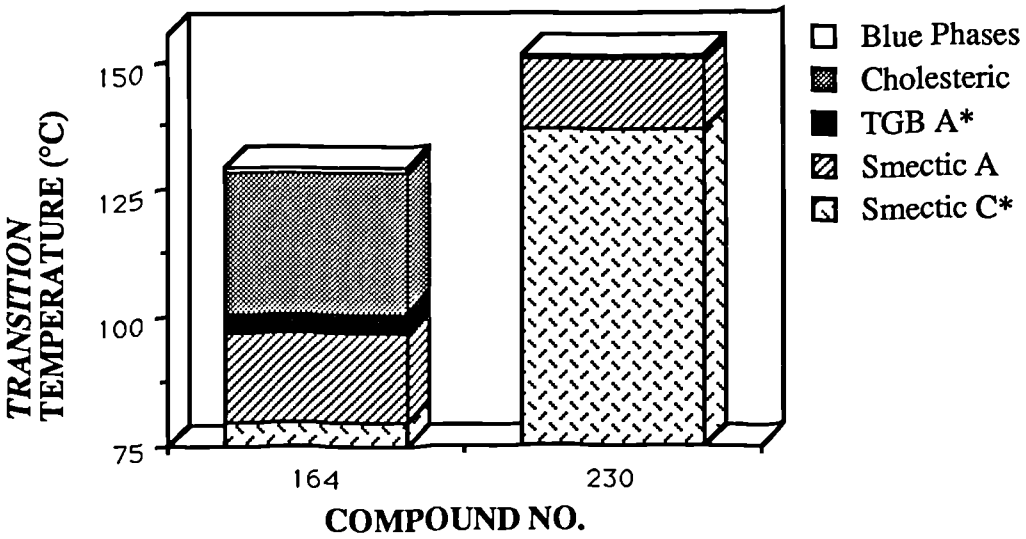
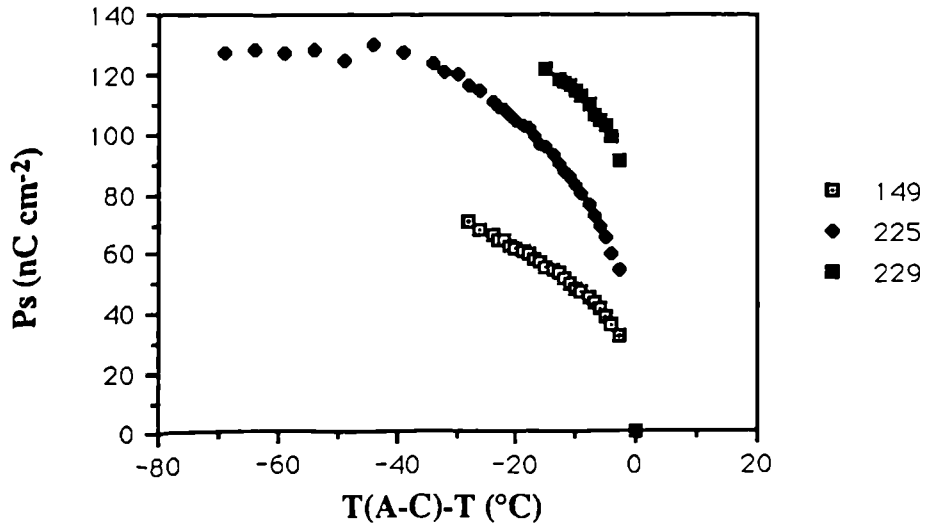


Figure 159. A Comparison of the Phase Behaviour Associated with Compounds 164 and 230 (the analogous members of series X and XXV).

From figure 159 it can be seen that the clearing point is lower in the material in which both ester groups point in the same direction (**164**) compared to where they oppose one another. Secondly, although both materials possess a cholesteric phase, only compound **164** exhibits blue phases. The TGB A* phase temperature range in compound **164** is much longer, whereas the range in compound **230** is very short. The thermal stability of the smectic C* phase in compound **230**, however, is greatly enhanced, whereas the temperature range of the A phase is approximately the same in each material.

In order to assess how the presence of a triple bond in the core structure, and the reversal of an ester linkage effects the spontaneous polarization in the smectic C* phase, a comparison was made between three analogous compounds **149**, **225**, and **229**. The results obtained along with the structures of these materials can be seen in figure 160.



149 $C_9H_{19}O-C_6H_4-CO_2-C_6H_4-C_6H_4-CO_2CH_2C^*H(Cl)C^*H(CH_3)CH_2CH_3$

225 $C_9H_{19}O-C_6H_4-CO_2-C_6H_4-C_6H_4-O_2CC^*H(Cl)C^*H(CH_3)CH_2CH_3$

229 $C_9H_{19}O-C_6H_4-C\equiv CCO_2-C_6H_4-C_6H_4-O_2CC^*H(Cl)C^*H(CH_3)CH_2CH_3$

Figure 160. The Spontaneous Polarization as a Function of Temperature in Compounds 149, 225, 229.

It can be seen from figure 160 that the material with the lowest spontaneous polarization (taken at 10 °C below the A-C* transition) is compound **149**. On reversal of the ester linkage the chiral centre moves from the 2- to the 1-position, and the polarization is seen to increase considerably. This may be a consequence of two factors, firstly an increase in the rotational hindrance of the chiral centre, and secondly a coupling between the carbonyl moiety of the ester linkage and the chlorine atom at the chiral centre may be enhanced. When the benzoate (**225**) is compared with the analogous propiolate (**229**), it is found that the value of the spontaneous polarization increases more sharply for compound **229**, giving a higher value. Unfortunately, recrystallization occurred quite

quickly in compound **229** and so the saturation value for the polarization could not be achieved and a full comparison of the temperature/spontaneous polarization profile of the two compounds could not be made. It is interesting to note that the polarization is highest in the reverse ester (**225**), suggesting a high degree of chirality. This material, however, did not exhibit blue phases which suggests a low degree of chirality. If these statements hold true it must be assumed that the degree of chirality that a molecule imparts to a phase is dependent on the structure of the phase.

8.18 Non-Chiral Dimeric Esters (Series XXVI).

The materials in this series (**248-251**) were synthesized in an attempt to prepare compounds that would show an edge dislocation phase at the transition from nematic to smectic A, in a non-chiral system. This type of dislocated modification was predicted to occur by de Gennes[95], in a similar way to how the chiral modification was stabilised by the incorporation of screw dislocations into the smectic A phase. In order to produce this type of macrostructure, molecules that have a bent shape were prepared in the hope of inducing multiple edge dislocations into the phase. It was hoped that layers of bent molecules would contain discontinuities as depicted in figure 161, where the bent molecules radiate to give a curved leading edge at the dislocation point.

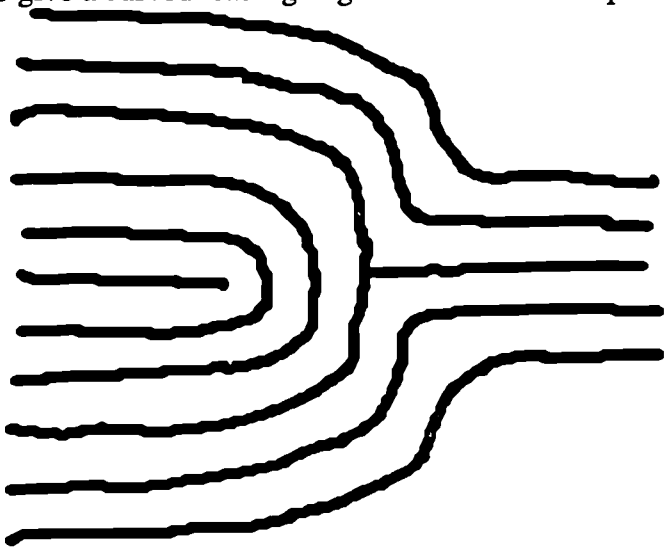
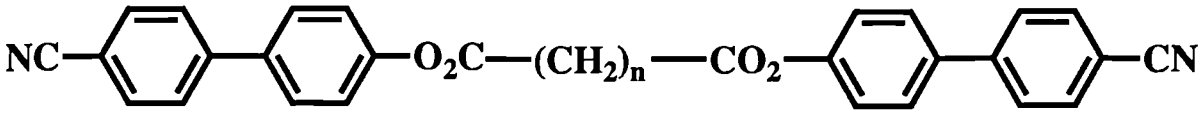


Figure 161. An Edge Dislocation (+ π) may be Produced by Bent Molecules.

The general structure of the first series of materials (XXVI) that were prepared of this type prepared is shown in figure 162.



n = 5 to 10

Figure 162. The General Structure of the Achiral Dimers.

The degree of 'bentness' associated with the materials in this series is related to a number of things, firstly whether the chain length (n) is an odd or an even number, secondly whether the alkyl chain adopts predominantly an all *trans* configuration, and thirdly the types of conformational species that are found to be most stable. An example of this is given in figure 163, where the two materials with n = to 5 (**248**), and 6 (**249**) are shown with an all *trans* configuration in which the two esters linking groups have carbonyl functions that point in opposite directions.

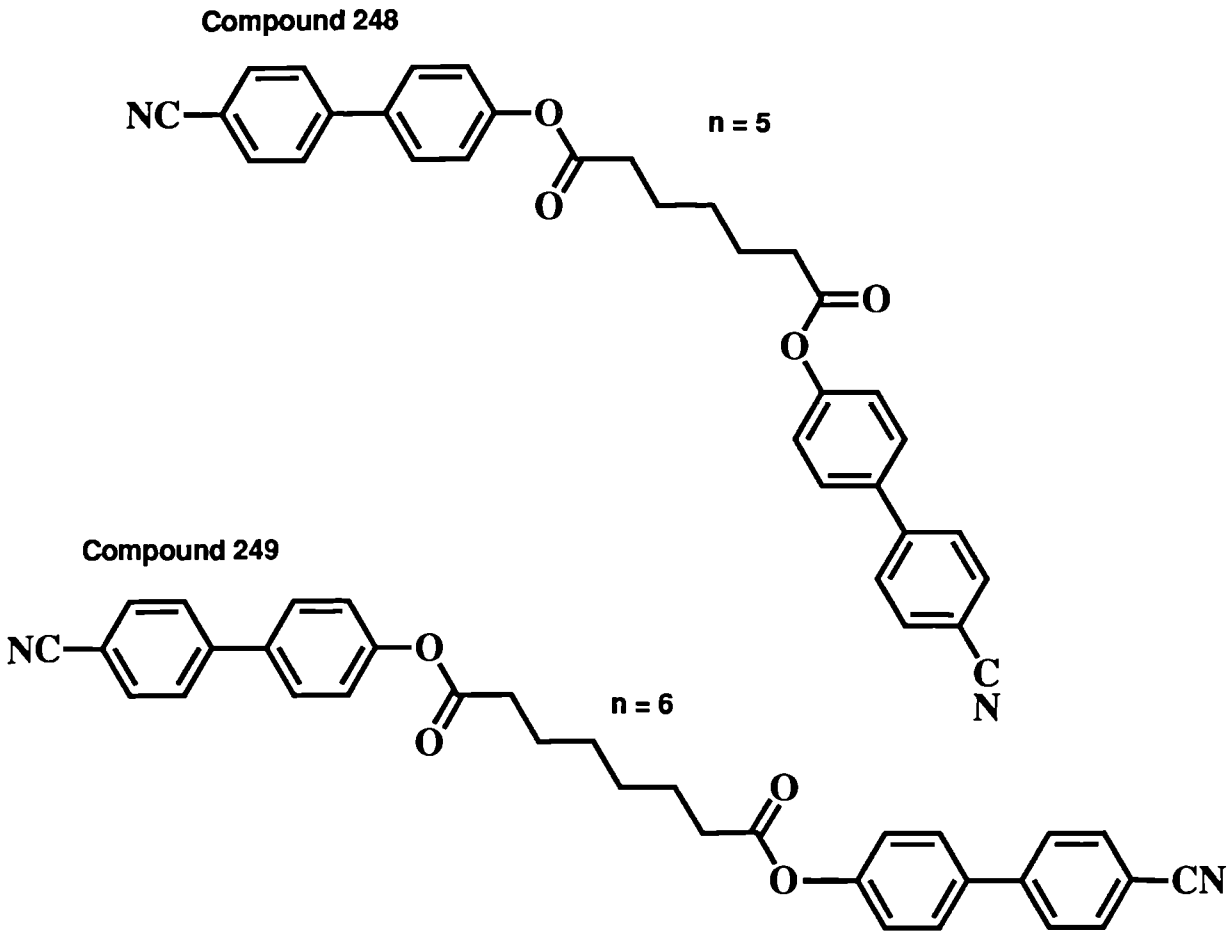


Figure 163. The All *Trans* Configuration of Two Dimeric Materials (n = 5 and 6).

In figure 163 it can be clearly seen that if the molecules adopt these configurations, then the material with an odd number of carbon atoms in its central alkyl chain would adopt a greater degree of 'bentness', and so may be more likely to exhibit frustrated phases. It must be remembered, however, that in order to exhibit the desired behaviour, the materials synthesised would have to show the correct phase sequence, that is isotropic liquid to nematic to smectic A, with possibly an underlying transition that may increase the fluctuations at the nematic to smectic A transition.

The results acquired for the series of dimers are listed in table 47, and illustrated in figure 164.

No.	n	Mpt.	I-N	Rec.
248	5	198.5	196.0	158.7
249	6	198.6	229.1	177.6
250	7	143.9	188.4	135.7
251	8	152.8	205.1	138.4
252	9	137.0	177.2	125.0
253	10	147.0	186.5	120.2

Table 47. The Transition Temperatures (°C) for the Non-Chiral Dimers (248-253).

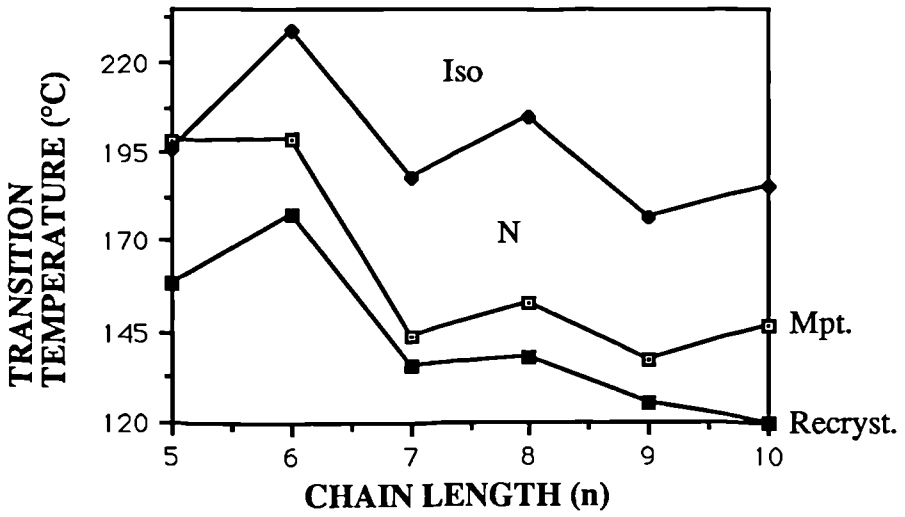


Figure 164. The Phase Behaviour of Compounds 248 to 253.

From table 47 and figure 164 it can be seen that the materials in this series of compounds exhibit an isotropic to nematic phase sequence, with no underlying smectic A phase. The desired transition sequence was therefore not obtained in these materials, and so the possibility of frustrated phases occurring was negated. The materials, because of the fact that they possessed four phenyl rings in their molecular structures, and terminal cyano groups, were quite high melting. The melting points were found to fall with increasing alkyl chain length. The clearing points were found to be dependent on a pronounced odd/even effect, with the transition from the isotropic liquid to the nematic phase

occurring at a much higher temperature in the members of the series with an alkyl chain that contained an even number of carbon atoms. This odd/even effect which is not quite as large at longer chain lengths was also reflected to some extent in the melting and recrystallization temperatures. The fact that the odd members of the series have lower clearing points may indicate that they do indeed possess a non-linear structure, which reduces the ability of the molecules to pack and therefore produce an ordered phase.

In order to utilise one of the previously prepared propiolic acids (**70**), that had been so successful in producing materials with TGB phases, and to reduce the melting point in the dimeric materials, one more non-chiral material was prepared (**267**). The structure of this dimer is illustrated in figure 165.

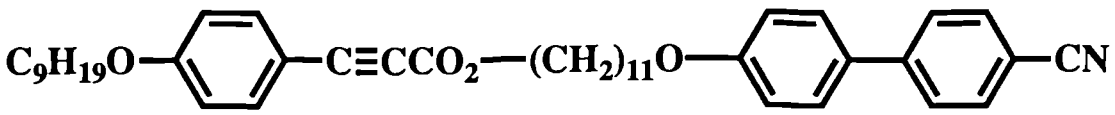


Figure 165. The Structure of Compound 267.

With the reduction in the number of phenyl rings from four to three, and only one nitrile in the molecule it was expected that this material would show a much reduced melting point and recrystallization temperature, and possibly the desired nematic to smectic A phase sequence. The transition temperatures obtained for this material (**267**) are illustrated in table 48.

No.	Mpt.	Rec.	I-N @
267	91.6	81.9	66.7

@ phase transition determined on fast cooling (10 °C min^{-1}), achieved using cardice.

Table 48. The Transition Temperatures (°C) of the Achiral Dimer 267.

It can be seen from the results shown in table 48 that the melting and recrystallization temperatures for compound **267** are much reduced compared to the previous series of

materials. Unfortunately, the liquid-crystalline properties of this material are also substantially reduced, with no phase behaviour being observed unless fast cooling was employed. On fast cooling a nematic phase was observed, but once again there was no suggestion of the presence of the desired smectic A phase.

8.19 Chiral Dimeric Esters (Series XXVII).

Although the desired phase sequence was not found in the non-chiral dimers (series XXVI), it was decided to try and produce dimers that may be bent and also optically active in order to possibly induce frustration in two ways, leading to a phase that would contain both bend and twist dislocations. Two materials were prepared in this series (XXVII) in order to see if this was possible. The first material (**261**) was similar to the series of non-chiral dimers discussed earlier (**248-253**), except that it contained a chiral branching point in the alkyl chain (see figure 166). The second material (**264**) was based on a commercially available alcohol (**263**) that possessed two chiral centres. This alcohol was then reacted with the heptyloxybiphenylcarboxylic acid **55** to produce the final product which was a di-ester (see figure 167).

Compound 261

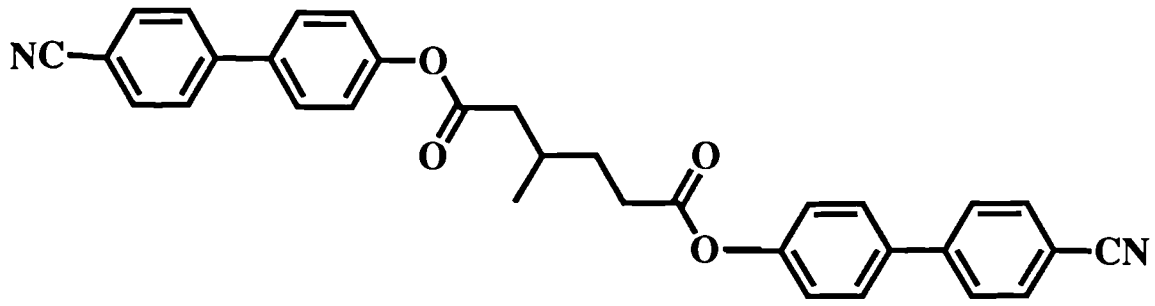


Figure 166. The Structure of the Chiral Dimeric Material 261.

Compound 264

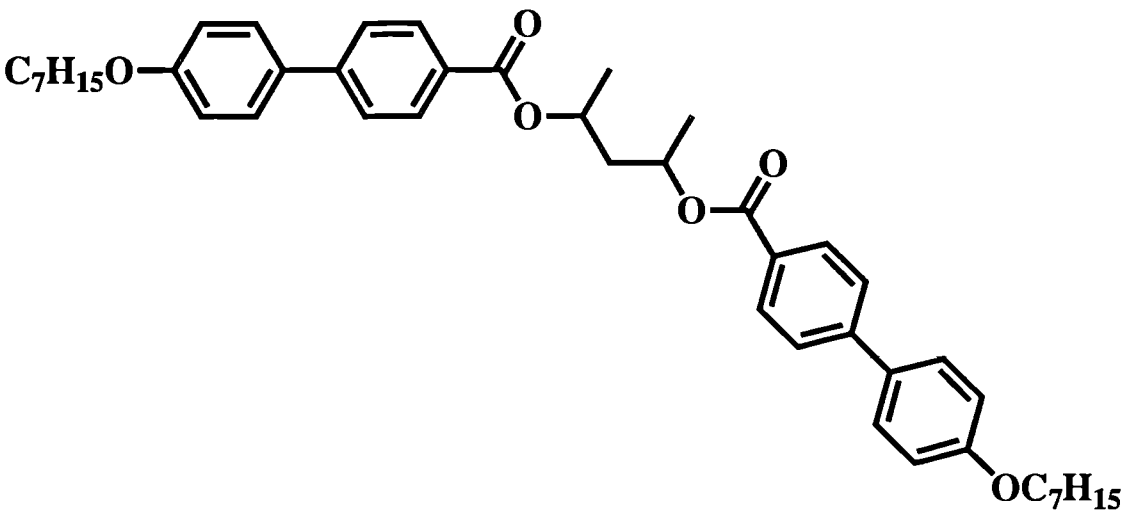


Figure 167. The Structure of the Chiral Dimeric Material 263.

The transition temperatures for these two materials are listed in table 49.

No.	Mpt.	I-Ch	I-B*	B*-E*	Rec.
261	167.3	212.7			143.0
264	113.1		116.9	111.4	108.0

Table 49. The Phase Behaviour of Compounds 261 and 264.

From table 49 it is clear that compound **261** exhibits phase behaviour that is very similar to that obtained for the related non-chiral analogues. For instance the chiral centre induces optical activity into the mesophase (cholesteric rather than nematic), but does not radically alter the phase behaviour. The elusive A phase is once again not present in this material. The second material (**264**) was crystalline in nature, exhibiting two soft-crystal modifications over a very narrow temperature range. It was obvious from the results that this type of structure did not give rise to the desired level of liquid-crystallinity. Having failed to produce materials that gave a bend or a twist/bend dislocation phase, this area of the project was halted due to time constraints.

Calorimetric studies gave results that were consistent with microscopic observations for all of the dimeric materials discussed. The transitions that occurred for compound **264**, however, were not well resolved as the temperature ranges of the phases were short.

8.20 The Characteristic Textures Exhibited by The TGB A* Phase.

A great deal of the work carried out in this thesis has been devoted to the preparation and characterisation of materials that exhibit a TGB A* phase. As this modification is still relatively novel the type of texture it exhibits in the polarizing microscope is not widely known. The following section is therefore devoted to giving an insight of what may be expected when materials that exhibit a TGB A* phase are examined by polarizing optical microscopy.

On heating from a homeotropic smectic A phase the TGB A* phase appears as filaments that eventually coalesce to give the fingerprint texture of a cholesteric phase. This is illustrated in plates 23 and 24, for the benzoate **158** (from series IX) and the propiolate **164** (from series X) respectively. On cooling the fingerprint texture breaks up into filaments which gradually reduce in size to leave the homeotropic smectic A texture. If the sample is cooled from a cholesteric phase that has been momentarily stressed to produce a Grandjean texture then on cooling into the TGB A* phase the plane texture takes on a platelet like appearance (see plate 25), further cooling leads to the formation of what appear to be pitch bands (see plate 26).

The microscopic structure of the filaments especially with regard to the TGB helix direction has been the subject of some debate, and still remains unresolved.

Plate 23. The Filament Texture Exhibited by *(S)*-2-Chloro-4-methylpentyl 4'-(4-nonyloxybenzoyloxy)-4-biphenylcarboxylate (158) on Heating from the Smectic A Phase.

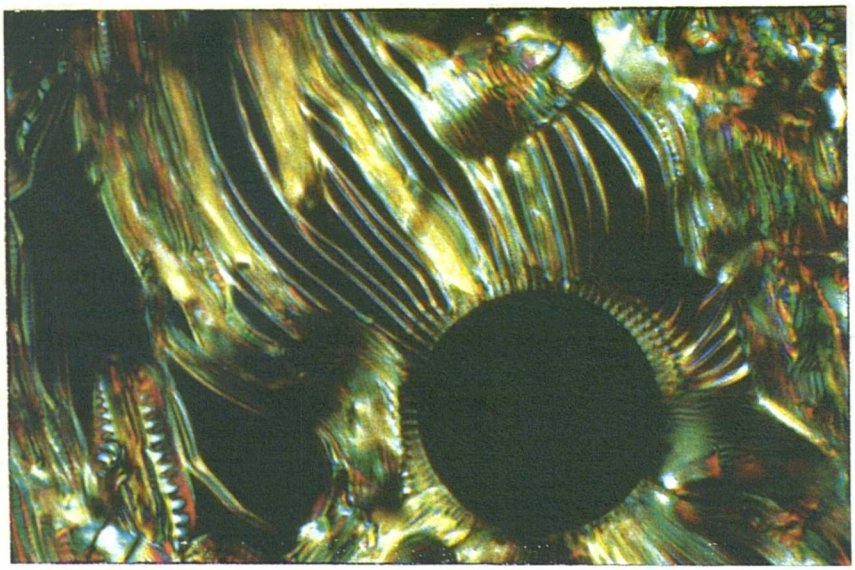


Plate 24. The Filament Texture Exhibited by *(S)*-2-Chloro-4-methylpentyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (164) on Heating from the Smectic A Phase.

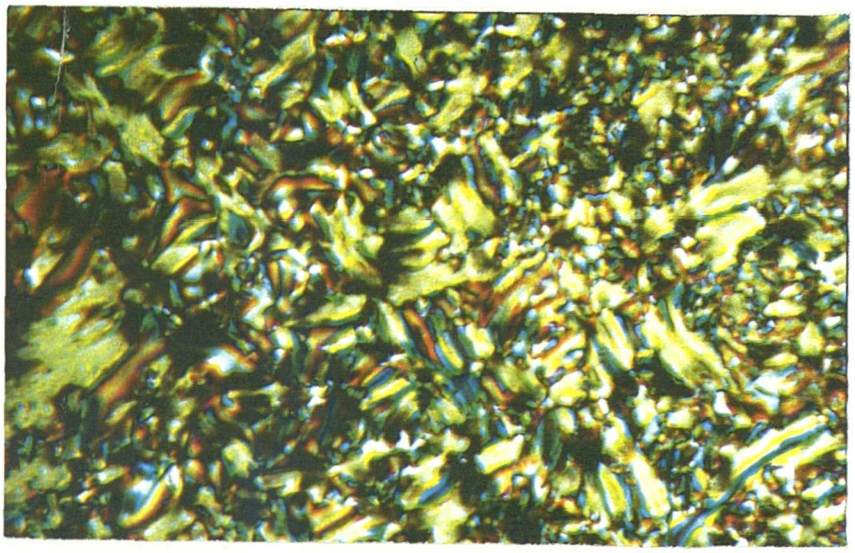


Plate 25. The Platelet-like Texture Exhibited by *(S)*-2-Chloro-4-methylpentyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (164) on Cooling from the Cholesteric Phase

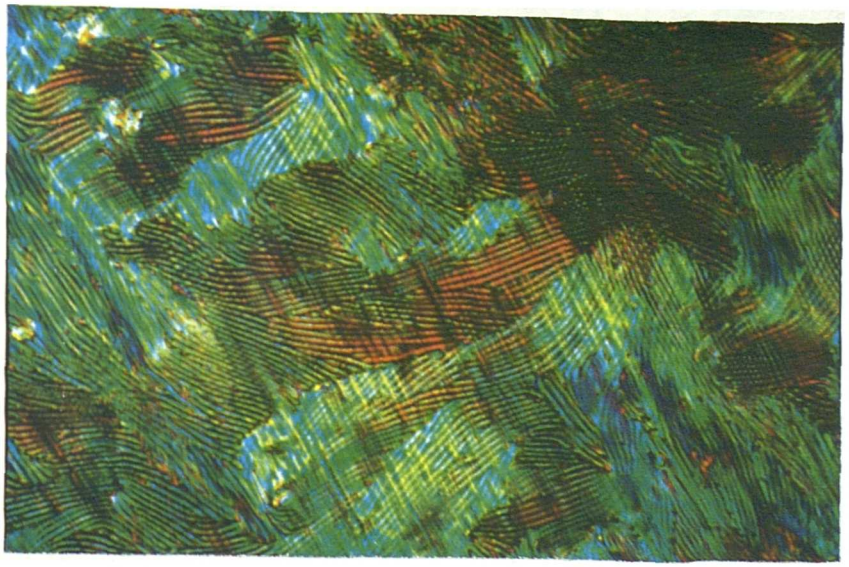


Plate 26. The Pitch Bands that are Exhibited by *(S)*-2-Chloro-4-methylpentyl 4'-(4-nonyloxyphenylpropioloyloxy)-4-biphenylcarboxylate (164) on Cooling from the Platelet-like Texture.

9. CONCLUDING REMARKS.

A large number of materials were prepared and their physical properties evaluated. In order to systematically draw conclusions from the results obtained, this chapter will be divided into a number of sections that are listed below.

a. materials based on the 2-chloroalkyl chiral moiety (branched chain)

   i. benzoate esters (series III, V, VII, IX, XVI, XVII,)

   ii. phenylpropiolate esters (series IV, VI, VIII, X, XVI, XVII)

b. materials based on the 2-chloroalkyl chiral moiety (normal chain)

   i. benzoate esters (series I, XI, XII, XIII, XIV, XV)

   ii. phenylpropiolate esters (series II, XI, XII, XIII, XIV, XV, XVIII)

c. materials based on a 2-halogeno-4-methylpentyl chiral moiety (series IX, X, XVI, XVII)

d. materials with a cyclohexane or napthalene core sub-unit (series XIX, XX, XXI, XXII, XXIII)

e. materials in which one ester group is reversed (series XXIV, XXV)

f. dimeric materials (series XXVI, XXVII)

Each individual section will now be discussed separately.

a (i). The general structure of the benzoate esters described in this section is shown in figure 168.

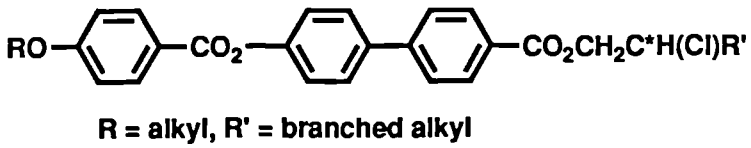


Figure 168. The General Structure of the Benzoates with a Branched Chiral Alkyl Chain.

The materials in this section had an isotropic liquid to blue phase to cholesteric to TGB A* to smectic A to smectic C*, or an isotropic to smectic A to smectic C* phase sequence depending on the length of alkoxy chain associated with the molecule. The alkoxy chain length at which the nematogenic tendency was seen to disappear was dependent on the chiral moiety present at the opposite end of the molecule. As the total length of the chiral group was increased (for example butyl to pentyl) the TGB A* and blue phase temperature ranges increased, except for compound **154** (that had two chiral centres with an *(S,R)* configuration in its structure) which did not possess a TGB A* phase. Compound **142** (the octadecyloxy member of series V) was shown to possess a new blue phase modification BPS[150]. The series of materials with the longest TGB A* temperature range was based on the 2-chloro-4-methylpentyl chiral moiety, suggesting that the effective chirality for these materials was the highest. This was supported by tilt angle and pitch length studies carried out for the smectic C* phases of compounds **143** and **158** (the nonyloxy members of series V and IX). Calorimetric studies on these materials revealed that there are measurable enthalpies associated with the transitions from cholesteric to TGB A* and TGB A* to smectic A. This indicates that the TGB A* phase is a thermodynamically stable state of matter.

The racemic version of compound **158** (**169**) was found to possess a simple isotropic to nematic to smectic A to smectic C phase sequence, with no TGB A* phase being observed in the phase sequence. The clearing point and nematic to smectic A transitions occurred at a higher temperature in this material (the racemate) than in the optically active variant (**158**), a result which is in keeping with theoretical predictions[95]. This elevation in transition temperatures for the racemate did not extend to the smectic A to smectic C/C* transition. A phase diagram produced by making binary mixtures of compounds **158** and **164** indicated that the TGB A* and blue phases were stable in mixtures of up to 75 % racemate. This result indicates that optical purity is an important

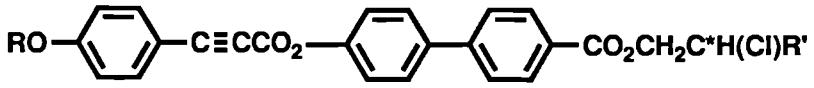
factor in determining if a TGB A* phase will be formed. Mixture studies involving compound **158** and a standard material (**15P1M7**) that exhibits a TGB A* phase were also carried out, but complete miscibility of the TGB A* phase across the phase diagram was not obtained.

When the two materials with sequential chiral centres in their structures were evaluated (**143** and **154**) it was found that the material with an *(S,S)* configuration of the chiral centres (**143**) had larger blue phase and TGB A* temperature ranges (**154** did not possess a TGB A* phase). This suggests in this instance that the *(S,S)* configuration imparts the greatest degree of chirality to the system.

When the properties of the smectic C* phases in these materials were evaluated, unusual behaviour was noted for a number of compounds. The helical twist sense in the series of materials based on the 2-chloro-3-methylbutyl chiral moiety (**128-135**) appeared to alternate with alkoxy chain length, i.e., there appeared to be an odd/even effect with regard to the helix direction in the smectic C* phase. In the nonyloxy member of this series (**130**) the smectic C* helix appeared to invert with respect to temperature. This inversion took place *via* a non-helical smectic C phase, with no related inversion in the direction of the spontaneous polarization. This type of inversion may have occurred in other members of series III, but at a temperature too close to the smectic A to smectic C* transition to detect. Inversions of this nature were also present in a number of materials that were based on the 2-chloro-4-methylpentyl chiral moiety (**156-163**), and were explained in terms of a temperature dependent interconversion between different conformational species that have different twisting powers and directions. The hypothesis suggests that liquid crystal systems are inhomogeneous in terms of conformer distribution. The materials that possessed two chiral centres exhibited normal behaviour in the smectic C* phase, the compounds with an *(S,S)* sequence (**141-148**) being

classified as ***S* e *d*LH** (for the chiral centre closest to the core), or ***S* o *d*LH** (chiral centre furthest from the core), and the material (**154**) with an *(S,R)* configuration being classified as ***S* e *L*LH** (for the chiral centre closest to the core), or ***R* o *L*RH** (for the chiral centre furthest from the core). The values of the spontaneous polarization associated with the materials in this section are thought to be only moderate, for example compound **146** (the dodecyloxy member of series VII) was found to have a value of 20 nC cm^{-2} at 10 °C below the A to C* transition.

a (ii). The general structure of the materials in this section is illustrated in figure 169.



R = alkyl, R' = branched alkyl

Figure 169. The General Structure of the Phenylpropiolates with a Branched Chiral Alkyl Chain.

The propiolates exhibited similar phase sequences to the analogous benzoates. The nematogenic tendency was, however, found to be greater in these materials. The transition temperatures of the propiolates were greatly reduced relative to the benzoates. The blue phase temperature ranges for the propiolates were generally shorter than in the previous benzoates indicating a reduction in chirality on insertion of the triple bond. This was somewhat expected due to the greater individual freedom of rotation of the aromatic units within the core structure, and the dilution effect caused by an addition of two carbon atoms *via* the acetylene linkage. The TGB A* temperature range was, however, much longer in the propiolates relative to the benzoates. This is possibly a consequence of one or both of the two following effects. Firstly, a weakening of the layer ordering, or secondly as a result of perturbations at the cholesteric to smectic A transition caused by a nearby chiral phase (e.g., a smectic C* phase). The smectic A temperature range in the propiolates was somewhat shorter than in the analogous benzoate esters, effectively

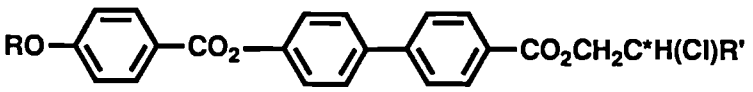
bringing the cholesteric to smectic A transition closer to the smectic A to smectic C* transition. Greater fluctuations at the cholesteric to smectic A transition may therefore be generated. The results of switching studies did, however, suggest that the layer ordering was much weaker in the propiolates.

The TGB A* temperature range was found to be greatest for materials that possessed a 2-chloro-4-methylpentyl chiral moiety (**164-168**). The temperature range of this phase decreasing with increasing alkoxy chain length. For the materials (**149** and **155**) with two chiral centres in the terminal chain it was surprisingly found that the material with an *(S,R)* sequence of chiral centres had the largest TGB A* temperature range (c.f., the benzoates). Miscibility studies for the nonyloxy member of series X (**164**) and a standard material that exhibited a TGB A* phase (**14P1M7**) did not show complete miscibility across the phase diagram. This immiscibility indicates that another chiral phase must be in close proximity to the cholesteric/isotropic to smectic A transition for a TGB A* phase to be present.

The helix direction in the materials with an 2-chloro-3-methylbutyl chiral moiety was found to be consistent throughout the series, and was classified as ***S* e ∠ RH**. The materials that have a 2-chloro-3-methylpentyl chiral group (**149** to **153** and **155**) were classified as ***S* e ∠LH**, or ***S* o ∠LH** for the *(S,S)* sequence of chiral centres, and ***S* e ∠ RH**, or ***R* o ∠ RH** for the *(S,R)* configuration. The materials with the 2-chloro-4-methylpentyl chiral end group, showed abnormal behaviour in the smectic C* phase with the helical twist sense inverting for a number of examples. The inversion of twist sense was proved by contact studies with a material of known helical twist sense (**178**). The polarization direction in all of the materials in which it was determined (at least one material from every series) was found to be positive, except in the case of compound **155** that has an *(S,R)* configuration of chiral centres, for which it was found to be negative. The value of

the spontaneous polarization (measured for the nonyloxy members of each series) was found to be highest in compound **155** (based on an *S,R* 2-chloro-3-methylpentyl chiral group), and lowest in compound **164** (based on a 2-chloro-4-methylpentyl chiral group), with the other two materials studied (**136** and **149**) having an almost identical spontaneous polarization/temperature profile. This result is quite surprising as the compound with the lowest polarization, and therefore possibly the least degree of molecular chirality, possessed the largest TGB A* temperature range. The results do indicate, however, that for a molecule with two sequential chiral centres, the absolute spatial configuration of the second one is very important in terms of the physical properties of the system. And that this is the case even when the dipole associated with the second optically active is relatively small compared to that associated with the first.

b (i). The general structure of the materials discussed in this section is illustrated in figure 170.



R = alkyl, R' = normal alkyl

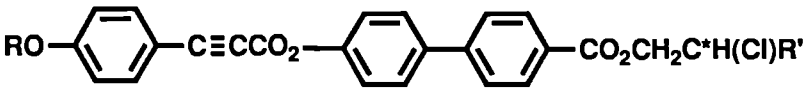
Figure 170. The General Structure of the Benzoates with a Normal Chiral Alkyl Chain.

The materials described in this section possessed a phase sequence that was dependent to a large extent on both the length of alkoxy chain associated with the molecule, and the length of alkyl chain attached to the peripheral side of the chiral centre. The series of materials in which the alkyl chain attached to the chiral centre was a methyl group (**115-122**) exhibited an isotropic liquid to cholesteric to smectic A to smectic C* phase sequence. The cholesteric phase disappeared when the alkoxy chain reached nine carbon atoms in length, and the smectic C* phases were all monotropic in nature. For the 2-chloropentyl and 2-chlorohexyl (**170** and **172**) systems an isotropic liquid to blue phase to

cholesteric to TGB A* to smectic A to smectic C* phase sequence was observed. The blue phase, cholesteric and TGB A* temperature ranges were all found to be less in these materials in comparison to the analogous branched chain materials (**130, 143, 154, 158**). As the alkyl chain, attached to the peripheral side of the chiral centre, was extended in length, the nematogenic tendency decreased. In some materials a direct transition from a blue phase to the smectic A was observed, whereas in other compounds that had longer alkoxy chains associated with their structures, a direct isotropic liquid to smectic A transition was found (e.g., compounds **179** and **182** respectively from the series of materials with a chiral decyl chain).

When the properties of the smectic C* phases were evaluated for these materials, all of the compounds were classified as ***S* e *d* LH Ps +**, except those form the first series (I) (**115-122**) which were classified as ***S* e *L* RH**, (the polarization direction was not determined for the materials in series I). The materials from the first series are the only ones therefore that are in agreement with the Goodby/Leslie hypothesis[39]. Although the actual pitch length was not measured for any of the materials in this section, microscopic observations of free standing films suggested that it was quite long in comparison to the materials that had branching associated with their chiral aliphatic chains.

b (ii). The materials discussed in this section had a general structure that is illustrated in figure 171.



R = alkyl, R' = normal alkyl

Figure 171. The General Structure of the Phenylpropiolates with a Normal Chiral Alkyl Chain.

The materials discussed in this section exhibited an isotropic liquid to blue phase to cholesteric to TGB A* to smectic A to smectic C* phase sequence, except for the material that had the shortest peripheral alkyl chain attached to the chiral centre (**130**). This material exhibited an isotropic liquid to cholesteric to smectic A phase sequence. The clearing points fell with increasing alkyl chain length, as did the cholesteric phase temperature range, except for compound **130** where the cholesteric temperature range was shorter than in compounds **171** and **173** (the materials based on a 2-chloropentyl and 2-chlorohexyl chiral moiety). The transition temperatures of the propiolates were reduced in comparison to the benzoates, but the TGB A* temperature ranges were greater in the propiolates. This behaviour is consistent with that observed for the branched alkyl systems. The TGB A* temperature ranges were, however, reduced in comparison to the materials that possessed branching positions in their chiral moiety.

The cholesteric phase in compound **130** (the propiolate based on a 2-chloropropyl chiral group) exhibited unusual behaviour in that the helix was found to invert with respect to temperature. This result was confirmed through contact studies with a material of known twist sense, and pitch measurements. A model involving conformational interchanges is suggested to explain this.

When the properties of the smectic C* phase were investigated (in the five materials that exhibited a smectic C* phase), it was found that the microscopic and macroscopic properties could be related in the following way for all of the materials ***S*** **e** ***d*** **LH**. The direction of the spontaneous polarization was classified as being positive for all of the compounds studied. Investigations into the magnitude of the spontaneous polarization with respect to temperature revealed that the highest values were obtained when the chiral alkyl chain was six carbons in total length (**173**). Longer chain lengths appeared to dilute the chirality of the system (thereby reducing the value of the spontaneous polarization),

whereas shorter chain lengths allowed for a greater freedom of rotation of the optically active centre thereby producing a smearing out effect of the lateral dipole leading to a lower spontaneous polarization value.

The electroclinic response in these materials was evaluated and found to be quite large considering the moderate values for the spontaneous polarization that were obtained. It is likely that this may be due to the ease of layer deformation in the smectic A phase, which is characterized by striped shaped domains that appear on the application of an electric field.

c. The general structures of the materials discussed in this section are illustrated in figure 172.

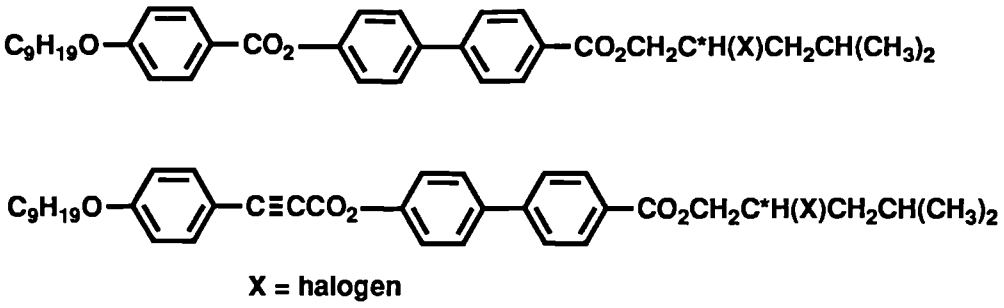


Figure 172. The General Structures of Materials With Various Halogens Present at the Chiral Centre.

The materials discussed in this section possessed various halogeno substituents at the chiral centre. The first family had a bromine atom positioned at the chiral centre (**189-193**), and exhibited an isotropic to cholesteric to smectic A to smectic C* phase sequence. The transition temperatures were lower for the propiolate (**193**) relative to its benzoate analogue (**191**). The helix direction in the smectic C* phase of the bromo compounds was classified as left-handed, and the direction of the spontaneous polarization was shown to be positive. The value of the spontaneous polarization, however, was found to

be too low to measure for compound **193**, which suggests that the material has a reduced chirality (in comparison to the analogous chloride **158**) possibly because of synthetic problems lowering the optical purity.

The chlorine based materials were discussed earlier (section a). It is worth noting, however, that they were found to have the longest TGB A* temperature range out of all the materials described in this section. Conversely, the value of the spontaneous polarization for the smectic C* phase was lower in the chloro substituted compound (**164**), than the value found in the analogous fluoro substituted material (**196**). This suggests that the size of the dipole associated with the chiral centre plays an important role in determining the value of the spontaneous polarization, but not necessarily the TGB A* temperature range.

The fluorine containing materials (**194** and **195**) possessed an isotropic liquid to blue phase to cholesteric to TGB A* to smectic A to smectic C* phase sequence. The blue phase temperature range was slightly shorter than that found in the chloro analogues (**158** and **164**). Increasing the size of the halogen atom located at the chiral centre, i.e., fluorine to chlorine to bromine, caused a reduction in the clearing point, and the smectic A to smectic C* transition temperature. The same process increasing the smectic A temperature range.

d. Templates that indicate the type of structures discussed in this section are illustrated in figure 173.

The materials in this section were prepared in order to ascertain what the effects of altering the core structures of the molecules would have on certain physical properties. In particular the effects associated with the temperature range of the TGB A* phase were of

great interest. Compound **198** (based on a cyclohexyl core sub-unit) possessed a blue phase to smectic A to smectic B phase sequence, indicating that the substitution of an alicyclic for an aromatic ring in this case leads to a greater incidence of orthogonal smectics.

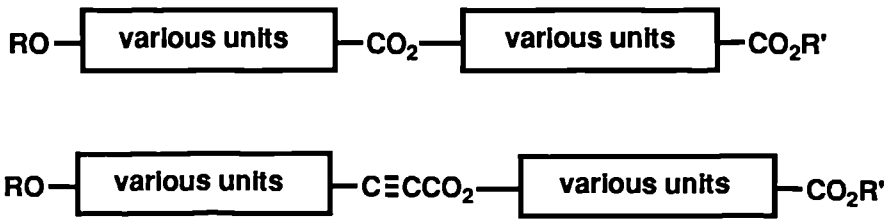


Figure 173. Templates that Indicate the General Structures of the Materials Discussed in Section d.

The substitution of a naphthalene unit for the biphenyl group in the core system (compounds **199** to **202**) led to a reduction in transition temperatures, a larger nematogenic tendency, and a reduction in the blue phase and TGB A* temperature ranges (c.f., compounds **158**, **164**, **169**, and **196**). As with the biphenyl analogues (**158** and **169**), the naphthalene derivatives showed an elevation in clearing point and the temperature of the nematic to smectic A transition for the racemic form (**201**) in comparison to the enantiomer (**200**). These effects were predicted by de Gennes[95].

Compounds **204** to **207**, based on a 2,6-disubstituted naphthalene core unit showed a reduced liquid-crystallinity and blue phase temperature range, but a broader TGB A* temperature range in comparison to the analogous materials with a phenyl core sub-unit. Similarly, the liquid-crystalline phase ranges for compounds **209** to **212**, based on the 1,4-disubstituted core unit were much lower than the phenyl analogues, with only compound **209** showing any liquid crystal phases.

Compounds **214** to **217** exhibited high clearing points and an increased mesogenicity relative to the other materials discussed in this section. The materials all exhibited smectic phases and had no tendency to form nematic or cholesteric phases. Three of the materials also exhibited a smectic C* phase.

e. The general structures of the materials discussed in this section are illustrated in figure 174.

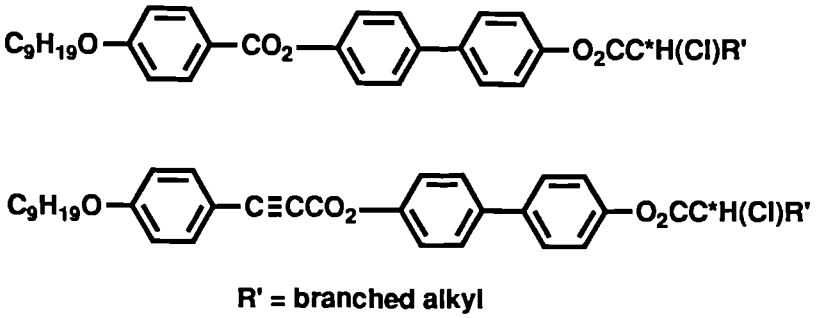


Figure 174. The General Structures of Materials with a Reversed Ester Linkage.

The first materials to be discussed are the benzoates (**223** to **226**). All of the materials exhibited blue phases and/or a cholesteric phases, and smectic C* phases. Only two of the materials were found to possess a smectic A phase, accompanied by a TGB A* phase (**223** and **226**). Compounds **223** and **224** also exhibited higher order modifications. The clearing points were in general higher than those observed for the analogous compounds in which the direction of the ester group had not been reversed (see section a). Similarly the transitions to the smectic C* phase occurred at a much higher temperature. Two of the materials (**224** and **225**) exhibited an inversion of helical twist sense in the smectic C* phase. This inversion was found to be similar in nature to that reported in other materials discussed earlier.

The phenylpropiolate esters (**227** to **230**) appeared to have a reduced level of 'chirality', with only one material exhibiting blue phases (**229**). The clearing points were found to

be lower than those observed for compounds **223** to **226** (the benzoates), with only two liquid crystal phases being apparent, i.e., a cholesteric phase and a smectic C* phase. This configuration of ester linkages was found to give the highest value of the spontaneous polarization in the smectic C* phase for all of the materials studied in this research program.

f. The materials discussed in this section had structures based on the molecular template illustrated in figure 175.

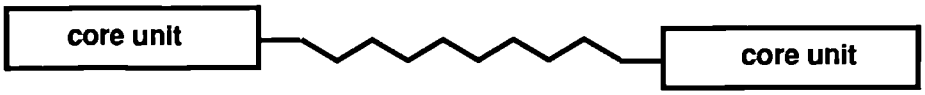


Figure 175. A Template that Indicates the General Structures of the Materials Discussed in Section e.

The first series of dimeric materials produced (**248** to **253**) exhibited only a nematic phase, with the chiral analogue (**261**) showing a cholesteric phase. A desirable smectic A phase underlying the cholesteric phase was not present in any of these materials. Compound **267** exhibited a nematic phase that was monotropic in nature. Compound **264** was found to exhibit higher order smectic modifications.

Briefly:-

1. Materials have been produced that possess a TGB A* phase, the thermal stability of this phase being critically dependent on the steric and dipolar properties of the chiral centre. These materials are the first to experimentally prove the Renn and Lubensky model[90], and the de Gennes analogy[95].
2. The temperature range of the TGB A* phase is increased if branching is introduced into the peripheral alkyl chain attached to the chiral centre, and is also found to be dependent on the length of this chain.

3. The size of atom and strength of the effective dipole associated with the chiral centre are important in determining the TGB A* temperature range.

4. The core structure is important in determining the TGB A* phase range. The introduction of a triple bond increases this range by weakening the layer ordering.

5. The nematogenicity is also increased on the introduction of a triple bond into the structure.

6. These materials are potentially the first to exhibit a TGB C* phase as predicetd by Renn and Lubensky[99].

7. Some of the materials exhibited inversions of helical twist in the cholesteric phase, whilst others showed this phenomenom in the smectic C* phase. The inversions in the smectic C* phase were not accompanied by an inversion in the direction of the spontaneous polarization. The materials were the first of their type, i.e., having only one chiral centre in their molecular architecture, to show these types of helix inversion.

7. Reversal of one ester linkage in the materials increased the tendency to form smectic C* phases, as well as increasing the value of the spontaneous polarization.

8. The dimeric materials did not give the desired nematic to smectic A phase sequence.

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