THE UNIVERSITY OF HULL

# Investigation of the Structure/Property Relationships in Triphenylene Discotic Liquid Crystals

Being a Thesis submitted for the Degree of Doctor of Philosophy
in the University of Hull

by

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**"If it were done when 'tis done, then 'twere well**
**It were done quickly"**
**Macbeth, Act I, Scene VII, Line 1**

**... and he certainly ain't talking about writing a PhD thesis!!!**

# *PUBLICATIONS*

## *Papers*

1. Triphenylene Hexa-*n*-alkylcyclohexanoates: A New Series of Disc-like Liquid Crystals, D.R. Beattie, P. Hindmarsh, J.W. Goodby, S.D. Haslam and R.M. Richardson, *J. Mater. Chem.*, 1992, **2**, 1261-1266.

2. Lateral Substitution in the Peripheral Moieties of Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-alkoxybenzoate)s: Dimethyl-substituted Systems, P. Hindmarsh, M. Hird, P. Styring and J.W. Goodby, *J. Mater. Chem.*, 1993, **3**, 1117-1128.

3. Investigation of the Effect of Bulky Lateral Substituents on the Discotic Mesophase Behaviour of Triphenylene Benzoates, P. Hindmarsh, M.J. Watson, M. Hird and J. W. Goodby, *J. Mater. Chem.*, 1995, **5**, 2111-2123.

4. The Synthesis and Transition Temperatures of some *ortho* Dichloroterphenyls for Ferroelectric Mixtures, M. Hird, K.J. Toyne, P. Hindmarsh, J.C. Jones and V. Minter, *Mol. Cryst. Liq. Cryst.*, 1995, **260**, 227-240.

## *Patents*

Discotic Compounds, Mixtures and Devices containing Discotic Compounds, J.W. Goodby, M. Hird, D.R. Beattie, P. Hindmarsh and G.W. Gray, Patent Application No. 9212354.6, 19th June 1992.

## *Oral and Poster Presentations at Conferences*

1. Lateral Substitution in the Peripheral Moieties of Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-alkoxybenzoate)s: Dimethyl-substituted Systems, P. Hindmarsh, M. Hird, P. Styring and J.W. Goodby, Oral Presentation, 8th Annual British Liquid Crystal Society Conference, 1993, University of Manchester.

2. Investigation of the Effect of Bulky Lateral Substituents on the Discotic Mesophase Behaviour of Triphenylene Benzoates, P. Hindmarsh, M. Hird and J.W. Goodby, Poster Presentation, 9th Annual British Liquid Crystal Society Conference, 1994, University of Hull.

   *and* Poster Presentation, 15th International Liquid Crystal Conference, 1994, Budapest, Hungary.

3. The Synthesis and Transition Temperatures of some *ortho* Dichloroterphenyls for Ferroelectric Mixtures, M. Hird, K.J. Toyne, P. Hindmarsh, J.C. Jones and V. Minter, Poster Presentation, 9th Annual British Liquid Crystal Society Conference, 1994, University of Hull.

   *and* Poster Presentation, 15th International Liquid Crystal Conference, 1994, Budapest, Hungary.

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# *FOREWORD*

This thesis has been structured into chapters so that the production of papers for publication is simplified. It will no doubt be apparent that Chapters 3 and 4 have already been seen in print in *Journal of Materials Chemistry*. This style was also chosen to enable greater freedom of movement and access to a particular area of interest, by preventing the reader from being swamped with unnecessary details that belong to other areas of research.

# *ABSTRACT*

This thesis presents a detailed investigation of the relationship that exists between the molecular structure and the mesomorphic behaviour in discotic liquid crystals. This was achieved by the systematic alteration of the molecular architecture of one class of discotic liquid crystals - the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s which were first studied in 1981.

It was shown, by the systematic increase in the lateral substituents (from hydrogen through to *tert*-butyl, both mono- and di-substituted) in both the outer and inner regions of the peripheral phenyl rings of these triphenylene benzoates, that both the position and size of the substituents greatly affect the melting points, transition temperatures and phase morphology. Studies on lateral substitution were also conducted using polar units and these results were equally remarkable. Examination of the effects of lengthening the peripheral arms, without lateral substituents of the triphenylene benzoates was also performed and with the results obtained, it allowed at last, the construction of a complete theoretical model for the relationship that exists between the molecular structure of discotic liquid crystals and the mesophase behaviour.

# *PART I*

# *THE INTRODUCTION*

# *CHAPTER 1*

## *The Introduction*

### *1.1 Historical Background*

Liquid-crystalline materials have been studied for just over a century now,[1] but it has been the last twenty to thirty years that have witnessed the most phenomenal explosion of research and development of this exciting field of science, which combines aspects of chemistry, biology, mathematics, physics and engineering.

LCD's, or liquid crystal displays to be exact, are now pretty much household names and appear in watches, calculators and videos (to name but a few). This would not have been possible if it was not for a number of significant and very important breakthroughs which have inevitably led to the resulting avalanche of interest into this particular research area that many scientists are still involved in to this day; in 1964, Fergason[2,3] reported that chiral nematic liquid crystals could be used as temperature indicators, in 1968 Heilmeier[4,5] demonstrated a liquid crystal device operating at room temperature, in 1971 Schadt and Helfrich[6] and independently Fergason invented the twisted nematic display device, and finally, in 1973 the first stable, commercially-viable, room temperature nematic liquid crystals - the 4-alkyl-4'-cyanobiphenyls - were synthesized by Gray *et al.*[7,8]

A great deal of fresh science was unearthed; new ideas were postulated and old ones correctly resolved, but primarily, research and development into liquid crystals had involved the study, either theoretical or experimental, of materials that possessed a central *rod*-shaped core, either of a low molar mass or of a polymeric variety.

It was during the important period ranging from the early 1950's through to 1970's that a number of isolated reports were published which detailed interesting studies of the possibility of mesomorphism being exhibited from materials that contained a ***non-rod***-like central core. Theoretical calculations indicated that it was possible for a *plate*- or *disc*-like compound to exhibit a nematic-like mesophase.[9-12] In 1965 Brooks and Taylor[13] experimentally observed this phenomenon while studying the carbonization of heavy petroleum residues and coal tars at very high temperatures. The chemistry of this liquid phase carbonization is very complex, but it is now understood that at temperatures between 350 and 550 °C a transformation occurs, whereby the large planar molecules (formed by the reactions of thermal cracking and aromatic polymerization) orientate approximately parallel to form an optically anisotropic phase. This was called the *carbonaceous* mesophase and its birefringent texture when viewed by optical polarizing microscopy closely resembled that of a classical nematic phase, but the lifetime of this nematic-like mesophase was unfortunately limited due to its hardening to a semi-coke. Further investigations were conducted concerning, for example, geometrical aspects and practical functions[14-16] and it became evident that there was a need for the synthesis of stable pure mesogens giving this type of mesophase[17-19] so that a thorough understanding could be attained regarding this new and very interesting area of liquid crystal research.

During 1977 and 1978, success was achieved by several research groups with the synthesis of the benzen-1,2,3,4,5,6-hexayl hexakis(*n*-alkanoate)s[20] and the 2,3,6,7,10,11-hexakis(*n*-alkyloxy)triphenylenes[21-23] (see structures **I** and **II**, Figure 1.1) which exhibit a very viscous and birefringent mesophase between the crystalline solid and the isotropic liquid phases. The structure of this novel mesophase, quite distinct from the smectic and nematic phases of calamitic materials, was deduced to be of a *columnar* arrangement where the molecules are stacked on top of one another into columns which are furthermore packed into an hexagonal lattice.[20-24]

Additional types of columnar mesophases were also revealed with the synthesis of the triphenylen-2,3,6,7,10,11-hexayl hexakis(*n*-alkanoate)s (see structure **III**, Figure 1.1).[25-29] In addition to the columnar mesophases, a highly birefringent, fluid mesophase was observed for some triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s and hexakis(4-alkylbenzoate)s[30,31] (see structure **IV**, Figure 1.1). This fluid mesophase was identified as the discotic nematic ($N_D$) phase which had previously been theoretically predicted to exist.[9-12]

The term *discotic* was proposed for these mesophases, meaning that they are generated by *disc*-shaped molecules, as opposed to *calamitic* phases exhibited by rod-like molecules.[22,32] Unfortunately, the same term has also used to describe the compounds themselves. Recently, some confusion concerning the nomenclature has arisen as it appears that *discotic* mesophases, or to be more precise, *columnar* mesophases can in fact be exhibited by non-disc-like materials.[33,34]

The field of discotic liquid crystals has flourished with the publication of many papers, several reviews[33,35-39] and a bibliography.[40]

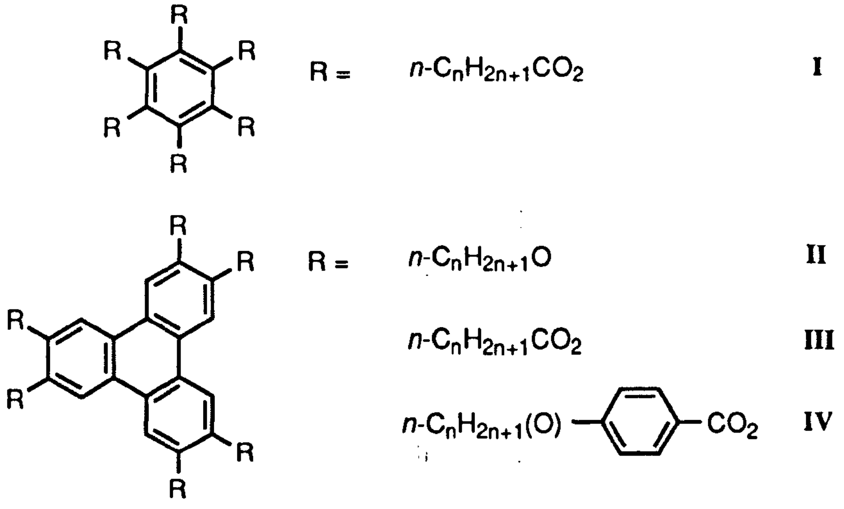


**Figure 1.1**

## 1.2 The Melting Behaviour of Crystals and Liquid Crystals[41,42]

A crystalline solid phase possesses a structure in which the molecules are highly rigid, and possess long-range positional **and** orientational order in a three-dimensional lattice. A liquid has neither positional nor orientational ordering, but attractive forces still exist which are just strong enough to hold the molecules together in a loose array and thus, the phase has a physical form. A gas has no order between the constituent molecules, therefore possesses no physical form and so the molecules are able to distribute themselves randomly.

The melting of a crystalline solid essentially involves the abrupt breakdown of the three-dimensional lattice, due to the thermal energy of the molecules overcoming the associative forces and this results in the formation of a randomly ordered state, called an *isotropic* liquid.

Most liquid crystalline materials do not follow the aforementioned, highly destructive procedure and display a *stepwise* breakdown in the intermolecular forces of attraction (which is described in detail below). However, some liquid crystalline compounds *do* simply melt from their crystalline form to the isotropic liquid. Those compounds in the former category exhibit mesophases on both their heating and cooling cycles and their mesophases are termed *enantiotropic*; those materials from the latter category only exhibit mesophases on their cooling cycle, which are found *below* the melting point in a region of supercooling, and these mesophases are termed *monotropic*.

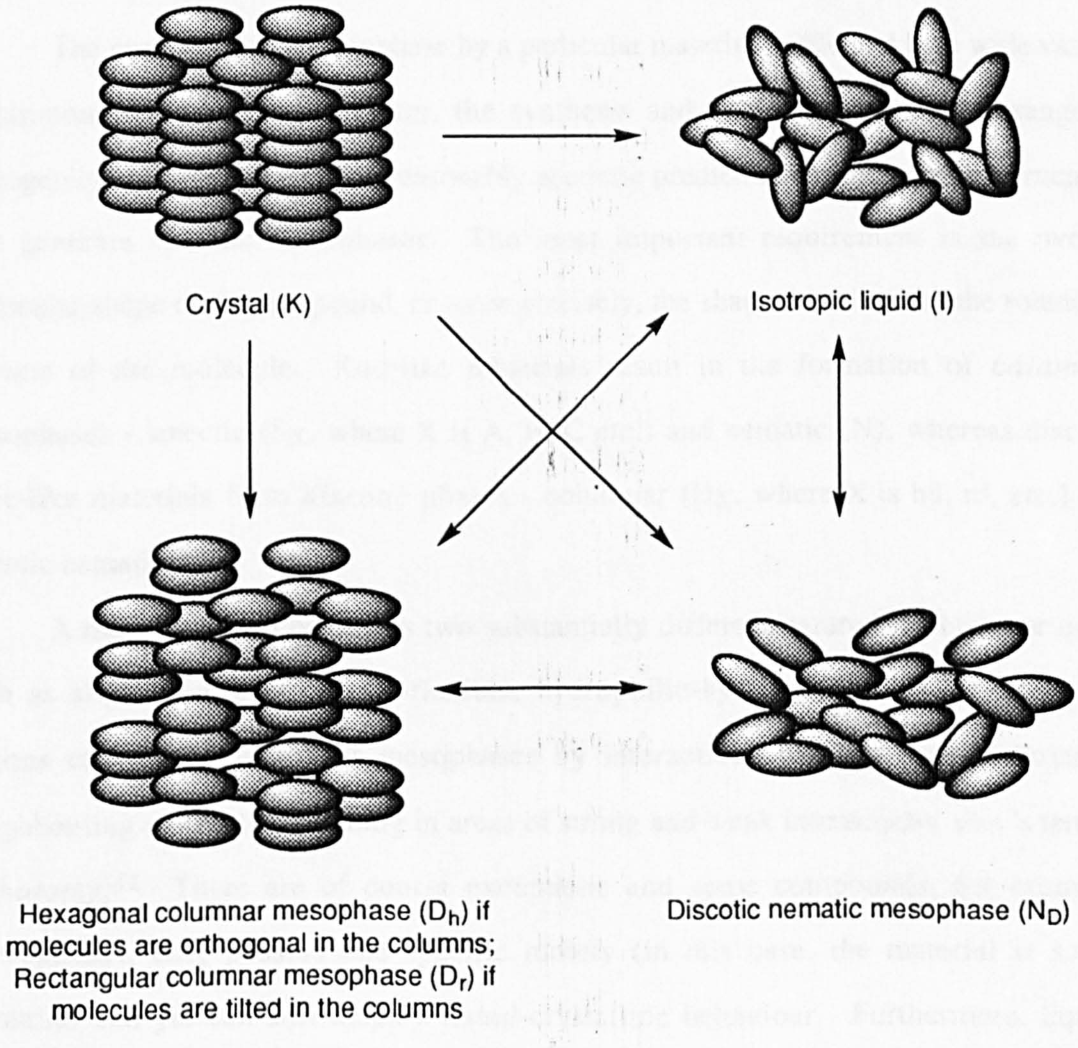


**Figure 1.2 : Possible Melting Processes For a Mesogenic Discotic Material**

The stepwise "melting" process will occur when molecules (that rotate about a long molecular axis) lose their long-range positional order but maintain some degree of short-range order, whilst retaining their long-range orientational order. On further heating, only long-range orientational order of the constituent molecules is left after the breakdown of the positional order, and finally, on further heating, the isotropic state is achieved after the orientational order is subsequently lost. The term *liquid crystallinity* is used to describe this remarkable situation and it represents the formation of a series of uniquely structured mesophases which retain properties of both the crystalline and fluid states. This melting process is represented in Figure 1.2, and is described using disc-like molecules.

## *1.3 Molecular Requirements and Classification of Liquid Crystals*[41,42]

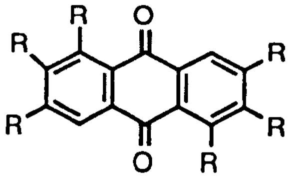
The generation of a mesophase by a particular material is affected by a wide variety of structural influences. However, the synthesis and evaluation of a wide range of mesogenic materials has enabled reasonably accurate predictions of the types of structures that generate specific mesophases. The most important requirement is the overall molecular shape of the compound, or more precisely, the shape described by the rotational volume of the molecule. Rod-like materials result in the formation of *calamitic* mesophases - smectic ($S_X$, where X is A, B, C *etc.*) and nematic (N), whereas disc- or plate-like materials form *discotic* phases - columnar ($D_X$, where X is hd, rd, *etc.*) and discotic nematic ($N_D$).

A material which possesses two substantially different natured moieties, or units, such as aliphatic-aromatic, rigid-flexible, hydrophilic-hydrophobic, non-polar-dipolar regions can aid formation of mesophases by interactions between like moieties of neighbouring molecules, resulting in areas of strong and weak interactions; this is termed *dichotomy*.[41] There are of course exceptions and some compounds, for example, quatraphenyl, only possess one specific moiety (in this case, the material is solely aromatic) and yet can still display liquid-crystalline behaviour. Furthermore, liquid-crystalline phase formation is influenced by the relative strength of the intermolecular associations. If the stronger core-to-core (or face-to-face) associations dominate over the weaker edge-to-edge (or side-to-side) ones, or *vice versa*, then the tendency to form mesophases is reduced. There needs to be a balance between these interactions so that they can both operate but in a locally restricted manner.[41]

Discotic liquid crystals are recognised by their distinctive and quite obvious disc-like core. There appears to be no universal rules as to the structural requirements for what constitutes a discotic liquid crystal. Originally, they were thought to be generally flat, predominantly aromatic and possessing six or eight peripheral arms, but it has now been proven that all three of these factors are not necessary in the generation of discotic mesophases. A number of non-*disc*-like materials[33,34] have been found to exhibit mesophase-types normally associated with discotic liquid crystals, for example, the hexagonal and rectangular disordered columnar mesophases ($D_{hd}$ and $D_{rd}$). Some examples of discotic liquid crystals are shown above in Figure 1.1 and below in Figure 1.3.

Liquid crystals can be divided into two different forms - *thermotropic*[43] and *lyotropic*.[44] In each case the mesophases are respectively formed by either a change in temperature, or by the action of a second component, such as a solvent on an *amphiphilic* material. These two classifications can be re-linked by a relatively rare group of compounds which exhibit mesomorphic characteristics of both sections and are called *amphitropic* compounds.

This thesis is only concerned with thermotropic liquid crystals and these can be further sub-divided into *calamitic* and *discotic* forms. Traditionally, these sections were thought to be separate entities but recently, the division lines have become blurred and another group of materials - *phasmidic* and *polycatenar*[34] - have been recognised which have properties of both thermotropic classifications. The divisions are illustrated in Figure 1.4.



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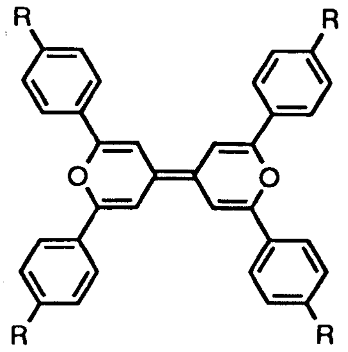

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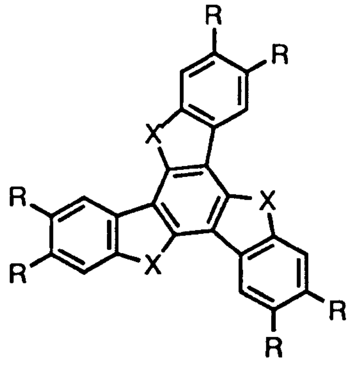

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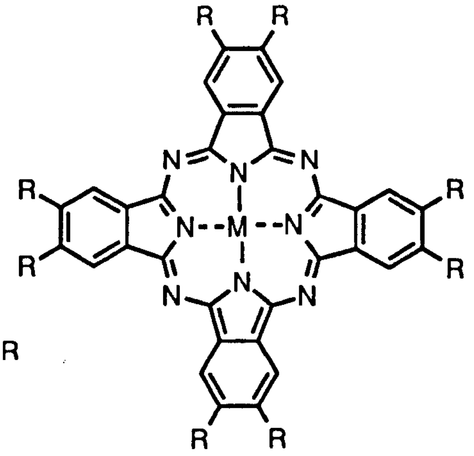

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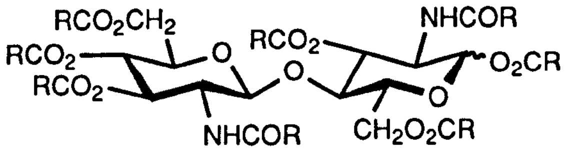

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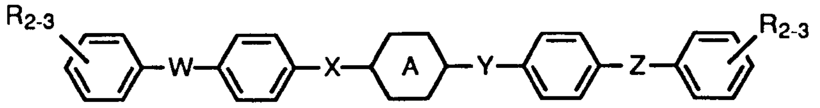

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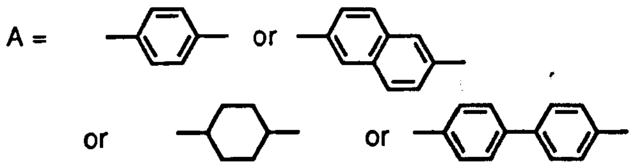

W, X, Y, Z = $-CO_2-$, $-O_2C-$, -N=CH-, -CH=N-, $-CH_2O-$, $-OCH_2-$

R = $C_nH_{2n+1}(O)-$, $C_nH_{2n+1}CO_2-$, $C_nH_{2n+1}(O)C_6H_4CO_2-$

**Figure 1.3 : Examples of Discotic Liquid Crystals: hexa-substituted anthraquinones (V); tetra-arylbipyranylidenes (VI); hexa-substituted truxenes with oxygenated and sulfurated analogues (VII); octa-substituted phthalocyanine complexes (VIII); acylated chito-oligosaccharides (IX); polysubstituted phasmids and polycatenars (X)**

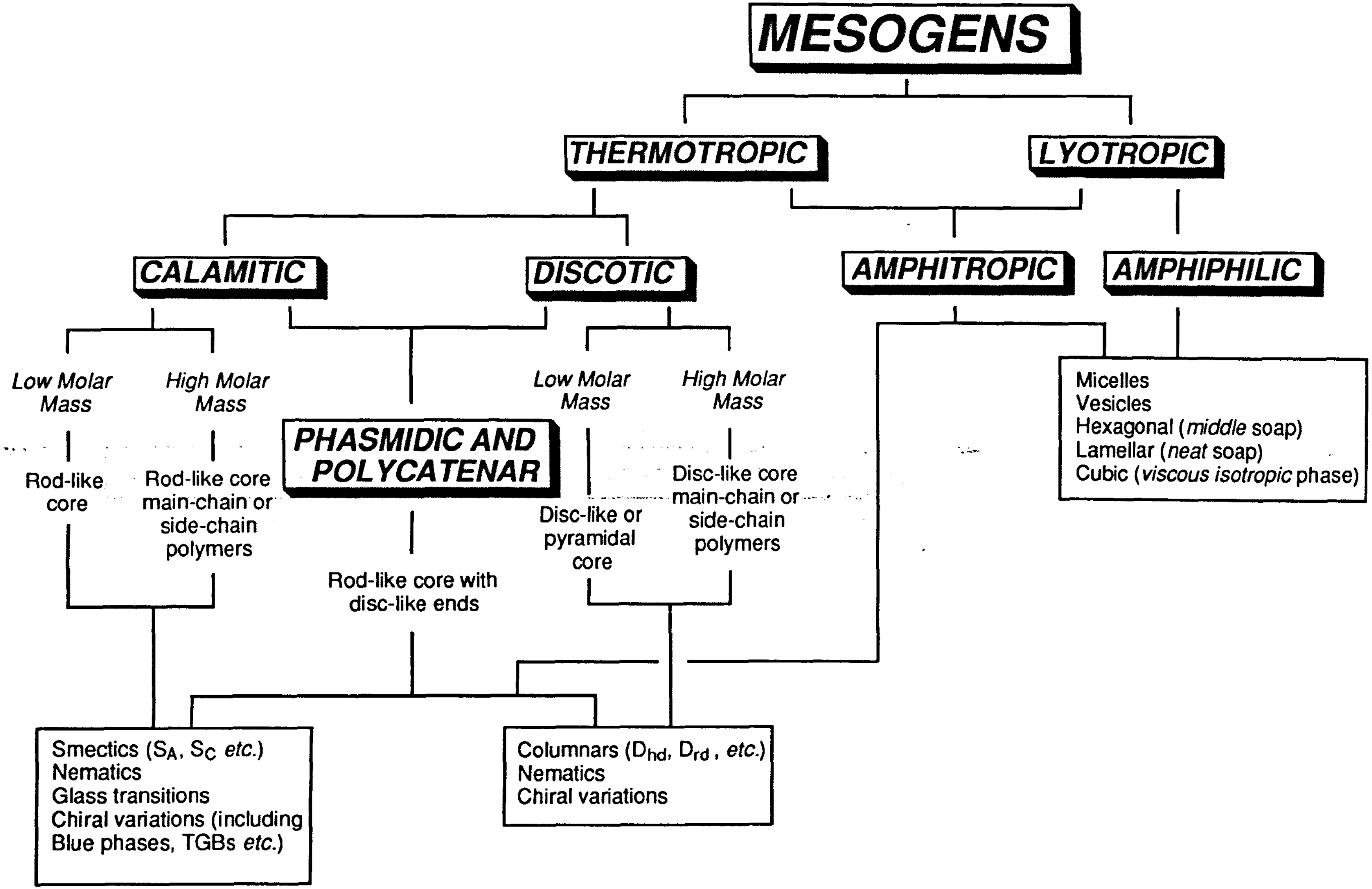

Figure 1.4 : A Classification of Liquid Crystals

## 1.4 The Mesophases of Discotic Liquid Crystals

The nomenclature of the mesophases is based upon the *structure* of the phase, in contrast to the situation of smectics which are named *alphabetically*. The capital letter 'S' was logically chosen to denote a smectic (from the greek word *smectos* meaning soap-like) and an 'N' for a nematic (from the greek word *nematos* meaning thread-like). Unfortunately, a 'D' was assigned to indicate the mesophases of discotic liquid crystals as they were generated by *disc-shaped molecules*. So, instead of using a 'C', columnar mesophases are denoted by use of a 'D'; a discotic nematic is designated '$N_D$'.[45]

At the time, 'D' was acceptable because columnar mesophases were only found with *discotic* liquid crystals, but now there are many examples of liquid crystals that do not possess a *disc*-like core ***and*** yet exhibit columnar mesomorphism.[33,34]

The complex polymorphism possible for the columnar phases is dealt with in the nomenclature system by further divisions to characterise the various columnar arrangements.[26,45-47] The possibilities for the two-dimensional lattice symmetry are covered by the following symbols: *h*exagonal ($D_h$), *r*ectangular ($D_r$) or *ob*lique ($D_{ob}$). The order or disorder of the molecular stacking within a column is defined by further subscripts ($_o$ or $_d$). Therefore, a hexagonal lattice of columns with an ordered stacking of disc-like molecules is conveniently denoted $D_{ho}$, the notations $D_{hd}$, $D_{rd}$ or $D_{ob.d}$ are then obvious.[37,48,49] The phases that are exhibited by discotic materials are more thoroughly discussed in the following sections.

### 1.4.1 The Columnar Mesophases

#### 1.4.1.1 The $D_h$ Hexagonal Phases

There are two phases in this category - the hexagonal ordered ($D_{ho}$) and the hexagonal disordered ($D_{hd}$), which are illustrated in Figure 1.5. The discotic molecules are packed orthogonally into columns with either regular or irregular spacing, and then the columns are arranged into an overall two-dimensional hexagonal lattice. The arrangement of molecules within the $D_{ho}$ is strongly ordered and "crystalline" in appearance (see Figure

1.5). As a consequence of this high degree of ordering, the enthalpies of transition for the $D_{ho}$ to Iso ($\Delta H_{D_{ho}\text{-Iso}}$) are quite high,[23] thus implying that the phase is probably better defined as a crystal phase rather than a liquid crystal mesophase. However, it should be noted that although the intermolecular distances within the columns are fixed, the columns themselves are able to move allowing some degree of *disorder* to exist; this phase is akin to the G, J *etc.* phases of calamitic liquid crystals. The enthalpies of transition for the $D_{hd}$ to Iso ($\Delta H_{D_{hd}\text{-Iso}}$) are much smaller[23] and therefore, more typical for liquid crystal mesophase transitions.

Originally, it was thought that these phases were only encountered when the linkages between the peripheral arms and the core were not very bulky, *ie*, alkyl chain ethers or esters,[22,23,25,52-54] but certain laterally substituted triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s also display these columnar mesophases.[55]

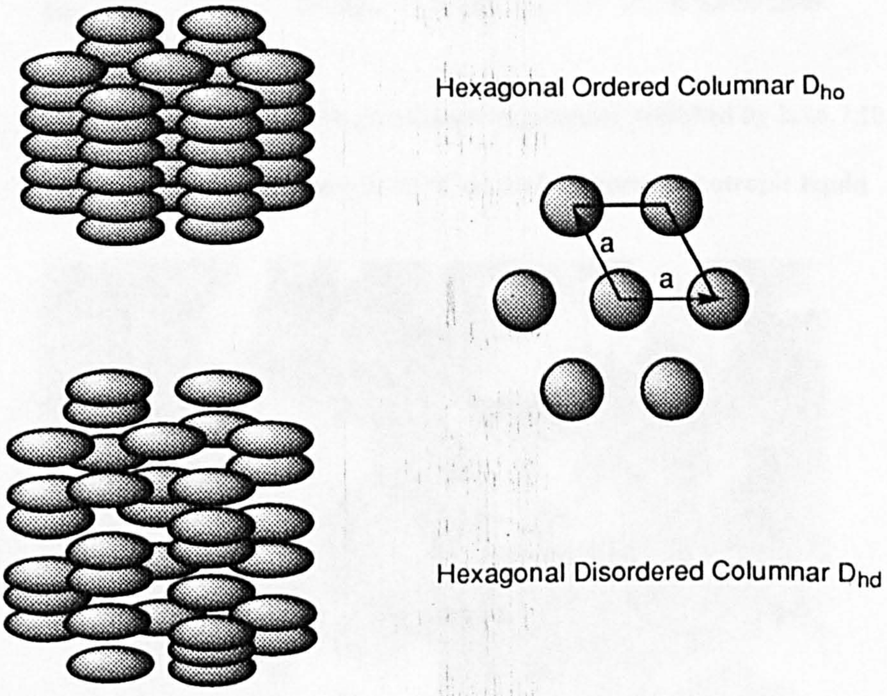

**Figure 1.5 : Schematic Representation of the Hexagonal Columnars**

Textures of both phases are relatively easy to identify using thermal optical polarizing microscopy. On cooling from the isotropic liquid, a $D_{ho}$ appears as a mosaic which is formed from the coalescence of regions of digitated stars (see Plates 1.1 and 1.2);[50] the resulting overall appearance is somewhat crystalline. Similarily, a $D_{hd}$ grows like a crystal on cooling from the isotropic liquid, without a mosaic texture and finally appears focal-conic (see Plate 1.3) or fan-like (see Plate 1.4). Both phases have negative uniaxial interference[§] figures.[22,24,32,50,51]

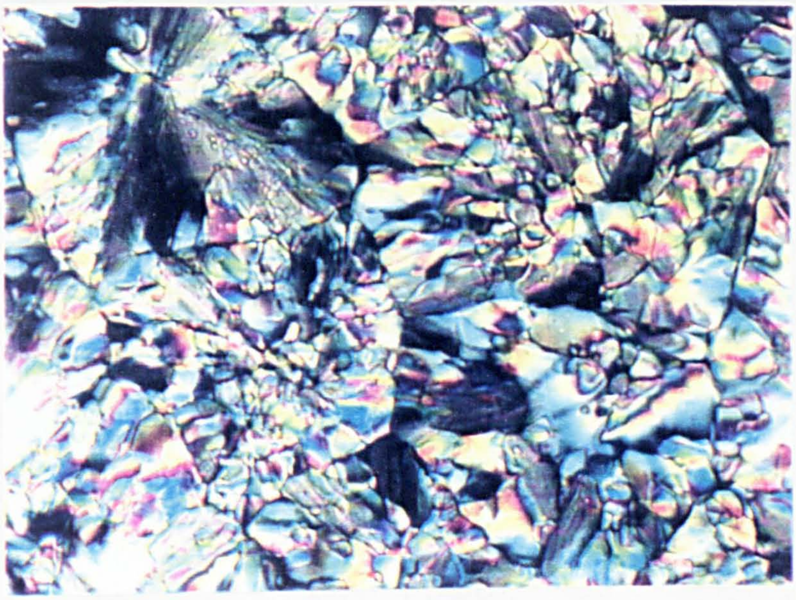

**Plate 1.1 : Hexagonal ordered ($D_{ho}$) columnar mesophase exhibited by 2,3,6,7,10,11-hexakis(octyloxy)triphenylene at 83 °C on cooling from the isotropic liquid**

**Plate 1.2 : Hexagonal ordered ($D_{ho}$) columnar mesophase exhibited by 2,3,6,7,10,11-hexakis(decyloxy)triphenylene at 67 °C on cooling from the isotropic liquid**

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[§] See Section 1.6 "*Optical Properties: Birefringence*' and Section 1.5.1 "*Thermal Optical Microscopy*"

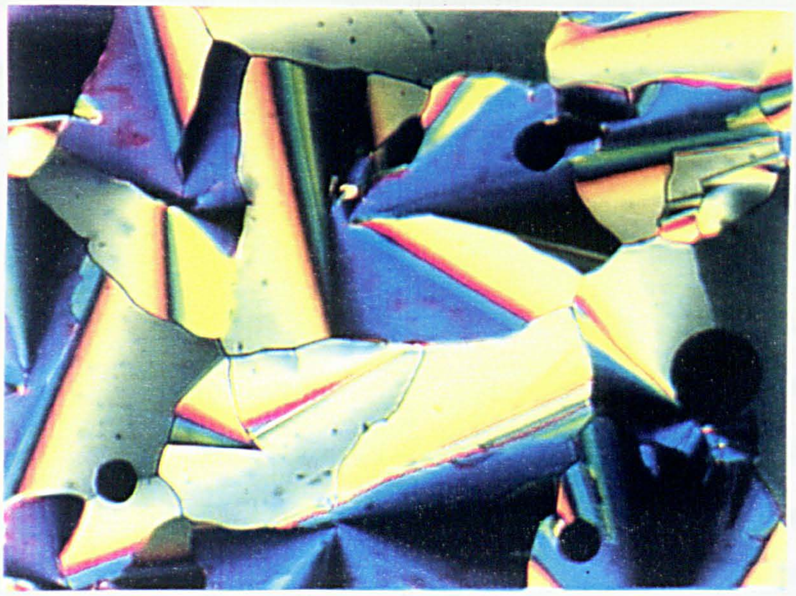


**Plate 1.3 : Hexagonal disordered ($D_{hd}$) columnar mesophase exhibited by triphenylen-2,3,6,7,10,11-hexayl hexakis(octanoate) at 120 °C on cooling from the isotropic liquid**

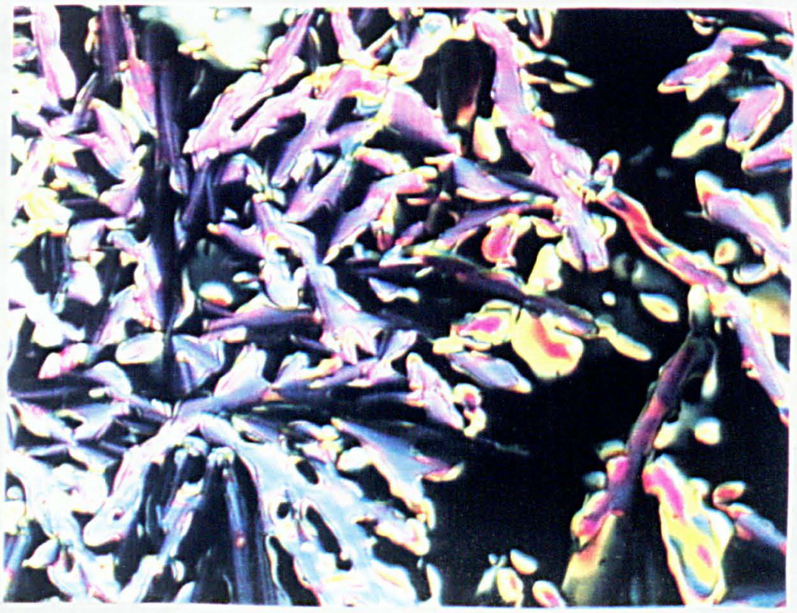
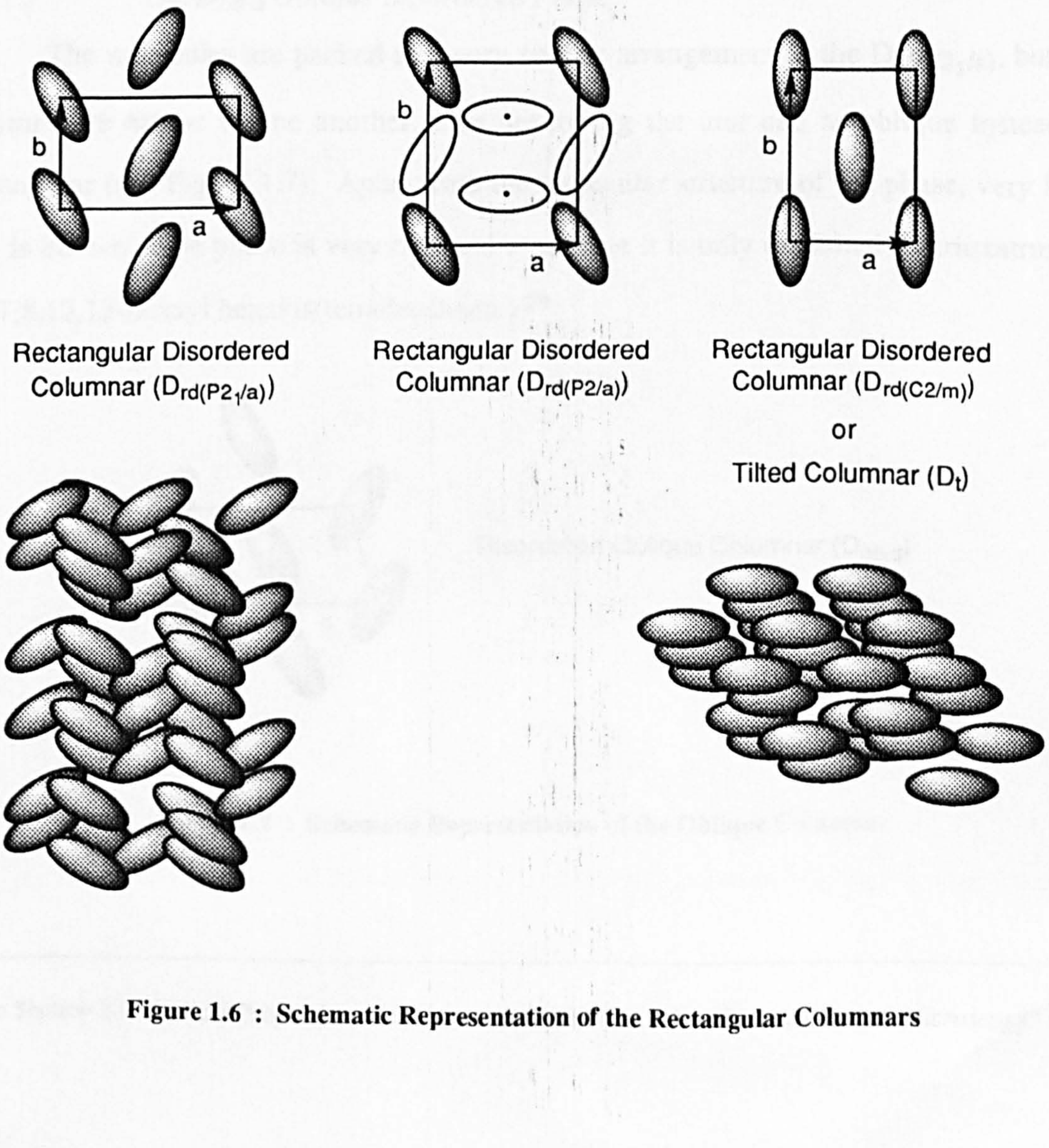


**Plate 1.4 : Hexagonal disordered columnar ($D_{hd}$) mesophase exhibited by triphenylen-2,3,6,7,10,11-hexayl hexakis(tetradecanoate) at 108 °C on cooling from the isotropic liquid**

### 1.4.1.2 *The $D_r$ Rectangular Phases*

At present, the acceptance of a rectangular ordered ($D_{ro}$) phase is still to be established. A number of reports exist,[56-60] but no firm confirmation has been made. It is again debatable whether this phase (if it exists at all) can be classified as a liquid crystal mesophase (using the same argument as for the hexagonal ordered [$D_{ho}$] phase) because the molecules possess order in three-dimensions, thus suggesting a crystalline form.

There are three accepted rectangular disordered mesophases which are depicted in Figure 1.6. The molecules are randomly spaced throughout the columns and are tilted, the the angles of which are not accurately known.[37,61] The columns are again packed into a hexagonal lattice, but the repeating unit cell is rectangular, hence the classification. There are three different symmetries within the $D_{rd}$ corresponding to the tilted arrangements of the discotic molecules with respect to the column axis: $D_{rd(P2_1/a)}$, $D_{rd(P2/a)}$ and $D_{rd(C2/m)}$[37] - these are the conventional crystallographic notations for the space groups.[62]



Rectangular Disordered Columnar ($D_{rd(P2_1/a)}$)

Rectangular Disordered Columnar ($D_{rd(P2/a)}$)

Rectangular Disordered Columnar ($D_{rd(C2/m)}$)
or
Tilted Columnar ($D_t$)

**Figure 1.6 : Schematic Representation of the Rectangular Columnars**

The enthalpies of transition for $D_{rd}$ to $D_{hd}$ ($\Delta H_{D_{rd}\text{-}D_{hd}}$) are typically small[25] as the transition is second order - there is only a change in the tilting of the molecules within the columns. The enthalpies of transition for $D_{rd}$ to Iso ($\Delta H_{D_{rd}\text{-}Iso}$) are variable, for example, small for short chain length triphenylen-2,3,6,7,10,11-hexayl hexakis(*n*-alkanoate)s[23] and large for benzen-1,2,3,4,5,6-hexayl hexakis(*n*-alkanoate)s.[20]

All three $D_{rd}$ phases are biaxial;[§] there are two optic axes - one found to be parallel with the column direction and one found to be parallel with the short molecular axes of the molecules themselves. There are no typical optical textures associated with the first two variations, but mosaic textures similar to those of the G phase of calamitic liquid crystals have been observed for the $D_{rd(C2/m)}$ phase.[30] For some examples, see Plates 1.5 and 1.6.

Finally, there have also been reports of another mesophase, the *tilted columnar* ($D_t$),[31,46,63] but this is in fact just the $D_{rd(C2/m)}$.[64]

### *1.4.1.3 The $D_{ob.d}$ Oblique Disordered Phase*

The molecules are packed in a very similar arrangement to the $D_{rd(P2_1/a)}$, but the columns are askew to one another, thus describing the unit cell as oblique instead of rectangular (see Figure 1.7). Apart from the molecular structure of the phase, very little else is known. The phase is very rare and at present it is only exhibited by trioxatruxen-2,3,7,8,12,13-hexayl hexakis(tetradecanoate).[29]

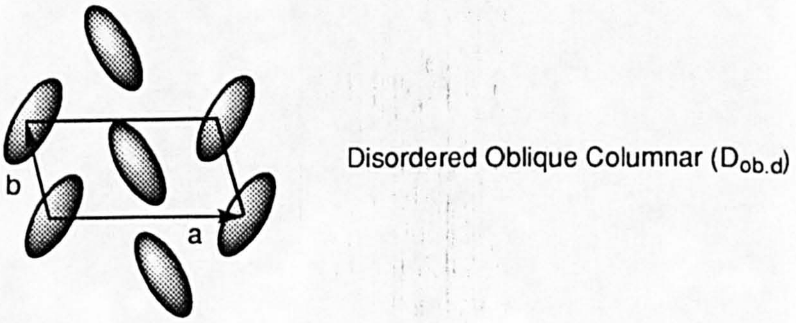


**Figure 1.7 : Schematic Representation of the Oblique Columnar**

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[§] See Section 1.6 "*Optical Properties: Birefringence*' and Section 1.5.1 "*Thermal Optical Microscopy*"

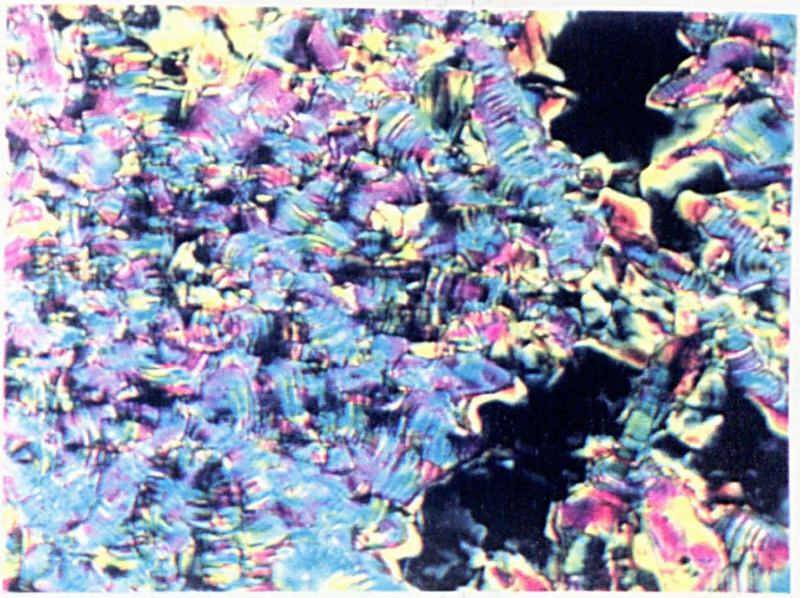

Plate 1.5 : Rectangular disordered ($D_{rd}$) columnar mesophase exhibited by triphenylen-2,3,6,7,10,11-hexayl hexakis(tetradecanoate) at 90 °C on cooling from the $D_{hd}$ mesophase

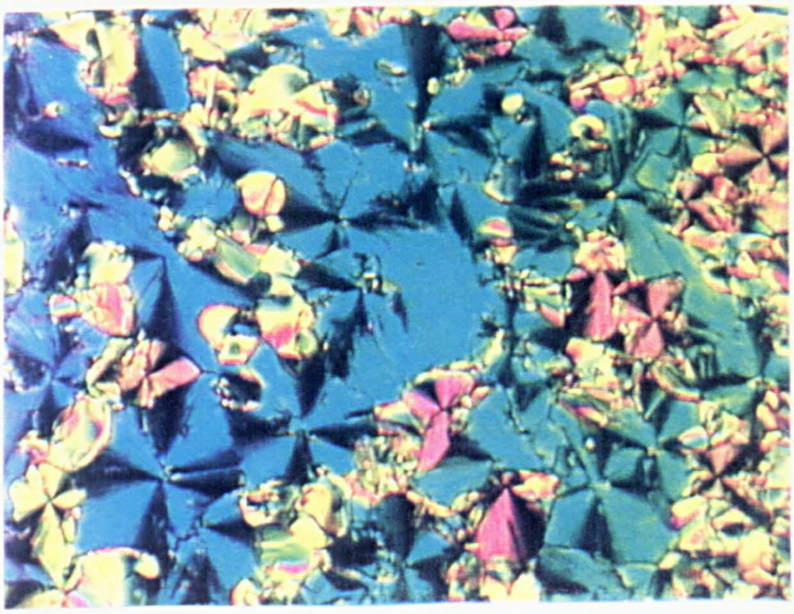

Plate 1.6 : Rectangular disordered ($D_{rd}$) columnar mesophase exhibited by triphenylen-2,3,6,7,10,11-hexayl hexakis(4-octyloxybenzoate) at 160 °C on cooling from the $N_D$ mesophase

### *1.4.2 The Nematic Mesophases*

#### *1.4.2.1 The $N_D$ and $N_D^*$ Discotic Nematic Phases*

The description of the discotic nematic ($N_D$) phase is topologically identical to the classical nematic mesophase exhibited by rod-like molecules. The discogens have complete orientational and rotational freedom but their planes are, on average, parallel to one another, and this phase structure was confirmed by X-ray and magnetic measurements.[37,51] The director (**n**) is found to be parallel to the short molecular axes of the discotic molecules. The discotic nematic ($N_D$) phase is illustrated in Figure 1.8.

The optical texture is also identical to that of the classical nematic phase, marbled or threaded with four and two point brush defects and very strong thermal fluctuations, especially at the $N_D$-Iso transition (see Plates 1.7 and 1.8). The enthalpies of transition ($\Delta H_{N_D\text{-Iso}}$) are very small, indicating that the transition is probably approaching second order in nature,[55] and are much smaller than typical enthalpies for the N-Iso transitions for calamitic liquid crystals. This would suggest that the structure of the discotic nematic phase is already very similar to that of the isotropic liquid.

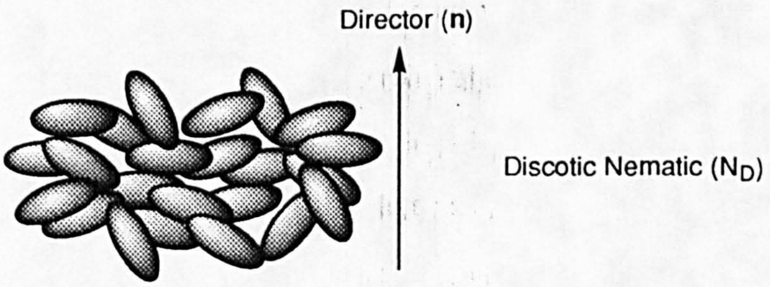

**Figure 1.8 : Schematic Representation of the Discotic Nematic**

The optical and diamagnetic anisotropies ($\Delta n$ and $\Delta\chi$) are negative, and the macroscopic viscosity is markedly higher than that of the classical calamitic nematic phase.[65] The dielectric anisotropy ($\Delta\varepsilon$) may be positive, in the case of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s due to the permanent dipoles associated with the six ester linkages,[66] or negative, in the case of the hexakis[2-(4-alkylphenyl)ethyn-1-yl]benzenes because these materials have no permanent dipoles.[67]

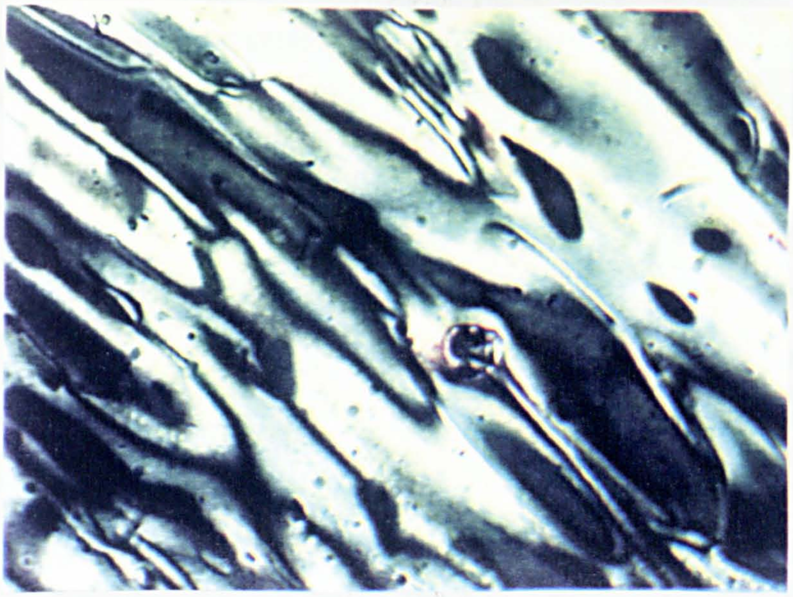

**Plate 1.7 : Discotic nematic ($N_D$) mesophase exhibited by triphenylen-2,3,6,7,10,11-hexayl hexakis(4-octyloxybenzoate) at 235 °C on cooling from the isotropic liquid**

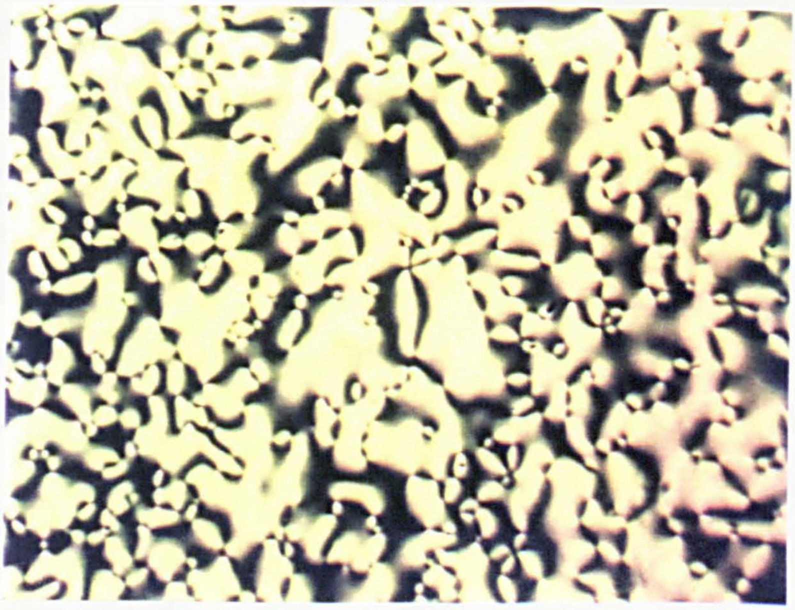

**Plate 1.8 : Discotic nematic ($N_D$) mesophase exhibited by triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxybenzoate) at 195 °C on cooling from the isotropic liquid**

Very few quantitative measurements of the physical properties of discotic liquid crystals have been reported. This mesophase was first exhibited by the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-benzoate)s and hexakis(4-alkylbenzoate)s.[30,31] The presence of the bulky phenyl rings weakened the molecular face-to-face interactions between the discs sufficiently to permit the discotic nematic mesophase to be formed.

Initial attempts[68] at obtaining the chiral discotic nematic mesophase were unsuccessful; the discogens all possessed a chiral centre in each of their terminal aliphatic chains, but the materials just exhibited columnar phases and unfortunately, only exhibited the chiral discotic nematic phase in mixtures with a discotic nematogenic host.

In 1981, it was reported that a pure discotic liquid crystal had been found that exhibited the chiral discotic nematic ($N_D^*$),[69] but also noted within the same publication were other discotic materials that possessed chiral centres and did *not* exhibit the chiral discotic nematic mesophase. It appeared that simply incorporating a chiral centre into the terminal aliphatic chains would not induce chirality into the mesophases as easily as was found in the research of chiral calamitic liquid crystals.

The optical texture is similar to that of the classical chiral nematic - fingerprint pattern which, when sheared displays the Grandjean planar texture. Marked differences are apparent - the fingerprint texture usually appears only in small regions throughout a somewhat non-descript marbled texture; and also, the viscosity is larger still than its achiral variation and so, the Grandjean texture is very difficult to obtain because the mesophase resists the shearing action.

As mentioned previously, the director (**n**) is found to be parallel to the short molecular axes of the discotic molecules, whereas the director (**n**) of calamitic molecules is found to be parallel to the long molecular axes. When the helix of the mesophase is formed for the chiral nematic, calamitic molecules lie perpendicular to the helix director, but discotic molecules lie parallel, as illustrated in Figure 1.9.

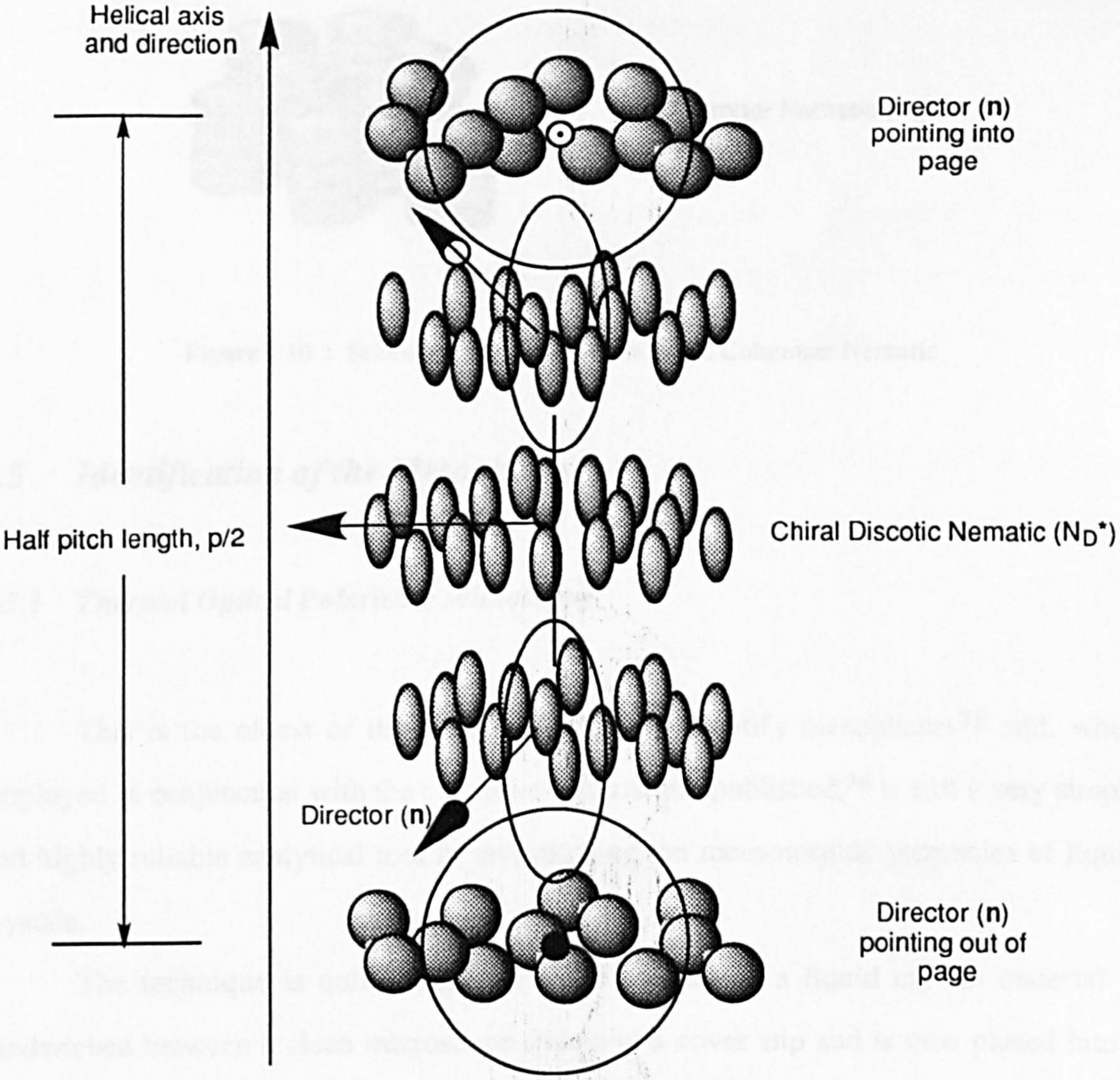

**Figure 1.9 : Schematic Representation of the Chiral Discotic Nematic**

### *1.4.2.2 The $N_C$ and $N_C^*$ Columnar Nematic Phases*

There are no published reports of the $N_C$ columnar nematic mesophase being exhibited by single systems; most often the systems under investigation have been doped[58,70-72] or are discotic polymers.[33,35,39,73] It is reported that the phase exhibits a similar optical texture as the discotic nematic ($N_D$), but its viscosity is markedly greater, and the structure of the phase is thought to be small columns of discogens, approximately four or five molecules long, which are arranged into an overall discotic nematic ($N_D$) arrangement. A possible structure of the phase is shown in Figure 1.10. Recently, a chiral variant has been reported[74] but, very little information has been mentioned.

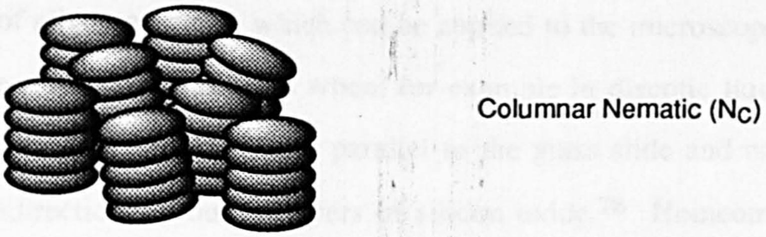

**Figure 1.10 : Schematic Representation of the Columnar Nematic**

## 1.5 *Identification of the Mesophases*

### 1.5.1 *Thermal Optical Polarizing Microscopy*

This is the oldest of the techniques used to identify mesophases[75] and, when employed in conjunction with the extensive information published,[76] is still a very simple and highly reliable analytical tool in investigating the mesomorphic properties of liquid crystals.

The technique is quite simple, a small amount of a liquid crystal material is sandwiched between a clean microscope slide and a cover slip and is then placed into a hot-stage that is positioned between the optical lens(es) of a polarizing microscope and an illuminating source, which is a pencil beam of light (Kohler illumination).[77] The textures of each phase are unique because of defect structures that are particular to each mesophase, and so to eliminate any defects which could cause confusion in the assignment of the mesophase, such as from crystal forms, the technique is best started from the isotropic liquid.

On cooling from the isotropic liquid, the first mesophase observed will exhibit the *natural* texture, which is the texture that is free from other textural influences because the texture of the preceding phase is optically extinct. On further cooling, the next mesophase to be seen will exhibit a *paramorphotic* texture, which is a texture that has been affected by prevailing defects from the preceding phase.

The molecules constituting a mesophase can align in one of two ways - *homogeneously* or *homeotropically* - and they can align in these fashions either naturally or with the aid of aligning agents, which can be applied to the microscope slides prior to use. Homogeneous alignment occurs when, for example in discotic liquid crystals, the short molecular axes lie approximately parallel to the glass slide and cover slip and is achieved by unidirectionally buffed layers of silicon oxide.[78] Homeotropic alignment occurs when, for example in discotic liquid crystals, the short molecular axes lie approximately perpendicular to the glass substrates and is obtained by the use of rufigallol, hexaphenol or 2,3,6,7,10,11-hexahydroxytriphenylene.[78]

The optical microscope is also used in investigating subtle structural and optical properties of the mesophase by such techniques as conoscopy. Under conoscopic observation, specific interference figures (isogyres) are formed which are indicative of uniaxiality or biaxiality.[77] Conoscopic studies depend on using the microscope in the wide aperture mode with a thick, homeotropic sample preparation. Unaxial liquid crystals result in isogyres which appear as "Maltese Cross" type patterns; biaxial materials give isogyres which are split, but will recombine when the sample is rotated.

### *1.5.2 Miscibility Studies*[79]

When a mesophase cannot be fully identified because the texture is ambiguous and it is thought to be one of perhaps two possible mesophases, then miscibilty studies may be employed. A number of mixtures of mass % compositions are made up, consisting of the test compound and a material of known mesophase behaviour, which has one of the mesophase possibilities in question, and the results obtained from microscopic examination are plotted as a binary phase diagram. It is advisable that the test compound and the literature material have similar or at least related structures. If the phase under examination extends across the binary phase diagram then the materials have identical phase types, but occasionally immiscibility occurs where a phase of one compound will not mix with the same phase of another compound,[79] and so a great deal of caution is required. However, the test is one of miscibility not immiscibility, and so if two mesophases are not miscible, it does not necessarily mean that they are not of the same phase type.

### *1.5.3 Differential Scanning Calorimetry*

This is a commonly used technique for mesophase temperature assignment and measures the enthalpies associated with each transition; unfortunately, it can give no information regarding the mesophase structure, but the size of the enthalpy of a transition can give an indication as to what transformation is occurring, *ie,* a first or second-order transition.

Differential Scanning Calorimetry (DSC) operates by maintaining a reference material and the test compound at the same temperature whilst heating or cooling. As the temperature range of the test compound is scanned, any emitted or absorbed heat energy detected from transitions is compensated for by the action of giving heat energy to, or taking heat energy from, the reference material.

### *1.5.4 X-Ray Diffraction*

This is the only analytical tool available that will give information that is directly related to the mesophase structure. By fully utilizing the information of crystallography, it is possible to relate the intensities and line positions to the nature and relative lattice positions of the atomic scattering sites. Small-angle X-ray scattering (SAXS) gives an indication of the geometry of the phase (hexagonal or rectangular) and the lattice parameters (dimensions of the unit cell). Wide-angle X-ray scattering (WAXS) gives an indication of the distances between the molecules in a mesophase.

## *1.6 Optical Properties: Birefringence*

If light that has been polarized in one plane, *ie,* the $x$-axis, travels from a source at the centre point of a medium, such as glass, it is found at any time interval that the light has travelled an equal distance in any direction; this situation is found to be identical if the light has been polarized in the $y$-axis also. This medium is described as being *optically isotropic* - the index of refraction has same value in each case.

When polarized light travels through a liquid crystal material, the values of the indices of refraction are different for *x*-polarized light and *y*-polarized light. This means that light is travelling at a different velocity depending on which direction the light has been polarized. With the exception of the cubic phases, the mesophases of liquid crystals are found to be *optically anisotropic*. Thus, if light containing both *x*-polarized and *y*-polarized light travels through the liquid crystal material, it is found that the two polarizations have different indices of refraction and therefore travel along two different directions in the material. This phenomenon is called *birefringence* or *double-refraction*.

The two polarizations are termed the ordinary ray (O), which is polarized perpendicular to the plane of the optic axis and the direction of propagation, and the extraordinary ray (E), which is polarized in the plane of the optic axis and the direction of propagation. Each ray will have a different velocity ($v_o$ and $v_e$) depending upon the material under examination. The difference in the respective refractive indices ($n_o$ and $n_e$) is termed optical anisotropy or birefringence ($\Delta n$) and may be positive or negative in sign. Double refraction cannot occur along optic axes ($n_o = n_e$ and $v_o = v_e$); materials with one or two axes are termed *uniaxial* or *biaxial* respectively.

No light emerges from crossed-polarizers, because the light emerging from the first polarizer is blocked by the second polarizer. When an isotropic material is inserted between the two polarizers, there is no change to the polarization of light and thus, no light is seen through the second polarizer. When an anisotropic material is inserted between the two polarizers, there is a change to the polarization of light and some light is seen through the second polarizer. This is only true if the direction of polarization makes an angle other than 0° or 90° with the director of the liquid crystal. In passing through the liquid crystal, the light polarized along the director and the light polarized perpendicular to the director are shifted out of phase to one another, and therefore emerge as elliptically polarized light. Since the electric field of elliptically polarized light is constantly rotating completely around during each cycle, it is parallel to the polarization axis of the second polarizer twice during each cycle. Some light will therefore emerge from the second polarizer.

Liquid crystals usually appear bright when viewed between crossed-polarizers, but there are two conditions when they continue to appear black. If the polarized light incident on the liquid crystal has its polarization direction either parallel or perpendicular to the director, all light is polarized along this one direction in the liquid crystal and there is no need to consider light polarized at 90° to this direction. Since only one polarization is present, it propagates through the liquid crystal at one velocity and emerges polarized along the same direction. It is therefore blocked by the second polarizer, and no light is seen.

### *1.6.1 The Hexagonal Columnar ($D_{ho}$ and $D_{hd}$) and Discotic Nematic ($N_D$) Mesophases*

The optic axis for the hexagonal columnar ($D_{ho}$ and $D_{hd}$) mesophases is parallel to the director, and the optic axis for the discotic nematic ($N_D$) mesophase is essentially parallel to the director. Figure 1.11 represents the velocity surface of the wavefronts of both the O- and E-rays as they travel through an hexagonal columnar ($D_{ho}$ and $D_{hd}$) mesophase or a discotic nematic ($N_D$) mesophase from point A at an unspecified time. As mentioned previously, the O- and E-rays experience identical velocities and therefore have the same refractive indices along the optic axis; this is because both rays can couple only with the long molecular axis of the molecules, which is essentially identical in all directions. But, in all other directions, the velocity of the E-ray ($v_e$) is greater than that of the O-ray ($v_o$).

The optical anisotropy or birefringence is given by:

$$\Delta n = n_e - n_o$$

and the refractive indices ($n_e$ and $n_o$) are given by:

$$n_e = c / v_e \text{ and } n_o = c / v_o$$

where c is the velocity of light.

So, if $v_e > v_o$

then $n_e < n_o$,

and therefore, the optical anisotropy, $\Delta n = n_e - n_o$ = negative value.

This briefly explains why the mesophases in question are termed both uniaxial and optically negative.

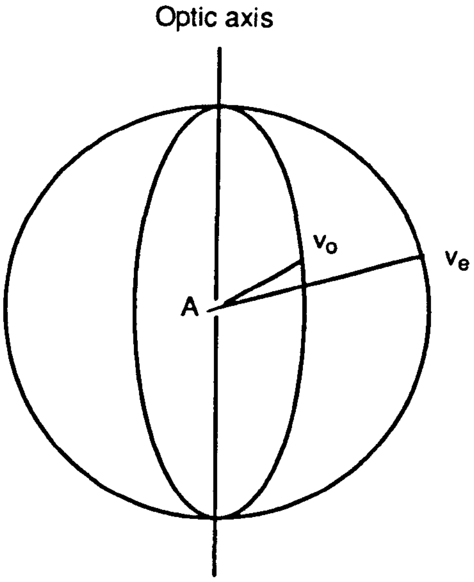

**Figure 1.11 : Wavefront velocity diagram for a uniaxial and optically negative hexagonal columnar ($D_{ho}$ and $D_{hd}$) mesophase or a discotic nematic ($N_D$) liquid crystal mesophase**

## *1.7 Applications*

Research into discotic liquid crystals has now been conducted for nearly two decades and the availability of materials has increased somewhat due to developments in the synthesis of these particular liquid crystals, which has primarily arisen because of greater involvement of more research groups.

At present, there are no applications for discotic liquid crystals, but their physical properties have suggested that some applications are possible. Semi-conductor properties have been built into discotic liquid crystals, *ie*, the 2,3,6,7,10,11-hexakis(alkyloxy)-triphenylenes, by treatment with an inorganic dopant such as a Lewis acid; doping the hexagonal disordered ($D_{hd}$) columnar mesophase with the Lewis acid converts it from an insulator into an anisotropic semiconductor.[80,81]

Formation of charge transfer complexes by doping electron-rich discotic liquid crystals with electron-poor materials, *ie*, trinitrofluorenone, have recently been of considerable interest as novel induced mesophases[58,60,70-72,74] and unique magnetic and conduction properties have been produced.[82-84]

Research by German research groups into the photoconductivity properties of the 2,3,6,7,10,11-hexakis(alkyloxy)- and 2,3,6,7,10,11-hexakis(alkylthio)triphenylenes[85,86] has been met with success as some of these materials possess the largest charge carrier mobilities ever seen for organic conductors;[86] only single crystals have larger values but these materials are difficult and expensive to make, as well as sometimes being too rigid to be useful. As a result of the fast conduction and response to light properties, sharper images could be possible if these discotic liquid crystals were able to be incorporated into flat-screen liquid crystal displays and photocopiers.

Further display-oriented research has uncovered the first discotic liquid crystals with ferroelectrically-switchable columnar mesophases;[87,88] these materials have been shown to possess quite strong electro-optical switching properties and so the possibility of employing discotic liquid crystals in devices comes ever closer.

## *1.8 Aims of the Research*

In the field of discotic liquid crystals, compounds incorporating the cores of benzene and triphenylene have been widely investigated and appear to possess the most scope for mesomorphism.[38] This is not to say that they show the most interesting mesomorphic properties, as liquid crystal materials incorporating, for example, a truxene core show some quite remarkable properties,[38] but the relative ease of synthesis of the benzene or triphenylene core units is the overriding factor in the decision to design, synthesize and investigate discotic liquid crystals incorporating these particular core units.

Research into discotic liquid crystals at Hull[89] had made some progress with the production of a number of novel discogens incorporating the triphenylene core,[89,90] so it was logical that further research of discotic liquid crystals should continue along the avenues already under scrutiny, such as the lateral methyl-substitution of the peripheral phenyl rings of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s.[89]

From the initial research data collected by Beattie,[89] a theoretical model was built[91] that relates molecular architecture to mesophase behaviour (see Figure 1.12). The idea was two-fold; firstly, by filling in the space that lay between the peripheral arms and the core with bulky and/or polar substituents, the central cores would be pushed away from each other, thus weakening the core-core interactions and hence, promote nematic phase formation by the suppression of columnar mesophase formation; and secondly, by extending the peripheral arms with spacer groups or more rigid aromatic units, *ie,* biphenyl, the mesomorphic properties would be lost - the peripheral arms would be now too rigid to allow the discotic molecules to pack into a structure suitable for mesophase formation, and so would probably promote crystal phases.

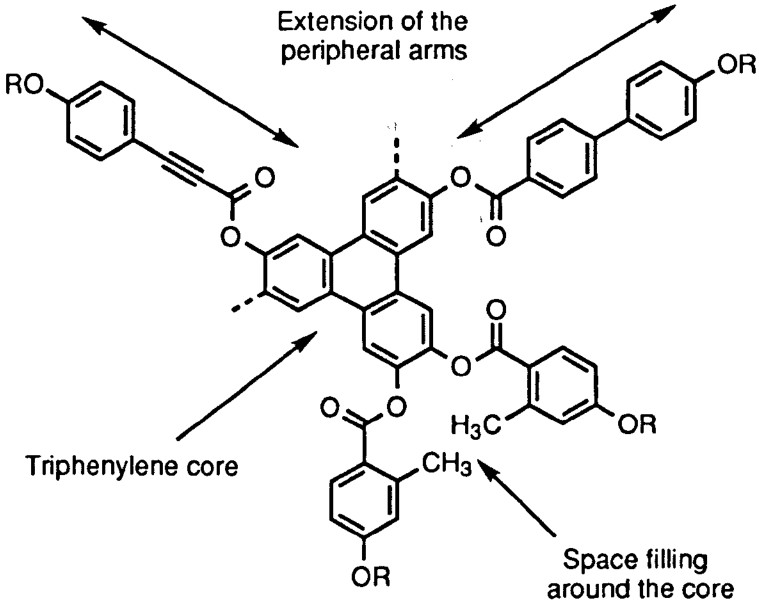

**Figure 1.12 : Schematic representation of a theoretical model for the relationship between structure and mesophase morphology**

This research programme was designed to expand further the aforementioned ideas of the theoretical model by conducting a systematic and detailed investigation of the relationship that exists between structure design and mesophase formation. A prerequisite to the research study was that, whilst altering the structure of the liquid crystal material, the discotic nematic ($N_D$) mesophase had to be hopefully maintained in the exhibited mesophases of each novel discotic liquid crystal. If nematogenic discotic liquid crystals are to be used in display devices, then the columnar mesophases must be eliminated by applying the same arguments that were originally directed towards device-oriented research of calamitic liquid crystals; these materials do not exhibit crystal phases such as B, E, G, H, J and K.

The aims of the research are further discussed at the start of each of the subsequent chapters, concentrating on the specific area under investigation.

## *1.9 Experimental Information*

### *1.9.1 Assessment of Materials*

Spectral analyses of the all final products and intermediates were carried out using a combination of infrared (IR) spectroscopy (Perkin-Elmer 783 Infrared Spectrophotometer), nuclear magnetic resonance (NMR) spectroscopy (JEOL JNM-GX270 FT NMR Spectrophotometer utilizing TMS as an internal standard), mass spectrometry (MS, Finnigan MAT 4500B EI/CI Mass Spectrometer) and elemental analysis (CHN, Fisons E1108 Elemental Analyser). Specific optical rotations, $[\alpha]_D$, were determined at ambient temperature (22-24 °C) in chloroform using a Bendix-NPL Automatic Type 143A optical unit and control unit. Thin-layer chromatographic (TLC) analyses were performed using aluminium-backed silica gel plates (60 F254 Merck) and various solvent systems, depending upon the compound in question; detection of the compounds on the TLC plate was aided by the use of a UV light source or development of the TLC plate using iodine.

The NMR data for the triphenylene esters were simplified to illustrate the important primary signals, and only one representative example is reported as all six peripheral ester moieties are identical. Mass spectral data are not reported for the final triphenylene products as their molecular masses are too large for detection by the spectrometer at Hull. Instead, elemental analysis was employed for the triphenylene compounds.

The purities of the final discotic liquid crystal compounds were initially determined by the condition of the NMR traces and the reversibility of the transition temperatures by thermal optical microscopy and DSC. The purities of the discogens were then investigated using HPLC but this was subsequently abandoned due to solubility problems. In order to calculate the purity of the materials, a single sharp peak on the analysis trace is required, but unfortunately a broad 'hump' was obtained instead indicating that the discotic material was continually dropping in and out of solution while travelling down the HPLC column.

Some measure of purity was needed and so it was decided to try gel permeation chromatography (GPC). The following pieces of equipment were used - two 300 x 7.5 mm columns (PLgel, 5μ, MIXED-D) in series with HPLC-grade THF as the mobile phase and HPLC-grade toluene as the internal standard, ERMA INC. ERC 7510 RI detector, Kontron Instruments HPLC pump 420 and Polymer Labs. software operated by a BBC computer. All the final discotic materials gave a single peak, but the software incorrectly calculated the molecular masses to be greater than they actually are. This problem is thought to be due to the shape of the discotic molecules. GPC columns are designed for polymers, *ie*, *plank*-shaped compounds, and the larger the molecule, the quicker they travel through the columns and are detected by the apparatus. As the discogens are circular, they therefore travel through the columns differently and, in this case, faster (as the software treats the materials as if they were larger than they really are).

Phase identification and the determination of transition temperatures were made by using thermal polarized light microscopy (Olympus BH2 or Zeiss Universal polarizing microscope) in conjunction with a Mettler FP90 microfurnace and FP82HT temperature controller. Photomicrographs were initially obtained using an RCA newvicon video camera (but this was later upgraded with an Hitachi KP C550 CCD colour video camera) attached to the Zeiss polarizing microscope and linked to a VY-200A Hitachi videoprinter. Differential scanning calorimetry (DSC) (Perkin-Elmer DSC7) was used as a complementary tool in the confirmation of transition temperatures and melting points of the materials, and also to determine the enthalpy of each transition. Enthalpies and transition temperatures were determined relative to an indium standard (measured onset 156.68 °C, ΔH 28.47 J $g^{-1}$; literature onset, 156.60 °C, ΔH 28.45 J $g^{-1}$).[92]

Molecular modelling studies were performed on a Silicon Graphics workstation (Indigo, XS24, 4000) using the programs QUANTA and CHARMm. Within CHARMm, the Adopted Basis Newton-Raphson (ABNr) algorithm was used to locate the molecular conformation with the lowest potential energy. The minimisation calculations were performed until the root mean square (RMS) force reached $10^{-6}$ kcal $mol^{-1}$ $Å^{-1}$. The RMS force is a direct measure of the tolerance applied to the energy gradient (*ie*, the rate of change of potential energy with step number) during each cycle of minimisation. If the average energy gradient was less than the specified value, the calculation was terminated. The molecular mechanics calculations assume the molecules to be a collection of hard particles held together by elastic forces, in the gas phase, at absolute zero and in an ideal motionless state.

### *1.9.2 Abbreviations and Nomenclature*

In the following text, IUPAC nomenclature has been employed throughout, except where clarity and consistency directed otherwise. The following lists show the abbreviations commonly used in this thesis.

#### *1.9.2.1 Chemicals*

| | | | |
|---|---|---|---|
| HMTP: | 2,3,6,7,10,11-hexamethoxytriphenylene, | | |
| HHTP: | 2,3,6,7,10,11-hexahydroxytriphenylene, | | |
| DMAP: | 4-(*N*,*N*-dimethyl)aminopyridine, | THF: | tetrahydrofuran, |
| DMF: | *N*,*N*-dimethylformamide, | *n*-BuLi: | *n*-butyllithium, |
| $CH_2Cl_2$: | dichloromethane, | $CHCl_3$: | chloroform, |
| TMS: | tetramethylsilane. | | |

#### *1.9.2.2 Physical Measurements*

K: crystalline solid,

I: isotropic liquid,

$D_X$: columnar mesophase, where X denotes the phase structure, *ie*, ho, hd, etc,

$N_D$: discotic nematic mesophase.

### *1.9.3 Purification and Drying of Solvents*

The following procedures were carried out in accordance with the recommendations laid out in:

D. D. Perrin and W. L. F. Amarago - *Purification of Laboratory Chemicals*, 3rd ed., Pergamon Press, Oxford, 1988.

Dichloromethane: freshly distilled (41-42 °C) from calcium hydride or phosphorus pentoxide, and then stored over molecular sieves (4Å);

Tetrahydrofuran: freshly distilled (65-67 °C) from potassium and benzophenone, and then stored over molecular sieves (4Å);

Pyridine: freshly distilled (113-115 °C) from potassium hydroxide pellets, and then stored over potassium hydroxide pellets;

Diethyl ether: stored over sodium wire for at least 48 hours prior to use;

Chloroform: freshly distilled (61-62 °C) from calcium chloride, and then stored over calcium chloride; amylene was used as the stabilizer.

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# *PART II*
# *THE RESEARCH*

# *CHAPTER 2*

# *Synthesis of the Triphenylene Cores*

## *2.1 Introduction*

After scrutiny of several reviews[1-3] and a number of published reports of research on triphenylene-based discotic liquid crystals,[3-6] it appeared that two key intermediates had to be synthesized if work was to be conducted into such discotic liquid crystals. These were 2,3,6,7,10,11-hexahydroxytriphenylene (**3**) and 2,3,6,7,10,11-hexabromotriphenylene (**7**); compound **3** for ether and ester-linked peripheral arms and compound **7** for alkyne-linked peripheral arms.

The syntheses of 2,3,6,7,10,11-hexahydroxytriphenylene (**3**) and 2,3,6,7,10,11-hexabromotriphenylene (**7**) are detailed in Schemes 2.1 and 2.2 respectively. The preparations of both compounds were crucial for the synthesis of the target discogens.

## *2.2 Experimental*

The preparation of 2,3,6,7,10,11-hexamethoxytriphenylene (**2**) was reported by Matheson, Musgrave and Webster[7-9] and modified by ICI.[10] The reaction involved the oxidative trimerization of three equivalents of 1,2-dimethoxybenzene (veratrole) with one equivalent of tetrachloro-1,4-benzoquinone (chloranil) (*Method A*). Although the initial reaction was simple enough, the work up was an extremely long and laborious procedure which required large quantities of solvents. The crude product was purified by column chromatography and the best results were obtained when TLC grade silica gel was used. However, patience was a virtue, and despite the very low yields (on average, 15%) a remarkably clean and highly pure product was obtained that did not require recrystallization. Fortunately, this procedure was only carried out three times as on average, it took three weeks to obtain just one batch of compound **2**.

An alternative method was developed in 1965 by Piatelli *et al.*[11] involving the use of iron(III) chloride and water in the oxidative cyclization of 1,2-dimethoxybenzene (veratrole) to produce 2,3,6,7,10,11-hexamethoxytriphenylene (**2**), but yields were very low. Recently, this method has received much new attention and has undergone further refinements by Boden *et al.*[12,13] and Naarmann *et al.*[14] to allow near quantitative yields of compound 3. This new method (*Method B*) has replaced the original procedure and very large batches of the required intermediate (**2**) can be obtained in just one day (compared to three weeks using *Method A*).

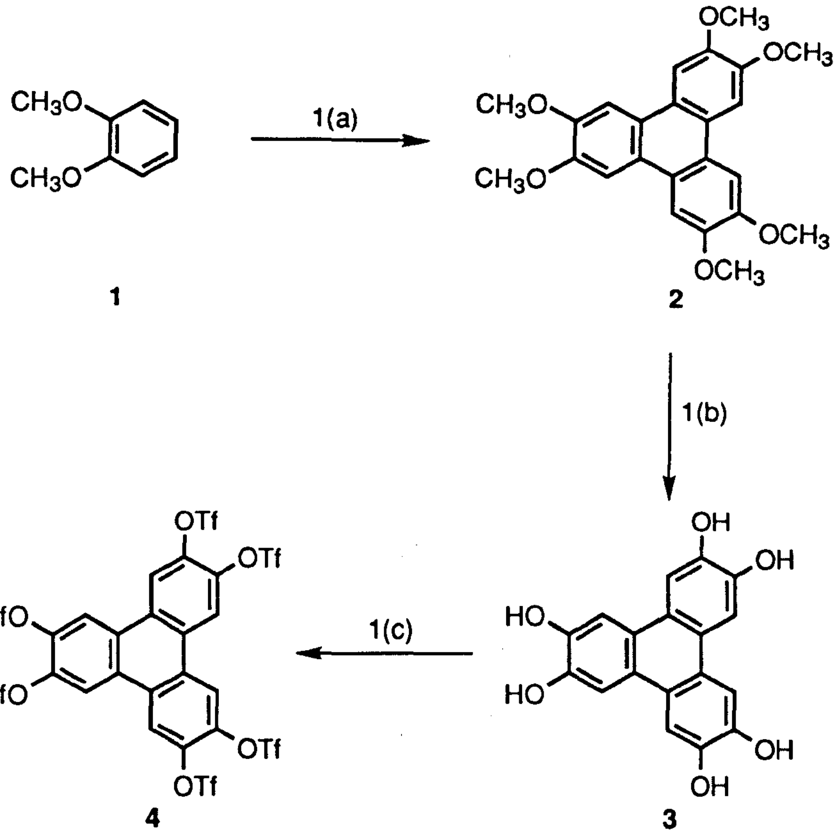
The demethylation of 2,3,6,7,10,11-hexamethoxytriphenylene (**2**) to give 2,3,6,7,10,11-hexahydroxytriphenylene (**3**) was expected to be a demanding process because of the required removal of six methyl substituents. The use of 48% (w/v) hydrobromic acid and glacial acid (reported by Piatelli *et al.*[11]) by Beattie[10] resulted in unsatisfactorily low yields, but the use of boron tribromide (reported by McOmie *et al.*[15]) resulted in better quantities of the desired product (**3**).[10] The latter procedure was utilized in this project and is detailed in Scheme 2.1; near quantitative yields were obtained on every application of this method, whether on a small or a large scale, despite previous reports of moderate yields[10] or the use of recrystallization.[10] The scale of the reaction was never raised to a level where more than 200 g of boron tribromide was needed as this material is extremely hazardous to handle. 2,3,6,7,10,11-Hexahydroxytriphenylene (**3**) was then used in the synthesis of the target discotic liquid crystals, which are detailed in the following chapters.

Triphenylen-2,3,6,7,10,11-hexayl hexakistriflate (**4**) was synthesized as an alternative to the use of instead of 2,3,6,7,10,11-hexabromotriphenylene (**7**) in the synthesis of directly-linked or alkyne-linked discotic liquid crystals. Compound **4** was produced by the use of trifluoromethanesulfonic anhydride[16] and a suitable base, in this case pyridine.

Triphenylene (**6**) is commercially available from Aldrich Chemical Co. but it is quite expensive. It can be prepared *via* the photocyclization of *ortho*-terphenyl[17-21] and self-condensation of 1,2-dihalogenobenzenes,[22,23] but a number of other methods do also exist, such as the self-condensation of cyclohexanone using sulfuric acid;[24] from 2-cyclohexyl-1-phenylcyclohexan-1-ol[25] or 2-(1-cyclohexen-1-yl)-1-phenylcyclohexan-1-ol[26] by dehydrogenation; from 9-phenanthryl magnesium bromide and succinic anhydride followed by reduction, cyclization and dehydrogenation;[27] by electrolytic oxidation of cyclohexanone;[28] whereas hexamethoxytriphenylene (**2**) is obtained with electrochemical trimerization of 1,2-dimethoxybenzene (veratrole) on a platinium electrode.[29] Modifications of the methods of self-condensation of mono- and dihalogenobenzenes[22,23,30,31] have been reported recently by Fossatelli and Brandsma[32] which have proven to be quite efficient in synthesizing triphenylene (**6**) and this method was used in Scheme 2.2 with comparable results.

Recently, the use of palladium-catalyzed-cross-coupling reactions using arylzinc halides[33] (combined with the photocyclization method[17-21]) or using boronic acids[34] (combined with the iron(III) chloride-catalyzed oxidative cyclization[12-14]) to synthesize asymmetrically-substituted triphenylene-based liquid crystals have been reported. Asymmetrically-substituted triphenylene-based liquid crystals were originally synthesized by Tinh *et al.*[35] using the Musgrave and Webster procedure (Scheme 2.1, 1(a) *Method A*) but unfortunately, four differently substituted triphenylenes were obtained because two differently substituted 1,2-dialkoxybenzenes were used in the synthesis and each final material had to be laboriously separated and identified as each final compound was virtually identical with one another. This was not a problem using the two new methods[33,34] because the triphenylene core was built gradually and each stage of the building process was carefully monitored so that only the desired intermediate was obtained before the next reaction in the sequence was tackled.

Triphenylene (**6**) was successfully brominated in all the desired positions using a procedure detailed by Breslow *et al.*[36] This material was then used in the synthesis of the target materials, which are detailed in the following chapters.



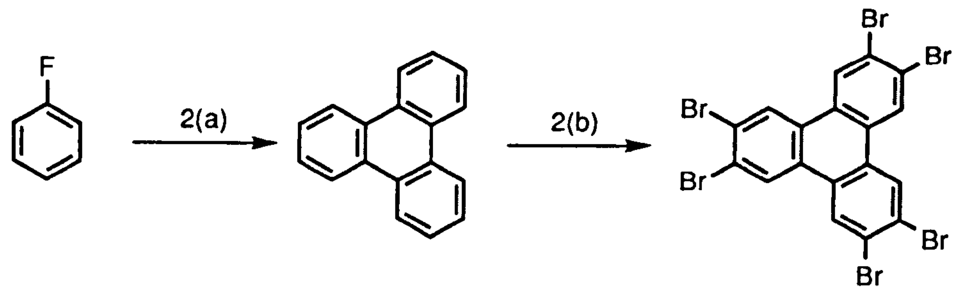
1(a) ..... *Method A* 70% (v/v) $H_2SO_4$, tetrachloro-1,4-benzoquinone, 8 days.

1(a) ..... *Method B* $FeCl_3$, conc. $H_2SO_4$, $CH_2Cl_2$.

1(b) ..... (i) $BBr_3$, $CH_2Cl_2$; (ii) $H_2O$.

1(c) ..... Trifluoromethanesulfonic anhydride, pyridine.

**Scheme 2.1 : Synthetic route for the preparation of 2,3,6,7,10,11-hexamethoxytriphenylene (2), 2,3,6,7,10,11-hexahydroxytriphenylene (3) and triphenylen-2,3,6,7,10,11-hexayl hexakistriflate (4)**



**5** **6** **7**

2(a) ..... (i) *n*-BuLi, THF, -50 °C; (ii) NaOBu$^t$, THF, -100 °C.

2(b) ..... $Br_2$, Fe powder, nitrobenzene.

**Scheme 2.2 : Synthetic route for the preparation of triphenylene (6) and 2,3,6,7,10,11-hexabromotriphenylene (7)**

### *2.2.1 Preparation of the Triphenylene Cores* (2, 3, 4, 6 and 7)

*2,3,6,7,10,11-Hexamethoxytriphenylene (HMTP)* (2)

*Method A*

1,2-Dimethoxybenzene (**1**, veratrole) (90.0 g, 0.65 mol) was added to a stirred suspension of tetrachloro-1,4-benzoquinone (chloranil) (200.0 g, 0.81 mol) in aqueous sulfuric acid (70 % v/v, 1400 ml) under a nitrogen atmosphere. The reaction mixture was stirred for eight days and then poured onto ice (5.0 kg). The resultant mixture was diluted with water (20,000 ml) and the suspension was allowed to stand overnight. The crude product was filtered off and washed successively with water (4000 ml), water/methanol (8:1, 4500 ml), methanol/water (10:1, 2200 ml) and finally methanol (2500 ml). The crude product was then dissolved in chloroform and filtered to remove any undissolved material. The solvent was removed and the crude product was washed successively with toluene (750 ml, x3) and then acetone (600 ml, x2). The crude product was taken up in chloroform and purified by column chromatography (TLC grade silica gel/chloroform). The pure product was isolated as a light-grey powder from the fractions by precipitation with methanol/toluene (2:1, 900 ml) and collected by filtration.

Yield: 15.0 g (17%) Mp: 314-315 °C (lit. 314-315 °C$^{7-9}$)

$^1$H NMR ($CDCl_3$ and TMS) δ: 4.15(18H, s), 7.55(6H, s).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 3000, 1625, 1520, 1465, 1265, 1050, 835, 780.

MS (*m/z*): 408($M^+$), 204, 188, 159, 138, 110, 82, 69, 58.

*Method B*

1,2-Dimethoxybenzene (**1**, veratrole) (23.0 g, 0.166 mol) was added slowly to a stirred solution of iron(III) chloride (81.0 g, 0.50 mol) and conc. $H_2SO_4$ (1.6 g) in $CH_2Cl_2$ (500 ml). Hydrogen chloride gas was emitted and the reaction mixture began to boil (no heat source). The reaction mixture was stirred for a further 2 h and the solid product was filtered off. The product was washed with large amounts of methanol to leave a light grey solid which was dried *in vacuo*.

Yield: 19.7 g (86%)

Spectral data as described in *Method A*.

*2,3,6,7,10,11-Hexahydroxytriphenylene (HHTP)* (**3**)

Boron tribromide (75.0 g, 0.30 mol) was added dropwise to a stirred, cooled (-78 °C) solution of compound **2** (12.0 g, 0.03 mol) in dry $CH_2Cl_2$ (800 ml) under dry nitrogen. The reaction mixture was allowed to warm to room temperature overnight, and diluted very carefully with water. The $CH_2Cl_2$ was removed, the crude product was filtered off and recrystallized from water to yield grey needles.

Yield: 11.4 g (98%) Mp: >310 °C (lit. >310 °C[11])

$^1H$ NMR ($CDCl_3$ and TMS) δ: 7.70(6H, s), 8.75(6H, s).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 3500-3000(broad), 1630, 1540, 1450, 1230, 1150, 1000, 860, 790, 620.

MS (*m/z*): 324($M^+$), 295, 271, 249, 221, 214, 197, 175, 162, 145.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakistriflate* (**4**)

Trifluoromethanesulfonic anhydride (26.1 g, 92.6 mmol) was added dropwise to a stirred, cooled (0 °C) solution of compound **3** (3.0 g, 9.26 mmol) in pyridine (100 ml) under dry nitrogen. The reaction mixture was stirred overnight and then poured onto a mixture of conc. HCl and ice. The crude product was extracted into ether (150 ml, x2), washed with water (200 ml), 10% sodium hydrogen carbonate (200 ml), water (200 ml) and dried ($MgSO_4$). The solvent was removed, the crude product was purified by column chromatography (silica gel/$CH_2Cl_2$) to yield a sandy coloured solid.

| | |
|---|---|
| Yield: 3.59 g (35%) | |
| $^1$H NMR ($CDCl_3$ and TMS) $\delta$: | 8.54(6H, s). |
| IR (KBr) $\nu_{max}$ $cm^{-1}$: | 1510, 1430, 1230, 1130, 1000, 890, 855, 810, 770, 680, 610, 505. |
| MS (*m*/*z*): | No data obtainable. |

*Triphenylene* (**6**)

Fluorobenzene (11.5 g, 0.12 mol) was added to a stirred, cooled (-50 °C) solution of *n*-butyllithium (63.0 ml, 1.6 mol $dm^{-3}$ in hexane, 0.10 mol) and then the reaction mixture was further cooled to -100 °C. A solution of sodium *tert*-butoxide (9.6 g, 0.10 mol) in THF (100 ml) was added over 2 mins whilst maintaining -100 °C. The solution was stirred for 10 mins and then warmed to -30 °C, at which point a strong exothermic reaction began. The whole reaction vessel was *promptly* immersed in liquid nitrogen and the temperature rose to just above 20 °C for a few seconds. The resulting black slurry was treated with ice (100 g) and then the product was extracted with ether (50 ml, x3). The combined organic layers were dried ($MgSO_4$) and the solvent was removed *in vacuo*. The product was recrystallized from chloroform to yield colourless needles.

| | |
|---|---|
| Yield: 4.0 g (53%) | Mp: 189-191 °C (lit. 189-191 °C[37]) |
| $^1$H NMR ($CDCl_3$ and TMS) $\delta$: | 7.65(6H, ddd), 8.65(6H, dd). |
| IR (KBr) $\nu_{max}$ $cm^{-1}$: | 1490, 1430, 1240, 740, 620. |
| MS (*m*/*z*): | 228($M^+$), 113. |

*2,3,6,7,10,11-Hexabromotriphenylene* (**7**)

Bromine (24.0 g, 8 ml, 0.15 mol) was added dropwise over 5 mins to a solution of compound **6** (4.0 g, 0.018 mol) and iron powder (0.36 g) in nitrobenzene (150 ml). The solution was allowed to stand for 10 h and then heated under reflux at 200 °C for 2 h. The mixture was cooled, mixed with ether (200 ml) and filtered. The crude product was recrystallized from 1,2-dichlorobenzene to yield an off-white solid.

Yield: 9.0 g (72%) Mp: 500-502 °C (lit. 500-502 °C; sealed capillary, dec.[36])

$^1$H NMR (CDCl$_3$ and TMS) δ: No distinguishable signal.

$^1$H NMR (C$_2$D$_2$Cl$_4$ at 145 °C) δ: 8.74(6H, s).[36]

IR (KBr) $\nu_{max}$ cm$^{-1}$: 1450, 1360, 1070, 870, 860, 655, 430.

MS ($m/z$): 708(M$^+$), 706(M$^+$), 704(M$^+$), 702(M$^+$), 700(M$^+$), 698(M$^+$), 696(M$^+$), 625, 623, 621, 619, 545, 543, 541, 539, 537, 382, 222, 111.

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# *CHAPTER 3*

# *Lateral Substitution in the Peripheral Moieties of Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-alkoxybenzoate)s: Dimethyl-substituted Systems*

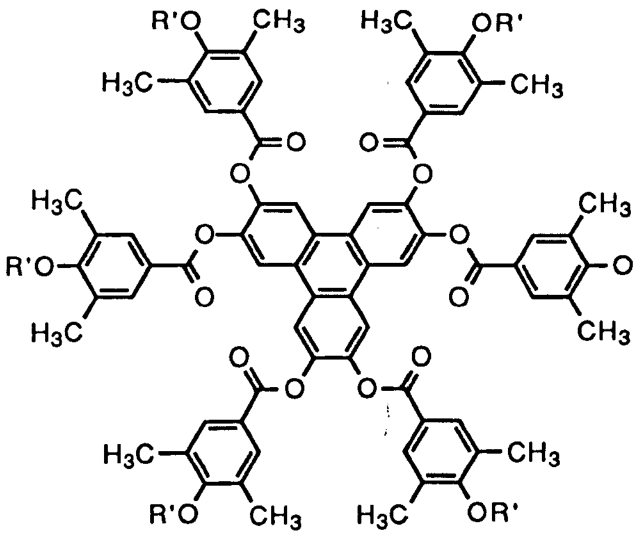
## *3.1 Introduction*

Lateral substitution in the peripheral phenyl groups of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s was first investigated by Beattie[1] using methyl substituents positioned either *ortho* to the terminal alkoxy chain (the *outer* position) or *ortho* to the ester linking group (the *inner* position). A suppression of the columnar mesophases by the methyl-substituents in both substituted positions was reported. Reductions in the melting points and clearing temperatures were also observed, but this was especially noticable in the inner-substituted series.

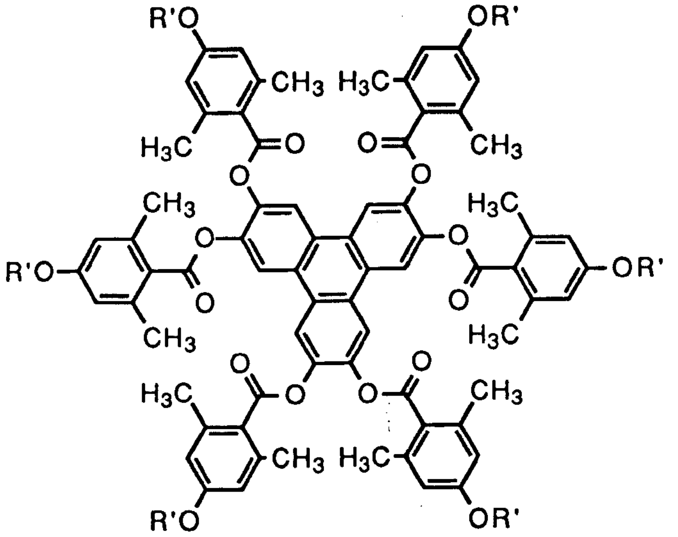
Examination of the effects of lateral substitution of the peripheral phenyl rings was developed by logically incorporating *two* methyl groups, one on either side of each of the phenyl rings, again *ortho* to the alkoxy chain or *ortho* to the ester linking group. The scope of the investigation was expanded by incorporating branched methyl substituents in the terminal alkoxy chain in order to determine further how the mesophase behaviour would be affected.

It is well known for calamitic (*rod*-like) materials that lateral substitution in the core and/or branching in the terminal peripheral aliphatic chains can reduce melting points and also radically affect mesophase morphology and transition temperatures.[2] Our objectives were to position bulky groups in the lateral positions of the peripheral phenyl groups and the terminal chains of triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoates), in order to investigate the effects of their presence on phase morphology, transition temperatures and melting points.

Thus, in this chapter the synthesis and properties of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-3,5-dimethylbenzoate)s and (-2,6-dimethylbenzoate)s are discussed (see structures **I** and **II**, Figure 3.1).



I



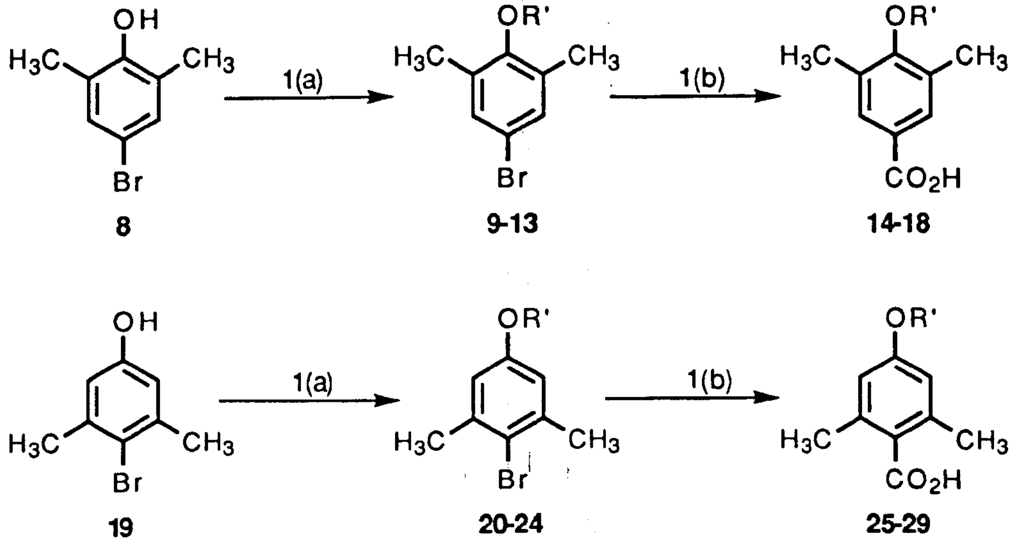
II

R' = $C_nH_{2n+1}$ (n = 6, 8, 10 and 12) or $C_6H_{13}CH(CH_3)$

**Figure 3.1 : Structures of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-3,5-dimethylbenzoate)s or (-2,6-dimethylbenzoate)s (structures I and II)**

## *3.2 Experimental*

The materials were prepared by the routes shown in Schemes 3.1 and 3.2. The preparation of 2,3,6,7,10,11-hexahydroxytriphenylene (**3**, HHTP) has been reported in Chapter 2. The various substituted acids were prepared by the synthetic routes shown in Scheme 3.1. Compounds **8** and **19** were purchased from Aldrich Chemical Co. and were *O*-alkylated with appropriate *n*-alkyl bromides in good yields using anhydrous potassium carbonate in butanone. In the case of the 1-methylheptyloxy derivatives, *O*-alkylation was achieved by using racemic octan-2-ol in the presence of diethyl azodicarboxylate (DEAD) and triphenylphosphine.[3] The replacement of the bromine in compounds **9-13** and **20-24** was achieved by lithiation using *n*-butyllithium at -78 °C; in each case the reaction mixture was then poured onto a slurry of solid $CO_2$ and dry ether, acidified, and the product purified (compounds **14-18** and **25-29**). The final liquid-crystalline materials (**30-34** and **35-39**) were prepared by the esterification of HHTP with the respective 4-alkoxy-3,5- or -2,6-dimethylbenzoyl chlorides in the presence of pyridine (Scheme 3.2).

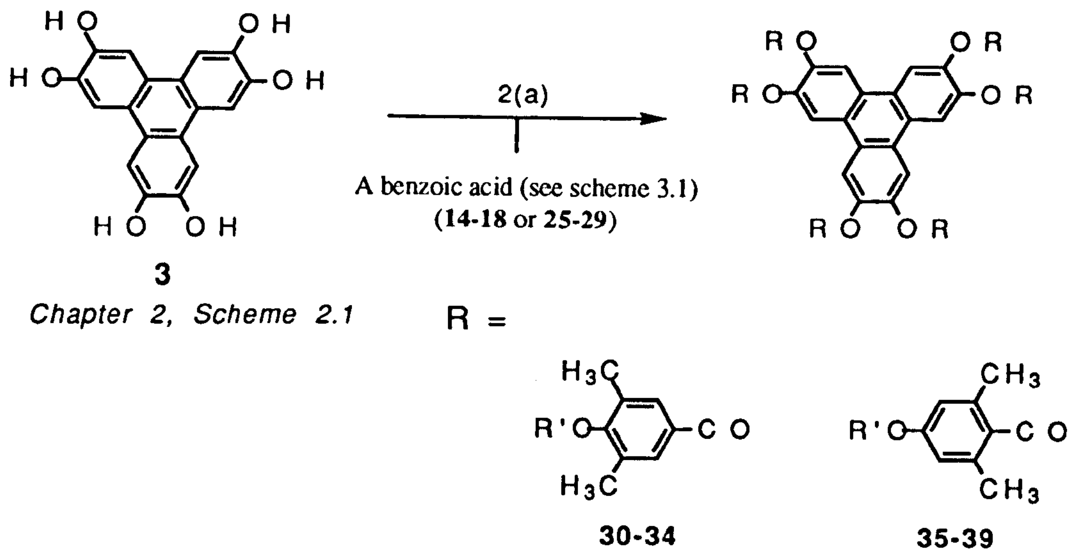


R' = $C_nH_{2n+1}$ (n = 6, 8, 10 and 12) or $C_6H_{13}CH(CH_3)$

1(a) ..... RBr, $K_2CO_3$, butanone; or octan-2-ol, DEAD, $PPh_3$, THF.

1(b) ..... (i) *n*-BuLi, THF; (ii) $CO_2$ (solid), $Et_2O$.

**Scheme 3.1 : Synthetic route for the preparation of the 4-alkoxy-3,5-dimethylbenzoic and -2,6-dimethylbenzoic acids (14-18 and 25-29)**



R' = $C_nH_{2n+1}$ (n = 6, 8, 10 and 12) or $C_6H_{13}CH(CH_3)$

2(a) ..... Acid chloride (oxalyl chloride, DMF, $CH_2Cl_2$), pyridine.

**Scheme 3.2 : Synthetic route for the preparation of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-3,5-dimethylbenzoate)s and (-2,6-dimethylbenzoate)s (30-34 and 35-39)**

### *3.2.1 Preparation of the 4-*n*-Alkoxy-1-bromo-3,5- or 4-*n*-Alkoxy-1-bromo-2,6-dimethylbenzenes* (9-12 and 20-23)

The general synthetic method is exemplified by the following procedure.

*1-Bromo-4-hexyloxy-3,5-dimethylbenzene* (9)

A solution of 1-bromohexane (9.08 g, 0.055 mol) in butanone (50 ml) was added dropwise to a stirred mixture of 4-bromo-2,6-dimethylphenol (**8**) (10.0 g, 0.049 mol) and anhydrous potassium carbonate ($K_2CO_3$) (30.0 g, 0.2 mol) in butanone (200 ml). The stirred mixture was then heated under reflux for 24 h. The $K_2CO_3$ was filtered off and the solvent was removed. The residue was distilled under reduced pressure to yield a colourless liquid.

| | |
|---|---|
| Yield: 12.95 g (93%) | Bp: 106-120 °C at 0.01 mmHg |
| $^1$H NMR ($CDCl_3$ and TMS) $\delta$: | 0.90(3H, t), 1.35(6H, m), 1.75(2H, m), 2.20(6H, s), 3.70(2H, t), 7.10(2H, s). |

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2810, 1450, 1350, 1200, 980, 830.

MS ($m/z$): 286(M$^+$), 284(M$^+$), 201, 200, 121, 103, 91, 85, 76, 65, 55, 42.

*1-Bromo-3,5-dimethyl-4-octyloxybenzene* **(10)**

Yield: 12.45 g (88%) Bp: 120-138 °C at 0.01 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.85(3H, t), 1.35(10H, m), 1.75(2H, m), 2.20(6H, s), 3.70(2H, t), 7.10(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2900, 2820, 1450, 1345, 1190, 980, 830.

MS ($m/z$): 314(M$^+$), 312(M$^+$), 201, 200, 137, 122, 97, 71, 57, 43.

*1-Bromo-4-decyloxy-3,5-dimethylbenzene* **(11)**

Yield: 12.00 g (88%) Bp: 150-160 °C at 0.01 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.85(3H, t), 1.25(14H, m), 1.75(2H, m), 2.20(6H, s), 3.70(2H, t), 7.10(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1465, 1380, 1200, 860.

MS ($m/z$): 342(M$^+$), 340(M$^+$), 201, 200, 183, 135, 121, 104, 91, 85, 77, 71, 43.

*1-Bromo-4-dodecyloxy-3,5-dimethylbenzene* **(12)**

Yield: 12.91 g (87%) Bp: 160-175 °C at 0.01 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.85(3H, t), 1.35(18H, m), 1.75(2H, m), 2.20(6H, s), 3.70(2H, t), 7.10(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2910, 2820, 1440, 1340, 1180, 960, 825.

MS ($m/z$): 370(M$^+$), 368(M$^+$), 314, 202, 201, 149, 137, 121, 97, 85, 71, 43.

*1-Bromo-4-hexyloxy-2,6-dimethylbenzene* **(20)**

Yield: 7.81 g (56%) Bp: 125-135 °C at 0.1 mmHg

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.85(3H, t), 1.25(6H, m), 1.75(2H, m), 2.75(6H, s), 3.85(2H, t), 6.60(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2960, 2860, 1560, 1460, 1320, 1170, 850.

MS (*m*/*z*): 286(M$^+$), 284(M$^+$), 201, 200, 185, 171, 134, 121, 103, 91, 77, 65, 55, 51.

*1-Bromo-2,6-dimethyl-4-octyloxybenzene* (**21**)

Yield: 9.63 g (68%) Bp: 120-140 °C at 0.05 mmHg

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.85(3H, t), 1.25(10H, m), 1.75(2H, m), 2.35(6H, s), 3.85(2H, t), 6.60(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1560, 1460, 1320, 1170, 820.

MS (*m*/*z*): 314(M$^+$), 312(M$^+$), 213, 201, 200, 185, 135, 121, 104, 91, 77, 62, 55.

*1-Bromo-4-decyloxy-2,6-dimethylbenzene* (**22**)

Yield: 10.00 g (74%) Bp: 150-170 °C at 0.01 mmHg

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.85(3H, t), 1.25(14H, m), 1.75(2H, m), 2.35(6H, s), 3.85(2H, t), 6.60(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1580, 1460, 1320, 1170, 1070, 1020, 850.

MS (*m*/*z*): 342(M$^+$), 340(M$^+$), 201, 200, 185, 135, 121, 104, 91, 83, 69, 43.

*1-Bromo-4-dodecyloxy-2,6-dimethylbenzene* (**23**)

Yield: 11.79 g (80%) Bp: 160-175 °C at 0.01 mmHg

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.85(3H, t), 1.25(18H, m), 1.75(2H, m), 2.35(6H, s), 3.85(2H, t), 6.60(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2900, 2820, 1560, 1450, 1310, 1150, 820.

MS (*m*/*z*): 370(M$^+$), 368(M$^+$), 314, 201, 200, 149, 137, 121, 97, 85, 71, 43.

### *3.2.2 Preparation of 1-Bromo-3,5- or 1-Bromo-2,6-dimethyl-4-(1-methylheptyloxy)-benzene* (13 and 24)

The general synthetic method is exemplified by the following procedure.

*1-Bromo-3,5-dimethyl-4-(1-methylheptyloxy)benzene* (**13**)

A solution of triphenylphosphine (11.79 g, 0.045 mol) in dry THF (100ml) was added to a stirred mixture of 4-bromo-2,6-dimethylphenol (**8**) (9.0 g, 0.045 mol), octan-2-ol (5.85 g, 0.045 mol) and diethyl azodicarboxylate (DEAD) (7.83 g, 0.045 mol) in dry THF (100 ml) under dry nitrogen. The solution was stirred overnight and the solvent was removed. The crude product was purified by column chromatography (silica gel/dichloromethane) to give a liquid which was distilled under reduced pressure to yield a colourless liquid.

Yield: 11.56 g (82%) Bp: 100-117 °C at 0.07 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.85(3H, t), 1.35(13H, m), 2.30(6H, s), 4.00(1H, m), 7.10(2H, s).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 2920, 2860, 1465, 1380, 1200, 1110, 850.

MS (*m*/*z*): 314($M^+$), 312($M^+$), 201, 200, 121, 104, 91, 77, 65, 57, 51.

*1-Bromo-2,6-dimethyl-4-(1-methylheptyloxy)benzene* (**24**)

Yield: 10.84 g (77%) Bp: 100-117 °C at 0.07 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.85(3H, t), 1.30(13H, m), 2.35(6H, s), 4.30(1H, m), 6.60(2H, s).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 2920, 2860, 1580, 1460, 1315, 1165, 1020, 855.

MS (*m*/*z*): 314($M^+$), 312($M^+$), 201, 200, 171, 148, 131, 121, 104, 91, 77, 65, 55, 51.

### *3.2.3 Preparation of the 4-Alkoxy-3,5- or 4-Alkoxy-2,6-dimethylbenzoic Acids* **(14-18 and 25-29)**

The general synthetic method is exemplified by the following procedure.

*4-Hexyloxy-3,5-dimethylbenzoic Acid* **(14)**

A solution of *n*-butyllithium (4.5 ml, 10.0 M in hexane, 0.045 mol) was added dropwise to a stirred, cooled (-78 °C) solution of 1-bromo-4-hexyloxy-3,5-dimethylbenzene (**9**) (12.95 g, 0.045 mol) in dry THF (250 ml) under dry nitrogen. The stirred mixture was maintained under these conditions for 1 h, and then poured into a slurry of solid carbon dioxide and dry ether. The product was acidified with 36% hydrochloric acid, and extracted into ether (200 ml) which was washed with water (300 ml). The ethereal extract was dried ($MgSO_4$) and the solvent removed to give a colourless solid which was recrystallized from petroleum ether (bp 40-60 °C, 75 ml) to yield colourless crystals.

Yield: 9.38 g (84%) Mp: 93-95 °C

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.30(6H, m), 1.85(2H, m), 2.35(6H, s), 3.80(2H, t), 7.80(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3200-2400(broad), 2920, 2860, 1675, 1600, 1440, 1310, 1210.

MS (*m*/*z*): 250(M$^+$), 202, 179, 166, 149 ,121, 103, 91, 85, 77, 65, 43.

*3,5-Dimethyl-4-octyloxybenzoic Acid* **(15)**

Yield: 9.06 g (82%) Mp: 79-81 °C

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.30(10H, m), 1.80(2H, m), 2.35(6H, s), 3.80(2H, t), 7.75(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3200-2400(broad), 2920, 2860, 1690, 1600, 1420, 1310, 1210.

MS (*m*/*z*): 278(M$^+$), 179, 166, 149, 135, 121, 102, 91, 77, 65, 57, 43.

### *4-Decyloxy-3,5-dimethylbenzoic Acid* (**16**)

Yield: 4.44 g (37%) Mp: 77-78 °C

$^1H$ NMR ($CDCl_3$ and TMS) $\delta$: 0.85(3H, t), 1.30(14H, m), 1.85(2H, m), 2.35(6H, s), 3.85(2H, t), 7.80(2H, s).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 3200-2400(broad), 2920, 2860, 1690, 1600, 1430, 1340, 1210.

MS (*m/z*): 306($M^+$), 166, 149, 121, 107, 85, 77, 71, 57, 43.

### *4-Dodecyloxy-3,5-dimethylbenzoic Acid* (**17**)

Yield: 8.02 g (69%) Mp: 80-81 °C

$^1H$ NMR ($CDCl_3$ and TMS) $\delta$: 0.85(3H, t), 1.30(18H, m), 1.80(2H, m), 2.35(6H, s), 3.80(2H, t), 7.80(2H, s).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 3200-2400(broad), 2920, 2850, 1690, 1600, 1420, 1320, 1205.

MS (*m/z*): 334($M^+$), 298, 186, 166, 149, 121, 97, 91, 77, 57, 43.

### *3,5-Dimethyl-4-(1-methylheptyloxy)benzoic Acid* (**18**)

Yield: 5 g (crude) Mp: impure*

$^1H$ NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(13H, m), 2.35(6H, s), 4.25(1H, m), 7.75(2H, s).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 3500-2500(broad), 2920, 2860, 1680, 1600, 1480, 1310, 1200, 1110.

MS (*m/z*): 278($M^+$), 199, 166, 148, 120, 91, 77, 69, 55.

---

[*] The amount of impurity found was not too great, therefore the crude product was used in the esterification reaction of HHTP.

*4-Hexyloxy-2,6-dimethylbenzoic Acid* **(25)**

Yield: 3.35 g (50%) Mp: 77-78 °C

$^1$H NMR ($CDCl_3$ andTMS) $\delta$: 0.90(3H, t), 1.35(6H, m), 1.75(2H, m), 2.45(6H, s), 3.95(2H, t), 6.60(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3400-2500(broad), 2920, 2860, 1700, 1660, 1600, 1320, 1270, 1015, 850.

MS (*m/z*): 250(M$^+$), 179, 166, 148, 121, 91, 77, 58.

*2,6-Dimethyl-4-octyloxybenzoic Acid* **(26)**

Yield: 5.17 g (60%) Mp: 88-90 °C

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(10H, m), 1.75(2H, m), 2.45(6H, s), 3.95(2H, t), 6.60(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3300-2500(broad), 2920, 2860, 1670, 1600, 1440, 1310, 1280, 1170, 1050, 850.

MS (*m/z*): 278(M$^+$), 179, 166, 148, 137, 119, 90, 77, 69, 65, 57.

*4-Decyloxy-2,6-dimethylbenzoic Acid* **(27)**

Yield: 2.64 g (30%) Mp: 80-81 °C

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.85(3H, t), 1.25(14H, m), 1.75(2H, m), 2.40(6H, s), 3.95(2H, t), 6.60(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3400-2600(broad), 2920, 2860, 1700, 1680, 1600, 1440, 1340, 1175, 1060, 845.

MS (*m/z*): 306(M$^+$), 166, 136, 122, 91, 77, 69, 55.

*4-Dodecyloxy-2,6-dimethylbenzoic Acid* **(28)**

Yield: 7.72 g (72%) Mp: 86-87 °C

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.85(3H, t), 1.25(18H, m), 1.75(2H, m), 2.40(6H, s), 3.95(2H, t), 6.60(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3400-2600(broad), 2920, 2860, 1700, 1680, 1600, 1420, 1320, 1300, 1170, 1060, 845.

| | |
|---|---|
| MS (*m*/*z*): | 334(M$^+$), 319, 289, 179, 166, 148, 138, 120, 97, 87, 83, 69. |

*2,6-Dimethyl-4-(1-methylheptyloxy)benzoic Acid* (**29**)

| | |
|---|---|
| Yield: 4.98 g (58%) | Mp: 63-65 °C |
| $^1$H NMR (CDCl$_3$ and TMS) δ: | 0.85(3H, t), 1.30(13H, m), 2.45(6H, s), 4.40(1H, m), 6.60(2H, s). |
| IR (KBr) $\nu_{max}$ cm$^{-1}$: | 3400-2500(broad), 2960, 2920, 1680, 1600, 1320, 1180, 850. |
| MS (*m*/*z*): | 278(M$^+$), 199, 166, 148, 120, 91, 77, 69, 55. |

### 3.2.4 *Preparation of the Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-alkoxy-3,5-benzoate)s or (-2,6-dimethylbenzoate)s* (30-34 and 35-39)

The general synthetic method for the preparation of the hexa-esters is exemplified by the following method.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-hexyloxy-3,5-dimethylbenzoate)* (**30**)

A solution of oxalyl chloride (5.04 g, 0.04 mol) in dry dichloromethane (50 ml) was added dropwise to a stirred solution of 4-hexyloxy-3,5-dimethylbenzoic acid (**14**) (9.00 g, 0.036 mol) and DMF (10 drops) in dry dichloromethane (100 ml). The reaction mixture was stirred at room temperature overnight and the solvent and the excess of oxalyl chloride were removed *in vacuo*. The residual acid chloride was used immediately without further purification.

A mixture of HHTP (**3**) (1.16 g, 0.0036 mol) in dry pyridine (100ml) was added to the residual acid chloride (0.036 mol) under dry nitrogen, and the resulting mixture was heated under reflux for 8 h. The reaction mixture was cooled and poured onto a mixture of concentrated hydrochloric acid and ice. The crude product was extracted into ether (150 ml, x2), washed with water (200 ml), 10% sodium hydrogen carbonate (200 ml) water (200 ml) and dried (MgSO$_4$). The solvent was removed, the crude product was purified by column chromatography (silica gel/dichloromethane) and recrystallised from ethanol/ethyl acetate to yield a white solid.

Yield: 4.09 g (66%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(6H, m), 1.75(2H, m), 2.10(6H, s), 3.70(2H, t), 7.65(2H, s), 8.45(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1310, 1170.

CHN analysis: % expected - C 75.00, H 8.33;
% found - C 74.48, H 8.30.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(3,5-dimethyl-4-octyloxybenzoate)* (**31**)

Yield: 4.10 g (68%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(10H, m), 1.75(2H, m), 2.10(6H, s), 3.70(2H, t), 7.65(2H, t), 8.45(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1310, 1170.

CHN analysis: % expected - C 75.95, H 8.86;
% found - C 75.70, H 8.71.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-3,5-dimethylbenzoate)* (**32**)

Yield: 0.28 g (11%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.85(3H, t), 1.30(14H, m), 1.75(2H, m), 2.20(6H, s), 3.20(2H, t), 7.65(2H, s), 8.45(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2900, 2820, 1740, 1300, 1170.

CHN analysis: % expected - C 76.74, H 9.30;
% found - C 76.28, H 9.19.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-dodecyloxy-3,5-dimethylbenzoate)* (**33**)

Yield: 3.45 g (70%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(18H, m), 1.75(2H, m), 2.05(6H, s), 3.65(2H, t), 7.60(2H, s), 8.45(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1315, 1180.

CHN analysis: % expected - C 77.42, H 9.68;
% found - C 76.98, H 9.52.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis[3,5-dimethyl-4-(1-methylheptyloxy)benzoate]* **(34)**

Yield: 1.39 g (41%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.15(3H, d), 1.35(8H, m), 1.65(2H, m), 2.20(6H, s), 4.15(1H, m), 7.80(2H, s), 8.75(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1310, 1175.

CHN analysis: % expected - C 75.95, H 8.86;
% found - C 75.38, H 8.77.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-hexyloxy-2,6-dimethylbenzoate)* **(35)**

Yield: 1.43 g (64%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.30(6H, m), 1.80(2H, m), 2.35(6H, s), 3.95(2H, t), 6.55(2H, s), 8.45(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1750, 1600, 1320, 1235, 1160, 1035.

CHN analysis: % expected - C 75.00, H 8.33;
% found - C 74.63, H 8.20.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(2,6-dimethyl-4-octyloxybenzoate)* **(36)**

Yield: 2.13 g (60%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.30(10H, m), 1.80(2H, m), 2.35(6H, s), 3.95(2H, t), 6.55(2H, s), 8.45(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1750, 1600, 1320, 1235, 1160, 1035.

CHN analysis: % expected - C 75.95, H 8.86;
% found - C 75.68, H 8.80.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-2,6-dimethylbenzoate)* (**37**)

Yield: 0.67 g (38%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.85(3H, t), 1.30(14H, m), 1.80(2H, m), 2.35(6H, s), 3.95(2H, t), 6.55(2H, s), 8.45(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1750, 1600, 1320, 1240, 1160, 1035.

CHN analysis: % expected - C 76.74, H 9.30;
% found - C 76.29, H 9.09.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-dodecyloxy-2,6-dimethylbenzoate)* (**38**)

Yield: 1.75 g (75%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.85(3H, t), 1.30(18H, m), 1.80(2H, m), 2.35(6H, s), 3.95(2H, t), 6.55(2H, s), 8.45(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1750, 1600, 1320, 1240, 1160, 1040.

CHN analysis: % expected - C 77.42, H 9.68;
% found - C 76.90, H 9.41.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis[2,6-dimethyl-4-(1-methylheptyloxy)benzoate]* (**39**)

Yield: 1.83 g (61%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.40(12H, m), 1.70(1H, m), 2.40(6H, s), 4.40(1H, m), 6.55(2H, s), 8.50(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1750, 1600, 1315, 1230, 1160, 1030.

CHN analysis: % expected - C 75.95, H 8.86;
% found - C 75.22, H 8.48.

## *3.3 Results*

### *3.3.1 Differential Scanning Calorimetry*

Calorimetric studies were carried out on each series of the esters prepared. Benzoate esters **30-34** with the methyl substituents pointing away from the triphenylene core will be discussed first. Typical results for the first heating cycles are shown in Figure 3.2. Compounds **31, 32** and **34** all show a sharp melting endotherm for the transition from the crystal to the discotic mesophase. This was followed on further heating by a phase change that had a smaller enthalpy peak indicating a liquid crystal to liquid crystal transition, and finally an endotherm marking the transition from the liquid crystal to the isotropic liquid. For each ester the enthalpy peak for the clearing transition was found to be weakly first order and even almost approaching a second order phase change. With cooling, the mesophase transitions were all found to be reversible. Compounds **30** and **33** were found to be different, the former showing a significant amount of decomposition rendering analysis difficult, and the latter showing no melting transition indicating that the material was already in a mesophase at the starting temperature of the first heating cycle (25 °C).

For the second series, compounds **35-38**, with the methyl substituents pointing in towards the core sharp melting endotherms were found, followed by a second peak (which is not reproducible on further heating and cooling runs). Further heating produced a transition to the isotropic liquid of similar size in enthalpy to the analogous series discussed above, *ie*, the clearing transitions were found to be very weakly first order in nature. Compound **35** showed an enthalpy for the recrystallization transition, but compounds **36-38** only exhibited transitions from the isotropic liquid to a mesophase, followed by a glass transition, which appears as a broad inflexion in the base-line of the thermogram. Compound **39** only showed a transition from crystal to the isotropic liquid. A complete set of heating thermograms for this series is shown in Figure 3.3, and the enthalpies of all of the transitions are incorporated in Tables 3.1 and 3.2.

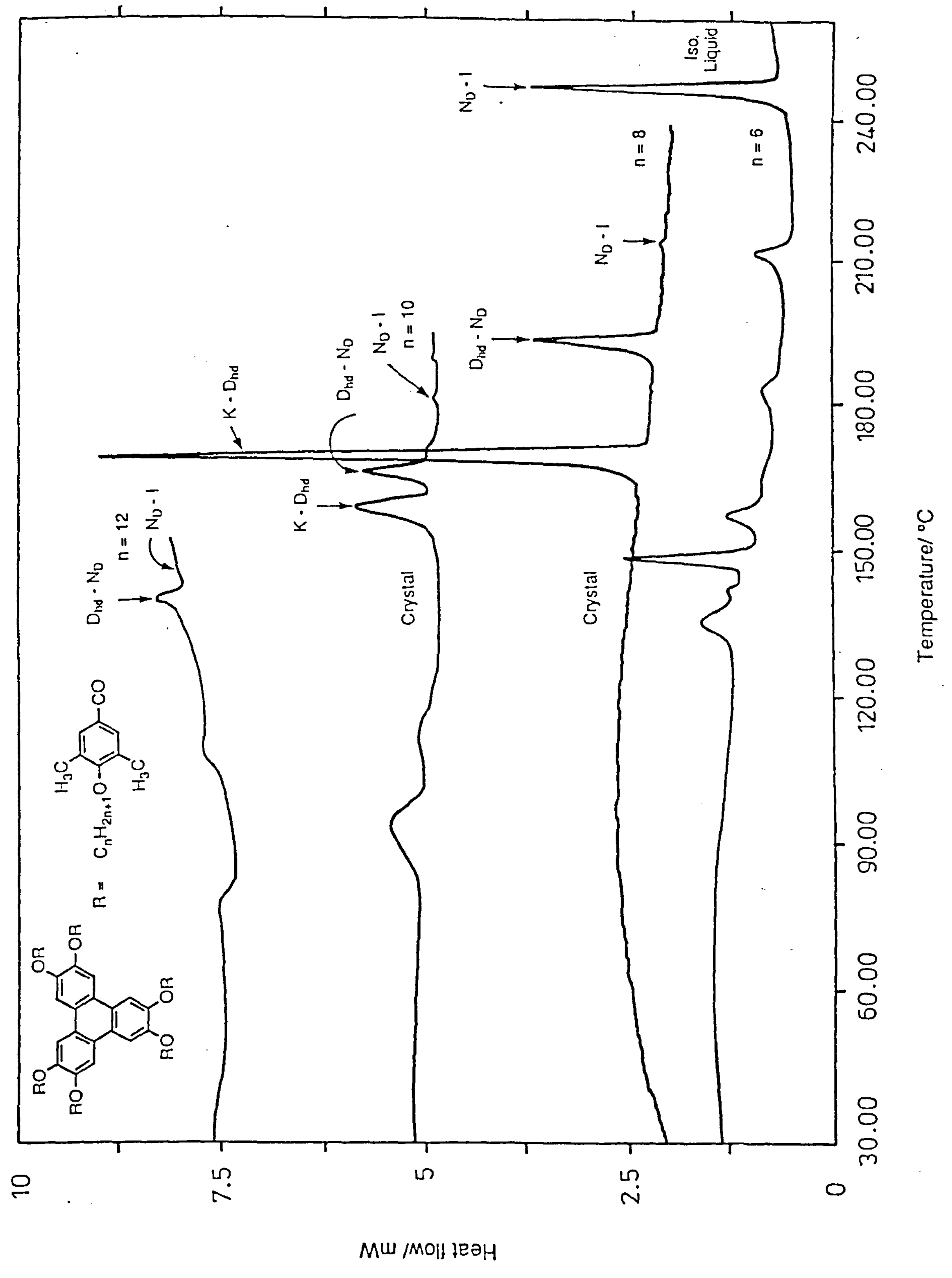


Figure 3.2 : DSC thermogram of the first heating cycle for each of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-3,5-dimethylbenzoate)s (30-33)

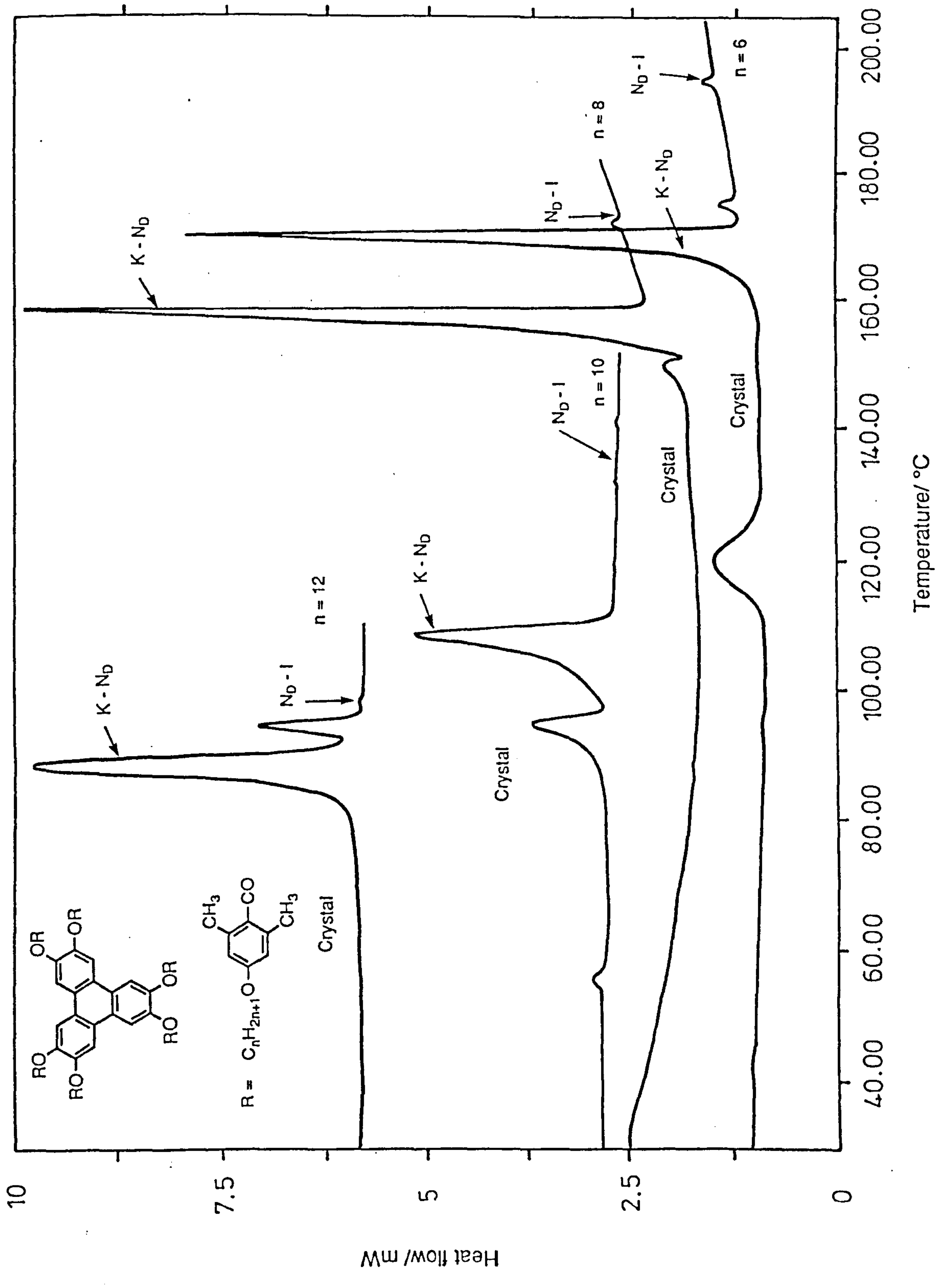


**Figure 3.3 : DSC thermogram of the first heating cycle for each of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-2,6-dimethylbenzoate)s (35--38)**

### *3.3.2 Thermal Optical Microscopy*

Compounds **30-34** with methyl substituents pointing away from the triphenylene core will again be discussed first. On heating each material from the crystal, under microscopic observation, the first discernible transition to be seen was that for the transformation to the nematic discotic phase. Plate 3.1 shows a typical texture of the nematic discotic phase of the octyloxy homologue formed on melting of the crystal. A threaded and *schlieren* texture is formed with the phase showing typical flow properties and Brownian motion that are expected of a nematic phase. Upon slow cooling from the isotropic liquid the nematic phase formed quintessential *schlieren* textures for each homologue. Plate 3.2 shows the *schlieren* texture for the dodecyloxy member; two and four brush singularities are clearly seen in this plate, thereby confirming the identification of the mesophase as nematic. Further slow cooling of each material resulted in the formation of a columnar phase. The textures of this phase were either mosiac or fan-like in appearance. The fan texture showed smooth fan-like regions and rectilinear δ lines. These two observations confirm that the phase has hexagonal symmetry and that there is no long range order in the columns, hence the phase is classified as $D_{hd}$.

Generally no recrystallization is observed under the microscope suggesting that the materials form glasses on cooling, however, a transition is observed in the DSC thermograms.

Other unusual observations were also made under microscopic examination, particularly in respect to the investigation of free-standing droplets. It was found, in very thin areas of the preparation where the material is essentially present on only one surface of the glass, that the glass substrate had an orienting influence on the material. Thus, the surface served to produce nucleation sites for the formation of the columnar phase. Surprisingly this effect took place even in the isotropic liquid phase. For example, when a material was heated to temperatures above its clearing point, at the edges of the sample and in free-standing droplets of the liquid, a columnar phase was formed. Plate 3.3 shows the fan texture of the hexagonal disordered columnar ($D_{hd}$) phase of the decyloxy homologue in a free-standing droplet at a temperature above the clearing ($N_D$-I) point. Plate 3.4

shows another area of the same preparation where the meniscus of the liquid and a film of the material meet. The free-standing film shows a fan-like texture and around the edge of the meniscus of the liquid droplet mosaic domains are seen. In this specimen it should be noted that the liquid droplet touches the surface of the cover-slip and the microscope slide, whereas the film is only in contact with the glass slide. This experiment clearly demonstrates that the disc-like molecules become ordered near surfaces which act as nucleation sites for the formation of the columnar phase. Moreover, this result is also indicative that the molecules in the isotropic liquid probably have short-range liquid crystal order of a cybotactic nature. This last observation is supported to some degree by the fact that the clearing point enthalpies of the compounds are very small, which suggests that there is not much difference in the local structure between the nematic discotic phase and the amorphous liquid.

Compounds **35-38** were more straightforward in their mesomorphic behaviour. Each material showed a clean transition to the discotic nematic ($N_D$) mesophase from the crystal and then on further heating a transition to the isotropic liquid. On cooling, the nematic phase was observed but only compound **35** showed any form of recrystallization. Compounds **36-38**, as their DSC thermograms indicate, exhibited glass transitions. The viscosity of the nematic phase was found to increase until the sample was unable to be sheared and the glass transition had been reached. The texture of the glass was found to be the same as that of the nematic phase. Compound **39** was non-mesogenic and showed only a melting transition to the isotropic liquid.

The transition temperatures for the two homologous series, determined by thermal polarized light microscopy, are given in Tables 3.1 and 3.2, and are plotted as a function of terminal *n*-alkoxy chain length in Figures 3.4 and 3.5, respectively. The enthaply values determined by differential scanning calorimetry are reported, where possible, along with each optical transition in Tables 3.1 and 3.2. It should be noted that the transition temperatures for both series of compounds show a linear relationship of temperature against number of carbon atoms in the terminal alkoxy chain.

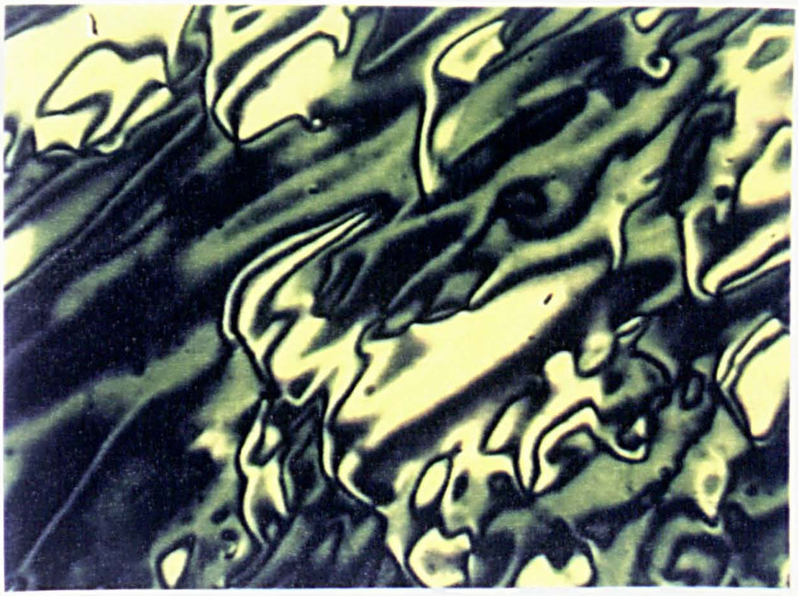


Plate 3.1 : Sheared *schlieren* and threaded texture of the discotic nematic ($N_D$) exhibited by compound 31 at 205 °C on heating

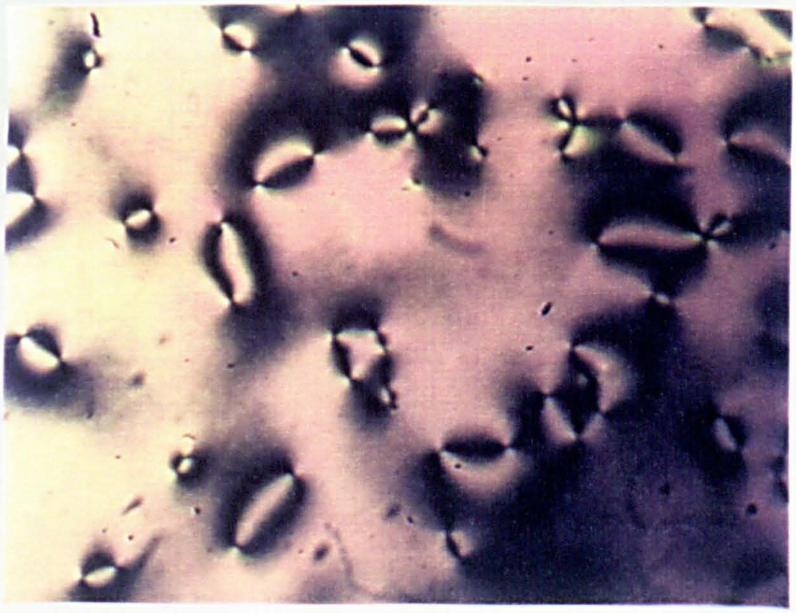


Plate 3.2 : Classical *schlieren* texture of the discotic nematic ($N_D$) showing singularities with two and four brushes, exhibited by compound 33 at 147 °C on cooling from the isotropic liquid

**Plate 3.3 : Fan texture of the hexagonal disordered ($D_{hd}$) columnar exhibited by compound 32. The sample is a thin film formed on a single surface at 184 °C (above the $N_D$-I temperature)**

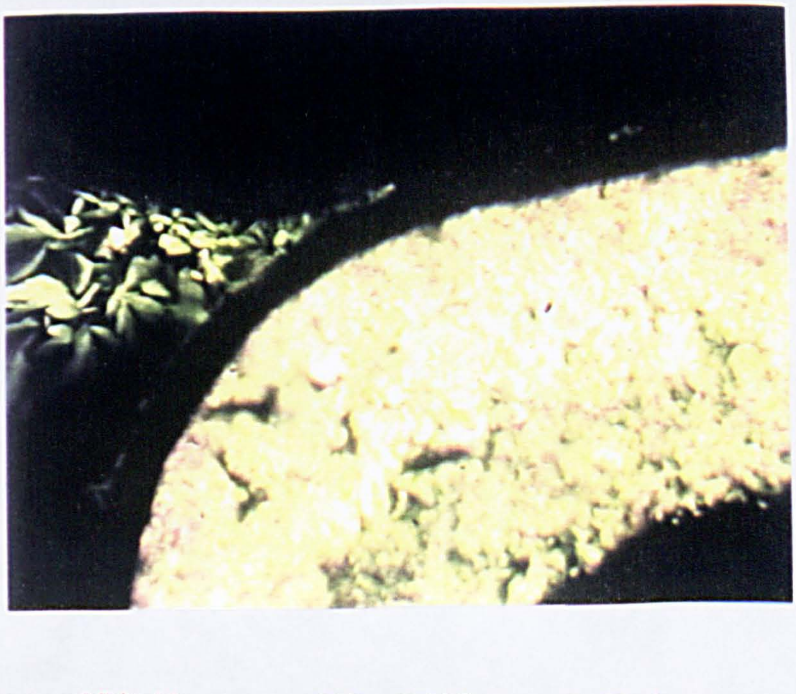
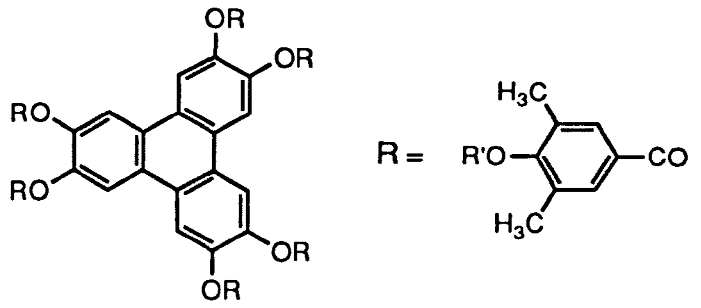


**Plate 3.4 : Textures exhibited by compound 32 at 182 °C (above the $N_D$-I temperature). Fan texture of the hexagonal disordered ($D_{hd}$) columnar on the left-hand side (thin film on one surface), mosaic domains of the $D_{hd}$ phase at the liquid/air interface and isotropic liquid at the bottom right-hand corner (film touching both glass substrates)**



| No. | R' | K | | $D_{hd}$ | | $N_D$ | | I |
|---|---|---|---|---|---|---|---|---|
| **30** | $C_6H_{13}$† | * | 150 (6.95) | * | 210 (2.80) | * | 243 (6.86) | * |
| **31** | $C_8H_{17}$ | * | 170 (31.16) | * | 195 (8.27) | * | 215 (0.13) | * |
| **32** | $C_{10}H_{21}$ | * | 157 (9.73) | * | 167 (5.29) | * | 182 (0.16) | * |
| **33** | $C_{12}H_{25}$ | * | @ | * | 143 (2.06) | * | 151 (0.38) | * |
| **34** | $C_6H_{13}CH(CH_3)$ | * | 125 (6.93) | * | 156 (4.33) | * | 183 (0.26) | * |

**Table 3.1 : Transition temperatures for triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-3,5-dimethylbenzoate)s**

† DSC data; material decomposes under microscopic examination.

@ No melting transition could be detected by DSC or thermal optical microscopy.

Enthalpies for each transition are given in parenthesis ($\Delta H$/kJ mol$^{-1}$).

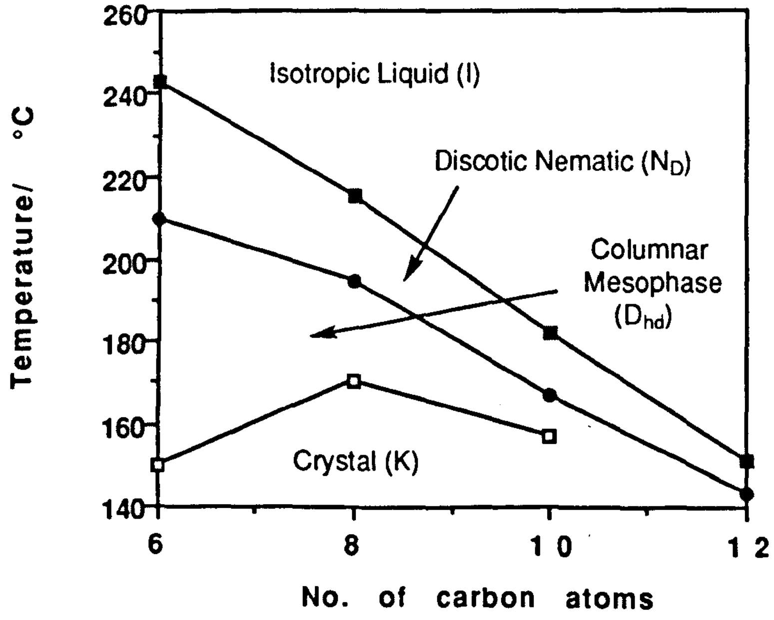
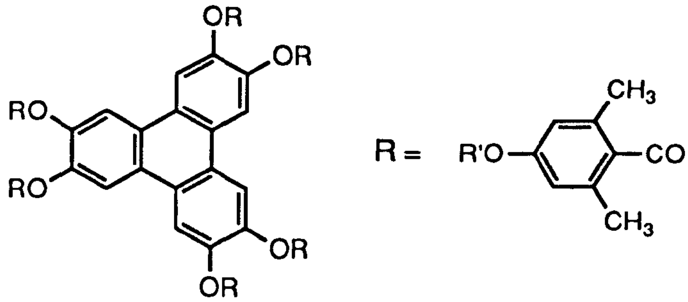


**Figure 3.4 : Transition temperatures plotted against the number of carbon atoms in the terminal chain for the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-3,5-dimethylbenzoate)s (30-33)**



| No. | R' | K | | $N_D$ | | I |
|---|---|---|---|---|---|---|
| 35 | $C_6H_{13}$ | * | 170 (33.57) | * | 196 (0.46) | * |
| 36 | $C_8H_{17}$ | * | 155 (42.28) | * | 170 (0.25) | * |
| 37 | $C_{10}H_{21}$ | * | 108 (21.01) | * | 134 (0.04) | * |
| 38 | $C_{12}H_{25}$ | * | 88 (34.17) | * | 99 (0.07) | * |
| 39 | $C_6H_{13}CH(CH_3)$ | * | 161 (@) | ——— | | * |

**Table 3.2 : Transition temperatures for triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-2,6-dimethylbenzoate)s**

Enthalpies for each transition are given in parenthesis ($\Delta H$/kJ mol$^{-1}$).

@ Not determined.

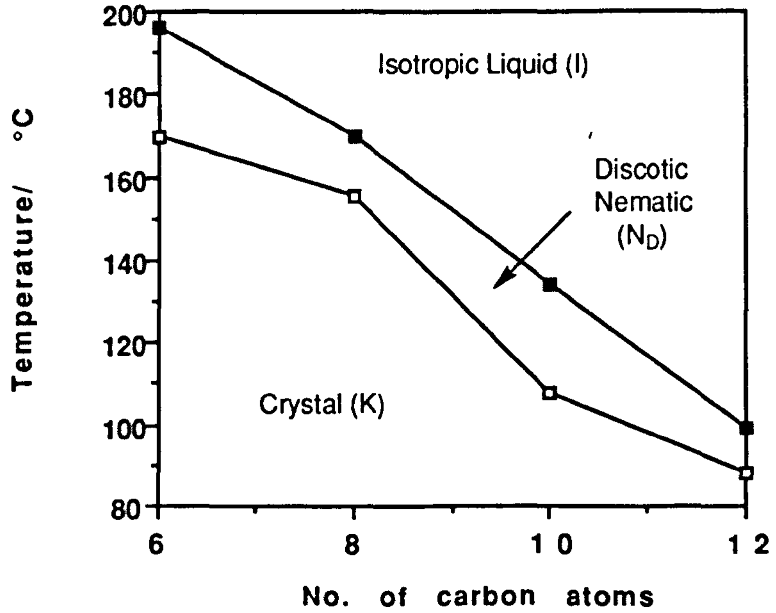


**Figure 3.5 : Transition temperatures plotted against the number of carbon atoms in the terminal chain of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-2,6-dimethylbenzoate)s (35-38)**

### *3.3.3 Miscibility Studies*

Mixture work was carried out in order to confirm the phase identification made by microscopy, to investigate whether unsymmetrical systems would exhibit lower transition temperatures than the pure materials and to examine the potential ability of materials in the second (*ie*, inner methyls) series to exhibit columnar mesophases. Thus, the following four binary systems were investigated:

a) a miscibilty study between the standard, triphenylen-2,3,6,7,10,11-hexayl hexakis(4-octyloxybenzoate) (**41**) and triphenylen-2,3,6,7,10,11-hexayl hexakis(3,5-dimethyl-4-octyloxybenzoate) (**31**, series 1),

b) two outer dimethyl-substituted materials from the first series with $C_8$ (**31**) and $C_{12}$ (**33**) chains respectively,

c) two inner dimethyl-substituted materials from the second series with $C_8$ (**36**) and $C_{12}$ (**38**) chains respectively,

d) one outer dimethyl-substituted (**31**) and one inner dimethyl-substituted material (**35**) both with $C_8$ chains.

#### *3.3.3.1 Binary System A*

A binary phase diagram was constructed for mixtures of the standard material triphenylen-2,3,6,7,10,11-hexayl hexakis(4-octyloxybenzoate) (**41**, $D_{rd}$, $N_D$ phases)[4] and the test compound triphenylen-2,3,6,7,10,11-hexayl hexakis(3,5-dimethyl-4-octyloxybenzoate) (**31**). It is clear from the phase diagram shown in Figure 3.6 that the phases of the test material (**31**) are **not** fully compatible with those of the standard compound (**41**). This result confirms the identification of the discotic nematic ($N_D$) mesophase in compound **31** and that the columnar phases exhibited by both compounds are **not** identical. This does not confirm that the mesophase exhibited by compound **31** is a hexagonal disordered ($D_{hd}$), but it does indicate that the mesophase in question is probably **not** a rectangular disordered ($D_{rd}$). However, it should be remembered that immiscibility is not a criterion on which to base phase classification.[5]

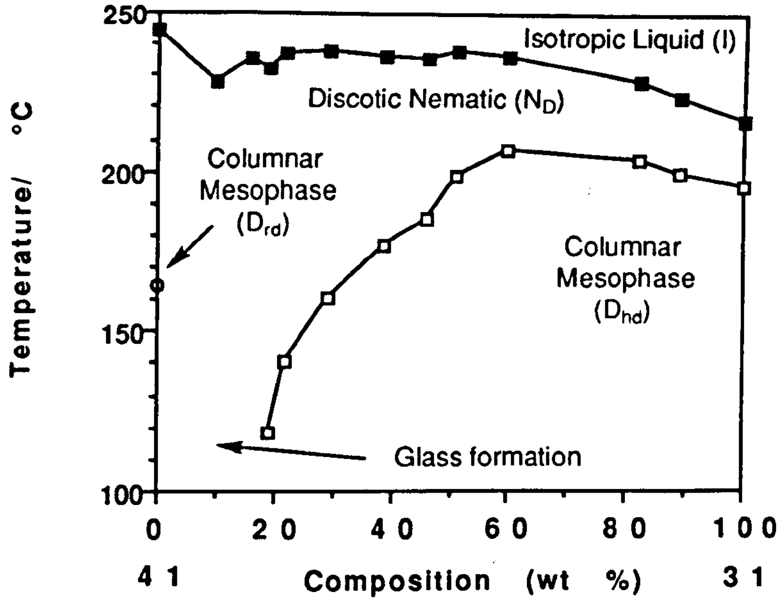


**Figure 3.6 : Binary phase diagram of transition temperatures plotted against '% by weight' for compounds 41 and 31**

### *3.3.3.2 Binary System B*

A binary phase diagram (Figure 3.7) between members of the first homologous series (*ie*, outer methyls) was constructed for mixtures of the $C_8$ and $C_{12}$ members. This phase diagram was investigated in order to examine how molecules with different disc-diameters mix to form mesophases. In particular it was expected that the different disc-sizes would disrupt the molecular packing in the columnar phase, thereby depressing the $N_D$ to $D_{hd}$ transition temperatures in the centre of the phase diagram. However, this was not observed, and instead the $N_D$ to $D_{hd}$ transition temperatures varied almost linearly with concentration. This suggests that the phase transitions vary almost ideally with temperature. This result complements the observation that the transition temperatures fall almost linearly as a function of alkoxy chain length in the homologous series (see Figure 3.7).

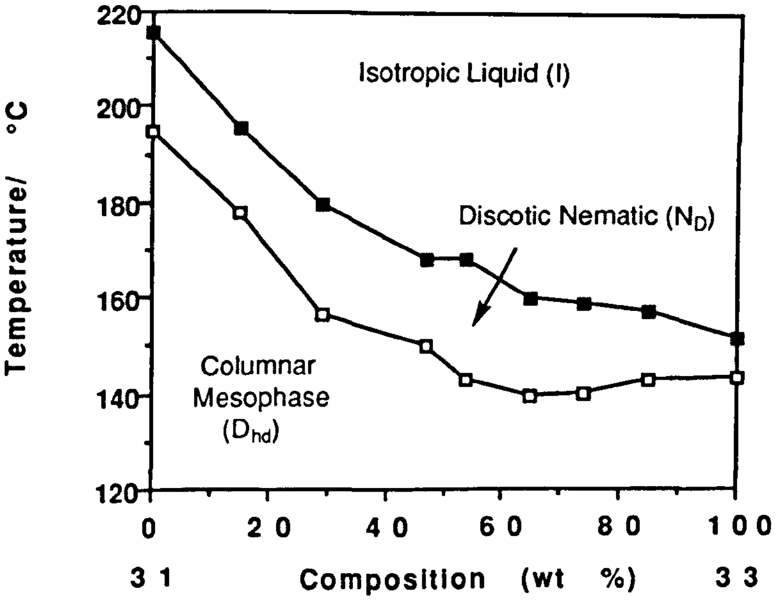


**Figure 3.7 : Binary phase diagram of transition temperatures plotted against '% by weight' for compounds 31 and 33**

### *3.3.3 Binary System C*

The effect of mixing materials with different disc-sizes on the nematic discotic to isotropic liquid and nematic discotic to crystal transitions was investigated *via* examination of binary phase diagrams constructed for members of the second series (*ie*, inner methyls). In this case the binary phase diagram for the octyloxy and dodecyloxy homologues is selected as a typical example (see Figure 3.8).

As with the pure materials, no recrystallization was observed for the binary mixtures where glasses were formed on cooling the nematic phase. Therefore, melting points were found using a rough method of slowly heating the sample, while continually attempting to shear the material until movement was detected. This point was used as the melting transition of the mixture. Again, as with the previous study, the $N_D$ to isotropic transition temperature was found to vary almost linearly with respect to concentration. Surprisingly, very little depression was found in the melting points with respect to concentration, and again these behaved almost linearly, with a small depression at about 60% by wt. of the dodecyloxy homologue. It may be that the lack of a depression in the eutectic phase diagram could be related to the fact that the mixtures form glasses on cooling. The structure of the glass phase could be closely related to that of the mesophase, thereby reducing the effects of mixing, *ie*, the formation of a eutectic depression in the melting point.

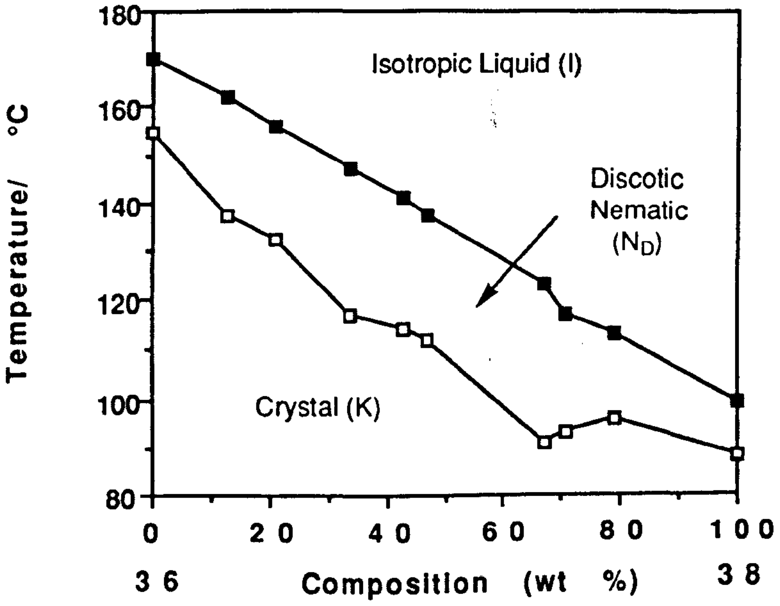


**Figure 3.8 : Binary phase diagram of transition temperatures plotted against '% by weight' for compounds 36 and 38**

### *3.3.3.4 Binary System D*

Binary mixtures between compounds of the two different series (**31** and **36**) were investigated in order to confirm the presence of the nematic discotic phase in the second series *via* use of the standardized members of the first series, and to examine the potential of members of the second series to exhibit columnar phases. A typical phase diagram for the mixtures between the octyloxy homologues of each series is shown in Figure 3.9. Again, the $N_D$ to isotropic liquid transition temperature for the mixtures behaved almost ideally, and varied nearly linearly with concentration.

As in all the previous mixture work, the binary mixtures did not show recrystallisation. Below the 50% value of compound **36**, the recrystallized state showed a columnar texture and above the 50% value of compound **36** in the mixtures, the familiar nematic glass formation was again encountered. However, the phase diagram confirms that the members of the second series exhibit nematic discotic phases and it also provides excellent proof that the inner dimethyl-substituted materials are purely nematogenic because the columnar mesophase falls sharply away just above 50% by wt. of the inner dimethyl compound in the binary mixtures, thereby demonstrating a suppression in columnar properties.

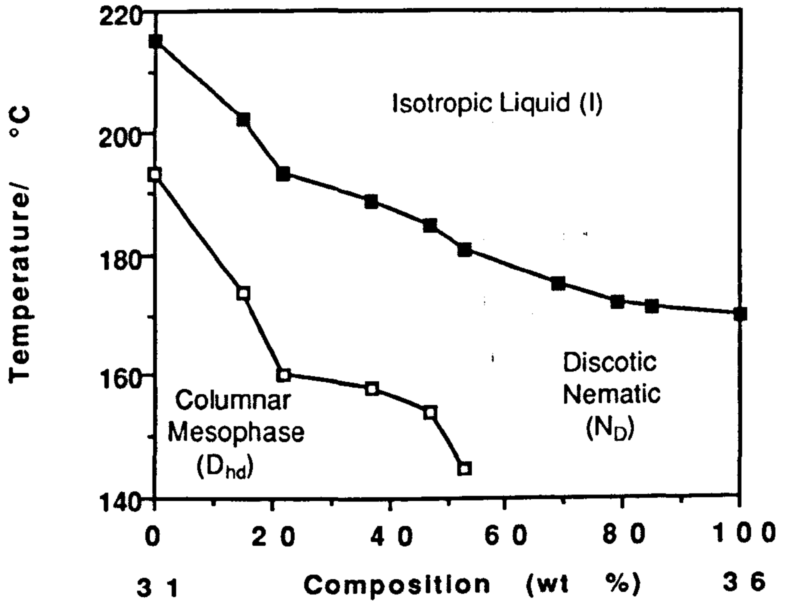


**Figure 3.9 : Binary phase diagram of transition temperatures plotted against '% by weight' for compounds 31 and 36**

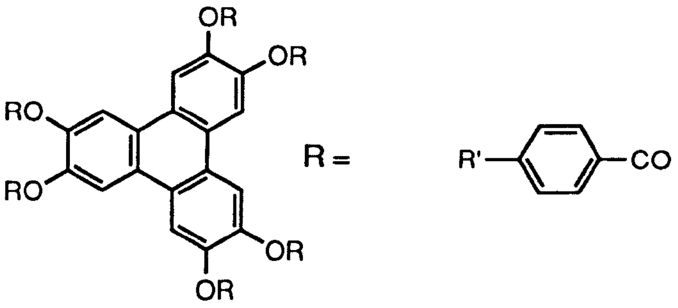
Further miscibility tests were attempted with two other compounds; triphenylen-2,3,6,7,10,11-hexayl hexakis(*n*-octanoate) and triphenylen-2,3,6,7,10,11-hexayl hexakis(4-heptylcyclohexanoate). Both of these materials were known to exhibit the hexagonal disordered columnar ($D_{hd}$)$^{6,7}$ and therefore they were used in binary phase diagrams with the test material triphenylen-2,3,6,7,10,11-hexayl hexakis(3,5-dimethyl-4-octyloxy-benzoate) (**31**) in order to attempt to confirm the identification of the columnar mesophase. Co-miscibility was not achieved in either case because of incompatabilities with respect to the transition temperatures of the standard materials with the test compound (**31**). The first standard material cleared into the isotropic liquid 40 °C below the *melting point* of the test compound and so the mixtures obtained were biphasic. The second miscibility test failed due to similar reasons; the test material decomposed on heating into the isotropic liquid as the clearing point of the standard material was some 30 °C higher than that for compound **31**. Consequently, mixtures with large biphasic regions were again obtained due to the products of decomposition. These regions rendered identification of mesophases by optical microscopy almost impossible.

## *3.4 Discussion*

The objective of this research programme was to position bulky groups in the lateral positions of the peripheral phenyl groups in the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s in order to investigate the effects of their presence on the phase morphology, transition temperatures and melting points. The effects of lateral substitution were predicted to reduce melting points and suppress columnar mesophases, and produce nematogenic discotic materials.

In this context, the unsubstituted compounds synthesised by Tinh,[4] exhibit both columnar and nematic polymorphism (compounds **40-45**, Table 3.3). These materials are directly comparable to the dimethyl analogues reported here (compounds **30-33** and compounds **35-38** shown in Tables 3.1 and 3.2).

Both alkyl and alkoxy derivatives prepared by Tinh have higher transition temperatures than either of the dimethyl substituted series. Thus, the first point concerning the lowering of melting points is borne out, and clearly lateral substitution, particularly when the substituents are pointing towards the more sterically crowded core, has the effect of markedly lowering transition temperatures (see Figure 3.10).



| No. | R' | K | | $D_T$† | | $D_{rd}$ | | $N_D$ | | I |
|---|---|---|---|---|---|---|---|---|---|---|
| **40** | $C_6H_{13}O$ | * | 186 | * | 193 | — | | * | 274 | * |
| **41** | $C_8H_{17}O$ | * | 152 | — | | * | 168 | * | 244 | * |
| **42** | $C_{10}H_{21}O$ | * | 142 | — | | * | 191 | * | 212 | * |
| **43** | $C_{12}H_{25}O$ | * | 146 | — | | * | 174 | — | | * |
| **44** | $C_8H_{17}$ | * | 208 | — | | — | | * | 210 | * |
| **45** | $C_{10}H_{21}$ | * | 185 | — | | * | 189 | — | | * |

**Table 3.3 : Transition temperatures for some triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s and (4-alkylbenzoate)s**

† Tinh stated that this phase was a tilted columnar.[4] See Chapter 1, Section 1.4.1.2.

If the transition temperatures and mesophase morphology of the three series are compared, it is seen that the unsubstituted system has a much stronger affinity for forming columnar structures. Additionally it is clear that columnar phase formation is suppressed across the three families of series as follows:

$$\underset{\text{Suppression of columnar mesophases}}{\xrightarrow{\text{Unsubstituted < 3,5 dimethyl substituted < 2,6 dimethyl substituted}}}$$

For example, for the dodecyloxy homologue, the unsubstituted system (**43**) exhibits a columnar phase (and $D_{rd}$ to Iso liquid ) at higher temperatures rather than the nematic discotic phase (and $N_D$ to Iso) found to occur for the analogous dimethyl substituted compounds (**33** and **38**). Thus, lateral substitution depresses the columnar phase stability by much more than the $N_D$ phase stability and in the process lowers transition temperatures.

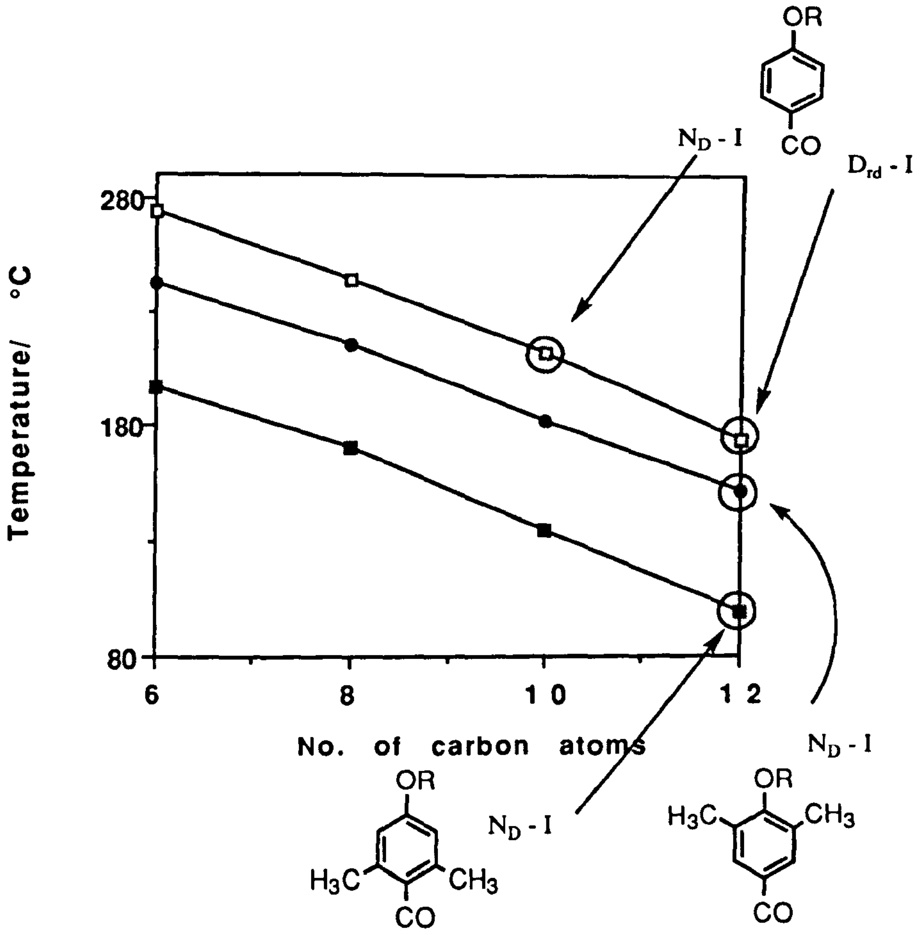


**Figure 3.10 : Graph of clearing temperatures plotted against the number of carbon atoms in the terminal chain for compounds 30-33, 35-38 and 40-43[2]**

Another interesting point that this graphical comparison raises is that the clearing point temperatures fall almost linearly with alkoxy chain length. This is very unusual behaviour which is rarely observed for calamitic materials, where the transition temperatures often do not vary linearly with chain length. In calamitic systems the transition temperatures usually either fall sharply at first or increase rapidly before levelling off as an homologous series is ascended.[8] The linear fall in transition temperatures in disc-like systems could be attributed to the molecular shapes and interactions of the molecules. In packing of disc-like materials together there will be two principally important interactions to consider, the face to face and the edge to edge associations of the discs. The stronger interaction of the two is expected to be the side to side association because it involves interactions between the aromatic cores. In increasing the alkoxy chain length, the edge to edge interactions will change but the overall packing will still be dominated by the core-core associations which do not vary much. As the alteration in alkoxy chain length is symmetrical around the periphery of the disc, then any change in edge to edge interactions will be isotropic in the planes of the molecules. As the aliphatic interactions are much weaker than the strong aromatic associations, extension of the alkoxy chains will serve only to dilute the effect of the core-core interactions. Coupling of these two factors therefore may be expected to lead to an incremental weakening of the core-core interactions per unit volume of material. Hence, if the phase stability is closely related to these interactions and their strengths, then one might expect that the clearing points might also vary linearly as well with respect to chain length.

The structural effects of methyl substitution on mesophase stability will now be examined; in the unsubstituted systems, the benzoate rings are able to arrange to be coplanar with respect to the triphenylene core, *ie*, there is enough space around the rim of the disc-like core for the aromatic regions to lie relatively flat with respect to one another. This situation is conducive towards allowing strong inter-disc attractions, because the molecules can pack closely one on top of another, and hence the formation of columnar mesophases is preferred. Furthermore these materials also have very high $N_D$ phase stability which appears to be related to the higher degree of disruption in the packing of the molecules required to form the isotropic liquid. Thus, these materials have high melting points, clearing points and columnar mesophase stability because of the stronger interactions caused by the ability of the molecules to pack closely together.

The addition of the bulky methyl groups in both the external and internal positions of the peripheral arms has the effect of increasing the thicknesses of the molecular discs which in turn weakens the side to side interactions.

For compounds **31-34** with the methyl substituents pointing outwards from the triphenylene core, the overall disc thickness has increased. Plates 3.5, 3.6 and 3.7 show molecular modelling minimized structures for the core regions of the molecules. The methyl substituents are found to cause some steric hindering leading to disc broadening. This should effectively weaken the side to side interactions which should result in lower clearing points and suppression of the columnar mesophases. Although a depression in the clearing points is found, the columnar phases are slightly more stable in the shorter alkoxy dimethyl substituted compounds than they are in the unsubstituted analogues. This may be due to a locking in of the cores at shorter alkoxy chain lengths leading to stronger core interactions, whereas for the longer alkoxy chains disruption might be caused in this packing arrangement by the longer chains. The additional use of a branched terminal chain (compound **34**) has no effect on the mesophase types but melting points and phase stabilities have all been reduced by approximately 50 °C. With the very high temperatures involved, it is perhaps not surprising that compound **30** decomposes and so little analysis can be obtained accurately.

In the second series of compounds (**35-39**, with lateral methyl substituents pointing towards the crowded inner core region, *ie*, in the 2 and 6 positions of the peripheral phenyl groups), the results are remarkable. The ordered columnar phase has been totally eliminated and the materials are purely nematogenic. Furthermore, the melting points for the longer chain homologues are substantially reduced. The most significant comparision to be made is that compound **38** clears to the isotropic liquid at less than 100 °C, a reduction of some 75 °C compared to the parent compound (**43**). Compound **38** also shows nematic mesomorphism, albeit over just 10 °C, but compound **43** did not exhibit a nematic phase at all. It appears the methyl groups in these inner-core positions force the peripheral phenyl moieties out of plane with respect to the triphenylene core (see Plate 3.7 which shows a computer modelling simulation of the core structure of this material); this disrupts the inter-disc packing of the molecules and eliminates columnar mesophases, but as the anisotropic disc-like shape is still present, the nematic phase is formed. A schematic diagram of this situation can be seen in Figure 3.11. In this figure the lateral steric interactions are shown to force the peripheral benzoate rings out of the plane of the triphenylene core.

It is interesting to note that the branched chain derivative, compound **39**, was found to be non-mesogenic. The nematic phase stability has now been lowered below the recrystallization point. The presence of the branched methyl substituent on the terminal alkoxy chain prevents the terminal chains from packing in the space between the benzoate groups and together with the twist of the peripheral phenyl group at the ester linkage, due to the internal methyl-substitution, has been enough to suppress the mesomorphism completely by pushing the discs too far apart for strong side to side interactions to be possible.

The effect on transition temperatures of bulky methyl-substituents in calamitic systems is usually considerable, often to the point of rendering a material non-mesogenic.[2,9] However, the results shown here reveal the greater tolerance of discotic materials towards bulky lateral substituents in terms of the depression of the nematic phase stability.

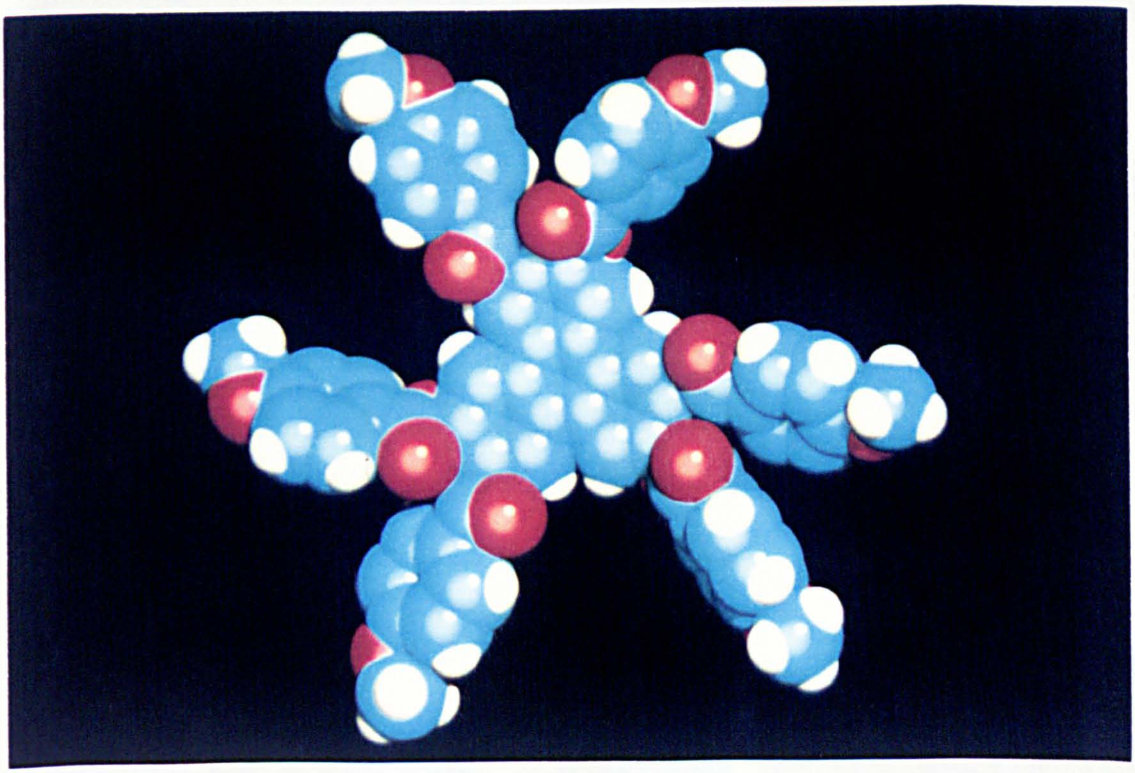


**Plate 3.5 : Minimized structure of the non-substituted triphenylene ester. The terminal aliphatic chains have been omitted for reasons of clarity. The space around the triphenylene core allows for optimum disc-to-disc interactions**

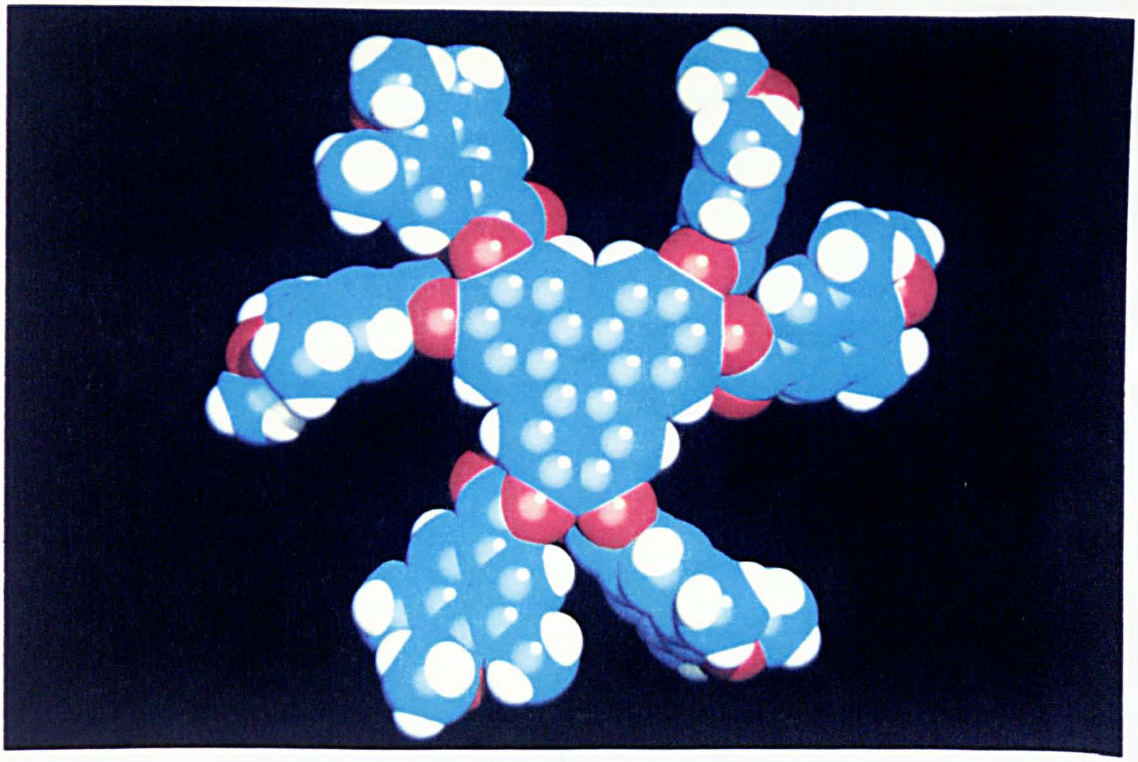


Plate 3.6 : Minimized structure of the outward methyl-substituted triphenylene ester. Here the methyl groups add breadth to the molecule in the outer region of the disc-like core

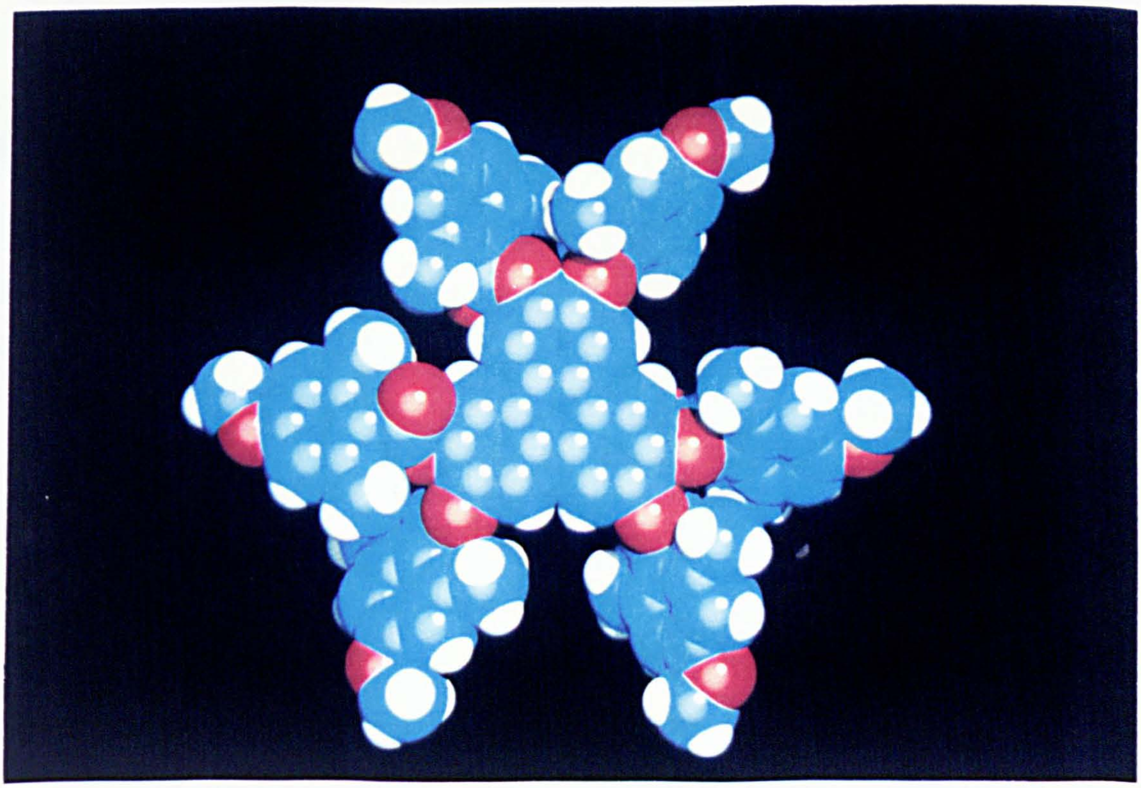


Plate 3.7 : Minimized structure of the inward methyl-substituted triphenylene ester. In this case the methyl-substituents can be clearly seen to overlap causing twisting around the central triphenylene unit. This makes the molecule thicker and hence weakens the disc-to-disc interactions

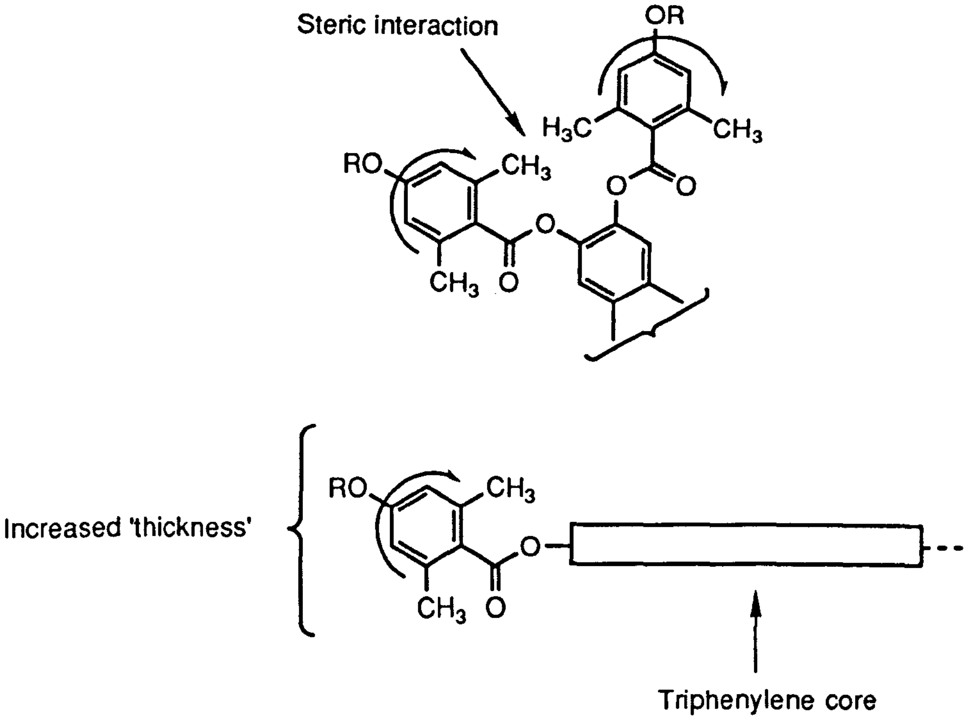


**Figure 3.11 : Schematic representation of the positioning of the peripheral arms due to steric crowding of the laterally substituted methyl groups**

## *3.5 Conclusions*

1. The triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s have high melting points and high mesophase stability of the columnar mesophases. Lateral substitution in the peripheral benzoate rings reduces transition temperatures considerably.

2. The discotic materials (**31-34**) with lateral dimethyl-substituents positioned in the spacious outer core region are found to have high melting points, high mesophase stability and exhibit columnar mesophases.

3. Lateral dimethyl-substituents directed towards the core have a much greater effect in reducing melting points and the nematic phase stability, furthermore columnar mesophases are totally eliminated.

4. The use of a lateral methyl-substitution as part of the terminal alkoxy chain further reduces melting points and nematic phase stabilities (compounds **34** and **39**). However, in the case of compound **39**, the effect has been to reduce the nematic phase stability below the crystallization temperature rendering the compound non-mesogenic.

5. There is a very delicate balance between substitution that will reduce melting points and eliminate ordered columnar mesophases and substitution that will destroy the mesogenic nature of the material.

6. A steric model that utilizes changes in the face to face and edge to edge interactions of the disc-like molecules allows a good interpretation of the results.

## *3.6 References*

1) D.R. Beattie, *Ph. D. Thesis*, University of Hull, 1993.

2) K.J. Toyne, in *'Thermotropic Liquid Crystals'*, ed. G. W. Gray, Wiley, Chichester, 1987.

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4) N.H. Tinh, H. Gasparoux and C. Destrade, *Mol. Cryst. Liq. Cryst.*, 1981, **68**, 101.

5) H. Sackman and D. Demus, *Mol. Cryst. Liq. Cryst.*, 1966, **2**, 81.

6) D.R. Beattie, P. Hindmarsh, J.W. Goodby, S.D. Haslam and R.M. Richardson, *J. Mater. Chem.*, 1992, **2**, 1261.

7) C. Destrade, P. Foucher, H. Gasparoux and N.H. Tinh, *Mol. Cryst. Liq. Cryst.*, 1984, **106**, 121.

8) For example, G.W. Gray, in *Liquid Crystals and Plastic Crystals*, eds. G.W. Gray and P.A. Windsor, Wiley, Chichester, 1974, p 103-152.

9) M. Hird and K.J. Toyne, unpublished results.

# *CHAPTER 4*

# *Investigation of the Effect of Bulky Lateral Substituents on the Discotic Mesophase Behaviour of Triphenylene Benzoates*

## *4.1 Introduction*

Firstly, it should be noted that the molecular modelling results detailed in section 4.4 of this chapter are reproduced by kind permission of Mr. M. J. Watson, and will also appear in his thesis.

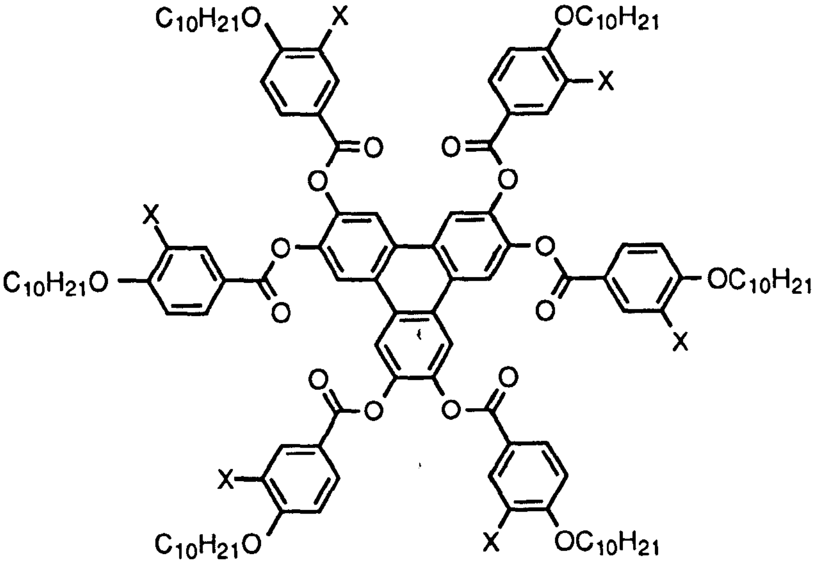
In a development of the work that was discussed in Chapter 3, bulkier groups (*ie*, ethyl, *iso*-propyl and *tert*-butyl) were positioned in the lateral positions of the peripheral phenyl groups of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s[1] in order to investigate the effect of the *size* of the lateral substituent, as well as the position, on phase morphology, transition temperatures and melting points.

It has already been reported that lateral methyl substitution in the peripheral phenyl groups can suppress columnar phases, thereby enhancing the discotic nematic temperature ranges in comparision to the unsubstituted systems[2,3] (see also Chapters 3 and 5). Lateral substitution was shown to cause twisting of the peripheral phenyl rings out of the plane containing the triphenylene disc-like core. The twisting disrupts the face to face interactions, thereby suppressing the tendency to form columnar structures. This reduces the incidence of columnar phases and as a consequence, allows the nematic phase to be observed over a wider temperature range (even though in some cases the $T_{N_D\text{-}I}$ may lower).[2,3]

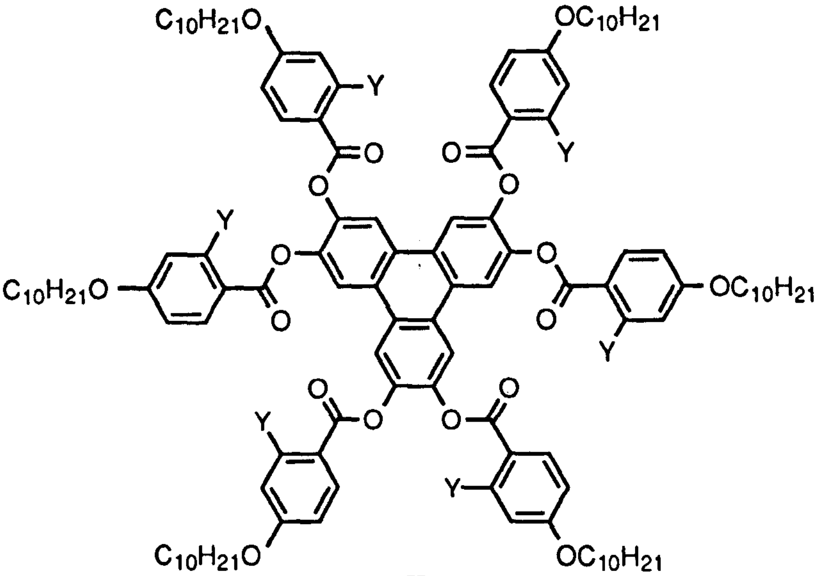
Therefore, a systematic study was carried out on the steric effects caused by the sequential increase in the size of the aliphatic lateral groups in the peripheral phenyl rings. Thus, mono-substituted systems in the inner and outer positions were studied, and the substituent was sequentially increased in size from methyl to *tert*-butyl.

Studies by Beattie on the mono-methyl derivatives have already been reported,[3] but the results were highly unreliable and the purity of materials was questionable. Therefore, the transition temperature data detailed for the mono-methyl derivatives in this chapter are those quoted from freshly made materials discussed in Chapter 5.

Thus, in this chapter the synthesis and properties of the triphenylen-2,3,6,7,10,11-hexayl hexakis(3-alkyl-) and (2-alkyl-4-decyloxybenzoate)s is discussed (see structures **I** and **II**, Figure 4.1). An examination was made on how lateral substitution of the peripheral phenyl rings affected the mesomorphism of these liquid crystals, and an attempt was made to simulate the inter-disc steric interactions by computer modelling.



**I**



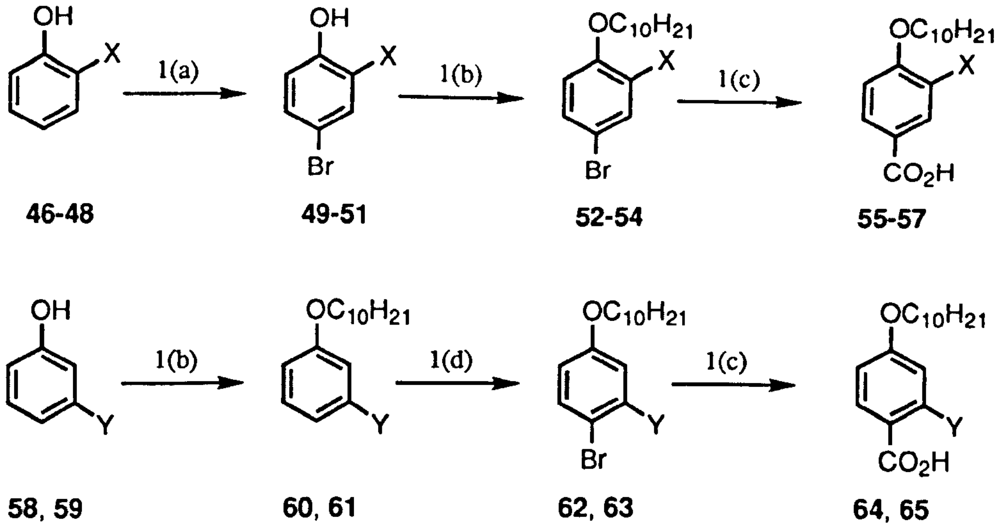
**II**

**Figure 4.1 : Stuctures of the triphenylen-2,3,6,7,10,11-hexayl hexakis(3-alkyl-) and (2-alkyl-4-decyloxybenzoate)s (structures I and II); structure I: X = methyl, ethyl, *iso*-propyl and *tert*-butyl; structure II: Y = methyl, ethyl and *iso*-propyl**

## *4.2 Experimental*

The materials were prepared by the routes shown in Schemes 4.1 and 4.2. The various substituted acids were prepared by the synthetic routes shown in Scheme 4.1. Compounds **46-48, 58** and **59** were purchased from Aldrich Chemical Co. Compounds **46-48** were brominated in good yields using bromine and glacial acetic acid at 0 °C. Compounds **58** and **59** were unable to be brominated solely in the desired position (*ie, para-* to the hydroxy function) due to the position of the alkyl substituent; poly-bromination occurred and an inseparable mixture was obtained. Therefore, compounds **58** and **59** were first *O*-alkylated with 1-bromodecane using anhydrous potassium carbonate in butanone to provide good yields of compounds **60** and **61**. Compounds **49-51** were also *O*-alkylated in this manner to give compounds **52-54**, in similarly good yields. Addition of the bromine in the desired position to compounds **60** and **61** was achieved by adding bromine dropwise to a gently refluxing solution of these compounds in dry chloroform; bromination was found not to occur at the *ortho* position to the alkoxy chain. The replacement of the bromine in compounds **52-54, 62** and **63** was achieved by lithiation using *n*-butyllithium at -78 °C; in each case the reaction mixture was then poured onto a slurry of solid $CO_2$ and dry ether, acidified, and the product purified (compounds **55-57, 64** and **65**). The final liquid-crystalline materials (**66-70**) were prepared by the esterification of HHTP (**3**) with the respective benzoyl chlorides in the presence of pyridine.

An inwards substituted *tert*-butyl analogue was unable to be obtained as bromination of 1-*tert*-butyl-3-decyloxybenzene to yield 1-bromo-2-*tert*-butyl-4-decyloxybenzene was unsuccessful, probably because of steric hindrance.



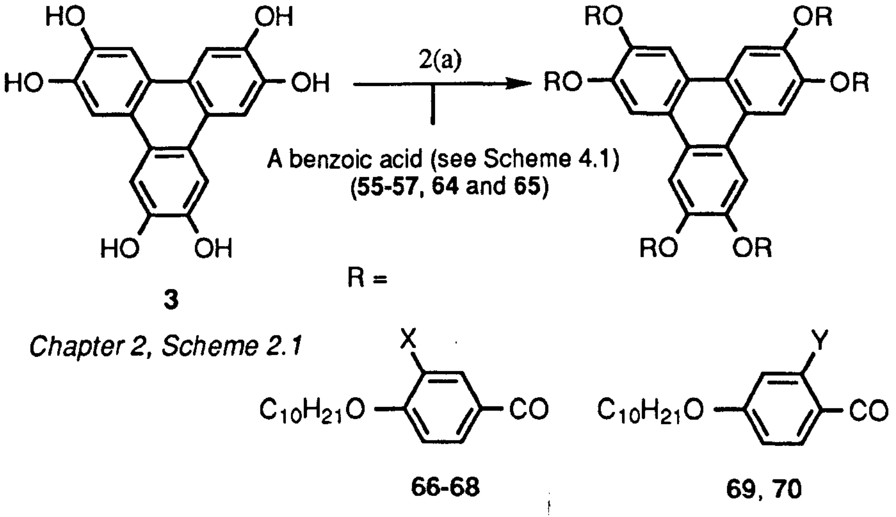
1(a) ..... $Br_2$, acetic acid, 0 °C.

1(b) ..... 1-Bromodecane, $K_2CO_3$, butanone.

1(c) ..... (i) *n*-BuLi, THF; (ii) $CO_2$ (solid), $Et_2O$.

1(d) ..... $Br_2$, dry $CHCl_3$, reflux.

**Scheme 4.1 : Synthetic route for the preparation of the 3-alkyl- and 2-alkyl-4-decyloxybenzoic acids; 55-57: X = ethyl, *iso*-propyl or *tert*-butyl, 64 and 65: Y = ethyl or *iso*-propyl**



2(a) ..... Acid chloride (oxalyl chloride, DMF, $CH_2Cl_2$), pyridine.

**Scheme 4.2 : Synthetic route for the preparation of the triphenylen-2,3,6,7,10,11-hexayl hexakis(3-alkyl-) and (2-alkyl-4-decyloxybenzoate)s; 66-68: X = ethyl, *iso*-propyl or *tert*-butyl, 69 and 70: Y = ethyl or *iso*-propyl**

### *4.2.1 Preparation of the 2-Alkyl-4-bromophenols* (49-51)

The general synthetic method is exemplified by the following procedure.

*4-Bromo-2-ethylphenol* (**49**)

A solution of bromine (12.96 g, 0.082 mol) in acetic acid (20 ml) was added to a cooled (0 °C), stirred solution of 2-ethylphenol (**46**) (10.00 g, 0.082 mol) in acetic acid (150 ml) as rapidily as possible without causing excessive heating. The temperature was maintained below 35 °C and the addition took *ca.* 2 minutes. The reaction mixture was stirred for a further 5 minutes and then poured into water (1500 ml). The aqueous solution was extracted into dichloromethane (twice) and the combined organic layers were washed with water (twice) and dried ($MgSO_4$). The solvent was removed and the crude residue was distilled to yield a colourless liquid.

Yield: 10.93 g (67%)    Bp: 85-88 °C at 0.4 mmHg

$^1H$ NMR ($CDCl_3$ and TMS) $\delta$: 1.22(3H, t), 2.60(2H, q), 4.75(1H, s), 6.62(1H, d), 7.15(1H, dd), 7.25(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3700-3100(broad), 2960, 1600, 1580, 1490, 1410, 1320, 1260, 1200, 1165, 1115, 860, 810, 760, 630.

MS (*m*/*z*): 202(M$^+$), 200(M$^+$), 187, 185, 121, 102, 91, 77, 63, 59, 51.

*4-Bromo-2-iso-propylphenol* (**50**)

Yield: 12.00 g (76%)    Bp: 120-125 °C at 0.4 mmHg

$^1H$ NMR ($CDCl_3$ and TMS) $\delta$: 1.23(6H, d), 3.16(1H, m), 4.78(1H, s), 6.62(1H, d), 7.15(1H, dd), 7.25(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3700-3100(broad), 2960, 1600, 1490, 1410, 1330, 1260, 1200, 1170, 1095, 880, 810, 740, 630.

MS (*m*/*z*): 216(M$^+$), 214(M$^+$), 201, 199, 135, 120, 102, 91, 77, 63, 51.

*4-Bromo-2-tert-butylphenol* (**51**)

Yield: 12.44 g (81%) Bp: 150-155 °C at 0.4 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 1.23(9H, s), 4.83(1H, s), 6.55(1H, d), 7.15(1H, dd), 7.35(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3700-3100(broad), 2960, 1600, 1490, 1395, 1360, 1320, 1250, 1200, 1165, 1080, 880, 805, 705, 630.

MS (*m*/*z*): 230(M$^+$), 228(M$^+$), 215, 213, 187, 185, 134, 115, 105, 89, 77, 63, 57, 51.

### 4.2.2 *Preparation of the 2-Alkyl-4-bromo-1-decyloxybenzenes and 1-Alkyl-3-decyloxybenzenes* (52-54, 60 and 61)

The general synthetic method is exemplified by the procedure reported in Chapter 3 for compound **9**.

*4-Bromo-1-decyloxy-2-ethylbenzene* (**52**)

Yield:16.43 g (88%) Bp: 187-189 °C at 0.4 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.18(3H, t), 1.30(14H, m), 1.80(2H, m), 2.60(2H, q), 3.90(2H, t), 6.66(1H, d), 7.22(2H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1485, 1460, 1240, 1135, 805, 640.

MS (*m*/*z*): 342(M$^+$), 340(M$^+$), 202, 200, 187, 185, 122, 107, 91, 85, 69.

*4-Bromo-1-decyloxy-2-iso-propylbenzene* (**53**)

Yield: 18.54 g (94%) Bp: 177-179 °C at 0.4 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.18(6H, d), 1.30(14H, m), 1.80(2H, m), 3.27(1H, m), 3.90(2H, t), 6.66(1H, d), 7.21(1H, dd), 7.26(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1490, 1470, 1245, 805, 645.

MS ($m/z$): 356($M^+$), 354($M^+$), 216, 214, 201, 199, 136, 121, 107, 91, 77, 69, 55.

*4-Bromo-2-tert-butyl-1-decyloxybenzene* (**54**)

Yield: 19.02 g (94%) Bp: 167-169 °C at 0.4 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.25(9H, s), 1.30(14H, m), 1.85(2H, m), 3.90(2H, t), 6.70(1H, d), 7.21(1H, dd), 7.34(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1490, 1470, 1390, 1245, 1090, 805, 645.

MS ($m/z$): 370($M^+$), 368($M^+$), 230, 228, 215, 213, 185, 135, 107, 91, 85, 57.

*1-Decyloxy-3-ethylbenzene* (**60**)

Yield: 10.40 g (97%) Bp: 150-155 °C at 0.5 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.23(3H, t), 1.30(14H, m),1.75(2H, m), 2.63(2H, q), 3.93(2H, t), 6.75(3H, m), 7.17(1H, t).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1600, 1580, 1450, 1260, 1155, 1000, 700.

MS ($m/z$): 262($M^+$), 122, 107, 77, 55.

*1-Decyloxy-3-iso-propylbenzene* (**61**)

Yield: 10.21 g (100%) Bp: 167-169 °C at 0.5 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.30(20H, m), 1.80(2H, m), 2.89(1H, m), 3.95(2H, t), 6.71(1H, m), 6.78(2H, m), 7.20(1H, t).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1600, 1580, 1450, 1290, 1260, 1190, 1050, 750.

MS ($m/z$): 276($M^+$), 136, 121, 91, 77.

### *4.2.3 Preparation of the 2-Alkyl-1-bromo-4-decyloxybenzenes* (**62** and **63**)

The general synthetic method is exemplified by the following procedure.

*1-Bromo-4-decyloxy-2-ethylbenzene* (**62**)

A solution of bromine (6.00 g, 0.038 mol) in dry chloroform (10 ml) was added dropwise to a stirred, gently refluxing (65 °C) solution of 1-decyloxy-3-ethylbenzene (**61**) (10.00 g, 0.038 mol) in dry chloroform (75 ml). The reaction mixture was allowed to cool, washed with water and dried ($MgSO_4$). The solvent was removed and the residue distilled to yield a colourless oil.

Yield: 7.60 g (59%) Bp: 160-165 °C at 0.3 mmHg

$^1H$ NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(17H, m), 1.75(2H, m), 2.70(2H, q), 3.90(2H, t), 6.60(1H, dd), 6.80(1H, d), 7.40(1H, d).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 2920, 2860, 1580, 1565, 1460, 1290, 1270, 1255, 1235, 1170, 1060, 1010, 870, 800, 640.

MS (*m*/*z*): 342($M^+$), 340($M^+$), 263, 202, 200, 187, 185, 122, 107, 91, 77, 69, 55.

*1-Bromo-4-decyloxy-2-iso-propylbenzene* (**63**)

Yield: 11.03 g (84%) Bp: 195-200 °C at 0.4 mmHg

$^1H$ NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(20H, m), 1.75(2H, m), 3.35(1H, m), 3.90(2H, t), 6.60(1H, dd), 6.83(1H, d), 7.40(1H, d).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 2920, 2860, 1580, 1565, 1460, 1285, 1240, 1230, 1190, 1010, 870, 800, 640.

MS (*m*/*z*): 356(M+), 354(M+), 216, 214, 202, 200, 120, 91, 69, 55, 43.

### 4.2.4 *Preparation of the 3-Alkyl- or 2-Alkyl-4-decyloxybenzoic Acids* (55-57, 64 and 65)

The general synthetic method is exemplified by the procedure reported in Chapter 3 for compound **14**.

*4-Decyloxy-3-ethylbenzoic Acid* (**55**)

Yield: 10.83 g (74%)
Mp: 104-106 °C
$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.35(17H, m), 1.80(2H, m), 2.67(2H, q), 4.00(2H, t), 6.85(1H, d), 7.92(1H, d), 7.96(1H, dd).
IR (KBr) $\nu_{max}$ cm$^{-1}$: 3300-2400(broad), 2920, 2860, 1675, 1600, 1425, 1320, 1265, 1140, 770, 650.
MS (*m*/*z*): 306(M$^+$), 166, 151, 121, 77, 57, 43.

*4-Decyloxy-3-iso-propylbenzoic Acid* (**56**)

Yield: 10.00 g (60%)
Mp: 99-101 °C
$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.35(20H, m), 1.85(2H, m), 3.35(1H, m), 4.05(2H, t), 6.85(1H, d), 7.95(2H, m).
IR (KBr) $\nu_{max}$ cm$^{-1}$: 3300-2500(broad), 2920, 2860, 1680, 1600, 1475, 1410, 1310, 1260, 1245, 1150, 770, 735, 650.
MS (*m*/*z*): 320(M$^+$), 180, 165, 91, 55, 43.

*3-tert-Butyl-4-decyloxybenzoic Acid* (**57**)

Yield: 10.00 g (58%)
Mp: 139-141 °C
$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.35(23H, m), 1.87(2H, m), 4.05(2H, t), 6.90(1H, d), 7.95(1H, dd), 8.05(1H, d).
IR (KBr) $\nu_{max}$ cm$^{-1}$: 3300-2500(broad), 2920, 2860, 1675, 1600, 1475, 1420, 1275, 1245, 1200, 1140, 1020, 820, 770, 710, 650.
MS (*m*/*z*): 334(M$^+$), 320, 194, 179, 151, 91, 85, 69, 43.

*4-Decyloxy-2-ethylbenzoic Acid* (**64**)

Yield: 3.41 g (51%) Mp: 74-76 °C

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(17H, m), 1.80(2H, m), 3.05(2H, q), 4.00(2H, t), 6.78(1H, dd), 6.80(1H, d), 8.05(1H, d).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 3300-2500(broad), 2920, 2860, 1685, 1605, 1560, 1295, 1255, 1225, 1155, 775, 645.

MS (*m/z*): 306($M^+$), 166, 149, 91, 77, 69, 57, 41.

*4-Decyloxy-2-iso-propylbenzoic Acid* (**65**)

Yield: 7.30 g (74%) Mp: 103-105 °C

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(20H, m), 1.80(2H, m), 4.00(2H, t), 4.07(1H, m), 6.72(1H, dd), 6.92(1H, d), 8.00(1H, d).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 3300-2500(broad), 2920, 2860, 1685, 1610, 1560, 1285, 1270, 1230, 870, 775, 650.

MS (*m/z*): 320($M^+$), 180, 147, 91, 69, 55, 43.

### *4.2.5 Preparation of the Triphenylen-2,3,6,7,10,11-hexayl Hexakis(3-alkyl-4-decyloxybenzoate)s or (2-alkyl-4-decyloxybenzoate)s* (66-70)

The general synthetic method for the preparation of the hexa-esters is exemplified by the method reported in Chapter 3 for compound **30**.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-3-ethylbenzoate)* (**66**)

Yield: 4.03 g (61%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.03(3H, t), 1.35(14H, m), 1.75(2H, m), 2.46(2H, q), 3.93(2H, t), 6.62(1H, d), 7.75(1H, d), 7.85(1H, dd), 8.45(1H, s).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 2920, 2860, 1740, 1600, 1500, 1250, 1130, 1075, 905, 760.

CHN analysis: % expected - C 77.2, H 8.8;

% found - C 77.18, H 9.03.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-3-iso-propylbenzoate)* **(67)**

Yield: 4.04 g (61%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.13(6H, d), 1.35(14H, m), 1.80(2H, m), 3.35(1H, m), 3.96(2H, t), 6.77(1H, d), 7.95(2H, m), 8.55(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1745, 1600, 1500, 1245, 1185, 1120, 1065, 910, 765, 730.

CHN analysis: % expected - C 77.5, H 9.0;

% found - C 77.46, H 9.29.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(3-tert-butyl-4-decyloxybenzoate)* **(68)**

Yield: 3.79 g (59%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(23H, m), 1.80(2H, m), 3.96(2H, t), 6.78(1H, d), 7.97(1H, dd), 8.02(1H, d), 8.55(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1600, 1500, 1230, 1120, 1080, 910, 760, 730.

CHN analysis: % expected - C 77.8, H 9.2;

% found - C 77.83, H 9.42.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-2-ethylbenzoate)* **(69)**

Yield: 1.72 g (65%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.15(3H, t), 1.35(14H, m), 1.80(2H, m), 2.99(2H, q), 3.95(2H, t), 6.60(1H, dd), 6.72(1H, d), 8.09(1H, d), 8.43(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1600, 1560, 1500, 1230, 1120, 1030, 905, 770.

CHN analysis: % expected - C 77.2, H 8.8;

% found - C 77.06, H 8.99.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-2-iso-propylbenzoate)* (**70**)

Yield: 3.03 g (62%)

| | |
|---|---|
| $^1$H NMR ($CDCl_3$ and TMS) $\delta$: | 0.90(3H, t), 1.15(6H, d), 1.35(14H, m), 1.80(2H, m), 3.96(3H, m), 6.60(1H, dd), 6.89(1H, d), 8.08(1H, d), 8.46(1H, s). |
| IR (KBr) $\nu_{max}$ cm$^{-1}$: | 2920, 2860, 1730, 1605, 1560, 1230, 1110, 1035, 770. |
| CHN analysis: | % expected - C 77.5, H 9.0;<br>% found - C 77.35, H 9.26. |

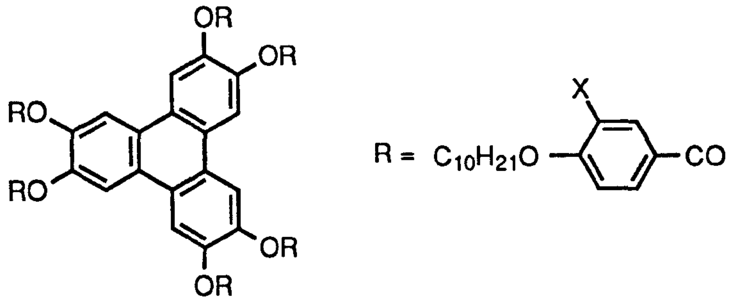
## *4.3 Results*

### *4.3.1 Transition Temperatures*

The transition temperatures for the previously reported[1,3] (see also Chapter 5) and newly synthesized materials were determined by a combination of thermal optical microscopy and differential scanning calorimetry. Typically the crystal to mesophase transitions were determined by calorimetry because of the difficulty in discerning this transition optically. The other transitions, including the recrystallization and glass transitions, were determined by microscopy. The results for the outer substituted systems are shown in Table 4.1, whereas the results for the inner substituted materials are given in Table 4.2. From Table 4.1, the clearing point transitions for the "outer" series fall initially and then rise with increasing size of the lateral substituent (*ie*, X = H to *tert*-butyl). The methyl and ethyl homologues (**99** and **66**) appeared to show a columnar phase upon cooling from the nematic phase. However, miscibility studies show this phase to be crystalline in nature rather than liquid-crystalline. The later members of the "outer" series, the *iso*-propyl- and *tert*-butyl-substituted homologues (**67** and **68**), only exhibit discotic nematic phases and no columnar phases were detected before recrystallization was encountered.

The recrystallization temperature gives an upper boundary limit to the presence of any columnar phases. The results initially show a suppression in recrystallization temperature as the "outer" series is ascended, but the recrystallization temperatures start to rise again for the larger substituents. Thus, suppression of columnar phases by increasing substituent size clearly occurs for the earlier homologues, but for the higher members this conclusion is only tentative.

Unlike the outer substituted series, the clearing points for the inner substituted series fall markedly with increasing substitution size (see Table 4.2). No columnar phases are observed in this series except for the parent unsubstituted compound (**42**, Y = H, see Chapter 3). In order to examine the limits of the presence of columnar phases in this particular series, the recrystallization processes were carefully studied. Even on substantial supercooling (*ca.* -40 °C) the presence of monotropic columnar phases could not be found. These results indicate that substitution at the inner position is extremely effective in suppressing columnar mesophases.

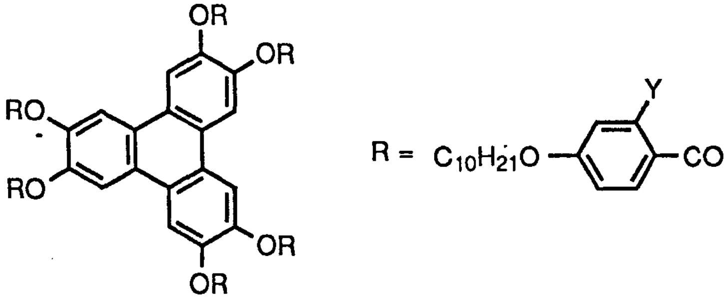


| No. | X | K | | $D_{rd}$ | | $N_D$ | | I | Recryst. | |
|---|---|---|---|---|---|---|---|---|---|---|
| **42** | H† | * | 142 | * | 191 | * | 212 | * | 80 | * |
| **99** | methyl‡ | * | 102 (35.46) | ———— | | * | 192 (0.39) | * | 110 | * |
| **66** | ethyl | * | 129 (20.30) | ———— | | * | 206 (0.62) | * | 102 | * |
| **67** | *iso*-propyl | * | 161 (30.29) | ———— | | * | 202 (0.96) | * | 146 | * |
| **68** | *tert*-butyl | * | 194 (52.57) | ———— | | * | 225 (1.07) | * | 174 | * |

**Table 4.1 : Transition temperatures for the triphenylen-2,3,6,7,10,11-hexayl hexakis(3-alkyl-4-decyloxybenzoate)s**

Enthalpies for each transition are given in parenthesis ($\Delta H$/kJ $mol^{-1}$).

†Literature compound.[1] ‡Literature compound,[3] (see also Chapter 5).



| No. | Y | K |  | $D_{rd}$ |  | $N_D$ |  | I | Recryst. |  |
|---|---|---|---|---|---|---|---|---|---|---|
| **42** | H† | * | 142 | * | 191 | * | 212 | * | 80 | * |
| **103** | methyl‡ | * | 107 (44.28) | ———— |  | * | 162 (0.16) | * | 51 | * |
| **69** | ethyl | * | 117 (42.52) | ———— |  | * | 131 (0.19) | * | 84 | * |
| **70** | *iso*-propyl | * | 93 (23.20) | ———— |  | * | [70 (0.15)] | * | {42} | * |

**Table 4.2 : Transition temperatures for the triphenylen-2,3,6,7,10,11-hexayl hexakis(2-alkyl-4-decyloxybenzoate)s**

Enthalpies for each transition are given in parenthesis (ΔH/kJ mol$^{-1}$).

Monotropic transitions are given in square brackets []. Glassy state transitions are given in curly braces {}.

†Literature compound.[1] ‡Literature compound,[3] (see also Chapter 5).

### *4.3.2 Differential Scanning Calorimetry*

Calorimetric studies were carried out on each series of the esters prepared. Typical results for the heating cycles of the "outer" series are shown in Figure 4.2 and Figure 4.3 shows the corresponding cooling cycles. All compounds show a sharp melting endotherm (except for the unsubstituted homologue [42] where the sharp endotherm corresponds to a mesophase-mesophase transition) and a much smaller endotherm marking the transition from the liquid crystal to the isotropic liquid. The enthalpy peak for the clearing transition was found to be rather small indicating that the transition from the liquid to the $N_D$ phase is weakly first order.

Compounds **99** and **66**, with the methyl- and ethyl-substituents, show an additional enthalpy between the largest peak and clearing endotherm, which corresponds to the point where the defect texture changes from *schlieren* to a platelet form. However, there is a large temperature hysterisis between the formation of this phase on cooling and its disappearance on heating. Usually, liquid crystal to liquid crystal transitions show small hystereses in temperatures because they have essentially liquid-like structures. In the case of the methyl and ethyl compounds (**99** and **66**), the large hystereses suggests that the phase which exhibits a platelet texture is more likely to have an ordered crystal-like structure. This is supported by the fact that the texture cannot be mechanically sheared in the microscope.

For the second set of compounds, with the substituents pointing towards the core, the results are shown in Figures 4.4 (heating) and 4.5 (cooling). Upon heating, all compounds show a sharp melting endotherm (except for compound **42** as mentioned previously) followed by a very small endotherm corresponding to the transition from the liquid crystal to isotropic liquid, *ie*, the transition, unlike the "outer" series, almost appears second order in nature. The *iso*-propyl analogue (**70**) is the exception and only shows a melting endotherm. No other transitions were detected on heating for this series.

Upon cooling, the mesophase transitions were all found to be reversible, with the exception again being the *iso*-propyl derivative (**70**). On cooling the expected signal for recystallization in compound **70** is not observed, instead a peak similar to those found for the first peak in the cooling thermograms (*ie*, isotropic to mesophase) for the compounds **66-69** and **42**, **99** and **103** is observed. There is no evidence for any recrystallization, indicating the possibility of a glassy state being present. A similar situation of glassy state formation was also found to occur for the inner dimethyl-substituted triphenylene benzoates reported previously[2] (see also Chapter 3).

### *4.3.3 Thermal Optical Microscopy*

For the outer substituted compounds **66-68** and **99**, when each material was heated from the crystal, under microscopic observation, the first discernible transition was that for the transformation to the nematic discotic phase. Plate 4.1 shows a typical texture formed on heating for the nematic discotic phase of compound **66** (ethyl-substituted). A threaded and *schlieren* texture is formed with the phase showing typical flow properties and Brownian motion that are expected of a nematic phase. Upon slow cooling from the isotropic liquid, the nematic phase formed the *schlieren* texture for each homolgue. Plate 4.2 shows the *schlieren* texture for compound **66** on cooling from the isotropic liquid; two and four brush singularities are shown in this texture, thereby confirming the identification of the mesophase as nematic.

Further slow cooling of each material resulted in recrystallization. In the case of the methyl- and ethyl-substituted homologues a mosaic texture, closely resembling a hexagonal columnar ($D_{hd}$ or $D_{ho}$) was observed, see Plate 4.3. Generally, columnar mesophases are fluid, albeit very viscous[4] as found for the rectangular disordered ($D_{rd}$) phase of the unsubstituted homologue (**42**). However, the platelet texture was unable to be sheared indicating that this phase is probably a transition to a crystal rather than to a columnar mesophase. On continued cooling, no other transition is observed for the methyl-substituted material (**99**) but recrystallization is seen for the ethyl-substituted homologue (**66**).

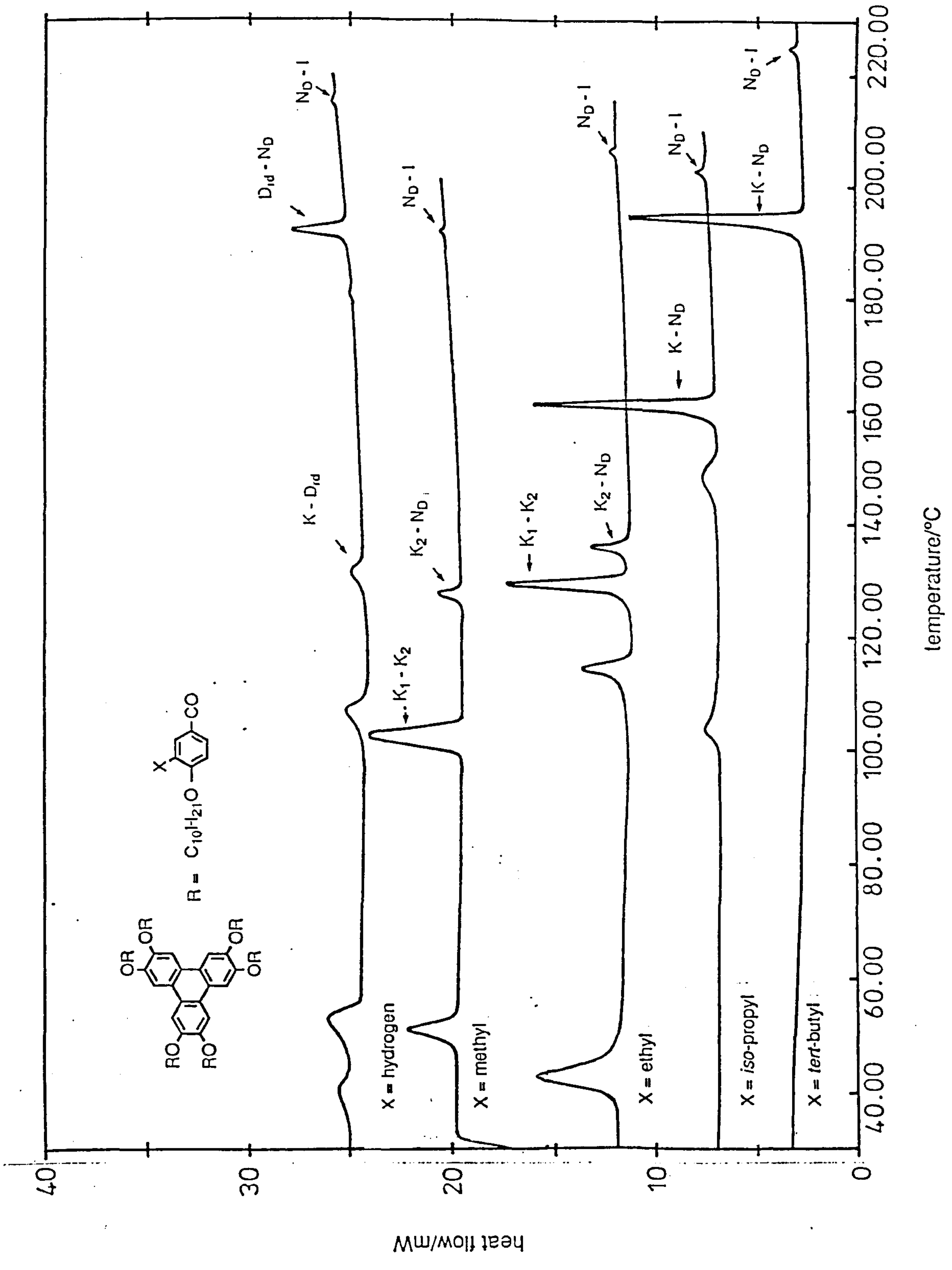


**Figure 4.2 : DSC thermogram of the first heating cycles of the triphenylen-2,3,6,7,10,11-hexayl hexakis(3-alkyl-4-decyloxybenzoate)s (42, 66-68 and 99)**

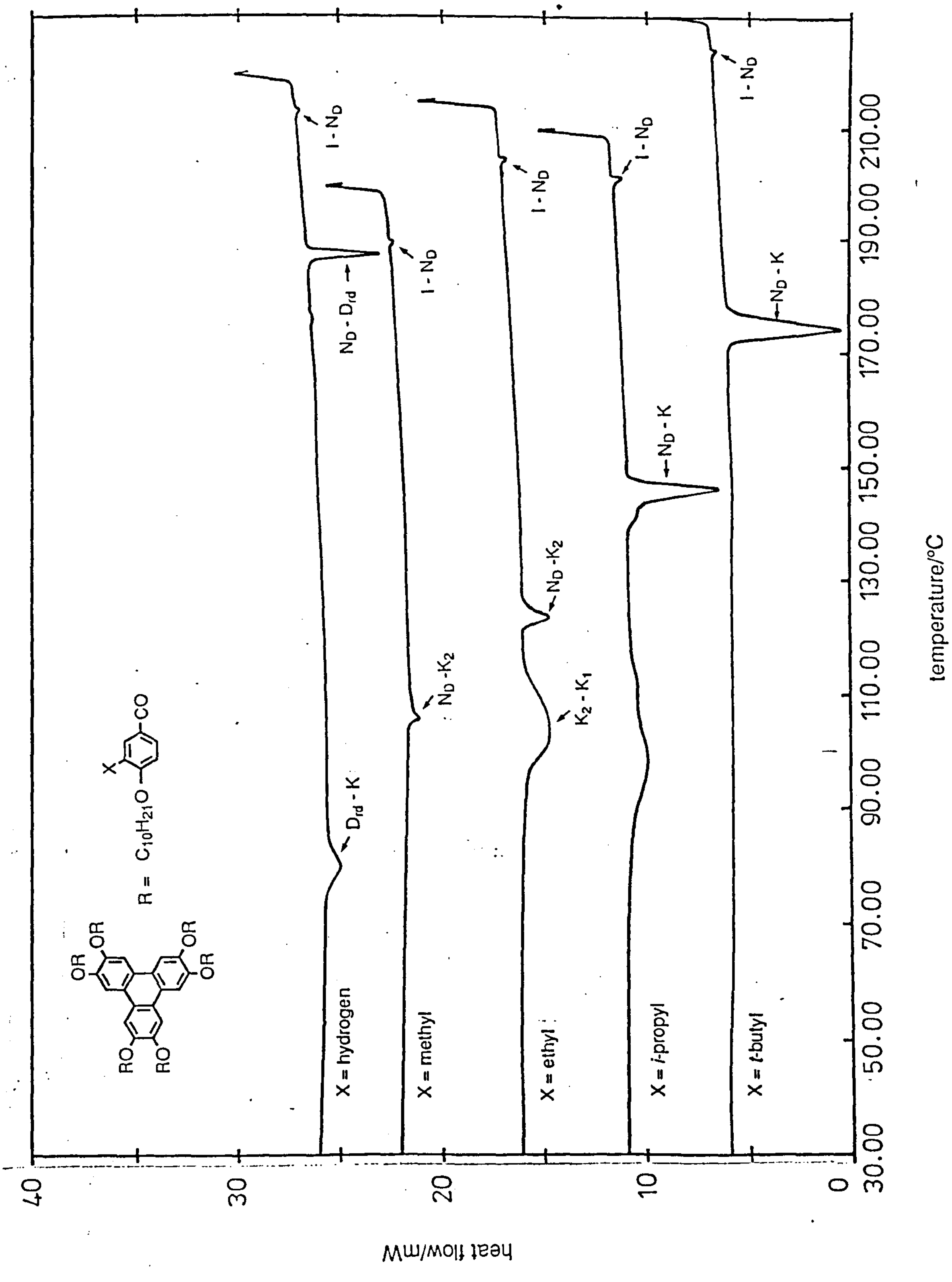


Figure 4.3 : DSC thermogram of the first cooling cycles of the triphenylen-2,3,6,7,10,11-hexayl hexakis(3-alkyl-4-decyloxybenzoate)s (42, 66-68 and 99)

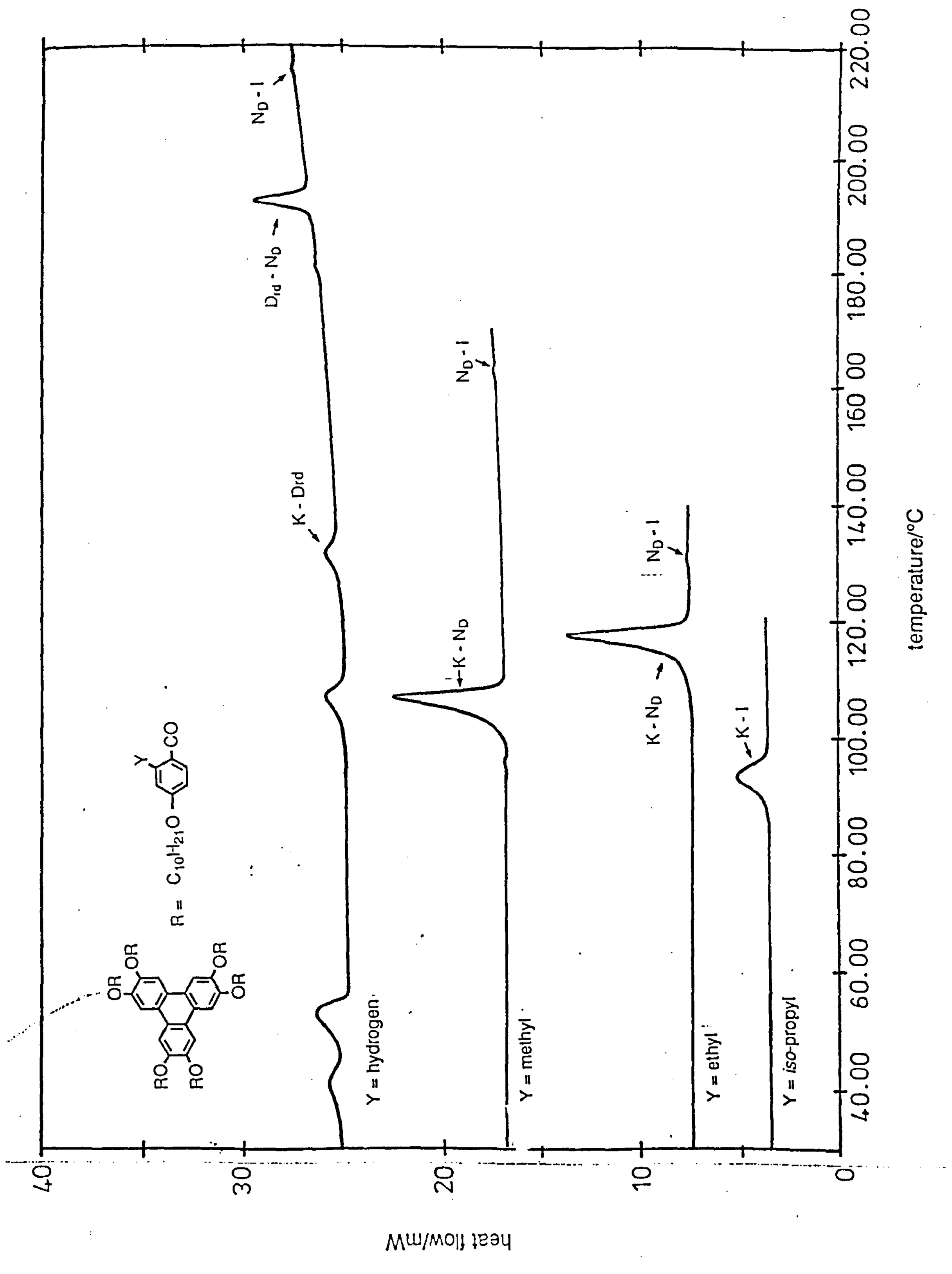


**Figure 4.4 : DSC thermogram of the first heating cycles of the triphenylen-2,3,6,7,10,11-hexayl hexakis(2-alkyl-4-decyloxybenzoate)s (42, 69, 70 and 103)**

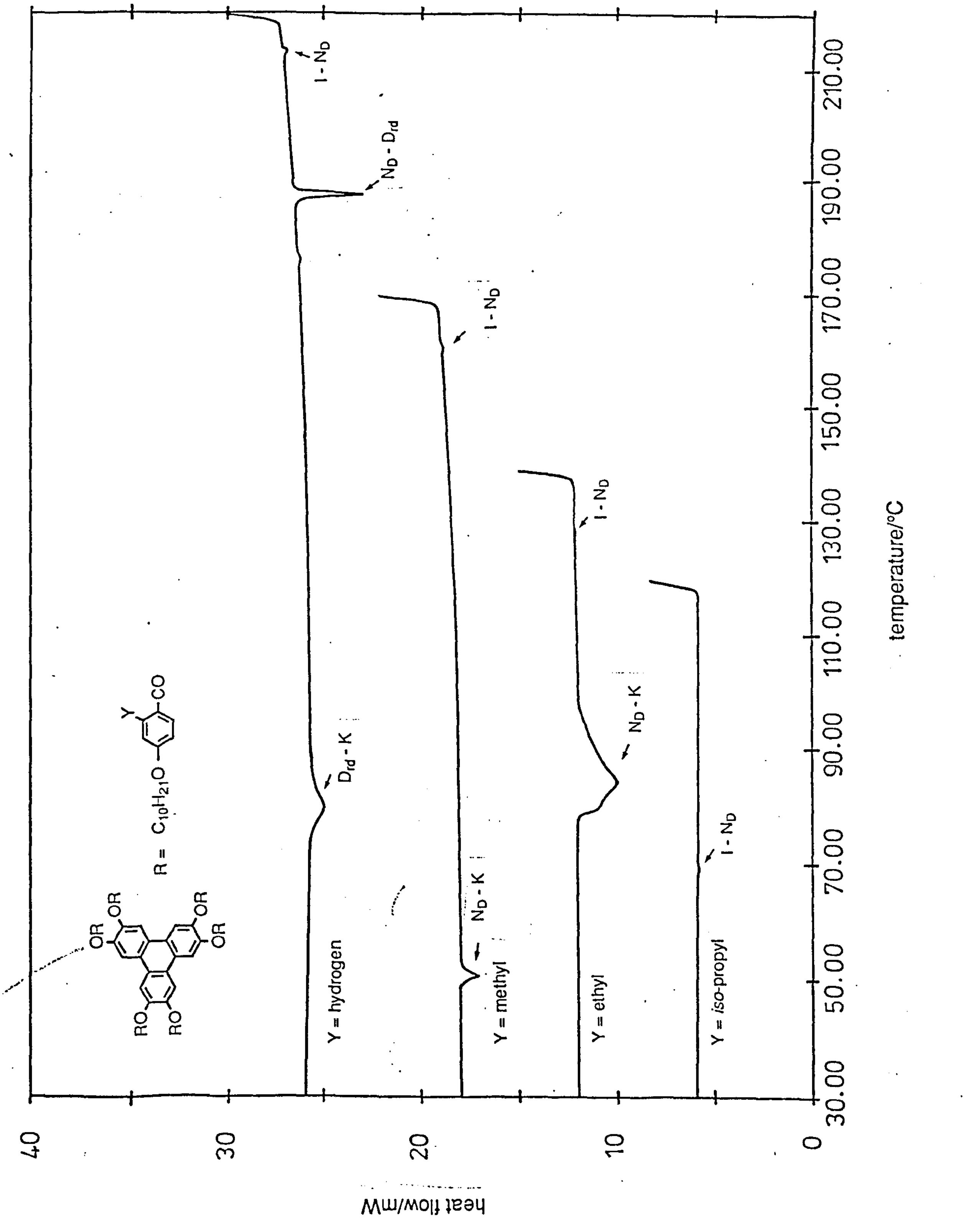


**Figure 4.5 : DSC thermogram of the first cooling cycles of the triphenylen-2,3,6,7,10,11-hexayl hexakis(2-alkyl-4-decyloxybenzoate)s (42, 69, 70 and 103)**

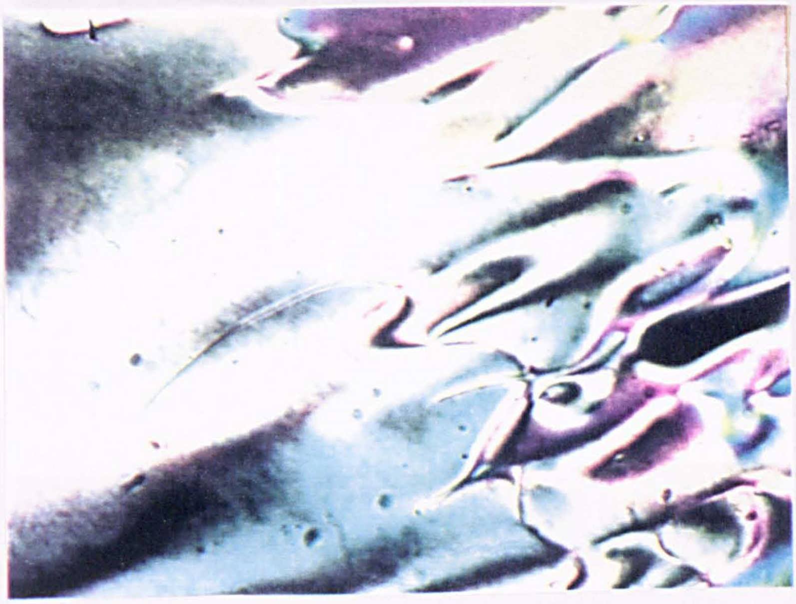


**Plate 4.1 : Sheared *schlieren* and threaded texture of the discotic nematic ($N_D$) exhibited by compound 66 at 183 °C on heating**

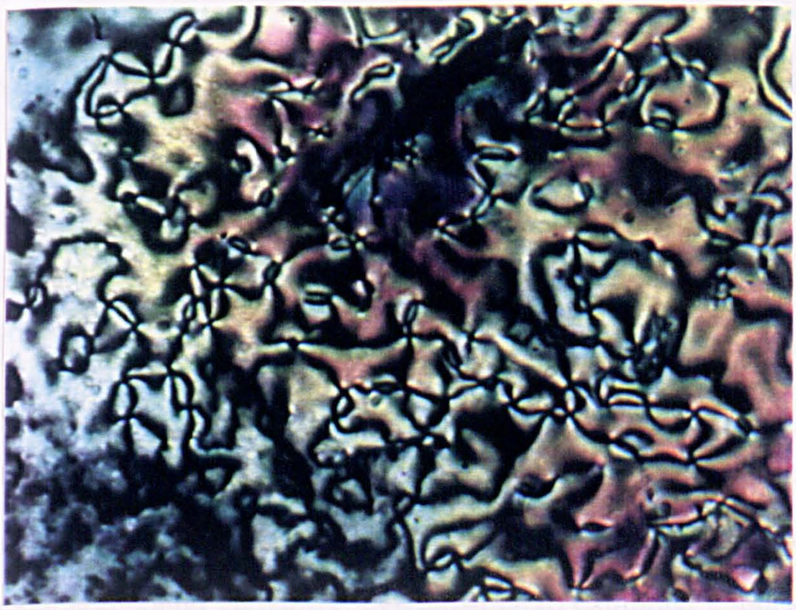


**Plate 4.2 : Classical *schlieren* texture of the discotic nematic ($N_D$) showing singularities with two and four brushes, exhibited by compound 66 at 195 °C on cooling from the isotropic liquid**

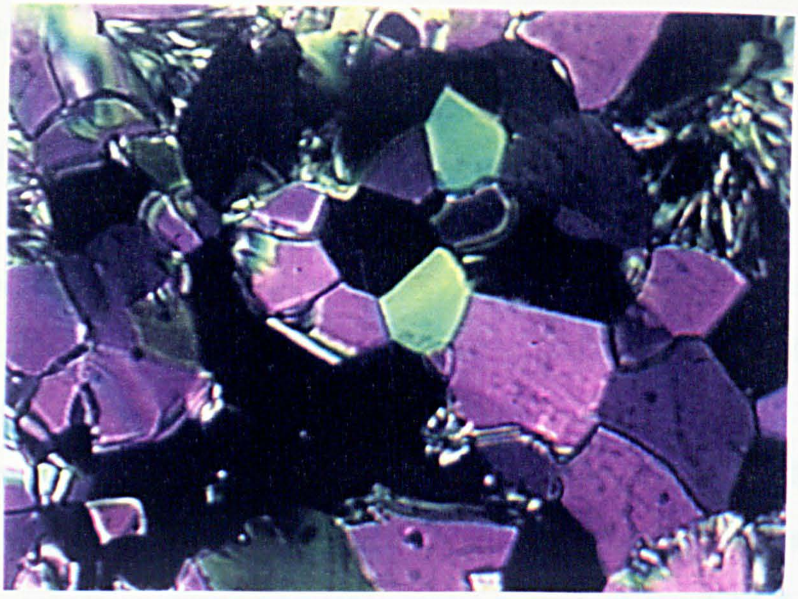


**Plate 4.3 : Mosaic texture of the ordered phase that resembles a hexagonal disordered ($D_{hd}$) exhibited by compound 66 at 124 °C on cooling from the $N_D$ mesophase**

The inner methyl- and ethyl-substituted compounds (**103** and **69**) showed transitions to the discotic nematic ($N_D$) mesophase from the crystal and then on further heating a transition to the isotropic liquid was seen. However, the *iso*-propyl-substituted material (**70**) did not show mesogenic behaviour on heating and melted directly to the isotropic liquid.

On cooling, the nematic phase was observed for all homologues. However, compound **70** (*iso*-propyl-substituted) only exhibited a monotropic $N_D$ mesophase approximately 20 °C lower than the clearing point transition whereas the $N_D$-I transition for the methyl- and ethyl-substituted materials (**103** and **69**) were found to be reversible. On further cooling, the inner methyl- and ethyl-substituted compounds (**103** and **69**) recrystallized, but compound **70** (*iso*-propyl-substituted) exhibited a transition to a glassy state which is supported by the data from the DSC thermogram as there is no evidence for a transition to the crystalline state. The viscosity of the nematic phase was found to increase with cooling until a point was reached where the sample was unable to be sheared and the glassy state had been reached. The texture of the glassy state was found to be almost the same as that of the nematic phase. A similar situation was also found for the inner dimethyl-substituted triphenylene benzoates[2] (see also Chapter 3).

### *4.3.4 Miscibility Studies*

Miscibility studies were carried out in order to try and confirm the phase identification of the suspected "columnar" phase exhibited by the outer methyl- and ethyl-substituted materials (**99** and **66**). It was expected that if the suspected phase was an hexagonal disordered ($D_{hd}$) columnar mesophase, then it would suppress the rectangular disordered ($D_{rd}$) columnar in the phase diagram. We had previously observed a similar depression in columnar properties when mixing triphenylen-2,3,6,7,10,11-hexayl hexakis(3,5-dimethyl-4-octyloxybenzoate) with its parent unsubstituted triphenylene benzoate[2] (see also Chapter 3).

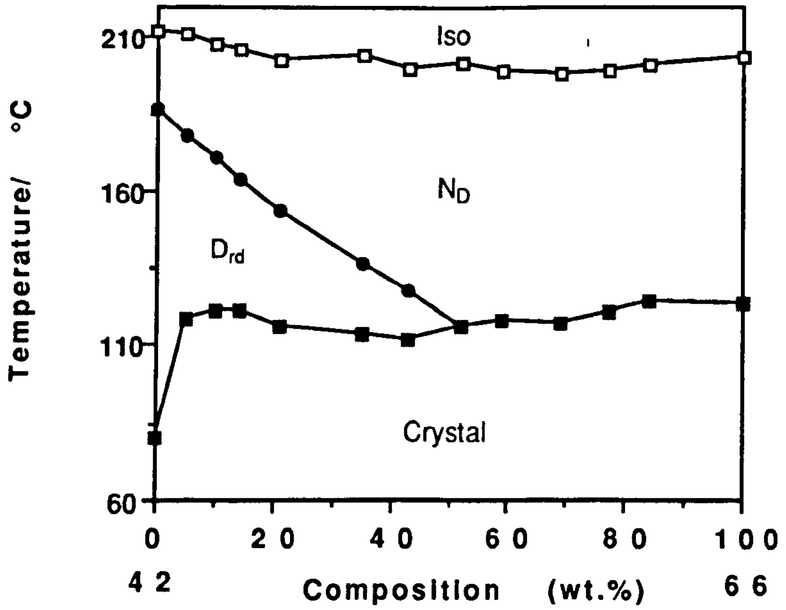


**Figure 4.6 : Binary phase diagram of transition temperatures plotted against '% by weight' for compounds 42 and 66**

It can be seen from Figure 4.6, that this is not the case. The phases of compound **66** are not fully compatible with those of the standard unsubstituted material (**42**). Nevertheless, the results confirm the presence of the discotic nematic ($N_D$) mesophase in compound **66**, however, the more ordered mesophase in question is not confirmed as being an hexagonal disordered phase ($D_{hd}$). Again, the ordered phase (40-100% of **66** in the phase diagram) showed no fluidity, whereas the rectangular disordered ($D_{rd}$) (found in the 0-40% of **66**) was able to be mechanically sheared. These results again suggest that the ordered phase is more than likely a crystal phase, and that lateral methyl- and ethyl-substitution does in fact suppress columnar mesophase formation.

The data and conclusions reached from the DSC cycles and thermal optical microscopy studies are shown graphically in Figure 4.7 for the outer substituted materials (compounds **66-68** and **99**), and in Figure 4.8 for the inner substituted materials (compounds **69**, **70** and **103**).

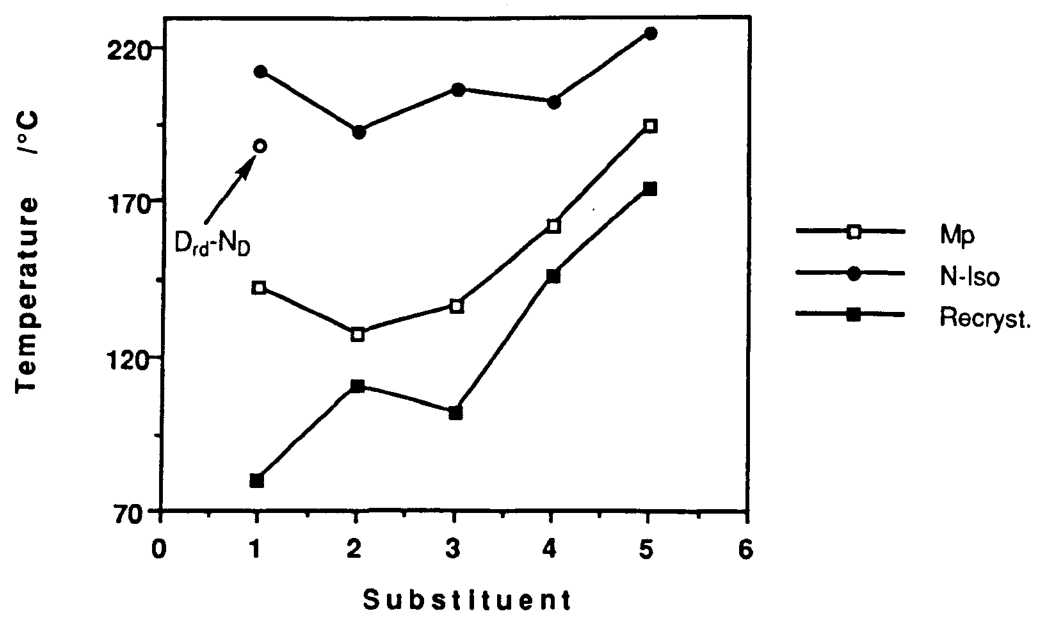


**Figure 4.7 : Transition temperatures plotted against size of substituent for the triphenylen-2,3,6,7,10,11-hexayl hexakis(3-alkyl-4-decyloxybenzoate)s; substituent: 1 - hydrogen (42); 2 - methyl (99); 3 - ethyl (66); 4 - *iso*-propyl (67); 5 - *tert*-butyl (68)**

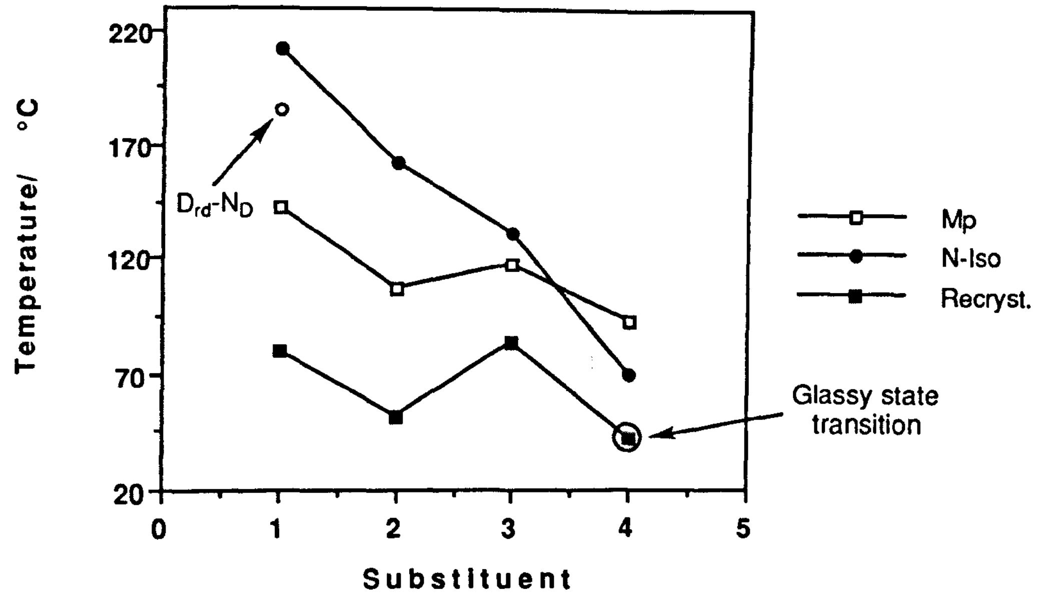
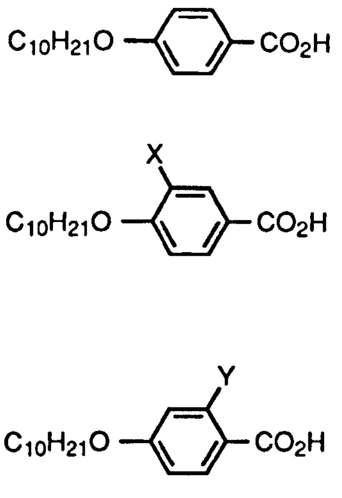


**Figure 4.8 : Transition temperatures plotted against size of substituent for the triphenylen-2,3,6,7,10,11-hexayl hexakis(2-alkyl-4-decyloxybenzoate)s; substituent: 1 - hydrogen (42); 2 - methyl (103); 3 - ethyl (69); 4 - *iso*-propyl (70)**

## *4.4 Molecular Modelling*

Molecular modelling studies were performed on the final discotic materials in order to obtain information about their molecular conformations and geometries, *ie,* in order to determine how the phenyl rings of neighbouring *arms* lie with respect to one another and/or with respect to the triphenylene core.

However, the modelling of the discotic triphenylene benzoates was performed only after the following benzoic acids - compounds **55-57, 64** and **65** (see Scheme 4.1), three literature benzoic acids (**71, 82** and **95**) detailed previously[1,3] (see also Chapter 5) and the unsynthesized benzoic acid (**72**) were investigated (see Figure 4.9). Studying the effect of the various substituents on the conformational structures of the benzoic acids was necessary as these materials are single systems and therefore much simpler in nature to investigate than their discotic counterparts. This allowed certain assumptions or inferences to be taken concerning the geometry about the benzoate *arms* of the triphenylene discogens.



**71**

**82** X = methyl
**55** X = ethyl
**56** X = *iso*-propyl
**57** X = *tert*-butyl

**95** Y = methyl
**64** Y = ethyl
**65** Y = *iso*-propyl
**72** Y = *tert*-butyl

Figure 4.9

### *4.4.1 Molecular modelling studies on the variously substituted benzoic acids* (55-57, 64, 65, 71, 72, 82 and 95)

Two different conformational searches (which are shown graphically in Figure 4.10 for the unsubstituted benzoic acid **71**) were performed on the resulting minimised structures for each of the benzoic acids **55-57**, **64**, **65**, **72**, **82** and **95**.

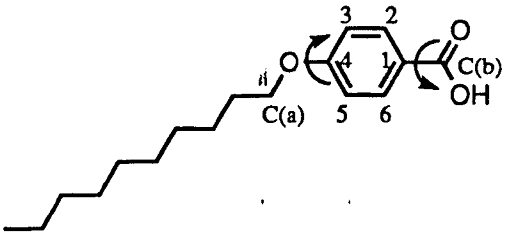


Figure 4.10

The first search was performed around the C(3)-C(4)-O-C(a) dihedral angle paying particular attention to the benzoic acids **55-57** and **82** which have substitution in the *ortho* position to the alkoxy chain. For this search, the remaining benzoic acids **64**, **65**, **72** and

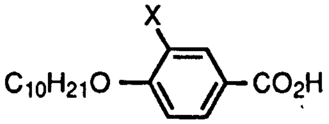
**95**, are of minor importance because steric interactions between the alkoxy group and the substituent are small or negligible.

Similarly, the second conformational search was performed around the C(2)-C(1)-C(b)-O dihedral angle and in this case, compounds **64**, **65**, **72** and **95** (which have the substituent *ortho* to the carboxylic acid group) are now of special interest since steric interactions between the carboxylic acid group and the substituent will be more significant than those encountered for compounds **55-57** and **82**.

The conformational searches were performed using a 360° grid scan of the dihedral angle with a 10° step size. At each step, the grid torsion was fixed to prevent the new conformational structure returning to the initial geometrically minimised structure. The resulting conformational structure was then further minimised using the ABNR algorithm and the number of iterations was limited to a small number (*ie*, 500) which was sufficient because complete geometrical optimisation had already been performed.

### 4.4.1.1 *Conformational studies concerning the alkoxy group*

The data obtained from the conformational search around the C(3)-C(4)-O-C(a) dihedral angle of the *meta* substituted benzoic acids **55-57** and **82** is found in Table 4.3; the unsubstituted benzoic acid (**71**) has been included for comparison. The values of ΔEa were determined from the rotation of the C(4)-O bond.



| No. | X | ΔEa / kcal mol$^{-1}$ |
|---|---|---|
| **71** | H | 2.24 |
| **82** | Methyl | 5.75 |
| **55** | Ethyl | 7.57 |
| **56** | *Iso*-propyl | 10.27 |
| **57** | *Tert*-butyl | 20.05 |

**Table 4.3 : Values of the energy barrier (ΔEa) to the rotation of the terminal alkoxy chain around the C(4)-O bond for the 3-alkyl-4-decyloxybenzoic acids**

It was found that the minimised structures of all the benzoic acids have a planar geometry (*ie,* the part of the alkoxy group near to the aromatic ring lies in the plane of the phenyl ring). As expected, as the size of the substituent *ortho* to the alkoxy group increases, the value of ΔEa also increases due to the steric interations between these two groups. As the size of the substituent is increased, the part of chain that is adjacent to the aromatic ring has less rotational freedom, and hence the value of the ΔEa increases accordingly. Thus, for the complete discotic molecular system, these results suggest that, as the peripheral alkoxy chain becomes stiffer, the effective diameter of the "rigid" central core of the system becomes larger.

For compounds **64, 65, 72** and **95**, the terminal alkoxy chain is not interfered with by the substituent whilst rotating around the C(3)-C(4)-O-C(a) dihedral angle. It was expected that the results of these modelling investigations would produce results similar to those obtained for the unsubstituted benzoic acid (**71**), and this was found to be true: the materials all have a planar geometry and ΔEa = 2.24 kcal $mol^{-1}$. Hence, for these compounds, the size or diameter of the "rigid" central core of their discotic counterparts remains effectively constant.

### *4.4.1.2 Conformational studies concerning the carboxylic acid group*

The conformational searches around the C(2)-C(1)-C(b)-O dihedral angle for the *ortho* substituted benzoic acids **64, 65, 72** and **95** gave the variation of the relative torsional energy as a function of the torsion angle for the rotation around the C(1)-C(b) bond; the plots obtained are overlayed in Figure 4.11.

When the torsion angle θ is *ca.* 0° or 180°, the carboxylic acid group and the phenyl ring lie in the same plane and so this conformer is highly conjugated. As the size of the substituent increases, so do the steric interactions between the substituent and carboxylic acid group and this is clearly seen by the fact that the conjugated configurations become less favourable.

When the torsion angle θ is *ca.* 90° or 270°, the carboxylic acid group and the phenyl ring lie in planes normal to one another and so this conformer has little or no conjugation at all. However, these configurations become more favourable as substituent size increases because the steric interactions between the substituent and carboxylic acid group are minimised (see Figure 4.11). An indication of the strength of the conjugation is found upon the addition of a methyl group (compound **95**); it is seen that the carboxylic acid group is in the same conformation as that seen for the unsubstituted benzoic acid (**71**).

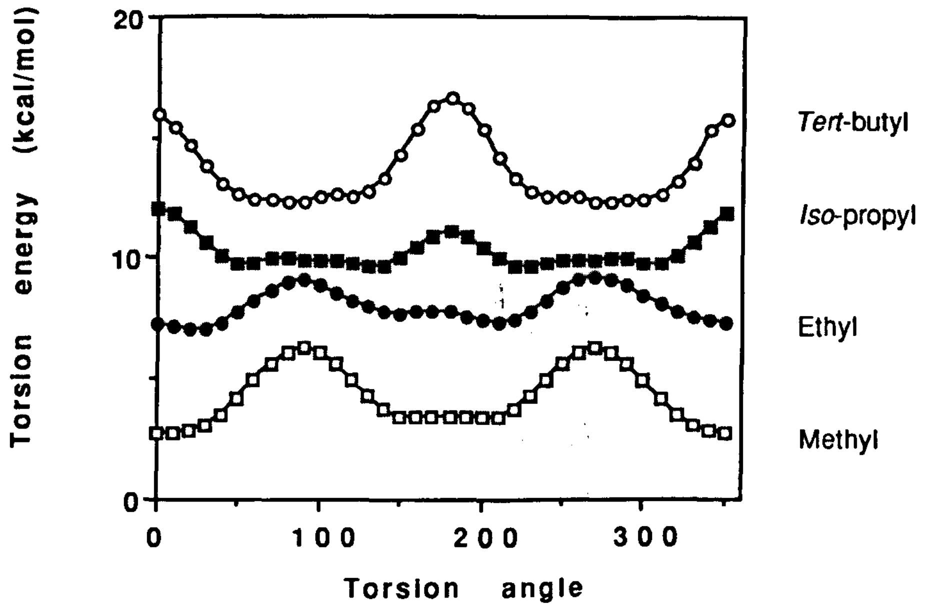


**Figure 4.11 : Comparision of the torsion energy diagrams of 64, 65, 72 and 95 for the C(2)-C(1)-C(b)-O dihedral angle**

Another aspect of the steric interaction between the lateral substituent Y and the carbonyl group of the acid moiety is that, as Y is increased in size, the effective conjugation between the carbonyl group and the phenyl ring is reduced. This has the effect of reducing the polarizability of the system and localizing the dipole associated with the carbonyl moiety of the carboxylic acid functional group. In addition, as Y is increased in size, the direction of the dipole will change as the conjugation is reduced. The relationship between polarizability and electron delocalization was previously investigated in a similar system.[5] For the overall discogen, this has the effect of altering the direction of the dipole from being radially distributed for small sizes of Y to tangential for larger sizes of Y. In this process, tangential orientations could also include out-of-plane directions, thereby increasing the inter-disc electrostatic repulsions. Consequently, it might be expected that as Y increases in size, "the effective molecular thickness" will also increase.

It was expected that for the methyl- to *tert*-butyl-substituted benzoic acids (**55-57** and **82**), the results of these modelling studies concerning the carboxylic acid group would be similar to the result obtained for the unsubstituted acid (**71**) and indeed, for these materials, this was found to be true.

### *4.4.2 Molecular modelling studies on the discotic materials* (**42, 66-70, 73, 99 and 103**)

Molecular modelling studies were carried out on the discotic materials **66-70** (see Scheme 4.2), three literature discotic compounds (**42, 99** and **103**) reported previously[1,3] (see also Tables 4.1 and 4.2; and Chapter 5) and an unsynthesized discotic molecule (**73**, which possesses a *tert*-butyl substituent *ortho* to the ester linkage; see Table 4.5). The molecular conformation with the lowest potential energy was obtained for each material using the same experimental procedure as described above for the laterally substituted benzoic acids.

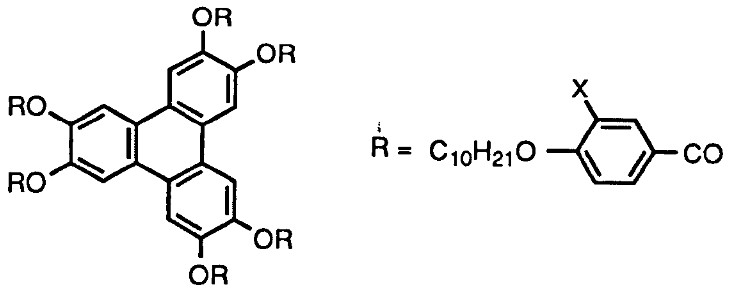
#### *4.4.2.1 Molecular modelling studies of the discogens with substitution in the outer regions*

The results obtained for the conformation studies for the discogens **42, 66-68** and **99** are shown in Table 4.4.

The torsion angles ($\lambda$) between the plane of the core and the plane of the peripheral phenyl ring are interesting in that they show an odd/even type trend as the size of the substituent increases. It might have been expected that the "rigid" central core thickness would follow a size accommodation trend of the form:

$$\mathrm{H} < \mathrm{Me} \sim \mathrm{Et} < i\text{-}\mathrm{Pr} << t\text{-}\mathrm{Bu}$$

However, the odd/even type trend in $\lambda$, together with the substitution size relationship described above, would lead to suggest that the core exhibits a general stepwise increase in thickness as the series is ascended (*ie*, from hydrogen to *tert*-butyl).



| No. | X | λ / ° | θ / ° |
|---|---|---|---|
| **42** | H | 80.7 ± 3.3 | negligible |
| **99** | Methyl | 60.9 ± 11.4 | negligible |
| **66** | Ethyl | 75.1 ± 11.3 | 13.6 |
| **67** | *Iso*-propyl | 61.2 ± 1.0 | 12.5 |
| **68** | *Tert*-butyl | 82.8 ± 3.3 | 10.5 |

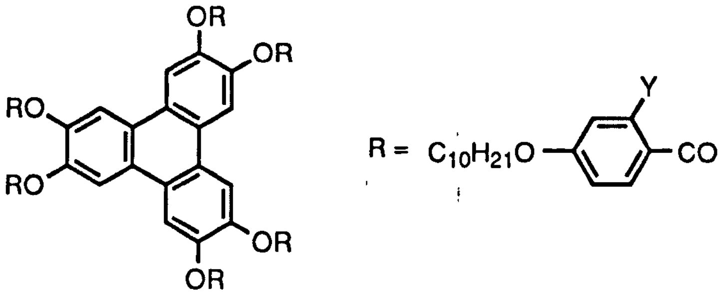
**Table 4 .4 : Geometrical observations for the minimised structures of the outer substituted discogens, where λ is the angle between the plane of the core and the plane of the peripheral phenyl ring and θ is the angle between the plane of the peripheral phenyl ring and the plane of the ester linkage. The values quoted are average ones and the limits are the corresponding standard deviations**

Finally, the dihedral angle (θ) between the plane of the peripheral phenyl ring and the ester linkage is small throughout the series, indicating that substitution in the outer regions has little or no effect on the conformation of the ester and phenyl rings. This was expected from the molecular modelling studies performed on the various related benzoic acids (**55-57** and **82**) where θ = 0°. The implication of such small θ values in the complete discotic molecules is that the local dipoles formed by the carbonyl groups will be small and largely independent of the substituent size and thus, electrostatic repulsion would not be expected to greatly affect the thickness of the central triphenylene core of the discogens.

### *4.4.2.2 Molecular modelling studies of the discogens with substitution in the inner regions*

The results obtained for the conformation studies for the inner-substituted discogens (**42, 69,70, 73** and **103**) are shown in Table 4.5.

The torsion angles (λ) between the planes of the core and the peripheral phenyl ring do not exhibit an odd/even-type trend as previously observed for the outer substituted discogens (*cf.* Table 4.4). After an initial drop in λ from the unsubstituted discogen (**42**) to the methyl-substituted analogue (**103**), λ then remains largely constant upon ascending the series. Therefore, a more linear increase in the "rigid" central core thickness of the discotic molecules is expected.



| No. | Y | λ / ° | θ / ° |
|---|---|---|---|
| **42** | H | 80.7 ± 3.3 | negligible |
| **103** | Methyl | 33.9 ± 3.5 | 32.4 ± 1.3 |
| **69** | Ethyl | 29.8 ± 0.5 | 35.7 ± 0.5 |
| **70** | *Iso*-propyl | 33.4 ± 4.6 | 30.8 ± 1.2 |
| **73** | *Tert*-butyl | 34.6 ± 9.2 | ~50 |

**Table 4.5 : Geometrical observations for the minimised structures of the inner substituted discogens, where λ is the angle between the plane of the core and the plane of the peripheral phenyl ring and θ is the angle between the plane of the peripheral phenyl ring and the plane of the ester linkage. The values quoted are average ones and the limits are the corresponding standard deviations**

Furthermore, as expected from the molecular modelling of the related benzoic acids (**64, 65, 72** and **95**), the angle (θ) between the planes of the peripheral ring and the ester linkage is significant, and similar values are found for the methyl-, ethyl- and *iso*-propyl-substituted compounds (**69**, **70** and **103**) whereas the largest value is observed for the *tert*-butyl-substituted homologue (**73**). As discussed previously, the larger the value of θ, the stronger the local dipoles formed by the out of plane carbonyl group, hence the greater the electrostatic repulsion between molecules that are face-to-face with one another and, ultimately, the thicker the "rigid" central core of the discogen.

### *4.4.3 Summary of the Modelling Studies*

From the modelling studies performed on the *meta* substituted benzoic acids (**55-57** and **82**) and the outer substituted discotic molecules (**66-68** and **99**), it is expected that the effective diameter of the outer substituted discotic molecule would increase with substituent size. Furthermore, it is expected that the central core thickness would be independent of electrostatic repulsions. From Plate 4.4, it is qualitatively shown that as substituent size increases, so does core thickness. Finally, it is thought that the thickness of the "rigid" central core will increase in a stepwise or odd/even manner with increasing substituent size.

The modelling studies on the *ortho* substituted benzoic acids (**64**, **65**, **73** and **95**) and the inner substituted discotic molecules (**69**, **70**, **73** and **103**) suggest that the electrostatic repulsion between adjacent inner substituted discotic molecules will increase due to a lowering of electron delocalization, thus increasing the effective thickness of the "rigid" central core. From Plate 4.5, it is qualitatively shown that the core thickness increases with substituent size. Finally, a near linear relationship is expected between substituent size and core thickness.

## *4.5 Discussion*

In our previous studies using methyl substitution, we had shown that "inner" methyl-substitution depresses mesophase transitions to a greater extent than the positioning of the methyl groups in the "outer" pointing positions in the peripheral phenyl units[3] (see also Chapter 5). Similarily, di-substitution appears to be even more effective in depressing the transition temperatures than mono-substitution[2] (see also Chapter 3). These property/structure correlations appear to indicate that interactions caused by the steric hindrance between the peripheral phenyl rings leads to a thickening of the molecular discs, *ie,* the steric hindrance of the methyl groups leads to a rotation of the peripheral phenyl rings out of plane of the central triphenylene core. The disc-thickening is expected to lead to a weakening of the core-core (face to face) interactions, ultimately leading to a reduction in the capacity of the system to form columnar phases and a depression of the clearing point temperatures.[2]

In this present study, we sought to examine the limits that substituent size has on mesophase stability and the formation of columnar phases. Thus, by increasing the size of lateral substituents the steric interactions/repulsions are expected to increase, thereby suppressing the overall tendency of the materials to exhibit mesophases. In addition, the columnar phases were expected to be suppressed totally with increasing substituent size.

By examining the data presented in Table 4.1 and Figure 4.7, it is clearly seen that lateral substitution in the "outer" region has greatly influenced the mesogenic behaviour. The discogens are all nematogenic, with two materials (the methyl- and ethyl-substituted homologues, **99** and **66**) exhibiting an additional crystal phase. There is an initial fall both in the melting point and in the clearing point when increasing the size of the substituent from hydrogen (**42**) to methyl (**99**), but from then on through to *tert*-butyl, a general increase in both transitions is observed.

The unusual and unexpected behaviour of the increasing clearing points can be explained from the molecular modelling studies of the variously substituted benzoic acids (**55-57** and **82**) and of the discotic materials (**66-68** and **99**). Plate 4.4 qualitatively indicates that as the substituent bulk increases, so does the central core thickness. It has been shown that electrostatic repulsion, which also contributes to core thickness, is small and largely independent of the substituent size in the outer-substituted series. Additionally, core thickness would appear to increase in a general odd/even manner as the size of the substituent increases. When the core thickness is larger, weaker core-core interactions are experienced and a *lowering* of the clearing points is observed.

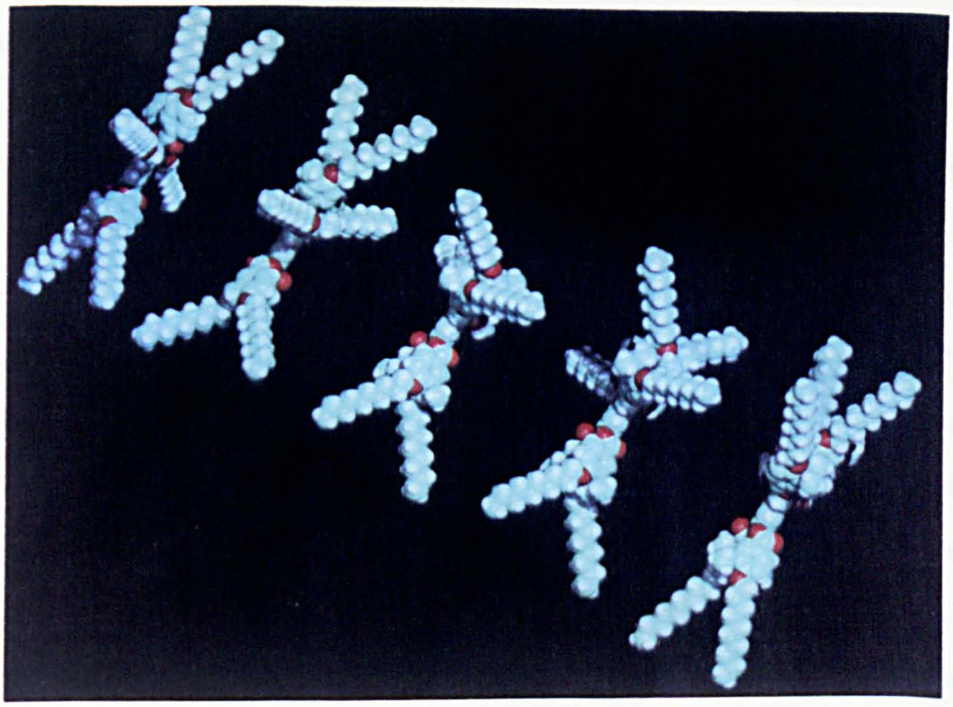


**Plate 4.4 : Photograph showing a side view of the outer-substituted discotic molecules, from left to right - hydrogen through to *tert*-butyl**

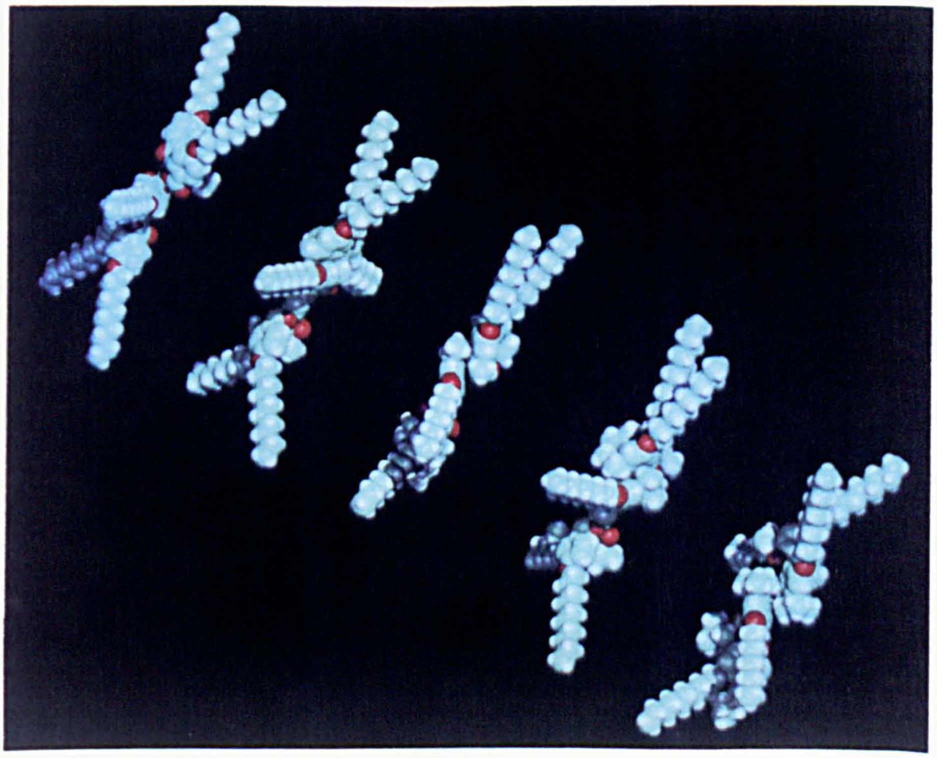


**Plate 4.5 : Photograph showing a side view of the inner-substituted discotic molecules, from left to right - hydrogen through to *tert*-butyl**

For the outer substituted systems, because of the rotational restriction of the first few carbon atoms in the alkoxy chain (caused by the increasing size of the lateral substituent), the "rigid" central core effectively appears larger. When the core size is increased, stronger core-core interactions are experienced, leading to higher clearing points. Thus in this system, a balance has been reached between one tendency to lower the clearing points, due to stepwise increase in core thickness, and another effect to increase the clearing points, caused by increasing the effective diameter of the central core which has given rise to the odd/even trend in the observed clearing points (see Figure 4.7).

In the second series of compounds (**69, 70** and **103**), with substitution in the "inner" regions, the results are quite remarkable (see Table 4.2 and Figure 4.8). There is a very clear trend in the reduction in the clearing points. All the compounds are purely nematogenic, however the *iso*-propyl derivative (**70**) has a monotropic discotic nematic phase. The effect of the size of the lateral substituent is quite exceptional. The trend in the clearing points again can be explained from the molecular modelling of the variously substituted benzoic acids (**64, 65, 72** and **95**) and of the discogens (**69, 70, 73** and **103**).

Plate 4.5 shows qualitatively that as the size of the substituent increases, the central core thickness also increases. As the disc has an uneven cross-sectional area, a lowering of clearing point temperatures may be expected. On the other hand, the diameter of the central core is not affected by inner substitution, implying that there would be no upward trend in the clearing point temperatures. Therefore, the sharp decrease in clearing point temperatures with substituent size (see Figure 4.8) can be explained by the fact the core thickness is increased by the bulky lateral substituent as well as electrostatic repulsions. The effect of such bulky lateral substituents in calamitic systems would easily render the materials non-mesogenic,[6] thus, our results reveal the greater tolerance of discotic phases towards the inclusion of bulky lateral substituents in terms of the depression of the nematic phase stability.

## *4.6 Conclusions*

We have demonstrated that there is a relationship between molecular disc thickness and phase formation in discotic liquid crystals. Thickening the molecular disc, and in due course weakening the face-to-face interactions has the effect of suppressing columnar phases, whereas nematic phase stability remains relatively unaffected.

## *4.7 References*

1) N.H. Tinh, H. Gasparoux and C. Destrade, *Mol. Cryst. Liq. Cryst.*, 1981, **68**, 101.

2) P. Hindmarsh, M. Hird, P. Styring and J.W. Goodby, *J. Mater. Chem.*, 1993, **3**, 1117.

3) D.R. Beattie, *Ph. D. Thesis*, University of Hull, 1993.

4) C. Destrade, P. Foucher, H. Gasparoux, N.H. Tinh, A.-M. Levelut and J. Malthête, *Mol. Cryst. Liq. Cryst.*, 1984, **106**, 121.

5) T.J. Phillips and J.C. Jones, *Liq. Cryst.*, 1994, **16**, 805.

6) K.J. Toyne, in *Thermotropic Liquid Crystals*, ed. G.W. Gray, Wiley, Chichester, 1987.

# *CHAPTER 5*

# *Lateral Substitution in the Peripheral Moieties of Triphenylene Benzoates: Mono-methyl-substituted Systems*

## *5.1 Introduction*

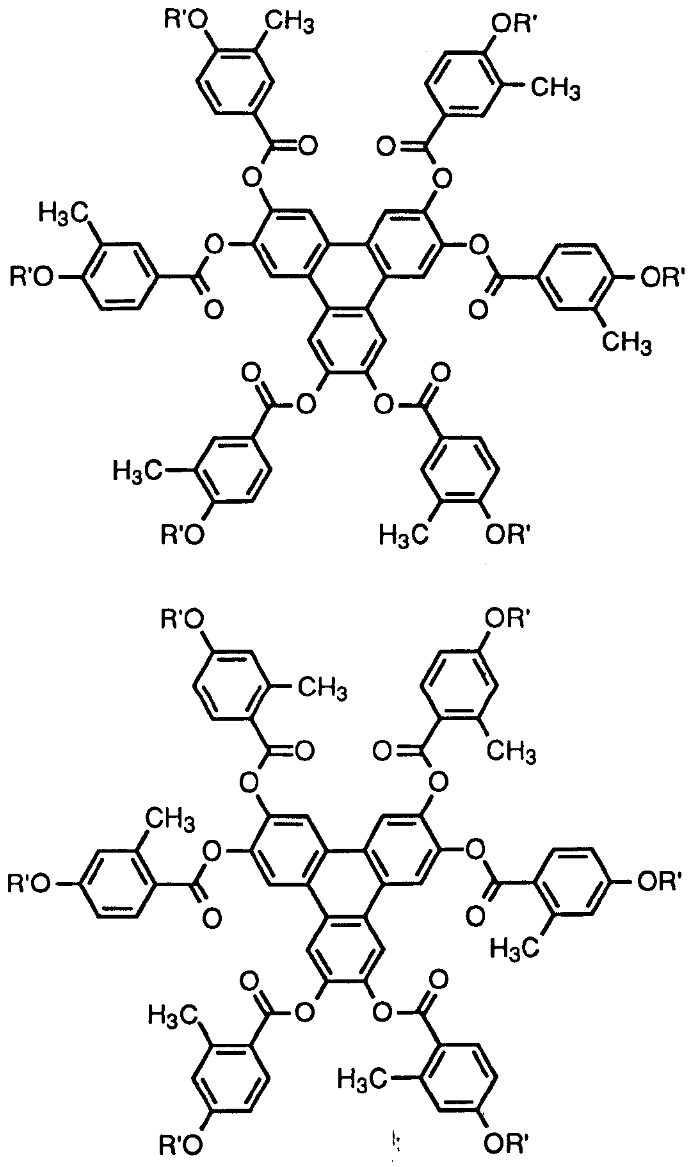
Research into the effects of mono-methyl substitution in the peripheral moieties of triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s was first conducted at Hull by Beattie[1] and the results were published in his thesis in 1993.

Beattie's synthetic approach to the production of these materials (see structures **I** and **II**, Figure 5.1) was elaborate and long-winded.[1] To obtain the various methyl-substituted benzoic acids, Beattie employed Fries Rearrangements and haloform reactions which were both time-consuming and inefficient in terms of yield.[1] The purities of the final discotic liquid crystals were questionable, and consequently, the results obtained for the liquid crystalline properties were highly unreliable.

This last point was previously raised in Chapter 4. It was during the study of the effects of the bulky-substituted triphenylene systems, that it was noted that the mono-methyl-substituted materials supplied by Beattie did not fit the liquid-crystalline behavioural patterns shown by the ethyl-, *iso*-propyl- and *tert*-butyl-substituted analogues.

To ensure accurate results were obtained, it was decided to re-synthesize and re-evaluate the selected mono-methyl-substituted triphenylene benzoates. Hence, the synthetic organic chemistry and evaluation work conducted on the liquid-crystalline properties of these materials and detailed in this chapter is entirely fresh.

Thus, in this chapter the new synthesis and properties of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-3-methylbenzoate)s and (-2-methylbenzoate)s are discussed (see structures **I** and **II**, Figure 5.1).



I

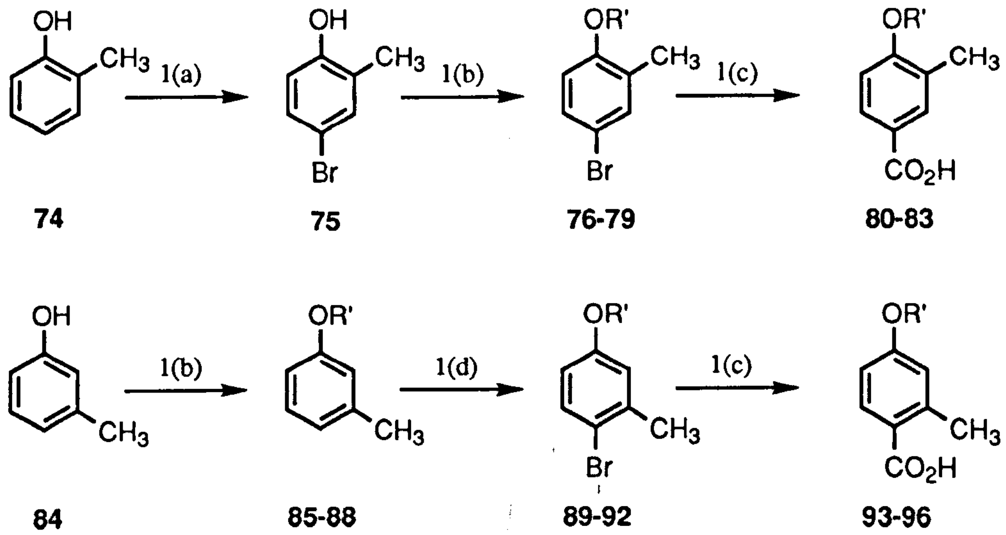
II

R' = $C_nH_{2n+1}$ (n = 6, 8, 10 and 12)

**Figure 5.1 : Structures of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-3-methylbenzoate)s and (-2-methylbenzoate)s (structures I and II)**

## *5.2 Experimental*

The materials were prepared by the routes shown in Schemes 5.1 and 5.2. The various substituted acids were prepared by the synthetic routes shown in Scheme 5.1. Compounds **74** and **84** were purchased from Aldrich Chemical Co. Compound **74** was brominated in a good yield using bromine and glacial acetic acid at 0 °C. Compound **84** was unable to be brominated solely in the desired position due to the position of the alkyl substituent. Therefore, compound **84** was first *O*-alkylated with the appropriate *n*-alkyl bromides in good yields using anhydrous potassium carbonate in butanone to provide compounds **85-88**. Compound **75** was also *O*-alkylated in this manner to give compounds **76-79**, in similarily good yields. Substitution of the bromine in the desired position to compounds **89-92** was achieved by adding bromine dropwise to a gently refluxing solution of these compounds in dry chloroform. The replacement of the bromine in compounds **76-79** and **89-92** was achieved by lithiation using *n*-butyllithium at -78 °C; in each case, the reaction mixture was then poured onto a slurry of solid $CO_2$ and dry ether, acidified, and the product purified (compounds **80-83** and **93-96**). The final liquid-crystalline materials (**97-104**) were prepared by the esterification of HHTP (**3**) with the respective benzoyl chlorides in the presence of pyridine.



R' = $C_nH_{2n+1}$ (n = 6, 8, 10 and 12)

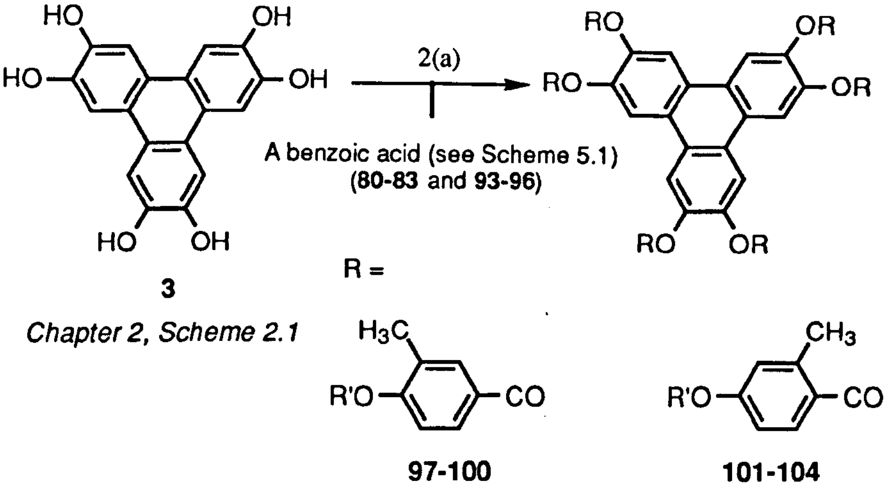
1(a) ..... $Br_2$, acetic acid, 0 °C.

1(b) ..... RBr, $K_2CO_3$, butanone.

1(c) ..... (i) *n*-BuLi, THF; (ii) $CO_2$ (solid), $Et_2O$.

1(d) ..... $Br_2$, dry $CHCl_3$, reflux.

**Scheme 5.1 : Synthetic route for the preparation of the 4-alkoxy-3-toluic and -2-toluic acids (80-83 and 93-96)**



R' = $C_nH_{2n+1}$ (n = 6, 8, 10 and 12)

2(a) ..... Acid chloride (oxalyl chloride, DMF, $CH_2Cl_2$), pyridine.

**Scheme 5.2 : Synthetic route for the preparation of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-3-methylbenzoates) and (-2-methylbenzoates) (97-104)**

### *5.2.1 Preparation of 4-Bromo-2-cresol* (75)

The synthetic method is exemplified by the procedure reported in Chapter 4 for compound 49.

| | |
|---|---|
| Yield: 69.35 g (81%) | Bp: 130-132 °C at 17 mmHg |
| $^1$H NMR ($CDCl_3$ and TMS) δ: | 2.20(3H, s), 5.06(1H, s broad), 6.61(1H, d), 7.15(1H, dd), 7.25(1H, d). |
| IR (KBr) $\nu_{max}$ cm$^{-1}$: | 3700-3100(broad), 2960, 1690, 1580, 1490, 1460, 1390, 1320, 1260, 1230, 1200, 1170, 1115, 870, 810, 760, 630. |
| MS (*m/z*): | 188(M$^+$), 186(M$^+$), 107, 51, 43. |

### 5.2.2 *Preparation of the 2-Alkoxy-5-bromotoluenes and 3-Alkoxytoluenes* (76-79 and 85-88)

The general synthetic method is exemplified by the procedure reported in Chapter 3 for compound **9**.

*5-Bromo-2-hexyloxytoluene* (**76**)

Yield: 6.68 g (57%)  Bp: 155-160 °C at 0.4 mmHg

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.30(6H, m), 1.80(2H, m), 2.18(3H, s), 3.90(2H, t), 6.65(1H, dd), 7.22(2H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1485, 1460, 1240, 1190, 1135, 800, 640.

MS (*m/z*): 272($M^+$), 270($M^+$), 188, 186, 107, 85, 78, 43.

*5-Bromo-2-octyloxytoluene* (**77**)

Yield: 8.35 g (76%)  Bp: 165-170 °C at 0.4 mmHg

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.30(10H, m), 1.80(2H, m), 2.15(3H, s), 3.90(2H, t), 6.65(1H, dd), 7.22(2H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1485, 1460, 1245, 1190, 1130, 800, 640.

MS (*m/z*): 300($M^+$), 298($M^+$), 188, 186, 107, 77, 57, 43.

*5-Bromo-2-decyloxytoluene* (**78**)

Yield: 8.13 g (71%)  Bp: 175-180 °C at 0.4 mmHg

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.30(14H, m), 1.80(2H, m), 2.17(3H, s), 3.90(2H, t), 6.65(1H, dd), 7.22(2H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1485, 1460, 1245, 1190, 1130, 800, 640.

MS (*m/z*): 328($M^+$), 326($M^+$), 188, 186, 107, 77, 57, 43.

*5-Bromo-2-dodecyloxytoluene* (**79**)

Yield: 6.37 g (56%)  Bp: 185-190 °C at 0.4 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.30(18H, m), 1.80(2H, m), 2.17(3H, s), 3.90(2H, t), 6.65(1H, dd), 7.22(2H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1485, 1460, 1245, 1190, 1130, 800, 640.

MS (*m/z*): 356(M$^+$), 354(M$^+$), 188, 186, 107, 77, 57, 43.

*3-Hexyloxytoluene* (**85**)

Yield: 3.24 g (72%) Bp: 130-135 °C at 0.5 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.30(6H, m), 1.75(2H, m), 2.30(3H, s), 3.92(2H, t), 6.71(3H, m), 7.13(1H, ddd).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1730, 1600, 1580, 1490, 1260, 1155, 1050, 770, 690.

MS (*m/z*): 192(M$^+$), 108, 91, 77, 43.

*3-Octyloxytoluene* (**86**)

Yield: 3.74 g (92%) Bp: 140-145 °C at 0.5 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.30(10H, m), 1.75(2H, m), 2.30(3H, s), 3.92(2H, t), 6.71(3H, m), 7.13(1H, ddd).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1730, 1600, 1580, 1490, 1260, 1170, 1070, 765, 690.

MS (*m/z*): 200(M$^+$), 108, 91, 77, 43.

*3-Decyloxytoluene* (**87**)

Yield: 4.99 g (55%) Bp: 150-155 °C at 0.5 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.30(14H, m), 1.75(2H, m), 2.30(3H, s), 3.92(2H, t), 6.71(3H, m), 7.13(1H, ddd).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1600, 1580, 1490, 1460, 1290, 1260, 1155, 1050, 770, 690.

MS (*m/z*): 248(M$^+$), 108, 91, 55, 43.

*3-Dodecyloxytoluene* (**88**)

Yield: 7.47 g (73%) Bp: 160-165 °C at 0.5 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.30(18H, m), 1.75(2H, m), 2.30(3H, s), 3.92(2H, t), 6.71(3H, m), 7.13(1H, ddd).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1600, 1580, 1490, 1460, 1290, 1260, 1155, 1050, 770, 690.

MS (*m*/*z*): 276(M$^+$), 108, 91, 55, 43.

### *5.2.3 Preparation of the 5-Alkoxy-2-bromotoluenes* (89-92)

The general synthetic method is exemplified by the procedure reported in Chapter 4 for compound **62**.

*2-Bromo-5-hexyloxytoluene* (**89**)

Yield: 3.84 g (84%) Bp: 155-160 °C at 0.4 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(6H, m), 1.75(2H, m), 2.35(2H, s), 3.90(2H, t), 6.60(1H, dd), 6.80(1H, d), 7.37(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1590, 1570, 1460, 1290, 1240, 1170, 1020, 870, 800, 640.

MS (*m*/*z*): 272(M$^+$), 270(M$^+$), 188, 186, 117, 107, 101, 73, 43.

*2-Bromo-5-octyloxytoluene* (**90**)

Yield: 4.25 g (84%) Bp: 165-170 °C at 0.4 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(10H, m), 1.75(2H, m), 2.34(2H, s), 3.90(2H, t), 6.60(1H, dd), 6.77(1H, d), 7.38(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1590, 1570, 1465, 1290, 1240, 1170, 1020, 870, 800, 640.

MS (*m*/*z*): 300(M$^+$), 298(M$^+$), 188, 186, 117, 107, 101, 43.

*2-Bromo-5-decyloxytoluene* (**91**)

Yield: 5.01 g (77%) Bp: 175-180 °C at 0.4 mmHg

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.35(14H, m), 1.75(2H, m), 2.34(2H, s), 3.90(2H, t), 6.59(1H, dd), 6.77(1H, d), 7.38(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1590, 1570, 1465, 1290, 1240, 1170, 1020, 870, 800, 640.

MS (*m/z*): 328(M$^+$), 326(M$^+$), 188, 186, 117, 107, 101, 73, 43.

*2-Bromo-5-dodecyloxytoluene* (**92**)

Yield: 6.94 g (73%) Bp: 185-190°C at 0.4 mmHg

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.35(18H, m), 1.75(2H, m), 2.34(2H, s), 3.90(2H, t), 6.59(1H, dd), 6.77(1H, d), 7.38(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1590, 1570, 1465, 1290, 1240, 1170, 1020, 870, 800, 640.

MS (*m/z*): 356(M$^+$), 354(M$^+$), 188, 186, 117, 107, 101, 73, 43.

### *5.2.4 Preparation of the 4-Alkoxy-3-toluic or 4-Alkoxy-2-toluic Acids* (80-83 and 93-96)

The general synthetic method is exemplified by the procedure reported in Chapter 3 for compound **14**.

*4-Hexyloxy-3-toluic Acid* (**80**)

Yield: 3.08 g (52%) Mp: 129-131 °C

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.35(6H, m), 1.80(2H, m), 2.26(3H, s), 4.03(2H, t), 6.84(1H, d), 7.88(1H, d), 7.93(1H, dd).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3300-2400(broad), 2920, 2860, 1675, 1600, 1430, 1325, 1305, 1265, 1140, 940, 770, 650.

MS (*m/z*): 236(M$^+$), 152, 135, 107, 77, 55, 43.

*4-Octyloxy-3-toluic Acid* (**81**)

Yield: 4.19 g (57%)
Transitions (°C): K 115 (N 102) I
$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.35(10H, m), 1.80(2H, m), 2.26(3H, s), 4.03(2H, t), 6.85(1H, d), 7.88(1H, d), 7.93(1H, dd).
IR (KBr) $\nu_{max}$ $cm^{-1}$: 3300-2400(broad), 2920, 2860, 1675, 1600, 1430, 1330, 1305, 1270, 1140, 770, 650.
MS (*m*/*z*): 264($M^+$), 152, 135, 107, 77, 57, 43.

*4-Decyloxy-3-toluic Acid* (**82**)

Yield: 4.79 g (66%)
Transitions (°C): K 107 (N 94) I
$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.35(14H, m), 1.80(2H, m), 2.25(3H, s), 4.04(2H, t), 6.85(1H, d), 7.87(1H, d), 7.92(1H, dd).
IR (KBr) $\nu_{max}$ $cm^{-1}$: 3300-2400(broad), 2920, 2860, 1675, 1600, 1430, 1330, 1305, 1265, 1140, 770, 650.
MS (*m*/*z*): 292($M^+$), 152, 135, 107, 57, 43.

*4-Dodecyloxy-3-toluic Acid* (**83**)

Yield: 3.63 g (63%)
Mp: 106-108 °C
$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.35(18H, m), 1.80(2H, m), 2.25(3H, s), 4.03(2H, t), 6.84(1H, d), 7.88(1H, d), 7.93(1H, dd).
IR (KBr) $\nu_{max}$ $cm^{-1}$: 3300-2400(broad), 2920, 2860, 1675, 1600, 1430, 1320, 1305, 1265, 1140, 770, 650.
MS (*m*/*z*): 320($M^+$), 153, 135, 107.

*4-Hexyloxy-2-toluic Acid* (**93**)

Yield: 1.93 g (58%)
Transitions (°C): K 72 N 75 I
$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.35(6H, m), 1.80(2H, m), 2.64(3H, s), 4.01(2H, t), 6.75(2H, m), 8.06(1H, d).
IR (KBr) $\nu_{max}$ $cm^{-1}$: 3300-2400(broad), 2920, 2860, 1670, 1600, 1325, 1290, 1240, 1150, 1030, 850, 770, 640.

MS (*m*/*z*): 236($M^+$), 152, 134, 77, 58, 43.

*4-Octyloxy-2-toluic Acid* (**94**)

Yield: 2.88 g (78%) Transitions (°C): K 72 (N 69) I

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(10H, m), 1.80(2H, m), 2.63(3H, s), 4.00(2H, t), 6.74(2H, m), 8.05(1H, d).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 3300-2400(broad), 2920, 2860, 1675, 1605, 1560, 1290, 1250, 1160, 1090, 865, 775, 650.

MS (*m*/*z*): 264($M^+$), 152, 134, 58, 43.

*4-Decyloxy-2-toluic Acid* (**95**)

Yield: 3.00 g (69%) Transitions (°C): K 77 (N 61) I

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(14H, m), 1.80(2H, m), 2.64(3H, s), 4.00(2H, t), 6.74(2H, m), 8.05(1H, d).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 3300-2400(broad), 2920, 2860, 1675, 1605, 1560, 1290, 1245, 1155, 1090, 865, 770, 650.

MS (*m*/*z*): 292($M^+$), 152, 134, 58, 43.

*4-Dodecyloxy-2-toluic Acid* (**96**)

Yield: 3.90 g (63%) Transitions (°C): K 81 (N 58) I

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(18H, m), 1.80(2H, m), 2.64(3H, s), 4.02(2H, t), 6.75(2H, m), 8.05(1H, d).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 3300-2400(broad), 2920, 2860, 1675, 1600, 1560, 1290, 1250, 1155, 1090, 865, 770, 650.

MS (*m*/*z*): 320($M^+$), 152, 134, 77, 57, 43.

### 5.2.5 *Preparation of the Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-alkoxy-3-methylbenzoate)s or (-2-methylbenzoate)s* (97-104)

The general synthetic method for the preparation of the hexa-esters is exemplified by the procedure reported in Chapter 3 for compound **30**.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-hexyloxy-3-methylbenzoate)* (**97**)

Yield: 1.27 g (60%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(6H, m), 1.75(2H, m), 2.06(3H, s), 3.93(2H, t), 6.64(1H, d), 7.78(1H, d), 7.88(1H, dd), 8.46(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1605, 1500, 1240, 1130, 1075, 755.

CHN analysis: % expected - C 75.00, H 7.35

% found - C 75.33, H 7.66.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(3-methyl-4-octyloxybenzoate)* (**98**)

Yield: 2.36 g (82%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(10H, m), 1.80(2H, m), 2.08(3H, s), 3.96(2H, t), 6.66(1H, d), 7.81(1H, d), 7.91(1H, dd), 8.49(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1735, 1600, 1500, 1250, 1175, 1130, 1075, 760.

CHN analysis: % expected - C 76.00, H 8.00

% found - C 76.20, H 8.38.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-3-methylbenzoate)* (**99**)

Yield: 2.20 g (70%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(14H, m), 1.75(2H, m), 2.06(3H, s), 3.94(2H, t), 6.67(1H, d), 7.76(1H, d), 7.87(1H, dd), 8.45(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1600, 1500, 1250, 1175, 1130, 1075, 755.

CHN analysis: % expected - C 76.83, H 8.54
% found - C 76.97, H 8.72.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-dodecyloxy-3-methylbenzoate)* **(100)**

Yield: 2.09 g (89%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(18H, m), 1.76(2H, m), 2.04(3H, s), 3.95(2H, t), 6.60(1H, d), 7.74(1H, d), 7.83(1H, dd), 8.45(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1600, 1560, 1500, 1290, 1250, 1175, 1140, 1080, 755.

CHN analysis: % expected - C 77.53, H 8.99
% found - C 77.71, H 9.30.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-hexyloxy-2-methylbenzoate)* **(101)**

Yield: 0.45 g (35%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(6H, m), 1.76(2H, m), 2.55(3H, s), 3.95(2H, t), 6.60(1H, dd), 6.68(1H, d), 8.08(1H, d), 8.46(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1720, 1605, 1560, 1500, 1235, 1120, 1035, 770.

CHN analysis: % expected - C 75.00, H 7.35
% found - C 75.38, H 7.53.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(2-methyl-4-octyloxybenzoate)* **(102)**

Yield: 0.96 g (48%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.90(3H, t), 1.35(10H, m), 1.77(2H, m), 2.55(3H, s), 3.95(2H, t), 6.59(1H, dd), 6.66(1H, d), 8.08(1H, d), 8.45(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1720, 1600, 1560, 1500, 1235, 1120, 1030, 760.

CHN analysis: % expected - C 76.00, H 8.00

% found - C 76.37, H 8.02.

### *Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-2-methylbenzoate)* (**103**)

Yield: 0.43 g (22%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.90(3H, t), 1.35(14H, m), 1.77(2H, m), 2.54(3H, s), 3.95(2H, t), 6.59(1H, dd), 6.67(1H, d), 8.07(1H, d), 8.43(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1720, 1600, 1560, 1500, 1240, 1120, 1035, 765.

CHN analysis: % expected - C 76.83, H 8.54

% found - C 76.47, H 8.70.

### *Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-dodecyloxy-2-methylbenzoate)* (**104**)

Yield: 1.38 g (54%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.90(3H, t), 1.35(18H, m), 1.76(2H, m), 2.56(3H, s), 3.95(2H, t), 6.59(1H, dd), 6.68(1H, d), 8.08(1H, d), 8.44(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1720, 1600, 1560, 1500, 1240, 1120, 1035, 765.

CHN analysis: % expected - C 77.53, H 8.99

% found - C 77.27, H 9.31.

## *5.3 Results*

### *5.3.1 Transition Temperatures*

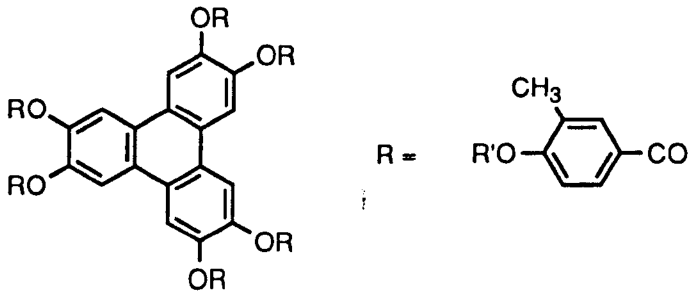
The transition temperatures were determined by a combination of thermal optical microscopy and differential scanning calorimetry. Typically, the crystal to mesophase transitions were determined by calorimetry because of the difficulty in discerning this transition optically. The results for the outer substituted systems are shown in Table 5.1, and the results for the inner substituted materials are given in Table 5.2. From Table 5.1, the clearing point transitions for the "outer" series (compounds **97-100**) fall almost linearly with increasing chain length. It is suspected that some decomposition has taken place in the hexyloxy analogue (compound **97**) as the transition temperature data acquired for this compound are slightly out of character in comparison to the data obtained for the other materials in this series. All the materials showed a possible columnar phase upon cooling from the nematic phase. However, miscibility studies show this phase to be crystalline in nature rather than liquid-crystalline (see Chapter 4, Section 4.3.1).

The results for the inner substituted series (compounds **101-104**) were straightforward and are shown in Table 5.2. The melting points and clearing points fall markedly with increasing chain length. All materials are purely nematogenic; even on substantial supercooling (*ca.* -40 °C) the presence of monotropic columnar phases could not be found.

### *5.3.2 Differential Scanning Calorimetry*

Calorimetric studies were carried out on each series of the esters prepared. Typical results for the heating and cooling cycles of the "outer" series (compounds **97-100**) are shown in Figures 5.2 and 5.3 respectively. All compounds show a sharp melting endotherm, which is then followed by a smaller enthalpy peak and finally by a small endotherm which marks the transition from the liquid crystal mesophase to the isotropic liquid. The enthalpy peak for the clearing transition was found to be rather small indicating that the transition from the liquid to $N_D$ mesophase is weakly first order. The second enthalpy peak corresponds to the point where the defect texture changes from the platelet to a *schlieren* form. This particular incident was first discussed in Chapter 4, Section 4.3.2 where it was concluded that the phase which exhibits the platelet texture probably has an ordered crystal-like structure.

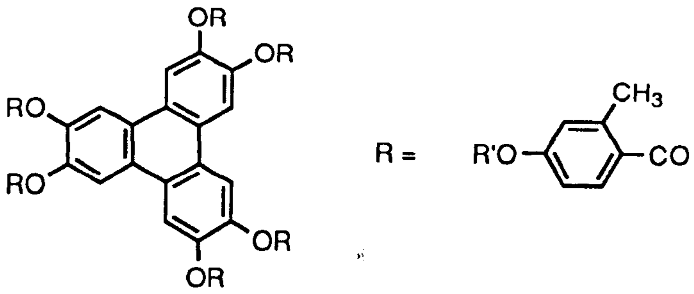
For the second set of compounds, compounds **101-104**, with the methyl substituents pointing in towards the core, the results are shown in Figures 5.4 (heating) and 5.5 (cooling). Upon heating, all compounds show a sharp melting endotherm followed by a very small endotherm corresponding to the transition from the liquid crystal to isotropic liquid; the clearing point transition almost appears second order in nature. No other transitions were detected on heating for this series. Upon cooling, the mesophase transitions were all found to be reversible.



| No. | R' | K | | $N_D$ | | I | Recryst. | |
|---|---|---|---|---|---|---|---|---|
| **97** | $C_6H_{13}$ | * | 126 (31.92) | * | 233 (0.90) | * | 220 | * |
| **98** | $C_8H_{17}$ | * | 134 (38.79) | * | 223 (0.49) | * | 139 | * |
| **99** | $C_{10}H_{21}$ | * | 103 (35.46) | * | 192 (0.39) | * | 106 | * |
| **100** | $C_{12}H_{25}$ | * | 99 (30.05) | * | 163 (0.38) | * | 102 | * |

**Table 5.1 : Transition temperatures for the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-3-methylbenzoate)s**

Enthalpies for each transition are given in parenthesis ($\Delta H$/kJ mol$^{-1}$).



| No. | R' | K | | $N_D$ | | I | Recryst. | |
|---|---|---|---|---|---|---|---|---|
| **101** | $C_6H_{13}$ | * | 172 (60.45) | * | 230 (0.34) | * | 126 | * |
| **102** | $C_8H_{17}$ | * | 126 (44.48) | * | 198 (0.31) | * | 139 | * |
| **103** | $C_{10}H_{21}$ | * | 109 (44.28) | * | 165 (0.16) | * | 52 | * |
| **104** | $C_{12}H_{25}$ | * | 105 (42.04) | * | 129 (0.11) | * | 35 | * |

**Table 5.2 : Transition temperatures for the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-2-methylbenzoate)s**

Enthalpies for each transition are given in parenthesis ($\Delta H$/kJ mol$^{-1}$).

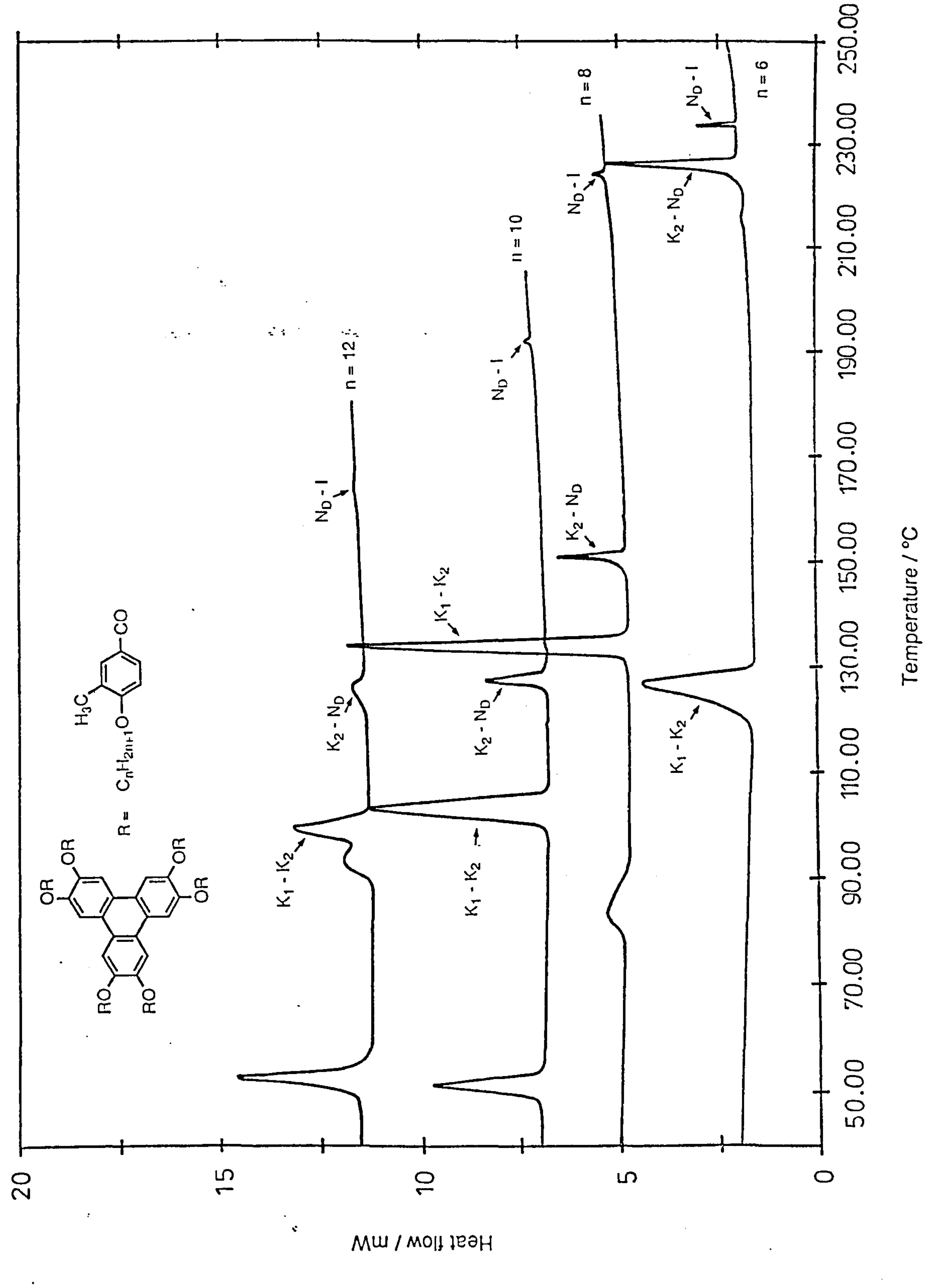


Figure 5.2 : DSC thermogram of the first heating cycle for each of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-3-methylbenzoate)s (97-100)

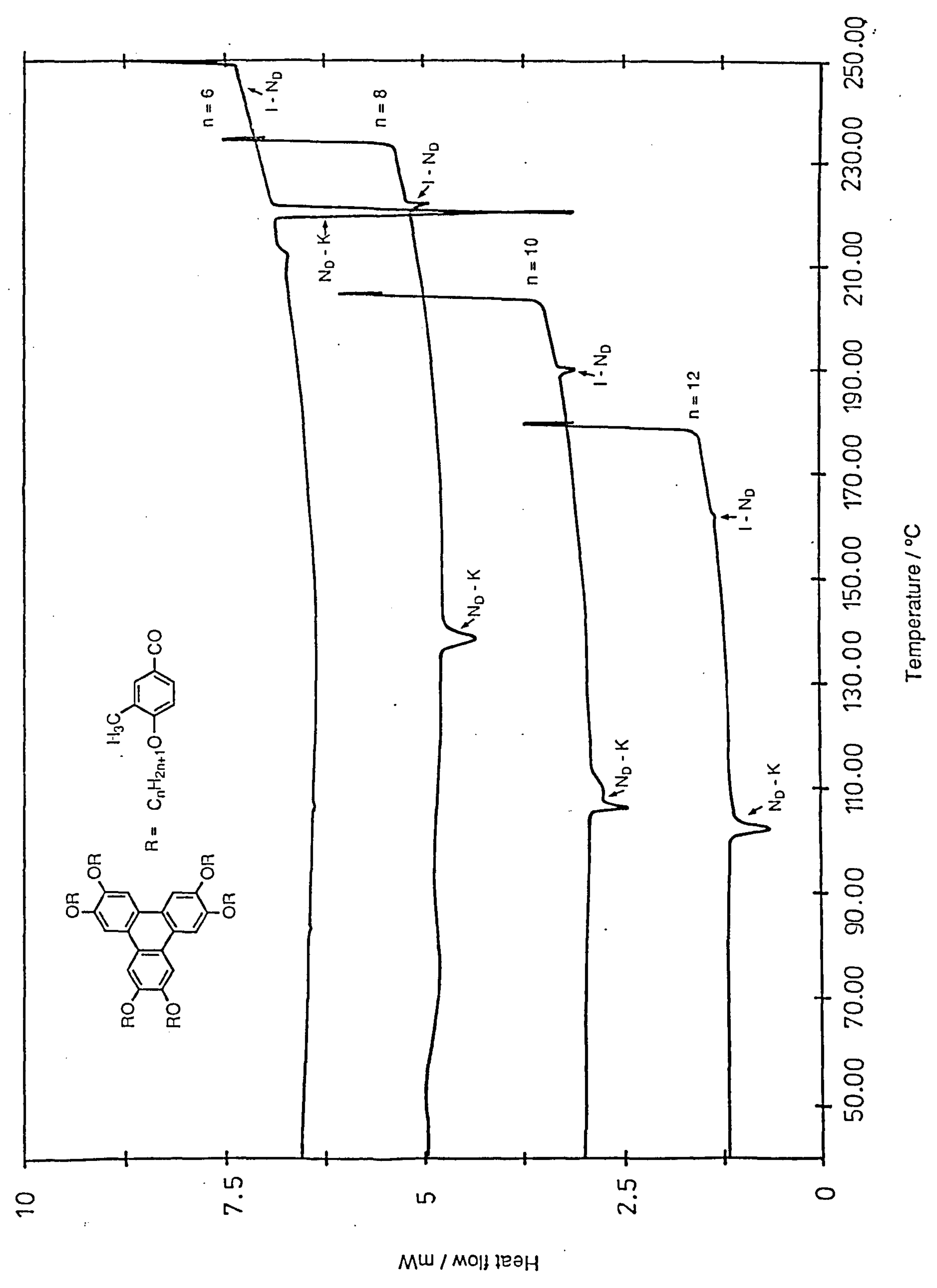


**Figure 5.3 : DSC thermogram of the first cooling cycle for each of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-3-methylbenzoate)s (97-100)**

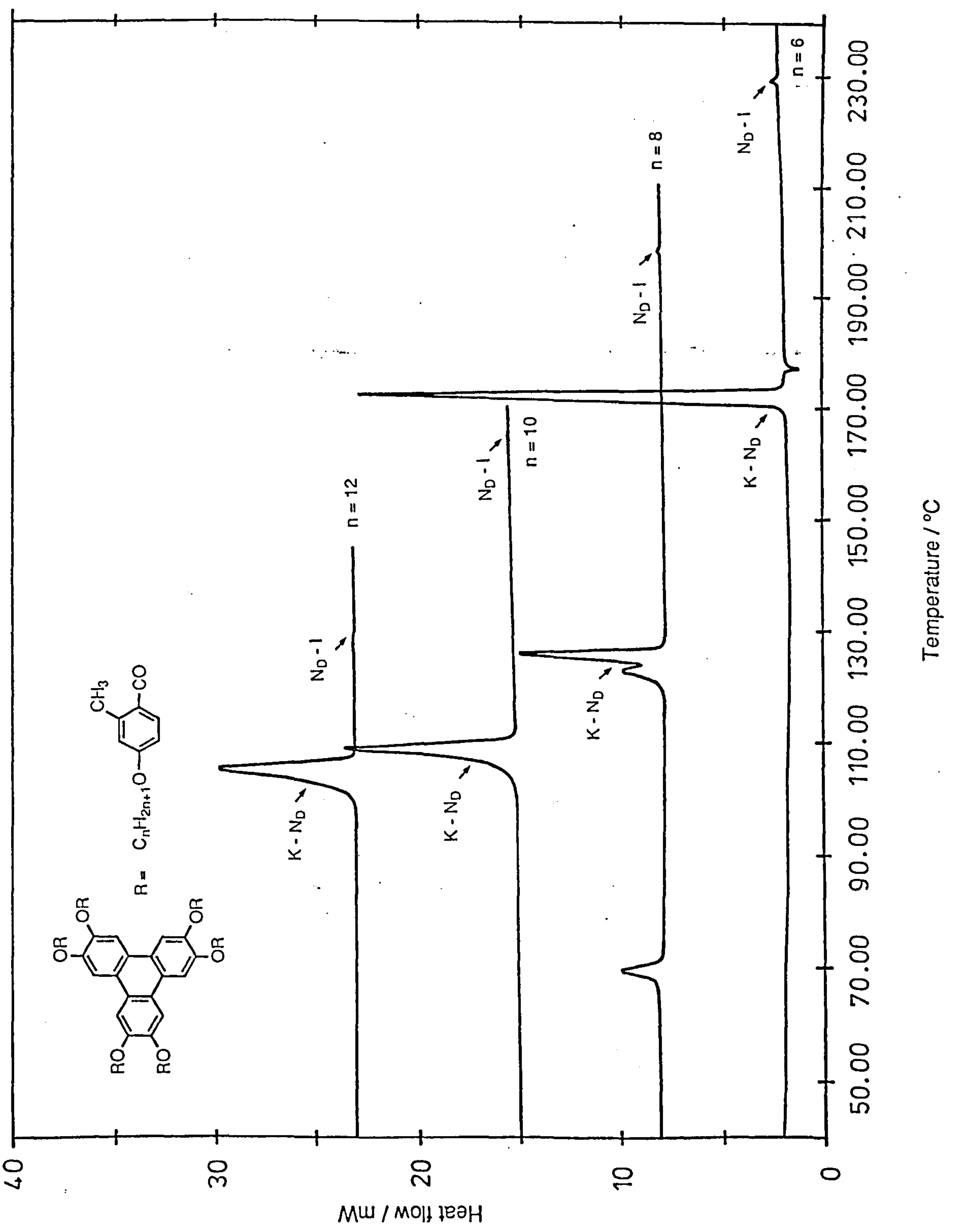


Figure 5.4 : DSC thermogram of the first heating cycle for each of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-2-methylbenzoate)s (101-104)

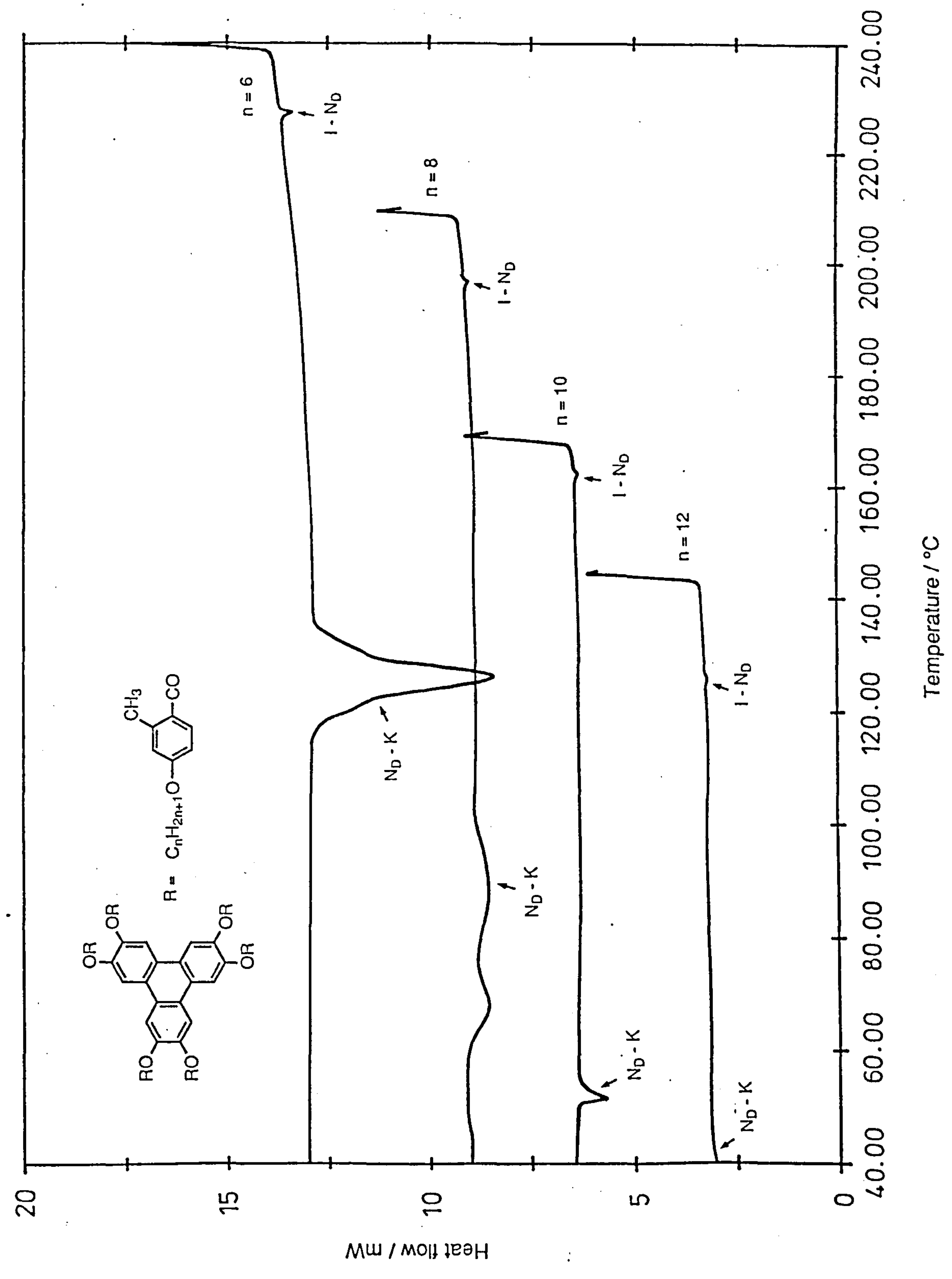


**Figure 5.5 : DSC thermogram of the first cooling cycle for each of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-2-methylbenzoate)s (101-104)**

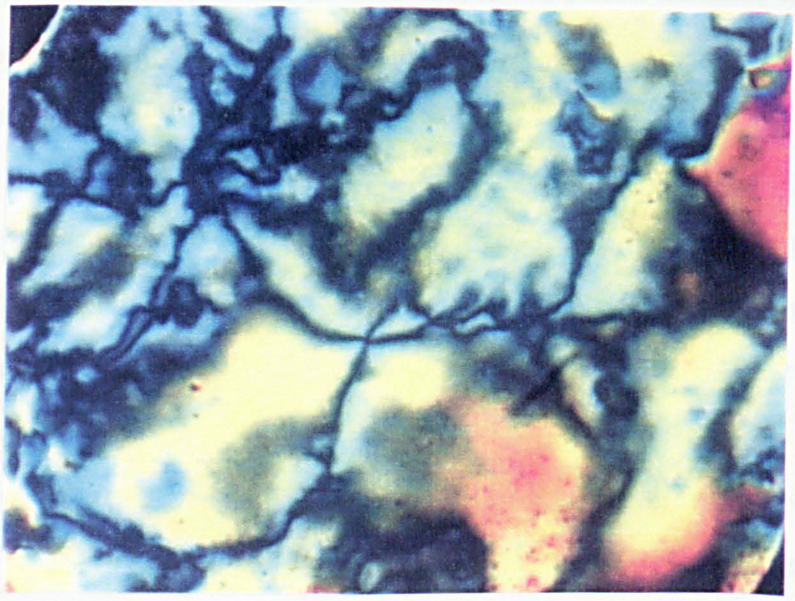


**Plate 5.1 : Sheared *schlieren* and threaded texture of the discotic nematic ($N_D$) exhibited by compound 99 at 180 °C on heating**

**Plate 5.2 : Mosaic texture of the ordered phase that resembles an hexagonal columnar exhibited by compound 99 at 104 °C on cooling from the $N_D$ mesophase**

### *5.3.3 Thermal Optical Microscopy*

For the outer substituted compunds **97-100**, when each material was heated from the crystal, under microscopic examination, the first discernible transition was that for the transformation to the discotic nematic mesophase. Plate 5.1 shows a typical texture formed on heating for the discotic nematic phase of the decyloxy homologue (compound **99**). A threaded and *schlieren* texture is formed with the phase showing typical flow properties and Brownian motion that are expected of a nematic mesophase. Upon slow cooling from the isotropic liquid, the discotic nematic phase formed the *schlieren* texture for each homologue.

Further slow cooling of each material resulted in the observation of a platelet texture, closely resembling a hexagonal columnar (see Plate 5.2). The platelet texture was unable to be sheared suggesting that this phase is probably a transition to a crystal rather than to a columnar mesophase. This particular situation was discussed in Chapter 4, Section 4.3.3.

The inner-substituted materials (compounds **101-104**) were more straightforward in their mesomorphic behaviour. Each homologue showed a clean transition to the discotic nematic mesophase from the crystal and then on further heating, a transition to the isotropic liquid. On cooling, the nematic phase was observed which was then followed by recrystallization.

The data and conclusions reached from the DSC cycles and thermal optical microscopy studies (and from discussions in Chapter 4, Section 4.3) are shown graphically in Figure 5.6 for the outer-substituted materials (compounds **97-100**), and in Figure 5.7 for the inner-substitued materials (compounds **101-104**).

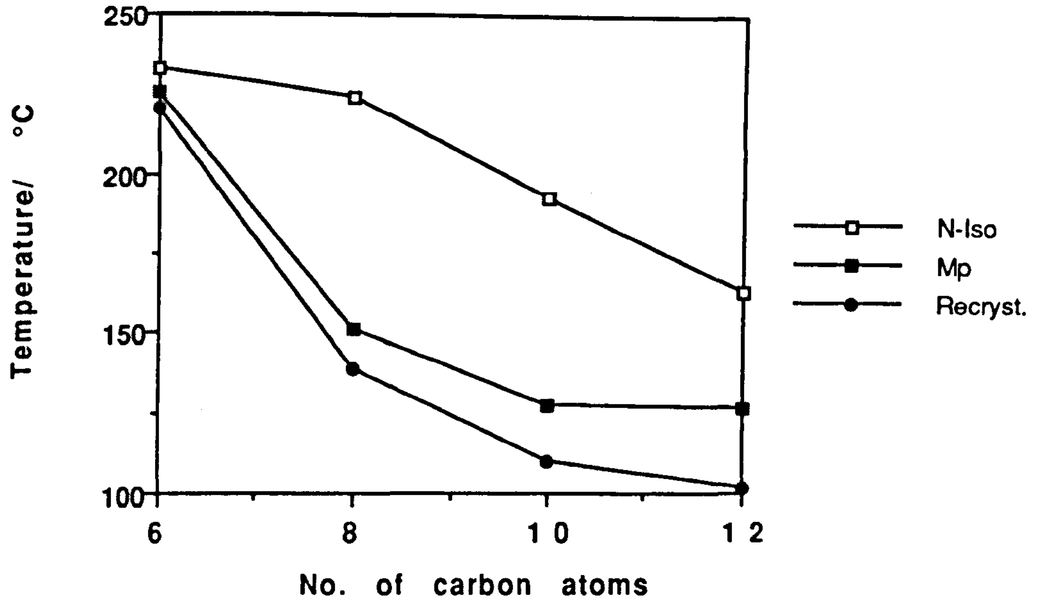


Figure 5.6 : Transition temperatures plotted against the number of carbon atoms in the terminal chain for the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-3-methylbenzoate)s (97-100)

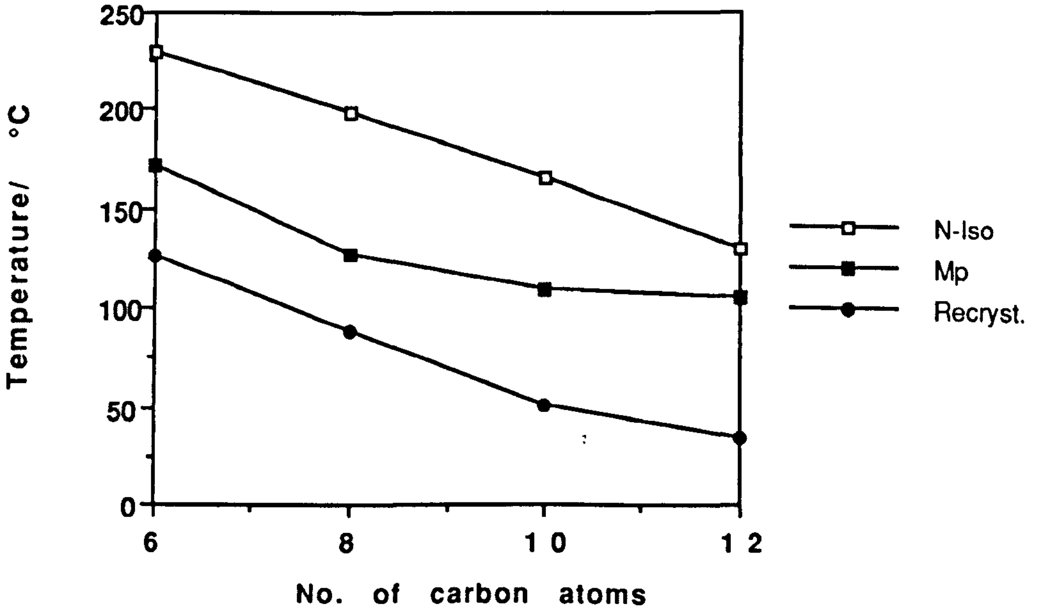


Figure 5.7 : Transition temperatures plotted against the number of carbon atoms in the terminal chain for the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-2-methylbenzoate)s (101-104)

## 5.4 *Discussion*

The objective of this research study was to re-synthesize the mono-methyl-substituted triphenylene benzoates, originally produced by Beattie,[1] in order that a successful evaluation of their mesomorphic properties could be performed.

The effects of lateral substitution were predicted to reduce melting points and suppress columnar mesophases, and produce nematogenic discotic materials. This was the original objective which led Beattie to study the area of lateral substitution using methyl groups positioned in the peripheral phenyl rings of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s, first synthesized by Tinh.[2] The findings from Beattie's research suggested that the theoretical model (see Chapter 1, Section 1.8) was acceptable and that lateral substitution indeed forced the peripheral phenyl rings to twist more out of the plane of the central core compared to peripheral phenyl groups of the unsubstituted materials. Beattie reported in his thesis that reductions were observed in both the melting and the clearing points compared to the parent systems. He also reported that columnar mesophase formation had been suppressed in the inner-substituted series, but due to the materials undergoing glassy-state transitions, he could not be certain of his observations. He was also unable to confirm that the columnar phases were totally suppressed in the outer-substituted series as well, due to the appearance of a number of crystal phases.

It was a direct consequence of Beattie's research that the dimethyl-substituted analogues[3] (see Chapter 3) were studied. The data obtained from studying the effects of incorporating *two* methyl-substituents further confirmed the validity of the theoretical model. However, it was only during the subsequent investigation of how the *size* of the substituent affected the mesophase behaviour[4] (see Chapter 4) that it was discovered that there were some pecularities in the mesomorphic properties of Beattie's original samples. Melting points and clearing points for the outer-substituted series were not consistent with the mesomorphic behavioural pattern built up by the unsubstituted parent material (**42**)[2] and the ethyl-, *iso*-propyl- and *tert*-butyl substituted compounds (**66-68**)[4] (see Chapter 4).

This unfortunate situation forced the re-synthesis of a selected number of Beattie's mono-methyl-substituted triphenylene benzoates, so that the correct results would be obtained in the study of the effect of the substituent size on the mesophase behaviour[4] (see Chapter 4).

The results for the melting and clearing points as well as the mesomorphic behaviour detailed in this chapter for both the outer- and inner-substituted series of triphenylene benzoates are consistent with the data previously obtained for the unsubstituted,[2] dimethyl-substituted[3] (see also Chapter 3) and bulky-substituted systems[4] (see also Chapter 4).

## *5.5 Conclusions*

With the accurate data now obtained for the mono-methyl-substituted triphenylene benzoates, a complete picture is formed of the relationship between the positioning and size of the lateral sterically-based substituent, ranging from the small hydrogen through to the immense *tert*-butyl, and the subsequent effect upon the mesogenic behaviour.

## *5.6 References*

1) D.R. Beattie, *Ph. D. Thesis*, University of Hull, 1993.

2) N.H. Tinh, H. Gasparoux and C. Destrade, *Mol. Cryst. Liq. Cryst.*, 1981, **68**, 101.

3) P. Hindmarsh, M. Hird, P. Styring and J.W. Goodby, *J. Mater. Chem.*, 1993, **3**, 1117.

4) P. Hindmarsh, M. J. Watson, M. Hird and J. W. Goodby, *J. Mater. Chem.*, 1995, **5**, 2111.

# CHAPTER 6

# *Investigation of the Tolerance Limits of the Mesophase Stabilities with the Inclusion of Two Bulky Lateral Substituents in Triphenylene Benzoates*

## *6.1 Introduction*

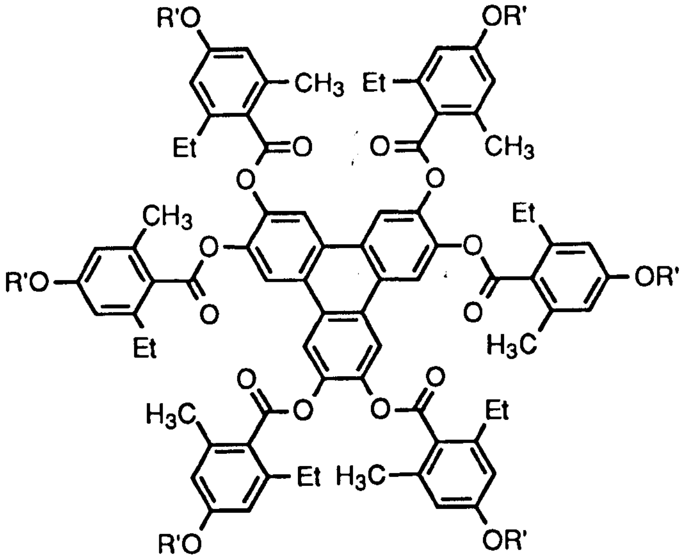
Investigation of the effects of lateral substitution in the peripheral phenyl rings of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s has been extensively reported in the previous chapters.

The research programme designed to study the possible relationship between molecular architecture and mesophase behaviour was first started by Beattie.[1] He originally investigated the effects upon mesomorphism by incorporating lateral methyl units into the molecular structure of the parent unsubstituted triphenylene benzoates, first synthesized by Tinh *et al.*;[2] Beattie's research was partially repeated and is detailed in Chapter 5. The research programme at Hull was further developed by the undertaking of a study into the effects of *two* lateral methyl units upon the mesophase behaviour of these particular discotic liquid crystals;[3] this work was reported in Chapter 3.

The research so far uncovered the effects of the *position* of the lateral substituent upon the mesogenicity, and so the direction of study was changed to examine the significance of the *size* of the lateral substituent. This was achieved by a systematic study of the steric effects caused by the sequential increase in the lateral substituent from methyl to *tert*-butyl;[4] this work was detailed in Chapter 4.

In this chapter, the last in the series discussing the effects upon the mesomorphic properties caused by lateral *steric* groups, the objective is to ascertain the tolerance limits of the relationship between the position(s) and size(s) of the lateral substituents and the mesogenic behaviour of the triphenylene benzoates. In Chapter 3, we discovered that the discotic materials were mesomorphic even with *two* methyl substituents situated in the very crowded regions around the triphenylene core, and in Chapter 4, it was found that the very bulky *iso*-propyl-inner-substituted triphenylene benzoate still exhibited the discotic nematic mesophase. Thus, the research elements of both the previous chapters are combined in this study in order that the position and size limits of the lateral substituents can be determined, so that inevitably a room temperature discotic nematogenic compound can be obtained.

Thus, in this chapter the synthesis and properties of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-2-ethyl-6-methylbenzoate)s are discussed (see structure **I**, Figure 6.1).



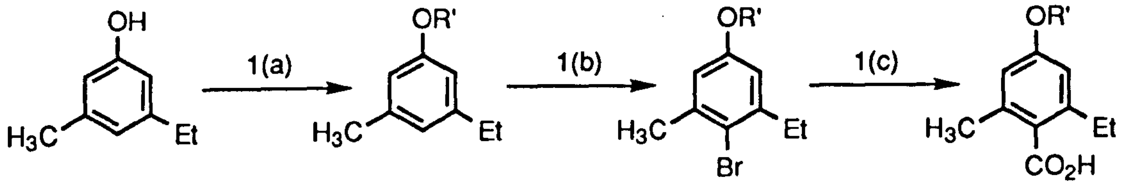
**I**

R' = $C_nH_{2n+1}$ (n = 6, 8, 10 and 12)

**Figure 6.1 : Structure of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-2-ethyl-6-methylbenzoate)s (structure I)**

## *6.2 Experimental*

The materials were prepared by the routes shown in Schemes 6.1 and 6.2. The various substituted acids were prepared by the synthetic routes shown in Scheme 6.1. Compound **105** was obtained from Kodak Eastman and was *O*-alkylated with the appropriate *n*-alkyl bromdes in good yields using anhydrous potassium carbonate in butanone. Substitution of the bromine in the desired position to compounds **106-109** was achieved by adding bromine dropwise to a gently refluxing solution of these compounds in dry chloroform. The replacement of the bromine in compounds **110-113** was achieved by lithiation using *n*-butyllithium at -78 °C; in each case the reaction mixture was then poured onto a slurry of solid $CO_2$ and dry ether, acidified, and the product purified (compounds **114-117**). The final discotic materials (**118-121**) were prepared by the esterification of HHTP (**3**) with the respective benzoyl chlorides in the presence of pyridine.



**105** **106-109** **110-113** **114-117**

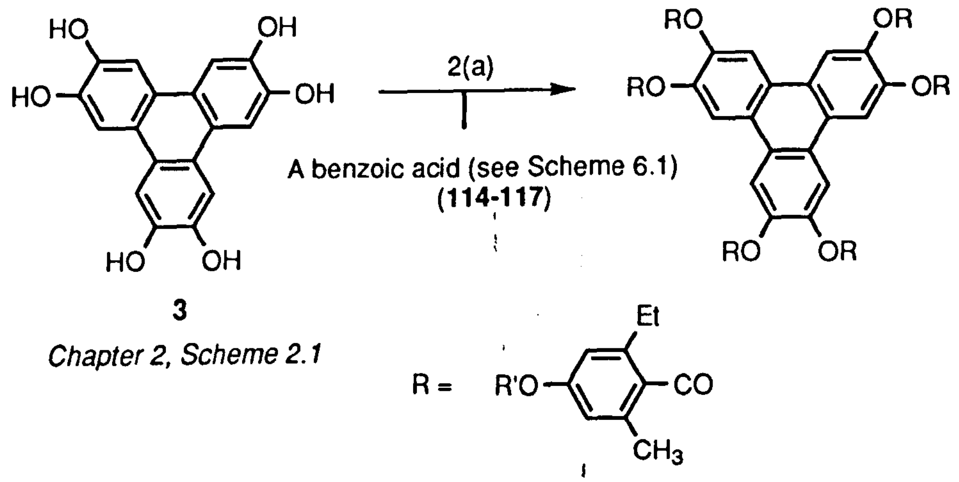
R' = $C_nH_{2n+1}$ (n = 6, 8, 10 and 12)

1(a) ..... RBr, $K_2CO_3$, butanone.

1(b) ..... $Br_2$, dry $CHCl_3$, reflux.

1(c) ..... (i) *n*-BuLi, THF; (ii) $CO_2$ (solid), $Et_2O$.

**Scheme 6.1 : Synthetic route for the preparation of the 4-alkoxy-6-ethyl-2-toluic acids (114-117)**



**3**

*Chapter 2, Scheme 2.1*

**118-121**

R' = $C_nH_{2n+1}$ (n = 6, 8, 10 and 12)

2(a) ..... Acid Chloride (oxalyl chloride, DMF, $CH_2Cl_2$), pyridine.

**Scheme 6.2 : Synthetic route for the preparation of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxy-2-ethyl-6-methylbenzoates) (118-121)**

### *6.2.1 Preparation of the 3-Alkoxy-5-ethyltoluenes* (**106-109**)

The general synthetic method is exemplified by the procedure reported in Chapter 3 for compound **9**.

*3-Ethyl-5-hexyloxytoluene* (**106**)

Yield: 7.16 g (88%) Bp: 120-130 °C at 0.1 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.23(3H, t), 1.35(6H, m), 1.77(2H, m), 2.30(3H, s), 2.58(2H, q), 3.94(2H, t), 6.54(2H, s), 6.58(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1590, 1455, 1330, 1285, 1160, 1070, 840, 640.

MS (*m/z*): 220(M$^+$), 136, 121, 91, 77, 55, 43.

*3-Ethyl-5-octyloxytoluene* (**107**)

Yield: 7.91 g (86%) Bp: 120-135 °C at 0.05 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.89(3H, t), 1.22(3H, t), 1.35(10H, m), 1.75(2H, m), 2.30(3H, s), 2.57(2H, q), 3.92(2H, t), 6.54(2H, s), 6.58(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1590, 1455, 1330, 1290, 1160, 1070, 840, 640.

MS (*m/z*): 248(M$^+$), 137, 121, 91, 77, 55, 43.

*3-Decyloxy-5-ethyltoluene* (**108**)

Yield: 7.98 g (88%) Bp: 145-155 °C at 0.01 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.22(3H, t), 1.35(14H, m), 1.75(2H, m), 2.30(3H, s), 2.56(2H, q), 3.92(2H, t), 6.54(2H, s), 6.58(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1590, 1455, 1330, 1290, 1160, 1070, 840, 640.

MS (*m/z*): 276($M^+$), 136, 121, 91, 77, 55, 43.

*3-Dodecyloxy-5-ethyltoluene* (**109**)

Yield: 8.61 g (98%) Bp: 155-160 °C at 0.01 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.22(3H, t), 1.35(18H, m), 1.75(2H, m), 2.30(3H, s), 2.57(2H, q), 3.92(2H, t), 6.54(2H, s), 6.58(1H, s).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 2920, 2860, 1590, 1455, 1330, 1290, 1160, 1070, 840, 640.

MS (*m/z*): 304, 136, 121, 91, 55, 43.

### *6.2.2 Preparation of the 5-Alkoxy-2-bromo-3-ethyltoluenes* (110-113)

The general synthetic method is exemplified by the procedure reported in Chapter 4 for compound **62**.

*2-Bromo-3-ethyl-5-hexyloxytoluene* (**110**)

Yield: 5.79 g (59%) Bp: 140-150 °C at 0.1 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.22(3H, t), 1.35(6H, m), 1.75(2H, m), 2.38(3H, s), 2.74(2H, q), 3.90(2H, t), 6.65(2H, d).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 2920, 2860, 1590, 1455, 1330, 1305, 1165, 1090, 840, 640.

MS (*m/z*): 300($M^+$), 298($M^+$), 220, 216, 214, 201, 199, 136, 121, 91, 55, 43.

*2-Bromo-3-ethyl-5-octyloxytoluene* (**111**)

Yield: 7.33 g (70%) Bp: 130-145 °C at 0.05 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.22(3H, t), 1.35(10H, m), 1.75(2H, m), 2.39(3H, s), 2.74(2H, q), 3.92(2H, t), 6.65(2H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1590, 1455, 1330, 1305, 1165, 1070, 840, 640.

MS ($m/z$): 328($M^+$), 326($M^+$), 248, 216, 214, 201, 199, 136, 121, 91, 55, 43.

*2-Bromo-5-decyloxy-3-ethyltoluene* (**112**)

Yield: 7.44 g (75%) Bp: 155-160 °C at 0.01 mmHg

$^1H$ NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.22(3H, t), 1.35(14H, m), 1.75(2H, m), 2.38(3H, s), 2.74(2H, q), 3.92(2H, t), 6.65(2H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1590, 1455, 1330, 1305, 1165, 1070, 840, 640.

MS ($m/z$): 356($M^+$), 354($M^+$), 276, 216, 214, 201, 199, 136, 121, 91, 55, 43.

*2-Bromo-5-dodecyloxy-3-ethyltoluene* (**113**)

Yield: 8.87 g (83%) Bp: 165-175 °C at 0.01 mmHg

$^1H$ NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.22(3H, t), 1.35(18H, m), 1.75(2H, m), 2.39(3H, s), 2.74(2H, q), 3.92(2H, t), 6.65(2H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1590, 1455, 1330, 1305, 1165, 1080, 840, 640.

MS ($m/z$): 384($M^+$), 382($M^+$), 304, 216, 214, 201, 199, 136, 121, 91, 55, 43.

### *6.2.3 Preparation of the 4-Alkoxy-6-ethyl-2-toluic Acids* (114-117)

The general synthetic method is exemplified by the procedure reported in Chapter 3 for compound **14**. The crude products were unable to be recrystallized and therefore, were purified by column chromatography (silica gel/dichloromethane : ethyl acetate, 4 : 1) to yield pale yellow oils.

*6-Ethyl-4-hexyloxy-2-toluic acid* (**114**)

Yield: 3.04 g (61%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.22(3H, t), 1.35(6H, m), 1.75(2H, m), 2.43(3H, s), 2.77(2H, q), 3.96(2H, t), 6.60(2H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3500-2500(broad), 2920, 2860, 1685, 1600, 1460, 1380, 1330, 1280, 1170, 1110, 860, 840, 660.

MS (*m*/*z*): 264(M$^+$), 180, 162, 136, 91, 77, 55.

*6-Ethyl-4-octyloxy-2-toluic acid* (**115**)

Yield: 3.57 g (54%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.22(3H, t), 1.35(10H, m), 1.75(2H, m), 2.43(3H, s), 2.77(2H, q), 3.94(2H, t), 6.60(2H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3500-2500(broad), 2920, 2860, 1685, 1590, 1455, 1380, 1330, 1285, 1165, 1110, 860, 840, 660.

MS (*m*/*z*): 292(M$^+$), 180, 162, 136, 91, 77, 55.

*4-Decyloxy-6-ethyl-2-toluic acid* (**116**)

Yield: 8.87 g (83%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.22(3H, t), 1.35(14H, m), 1.75(2H, m), 2.43(3H, s), 2.76(2H, q), 3.93(2H, t), 6.60(2H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3500-2500(broad), 2920, 2860, 1680, 1600, 1465, 1380, 1330, 1285, 1170, 1110, 860, 840, 660.

MS (*m*/*z*): 320(M$^+$), 180, 162, 136, 91, 77, 55.

*4-Dodecyloxy-6-ethyl-2-toluic acid* (**117**)

Yield: 8.87 g (83%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.22(3H, t), 1.35(18H, m), 1.75(2H, m), 2.40(3H, s), 2.74(2H, q), 3.92(2H, t), 6.60(2H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3500-2500(broad), 2920, 2860, 1670, 1600, 1460, 1380, 1330, 1285, 1170, 1110, 860, 840, 660.

MS ($m/z$): 348(M$^+$), 180, 162, 136, 91, 77, 55.

### *6.2.4 Preparation of the Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-alkoxy-2-ethyl-6-methylbenzoate)s* (118-121)

The general synthetic method for the preparation of the hexa-esters is exemplified by the method reported in Chapter 3 for compound **30**. The final compounds obtained were oils and therefore, were unable to be recrystallized.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(2-ethyl-4-hexyloxy-6-methylbenzoate)* (**118**)

Yield: 0.53 g (25 %)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.20(3H, t), 1.35(6H, m), 1.80(2H, m), 2.34(3H, s), 2.76(2H, q), 3.97(2H, t), 6.63(2H, d), 8.54(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1750, 1600, 1500, 1460, 1410, 1330, 1310, 1285, 1230, 1160, 1110, 1040, 890, 770.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(2-ethyl-6-methyl-4-octyloxybenzoate)* (**119**)

Yield: 0.31 g (13 %)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.20(3H, t), 1.35(10H, m), 1.80(2H, m), 2.36(3H, s), 2.75(2H, q), 3.96(2H, t), 6.61(2H, d), 8.52(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1745, 1600, 1500, 1460, 1410, 1330, 1310, 1285, 1235, 1160, 1110, 1040, 890, 770.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-2-ethyl-6-methylbenzoate)* (**120**)

Yield: 1.66 g (29 %)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.20(3H, t), 1.35(14H, m), 1.80(2H, m), 2.36(3H, s), 2.75(2H, q), 3.95(2H, t), 6.62(2H, d), 8.53(1H, s).

| | |
|---|---|
| IR (KBr) $\nu_{max}$ cm$^{-1}$: | 2920, 2860, 1745, 1600, 1500, 1460, 1410, 1330, 1310, 1285, 1240, 1160, 1110, 1040, 890, 770. |

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-dodecyloxy-2-ethyl-6-methylbenzoate)* (**121**)

Yield: 1.67 g (29 %)

| | |
|---|---|
| $^1$H NMR ($CDCl_3$ and TMS) δ: | 0.88(3H, t), 1.20(3H, t), 1.35(18H, m), 1.80(2H, m), 2.35(3H, s), 2.74(2H, q), 3.96(2H, t), 6.60(2H, d), 8.54(1H, s). |
| IR (KBr) $\nu_{max}$ cm$^{-1}$: | 2920, 2860, 1750, 1600, 1500, 1460, 1410, 1330, 1310, 1285, 1230, 1160, 1110, 1040, 890, 770. |

## *6.3 Results*

### *6.3.1 Transition Temperatures*

The final discotic materials (compounds **118-121**) were obtained as oils, despite many efforts to crystallize them. Therefore, unfortunately there are no transition temperatures to report or mesomorphic properties to discuss .

### *6.3.2 Differential Scanning Calorimetry*

Calorimetric studies were carried out on one homologue, the decyloxy analogue (compound **120**) to determine whether these materials could crystallize and from there assess the possibility that they could exhibit mesophases. No results were obtained, so therefore it was decided not to proceed with the calorimetric analysis of the other members of the series.

### *6.3.3 Thermal Optical Microscopy*

No melting points, mesophase textures or recrystallizations were observed for these materials under microscopic examination.

## *6.4 Discussion*

The objective of this study was to evaluate the tolerance limits of the mesophase stabilities of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s when bulky lateral substituents were incorporated in the peripheral phenyl rings.

The effects of lateral substitution were predicted to reduce melting points and suppress columnar mesophases, and produce nematogenic discotic materials. In Chapters 3 to 5, the research results quite unanimously proved that this prediction was correct, but the research still had some way to go in finding room temperature discotic nematogenic materials. The results from Chapters 3 to 5 for the inner-substituted discotic materials showed the most promise in aiding this investigation. For example, in Chapter 3 the clearing point temperatures for the inner-substituted series (compounds **35-38**) were 100-150 °C lower compared to the parent systems (compounds **40-43**) synthesized by Tinh *et al.*;[2] it was now possible to obtain the discotic nematic mesophase at temperatures below 100 °C. The evidence from the research in Chapter 4 strengthened the argument that the prediction was indeed correct because it was proven that the triphenylene benzoates were able to tolerate even bulkier lateral substituents than just methyl units *and still* exhibit the discotic nematic mesophase.

Thus, in this study triphenylene benzoates were synthesized which incorporate both methyl- and ethyl-substituents in the crowded "inner" region of the triphenylene core. It is quite obvious that the lateral substitution in the "inner" region has again greatly influenced the mesogenic behaviour. The discotic materials (compounds **118-121**) were obtained as oils and unfortunately devoid of any mesomorphic properties.

At first glance, these results appear to be a disappointment because we have not produced discotic compounds that exhibit the desired discotic nematic mesophase at room temperature, or for that matter any mesophases. However, these findings are roughly in keeping with the original prediction, previously discussed in Chapters 3 to 5, that inner-substituted bulky units will reduce melting and clearing points. These new materials *were* predicted to have low melting and clearing points, but unfortunately the available data suggest that the values, which at present have not been obtained, are much lower than previously proposed.

If the data are taken to be correct, and the materials are indeed oils and therefore liquids at room temperature, then the melting and clearing point values of these new compounds are not consistent with the research data detailed in Chapters 3 to 5. Therefore, until the new materials can be obtained in their crystalline state so that accurate and detailed analyses can be performed on the mesophase behaviour, then the discussion of this research programme investigating tolerance limits must unfortunately come to a close.

## *6.5 Conclusions*

The outcome of this piece of work clearly demonstrates that the mesomorphic behaviour is greatly influenced by the effects of the lateral substituents and in this case, the mesogenic properties appear to have been unfortunately eliminated altogether. It is quite obvious that there is a very delicate balance between substitution that will reduce melting and clearing points and eliminate ordered columnar mesophases and substitution that will destroy the mesogenic nature of the material.

## *6.6 References*

1) D.R. Beattie, *Ph. D. Thesis*, University of Hull, 1993.

2) N.H. Tinh, H. Gasparoux and C. Destrade, *Mol. Cryst. Liq. Cryst.*, 1981, **68**, 101.

3) P. Hindmarsh, M. Hird, P. Styring and J.W. Goodby, *J. Mater. Chem.*, 1993, **3**, 1117.

4) P. Hindmarsh, M.J. Watson, M. Hird and J.W. Goodby, *J. Mater. Chem.*, 1995, **5**, 2111.

# *CHAPTER 7*

# *Investigation of the Effect of Polar Lateral Substitution on the Discotic Mesophase Behaviour of Triphenylene Benzoates*

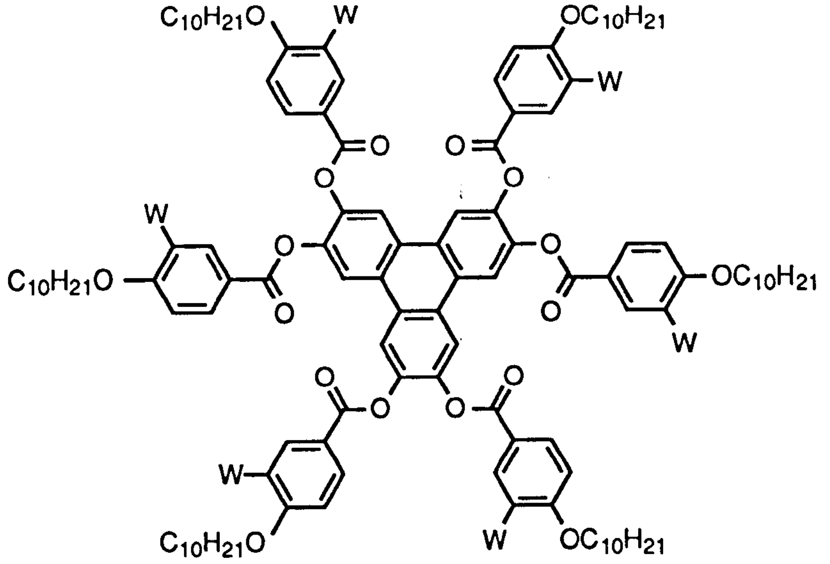
## *7.1 Introduction*

Research studies into the effects of lateral substitution in the peripheral phenyl moieties of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s using bulky groups, such as methyl to *tert*-butyl, on the mesomorphic behaviour have been extensively discussed in the previous chapters. It is now quite established that the steric effects, caused by the insertion of bulky groups into the crowded peripheral regions around the triphenylene core, do reduce the melting and clearing points and tend to produce discotic nematogenic materials. However, research into the effects of lateral substitution of the triphenylene benzoates cannot be completed until the area of substitution using *polar* groups, such as the halogens, nitro or cyano, has been examined.

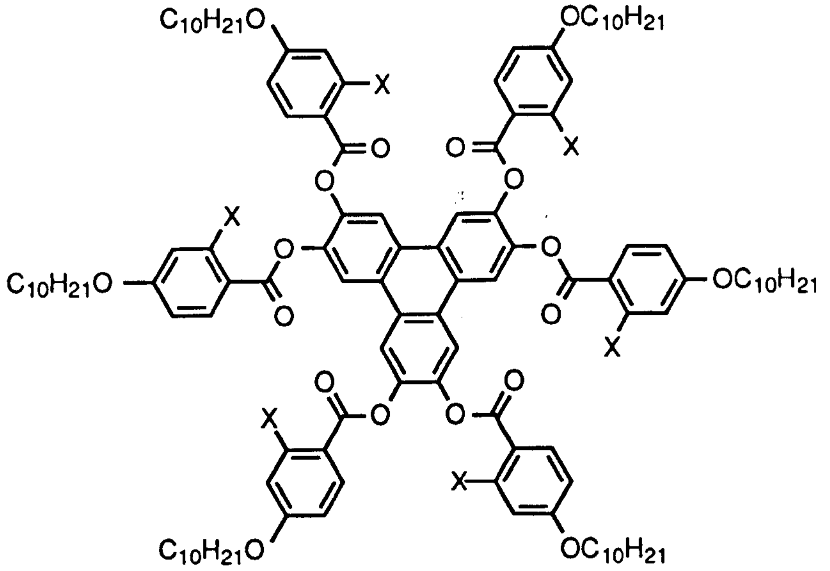
In the field of calamitic (*rod*-like) liquid crystals, the study of the effects of lateral substitution is concerned preferentially with the use of *polar* groups, because it was found that the use of bulky lateral units was detrimental to the production of the required mesophases, often to the point of rendering compounds non-mesogenic.[1,2] The major polar unit studied, the fluoro substituent, showed that despite its relatively small size, it could depress melting and clearing points considerably, and its presence had a much greater effect on smectic mesophase thermal stability by diminishing the efficiency of the packing of the molecules into layers. The ability of a lateral fluoro-substituent to diminish the stability of smectic mesophases relative to the nematic mesophase without significantly increasing viscosity was found to be useful in improving the molecular structures for materials for electrooptical devices.[1] Substituents larger than fluorine often destabilized smectic phases to an even greater extent, but they also gave compounds with even lower clearing points and unfortunately, increased viscosities.[1]

Therefore, our objective for this study was to position polar groups, however sterically small, into the lateral positions of the peripheral phenyl groups of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s, in order to investigate the effects on phase morphology, transition temperatures and melting points.

Thus, in this chapter the synthesis and properties of a variety of polar-substituted triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxybenzoate)s are discussed (see structures **I-IV**, Figures 7.1 and 7.2).

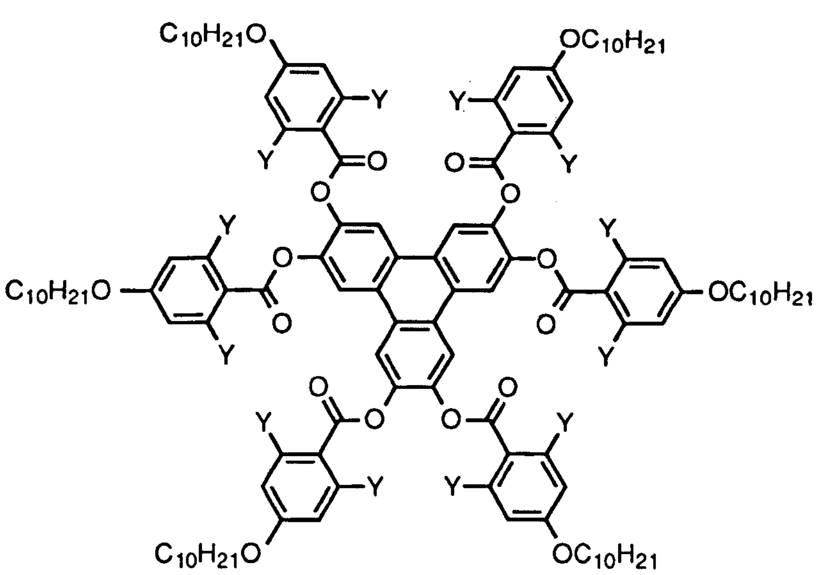


I



II

**Figure 7.1 : Structures of the mono-polar-substituted triphenylen-2,3,6,7,10-hexayl hexakis(4-decyloxybenzoate)s; structure I: W = fluoro, chloro and trifluoromethyl; structure II: X = fluoro, chloro and methoxy**


III

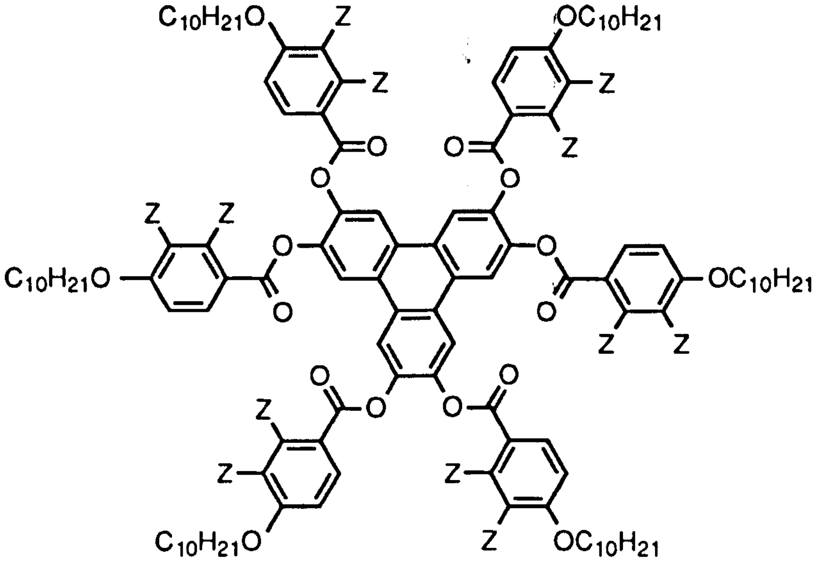

IV

**Figure 7.2 : Structures of the di-polar-substituted triphenylen-2,3,6,7,10-hexayl hexakis(4-decyloxybenzoate)s; structure III: Y = fluoro and chloro; structure IV: Z = fluoro and chloro**

## 7.2 Experimental

The materials were prepared by the routes shown in Schemes 7.1-7.6. The various substituted benzoic acids were prepared by the synthetic routes shown in Schemes 7.1-7.5. Compounds **122**, **128** and **131** in Scheme 7.1; **134**, **138**, **142** and **145** in Scheme 7.2; **148**, **152** and **155** in Scheme 7.3; **161** in Scheme 7.4; and, **169**, **173** and **176** in Scheme 7.5 were all purchased from Aldrich Chemical Co., whereas compound **125** was supplied by Merck Ltd (UK).

Scheme 7.1 will be discussed first. Compounds **122**, **125**, **128** and **131** were all *O*-alkylated with 1-bromodecane in good yields using anhydrous potassium carbonate in butanone to give compounds **123**, **126**, **129** and **132**. The replacement of the bromine in compound **123** was achieved by lithiation using *n*-butyllithium at -78 °C after 45 mins; the reaction mixture was then poured onto a slurry of solid $CO_2$ and dry ether, acidified, and the product purified (compound **124**). Compound **126** was hydrolyzed with concentrated sulfuric acid and water in glacial acetic acid under reflux conditions to give, *via* the amide, the carboxylic acid **127**. In compound **129**, there is a proton flanked on both sides by a fluoro-substituent, and in compound **132**, there is a proton flanked on only one side by a fluoro-substituent. Due to their inherent acidities, both these protons can be exploited by the use of *n*-butyllithium to allow the desired functional group to be incorporated onto the phenyl ring.[3] In both cases, the aryl-lithium salt formed at -78 °C after 2.5 hours is poured into solid $CO_2$ and worked up in an identical way as that for compound **124** as stated above.

In Scheme 7.2, a number of different strategies were used to generate the desired carboxylic acids. The methyl ester of compound **134** was simply obtained by heating up a solution of the acid **134** in methanol with a little concentrated sulfuric acid for a few hours. Compounds **135**, **138**, **142** and **145** were all *O*-alkylated with 1-bromodecane in good yields using the procedure described above to give compounds **136**, **139**, **143** and **146**. Addition of the bromine in the desired position to compound **139** was achieved by adding bromine dropwise to a gently refluxing solution of compound **139** in dry chloroform. The benzoic acid **137** was obtained by hydrolyzing the methyl ester **136** using sodium hydroxide in ethanol. The procedures involved in obtaining the benzoic acids **141**, **144** and **147** were described above for compounds **124**, **130** and **133**.

Scheme 7.3 details the synthetic strategies for the production of the trifluoromethyl-substituted benzoic acids. The synthesis of the benzoic acid that incorporates its substituent *ortho* to the terminal alkoxy chain was straightforward. Compound **148** was brominated in a good yield using bromine and glacial acetic acid at 0 °C. The phenol **149** was then *O*-alkylated as previously described to give compound **150**. The bromine was then replaced using *n*-butyllithium to form an aryl-lithium salt which was poured onto solid $CO_2$, which is also previously described, to give the benzoic acid **151**.

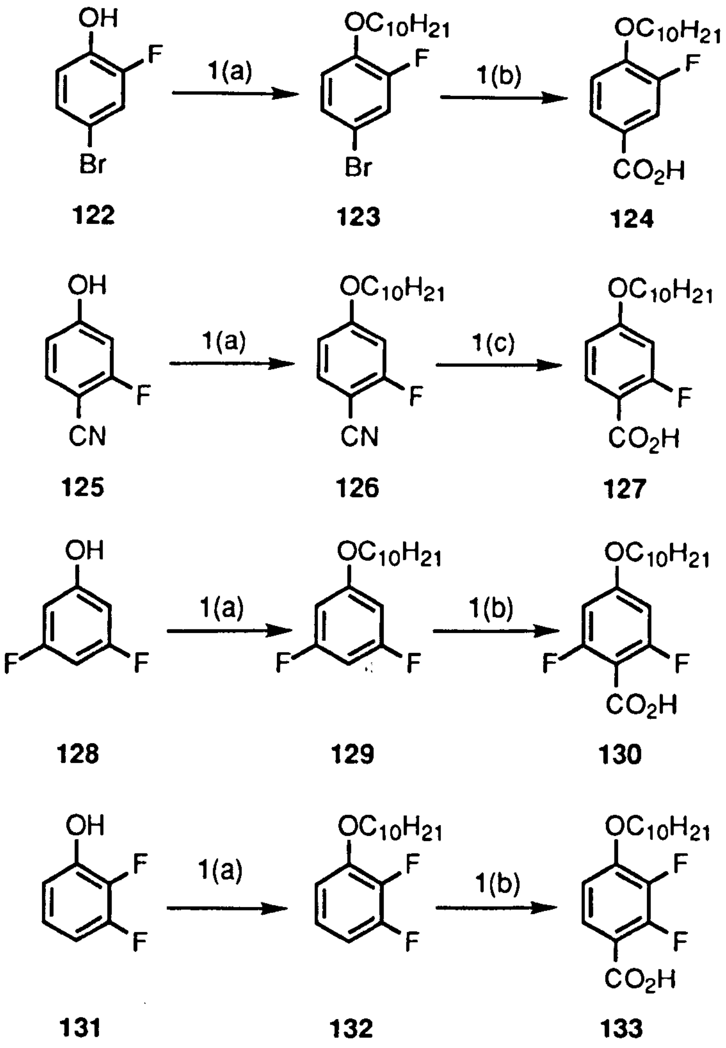
The synthesis of the analogous benzoic acid with the trifluoromethyl-substituent *ortho* to the carboxylic acid functional group was not so easy. Initially, it was hoped that the successful synthetic strategy already used to great effect (described in the Chapter 4) would suffice in obtaining the required intermediate with the desired substitution pattern (compound **154**). It appears that the very strong electron-withdrawing effect of the trifluoromethyl group renders the phenyl ring totally inactive to substitution *ortho* to its position; this bromination reaction was attempted on a number of occasions with no success and only compound **153** was recovered.

A more elaborate, but unfortunately very long-winded synthetic route was then devised. The bromination of the aniline **155** using NBS in dichloromethane at 0-5 °C is near quantitative. The subsequent diazotization using sodium nitrite in glacial acetic acid and concentrated sulfuric acid followed by the reaction of the cold diazonium salt with copper(I) cyanide (made *in situ*) was straightforward and a reasonably good yield of the benzonitrile **157** was obtained. The replacement of the bromine using *n*-butyllithium had to be performed at -100 °C otherwise the nitrile group would have been attacked by the *n*-butyllithium. This aryl-lithium salt, formed after 10 minutes was then quenched with trimethyl borate to form the phenylboronic acid. After hydrolyzing with hydrochloric acid, the boronic acid was oxidized to the phenol **158** using hydrogen peroxide in THF, heated under reflux for at least 6 hours. The hydrolysis of the benzonitrile **159** unfortunately failed to go to completion and only the corresponding benzoic acid amide was recovered; this hydrolysis reaction was repeated but without success.

Scheme 7.4 also details an elaborate and unfortunately long-winded synthetic route for the production of a benzoic acid incorporating both a fluoro- and methyl-substituent. The starting compound **161** had a substitution pattern that was as near to our requirements as possible and with a functional group, in this case the amino group, that could be exploited to aid the incorporation of other functionalities. The aniline **161** was brominated using bromine in chloroform to produce compound **162**, and then this material was deaminated; this was achieved by first converting the amino group of compound **162** into its corresponding diazonium salt, followed by quenching with hypophosphorus acid. The bromine of the toluene **163** was not removed using *n*-butyllithium due to the possibility that the lithium salt would transfer to the position *ortho* to the fluoro-substituent, which is known to be more stable environment. Therefore, a Grignard of compound **163** was formed using magnesium and 1,2-dibromoethane in THF, which was subsequently quenched with trimethyl borate. Upon hydrolysis with aqueous hydrochloric acid, the boronic acid was obtained, which was then oxidized to the phenol **164** as described above for compound **158**. The addition of the bromine to compound **165** was achieved using the procedure described above for compound **140**. Compound **166** was converted to the nitrile **167** using copper(I) cyanide in 1-methylpyrrolidin-2-one, instead of direct conversion to the benzoic acid using *n*-butyllithium and solid $CO_2$ again due to the possibility of transfer of the lithium salt to the more stable position between the fluoro-substituent and the alkoxy chain. Hydrolysis of the nitrile **167** to the benzoic acid **168** failed and a compound was obtained that possessed the same spectral data as compound **165**.

Scheme 7.5 details the last of the benzoic acids targetted for synthesis. Compound **169** was *O*-alkylated in a good yield, and compound **176** was selectively *O*-alkylated in the desired position also in a good yield; both using the procedure described above for compound **123**. Compound **177** was further *O*-alkylated using methyl iodide in a quantitative yield. Compound **173** was *O*-alkylated using decan-1-ol in the presence of DEAD and triphenylphosphine; this is the Mitsunobu reaction.[4] Compound **170** was brominated in the desired position using the procedure detailed for compound **140** and the conversion to the benzoic acid was also as described for compound **151**, with the exception that the lithiation only took 10 minutes and was performed at -100 °C to prevent attack of the nitrile group by the *n*-butyllithium. The hydrolysis of the esters **174** and **178** was described above for compound **137**.

The final discotic materials (**180-191**) were prepared by the esterification of HHTP (**3**) with the respective benzoyl chlorides in the presence of pyridine, see Scheme 7.6. Four final target materials (**183**, **184**, **190** and **191**) were not successfully synthesized; the reaction procedures were repeated and slightly altered; firstly, by adding a catalytic amount of DMAP in order to aid the esterification process and secondly, in the purification stage using column chromatography, the elution solvent (dichloromethane) was made more polar by the gradual addition of ethyl acetate until the elution solvent was solely ethyl acetate. Both alterations made no difference to the final outcome - these target materials (**183**, **184**, **190** and **191**) were not obtained.

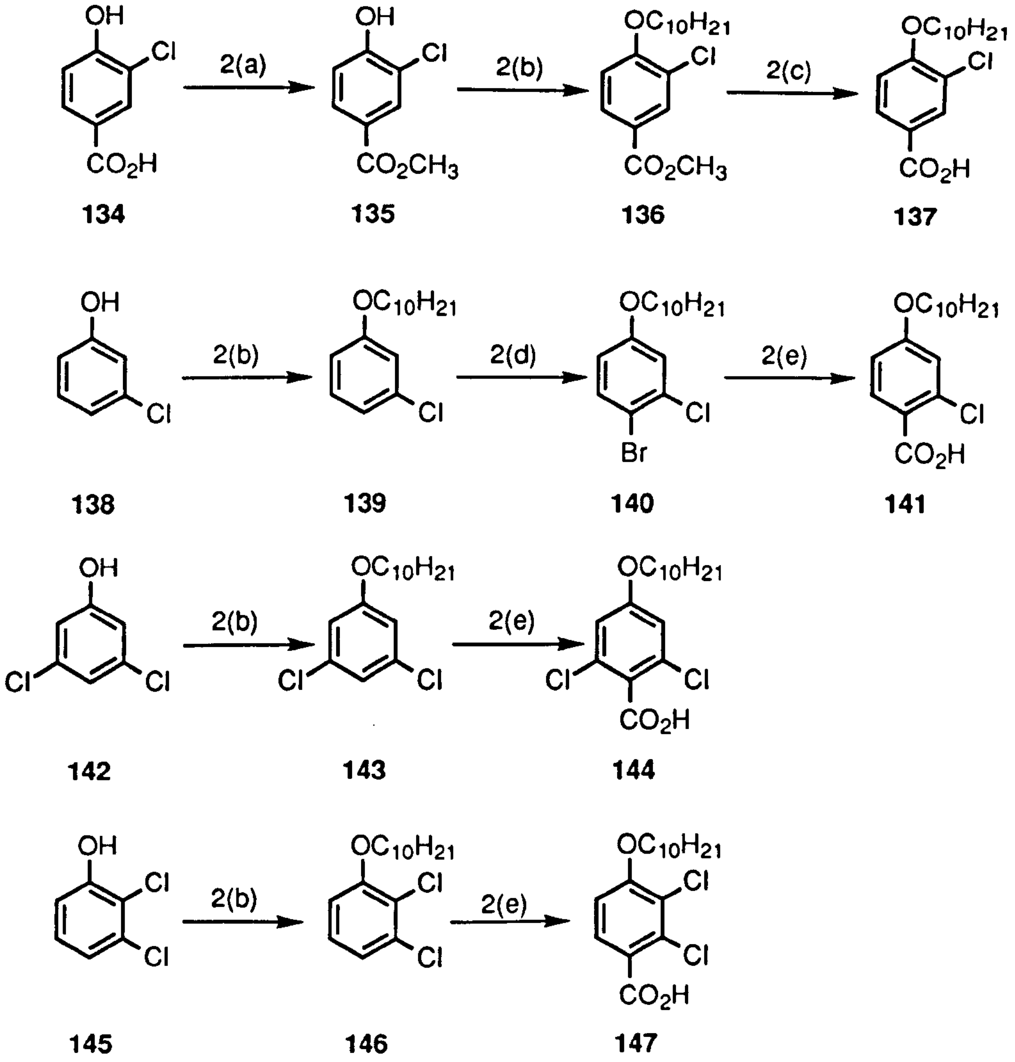


1(a) ..... 1-Bromodecane, $K_2CO_3$, butanone.

1(b) ..... (i) *n*-BuLi, THF; (ii) $CO_2$ (solid), dry $Et_2O$.

1(c) ..... conc. $H_2SO_4$, water, glacial acetic acid.

**Scheme 7.1 : Synthetic route for the preparation of the fluoro-substituted benzoic acids (124, 127, 130 and 133)**



2(a) ..... conc. $H_2SO_4$, methanol.

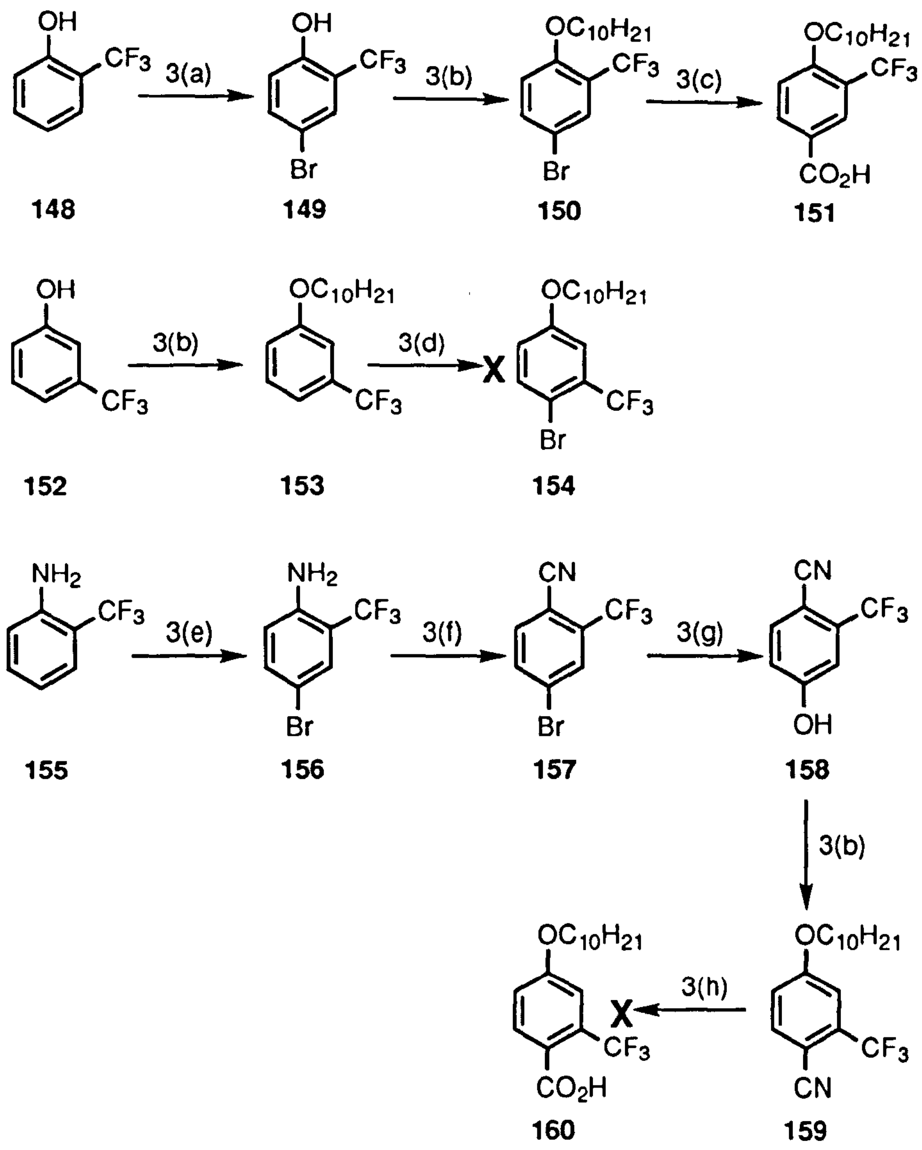
2(b) ..... 1-Bromodecane, $K_2CO_3$, butanone.

2(c) ..... NaOH, water, ethanol.

2(d) ..... $Br_2$, dry $CHCl_3$, reflux.

2(e) ..... (i) *n*-BuLi, THF; (ii) $CO_2$ (solid), dry $Et_2O$.

**Scheme 7.2 : Synthetic route for the preparation of the chloro-substituted benzoic acids (137, 141, 144 and 147)**



3(a) ..... $Br_2$, glacial acetic acid, 0 °C.

3(b) ..... 1-Bromodecane, $K_2CO_3$, butanone.

3(c) ..... (i) *n*-BuLi, THF; (ii) $CO_2$ (solid), $Et_2O$.

3(d) ..... $Br_2$, dry $CHCl_3$, reflux.

3(e) ..... NBS, $CH_2Cl_2$.

3(f) ..... (i) $NaNO_2$, conc. $H_2SO_4$, water, glacial acetic acid;

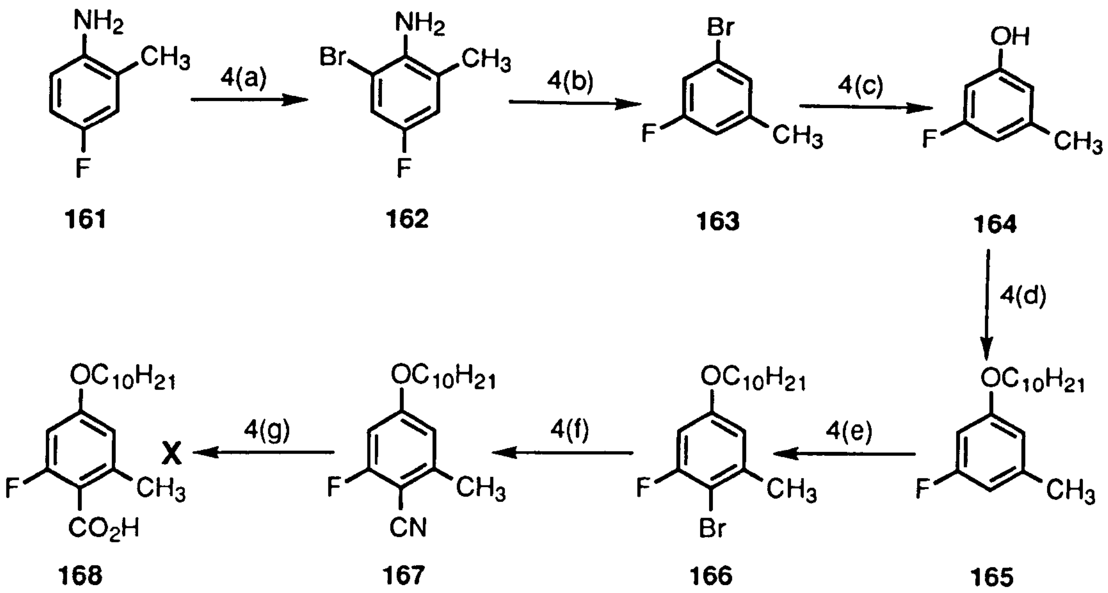
(ii) $CuSO_4.5H_20$, KCN.

3(g) ..... (i) *n*-BuLi, THF and hexane, -100 °C; (ii) $(MeO)_3B$, THF;

(iii) 10% HCl; (iv) 30% $H_2O_2$, THF, reflux.

3(h) ..... conc. $H_2SO_4$, water, glacial acetic acid.

**Scheme 7.3 : Synthetic route for the preparation of the trifluoromethyl-substituted benzoic acids (151 and 160)**



4(a) ..... $Br_2$, $CHCl_3$.

4(b) ..... (i) $NaNO_2$, aq. HCl; (ii) $H_3PO_2$.

4(c) ..... (i) Mg, 1,2-dibromoethane, THF; (ii) $(MeO)_3B$, THF;
(iii) 10% HCl; (iv) 30% $H_2O_2$, THF, reflux.

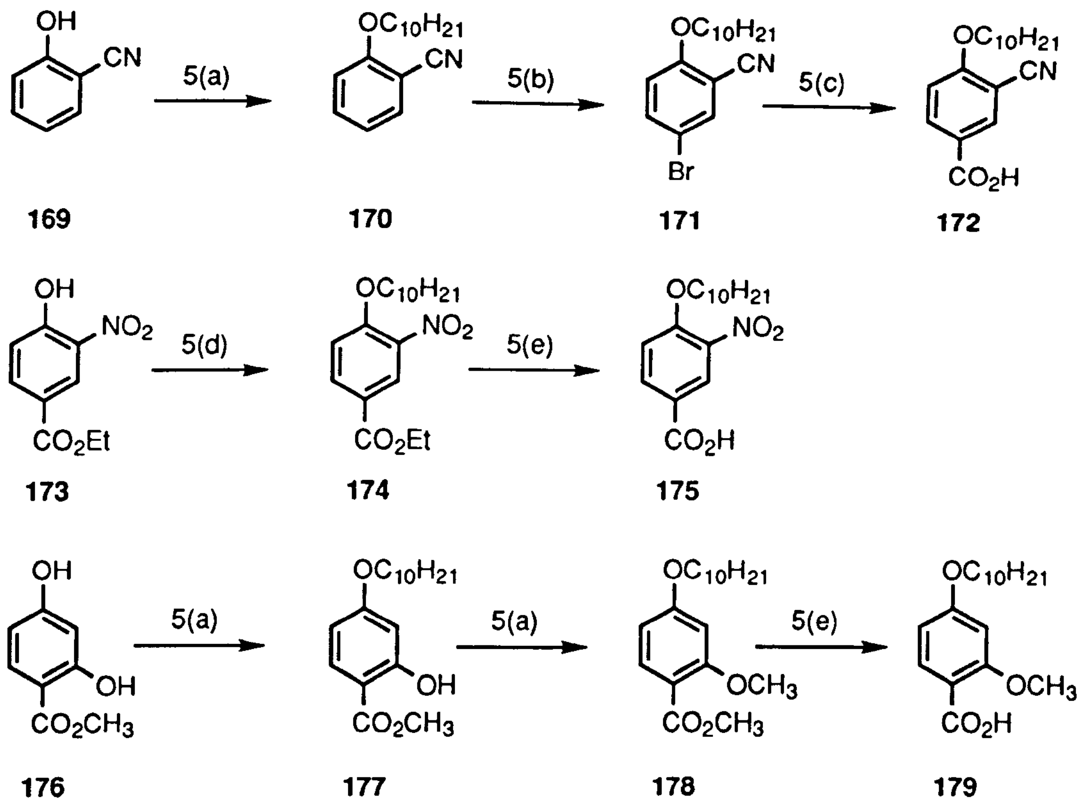
4(d) ..... 1-Bromodecane, $K_2CO_3$, butanone.

4(e) ..... $Br_2$, dry $CHCl_3$, reflux.

4(f) ..... CuCN, 1-methylpyrrolidin-2-one, 185 °C.

4(g) ..... conc. $H_2SO_4$, water, glacial acetic acid.

**Scheme 7.4 : Synthetic route for the preparation of 4-decyloxy-6-fluoro-2-toluic acid (168)**



5(a) ..... 1-Bromodecane or methyl iodide, $K_2CO_3$, butanone.

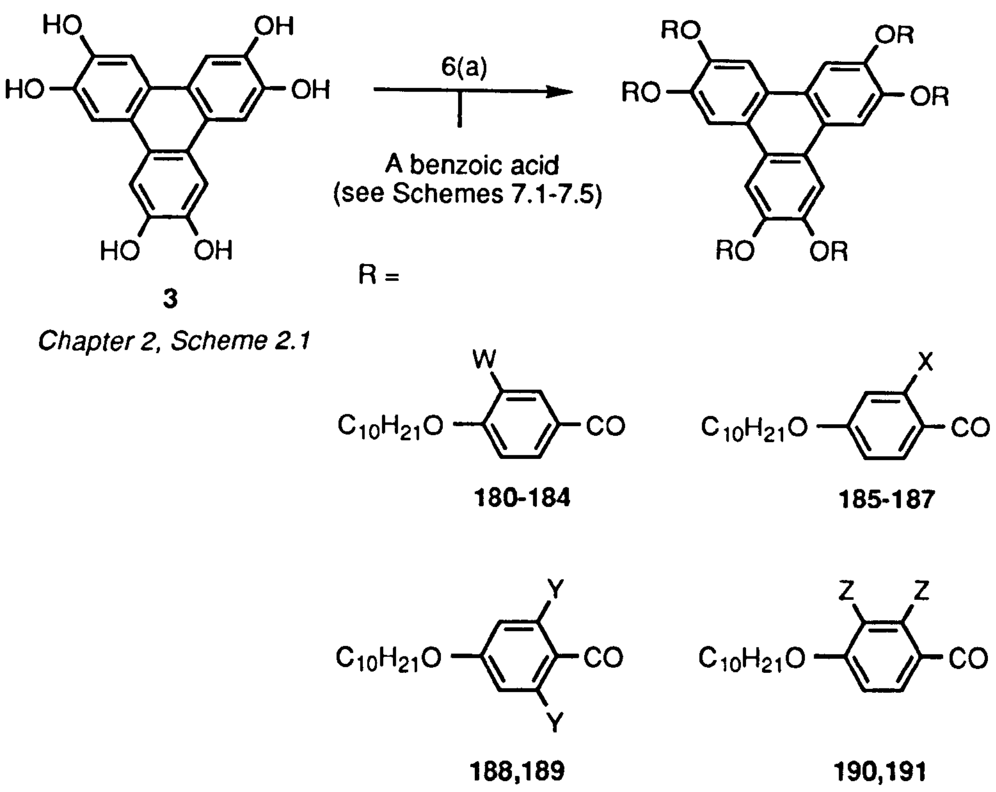
5(b) ..... $Br_2$, dry $CHCl_3$, reflux.

5(c) ..... (i) *n*-BuLi, THF and hexane, -100 °C; (ii) $CO_2$ (solid), dry $Et_2O$.

5(d) ..... Decan-1-ol, DEAD, $PPh_3$, THF.

5(e) ..... NaOH, water, ethanol.

**Scheme 7.5 : Synthetic route for the preparation of 3-cyano-4-decyloxybenzoic, 4-decyloxy-3-nitrobenzoic and 4-decyloxy-2-methoxybenzoic acids (172, 175 and 179)**



6(a) ..... Acid chloride (oxalyl chloride, DMF, $CH_2Cl_2$), pyridine.

**Scheme 7.6 : Synthetic route for the preparation of the polar-substituted triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxybenzoate)s; 180-184: W = fluoro, chloro, trifluoromethyl, cyano or nitro; 185-187: X = fluoro, chloro or methoxy; 188 and 189: Y = fluoro or chloro; 190 and 191: Z = fluoro or chloro**

### 7.2.1 *Preparation of 1-Bromo-4-decyloxy-3-fluorobenzene, 4-Decyloxy-2-fluorobenzonitrile, 1-Decyloxy-3,5-difluorobenzene and 1-Decyloxy-2,3-difluorobenzene* (123, 126, 129 and 132)

The general synthetic method is exemplified by the procedure reported in Chapter 3 for compound **9**.

*1-Bromo-4-decyloxy-3-fluorobenzene* (**123**)

Yield: 19.8 g (100%) Bp: 125-130 °C at 0.05 mmHg

$^1H$ NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.27(14H, m), 1.78(2H, m), 3.96(2H, t), 6.79(1H, t), 7.16(2H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2930, 2880, 1510, 1470, 1310, 1270, 1210, 930, 880, 860, 800.

MS ($m/z$): 333 (M$^+$), 331 (M$^+$), 192, 191, 163, 140, 111, 96, 83, 69.

*4-Decyloxy-2-fluorobenzonitrile* (**126**)

Yield: 8.48 g (70%) Mp: 31-32 °C

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.28(14H, m), 1.79(2H, m), 3.98(2H, t), 6.72(2H, m), 7.50(1H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 2230, 1640, 1570, 1520, 1290, 1180, 1120, 870, 810.

MS ($m/z$): 277 (M$^+$), 150, 138, 120, 111, 97, 85, 71, 43.

*1-Decyloxy-3,5-difluorobenzene* (**129**)

Yield: 10.26 g (100%) Bp: 106-116 °C at 0.2 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.85(3H, t), 1.30(14H, m), 1.75(2H, m), 3.90(2H, t), 6.40(3H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1620, 1595, 1455, 1350, 1150, 1110, 995, 840, 620.

MS ($m/z$): 270(M$^+$), 140, 130, 111, 97, 85, 71, 57.

*1-Decyloxy-2,3-difluorobenzene* (**132**)

Yield: 10.0 g (74%) Bp: 106-116 °C at 0.2 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.85(3H, t), 1.25(14H, m), 1.80(2H, m), 4.00(2H, t), 6.25(2H, m), 6.95(1H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2880, 1620, 1510, 1480, 1250, 1080, 760, 710.

MS ($m/z$): 270 (M$^+$), 140, 135, 130, 111, 97, 85, 69, 57, 43.

## *7.2.2 Preparation of the 4-Decyloxy-3-fluorobenzoic, 4-Decyloxy-2-fluorobenzoic, 4-Decyloxy-2,6-difluorobenzoic and 4-Decyloxy-2,3-difluorobenzoic Acids* (124, 127, 130 and 133)

The general synthetic method for compounds **124**, **130** and **133** is exemplified by the procedure reported in Chapter 3 for compound **14**.

*4-Decyloxy-3-fluorobenzoic Acid* (**124**)

Yield: 9.7 g (55%) Transitions (°C): K 105.3 $S_C$ 109.4 N 113.8 I

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.30(14H, m), 1.85(2H, m), 4.10(2H, m), 6.95(1H, t), 7.80(2H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3500-2500(broad), 1690, 1620, 1520, 1470, 1450, 1310, 1290, 1215, 770, 640.

MS (*m/z*): 296 ($M^+$), 234, 156, 140, 128, 110, 97, 82, 68.

*4-Decyloxy-2-fluorobenzoic Acid* (**127**)

A mixture of concentrated sulfuric acid (100 ml) and water (100 ml) was added dropwise to a stirred solution of compound **126** (8.48 g, 0.031 mol) in glacial acetic acid (200 ml). The stirred mixture was heated under reflux (8 h), cooled and the product was filtered off. The product was taken up in ether (100 ml), washed with water (150 ml) and dried ($MgSO_4$). The solvent was removed and the product recrystallized from ethanol to yield an off-white solid.

Yield: 4.93 g (54%) Transitions (°C): K 92.1 N 107.4 I

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(14H, m), 1.75(2H, m), 4.00(2H, t), 6.65(2H, m), 7.95(1H, t).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3300-2500(broad), 2920, 2860, 1680, 1620, 1450, 1290, 1150, 850.

MS (*m/z*): 296 ($M^+$), 169, 156, 139, 111, 97, 83, 69, 55.

*4-Decyloxy-2,6-difluorobenzoic Acid* (**130**)

Yield: 7.7 g (65%) Mp: 93-94 °C

$^1$H NMR (CDCl$_3$ and TMS) δ: 6.50(2H, d) 3.90(2H, t), 1.80(2H, t), 1.30(14H, m), 0.85(3H, t).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3500-2400(broad), 2920, 2850, 1680, 1620, 1570, 1350, 1280, 1160, 1050, 840.

MS (*m*/*z*): 314(M$^+$), 175, 157, 140, 111, 85, 71, 57.

*4-Decyloxy-2,3-difluorobenzoic Acid* (**133**)

Yield: 8.53 g (73%) Transitions (°C): K 112.0 (S$_C$ 111.0) I

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.85(3H, t), 1.35(14H, m), 1.85(2H, m), 4.10(2H, t), 6.75(1H, m), 7.75(1H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2850, 1690, 1620, 1460, 1300, 1090, 1080, 770.

MS (*m*/*z*): 314 (M$^+$), 175, 157, 140, 111, 97, 85, 71, 57, 43.

### *7.2.3 Preparation of Methyl 3-chloro-4-hydroxybenzoate* (135)

A solution of 3-chloro-4-hydroxybenzoic acid (25.0 g, 0.15 mol) in methanol (120 ml) and concentrated sulfuric acid (2.5 ml) was heated under reflux for 4 h. The reaction mixture was allowed to cool and the methanol was removed *in vacuo*. The crude product was dried *in vacuo* and used without further purification.

Yield: 27.00 g (100%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 3.90(3H, s), 7.04(1H, d), 7.88(1H, dd), 8.05(1H, d), 8.70(1H, s broad).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3340(broad), 1690, 1600, 1440, 1300, 1270, 1215, 775, 710.

MS (*m*/*z*): 188(M$^+$), 186(M$^+$), 157, 155, 58, 43.

### *7.2.4 Preparation of Methyl 3-chloro-4-decyloxybenzoate, 1-Chloro-3-decyloxybenzene, 1,3-Dichloro-5-decyloxybenzene and 1,2-Dichloro-3-decyloxybenzene* (136, 139, 143 and 146)

The general synthetic method is exemplified by the procedure reported in Chapter 3 for compound **9**.

*Methyl 3-chloro-4-decyloxybenzoate* (**136**)

Yield: 9.21 g (88%)

$^{1}$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(14H, m), 1.85(2H, m), 3.88(3H, s), 4.06(2H, t), 6.89(1H, d), 7.90(1H, dd), 8.04(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1670, 1600, 1500, 1460, 1430, 1310, 1270, 1110, 1060, 765, 720.

MS (*m*/*z*): 328(M$^+$), 326(M$^+$), 188, 186, 157, 155, 43.

*1-Chloro-3-decyloxybenzene* (**139**)

Yield: 8.37 g (80%)

$^{1}$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.30(14H, m), 1.77(2H, m), 3.93(2H, t), 6.77(1H, dd), 6.88(2H, m), 7.18(1H, ddd).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2850, 1595, 1570, 1460, 1280, 1200, 1245, 1230, 1070, 1030, 860, 770, 680.

MS (*m*/*z*): 270(M$^+$), 268(M$^+$), 130, 128, 57, 43.

*1,3-Dichloro-5-decyloxybenzene* (**143**)

Yield: 7.58 g (82%)

$^{1}$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(14H, m), 1.76(2H, m), 3.91(2H, t), 6.77(2H, dd), 6.90(1H, dd).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1585, 1565, 1440, 1260, 1105, 1040, 830, 800, 670.

MS (*m*/*z*): 304(M$^+$), 302(M$^+$), 164, 162, 85, 71, 57.

*1,2-Dichloro-3-decyloxybenzene* (**146**)

Yield: 8.70 g (93%) Bp: 172-174 °C at 0.15 mmHg

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.30(14H, m), 1.40(3H, t), 1.80(2H, m), 4.00(2H, t), 6.78(1H, dd), 7.04(1H, dd), 7.10(1H, dd).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 2920, 2860, 1570, 1450, 1380, 1290, 1265, 1050, 1030, 765, 700, 650.

MS (*m/z*): 306($M^+$), 304($M^+$), 302($M^+$), 166, 164, 162, 140, 111, 97, 69, 57, 43.

### *7.2.5 Preparation of 1-Bromo-2-chloro-4-decyloxybenzene* (140)

The general synthetic method is exemplified by the procedure reported in Chapter 4 for compound **62**.

Yield: 9.60 g (90%) Bp: 124-128 °C at 0.17 mmHg

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.30(14H, m), 1.73(2H, m), 3.89(2H, t), 6.66(1H, dd), 7.00(1H, d), 7.44(1H, d).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 2920, 2860, 1585, 1460, 1380, 1280, 1230, 1060, 1030, 860, 840, 800, 640.

MS (*m/z*): 350($M^+$), 348($M^+$), 346($M^+$), 270, 268, 210, 208, 206, 130, 128, 69, 55.

### *7.2.6 Preparation of 3-Chloro-4-decyloxybenzoic, 2-Chloro-4-decyloxybenzoic, 2,6-Dichloro-4-decyloxybenzoic and 2,3-Dichloro-4-decyloxybenzoic Acids* (137, 141, 144 and 147)

*3-Chloro-4-decyloxybenzoic Acid* (**137**)

A solution of compound **136** (9.21 g, 0.028 mol) and sodium hydroxide (6.60 g, 0.165 mol) in ethanol (150 ml) and water (15 ml) was heated under reflux for 2 h. The reaction mixture was then allowed to cool and dilute hydrochloric acid (100 ml) was added. The crude product was filtered off, washed with water and then dried *in vacuo*. The crude product was recrystallised from ethanol to yield colourless crystals.

Yield: 7.55 g (86%) Transitions (°C): K 100 ($S_C$ 84 N 89) I

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.35(14H, m), 1.85(2H, m), 4.10(2H, t), 6.92(1H, d), 7.97(1H, dd), 8.13(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3400-2500(broad), 2920, 2860, 1680, 1590, 1500, 1460, 1430, 1320, 1300, 1275, 1060, 765, 715.

MS (*m/z*): 314(M$^+$), 312(M$^+$), 172, 84, 70, 57.

The general synthetic method for the following compounds is reported by the procedure reported in Chapter 3 for compound **14**.

*2-Chloro-4-decyloxybenzoic Acid* (**141**)

Yield: 4.92 g (56%) Transitions (°C): K 86 (N 64) I

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.30(14H, m), 1.76(2H, m), 4.00(2H, t), 6.83(1H, dd), 6.97(1H, d), 8.03(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3330-2400(broad), 2920, 2860, 1680, 1590, 1550, 1465, 1405, 1290, 1230, 1065, 860, 640.

MS (*m/z*): 314(M$^+$), 312(M$^+$), 172, 85, 69, 55.

*2,6-Dichloro-4-decyloxybenzoic Acid* (**144**)

Yield: 5.44 g (63%) Mp: 55-57 °C

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.30(14H, m), 1.76(2H, m), 3.95(2H, t), 6.85(2H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3330-2400(broad), 2920, 2860, 1710, 1590, 1550, 1465, 1380, 1290, 1250, 1150, 1050, 1020, 815, 640.

MS (*m/z*): 348(M$^+$), 346(M$^+$), 207, 111, 97, 85, 71, 57.

#### *2,3-Dichloro-4-decyloxybenzoic Acid* (**147**)

Yield: 3.44 g (34%) Mp: 101-103 °C

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.30(14H, m), 1.40(3H, t), 1.85(2H, m), 4.20(2H, t), 6.88(1H, d), 7.98(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3400-2400(broad), 2920, 2860, 1690, 1575, 1270, 1250, 1025, 770, 680.

MS (*m*/*z*): 346(M$^+$), 348(M$^+$), 350(M$^+$), 210, 208, 206, 189, 140, 111, 97, 85, 70, 57.

### *7.2.7 Preparation of 5-Bromo-2-hydroxybenzotrifluoride* (**149**)

The general synthetic method is exemplified by the procedure reported in Chapter 4 for compound **49**.

Yield: 9.19 g (62%) Mp: 32-34 °C

$^1$H NMR (CDCl$_3$ and TMS) δ5.56(1H, s broad), 6.85(1H, d), 7.50(1H, m), 7.62(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3400(broad), 1600, 1420, 1310, 1170, 1130, 1050, 890, 820, 680, 630.

MS (*m*/*z*): 242(M$^+$), 240(M$^+$), 222, 220, 194, 192, 113, 63.

### *7.2.8 Preparation of 2-Amino-5-bromobenzotrifluoride* (**156**)

*N*-Bromosuccinimde ( 55.2 g, 0.31 mol) was added in small portions over 45 mins to a stirred, cooled (< 5 °C) solution of 2-aminobenzotrifluoride (50.0 g, 0.31 mol) in dry dichloromethane (200 ml). The mixture was stirred for 1 h and washed with copious amounts of water. The aqueous layer was washed with dichloromethane and the combined organic phases were washed with water and dried (MgSO$_4$). The solvent was removed to give a red liquid which was distilled to yield a pale orange liquid.

Yield: 68.01 g (92%) Bp: 100-101 °C at 17mmHg

$^1$H NMR ($CDCl_3$ and TMS) δ:4.17(2H, s broad), 6.63(1H, d), 7.37(1H, dd), 7.53(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3500, 3405, 1625, 1600, 1575, 1485, 1420, 1325, 1290, 1260, 1170, 1140, 1110, 1070, 1040, 890, 850, 815, 670, 630, 520.

MS (*m/z*): 241(M$^+$), 239(M$^+$), 221, 219, 194, 192, 120, 113, 70, 58.

### *7.2.9 Preparation of 4-Bromo-2-(α,α,α-trifluoromethyl)benzonitrile* (**157**)

Concentrated sulfuric acid (50 ml) was added dropwise to a stirred mixture of compound **156** (34.0 g, 0.14 mol), water (100 ml) and glacial acetic acid (150 ml). The clear solution was cooled to -5 °C and a solution of sodium nitrite (11.73 g, 0.17 mol) in water (70 ml) was added dropwise; the stirred mixture was maintained at -5 °C for 20 min.

A solution of potassium cyanide (45.5 g, 0.70 mol) in water (200 ml) was added dropwise to a stirred solution of copper(II) sulfate pentahydrate (49.8 g, 0.20 mol) in water (200 ml) and ice (200 g) at 10-20 °C. Sodium hydrogen carbonate (168.0 g, 2.0 mol) and cyclohexane (300 ml) were added, the temperature was raised to 50 °C and the cold diazonium salt mixture was added in portions with rapid stirring. The mixture was cooled, the organic layer was separated and the aqueous layer was washed with ether (twice). The combined organic extracts were washed with water, 10% sodium hydroxide, water and dried ($MgSO_4$). The solvent was removed to yield a dark red liquid which was distilled to yield a pale orange liquid.

Yield: 19.43 g (56%) Bp: 124-128 °C at 17mmHg

$^1$H NMR ($CDCl_3$ and TMS) δ: 7.71(1H, d), 7.85(1H, dd), 7.96(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2220, 1590, 1480, 1400, 1300, 1270, 1200, 1180, 1140, 1080, 1055, 900, 830, 745, 670, 550.

MS (*m/z*): 251(M$^+$), 249(M$^+$), 170, 99, 75, 69, 50.

### *7.2.10 Preparation of 4-Hydroxy-2-(α,α,α-trifluoromethyl)benzonitrile* (158)

*n*-Butyllithium (31.2 ml, 2.5M in hexane, 0.078 mol) was added dropwise to a stirred, cooled (-100 °C) solution of compound **157** (19.43 g, 0.078 mol) in dry THF (200 ml) and dry hexane (70 ml) under dry nitrogen. The reaction was maintained under these conditions for 10 mins then a solution of trimethyl borate (16.1 g, 0.16 mol) in dry THF (20 ml) was added dropwise. The reaction mixture was allowed to warm to room temperature overnight and then stirred for 1 h with 10% hydrochloric acid (100 ml). The product was extracted into ether (twice), and the combined organic extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude boronic acid was used without further purification.

30% Hydrogen peroxide (15.9 g, 53 ml, 0.47 mol) was added dropwise to a stirred refluxing solution of the boronic acid in THF (200 ml). The stirred mixture was heated under reflux overnight and then cooled. The reaction mixture was poured into water (1000 ml) and the product was extracted into dichloromethane (twice). The combined organic layers were dried ($MgSO_4$) and the solvent was removed *in vacuo* to yield a dark oil which was further purified by column chromatography (silica gel/dichloromethane) to yield a colourless liquid.

Yield: 7.30 g (50%)

| | |
|---|---|
| $^1H$ NMR ($CDCl_3$ and TMS) $\delta$: | 6.30, (1H, s broad), 7.09(1H, dd), 7.25(1H, d), 7.73 (1H, d). |
| IR (KBr) $\nu_{max}$ $cm^{-1}$: | 3600-3000(broad), 2220, 1610, 1450, 1330, 1270, 1180, 1140, 1045. |
| MS (*m/z*): | 187($M^+$), 168, 139, 88, 69, 63. |

### *7.2.11 Preparation of 5-Bromo-2-decyloxybenzotrifluoride, 3-Decyloxybenzotrifluoride and 4-Decyloxy-2-($\alpha,\alpha,\alpha$-trifluoromethyl)benzonitrile* (150, 153 and 159)

The general synthetic method is exemplified by the procedure reported in Chapter 3 for compound **9**.

*5-Bromo-2-decyloxybenzotrifluoride* (**150**)

Yield: 12.38 g (86%) Bp: 165-167 °C at 0.4 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(14H, m), 1.85(2H, m), 4.01(2H, t), 6.85(1H, d), 7.55(1H, dd), 7.63(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1600, 1490, 1460, 1410, 1310, 1300, 1280, 1250, 1140, 1050, 890, 810, 675.

MS (*m*/*z*): 382(M$^+$), 380(M$^+$), 320, 242, 240, 222, 220, 140, 111, 97, 85.

*3-Decyloxybenzotrifluoride* (**153**)

Yield: 15.22 g (91%) Bp: 167-169 °C at 0.4 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.30(14H, m), 1.80(2H, m), 3.95(2H, t), 7.05(1H, ddd), 7.11(1H, dd), 7.20(1H, ddd), 7.40(1H, dd).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1610, 1590, 1490, 1450, 1330, 1295, 1240, 1170, 1130, 1065, 1035, 880, 790, 700, 660.

MS (*m*/*z*): 302(M$^+$), 162, 140, 111, 97, 85, 69, 57, 43.

*4-Decyloxy-2-($\alpha,\alpha,\alpha$-trifluoromethyl)benzonitrile* (**159**)

Yield: 12.67 g (100%) Bp: 150-160 °C at 0.03 mmHg

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(14H, m), 1.80(2H, m), 4.05(2H, t), 7.09(1H, dd), 7.25(1H, d), 7.74(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2850, 2210, 1605, 1500, 1440, 1335, 1315, 1270, 1240, 1180, 1140, 1040, 890, 840, 550.

MS ($m/z$): 327(M$^+$), 280, 205, 190, 135, 97, 91, 85, 71, 56.

### *7.2.12 Preparation of 2-Bromo-5-decyloxybenzotrifluoride* (**154**; Attempted)

The general synthetic method is exemplified by the procedure reported in Chapter 4 for compound **62**. The reaction failed and the compound **153** was recovered.

### *7.2.13 Preparation of 4-Decyloxy-3-(α,α,α-trifluoromethyl)benzoic and 4-Decyloxy-2-(α, α, α-trifluoromethyl)benzoic Acids* (151 and 160)

The general synthetic methods are exemplified by procedures reported in Chapter 3 (compound **14**) for compound **151** and in this Chapter (compound **127**) for compound **160**.

*4-Decyloxy-3-(α,α,α-trifluoromethyl)benzoic Acid* (**151**)

Yield: 6.52 g (57%) Mp: 76-78 °C

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.35(14H, m), 1.85(2H, m), 4.12(2H, t), 7.02(1H, d), 8.25(1H, dd), 8.35(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3300-2400(broad), 2920, 2860, 1680, 1610, 1420, 1285, 1190, 1050, 930, 770, 675.

MS ($m/z$): 346(M$^+$), 206, 186, 140, 111, 97, 85, 71, 44.

*4-Decyloxy-2-(α,α,α-trifluoromethyl)benzoic Acid* (**160**; Attempted)

The reaction failed to hydrolyse the nitrile group completely and a quantitative amount of the benzoic acid amide was recovered. The amide would not hydrolyse even on repeated attempts.

Yield: 6.73 g (100%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.35(14H, m), 1.85(2H, m), 4.12(2H, t), 5.75(2H, s broad), 7.05(1H, dd), 7.20(1H, d), 7.57 (1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3500-3250(broad), 3250-3000(broad, 2920, 2860, 1650, 1610, 1430, 1310, 1245, 1170, 1130, 1040, 875, 830, 620.

MS (*m/z*): 346(M$^+$), 206, 189, 146, 85, 71, 57.

### *7.2.14 Preparation of 2-Bromo-4-fluoro-6-methylaniline* (162)

Bromine (31.6 g, 10.5 ml, 0.2 mol) was added dropwise to a stirred solution of compound **161** (25.0 g, 0.2 mol) in chloroform (200 ml) and a fine precipitate was obtained. The reaction mixture was left to stir for 1 h and then washed with water and dried ($MgSO_4$). The solvent was removed to yield a red liquid.

Yield: 40.6 g (100%)

$^1$H NMR ($CDCl_3$ and TMS) δ: 2.37(3H, s), 3.80(2H, s broad), 6.85(1H, dd), 7.12 (1H, dd).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3500-2500(broad), 1590, 1460, 1280, 1220, 1170, 1120, 1060, 860, 460, 360.

MS (*m/z*): 205(M$^+$), 203(M$^+$), 192, 190, 149, 124, 108, 75, 43.

### *7.2.15 Preparation of 3-Bromo-5-fluorotoluene* (163)

A solution of sodium nitrite (20.7 g, 0.3 mol) in water (150 ml) was added dropwise to a stirred, cooled solution (< 5 °C) of compound **162** (40.6 g, 0.2 mol) in 36% hydrochloric acid (500 ml) and water (200 ml) and the mixture was left stirring for 30 min. The temperature was maintained while hypophosphorus acid (396.0 g, 328 ml, 6.0 mol) was added dropwise, and then the mixture was stirred at room temperature overnight. Water and dichloromethane were added and the separated aqueous layer was washed with dichloromethane. The combined organic extracts were washed with water and dried ($MgSO_4$). The solvent was removed and the crude product was purified by column chromatography (silica gel/dichloromethane) to yield a colourless oil.

Yield: 15.52 g (41%)

| | |
|---|---|
| $^1$H NMR ($CDCl_3$ and TMS) δ: | 2.33(3H, s), 6.80(1H, dd), 7.05(1H, dd), 7.12(1H, d). |
| IR (KBr) $\nu_{max}$ $cm^{-1}$: | 1605, 1580, 1450, 1265, 1140, 1090, 960, 840, 820, 670. |
| MS (*m*/*z*): | 190($M^+$), 188($M^+$), 109, 107, 83, 63, 43. |

### *7.2.16 Preparation of 5-Fluoro-3-cresol* (164)

A 20% portion of a solution of compound **163** (15.52 g, 0.083 mol) in dry THF (30 ml) was added to a mixture of magnesium turnings (2.4 g, 0.1 mol) and 1,2-dibromoethane (3 drops) in dry THF (120 ml) under dry nitrogen. The reaction mixture was heated gently until the mixture became cloudy and the solvent began to boil without the need for external heat. The remainder of compound **163** in dry THF was added dropwise whilst maintaining a gentle reflux. The reaction mixture was heated under reflux for a further 45 mins and cooled to -78 °C. Trimethyl borate (25.8 g, 0.25 mol) was added dropwise and the reaction mixture was allowed to warm to room temperature overnight. 10% Hydrochloric acid (150 ml) was added and the mixture was stirred at room temperature for 1 h. The product was extracted into dichloromethane (twice) and the combined organic extracts were washed with water and dried ($MgSO_4$). The solvent was removed and the boronic acid was used without further purification.

30% Hydrogen peroxide (17.0 g, 57 ml, 0.50 mol) was added dropwise to a stirred refluxing solution of the boronic acid in THF (200 ml). The stirred mixture was heated under reflux overnight and then cooled. The reaction mixture was poured into water (1000 ml) and the product was extracted into dichloromethane (twice). The combined organic layers were dried ($MgSO_4$) and the solvent was removed *in vacuo* to yield a dark oil which was further purified by column chromatography (silica gel/dichloromethane) to yield a colourless liquid.

Yield: 7.36 g (70%)

| | |
|---|---|
| $^1$H NMR ($CDCl_3$ and TMS) δ: | 2.30(3H, s), 5.65(1H, s), 6.34(1H, dd), 6.36(1H, d), 6.44(1H, dd). |

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3700-2700(broad), 1620, 1600, 1460, 1330, 1150, 1130, 1050, 965, 840, 680.

MS (*m/z*): 126(M$^+$), 108, 97, 58.

### *7.2.17 Preparation of 3-Decyloxy-5-fluorotoluene, 2-Decyloxybenzonitrile, Ethyl 4-decyloxy-3-nitrobenzoate, Methyl 4-decyloxy-2-hydroxybenzoate and Methyl 4-decyloxy-2-methoxybenzoate* (165, 170, 174, 177 and 178)

The general synthetic procedures are exemplified by procedures reported in Chapter 3 (compound **13**) for compound **174** and (compound **9**) for all others. Methyl iodide was used in the preparation of compound **178**. Compounds **174**, **177** and **178** were not distilled but were purified by column chromatography (silica gel/dichloromethane) to yield colourless oils.

*3-Decyloxy-5-fluorotoluene* (**165**)

Yield: 9.09 g (59%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.30(14H, m), 1.80(2H, m), 2.30(3H, s), 4.05(2H, t), 6.45(3H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1610, 1580, 1460, 1330, 1160, 1140, 1050, 830, 680.

MS (*m/z*): 266(M$^+$), 126, 108, 97, 88, 69, 55.

*2-Decyloxybenzonitrile* (**170**)

Yield: 21.63 g (99%) Bp: 167-169 °C at 0.4 mmHg

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.30(14H, m), 1.80(2H, m), 4.05(2H, t), 6.95(2H, m), 7.51(2H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 2215, 1600, 1580, 1490, 1450, 1290, 1260, 1160, 1110, 750.

MS (*m/z*): 259(M$^+$), 140, 119, 97, 91, 85, 69, 43.

*Ethyl 4-decyloxy-3-nitrobenzoate* (**174**)

Yield: 8.58 g (85%)

| | |
|---|---|
| $^1$H NMR ($CDCl_3$ and TMS) $\delta$: | 0.88(3H, t), 1.30(14H, m), 1.40(3H, t), 1.85(2H, m), 4.15(2H, t), 4.38(2H, q), 7.10(1H, d), 8.20(1H, dd), 8.50(1H, d). |
| IR (KBr) $\nu_{max}$ cm$^{-1}$: | 2920, 2860, 1705, 1610, 1530, 1460, 1350, 1260, 1160, 840, 760. |
| MS (*m/z*): | 274(M$^+$), 134, 89, 58, 43. |

*Methyl 4-decyloxy-2-hydroxybenzoate* (**177**)

Yield: 16.06 g (88%)

| | |
|---|---|
| $^1$H NMR ($CDCl_3$ and TMS) $\delta$: | 0.88(3H, t), 1.35(14H, m), 1.76(2H, m), 3.91(3H, s), 3.98(2H, t), 6.43(2H, m), 7.73(1H, m), 10.96(1H, s). |
| IR (KBr) $\nu_{max}$ cm$^{-1}$: | 3200(broad), 2920, 2860, 1670, 1615, 1575, 1500, 1470, 1440, 1355, 1320, 1250, 1200, 1180, 1135, 1015, 840, 780, 645. |
| MS (*m/z*): | 308(M$^+$), 244, 190, 168, 149, 136, 121, 108, 95, 83, 69, 43. |

*Methyl 4-decyloxy-2-methoxybenzoate* (**178**)

Yield: 15.36 g (92%)

| | |
|---|---|
| $^1$H NMR ($CDCl_3$ and TMS) $\delta$: | 0.88(3H, t), 1.35(14H, m), 1.80(2H, m), 3.85(3H, s), 3.90(3H, s), 4.00(2H, t), 6.48(2H, m), 7.83(1H, m). |
| IR (KBr) $\nu_{max}$ cm$^{-1}$: | 2920, 2860, 1700, 1605, 1480, 1440, 1420, 1280, 1210, 1170, 1150, 1040, 845, 760. |
| MS (*m/z*): | 322(M$^+$), 291, 182, 151, 121, 107, 69. |

### *7.2.18 Preparation of 2-Bromo-5-decyloxy-3-fluorotoluene and 5-Bromo-2-decyloxybenzonitrile* (166 and 171)

The general synthetic method is exemplified by the procedure reported in Chapter 4 for compound **62**.

*2-Bromo-5-decyloxy-3-fluorotoluene* (**166**)

Yield: 9.75 g (82%)

| | |
|---|---|
| $^1$H NMR ($CDCl_3$ and TMS) $\delta$: | 0.88(3H, t), 1.35(14H, m), 1.85(2H, m), 2.35(3H, s), 4.05(2H, t), 6.50(1H, dd), 6.63(1H, d). |
| IR (KBr) $\nu_{max}$ cm$^{-1}$: | 2920, 2860, 1600, 1580, 1460, 1330, 1160, 1040, 840, 660. |
| MS (*m*/*z*): | 346(M$^+$), 344(M$^+$), 206, 204, 125, 96, 85, 69, 55. |

*5-Bromo-2-decyloxybenzonitrile* (**171**)

Yield: 21.79 g (88%)

| | |
|---|---|
| $^1$H NMR ($CDCl_3$ and TMS) $\delta$: | 0.88(3H, t), 1.35(14H, m), 1.85(2H, m), 4.05(2H, t), 6.84(2H, d), 7.59(1H, dd), 7.62(1H, d). |
| IR (KBr) $\nu_{max}$ cm$^{-1}$: | 2920, 2860, 2210, 1590, 1470, 1390, 1280, 1260, 1130, 1010, 820, 640, 490. |
| MS (*m*/*z*): | 359(M$^+$), 357(M$^+$), 199, 140, 111, 97, 84, 70, 43. |

### *7.2.19 Preparation of 2-Fluoro-4-decyloxy-6-methylbenzonitrile* (167)

A solution of compound **166** (9.75 g, 0.028 mol) in dry *N*-methylpyrrolidin-2-one (30 ml) was added to a stirred suspension of dried copper(I) cyanide (4.5 g, 0.05 mol) in dry *N*-methylpyrrolidin-2-one (40 ml). The reaction mixture was heated at 185 °C for 4 h and allowed to cool to room temperature. The reaction mixture was poured into water and the product was extracted into dichloromethane (twice). The combined organic extracts were washed with water and dried ($MgSO_4$). The solvent was removed and the product was purified by column chromatography (silica gel/dichloromethane) to yield a pale yellow oil.

Yield: 6.91 g (85%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.35(14H, m), 1.85(2H, m), 2.46(3H, s), 4.05(2H, t), 6.49(1H, dd), 6.57(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 2210, 1620, 1565, 1465, 1335, 1150, 1050, 845, 720.

MS (*m/z*): 291(M$^+$), 160, 151, 140, 126, 112, 97, 85, 71, 58.

### ***7.2.20 Preparation of 4-Decyloxy-6-fluoro-2-toluic, 3-Cyano-4-decyloxybenzoic, 4-Decyloxy-3-nitrobenzoic and 4-Decyloxy-2-methoxybenzoic Acids* (168, 172, 175 and 179)**

The general synthetic methods are exemplified by procedures reported in Chapter 3 (compound **14**) for compound **172** and this Chapter (compound **137**) for compounds **168**, **175** and **179**.

*4-Decyloxy-6-fluoro-2-toluic Acid* (**168**; Attempted)

The reaction failed and the isolated material obtained had the same spectral data as compound **165**, indicating that the nitrile group had been cleaved.

*3-Cyano-4-decyloxybenzoic Acid* (**172**)

Yield: 7.80 g (87%) Mp: 117-119 °C

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.35(14H, m), 1.88(2H, m), 4.15(2H, t), 7.02(1H, d), 8.25(1H, dd), 8.30(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3300-2500(broad), 2920, 2860, 2215, 1685, 1600, 1280, 1160, 1005, 770, 640.

MS (*m/z*): 303(M$^+$), 163, 141, 97, 85, 71, 43.

*4-Decyloxy-3-nitrobenzoic Acid* (**175**)

Yield: 7.70 g (100%) Mp: 94-96 °C

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.30(14H, m), 1.85(2H, m), 4.17(2H, t), 7.12(1H, d), 8.23(1H, dd), 8.56(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3300-2400(broad), 2920, 2860, 1690, 1605, 1535, 1420, 1310, 1280, 1140, 770, 690, 640.

MS (*m/z*): 246(M$^+$), 183, 140, 97, 85, 71, 57, 43.

*4-Decyloxy-2-methoxybenzoic Acid* (**179**)

Yield: 14.25 g (96%) Mp: 84-86 °C

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(3H, t), 1.30(14H, m), 1.80(2H, m), 4.00(2H, t), 4.05(3H, s), 6.51(1H, d), 6.62(1H, dd), 8.13(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2850, 1690, 1660, 1605, 1565, 1465, 1440, 1280, 1250, 1200, 1160, 1095, 1030, 840, 760, 640.

MS (*m/z*): 308(M$^+$), 168, 151, 139, 121, 95, 69, 55, 43.

### *7.2.21 Preparation of the Polar-Substituted Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxybenzoate)s* (180-191)

The general synthetic method for the preparation of the hexa-esters is exemplified by the procedure reported in Chapter 3 for compound **30**.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-3-fluorobenzoate)* (**180**)

Yield: 1.6 g (25%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.85(3H, t), 1.30(14H, m), 1.80(2H, m), 3.95(2H, t), 6.65(1H, t), 7.50(1H, m), 7.65(1H, m), 8.25(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1610, 1520, 1285, 1190, 750.

CHN analysis: % expected - C 72.29, H 7.53;
% found - C 72.08, H 7.72.

### *Triphenylen-2,3,6,7,10,11-hexayl Hexakis(3-chloro-4-decyloxybenzoate)* (**181**)

Yield: 2.81 g (71%)

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.35(14H, m), 1.81(2H, m), 3.95(2H, t), 6.58(1H, d), 7.73(1H, dd), 7.82(1H, d), 8.25(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1600, 1500, 1270, 1230, 1125, 1090, 1055, 900, 750.

CHN analysis: % expected - C 68.97, H 7.18;
% found - C 68.78, H 6.82.

### *Triphenylen-2,3,6,7,10,11-hexayl Hexakis[4-decyloxy-3-(α,α,α-trifluoromethyl)-benzoate]* (**182**)

Yield: 2.09 g (57%)

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.35(14H, m), 1.79(2H, m), 3.90(2H, t), 6.63(1H, d), 7.92(1H, dd), 7.99(1H, d), 8.30(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1610, 1500, 1280, 1240, 1130, 1050, 900, 760, 735.

CHN analysis: % expected - C 65.97, H 6.54;
% found - C 65.68, H 6.54.

### *Triphenylen-2,3,6,7,10,11-hexayl Hexakis(3-cyano-4-decyloxybenzoate)* (**183**; Attempted)

The reaction failed on two attempts; in one of the reactions, a small amount of DMAP was added to aid the esterification process, but without success.

### *Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-3-nitrobenzoate)* (**184**; Attempted)

The reaction failed on two attempts; in one of the reactions, a small amount of DMAP was added to aid the esterification process, but without success.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-2-fluorobenzoate)* **(185)**

Yield: 2.68 g (58%)

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.85(3H, t), 1.35(14H, m), 1.85(2H, m), 3.95(2H, t), 6.60(2H, m), 8.00(1H, t), 8.50(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1615, 1500, 1250, 1140, 1060.

CHN analysis: % expected - C 72.29, H 7.53;
% found - C 72.48, H 7.34.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(2-chloro-4-decyloxybenzoate)* **(186)**

Yield: 2.62 g (78%)

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.35(14H, m), 1.78(2H, m), 3.92(2H, t), 6.59(1H, dd), 6.81(1H, d), 8.04(1H, d), 8.38(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1750, 1600, 1500, 1240, 1120, 1080, 1030, 755.

CHN analysis: % expected - C 68.97, H 7.18;
% found - C 68.88, H 7.37.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-2-methoxybenzoate)* **(187)**

Yield: 0.27 g (11%)

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.35(14H, m), 1.78(2H, m), 3.77(3H, s), 3.96(2H, t), 6.40(2H, m), 8.00(1H, d), 8.49(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1600, 1560, 1490, 1455, 1405, 1230, 1120, 1030, 825, 750.

CHN analysis: % expected - C 73.26, H 8.14;
% found - C 72.96, H 8.30.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-2,6-difluorobenzoate)* **(188)**

Yield: 3.00 g (60%)

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.90(3H, t), 1.30(14H, m), 1.80(2H, m), 3.95(2H, t), 6.50(2H, d), 8.55(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1755, 1740, 1630, 1570, 1450, 1350, 1245, 1160, 1075, 1045, 840.

CHN analysis: % expected - C 68.57, H 6.86;
% found - C 68.41, H 6.89.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(2,6-dichloro-4-decyloxybenzoate)* (**189**)

Yield: 2.42 g (66%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(14H, m), 1.78(2H, m), 3.96(2H, t), 6.88(2H, d), 8.63(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1760, 1590, 1550, 1300, 1240, 1100, 1030, 815.

CHN analysis: % expected - C 62.83, H 6.28;
% found - C 63.11, H 6.27.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxy-2,3-difluorobenzoate)*
(**190**; Attempted)

The reaction failed on two attempts; in one of the reactions, a small amount of DMAP was added to aid the esterification process, but without success.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(2,3-dichloro-4-decyloxybenzoate)*
(**191**; Attempted)

The reaction failed on two attempts; in one of the reactions, a small amount of DMAP was added to aid the esterification process, but without success.

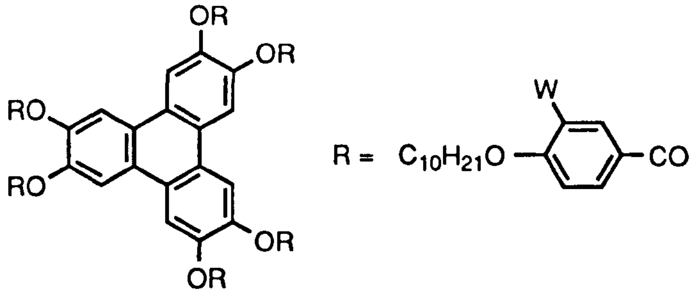
## *7.3 Results*

### *7.3.1 Transition Temperatures*

The transition temperatures for the discotic materials were determined by a combination of thermal optical microscopy and differential scanning calorimetry. Typically, the crystal to mesophase transitions were determined by calorimetry due to the difficulty in discerning this transition optically. All other transitions, including recrystallization and glassy-state transitions, were determined by microscopy. The results for the mono-substituted "outer" series (compounds **180-182**) are shown in Table 7.1, whereas the results for the mono- (compounds **185-187**) and di-substituted materials (compounds **188** and **189**) with the substituents in the "inner" regions are given in Tables 7.2 and 7.3 respectively; all three tables are shown with the parent, unsubstituted analogue (compound **42**)[6] for comparision. The enthalpy values determined by DSC analysis are reported, where possible, along with each optical transition temperature in Tables 7.1-7.3.

From Table 7.1, it is quite clear that position of the polar substituent in the "outer" regions has radically affected the mesophase behaviour, now rendering all the materials effectively non-mesogenic. The presence of the substituent has had an adverse effect upon the mesomorphic properties as the melting points are all above 300 °C! These results are highly uncharacteristic of the trends that have been previously reported in Chapters 3 to 6.

However, the results for the inner-substituted discotic materials are all in keeping with the established trends that are expected of discotic liquid crystals that have substituents in the crowded "inner" region next to the triphenylene core. Unlike the outer-substituted series, the clearing points for both inner-substituted series (compounds **185-189**) fall with increasing substituent size (see Tables 7.2 and 7.3). No columnar mesophases are observed in either series, even with substantial supercooling (*ca.* -40 °C), except however with the mono-chloro inner-substituted homologue (compound **186**) which appeared to show a possible columnar phase upon cooling from the discotic nematic mesophase. This particular phase, which had a platelet texture, was unable to be mechanically sheared; similar observations have been previously discussed for the outer-substituted methyl- and ethyl- derivatives (**99** and **66**)[5] (see also Chapters 4 and 5).



| No. | W | K | | $D_{rd}$ | | $N_D$ | | I |
|---|---|---|---|---|---|---|---|---|
| **42** | H§ | * | 142 | * | 191 | * | 212 | * |
| **180** | F | * | >300 | — | | | | * |
| **181** | Cl | * | >300 | — | | | | * |
| **182** | $CF_3$ | * | >300 | — | | | | * |

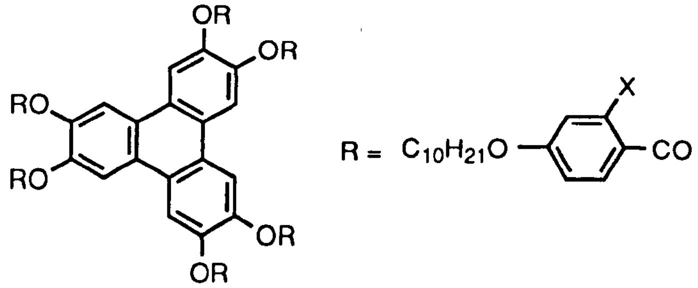
**Table 7.1 : Transition temperatures for the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxy-3-substitutedbenzoate)s**

§Literature compound.[6]

### *7.3.2 Differential Scanning Calorimetry*

Calorimetric studies were carried out on each discotic material prepared, except where indicated.

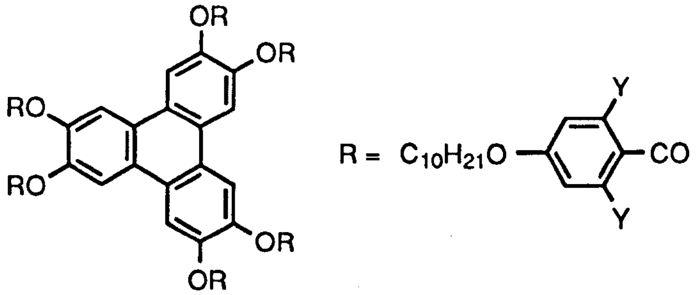
The outer-substituted series, incorporating either a fluoro-, chloro- or trifluoromethyl-substituent (compounds **180-182**), will be discussed first. Compound **180**, with the fluoro-substituent, was the only material of this series to be investigated. This material had not melted by 300 °C and *ca.* 450 °C rapidly decomposed, resulting in leakage of the spoiled compound onto the heating element of the DSC apparatus. Consequently, the remaining materials **181** and **182**, with the chloro- and trifluoromethyl-substituents respectively, were not analyzed. Throughout the DSC scan, there were no traces of enthalpy changes denoting possible mesophase transitions, but instead a rising



| No. | X | K | | $D_{rd}$ | | $N_D$ | | I | Recryst. | |
|---|---|---|---|---|---|---|---|---|---|---|
| **42** | H§ | * | 142 | * | 191 | * | 212 | * | 80 | * |
| **185** | F | * | 159 (30.08) | ——— | | * | 184 (0.68) | * | 149 | * |
| **186** | Cl | * | 80 (18.44) | ——— | | * | 193 (0.36) | * | 105 | * |
| **187** | OMe | * | 158 (36.95) | ——— | | * | 162 (0.37) | * | 117 | * |

**Table 7.2 : Transition temperatures for the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxy-2-substitutedbenzoate)s**

Enthalpies for each transition are given in parenthesis ($\Delta H$/kJ mol$^{-1}$). §Literature compound.[6]



| No. | Y | K | | $D_{rd}$ | | $N_D$ | | I | Recryst. | |
|---|---|---|---|---|---|---|---|---|---|---|
| **42** | H§ | * | 142 | * | 191 | * | 212 | * | 80 | * |
| **188** | F | * | 138 (@) | ——————— | | | | * | 124 | * |
| **189** | Cl | * | 130 (61.95) | ——— | | * | [98 (0.18)] | * | 64 | * |

**Table 7.3 : Transition temperatures for the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxy-2,6-disubstitutedbenzoate)s**

Enthalpies for each transition are given in parenthesis ($\Delta H$/kJ mol$^{-1}$).

Monotropic transitions are given in square brackets []. @ Not determined.

§Literature compound.[6]

baseline was seen which finally became a jumble of enthalpy signals indicating decomposition of the sample.

The analysis of the mono-substituted "inner" series, incorporating either a fluoro-, chloro- or methoxy-substituent (compounds **185-187**), was straightforward. Typical results for the heating and cooling cycles for compounds **185** and **186** are shown in Figures 7.3 and 7.4 respectively; the DSC heating and cooling traces for compound **187**, the methoxy-substituted analogue, are illustrated in Figures 7.5 and 7.6 respectively, with the corresponding methyl- and ethyl-substituted derivatives (compounds **103** and **69**, see Chapters 4 and 5) shown for comparision. Each material had both a melting endotherm and a much smaller enthalpy peak corresponding to the clearing point, which is characteristic of a discotic nematic ($N_D$) to isotropic liquid transition[7] (see also Chapter 3). All mesophase transitions were found to be reversible.

The chloro-substituted derivative (**186**) had an additional endotherm between the melting and clearing point peaks, which corresponds to the point where the defect texture changes from a *schlieren* to a platelet form upon cooling. However, there is a large temperature hysteresis between the formation of this phase on cooling and its disappearance on heating. This situation was previously reported for the outer-substituted methyl- and ethyl- analogues (**99** and **66**)[5] (see also Chapters 4 and 5).

The analyses of the di-substituted "inner" materials, incorporating either fluoro- or chloro-substituents (compounds **188** and **189**) were also straightforward. The difluoro-substituted homologue (**188**) only showed a melting endotherm on heating and upon cooling, simply recrystallized. The dichloro-substituted material (**189**) also showed only a melting endotherm on heating, but however, on cooling this derivative showed a very small enthalpy peak, characteristic for isotropic liquid to discotic nematic transitions, before a recrystallization peak. This particular situation was first observed for the inner-substituted *iso*-propyl analogue (**70**, see Chapter 4).

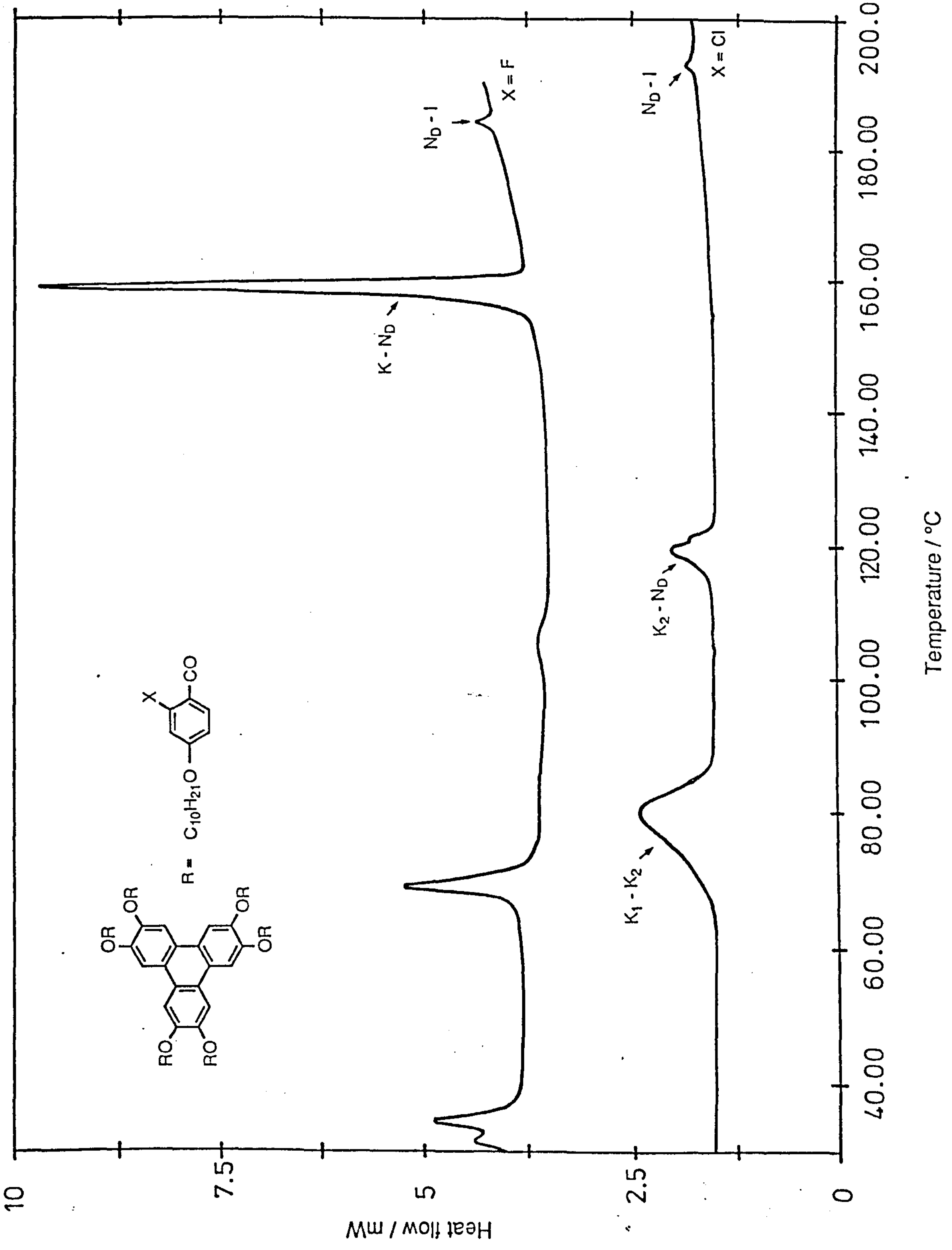


**Figure 7.3 : DSC thermogram of the first heating cycle of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxy-2-substitutedbenzoate)s (185 and 186)**

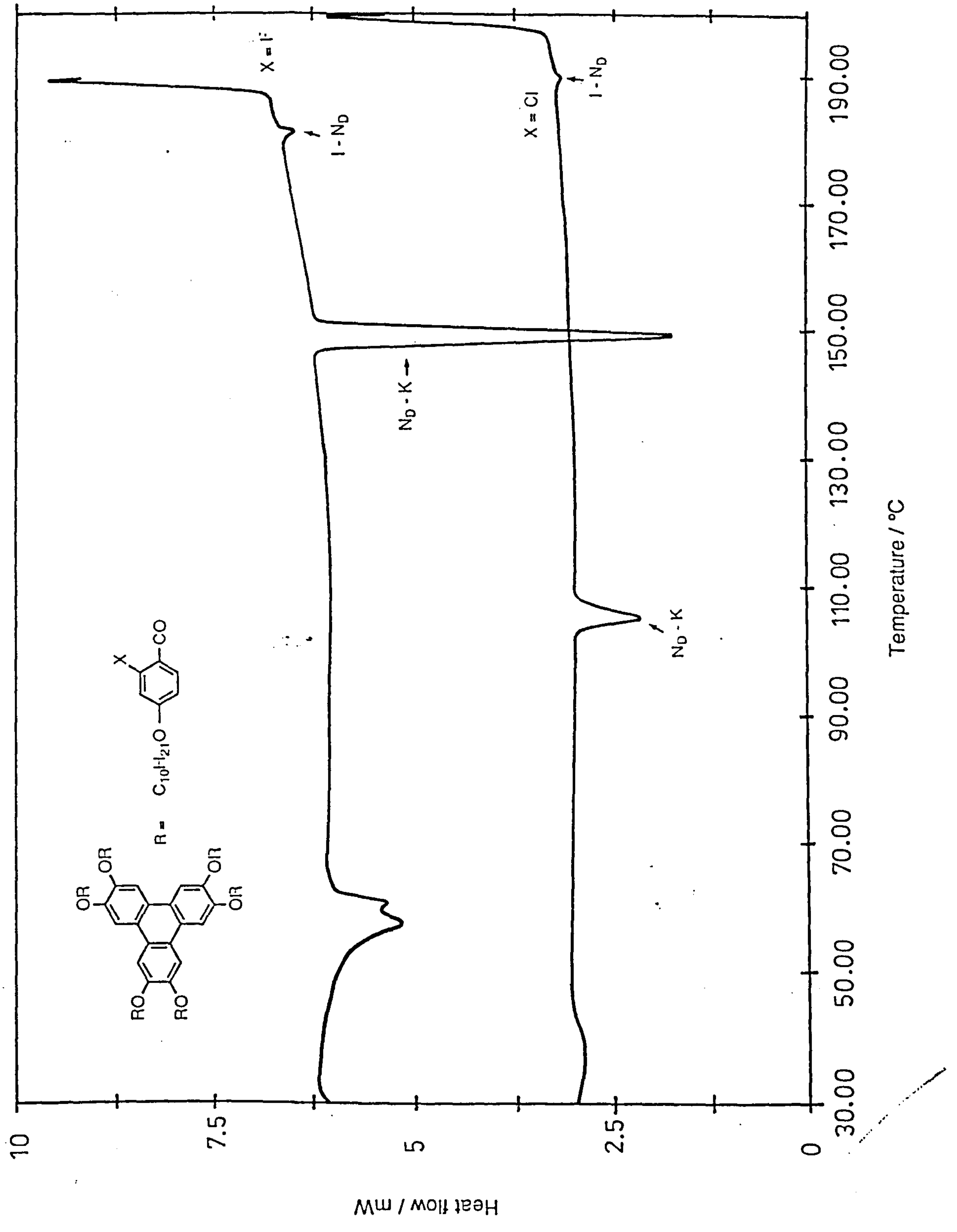


Figure 7.4 : DSC thermogram of the first cooling cycle of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxy-2-substitutedbenzoate)s (185 and 186)

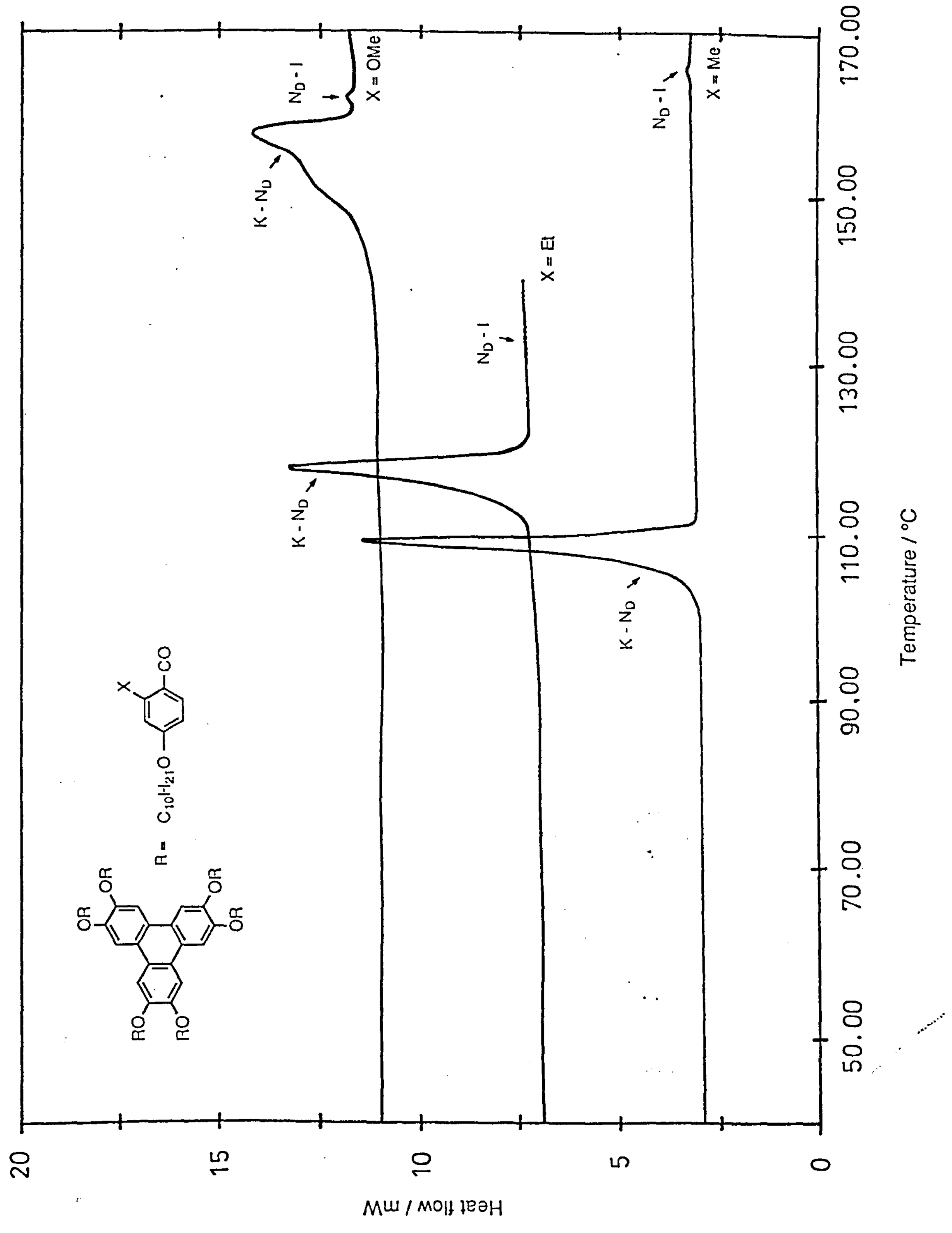


Figure 7.5 : DSC thermogram of the first heating cycle of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxy-2-substitutedbenzoate)s (69, 103 and 187)

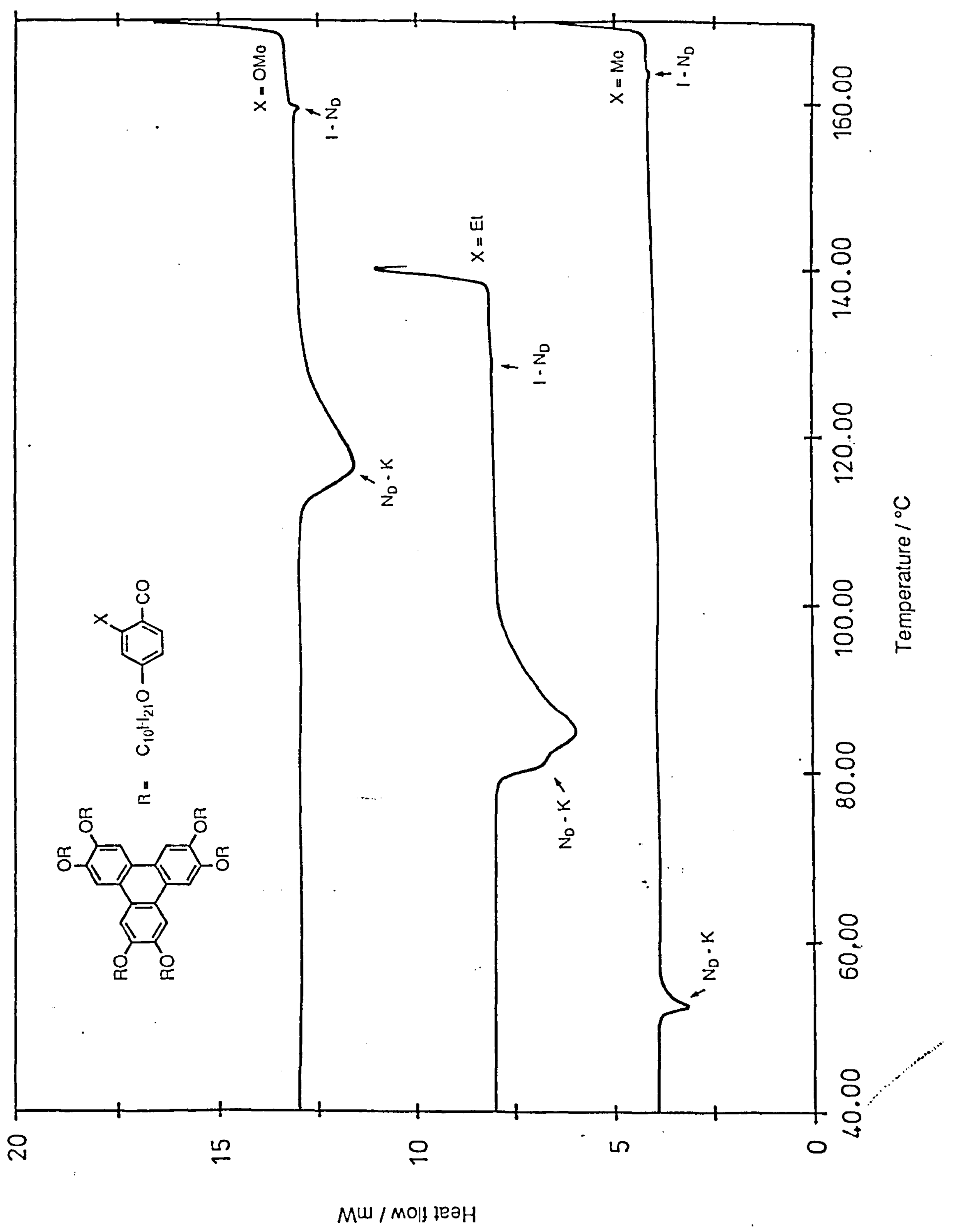


**Figure 7.6 : DSC thermogram of the first cooling cycle of the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxy-2-substitutedbenzoate)s (69, 103 and 187)**

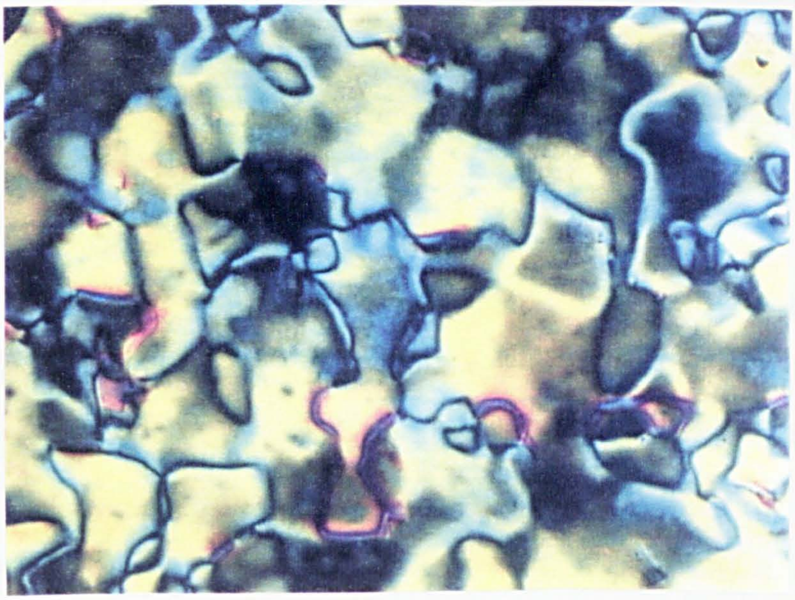


**Plate 7.1 : Sheared *schlieren* and threaded texture of the discotic nematic ($N_D$) exhibited by compound 186 at 185 °C on heating**

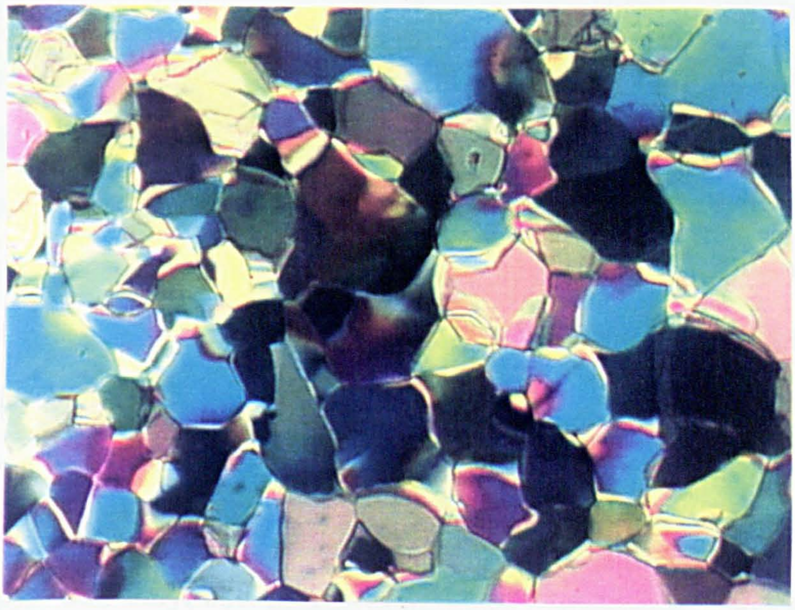


**Plate 7.2 : Mosaic texture of the ordered phase that resembles a hexagonal columnar exhibited by compound 186 at 105 °C on cooling from the $N_D$ mesophase**

### *7.3.2 Thermal Optical Microscopy*

For the mono-substituted "outer" compounds, incorporating either a fluoro-, a chloro- or a trifluoromethyl-substituent (compounds **180-182**), when each material was heated from the crystal, under microscopic examination, neither a melting point could be detected nor crystal to crystal transitions and/or mesophase transformations observed. The heating element of the Mettler FP90 microfurnace was only capable of reaching 300 °C, and up until this temperature, no birefringent textural differences had been detected. Therefore, no further analysis using this technique was performed on these particular derivatives.

However, the microscopic examinations were straightforward for the mono-substituted "inner" materials, incorporating either a fluoro-, a chloro- or a methoxy-substituent (compounds **185-187**). When each material was heated from the crystal, the first discernible transition was that to the discotic nematic ($N_D$) mesophase. Plate 7.1 shows a typical texture formed on heating for the discotic nematic phase of compound **186** (chloro-substituted). A threaded and *schlieren* texture is formed with the phase showing typical flow properties and Brownian motion that are expected of a nematic phase. Upon slow cooling of each material from the isotropic liquid, the discotic nematic formed the *schlieren* texture, with two and four brush singularities. Further slow cooling of the fluoro- and methoxy-substituted materials (**185** and **187**) resulted in recystallization, but in the case of the chloro-substituted homologue (**186**), a mosaic texture was observed which closely resembled a hexagonal columnar ($D_{hd}$ or $D_{ho}$) (see Plate 7.2). The platelet texture was unable to be sheared indicating that it is probably a transition to a crystal rather than a columnar phase; columnar phases have been reported to be sheared.[8] On continued cooling, no recrystallization was observed. A similar situation was first encountered for the outer methyl- and ethyl-substituted derivatives[5] (compounds **99** and **66**, see also Chapters 4 and 5).

The microscopic examinations of the di-substituted "inner" materials, incorporating either fluoro- or chloro-substituents (compounds **188** and **189**), also presented no difficulties. Compound **188** (fluoro-substituted) on heating simply melted to the isotropic liquid and then on cooling, merely recrystallized. Likewise, the chloro-substituted homologue (**189**) also melted from the crystal state to the isotropic liquid, however upon cooling, the discotic nematic ($N_D$) mesophase was observed. No recrystallization was seen, suggesting a possible glassy-state transition; data from the DSC thermogram support this conclusion as there is no evidence for a transition to the crystalline state detected. The viscosity of the nematic phase was found to increase with cooling until a point was reached where the sample was unable to be mechanically sheared and thus, the glassy state had been reached. The texture of the glassy state was found to be almost the same as that for the nematic phase. A similar situation was also found for the inner dimethyl-substituted triphenylene benzoates[7] (compounds **35-38**, see also Chapter 3).

The data and conclusions reached from the DSC cycles and thermal optical microscopy studies are shown graphically in Figure 7.7 for the mono-substituted "inner" materials (**185-187**), and in Figure 7.8 for the di-substituted "inner" materials (**188-189**). In both cases, bulky-substituted analogues [methyl- and ethyl-substituted (**103** and **69**) in Figure 7.7, and dimethyl-substituted (**37**) in Figure 7.8] have been included for comparisions in order that the effect of increasing substituent size can be seen.

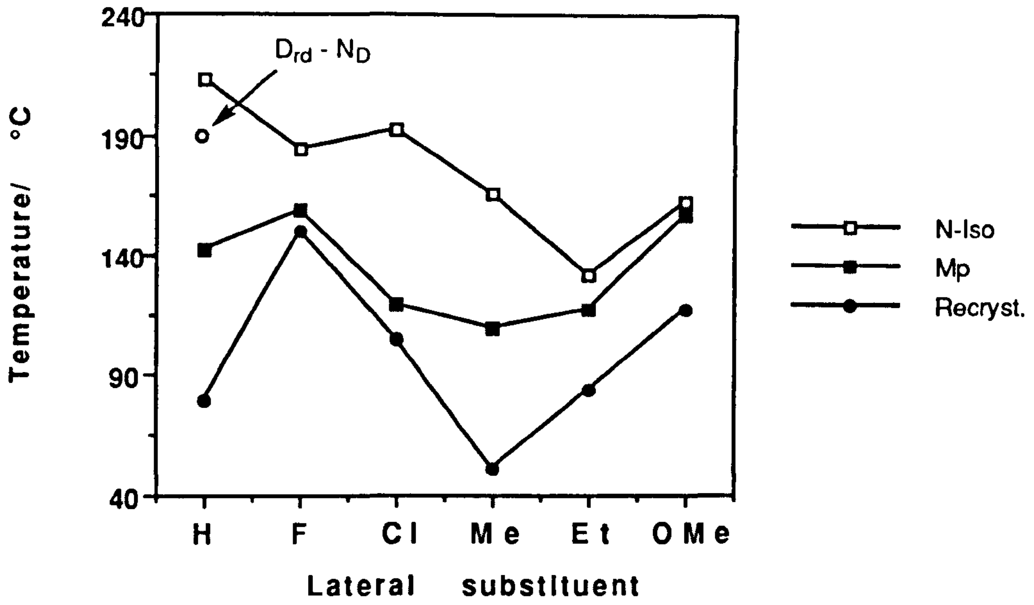


Figure 7.7 : Transition temperatures plotted against the lateral substituent on the peripheral phenyl ring for the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxy-2-substitutedbenzoate)s

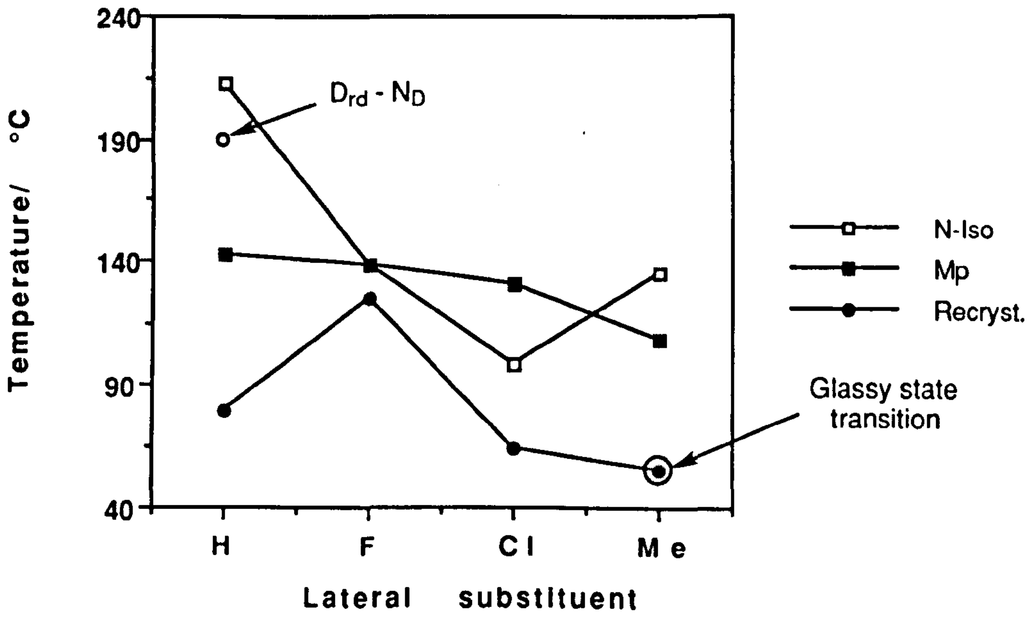


Figure 7.8 : Transition temperatures plotted against the lateral substituent on the peripheral phenyl ring for the triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxy-2,6-disubstitutedbenzoate)s

## 7.4 *Discussion*

The objective of this research programme was to position polar groups in the lateral positions of the peripheral phenyl groups in triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxybenzoate) in order to investigate the effects of their presence on the phase morphology, transition temperatures and melting points.

In our previous studies using bulky substituents[5,7] (see Chapters 3 to 6), we had shown that interactions caused by the steric hindrance between the peripheral phenyl rings led to a thickening of the molecular discs. The disc-thickening led to a weakening of the core-to-core interactions, which ultimately reduced the capacity of the system to form columnar phases and depressed the clearing point temperatures.

In this present study, we have found that the presence of polar substituents has had remarkable and varied effects upon the discotic mesophase behaviour. By examining the data presented in Table 7.1, it is clearly seen that lateral substitution in the "outer" region has uncharacteristically influenced the mesogenic behaviour. The discogens **180-182** are all very high melting materials (>300 °C) and have been found not to exhibit mesomorphism because of the extreme temperatures involved. The results suggest, and this is purely speculative, that polar substitution in these "outer" regions actually promotes crystal and/or columnar phase formation; this is quite the opposite effect that we have previously witnessed for other materials with lateral substituents in these same positions[5,7] (see Chapters 3 to 6). Presently, there is no evidence that can support this claim and none that can confirm what actual effect(s) the polar substituent is having upon the molecular structure.

For the mono-substituted "inner" compounds **(185-187)**, the mesogenic behavioural results are consistent with the data already acquired for the discogens that possess bulky substituents in the crowded "inner" regions of the triphenylene core (see Table 7.2 and Figure 7.7). There is a clear general trend in the reduction of the clearing points but the effect of the substituent size is not as prominent as that found for the analogous bulky-substituted materials (methyl- and ethyl-, **103** and **69**). This is to be somewhat expected as the steric effects of a fluoro-substituent, which is not much bigger than a hydrogen, are not going to compare to those of either a methyl- or ethyl-substituent. However, in comparison to the unsubstituted analogue (**42**), the presence of the fluoro-substituent in the derivative **185** has had a significant effect on the mesophase behaviour; the fluoro-substituted material is now purely nematogenic, as are the chloro- and methoxy-substitued discogens (**186** and **187**) but the chloro derivative exhibits an additional crystal phase.

The sizes of a methoxy-substituent and an ethyl group are quite similar, but their effects upon the mesophase behaviour of the discogens (**187** and **69**) are not. Both the melting point and clearing point in the methoxy derivative are higher than the ethyl-substituted compound and the nematic phase temperature range is very small (*ca.* 4 °C compared to *ca.* 15 °C).

In the third series of compounds (**188** and **189**), with two substituents in the "inner" regions, the results are somewhat unusual (see Table 7.3 and Figure 7.8). Melting points and clearing points have been reduced by substantial amounts compared to the unsubstituted analogue (**42**). Both materials exist in their isotropic liquid states at similar temperatures; however, the difluoro- material (**188**) is non-mesogenic, whereas the dichloro- compound (**189**) only exhibits the discotic nematic ($N_D$) mesophase monotropically. The presence of two polar substituents has now had much more influence upon the mesophase behaviour compared to just one unit (compounds **185** and **186**).

## *7.5 Conclusions*

The effect of bulky lateral substituents in calamitic systems would easily render the materials non-mesogenic,[1] so the much smaller polar substituents are preferred. However, it has been proven that the molecular structure of triphenylene-based discotic liquid crystals *can* accommodate the large steric effects and still display mesomorphism.[5,7] Nevertheless, investigations into the effects of the much smaller polar groups had to be conducted and now, they have yielded both results that are consistent with established trends, *and* findings that were highly surprising and very uncharacteristic. The use of polar substituents may not have had such a significant influence upon the melting points or clearing points as bulky substituents, but their presence *has* had quite a prominent effect upon the phase morphology of triphenylene-based discotic liquid crystals.

## *7.6 References*

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7) P. Hindmarsh, M. Hird, P. Styring and J.W. Goodby, *J. Mater. Chem.*, 1993, **3**, 1117.

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# CHAPTER 8

# Investigation of the Effect of Chirality on the Discotic Mesophase Behaviour of Triphenylene Benzoates

## 8.1 Introduction

The concept of chirality in liquid crystals has been evident from their discovery in 1888;[1] the first materials investigated were derivatives of cholesterol, *eg*. cholesteryl benzoate and cholesteryl acetate and the liquid crystal mesophase exhibited by both materials was termed the *cholesteric* mesophase (Ch). Nowadays, this mesophase is termed the *chiral nematic* mesophase ($N^*$) because most chiral liquid crystals do not have any structural connections with cholesterol, and so the term *cholesteric* mesophase (Ch) seems inappropriate.

Today, chirality plays an enormous rôle in the research of calamitic liquid crystals;[2] chiral calamitic liquid crystals find extensive use as thermochromic materials[3] and are important for ferroelectric and related applications.[4]

Investigations into the effect of chirality upon the mesophase behaviour of calamitic liquid crystals have revealed a great deal of new information. Incorporation of a chiral centre into a molecule results in the property of *handedness* due to a reduction of the compound's symmetry. Consequently, in many cases, the molecules cannot pack into the same mesomorphic structures as their achiral analogues, and the organization of the chiral molecules leads to helical mesomorphic structures. Sometimes the molecules are unable to pack in any sort of "uniform" fashion at all, and the structures of the resultant mesophases have been termed *frustrated*; examples of these mesophase-types are blue phases (BPI, BPII and BPIII),[5] twist grain boundary phases ($TGB_A$ and $TGB_C$)[6-8] and fog phases.[9,10] The liquid crystal properties of the chiral liquid crystal are greatly affected by what substituent is actually present at the chiral centre; investigations into the effects of substituting halogens or large bulky chains at the chiral centre were conducted by Slaney and Nishiyama respectively.[6,7]

Research conducted into the effects of chirality on the mesophase behaviour of discotic liquid crystals has not been as well documented as for calamitic materials. The first report was by Destrade *et al.*[11] in 1980 who studied optically active aliphatic esters of benzene, triphenylene and truxene (see structures **I-III**, Figure 8.1). The benzene derivatives were non-mesogenic, while the others unfortunately only exhibited columnar mesophases. It appeared that simply introducing chirality into the molecular structure was insufficient to alter the *nature* of the phases. However, when mixed with triphenylen-2,3,6,7,10,11-hexayl hexakis(4-heptyloxybenzoate), which in its pure state exhibits the discotic nematic phase ($N_D$),[12] typical chiral nematic textures were obtained.[11] Unlike the classical nematic, a relatively high concentration (*ca.* 50%) of the chiral dopant was required to produce an appreciable twist, whereas in calamitic mixtures, only a very small amount of the chiral dopant (*ca.* 5%) is necessary. Furthermore, the chiral discotic nematic ($N_D$*) texture was only seen at higher temperatures after the initial appearance of a nematic texture, which suggested a very high temperature dependence of the pitch.[11]

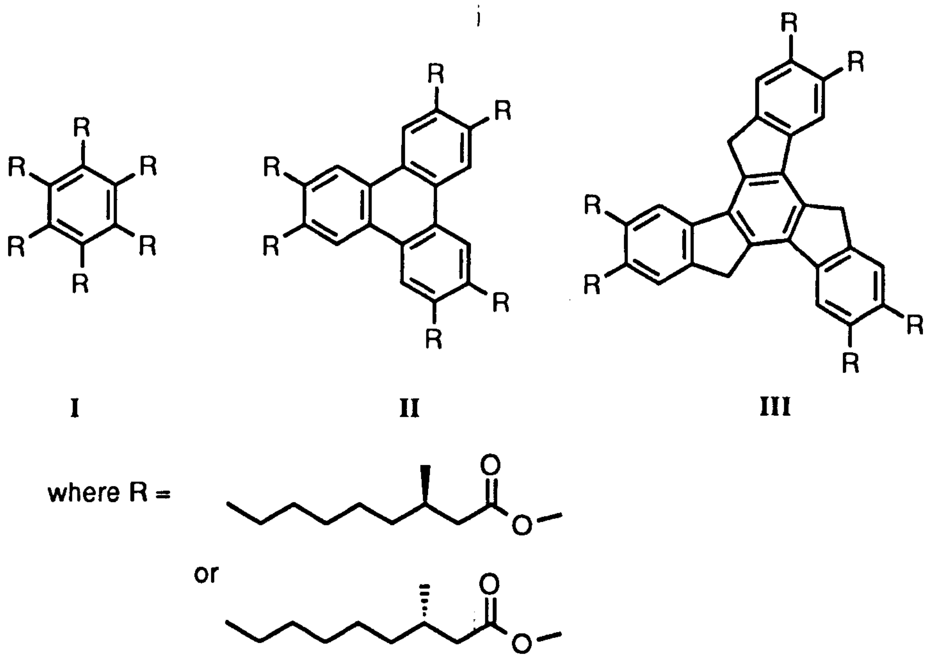


**Figure 8.1 : Structures of the benzen-1,2,3,4,5,6-hexayl, triphenylen-2,3,6,7,10,11-hexayl or truxen-2,3,7,8,12,13-hexayl hexakis[(*R*) - or (*S*) - 3-methylnonanoate)s (structures I--III)**

Shortly after the first publication of chiral discotic materials, Malthête reported details of the first discotic liquid crystal to exhibit the chiral discotic nematic mesophase ($N_D^*$) in its pure state.[13] The compound was triphenylen-2,3,6,7,10,11-hexayl hexakis[(*S*)-(+)-4-(4-methylhexyloxy)benzoate] (see structure **IV**, Figure 8.2) and the mesophase was entirely miscible with that of the achiral discotic nematic ($N_D$) mesophase. Two more chiral derivatives were reported (see structures **V** and **VI**, Figure 8.2) but they did not exhibit the chiral discotic nematic mesophase; instead, one showed a rectangular disordered columnar ($D_{rd}$) phase (structure **V**) and the other was non-mesogenic (structure **VI**). By comparing structures **IV** and **VI**, it is seen that the chiral centre in the former compound is further away from the peripheral phenyl ring *and* the terminal alkyl chain is **shorter** than that of the latter material, and yet, it still displays the desired chiral discotic nematic mesophase. It seems that the *position* of the chiral centre is *the* important factor affecting the inducement of chirality into the mesomorphic properties, and not the length of the terminal alkyl chain.

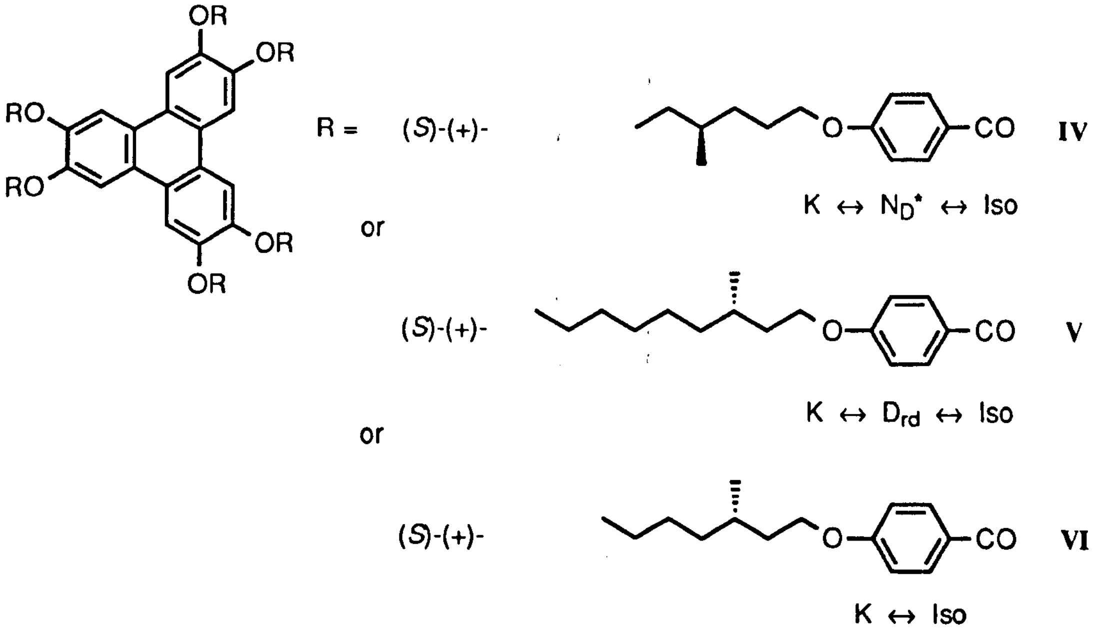


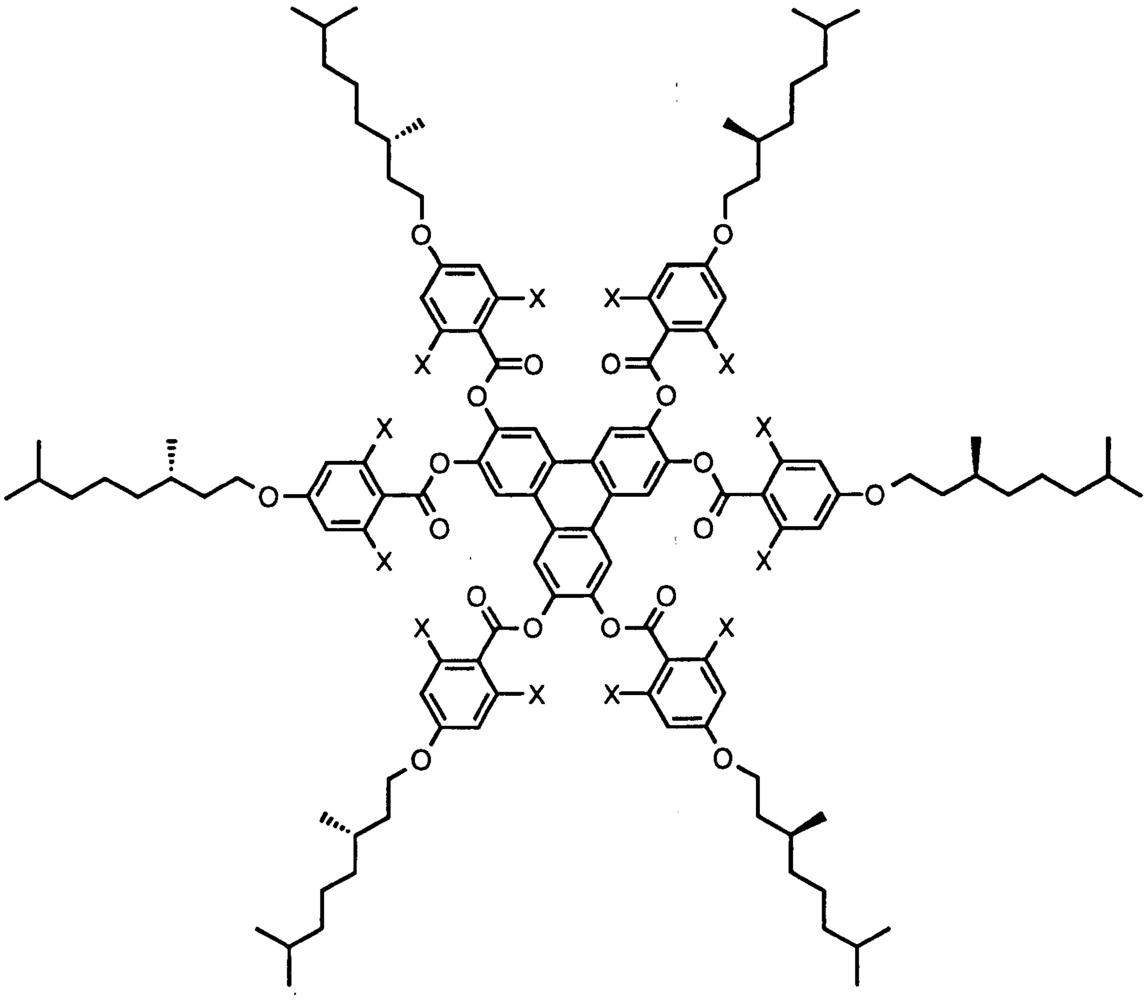
**Figure 8.2 : Structures of triphenylen-2,3,6,7,10,11-hexayl hexakis[(*S*) - (+) - 4-(4-methylhexyloxy)benzoate], hexakis[(*S*)-(+)-4-(3-methylnonyloxy)benzoate] and hexakis[(*S*)-(+)-4-(3-methylheptyloxy)benzoate] (structures IV-VI)**

Publications of research into discotic liquid crystals exhibiting the chiral discotic nematic ($N_D^*$) mesophase, whether in their pure states[13,14] or in mixtures[11,15,16] have been somewhat scarce. Recently, Praefcke and co-workers reported work conducted on chiral discotic multiynes,[17] of which the achiral analogues have been studied quite extensively.[18-22] The synthesized materials incorporated (*S*)-2-methylbutyl- and (*S*)-3,7-dimethyloctyloxy- terminal chains and in all cases, the desired chiral discotic nematic mesophase was observed. It was also noted that both the phenomenon of the selective reflection of light and a temperature induced helix inversion of the chiral discotic nematic mesophase were witnessed; this is the first report of helix inversion in discotic liquid crystals, whereas in calamitic systems, it has been observed in both the chiral nematic and chiral smectic C mesophases.[23-25] Observations of the selective reflections of light and even the appearance of discotic blue phases ($BP_DI$, $BP_DII$ and $BP_DIII$) have been previously reported when multiynes have been used in mixture work with cellobiose derivatives as the chiral dopants.[26]

Recently, the topic of interest in the research of chiral discotic liquid crystals has shifted slightly from chiral discotic nematic mesophases to chiral columnar mesophases. The property of ferroelectricity in discotic liquid crystals has been reported by both Bock and Helfrich,[27-29] and by Scherowsky and Chen.[30,31] This is clearly quite a major step forward for application-based research in the field of discotic liquid crystals, which for many years have been subject to only basic physical studies.

As mentioned previously, very few chiral discotic liquid crystals are known to exhibit the chiral discotic nematic ($N_D^*$) mesophase. The triphenylen-2,3,6,7,10,11-hexayl hexakis(4-alkoxybenzoate)s were the first discotic materials to exhibit the discotic nematic ($N_D$) mesophase,[12] and it was a chiral analogue which was the first discogen to show the chiral discotic nematic ($N_D^*$) mesophase in its pure state.[13]

Thus, in this chapter the synthesis and properties of two novel compounds, triphenylen-2,3,6,7,10,11-hexayl hexakis[(*S*)-(-)-4-(3,7-dimethyloctyloxy)benzoate] and hexakis[(*S*)-(-)-2,6-dimethyl-4-(3,7-dimethyloctyloxy)benzoate] are discussed (see structure **VII**, Figure 8.3). Our objective was to evaluate the relationship that exists between the position of the chiral centre in the terminal alkoxy chain and its effect upon the discotic mesogenic behaviour in relation to known materials.

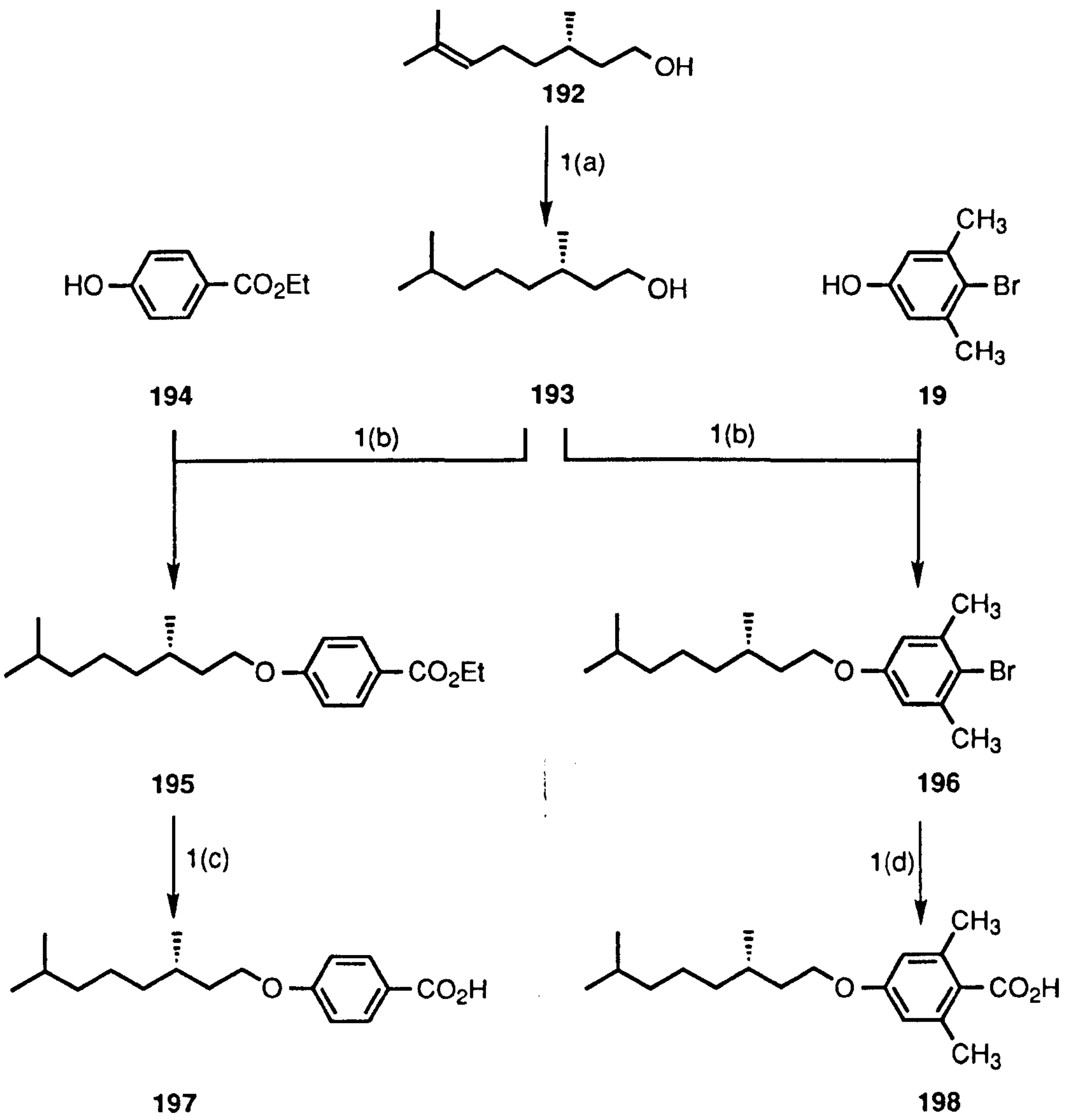


**VII**

Figure 8.3 : Structures of the triphenylen-2,3,6,7,10,11-hexayl hexakis[(*S*) - 4-(3,7-dimethyloctyloxy)benzoate] (X = hydrogen) and hexakis[(*S*) - 2,6-dimethyl-4-(3,7-dimethyloctyloxy)benzoate] (X = methyl)

## 8.2 *Experimental*

The materials were prepared by the routes shown in Schemes 8.1 and 8.2. Compounds **19**, **192** and **194** were all purchased from Aldrich Chemical Co. The double bond of (*S*)-(-)-citronellol (**192**) was removed using hydrogen and a catalyst, 10% palladium on carbon, whilst dissolved in ethyl actetate, to give compound **193**. Compounds **19** and **194** were *O*-alkylated with compound **193** in the presence of DEAD and triphenylphosphine (the Mitsunobu reaction[32]) to give moderate yields of compounds **195** and **196**. The benzoic acid **197** was obtained by hydrolyzing the ethyl ester **195** with sodium hydroxide in an aqueous solution of ethanol. The replacement of the bromine in compound **196** was achieved by lithiation using *n*-butyllithium at -78 °C; the reaction mixture was then poured onto a slurry of solid $CO_2$ and dry ether, acidified, and the product purified (compound **198**). The final liquid-crystalline materials were prepared by the esterification of HHTP (**3**) with the respective benzoyl chlorides in the presence of pyridine, see Scheme 8.2.



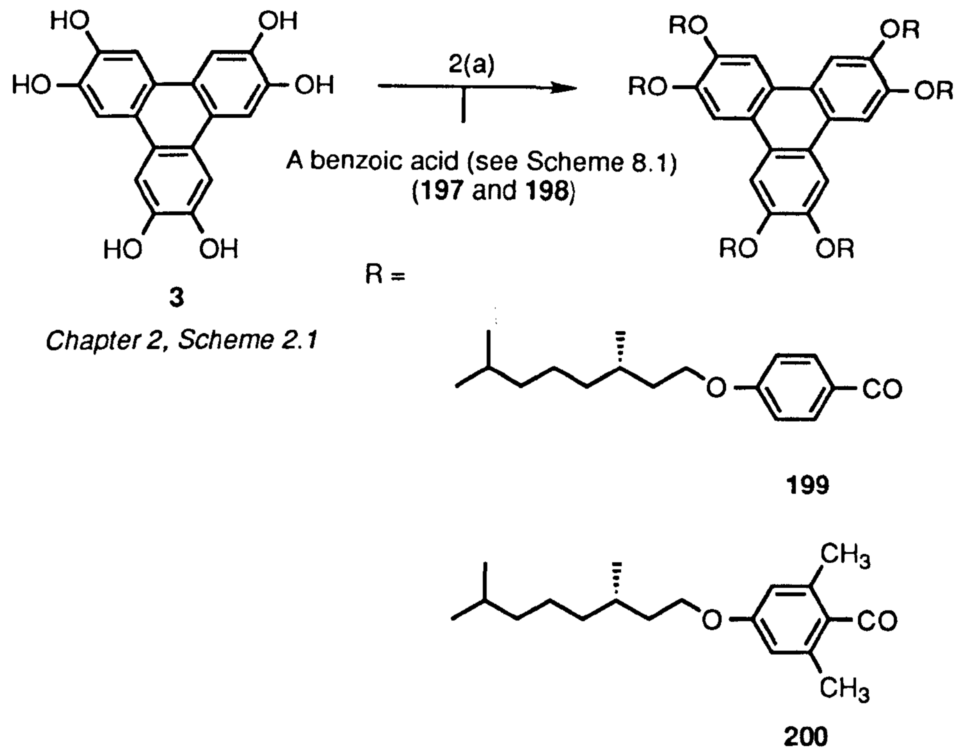
1(a) ..... $H_2$, 10% palladium on carbon, ethyl acetate.

1(b) ..... DEAD, $PPh_3$, THF.

1(c) ..... NaOH, water, ethanol.

1(d) ..... (i) *n*-BuLi, THF; (ii) $CO_2$ (solid), dry $Et_2O$.

**Scheme 8.1 : Synthetic route for the preparation of the (*S*)-(-)-4-(3,7-dimethyloctyloxy)benzoic and (*S*)-(-)-2,6-dimethyl-4-(3,7-dimethyloctyloxy)benzoic acids (197 and 198)**



2(a) ..... Acid chloride (oxalyl chloride, DMF, $CH_2Cl_2$), pyridine.

**Scheme 8.2 : Synthetic route for the preparation of triphenylen-2,3,6,7,10,11-hexayl hexakis[(*S*)-(-)-4-(3,7-dimethyloctyloxy)benzoate] and hexakis[(*S*)-(-)-2,6-dimethyl-4-(3,7-dimethyloctyloxy)benzoate] (199 and 200)**

### *8.2.1 Preparation of (S)-(-)-3,7-Dimethyloctan-1-ol* (193)

A stirred mixture of compound **192** (25.0 g, 0.16 mol) and 10% palladium on carbon (1 g) in ethyl acetate (100 ml) was kept under an atmosphere on $H_2$ (3.6 $dm^3$, 0.16 mol). The reaction mixture was then filtered and the solvent was removed to yield a colourless oil.

Yield: 25.3 g (100%)

| | |
|---|---|
| $^1H$ NMR ($CDCl_3$ and TMS) $\delta$: | 0.84(6H, d), 0.86(3H, d), 1.15(3H, m), 1.30(5H, m), 1.55(3H, m), 3.70(2H, m). |
| IR (KBr) $\nu_{max}$ $cm^{-1}$: | 3600-3100(broad, 2920, 2860, 1460, 1380, 1360, 1050, 1010. |
| MS (*m/z*): | 158($M^+$), 112, 84, 69, 56, 43. |

$[\alpha]_D$: 0° (0.02187 g/ml at 26 °C).

### *8.2.2 Preparation of (S)- (-)-Ethyl 4-(3, 7-dimethyloctyloxy)benzoate and (S)-(-)-1-Bromo-2,6-dimethyl-4-(3,7-dimethyloctyloxy)benzene* (195 and 196)

The general synthetic method is exemplified by the procedure reported in Chapter 3 for compound **13**.

*(S)-(-)-Ethyl 4-(3,7-dimethyloctyloxy)benzoate* (**195**)

Yield: 8.26 g (77%)

$^1H$ NMR ($CDCl_3$ and TMS) $\delta$: 0.87(6H, d), 0.94(3H, d), 1.15(3H, m), 1.30(4H, m), 1.37(3H, t), 1.58(2H, m), 1.83(1H, m), 4.04(2H, m), 4.34(2H, q), 6.90(2H, dd), 7.98(2H, dd).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1710, 1605, 1510, 1460, 1355, 1270, 1250, 1165, 1100, 1020, 850, 770, 700.

MS (*m/z*): 306(M$^+$), 252, 202, 166, 138, 121, 111, 85, 70.

$[\alpha]_D$: -0.6° (0.01914 g/ml at 26 °C).

*(S)-(-)-1-Bromo-2,6-dimethyl-4-(3, 7-dimethyloctyloxy)benzene* (**196**)

Yield: 6.30 g (56%)

$^1H$ NMR ($CDCl_3$ and TMS) $\delta$: 0.86(6H, d), 0.92(3H, d), 1.15(3H, m), 1.30(4H, m), 1.56(2H, m), 1.79(1H, m), 2.37(6H, s), 3.93(2H, m), 6.64(2H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2940, 2920, 2860, 1580, 1460, 1320, 1170, 1070, 1020, 850.

MS (*m/z*): 342(M$^+$), 340(M$^+$), 202, 200, 120, 90, 71.

$[\alpha]_D$: -1.1° (0.02270 g/ml at 26 °C).

### *8.2.3 Preparation of (S)-(-)-4-(3, 7-Dimethyloctyloxy)benzoic and (S)-(-)-2,6-Dimethyl-4-(3,7-dimethyloctyloxy)benzoic Acids* (**197** and **198**)

The general synthetic methods are exemplified by procedures reported in Chapter 7 (compound **137**) for compound **197**, and in Chapter 3 (compound **14**) for compound **198**, which was purified by column chromatography (silica gel/dichloromethane : ethyl acetate, 4 : 1) to yield a colourless oil.

*(S)-(-)-4-(3, 7-Dimethyloctyloxy)benzoic Acid* (**197**)

Yield: 7.54 g (100%) Mp: 92-93 °C

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.86(6H, d), 0.92(3H, d), 1.15(3H, m), 1.42(4H, m), 1.60(2H, m), 1.85(1H, m), 4.05(2H, m), 6.92(2H, dd), 8.05(2H, dd).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2940, 2920, 2860, 1580, 1460, 1320, 1170, 1070, 1020, 850.

MS (*m/z*): 278(M$^+$), 138, 121, 85, 70, 57, 43.

$[\alpha]_D$: -14.5° (0.00330 g/ml at 24 °C).

*(S)-(-)-2,6-Dimethyl-4-(3,7-dimethyloctyloxy)benzoic Acid* (**198**)

Yield: 5.81 g (100%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.86(6H, d), 0.90(3H, d), 1.13(3H, m), 1.40(4H, m), 1.55(2H, m), 1.80(1H, m), 2.45(6H, s), 4.00(2H, m), 6.60(2H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2940, 2920, 2860, 1680, 1595, 1460, 1315, 1280, 1170, 1050, 855, 650.

MS (*m/z*): 306(M$^+$), 1200, 166, 148, 135, 122, 91, 77, 69, 55.

$[\alpha]_D$: -11.3° (0.00941 g/ml at 21 °C).

### 8.2.4 *Preparation of Triphenylen-2,3,6,7,10,11-hexayl Hexakis[(S)-(-)-4-(3,7-dimethylocyloxy)benzoate] and Hexakis[(S)-(-)-2,6-dimethyl-4-(3,7-dimethyloctyloxy)benzoate]* (199 and 200)

The general synthetic method for the preparation of the hexa-esters is exemplified by the procedure reported in Chapter 3 for compound **30**.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis[(S)-(-)-4-(3,7-dimethyloctyloxy)benzoate]* **(199)**

Yield: 1.14 g (22%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.86(6H, d), 0.92(3H, d), 1.15(3H, m), 1.40(4H, m), 1.56(2H, m), 1.83(1H, m), 3.95(2H, m), 6.73(2H, dd), 7.95(2H, dd), 8.42(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2940, 2920, 2860, 1740, 1600, 1505, 1245, 1170, 1070, 1010, 840, 760.

CHN analysis: % expected - C 76.43, H 8.28;
% found - C 76.31, H 8.56.

[α]$_D$: -3.6° (0.01000 g/ml at 21 °C).

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis [(S)-(-)-2,6-dimethyl-4-(3,7-dimethyloctyloxybenzoate]* **(200)**

Yield: 1.84 g (47%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.86(6H, d), 0.92(3H, d), 1.15(3H, m), 1.40(4H, m), 1.57(2H, m), 1.85(1H, m), 2.33(6H, s), 4.00(2H, m), 6.53(2H, d), 8.43(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2940, 2920, 2860, 1750, 1600, 1505, 1320, 1245, 1160, 1045, 900, 850.

CHN analysis: % expected - C 77.19, H 8.77;
% found - C 76.95, H 8.74.

[α]$_D$: -3.2° (0.00742 g/ml at 21 °C).

## *8.3 Results*

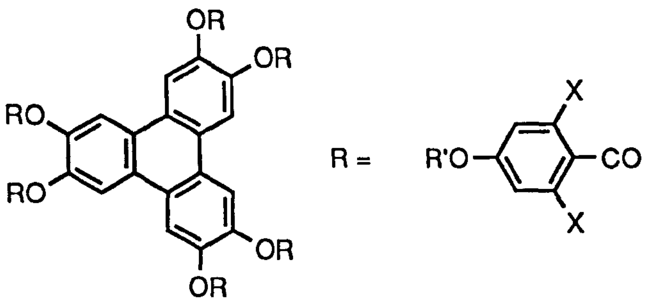
### *8.3.1 Transition Temperatures*

The transition temperatures for the previously reported[12,33] (compounds **36** and **41**, see Chapter 3) and newly synthesized discotic liquid crystals were determined by a combination of thermal optical microscopy and differential scanning calorimetry. Typically, the crystal to mesophase transitions were determined by calorimetry because of the difficulty in discerning the transition optically. The other transitions, including the recystallization and glass transitions, were determined by microscopy. The transition temperature results are shown in Table 8.1. The clearing point temperatures fall, as first the chiral terminal chains are incorporated into the system (compound **199**) and then the two lateral dimethyl-substituents are positioned onto the peripheral phenyl rings (compounds **36** and **200**), in comparison to the parent material **41**, but their melting points remain fairly similar. In the unsubstituted chiral material **199**, the only mesophase to be observed is the rectangular disordered ($D_{rd}$), whereas the analogous dimethyl-substituted discogen **200** exhibits the desired chiral discotic nematic ($N_D^*$) mesophase.

### *8.3.2 Differential Scanning Calorimetry*

Calorimetric studies were carried out on both of the chiral triphenylene esters prepared (compounds **199** and **200**). The results for the first heating and cooling cycles are shown in Figures 8.4 and 8.5 respectively, and the enthalpies of all the transitions, where possible, are incorporated in Table 8.1.

Both materials show a sharp melting endotherm for the transition from their crystal forms to their respective mesophases. In the case of compound **199** which has no lateral substituents, the enthalpy of the endotherm associated with the transition from the mesophase to the isotropic liquid is quite large, indicating that the mesophase is somewhat ordered and suggests that the transition is from a columnar mesophase to the isotropic liquid. However, the enthalpy for the peak indicating the mesophase to isotropic liquid for



| No. | R' | X | K | | $D_{rd}$ | | $N_D$ | | I | Recryst. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **41** | Oct§ | H | * | 152 | * | 168 | * | 244 | * | 99 | * |
| **199** | Cit | H | * | 131 (16.52) | * | 210 (11.64) | — | — | * | 52 | * |
| **36** | Oct† | Me | * | 155 | — | — | * | 170 | * | 50 | * |
| **200** | Cit | Me | * | 120 (29.02) | — | — | * | 138 (0.23) | * | {45} | * |

**Table 8.1 : Transition temperatures for the variously substituted triphenylen-2,3,6,7,10,11-hexayl hexakis(benzoate)s**

Enthalpies for each transition are given in parenthesis ($\Delta H$/kJ mol$^{-1}$).

Glassy state transitions are given in curly braces { }.

Oct: octyl; Cit: (*S*)-(-)-3,7-dimethyloctyl.

§Literature compound.[12] †Literature compound,[33] (see also Chapter 3).

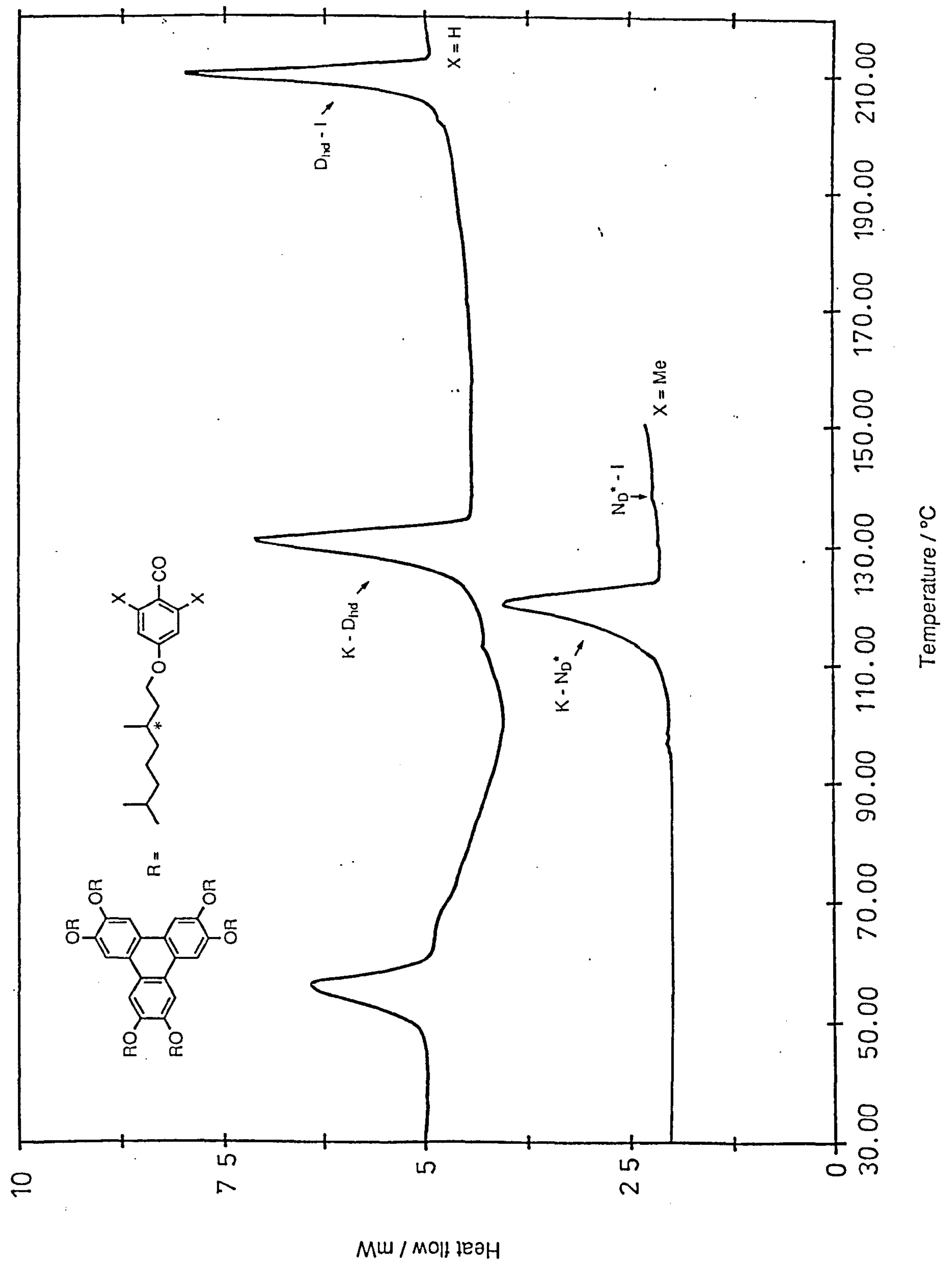


Figure 8.4 : DSC thermogram of the first heating cycle for the triphenylene esters (199 and 200)

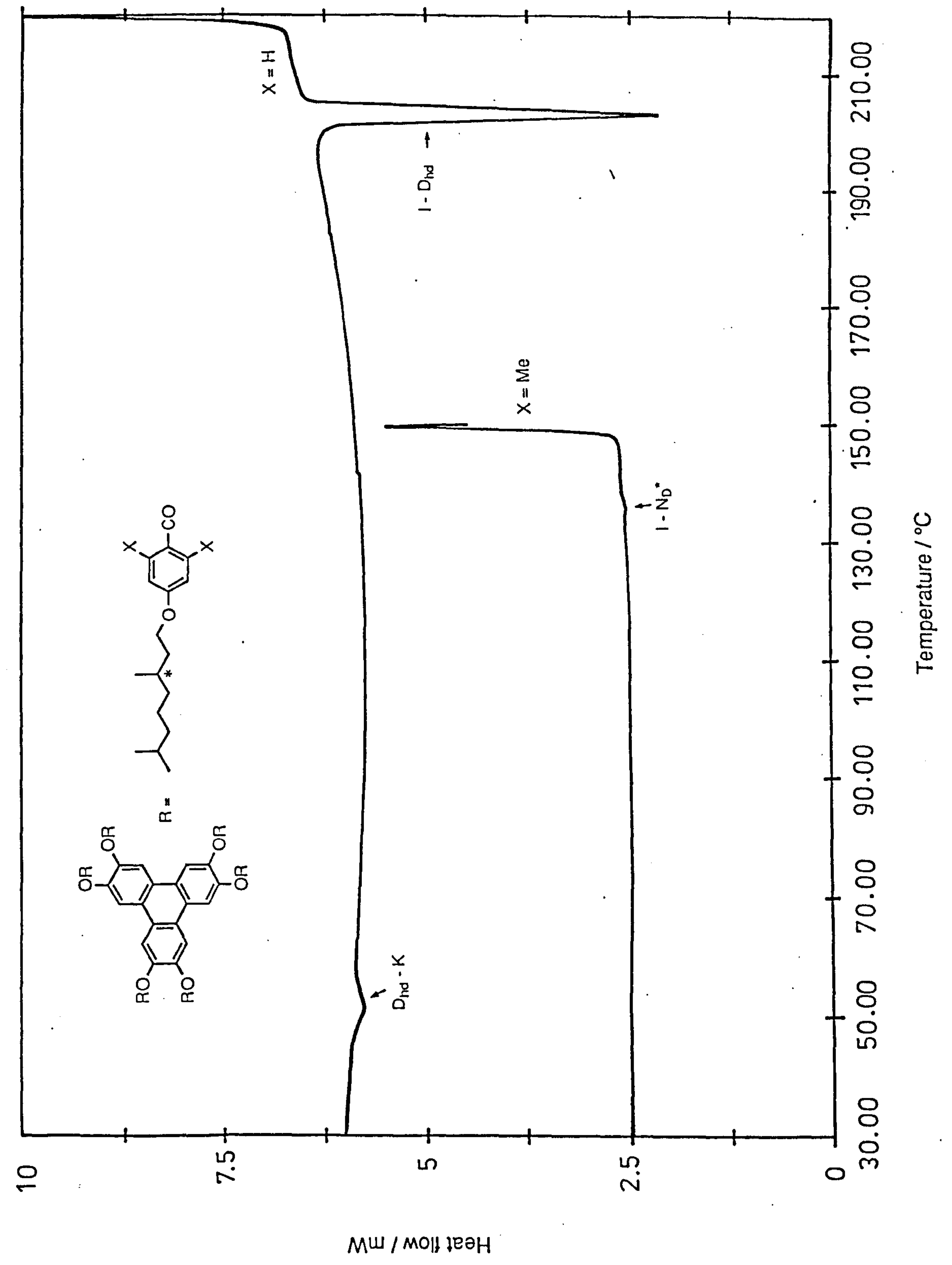


Figure 8.5 : DSC thermogram of the first cooling cycle for the triphenylene esters (199 and 200)

the dimethyl-substituted discogen (compound **200**), is very small and characteristic for discotic nematic ($N_D$) to isotropic transitions[33,34] (see Chapter 3 and 4).

The transition from the isotropic liquid to the mesophase for compound **199** was found to be reversible, but the recrystallization transition supercooled to *ca.* 50 °C. For compound **200**, the only transition exhibited was that for the isotropic liquid to mesophase, which was followed by a glassy-state transition that appeared as a broad inflexion in the base-line of the thermogram. This particular trait was first observed for the achiral dimethyl-substituted analogues which have been previously reported[33] (see Chapter 3).

### *8.3.3 Thermal Optical Microscopy*

The mesomorphic behaviour for non-substituted discotic material (**199**) will be discussed first. On heating the material, under microscopic observation, the first discernible transition to be seen was that for the clearing transition to the isotropic liquid. It was impossible to visually detect the melting transition to the columnar mesophase. Cooling the material from the isotropic liquid resulted in the formation of a columnar phase. The textures of this phase were either mosaic or fan-like in appearance (see Plate 8.1). The same fan texture was observed for the chiral triphenylene benzoates synthesized by Malthête *et al.*[13] (see Figure 8.2) and was denoted as the rectangular disordered ($D_{rd}$) columnar phase. No recrystallization was observed under the microscope which suggests that the material has formed a glass, however, a recrystallization transition is seen on the DSC cooling thermogram.

For compound **200**, which has the two lateral methyl-substituents, the first transition observed was that from the crystal to the chiral discotic nematic ($N_D$*) and then on further heating, a transition to the isotropic liquid. On cooling from the isotropic liquid, the chiral discotic nematic swept in rapidly and did not show any distinctive textural features, *ie,* a fingerprint texture. The birefringent texture covering the entire slide was of one colour only, which, of course, was temperature dependent (blue at high temperatures and red at low temperatures). This situation was true for both thick and thin slide preparations and gave some indication that the mesophase could be aligned quite easily.

With thin slide preparations, the handedness of the helix of the chiral discotic nematic ($N_D^*$) was able to be determined by a simple optical rotation experiment, which involved the rotation of one of the microscope's polarizers. A colour variation was observed when the polarizer was rotated in one direction and nothing different was noted in the other direction; in this case, the helix of the chiral discotic nematic was found to be left-handed. The material was able to be sheared quite easily, and the texture obtained was a Grandjean planar texture (see Plate 8.2). This material did not recrystallize and, as the DSC cooling thermogram suggests, exhibits a glassy-state transition. The viscosity of the chiral discotic nematic phase was found to increase until the sample was unable to be mechanically sheared and thus, the glass transition had been reached. The texture of this glassy state was found to be similar for the chiral discotic nematic mesophase.

The transition temperatures for the two chiral discotic materials (compounds **199** and **200**) are given in Table 8.1, and are shown graphically in Figure 8.6, along with two achiral derivatives for comparison (compounds **41**, unsubstiuted and **36**, dimethyl-substituted). The enthalpy values determined by DSC are also reported in Table 8.1, where possible.

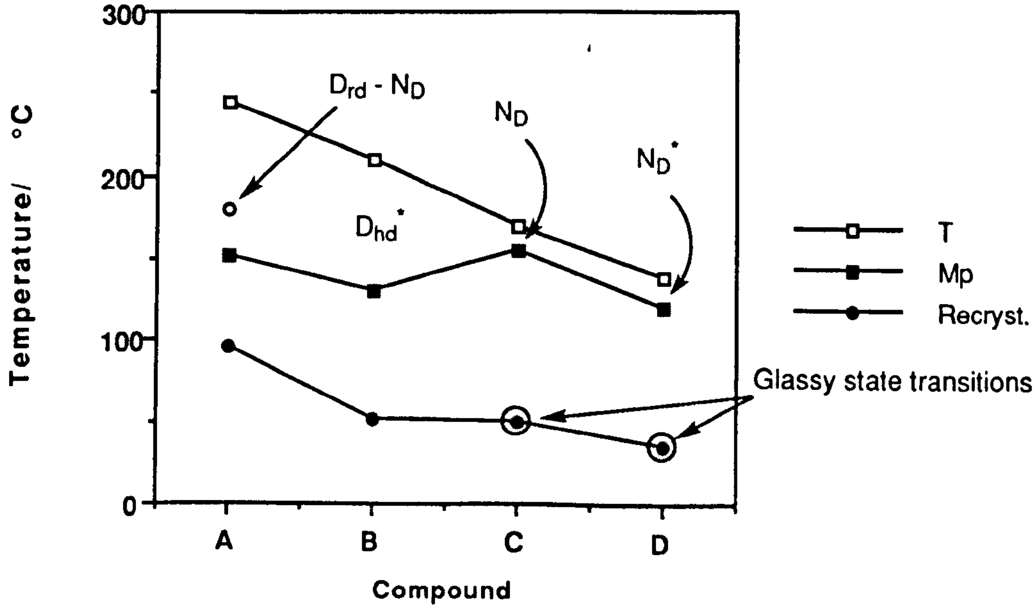


**Figure 8.6 : Transition temperatures plotted against size of substituent for the triphenylen-2,3,6,7,10,11-hexayl hexakis(benzoate)s; compound: A - 41 (see Chapter 3)[12]; B - 199; C - 36; D - 200**

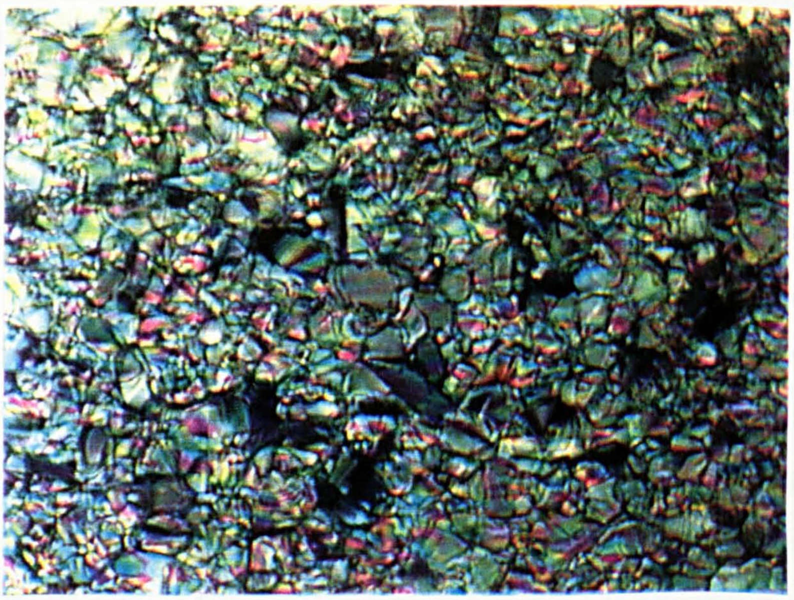


**Plate 8.1 : Mosaic texture of the rectangular disordered ($D_{rd}$) columnar exhibited by compound 199 at 190 °C on cooling from the isotropic liquid**

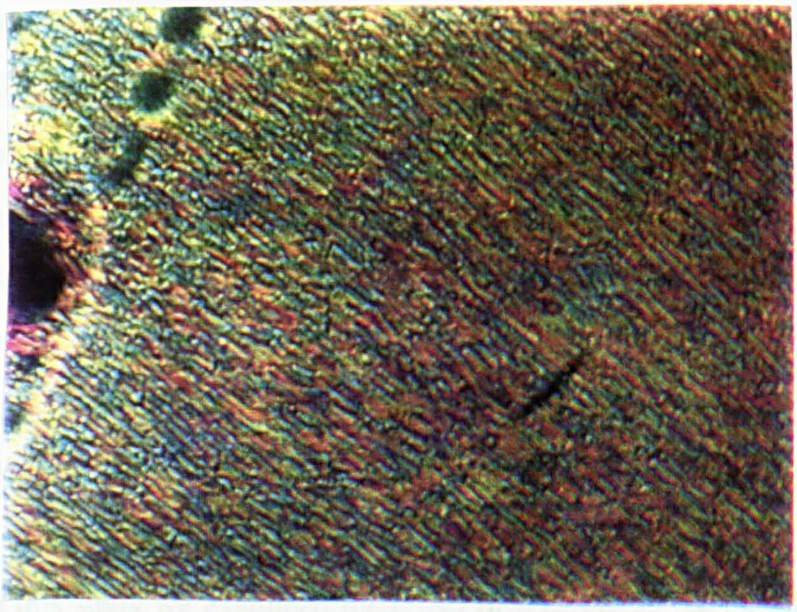


**Plate 8.2 : Grandjean planar texture of the chiral discotic nematic ($N_D$*) exhibited by compound 200 at 120 °C on cooling from the isotropic liquid**

## 8.4 *Discussion*

In 1981, Malthête *et al.*[13] had reported the mesomorphic properties of three laterally unsubstituted triphenylene benzoates (see structures **IV-VI**, Figure 8.2) and had noted that the positioning of the chiral centre in the terminal alkoxy chain, *and* the length of the terminal alkoxy chain affected the mesophase behaviour quite considerably. In structure **IV**, the chiral centre is positioned at the fourth carbon in the terminal alkoxy chain which is relatively small ($C_6$), and the material exhibits the desired chiral discotic nematic ($N_D^*$) mesophase. However, in structures **V** and **VI** the chiral centre is at the third position and the chain lengths are long ($C_9$) and small ($C_6$) respectively, and both materials do not exhibit the desired mesophase; structure **V** exhibits a rectangular disordered ($D_{rd}$) columnar phase and structure **VI** is non-mesogenic. Malthête had demonstrated that the correct positioning of the chiral centre in the terminal chain was crucial to allow the discotic molecules to pack in the desired mesmorphic structures.

In separate studies[33] (compound **39**, see Chapter 3), we had found that positioning the branched chain at the first carbon of the terminal alkoxy chain also totally destroyed the mesogenic properties of the system.

Therefore, from the evidence above, it is apparent that the positioning of the chiral centre at the third position and lower in the terminal alkoxy chain (*ie*, moving the chiral centre closer to the peripheral phenyl ring) is detrimental in allowing the system to form the chiral discotic nematic mesophase. However, in their research of triphenylene multiynes, Praefcke and co-workers[17] have used chiral terminal chains with the chiral centre at the third position and have not just obtained mesomorphism, but the chiral discotic nematic mesophase that they desired.

So, it now appears that the actual design of the discotic molecule as a whole is also a factor in affecting the production of the desired mesophases.

Thus, in this study we examined the effect of positioning the chiral centre at the third position in an unsubstituted system (**199**), directly analogous to structure **V**, and then in a laterally dimethyl-substituted system (**200**). The chiral chain chosen in this study was (*S*)-(-)-3,7-dimethyloctyloxy and was easily obtained from (*S*)-(-)-citronellol (**192**), a relatively inexpensive chiral alcohol. This particular alcohol was selected because Praefcke and co-workers[17] had used this chiral alcohol in their research to successfully obtain discotic liquid crystals exhibiting the chiral discotic nematic ($N_D^*$) mesophase.

From the data in Table 8.1 and Figure 8.6, it is clear that both the position of the chiral centre in the terminal chain and the presence/absence of lateral substituents has affected the mesophase behaviour. The presence of chirality has lowered the melting and clearing points of compounds **199** and **200** in comparison to their achiral counterparts (compounds **36** and **41**). Both the new discotic materials (**199** and **200**) are mesogenic.

However, the unsubstituted compound (**199**) does not exhibit the desired chiral discotic nematic ($N_D^*$) mesophase, but instead shows a rectangular disordered ($D_{rd}$) columnar phase. This same result was obtained by Malthête *et al.*[13] for structure **V** (see Figure 8.2) when the chiral centre was in the third position in the terminal chain. It appears that the presence of the branched methyl group at the chiral centre prevents the discotic molecules from sliding over one another and in turn, by prohibiting the system to form the fluid nematic mesophase, promotes the formation of columnar phases.

On the other hand, the dimethyl-substituted derivative (**200**) *does* exhibit the $N_D^*$ mesophase. In our previous studies using lateral substitution[33,34] (see Chapters 3 to 6), we had shown that lateral substitution in the crowded "inner" region of the triphenylene core totally suppressed the formation of columnar mesophases and ultimately, promoted the capacity of the system to exhibit the discotic nematic mesophase. Thus, the use of lateral substituents in compound **200** has been of great benefit in weakening the core-to-core interactions and so reducing the capacity of these chiral systems to form columnar phases, thereby allowing the $N_D^*$ mesophase to be exhibited.

## *8.5 Conclusions*

There is clearly a very delicate balance between obtaining discotic liquid crystals that exhibit the chiral discotic nematic ($N_D^*$) mesophase and obtaining discogens that either exhibit columnar phases or are non-mesogenic. The position of the chiral centre is crucial in allowing the discotic molecules to pack in the desired mesomorphic structures.

Finally, the use of lateral substituents has again been of great benefit in lowering melting and clearing points and tending to produce nematogenic mesophases.

### *8.6 References*

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# CHAPTER 9

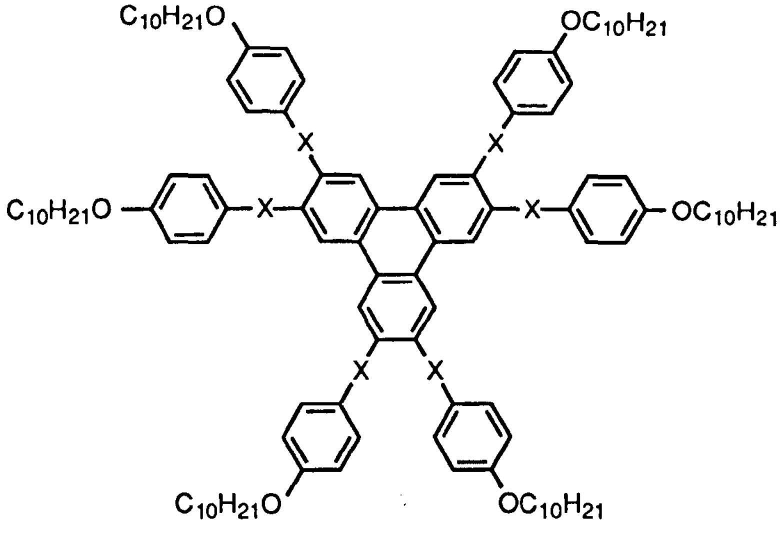
# *Investigation of the Effect of the Length of the Peripheral Linkages on the Discotic Mesophase Behaviour of Triphenylene Benzoates*

## *9.1 Introduction*

In our previous studies, we have extensively discussed the effects of filling in the empty space between the peripheral phenyl rings around the central triphenylene core with both large bulky substituents and with polar substituents. From our findings, it was clear that a relationship existed between the position and the size of the substituent(s) and the mesophase(s) exhibited. The research conducted throughout Chapters 3 to 8 all focused on the same objective and was attributed to the preliminary findings of Beattie who first used lateral substituents in the triphenylene benzoates.[1]

However, in our aims of research for this thesis (see Chapter 1, Section 1.8), the topic of lateral substitution was not the sole idea to be investigated. Thus in this chapter, we now turn our attention to further developing another area of study that Beattie first touched upon - extension of the peripheral arms of the triphenylene benzoates. Beattie synthesized a number of triphenylene biphenyl-4-yl carboxylates and a triphenylene phenylpropiolate, but none of the materials exhibited mesomorphism. It was thought that this situation was attributed to the fact that the peripheral arms were to rigid to have any effect upon the core-to-core interactions which were then able to promote crystal or columnar phase formation instead of nematic mesophases.

This new topic of research somewhat clashes with the ideas behind our previous studies, in that now we are actively prohibiting the filling of the empty space around the triphenylene core by lengthening the linking group between the triphenylene unit and the peripheral phenyl rings (see structure **I**, Figure 9.1). However, in this study we are systematically extending (or removing) the linking group from a literature material of known mesomorphism, triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxybenzoate)[2] (compound **42**, see Chapter 3), instead of examining extreme cases with the hope of finding mesmorphic properties as performed by Beattie.[1]



**I**

**Figure 9.1 : Structure of 2,3,6,7,10,11-hexakis(4-decyloxyphenyl)triphenylene, X = direct link; and triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxybenzoate), X = $CO_2$; hexakis(4-decyloxyphenylacetate); X = $CH_2CO_2$; and hexakis(4-decyloxycinnmate), X = $CH=CHCO_2$**

Thus, in this chapter the synthesis and properties of a number of novel discotic materials are discussed and an attempt is made to establish a relationship theory that connects the length of the linkage of the peripheral arm with the mesophase behaviour.

## 9.2 *Experimental*

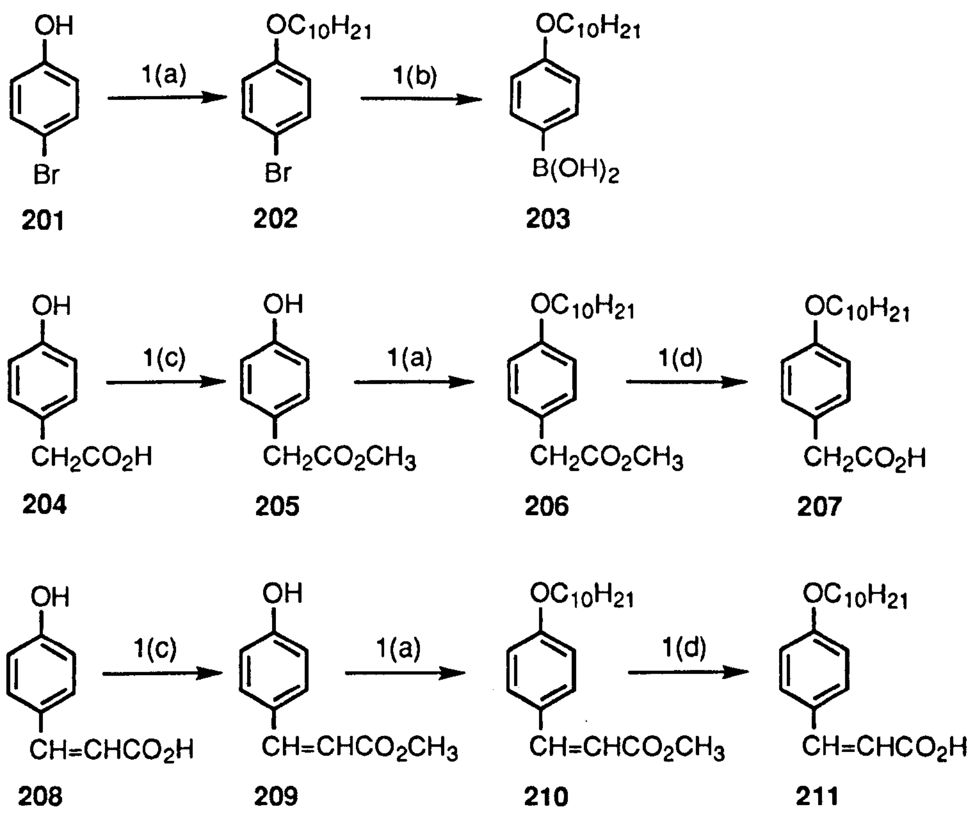
The materials were prepared by the routes shown in Schemes 9.1-9.4. Compounds **201**, **204**, **208** and **212** were all purchased from Aldrich Chemical Co. The methyl esters **205** and **209** were easily prepared by heating up the acids **204** and **208** in methanol with a few mls of concentrated sulfuric acid. Compounds **201**, **205**, **209** and **212** were all *O*-alkylated with 1-bromodecane in good yields using anhydrous potassium carbonate in butanone to give compounds **202**, **206**, **210** and **213**. The replacement of the bromine in compound **202** was achieved by lithiation using *n*-butyllithium at -78 °C; the aryl-lithium salt was then quenched with trimethyl borate and after subsequent hydrolysis with aqueous hydrochloric acid, the boronic acid **203** was obtained. The benzoic acids **207** and **211** were obtained by hydrolyzing the methyl esters **206** and **211** in aqueous ethanol using sodium hydroxide.

The protecting benzyl group in compound **213** was removed using hydrogen and a catalyst, 10% palladium on carbon, whilst dissolved in a mixture of THF and ethanol. Compound **214** was then *O*-alkylated with benzyl 2-bromoacetate using the same procedure as described above for compounds **202, 206** and **210**. The benzyl protecting group of the ester **215** was removed in an identical manner described for compound **214**.

The final discotic materials (**217-220**) were prepared by either the palladium-catalyzed cross-coupling of the arylboronic acid **203** with the triphenylene triflate **4**, or by the esterification of HHTP (**3**) with the respective benzoyl chlorides in the presence of pyridine.

The use of hexabromotriphenylene (**7**) was unsuccessful in the cross-coupling reaction to synthesize compound **217**, despite literature reports to the contrary.[3-8] The solubility of the halide **7** in DME was poor whereas triphenylen-2,3,6,7,10,11-hexayl hexakis(triflate) dissolved quite readily.

Compound **220** was the only target material that was not successfully synthesized Although the reaction procedure was repeated on several occasions and the conditions slightly altered, firstly, by adding a catalytic amount of DMAP to aid the esterification process and secondly, in the purification stage using column chromatography, the elution solvent (dichloromethane) was made more polar by the gradual addition of ethyl acetate until the elution solvent was solely ethyl acetate no final material (**220**) was obtained.



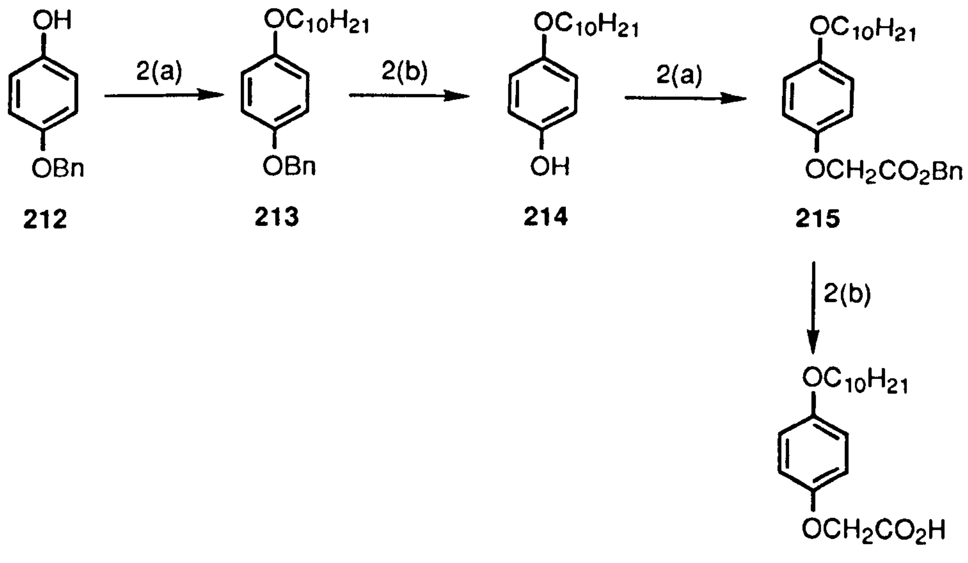
1(a) ..... 1-Bromodecane, $K_2CO_3$, butanone.

1(b) ..... (i) *n*-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl.

1(c) ..... conc. $H_2SO_4$, methanol.

1(d) ..... NaOH, water, ethanol.

**Scheme 9.1 : Synthetic route for the preparation of 4-decyloxyphenylboronic, 4-decyloxyphenylacetic and 4-decyloxycinnamic acids (203, 207 and 211)**

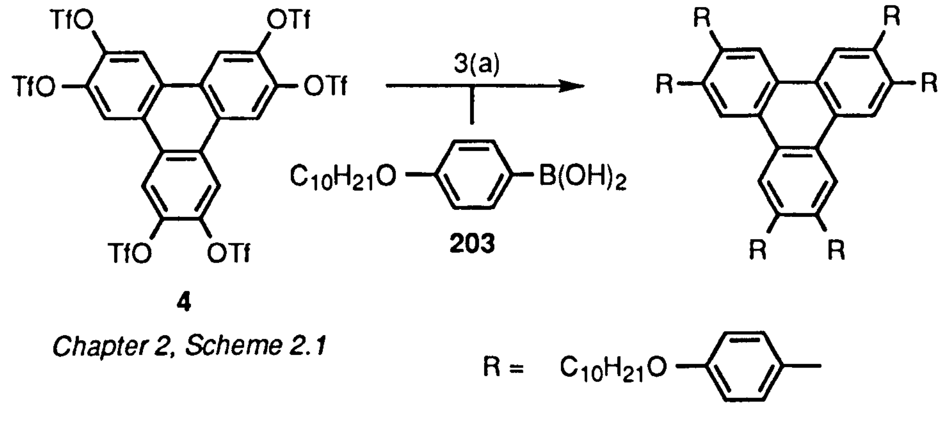


**212** **213** **214** **215** **216**

2(a) ..... 1-Bromodecane or benzyl 2-bromoacetate, $K_2CO_3$, butanone.

2(b) ..... $H_2$, 10% palladium on carbon, THF and ethanol.

**Scheme 9.2 : Synthetic route for the preparation of (4-decyloxyphenoxy)acetic acid (216)**

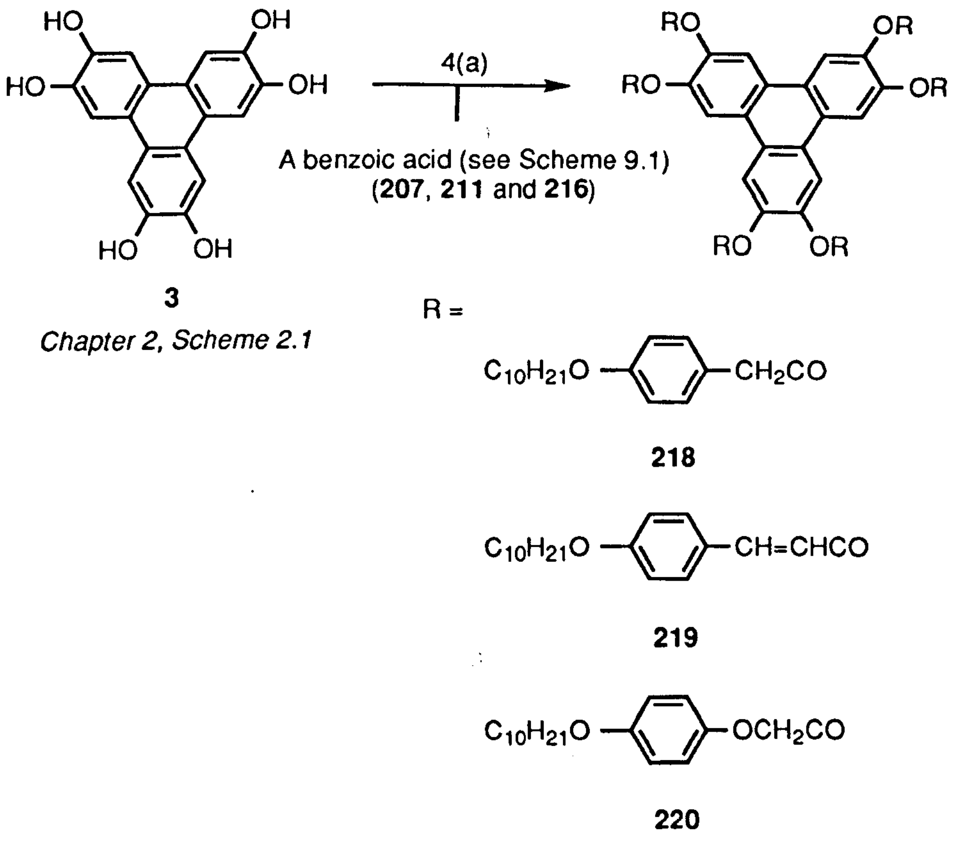


**4** **203** **217**

3(a) ..... $Pd(PPh_3)_4$, 2M $Na_2CO_3$, LiCl, DME.

**Scheme 9.3 : Synthetic route for the preparation of**

**2,3,6,7,10,11-hexakis(4-decyloxyphenyl)triphenylene (217)**



4(a) ..... Acid chloride (oxalyl chloride, DMF, $CH_2Cl_2$), pyridine.

**Scheme 9.4 : Synthetic route for the preparation of triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxyphenylacetate), hexakis(4-decyloxycinnamate) and hexakis[(4-decyloxyphenoxy)acetate] (218, 219 and 220)**

### *9.2.1 Preparation of Methyl 4-hydroxyphenylacetate and Methyl 4-hydroxycinnamate* (205 and 209)

The general synthetic method was exemplified by the procedure reported in Chapter 7 for compound 135.

*Methyl 4-hydroxyphenylacetate* (205)

Yield: 32.70 g (100%)

$^1$H NMR ($CDCl_3$ and TMS) δ: 3.56(2H, s), 3.70(3H, s), 6.45(1H, s broad), 6.75(2H, dd), 7.10(2H, dd).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 3600-2500, 1760, 1610, 1510, 1440, 1350, 1230, 1170, 1060, 1010, 840, 600.

MS (*m/z*): 166($M^+$), 107, 77, 58, 51.

*Methyl 4-hydroxycinnamate* **(209)**

Yield: 27.06 g (100%)

$^1H$ NMR ($CDCl_3$ and TMS) δ: 3.80(3H, s), 4.15(1H, s broad), 6.25(1H, d), 6.84(2H, dd), 7.39(2H, dd), 7.60(1H, d).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 3380 (broad), 1685, 1600, 1430, 1200, 1180, 990, 835.

MS (*m/z*): 178($M^+$), 147, 119, 91, 73, 65, 58, 51, 45.

### *9.2.2 Preparation of 1-Bromo-4-decyloxybenzene, Methyl 4-decyloxyphenylacetate, Methyl 4-decyloxycinnamate and 1-Benzyloxy-4-decyloxybenzene* **(202, 206, 210 and 213)**

The general synthetic method is exemplified by the procedure reported in Chapter 3 for compound **9**.

*1-Bromo-4-decyloxybenzene* **(202)**

Yield: 36.42 g (97%) Bp: 160-163 °C at 0.4 mmHg

$^1H$ NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.30(14H, m), 1.80(2H, m), 3.90(2H, t), 6.75(2H, dd), 7.37(2H, dd).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 2920, 2860, 1590, 1485, 1465, 1390, 1285, 1245, 1170, 1070, 1000, 820, 640, 510.

MS (*m/z*): 314($M^+$), 312($M^+$), 174, 172, 69, 55.

*Methyl 4-decyloxyphenylacetate* **(206)**

Yield: 11.00 g (100%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.35(14H, m), 1.75(2H, m), 3.56(2H, s), 3.70(3H, s), 3.94(2H, t), 6.86(2H, dd), 7.20(2H, dd).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 2920, 2860, 1740, 1610, 1510, 1245, 1155, 1020, 820.

MS (*m/z*): 306($M^+$), 247, 166, 121, 106, 69, 55.

*Methyl 4-decyloxycinnamate* (**210**)

Yield: 18.38 g (86%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(14H, m), 1.76(2H, m), 3.80(3H, s), 3.96(2H, t), 6.30(1H, d), 6.89(2H, dd), 7.47(2H, dd), 7.65(1H, d).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 2920, 2860, 1710, 1600, 1510, 1285, 1175, 1020, 840.

MS (*m/z*): 318($M^+$), 287, 178, 147, 118, 91.

*1-Benzyloxy-4-decyloxybenzene* (**213**)

Yield: 13.09 g (77%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.30(14H, m), 1.75(2H, t), 3.80(2H, t), 5.05(2H, s), 6.85(4H, m), 7.38(5H, m).

IR (KBr) $\nu_{max}$ $cm^{-1}$: 2920, 2850, 1510, 1240, 1030, 825, 735, 690.

MS (*m/z*): 340($M^+$), 249, 200, 109, 91, 85, 71, 65, 43.

### *9.2.3 Preparation of 4-Decyloxyphenylboronic Acid* (203)

*n*-Butyllithium (15.2 ml, 2.5M in hexane, 0.038 mol) was added dropwise to a stirred, cooled (-78 °C) solution of compound **202** (11.0 g, 0.035 mol) in dry THF (200 ml) under dry nitrogen. The reaction was maintained under these conditions for 45 mins then a solution of trimethyl borate (10.3 g, 0.10 mol) in dry THF (20 ml) was added dropwise. The reaction mixture was allowed to warm to room temperature overnight and then stirred for 1 h with 10% hydrochloric acid (100 ml). The product was extracted into ether (twice), and the combined organic extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude boronic acid was used without further purification.

Yield: 9.77 g (100%)

### *9.2.4 Preparation of 4-Decyloxyphenol* (214)

A stirred solution of compound **213** (13.09 g, 0.039 mol) and 10% palladium on carbon in THF was kept under an atmosphere on $H_2$ (0.86 $dm^3$, 0.039 mol). The reaction mixture was then filtered and the solvent was removed. The crude product was recrystallized from ethanol to yield colourless crystals.

Yield: 6.86 g (70%)

| | |
|---|---|
| $^1H$ NMR ($CDCl_3$ and TMS) $\delta$: | 0.88(3H, t), 1.30(14H, m), 1.75(2H, m), 2.70(1H, s broad), 3.90(2H, t), 6.77(4H, m). |
| IR (KBr) $\nu_{max}$ $cm^{-1}$: | 3600-3100(broad), 2920, 2850, 1510, 1240, 820, 720. |
| MS (*m/z*): | 250($M^+$), 123, 110, 81, 65, 55. |

### *9.2.5 Preparation of Benzyl (4-decyloxyphenoxy)acetate* (215)

The general synthetic method was exemplified by the procedure reported in Chapter 3 for compound **9**.

Yield: 9.8 g (77%)

| | |
|---|---|
| $^1H$ NMR ($CDCl_3$ and TMS) $\delta$: | 0.88(3H, t), 1.30(14H, m), 1.75(2H, m), 3.90(2H, t), 4.62(2H, s), 5.24(2H, s), 6.81(4H, m), 7.36(5H, m). |
| IR (KBr) $\nu_{max}$ $cm^{-1}$: | 2920, 2860, 1760, 1500, 1450, 1200, 1080, 825, 730, 700. |
| MS (*m/z*): | 398($M^+$), 320, 180, 165, 123, 107, 91. |

### 9.2.6 *Preparation of 4-Decyloxyphenylacetic, 4-Decyloxycinnamic and (4-Decyloxphenoxy)acetic Acids* (207, 211 and 216)

The general synthetic method is exemplified by procedures reported in Chapter 7 (compound **137**) for compounds **207** and **211**, and in this Chapter (compound **214**) for compound **216**) .

*4-Decyloxyphenylacetic Acid* (**207**)

Yield: 7.63 g (73%) Mp: 84-85 °C

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.35(14H, m), 1.75(2H, m), 3.60(2H, s), 3.95(2H, t), 6.86(2H, dd), 7.20(2H, dd).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3300-2500 (broad), 2960, 2860, 1690, 1510, 1250, 820, 795.

MS (*m/z*): 292(M$^+$), 152, 107, 77, 69, 55.

*4-Decyloxycinnamic Acid* (**211**)

Yield: 15.82 g (90%) Transitions (°C): K 136 $S_C$ 150 N 169 I

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.35(14H, m), 1.75(2H, m), 3.95(2H, t), 6.31(1H, d), 6.90(2H, dd), 7.49(2H, dd), 7.73(1H, d).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3500-2400 (broad), 2920, 2850, 1670, 1620, 1600, 1500, 1420, 1305, 1245, 1215, 1170, 980, 830.

MS (*m/z*): 304(M$^+$), 279, 177, 164, 147, 129, 119, 107, 97, 85, 77, 69, 65.

*(4-Decyloxyphenoxy)acetic Acid* (**216**)

Yield: 7.59 g (100%) Mp: 116-118 °C

$^1$H NMR ($CDCl_3$ and TMS) δ: 0.88(3H, t), 1.30(14H, m), 1.75(2H, m), 3.90(2H, t), 4.63(2H, s), 6.86(4H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1730, 1700, 1605, 1465, 1440, 1230, 1085, 820.

MS ($m/z$): 308($M^+$), 258, 168, 123, 109, 91.

### *9.2.7 Preparation of 2,3,6,7,10,11-Hexakis(4-decyloxyphenyl)triphenylene, and Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxyphenylacetate), Hexakis(4-decyloxycinnamate) and Hexakis[(4-decyloxyphenoxy)acetate]* **(217-220)**

*2,3,6,7,10,11-Hexakis(4-decyloxyphenyl)triphenylene* (**217**)

Tetrakis(triphenylphosphine)palladium(0) (1.0 g, 0.9 mmol) and compound **203** (5.0 g, 0.018 mol) were added sequentially to a stirred mixture of compound **4** (1.0 g, 0.9 mmol), aqueous sodium carbonate (20 ml, 2 mol dm$^{-3}$), lithium chloride (0.76 g, 0.018 mol) in 1,2-dimethoxyethane (50 ml) under dry nitrogen and the mixture was heated under reflux overnight. The mixture was cooled, the product extracted into dichloromethane (twice), and the combined organic extracts washed with brine and dried ($MgSO_4$). The solvent was removed in vacuo and the crude product was purified by column chromatography (silica gel/ petroleum fraction : dichloromethane, 2 :1) to yield a colourless solid which was recrystallized from ethanol/ethyl acetate to yield a colourless solid.

Yield: 0.63 g (43%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.89(3H, t), 1.30(14H, m), 1.79(2H, m), 3.97(2H, t), 6.83(2H, dd), 7.23(2H, dd), 8.63(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1605, 1510, 1470, 1240, 1170, 830, 590.

CHN analysis: % expected - C 84.44, H 9.63;
% found - C 84.24, H 9.94.

The general synthetic method for the preparation of the hexa-esters is exemplified by the procedure reported in Chapter 3 for compound **30**.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxyphenylacetate)* (**218**)

Yield: 1.56 g (35%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.89(3H, t), 1.30(14H, m), 1.79(2H, m), 3.54(2H, s), 3.87(2H, t), 6.85(2H, dd), 7.22(2H, dd), 8.16(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1755, 1610, 1510, 1420, 1240, 1300, 1250, 1120, 920, 880, 800.

CHN analysis: % expected - C 76.83, H 8.54;
% found - C 76.50, H 8.74.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-decyloxycinnamate)* (**219**)

Yield: 1.08 g (38%)

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.89(3H, t), 1.30(14H, m), 1.79(2H, m), 3.90(2H, t), 6.45(1H, d), 6.73(2H, dd), 7.32(2H, dd), 7.83(1H, d), 8.26(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1730, 1620, 1600, 1500, 1420, 1230, 1200, 1170, 1130, 1010, 980, 820.

CHN analysis: % expected - C 77.65, H 8.24;
% found - C 77.69, H 8.51.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis[(4-decyloxyphenoxy)acetate]* (**220**; Attempted)

The reaction failed on several attempts; the reaction procedure was modified by the addition a catalytic amount of DMAP to aid the esterification process, but without success.

## *9.3 Results*

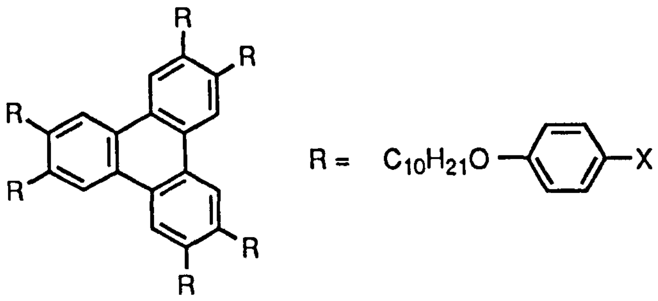
### *9.3.1 Transition Temperatures*

The transition temperatures for the previously reported[2] (compound **42**, see Chapter 3) and newly synthesized materials were determined by a combination of thermal optical microscopy and differential scanning calorimetry. Typically, the crystal to mesophase transitions were determined by calorimetry because of the difficulty in discerning this transition optically. The other transitions, including the recrystallization and glass transitions, were determined by microscopy.

The results are shown in Table 9.1, where it is clearly seen that altering the linkage group radically affects the mesophase behaviour of these discotic liquid crystals. When no linking group is present as in compound **217**, the discotic compound is non-mesogenic. In the case of compound **218**, which has a methylene group between the carbonyl group and the phenyl ring, the discotic nematic ($N_D$) mesophase has been eliminated and only an hexagonal disordered ($D_{hd}$) columnar phase is present. However, the $N_D$ mesophase has been re-established, and the columnar phases suppressed in compound **219** when the linkage is extended to an "ethene" group. Finally, in contrast to the new discotic materials, in the case of the literature material (**42**), both the rectangular disordered ($D_{rd}$) columnar phase and the discotic nematic ($N_D$) mesophase are observed.

### *9.3.2 Differential Scanning Calorimetry*

Calorimetric studies were carried out on each of the new discotic materials prepared. Typical results for the heating and cooling cycles are shown in Figures 9.2 and 9.3 respectively. All compounds were found to have different magnitudes of melting endotherms, followed by enthalpy peaks denoting mesophase-mesophase transitions or mesophase to isotropic liquid. The enthalpy peak for the clearing point transition from the discotic nematic was found to be rather small, indicating that the transition from the



| No. | X | K | | $D_{rd}$ | | $D_{hd}$ | | $N_D$ | | I | Recryst. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **217** | — | * | 86 (@) | — | — | — | — | — | — | * | {55} | * |
| 42 | $CO_2$† | * | 142 | * | 191 | — | — | * | 212 | * | 80 | * |
| **218** | $CH_2CO_2$ | * | 113 (22.30) | — | — | * | 183 (5.75) | — | — | * | 99 | * |
| **219** | $CH=CHCO_2$ | * | 170 (3.31) | — | — | — | — | * | 212 (0.37) | * | 162 | * |

**Table 9.1 : Transition temperatures for 2,3,6,7,10,11-hexakis(4-decyloxyphenyl)triphenylene, and triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxybenzoate), hexakis(4-decyloxyphenylacetate) and hexakis(4-decyloxycinnamate)**

Enthalpies for each transition are given in parenthesis ($\Delta H$/kJ $mol^{-1}$). Glassy state transitions are given in curly braces { }.

†Literature compound,[2] (see also Chapter 3). @ Not determined.

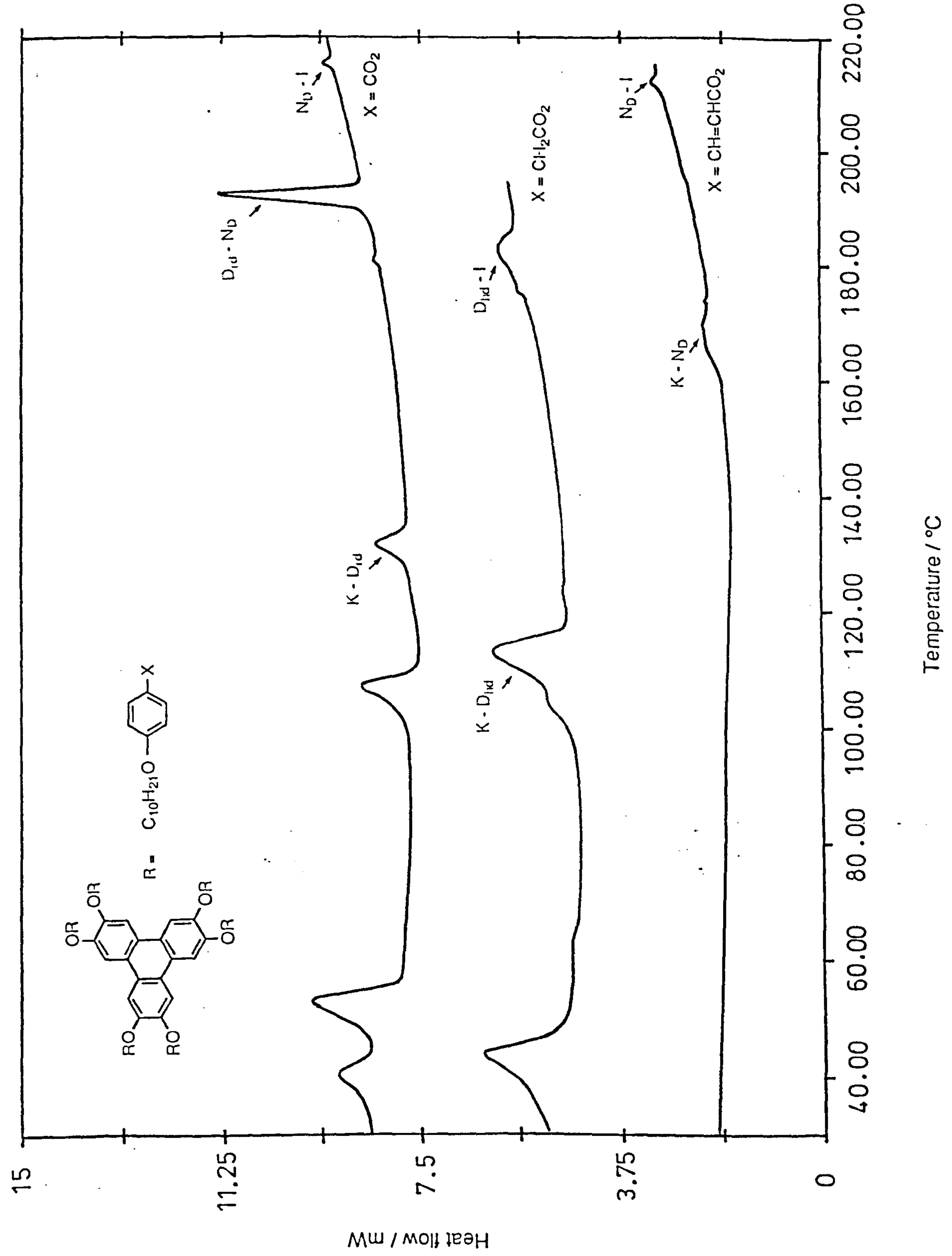


Figure 9.2 : DSC thermogram of the first heating cycles of the triphenylene materials (42, 217-219)

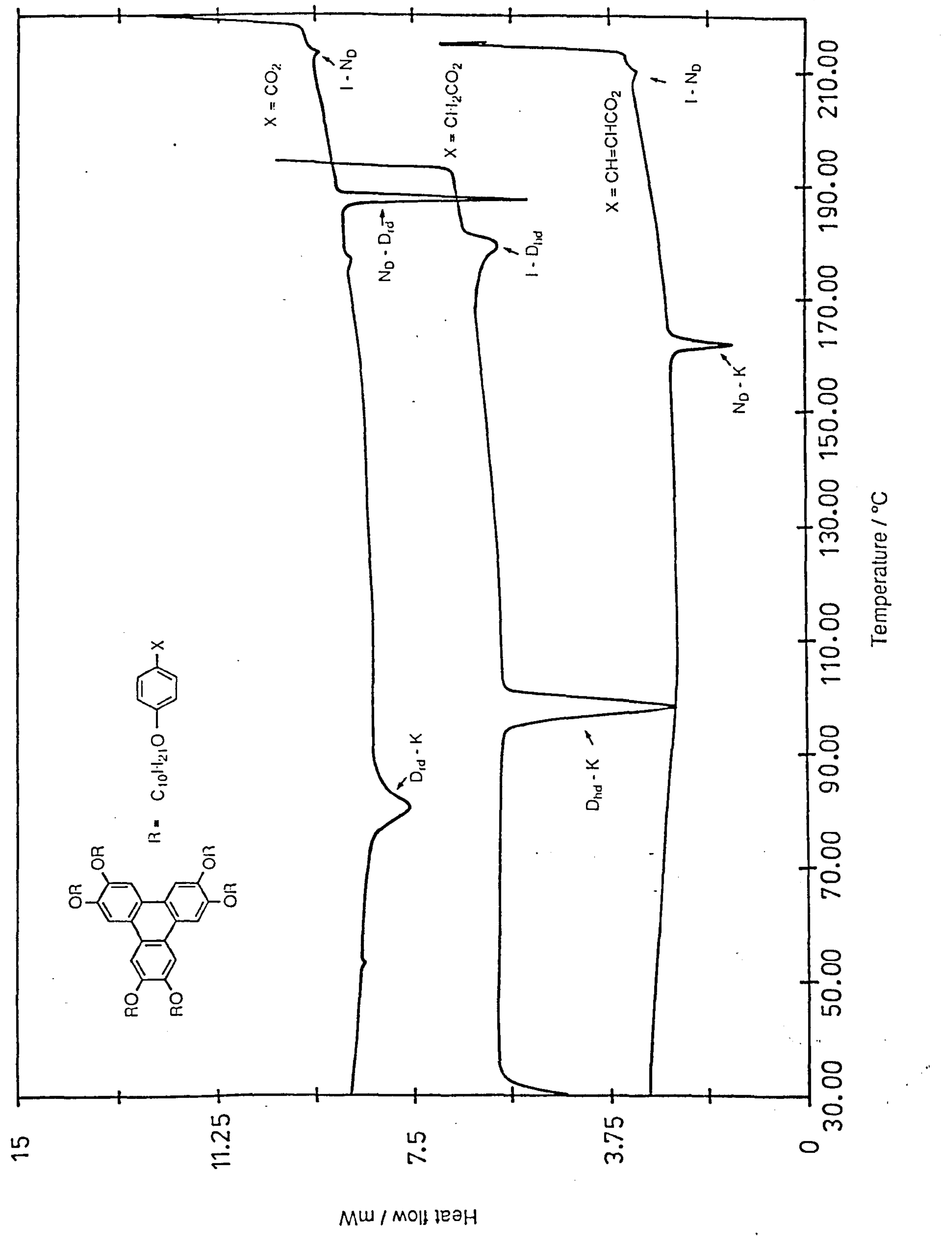


Figure 9.3 : DSC thermogram of the first cooling cycles of the triphenylene materials (42, 217-219)

nematic to isotropic liquid is weakly first order. In comparision, the enthalpy peak for the clearing point transition from the hexagonal disordered ($D_{hd}$) columnar phase was much larger and therefore, indicative of the clearing point transition of a more ordered phase. The transitions were all found to be reversible.

### *9.3.3 Thermal Optical Microscopy*

When each material was heated from the crystal, under microscopic observation, the first discernible transition was that for the transformation to either the discotic nematic mesophase (compounds **42** and **219**) or to the isotropic liquid state (compounds **217** and **218**).

The material without a linkage (**217**) simply melted on heating to the isotropic liquid. On cooling a transition to a glassy-state was observed which was supported by data from the DSC thermogram and there was no evidence for a transition to a crystalline state.

Compound **218** which possesses a methylene group, appeared to have only a melting transition because it was not possible to observe a distinct transition from the crystalline state to the hexagonal disordered columnar phase. However, upon slow cooling from the isotropic liquid, batonnets were observed which coalesced into either a mosaic or fan-like texture. The fan texture showed smooth fan-like regions and rectilinear δ lines, which confirm that the phase has hexagonal symmetry and no long range order in the columns, thereby classifying the phase as $D_{hd}$. Plate 9.1 shows batonnets growing on slow cooling from the isotropic liquid for this compound.

Compound **219** which possesses the "ethene" group, melted to the discotic nematic mesophase on heating from its crystalline state. Plate 9.2 shows a typical texture formed on heating for the discotic nematic phase for this compound. A threaded and *schlieren* texture is formed with the phase showing typical flow properties and Brownian motion that are expected on a nematic mesophase. Upon slow cooling from the isotropic liquid, the nematic phase formed the *schlieren* texture.

Generally, no recrystallization was observed under the microscope suggesting that the materials had formed glasses on cooling, however, transitions were observed in the DSC thermograms.

**Plate 9.1 : Batonnets growing from the isotropic liquid at 180 °C on slow cooling for the hexagonal disordered ($D_{hd}$) columnar exhibited by compound 218**

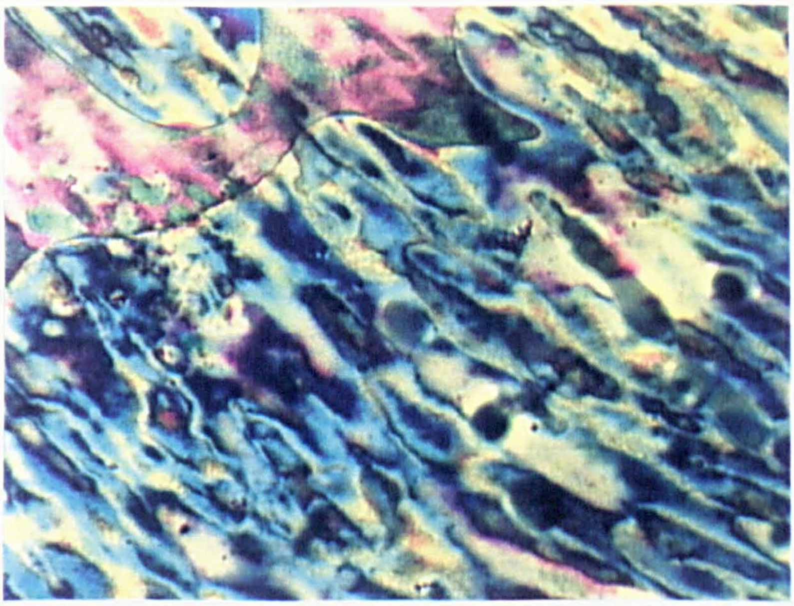


**Plate 9.2 : Sheared *schlieren* and threaded texture of the discotic nematic ($N_D$) exhibited by compound 219 at 195 °C on heating**

The data and conclusions reached from the DSC cycles and the thermal optical microscopy studies are shown graphically in Figure 9.4.

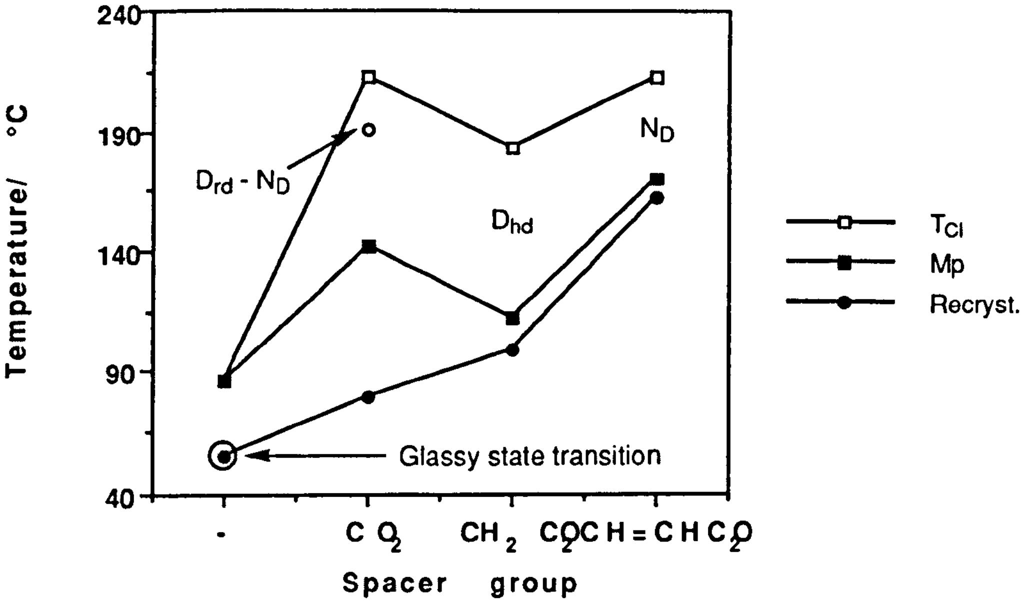


**Figure 9.4 : Transition temperatures plotted against the size of the spacer group for 2,3,6,7,10,11-hexakis(4-decyloxyphenyl)triphenylene, and triphenylen-2,3,6,7,10,11-hexayl hexakis(4-decyloxybenzoate), hexakis(4-decyloxyphenylacetate) and hexakis(4-decyloxycinnamate)**

## *9.4 Discussion*

The objective of this research study was to extend, or remove, the linking group between the triphenylene core and each of the peripheral phenyl rings in order to investigate the effects on the phase morphology, transition temperatures and melting points. It was predicted that by "creating" space around the crowded core area by the removal of the bulky phenyl groups, then the intermolecular forces between neighbouring triphenylene units would not be weakened to the same extent as previously encountered (see Chapters 3 to 8). Thus, the discotic system as a whole would prefer to form crystal or columnar phases instead of the discotic nematic mesophase.

The results shown in Table 9.1 and in Figure 9.4 illustrate that altering the linking group does have quite a radical affect upon the discotic mesophase behaviour.

The removal of the ester linkage in the directly-linked discogen **217** has resulted in the destruction of all mesogenicity, but the melting point of this material is considerably lower than that of the standard system (**42**).[2] Upon cooling, the discogen does not recrystallize but appears to go through a glassy-state transition.

The data obtained for the discotic compound (**218**) with a methylene group inserted between each of the peripheral phenyl rings and the ester linkages is consistent with the original prediction. The addition of the methylene spacer group has allowed the peripheral arm more flexibility which has weakened the triphenylene core to core interactions. This has thus lowered both the melting and clearing points in comparison to the parent system (compound **42**). The intermolecular interactions have not been weakened enough for the system to display discotic nematic ($N_D$) mesomorphism, and so this compound only displays an hexagonal disordered ($D_{hd}$) columnar phase.

However, the data for the cinnamate **219**, are unexpected. This material has now regained the ability to exhibit the discotic nematic ($N_D$) mesophase and has totally eliminated columnar phase formation. Unfortunately, both the melting and clearing points are higher than the previous compound (**218**).

## *9.5 Conclusions*

It is clear that there is a relationship between the linkage of the peripheral arm and the type of mesophase exhibited by discotic liquid crystals. However, at present there are insufficient data available to clarify any possible theories due to the limited number of discotic materials synthesized for this area of study. It is obvious that there is still much to discover regarding the effects on the discotic mesophase behaviour by the alteration of the molecular architecture.

## 9.6 References

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# *CHAPTER 10*

# *Miscellaneous Triphenylene Esters*

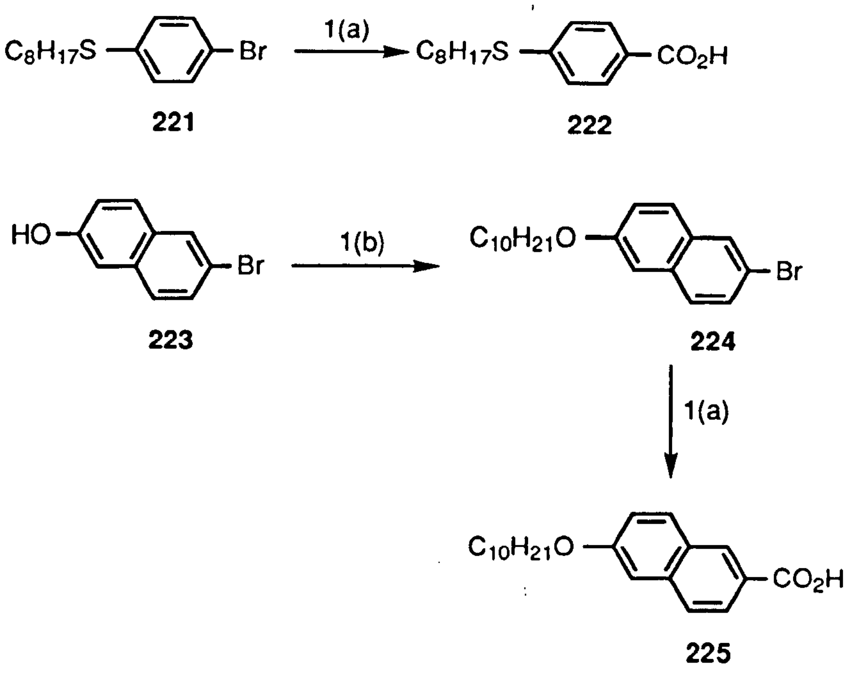
## *10.1 Introduction*

In this the last of the research chapters, those discotic materials that are unable to fit into any other area of this thesis, are collected together and their mesomorphic properties are discussed.

## *10.2 Experimental*

The materials were prepared by the routes shown in Schemes 10.1-10.3. Compounds **223**, **226**, **230** and **234** were all purchased from Aldrich Chemical Co., whereas compound **221** was donated by A. Seed.[1] The methyl esters **227**, **231** and **235** were easily prepared by heating up the acids **226**, **230** and **224** in methanol with a little concentrated sulfuric acid. Compounds **223**, **227**, **231** and **235** were all *O*-alkylated with 1-bromodecane in good yields using anhydrous potassium carbonate in butanone to give compounds **224**, **228**, **232** and **236**. The replacement of the bromine in compounds **221** and **224** was achieved by lithiation using *n*-butyllithium at -78 °C; in each case, the reaction mixture was poured onto a slurry of solid $CO_2$ and dry ether, acidified, and then the product purified (compounds **222** and **225**). The benzoic acids **229**, **233** and **237** were obtained by hydrolyzing the methyl esters **228**, **232** and **236** in aqueous ethanol using sodium hydroxide.

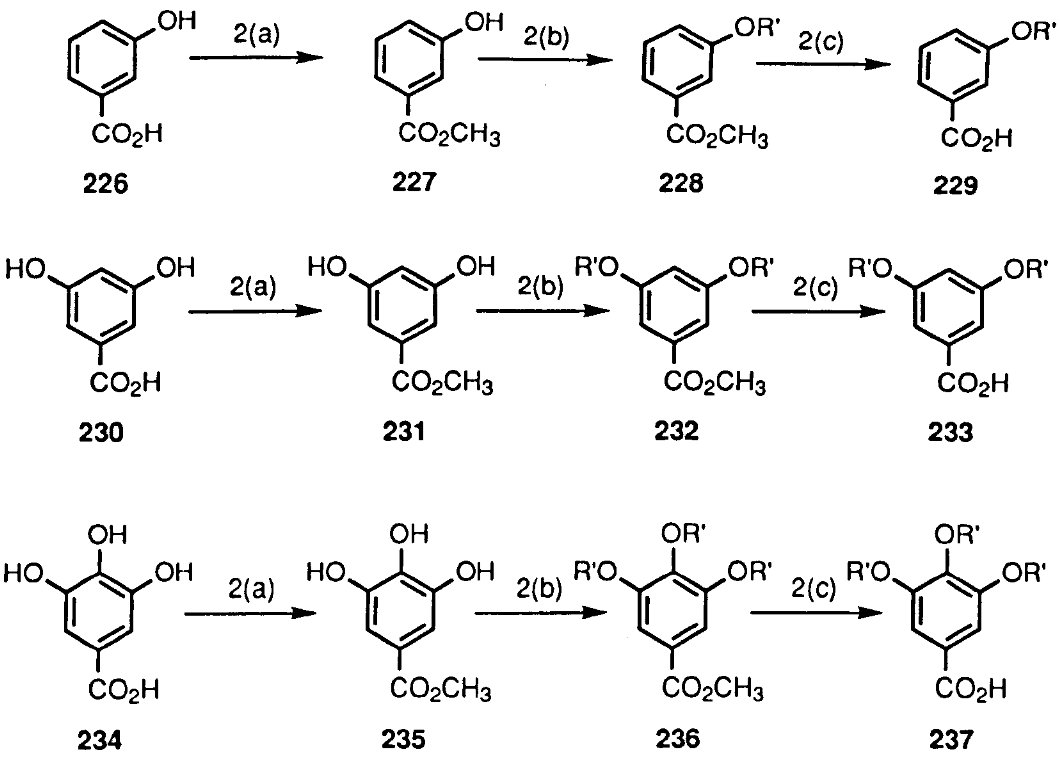
The final discotic materials (**238-242**) were prepared by the esterification of HHTP (**3**) with the respective acid chlorides in the presence of pyridine, see Scheme 10.3. Compounds **241** and **242** were the only target materials that were not successfully synthesized; it was suspected that a wet batch of pyridine was mistakenly used. Unfortunately, due to time constraints, these particular compounds were never resynthesized.



1(a) ..... (i) *n*-BuLi, THF; (ii) $CO_2$ (solid), dry $Et_2O$.

1(b) ..... 1-Bromodecane, $K_2CO_3$, butanone.

**Scheme 10.1 : Synthetic route for the preparation of 4-octylsulfanylbenzoic and 6-decyloxy-2-naphthoic acids (222 and 225)**

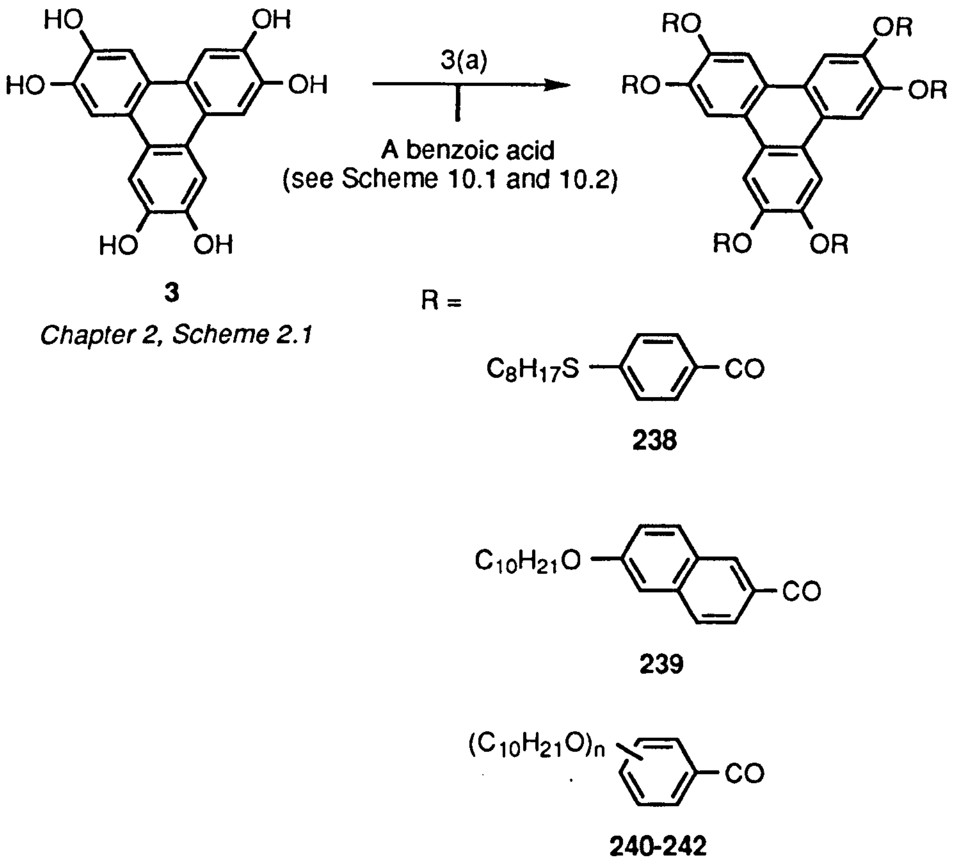


2(a) ..... conc. $H_2SO_4$, methanol.

2(b) ..... 1-Bromodecane, $K_2CO_3$, butanone.

2(c) ..... NaOH, water, ethanol.

**Scheme 10.2 : Synthetic route for the preparation of 3-decyloxybenzoic, 3,5-didecyloxybenzoic and 3,4,5-tridecyloxybenzoic acids (229, 233 and 237)**



3(a) ..... Acid chloride (oxalyl chloride, DMF, $CH_2Cl_2$), pyridine.

**Scheme 10.3 : Synthetic route for the preparation of triphenylen-2,3,6,7,10,11-hexayl hexakis(4-octylsulfanylbenzoate), hexakis(6-decyloxy-2-naphthoate), hexakis(3-decyloxybenzoate), hexakis(3,5-didecyloxybenzoate) and hexakis(3,4,5-tridecyloxybenzoate) (238-242)**

### *10.2.1 Preparation of Methyl 3-hydroxybenzoate, Methyl 3,5-dihydroxybenzoate and Methyl 3,4,5-trihydroxybenzoate* (227, 231 and 235)

The general synthetic method is exemplified by the procedure reported in Chapter 7 for compound **135**.

*Methyl 3-hydroxybenzoate* (**227**)

Yield: 32.98 g (100%)

$^1H$ NMR ($CDCl_3$ and TMS) $\delta$: 3.90(3H, s), 5.10(1H, s), 7.05(1H, m), 7.32(1H, m), 7.53(1H, m), 7.62(1H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3480 (broad), 1690, 1600, 1440, 1310, 1240, 1110, 1075, 970, 880, 760, 610.

MS ($m/z$): 152(M$^+$), 121, 93, 74, 65, 63, 59, 50, 43.

*Methyl 3,5-dihydroxybenzoate* **(231)**

Yield: 32.76 g (100%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$3.84(3H, s), 6.59(1H, m), 6.99(2H, s broad), 7.02(2H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3700-3000 (broad), 3400, 3250, 1690, 1610, 1350, 1175, 1000, 770.

MS ($m/z$): 168(M$^+$), 137, 109, 81, 69, 63, 53, 43.

*Methyl 3,4,5-trihydroxybenzoate* **(235)**

Yield: 32.12 g (100%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 3.83(3H, s), 5.65(3H, s broad), 7.12(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3600-2500 (broad), 3500, 3460, 3300, 1695, 1615, 1440, 1310, 1250, 1200, 1050, 1005, 770, 640, 550.

MS ($m/z$): 184(M$^+$), 153, 136, 125, 107, 79, 67, 58, 51.

### *10.2.2 Preparation of 2-Bromo-6-decyloxynaphthalene, Methyl 3-decyloxybenzoate, Methyl 3,5-didecyloxybenzoate and Methyl 3,4,5-tridecyloxybenzoate* **(224, 228, 232 and 236)**

The general synthetic method is exemplified by the procedure reported in Chapter 3 for compound **9**.

*2-Bromo-6-decyloxynaphthalene* **(224)**

Yield: 12.68 g (97%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(14H, m), 1.85(2H, m), 4.05(2H, t), 7.08(1H, m), 7.16(1H, m), 7.48(1H, m), 7.58(1H, d), 7.64(1H, d), 7.90(1H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1620, 1585, 1495, 1465, 1390, 1260, 1210, 850, 815

MS (*m/z*): 365(M$^+$), 363(M$^+$), 225, 223, 193, 156, 143, 126, 114.

*Methyl 3-decyloxybenzoate* (**228**)

Yield: 9.64 g (100%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.85(3H, t), 1.35(14H, m), 1.82(2H, m), 3.90(3H, s), 3.98(2H, t), 7.05(1H, m), 7.35(1H, m), 7.55(1H, m), 7.62(1H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1720, 1600, 1585, 1440, 1290, 1280, 1230, 1100, 755.

MS (*m/z*): 292(M$^+$), 220, 152, 135, 121, 97, 85, 69, 55.

*Methyl 3,5-didecyloxybenzoate* (**232**)

Yield: 10.75 g (100%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(6H, t), 1.35(28H, m), 1.75(4H, m), 3.90(3H, s), 3.96(4H, t), 6.65(1H, m), 7.15(2H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1720, 1600, 1440, 1390, 1320, 1240, 1160, 1050, 860, 760, 720.

MS (*m/z*): 448(M$^+$), 308, 168, 152, 137, 121, 97, 83, 69, 55.

*Methyl 3,4,5-tridecyloxybenzoate* (**236**)

Yield: 12.59 g (100%)

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.88(9H, t), 1.35(42H, m), 1.75(6H, m), 3.92(3H, s), 4.04(6H, t), 7.27(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1720, 1590, 1500, 1430, 1330, 1220, 1110, 1020, 765.

MS (*m/z*): 604(M$^+$), 465, 324, 197, 184, 152, 97, 85, 71.

### *10.2.3 Preparation of 4-Octylsulfanylbenzoic, 6-Decyloxy-2-naphthoic, 3-Decyloxybenzoic, 3,5-Didecyloxybenzoic and 3,4,5-Tridecyloxybenzoic Acids* **(222, 225, 229, 233 and 237)**

The general synthetic methods are exemplified in procedures reported in Chapter 3 (compound **14**) for compounds **222** and **225**, and in Chapter 7 (compound **137**) for compounds **229**, **233** and **237**.

*4-Octylsulfanylbenzoic Acid* (**222**)

Yield: 9.37 g (90%)

Transitions (°C): K 104.4 N 106.2 I

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.85(3H, t), 1.25(10H, m), 1.70(2H, m), 3.00(2H, t), 7.30(2H, dd), 8.00(2H, dd).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1680, 1595, 1420, 1290, 1280, 810.

MS (*m/z*): 266 (M$^+$), 200, 167, 154, 137, 123, 109, 77, 69, 65.

*6-Decyloxy-2-naphthoic Acid* (**225**)

Yield: 6.18 g (54%)

Transitions (°C): K 130 $S_C$ 143 $S_A$ 145 N 180 I

$^1$H NMR (CDCl$_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(14H, m), 1.85(2H, m), 4.10(2H, t), 7.16(1H, m), 7.21(1H, m), 7.76(1H, d), 7.86(1H, d), 8.05(1H, m), 8.60(1H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3200-2100 (broad), 2920, 2850, 1670, 1620, 1480, 1470, 1390, 1290, 1210 .

MS (*m/z*): 328(M$^+$), 188, 171, 159, 143, 115, 69, 55, 43.

*3-Decyloxybenzoic Acid* (**229**)

Yield: 7.60 g (82%)

Mp: 85-86 °C

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.85(3H, t), 1.30(14H, m), 1.80(2H, m), 4.00(2H, t), 7.15(1H, m), 7.37(1H, m), 7.60(1H, m), 7.69(1H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3300-2400 (broad), 2920, 2860, 1680, 1600, 1590, 1450, 1310, 1250, 1120, 755.

MS (*m/z*): 278(M$^+$), 138, 121, 106, 97, 77, 65, 55.

*3,5-Didecyloxybenzoic Acid* (**233**)

Yield: 5.82 g (45%) Mp: 58-60 °C

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(6H, t), 1.35(28H, m), 1.75(4H, m), 4.00(4H, t), 6.68(1H, m), 7.21(2H, m).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3300-2500, 2920, 2860, 1690, 1610, 1470, 1445, 1320, 1170, 860, 740.

MS (*m/z*): 434(M$^+$), 294, 195, 154, 111, 97, 83, 67, 55.

*3,4,5-Tridecyloxybenzoic Acid* (**237**)

Yield: 10.71 g (86%) Mp: 273-275 °C

$^1$H NMR (CDCl$_3$ and TMS) δ: 0.88(9H, t), 1.30(42H, m), 1.63(6H, m), 3.75(6H, t), 7.06(2H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 3600-2500 (broad), 2920, 2860, 1680, 1580, 1560, 1425, 1360, 1325, 1220, 1110.

MS (*m/z*): 590(M$^+$), 450, 244, 216, 184, 170, 152, 124, 92, 87, 64, 57, 45.

### *10.2.4 Preparation of Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-octylsulfanylbenzoate), Hexakis(6-decyloxy-2-naphthoate), Hexakis(3-decyloxybenzoate), Hexakis(3,5-didecyloxybenzoate) and Hexakis(3,4,5-tridecyloxybenzoate) (238-242)*

The general synthetic method for the preparation of the hexa-esters is exemplified by the procedure reported in Chapter 3 for compound **30**.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(4-octylsulfanylbenzoate)* (**238**)

Yield: 0.42 g (7%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(10H, m), 1.70(2H, m), 2.90(2H, t), 6.95(2H, dd), 7.70(2H, dd), 8.35(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1590, 1270, 1090.

CHN analysis: % expected - C 71.52, H 7.28;
% found - C 71.83, H 7.14.

*Triphenyen-2,3,6,7,10,11-hexayl Hexakis(6-decyloxy-2-naphthoate)* (**239**)

Yield: 1.66 g (40%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.90(3H, t), 1.35(14H, m), 1.78(2H, m), 3.90(2H, t), 6.60(1H, m), 6.77(1H, m), 7.03(1H, d), 7.16(1H, d), 7.57(1H, m), 8.27(1H, m), 8.58(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1625, 1465, 1270, 1190, 1120, 1070.

CHN analysis: % expected - C 79.12, H 7.69;
% found - C 78.84, H 7.85.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(3-decyloxybenzoate)* (**240**)

Yield: 4.83 g (95%)

$^1$H NMR ($CDCl_3$ and TMS) $\delta$: 0.88(3H, t), 1.30(14H, m), 1.70(2H, m), 3.70(2H, t), 7.00(1H, m), 7.15(1H, m), 7.50(1H, m), 7.60(1H, m), 8.49(1H, s).

IR (KBr) $\nu_{max}$ cm$^{-1}$: 2920, 2860, 1740, 1600, 1270, 1210, 1050, 740.

CHN analysis: % expected - C 76.43, H 8.28;
% found - C 76.28, H 8.61.

*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(3,5-didecyloxybenzoate)* (**241**; Attempted)

It was suspected that a wet batch of pyridine was mistakenly used. Unfortunately, due to time constraints, this compound was never resynthesized.

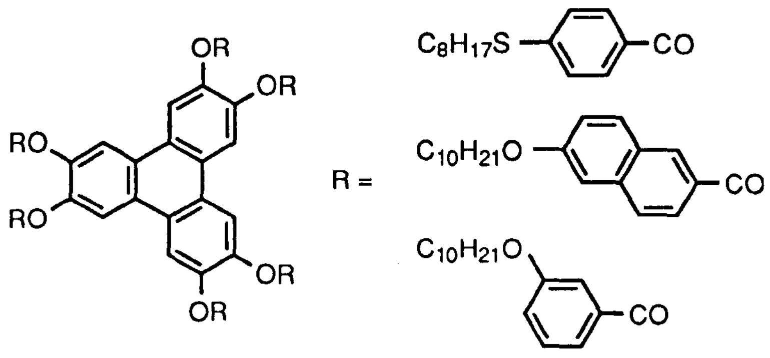
*Triphenylen-2,3,6,7,10,11-hexayl Hexakis(3,4,5-tridecyloxybenzoate)* (**242**; Attempted)

It was suspected that a wet batch of pyridine was mistakenly used. Unfortunately, due to time constraints, this compound was never resynthesized.

## *10.3 Results*

### *10.3.1 Transition Temperatures*

The transition temperatures for the newly synthesized materials were determined by a combination of thermal optical microscopy and differential scanning calorimetry. Typically, the crystal to mesophase transitions were determined by calorimetry because of the difficulty in discerning this transition optically. All other transitions were determined by microscopy. The results are shown in Table 10.1. The melting point for compound **238** with the octylsulfanyl chain is over 300 °C and is outside the maximum range of the Mettler heating stage; this situation was previously encountered for the "outer" fluoro-, chloro- and trifluoromethyl-substituted discotic materials discussed in Chapter 7. Compound **240** does not display mesomorphism and simply melts to the isotropic liquid. The naphthoate derivative (compound **239**) is the only material to exhibit a mesophase, in this case the discotic nematic ($N_D$) phase, but unfortunately experiences some decomposition at the clearing point transition.



| No. | | K | | $N_D$ | | I |
|---|---|---|---|---|---|---|
| **238** | 4-octylsulphanylbenzoate | * | > 300 | — | — | * |
| **239** | 6-decyloxynaphthoate | * | 250 | * | *ca.* 280 (decomposes) | * |
| **240** | 3-decyloxybenzoate | * | 134 | — | — | * |

**Table 10.1 : Transition temperatures for triphenylen-2,3,6,7,10,11-hexayl hexakis(4-octylsulphanylbenzoate), hexakis(6-decyloxynaphthoate) and hexakis(3-decyloxybenzoate)**

### *10.3.2 Differential Scanning Calorimetry*

Calorimetric studies were carried out on the three materials prepared. The octylsulfanyl material **238** had not melted by 300 °C and *ca.* 360 °C rapidly decomposed, resulting in leakage of the spoiled compound onto the heating element of the DSC apparatus. Throughout the DSC scan, there were no traces of enthalpy changes that could significantly denote possible mesophase transitions, but instead a rising baseline was observed which finally became a jumble of enthalpy signals indicating that the discotic material had decomposed.

The naphthoate derivative **239** showed both a melting endotherm and a clearing point transition; both signals were small and the baseline was very noisy, especially at the transition to the isotropic liquid, indicating that the material was decomposing. Upon cooling, there was a signal for the isotropic to nematic and further slow cooling resulted in recrystallization. Degeneration of the transition temperatures was experienced upon further heating and cooling cycles.

The 3-decyloxybenzoate **240** only showed a melting endotherm and upon cooling experienced a glassy-state transition which was seen as a gradual change in the baseline.

### *10.3.3 Thermal Optical Microscopy*

The naphthoate discotic material **239** was the only compound to display mesomorphism. When heated under microscopic observation, the material was seen to melt from its crystal state to the discotic nematic phase. A threaded and *schlieren* texture was formed, showing typical flow properties and Brownian motion that are expected of a nematic phase. Some decomposition was observed at the transition from the nematic phase to the isotopic liquid. This subsequently spoilt the classical *schlieren* texture of the discotic nematic phase when the material was cooled from the isotropic liquid.

## *10.4 Discussion*

This last chapter collects together those discotic materials that do not fit into any specific areas of this research programme. Consequently, there is no theme in this chapter and so the compounds are discussed separately.

Compound **238**, with the octylsulfanyl chain, was synthesized in order to investigate the presence of the sulfur unit on the mesophase behaviour. The effect upon the mesophase has been significant; the material is now effectively non-mesogenic and suffers severe decomposition at *ca.* 360 °C. No mesophases or crystal transitions were observed at all below 300 °C. In comparision, the parent octyloxy analogue (compound **41**, see Chapter 3), synthesized by Tinh *et al.*,[2] exhibits a rectangular disordered ($D_{rd}$) columnar phase at 152 °C, the discotic nematic ($N_D$) mesophase at 168 °C and clears into the isotropic liquid at 244 °C. The effect of the sulfur unit appears to have promoted crystal formation in the discotic system which has raised the temperatures of all possible transitions; as yet, the reasons behind this situation cannot be explained.

The mesomorphic behaviour of the naphthoate discogen **239** is somewhat straightforward. The material exhibits the discotic nematic mesophase and no columnar phases, whereas its benzoate analogue (compound **42**, see Chapter 3), does exhibit a rectangular disordered ($D_{rd}$) columnar phase. However, both the melting and clearing point transition temperatures are much higher in the naphthoate material **239** (K 250 $N_D$ 280 Iso) than they are in the benzoate analogue **42** (K 142 $D_{rd}$ 191 $N_D$ 212 Iso). At present, no explanation for this situation can be given.

The final material in this section is the 3-decyloxybenzoate **240**. This material does not display any mesomorphism unlike its 4-decyloxy analogue (compound **42**). This point also can not be explained. However, its occurence has strengthened arguments regarding molecular structure of discotic liquid crystals. There is a very fine line between discotic materials which do display mesomorphism and those discotic materials which do not.

## *10.5 Conclusions*

The design of the discotic molecular architecture needs to be conducted very carefully so that discotic materials which do display mesomorphism can be synthesized in preference to those discotic materials which do not. There is a very fine line in the field of discotic liquid crystals that can easily be traversed; on one hand, the structure of discotic liquid crystals tolerates large bulky substituents and allows mesomorphism and conversely, supports small polar substituents which prohibit mesomorphism. There is obviously still a great deal of information yet to be uncovered and no doubt, in future studies the number of non-mesogenic novel discogens will far outweigh those novel derivatives that do possess mesogenicity.

## *10.6 References*

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# *CHAPTER 11*

# *Discussion of Major Synthetic Routes and Methods*

## *11.1 Introduction*

In this chapter, an attempt is not made to describe every step in mechanistic terms of all the synthetic routes used throughout this thesis. Many of the reactions detailed in the previous chapters have been well documented, so in this chapter those steps that are of major interest will be discussed. Thus, this chapter is concerned solely with the synthetic routes to the preparations of the final discotic liquid crystals in Chapters 3 to 10.

## *11.2 Synthesis of the Final Triphenylene Discotic Materials*

The final reaction step to the production of the triphenylene discotic compounds was the esterification reaction using 2,3,6,7,10,11-hexahydroxytriphenylene (**3**, see Chapter 2), except for one material (**217**, see Chapter 9) which was synthesized using a palladium-catalyzed cross-coupling method using triphenylen-2,3,6,7,10,11-hexayl hexakis(triflate) (**4**, see Chapter 2).

### *11.2.1 The Acid Chloride Esterification Reaction*

All the final triphenylene esters were synthesized in the same way. The methodology followed throughout was the classical approach of converting the acid into its respective acid chloride using oxalyl chloride,[1] and then under base-catalyzed conditions, esterification with 2,3,6,7,10,11-hexahydroxytriphenylene (**3**).[2,3] Pyridine was the only solvent system used throughout this work. A mechanism for the esterification reaction is shown in Figure 11.1.

As acid chlorides are moisture sensitive, it was imperative that the esterification reactions were performed under dry conditions. The pyridine was dried by distillation from potassium hydroxide pellets, and subsequent storage was also over potassium hydroxide pellets.[4] The esterification reaction was performed under an atmosphere of dry nitrogen and at a temperature to maintain the pyridine solvent under reflux conditions.

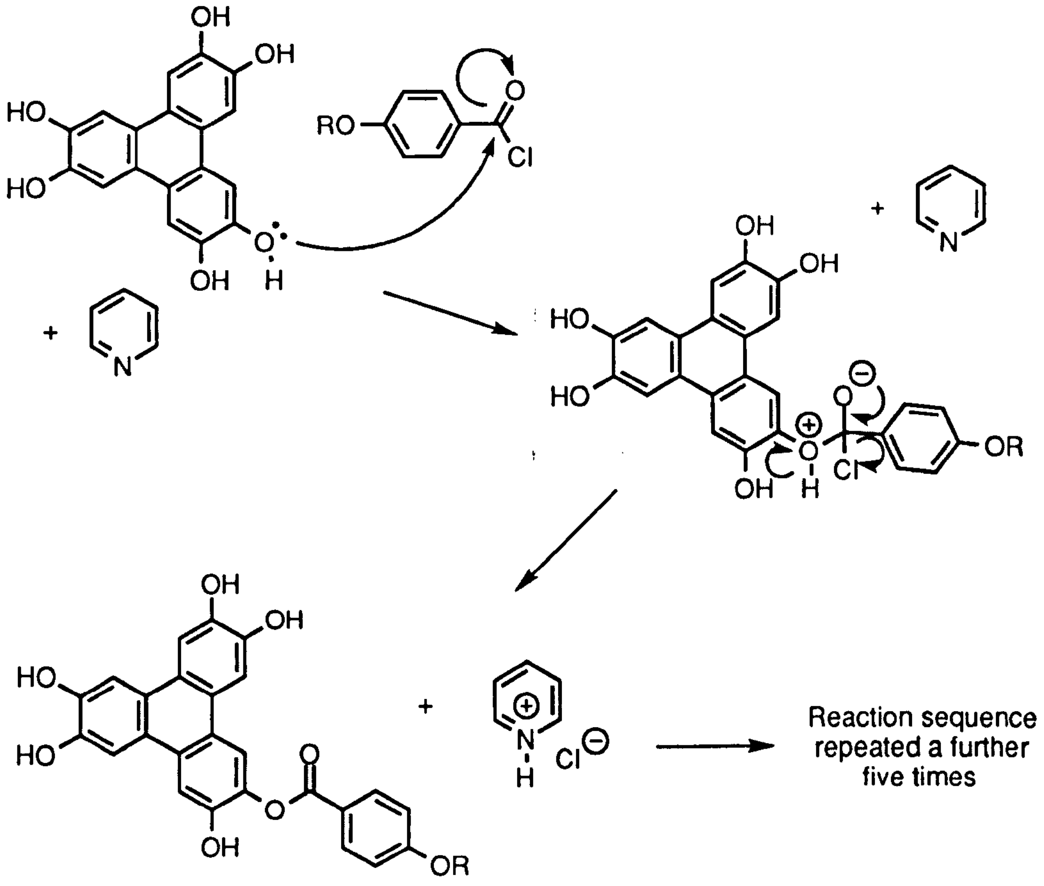


**Figure 11.1 : Mechanism for the acid chloride esterification reaction**

Initial attempts to produce final discotic esters in this research project resulted in very poor yields (*ca.* 10-20%) using the methods of Beattie.[5] His synthetic methodology advised to :

1) use twenty times excess of the acid in comparision to the phenol (**3**),

2) leave the esterification reaction for two hours,

3) use flash chromatography, and

4) use ethanol or *iso*-propyl alcohol in the recrystallizations,

and after six months into the research project, all the aforementioned advice was subsequently ignored.

It did not take long to discover some solutions to the problems posed by Beattie's synthetic methodology. Firstly, the maximum excess of acid needed for the esterification reaction was found to be only ten times. There were two main reasons:

1) Cost - there were only six hydroxy positions on the triphenylene core material (**3**) to be substituted, so it was unnecessary to waste so much extra acid chloride.
2) Cleaning-up - acids **can** travel through a column with the right solvent system and so any more excess acid than is really necessary will cause unwanted extra work-ups.

Secondly, the time allowed by Beattie for the completion of the reaction was only **two** hours. Considering the temperature of the esterification reaction was *ca.* 115 °C (the boiling point of pyridine), this would easily give some indication as to the difficulty in esterifying the acids with the phenol (**3**). Beattie claimed that there was no visible trace of the starting triphenylene phenol **3** left on the TLC plate after two hours. There would be very little final product in the reaction mixture after this length of time; clearly, there would be every permutation between mono- and hexa-substituted triphenylene. So, it was decided to simply leave the esterification reaction to continue for longer; it was soon determined that the optimum length of time for this reaction was **eight** hours. Some reactions were left for longer times again, but their products yields had not increased significantly; the average yield for the triphenylene esters was *ca.* 60%. Occasionally, the addition of DMAP was required to aid the esterification process.

The third point raised, regarding flash chromatography, has already been raised in the first part of this discussion. Acids **can** travel through a column with the right solvent system, and even more so if external pressure is applied as in flash chromatography. Beattie used a twenty times excess of acid in his esterification reactions, and so it is clear that he would have had a difficult time separating his desired final product from the excess acid that was also present. If he was unable to separate the excess acid, his attempts to recrystallize the discotic liquid-crystalline materials would have been obviously hampered.

The problem over separation of the excess acid from the target materials was very simply dealt with. Firstly, and as mentioned previously, the excess of acid was reduced to ten times. Secondly, the use of flash chromatography was discontinued and instead, gravity column chromatography was utilized. The solvent system used was still pure dichloromethane, but the discotic materials were now obtained much more easily and cleaner. For some of the final discotic materials, the solvent system was altered to become more polar; this was achieved by the gradual addition of ethyl acetate to dichloromethane, but no extra complications were encountered with this modification.

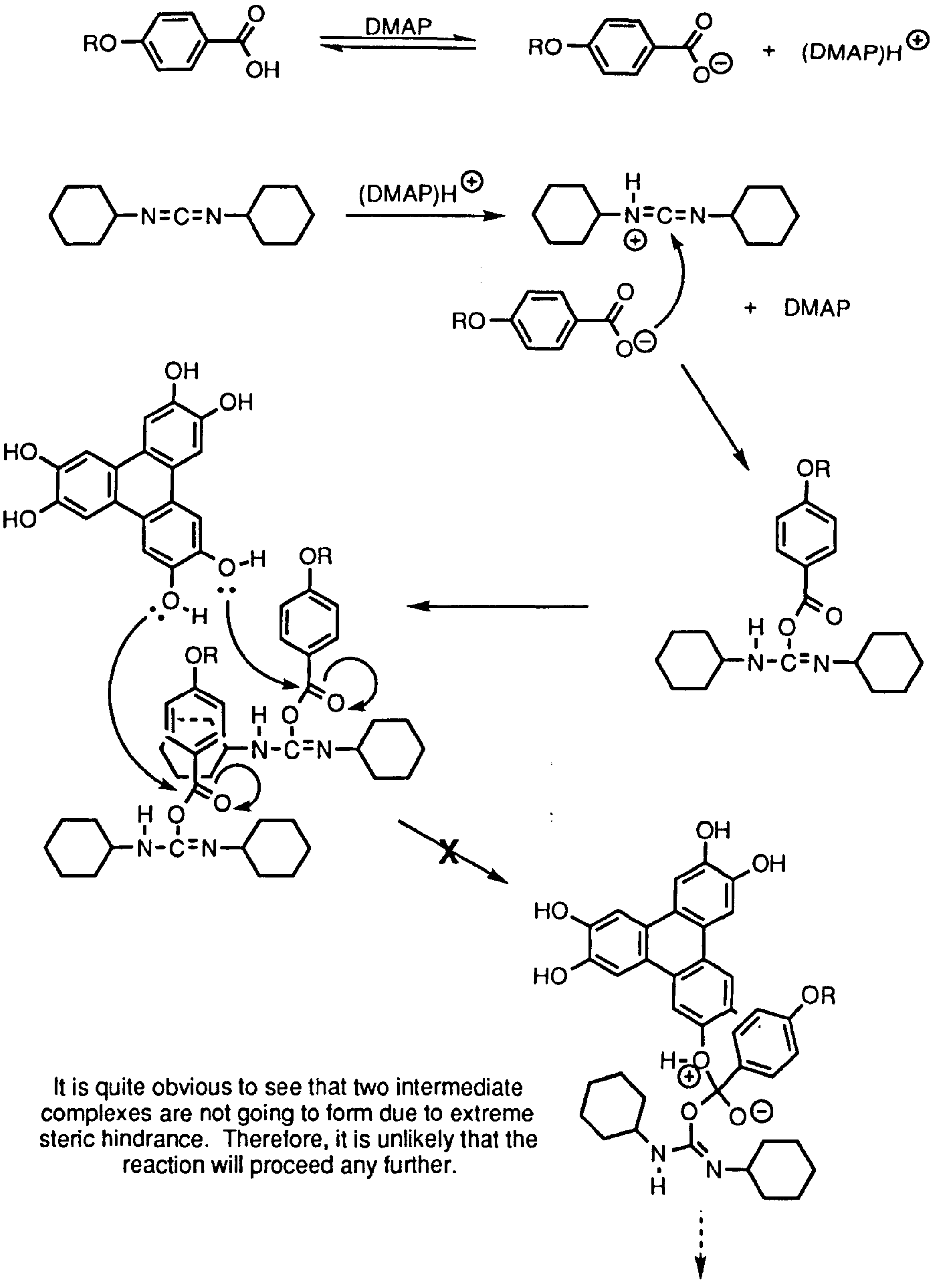
With these purification problems solved, this obviously meant that the recrystallizations would be also relatively problem-free. In all the recrystallizations performed, there was only one solvent system exclusively applied - ethanol with the gradual addition of ethyl acetate. All the final discotic materials in Chapters 3 to 10 were obtained as colourless or off-white crystals or solids. Pure ethanol could **not** dissolve the discotic liquid crystals, and therefore, Beattie could not have obtained his materials in a pure state.

The acid chloride method is not the sole procedure for esterification reactions. Other methods do exist but they were not implemented for reasons that are now discussed.

### *11.2.2 The DCC-DMAP Esterification Reaction*

The use of the *N,N'*-dicyclohexylcarbodiimide (DCC) method for the esterification of acids has been well known.[6] It is a very simple procedure and so well liked. However, for the esterification of acids and alcohols in very sterically-hindered environments, the procedure is not recommended. As illustrated in Figures 11.2 and 11.3, the mechanism for the DCC reaction involves the use of quite a large intermediate complex. To form two such complexes in very close proximity is quite impossible and therefore, the reaction does not proceed to completion.

It has been known that if an alcohol or a phenol used in an esterification does not react with the complex, then the acid will form an anhydride with another acid nearby.[7] In a few trial reactions,[8] it was discovered that the acid anhydrides were formed preferentially with this procedure when the triphenylene phenol **3** was used. This was further evidence to abandon the idea of using the DCC-DMAP esterification reaction to produce the target discotic materials for this research programme.



It is quite obvious to see that two intermediate complexes are not going to form due to extreme steric hindrance. Therefore, it is unlikely that the reaction will proceed any further.

**Figure 11.2 : Mechanism for the DCC-DMAP esterification reaction (Part 1)**

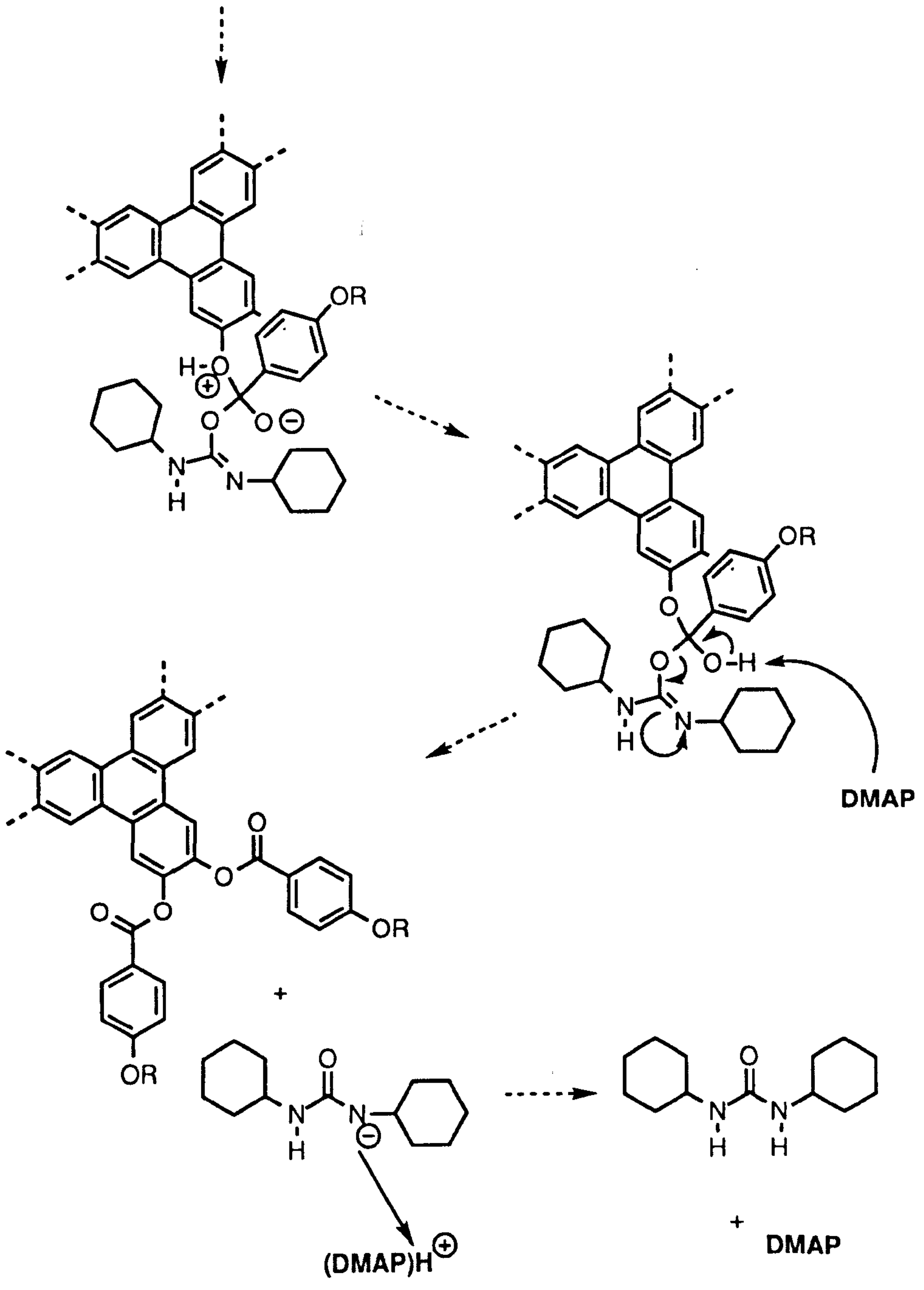
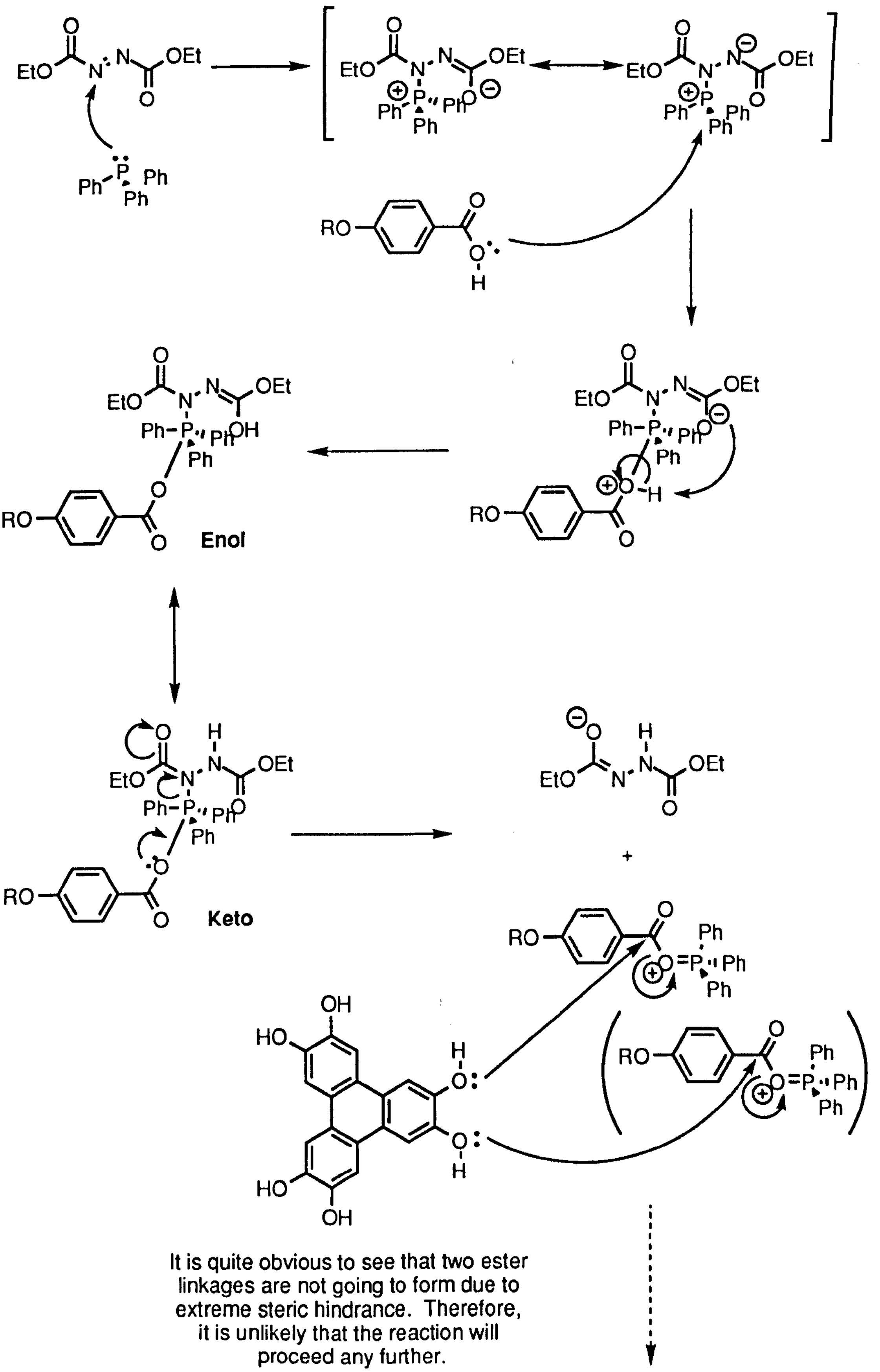


Figure 11.3 : Mechanism for the DCC-DMAP esterification reaction (Part 2)

### *11.2.3 The Mitsunobu or DEAD Esterification Reaction*[9]

This particular procedure is of great importance in esterification or etherification reactions involving the use of chiral alcohols.[10-12] The handedness of the chiral alcohol is completely inverted during the reaction and as yet there has been no reports of racemization occurring.



It is quite obvious to see that two ester linkages are not going to form due to extreme steric hindrance. Therefore, it is unlikely that the reaction will proceed any further.

**Figure 11.4 : Mechanism for the Mitsunobu or DEAD esterification reaction (Part 1)**

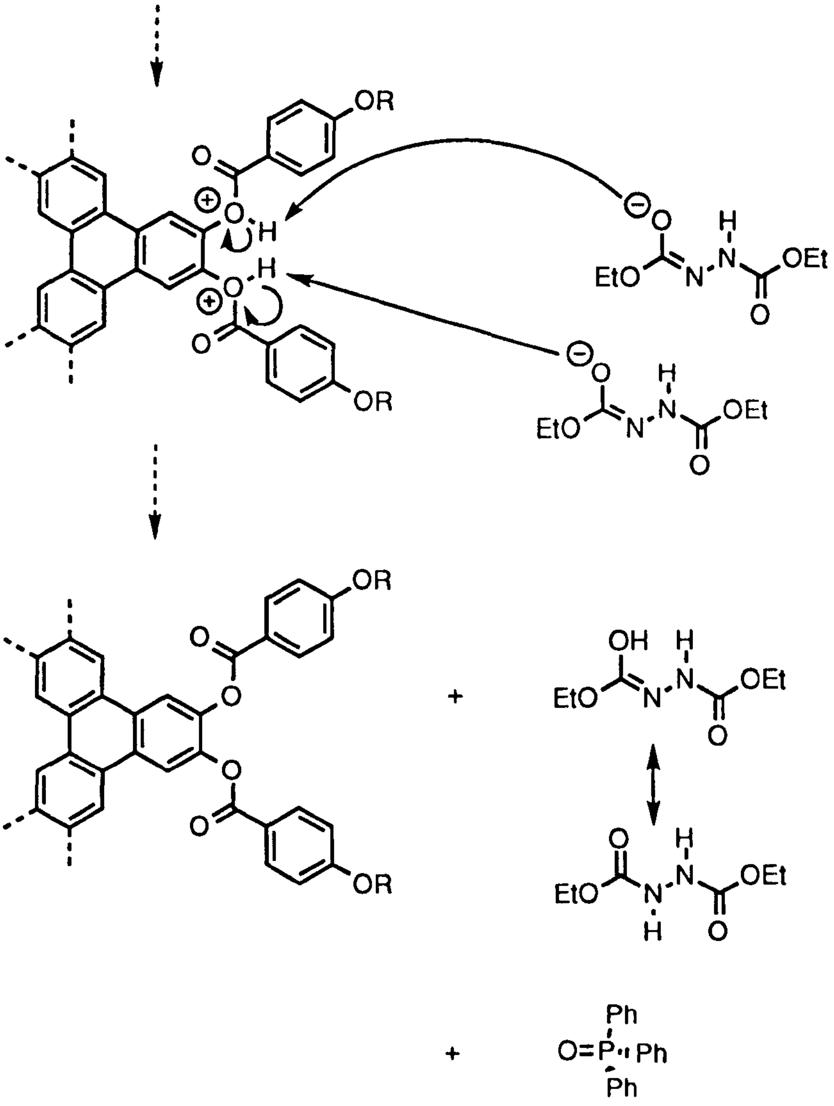


Figure 11.5 : Mechanism for the Mitsunobu or DEAD esterificaton reaction (Part 2)

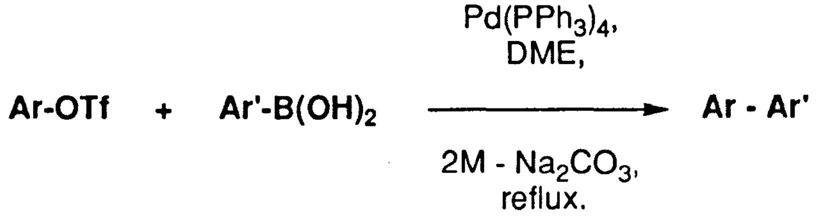
However, the reaction can still be used in the esterification or etherification of achiral systems, but when cost is an issue, the choice of procedure will always be the DCC-DMAP reaction.

The reaction procedure is as straightforward as the DCC-DMAP reaction but, the mechanism for the DEAD reaction also involves the use of quite a large intermediate complex, as illustrated in Figures 11.4 and 11.5. To form two such complexes in very close proximity is quite impossible and therefore, the reaction does not proceed to completion.

In a few trial reactions,[8] it was found that no products were synthesized at all using this reaction. As in the case for the DCC-DMAP reaction, the idea of using the DEAD esterification reaction to produce the target discotic materials for this research programme was abandoned.

### *11.2.4 The Palladium-catalyzed Cross-coupling Reaction*

Palladium-catalyzed cross-coupling reactions between aryl boronic acids and aryl halides have been used extensively at Hull.[13-15] However, cross-coupling reactions can also be performed between arylboronic acids and phenol-triflates,[16] but a three-fold excess of lithium chloride[17,18] has to be added to the basic reagents (as shown in Figure 11.6).



$$\text{Ar-OTf} + \text{Ar'-B(OH)}_2 \xrightarrow[\substack{\text{2M - Na}_2\text{CO}_3\text{,} \\ \text{reflux.}}]{\substack{\text{Pd(PPh}_3\text{)}_4\text{,} \\ \text{DME,}}} \text{Ar - Ar'}$$

**Figure 11.6 : The Triflate-Boronic Acid Palladium-catalyzed Cross-coupling Reaction**

Despite literature reports of the successful use of 2,3,6,7,10,11-hexabromotriphenylene (**7**) in cross-coupling reactions to synthesize alkyne-linked triphenylene discotic liquid crystals,[19-24] the desired final discotic material **217** was not obtained by the standard procedure using arylboronic acids and aryl halides. It is thought that the use of bis(triphenylphosphine)palladium(II) chloride as a catalyst is far superior than tetrakis(triphenylphosphine)palladium(0),[25] and also, the solubility of hexabromotriphenylene (**7**) in DME is very poor whereas triphenylen-2,3,6,7,10,11-hexayl hexakis(triflate) dissolves quite readily. Therefore, the palladium-catalyzed cross-coupling reaction utilized in Chapter 9 to synthesize the directly-linked discogen **217** was the triflate procedure.[16]

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