THE UNIVERSITY OF HULL

THE SYNTHESIS OF NOVEL LIQUID CRYSTAL MATERIALS DESIGNED FOR ELECTRO-OPTIC DISPLAYS

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on

THE SYNTHESIS OF NOVEL LIQUID CRYSTAL MATERIALS DESIGNED FOR ELECTRO-OPTIC DISPLAYS

Liquid crystals represent a fourth state of matter whose properties are intermediate between those of a crystalline solid and an amorphous isotropic liquid. Over recent years, the general area has progressed from a small academic field to the present situation involving worldwide interest from many different standpoints, primarily because of the applications of thermotropic nematic liquid crystals in electro-optic displays.

Nematic liquid crystals are well suited for such applications as they uniquely combine the fluid nature of an isotropic liquid with the anisotropic properties of more ordered systems, and it was within the general area of nematics that this work was undertaken.

The current micro-electronic revolution has meant that the new materials of the early 1970's now present significant problems and limitations relating to their use in some of the more sophisticated display applications. Consequently, there is a great demand for a superior generation of liquid crystals to meet this need.

The broad objectives of this work involved the synthesis of novel materials to try and improve the properties of existing systems, and to carry out this work in a reasonably systematic manner such that the properties (physical and electro-optic) could, as far as possible, be related to molecular structure.

Over twenty-five different structural types were examined, and in many cases useful properties were observed. These structural types were derived from variations in the ring system (benzene, naphthalene, biphenyl, *trans*-cyclohexane, bicyclo(2.2.2) octane), the terminal (alkyl, alkoxy, hydrogen, cyano) and lateral (hydrogen, fluorine) substituents, and the inter-ring linkage (-CH_2O-, single bond, -CO.O-, -CH_2CH_2-). The best of these materials do in fact exhibit superior properties compared with some commercial materials. Furthermore, in some cases, it has been possible to relate the properties to molecular structure, whilst in other cases ideas are developed concerning those properties that are less well understood.

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NOTATION

R = normal-alkyl, unless otherwise specified

( ) = monotropic transition temperature

[ ] = virtual transition temperature

T_{N-I}, etc = temperature of the transition from the nematic state to the isotropic liquid, etc

 = 1,4-disubstituted cyclohexane ring in the *trans*-configuration

PREFACE AND HISTORICAL ASPECTS OF LIQUID CRYSTALS

1.1 *PREFACE*

Over the last ten or fifteen years, the subject of liquid crystals has been transformed from one perhaps little known outside academic circles into one relating to a commercial industry which now has an annual turnover in the multi-million pound bracket. Although liquid crystals themselves have several uses, it is their incorporation in electro-optic display devices that is mainly responsible for the remarkable success of these materials. The commercial outlet for liquid crystal displays, particularly in the form of digital watches and calculators, has meant that the term 'liquid crystal' is now almost as familiar to the layman as it is to a specialist in the field.

However, it should be emphasised that the commercial success of liquid crystal electro-optic display devices is not simply a case of economic production and efficient marketing. The origins of this success may be traced back a little further than that. Liquid crystals themselves have been known for many years, but it is only over the last decade that suitable liquid crystal materials have been synthesised that meet the demands of the modern display device industry. The present interest and volume of work connected with the liquid crystal field are highly unlikely to have been as great without the production of suitable materials by synthetic organic chemists.

In recent years, the tailoring of simple organic molecules to meet the fairly rigorous demands set by the display device manufacturers has been no mean achievement. However, the consequent success of the display devices has been such that the revolutionary new materials of the early 1970's can no longer keep pace with the ever increasing demands of the display device industry to widen the scope of the display systems. From the small, relatively simple displays of the digital watch and calculator, many further applications for liquid crystal displays can now be foreseen. In these, complex alphanumeric data must be presented or stored (for example, when the system is computer controlled) and the display must operate efficiently over a wider temperature range than is presently accessible (for usage in the automobile industry, etc). Also, the economic production of coloured and large area displays will open up markets that are currently of very limited interest to liquid crystal display device manufacturers. In fact, any system which stores or presents information now has relevance to the liquid crystal display industry. Although a long way off, the ultimate goal would be to achieve a liquid crystal, flat panel television display which would be of large area, lightweight and robust, with obvious advantages over the present television system. Currently this can be achieved only with small area screens, with black and white presentation and definite viewing angle problems.

It was with the objective of producing improved liquid crystal materials to meet at least some of the developing requirements of the display industry that the present work was undertaken. The research was therefore aimed at the synthesis of novel liquid crystal materials that were designed to be superior to the existing display materials, so overcoming some of the problems that these earlier materials have encountered and thereby making some of the more sophisticated display devices more commercially viable.

1.2 *HISTORICAL ASPECTS*

For a more detailed treatment of the history of liquid crystals the reader is referred to a review article by Kelker.[1]

The first recorded examples of liquid crystals appeared in the middle of the last century. These early examples were not of the more familiar thermotropic (temperature induced) liquid crystal type, but of lyotropic (solvent induced) liquid crystal type. This is perhaps because scientists at that time were particularly concerned with the problems posed by emulsions and colloidal solutions.

The discovery of thermotropic liquid crystals was centred around observations involving esters of cholesterol. Progress in this area was slow, possibly due to the fact that no suitable theory of atomic and molecular structure existed at that time, coupled with the uncertainty of the chemical composition of these esters. The work of Planer[2] (1861) and Löbisch[3] (1872) was prominent at this time, as well as that of Raymann[4] (1887). A year later, Reinitzer[5] gave the first detailed description of certain striking colour phenomena associated with the cholesteryl esters. Rather puzzled by his observations, he sent his samples to the crystallographer Lehmann, asking for his opinions. A quote from the communication of Reinitzer to Lehmann reads:

> "The substance has two melting points, if it can be expressed in such a manner. At 145.5°C it melts to a cloudy, but fully liquid melt which at 178.5°C suddenly becomes completely clear. On cooling, a violet and blue colour phenomenon appears, which then quickly disappears, leaving the substance cloudy but still liquid. On further cooling, the violet and blue colouration appears again and immediately afterwards the substance solidifies to a white, crystalline mass."

A satisfactory explanation of these observations was still some thirty years away at that time.

Lehmann used several different terms to describe the cloudy, but fluid state: 'flowing crystals'(1889), 'crystalline liquid' (1890), and finally 'liquid crystals' appeared for the first time in 1900.[6] No great advances were made until the 1920's, but the work of Schenck[7] (establishing the homogeneity of the liquid crystal phase), Vorlander[8] (on the synthesis of new materials exhibiting similar characteristics), and Bose[9] (on a theory of the liquid crystal phase which later developed into the so-called 'Swarm' theory) is most noteworthy.

The work of Friedel,[10] published in 1922, was a major step forward in understanding the underlying principles of the liquid crystal phase. He used the descriptive term 'mesophase' (Greek 'mesos' = intermediate), and by the careful optical study of many different mesogens (compounds capable of giving mesophases), he was able to differentiate three different classes of mesophase, and to classify the various microscopic textures that were exhibited by each particular type of mesophase. The three basic types of mesophase he identified were:

(i) a highly viscous, turbid phase, more resembling a crystalline solid than a liquid *(the smectic phase)*;

(ii) a turbid, mobile phase more like a liquid than a solid *(the nematic phase)*;

(iii) a turbid, mobile phase similar to the nematic phase, but in addition, possessing unique optical properties *(the cholesteric phase)*

From his studies, Friedel was also able to reach reliable conclusions about the molecular arrangements within the mesophases, and it is this work which is generally thought of as providing the foundation upon which is built most of present day knowledge concerning the liquid crystalline state.

The work of Friedel certainly clarified the somewhat confused situation surrounding the mesomorphic state at that time, allowing theoretical work to be developed with relative ease. The physicist Oseen[11] developed the early 'Continuum Theory' in 1929 (of which some aspects are still valid today), and this was advanced both by Zocher,[12] and then extensively by Frank[13] some time later.

The following thirty years saw steady, but unspectacular progress (possibly due to the intervention of the War years) in the liquid crystal area as a whole.

The late 1950's and the 1960's saw several advances on both the experimental and theoretical sides of the subject. The theoretical work of Maier and Saupe[14] is of great importance, and the monograph by Gray[15] on the structure and properties of liquid crystals may be regarded as a milestone in the development of the field. The electro-optic effect utilising liquid crystals, as devised by Schadt and Helfrich[16] in the early 1970's, was largely responsible for the huge commercial interest created in liquid crystal display devices, such that when suitable materials became available a year or so later, the field as a whole expanded at a colossal rate, and it has been increasing in scope and activity ever since.

INTRODUCTION

2.1 *TYPES OF MESOPHASE*

A simple explanation for the existence of mesomorphism may be obtained by assuming that, in general, the required molecular structure is of a long, linear and rigid nature, as represented by the ellipsoids in Figure 1.

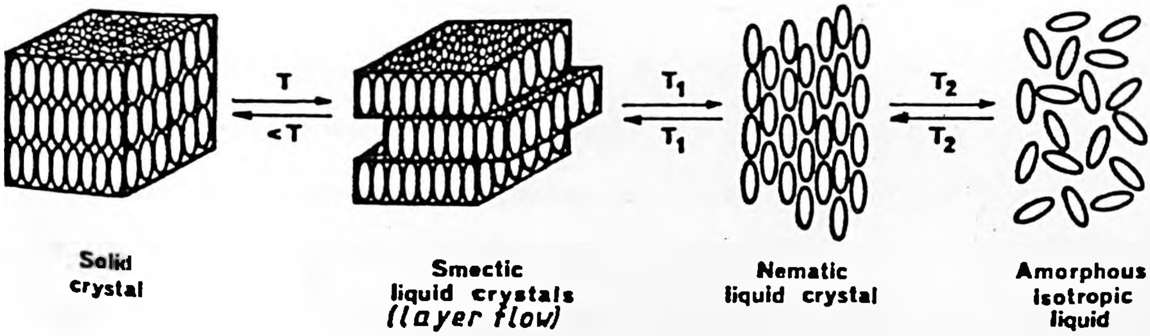


FIGURE 1

Sequence of possible changes on heating a layer crystal lattice composed of elongated molecules

In the crystalline state, the molecules assume the lowest energy configuration, resulting in a regularly ordered, efficiently packed crystal where the molecules execute small vibrations about fixed lattice points, without molecular rotation. Frequently, this lattice is of a layer type. Two different types of intermolecular force (similar in nature, but differing in potential) may then be associated with such a system, ie, the forces between the ends of the molecules (the terminal forces) and those between the sides of the molecules (the lateral forces). Due to the molecular shape and crystal packing, these two types of intermolecular interaction are not necessarily equivalent, and the terminal forces are generally found to be weaker than the lateral forces. If energy is supplied to the crystal (ie, by heating), a certain temperature is reached at which the terminal forces are broken down, but the lateral forces are still sufficiently strong to maintain a layer arrangement. This produces two-dimensional layers of molecules which, in some cases at least, are free to slide over one another (the smectic mesophase). Further heating of the sample may produce the isotropic liquid by overcoming the residual lateral forces. However, if these lateral forces are simply further weakened, but the molecules retain a statistically parallel arrangement, the nematic mesophase is produced. This phase has one-dimensional order. It need not necessarily be produced from a smectic mesophase, as it may also be obtained directly from the crystalline solid. As before, further heating of the nematic mesophase will give rise to the isotropic liquid, which is characterised by relatively unhindered molecular rotation and no long range order.

A third type of mesophase (the cholesteric mesophase) is produced in a similar manner to the nematic phase, except that here the system contains molecules having an optically active centre.

In the great majority of cases, the transitions (mesophase-mesophase and mesophase-isotropic liquid) are precisely reversible. This is an important characteristic of liquid crystal transitions and is very useful in helping to prove the existence of a mesophase. The crystalline solid-mesophase transition is not usually reversible due to the phenomenon of supercooling. Consequently, it is possible for a compound to exhibit one or several monotropic mesophases (observed only on cooling cycles), as opposed to the more common enantiotropic mesophases (observed both on heating and cooling cycles).

The intermolecular interactions that are primarily responsible for the formation of liquid crystal mesophases consist of three general types and involve:

(i) direct dipole-dipole interactions, due to the direct interaction of permanent molecular dipoles;

(ii) induced-dipole interactions, arising from the mutual polarisation of the molecules by virtue of their permanent dipoles;

(iii) dispersion (London) forces, produced by the spontaneous oscillation of the electron clouds of the molecules and resulting in nett attractive interactions between instantaneous dipoles.

In addition to these interactions, other specific intermolecular attractions and also repulsions may be significant. Important amongst these are hydrogen bonding and steric factors.

The three main types of thermotropic mesophase will now be discussed in a more detailed manner.

2.1.1 *The Smectic Mesophase*

Only a brief account of the markedly polymorphic smectic mesophase will be given here, as most of this work has centred around the development of novel nematogenic materials. Further details can be found in the texts by Demus and Richter,[17] and Gray and Goodby.[18]

The smectic phase was first noted by Grandjean,[19] and more extensively investigated by Friedel who likened the smectic phase (smectic A as it later turned out) to the droplets produced by the evaporation of soap films, and hence derived the name 'smectic', from smectos (Greek) = soap-like.

At first, the smectic phase was believed to exist only as a single phase, but gradually evidence was obtained to show that several different types of smectic phase exist. The number of smectic polymorphic forms has grown, particularly over the last ten or fifteen years, such that there are now eleven different sub-classes of smectic mesophase established beyond doubt, whilst one or two others remain to be verified.[20]

Each different phase-type is unambiguously defined by a lettered subscript following the word *smectic*, usually abbreviated to the letter *S*, ie, S_A, S_B, . . . S_J.[21] No single compound has been found that exhibits all of the eleven possible smectic phases, six being the most so far observed.

As previously mentioned, smectic mesophases consist of layers of molecules and may therefore be regarded as two-dimensional solids. Indeed, some smectic phases appear to be very similar to the crystalline state, and correlations between the ends of molecules in neighbouring layers persist to varying extents, ie, weakening of the terminal interactions between molecules is minimal in these cases. In these instances, only an experienced observer can distinguish microscopically between the ordered smectic phase and the crystalline solid. A similar situation exists in trying to differentiate between some of the different smectic phase-types, and this situation can be further complicated by the fact that each phase may adopt one of several different textures. Examples of these textures are the homeotropic texture (where the molecules are aligned perpendicular to the surfaces of the thin film under observation), the focal-conic or fan texture (where the molecules lie in regions filled by equidistant parallel, but curved strata which give rise to characteristic ellipsoids and hyperbolae), the related polygonal texture, the mosaic texture (where individual small areas have a characteristic birefringence), and the *schlieren* texture (which has a streaky, oily appearance). Development of certain smectic phases from the isotropic liquid, eg, S_A, S_C, occurs through the formation of elongated, birefringent particles called bâtonnets.[10] These distinctive ornate particles have rounded surfaces and are the precursors of the focal-conic domains. The particular texture that is produced depends on several factors, such as the method of sample preparation (cleaning of the glass), the sample thickness, the rate of heating/cooling used, the preceding state from which the sample was produced, etc.

Optical microscopy is very important in the area of smectic liquid crystals, but also extremely useful are the techniques of miscibility and differential scanning calorimetry (DSC). A smectic compound of undetermined phase-type may be classified by the use of miscibility experiments as originated by Sackmann and Demus.[22] If two smectic phases have complete miscibility over the whole composition range, in a continuous manner, then they belong to the same smectic class. Thus, the material exhibiting an unknown smectic phase is mixed in a range of compositions with a standard of known smectic classification to see if over some suitably selected temperature range the two phases are compatible. Note that if complete miscibility is not observed, this does not prove that the smectic phases are different. Solubility factors can obviously affect the miscibility of the compounds.

As the majority of mesophase to mesophase transitions (smectic-smectic and smectic-nematic) are reversible and involve an energy change (albeit small in some cases), the use of DSC for detecting 'hidden' phases is very valuable. Not only can DSC prove the existence of phases that are difficult to observe directly, but melting points may be distinguished from internal mesophase transitions due to the phenomenon of supercooling. Although DSC gives information on phase transitions, no information is given on the types of phase involved. These have to be established by the use of optical microscopy and miscibility studies, or of course by X-ray methods.

Consequently, the complete analysis of a smectic liquid crystal (especially in the case of a compound with several different smectic phases) is only possible by using the three techniques (DSC, optical microscopy, and miscibility) hand in hand.

The molecular structure of the different smectic phase-types varies from being reasonably straightforward to being fairly involved. The use of X-ray techniques in structure elucidation is particularly important, if not essential, in this respect. In fact, for some of the less common phases the molecular structure is not completely understood and much remains to be done. The symmetry of packing of the molecules in the phases is often fairly simple, eg, hexagonal or cubic, and the molecules may be arranged in monolayers or bilayers, whilst being orthogonal or tilted with respect to the layer planes. The structure of two of the more common smectic phases (S_A and S_B) will now be briefly described, as these were the only smectic mesophases encountered during the course of this work.

The S_A phase is the least ordered of all the smectic structures and consists of layers of molecules with their molecular long axes perpendicular to the layer planes. The centres of gravity of the molecules are not ordered within each layer. The most common texture of the S_A phase is the focal-conic texture as shown in Plate 1.

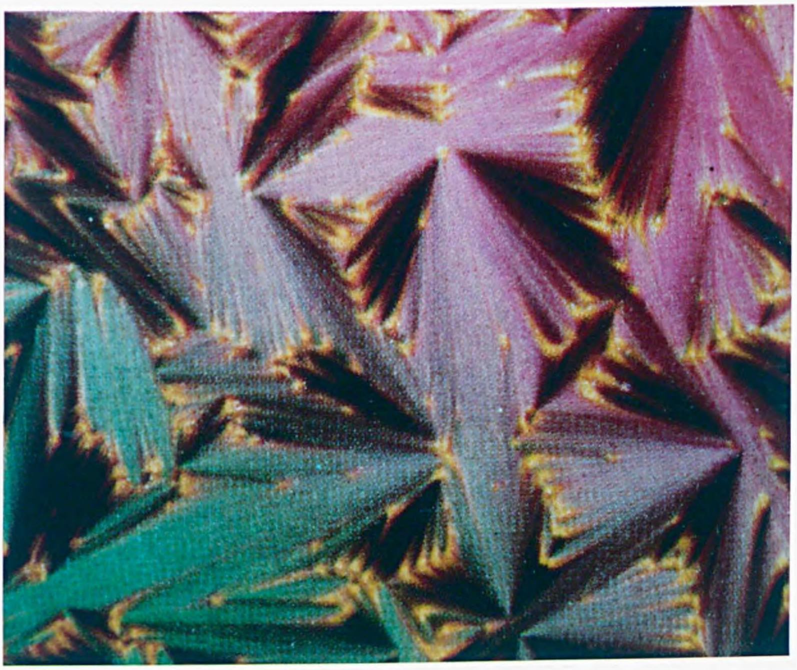


PLATE 1

The focal-conic texture of the S_A mesophase

The focal-conic domains are defined by ellipses of various shapes and by hyperbolae of various eccentricities, each domain being filled by a series of concentric, equidistant, parallel, curved strata, such that the molecules lie with their long axes normal to the layers.

Often this focal-conic texture is formed from bâtonnets as the phase is cooled from the isotropic liquid.

The related polygonal texture may be observed in certain cases, ie, in relatively thick sample preparations. Here, ellipses of various size are packed together, such that they touch tangentially. The observed film actually consists of focal-conic domains packed together with their bases (the ellipses) on the upper and lower surfaces, and their apices on the lower and upper surfaces respectively.

The optically extinct S_A homeotropic texture may also be observed. This texture is produced when the molecules are arranged perpendicular to the glass surfaces, and usually occurs when the glass surfaces are either scrupulously clean or have been pre-treated in some manner, eg, with a thin film of lecithin.

The molecules in the S_B phase are arranged in layers, similar to those of the S_A phase, but now the centres of gravity of the molecules within the layers are ordered in a hexagonally close packed structure. The molecules themselves lie with their long axes normal to the layer planes.

Two types of S_B phase are now recognised:

(i) in which the hexagonal arrangement is correlated over a large number of layers;

(ii) in which there is no correlation of structure from one layer to another.

S_B phases of type (i) are called crystal B phases, S_B(cryst), and those of type (ii) are termed hexatic or liquid crystal S_B phases, S_B(hex).

The most common textures adopted by the S_B phase are the focal-conic texture (similar, but not identical to that of the corresponding S_A texture) and the mosaic texture. Plate 2 shows the mosaic texture, which is the natural texture, ie, that formed on cooling an isotropic liquid.

The molecules within each particular birefringent area lie in plane layers with a uniform orientation of the director, and the differences in birefringence from one area to another are due to the different orientations of the directors from area to area. This arises from the different angles made by the layer planes with respect to the glass surfaces.

PLATE 2

The mosaic texture of the S_B mesophase

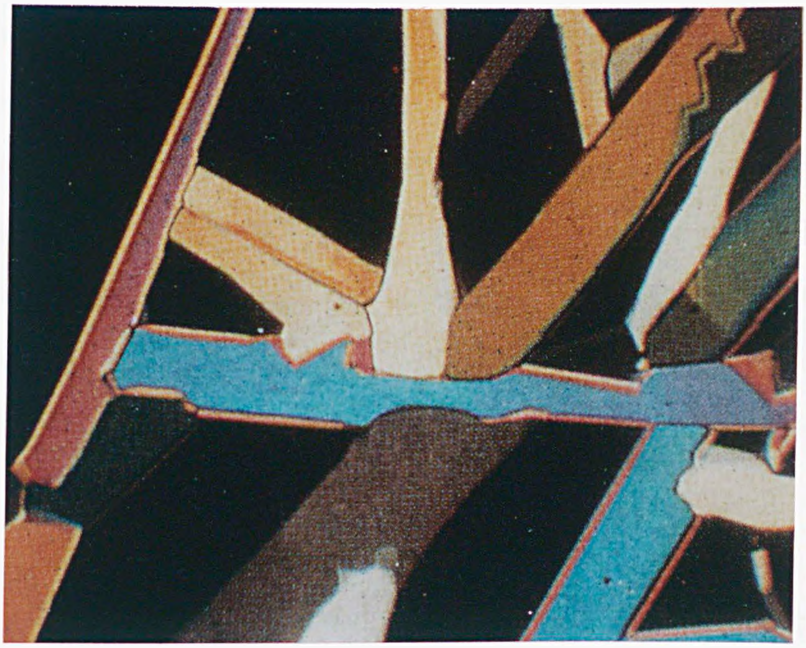


PLATE 3

The rod-like texture of the S_B mesophase

Most of the other textures exhibited by the S_B phase (eg, homeotropic, focal-conic, polygonal) are usually paramorphotic textures imposed by other preceding phases (often S_A).

Plate 3 shows the characteristic rod-like particles[23] observed on cooling to obtain the S_B phases of many of the S_B materials examined during the course of this work. On cooling, the long, thin rods (not bâtonnets) quickly form from the nematic or isotropic liquid. They then spread out and eventually cover the whole field of view.

From studies of many different polymorphic smectogens, a general order of thermal stability has been reached for the different phase-types, ie,

$$S_H < S_E < S_G < S_J < S_F < S_B(\text{cryst}) < S_I < S_B(\text{hex}) < S_C < S_D < S_A < \text{Ch or N}$$

This sequence is useful in certain cases. For example, suppose a trimorphic smectic compound has been shown to exhibit a S_A phase, and also a S_B(hex) phase which is the least thermally stable form. Then the order of thermal stability tells us that the remaining unclassified phase is either S_C or S_D. Microscopy and miscibility experiments may then be carried out to establish the exact nature of this phase.

With reference to a rod-like molecular structure of the form

unlike the situation for nematic and cholesteric liquid crystals, it has not been possible to establish a terminal group (X) efficiency order for the promotion of either smectic properties in general, or each of the various polymorphic smectic forms. Too few systems have yet been investigated to be sure of either the efficiency order relating to a given smectic phase-type, or if the order changes generally with the smectic phase-type. The fact that order inversions have been found with X = -CN and $-OCH_3$ in different systems, relative to the behaviour of the unsubstituted compounds, with X = H,[24] illustrates that the effects are rather unpredictable.

Due to their relatively viscous nature, smectic liquid crystals have not found the widespread applications of their nematic, and to a lesser extent cholesteric, counterparts. The most promising application to date is a smectic laser addressed display device which requires a S_A material. This particular use for smectic materials will be discussed more fully, along with the other electro-optical effects of liquid crystals, in Section 2.2.1.

2.1.2 *The Nematic Mesophase*

The nematic phase is perhaps the simplest, yet most important mesomorphic state, as it is used extensively in the electro-optic display devices that are now commonplace on a worldwide basis.

The phase itself is much less viscous than the smectic state and can be regarded more as a liquid than a crystalline solid. The molecules themselves pack together in the lowest energy form, which, because of their geometry, is one in which the molecules lie with their long axes in one particular direction. There is no ordering of the molecular centres of gravity, so the nematic phase has only one-dimensional ordering.

Unlike the smectic phase, no evidence has been found for the existence of any polymorphic forms of the phase. As a result of this, coupled with the lower ordering of the system, the nematic phase is much simpler to deal with than the smectic phase from both the experimental and theoretical standpoints.

The first theory of the nematic phase was proposed by Bose[9] in 1909 and is termed the Swarm Theory. Here, the molecules were thought to form aggregates (termed swarms) of up to one million molecules all lying parallel to one another. However, sound evidence for the existence of swarms has never been obtained and the theory was superseded by the Continuum Theory proposed by Zocher[12] and Oseen[11] towards the end of the 1920's; later the theory was simplified by Frank.[13] Much of this theory is still valid today, and it states that at any point in the nematic bulk, there is a certain preferred direction for the orientation of the long axes of the molecules (the director). However, the director is not fixed throughout the bulk and is considered to vary, but continuously, throughout the nematic phase, except at singularities where the nematic director suddenly changes its direction of orientation. Thus, the nematic phase is anisotropic, effectively combining order and disorder, and having a very mobile, elastic construction.

When viewed microscopically, a sample of the nematic phase mounted between crossed polarisers appears birefringent (unless it is homeotropic) and may adopt one of several textures. This fact, coupled with evidence from X-ray experiments that the nematic phase produces diffraction patterns qualitatively similar to those obtained for isotropic liquids, again illustrates the intermediate characteristics of the phase when compared with those of a solid and a liquid.

Generally, the same sort of factors that govern the nature of a smectic texture also determine which nematic texture is observed. Plate 4 shows the threaded nematic texture. This is one of the least common textures and is so named because of the thin, dark lines (threads) that are present in the preparation. In this case, the thread in the centre is joined to two molecular discontinuity lines in the nematic bulk. Their exact nature is not fully understood, and the threads (optical discontinuities) may either move freely within the sample or have one or both ends fixed to the cell surface. New threads are constantly generated within the nematic sample, whilst existing threads may disappear. This texture is often observed with relatively thick sample preparations.

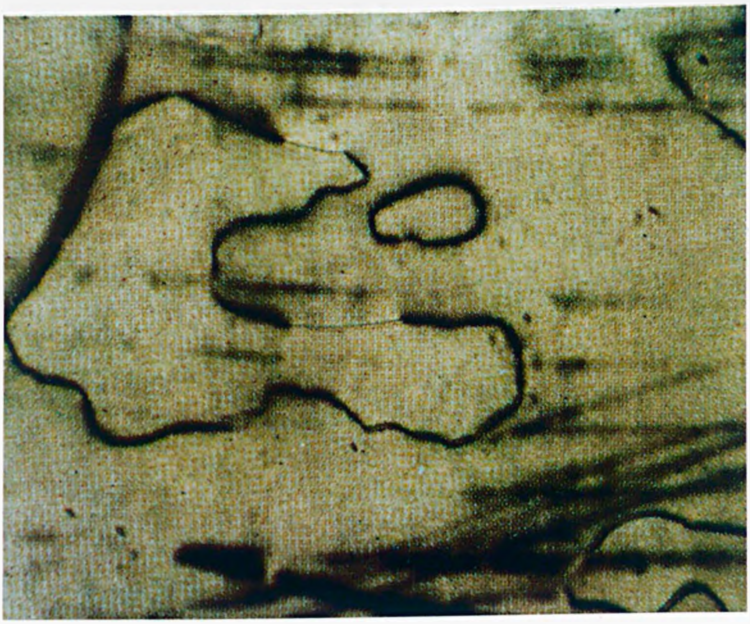


PLATE 4

The threaded texture of the nematic mesophase

The marbled texture (see Plate 5) is often produced with mixtures of nematogens. The dark areas are homeotropic or near-homeotropic regions where the optical axis (the director or direction of the molecular long axes) is normal to the supporting surfaces, ie, along the direction of viewing, so producing optical extinction. The coloured areas have varying orientations of the optical axis relative to the plane of the nematic film.

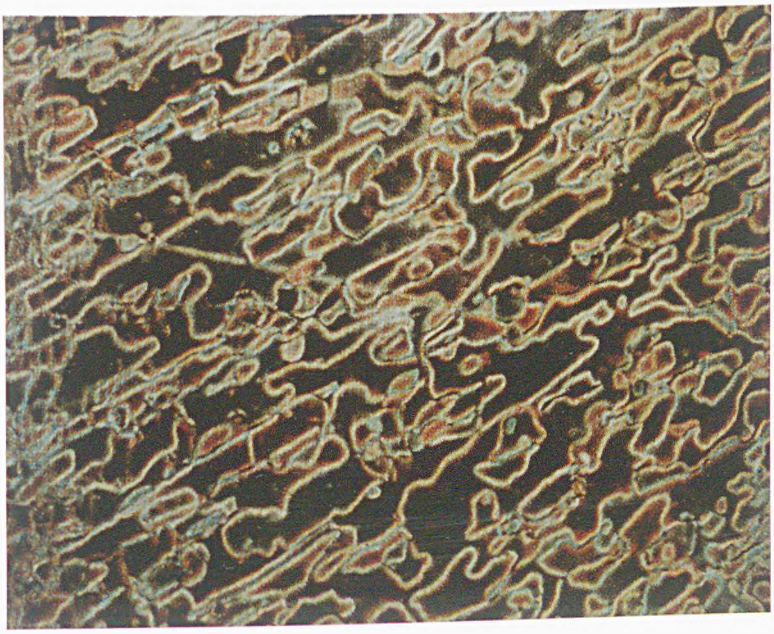


PLATE 5

The marbled texture of the nematic mesophase

When the nematic phase is produced by slowly cooling the isotropic liquid, small characteristic droplets of the mesophase appear as the system passes through a narrow two-phase region (see Plate 6). These spherical droplets have a cross of extinction, frequently distorted, which remains static even when the preparation is rotated, showing

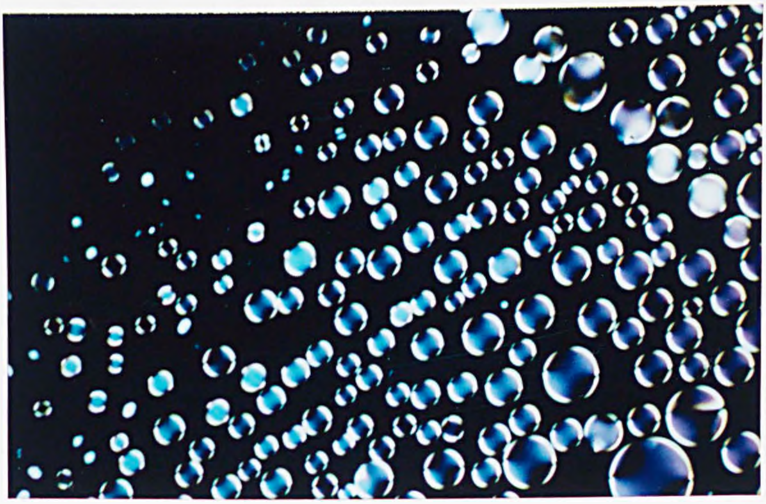


PLATE 6

Nematic droplets obtained on cooling an isotropic liquid

that the droplets have a spherically symmetric arrangement of the rod-like molecules, ie, radiating from the droplet centre. These droplets quickly coalesce on cooling, as the rest of the liquid becomes nematic, and the phase often adopts the *schlieren* texture, as shown in Plate 7. This texture has a fairly even birefringence which changes only gradually across the preparation. The texture is characterised by point singularities which are observed as tiny black spots. These may in fact be insoluble dust particles present in the sample and around which the nematic structure is radiating or circulating. These singularities form the focal points for either one or two pairs of distinctive black brushes of extinction. Often the nematic phase, and particularly the *schlieren* texture, can be seen to be in continuous, vibrational, Brownian motion. This effect is usually referred to as 'shimmering'.

Other textures that may be observed for the nematic phase include the optically extinct homeotropic texture, and the homogeneous

PLATE 7

The schlieren *texture of the nematic mesophase*

texture (see Plate 8) in which the molecular long axes (and the optical axis) are normal to the direction of viewing.

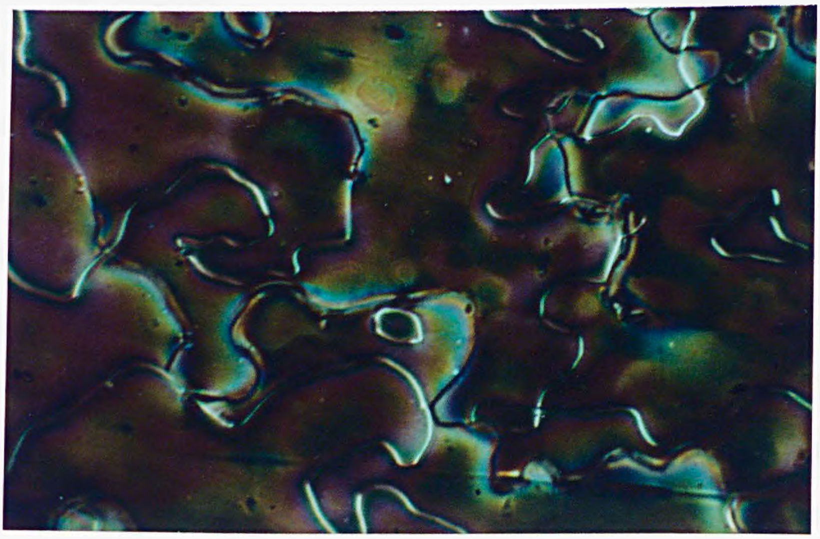


PLATE 8

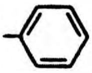
The homogeneous texture of the nematic mesophase

Although optically extinct, the homeotropic phase may be distinguished from a homeotropic smectic or an isotropic phase by lightly disturbing the sample. This produces immediate flashes of light as the director (the optical axis) is momentarily disrupted from its orientation normal to the plane of the preparation. This effect is observed neither in the more viscous smectic textures nor, obviously, in the isotropic liquid.

Transitions involving the change from the nematic phase to either a smectic phase or the isotropic liquid are temperature reversible. Only transitions to the highly ordered crystalline solid involve significant supercooling effects. It is also worth noting that both the sharpness of the transition (the temperature range over which the transition occurs) and the preciseness of reversibility of the transition give a good indication as to the purity of the sample, ie, the sharper and more precisely reversible the transition is, the purer is the sample.

It is possible to produce certain nematic textures (eg, the homogeneous and the homeotropic textures) very precisely and over large areas and volumes of phase by the use of either magnetic or electric fields. Moreover, these uniformly oriented states may be rapidly interchanged, by application of suitable external fields, due to the fluid, mobile character of the nematic phase. It is these properties that provide the basis of the electro-optic display devices in which nematic liquid crystals feature, and which are to be discussed more fully in Section 2.2.1.

Most terminal substituents tend to affect the anisotropy of the intermolecular attractions favourably such that, relative to the parent unsubstituted compound, the nematic thermal stability (the temperature of the nematic-isotropic transition - T_{N-I}) is raised. The general nature of this effect allows one to quote the following general order of nematic terminal group efficiency:

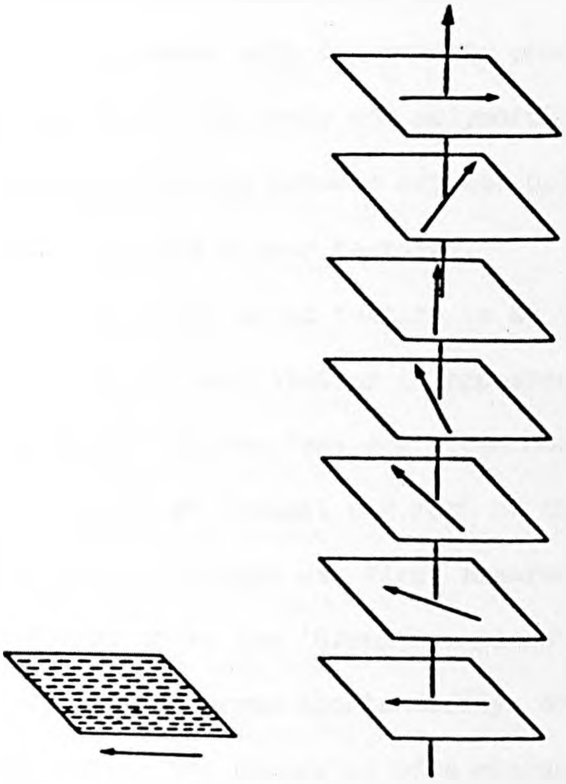

$$> -NHCOCH_3 > -CN > -OCH_3 > -NO_2 > -Cl > -Br \simeq -N(CH_3)_2$$
$$> -CH_3 > -F > -H$$

This order of decreasing T_{N-I} values is an *average* efficiency order derived from studies of many related and unrelated materials, and it is possible to find some examples of exceptions and deviations from the order. In general, the smallest increases in T_{N-I} value are obtained with small, weakly conjugating substituents (eg, halogeno, $-CH_3$) or those with an off-axis dipole (eg, $-N(CH_3)_2$), whilst the largest effects are obtained with substituents capable of enhancing conjugative interactions in the molecule, and hence the axial molecular polarisability (eg, phenyl, -CN).

2.1.3 *The Cholesteric Mesophase*

The study of cholesteric liquid crystals formed little or no part of this work, so as with the smectic mesophase, this discussion will be reasonably brief.

The cholesteric mesophase is so named because the first compounds known to exhibit this phase were esters of cholesterol. Derivatives of other naturally occurring sterols also exhibit this phase, but many other structurally unrelated compounds have also been found to be cholesterogens. In fact, the only pre-requisites for the formation of a cholesteric mesophase are that the molecules should have an elongated structure compatible with nematic behaviour and they should possess an optically active (ie, chiral or asymmetric) centre. This asymmetry of the molecules produces a twisted, helical-like structure due to the asymmetry of the intermolecular polar and steric effects, and it is this helical structure which is responsible for producing the unique physical (mainly optical) properties of the cholesteric phase. The cholesteric phase is therefore a spontaneously twisted nematic phase.



The helical, sheet-like arrangement of molecules in the cholesteric mesophase, showing a half-pitch length; the arrow in each sheet denotes the director

FIGURE 2

Figure 2 shows the general principle behind the formation of the cholesteric phase. Each sheet consists of molecules aligned in the same direction, in much the same way as for the nematic mesophase.

However, in the cholesteric mesophase, the molecular directors in successive sheets are turned progressively through a similar, small angle. This produces a helical arrangement of the molecular long axes, the helical axis being normal to the molecular director; it is this helical axis which is called the cholesteric director. This twisted structure is responsible for the special optical rotary properties of the cholesteric phase. For example, the specific rotation is approximately 15 min arc per sheet (or ~1000^0 per mm) which may be compared with the value for normal organic compounds which rarely exceeds 300^0 mm^{-1}.

In common with the nematic phase, the cholesteric phase has been found to exhibit only one polymorphic form; two main textures are usually observed between crossed polarisers. These are the focal-conic and the planar textures.

The focal-conic texture is by far the most common texture of the two. It is very similar in appearance to the focal-conic texture of smectics, but the fans are often much smaller.

Although Friedel did much of the early work on cholesterogens, the planar texture was first observed by Grandjean and is often referred to as the 'Grandjean plane' texture (see Plate 9). It is only rarely formed spontaneously, and must usually be induced by disturbing the coverslip of a microscope slide preparation. This encourages the molecules to lie flat to the glass with the cholesteric director normal to the cell surfaces. The texture then has a fairly even birefringence when viewed between crossed polarisers, with characteristic lines of structural discontinuity criss-crossing the preparation.

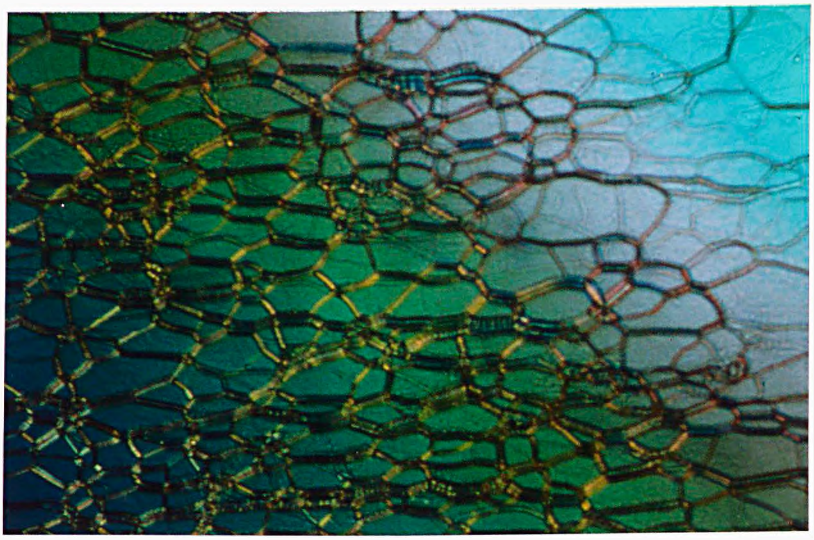


PLATE 9

The 'Grandjean plane' texture of the cholesteric mesophase

Cholesteric liquid crystals are of great interest, because, in the plane texture, the phase can reflect a particular wavelength of light. If this wavelength is within the region of the visible spectrum, it is observed as a particular colour. The selection of the particular wavelength is dependent upon the pitch length of the cholesteric phase (which must be of the order of the wavelength of visible light). The temperature of the sample is also very important, as the pitch length is often temperature dependent. These principles are discussed more fully in Section 2.2.2.

It should be pointed out that the formation of a cholesteric mesophase may also be achieved by doping a nematic phase with only a small amount, eg, less than 5%, of a cholesterogen or even a non-mesogen that is optically active. Apparently, the presence of such quantities of a chiral additive is enough to force the system to adopt the helical structure, which at such low concentrations will have a long pitch. This shows that the nematic and cholesteric phases have very similar structures. Further evidence of this is provided by the work of Gray[25] and Billard.[26] The resolved optical isomers of a racemic compound were shown each to have the same cholesteric properties, but with opposite twist senses, whilst the racemic system itself was nematic. Furthermore, the identical cholesteric to isotropic liquid transition temperatures of the optical isomers were found to be the same as the nematic to isotropic liquid transition temperature of the racemic system.

Cholesteric liquid crystals are therefore frequently regarded as simply nematic liquid crystals possessing a spontaneous structural twist. Further support for this is given by the following results. As the T_{Ch-I} value for an optically active isomer is identical to the T_{N-I} value for the racemic modification, it might be expected that the terminal group efficiency order for promoting T_{Ch-I} relative to that for the unsubstituted compound might be similar to that for the promotion of T_{N-I}. Although fewer cholesteric systems have been investigated, such a relationship has in fact been found,[27] so that the general efficiency for terminal substituents in promoting T_{Ch-I} values is given by the order on page 23.

However, it is perhaps unwise to take the comparison between these two mesophases too far, for we should remember that the cholesteric phase also has properties in common with the smectic phase (eg, each may exhibit the focal-conic texture). This really emphasises that close relationships exist for all of the three main types of thermotropic mesophase, but since individually they retain their own very characteristic properties, it is probably best to consider each as a separate entity.

2.1.4 *Additional Classes of Mesophase*

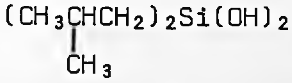
In addition to the three main classes of mesophase just described, there exist several other forms of matter that have structures intermediate between those of crystalline solids and the disorder of an isotropic phase. Examples of these mesophases are provided by lyotropic liquid crystals, plastic crystals, discotic (or columnar) liquid crystals, and polymeric liquid crystals. A brief description of each will now be given.

Lyotropic liquid crystals are produced by the action of solvent (eg, water) in limited quantity on the crystalline lattices of suitable materials (amphiphiles). By varying the amount of solvent, different lyotropic mesophases may be produced, before an isotropic solution is obtained. In addition, these phases are temperature dependent so it can be appreciated that lyotropic liquid crystals are very complex systems.

Soaps provide examples of lyotropic liquid crystals, which consist of alkali metal salts of long chain carboxylic acids with water as the solvent. An understanding of lyotropic liquid crystals is therefore of fundamental importance in the detergent industry and lyotropic liquid crystals are also very important because of their vital role in biological systems (biological membranes, solutions of bile acids, etc). However, further discussion on this subject is beyond the scope of the present work and the reader is referred to the literature for further information upon the subject.[28-31]

Plastic crystals are formed by certain molecules that have a roughly spherical molecular geometry. The molecules are organic in nature (non-amphiphilic) and, after melting has occurred, these still occupy fixed lattice positions, usually in a cubic arrangement. However, the molecules now have freedom of rotation. Thus, the phase, which is optically isotropic, has no orientational order, but does possess positional order of the molecules. Examples of compounds exhibiting a plastic crystal mesophase are cyclohexane, $C(CH_3)_4$, CCl_4, camphor, and adamantane.

Discotic liquid crystals were first recorded in 1977 by Chandrasekhar[32] as a new family of thermotropic liquid crystals. The compounds studied were fully esterified derivatives of hexahydroxybenzene, whose molecules stacked flat on top of one another giving columns which then formed a hexagonal array. This produces a liquid crystal phase different from those of the more conventional type and having distinctive optical textures. In fact, similar optical textures had been reported for the compound di-isobutylsilanediol



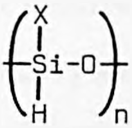
$$(\mathrm{CH_3}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}\mathrm{HCH_2})_2\mathrm{Si(OH)_2}$$

over twenty years earlier,[33,34] but the nature of the phase remained an enigma until the publication of Chandrasekhar's work. It was then realised[35] that the phase was discotic, dimers of di-isobutylsilanediol forming the disc-like units of the columns.

Several other molecules possessing a disc-like structure have now been shown to form phases with similar properties,[36] and in addition to different polymorphic forms of the columnar discotic phase, discotic nematics and cholesterics are now recognised. Future developments in this area of liquid crystals are awaited with great interest.

The molecules of polymeric liquid crystals are comprised either of a long polymeric main chain incorporating mesogenic units linked together by flexible spacer units or of a fairly flexible backbone to which regularly spaced mesogenic side groups are attached by means of flexible spacer groups.

The latter type is probably the more important. The backbone is often a polymer of a substituted (eg, X = methyl) hydrogensiloxane



$$\left(-\overset{\overset{X}{|}}{\underset{\underset{H}{|}}{\mathrm{Si}}}-O- \right)_n$$

in which the reactive hydrogen atoms are regularly distributed along the backbone. The mesogenic side groups are often very similar in structure to conventional liquid crystals, except that some sort of reactive function is required to attach these groups to the backbone by chemical reaction with the reactive hydrogen atoms. Usually, this function is a double bond situated terminally in an alkylene chain, the chain acting as a flexible spacer between the backbone and the core structure of the side group.

The mesophases obtained by heating polymeric liquid crystal materials above Tg are analogous to the smectic, nematic, and cholesteric phases obtained from normal low molar mass liquid crystal materials, although the microscopic textures obtained can be quite different in appearance. In this context, the use of DSC for determining polymeric glass transition and other transition temperatures has been found to be essential.

The uses of polymeric liquid crystals are as yet fairly limited, although, as with discotic liquid crystals, this may be due to the fact that their study is still very much in its infancy. However, the electric field-switching capabilities of suitable side groups are being investigated as one possible application. Here, the side groups follow an applied electric or magnetic field (above Tg) by the same principles as for normal liquid crystals. As the backbone becomes fixed below Tg, an electro-optical storage effect is obtained by quenching to form the rigid, flow-free polymeric material. This effect would require a nematic or a smectic polymer. Applications for cholesteric polymers have already been realised. The optical effects of the polymer are 'locked-in' below Tg, and in this way, foils can easily be prepared for use as selective filters or reflectors.

2.2 USES AND APPLICATIONS OF LIQUID CRYSTALS

2.2.1 *Electro-optic Display Devices*

The commercial success of liquid crystals over the last ten or fifteen years is due almost entirely to the development and use of nematic liquid crystals in electro-optical display devices. Practical applications of smectic and cholesteric liquid crystals have met with limited success by comparison with their nematic counterparts, although, as we shall see, significant advances have been made recently in these areas.

Nematic liquid crystals may be used in several different modes of display device operation. However, it is the 'Twisted Nematic' display mode[16] (TN) that is mainly responsible for the world-wide production of many millions of liquid crystal digital displays, an example of which is shown in Plate 10.

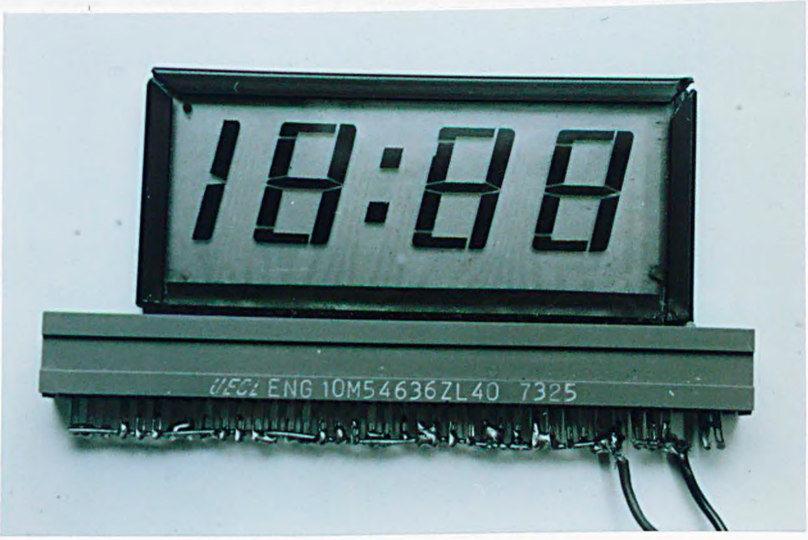


PLATE 10

An electro-optic display device incorporating nematic liquid crystals

The main operating principles of the TN device are as follows (see Figure 3).

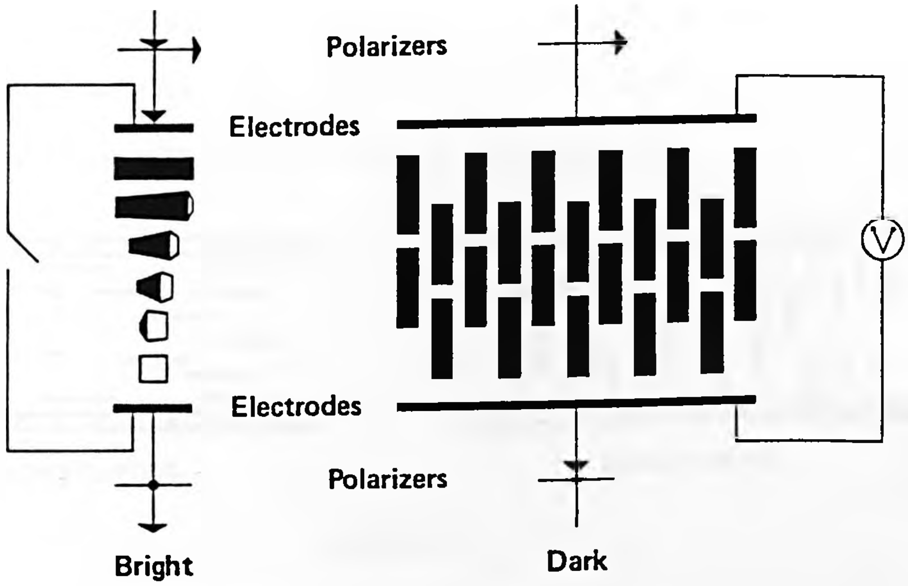
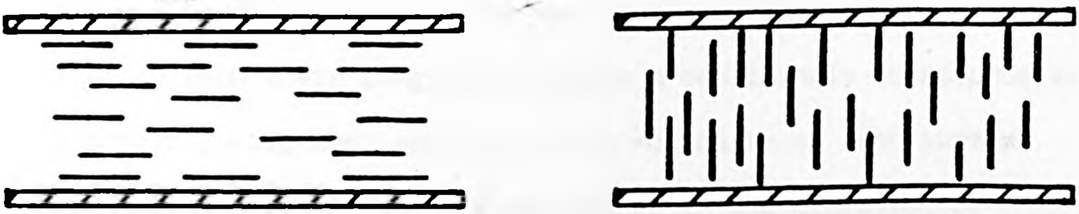


FIGURE 3

Operating principles of the twisted nematic shutter

The cell itself is very thin, usually 6-12 μm thick, which allows the display to have fast response times (ie, switch 'ON' and switch 'OFF' times), whilst still having a sufficiently good contrast ratio between the 'ON' and the 'OFF' elements.

The inner surfaces of the glass plates of the cell are treated in two ways. Firstly, a transparent conductive coating is applied to those areas that are required to be switched 'ON'; these areas usually consist of the seven independent bar electrodes required to display the number *eight* (which can also be seen in Plate 10) for each digit present, plus one or two dot elements which are used to break up the numerals as required. The conductive coating is usually formed by using indium-tin oxide or one of these oxides. Secondly, each surface is treated so that the molecules lie with their long axes in a single, preferred direction and in the same plane as the cell plate. This induces a homogeneous molecular surface alignment. The other type of surface alignment used in other display modes is homeotropic; in this case, the molecular long axes are persuaded to lie perpendicular to the cell plates (see Figure 4).



HOMOGENEOUS HOMEOTROPIC

FIGURE 4

Two main types of molecular alignment

Homogeneous alignment may be obtained by coating the cell plates with polyvinyl alcohol. This deposition technique leaves a covering of the alcohol a few molecules thick on the substrate and by rubbing with a tissue in a uniform direction, molecular grooves are created along which the rod-like nematogenic molecules prefer to lie.

It is possible to achieve both of these surface conditions together, as certain processes involving the production of the conducting surfaces by sputtered vapour deposition naturally produce surfaces that favour homogeneous alignment. By comparison, homeotropic alignment may be obtained by treating the cell plates with certain acids (eg, chromic acid), coating the surface with a suitable lipid (eg, lecithin), or doping the liquid crystal with a suitable surface active agent.

However, the important point to note is that in the TN mode the two cell surfaces are placed with their alignment directions perpendicular to one another. This means that the molecules at the two surfaces, although homogeneously aligned, have their long axes oriented at 90°. Due to the elastic properties of nematic liquid crystals, and also to the relatively thin nature of the cell, the majority of the molecules which are in the bulk of the cell are forced to turn their long axes through a small angle to compromise the opposing alignment effects of the molecules at each surface. This in fact results in a gradual change in the direction of orientation of the molecular long axes on passing through the cell, so that a quarter-helical turn is produced. It is for this reason that the TN display has been so named.

On the outer surfaces of each of the cell plates is affixed a sheet of polariser. The polariser is so arranged at *each* surface that the direction of the plane of polarisation is in the same direction as the long axes of the nematogenic molecules. Thus, as is the case with the surface alignment directions, the directions of plane polarisation at each surface are orthogonal to one another.

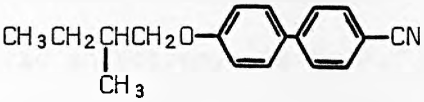
Now, consider a ray of ambient light entering the cell in this, the 'OFF' state. Firstly, the light is plane polarised and encounters the molecules of the nematic liquid crystal with its direction of vibration in the same direction as the molecular long axes. On passing through the cell, the plane of polarisation of the incident light follows the turn in the direction of orientation of the molecular long axes and is guided through 90°. Therefore, the light reaches the other cell plate having had its plane of polarisation state, which is switched to the homogeneous texture in the 'ON' state if the molecules are of negative dielectric anisotropy. Alternatively, if the material used is of positive dielectric anisotropy, application of the field will produce the homeotropic state from the homogeneous alignment. Polarisers are used in both cases, the homeotropic state appearing dark, and the homogeneous state appearing birefringent. As with the TN device, switch-off produces a rapid reattainment of the original alignment through the effect of surface forces.

The dynamic scattering effect requires a nematic liquid crystal of negative dielectric anisotropy ($\Delta\varepsilon \simeq -0.2$ to -0.5) doped with a small amount of conducting material (or ions). In the 'OFF' state, with a black back-plate, the cell appears dark, but when the cell is switched 'ON', turbulence occurs through ionic conduction; the scattering state so produced makes the display appear bright. On switch-off, the cell again becomes dark.

These two display modes have now become almost obsolete due to the phenomenal success of the TN mode.

However, the TN device does have certain limitations. For example, most of the TN displays marketed commercially are of the standard black on white (or white on black if one of the polarisers is rotated through 90^{0}) type. Production of a display presenting coloured information on a contrasting coloured background would therefore seem to offer widespread commercial possibilities.

TN coloured displays can be produced in two ways. Firstly, one or both, of the conventional neutral polarisers may be replaced by a coloured polariser which transmits light of only one particular wavelength. However, this is relatively expensive and the resulting furthermore, the response times are very fast (<100 ms at room temperature). It should also be mentioned that a small percentage of a cholesterogen having a pitch length approximately four times the cell thickness, is usually added to the nematic mixture. This additive serves the purpose of inducing a uniform twist sense throughout the sample, thereby preventing localised areas of reverse twist which give rise to patchy regions within the display.[37] As an example, about 1% of the compound



is frequently added to the commercial mixture E7 (BDH Chemicals Limited, Poole, Dorset).

Usually, the display is viewed in reflection, as opposed to transmission, and this requires a reflective back-plate to be placed on the outside of the analyser. A useful advantage of using ambient light is that the brighter the light source, the better is the display contrast. However, the main advantage of the TN display is that it is able to provide a continuous display with a low power (~2 μW cm^{-2}) and voltage (1-3 volts) supply.

The TN device was, in fact, not the first display to be marketed commercially. Earlier display modes were tried with limited success, mainly due to the fact that sufficiently good nematic materials, with the required physical parameters and stability, were not available at that time. These early display devices utilised the Fréedericksz effect or the Dynamic Scattering effect.

The Fréedericksz[38] effect is perhaps the simplest display mode in that the 'OFF' state requires the molecules to be in the homeotropic state, which is switched to the homogeneous texture in the 'ON' state if the molecules are of negative dielectric anisotropy. Alternatively, if the material used is of positive dielectric anisotropy, application of the field will produce the homeotropic state from the homogeneous alignment. Polarisers are used in both cases, the homeotropic state appearing dark, and the homogeneous state appearing birefringent. As with the TN device, switch-off produces a rapid reattainment of the original alignment through the effect of surface forces.

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TN coloured displays can be produced in two ways. Firstly, one or both, of the conventional neutral polarisers may be replaced by a coloured polariser which transmits light of only one particular wavelength. However, this is relatively expensive and the resulting contrast between the 'ON' and 'OFF' elements is unexceptional. Some examples of coloured TN displays produced in this way are given in Plate 11.

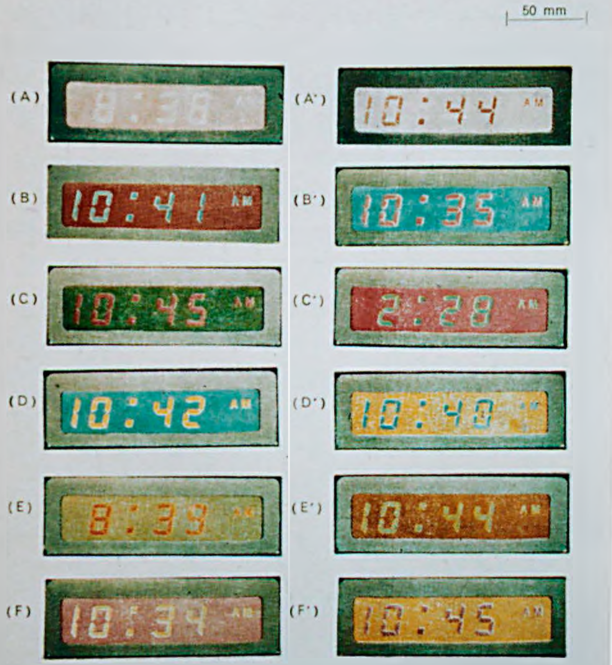


Figure 1 Multi-color indication panels with twisted nematics for clocks. (A), (A') are mono-color and others are bi-colors. These were produced by combining a neutral-color polarizer and dichroic-color polarizers. Light source is ordinary white light. Devices are operated at 6 V (ac rms).

PLATE 11

The second method involves the use of a dichroic dye which is incorporated in the desired nematic host in a relatively low concentration (<1%). The general principles of light absorption by dichroic dyes are illustrated in Figure 5, the use of which in nematic displays was first suggested by Heilmeier and Zanoni.[39]

The dye molecules absorb polarised light strongly only in one orientation of their molecular long axes so that the transmitted light appears coloured, whereas the light from other planes of polarisation is not absorbed, and so remains colourless. The geometrical shape of

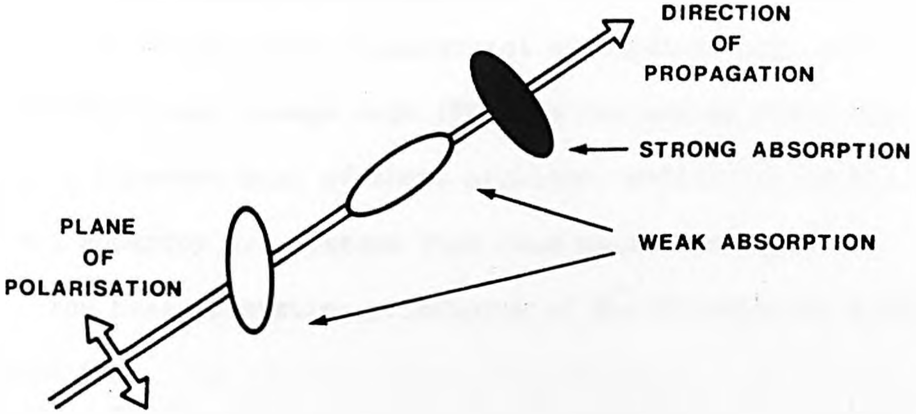


FIGURE 5

The absorption of plane polarised light by dichroic dye molecules in different orientations

the dye molecules is chosen to be similar to that of the nematic host (ie, elongated rigid rods), so enabling the dye molecules to align with the nematic molecules. This is an essential feature of this type of display mode, as the nematic director is changed from one orientation to another from the 'OFF' to the 'ON' states, thereby producing a coloured to colourless transition.

There are, however, several disadvantages with this, the so-called *twisted nematic guest-host* display. In particular, dyes having the desired physical properties such as adequate solubility, stability (thermal, photochemical and electrochemical), and order parameter have been very difficult to obtain. In fact, it is only recently that promising dyes have become available. These dyes have the anthraquinone unit as their basic building block, as opposed to the earlier azo type dyes. However, the contrast ratio, brightness, and economic viability weigh against the TN guest-host display device. This is to a large extent due to the fact that the main competition to the TN device, from a commercial standpoint, the dyed cholesteric to nematic phase change mode (PC), as devised by White and Taylor,[40] largely bypasses most of these problems, whilst now taking advantage of the superior dye systems that have become available.

The basic operating principles of the PC mode are shown in Figure 6.

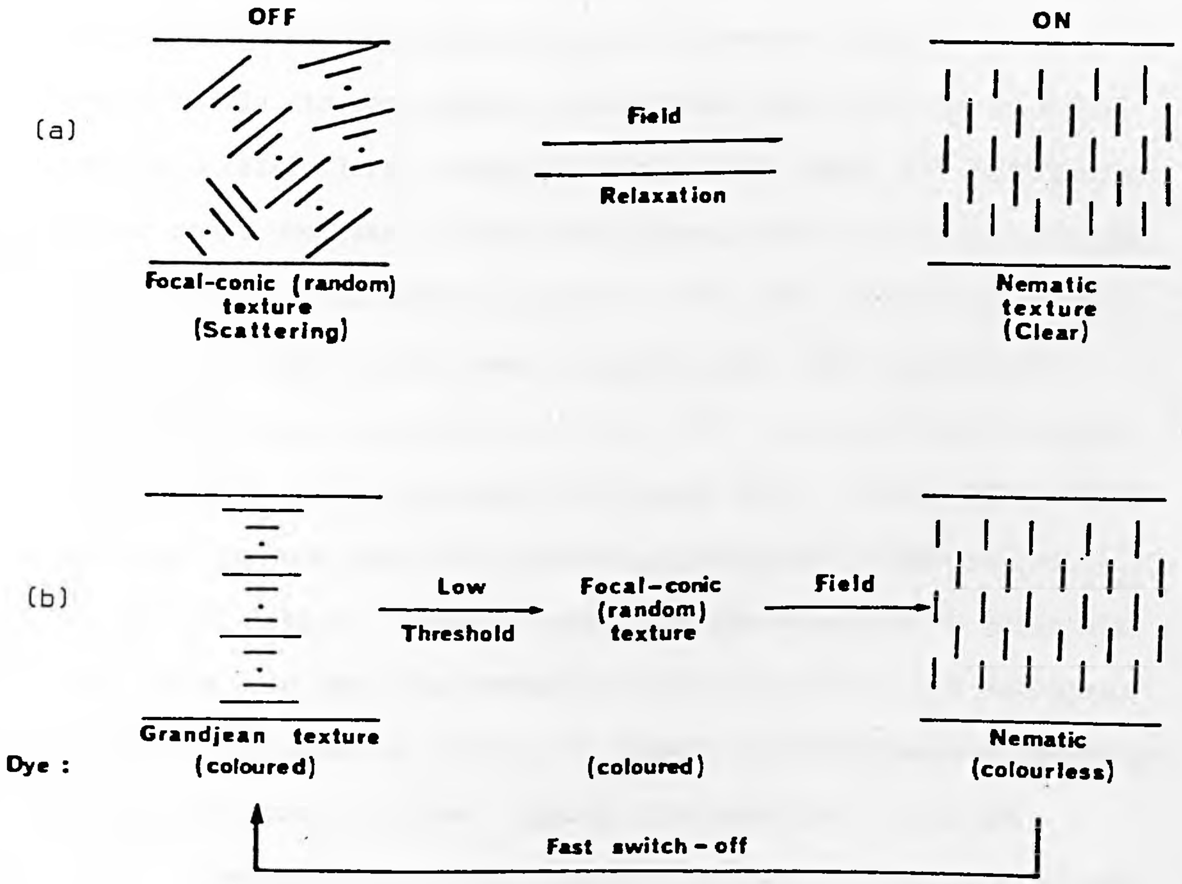


FIGURE 6

Operating principles of the cholesteric to nematic phase-change display

In the 'OFF' state, the helices may be arranged randomly (ie, in the focal-conic texture), so that the cell scatters light and appears bright. When the display is switched 'ON', the electric field effectively unwinds the helices so that the molecules (which must be of positive dielectric anisotropy) assume the homeotropic, pseudo-nematic alignment which is non-scattering, and so appears clear (Figure 6(a)). Switch-off reproduces the random arrangement of the cholesteric helices as a direct result of the molecular asymmetry. This action occurs very quickly and is almost independent of any surface effects, so that this form of the PC display appears to have the advantage of requiring little or no surface alignment. Unfortunately, in some cases, unless relatively thick cells, which require a fairly large threshold voltage, are used, the contrast is rather poor. However, as mentioned above, the use of a dichroic dye vastly improves the contrast such that the 'OFF' state is coloured and the 'ON' state colourless. In this case, the cholesteric Grandjean texture is preferred in the 'OFF' state, as this produces the strongest colour transmission (Figure 6(b)). The electric field turns the helices over and unwinds the structure to produce the homeotropic texture, thereby forcing the dye molecules to align with their molecular long axes normal to the cell plates. The Grandjean texture is reformed on switch-off, without the intermediate formation of the focal-conic texture. Again, this switch-off is rapid.

If a homogeneous surface alignment is used to produce a uniform display, contrast ratios of greater than 10:1 may be achieved with normal cell thicknesses at threshold voltages of ~4V.

Usually, a cholesteric material of pitch length 1-5 μm and positive dielectric anisotropy is used, and this is often obtained by mixing a suitable short pitch cholesterogen with a nematic host material of positive dielectric anisotropy in the ratio of about 1:10. This type of display mode produces white information on a coloured background, and is often referred to as a negative contrast, dyed phase change display.

It is also possible to produce a positive contrast, dyed phase change display, where coloured information is presented on a white background.[41] Overall, the dielectric anisotropy of the cholesteric mixture is required to be about -4, and this is achieved by incorporating suitable cholesteric dopants and dyes into a nematic host of strongly negative dielectric anisotropy. The pitch length, P, is arranged to be about half the cell thickness, d (ie, $P = \frac{1}{2}d$), and a homeotropic surface alignment is used. The surface forces effect an unwinding of the cholesteric helices and the 'OFF' state becomes a pseudo-nematic, homeotropic arrangement. This appears *colourless*. In the 'ON' state, the molecules are forced to turn through 90°, and in doing so, generate a cholesteric planar texture; the 'ON' areas now appear coloured. The numerical value of P is selected as half the cell thickness as a compromise between allowing the surface forces to unwind the helices effectively, and obtaining a good colour absorption in the 'ON' state. Thus, coloured information is presented on a white background, and for many applications this is considered preferable to the reverse situation obtained with the negative contrast display mode.

Although the majority of the present-day commercial display devices incorporate the TN mode, it is likely that the PC mode, in one form or another, will feature more as time progresses. The TN mode is reasonably adequate for the relatively simple black on white display devices, but as the demand grows for more sophisticated display, both of the neutral and coloured types, so the PC mode will become more commercially viable.

In general terms, the PC mode offers the advantages of increased brightness and economic efficiency (as external polarisers are not required), faster response times and an absence of viewing angle problems when compared with the TN mode. Although recent improvements in the PC mode have reduced the required threshold voltage, because thick films are no longer a necessity, there are still several problems remaining. For example, the variation of threshold voltage with temperature is often unacceptably high for multiplexed addressing. The above mentioned physical and electro-optic parameters will be discussed more fully in the first part of the Results and Discussion Section.

A further type of display mode that incorporates nematic liquid crystals, is the so-called two frequency switching display mode.

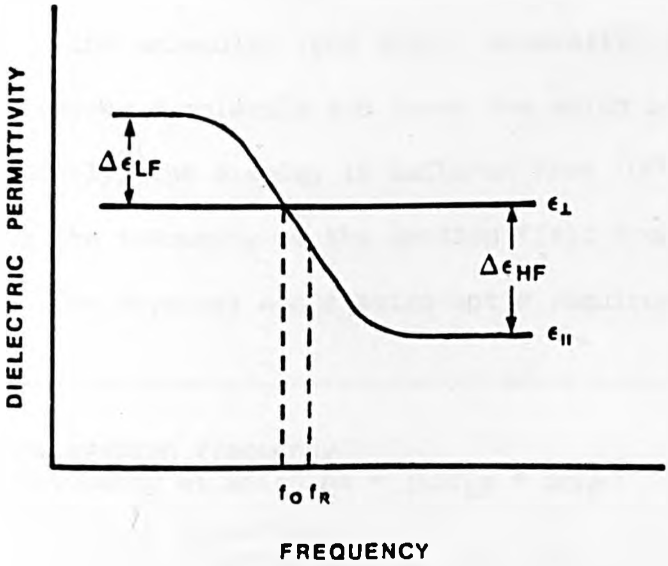


FIGURE 7

Dielectric switching by variation of the applied field frequency

Figure 7 shows schematically the general parameters and principles involved in two-frequency switching. At low frequencies of the applied electric field (as used with most other display modes), the nematic material is chosen so that $\varepsilon_{\parallel}$ is greater than $\varepsilon_{\perp}$ and hence $\Delta\varepsilon$ at low frequency (ie, $\Delta\varepsilon_{LF}$) is positive. However, as the frequency of the applied field is increased, so $\varepsilon_{\parallel}$ becomes less positive, and eventually has a value lower than $\varepsilon_{\perp}$ which remains virtually constant. Consequently, at high frequencies of the applied field $\Delta\varepsilon_{HF}$ is negative.

The reason for the switch in $\Delta\varepsilon$ from positive to negative with increasing field frequency is that below f_R,[†] the relaxation frequency, the component of the molecular dipole parallel to the director is able to follow the alternating electric field and so makes a significant contribution to $\varepsilon_{\parallel}$. However, as the frequency of alternation of the field increases, this component of the dipole is unable to follow the field and this contribution to $\varepsilon_{\parallel}$ is lost. This effect is believed to be due to hindering, because of steric crowding by neighbouring molecules, of the rotation of the molecules about an axis normal to the molecular long axis. Generally, the more sterically hindered a molecule the lower the value of f_R.

Consequently, the display is switched from 'OFF' to 'ON' simply by increasing the frequency of the applied field from suitable low to high values. The physical and electro-optic requirements for a good

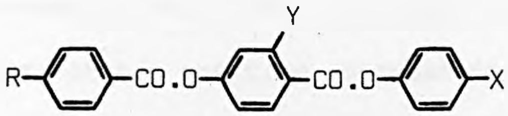
---

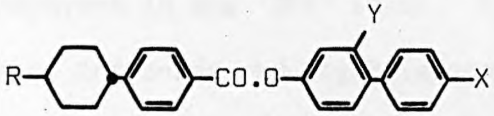
[†] f_R = relaxation frequency
= frequency at which $\Delta\varepsilon = \frac{1}{2}(\Delta\varepsilon_{LF} + \Delta\varepsilon_{HF})$

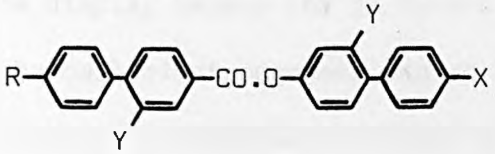
f_0 = crossover frequency
= frequency at which $\varepsilon_{\parallel} = \varepsilon_{\perp}$, ie, $\Delta\varepsilon = 0$

two-frequency material are a large positive $\Delta\varepsilon_{LF}$ and a large negative $\Delta\varepsilon_{HF}$, a low f_0 (typically 0.5 to 10 kHz), a weak temperature dependence of f_0, a low melting point and viscosity (<50 cP at 20^oC) for the eutectic nematic mixture, and an optical anisotropy of greater than 0.14.

The materials presently used consist, in the main, of very long, rigid, laterally substituted molecules, as it has been found that f_R is lowered for such materials. Typical examples are mono- and di-esters such as:







etc

where

R = n-alkyl, n-alkoxy
X = halogen, -CN
Y = -Cl, -F, $-CH_3$

There is considerable potential for two-frequency applications in the area of twisted nematic displays, both in terms of static drive displays which can be operated as fast shutters, and as multiplexed drive displays. However, there are several problems to be overcome before such display devices become realistic commercial possibilities. These problems include the low solubility of some of the components of the mixtures, high mixture viscosities, high temperature dependence of f_0, etc, and much remains to be done in this area.

The use of smectic liquid crystals in electro-optic display devices has, to-date, met with limited success by comparison with that of nematic, and to a lesser extent cholesteric, liquid crystals. This is due mainly to the highly viscous nature of the smectic phases, but significant progress has been made recently with a display device that incorporates a S_A material.

This display has a memory facility and uses an infra-red laser beam for information writing. The display cell consists of a S_A material (often a mixture) homeotropically aligned in a cell of approximate thickness 20 µm. Often a suitable dye is incorporated into the mixture so that a positive contrast is obtained. The cell is therefore transparent in the 'OFF' state. The application of a narrow laser beam of infra-red red light (approximately 30 µm diameter) onto the display causes the S_A material to go isotropic. This is because the cell electrodes are chosen to be infra-red absorbant, and the local temperature increase at the cell surface causes the smectic material to become isotropic. It is therefore necessary to chose the T_{S_A-I} value[†] to optimise the opposing effects of ambient temperature interference at low T_{S_A-I} values, and poor response to the infra-red beam at high T_{S_A-I} values. Typical T_{S_A-I} values are in the region of 50°C.

The infra-red beam is directed onto any given area of the cell for only a very short time so that on its removal, the isotropic

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[†] Advantages are said to arise from the use of a material with a short (1-2°C) nematic phase between the smectic phase and the isotropic liquid, particularly with regard to the alignment of the material on erasure.

liquid rapidly cools to the smectic state, and reforms, not the initial homeotropic alignment, but the thermodynamically more stable focal-conic texture. This texture is scattering, so that in the 'ON' state the display is coloured, depending on the dye used. If a coloured display is not required, bright information can be displayed on a dark background by using a black reflective back-plate.

This is one of the special features of the S_A display mode, in that the 'ON' state is produced, not by a field effect, as is the case with the nematic and cholesteric display modes, but by a heating effect caused by electromagnetic irradiation.

The high thermodynamic stability of the scattering focal-conic texture means that the information may be displayed or stored for almost any required length of time, thus providing an efficient memory bank for the device. The information is erased by selective redirection of the laser beam and application of an electric field of suitable frequency to the cell. The homeotropic alignment is then produced on cooling from the isotropic liquid (via the nematic phase, if present) as the material is chosen to have a positive dielectric anisotropy.

The advantage of this type of display is that it is possible to obtain a high resolution, bright display with the capabilities of selective erasure, built-in memory facilities and the capability of projection onto a large area screen if desired. However, there are several weaknesses in this display mode, especially poor temperature control and writing speed (presently at 60-80 mm s^{-1}). Also, the white on black contrast could be improved and there is a need to increase the resolution (presently at about 1000 lines) and addressability for some of the more sophisticated applications. Current developments in these areas are centred around the use of a higher resolution deflector to enable the attainment of 3000-4000 line resolution and an improved light source by using infra-red laser diodes.

A second electro-optic effect using a smectic liquid crystal is the ferroelectric S_C display mode. Structurally, the S_C mesophase is related to the S_A phase, except that the molecules within the smectic layers are tilted at some angle to the layer normal. By using a material incorporating an asymmetric centre in the molecule, successive layers have an associated small, regular twist of the molecular tilt direction. Consequently, a chiral S_C material has a helical structure with a corresponding pitch length in much the same way as for cholesteric liquid crystals.

If the chiral S_C material has a significant lateral molecular dipole, each layer has a spontaneous polarisation in the plane of the layer. The direction of this polarisation will therefore also rotate on passing through successive smectic layers. The application of an electric field may then unwind the helical structure, thus creating a switching effect which is the basis for a S_C device.

It should also be mentioned that for chiral S_C materials of suitable pitch lengths, iridescence effects are observed as for the cholesteric mesophase. For certain materials, the colour of this iridescence is temperature dependent, thus theoretically providing the basis for a temperature sensing device, the general principles of which are to be discussed more fully in terms of cholesteric materials in the following section.

2.2.2 *Surface Thermography and Pollutant Detection*

As noted earlier (Section 2.1.3), the cholesteric mesophase has a helical axis which gives rise to some special optical effects. These optical effects can often be observed as a colouration of the sample, depending on the particular material.

Consider the reflection of electromagnetic radiation from equidistant planes, as given by the Bragg[42] equation:

$$n\lambda = 2\ d \sin\theta$$

where

n = order of reflection
d = plane thickness
θ = angle of incidence
λ = wavelength of the reflected radiation

This mathematical description can, in fact, be applied to the cholesteric mesophase. In this case, the layer planes correspond to half the pitch length of the cholesteric material ($^{P}/2$), so that the wavelength of the reflected radiation is dependent on the angle of incidence and the cholesteric pitch length; hence, for a first order reflection

$$\lambda = P \sin\theta$$

Thus, for a given angle of incidence only one particular wavelength will be reflected, and this value is dependent on the pitch length.

If the cholesteric pitch length is of the order of the wavelength of visible light, then by the above principle, visible light of a particular wavelength will be reflected from the cholesteric material and this is observed as a characteristic colour. Light transmitted has therefore had this wavelength of light removed, so that when viewed in transmission, the light appears as the colour compliment to that reflected.

As well as being pitch-length dependent, the colour observed on reflection or transmission is often temperature dependent. These properties are, in fact, related, because the pitch length of the cholesteric material in such cases is temperature sensitive - the pitch length generally shortens with increasing temperature. A change or difference in ambient or surface temperatures may therefore be monitored relatively easily by observing colour variations in cholesteric liquid crystals. Actually, no single component cholesteric material is used, but several cholesteric compounds (often esters of cholesterol) are mixed together, the composition being dependent upon the required properties. By 'tuning' suitable mixtures in this way, large or small temperature changes may be detected with reasonable sensitivity (ie, <0.1^{o}C) in the range 0 to 100^{o}C.

In practice, the cholesteric mixture is encapsulated by emulsifying the material in an aqueous solution of a polymeric material. Micro-droplets of diameter 10-30 μm of the cholesteric material then become coated with the polymer. This technique largely by-passes most of the earlier addressing problems of cholesteric films, though colour brightness is affected.

Commercially, cholesteric liquid crystals are used in digital thermometers. Each numeral has a slightly different pitch length associated with it, through the use of slightly different cholesteric mixture compositions. As the numerical value of the digits increase, so too does the corresponding pitch length. Thus, as the temperature increases, the pitch length of all the mixtures decrease, but at any one temperature only one of the cholesteric pitch lengths is within the wavelength range of visible light. This corresponds to the 'ON' element. The digits below and above this value are reflecting light in the ultra-violet and infra-red regions of spectrum, respectively.

In practice, the numerals of the display are cut into transparent plastic strips under which are housed the encapsulated cholesteric liquid crystal mixture sealed onto a black background. Therefore, the 'ON' state is coloured (as desired) and the 'OFF' state and background are black.

As commercial processes and techniques are improved, and the encapsulation procedures perfected, other areas may be envisaged where cholesteric thermochromic materials may be useful. Examples of these areas are given below.

(i) In the foodstuffs industry, it is required by Law that certain perishable goods shall be maintained below a defined temperature. An irreversible temperature sensor could then be used to indicate if such a temperature threshold had been exceeded.

(ii) For road users, it is important to indicate when the road surface temperature has fallen to such a level that ice formation is a possibility. Here the thermochromic material could be incorporated into the cats'-eyes used in the road.

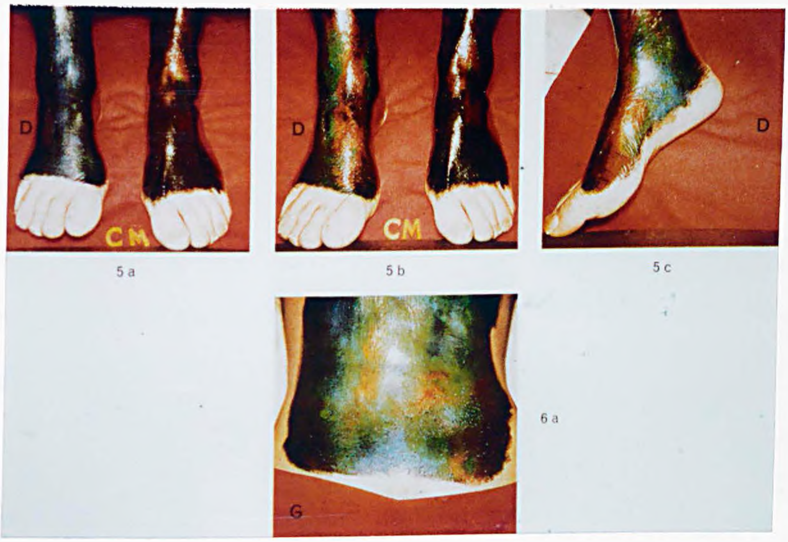
(iii) For large area domestic usage, commercial interest exists in the production of thermochromic wall displays whereby the imaged cholesteric film is placed in a conventional frame; indeed the whole available wall-surface area could be covered by the cholesteric film. Alternative effects could be produced by the incorporation of the encapsulated cholesteric micro-spheres into selected wallpaper or paints.

Although some of these applications may appear a little unrealistic at the present time, the potential of cholesteric thermochromic liquid crystals is in fact very real, and many other uses can be envisaged in which temperature effects or changes in temperature are involved. For example, they are also of tremendous potential in the widely different areas of medicine and industry.

In medicine, the variation by as little as 0.1 - 0.2°C in the local skin temperature of a patient may be indicative of some disorder. For example, tumours, breast cancer, blood clots in veins and arteries, certain other cancers, etc, all result in either small temperature rises in the affected areas or some temperature anomaly. By using an encapsulated cholesteric material incorporated in a thin elastic sheet, a convenient method of preliminary assessment is provided, and this has the desirable advantages of speed, low cost, availability, and re-usage potential, whilst causing the minimum amount of distress to the patient.

Such an application is illustrated in Plate 12, where the upper half shows a patient with an ailment of the inside of the right foot (blue area), causing the rest of the foot and leg to rise slightly in temperature when compared with the corresponding areas of the other leg (red colouration).

The lower half of Plate 12 is a thermograph of a pregnant



5 a

5 b

5 c

6 a

PLATE 12

The use of cholesteric liquid crystals for detecting small differences in surface temperatures

woman's stomach; this allows the placenta to be located with relative ease (blue area).

The pitch length of the cholesteric helix is also very sensitive to any impurities that may be present (to a few parts per million). Thus, great care and cleanliness are important when working with cholesteric materials. However, this apparent disadvantage of cholesteric materials may be turned into a possible advantage in the area of pollutant detection.

Certain esters of cholesterol (eg, cholesteryl oleyl carbonate) have been found to be fairly sensitive to small traces of various additives. Generally, the pitch length increases with increasing concentration of the additive as might be expected. This could provide the basis for an industrial vapour indicator, although this particular application of cholesteric liquid crystals is a long way from commercial development. Such a device could be envisaged as operating in industrial areas that may be susceptible to unacceptably high concentrations of toxic gases, eg, parts of an oil refinery or chemical plant, etc. Also, such a device could be used in testing for possible leakages during the piping and transportation of chemicals. The unacceptably high concentration of pollutant would be monitored by the cholesteric detector and observed as a colour change. However, such applications would necessitate very effective thermostatic control of the detector to avoid thermal interference. The alternative would be to use a temperature insensitive cholesteric material which retains a high degree of pollutant sensitivity, but this is probably not practicable, as both phenomena rely on the same principle, ie, the variation of the cholesteric pitch length. A further problem is how to sensitise the detector to the required pollutant or pollutants, so that the device remains insensitive to atmospheric dust, smoke, ions, and perhaps other harmless vapours, etc. Consequently, there are fairly large problems associated with the development of a cholesteric pollutant detection device, but hopefully these are not insurmountable.

Finally, brief mention is made of other possible industrial uses of thermochromic liquid crystals. Welds may be non-destructively screened for flaws and imperfections in the metal structure, using encapsulated cholesteric materials. If a voltage is applied to the system, any faults (as small as 25 μm in diameter) in the structure may be detected, due to a small local temperature rise caused by an increase in the electrical resistance. Temperature differentials are also produced in large metal superstructures that are subject to various stresses and strains resulting in hot and cold spots. The use of suitable thermochromic materials not only pinpoints the suspect areas, but also allows the design of metal structures (eg, bridges, etc) to be improved and made safer.

2.2.3 *Physical Analysis*

Liquid crystals are also of considerable use in several different areas of experimental physical analysis. Nematic liquid crystals are mainly used, and, as with their application in display devices, it is the combination of their fluidity and their structural anisotropy that produces superior results, in many cases, when compared with conventional techniques.

Both smectic and nematic liquid crystals have been used as the stationary 'liquid' phase in gas-liquid chromatography,[43] and this technique has been applied with considerable success to certain systems. For example, standard glc techniques are often unable to separate materials that are structurally very similar, eg, geometrical isomers, etc. The use of liquid crystals gives rise to different retention times of the isomers, thus effecting good separations. This is because the relatively structured nature of the anisotropic liquid crystal stationary phase renders it particularly sensitive to small differences in the molecular shape of a solute. As a result, differences in the adsorption activities of the isomers are magnified, and better resolution results.

Nuclear magnetic resonance studies of certain solutes have been found to yield a greater amount of structural information when the work is carried out using a nematic liquid crystal as the solvent.[44] In this case, the host nematic orientates the solute molecules to such an extent that all of the dipole-dipole interactions are not averaged out, as is normally the case, and the effects may be interpreted by computer processing to yield useful information about the anisotropy of chemical shifts, direct magnetic dipole-dipole interactions, indirect spin couplings, bond angles and lengths, and molecular order and relaxation processes. However, the spectra obtained may be more complex than normal, and care must be taken when analysing data obtained in this way.

Similar studies have been carried out using electron-spin resonance techniques incorporating spin probes in liquid crystal solvents.[45-47] The information obtained relates not only to the solute-solute intermolecular interactions, but also to solvent-solvent interactions, as well as those between the solute and the solvent.

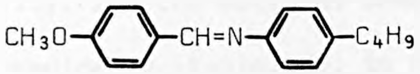
AIMS OF THE WORK

3.1 *GENERAL AIMS*

Ever since the discovery of liquid crystals by Reinitzer,[5] scientists have been trying to interpret their experimental observations and the trends in the properties of these systems in terms of various theories and postulates. The relationships between the physical parameters of liquid crystals and their molecular structure have in fact evolved to such an extent that it can be said, in general terms, that a broad correlation between the two exists. For example, the approximate change in T_{N-I} value may be estimated for a particular compound which has resulted from some reasonable change in the molecular structure of a known nematogen, eg, the substitution of a lateral or terminal substituent, the variation of a central linking group, etc. Such estimations are usually based on the effects of similar structural changes in different molecular systems, the assumption being made that the effect will be virtually the same for the system under examination.

In the case of T_{N-I} values, such predictions are often very reasonable, but there are many examples where the predicted and experimental values differ greatly. However, even the partial understanding achieved by way of the influence of structural change on T_{N-I} values may be considered to be advanced by comparison with the relationships that exist for many of the other parameters associated with liquid crystals (eg, viscosities, electro-optical properties, melting point transitions, etc). It is therefore clear that we are a long way from a complete understanding of the physical behaviour of liquid crystals in terms of their molecular structure. Consequently, one of the aims of this work was to advance the development of such relationships, whilst at the same time producing novel liquid crystals that were not simply of academic interest, but might be of some value in the area of display device applications.

Many of the early commercial liquid crystal display devices incorporated the Fréedericks display mode[38] (Section 2.2.1). Usually the homeotropic 'OFF' state and homogeneous 'ON' state were used, so that the materials were required to be of negative dielectric anisotropy. In this context, 4-methoxybenzylidene-4'-butylaniline (MBBA), C 21° N 47° I, was widely used as it was one of the then



MBBA

rare liquid crystal materials having a reasonably wide nematic range around room temperature. By using mixtures incorporating different homologues, the melting point could be lowered whilst retaining or even raising the reasonably high T_{N-I} value. Thus, display devices operating over a range of approximately 40 or 50° could be produced. Although this operating temperature range is fairly modest by present day standards, other more serious drawbacks were the limiting factors on the operating lifetime of these displays. Such Schiff's bases as MBBA are difficult to obtain and maintain in a high degree of purity,[48] since they are susceptible to atmospheric moisture, oxygen and other pollutants. Azoxy liquid crystals[49,50] (which were also found to have reasonable liquid crystal temperature ranges) had the advantage of being stable in the atmosphere, but these materials had a yellow colouration and deteriorated in UV light. Consequently, until about ten years ago, the display devices that were available were seriously limited in terms of both operating temperature range and operating lifetime.

The general requirements for a liquid crystal material to be commercially viable at that time were

(i) a reasonable nematic temperature range, eg, 0-60°C;

(ii) a colourless appearance - to increase the contrast ratio and produce neutral colour imaging;

(iii) stability - this was, and still is, a major requirement of any material. It applies to several different aspects of stability, ie, the material should be

  (a) chemically stable, eg, to hydrolysis by atmospheric moisture, oxidation, etc

  (b) photochemically stable, particularly with respect to UV light

  (c) electrochemically stable - since a potential difference has to be applied to any cell containing the material

  (d) commercially 'stable', in the sense that the materials must be safe (non-toxic, etc) and easy to handle at all stages from the laboratory synthesis through to the sale and distribution of the displays.

Thus, although the device technology existed and the commercial potential for the nematic liquid crystal display devices was recognised in the period 1970-1971, the lack of suitable materials prevented any large-scale and sound commercial development.

Fortunately, this highly unsatisfactory situation was changed quite dramatically with the discovery of the 4-n-alkyl- and 4-n-alkoxy-4'-cyanobiphenyls (CB's) in 1972 by Gray and Harrison.[51-53] These materials fulfilled the above requirements in that they are colourless, low melting nematogens that have good overall stabilities and are readily amenable to purification. Using the related 4-n-alkyl-4"-cyano-*p*-terphenyls[54,55] to produce suitable eutectic mixtures (to be discussed more fully in the Results and Discussion Section), these materials were found to be just what was needed for electro-optical display devices, and quickly met the commercial requirements of the TN display mode.

Such has been the impact of these, and other subsequent materials (eg, *trans*-1-n-alkyl-4-(4'-cyanophenyl)cyclohexanes[56] (PCH's) and esters of 4-n-alkylbenzoic acids[57] and *trans*-4-n-alkylcyclohexane-1-carboxylic acids[58]), that the present worldwide annual production of TN display devices now runs into hundreds of millions.

Thus, over a period of ten years, liquid crystals have progressed from relative obscurity to become systems that are fairly familiar to most people.

However, the widespread success of these electro-optic display devices has in its turn had several repercussions in the liquid crystal area itself. One obvious factor is the large increase in the number of people currently involved (in one capacity or another) with liquid crystals, with most being concerned mainly with nematogens and the related display-device technology. Whilst this arguably may have moved some of the research emphasis away from other less commercially oriented, but no less interesting aspects of liquid crystals, the progress and understanding of display devices in terms of electronics, chemistry and physics of liquid crystals has been tremendous. Consequently, the general requirements and performance figures for display devices that were applicable ten years ago have been greatly refined. This is due to advances in technology, particularly on the electronics side, with the advent of solid state semi-conductor micro-electronics etc, leading to developments that now allow devices to retain and display a much greater amount of information, whilst at the same time reducing the overall size of the units involved. Thus, from the relatively bulky early devices with simple four or five digit displays, the more complex present-day devices are slim, multi-function displays involving a mixture of alphanumerics and other forms of imaging, memories, alarms, timers, mathematical programs etc, such that, in some cases, they can essentially be considered as mini-computers.

However, this relatively rapid progress has been the source of major problems for the materials scientist as the advances made in relation to the technology and drive electronics of displays have outpaced the advances made in new materials. As a result of this, the materials presently available are less well tuned than is desirable to the now very demanding requirements for the sophisticated levels of display device that are technically attainable. For example, for liquid crystal display devices to be used in the areas of automobile and aircraft instrumentation, domestic and pocket television, large and small scale information displays, computer controlled devices, and various military applications, etc, new materials need to be developed that incorporate several advantageous properties that include wider nematic ranges, lower viscosities, good solubility characteristics, high multiplexing performance (sharp threshold voltage, weak temperature dependence, etc), suitable optical and dielectric anisotropies, acceptable elastic deformations, high order parameters (particularly if dye systems are to be incorporated into the host), etc.

It can be seen from this by no means exhaustive list that there are many variable parameters to consider when assessing liquid crystal materials. Some of these parameters are judged to be more important than others, depending on the exact application, and often a compromise situation arises because one parameter must be optimised at the expense of another. No single component liquid crystal is ever likely to approach these current demands, and it must probably be accepted that even multi-component mixtures will probably always fall somewhat short of satisfying such conditions fully. Nevertheless, small, but significant, advances may be expected from novel liquid crystals, and therefore it is only by pursuing such goals that any progress can be anticipated. Consequently, it was with the above-mentioned requirements and physical parameters in mind that the work presented in this thesis was carried out.

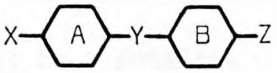
Broadly speaking, the general aims of the work were two-fold: namely,

(i) the synthesis of novel liquid crystal materials and additives that might meet more fully the stringent requirements of present-day, sophisticated, electro-optical display devices;

(ii) the systematic accumulation of information concerning relationships between molecular structure and observed physical properties.

3.2 SPECIFIC AIMS

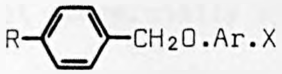
Most of the nematogens developed for display device applications have been compounds whose general structure (1) has consisted of



(1)

two ring systems, A and B, joined together by an appropriate central linking group Y and carrying terminal substituents X and Z. Thus, fully aromatic Schiff's bases (Y = -N=CH-) and azoxy compounds (Y = $\overset{\text{O}}{\overbrace{\text{-N=N-}}}$), were amongst the first liquid crystals to be used to any significant extent in display devices. However, as mentioned earlier (Section 3.1), the problems of chemical/photochemical stability and the colour associated with these compounds were a major drawback to their widespread commercial use. In contrast, the success of the CB's and PCH's (where no central linking group Y is present) illustrates the dramatic difference that the central linking group can have upon the properties of a nematogen. Therefore, the role of this unit is very important, and any programme of work on new mesogens must give careful consideration to the choice of Y.

In accordance with this, it was thought useful to investigate compounds that had as their inter-ring linking group the unit $-CH_2O-$. Compounds of general structure (2) were therefore synthesised and



(2)

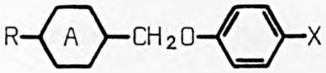
where

Ar = 1,4-disubstituted benzene
2,6-disubstituted naphthalene
4,4"-disubstituted biphenyl

X = cyano, n-alkoxy

assessed. Materials containing this ether function as a central linking group had not been previously investigated, due to the expected lability (particularly in the presence of acid) of the benzylic ether linkage. However, in sealed display cells, acid contamination should not be a problem, and the investigation of these systems seemed an attractive proposition.

Alicyclic ring systems have been shown by several workers[56,58,59] to give rise to useful liquid crystal properties when these rings are incorporated into suitable systems. Therefore, the investigation of compounds of general structure (3), closely related to the compounds of structure (2), was also planned.



(3)

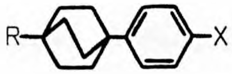
where

(i) A = *trans*-1,4-disubstituted cyclohexane
X = n-alkyl, n-alkoxy

(ii) A = 1,4-disubstituted bicyclo(2.2.2)octane
X = cyano, n-alkyl, n-alkoxy

These materials now no longer contain the potentially labile benzylic ether function. They should therefore be highly stable materials that offer other useful physical properties associated with the saturated ring systems, ie, lower viscosity and greater nematic thermal stability by comparison with the fully aromatic analogues.

CB's were the first commercially successful nematic materials to show that a central linking group was not an essential prerequisite for mesophase formation. As mentioned above, the use of alicyclic rings can also produce favourable results, and in this context the PCH's were the first compounds to combine successfully both of these effects. A fairly obvious extension of this theme is to employ the potentially useful bicyclo(2.2.2)octane ring in a similar system which involves no central linking group. The synthesis of a range of compounds with the general structure (4) was therefore planned.



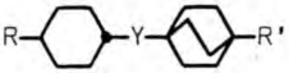
(4)

where

X = n-alkyl, n-alkoxy

It is worth mentioning at this point that both materials of high dielectric anisotropy and low (weakly positive or negative) dielectric anisotropy are of equal interest from the point of view of display devices. This is because some of the most useful nematic mixtures are comprised of a host nematic of strongly positive dielectric anisotropy containing a component of weakly positive or weakly negative dielectric anisotropy. This aspect of display devices will be dealt with more fully in Section 4.1.2.

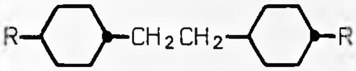
Generally speaking, the low dielectric anisotropy components of commercially available nematic mixtures have been terminally dialkyl or alkyl-alkoxy substituted phenyl benzoates or phenyl cyclohexanoates, although terminally dialkyl and alkyl-alkoxy substituted phenylcyclohexanes are now attracting much interest. An alternative approach to searching for quite novel materials of superior stability to esters is to develop new esters that have comparable stability characteristics, but are superior in other respects, eg, lower melting points, wider nematic ranges, lower viscosities, lower smectic tendencies, etc. With these points in mind, a range of fully aliphatic esters of general structure (5) was prepared.

 (5)

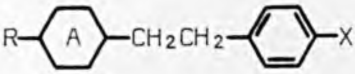
where

Y = -CO.O-, -O.CO-

The most stable liquid crystal materials to date have, as already mentioned, no central linking group, ie, the two ring systems are joined by a single bond (carbon-carbon). Therefore, if a central linking unit consisting of only C-C bonds were used, with no hetero-atoms involved, this should also provide extremely stable systems. Consequently, the inter-ring linkage $-CH_2CH_2-$ was incorporated into several different types of structure. Firstly, for ease of synthesis, compounds (6) were prepared. These are amongst the first fully aliphatic, hydrocarbon liquid crystals to be made,[60] and may be regarded, perhaps, as the ultimate in terms of stability.

 (6)

Then a range of compounds of general structure (7) was prepared. Thus, the ring structure A was varied, as well as the nature of the aromatic substituent X.

 (7)

where

(i) A = 1,4-disubstituted benzene;
X = n-alkyl

(ii) A = *trans*-1,4-disubstituted cyclohexane;
X = cyano, hydrogen, n-alkyl, n-alkoxy

(iii) A = 1,4-disubstituted bicyclo(2.2.2)octane;
X = cyano, hydrogen, n-alkyl, n-alkoxy

In summary, the aim of this work was to produce novel liquid crystal materials that might be superior to those presently used in electro-optic display devices and to vary the molecular parameters in a reasonably systematic manner in order to gain information relevant to the optimisation of various physical and electro-optic properties.

RESULTS AND DISCUSSION

4.1 PHYSICAL AND ELECTRO-OPTIC PARAMETERS

As the level of complexity of electro-optic display devices increases, the demands on the liquid crystal materials used are also made much greater. The usefulness of a particular liquid crystal material, or mixture, is usually assessed in terms of several related and unrelated physical properties. It therefore seems appropriate to discuss the more relevant of these parameters, in order both to define and to clarify the significance of each.

4.1.1 Viscosity Coefficients

The viscosity of a material is the property which opposes the relative motion of adjacent volume elements or layers of the material, and is often regarded as a type of internal friction or resistance to flow.

Usually, the viscosities of materials are compared by their relative coefficients of viscosity, η. This coefficient is defined as the force per unit area (N m^{-2}) required to maintain a unit difference in velocity (1 m s^{-1}) between two parallel layers of a material separated by unit distance (1 m). The units of η are therefore N. s. m^{-2}, or the more commonly used c.g.s. units dyne. s. cm^{-2} (1 N. s. m^{-2} = 10^4 dyne. s. cm^{-2}) which is termed a poise, P.

With liquid crystalline systems which are aligned, the viscosity is, of course, an anisotropic property, and as the macroscopic, flow aligned viscosities (see below) of most liquid crystalline systems are relately low, the viscosity coefficient (often termed simply 'viscosity') is usually expressed in centipoise, cP.

The effect of temperature on viscosity is of an Arrhenius-type, exponential form (see Equation (1)).

$$\eta = \eta_0 \, e^{\frac{-Ea}{RT}} \qquad (1)$$

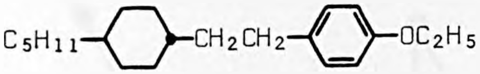
where

η_0 = a constant, representing the viscosity at a temperature of absolute zero;

Ea = the activation energy required for the molecules to flow past one another;

R = the gas constant

Such an expression has been found to be applicable both to isotropic liquids and nematic liquid crystals.[61] As an example, the effect of temperature on viscosity for the compound



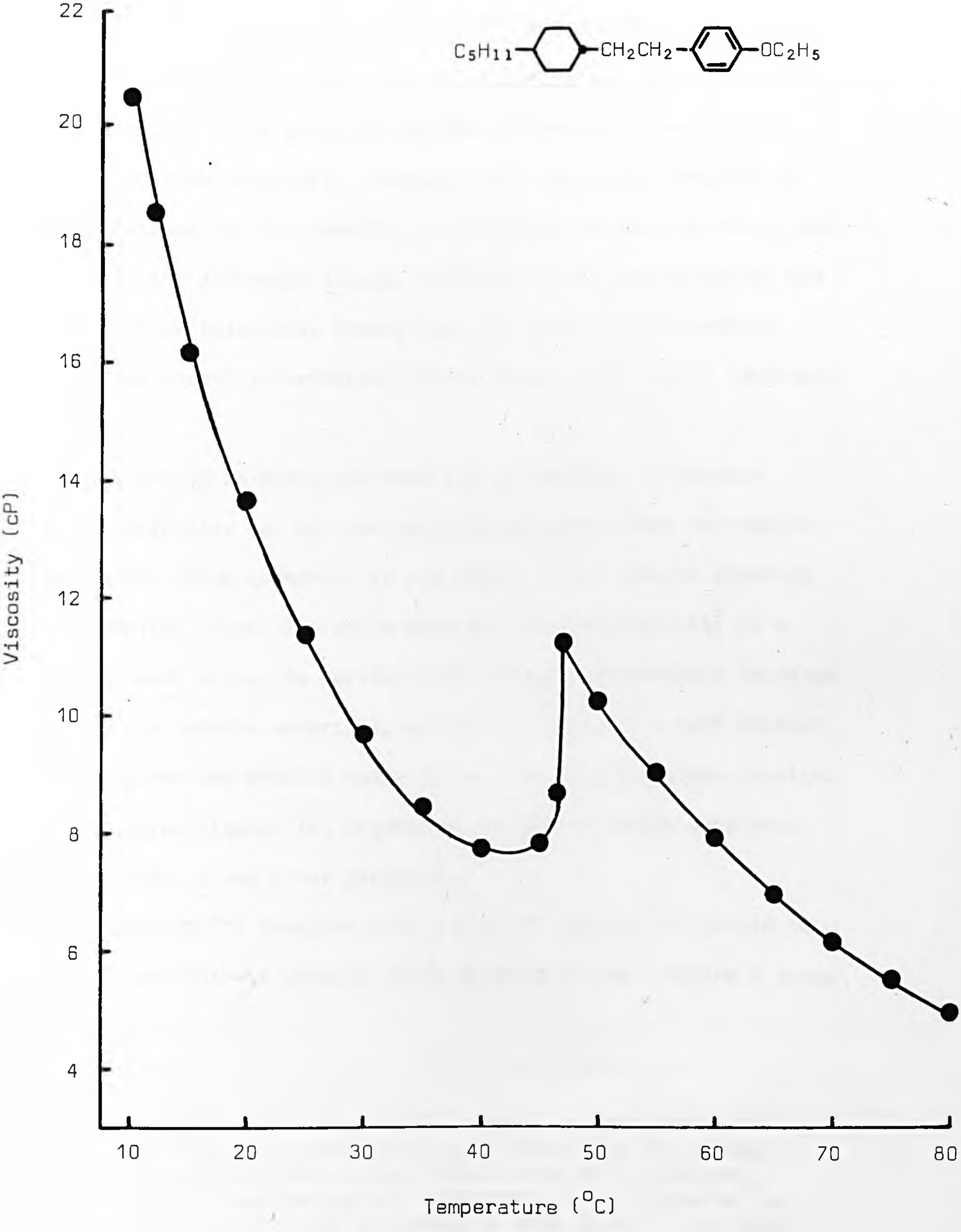
PECH 5.02

(to be discussed more fully later) is shown in Figure 8, both for the isotropic liquid and the nematic states. This is a fairly typical plot for a nematogen, with the general shape of the curve corresponding to each of the two states being similar (as would be expected if each state is to fit Equation (1)). Also, the viscosity increase at the N-I transition temperature is relatively characteristic.

An important point to note is that if the nematic and isotropic regions of the plot are extrapolated, the nematic viscosity is lower than the isotropic viscosity at the same temperature. At first sight, this may seem surprising in view of the one-dimensional ordering within the nematic phase, compared

FIGURE 8

Graph of viscosity against temperature for the compound



with the zero-dimensional ordering of the isotropic liquid. However, it must be remembered that the standard methods of measuring the nematic viscosity coefficient (Ostwald viscometer, rotating cone, etc) relate to a flow-aligned situation,[†] in which the molecules slide past one another in the direction of their long axes (the director). Consequently, the value obtained by these methods for the nematic viscosity coefficient is lower than that for the isotropic liquid, because the aligned molecules are able to flow relatively freely past one another with reduced molecular steric interference compared with that in the isotropic state.

It should be mentioned that the viscosities of smectic liquid crystals, eg, S_A, are much greater than those for nematic materials, being generally in the range 100 to several thousand centi-poise. Also, the value obtained for the viscosity of a smectic such as S_A, is particularly strongly anisotropic (more so than for a nematic material), as there is usually a much greater tendency for the smectic material to flow in a direction parallel to the layer planes, ie, orthogonal to the molecular long axes, rather than in any other direction.

Equation (1) predicts that a plot of log η v $^1/T$ should be linear, and this is usually found to be the case. Figure 9 shows

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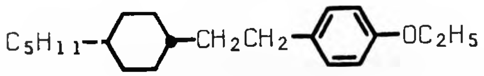
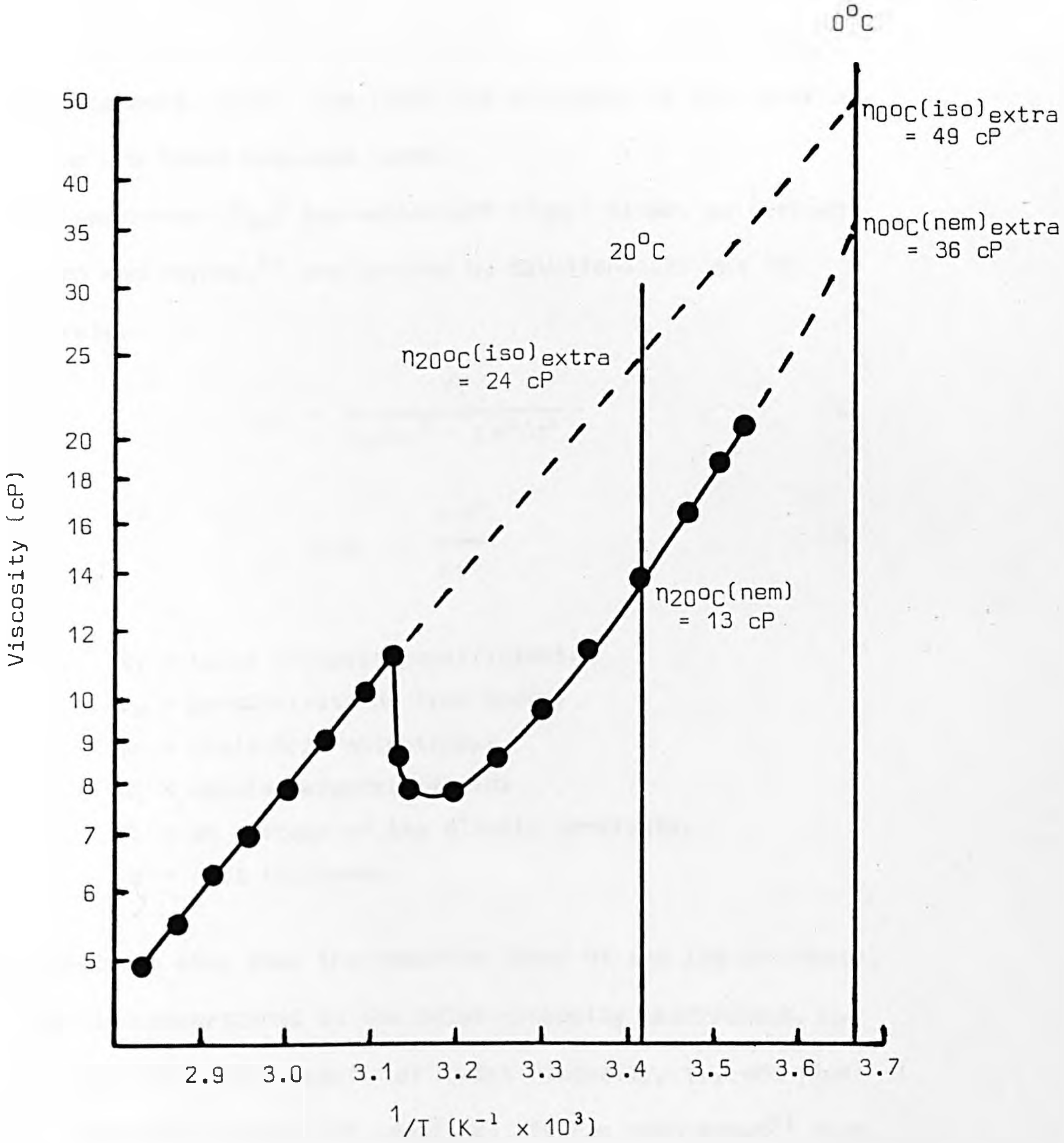
[†] For the anisotropic nematic state, several viscosity coefficients are required to define fully the viscous properties (splay, twist, bend, etc) of the system. Leslie[62] has defined six viscosity coefficients (α_1 to α_6) and particular reference is made later to the twist viscosity coefficient, γ_1 ($\gamma_1 = \alpha_3 - \alpha_2$).

FIGURE 9

Graph of log viscosity against inverse temperature for the compound





such a plot, again for the compound PECH 5.02, and it can be seen that almost perfect behaviour is observed for the isotropic liquid state, whereas there is some deviation from linearity for the nematic state.

With respect to electro-optic display devices, the main use of the viscosity coefficients is in the estimation of the response times of the nematic material to external forces (electric fields, surface alignment, etc). The lower the viscosity of the material, the faster are these response times.

The switch-on (T_{ON}) and switch-off (T_{OFF}) times, as derived by Jakeman and Raynes,[63] are defined by Equations (2) and (3) respectively.

$$T_{ON} = \frac{\gamma_1}{\varepsilon_0 \Delta\varepsilon E^2 - K\pi^2/d^2} \qquad (2)$$

$$T_{OFF} = \frac{\gamma_1 d^2}{K\pi^2} \qquad (3)$$

where

γ_1 = twist viscosity coefficient;
ε_0 = permittivity of free space;
$\Delta\varepsilon$ = dielectric anisotropy;
E = applied electric field;
K = an average of the elastic constants;
d = cell thickness.

These equations show that the response times of the liquid crystal are directly proportional to the twist viscosity coefficient, γ_1.

Although the coefficients of twist viscosity, γ_1, and flow aligned viscosity, η, are not identical, it has been shown[61] that γ_1 in Equations (2) and (3) may effectively be replaced by η without undermining the validity of these equations.

As mentioned earlier, it has been suggested that six independent viscosity coefficients[62] are needed to define the nematic viscosity exactly. Although such treatments may be preferable, enormous practical problems are involved in measuring the various coefficients, and the observed results do show that to a first approximation, the response times are directly proportional to the flow aligned viscosity.

Therefore, by simply measuring the flow aligned viscosity coefficient of a material, at one or preferably more temperatures, it is possible to estimate how this material would behave in a display cell, and so compare it with other liquid crystal materials that are available. In this way, it is possible to obtain very useful practical information from a relatively simple, physical experiment.

In practice, viscosity measurements are usually carried out at 20°C; this yields the coefficient η_{20^oC}. A second measurement at a different temperature (eg, 0°C giving η_{0^oC}) allows the values for Ea and η_0 to be calculated using Equation (1). The value for Ea is quite significant in that it is a measure of the rate of change of viscosity with temperature. For practical applications, it is not simply the viscosity of the material at normal temperatures that is important (as in many cases this is reasonably acceptable), but it is the viscosity of the material at low operating temperatures (eg, -30°C or lower) that is critical. Consequently, achievement of as low a value for Ea as possible is most desirable. Several viscosity measurements made at various temperatures are preferable in order to obtain an accurate value for Ea, and if an extensive range of temperatures is covered, the full viscosity-temperature characteristics for a material are revealed (as shown in Figures 8 and 9 for the compound PECH 5.02). As a rough guide, values for η_{20^oC} are generally within the range 15-50 cP for most simple nematogens, with corresponding values for T_{ON} and T_{OFF} being within the range 50-250 ms.

Often however, the material under test does not have a nematic phase at a practically accessible temperature, and particularly at 20^oC. For example, the melting point may be too high, the material may be smectic, the material may possess a low T_{N-I} value, or indeed the material may have no nematic phase at all. Although such materials may be considered less interesting because of these properties, it must be remembered that successful liquid crystal materials are mixtures of compounds, some components of which may have poor liquid crystal thermal properties, but other very useful physical properties, such that their incorporation into a mixture is advantageous. In view of this, it is often desirable to assess such materials for their potential as low viscosity additives.

There are two approaches to this problem. Firstly, if the material has a low (or virtual) T_{N-I} value, it may only be possible to carry out viscosity experiments on the isotropic liquid. As mentioned earlier, the isotropic viscosity is usually higher than the nematic viscosity at the same temperature, but generally both follow the same trend. Consequently, if the isotropic viscosity is low, then so too will be the nematic viscosity. Therefore, in the absence of a nematic phase (either for the test compound itself, or in terms of experimental accessibility), the isotropic viscosity alone is a useful pointer to the viscosity characteristics for a material.

The second approach to this problem is to use the material in admixture with a suitable nematogen. This procedure is applicable to materials of low T_{N-I} value (providing the T_{N-I} value of the mixture is not lowered unreasonably), to high melting point materials (providing the compound is adequately soluble in the host), and to smectogens (providing that the smectic tendencies of the mixture are sufficiently depressed). Such mixtures (eg, of 4-n-alkyl-4'-cyanobiphenyls - CB's) have been found by Constant and Raynes[64] to reveal an approximate logarithmic relationship which had previously been observed for isotropic liquids[65] - see Equation (4).

$$\log \eta = c_1 \log \eta_1 + c_2 \log \eta_2 \qquad (4)$$

where

η = viscosity of the mixture;
c_1, c_2 = concentration of component 1, 2;
η_1, η_2 = viscosity of component 1, 2.

The material under test is therefore mixed in a known concentration (usually 20 wt %) with the nematic host (usually ZLI 1132 - E Merck, Darmstadt, West Germany or E7[†]) and the

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[†] General data for the two eutectic mixtures E7 and ZLI 1132

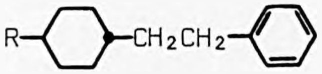
E7	ZLI 1132
C -10 N 60 I	C -6 N 70 I
$\eta_{20^\circ C}$ = 40.0 cP	$\eta_{20^\circ C}$ = 27.9 cP
Composition (wt %):	Composition (wt %):
CB 5 (51.0), CB 7 (25.0) CB 80 (16.0), T15 (8.0)	PCH 3 (24.0), PCH 5 (36.0) PCH 7 (25.0), BiCH 5 (15.0)

viscosity for the mixture determined. If the viscosity for the host itself is known at the desired temperature, then the nematic viscosity for the test material may be calculated. This value is essentially the nematic viscosity that the material under test would have if it were able to exhibit a nematic mesophase at that temperature.

However, the viscosity coefficients obtained by this method must be viewed with some caution. This is because the above logarithmic relationship has been developed for CB compounds and may not hold true for other systems. Related materials possessing similar dielectric behaviour and intermolecular forces, etc, are likely to be fairly well described by such a relationship, but other materials of a widely different nature may deviate markedly from the predicted value. Consequently, the viscosity coefficient obtained by this method may vary depending upon the host employed, and perhaps the most satisfactory situation is to use a host of a similar nature to the material under test. This is not however always done in practice and the Merck mixture, ZLI 1132, is often used rather indiscriminately.

Thus, overall, it is possible to obtain information on the viscosity behaviour of most materials either directly from the nematic phase, by using the isotropic liquid, or by dissolving the test material in a suitable nematic host.

Some general trends may be observed for the variation of viscosity with molecular structure, but in many cases there is no direct correlation between the two. In terms of molecular size, as might be expected, smaller molecules generally give a lower viscosity than do molecules of a high molecular weight. For example, mesogens incorporating only a single ring structure have lower viscosities than those containing two ring systems, and in turn, these have lower viscosities than systems with three rings, etc. However, within each of these groups, it is not possible to predict the order of the viscosities for different substituents with any degree of certainty. For a given homologous series the viscosity usually increases with hydrocarbon chain length. Figure 10 shows this effect for the isotropic viscosities of the series of compounds



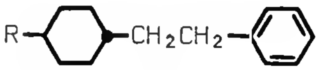
PECH R·H

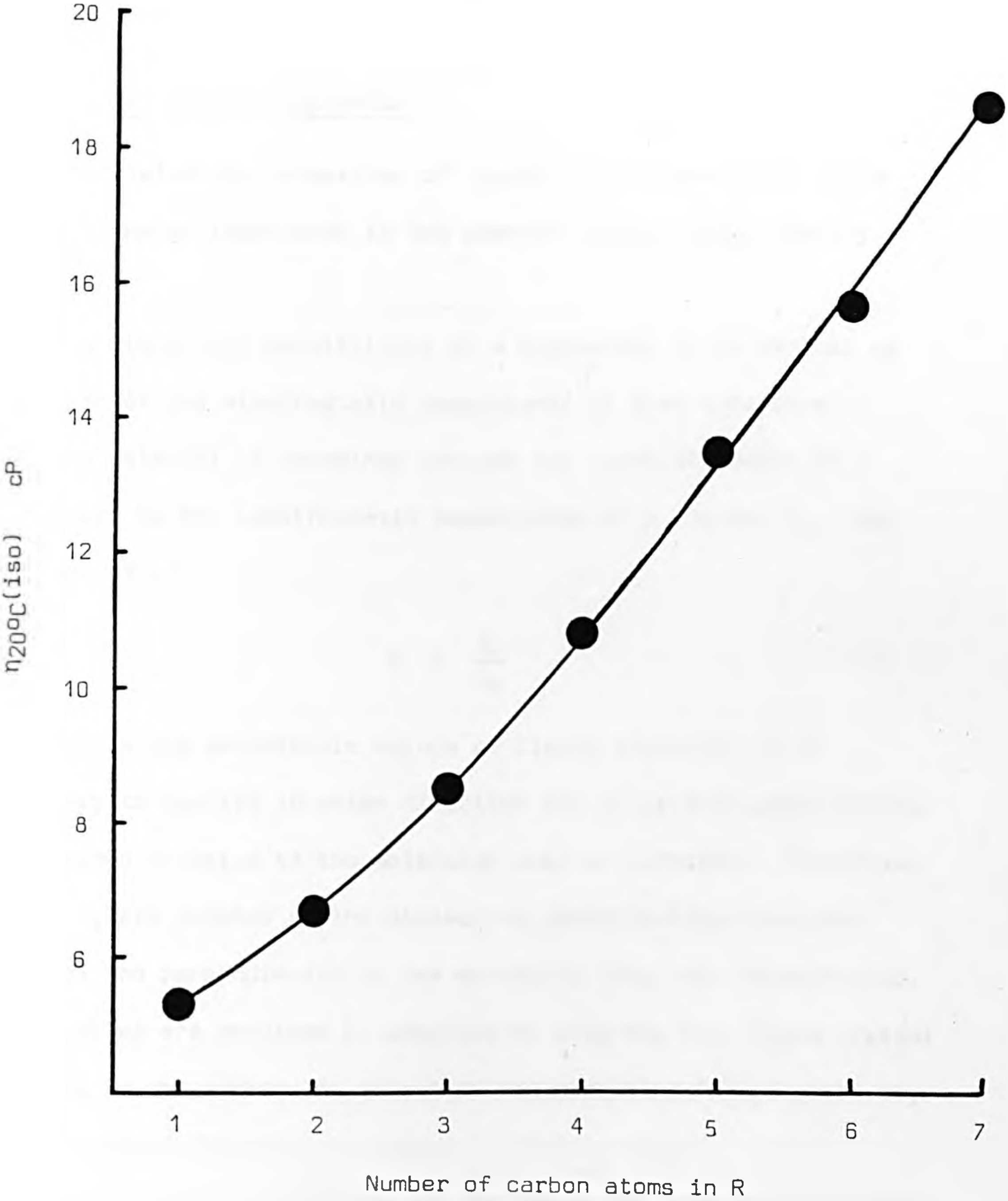
The steady increase in the viscosity as the alkyl chain length, R, increases may be interpreted in terms of the greater intermolecular attractive (Van der Waals) forces resisting the flow of the molecules past one another.

Other molecular structural relationships relating to viscosity coefficients include the effect of polar groups,[66] which tend to increase the viscosity due to increased intermolecular attractions by way of dipole-dipole interactions. Also, lateral substituents generally adversely affect the viscosity of a material (single component or a mixture), primarily due to the geometry of the molecule and introduction of a 'drag' into the system. It is usually observed that a compound incorporating the *trans*-1,4-disubstituted cyclohexane ring has a lower viscosity than the analogous compound incorporating a 1,4-disubstituted benzene ring. The reason for this is probably that an aromatic ring possesses polarisable electrons, capable of induced-dipolar intermolecular interactions, etc, whereas this is not the case for an alicyclic cyclohexane ring.

FIGURE 10

Graph of viscosity against number of carbon atoms in R for the series





However, generalisations beyond these broad conclusions are of limited value, and this serves to illustrate the complexities involved in molecular viscosities.

4.1.2 *Dielectric Properties*

The dielectric properties of liquid crystal materials are a factor of major importance in the area of electro-optic display devices.

The dielectric permittivity of a substance, ε, is defined as the ratio of the electrostatic capacitance of that substance, C, when the material is contained between the parallel plates of a condenser, to the electrostatic capacitance of a vacuum, C_0 - see Equation (5).

$$\varepsilon = \frac{C}{C_0} \tag{5}$$

Due to the anisotropic nature of liquid crystals, it is necessary to specify in which direction the dielectric permittivity is measured relative to the molecular axis or director. Therefore, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are defined as the dielectric permittivities measured parallel and perpendicular to the molecular long axis respectively. These values are obtained in practice by aligning the liquid crystal material in one particular direction and measuring the permittivity in the desired direction by using an electric field.

The dielectric anisotropy is defined as the difference between the permittivity values measured parallel and perpendicular to the molecular long axis - see Equation (6).

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \qquad (6)$$

When a liquid crystal passes into the isotropic liquid, the system is of course no longer anisotropic. In this case the isotropic permittivity, ε_{iso}, is obtained, and this is directly comparable with the average permittivity, $\bar{\varepsilon}$, of the nematic phase where

$$\bar{\varepsilon} = \frac{1}{3}(\varepsilon_{\parallel} + 2\varepsilon_{\perp}) \qquad (7)$$

In the case of normal nematogens, a plot of $\bar{\varepsilon}$ and ε_{iso} against temperature is therefore continuous from the nematic state through into the isotropic liquid. This point will be discussed in more detail later in the context of molecular antiparallel dimerisation effects.

If a magnetic field is used instead of an electric field to measure the permittivities of the liquid crystal, then the corresponding diamagnetic parameters, and therefore the diamagnetic anisotropy, $\Delta\chi$, may be obtained. However, these are used to a much lesser extent than the dielectric properties in relation to display devices.

As dielectric properties are not temperature independent, to be strictly accurate, the temperature at which the permittivity measurements are made should be quoted. Also, as discussed earlier (Section 2.2.1), the dielectric properties are dependent upon the frequency of the applied field, and this value should also be quoted. Whenever possible, measurements are carried out at 20°C or some fixed reduced temperature, T (where $^{T}/T_{N-I}$ = constant), at a frequency of 1 KHz with a driving voltage of 1 volt.

The significance of the dielectric anisotropy in connection with display devices may be seen from Equation (2), given in the previous section. The larger the value of $\Delta\varepsilon$, the shorter will be the turn-on time of the cell when the electric field is applied. Although in principle materials of low dielectric anisotropy can be made to have fast turn-on times by increasing the applied field (as $\Delta\varepsilon \times E^2$ = constant), this would seriously reduce one of the main advantages of liquid crystal display devices, namely, that they involve only a very small power consumption (typically 2 μW cm^{-2}).

Note from Equation (3) that the turn-off time is independent of the dielectric anisotropy as only surface and intermolecular forces are involved.

In designing materials with particularly high or low values for $\Delta\varepsilon$, depending upon the application, it is often easiest to adjust the magnitude of $\varepsilon_{\parallel}$ rather than $\varepsilon_{\perp}$. Strongly electron attracting groups such as cyano, nitro or halogeno, when incorporated into a liquid crystalline structure, tend to induce a dipole moment due to the unsymmetrical distribution of electrons throughout the molecule. This is often achieved, with much better results both in terms of ease of synthesis and polarisability effects, in the terminal position of a molecule rather than a lateral position. This is illustrated by the fact that it is possible to obtain positive values of $\Delta\varepsilon$ up to approximately +25, but it is difficult to obtain more negative values than $\Delta\varepsilon = -10$ at normal temperatures. As an example, the CB's have approximate values of $\Delta\varepsilon = +11$ ($\varepsilon_{\parallel} = 18$ and $\varepsilon_{\perp} = 7$).

Although it would appear that values of $\Delta\varepsilon$ as large as possible (positive or negative) are required for the fast response times of display devices, there are other factors to consider, and it has been found that the optimum value for $\Delta\varepsilon$ generally lies between 2.5 and 5.0.

This is because one of the major factors related to the magnitude of $\Delta\varepsilon$ is the threshold voltage sharpness of the display (to be discussed more fully in section 4.1.4), ie, the display should preferably be turned fully 'ON' from the 'OFF' state over as small a range of the applied voltage as possible. It has been shown[67] that the display sharpness is inversely proportional to the ratio $\frac{\Delta\varepsilon}{\varepsilon_\perp}$, ie, the sharpness is increased by lowering the value of $\frac{\Delta\varepsilon}{\varepsilon_\perp}$. This value is obviously lowered as $\Delta\varepsilon$ tends to zero, and this is the opposite situation for $\Delta\varepsilon$ as implied for fast response times by Equation (2); hence, the compromise situation of $\Delta\varepsilon = 2.5 - 5.0$ arises.

This effect of threshold sharpness dependency on $\Delta\varepsilon$ is typically illustrated in the case of CB's (high $\Delta\varepsilon$) in admixture with ester materials of low $\Delta\varepsilon$. At high concentrations of the CB, the threshold sharpness is poor. As significant amounts of suitably substituted phenyl benzoates or phenyl cyclohexanoates are added, so the $\Delta\varepsilon$ value for the mixture is reduced, until, at a concentration of about 30% ester, the display sharpness is at a maximum. The addition of further amounts of ester serves only to reduce $\Delta\varepsilon$ without further increasing the threshold sharpness of the display.

The function of the ester additive is believed to involve a breakdown of the antiparallel molecular pairing which has been found to occur in CB systems. Figure 11 illustrates schematically

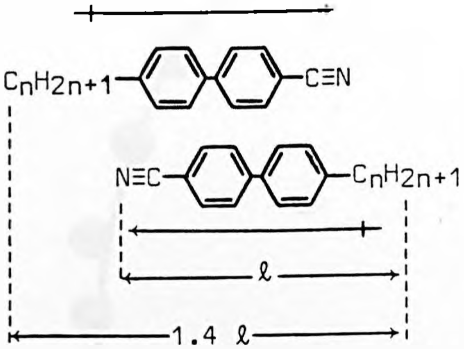


FIGURE 11

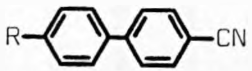
Antiparallel molecular correlation for the CB's

how the CB molecules are effectively interdigitated. This situation arises because of intermolecular charge effects, ie, it is apparently energetically most favourable for the molecules to pair with their axes of maximum polarity in opposite directions. As a result, the effective overall length of such a pair is about 1.4 x the molecular length. As the dipolar axes of the molecules in each pair are opposed, this serves somewhat to reduce the value of $\Delta\varepsilon$, so that a pure CB exhibits a lower $\Delta\varepsilon$ value than might be expected.

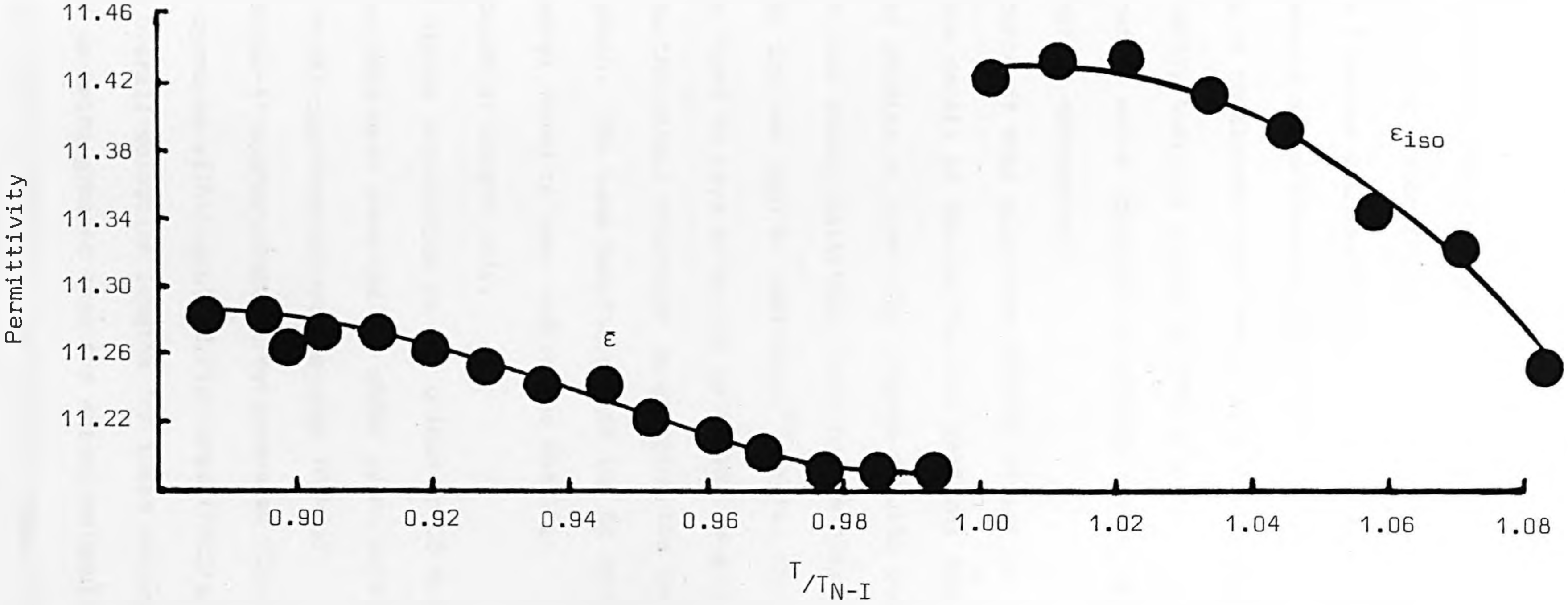
Confirmation of this molecular pairing situation is obtained from dielectric permittivity data for CB's both in the nematic and isotropic liquid states (see Figure 12). As mentioned above, for a normal, unpaired system, a plot of $\bar{\varepsilon}$ and ε_{iso} against temperature is continuous, even at the N-I transition temperature. As can be

FIGURE 12

Graph of permittivity against reduced temperature for a ternary mixture of



(R = C_3H_7–:C_5H_{11}–:C_7H_{15}–; 30:40:30 wt %)



seen from Figure 12, this is not the case for a CB system, and the plots of $\bar{\varepsilon}$ and ε_{iso} v T are discontinuous at the N-I transition temperature. As the $\bar{\varepsilon}$ values are lower than the ε_{iso} values, this means that in the nematic state there is some factor effectively reducing $\bar{\varepsilon}$, and this is consistent with the antiparallel pairing situation. Significantly too, the height of the step or discontinuity referred to above decreases on adding low $\Delta\varepsilon$ materials which disrupt the pairing arrangement.

Supporting evidence of this molecular pairing effect is obtained from the fine detail of the diffraction patterns from high resolution X-ray studies of carefully aligned nematic phases of these and related (see below) materials, both in the pure state and in admixture with low and high $\Delta\varepsilon$ additives.[68] Here, the pure cyano components are found to have effective molecular lengths roughly equivalent to the actual molecular length plus the length of the hydrocarbon chain. The same materials with low $\Delta\varepsilon$ additives incorporated are however found to have end-to-end spacings equivalent to the molecular length only.

This effect of dipole correlation is not unique to CB molecules, as similar properties have been observed for other cyano systems, eg, *trans*-1-n-alkyl-4-(4'-cyanophenyl)cyclohexanes (PCH's), *trans*-1-n-alkyl-4-(*trans*-4'-cyanocyclohexyl)cyclohexanes (CCH's), and 1-n-alkyl-4-(4'-cyanophenyl)bicyclo(2.2.2)octanes (PBCO's). Again the effective overall molecular lengths for these materials have been calculated as being greater than the actual molecular length. The PCH's and PBCO's represent intermediate cases in which just the cyanophenyl groups pair in an antiparallel manner, whereas in the case of the CCH's, wherein no aromatic rings are present, the main charge distribution is located on the cyano group, so that only these groups pair up antiparallel in order to optimise attractive and minimise repulsive molecular interactions. This gives an overall length for the CCH dimer of approximately 1.8 x the molecular length (see Figure 13).

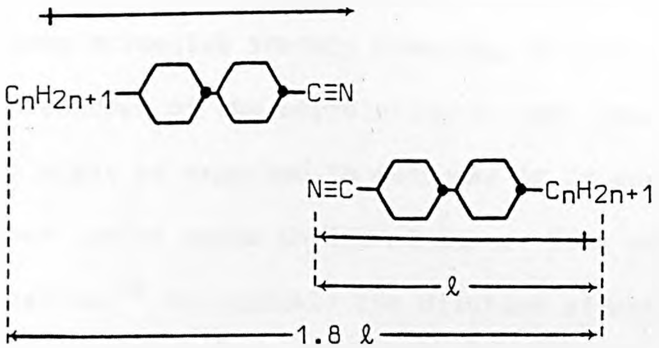


FIGURE 13

Antiparallel molecular correlation for the CCH's

Such dynamic systems of paired molecules may in fact be the reason why terminally cyano-substituted materials have such high T_{N-I} values and the cyano substituent heads the nematic terminal group efficiency order - ie, the effective molecular length is between 1.4 and 1.8 x the actual molecular length.

Also, a similar pairing situation exists for cyano materials incorporating the $-CH_2CH_2-$ inter-ring linkage, as will be discussed in Section 4.5.2.

The overall effect of antiparallel correlation with respect to electro-optic display devices is to not only increase the threshold voltage because of the effective reduction in $\Delta\varepsilon$, but also to reduce the sharpness of the threshold. It is believed that such low $\Delta\varepsilon$ additives, which are incapable of similar dipole correlation effects themselves, serve to break up the molecular dimers, so that the cyano/ester mixed system is virtually correlation free. In molecular terms it is envisaged that an ester molecule penetrates, either fully or partially, the pair of correlated cyano molecules thereby breaking up such interactions. The initial breakdown of the correlation at very low ester concentration might be expected to *increase* $\Delta\varepsilon$ if any polar order of the 'monomer' units arose in the mixture. Some evidence for this effect exists,[69] but quickly the dilution effect of adding the low $\Delta\varepsilon$ ester predominates and lowers $\Delta\varepsilon$. This mechanism would require a molecular concentration ratio of approximately 2:1 of high $\Delta\varepsilon$:low $\Delta\varepsilon$ material which is in fair agreement with the optimum experimentally determined concentration of about 30-40% ester.

As a result of the addition of low $\Delta\varepsilon$ components to purely cyano systems, the threshold sharpness is greatly improved (the overall value for $\Delta\varepsilon$ being a weighted average of the materials used in the mixture), and the threshold voltage is only slightly increased.

Further support for these ideas comes from the experimental observations that other low $\Delta\varepsilon$ materials, apart from esters, are just as efficient in breaking up these antiparallel correlation effects of cyano compounds. These systems include low Δε materials incorporating the -CH_2CH_2- linkage, again to be discussed later. Phenyl benzoate and phenyl cyclohexanoate based esters are used commercially because they have themselves nematic liquid crystal phases (ie, the T_{N-I} value of the mixture is not drastically reduced), as well as other acceptable properties such as moderate viscosity, high birefringence, adequate solubility, etc, and the fact that they can be produced economically on a large scale. However, some of the properties of these ester materials could be improved upon with regard to increased molecular stability, lower viscosity, lower smectic tendencies, etc. Therefore, it can be seen that the search for new, improved materials of low Δε is just as important as that for new, improved materials of high Δε.

With these factors in mind, it is therefore desirable that novel liquid crystals are screened for their dielectric permittivities as well as for their other characteristic physical and electro-optic properties.

Ideally, permittivity measurements are carried out on the pure material in the nematic state, usually at 20°C or some fixed reduced temperature. Results obtained in this way then allow a direct comparison with similar data for other materials, ie, the magnitude of Δε is obtained under standard conditions.

By obtaining permittivity measurements over a range of temperatures, information may also be acquired concerning molecular correlation effects, particularly if this temperature range includes the T_{N-I} value, so that measurements are made on both the nematic and isotropic liquid states.

However, if it is not possible to carry out permittivity measurements on the pure material (eg, the melting point is too high, the material is smectic, or it has no nematic phase, etc), then measurements may be conducted using a mixture of the compound in a suitable nematic host such as E7, ZLI 1132 or a low $\Delta\varepsilon$ system. As much of the test material as possible should be incorporated into the host, dependent upon the solubility, T_{N-I} value, etc, of the particular compound. If the dielectric properties of the host are known, and those of the mixture measured, then by assuming that the values are additive (ie, a linear function of mixture composition), the permittivities for the test material may be obtained by extrapolation to zero concentration for the host.

4.1.3 Optical Properties

The anisotropic nature of liquid crystals not only applies to their electric and magnetic characteristics, but is also evident from their optical properties.

When a ray of light is passed through a smectic, nematic or cholesteric liquid crystal, it is split into two separate components which travel with different velocities through the medium. Consequently, these components are refracted to different extents so that the two rays follow different paths. These two rays are termed the *ordinary* ray and the *extraordinary* ray. The ordinary ray (refractive index n_o) is classified as the ray for which the electric vector vibrates normal to the liquid crystal molecular director. Similarly, the extraordinary ray (refractive index n_e) has its electric vector vibrating parallel to the molecular director.

The optical anisotropy of a material, often termed the birefringence, Δn, is the difference between the refractive indices of the extraordinary and ordinary rays, ie,

$$\Delta n = n_e - n_o$$

Experimentally the values for n_e and n_o are measured by some suitable optical method, such as a refractometer. In the case of nematic liquid crystals, the material is usually aligned first (for example, by lecithin to give a homeotropic alignment) so that accurate and reproducible values for the refractive indices are obtained. As the birefringence of a liquid crystal is often temperature dependent, such measurements are usually carried out at some specific temperature, such as 20°C, or preferably some reduced temperature. Usually, a ray of monochromatic light, such as the sodium-D line (λ = 589.6 nm) is employed as the incident irradiation.

If it is not possible to obtain birefringence data for a particular material, an estimate for these values can be obtained by incorporating the test material into a suitable host. This may be necessary if the material has no nematic phase (resulting in virtual index values) or has a nematic phase that is not easily accessible on the temperature scale, etc. As with dielectric permittivities, the optical anisotropies are assumed to be a linear function of mixture composition, so that by knowing the values for the host, the data for the mixture can be extrapolated to yield the corresponding results for the material under test.

The birefringence value for a liquid crystal is important for the successful operation of electro-optic display devices. In the case of the twisted nematic display, a sufficiently high optical anisotropy (roughly between 0.1 and 0.3) is required to maintain an acceptable contrast between the 'ON' and 'OFF' states. For the cholesteric-nematic phase change display, low values for the optical anisotropy (<0.1) are required to avoid the partial imaging of unselected elements. An example of the birefringence of two commercially used mixtures for twisted nematic applications is provided by E7, $\Delta n = 0.23$ and ZLI 1132, $\Delta n = 0.14$ - both values being measured at 20°C and 589.6 nm.

4.1.4 *Voltage Characteristics and Addressing Techniques*

The transition of a liquid crystal display cell from the 'OFF' to the 'ON' state is not a simple one-step process, but is brought about rather by a gradual change in the orientation of the molecules. Although primarily a field effect, this process of molecular reorientation or its assessment is observed to be dependent on such factors as the applied voltage, temperature, viewing angle, etc. Each display cell is therefore assessed in terms of these variables so that it is possible to compare the different liquid crystal materials used under standard conditions.

In the 'OFF' state, a twisted nematic liquid crystal display allows incident light to pass through it. As a voltage is applied across the cell, a point is reached at which the transmission of light starts to decrease. As this point, the display is just beginning to be switched 'ON', so that the corresponding applied voltage is termed the threshold voltage, V_T. Further increasing the voltage reduces the transmission until eventually the cell is fully 'ON'. The percentage transmission against voltage is shown graphically in Figure 14, and it can be seen that different characteristics are obtained depending on the angle from which the display is viewed. The angles shown are deviations from the cell normal so that, for a given applied voltage, the display appears to be more 'ON' (ie, there is a lower % transmission) when it is viewed at an angle, rather than normal to the cell.

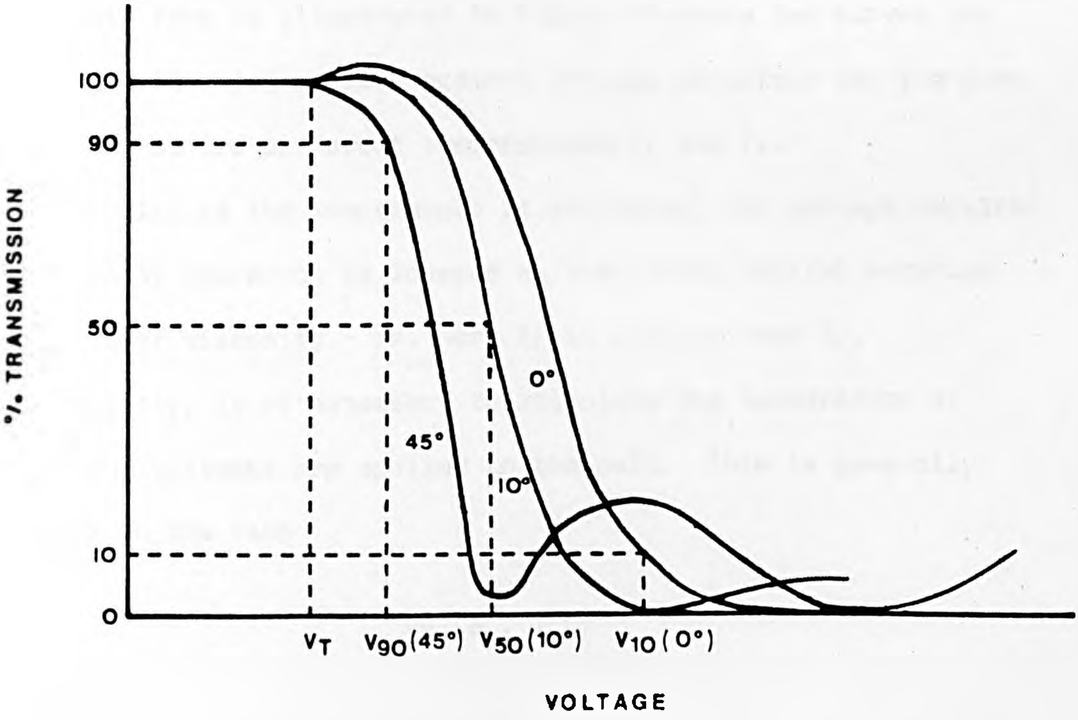


FIGURE 14

General plot of transmission against voltage for a TN-display as a function of viewing angle

An observer usually decides that such a display is completely 'OFF' at all viewing angles if the applied voltage, V, is such that

$$V < V_{90}\ (45^{\circ})$$

where $V_{90}\ (45^{\circ})$ is the voltage required to produce 90% transmission as measured at an angle of 45° to the cell normal.

Similarly the display is judged to be 'ON' when

$$V > V_{10}\ (0^{\circ})$$

A major drawback with liquid crystal displays is that usually the voltages required either to leave the display 'OFF' or to turn it fully 'ON' vary significantly with temperature, ie, $\frac{dV}{dT}$ is non-zero.

This fact is illustrated in Figure 15 where two curves are shown for the transmission against voltage behaviour for the same cell, but at two different temperatures, T_1 and T_2.

Usually as the temperature is increased, the voltage required for display operation is lowered as the liquid crystal material has a lower viscosity - ie, here T_2 is greater than T_1. Consequently, it is necessary to stipulate the temperature at which the voltages are applied to the cell. This is generally written in the form

$$V_X\ (\theta^{\circ},\ T^{\circ}C)$$

where

X = percentage transmission
θ = viewing angle
T = temperature at which the voltage is applied

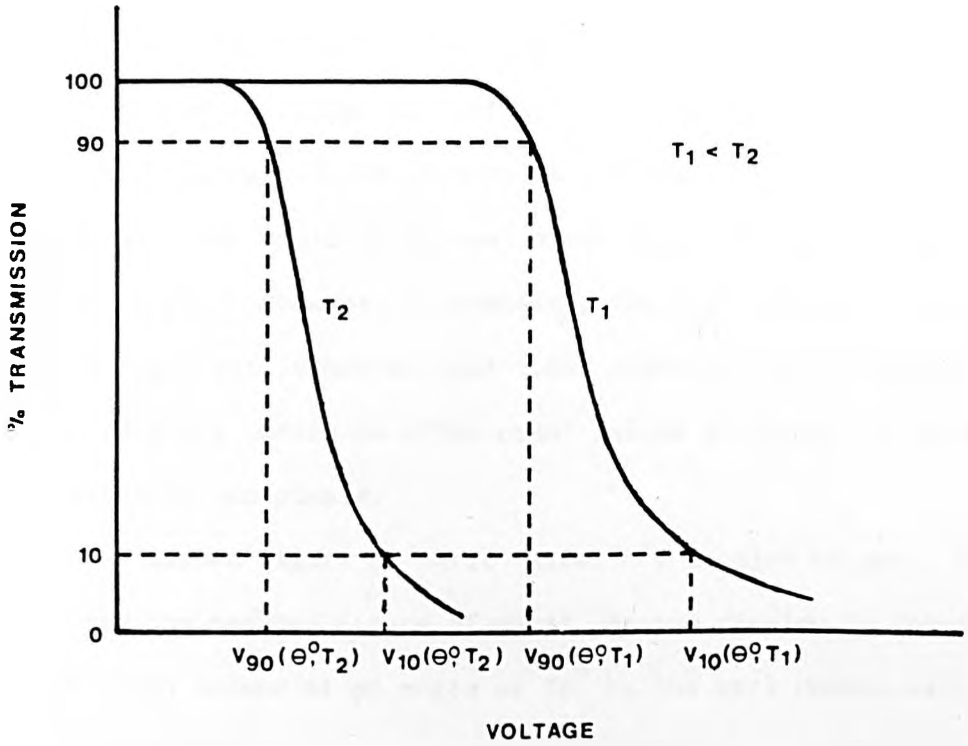


FIGURE 15

General plot of transmission against voltage for a TN-display as a function of temperature

Many electro-optic measurements are carried out at 20°C, so that the appropriate 'OFF' and 'ON' state voltages are given by

$$V < V_{90}\ (45^{\circ},\ 20^{\circ}C) \qquad \text{OFF}$$
$$V > V_{10}\ (0^{\circ},\ 20^{\circ}C) \qquad \text{ON}$$

By using these characteristic voltages it is possible to assign a figure of merit value, M, which is used to assess each particular material. At 20°C, M is defined as

$$M_{20^{\circ}C} = \frac{V_{10}\ (0^{\circ},\ 20^{\circ}C)}{V_{90}\ (45^{\circ},\ 20^{\circ}C)}$$

ie, the figure of merit is defined as a ratio of the 'ON' to 'OFF' voltages. In an ideal case, the transmission *v* voltage curve is as steep as possible, so that only a very small change in the applied voltage is required to switch from the 'OFF' to the 'ON' states. This would give a value for M_{20^oC} of, or just greater than, unity. However, in practice, the best materials to date have M_{20^oC} little better than 1.60, although for three-way multiplexing (which is often used) values of $M_{20^oC} < 1.92$ are reasonably acceptable.

A second figure of merit value, M^1, is also of use. This is termed the *reduced* figure of merit, as the display is considered 'ON' when viewed at an angle of 10^0 to the cell normal with 50% transmission.

ie,
$$M^1{}_{20^oC} = \frac{V_{50}\ (10^o,\ 20^oC)}{V_{90}\ (45^o,\ 20^oC)}$$

The value of M^1 is always less than M, for a given material and temperature, so that the number of lines that can be multiplexed is always increased when the reduced viewing conditions are used.

As the voltage characteristics vary significantly with temperature, it is also necessary to be able to assess materials over a range of temperatures. To do this, usually a temperature range of 0 to 40^oC is used, whereby the display is considered to be 'OFF' at 40^oC and 'ON' at 0^oC, so that the minimum and maximum possible voltages are involved, respectively. The corresponding figures of merit are therefore defined as

$$M_{0-40^oC} = \frac{V_{10}\ (0^o,\ 0^oC)}{V_{90}\ (45^o,\ 40^oC)}$$

$$M^1_{0-40^oC} = \frac{V_{50}\ (10^o,\ \ 0^oC)}{V_{90}\ (45^o,\ 40^oC)}$$

These figures of merit are always greater than the corresponding value obtained at constant temperature, so that few materials conform to the requirement of $M_{0-40^oC} < 1.92$ for three-way multiplexing.

The actual figure of merit that is most applicable for a given material depends upon the application for which the display device is to be used. For example, for applications involving temperature-uncompensated voltage drive (watches, pocket calculators, etc) the relevant figures of merit are M_{0-40^oC} and $M^1_{0-40^oC}$, whereas for more involved applications which require a temperature-compensated drive M_{20^oC} and $M^1_{20^oC}$ are applicable.

As already mentioned, the display transmission is changed, for a given applied voltage, as the temperature is altered. This is an obvious drawback of liquid crystal display devices, because, with an increase in temperature, for example, unselected elements (ie, 'OFF' elements) may suffer a reduction in the amount of light transmitted. These elements then appear to be either fully or partially 'ON' - ie, there is 'cross-talk' of the elements.

Ideally, the temperature dependence of the transmission *v* voltage curves should be measured for various parts of the curves, but in practice the normalised rate of change of the voltage with temperature, $\frac{1}{V}\left(\frac{dV}{dT}\right)$, does not vary greatly with either the viewing angle or the applied voltages, so that a single measurement at each temperature, using normal incidence, is usually adequate. This voltage dependence on temperature is defined as:

$$\frac{1}{V}\left(\frac{dV}{dT}\right) = \frac{1}{\frac{1}{2}\left[V_{10}\,(0^{o},\,T_1) + V_{10}\,(0^{o},\,T_2)\right]} \cdot \frac{V_{10}\,(0^{o},\,T_1) - V_{10}\,(0^{o},\,T_2)}{T_1 - T_2} \times 100$$

(in % $^{o}C^{-1}$ units)

by reference to Figure 15.

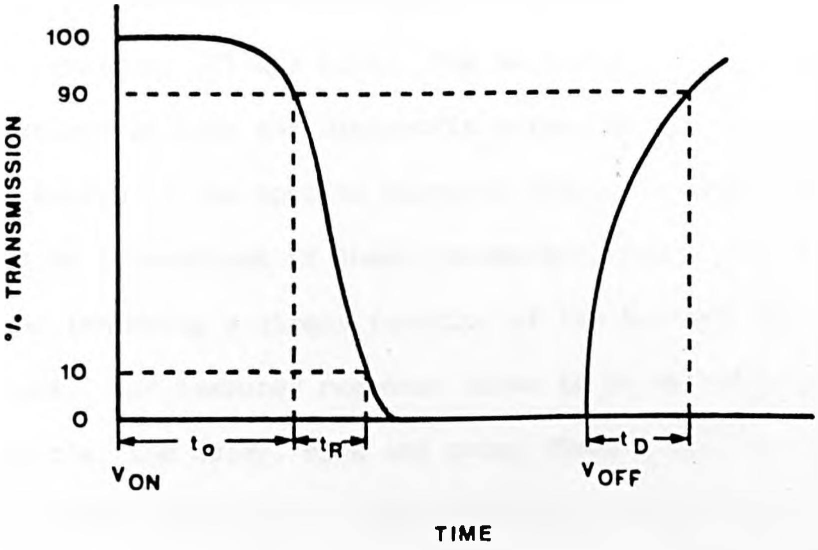
As examples, values of $\frac{1}{V}\left(\frac{dV}{dT}\right)$ = 0.84% $^{o}C^{-1}$ and 0.79% $^{o}C^{-1}$ are obtained for the commercial mixtures E7 and ZLI 1132, respectively. Obviously, as low a rate of change as possible is desirable, and values below 0.30% $^{o}C^{-1}$ have been recorded, eg, 0.28% $^{o}C^{-1}$ for the high voltage mixture ZLI 1216 prepared by E Merck, Darmstadt, West Germany. Note that due to the inverse relationship of the voltage with temperature, the above values should be -0.84% $^{o}C^{-1}$ for E7, etc, but often the negative sign is omitted.

The response times (switch-on and switch-off times) for a display device are also very important characteristics. These times should be as short as possible, and Figure 16 illustrates how such optical responses are derived from a plot of the transmission against time curve for a twisted nematic cell.

The voltage, V, is applied at time t = 0 (V_{ON}); the switch-on time (T_{ON}) consists of a delay component (t_D), which is the time taken for the transmission to be reduced from 100% to 90%, and a rise time component (t_R), which is the time required for the display to become fully 'ON' (10% transmission).

The switch-off time (T_{OFF}) is defined as the decay time (t_D) required for the transmission to rise to 90% (the usual 'OFF' condition) from the instant that the applied voltage is removed.

As can be seen from Equations (2) and (3) (Section 4.1.1), the response times are directly proportional to the twist viscosity



t_0 = delay time
t_R = rise time
t_D = decay time

T_{ON} (switch-on time) = $t_0 + t_R$
T_{OFF} (switch-off time) = t_D

FIGURE 16

General effect of the applied voltage on the transmission against time characteristics for a TN-display

coefficient, γ_1, of the material, and to a first approximation, also to the simple experimental property of flow aligned viscosity, η. Therefore, sufficiently fast optical response times are only obtained with materials of suitably low viscosity values, and this is the reason why viscosity coefficients are so important when assessing a particular material for application in electro-optic display devices.

As well as the influence of viscosity upon the response times, other parameters of the material need also to be considered (again see Equations (2) and (3)). The switch-on time is inversely dependent on both the dielectric anisotropy of the material and the square of the applied electric field. However, the switch-off time is independent of these parameters, due to the switch-off mechanism being a direct function of the surface and intermolecular forces. For measured response times to be as comparable as possible, the delay, rise and decay times should be measured at a constant temperature, applied electric field, and cell thickness.

As an example, E7 produces response times of about 60 ms when driven at 3 volts in a 10 μm thick cell at 20^{o}C, although significantly faster response times are now accessible by using more recently developed materials.

The advances that have been made in recent years concerning the types of information stored and displayed, and the functions performed by LCD devices have been achieved only after overcoming major problems relating to the assembly electronics of such displays. The problem is that each of the seven independent elements that make up each individual numeral require a separate electrical connection. Consequently, for a display with n digits, 7 x n individual element connections are required. For the relatively simple display devices where n is small, this presents no real problem. However, with more complicated displays, where n is large, it can be seen that the number of connections required will be extremely large, so increasing the bulk of the display (a disadvantage) and making the cost of the assembly process more and more prohibitive. In fact, when n exceeds about 15 (over 100 elements), it becomes very difficult to fabricate a display with direct external electrical access to each individual element. The uneconomic nature of this type of display assembly is illustrated by the fact that the first mass-produced commercial calculators (utilising 67 individually driven display leads) were soon rendered uncompetitive when compared with single integrated circuit calculators.

In order to get around this problem, it is necessary to use a matrix-addressing (often termed multiplexing) technique which greatly reduces the number of external lines that must be driven (hence also the number of drivers required), as well as the number of electrical interconnections involved. Such a technique has the advantages of simplifying system-assembly and packaging, thereby saving time. As a consequence, the display is a more compact unit produced at a more economic rate, and having a potential for displaying more complex information. This situation is now possible, because each element is no longer individually driven; instead, several elements are arranged to share the same electrical line. However, it should be mentioned that there is almost always a trade-off between the multiplexing capacity and the optical performance of the display, although the advent of superior materials would serve to reduce this adverse effect.

The general principles of matrix-addressing may be illustrated by considering an X-Y grid (see Figure 17), the lines of which represent the electrical circuitry connecting the elements, with the intersections representing the display elements themselves.

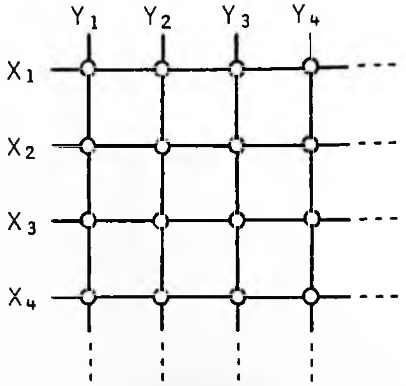


FIGURE 17

Schematic representation of display operation by the matrix-addressing technique

In the simplest case, the matrix lines are supplied with a steady voltage, ±V, as appropriate, which is just below the threshold voltage, V_T. At the desired intersections, where both the row and column lines have a voltage applied, the voltage difference (ie, +V - (-V) = 2 V) activates the central element as shown in Figure 18.

This is termed static matrix-addressing, where the voltage at each element is defined as the difference between the corresponding row and column voltages. Although the electrodes may be connected to the elements in many different ways, it is possible to define a 7 element numeral by a 3 x 3 matrix. This allows a 20 digit display to consist of a 3 x 60 matrix which requires 63 electrode terminals. The advantage of matrix addressing can be seen by comparing this with the fact that, with

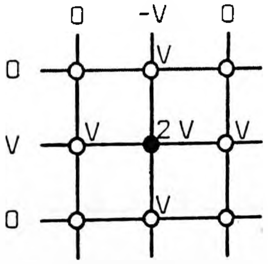


FIGURE 18

Schematic representation of the static matrix-addressing technique

this number of connections, only 9 digits may be displayed if each of the elements is independently driven. However, the main limitation of static addressing is its inability to display all possible patterns. For example, a closed outline, with none of the central elements activated, cannot be displayed, as this would involve the requirement that the same row and column voltages would simultaneously lead to some elements being 'ON', whilst neighbouring elements were 'OFF'. Despite such drawbacks, static matrix-addressing may be used for many applications in which the information to be displayed is not restricted in this way.

To display more complex types of information (including that which the static addressing technique cannot handle), it is necessary to use dynamic (time-shared) matrix-addressing. Here, steady-state voltages, ±V, again just below the threshold voltage V_T, are used to drive the column electrodes, with the rows being scanned sequentially, using a pulsed voltage, 2 V (see Figure 19).

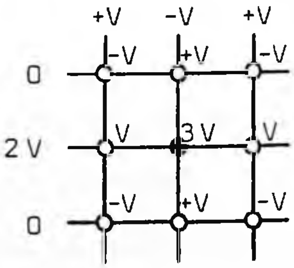


FIGURE 19

Schematic representation of the dynamic matrix-addressing technique

For most applications, it is sufficient to use only 3 rows in combination with the columns to display the seven electrodes required for each digit. This is termed 1 in 3 addressing. Also, the ratio of voltages for the 'OFF' and 'ON' elements is given by

$$\frac{V_{UNSELECTED}}{V_{SELECTED}} = \frac{1}{3}$$

so that overall this mode of addressing is termed the 1 in 3, $\frac{1}{3}$ way select case.

Using this technique, it is now possible to display more intricate patterns by arranging that elements receive appropriate varying voltage frequencies. As the scanning row voltage is used to activate the desired elements, it is necessary for the cycle-scanning time to be lower than the decay time, t_D, of the elements, so that the activated elements remain 'ON'. This requirement therefore restricts the number of rows that can be efficiently addressed, ie, for Y rows to be activated then

$$Y \times t_R < t_D$$

where t_R is the rise time for the elements. Thus, if the rise time of the element is very short, it is possible to address more rows. As the rise time is essentially the steepness of the transmission ν voltage curve (see Figure 14), it follows that for optimal multiplexing capacity, the slope of this curve must be as steep as possible. In practice, this means that the 'ON' elements are maintained just above V_T, whilst the 'OFF' elements are held just below V_T. Consequently, it is necessary for the elements to have very good sharpness characteristics, and this is reflected in the requirements for M_{20^oC} and M_{0-40^oC}, which must have even lower values than those demanded for independent element addressing.

As all of the elements in a display addressed by dynamic multiplexing are maintained as close as possible to V_T, there is a high risk of 'cross-talk' interfering with the display information, particularly if the voltage properties of the liquid crystal material are temperature dependent. A high value of $\frac{1}{V}\left(\frac{dV}{dT}\right)$ therefore reduces the number of lines that may be efficiently multiplexed, so that even lower values of voltage-temperature dependence than those currently accessible are necessary to enable displays to be multiplexed to a very high level.

Table 1 shows the level of matrix addressing attainable as a function of the voltage figure of merit and temperature dependency of the threshold voltage.

TABLE 1

Maximum limits of the performance parameters required of liquid crystal materials in relation to the number of multiplexible lines in a TN-display

Number of multiplexed lines	M_{20^oC}	$\frac{-1}{V}\left(\frac{dV}{dT}\right)$ % $^oC^{-1}$
4	1.73	1.07
8	1.41	0.74
12	1.35	0.60
16	1.29	0.51
25	1.22	0.40
50	1.15	0.28
100	1.11	0.21

It should be mentioned that these values are the maximum tolerances permitted, and that for practical applications it may be desirable to have M_{20^oC} and $\frac{1}{V}\left(\frac{dV}{dT}\right)$ values lower than this.

It is also possible to assess different liquid crystal materials in terms of a *margin* which helps to decide the level to which the material is capable of being multiplexed

ie,

$$\text{margin (\%)} = \left(\frac{M^{-1} - N}{M^{-1} + N}\right) \times 100$$

where

$$N = \frac{V_{UNSELECTED}}{V_{SELECTED}} = \left(\frac{n}{n+8}\right)^{\frac{1}{2}} \text{ for } n \leqslant 4, \text{ or } = \left(\frac{\sqrt{n}-1}{\sqrt{n}+1}\right)^{\frac{1}{2}} \text{ for } n > 4$$

n = level of matrix addressing, 1 in n^{70}

M = M_{20^oC}, M_{0-40^oC}, $M^1_{20^oC}$, $M^1_{0-40^oC}$, as appropriate

Effectively, the margin is the percentage by which the power supply may be varied such that the display elements remain almost unaffected (ie, there is negligible cross-talk). Therefore, as high a value as possible is required for the margin. By assessing the margin at a particular level of multiplexing (eg, 1 in 3), the margin at any other level (eg, 1 in 2, 1 in 4, etc) may be calculated from this equation.

Examples of such values (for the 1 in 3, $\frac{1}{3}$ select case) are 10.5% and 12.1% for the specifically designed, commercial multiplexible mixtures E35MX (BDH Chemicals Limited) and ZLI 1216 (E Merck, Darmstadt, West Germany), respectively.

For general applications, such as the TN-displays used in watches and calculators, 3- or 4-way multiplexing is usually sufficient. In these cases, the materials presently available have no great difficulty in reaching the required electro-optic performance. However, for more complex applications involving 8-, 16- or possibly even 32-way matrix-addressing, severe restrictions are imposed by the liquid crystal material. For example, the best currently available high level multiplexible mixtures (BDH eutectics E120, E130, and E140) are capable of only up to around 8-way multiplexing. From this it can be seen that there is an enormous demand for new liquid crystal materials and mixtures that are able to satisfy the demands of 8-way and higher multiplexing.

4.1.5 *Elastic Constants*

Although not particularly well understood in molecular terms, the elastic constants of liquid crystals are very important with particular reference to display cells.

Consider a nematic liquid crystal sandwiched between the two plates of a cell. In the idealised situation, the molecules are all aligned with their long axes arranged in a uni-directional manner, such that the system adopts the lowest energy conformation. However, in reality, due to surface effects, and intermolecular interactions, the molecular arrangement tends to experience small, but significant distortions, such that the molecular alignment (and the nematic director) deviates from the idealised uni-directional form. It is possible to distinguish three different types of elastic distortion, termed *splay*, *twist*, and *bend*, which are characterised by the constants k_{11}, k_{22}, and k_{33}, respectively. These deformations are illustrated in Figure 20.

FIGURE 20

Elastic deformations of liquid crystals

Values for these elastic constants are of the order of 10^{-12} N, with larger values indicating a greater resistance to intermolecular deformation.

Elastic deformations are of importance in display devices when considering the rise and decay times for a cell and particularly in relation to the threshold sharpness. The relevant mathematical expressions (see Equations (2) and (3)) show that:

$$T_{ON} \quad \alpha \frac{1}{d^2\varepsilon_0\Delta\varepsilon E^2 - K\pi^2}$$

$$T_{OFF} \quad \alpha \frac{1}{K}$$

$$\text{Threshold sharpness} \quad \alpha \frac{1}{k_{33}/k_{11} + \dfrac{\Delta\varepsilon}{\varepsilon_\perp}}$$

where K is some average of the elastic constants depending on the particular effect, and the other terms have their usual meaning.

Hence, the switch-on times are lowered by low values of K, whilst the switch-off times are increased with low K values. In practice, it is found that such relationships are of less significance when compared with the dependencies of response times on cell thickness and particularly viscosity, so that in these cases, the effects of elastic constants are usually considered as only of secondary importance.

However, the main effect of elastic molecular deformations is on the threshold sharpness of the display. This is because absolute values of the elastic constants (for which the changes are usually much less than an order of magnitude); are no longer involved, now it is the ratio k_{33}/k_{11} which is of significance. Low values of k_{33}/k_{11} therefore increase the threshold sharpness and this ratio is quite sensitive to relatively small changes in the elastic constants, resulting in quite significant changes in the threshold sharpness. Consequently, to obtain good multiplexing performance, it is essential to keep k_{33}/k_{11} as low as possible. This in itself is a major problem, as the factors which are necessary to obtain a low k_{33}/k_{11} ratio are not particularly well understood. Although the relationships between molecular structure and elastic constants are somewhat vague, recent studies by various research groups, particularly that of RSRE, Malvern,[68] tend to indicate that some general principles may be emerging. These include the following 'rules of thumb', suggesting that low k_{33}/k_{11} values may be obtained for liquid crystal mixtures if

(i) rigid molecular cores are employed;

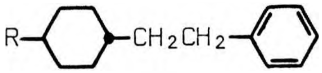
(ii) such cores are benzenoid in nature, as k_{33}/k_{11} increases in the order

(iii) low $\Delta\varepsilon$ materials are incorporated into the mixtures (thereby reducing antiparallel correlations);

(iv) the low $\Delta\varepsilon$ additives have long terminal alkyl chains;

(v) the strongly positive $\Delta\varepsilon$ components (eg, CB's) have short terminal alkyl chains.

It is worth noting that these principles come largely from work carried out using hosts based on CB's and related materials, and they may not be applicable to other systems. As more systems are investigated and data accumulated, it may however become easier to relate elastic constant behaviour to molecular structure. Indeed, it is only within the last year or so that such studies have revealed that the addition of low $\Delta\varepsilon$ additives other than dialkyl and alkyl-alkoxy esters will effectively reduce the k_{33}/k_{11} value of the mixture. Materials such as



(see Section 4.5.1) will also suffice. The function of these low $\Delta\varepsilon$ additives is to break up the anti-parallel correlation that persists in strongly positive mixtures (as discussed in Section 4.1.2), thereby reducing k_{33}/k_{11}, as well as $\Delta\varepsilon/\varepsilon_{\perp}$, as required for a sharp electro-optical performance.

However, it should be mentioned that the rules (i)-(v) are sometimes used in practice only to a limited extent, as they may conflict with other guidelines to be followed when preparing liquid crystal mixtures. For example, the requirement for benzenoid cores may limit the T_{N-I} value attainable, and the use of long alkyl chains may both introduce unwanted smectic properties and increase the viscosity. Consequently, there are many sets of considerations to be borne in mind when formulating mixtures of low k_{33}/k_{11}, and none is guaranteed to give success.

A further consideration is that the elastic constant values are often temperature dependent. An inverse correlation usually exists, the deformations becoming more pronounced at higher temperatures. Obviously it is desirable that such a temperature dependence is as low as possible. Values for the normalised rate of change, $\frac{-1}{K_{ii}}\left(\frac{dK_{ii}}{dT}\right)$, for CB's and PCH's are generally in the range -1.2 to -2.0% $^{o}C^{-1}$, although higher values are possible for mixtures.

The determination of elastic constants requires very accurate and well controlled experimental technique. Essentially, this involves the careful measurement of the capacitance-voltage characteristics of the homogeneously aligned nematic test material, which has been distorted by the application of a variable magnetic or electric field. The experimental points are then fitted to equations (usually by computer control) derived from Continuum Theory, and this enables the three elastic constants to be obtained. Using automatic control of the voltage, frequency, and temperature, it is possible for accuracies of $k_{11} < 2\%$, $k_{22} < 10\%$ and $k_{33} < 5\%$ to be obtained.

4.1.6 Order Parameters

Most of the physical properties of liquid crystals are related either directly or indirectly to the order parameter. The order parameter, S, is a measure of the microscopic or local ordering that exists within the system. The most useful order parameters are those for nematic materials for which the order parameter is defined by Equation (8)

$$S = \tfrac{1}{2} \langle 3\cos^2\theta - 1 \rangle \qquad (8)$$

where θ represents the angle between the long molecular axis and the nematic director. As all nematic materials are in a constant state of thermal fluctuation, it is necessary to use a space-time average of this dynamic motion, which is represented here by the brackets (< >).

Theoretical values of S vary from 1, which represents perfect order ($\theta = 0^{\circ}$, so that the director and the long molecular axes are uni-directional), to 0, where the system has maximum disorder (ie, the isotropic liquid).

The order parameter is important in the display device area, as it provides a measure of the optical contrast between the 'ON' and 'OFF' states, ie, the higher the value of S, the greater is the contrast. The variation of optical contrast with order parameter is even more critical when dyes are incorporated into the nematic system. Consequently, order parameters are particularly important for TN guest-host displays and dyed PC displays (see Section 2.2.1). The reasons may be summarised in the following terms. Generally, nematic materials have order parameters of $0.5 < S < 0.7$. The incorporation of similarly shaped dichroic dye molecules into the host then produces a marked absorption in the clear, homeotropic nematic state (the 'ON' state), with θ corresponding to an angle of $\approx 30^{\circ}$. By using longer dye molecules, it is possible to average out some of the liquid crystal fluctuations, so that dye order parameters of up to 0.8 may be obtained ($\theta \simeq 20^{\circ}$). Now the dye molecules give only a weak optical absorbance in the homeotropic nematic state, showing that there is a significant difference in performance for systems with dyes having order parameters of ~0.6 and those with order parameter >0.7.

As might be expected, the nematic order parameter varies significantly with temperature. Increasing temperature (energy) causes the thermal fluctuations of the molecules and θ to increase, so that the order parameter is lowered. It is therefore important that order parameters for different systems are compared at the same reduced temperature to eliminate temperature variations as far as possible.

There are several methods available for determining S (eg, X-ray studies, magnetic susceptibility and dielectric permittivity measurements, spectroscopic methods, etc), but the following two are most commonly used:

(i) *the use of refractive indices*[71] - This method is often used for pure nematogens or simple mixtures.

Here

$$S = \left(\frac{\bar{\alpha}}{\Delta\alpha}\right) \left(\frac{n_e^2 - n_o^2}{\bar{n}^2 - 1}\right)$$

where

n_e, n_o are as defined in Section 4.1.3;
$\bar{n}$ = mean refractive index, with $\bar{n}^2 = \frac{1}{3}(n_e^2 + 2n_o^2)$;
$\bar{\alpha}$ = mean molecular polarisability;
$\Delta\alpha$ = anisotropy of molecular polarisability

Hence, by measuring the refractive indices of the material at a given temperature, the order parameter may be determined at that temperature, if the polarisability characteristics of the material are known.

(ii) *the use of absorbance characteristics* - This method is generally applied to systems containing a dye dissolved in a nematic host.

Here

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}$$

where

A = -log[% absorbance] of light polarised parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the director of a homogeneously aligned film.

Thus, the dye order parameter is obtained by measuring the absorbances spectrophotometrically relative to those for the control nematic system with no dye present.

4.1.7 *Eutectic Mixtures*

Although there are many thousands of organic compounds that exhibit liquid crystalline phases, the majority of these materials having been developed in recent years, no single component material is able to meet the demands for a mesophase (particularly nematic) to extend over the temperature range -30 to +90°C as required for advanced display device applications. This condition, it is stressed, ignores *all* the other rigorous demands placed upon the material, so it can be seen that pure liquid crystal materials have extremely limiting properties.

The main problem with most pure materials is that their melting points are too high; only a limited number of compounds exhibit room temperature mesophases (and this is often because of supercooling effects), and very very few mesogens have melting points below 0°C. Consequently, the presently available liquid crystal materials are some way from having suitable thermal characteristics to enable them to be used as pure materials for commercial applications. Unfortunately, as an adequate correlation between melting temperature and molecular structure does not exist (generally, melting point trends are erratic and unpredictable), it is not possible to tailor the molecular geometry to meet the mp requirement.

The problem of attaining sufficiently high T_{N-I} values is not so acute, as many materials are known that have T_{N-I} values in excess of 100°C. Relationships between T_{N-I} value and molecular structure are more well defined, but it must be said that the rules that do exist (such as the orders in which functional groups, ring systems, terminal and lateral substituents, etc, promote T_{N-I} values) should only be used as general guidelines (the rules generally being developed for materials involving aromatic systems) and may not hold true for every specific example. However, as it is often possible (sometimes with a little trial and error) to obtain a single component material with a T_{N-I} value roughly in the region desired, the upper temperature mesophase requirement is not a real problem.

The major difficulty is therefore to reduce the melting point of liquid crystal materials to a suitable value for commercial applications.

This can be achieved by using mixtures of compounds. The mixture effectively has a lower melting point than any of its pure components, whilst the T_{N-I} value is an average value dependent on the composition of the mixture.

Figure 21 is a temperature/composition diagram of state for a binary system composed of pure components A and B.

It can be seen that the addition of either component to the other results in the melting temperature being depressed. At the point C-N(eut), the melting temperature is at a minimum for the system; this point is termed the eutectic point, and the corresponding mixture composition is termed the eutectic composition.

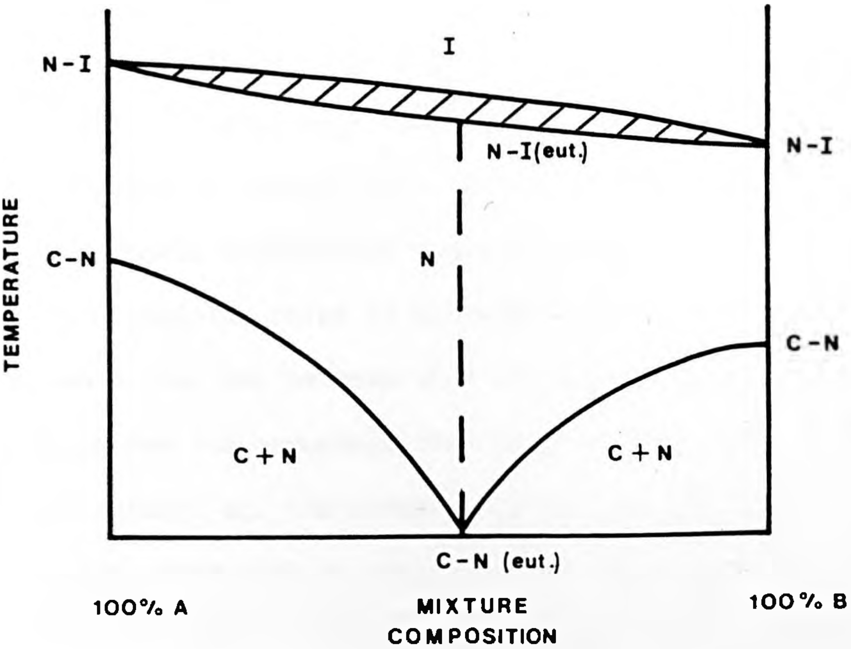


FIGURE 21

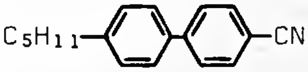
Diagram of state for two nematogens A and B

At this point the transition from the crystalline solid to the mesophase (nematic here) takes place at a single temperature, whereas for other mixture compositions this transition usually takes place over a temperature range which may be wide.

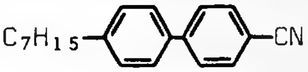
The T_{N-I} values for the mixtures do not show this fall to a minimum, but are usually a direct linear function of the mixture composition. The T_{N-I} value of the eutectic composition is given by $T_{N-I(eut)}$. The shaded region represents the temperature range for the two phase region consisting of co-existing nematic and isotropic phases. The extent of this shaded region represents the range over which the nematic-isotropic transition occurs for a given composition.

From this diagram, it can be seen that the nematic range for the eutectic composition (ie, from C-N(eut) to N-I(eut)) is significantly greater than that for either of the pure components. The effect of mixing pure components is therefore two-fold - the melting point is reduced to a minimum at the eutectic composition, and the nematic temperature range is widened.

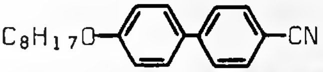
In principle, there is no restriction on the number of components that may be used in a mixture. Also, this mixing technique has the advantage that the materials used may be of a similar nature, eg, the closely related homologues of a given series will show such an effect. These points are illustrated by the fact that three different homologues of the CB series are used to make up the commercially available eutectic mixture E7. This is a quarternary mixture having the transition temperatures C -10 N 60 I. Thus, a nematic range of 70° has been produced from three biphenyl-based compounds (each of which has a relatively narrow nematic range) and a terphenyl component used to elevate the T_{N-I} value:



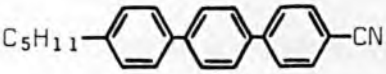
C 22 N 35.5 I



C 30 N 43 I



C 54.5 S_A 67 N 80 I



C 131 N 240 I

The melting point of E7 is therefore over 30° lower than the lowest melting point for the pure components. The effect of mixtures in lowering T_{C-N} values, as well as in widening the nematic range, is therefore quite striking, and is absolutely essential for producing materials capable of meeting the requirements for commercial applications.

The determination of the eutectic composition for a binary mixture is not experimentally difficult. However, for multicomponent mixtures (5, 6 or 7 components are often used) the task would be enormous. It is therefore necessary to have some means by which the eutectic composition may be calculated. This is provided by the equation of Schröder-Van Laar (9)[72,73]

$$\ln X_n = \frac{\Delta H_n}{R}\left(\frac{1}{T_n} - \frac{1}{T}\right) \qquad (9)$$

where

X_n = mole fraction of component n;
ΔH_n = enthalpy of fusion of component n;
T_n = melting temperature of component n;
T = melting temperature of the n component eutectic mixture;
R = gas constant

This equation predicts the mole fraction (concentration) for each of the n components that is required to produce the eutectic mixture, and also gives the melting point of this mixture. Therefore, there are n such equations for a given mixture (one for each component), and as there are n + 1 unknowns (X_1, X_2, X_3, . . . X_n, T), these may be solved simultaneously using the fact that the sum of the constituent mole fractions is unity, ie

$$\sum_{n=1}^{n} X_n = 1$$

An alternative procedure[74] pre-selects a value for T (as close as possible to the anticipated eutectic temperature) and evaluates the constituent mole fractions, $X_1, \ldots X_n$, accordingly. If

$$\sum_{n=1}^{n} X_n > 1$$

then T is greater than the eutectic melting temperature, and similarly if

$$\sum_{n=1}^{n} X_n < 1$$

then T is lower than the eutectic melting temperature. By using successive approximations for T, it is usually possible to obtain the eutectic melting temperature

$$(\text{ie, when } \sum_{n=1}^{n} X_n = 1)$$

and hence the eutectic mixture composition, with on average no more than five estimates for T. Also, as previously mentioned, the T_{N-I} value for the mixture is often a linear function of concentration, and this may be calculated by using the expression

$$T_{N-I(eut)} = \sum_{n=1}^{n} X_n (T_{N-I})_n$$

where

$$(T_{N-I})_n = T_{N-I} \text{ value of component } n$$

From this the nematic range for the mixture is then easily obtained.

For many multi-component mixtures, good agreement has been obtained between the theoretical and experimental values, in terms of both the accuracy of the eutectic melting temperature and the mixture composition.

Thus, by simply measuring the enthalpy of fusion and the melting point for each of the components used in the mixture, it is a relatively simple procedure to compute the required concentration for each component and the theoretical eutectic melting temperature.

In cases where there is good agreement between the theoretical and experimental data, then the mixture and the components are behaving almost ideally. When this is not the case, quite large differences may be observed between the observed and the predicted values. Such departures from ideality may arise for various reasons, eg, the existence of more than one solid modification for one (or more) of the pure components or the formation of mixed crystals (partial solid miscibility) by two or more of the constituents. Such phenomena give rise to metastable eutectic compositions for which the corresponding melting point may be either lower or higher than the true eutectic value. Great care must therefore be taken when evaluating eutectic data to ensure that only true eutectic values are obtained.

The enthalpy data required for the components to be used in a mixture may be conveniently obtained, along with the melting points, by the methods of DSC and DTA (to be discussed more fully in the Experimental Section). This information can then be inserted into the Schröder-Van Laar expression and the eutectic temperature and composition calculated. For binary or ternary mixtures this process is fairly straightfoward, but for multi-component mixtures, the data are usually obtained with the aid of computer facilities.

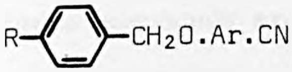
Finally, it should be mentioned that although even wider nematic ranges for mixtures may be obtained, either through the effects of supercooling or of metastable eutectic compositions, nucleation to give the crystalline solid can occur at any time at temperatures below the true eutectic melting point, where the nematic phase becomes metastable.

4.2 *COMPOUNDS INCORPORATING THE -CH_2O- INTER-RING LINKAGE*[75]

As mentioned earlier (Section 3.2), the central linking group of a molecule has a major influence upon the physical properties exhibited by the system. The use of the relatively novel -CH_2O- group in this context therefore offered the possibility of preparing a range of new liquid crystal materials, of either high or low dielectric anisotropy, with the possibility of achieving improved physical parameters in terms of viscosity, solubility, electro-optic properties, etc. Three broad classes of material were investigated; in these, the ring attached to the ether-oxygen was kept aromatic, whilst the other ring system was varied from 1,4-disubstituted benzene to *trans*-1,4-disubstituted cyclohexane to 1,4-disubstituted bicyclo(2.2.2)octane.

4.2.1 *Benzyl Ethers*

The first ethers prepared were fully aromatic compounds of interest as high birefrigence materials of positive dielectric anisotropy - see structure (8).

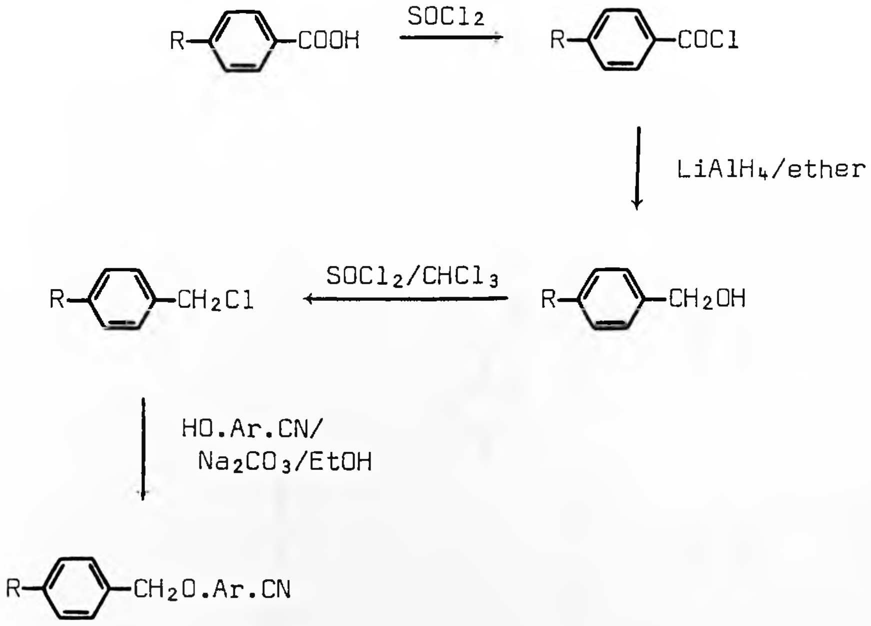


(8)

where

Ar = 1,4-disubstituted benzene;
2,6-disubstituted naphthalene;
4,4'-disubstituted biphenyl

The synthesis of these compounds was carried out according to the route illustrated in Scheme 1, starting from the 4-n-alkylbenzoic acids.



SCHEME 1

Synthetic route for benzyl ethers

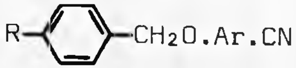
As these materials are ethers (generally considered a fairly stable class of compound), no problems in terms of thermal, photochemical or electrochemical instability were anticipated. Hydrolysis (catalysed by acid, for example) of the benzylic ether function was not considered a real problem, as the materials used in display devices are contained in fully sealed cells.

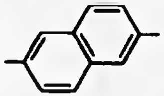
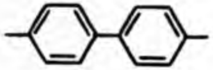
Thermal data for these compounds are given in Table 2.

Once obtained in the pure state, these compounds are in fact found to be both thermally and photochemically stable. This was established by leaving standard slide preparations of the compounds under ambient lighting conditions and at elevated temperatures for varying lengths of time (several hours to several weeks). On subsequent re-examination of the samples, no significant changes in the transition temperatures were observed.

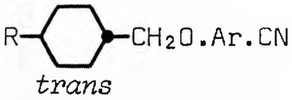
TABLE 2

Thermal data for some benzyl ethers of structure



R/Ar							
	C-I ($^{\circ}$C)	N-I ($^{\circ}$C)	C-I ($^{\circ}$C)	N-I ($^{\circ}$C)	C-S_A/N ($^{\circ}$C)	S_A-N/I ($^{\circ}$C)	N-I ($^{\circ}$C)
C_5H_{11}-	49	[-20]	82	(62)	91	-	147
C_6H_{13}-	48	[-3]	82	(56)	85	129	142
C_9H_{19}-	60	[5]	74	(71)	60	142	-

Some of these compounds may be compared with corresponding *trans*-cyclohexyl derivatives of general structure (9), prepared earlier by Gray and McDonnell[76] in a preliminary study of materials incorporating the -CH_2O- inter-ring linkage. Thermal data for these compounds are given in Table 3.



(9)

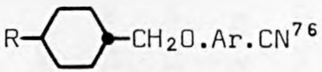
where

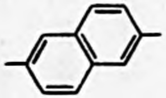
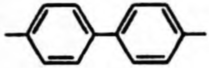
Ar is as defined for structure (8)

In general terms, the benzyl ethers usually have the lower melting points of the two systems, but unfortunately their T_{N-I} values are also reduced, and often to a much greater extent (40-70^0). As a result, the nematic ranges for the benzyl ethers are much smaller or the phases are strongly monotropic. This result was not entirely unexpected, in view of the effect on T_{N-I} values observed for other materials when a 1,4-disubstituted benzene ring is replaced by a *trans*-1,4-disubstituted cyclohexane ring,[56,58] ie, when relatively low temperatures are involved (as is the case here), by comparison with the 1,4-disubstituted benzene ring system, the *trans*-1,4-disubstituted cyclohexane ring enhances T_{N-I} values, whereas at much higher temperatures, it usually reduces T_{N-I} values. This dual nature of the *trans*-cyclohexane ring is quite general and has been observed for materials with directly linked rings in the core structure (CB's *v* PCH's), as well as for esters (phenyl benzoate *v* phenyl cyclohexanoate), etc. The effect is believed to be due[76] to the ability of the relatively flexible cyclohexane ring to absorb small amounts of energy at low temperatures (retaining a

TABLE 3

Comparative thermal data for some cyclohexylmethyl ethers of structure



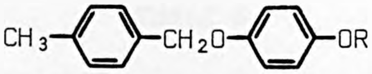
R/Ar							
	C-I (°C)	N-I (°C)	C-N (°C)	N-I (°C)	C-S_A (°C)	S_A-N (°C)	N-I (°C)
C_5H_{11}-	74.3	(48.6)	87.3	114.5	107.0	136.3	193.2
C_6H_{13}-	-	-	81.0	110.0	107.3	161.8	185.7

high proportion of equatorial-equatorial conformers) by way of non-disruptive conformational changes, thereby preserving the nematic order. The more rigid benzene ring is unable to undergo such conformational changes and is presumed therefore to fill space less efficiently, so that the nematic order is more easily broken down. However, when sufficiently high energies are involved, these conformational changes of the cyclohexane ring may become more serious in nature, thereby increasing the proportion of non-linear (axial-axial) conformers within the system, such that the T_{N-I} value falls below that of the aromatic analogue.

Although the benzyl ethers appear to have the *dis*advantage of reduced nematic thermal stability with respect to the cyclohexylmethyl ethers this does also apply to the smectic thermal stability - an advantage. Consequently, the biphenyl derivatives (the only materials here exhibiting smectic properties) of the benzyl ethers have $T_{S_A-N/I}$ values over 30^0 lower than those of the analogous cyclohexane derivatives.

Due to an increasing demand for materials of less strongly positive, or even weakly negative, dielectric anisotropy for multiplexing applications (see Section 4.1.2), it seemed a logical progression to prepare some benzyl ethers in which the terminal cyano group of structure (8) was replaced by an alkyl or alkoxy substituent. However, on the basis of the results in Table 2, it was to be expected that any dialkyl derivatives would have comparatively low T_{N-I} values (as cyano groups are usually found to be much more efficient at promoting nematic order compared with alkyl groups - see terminal group efficiency order in Section 2.1.2).

This would give rise to relatively uninteresting materials for display device applications. Consequently, the potential of the alkyl-alkoxy analogues was explored first. Two of these materials of structure (10) were therefore prepared by a similar route to that shown in Scheme 1 for the cyano-derivatives, except that a stronger base was required to give effective salt formation of the 4-alkoxyphenol (see Experimental Section). Data for these materials are recorded in Table 4.



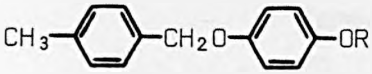
(10)

where

R = CH_3, C_4H_9

TABLE 4

Physical data for two benzyl ethers of structure



R	C-I (°C)	N-I (°C)	Viscosity† (cP) 20°C	Viscosity† (cP) 0°C
$-CH_3$	82	[-6]	35.4	SEGREGATION
$-C_4H_9$	76	[19]	43.6	SEGREGATION

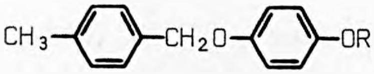
† viscosity values are for 10 wt % solutions in E7

From these results it can be seen that these alkyl-alkoxy derivatives have low T_{N-I} values, as well as fairly high melting points. Since the nematic viscosity of E7 is 40 cP at 20°C, the methoxy homologue has lowered the host viscosity at this temperature. This is a more encouraging result (even though the test material contains short alkyl and alkoxy chains), but unfortunately these materials appear to be fairly insoluble in E7 at low temperatures, so that viscosity measurements at 0°C could not be made due to segregation of one or more components of the mixture.

The results recorded in Table 5 are electro-optic data obtained using a general nematic host containing 12.5 wt % of each of the two compounds of structure (10); measurements were made at RSRE, Malvern.

TABLE 5

Physical and electro-optic data for 12.5 wt % of each of two benzyl ethers of structure



(R = $-CH_3$, $-C_4H_9$) when incorporated into a nematic host

		Temperature (°C)		
		20	30	40
V	V_{90} (45°)	0.98	0.89	0.72
	V_{50} (10°)	1.27	1.13	0.90
	V_{10} (0°)	1.68	1.47	1.21
ms	Rise time (at 3 V)	53	33	22
	Decay time (at 3 V)	65	52	48

$M_{20^\circ C} = 1.71$ $\qquad$ $M'_{20^\circ C} = 1.30$

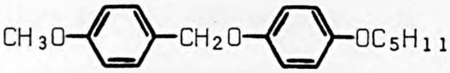
N-I (°C) = 44.2-45.8

Δn (20°C, 589 nm) = 0.175; $n_e = 1.705$; $n_o = 1.530$

$\Delta\varepsilon$ (0.95 T_{N-I}) = 9.8; $\varepsilon_{\parallel} = 16.7$; $\varepsilon_{\perp} = 6.9$

By comparison with other materials tested using this host, both the response times and the figures of merit, $M_{20^\circ C}$ and $M'_{20^\circ C}$, are very encouraging. The main drawbacks of these compounds are, however, their low solubility in nematic solutions and their low T_{N-I} values. Although the optimum chain lengths may not perhaps have been chosen for the compounds (10), it is unlikely that the use of other homologues would lead to a significant enhancement of these latter properties.

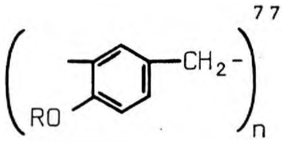
On the basis of these results, the dialkoxy-substituted benzyl ether derivatives were not expected to be very useful materials, particularly from the solubility point of view. Synthetic problems were encountered which prevented the preparation of sizeable, quantities of these compounds, but a small sample of compound (11) was obtained. As expected, the T_{N-I} value is higher than the values for the alkyl-alkoxy analogues. However, as anticipated, the crystallinity of the system has also been enhanced, as indicated by the higher melting point, an effect that is likely to make these materials generally even less soluble in nematic hosts than the alkyl-alkoxy analogues.



(11)

C-I 93°C, N-I [38°C]

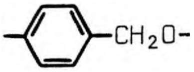
The synthetic problems encountered with these dialkoxy derivatives centred around the preparation of the 4-n-alkoxybenzyl chlorides from the corresponding alcohols, cf, Scheme 1. However, because of ring activation by the alkoxy group, the 4-n-alkoxybenzyl chlorides undergo rapid polymerisation, with the elimination of HCl, to produce polymers of the form



These chlorides are in fact stable at low temperatures (<-20^{0}C), but because of the disappointing transition temperatures for compound (11), it was not considered worthwhile to modify the synthetic route in order to obtain other homologues.

The results for the compounds of structures (10) and (11) more or less confirm the assumption that related benzyl ethers with two terminal alkyl groups would have rather low T_{N-I} values, and hence be relatively uninteresting materials. As a result, these compounds were not investigated.

In summary, the benzyl ethers provide a novel series of relatively stable mesogens which permit detailed comparisons to be made with other established liquid crystal materials. Although some properties of the benzyl ethers are quite acceptable for display device applications (low smectic tendencies, plus reasonable figures of merit and response times when incorporated into a nematic host) several properties, such as the low solubility in nematic solutions, along with unacceptably low T_{N-I} values, are serious disadvantages for these materials. The lowering of the T_{N-I} values of the cyano-substituted ethers relative to the analogous cyclohexyl materials of structure (9) was in fact expected on the basis of comparative data for other series of materials, and therefore provides further evidence for the ability of the cyclohexane ring to promote the nematic thermal stability of a system (at relatively low temperatures). However, the T_{N-I} values for the benzyl ethers were even lower than was anticipated, and this is probably related to other disruptive effects involving the unit,

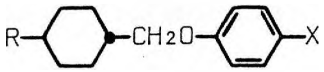


which will be discussed more fully in Section 4.2.3.

4.2.2 *Cyclohexylmethyl Ethers*

To try to increase the T_{N-I} values of the benzyl ethers and also possibly to improve other physical properties, eg, the solubility, the replacement of a 1,4-disubstituted benzene ring in the benzyl ether system by a *trans*-1,4-disubstituted cyclohexane ring seemed to be a logical step. As mentioned in the previous section, the cyclohexane ring has been found to be superior in several respects to the benzene ring (eg, for lowering viscosity, raising T_{N-I} etc) when it is incorporated into different systems.[56,58] This fact is also illustrated in the preceding section by comparing the cyano-benzyl ethers (Table 2) with the previously prepared cyano-cyclohexylmethyl ethers[76] (Table 3). The compounds investigated here were therefore materials containing only terminal alkyl and alkoxy substituents.[†] Scheme 2 illustrates the general synthetic route used to prepare compounds of general structure (12).

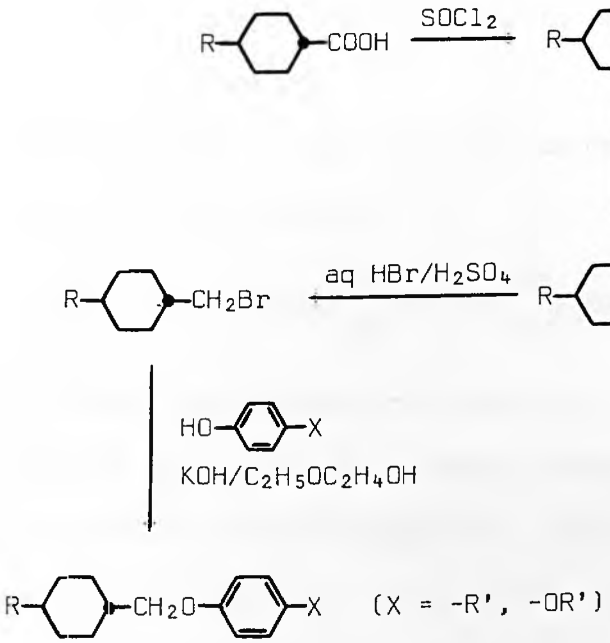
[†] Since the completion of this work, other research groups[78,79] have published data on a small number of identical compounds, as well as on other related materials.



(12)

where

X = n-alkyl, n-alkoxy



SCHEME 2

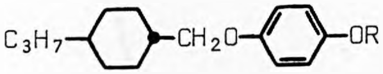
Synthetic route for cyclohexylmethyl ethers

Materials of structure (12) no longer contain the potentially labile benzylic ether function, and were expected to be particularly stable compounds.

The first materials prepared were the alkyl-alkoxy derivatives. With moderate lengths of the alkyl chain on the cyclohexane ring ($R = C_5H_{11}$- and C_6H_{13}-), smectic properties were observed with $X = -OC_4H_9$. Consequently, most of the alkyl-alkoxy derivatives chosen for study had the shorter propyl chain on the cyclohexane ring, the homologous series ranging up to $X = -OC_7H_{15}$. The transition temperatures for all of the alkyl-alkoxy materials of structure (12) prepared are recorded in Table 6.

In general terms, the melting points and T_{N-I} values are more favourable than those for the alkyl-alkoxy benzyl ethers, although the comparison is restricted in extent by the small number of benzyl ethers prepared.

Figure 22 shows a plot of transition temperatures against chain length, R, for the compounds



Several general points are worth mentioning. As the alkoxy chain lengthens the $T_{S_B-N/I}$ and T_{N-I} values increase, but there is no great variation in the melting points. Consequently, the liquid crystal phases progress from being virtual ($-OCH_3$) to monotropic ($-OC_2H_5$ to $-OC_6H_{13}$), and finally to enantiotropic ($-OC_7H_{15}$). As the relative smectic characteristics increase at a greater rate than the nematic, the last nematic phase is observed with $-OR = -OC_5H_{11}$. The T_{N-I} values quoted for the hexyloxy and heptyloxy compounds are therefore virtual values obtained by standard techniques using mixtures. In these experiments, smectogenic compounds (S_B) are involved, but in principle, there should be little difference between assessing virtual T_{N-I} values for two- or three-dimensional smectogens, as opposed to three-dimensional solids.

Figure 22 also illustrates the fairly common occurrence of the alternating, odd-even chain length effect on T_{N-I} values. That is, two distinct smooth curves are obtained by joining together the appropriate points for the T_{N-I} values; one curve is obtained for an

FIGURE 22

Graph of transition temperatures against number of carbon atoms in R for the series

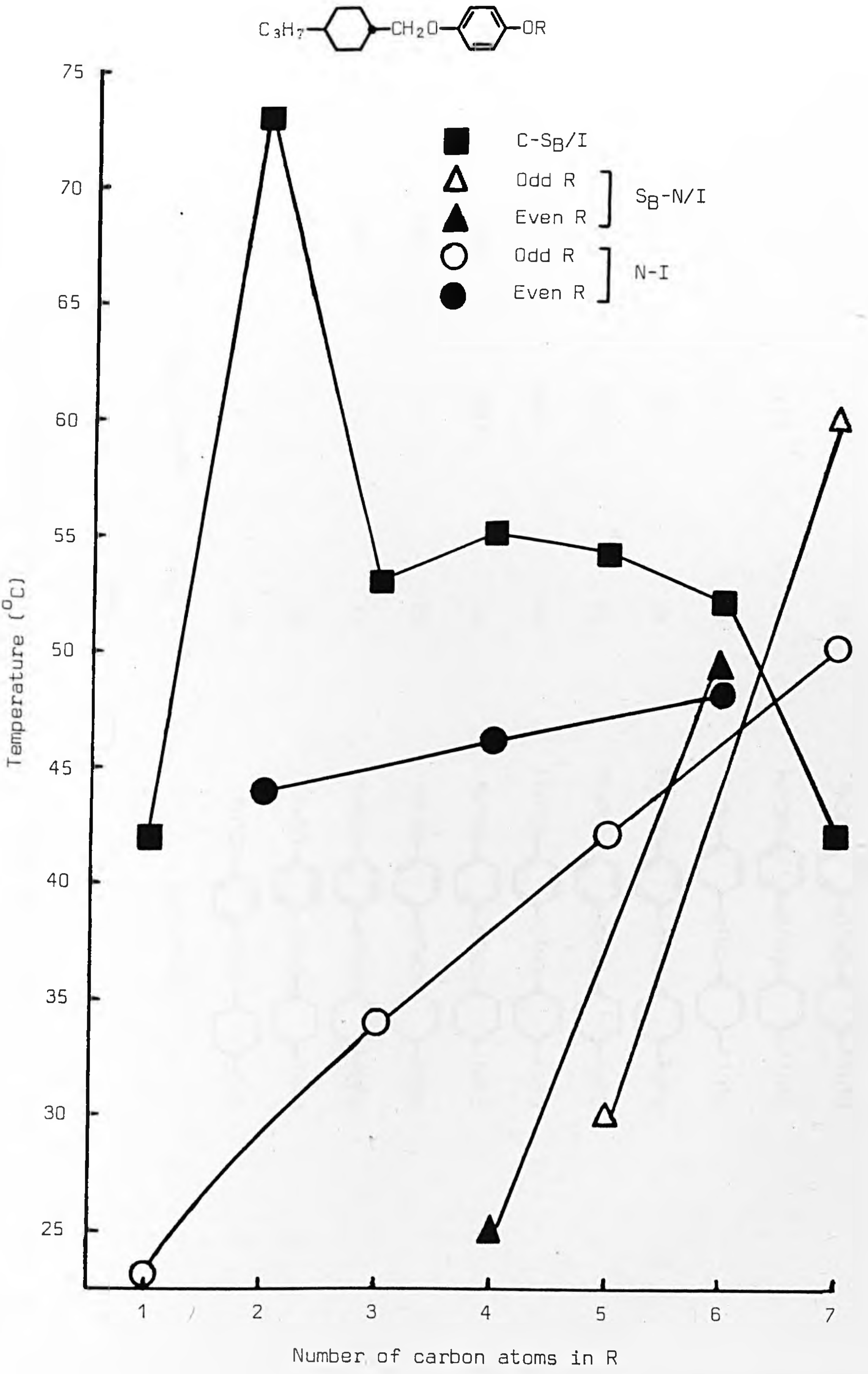
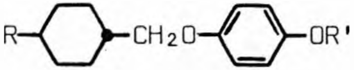
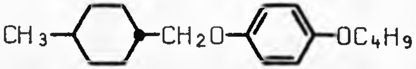
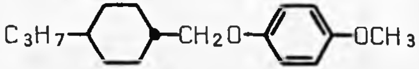
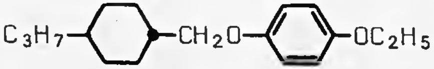
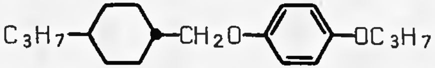
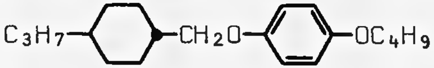
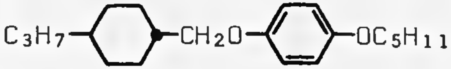
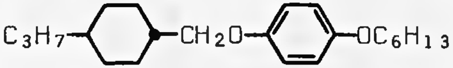
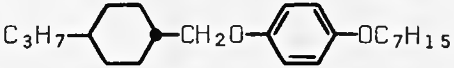
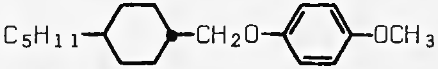
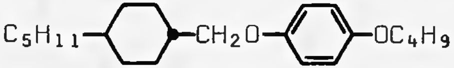
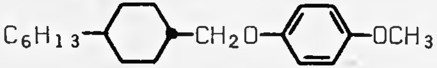
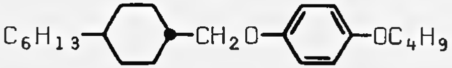


TABLE 6

Thermal data for some cyclohexylmethyl ethers of structure



Structure	C-S_B/I (°C)	S_B-N/I (°C)	N-I (°C)
	55	-	[18]
	42	-	[23]
	73	-	(44)
	53	-	(34)
	55	(25)	(46)
	54	(30)	(42)
	52	(49)	[48]
	42	60	[50]
	46	-	(38)
	55	(47)	(53)
	45	-	(36)
	54	(50)	-

odd number of carbon atoms in the alkoxy group, and the other for an even number of carbon atoms. In the case of terminal alkoxy substituents, it is usually found (as here) that the even T_{N-I} curve relates to higher temperatures than the odd T_{N-I} curve. In this example, both curves increase gradually with chain length (although at slightly different rates). This is often the case, but need not necessarily be so, as other shapes for the curves are also possible.[15] An explanation of these effects has been suggested based upon considerations of the geometry and polarisability of the molecules;[80] however, it should be stressed that no single approach accounts fully for all the various types and shapes of T_{N-I} curve that have so far been observed. However, in general terms, it is both the molecular length:breadth (l:b) ratio and the anisotropy of molecular polarisability ($\Delta\alpha$) that are considered to be particularly important. In both cases, high values are desirable - a high l:b ratio satisfies the simplistic model of liquid crystals as being composed of long, linear, rigid rods, and a high value for $\Delta\alpha$ complies with the requirement for maximum positive interaction (attraction) due to dispersion forces, as given by the Maier-Saupe theory of the nematic state.[14]

As an example, consider the addition of a methylene unit to an alkoxy group containing an odd number of carbon atoms. If the chain is considered to be in the all *trans* (planar, zig-zag) conformation[†]

[†] It should be mentioned, of course, that in any given system no one conformation alone exists. In effect, there is a dynamic equilibrium that involves all of the possible conformations, the proportion of each present being dependent on their relative stabilities.

(which is not unreasonable considering the intermolecular constraints required to maintain nematic order), such a change increases the l:b ratio and enhances the molecular polarisability in the direction of the molecular long axis by an amount approximately equal to twice that in a direction normal to this axis. As a result, the even N-I curve lies at higher temperatures than the odd N-I curve (as in Figure 22), and as the alkoxy chain lengthens, the two curves tend to converge, due to a damping of these effects as the chain becomes more flexible.

Similarly, due to the close geometrical relationship of an oxygen atom to a methylene group, the N-I curve for terminal alkyl chains containing an odd number of carbon atoms usually lies at higher temperatures than the N-I curve relating to even numbers of carbon atoms in the chain.

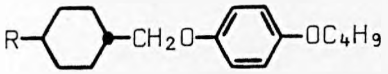
An overall consideration of the l:b ratio alone would lead to the general conclusion that if regular, planar, zig-zag chains are involved, the T_{N-I} values should fall as the homologous series is ascended as the l:b ratio falls with increasing chain length. As this is the opposite effect to that usually observed for series having relatively low T_{N-I} values, it is therefore assumed that the molecular polarisability factor is of greater significance in this case. However, it has been proposed[81] that at relatively high temperatures the l:b ratio becomes the predominant factor, not for the reasons stated above, but due to increased molecular fluctuations and chain flexing motions, etc, as a result of the high thermal energy of the system. In these terms, it is now possible to account for the fall in T_{N-I} values observed for many series of high nematic thermal stability as the series is ascended.

Two further points should be raised in connection with Figure 22.

(a) The alternation effect for the $T_{S_B\text{-}N/I}$ values is not of the opposite sense to that for the $T_{N\text{-}I}$ values. This is not consistent with earlier and still unexplained observations for other systems,[82] although unpublished exceptions exist.

(b) The crossing of the $T_{N\text{-}I}$ and $T_{S_B\text{-}N/I}$ transition lines carries the implication that the nematic phases have become *monotropic* with respect to the S_B phases. Except possibly in systems where re-entrant nematic phases occur, this is not observed in practice. The results in Figure 22 merely tell us that the potential of, for example, the ether with R' = $-C_7H_{15}$ to support nematic order in a *mixed nematic system* is equivalent to its having a $T_{N\text{-}I}$ value of 50°C - *if* it could exhibit such a phase as a single component material. In fact it does not show such a phase, and has a $T_{S_B\text{-}I}$ value of 60°C.

From Table 6 it is also possible to assess the general trends on varying the chain length of the alkyl group attached to the cyclohexane ring - ie, by a comparison of the data for the compounds



Here, the observations are similar to those just discussed. That is, the melting points are fairly constant as R increases, and the $T_{S_B\text{-}N/I}$ and $T_{N\text{-}I}$ values increase generally with R, with smectic properties first appearing for the 3.04 homologue. It therefore appears to make no great difference to the liquid crystal properties and thermal stability whether the chain length is varied on the cyclohexane ring (alkyl chain) or the aromatic ring (alkoxy chain).

Table 7 contains data from physical assessments made at RSRE, Malvern on a host nematic mixture incorporating two homologues of structure (13) of total concentration 45 wt % (R = $-CH_3$, 25 wt %; R = $-C_4H_9$, 20 wt %).

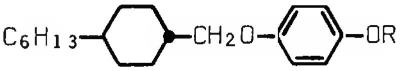
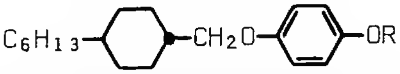

(13)

TABLE 7

Electro-optic data for two cyclohexylmethyl ethers of structure



($R = -CH_3$, 25 wt %; $R = -C_4H_9$, 20 wt %)
when incorporated into a nematic host

		Temperature (°C)		
		0	20	40
V	V_{90} (45°)	1.21	1.12	0.98
	V_{50} (10°)	1.64	1.47	1.26
	V_{10} (0°)	2.19	1.90	1.67
ms	Rise time (at 3 V)	350	100	-
	Decay time (at 3 V)	240	86	-

$M_{20^\circ C} = 1.70$ $\qquad M'_{20^\circ C} = 1.31$

$M_{0-40^\circ C} = 2.23$ $\qquad M'_{0-40^\circ C} = 1.67$

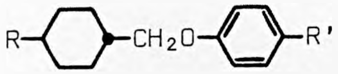
$\frac{-1}{V}\left(\frac{dV}{dT}\right)_{\%}$ $^\circ C^{-1}$	at V_{90} (45°)	0.51
	at V_{50} (10°)	0.65
	at V_{10} (0°)	0.68

N-I (°C) = 57.3

$\Delta\varepsilon$ (0.95 T_{N-I}) = 7.5; $\varepsilon_{\parallel}$ = 13.6; $\varepsilon_{\perp}$ = 6.1

These results may be compared with the similar, although not identical, data given in Table 5 for the alkyl-alkoxy benzyl ethers. The figures of merit are much the same, but a major drawback in the case of the cyclohexylmethyl ethers is the somewhat high value for the variation of threshold voltage with temperature. The differences in the T_{N-I} values, response times, and the dielectric properties may be attributed, partly to the different ring systems involved, but it must also be remembered that longer alkyl and alkoxy chain lengths and much higher concentrations of the test material were involved in the case of the experiments with the cyclohexylmethyl ethers.

Although the melting points for these compounds are not excessively high, it was felt that these values could profitably be lowered by preparing the corresponding dialkyl analogues - see general structure (14).



(14)

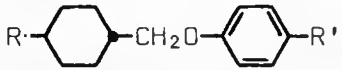
These materials were expected to have lower T_{N-I} values than the corresponding alkyl-alkoxy materials. This was not however considered a great problem (providing the magnitude of the depression was not too large), as the addition of suitable high T_{N-I} additives could be used to boost the N-I transition temperature of mixtures incorporating such ethers. Also, it was hoped that these materials would be less smectic in nature, less viscous, and more soluble in nematic hosts.

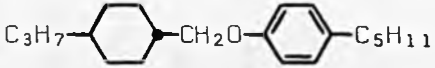
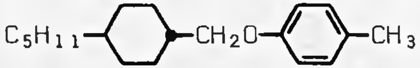
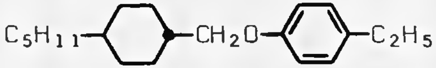
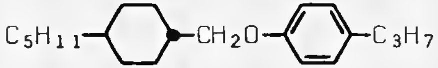
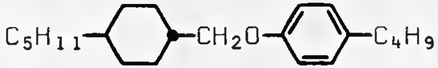
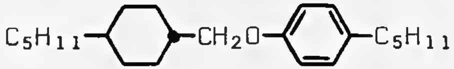
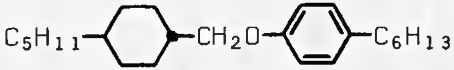
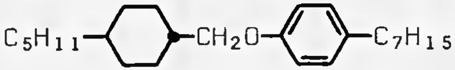
The transition temperatures for these materials are given in Table 8.

As expected, both the melting points and the T_{N-I} values are lower compared with the alkyl-alkoxy analogues (see Table 6). However, in this case, the T_{N-I} values have suffered most. Consequently, only two of the eight dialkyl compounds exhibit a nematic phase, and these are strongly monotropic, whereas seven of

TABLE 8

Thermal data for some cyclohexylmethyl ethers of structure

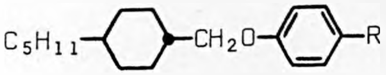


Structure	C-S_B/I (^oC)	S_B-I (^oC)	N-I (^oC)
	24	-	(4)
	47	-	[17]
	30	-	(5.5)
	32	(10)	[4]
	23	(21)	[-4]
	35	(31)	[21]
	30	36	[18]
	34	38	[26]

the twelve alkyl-alkoxy derivatives have a nematic phase (also monotropic).

The smectic tendencies for the two systems appear to be fairly similar. In the case of the dialkyl compounds, a smectic phase is first observed for the pentyl·propyl (5.3) homologue; a smectic phase is first observed in the alkyl-alkoxy series for the homologue 3.04. In both cases, the molecules are of a similar molecular length when the smectic phase is first observed, but it is worth mentioning that the smectic thermal stability is on average approximately 15^{o} lower in the case of the dialkyl compounds (eg, $T_{S_B-N/I}$ = 10^{o}C and 25^{o}C for the 5.3 and 3.04 homologues, respectively).

The variation in transition temperatures for



(15)

with different lengths of the alkyl group, R, is shown in Figure 23.

The behaviour of the T_{N-I} values observed for this series of compounds is significantly different to that observed for the corresponding alkyl-alkoxy materials (see Figure 22), although for both sets of compounds the trends for the more dominant smectic phases are similar.† The usual odd-even effect on T_{N-I} values is observed, but the main difference is in the actual shapes of the N-I curves. As the alkyl chain increases from $-CH_3$ to $-C_3H_7$ and from $-C_2H_5$ to $-C_4H_9$, the T_{N-I} values decrease. The T_{N-I} values then

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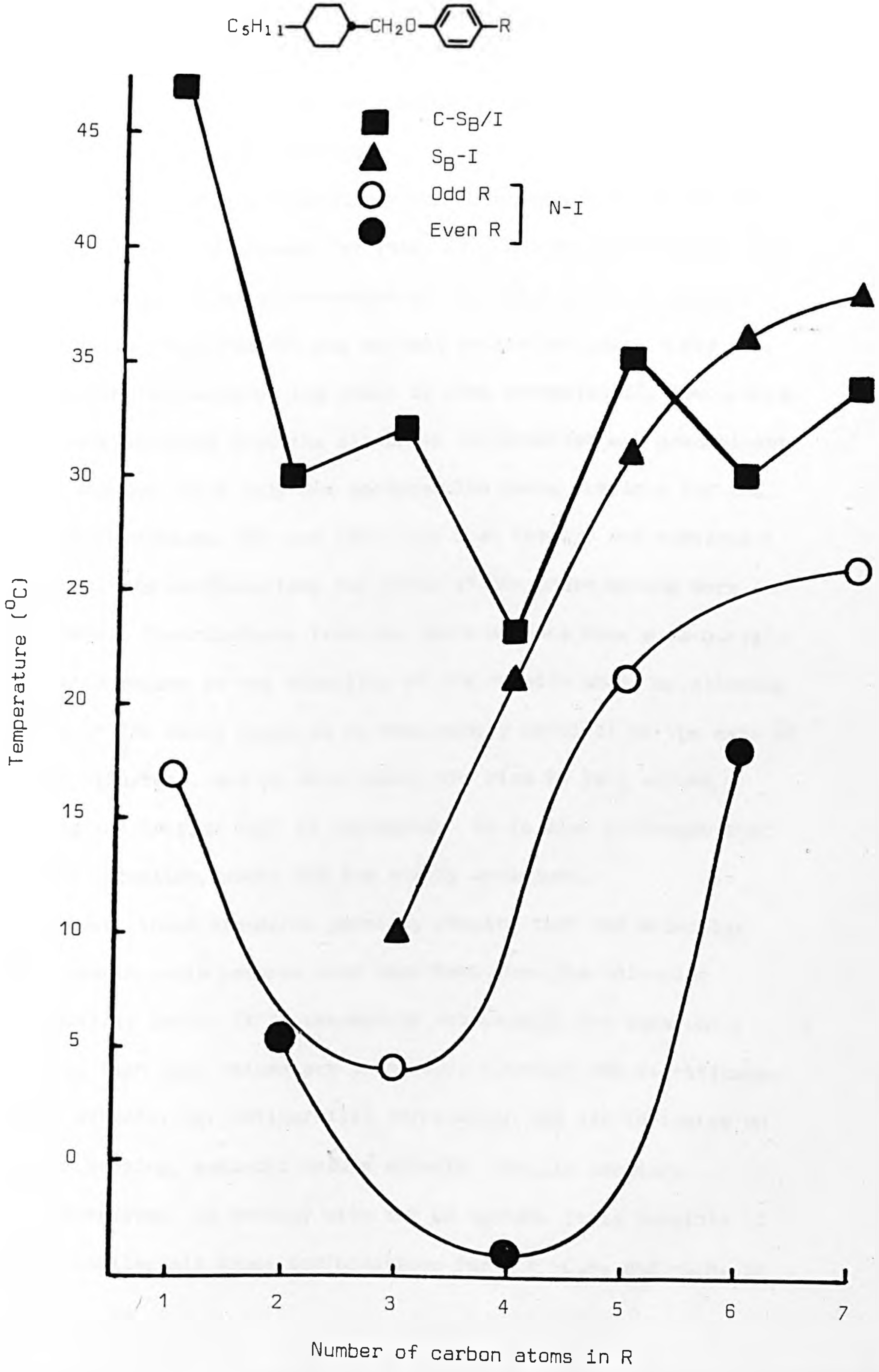
† Except that no alternation of the T_{S_B-I} values is observed for the dialkyl series.

FIGURE 23

Graph of transition temperatures against number of carbon atoms in R for the series



increase as the chain is further lengthened, so that a minimum is obtained for each curve. In the case of the alkyl-alkoxy analogues discussed above, both N-I curves gradually rise with chain length so that no such minima are observed.

This rather uncommon behaviour was first observed for the CB's (see Figure 24). To account for this, Gray and Mosley[80] argued that although the all *trans* conformation of the alkyl chain is usually energetically preferred, it may be that in certain cases a *cis* conformation for parts of the chain is also energetically favourable. Here it was proposed that the all *trans* conformation was predominant for CB3 and CB4 (with only one conformation being possible for the first two homologues, CB1 and CB2), but that for CB5 and subsequent homologues, *cis* conformations for parts of the chain become more significant. Contributions from *cis* conformations have a favourable effect with regard to the stability of the nematic phase by allowing the axis of the alkyl chain to be more nearly parallel to the axis of the core structure, and on this basis, the rise in T_{N-I} values following the initial fall is explained. It is also envisaged that a similar situation exists for the alkoxy analogues.

However, these arguments possibly require that the molecular length:breadth ratio becomes more important than the molecular polarisability (which it is assumed is not usually the case until relatively high T_{N-I} values are involved), although the significance of other effects, eg, antiparallel correlation and its influence on molecular packing, excluded volume effects, etc, is unclear.

Nevertheless, by analogy with the CB system, it is possible to envisage similar all *trans* conformations for R = $-C_3H_7$ and $-C_4H_9$ in

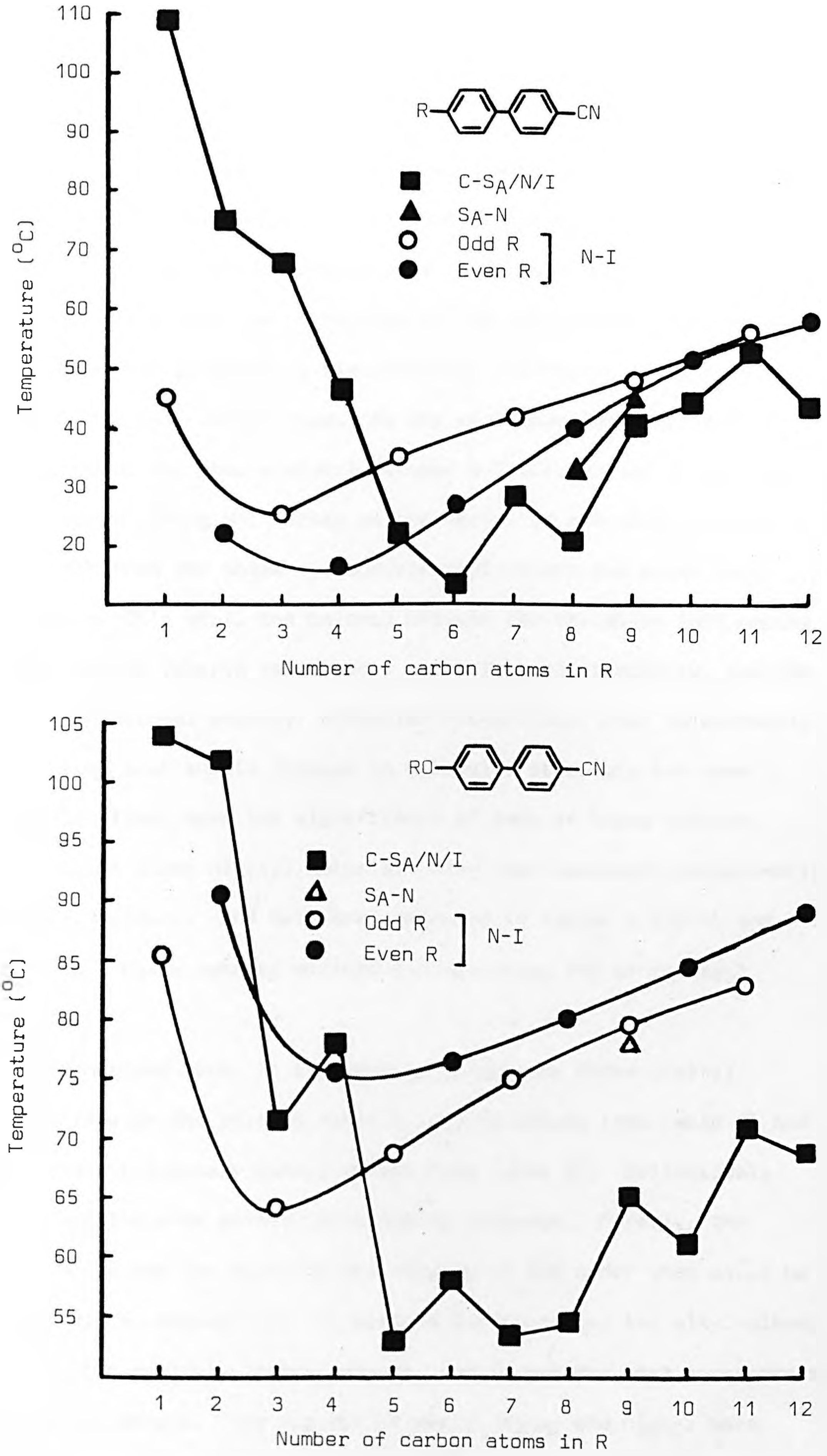
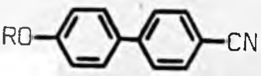


FIGURE 24

Graph of transition temperatures against number of carbon atoms in R for the series

R- and RO-



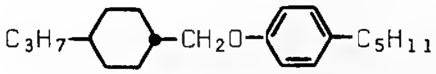
structure (15). Such conformations will effectively reduce the molecular length:breadth ratio, thereby reducing the thermal stability of the nematic phase. For homologues higher than butyl, it is possible that the proportion of the appropriate conformations containing *cis* linkages is significantly increased, so that as a result, the T_{N-I} values rise. As the corresponding alkyl-alkoxy analogues do not show similarly shaped N-I curves, but exhibit the more common rising N-I curves as the series is ascended, it must be concluded that for these cyclohexylmethyl ethers and other such materials (CB's etc), the balance between the variables influencing these changes (steric repulsions, molecular polarisability, packing and orientational entropy, molecular flexibility, etc) is extremely fine, such that subtle changes in molecular structure can have a dramatic effect upon the significance of each of these factors.

Two of these dialkyl materials have been assessed independently at RSRE, Malvern. The data are presented in Tables 9 and 10 and refer to a basic nematic mixture incorporating 40% of the test material.

From these data, it is possible to compare these dialkyl materials with the related alkyl-alkoxy materials (see Table 7) and with the alkyl-alkoxy benzyl ethers (see Table 5). Collectively, these results show several interesting features. Firstly, the T_{N-I} values for the mixtures are roughly in the order that would be expected, ie, highest for the mixture incorporating the alkyl-alkoxy substituted cyclohexylmethyl ethers, and lowest for that incorporating the benzyl ethers. The figures of merit, M_{20^oC} and M'_{20^oC}, have remained much the same irrespective of the system investigated,

TABLE 9

Physical and electro-optic data for 40 wt % of the cyclohexylmethyl ether of structure



when incorporated into a nematic host

		Temperature (^{o}C)			
		0	10	20	30
V	V_{90} (45^{o})	1.23	1.14	1.06	0.97
	V_{50} (10^{o})	1.62	1.53	1.39	1.25
	V_{10} (0^{o})	2.11	1.98	1.81	1.66
ms	Rise time (at 2 V)	-	-	200	112
	Decay time (at 2 V)	-	-	54	45
	Rise time (at 3 V)	258	135	73	47
	Decay time (at 3 V)	175	104	67	52

$M_{20^{o}C} = 1.71$ $M'_{20^{o}C} = 1.31$

$\frac{-1}{V}\left(\frac{dV}{dT}\right)\%\ ^{o}C^{-1}$		
	at V_{90} (45^{o})	0.82
	at V_{50} (10^{o})	0.89
	at V_{10} (0^{o})	0.83

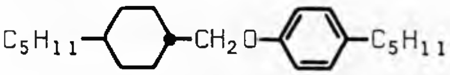
N-I (^{o}C) = 47.6-51.6

Δn (20^{o}C, 589 nm) = 0.1477; n_e = 1.6613; n_o = 1.5136

No smectic phase is observed down to -20^{o}C for this mixture

TABLE 10

Physical and electro-optic data for 40 wt % of the cyclohexylmethyl ether of structure



when incorporated into a nematic host

		Temperature (°C)			
		0	10	20	40
V	V_{90} (45°)	1.33	1.26	1.17	0.94
	V_{50} (10°)	1.75	1.64	1.53	1.22
	V_{10} (0°)	2.25	2.16	1.97	1.57
ms	Rise time (at 3 V)	245	144	83	33
	Decay time (at 3 V)	142	84	59	41
	Rise time (at 4 V)	126	76	45	21
	Decay time (at 4 V)	164	94	63	44

M_{20^oC} = 1.68 M'_{20^oC} = 1.31

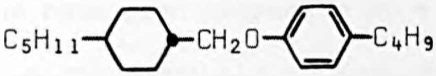
$\frac{-1}{V}\left(\frac{dV}{dT}\right)$ % $^oC^{-1}$	at V_{90} (45°)	0.83
	at V_{50} (10°)	0.87
	at V_{10} (0°)	0.86

N-I (°C) = 53.7-56.8

Δn (20°C, 589 nm) = 0.1518; n_e = 1.6615; n_o = 1.5097

A smectic phase is observed for this mixture in the region -15 to -10°C implying (at least for this host) only weak dependencies on the type of ring structure used (benzene or cyclohexane) and the nature of the terminal substituents (alkyl or alkoxy).

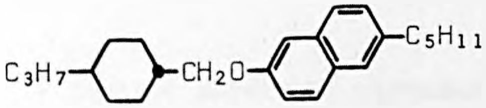
Unfortunately, the poor values for the variation of the threshold voltage with temperature obtained for the alkyl-alkoxy cyclohexylmethyl ethers have been worsened by using the dialkyl-substituted cyclohexylmethyl ethers. Consequently, for these materials, it would appear to be preferable to substitute the aromatic ring with a terminal alkoxy group rather than an alkyl group - with respect to reducing $^{dV}/dT$. On the other hand, as might be expected, the viscosity for the mixture, as judged by the electro-optic response times, is most favourable when using the dialkyl materials. The acceptable viscosity of the dialkyl system is illustrated by the compound



which has η_{20^oC} (iso) = 34 cP, and η_{20^oC} $(nem)_{extra}$ = 23 cP (from a 20 wt % solution in ZLI 1132). Therefore, if such materials were used as low dielectric anisotropy additives to replace esters (sometimes of relatively high viscosity), in nematic mixtures (typically of viscosity 30-40 cP), it would be expected that a lowering of the host viscosity would result.

The above results showing that apparently superior results are obtained for the cyclohexylmethyl ethers in terms of threshold voltage stability with temperature when alkyl-alkoxy substituents are used, whereas with dialkyl substituents, the materials are preferable in terms of viscosity, serve to illustrate the problems involved in obtaining materials of improved physical and electro-optic performance. Often an improvement in one parameter results in a loss in performance for another, so that it is virtually impossible to tune either a given compound, series of compounds, or even a multicomponent mixture to a pitch such that all of the physical and electro-optic parameters are optimised. Indeed, it is usually necessary to give priority to a small number of these parameters (depending upon the particular application) and to compromise as necessary with regard to other properties.

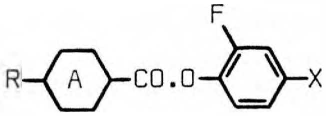
To try and produce an enantiotropic nematic mesophase from the dialkyl-substituted cyclohexylmethyl ether system, the 1,4-disubstituted benzene ring was replaced by a 2,6-disubstituted naphthalene ring. Compound (16) was subsequently prepared, but the material was found to be high melting. In fact, both the melting point and T_{N-I} value have been increased by a similar amount when compared with the 1,4-disubstituted benzene analogue (see Table 8). No further materials of this type were prepared.



(16)

C-I 99°C, N-I (78°C)

Another somewhat disappointing result was obtained by investigating a fluorinated dialkyl-substituted cyclohexylmethyl ether. Considering materials of low dielectric anisotropy, 2-fluorination of various phenyl esters of benzene, cyclohexane,[83] and bicyclo(2.2.2)octane[84] carboxylic acids of structure (17), has been found to produce some interesting results. For example, the



(17)

where

A = benzene, cyclohexane, bicyclo(2.2.2)octane

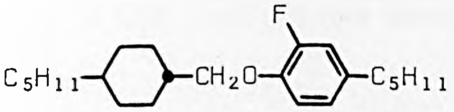
X = n-alkyl, n-alkoxy

lateral 2-fluoro-substituent (which is only slightly larger in size than hydrogen), has been found to depress greatly the smectic tendencies both of the parent compound itself, and those of various mixtures for which injected smectic phases can be a major problem. It is likely that the fluoro-substituent does this by reducing the lateral attractive forces through both intra- and inter-molecular steric effects. Other larger lateral substituents, for example -CN, $-CH_3$ etc, also produce a similar effect on the smectic characteristics of a system, but they have the disadvantage of severely reducing the T_{N-I} value relative to that of the unsubstituted compound. The use of fluorine as a lateral substituent has therefore been found to have the advantage of severely reducing the smectic tendencies of compounds of type (17), whilst often having no very adverse effects on the T_{N-I} values.

For example, if dialkyl esters of structure (17) are considered, then compared with the unfluorinated compounds, the T_{N-I} values are reduced by an average of $25^{o}C$, $11^{o}C$, and only $3^{o}C$ when ring A is benzene, cyclohexane, and bicyclo(2.2.2)octane respectively.

The use of other lateral halogeno-substituents has shown that T_{N-I} values are depressed in the order I > Br > Cl > F, indicating that the geometrical size of the substituent is perhaps now the most important consideration from the point of view of nematic thermal stability.

It was therefore hoped that in the compound (18), the fluoro-substituent would not depress the T_{N-I} value by more than about 10-15^{o} (as for the cyclohexanoate esters), but that there would be marked reductions in the melting point and smectic properties. As a result, much lower smectic characteristics would be obtained for the compound itself and for an equivalent mixture to that assessed in Table 10. Electro-optically, it was assumed that the 2-fluorinated compound would be similar to the parent compound (apart from having a more negative dielectric anisotropy), as this had been found to be the case for the analogous cyclohexanoate and bicyclo(2.2.2)octanoate esters. However, such effects are difficult to predict.



(18)

C-I 43^{o}C, N-I [-10^{o}C]

Compared with the unfluorinated compound (C-I 35^{o}C, S_B-I (31^{o}C), N-I [21^{o}C]), the melting point has been increased by 8^{o}C and the T_{N-I} value lowered by about 31^{o}C. Therefore, 2-fluorination of the cyclohexylmethyl ether system has had quite different effects compared with 2-fluorination of phenyl cyclohexanoates, although as expected, the smectic tendencies of the system have been repressed. To account for these differences, it is necessary to examine the molecular structural relationships between these ethers and esters. The difference between the two systems is governed only by the inter-ring linkage, ie, $-CH_2O-$ or -CO.O-. The $-CH_2O-$ group contains both sp^3 hybridised C and O atoms. This linking group is therefore quite flexible in nature and only weakly polarisable when compared with the -CO.O- unit, which is a rigid, planar group of relatively high polarisability, by virtue of the π-electron system (sp^2 hybridised C and O). It would seem that the poor results obtained on 2-fluorination of the cyclohexylmethyl ethers must be attributed to the $-CH_2O-$ group and its greater flexibility compared with the more rigid conjugated -CO.O- linking group. Intramolecular steric effects and repulsive interactions may therefore cause more severe twisting effects or possibly even bending within the core structure - factors which may more seriously effect the nematic order.

In view of this disappointing result, it was not considered worthwhile to prepare further fluorinated derivatives of the cyclohexylmethyl ethers.

To summarise, the cyclohexylmethyl ethers should possess superior thermal, photochemical, and electrochemical stabilities compared with related esters and benzyl ethers. The T_{N-I} values for these compounds in nematic hosts also appear to be better than those for the benzyl ethers. The voltage figures of merit are roughly comparable for these two systems. Whilst the T_{N-I} values, melting points, and viscosities for the cyclohexylmethyl ethers could desirably be improved, the main disadvantage of these compounds lies in the unacceptably high values for the threshold voltages of their mixtures with nematic hosts, coupled with a large dependence of these values on temperature. The high smectic characteristics exhibited by the compounds themselves also pose a problem.

4.2.3 *Bicyclo(2.2.2)octylmethyl Ethers*

The bicyclo(2.2.2)octane (BCO) ring was first investigated by Dewar *et al.*[85-88] for its potential when incorporated into liquid crystal systems. This ring system was chosen because the 1,4-bonds are both co-linear and co-axial, as desired for liquid crystal formation, and the molecular dimensions are similar to those for benzene. For example, from computer simulations, the molecular dimensions have been estimated as 2.55 Å and 2.78 Å for the C_1-C_4 distances, and as 5.61 Å and 4.31 Å for the diameters of the cylinders swept out by the lateral hydrogens on rotation about the C_1-C_4 axis, for bicyclo(2.2.2)octane and benzene respectively.

However, the first results obtained for the BCO ring, by incorporation into the tricyclic diesters of structure (19),[85] were generally rather unexciting. With a single BCO ring incorporated

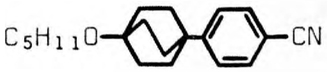
(19)

where

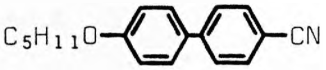
A, B, C = 1,4-disubstituted benzene
1,4-disubstituted bicyclo(2.2.2)octane

into this structure as ring B, the T_{N-I} value fell by 31°C, and when incorporated as ring A (or C), the T_{N-I} value fell by 79°C, relative to the fully aromatic diester[89] (R = $-CH_3$, see Table 15). With rings A and C, or all three ring structures as BCO, no liquid crystal properties were observed. These poor results were attributed to a diminution of π-electrons and conjugative interactions within the molecules, resulting in a reduction of the anisotropy of the molecular polarisability and consequently a lowering of the T_{N-I} value.

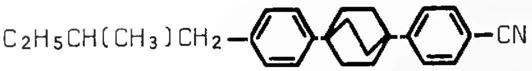
Further work by Gray and McDonnell[90] on the replacement of a benzene ring by a BCO ring in some biphenyl- and terphenyl-based systems (see below) tended to confirm the results of Dewar.



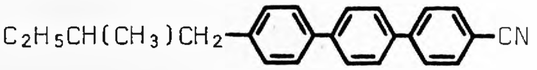
C-I >50°C, N-I <20°C



C 48 N 68 I



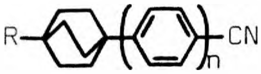
C 155 Ch 156 I



C 132 Ch 208 I

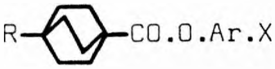
However, it now turns out, with good reason, that all of the above BCO systems do not in fact show what is now the accepted trend, ie, that when a BCO ring is incorporated into *suitable* systems an increase in the T_{N-I} value is obtained relative to both the benzene and the cyclohexane analogue. This subject will be discussed more fully later on in this section, in the context of some results obtained during the course of this work on BCO ethers, together with other results drawn from the liquid crystal area as a whole.

The results of Carr, Gray and Kelly on systems of type (20)[91] and (21)[59,92] provided the first sets of data that showed positively that the BCO ring could be successfully incorporated into liquid crystal materials and produce T_{N-I} values considerably higher than those for the analogous benzene and cyclohexane derivatives. Furthermore, some very encouraging electro-optic results were obtained for mixtures incorporating some of these BCO materials, particularly with respect to the variation of the threshold voltage with temperature. For example, values for $^{-1}/V\ (\frac{dV}{dT})$ as low as 0.28% $^{0}C^{-1}$ have been obtained for mixtures incorporating some BCO esters of type (21).[93]



(20)

n = 0 or 1



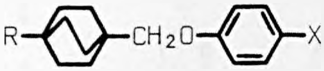
(21)

where

(i) Ar = 1,4-disubstituted benzene
X = n-alkyl, n-alkoxy, cyano

(ii) Ar = 2,6-disubstituted naphthalene, 4,4'-disubstituted biphenyl
X = cyano

In the light of these results, it was felt that interesting properties might be obtained with the BCO analogues (see structure (22)) of the benzyl and cyclohexylmethyl ethers discussed in the previous two sections.



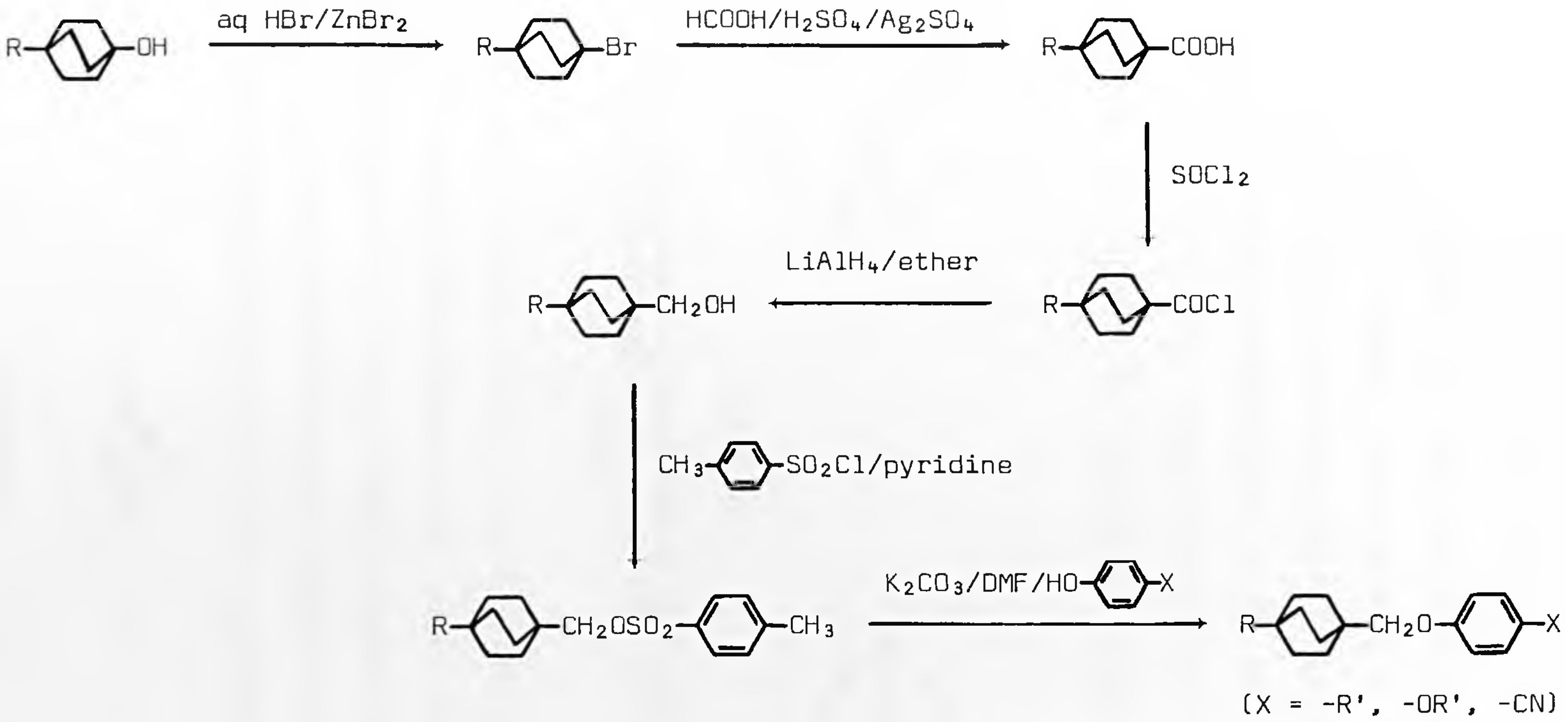
(22)

where

X = n-alkyl, n-alkoxy, cyano

Several bicyclo(2.2.2)octylmethyl ethers were therefore prepared by the route outlined in Scheme 3.

Although the bicyclo(2.2.2)octane and cyclohexane rings are both alicyclic and of similar molecular dimensions, their chemistry is often very different. For example, substitution reactions that take place fairly readily with cyclohexane are either very difficult or do not take place at all with BCO. This is because a large number of these reactions take place *via* a S_N2 mechanism, whereby an attacking nucleophile approaches the molecule from the opposite side to that from which the displaced group leaves. With 1,4-disubstituted cyclohexane



SCHEME 3

Synthetic route for bicyclo(2.2.2)octylmethyl ethers an attacking nucleophile is sterically hindered to some extent by the ring structure (see Figure 25), but is not totally excluded. This is borne out by the fact that S_N2 reactions take place with cyclohexyl systems, but at a slower rate than those with simple unhindered aliphatic compounds. However, in the case of 1,4-disubstituted bicyclo(2.2.2)octane, an approaching nucleophile finds it very difficult to displace the substituent X, due to the three-dimensional bulk of the ring structure. Consequently, such displacement reactions do not normally occur with BCO bridgehead systems.

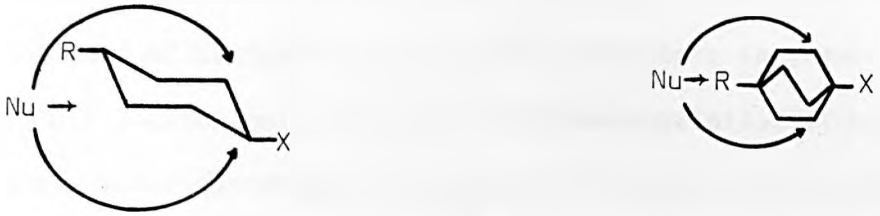


FIGURE 25

Possible approaches of an attacking nucleophile to the 1,4-disubstituted cyclohexane and bicyclo(2.2.2)octane rings

As a result of this, a lot of substitution reactions of BCO are forced to proceed by the S_N1 mechanism. Here, heterolytic fission of the C-X bond occurs to produce a highly reactive ionic species. This mechanism is unfavourable for the BCO ring in two respects. Firstly, the BCO cation produced (see Figure 26) is sp^2 hybridised at the

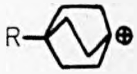
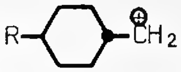


FIGURE 26

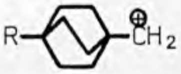
The bridgehead bicyclo(2.2.2)octyl carbocation positively charged C atom, and is therefore required to be planar at this point. However, because of the geometry of the ring, this is strongly resisted due to molecular strain factors. Secondly, there are no adjacent p- or π-orbitals available to assist with the delocalisation of the positive charge. The BCO cation is therefore a very difficult species to form, and once formed it is highly unstable and therefore extremely reactive.

Independent support for these points relating to the BCO ring has been obtained from kinetic experiments,[94] which have shown that the BCO ring undergoes substitution reactions almost exclusively by the S_N1 mechanism as opposed to the S_N2 route. Scheme 3 shows that in the case of bridgehead substitution reactions (eg, for 4-n-alkyl-bicyclo(2.2.2)octanol and n-alkyl-4-bromobicyclo(2.2.2)octane) strongly ionic conditions (ie, the use of very polar solvents) that are extremely forcing in nature are required in order to cleave the C-X (C-OH and C-Br) bond and allow the reaction to proceed by the S_N1 route.

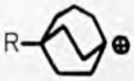
A further difference between the cyclohexane and BCO rings is revealed by the fact that the final ether formation step was carried out on the substituted methyl bromides for cyclohexane, but the analogous bicyclo(2.2.2)octylmethyl bromides could not be formed, due to chemical instability. Consequently, the tosylates of the BCO materials were used as intermediates for formation of the BCO ethers (compare Schemes 2 and 3). The reason for this difference between the two systems is a direct function of the properties of the two alicyclic ring structures involved. In the preparation of the cyclohexane compounds, the *trans*-4-n-alkylcyclohexylmethanol is brominated by simply heating the alcohol under reflux in an aqueous mixture of hydrobromic and sulphuric acids for 3 hours. The bromide is then obtained in a fairly good yield (80-90%) and can then be purified by reduced pressure distillation. However, if the corresponding 4-n-alkylbicyclo(2.2.2)octylmethanol is subjected to the same treatment, a mixture of products is obtained, with no substantial formation of the desired bromide. The most likely kinetics for this reaction are first order, ie, involving a S_N1 mechanism which (for cyclohexane) produces the intermediate



This primary carbocation is a relatively short lived species and will rapidly combine with a bromide anion to form the product. However, the corresponding bicyclo-octyl carbocation,



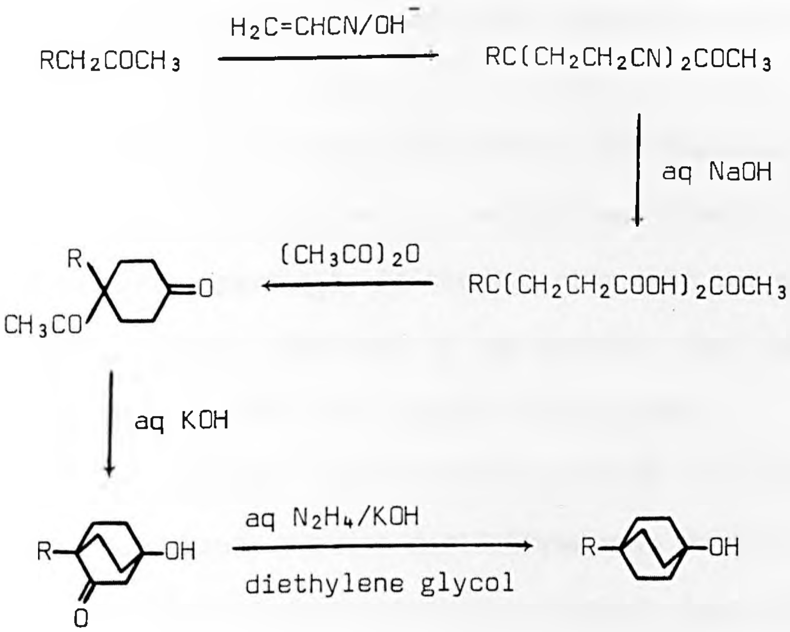
is capable of rearrangement by C-C bond cleavage, producing a tertiary carbocation



which is the energetically more stable species. This process is not as favourable for the cyclohexyl system as only a secondary carbocation can be produced. Consequently, in the case of BCO, bicyclo(3.2.2)-nonane derivatives are produced, and the reaction is further complicated by the fact that other rearrangements/side-products may be produced from the bicyclo(3.2.2)nonyl carbocation by way of hydride shifts, etc.[95]

It was therefore essential to avoid this bromination procedure in the preparation of the BCO ethers. Overall the yields obtained by the two routes were similar, and in principle, the tosylation procedure could equally well be applied to the preparation of the cyclohexylmethyl ethers, with the possible advantage that a crystalline and readily purified intermediate would be produced at the somewhat critical penultimate stage of the synthesis.

For reference, the starting alcohol given in Scheme 3 was prepared in five steps starting from the appropriate alkyl methyl ketone. This route is outlined in Scheme 4.



SCHEME 4

Synthetic route for 4-n-alkylbicyclo(2.2.2)octanols

Eight dialkyl derivatives of these BCO ethers were prepared. In addition, a single alkyl-alkoxy analogue was prepared, as well as two laterally fluorinated dialkyl derivatives. The thermal data for these compounds are given collectively in Table 11.

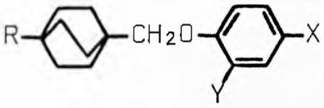
Compared with the corresponding cyclohexylmethyl ethers (see Tables 6 and 8 and compound (18)), the melting points and T_{N-I} values for the BCO materials are increased in all cases, the one exception being the laterally fluorinated di-pentyl compound which melts 5^{o} lower. Taken as an average over the ten compounds that are comparable, the melting points have increased by 18.6^{o} and the T_{N-I} values by 16.4^{o} for the bicyclo(2.2.2)octylmethyl ethers. Consequently, as the melting points have been increased slightly more than the T_{N-I} values, the nematic ranges would be expected to have been reduced. However, for these compounds, the real situation is that nematic phases are slightly more monotropic with respect to the melting points.

These and similar comparisons made in the previous section involving cyclohexane and benzene derivatives, provide confirmatory evidence for the superiority of the BCO ring over the cyclohexane ring, which is in turn superior to the benzene ring, from the point of view of promoting the T_{N-I} value of the system.

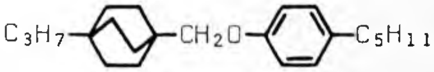
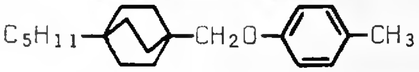
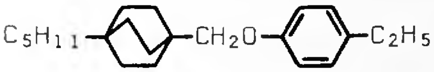
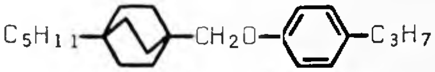
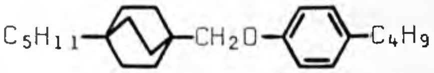
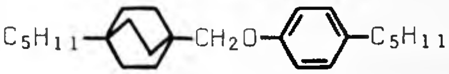
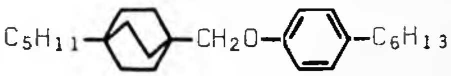
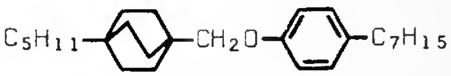
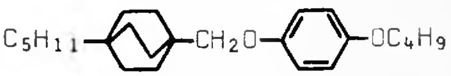
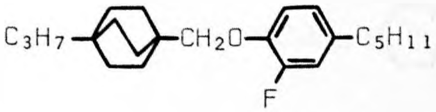
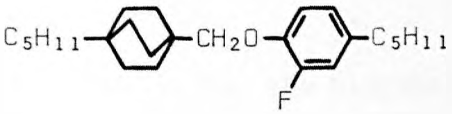
The relative smectic tendencies for the BCO and cyclohexane systems (no comparable benzene derivatives were prepared) indicate that those for the BCO derivatives are slightly lower than for the cyclohexane compounds in the case of the dialkyl derivatives, but slightly higher for the alkyl-alkoxy compounds. In the case of the dialkyl materials, the smectic phase first appears for the BCO series with the 5.6 homologue at $30^{o}C$. In the corresponding cyclohexane series, a smectic phase appears with the 5.3 homologue at $10^{o}C$, the 5.6 homologue having a T_{S_B-I} value of $36^{o}C$. The only alkyl-alkoxy

TABLE 11

Thermal data for some bicyclo(2.2.2)octylmethyl ethers of structure

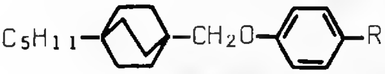


(X = R', OR'; Y = H, F)

	C-I (^{o}C)	S_B-N/I (^{o}C)	N-I (^{o}C)
	51	-	[21]
	69	-	(33.5)
	58	-	(20)
	56	-	(30)
	56	-	(19)
	47	-	(32)
	43	(30)	[27]
	47	(35.5)	(36)
	74	(61)	(68)
	41	-	[2]
	38	-	(11.5)

BCO analogue investigated (5.04) has a T_{S_B-N} value of 61°C (monotropic), whereas the 5.04 cyclohexylmethyl ether gives a similar monotropic phase, but some 14° lower at 47°C.

Figure 27 shows the change in transition temperatures with varying alkyl chain length for the compounds of general structure (23).

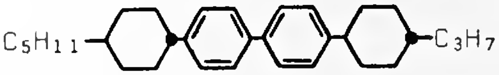


(23)

This plot shows the usual odd-even alternation of T_{N-I} values. Both T_{N-I} curves exhibit a minimum in a similar manner to the corresponding curves for the dialkylcyclohexylmethyl ethers discussed in the previous section (see Figure 23), although the curvature for the BCO compounds is less pronounced.

Table 12 contains physical data supplied by RSRE, Malvern for binary and ternary mixtures containing bicyclo(2.2.2)octylmethyl ethers, as well as similar data for two ester systems used commercially in nematic mixtures.

Each of the binary mixtures consists of two homologues (3.5 and 5.5) mixed in equal weight proportions. The ternary mixtures are the binary mixtures with 10 wt % of compound (24) added in order to enhance the T_{N-I} value of the mixture.



(24)

N-I 310°C

Generally, the bicyclo(2.2.2)octylmethyl ethers do not compare too favourably with the low Δε ester materials that they would be expected to replace in nematic mixtures. The data given in Table 12

FIGURE 27

Graph of transition temperatures against number of carbon atoms in R for the series

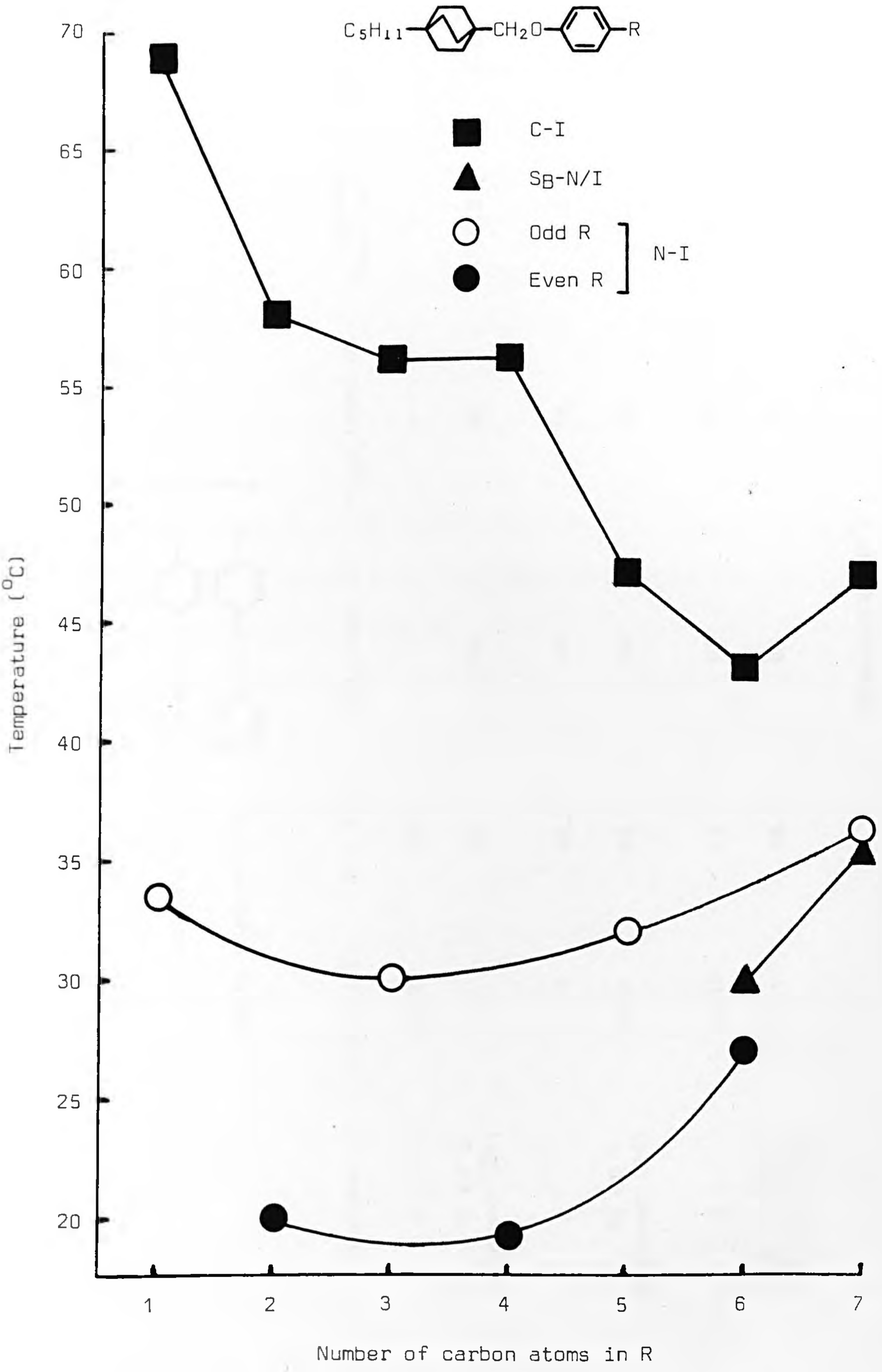
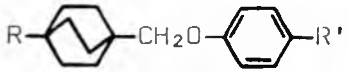


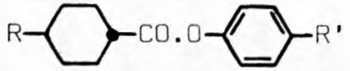
TABLE 12

Physical data for some mixtures of dialkyl substituted bicyclo(2.2.2)octylmethyl ethers, phenyl cyclohexanoates and phenyl benzoates

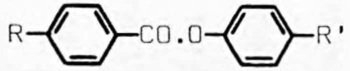
Binary mixture A =



Binary mixture B =



Binary mixture C =



R:R' = 3.5:5.5 in 50:50 wt %

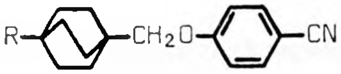
Mixture	C-N/I (^{o}C)	N-I (^{o}C)	$\eta_{0^{o}C}$(nem) cP	$\eta_{20^{o}C}$(nem) cP	E_a(nem) kcal mol^{-1}	Δn (20^{o}C)
A	30-31	23.7	-	-	-	-
A + 10 wt % compound (24)	27	50	274	89	8.9	0.06†
B	5-14	40.5	41	18	6.5	-
B + 10 wt % compound (24)	9-17	66	49	20	6.8	0.085
C	12-15	23	62	28	6.2	-
C + 10 wt % compound (24)	4-11	48.5	69	28	7.3	0.125

† measured at 40^{o}C

show that the melting points and viscosity values for the BCO ethers are particularly high, and the T_{N-I} values and nematic activation energies could be more promising. One advantage of the ether system would be the increase in stability of the mixture (chemical, photochemical and electrochemical) relative to the ester mixtures. Nevertheless, any possible advantages of the BCO ether systems are apparently far outweighed by their disadvantages, and it must be remembered also that commercially, the preparation of such systems would be much less economical by comparison with that for the less sophisticated phenyl cyclohexanoate or phenyl benzoate esters presently used.

Lateral 2-fluorination of the aromatic ring for the bicyclo(2.2.2)-octylmethyl ethers appears to be more favourable than in the case of the cyclohexylmethyl ethers. On average the melting points are depressed by 9.5^{o}, and the T_{N-I} values by 20^{o} by comparison with the unsubstituted materials. These results compare with a melting point *increase* of 8^{o} and a T_{N-I} decrease of 31^{o} for the fluorinated dipentyl cyclohexyl compound relative to its unsubstituted analogue. However, an average T_{N-I} depression of only 3^{o} is obtained on 2-fluorination of the phenyl ring for terminally disubstituted phenyl bicyclo(2.2.2)-octanoates. The intermediate T_{N-I} decrease obtained for the fluorinated bicyclo(2.2.2)octylmethyl ethers therefore appears to result from an increased shielding effect by the bulky BCO ring relative to that exercised by the cyclohexane ring in the cyclohexylmethyl ethers, but smaller conjugative interactions and a consequent increase in rotational freedom and flexibility relative to the bicyclo(2.2.2)octanoate esters.

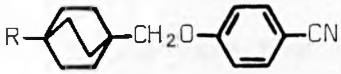
Three cyano derivatives of general structure (25) were prepared, and the thermal data are presented in Table 13.

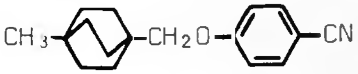
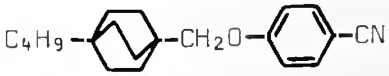
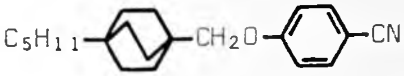


(25)

TABLE 13

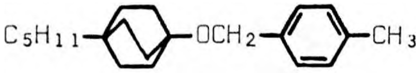
Thermal data for some bicyclo(2.2.2)octylmethyl ethers of structure



Structure	C-N/I ($^{\circ}$C)	N-I ($^{\circ}$C)
	89	[-44]
	79	(57)
	72	73.5

It is possible to compare the pentyl homologue with the analogous cyclohexane (see Table 3) and benzene (see Table 2) derivatives. Again these results illustrate the trend that the stabilising effect of these ring structures on the nematic phase decreases on passing from BCO, to cyclohexane, to benzene. For these compounds, the effect is quite pronounced, in that the T_{N-I} value for the benzyl ether is virtual, for the cyclohexylmethyl ether it is monotropic, and for the bicyclo(2.2.2)octylmethyl ether it is enantiotropic.

An interesting result was then obtained by reversing the $-CH_2O-$ inter-ring linkage of the 5.1 dialkyl derivative to produce the compound of structure (26).

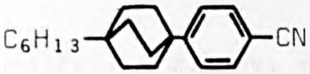


(26)

C-I 63°C, N-I [-210°C]

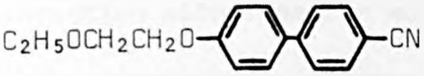
The preparation of this material again illustrates the unreactive nature of substituted bicyclo(2.2.2)octanes. By comparison, benzylation of a 4-substituted cyclohexanol takes place in a KOH medium to give approximately 70% of product after 4 hr at 150°C. However, with 4-pentylbicyclo(2.2.2)octanol, more forcing reaction conditions (6 hr at 215°C) gave less than 10% of the product.

Although the melting point for compound (26) and that for the corresponding bicyclo(2.2.2)octylmethyl ether (see Table 11) are similar, there is an incredible difference of well over 200° between the two T_{N-I} values. However, it was soon realised that, although this result was not anticipated, it followed a similar trend found for other materials containing ether linkages between saturated carbon atoms. For example, compound (27) has a good nematic thermal stability, whereas the corresponding alkoxy analogue (see page 152) does not. Also, compound (28)[96] shows a similar sharp decrease in T_{N-I} value resulting from the additional aliphatic ether linkage that has been incorporated into the alkoxy chain of CB5O - compound (29). Further circumstantial evidence for this effect is



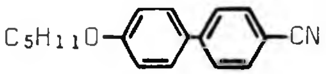
(27)

C 72 N 86 I



(28)

C-I 75.5°C, N-I [-15°C]



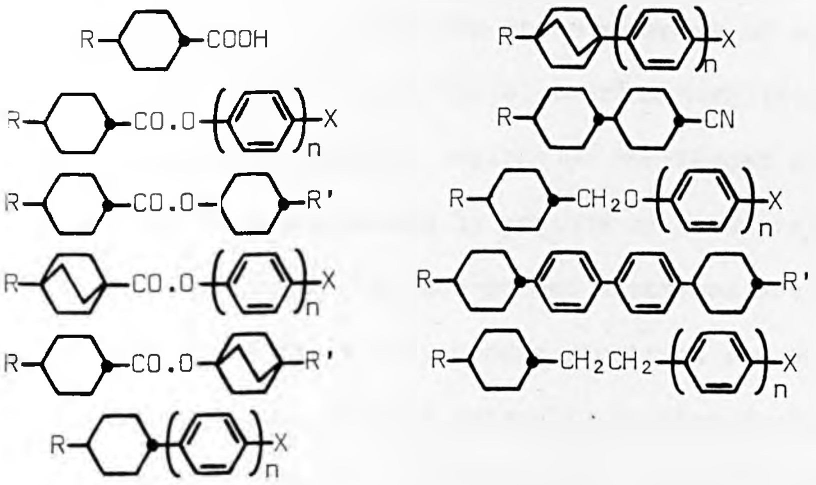
(29)

C 48 N 68 I

that for many of the best currently available liquid crystal materials containing alkyl-alicyclic ring functions, no *published* data exist on their structurally related alkoxy analogues - a list of such compounds (which is by no means exhaustive) is given in Table 14.

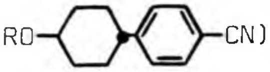
TABLE 14

A list of some useful liquid crystal materials containing alkyl-alicyclic ring functions for which no reports on the corresponding materials containing alkoxy-alicyclic ring functions have appeared - implying that the latter are poor mesogens



where

X = n-alkyl, n-alkoxy, cyano
n = 1 or 2

In private conversation with research workers from E Merck, Darmstadt, West Germany, it has been disclosed that certain examples of these alkoxy derivatives have been investigated (eg, 

)

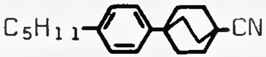
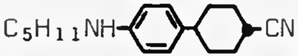
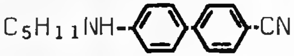
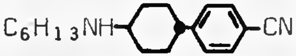
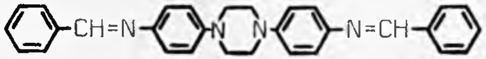
and found to have poor liquid crystal properties, and it is now widely accepted that such compounds have extremely poor liquid crystal thermal stability.

However, this behaviour is not confined simply to ether-based systems, and Table 15 reveals that pairs of structurally related compounds drawn from quite widely different molecular types can also exhibit this effect of unexpectedly large differences in liquid crystal thermal stability. In addition, many other miscellaneous examples are scattered throughout the literature.

The explanation for these effects is not obvious, but it may have its origins in the fundamental nature of the chemical bonding. Almost without exception, all of the known examples of materials that exhibit unexpectedly low liquid crystal thermal stability contain within the molecule *two* distinct regions of non-bonded or relatively weakly bonded electrons separated by regions of essentially inert, strongly bonded electrons. The non-bonded electrons are usually lone electron pairs, whilst the weakly bonded electrons are usually in *p*-type orbitals that can interact laterally to form conjugated π-electron systems. Lone-pair electrons on O atoms (2 x sp^3 orbitals) or N atoms (1 x sp^3 orbital), and interacting *p*-orbitals in aromatic systems, nitrile groups, ester functions, etc, provide examples of non-bonded and weakly bonded electron systems respectively. The strongly bonded electron systems involve σ-bonds that result from direct orbital interactions, eg, carbon-carbon and carbon-hydrogen bonds.

TABLE 15

Comparative thermal data for some liquid crystal materials and related derivatives of relatively low thermal stability

Compound	Transition Temperatures	Ref	Comparison	Transition Temperatures	Ref
	C 197 I, N (195) I	85		C 222 N 300 I	89
	C 185 N 269 I	85			
	C 189 N 221 I	85			
	C 103.5 I	97		C 221 S 228 I	98
	C 180 N 237 I	97		C 268 N 314 I	98
	C 178 N 207 I	97		C 306 N 315 I	99
	C 16 I, N [-25] I	100		C 30 N 55 I	56
	C 113 I, N [50] I	101		C 62 N 100 I	91
	C 80.7 I, N (16.9) I	102		C 86.3 N 90.7 I	102
	C 67.5 I, N (27.6) I	102		C 105.3 I, N (93.8) I	102
	C 59.8 I, N [16] I	103		C 48.5 N 79 I	58
	C 278 N 286 I	104		C 302 S 315 N >360 I	99

The exact nature of this effect is hardly understood, although Eidenschink[100] has proposed an interpretation based on antenna theory, the molecules being considered as having regions that function as energy receivers and emitters.

It seems likely however that the non-bonded and weakly bonded electron systems behave in a similar fashion, in that they introduce a significant component of lateral polarisability into the molecule in the form of either permanent or instantaneous electric dipoles. When *one* such region is present within a molecule, the system often tolerates this well, and indeed such a region may in fact be a contributory factor to the reasonably good thermal stability of the mesophase observed for many such materials. However, in a molecule where two such distinct regions are present, it seems that now such interactions become disadvantageous for mesophase formation, possibly by way of disruptive (repulsive) lateral intermolecular interactions. It is unlikely that other factors (eg, molecular flexibility, steric inhibition of conjugation, etc) alone are responsible for this effect when considering the data for compound (26) and its reverse isomer, and for numerous other examples in the literature. These other factors must never of course be ignored, as they can certainly help to determine the efficiency of packing of the molecules in the mesophase.

By using the above considerations, it is possible to derive the following general principle regarding liquid crystal thermal stability:

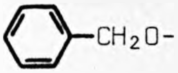
> If a molecule contains more than one distinct region of non-bonded (lone pair) or delocalised (π-type) electrons, it is likely to exhibit reduced liquid crystal thermal stability with respect to

some related system containing a single non-bonded/delocalised electron region.[†]

Although it may appear to be somewhat optimistic to expect liquid crystal behaviour in general to be summarised by such generalisations, no fully authenticated examples of exceptions to this principle are as yet known.

On the basis of the above arguments, it is now fairly clear why the initial erroneous conclusion was reached regarding the replacement of a 1,4-disubstituted benzene ring by a 1,4-disubstituted bicyclo(2.2.2)octane ring. The first systems incorporating the BCO ring all involved molecules containing more than a single region of non-bonded or delocalised electrons (see pages 151 and 152). In more normal systems, the BCO ring, without exception, enhances mesophase thermal stability with respect to the analogous benzene and, to a lesser extent, cyclohexane systems.

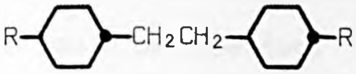
In the particular context of this work, it is possible to predict that, in general, any molecule containing the benzylic ether unit



will have relatively poor liquid crystal properties. The benzyl

---

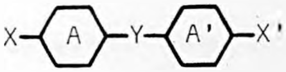
[†] Note however that totally σ-bonded systems (eg,



- to be discussed in Section 4.5.1) may also have high mesophase thermal stabilities.

ethers discussed in Section 4.2.1 belong to this general class of compound, and whilst the T_{N-I} values for these materials were expected to be lower than those for the analogous cyclohexylmethyl ethers, the extent of the depression was often much greater than expected - up to 70^{o} in some cases. Note too that compound (26) belongs to this general class of material.

By applying these general principles to materials other than ethers, it is possible quickly and simply to assess the mesomorphic potential for a range of compounds. For example, the derivatives of general structure (30) would appear to be only of limited value, for

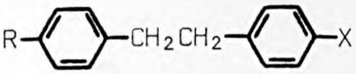


(30)

where

A = any aromatic ring system
X = any terminal substituent
Y = any linkage preventing inter-ring conjugation

if Y is as defined (eg, $-CH_2O-$, $-CH_2CH_2-$, $-(CH_2)_4-$, $-CH_2CH_2CO_2-$, $-CH_2CO_2CH_2-$, $-CH_2CO-$, $-CH_2NH-$, etc), it separates the two aromatic regions. Results from this work with A = benzene and Y = $-CH_2CH_2-$ (as well as $-CH_2O-$) appear to support this conclusion. For example, the compounds

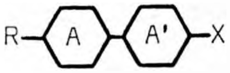


where

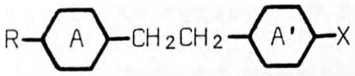
X = -R', -CN

have, by comparison with the analogous cyclohexyl derivatives, much lower T_{N-I} values than would be expected. These materials are to be discussed in Section 4.5.

On the positive side, such a principle would suggest that useful liquid crystal properties may be obtained with the following systems, for example:



(31)

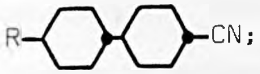


(32)

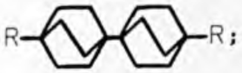
where

A = any alicyclic ring system
X = any terminal substituent

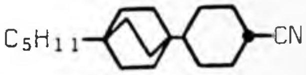
These general structures are highlighted because of their particular relationship to this work, and other cases could well be quoted; specific examples within structures (31) and (32) are, of course, known materials. These include the following materials, under structure (31):



;[105]

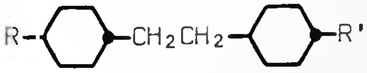


;[60]

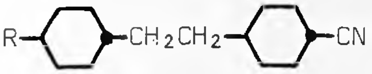


C 104 N 129 I;[101]

and under structure (32):



(see Section 4.5.1);



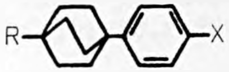
[106]

In each case, useful liquid crystal properties are observed, providing yet further support for the above general ideas.

To sum up this section on the bicyclo[2.2.2]octylmethyl ethers, these materials provide a novel series of stable liquid crystals which confirm that the BCO ring is the best single ring structure currently available for raising the nematic liquid crystal thermal stability of a system. Compared with ester derivatives, which these materials might be expected to replace in commercial nematic mixtures, the ethers do not however rate too favourably, their melting points and viscosity coefficients generally being higher, and their T_{N-I} values lower. Finally, the investigation of a system incorporating a reverse $-CH_2O-$ inter-ring linkage, coupled with previously unexplained results from other workers, has stimulated thinking about a groundrule governing aspects of the organisation within the molecules of mesogens of different kinds of electron distribution. The rule is entirely qualitative, but appears to be general and useful in application. Hopefully, it may prove to be of value in aiding the design of future liquid crystal materials.

4.3 *DERIVATIVES OF PHENYLBICYCLO(2.2.2)OCTANE*

The worldwide commercial usage of certain liquid crystals, such as the CB's[51-53] and PCH's,[56] has shown beyond doubt that a central linking group between ring structures is not a prerequisite for the formation of good liquid crystal materials. As mentioned in the previous section, the incorporation of the bicyclo(2.2.2)octane ring into similar structures[91] has produced materials of improved T_{N-I} values. It was against this background, and in the knowledge that some of the more adverse properties exhibited by materials incorporating the -CH_2O- inter-ring linkage may be attributed to the relatively flexible and weakly polarisable nature of this linking group, that an investigation of low $\Delta\varepsilon$ compounds of general structure (4) was planned.



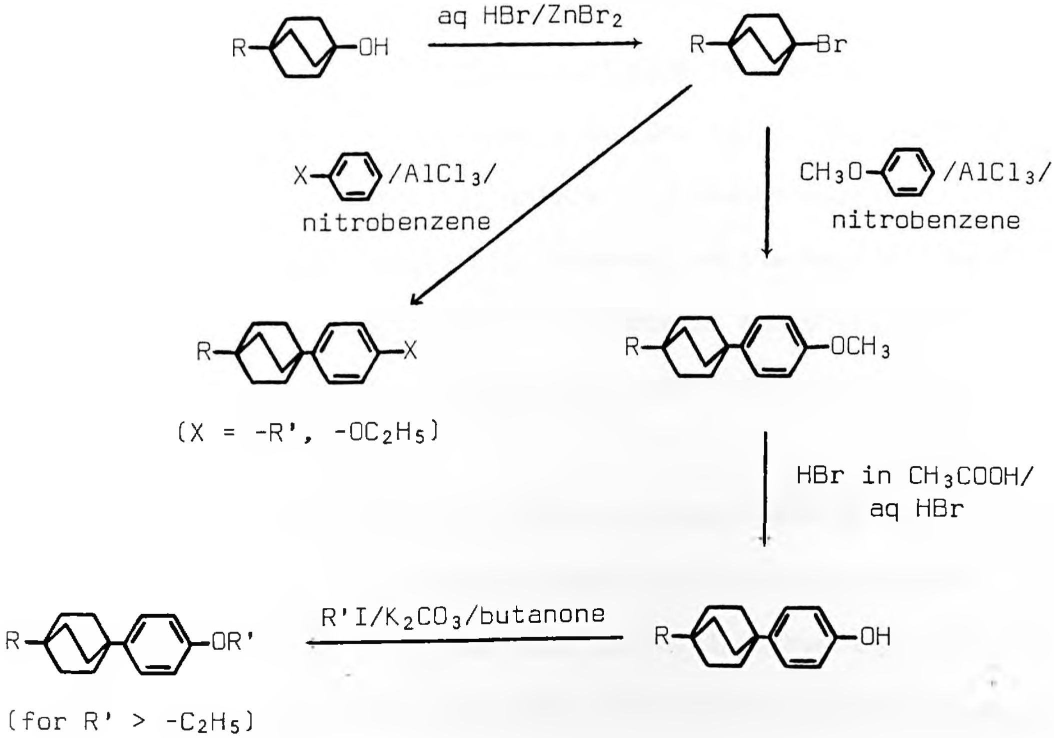
(4)

where

X = n-alkyl, n-alkoxy

The synthetic route for these materials is given in Scheme 5, starting from the appropriate 4-n-alkylbicyclo(2.2.2)octanol (prepared as in Scheme 4).

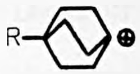
It is worth mentioning several points relating to the preparation of these phenylbicyclo(2.2.2)octane (PBCO) derivatives. The 1-n-alkyl-4-bromobicyclo(2.2.2)octane can be made to undergo a Friedel-Crafts alkylation reaction only if relatively forcing conditions are used. For example, it was found to be essential to use nitrobenzene as the solvent, rather than other more convenient solvents, eg, 1,2-dichloroethane etc. This may be attributed to the

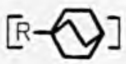


SCHEME 5

Synthetic route for disubstituted phenylbicyclo(2.2.2)octanes

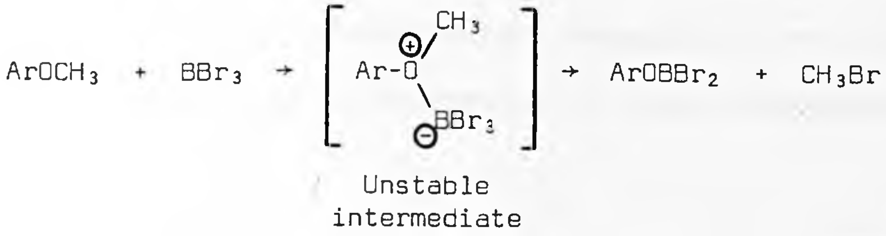
greater solvating properties of nitrobenzene for the BCO carbocation



(or the ion-pair $[AlCl_3Br]^-$ $^+$)

Also, this reaction was best carried out at an elevated temperature (80°C). Even so, the yields were never exceptionally high, being generally in the range 45-65%, reminding us of the fact that the bicyclo[2.2.2]octyl carbocation is difficult to form. In general, the product obtained by Friedel-Crafts alkylation of an aromatic system has an aromatic nucleus that is more electron-rich than the starting material due to electronic inductive effects. Consequently, the product is slightly activated relative to the starting material. As a result, di- and often tri-substitution of the aromatic nucleus may occur. This problem is usually avoided to a large extent by the slow addition of the alkyl halide to a reasonably large molar excess of the aromatic material. However, in the case of the PBCO's, the risk of further substitution is remote as the physical bulk of the BCO ring system makes attack at the more electron rich sites sterically unfavourable.

This alkylation step was found to proceed more or less independently of the alkyl chain present in the n-alkylbenzene. This was not, however, the case with the n-alkoxybenzenes. As the length of the alkoxy chain increased (particularly beyond ethoxy), the yield and the purity of the product were found to fall dramatically. This is because, under Friedel-Crafts conditions, long chain alkyl aryl ethers are prone to cleavage at the oxygen-aliphatic carbon bond, thereby producing a mixture of products. This behaviour has also been observed by other workers[96] using similar conditions in the Friedel-Crafts reactions. Such a side reaction in the presence of the Lewis acid, $AlCl_3$, is not of course surprising in view of the fact that another Lewis acid, BBr_3, is involved as the main attacking species in a highly successful demethylation procedure for structurally related aryl methyl ethers.[107] Here, the Lewis acid attacks the ether oxygen in order to reduce its own electron deficiency, the resulting intermediate rapidly losing methyl bromide as shown below:



$$\mathrm{ArOCH_3} + \mathrm{BBr_3} \rightarrow \left[\mathrm{Ar{-}\overset{\oplus}{O}}{}^{\diagup \mathrm{CH_3}}_{\diagdown \overset{\ominus}{\mathrm{B}}\mathrm{Br_3}}\right] \rightarrow \mathrm{ArOBBr_2} + \mathrm{CH_3Br}$$

Hydrolysis then produces the phenol ArOH.

As aluminium chloride is a much weaker Lewis acid than boron tribromide, the intermediate complex will be less easily formed. Consequently, Friedel-Crafts alkylation reactions involving anisole and phenetole are relatively free from this dealkylation problem. However, as the alkyl chain of the alkyl aryl ether lengthens, the presence of such an intermediate becomes more significant due to the stabilising influence of increased inductive effects which delocalise the positive charge on the oxygen atom. Also, increasing the alkyl chain length offers the possibility of rearrangement of the carbocation to the more stable secondary and, if possible, tertiary carbocation, and this may provide a driving force for the reaction.

As a result of this, the compounds with alkoxy side chains greater than ethoxy were prepared by a standard alkylation of the 4-substituted phenol which was in turn obtained by demethylation of the 4-substituted phenyl methyl ether.

In all, sixteen compounds of structure (4) were prepared, and their transition temperatures are recorded in Table 16.

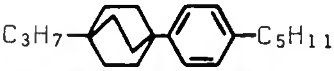
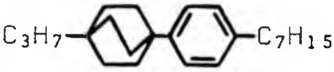
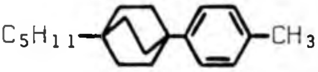
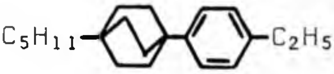
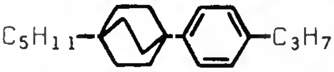
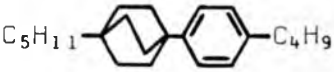
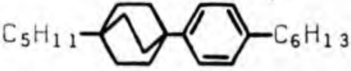
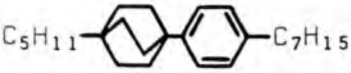
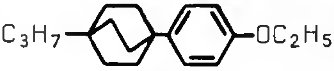
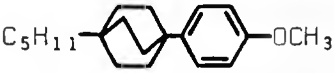
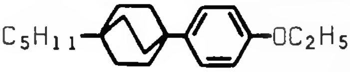
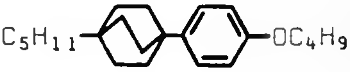
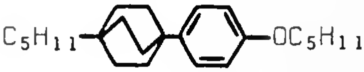
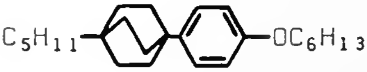
All of the ethers prepared gave a nematic phase, whilst only one of the dialkyl compounds was found to exhibit a nematic phase (monotropic). Overall, the T_{N-I} values provide yet further evidence for the superiority of the BCO ring, relative to benzene and cyclohexane rings, in promoting the nematic thermal stability of a system.

If the 3.5 and 3.7 derivatives are compared with the 5.3 and 5.5 homologues respectively, an increase in the alkyl chain attached to

TABLE 16

Thermal data for some phenylbicyclo(2.2.2)octanes of structure

(X = -R' , -OR')

Structure	C-N/I (^{o}C)	S_B-N/I (^{o}C)	N-I (^{o}C)
	57	-	[5]
	49	-	[8]
	64	-	[19]
	44	-	[0]
	50	-	[31]
	34	-	[2]
	52	-	(33)
	47	(30)	[15]
	52	(44)	[35]
	81	-	(74)
	64	-	70
	73	-	86
	72	-	(65)
	65	-	77
	75	(50)	(70.5)
	66	(54)	79

the BCO ring would appear to be more favourable than an increase in the chain on the aromatic ring for raising the T_{N-I} value. By comparison, the melting points do not vary to any great extent.

The smectic properties appear for equivalent homologues in the two series, ie, for the 5.6 and 5.05 derivatives, although the $T_{S_B-N/I}$ values for the dialkyl materials are significantly lower. Overall, these materials are less smectic in their tendencies than the related biphenyls, for which, in the case of the alkyl-alkoxy analogues, purely smectic properties occur with much shorter chain homologues. Full comparisons with the equivalent PCH derivatives are not possible as long chain homologues have not been prepared, but no smectic properties are observed for PCH3.5, PCH3.02 and PCH3.04 (these latter two compounds having T_{N-I} values of 37°C and 32°C respectively).

The effect on transition temperatures of removing the $-CH_2O-$ inter-ring linkage from the bicyclo(2.2.2)octylmethyl ethers, discussed in the previous section, can be obtained if the results in Table 16 are compared with those in Table 11. Taken as an average over the eight comparable dialkyl materials, the T_{N-I} values have dropped by approximately 10°C,[†] and the melting points by approximately 3.5°C. Consequently, the removal of the $-CH_2O-$ inter-ring linkage reduces the nematic characteristics of the system, but only to a relatively small extent. This more or less confirms the

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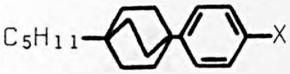
[†] No great importance should be attached to the exactness of this value, as over half of the transition temperatures involved are virtual values.

general conclusion of Section 4.2, that the $-CH_2O-$ unit is a useful, but generally unexceptional ring-bridging unit. On the other hand, a comparison of the 5.04 compounds reveals that the PBCO derivative has both a lower (-9°C) melting point and an increased (+11°C) T_{N-I} value relative to the $-CH_2O-$ linked derivative. The effect on the smectic properties of the system on removal of the $-CH_2O-$ unit is unclear, and no strong correlations appear to exist.

Figures 28 and 29 show the variations in transition temperatures with chain length for the two series



(X = -R, Figure 28 and X = -OR, Figure 29)

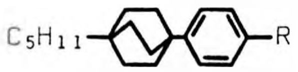
Within both series of compounds, the melting points do not vary greatly, and both families exhibit the usual odd-even chain length effect. In the case of the alkyl-alkoxy derivatives, a minimum is observed in both the odd and even T_{N-I} curves, as discussed in Section 4.2.2. However, this is not the case for the dialkyl derivatives, although it must be said that here the precise shapes of the curves are in question, due to the virtual nature of all but one of the N-I transition temperatures.

Table 17 contains data resulting from physical assessments of some of these materials at RSRE, Malvern.

The viscosity data show that, although the values for the dialkyl derivatives are markedly higher than those for the analogous biphenyl (η_{20^oC}(iso) ≃ 10 cP) and PCH (η_{20^oC}(iso) ≃ 8 cP) materials, they are not much greater than the viscosity values for some commercial ester materials of low $\Delta\varepsilon$. In this context, the response

FIGURE 28

Graph of transition temperatures against number of carbon atoms in R for the series



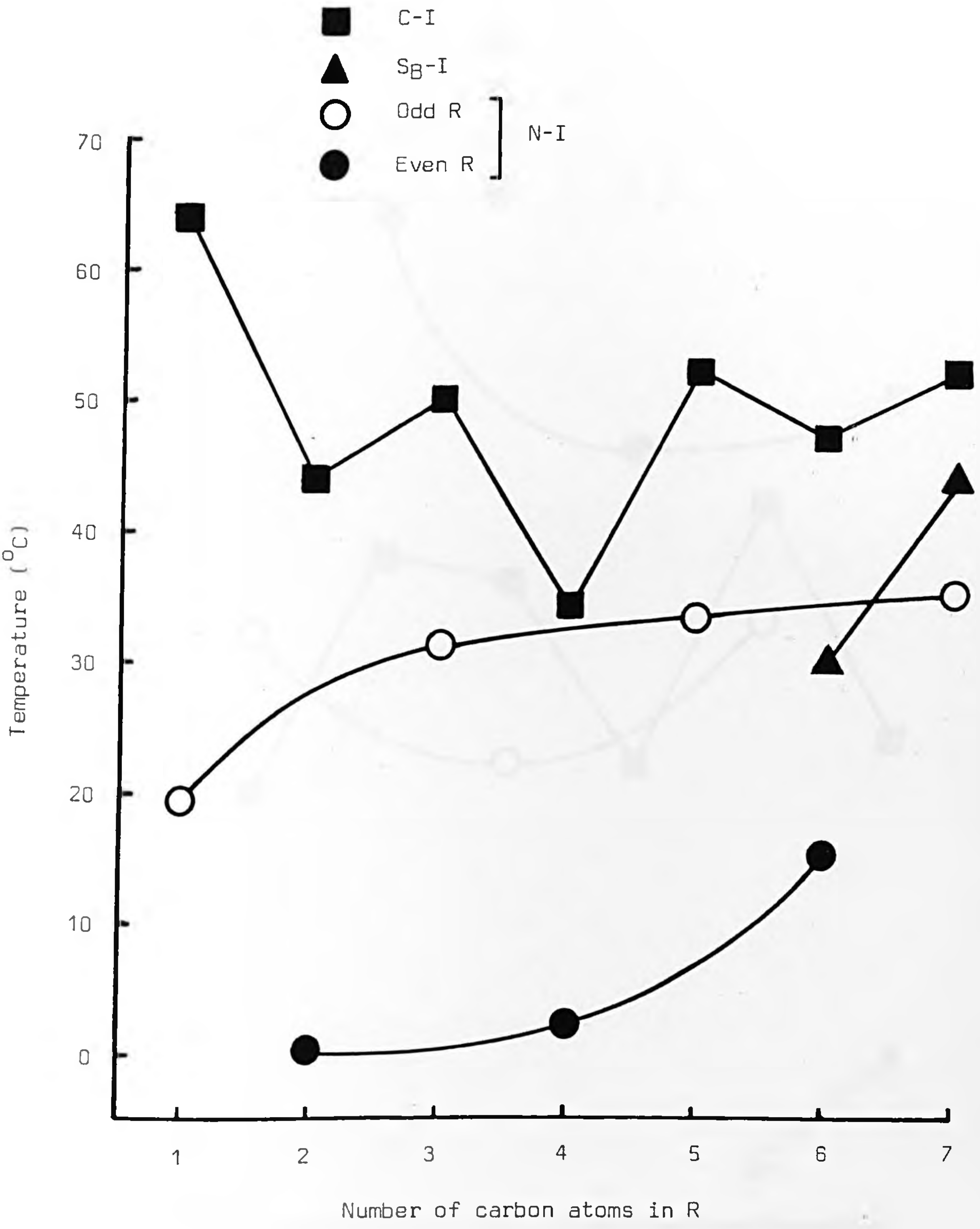


FIGURE 29

Graph of transition temperatures against number of carbon atoms in R for the series

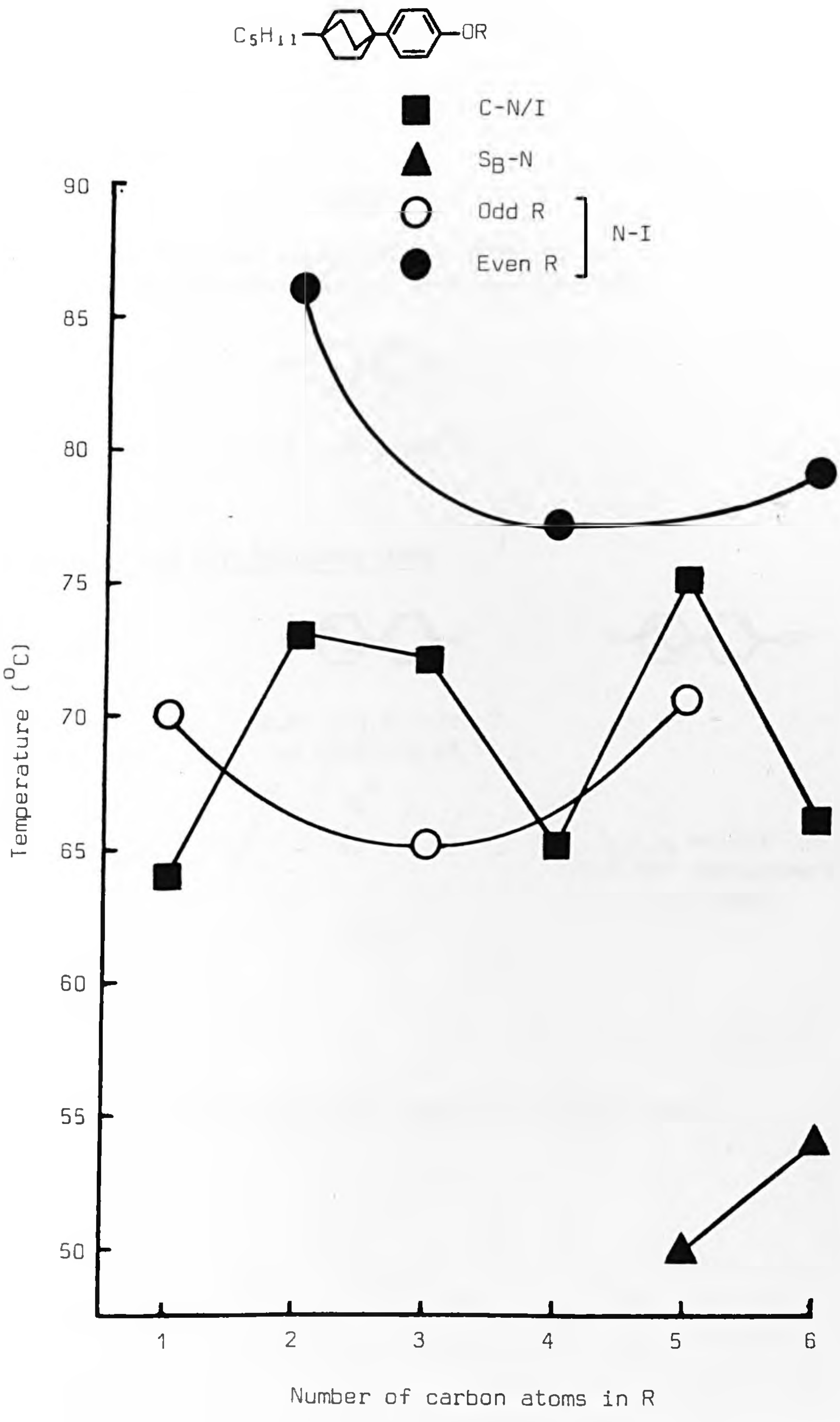
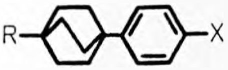


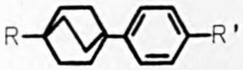
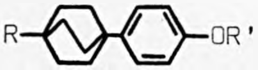
TABLE 17

Physical and electro-optic data for some phenylbicyclo(2.2.2)octanes of structure



(X = $-R'$, $-OR'$)

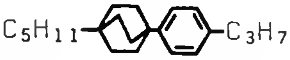
(a) *Viscosity and birefringence data*

	Structure		
	Mixture composition	R.R' = 3.5:3.7:5.7 in 25:25:50 wt %	–
cP	$\eta_{20^{o}C}$(nem)	35†	$T_{C/S-N}$ values too high for measurements to be made
	$\eta_{0^{o}C}$(iso)$_{extra}$	52	
	Δn (20°C)	0.05†	

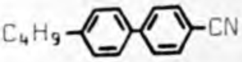
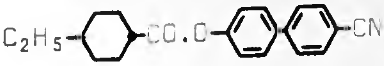
† measurement carried out close to the T_{N-I} value

TABLE 17 *(continued)*

(b) <u>*Electro-optic data*</u>††

		A = 	A = 	
		Temperature ($^\circ C$)	Temperature ($^\circ C$)	
		20	20	30
V	V_{90} (45°)	1.16	1.15	-
	V_{50} (10°)	2.13	2.10	-
	V_{10} (0°)	1.59	1.58	-
	$M_{20^\circ C}$	1.84	1.83	-
	$M'_{20^\circ C}$	1.37	1.37	-
ms	Rise time (at 3 V)	84	-	59
	Decay time (at 3 V)	50	-	48
$-\frac{1}{V}\left(\frac{dV}{dT}\right)$ % $^\circ C^{-1}$	at V_{90} (45°)	0.48	0.64	
	at V_{50} (10°)	0.58	0.82	
	at V_{10} (0°)	0.62	0.84	
	N-I ($^\circ C$)	79.0	60.5	

†† Data for compound A when incorporated into the following mixture:

Component	wt %
	15
	23
	10
	12
A	40

times of the mixture also appear to be quite acceptable.

As mentioned in Section 4.2.3, useful electro-optic properties (eg, low $\frac{-1}{V}\left(\frac{dV}{dT}\right)$ values) may be obtained for systems incorporating a BCO ring. In the case of the mixtures involving PBCO materials, although the M_{20^oC} values are a little higher than desired, the $\frac{-1}{V}\left(\frac{dV}{dT}\right)$ values are again found to be relatively low. However, although these latter values appear to provide advantages for the PBCO materials, they are still significantly higher than the corresponding values involving BCO esters. Consequently, it must be concluded that such electro-optic properties are not purely a function of the BCO ring itself, and that the molecular (and therefore intermolecular) environment into which the ring is placed is also significant.

Overall, the dialkyl and alkyl-alkoxy PBCO's provide two novel families of highly stable liquid crystals and again illustrate the fact that an inter-ring linking unit is not essential for mesophase formation. Whilst the melting points for these materials could profitably be lower, the T_{N-I} values are comparable with those for the esters of low $\Delta\varepsilon$ that they might be expected to replace in commercial nematic mixtures. Most of the other physical and electro-optic properties relating to mixtures of these materials are reasonably acceptable. Finally, comparisons with related benzene and cyclohexane derivatives again illustrate that the BCO ring gives the highest T_{N-I} values for these systems.

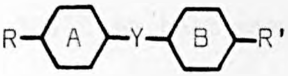
4.4 *ESTERS OF BICYCLO(2.2.2)OCTANE- AND CYCLOHEXANE-1-CARBOXYLIC ACIDS*

The search for materials of low dielectric anisotropy, as possible replacements for the ester components used in commercial nematic mixtures, has placed a high priority on obtaining very highly stable (chemically, electrochemically, photochemically, etc) materials. This is because, over long periods of time, these ester components gradually break down, both photochemically and because of the lability of the ester function -CO.O-.

An alternative approach is to develop new ester materials that have superior physical and electro-optic properties compared with those they replace, so that although little may be gained in terms of overall stability (display device lifetime), the electro-optic properties and multiplexing capabilities of the display devices may be significantly improved.

It has already been demonstrated, both during the course of this work and within the liquid crystal area as a whole, that the bicyclo(2.2.2)octane and *trans*-cyclohexane rings promote many of the desirable features necessary for the formation of good liquid crystals. Accordingly, the idea of producing a molecule into which *both* of these rings had been incorporated (the first instance of this kind) seemed to be an attractive proposition.

Consequently, several fully aliphatic esters of general structure (33) were prepared.



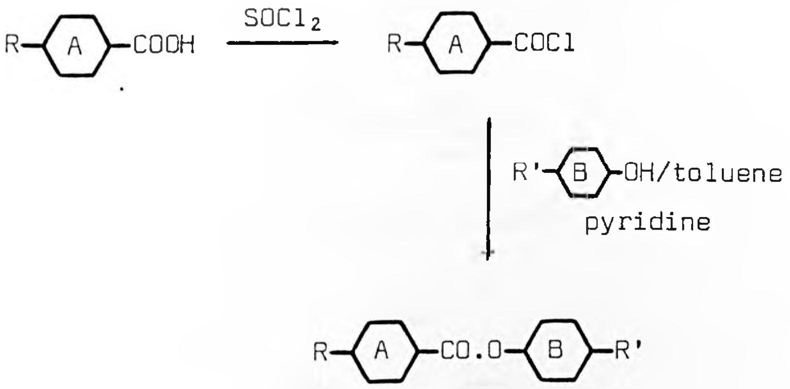
(33)

where

Y = -CO.O-, -O.CO-

A, B = *trans*-cyclohexane, bicyclo(2.2.2)octane
(A *and* B ≠ *trans*-cyclohexane)

These materials were prepared by the esterification route outlined in Scheme 6.



where

A, B = *trans*-cyclohexane, bicyclo(2.2.2)octane
(A *and* B ≠ *trans*-cyclohexane)

SCHEME 6

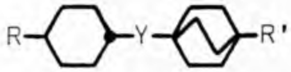
Synthetic route for bicyclo(2.2.2)octane- and cyclohexane-1-carboxylates

In general, esterification of a secondary or tertiary aliphatic alcohol with an aliphatic acid chloride takes place within a few hours under normal conditions. The fact that the above materials, when B = BCO, are only obtained in a reasonable yield after heating under reflux in toluene for 64 hr again illustrates the unreactive nature of the BCO compounds involved.

The transition temperatures for the esters are given in Table 18. All of these materials are in fact strongly smectic, ie, most of the compounds melt around, or below room temperature, and many have T_{S_B}-I values well above 100^{0}C so that smectic ranges of greater than 100^{0} are observed.

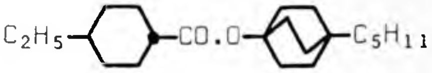
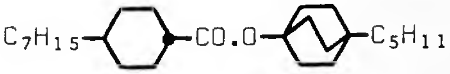
TABLE 18

Thermal data for some bicyclo(2.2.2)octanoates and cyclohexanoates of structure

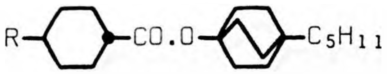


(Y = -CO.O-, -O.CO-)

and

Structure	C-S_B (^oC)	S_B-N/I (^oC)	N-I (^oC)
	22	49	[40]
	4	73	[59]
	1	88	[85]
	9	104.5	[92]
	-3	107	[100]
	19	115	[102]
	11	114	[103]
	18	79	92
	17	96	[92]
	40	191.5	[130]

The first of these materials prepared were the homologues of general structure (34).



(34)

The effect on transition temperatures of variation of the chain length, R, is shown in Figure 30.

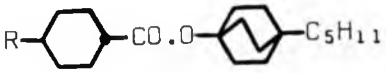
Within this series, the propyl and pentyl homologues were the first to be synthesised. It was hoped that by reducing the length of the alkyl chain, the smectic properties of the system could be sufficiently reduced to allow the formation of a nematic phase. However, even with R = $-CH_3$, the material is still highly smectogenic, illustrating the relatively strong intermolecular lateral cohesive forces that must be present in this type of aliphatic ester.

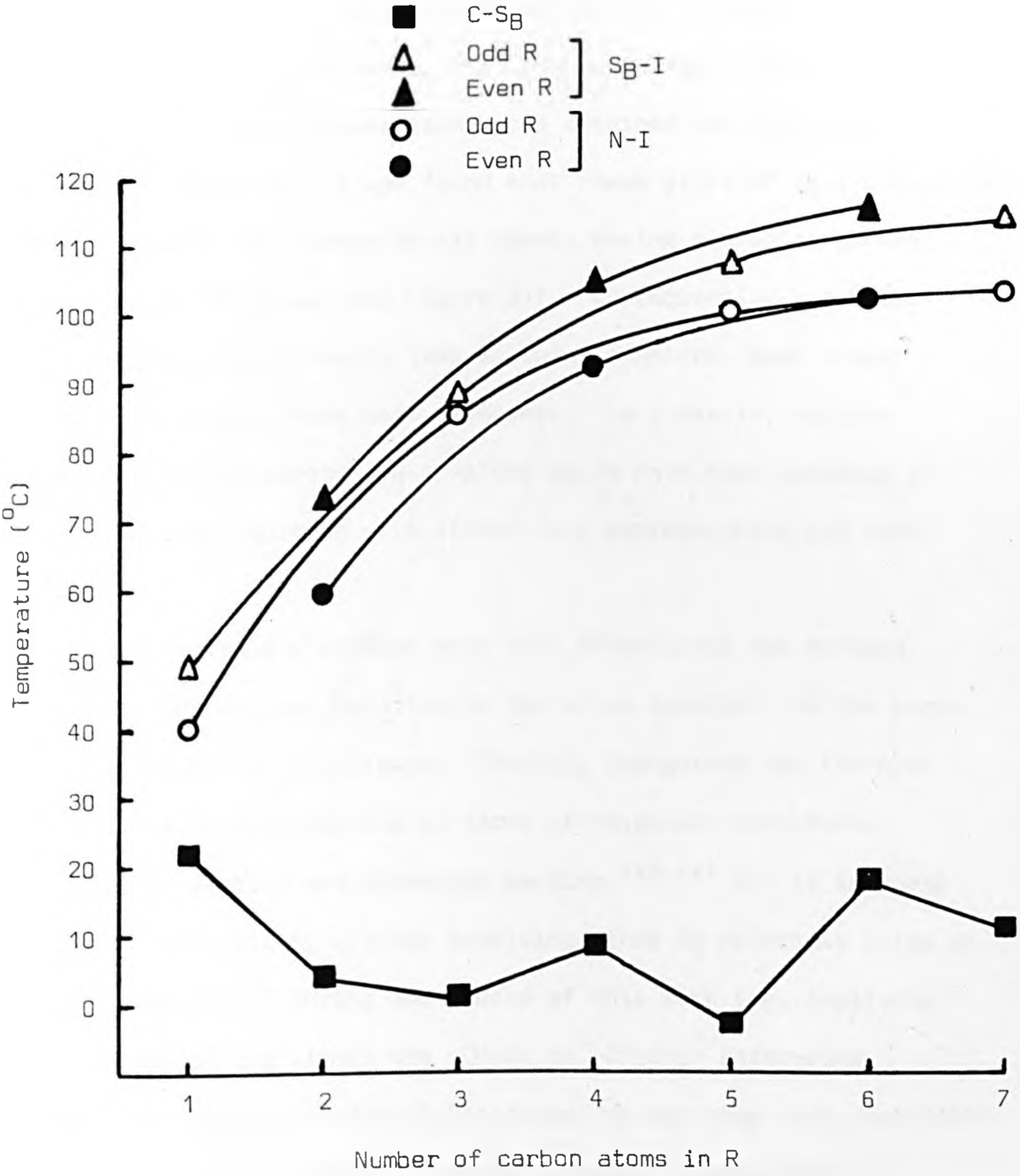
Generally, the melting points for these homologues are similar, but the T_{S_B-I} values increase sharply with chain length. To get some idea of the T_{N-I} values for these compounds, miscibility studies were carried out using the nematic eutectic mixture E7. Several interesting points emerged from these studies. The virtual T_{N-I} values obtained in this way are also plotted in Figure 30, and it can be seen that the shapes of the two curves (odd and even) are very similar to those of the two T_{S_B-I} curves. Throughout, the T_{N-I} virtual values are very close to the T_{S_B-I} values, less than 15^o separating the two values for all homologues investigated.

Attention is again drawn to the opposite sense of the odd-even alternation of the T_{S_B-I} and T_{N-I} virtual values, a situation which has been observed experimentally[82] for other systems for which the transitions are enantiotropic.

FIGURE 30

Graph of transition temperatures against number of carbon atoms in R for the series



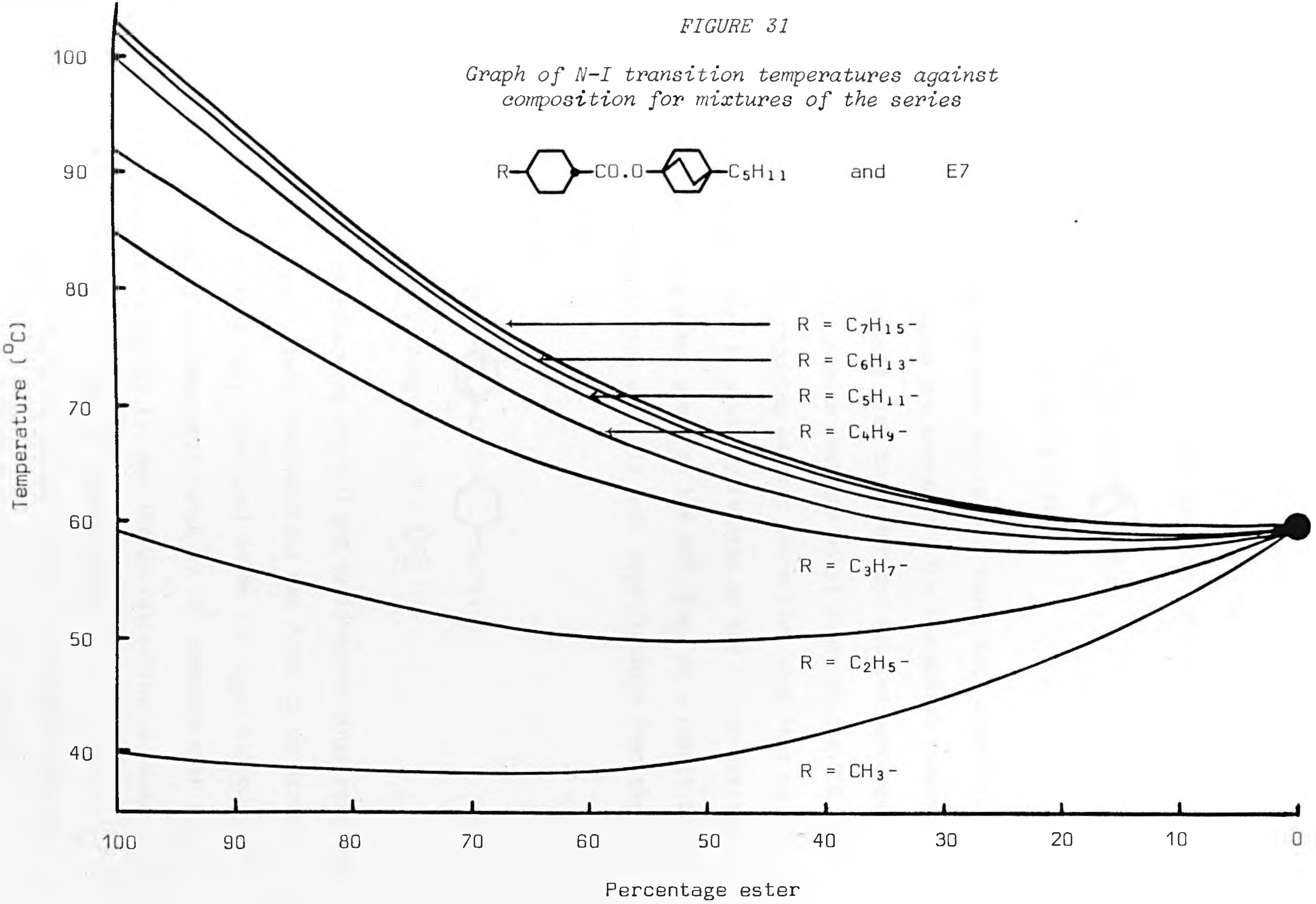


These aliphatic esters were found to be extremely soluble in host nematics, and very high concentrations of the ester (up to 90 wt %) could be used in the miscibility experiments. This reduced the length of the extrapolation of the curves, and consequently ensured a high degree of accuracy of the virtual values. This outcome was apparently somewhat fortuitous, because unlike the linear T_{N-I} v mixture composition plots obtained for many non-mesomorphic compounds, it was found that these plots of T_{N-I} v mixture composition were non-linear in all cases, having a similar general form for each homologue (see Figure 31). Consequently, had these materials been significantly less soluble in nature, much longer extrapolations would have been necessary. As a result, vastly different (and inaccurate) T_{N-I} values would have been obtained if the conventional approach of a linear T_{N-I} extrapolation had been adopted.

These miscibility studies show that effectively the mixture T_{N-I} values are reduced relative to the value expected on the basis of simple additivity principles. Possibly the esters and the host (E7) could be more compatible in terms of molecular structure, dielectric properties and molecular packing,[108,109] but it is worth noting that miscibility studies involving other S_B materials (also of low $\Delta\varepsilon$) investigated during the course of this work (eg, involving compounds containing either the $-CH_2O-$ or $-CH_2CH_2-$ inter-ring linkages, and phenylbicyclo(2.2.2)octanes) do not show such deviations from linearity. The structure of the S_B phase - correlated or uncorrelated (hexatic) - may well influence the properties of the mixture so that further miscibility and X-ray studies would seem to

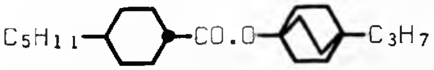
FIGURE 31

Graph of N-I transition temperatures against composition for mixtures of the series



be necessary in order to establish the exact nature of this behaviour.

The accuracy of the virtual T_{N-I} values for these esters was more or less confirmed by preparing compound (35) for which the alkyl

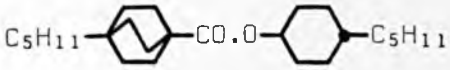


(35)

C 18 S_B 79 N 92 I

chain on the BCO ring has been shortened. Here, both enantiotropic smectic and nematic phases are produced. The transition temperatures for these phases agree well with those for the related homologues of structure (34), and illustrate that the alkyl chain on the BCO ring is more important for inducing smectic properties than that on the cyclohexane ring. This is possibly related to the higher positional order imposed on the alkyl group on the BCO ring, as a result of its attachment to the BCO ring which is much less flexible than the cyclohexane ring.

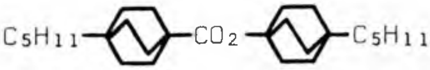
The compound



C 17 S_B 96 I, N-I [92]

shows the effect of reversing the BCO and cyclohexane rings relative to the ester linkage. Again, the material was found to be strongly smectic, with a virtual T_{N-I} value just below the T_{S_B-I} value. The reversal has lowered the mesogenic range by 31° compared with the parent compound (C -3 S_B 107 I), and the corresponding decreases in ΔT_{S_B-I} and ΔT_{N-I} are -11° and -8° respectively.

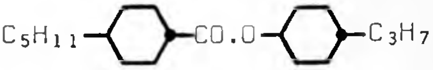
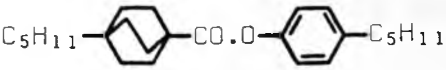
Also included in Table 18 are the transition temperatures for the bicyclo(2.2.2)octyl bicyclo(2.2.2)octanoate of structure



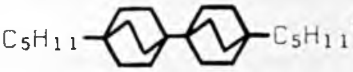
Along with comparative thermal data for other ester derivatives (see Table 19), the BCO ring is again seen to be superior to the *trans*-cyclohexane and benzene rings for promoting the T_{N-I} value of a system.

TABLE 19

Comparative thermal data for some related ester systems

Structure	C-S/N/I (°C)	S-N (°C)	N-I (°C)
	36	-	(26)
	37	-	48
	25	37	52
	68	-	(59)
	30	-	61.5

The effect of the ester linkage in this system may be judged by a comparison with the bicyclo(2.2.2)octylbicyclo(2.2.2)octane derivative



[60]

C 46 S 247 I

(S phase unclassified)

The effect of inserting the -CO.O- inter-ring linkage is therefore to significantly depress the liquid crystal properties, ie, the melting point is almost unchanged, but the T_{S-I} value is lowered by over 50^{o}, thereby markedly reducing the range of the smectic phase.

The transition temperatures for all of the compounds listed in Table 18 were obtained by a combination of optical microscopy and DSC. The DSC results were also used to establish that no other smectic polymorphic forms were present for any of these compounds. An example of a thermograph for compound (35) is given in Figure 32. The smectic phases were characterised by microscopy and miscibility studies with other smectic materials of known polymorphic form.

Due to the high solubility of these materials in nematic solutions, it was possible to assess some of their electro-optic properties when they were incorporated into nematic mixtures. Table 20 contains data from assessment work carried out at RSRE, Malvern, and Table 21 shows similar data from work carried out at E Merck, Darmstadt, West Germany. Also included in these data are comparative results for dialkyl and alkyl-alkoxy phenyl cyclohexanoates, which are commercially used ester additives.

Overall, the aliphatic esters appear to compare reasonably well with the commercial esters. The effects on T_{N-I} and viscosity values are moderate, whilst the birefringence values are lowered considerably, as would be expected from the aliphatic nature of these materials; the birefringence of compound (35) itself is 0.036 at $0.98 \times T_{N-I}$. However, the main effect of these aliphatic esters is to lower, quite markedly, the temperature dependence of the threshold voltage of the mixture. The commercial esters also reduce the $\frac{-1}{V}\left(\frac{dV}{dT}\right)$ values, but here the behaviour does not appear

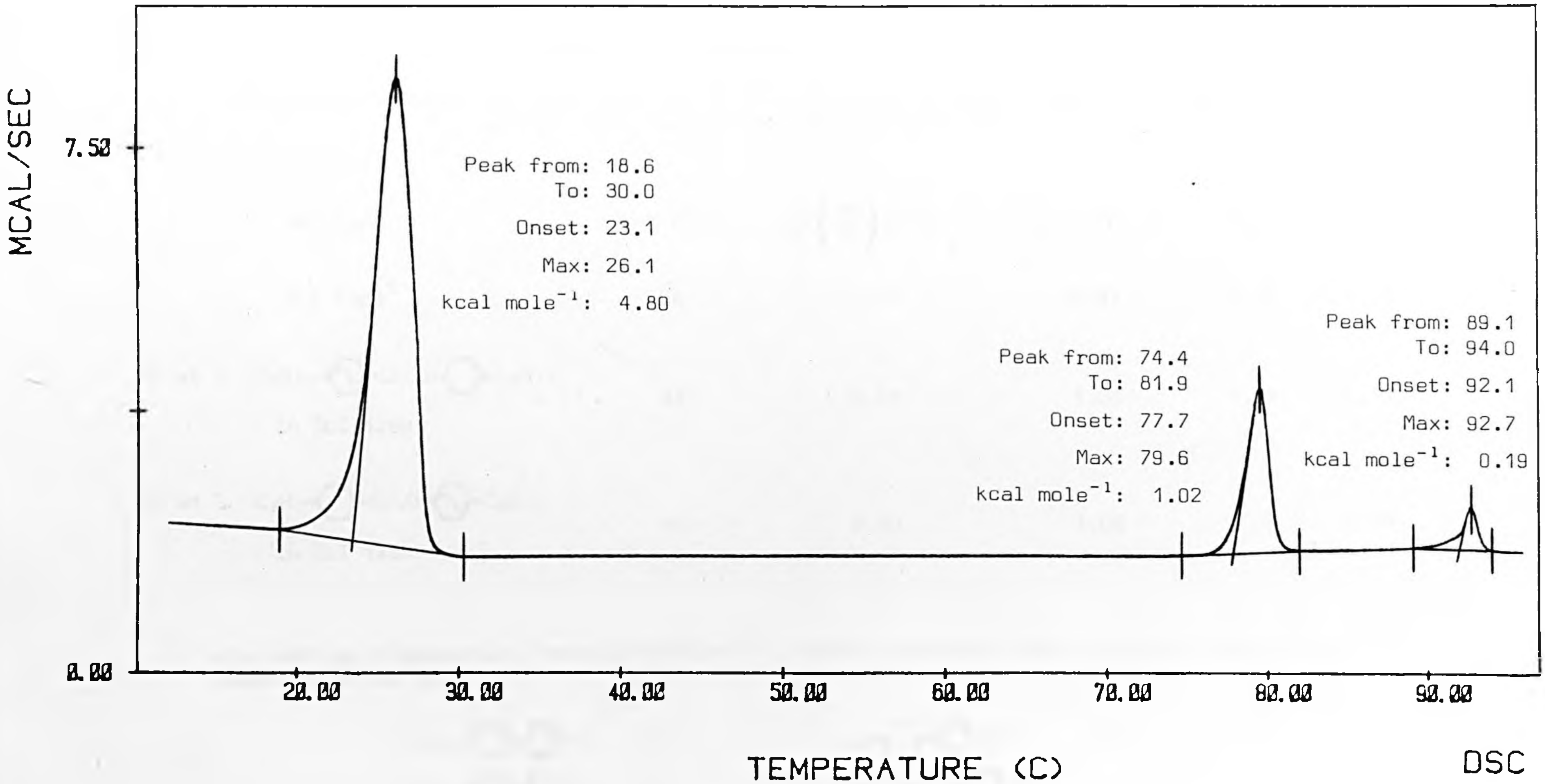


FIGURE 32

DSC thermograph for the ester of structure

TABLE 20

Electro-optic data for some mixtures of bicyclo(2.2.2)octanoate and cyclohexanoate esters when incorporated into nematic hosts

Mixture	N-I (°C)	$\frac{-1}{V}\left(\frac{dV}{dT}\right)$ % °C^{-1}	V_{90} (45°) V	M_{20}	M'_{20}
ZLI 1289†	64	0.47	0.91	1.87	1.33
30 wt %  in ZLI 1289	64	0.40	1.05	1.77	1.33
30 wt %  in ZLI 1289	59	0.40	1.05	1.77	1.34

† ZLI 1289 is a commercial nematic mixture of E Merck, Darmstadt, West Germany, having the composition (wt %):

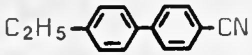
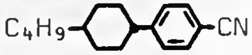
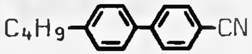
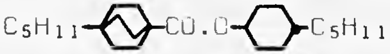
	14		22
	18		9
	21		16

TABLE 20 (continued)

Mixture	N-I (^{o}C)	$\frac{-1}{V}\left(\frac{dV}{dT}\right)$ % $^{o}C^{-1}$	V_{90} (45^{o}) V	M_{20}	M'_{20}
15 wt %  + 15 wt %  in ZLI 1289	60	0.40	1.01	1.79	1.36
40 wt %  in host X††	79	0.37	1.22	1.75	1.33

†† X has the composition (wt %):

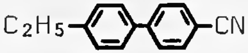
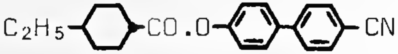
	25		15
	40		20

TABLE 21

Physical and electro-optic data for some mixtures of bicyclo(2.2.2)octanoate and cyclohexanoate esters when incorporated into nematic hosts

Mixture	N-I (^{o}C)	$\frac{-1}{V}\left(\frac{dV}{dT}\right)$ % $^{o}C^{-1}$	$\eta_{20^{o}C}$ (cP)	Δn (20^{o}C)
E7	57.3	0.75	37.8	0.232
20 wt %  in E7	57.2	0.65	37.6	0.192
20 wt %  in E7	58.6	0.72	33.2	0.203
20 wt %  in E7	55.5	0.76	38.6	0.203
ZLI 1132	71.5	0.55	28.1	0.145
20 wt %  in ZLI 1132	70.2	0.44	28.2	0.123
20 wt %  in ZLI 1132	68.9	0.52	24.2	0.129
20 wt %  in ZLI 1132	64.3	0.53	22.3	0.127

to be as general in nature, and often the extent of the lowering of the temperature dependency is not as great. The relatively large reduction of the $\frac{-1}{V}\left(\frac{dV}{dT}\right)$ values for the aliphatic ester mixtures may be attributed to the BCO ring, as similar properties have been observed for other related and unrelated BCO materials (eg, phenylbicyclo(2.2.2)octanoates and phenylbicyclo(2.2.2)octanes). These results therefore demonstrate that it is possible to produce superior multiplexible mixtures using these esters as low $\Delta\varepsilon$ additives.

In summary, these aliphatic esters generally appear to be better suited for use in multiplexible nematic mixtures than the ethers (Section 4.2) and phenylbicyclo(2.2.2)octanes (Section 4.3) previously discussed. Compared with such systems, the esters have higher T_{N-I} values (although mainly virtual), lower melting points, good solubility characteristics and particularly favourable low variations of the threshold voltage with temperature for nematic mixtures incorporating them. The viscosity and voltage figures of merit for such mixtures are reasonable, the main disadvantages of these compounds being their possible chemical instability over long periods of time and their strong smectic characteristics, which could particularly be a problem at low temperatures.

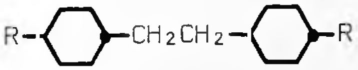
4.5 *COMPOUNDS INCORPORATING THE $-CH_2CH_2-$ INTER-RING LINKAGE*

One of the major reasons for the commercial success of materials such as the CB's and PCH's is the fact that they contain no reactive or partially labile centres within the molecules. Consequently, they are extremely stable materials. Therefore, as might be expected, hydrocarbon-based liquid crystal compounds should provide the most stable and long lasting materials for use in electro-optic displays.

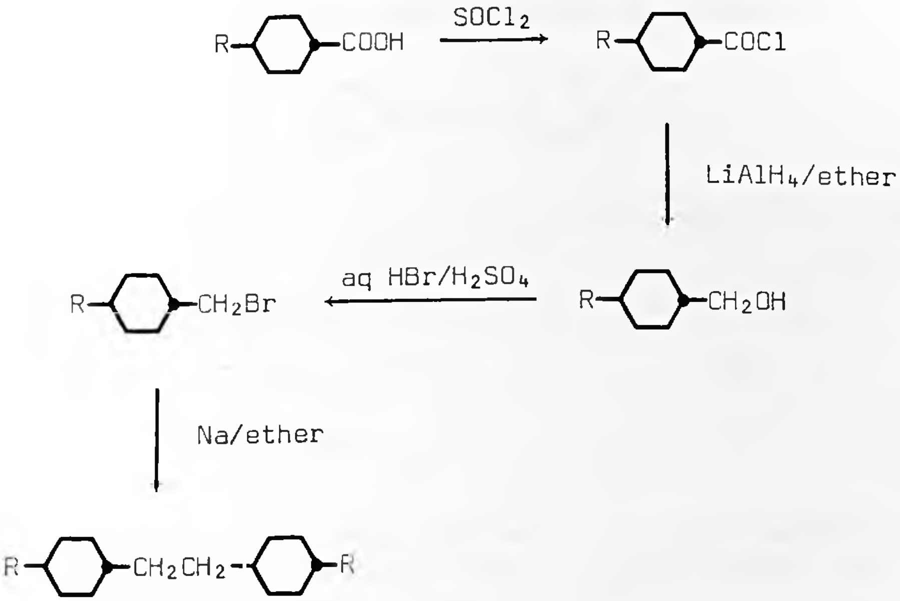
By incorporating the $-CH_2CH_2-$ unit into a molecule as an inter-ring linkage, the stability requirement is satisfied, and such systems would be expected to offer increased lifetimes relative to similar materials incorporating other inter-ring linking units, eg, $-CO.O-$, $-CH_2O-$, $-CH=N-$, $-N\underset{\substack{\downarrow\\ O}}{=}N-$, etc. Also, although it is now generally recognised that a central linking unit is not necessarily required for the formation of a mesophase, by using the $-CH_2CH_2-$ unit in such a position within the molecule (rather than as a means of increasing a terminal alkyl chain), a new family of liquid crystal materials, possibly with advantageous physical properties, becomes accessible. By varying the ring system involved (benzene, cyclohexane, bicyclo(2.2.2)octane, etc) and the terminal substituents ($-H$, $-R$, $-OR$, $-CN$, etc), many structural permutations are possible, each system having the probable advantage of good stability characteristics. Coupled with the semi-predictable structural effects on certain physical parameters (T_{N-I}, viscosity, dielectric and optical anisotropies, etc) and the less predictable effects on other properties (melting point, electro-optic performance, order parameter, solubility, elastic constants, etc), the preparation and investigation of such materials seemed to offer an attractive, interesting and wide-ranging study.

4.5.1 *Cyclohexylethyl Derivatives of Low Dielectric Anisotropy*

To get some idea of how this linking unit would influence transition temperatures and other simple properties, a system was chosen that would be fairly quickly accessible in terms of synthetic time and effort. Consequently, three compounds of general structure (6) were prepared as outlined in Scheme 7.



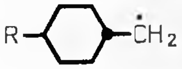
(6)



SCHEME 7

*Synthetic route for 1-(*trans*-4'-n-alkylcyclohexyl)-2-(*trans*-4"-n-alkylcyclohexyl)ethanes*

The final step in the preparation of these materials involves the production of the transient species

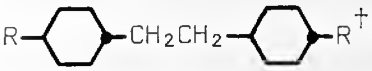


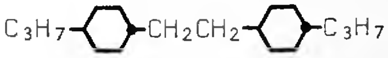
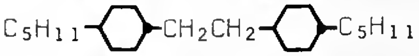
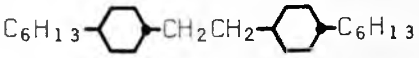
This is brought about by the sodium metal abstracting a halogen atom from the substituted methyl bromide. The radicals produced then undergo dimerisation to yield the symmetrical product.

These materials are aliphatic hydrocarbons, with no reactive centres within the molecule, and, as already said, may be regarded as the ultimate in stability for liquid crystal materials. The transition temperatures for these compounds are given in Table 22.

TABLE 22

Thermal data for some compounds of structure


[†]

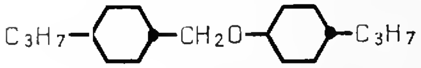
Structure	C-S_B (^oC)	S_B-I (^oC)	N-I (^oC)[††]
	36	71.5	[60]
 [110]	46	108	[74]
	46	113	[70]

[†] Since these materials were made, results on some of these compounds have been published by other workers (ie, R = C_3H_7-[111] and R = C_5H_{11}-[111,112])

[††] These T_{N-I} values were obtained from the data for mixtures of these compounds with the nematic eutectic E7, as discussed earlier (see page 133)

These derivatives illustrate that good mesophase thermal stabilities can be obtained for -CH_2CH_2- linked systems. In fact the 5.5 homologue has a similar T_{S_B-I} value to those of the corresponding bicyclo(2.2.2)octyl cyclohexanoate and cyclohexyl bicyclo(2.2.2)octanoate esters (see Table 18). Therefore, on this basis, the -CH_2CH_2- unit promotes mesophase (smectic) thermal stability, compared with the -CO.O- function, to roughly the same extent that the *trans*-cyclohexane ring lowers mesophase stability relative to the bicyclo(2.2.2)octane ring. Further evidence for the influence of the $-CH_2CH_2-$ unit can be obtained by comparing the 3.3 homologue with the following ester and ether derivatives:

C 22.8 N 36.6 I[103]



C 6.9 S 8.0 N 17.5 I[113]
(S phase unclassified)

In this context, the $-CH_2CH_2-$ inter-ring linkage compares favourably in that wide ranging mesophases (although smectic in nature) of high thermal stability are produced.

For all three cyclohexylethyl derivatives, no evidence for any smectic polymorphic forms other than S_B has been obtained, and for reference, Figure 33 gives a DSC thermograph for the 6.6 homologue.

Dielectric permittivity measurements have been carried out at RSRE, Malvern on mixtures incorporating these cyclohexylethyl derivatives into CB hosts. With regard to breaking up the anti-parallel correlation of the host, the effects ere similar to those observed when using either disubstituted phenyl benzoates or disubstituted phenyl cyclohexanoates as the low $\Delta\varepsilon$ additive. These results show that neither the ester function nor the aromatic ring system play any major role in this capacity, and that the observations can be explained satisfactorily in terms of the interpenetration of the paired molecules by any elongated molecule of low $\Delta\varepsilon$.

Compound (36), a fully aromatic analogue of the cyclohexane

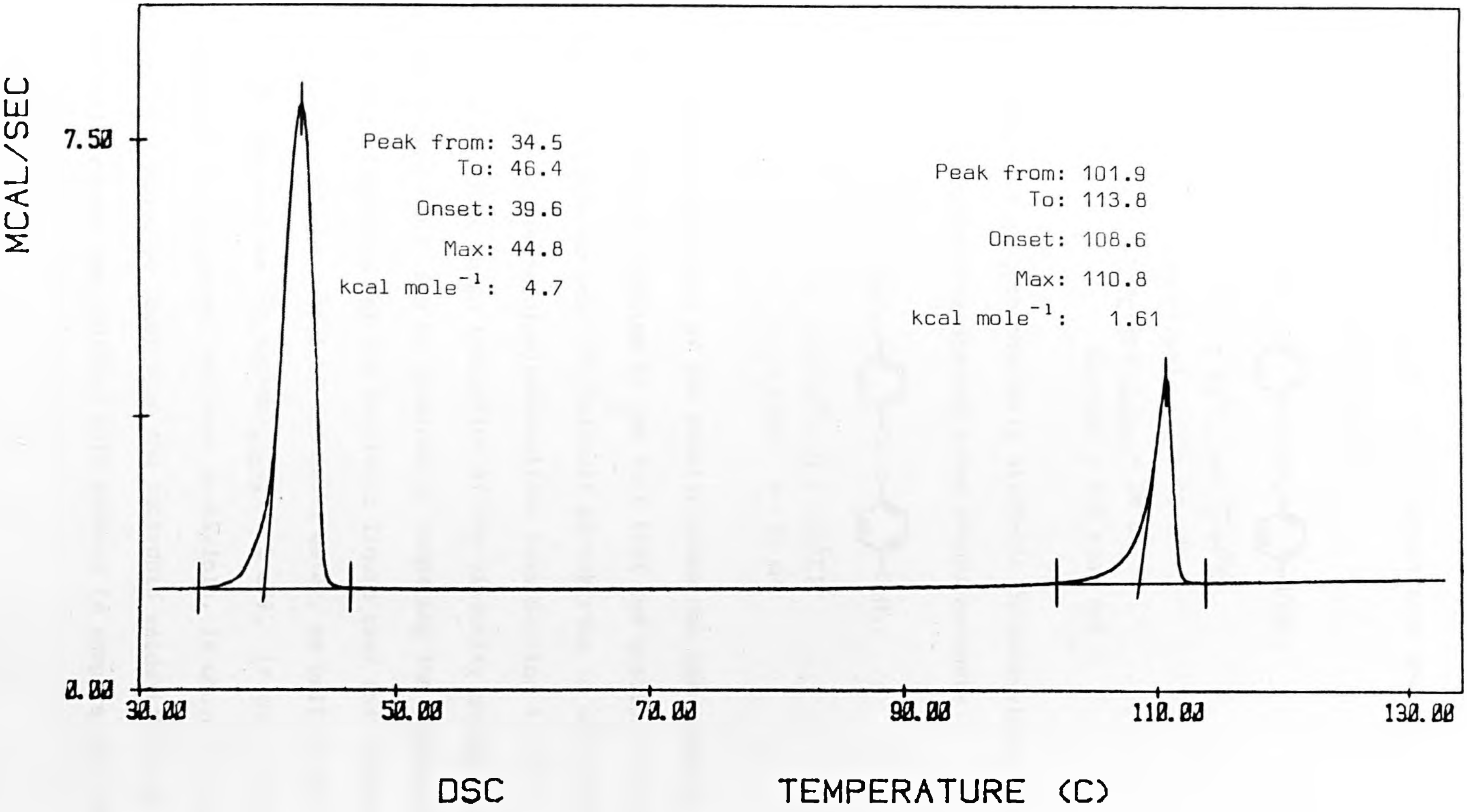
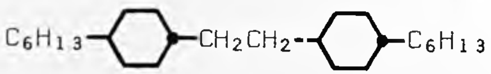
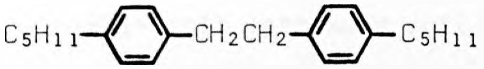


FIGURE 33

DSC thermograph for the hydrocarbon of structure



materials, was prepared by the route outlined in Scheme 7, except that 4-pentylbenzyl alcohol was converted into the chloride (by $SOCl_2$ in $CHCl_3$) rather than the bromide.



(36)

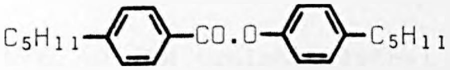
C-I 42°C, N-I [-44°C]

$\eta_{20^{\circ}C}(iso)_{extra} = 16$ cP

$\eta_{0^{\circ}C}(iso)_{extra} = 28$ cP

$E_a(iso) = 4.5$ kcal mol^{-1}

Relative to both the fully aliphatic cyclohexylethyl derivative and the corresponding disubstituted phenyl benzoate



C-I 36°C, N-I (26°C)

$\eta_{20^{\circ}C}(nem) \approx 29$ cP

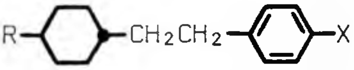
the thermal stability of the nematic phase has been greatly reduced. This is probably related to the fact that two distinct π-systems have been incorporated into the molecule giving rise to significant repulsive intermolecular interactions (see Section 4.2.3).

However, a rough indication of the viscosity characteristics for the $-CH_2CH_2-$ unit can be obtained by comparing the viscosity for this material (measured for the isotropic liquid over the temperature range 50-80°C) with that of the above ester, as well as with related $-CH_2O-$ derivatives ($\eta_{20^{\circ}C}(nem)_{extra} \simeq 25$ cP). If the nematic viscosity for compound (36) were accessible, it would be expected that this would be lower than the isotropic value (16 cP at 20°C), so that overall the $-CH_2CH_2-$ unit appears to compare very well.

The results on these four -CH_2CH_2- linked compounds suggest that it may be possible to obtain high mesophase (nematic) thermal stabilities together with reasonably low viscosity values by incorporating the -CH_2CH_2- unit into some suitable molecules. As might be expected, none of these compounds represent the optimum in terms of simple physical properties, and the next stage in developing related materials centred around effectively combining the known useful properties of the cyclohexylethyl compounds[†](high mesophase thermal stability), with those of the aromatic analogue (low viscosity), and hopefully also, suppressing the smectic tendencies of the system.

The high symmetry of the cyclohexylethyl derivatives may be partially responsible for the high smectic thermal stability, but it has been shown by other workers[111] that even the use of non-equivalent terminal alkyl chains is not sufficient to depress significantly the smectic properties and produce a nematic phase. However, there are several other approaches to reducing this high molecular symmetry. For example, one might use structurally different terminal groups or introduce lateral substituents into the molecule. Another simple approach is to combine in the same molecule some of the structural features of the above fully aromatic and fully alicyclic systems. This was adopted and gave the compounds of general type (37).

[†] The viscosity characteristics of these materials could not be easily assessed due to either solubility problems in suitable hosts or the high smectic tendencies of the solutions.

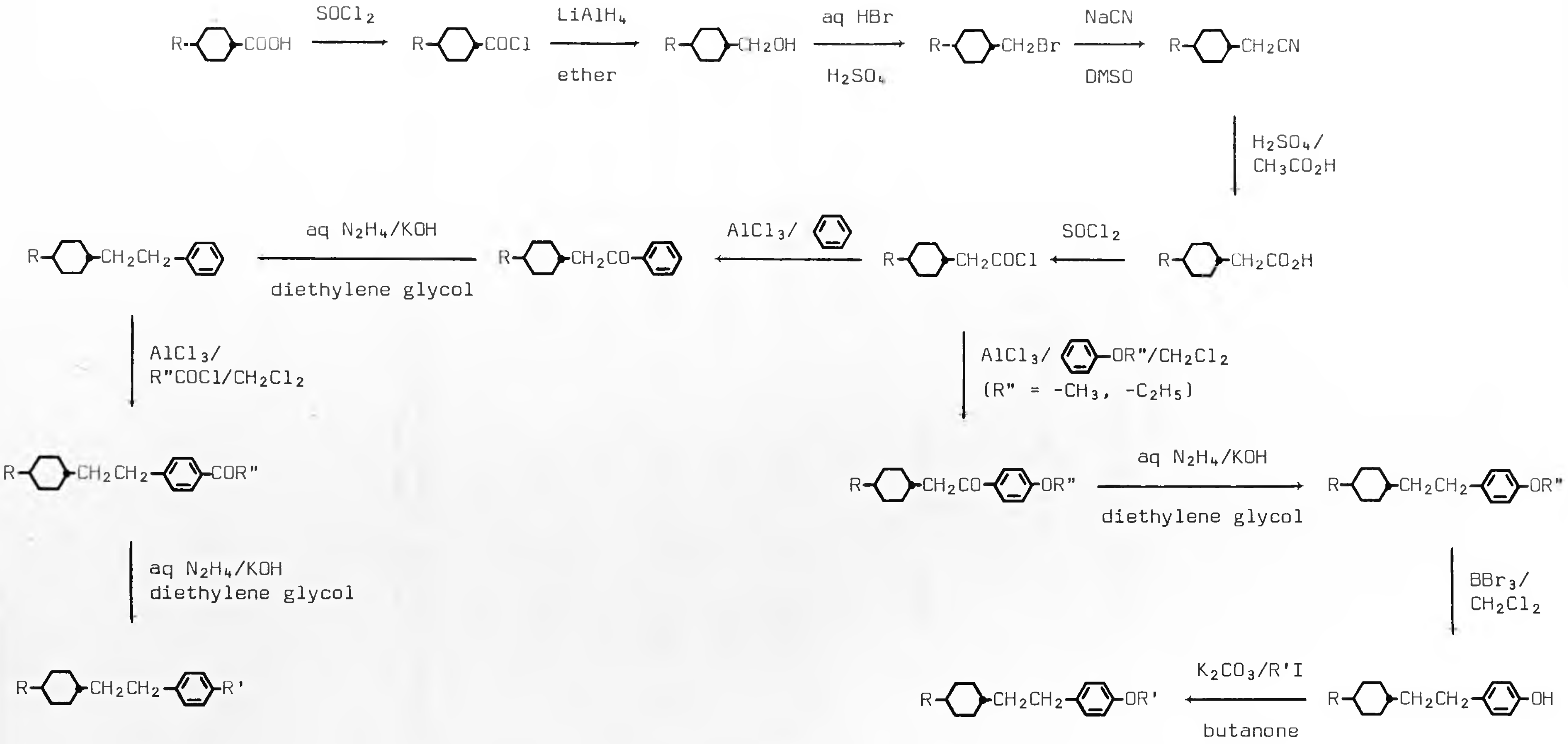

(37)

X = n-alkyl, n-alkoxy

The reduced symmetry of these cyclohexylethylphenyl or, alternatively, phenethylcyclohexyl (PECH) derivatives increases the length of their synthesis (relative to that for the fully saturated materials), but as most of the steps (see Scheme 8) were relatively straightforward (as required for any large scale production), this was not considered a major problem.

The first compounds prepared of this type were the PECH 5.0R derivatives. The synthesis of the higher derivatives was more involved than that for the lower homologues, due to the necessity for demethylation and subsequent re-alkylation in order to avoid chain cleavage at the ether function under Friedel-Crafts conditions. This reflects a similar situation to that described for the 1-(4'-n-alkoxyphenyl)-4-n-alkylbicyclo(2.2.2)octanes (see Section 4.3). The transition temperatures for these materials and a plot of these values against alkoxy chain length are given in Table 23 and Figure 34 respectively.

From these data, there are several points that should be mentioned. Compared with the fully saturated $-CH_2CH_2-$ linked compounds for which results were given in Table 22, the melting points and overall smectic thermal stability have been lowered, such that now several enantiotropic nematic phases are observed. The T_{N-I} values appear to remain fairly constant (within each odd or even chain length group), but this trend cannot be followed to any great extent due to the sharp rise in the smectic properties as the

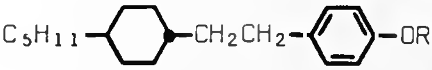


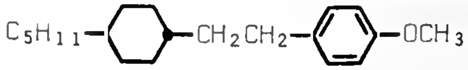
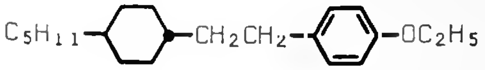
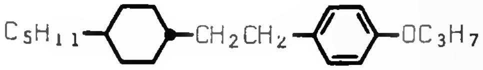
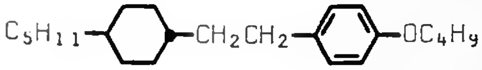
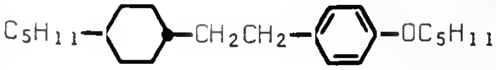
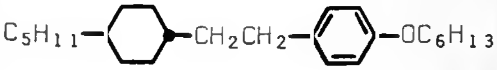
SCHEME 8

*Synthetic route for 1-(*trans*-4'-n-alkylcyclohexyl)-2-(4"-n-alkyl- or -alkoxy-phenyl)ethanes*

TABLE 23

Thermal data for some compounds of structure

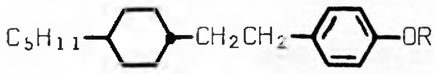


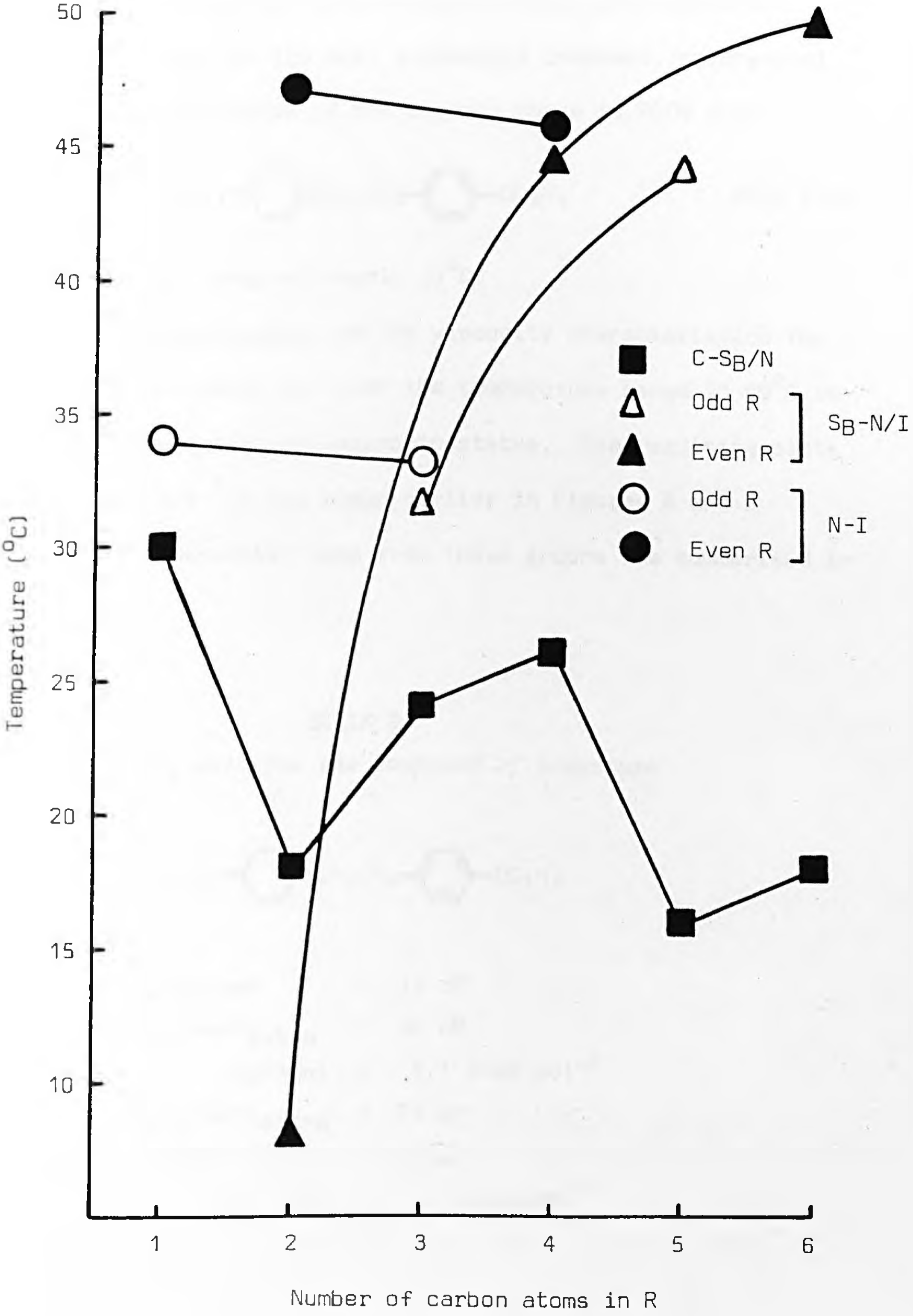
Structure	C-S_B/N (^oC)	S_B-N/I (^oC)	N-I (^oC)
	30	-	34
 [110]†	18	(8)	47
	24	31.5	33
	26	44.5	45.5
	16	44	-
	18	49.5	-

† This compound has been described recently by other workers[114] (C 18 N 46 I), but no smectic phase was reported

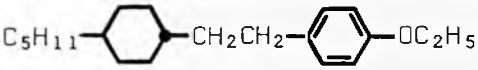
FIGURE 34

Graph of transition temperatures against number of carbon atoms in R for the series





homologous series is ascended. This increase in smectic tendencies has the effect of producing fully smectic compounds for the later members of the series; only the methyl homologue is purely nematic, and the ethyl to butyl ethers exhibit both types of mesophase. As a result, the most accessible compound for physical and electro-optical studies of the nematic phase is PECH 5.02



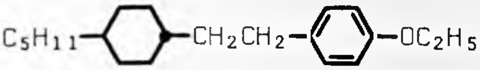
PECH 5.02

which has a nematic range of nearly 30°C.

A detailed investigation of the viscosity characteristics for this compound was carried out over the temperature range 10-80°C to include both the nematic and isotropic states. The resulting plots of η v T and log η v $^1/T$ are shown earlier in Figures 8 and 9 respectively; the essential data from these graphs are summarised in Table 24.

TABLE 24

Viscosity data for the compound of structure



η_{20^oC}(nem) = 13 cP

η_{0^oC}(nem)$_{extra}$ = 36 cP

E_a(nem) = 8.1 kcal mol^{-1}

η_{20^oC}(iso)$_{extra}$ = 24 cP

η_{0^oC}(iso)$_{extra}$ = 49 cP

E_a(iso) = 5.7 kcal mol^{-1}

The usual lowering of the viscosity for the nematic phase relative to that for the isotropic liquid is evident. Also, the measured nematic viscosity of 13 cP at 20°C is significantly lower than that for equivalent materials containing other inter-ring linkages (eg, esters, ethers, etc), and is only slightly greater than that observed if the $-CH_2CH_2-$ unit is not present - ie, for PCH 3.02 + PCH 3.04 (1:1), η_{20^oC}(nem) = 11.5 cP. These results demonstrate that, as was hoped, it is possible to produce materials containing the $-CH_2CH_2-$ inter-ring linkage that have a low viscosity and a relatively wide nematic range.

Tables 25 and 26 contain electro-optic data for mixtures incorporating PECH 5.02, as well as comparative data for related ester materials; the assessment work was carried out at RSRE, Malvern.

Taken as a whole, although the electro-optic properties vary slightly depending on the host, PECH 5.02 compares reasonably well with the various ester materials, and may therefore be considered to be quite a useful additive. Further work at RSRE, Malvern has indicated that the solubility characteristics of some high T_{N-I} additives in the pure material are relatively good. For example, the solubility of T15 is 1.5 wt % at -30°C, whereas with PCH R.OR' hosts, T15 is almost insoluble, and in PCH R.R' and dialkyl biphenyl compounds, the solubility is $\leqslant$1 wt % at -30°C. As might be expected from the relatively low viscosity of PECH 5.02, the response times of mixtures incorporating this material are fast, so that it would appear that the main advantages of the PECH R.OR' compounds lies not in their electro-optic properties, but in their viscosity and solubility characteristics.

TABLE 25

Electro-optic data for 30 wt % of component X when incorporated into ZLI 1289

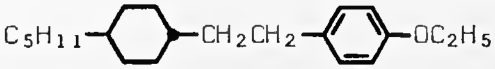
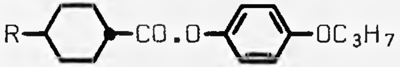
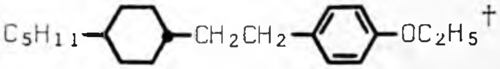
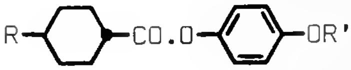
Component X	N-I (^{o}C)	V_{90} (45^{o}) V	$M_{20^{o}C}$	$M'_{20^{o}C}$	$\frac{-1}{V}\left(\frac{dV}{dT}\right)$ % $^{o}C^{-1}$	1:3 Margin (%)
ZLI 1289	64	0.91	1.87	1.41	0.47	-
	58	1.1	1.80	1.37	0.61	4.7
 (R = C_3H_7-:C_5H_{11}-, 1:1)	60	1.01	1.79	1.36	0.40	9.0

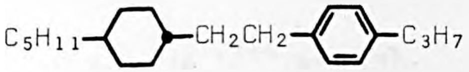
TABLE 26

Electro-optic data for mixtures incorporating component X, doped with CB 2 to have Δε = +2

Component X	$-\frac{1}{V}\left(\frac{dV}{dT}\right)$ % $^{\circ}C^{-1}$	$M'_{20^{\circ}C}$
	0.42	1.34
	0.6	1.28
	0.5	1.30
	0.5	1.23
	0.4	1.24

† Δn (20°C) = 0.07
Δε (20°C) = -0.3

For most families of materials, it is usually found that the viscosity of a dialkyl derivative is lower than that of the alkyl-alkoxy analogue. In the case of the PCH materials, the difference is quite marked, with the dialkyl compounds having η_{20^oC}(iso) = 7-10 cP and the alkyl-alkoxy compounds having η_{20^oC}(iso) = 17-20 cP, depending on the chain lengths involved. As the $-CH_2CH_2-$ compounds are so similar structurally to the PCH materials, it was clear that the dialkyl analogues, PECH R.R', offered the possibility of lowering the viscosity of the system even further. Therefore, if the T_{N-I} values of these compounds were not too adversely affected, such materials might prove to be extremely valuable.



PECH 5.3

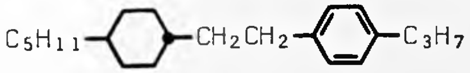
To give the best comparison with PECH 5.02, PECH 5.3 was prepared.

The initial synthesis of this compound proved to be somewhat troublesome, as a small amount of impurity (~2%) was found to be present in the sample, and this could not easily be removed by standard purification techniques. The synthetic route used in this case involved the Friedel-Crafts acylation of propylbenzene with *trans*-4-pentylcyclohexylacetyl chloride in dichloromethane, and the impurity may have been a small, but significant amount of *ortho*-isomer. The pure material was obtained only after extensive purification techniques had been employed, and as this significantly reduced the yield, it appeared to be more efficient to prepare such dialkyl materials by the route outlined in Scheme 8, which avoids the possibility of isomeric contaminants.

The transition temperatures and viscosity coefficients for this compound are recorded in Table 27. Compared with PECH 5.02, the melting point has been reduced by 15°, but the smectic tendencies have *increased*, with the result that no nematic phase is observed. An estimate of [3°C] for the T_{N-I} values was obtained by miscibility experiments, so that a drop of 44° in T_{N-I} value has occurred relative to PECH 5.02.

TABLE 27

Physical data for the compound of structure



C 3 S_B 16 I,[114] N-I [3]

$\eta_{20^{\circ}C}(iso) = 22$ cP

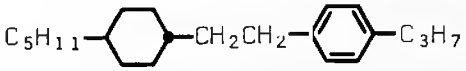
$\eta_{0^{\circ}C}(iso)_{extra} = 50$ cP

$E_a(iso) = 6.5$ kcal mol^{-1}

As PECH 5.3 has no nematic phase, only isotropic viscosity measurements were possible. These were carried out over the temperature range 17-80°C (see Figure 35 for a plot of log η *v* $^{1}/T$); the value obtained of 22 cP is only slightly lower than the isotropic viscosity value for PECH 5.02 (24 cP) at 20°C. The large anticipated drop in viscosity for the dialkyl compound has therefore not been realised. This fact, coupled with the increased smectic tendencies and much lower T_{N-I} value relative to PECH 5.02, shows that the general physical properties of PECH 5.3 are unexceptional.

FIGURE 35

Graph of log viscosity against inverse temperature for the compound



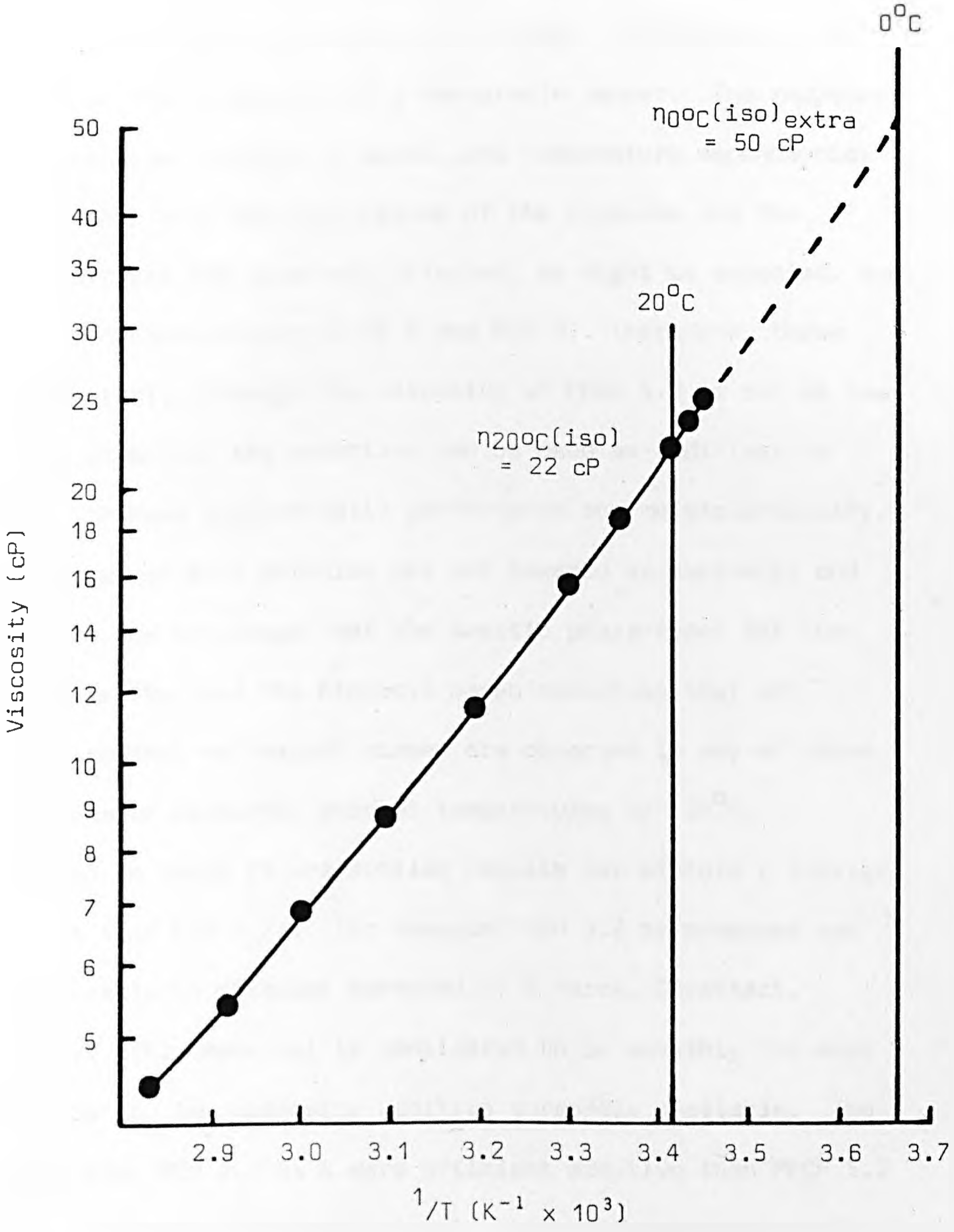
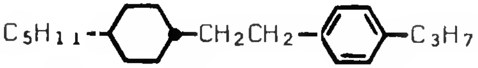


Table 28 contains electro-optic and viscosity data for mixtures incorporating PECH 5.3; the assessment work was carried out at RSRE, Malvern. In the case of mixtures X and Y, some of the highly positive $\Delta\varepsilon$, two ring components (CB 5 and PCH 5) have been removed from mixture A and replaced with PECH 5.3, whilst keeping the concentrations of high T_{N-I} additives the same. The effect is to change most of the parameters in a favourable manner. The response times, viscosities, figures of merit, and temperature dependencies are all lowered; only the T_{N-I} values of the mixtures and the threshold voltages are adversely affected, as might be expected, due to the lower concentrations of CB 5 and PCH 5. Therefore, these results show that, although the viscosity of PECH 5.3 is not as low as had been expected, the materials can be used as additives to mixtures to improve electro-optic performance and multiplexibility. The T_{N-I} values of such mixtures are not lowered excessively, and there is also the advantage that the smectic phase-types for the PECH materials (S_B) and the biphenyl-based materials (S_A) are immiscible, so that no smectic phases are observed in any of these and their related mixtures, even at temperatures of -20°C.

Included in Table 28 are similar results for mixture Z (mixture B plus 15 wt % of PCH 3.2). The compound PCH 3.2 is prepared and used commercially in mixtures marketed by E Merck, Darmstadt, West Germany. This material is considered to be possibly the most effective low $\Delta\varepsilon$, low viscosity additive currently available. The data reveal that PCH 3.2 is a more efficient additive than PECH 5.3 in terms of viscosity (response times), threshold sharpness, and figures of merit, but less efficient with respect to threshold temperature stability and T_{N-I} value.

TABLE 28

Physical and electro-optic data for the compounds of structure



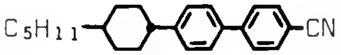
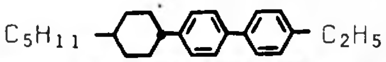
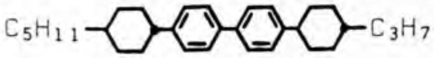
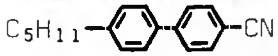
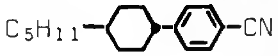
and

when incorporated into a nematic host

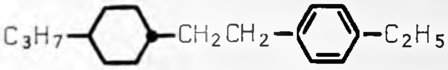
	Mixture	$A^{\dagger}$	X = $B^{\dagger}$ + 15 wt % PECH 5.3	Y = $C^{\dagger}$ + 30 wt % PECH 5.3	Z = $B^{\dagger}$ + 15 wt % PCH 3.2
	N-I (°C)	89	83	75	78
cP	$\eta_{20^{o}C}$(nem)	33	26	-	24
	$\eta_{0^{o}C}$(nem)	140	88	-	82
	$\eta_{-10^{o}C}$(nem)	330	230	-	175
	$\eta_{-30^{o}C}$(nem)$_{extra}$	3000	2000	-	1000
Extrapolated to -30°C,5 V drive (secs)	Rise Time	5.3	4.3	3.0	1.9
	Decay Time	4.0	3.0	2.7	1.2
	$V_{90}(45^{o})$ V	1.27	1.42	1.56	1.32
	$M_{20^{o}C}$	1.98	1.91	1.83	1.80
	$M'_{20^{o}C}$	1.45	1.42	1.37	1.38
	$\frac{-1}{V}\left(\frac{dV}{dT}\right)$ % $^{o}C^{-1}$	0.63	0.53	0.54	0.59

† Composition of mixtures A, B, and C are defined on page 213

TABLE 28 (continued)

Component	Code	Composition (wt %)		
		A	B	C
	BiCH 5	15	15	15
	BiCH 5.2	5	5	5
	CBC 5.3	8	8	8
	CB 5	36	28.5	21
	PCH 5	36	28.5	21

To obtain a better comparison with PCH 3.2, and to see if there was any great variation in viscosity with terminal alkyl chain length, the related material PECH 3.2



PECH 3.2

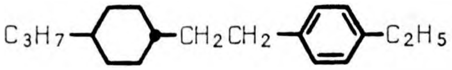
was prepared. The route used to prepare this compound is outlined in Scheme 8 (thereby avoiding the isomer problems experienced with PECH 5.3), and its physical properties are given in Table 29, alongwith those for PCH 3.2.

Both compounds are isotropic liquids of extremely low viscosity, but the PECH material apparently has a much higher virtual T_{N-I} value, perhaps because of its greater molecular length.

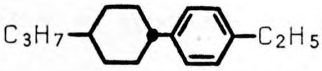
Under normal circumstances, a full investigation of the properties of this material and other homologues would have been carried out to substantiate the promise shown by these initial results. However, this programme was not undertaken due to a situation that arose concerning the patent rights for these

TABLE 29

Physical data for the compounds of structure



and



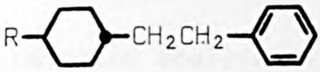
[115]

Compound	PECH 3.2	PCH 3.2
C-I (^{o}C)	-5	-1.5
N-I (^{o}C)	[-28]	[-75]
$\eta_{20^{o}C}$(nem)$_{extra}$ (cP)†	3	4

† by extrapolation from data for a 20 wt % solution in ZLI 1132

materials. It emerged that the Swiss company, F Hoffmann-La Roche, had also been working on these materials, and that their patent application[116] pre-dated our own UK Ministry of Defence application by just thirteen days. Consequently, the work on these PECH R.OR' and PECH R.R' materials was brought to an end at this point, with the general conclusion that the dialkyl compounds in particular were possibly as good, if indeed not better materials for use as low viscosity, low dielectric anisotropy additives as any others currently available.

It was soon discovered, however, that reasonably good properties could be obtained by using the compounds PECH R.H.



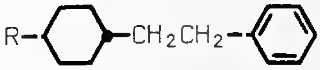
PECH R.H

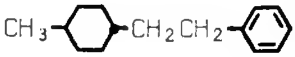
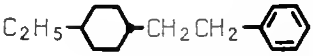
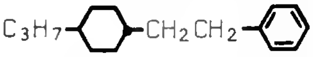
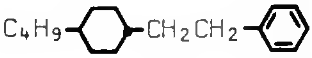
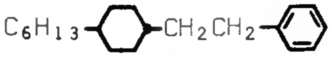
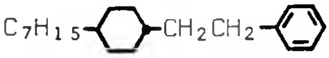
These materials had first arisen in this work as intermediates in the synthesis of the PECH R.R' derivatives (see Scheme 8), and differ from these compounds only in the fact that the aromatic ring is mono-substituted.

As mentioned in Section 2.1.2, almost any terminal substituent in a molecule raises the T_{N-I} value relative to that for the unsubstituted material. As the dialkyl derivatives had been found to have low liquid crystal thermal stabilities, it was not expected that any of the PECH R.H homologues would exhibit a mesophase. This was found to be the case, with none of the homologues up to heptyl exhibiting liquid crystal properties (see Table 30).

TABLE 30

Physical data for some compounds of structure

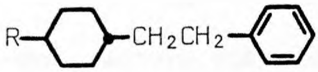


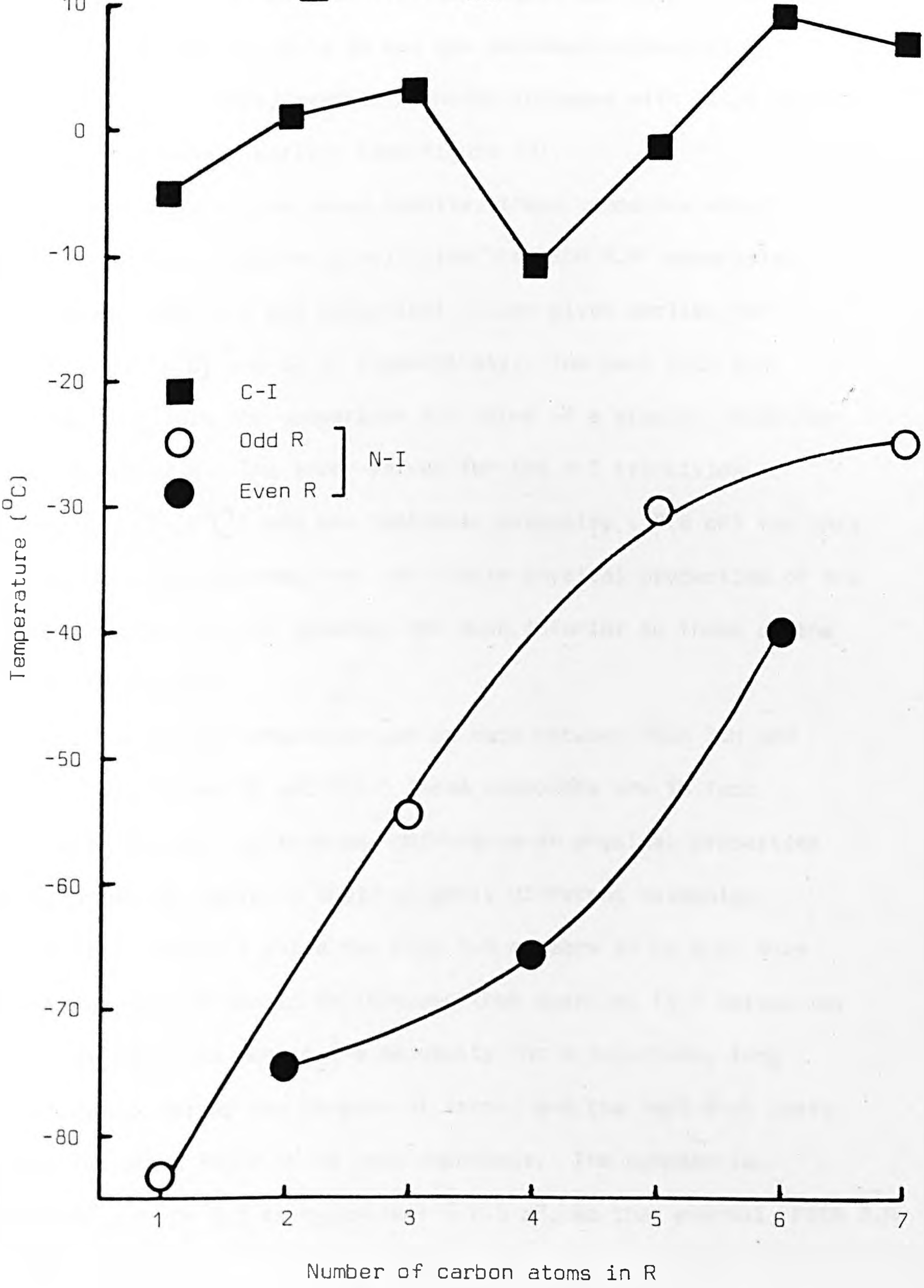
Structure	C-I (°C)	N-I (°C)	$\eta_{20^{\circ}C}$(iso) cP
	-5	[-83]	5.3
	1	[-75]	6.7
	3	[-55]	8.5
	-11	[-66]	10.8
	-1.5	[-30]	13.4
	9	[-40]	15.6
	7	[-25]	18.6

Consequently, no detailed analysis of the T_{N-I} values has been made, as they are all virtual values, but the plot of the transition temperatures against alkyl chain length (see Figure 36) does indicate that the T_{N-I} values are reasonably self-consistent, and that they increase as the series is ascended, for both the odd

FIGURE 36

Graph of transition temperatures against number of carbon atoms in R for the series





and even homologues. The melting points exhibit no particular trends within the series, although a minimum is observed for the butyl homologue, a common feature for several series of compounds.

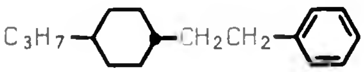
Also included in Table 30 are the isotropic viscosities measured at 20°C; these exhibit a smooth increase with alkyl chain length, as mentioned earlier (see Figure 10).

On the basis of the above results, these compounds would appear to compare reasonably well with the PECH R.R' materials. For example, the T_{N-I} and $\eta_{20^oC}(iso)$ values given earlier for PECH 5.3 are [3°C] and 22 cP respectively. The best PECH R.H material available for comparison (in terms of a similar molecular size) is PECH 7.H. The lower values for the N-I transition temperature ([-25°C]) and the isotropic viscosity (18.6 cP) for this 7.H compound demonstrates that the simple physical properties of the PECH R.H series are, in general, not much inferior to those of the PECH R.R' materials.

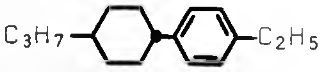
Another useful comparison can be made between PECH 3.H and PCH 3.2 (see Tables 29 and 30). These compounds are in fact structural isomers, so that any difference in physical properties should be attributable to their slightly different molecular structures. The T_{N-I} value for PECH 3.H appears to be much more favourable, but it should be stressed that such low T_{N-I} values may not be too accurate due to the necessity for a relatively long extrapolation across the diagram of state, and the fact that these values are often found to be host dependent. The comparable viscosity for PCH 3.2 is $\eta_{20^oC}(iso) = 7.5$ cP, so that overall, PECH 3.H compares well.

TABLE 31

Physical and electro-optic data for 27 wt % of the compounds of structure



and



when incorporated into a nematic host

	Mixture	Host† + 27 wt % of PECH 3.H	Host† + 27 wt % of PCH 3.2
	N-I (°C)	72	86.5
cP	$\eta_{20^\circ C}$(nem)	22	18.5
	$\eta_{10^\circ C}$(nem)	36	30
	$\eta_{0^\circ C}$(nem)	64	53
	$\eta_{-10^\circ C}$(nem)	135	103
$T = 0.8493 \times T_{N-I}$	$\varepsilon_\parallel$	7.66	7.36
	$\varepsilon_\perp$	3.45	3.35
	$\Delta\varepsilon$	4.21	4.01

† Host composition:

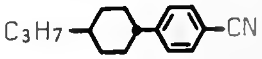
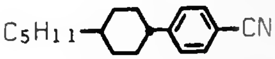
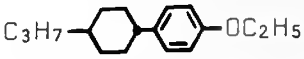
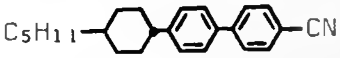
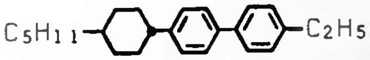
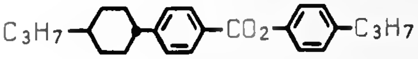
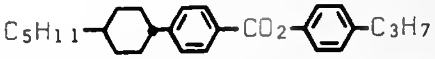
Compound	Code	wt %
	PCH 3	10
	PCH 5	5
	PCH 3.02	10
	BiCH 5	7
	BiCH 5.2	17
	CBC 5.3	10
	HP 3.3	8
	HP 5.3	6

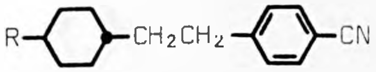
Table 31 contains further data for comparable mixtures incorporating either of these two materials; the assessment work was carried out at RSRE, Malvern. These results show that PECH 3.H is not in fact quite such a good mixture additive as PCH 3.2, as the viscosity coefficients are higher and the mixture T_{N-I} value is lower for the PECH compound, with perhaps only a small advantage being gained in terms of the dielectric anisotropy.

Measurements of the elastic constants of mixtures containing PECH 3.H were made at RSRE, Malvern as part of a broader programme of work, and valuable information concerning the relationship of elastic constants to molecular antiparallel correlations has emerged. A large decrease in k_{33}/k_{11} occurred when non-cyano (non-polar) materials, eg, PECH 3.H, dialkylphenyl benzoate esters, BiCH 5.2, etc, were used as additives to cyano-substituted hosts. This indicates that it is the dilution of the cyano host which plays the major part in reducing k_{33}/k_{11} for these mixtures. Also, $\frac{d\,(k_{33}/k_{11})}{dT}$ is much reduced, and these facts support the idea that it is a reduction in the local antiparallel ordering of the cyano host that is predominantly responsible for the effects, a conclusion verified by X-ray studies of the local ordering for such mixtures carried out at Exeter University.[117]

In summary, the PECH R.OR', R.R' and R.H compounds represent a very useful group of stable materials of low dielectric anisotropy that have reasonable nematic properties and low viscosities. Although the smectic tendencies for some of these materials are a little high, this has not presented any major problems when these materials are incorporated (up to 30 wt %) into nematic hosts.

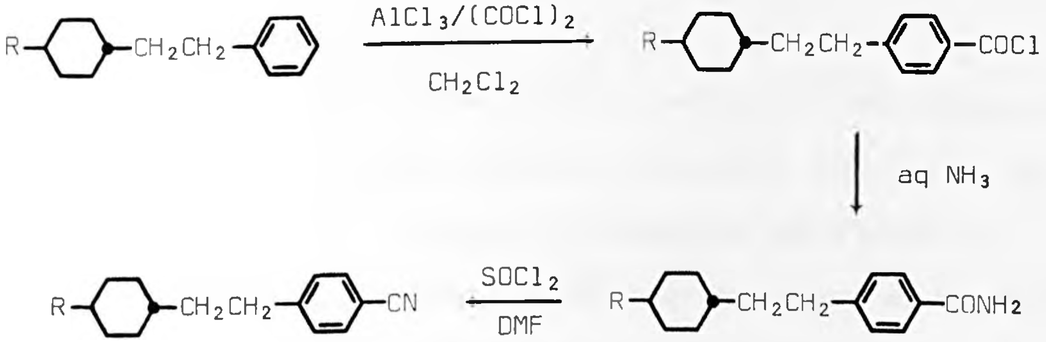
Furthermore, the electro-optic properties of such mixtures are reasonably good. A further advantage of these materials is that they appear to solubilise high T_{N-I} additives, making it possible to incorporate higher concentrations of such additives in mixtures.

4.5.2 *Cyclohexylethyl Derivatives of Highly Positive Dielectric Anisotropy*



PECH R[118,119]

Once the potential of the low dielectric anisotropy PECH compounds had been discovered (see previous section), it was an obvious step to prepare and investigate the related PECH R materials of highly positive dielectric anisotropy.



SCHEME 9

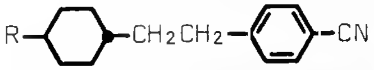
*Synthetic route for 1-(*trans*-4'-n-alkylcyclohexyl)-2-(4"-cyanophenyl)ethanes*

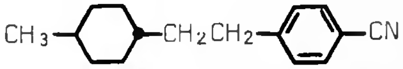
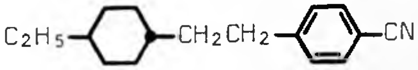
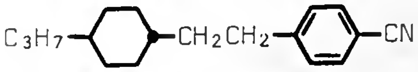
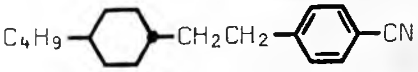
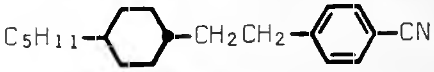
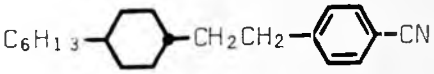
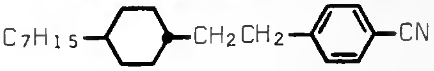
These cyano derivatives were prepared (see Scheme 9) from the PECH R.H materials (Scheme 8, page 203).

The transition temperatures for the series up to PECH 7 are given in Table 32, and a plot of these values against alkyl chain

TABLE 32

Thermal data for some compounds of structure



Structure	C-N/I (°C)	N-I (°C)
	51	(-10)
	43.5	(12)
	38	44.5
	27	38.5
	30	51
	35	47
	45	54.5

length is given in Figure 37.

The general shapes of the two T_{N-I} curves for these compounds are very similar to those for the PCH R compounds (see Figure 38), and contrast with those for the CB R materials (see Figure 24).

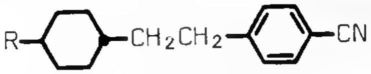
Although the T_{N-I} values for the later homologues of the PECH R and PCH R series are very similar, the initial slopes of the curves for the PECH series are less steep, due to the higher T_{N-I} values of the early homologues.

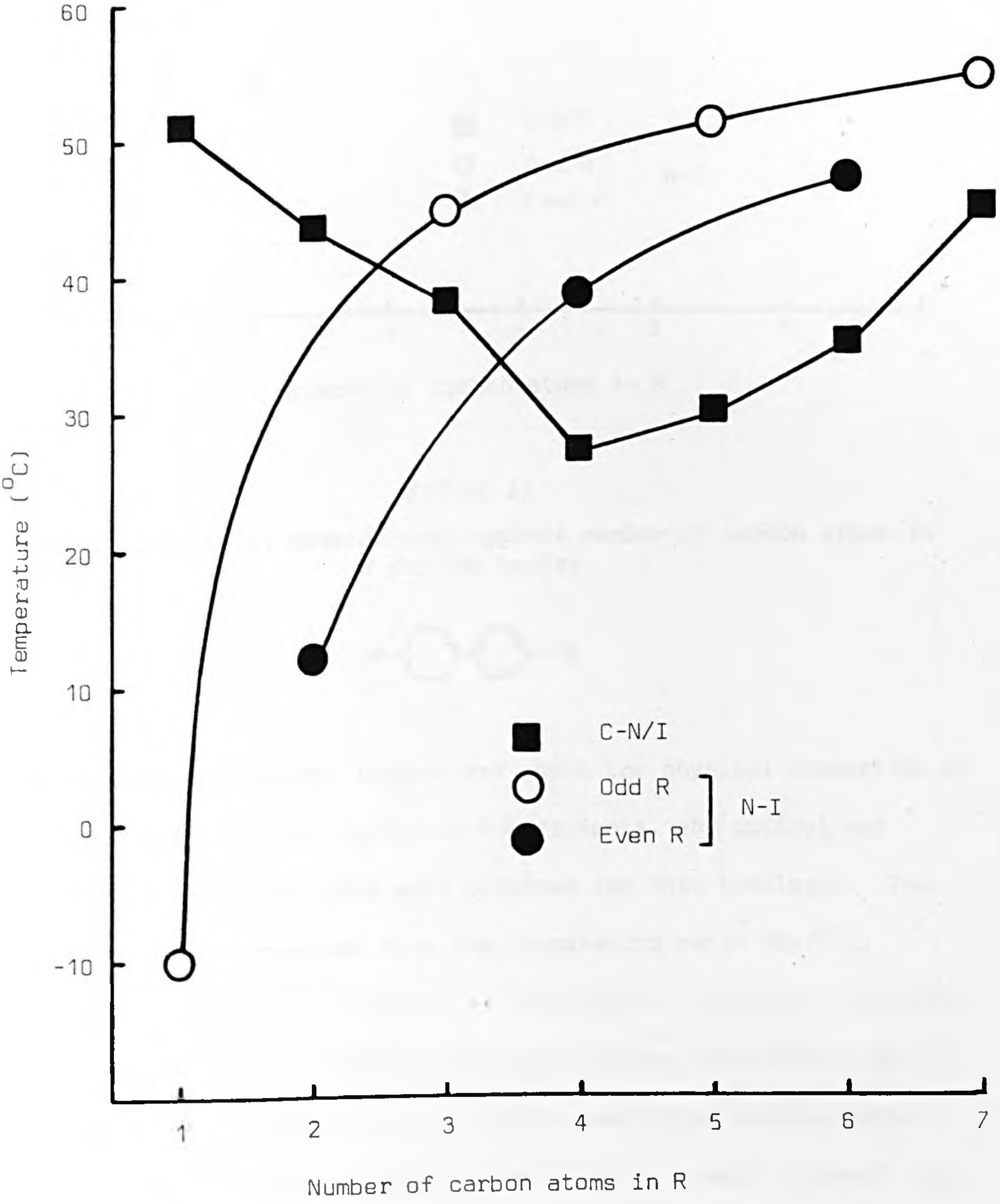
The melting points for the PECH R and PCH R series are of the same order, and show no obvious trends with change in alkyl chain length.

The first member of the series to be prepared was PECH 3. To

FIGURE 37

Graph of transition temperatures against number of carbon atoms in R for the series





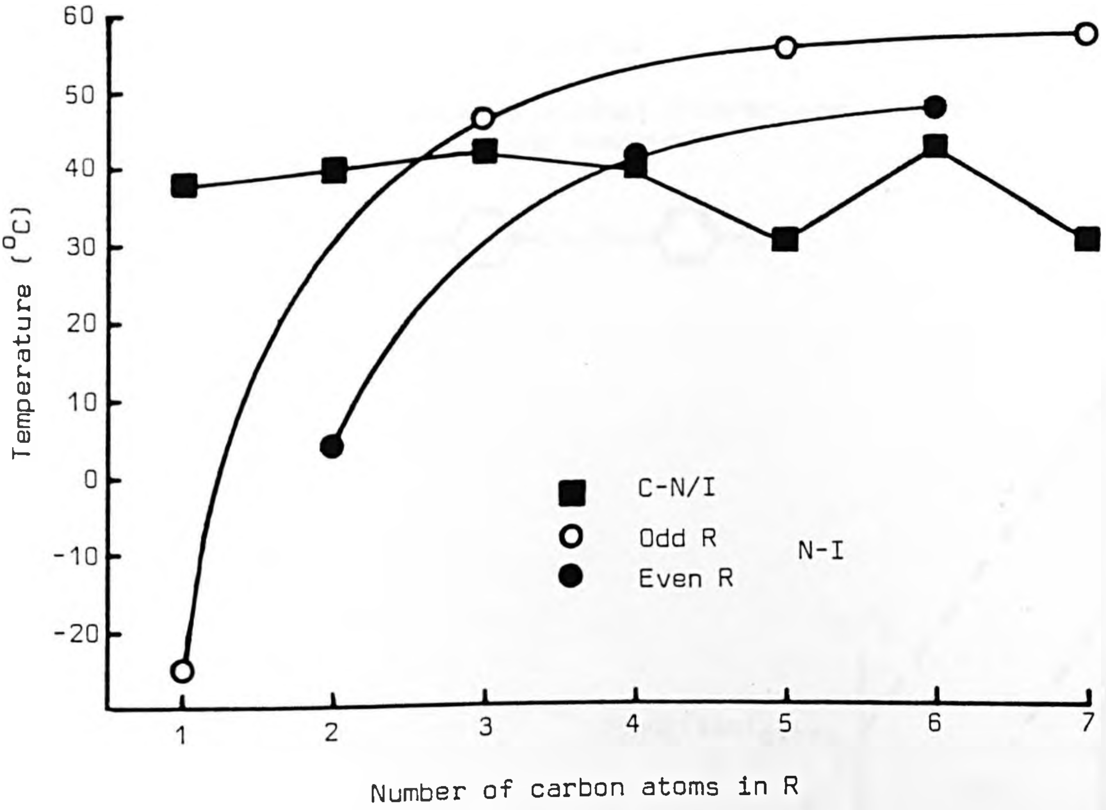
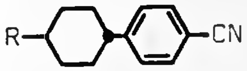


FIGURE 38

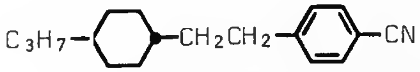
Graph of transition temperatures against number of carbon atoms in R for the series

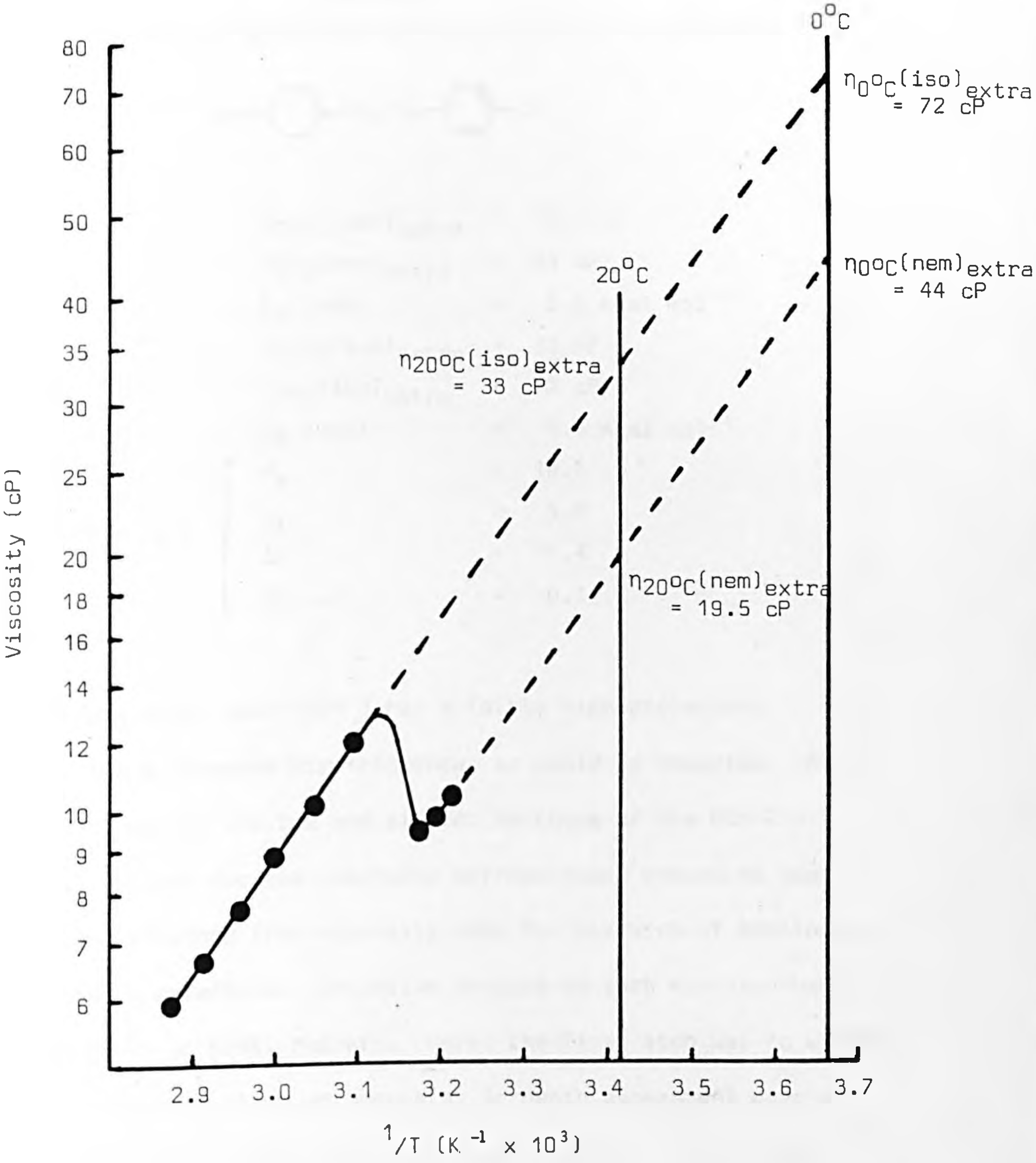


obtain some preliminary indications about the physical properties of this new cyano system, viscosity coefficients, and optical and dielectric anisotropy data were obtained for this homologue. The viscosities were measured over the temperature range 38-75^{o}C. Therefore, an accurate estimate of the change in isotropic viscosity with temperature was obtained, but only limited information could be gained for the nematic phase, due to restricted supercooling. Consequently, the extrapolated values for the nematic viscosity were obtained from the log η v ^{1}/T plot (see Figure 39), by assuming that

FIGURE 39

Graph of log viscosity against inverse temperature for the compound

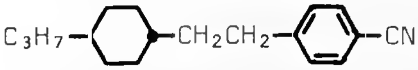




this region of the curve lies parallel to that for the isotropic region. This has been found to be the case for many materials. Table 33 summarises the data.

TABLE 33

Physical and electro-optic data for the compound of structure



$\eta_{20^oC}(\text{nem})_{\text{extra}}$ = 19.5 cP

$\eta_{0^oC}(\text{nem})_{\text{extra}}$ = 44 cP

E_a (nem) = 6.5 kcal mol^{-1}

$\eta_{20^oC}(\text{iso})_{\text{extra}}$ = 33 cP

$\eta_{0^oC}(\text{iso})_{\text{extra}}$ = 72 cP

E_a (iso) = 6.5 kcal mol^{-1}

$T = 0.98 \times T_{N-I}$ $\left[\begin{array}{l} \varepsilon_{\parallel} = 16.8 \\ \varepsilon_{\perp} = 5.4 \\ \Delta\varepsilon = 11.4 \\ \Delta n = 0.11 \end{array}\right.$

These data show that PECH 3 has a fairly high dielectric anisotropy and a moderate birefringence, as would be expected. Also, the viscosity values are low and similar to those of the PCH R compounds. Support for the viscosity extrapolation procedure used here has been obtained from viscosity data for mixtures of homologues of these PECH R materials. Extensive studies on such mixtures have been carried out at RSRE, Malvern. Here, the first step was to widen the nematic range to allow an accurate, in-depth assessment over a range of temperature, free from any boundary effects. To do this, a ternary mixture (non-eutectic) was prepared using the propyl, pentyl and heptyl homologues of concentration 30:40:30 wt % respectively. Table 34 summarises the physical and electro-optic properties for this mixture and gives comparative data for related mixtures of PCH's and CB's.

The similarity of the data for the PECH and PCH mixtures illustrates the point that there is, in general, no significant change in properties when the $-CH_2CH_2-$ inter-ring linkage is incorporated into the system. The properties of the CB's vary from being superior to inferior, relative to those for the PECH and PCH materials. Many of these property differences may reasonably be accounted for in terms of the basic difference in molecular structure.

The nematic range of the above ternary PECH mixture was further increased by adjusting the component concentrations and incorporating the related high T_{N-I}, three ring analogue BiECH 3, to give a broad range mixture (code-named JC10) with a narrow melting range. The physical and electro-optic properties for this mixture are given in Table 35.

Relative to the ternary PECH mixture, this mixture has a nematic phase that is wider by 30°C. The nematic viscosity has been increased slightly to 30 cP at 20°C, but is still relatively low; the elastic constants have also increased. The dielectric permittivities have remained much the same, whilst slight advantages have been gained in terms of the order parameter and birefringence.

Further properties of the JC 10 mixture are presented in Table 36, along with similar properties for a mixture of JC 10 with 30 wt % of the BCO ester

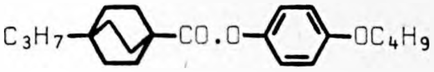


TABLE 34

Physical and electro-optic data for C_3H_7-:C_5H_{11}-:C_7H_{15}-: (30:40:30 wt %) mixtures of PECH's, PCH's and CB's

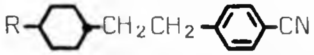
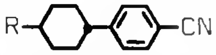
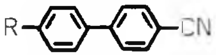
	Material			
	C-N (^{o}C)	0	0	-10
	N-I (^{o}C)	49	50	35
cP	$\eta_{20^{o}C}$(nem)	25	26	34
	$\eta_{0^{o}C}$(nem)	86	85	100
	E_a(nem) kcal mol^{-1}	9.8	9.4	8.6
$T = 0.9 \times T_{N-I}$	$\varepsilon_{\parallel}$	16.3	17.6	22.3
	$\varepsilon_{\perp}$	4.4	4.9	5.7
	$\Delta\varepsilon$	11.9	12.7	16.6
	k_{11} (10^{-12} N)	13.0	9.6	9.8
	k_{33} (10^{-12} N)	27.0	20.8	15.2
	k_{33}/k_{11}	2.08	2.17	1.55
	Sharpness M	1.95	1.91	1.97
	Δn	0.12	0.12	0.22
	S	0.67	0.65	0.62

TABLE 34 (continued)

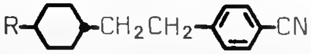
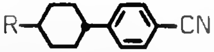
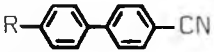
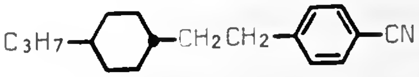
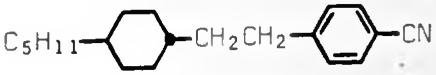
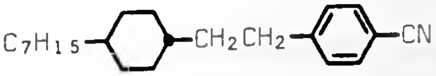
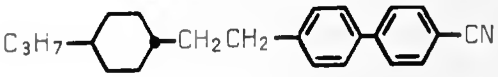
	Material			
% $^{\circ}C^{-1}$	$\frac{-1}{V}\left(\frac{dV}{dT}\right)$	0.82	0.79	1.21
	$\frac{-1}{k_{11}}\left(\frac{dk_{11}}{dT}\right)$	1.13	1.23	1.49
	$\frac{-1}{S}\left(\frac{dS}{dT}\right)$	0.38	0.59	0.69
%	Permittivity jump at T_{N-I} $\left[\frac{2\ (\varepsilon_{iso}-\bar{\varepsilon})}{\varepsilon_{iso}+\bar{\varepsilon}}\right]_{T_{N-I}}$	10	7	4

TABLE 35

Physical and electro-optic data for the PECH broad-range mixture JC 10†

	C-N (°C)	-10
	N-I (°C)	70
cP	$\eta_{20^\circ C}$(nem)	30
	$\eta_{0^\circ C}$(nem)	120
T = 20°C	$\varepsilon_{\parallel}$	16.2
	$\varepsilon_{\perp}$	4.2
	$\Delta\varepsilon$	12.0
	Δn	0.138
	S	0.71
	k_{11} (10^{-12} N)	14.7
	k_{22} (10^{-12} N)	7.9
	k_{33} (10^{-12} N)	34.1
	k_{22}/k_{11}	0.54
	k_{33}/k_{11}	2.32

† Composition of mixture JC 10:

Compound	Code	wt %
	PECH 3	32
	PECH 5	30
	PECH 7	19
	BiECH 3	19

(BiECH 3: C 77 N 194 I)

TABLE 36

Further electro-optic data for PECH based mixtures

Mixture	JC 10	JC 10 + 30 wt % BCO ester
N-I (^{o}C)	70	72
V_{90} (45^{o}) V	1.42	1.45
$M_{20^{o}C}$	1.97	1.85
$M'_{20^{o}C}$	1.46	1.40
$\frac{-1}{V}\left(\frac{dV}{dT}\right)$ % $^{o}C^{-1}$	0.7	0.5
Margin (%)	0	6

From these data, it can be seen that the useful multiplexing characteristics of the JC 10 mixture are further improved by the addition of an additive of low dielectric anisotropy; this is as expected and is in good agreement with results obtained from other mixtures. The alkyl-alkoxy BCO ester was chosen, as it has been found to be one of the most efficient additives in terms of increasing multiplexing performance. It can be seen that the figures of merit, the threshold temperature dependency and the margin are significantly improved.

One of the most promising features of the PECH mixtures, evident from the data in Tables 34 and 35, is the relatively high value for the order parameter, and its low variation with temperature. Consequently, further assessment work at RSRE, Malvern was concentrated upon investigating the properties of dichroic dyes when these were incorporated into the JC 10 host. As a result, order parameters and solubility characteristics were established for blue, yellow and red anthraquinone-based dyes. Data derived from these dye mixtures are presented in Table 37, together with similar data for the same dyes dissolved in broad range CB- (E 43) and PCH- (ZLI 1132) based hosts.

TABLE 37

Order parameters and solubility data for some dyes when incorporated into broad range mixtures at 20^oC

Mixture		JC 10	ZLI 1132	E 43
C-N (^oC)		-10	-6	-10
N-I (^oC)		70	70	80
Blue Dye	S	0.80	0.78	0.77
	Sol (%)	3.7	10.0	7.0
Yellow Dye	S	0.82	0.80	0.79
	Sol (%)	2.9	4.0	7.8
Red Dye	S	0.77	0.80	0.80
	Sol (%)	4	5	15

The increased nematic order parameters for PECH R materials therefore appear to have beneficially affected the order parameters of the dyes, in that the S values for the blue and yellow dyes (although not the red dye) are superior to those when these dyes are incorporated into the other hosts. Consequently, it should be possible to produce dyed display devices with increased colour contrast using PECH R materials. Although the dye solubilities in the JC 10 host are lower than in the other hosts, they are still quite acceptable for most types of dye display.

In addition to the above comparisons of mixtures derived from different families of materials, it is also possible to compare the properties of structural isomers of the PECH R and PCH R series (eg, PECH 3 *v* PCH 5; PECH 5 *v* PCH 7, etc). As well as having the same molar mass, these pairs of molecules have similar molecular lengths, dipole moments and polarisabilities, although the PECH molecules are likely to occupy a greater rotational volume on rotation about the molecular long axis, due to the flexible $-CH_2CH_2-$ unit. Overall, the properties for the pairs of materials are similar, particularly in relation to the T_{N-I} values, dielectric permittivities and refractive indices, but some variations are evident. These include the differences in order parameters (mentioned above for mixtures) and enthalpy values (ΔH) for the N-I transition. The S values for the PECH materials are higher by some 4%, and the ΔH values at T_{N-I} are significantly greater for the PECH compounds.

Table 38 contains these enthalpy data for three PECH homologues, as well as the enthalpies of melting. The DSC values for the onset of the transitions agree well with those obtained by optical microscopy (see Table 32). An example of a DSC thermograph is given in Figure 40 for PECH 7.

As indicated in Table 34, the PECH materials exhibit a significantly larger discontinuity in permittivity at the N-I transition than the PCH's and CB's. The reasons for the differences are not clear, but since the permittivity jump is a function of the strength of the antiparallel correlations, it is likely that the factors responsible (possibly involving increased intermolecular cohesive forces) may be related broadly to all of the slightly unusual properties of the PECH materials.

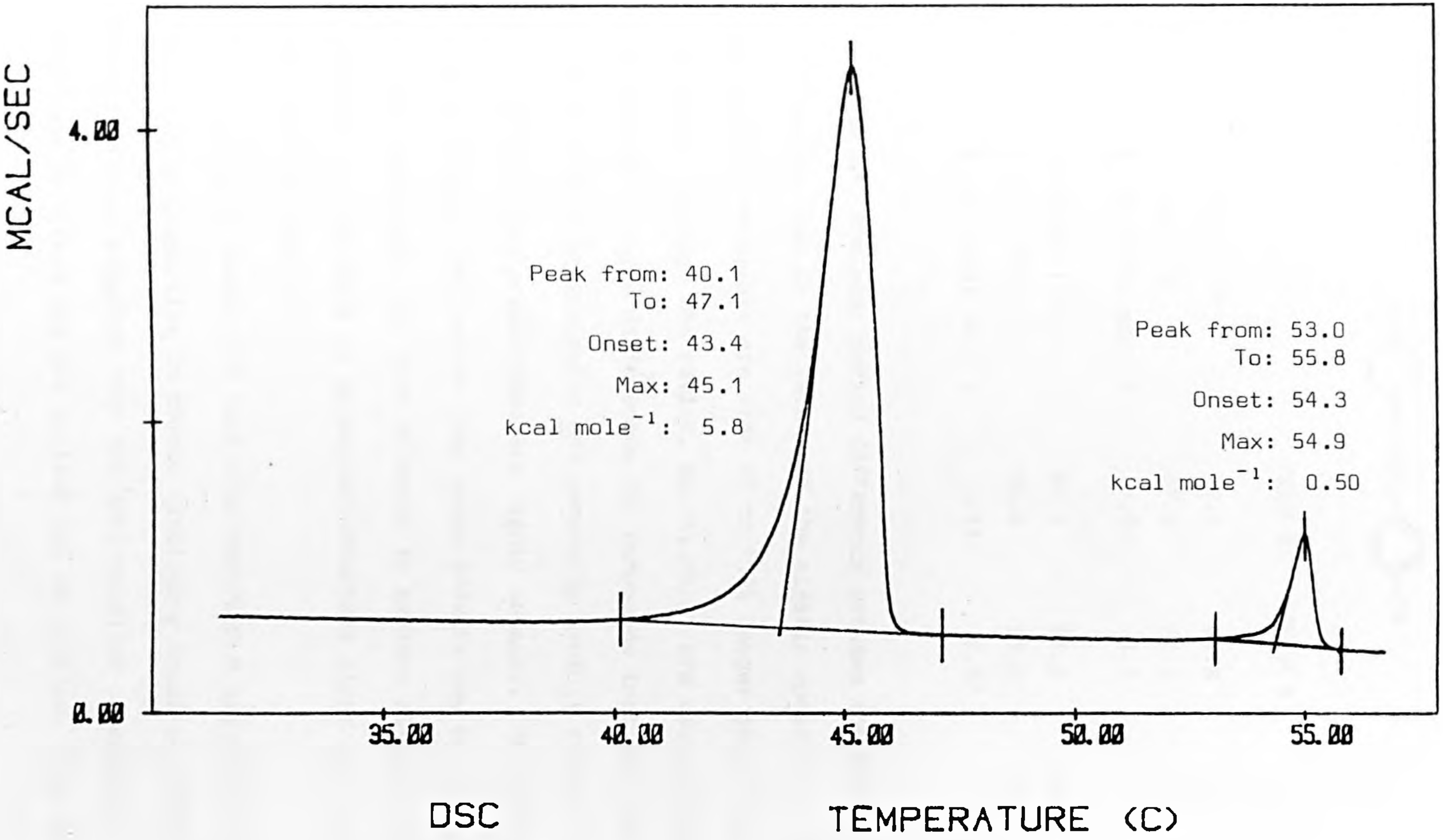


FIGURE 40

DSC thermograph for the nitrile of structure

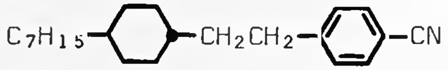
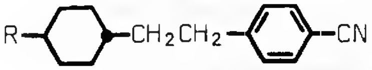


TABLE 38

Enthalpy data for three compounds of structure



		PECH 3	PECH 5	PECH 7
C-N	Onset (°C)	40.1	29.9	43.4
	Max (°C)	41.6	32.3	45.1
	ΔH (kcal mol^{-1})	3.9	3.5	5.8
N-I	Onset (°C)	46.1	51.8	54.3
	Max (°C)	46.6	53.0	54.9
	ΔH (kcal mol^{-1})	0.44	0.47	0.50

However, the most marked difference between the PECH R and PCH R series lies in the values of the elastic constants. Those for the PECH materials are from 40 to 100% larger than those for the PCH's, although the ratios, eg, k_{33}/k_{11}, are usually similar. Such extremely large differences for compounds that are very closely related structurally and generally exhibit similar physical and electro-optic properties, are highly unusual. On this basis, it is envisaged that subtle long range effects may be responsible for this behaviour, and that attempts to explain elastic constant behaviour on the basis of molecular structure alone must be viewed with some caution.[119]

In general terms, the fact that the PECH R and PCH R materials have so many properties in common (including their dielectric permittivities) suggests that the anti-parallel correlation arrangements within the two systems may be similar. The established

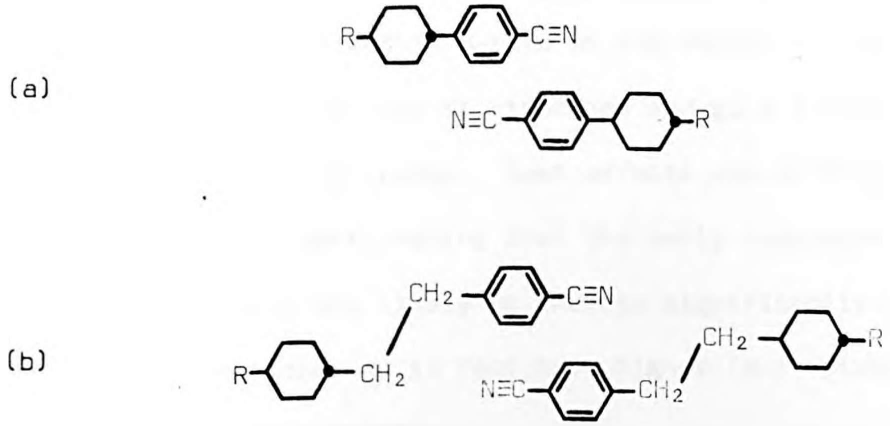


FIGURE 41

Antiparallel molecular correlation for (a) the PCH R, and (b) the PECH R materials

situation for the PCH compounds is shown diagrammatically in Figure 41(a). With the cyanophenyl groups so overlapped, the dimer has a resultant length approximately 1.4 x the molecular length. If a similar situation persists in the PECH system, then the molecular pairing will be like that shown in Figure 41(b). Independent evidence for the existence of such a paired system has been obtained from X-ray studies of the PECH R materials carried out at Exeter University.[117] It was found that the repeat spacings corresponded to approximately 1.5 x the molecular length, and this provides support for the existence of dimers of the type shown above.

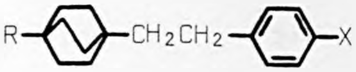
As the length of the dimers in the PECH system is slightly greater than that for the PCH's, it might be anticipated that the T_{N-I} values for the PECH materials would be slightly higher. As this is not generally found to be the case, it is possible that the effective increase in length of the molecular dimer is approximately cancelled out by the flexible nature of the $-CH_2CH_2-$ linkage. This will both increase molecular fluctuations and give a decrease in the effective length:breadth ratio. Such effects are difficult to quantify, but it is worth noting that the early homologues of the PECH R series, which are likely to undergo significantly fewer molecular deformations, do in fact have higher T_{N-I} values than the corresponding PCH homologues.

Finally, it should be mentioned that no smectic properties have been observed for the PECH R materials, either in the pure state or when incorporated into mixtures, even when extensive supercooling of the system occurs. The onset of smectic properties for the CB's occurs at the octyl homologue, and no smectic tendencies are evident for the PCH series up to PCH 9. Whilst the onset of smectic properties for the PECH series has not yet been established, the absence of smectic phases for the heptyl homologue suggests that these materials are at least comparable with the CB's and PCH's in this respect.

In summary, the PECH R materials provide a novel family of stable liquid crystal materials that have low melting points and good nematic ranges. These nematic phases have a low viscosity, a high dielectric anisotropy and a moderate birefringence. The high values for the permittivity discontinuity, the order parameter, and the enthalpy change at the N-I transition, plus the exceptionally large values for the elastic constants, have interesting theoretical implications. When these compounds are used in admixture with other suitable materials, broad range mixtures are produced that exhibit good electro-optic performance. The high order parameters of dyes dissolved in such mixtures mean that the PECH R materials are suitable for use in both twisted nematic and dyed cholesteric-nematic phase change displays.

4.5.3 *Bicyclo(2.2.2)octylethyl Derivatives*

To try and extend the impressive properties obtained for the PECH compounds (R.OR', R.R', R.H and R), the effect of replacing the *trans*-cyclohexane ring by a bicyclo(2.2.2)octane ring was investigated. The compounds under consideration have the structure



PEBCO

where

X = -H, -R', -OR', -CN

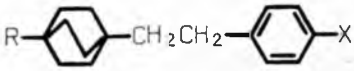
By analogy with the PECH compounds, these materials are referred to as PEBCO derivatives.

The preparation of these compounds was carried out essentially by the procedures used to prepare the related PECH materials (see Schemes 8 and 9), except that sulphonate esters, rather than the methyl bromides, were prepared from the bicyclo(2.2.2)octylmethanols (as discussed in Section 4.2.3).

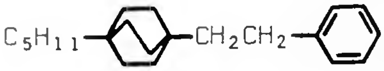
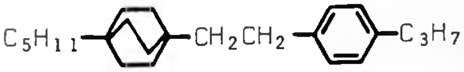
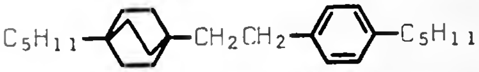
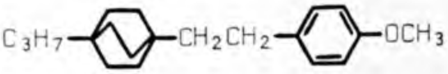
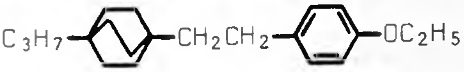
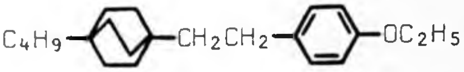
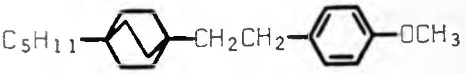
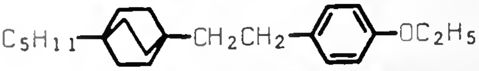
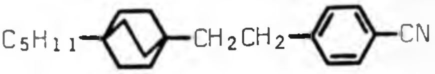
The transition temperatures for the PEBCO materials are given in Table 39, and on comparing the results for these compounds with those for other known materials incorporating the -CH_2CH_2- unit, particularly the PECH compounds, several trends emerge.

TABLE 39

Thermal data for some compounds of structure



(X = -H, -R', -OR', -CN)

Structure	C-S_B/N/I (^oC)	S_B-N (^oC)	N-I (^oC)
	24	-	(8.5)
	60	-	62
	45	58	62
	60	-	101
	57	-	76.5
	57	-	87
	29	-	89.5
	60	-	101
	76	-	113

The compound PEBCO 5.H has $\eta_{20^oC}(\mathrm{iso})$ = 38.5 cP and $\eta_{20^oC}(\mathrm{nem})_{\mathrm{extra}}$ = 24.5 cP (extrapolated from data for a 20 wt % solution in ZLI 1132). Therefore, compared with PECH 5.H (see Table 30), the melting point, T_{N-I} value and isotropic viscosity have all been increased (+25.5^oC, +38.5^oC, and +25.1 cP respectively). The increases in the transition temperatures are of a similar order to those found when such a structural change is made in other systems, and it is worth mentioning that the monotropic nematic phase for the PEBCO 5.H is the first liquid crystal phase to be observed directly for any mono-substituted, $-CH_2CH_2-$ linked material of this type. However, the large increase in viscosity is disappointing, although not exceptional for such a structural change, and serves to underline the difference between the relatively sleek, free-moving nature of the cyclohexane ring and the bulky, almost spherical nature of the bicyclo(2.2.2)octane ring.

The PEBCO R.R' compounds show a similar, although somewhat enhanced, effect on transition temperatures, as PEBCO 5.3 has a higher melting point by $+57^{o}C$ and a higher T_{N-I} value by $+59^{o}C$ than PECH 5.3 (see Table 27). Also, loose comparisons of the T_{N-I} values and viscosities for PEBCO 5.5, $\eta_{20^oC}(nem)_{extra}$ = 24 cP (extrapolated from data for a 20 wt % solution in ZLI 1132), for the corresponding fully aromatic analogue (see Section 4.5.1), $\eta_{20^oC}(iso)_{extra}$ = 16 cP, and for PECH 5.3 seem to be reasonably self-consistent.

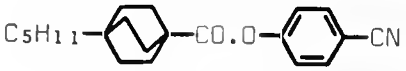
These PEBCO R.R' materials may also be compared with the corresponding derivatives with $-CH_2O-$ as the inter-ring linkage (see Table 11). The melting points for both series of compounds are very similar, but the changes in T_{N-I} value are $+32^{o}$ and $+30^{o}$ on going from the appropriate BCO ether to PEBCO 5.3 and PEBCO 5.5 respectively. However, no smectic properties are observed for the BCO ethers, whereas PEBCO 5.5 has a smectic range of 13^{o}.

The compounds PEBCO R.OR' have increased nematic ranges compared with the dialkyl materials. Here, the only homologues for which direct comparisons can be made are PEBCO 5.02 and PEBCO 5.3. The melting points are similar, but the T_{N-I} value for the alkoxy derivative is higher by 39°C.

In relation to the analogous cyclohexyl compounds (PECH R.OR'), the significant features are that the T_{N-I} values are increased by over 50°, where direct comparisons are possible, and that the viscosity is also substantially greater if the 5.O2 homologues are compared (see Tables 23 and 24). No smectic properties have been observed for the PEBCO R.OR' compounds, although the highest homologue prepared was the 5.O2 derivative. However, the corresponding PECH 5.O2 material has a monotropic S_B phase, albeit of low thermal stability.

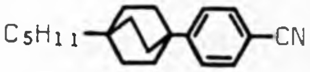
Table 11, given earlier, contains thermal data on only one related BCO alkyl-alkoxy derivative incorporating the inter-ring linkage, $-CH_2O-$. A direct homologous comparison with the PEBCO R.OR' compounds is not possible, but it is worth noting that all of the PEBCO R.OR' compounds listed in Table 39 have higher T_{N-I} values than that of the $-CH_2O-$ material, whilst having a reduced complement of carbon atoms in the terminal chains.

The final compound in Table 39 is the high dielectric anisotropy cyano derivative, PEBCO 5, which has good liquid crystal transition temperatures. Relative to the corresponding ester and the directly ring-linked material (compounds (38) and (39) respectively), PEBCO 5 has a nematic range that is at least as wide, coupled with a superior T_{N-I} value. In the case of the PEBCO R.R' and R'.OR' materials, although the nematic ranges are not as great as those for the corresponding esters, the T_{N-I} values for the $-CH_2CH_2-$ and $-CO.O-$ linked systems are comparable, and are much superior to those for



(38)

C 89 N 109 I



(39)

C 62 N 100 I

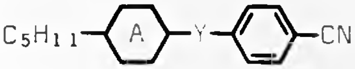
the related disubstituted phenylbicyclo(2.2.2)octanes (discussed in Section 4.3). Consequently, it would appear that from the standpoint of T_{N-I} values, the $-CH_2CH_2-$ inter-ring linkage may be best suited to systems incorporating the BCO ring. This may be because the BCO ring is a relatively rigid (although not incompressible) unit, and is able to compensate the flexible nature of the $-CH_2CH_2-$ linkage. In comparison, the *trans*-cyclohexane ring is very flexible, so that the PECH derivatives have lower T_{N-I} values compared with the analogous esters and similar values to the PCH materials. The low T_{N-I} values of the fully aromatic $-CH_2CH_2-$ derivatives have been discussed earlier.

However, although the transition temperatures for PEBCO 5 are good, the viscosity is very high, ie, $\eta_{20^oC}(nem)_{extra}$ = 101 cP (extrapolated from data for a 20 wt % solution in ZLI 1132). This value is similar to that for a ternary mixture of three homologues of type (39), where $\eta_{20^oC}(nem)$ = 96 cP. This result emphasises the fact that the incorporation of the BCO ring into a molecule markedly increases the viscosity. Consequently, the PECH materials would appear to represent the best compromise between increasing the T_{N-I} value and adversely affecting the viscosity of the system.

As well as comparing PEBCO 5 with the analogous ester and with the directly ring-linked system, it is also possible to compare, on a broader basis, all of the cyano derivatives containing the three different ring structures and involving the two linking units $-CH_2CH_2-$ and $-CH_2O-$, for which PEBCO 5 completes the series. Table 40 gives the transition temperatures for all of the relevant compounds.

TABLE 40

Comparative thermal data for some compounds of structure



$^{Y}/_{A}$				
$-CH_2CH_2-$	C-N/I (^{o}C)	62	30	76
	N-I (^{o}C)	[-24]	51	113
$-CH_2O-$	C-N/I (^{o}C)	49	74.3	72
	N-I (^{o}C)	[-20]	(48.8)	73

These data provide yet further conclusive evidence of the superiority of the BCO ring in relation to the benzene and *trans*-cyclohexane rings in promoting the nematic thermal stability of a system. The two linking groups appear to be comparable for the benzene and cyclohexane derivatives, with the main difference arising for the BCO derivatives, where the $-CH_2CH_2-$ unit appears to be much superior. These conclusions are found to hold broadly for the low $\Delta\varepsilon$ systems.

To sum up, the main drawback with all the PEBCO materials is their relatively high viscosity. However, the use of the $-CH_2CH_2-$ inter-ring linkage and the BCO ring together in a molecule does produce highly stable systems with very good T_{N-I} values. This group of compounds therefore represents an interesting and useful addition to the broad family of liquid crystal materials.

EXPERIMENTAL

5.1 *ASSESSMENT OF MATERIALS*

5.1.1 *Structure and Purity*

The molecular structure and/or purity of each final product and intermediate material was checked by a variety of physical analysis techniques.

In the case of the intermediate compounds, the appropriate physical constants (mp, bp, etc) were recorded and checked against known literature values if possible. For each of these materials infra-red spectroscopy, IR (Perkin-Elmer 457 and Unicam SP200), nuclear magnetic resonance spectroscopy, NMR (Jeol J NM-4H 100 MHz), mass spectroscopy, MS, and gas-liquid chromatography, GLC, were used as necessary.

All final products were assessed in a similar manner with GLC and high performance liquid chromatography, HPLC, playing a particularly important role in the estimation of product purity. Further purification was deemed necessary wherever these results indicated a purity of <99.8%. The purity of all materials was, of course, monitored throughout by thin layer chromatography, TLC, as a matter of routine.

5.1.2 *Transition Temperatures*.

Melting points were determined by the standard capillary method. Whenever this value was below ambient temperature or was not easily observed (in the case of some C-S transitions), a combination of low temperature microscopy and DSC or DTA (see later) was used.

Liquid crystal transition temperatures (eg, C-S, C-N, S-S, S-N, S-I, and N-I) were measured by optical microscopy using a Nikon L-Ke or Vickers M72C polarising microscope equipped with a Mettler FP52 heating/cooling stage coupled to a Mettler FP5 temperature control unit. Temperatures between ambient and -20°C were attained by passing dry, cooled gaseous nitrogen through the heating/cooling stage. The accuracy of temperature control with this instrument is ±0.1° below 100°C and ±0.2° above 100°C, the maximum working temperature being around 300°C.

When no nematic liquid crystal phase (monotropic or enantiotropic) was exhibited by the sample, due to either an unexpected high melting point or the predominance of smectic properties, a virtual or latent nematic-isotropic liquid transition temperature was determined, as discussed in Section 4.1.7.

5.1.3 Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA)

The analysis of a material by DSC (or DTA) provided useful information in two respects:

(i) the enthalpy for a given phase transition, ΔH, was determined;

(ii) transitions difficult to detect by other means (optical microscopy, etc) were often revealed.

As each phase transition (C-C, C-S, C-N, C-Ch, C-I, S-S, S-N, S-Ch, S-I, N-I, Ch-I) involves a change in energy (molecular ordering), there is consequently a corresponding enthalpy change associated with the transition. As a result, any enthalpy change observed upon heating or cooling the sample implies that some phase transition had occurred, and this fact was particularly useful for determining phase transitions that were not easily observed by optical microscopy, eg, for C-C, C-S, and S-S transitions in particular. By further establishing whether the transition was reversible at the same temperature over successive heating and cooling cycles, it was possible to distinguish between melting transitions (usually involving supercooling) and internal mesophase and mesophase-isotropic liquid changes (involving little or no supercooling). Moreover, as the magnitude of ΔH is proportional to the change in molecular ordering, it was often possible to further characterise some phase transitions. For example, C-C and C-S changes could be distinguished on this basis. Although transition temperatures were obtained by the DSC (or DTA) technique, the values quoted throughout this thesis are the exact values subsequently determined under standard conditions using optical microscopy.

As discussed in Section 4.1.7, to calculate the concentration of each component required for the formation of a eutectic mixture, it is necessary to have an accurate value for the enthalpy of fusion corresponding to each component. These values are relatively easily obtained by DSC (or DTA), and Table 38 contains some typical data for the PECH's which may be used to formulate nematic eutectic mixtures involving these materials.

DSC analyses were carried out using a Perkin-Elmer instrument (DSC-2C) coupled with a thermal analysis data station (3600) and graphics plotter (7225A). The following general procedure was used. A small amount of the test material, of accurately known weight (10-50 mg), encapsulated in a clean, dry DSC pan, and an inert reference material contained in another pan were simultaneously heated or cooled as required, at a suitable linear rate and under an atmosphere of dry nitrogen. Any enthalpy change occurring in the test material resulted in a temperature differential between the sample and the reference material, such that heat had either to be supplied to or removed from the sample (depending upon the sign of the enthalpy change) in order to keep the sample and reference material at the same temperature. The amount of energy involved was automatically recorded and a plot of ΔH *v* T produced.

The basic principles of DTA are similar to those of DSC, except that the temperature *difference* between the sample and inert reference material was recorded when a phase transition occurred. DTA measurements were made using a Stanton Redcroft (671) thermal analysis unit.

5.1.4 *Viscosity Coefficients*

The ideal situation for the measurement of the viscosity of a nematic phase is naturally when the material under test exhibits its nematic phase over the desired experimental temperature range, and particularly at 20°C. As this was not always the case, two alternative procedures were used to provide an estimate for the nematic viscosity. These procedures involved:

(i) measurement of the isotropic viscosity of the material at 20^{o}C, or over a suitable temperature range;

(ii) measurement of the viscosity of a solution of the test material in a suitable nematic host as solvent.

These procedures have been discussed more fully in Section 4.1.1.

Viscosities were measured using a calibrated semi-micro capillary viscometer (Poulten, Selfe, and Lee - Model 250). The viscometer was allowed to equilibrate for at least 30 min at the required temperature in a constant temperature bath before any measurements were made. Each viscosity was obtained using the average of three separate measurements, provided that the agreement between the values was good. The viscosity at a temperature T^{o}C, η_{T^oC}, was obtained from the expression

$$\eta_{T^oC}\ (cP) = t \times f$$

where

t = time of flow measured using the viscometer (in secs)
f = constant (the viscometer conversion factor)

5.2 *PREPARATION OF MATERIALS*

Each general experimental procedure in this section is illustrated by particular reference to a representative homologue.

5.2.1 *Compounds Incorporating the -CH_2O- Inter-Ring Linkage*

4-n-Alkylbenzyl alcohols

4-Pentylbenzoic acid (13.4 g, 0.07 mole) was added to thionyl chloride (120 cm^3) and the mixture heated under reflux for 90 min. The excess of thionyl chloride was removed from the cooled solution *in vacuo*; dry ether (50 cm^3) was then added and distilled off under reduced pressure (twice) to remove the last traces of thionyl chloride. A solution of the acid chloride in dry ether (80 cm^3) was added to a solution of lithium aluminium hydride (5.3 g, 0.14 mole) in dry ether (100 cm^3) at such a rate as to maintain gentle reflux of the ether. After the addition, the mixture was heated under reflux for 30 min. Then water (1.9 g, 0.105 mole) was cautiously added to the cooled solution, followed by dilute hydrochloric acid until coagulation of the inorganic salts seemed to be complete. The ethereal layer was decanted off and the remaining inorganic salts were washed with ether (3 x 30 cm^3). The combined ethereal extracts were washed with water (3 x 60 cm^3), dried (Na_2SO_4), and filtered, and the solvent was removed *in vacuo* to give a pale yellow liquid. This was distilled to yield the product as a colourless liquid. The yield of the alcohol was 11.6 g (93%), bp 114°C at 0.7 mm Hg.

Similarly prepared were the alcohols:

4-methylbenzyl alcohol (91%), mp 61°C;[†]
4-hexylbenzyl alcohol (94%), bp 120°C at 0.8 mm Hg;
4-nonylbenzyl alcohol (88%), bp 138°C at 2 mm Hg.

4-n-Alkylbenzyl chlorides

4-Pentylbenzyl alcohol (3.6 g, 0.02 mole) was added to a solution of thionyl chloride (2.9 g, 0.024 mole) in chloroform (60 cm^3) and the mixture heated at 80°C for 90 min. The solvent was removed *in vacuo* and the residual oil taken up in ether (50 cm^3). The ethereal solution was washed with 10% sodium bicarbonate solution (2 x 30 cm^3), dried (Na_2SO_4), and filtered, and the solvent was removed *in vacuo*. The residual product was purified by distillation which yielded a colourless liquid, 3.7 g (95%), bp 118°C at 2 mm Hg.

Similarly prepared were the chlorides:

4-methylbenzyl chloride (90%), bp 120°C at 4 mm Hg;[††]
4-hexylbenzyl chloride (91%), bp 120°C at 1.5 mm Hg;
4-nonylbenzyl chloride (84%), bp 130°C at 3 mm Hg.

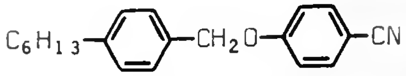
[†] Literature value,[120] mp 61°C

[††] Literature value,[121] bp 200-202°C

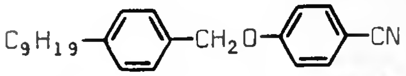
4-(4'-n-Alkylbenzyloxy)cyanobenzenes, 2-(4'-n-alkylbenzyloxy)-6-cyanonaphthalenes, and 4-(4"-n-alkylbenzyloxy)-4'-cyanobiphenyls

4-Pentylbenzyl chloride (2.0 g, 0.01 mole) was added dropwise to a mixture of 4-cyanophenol† (0.7 g, 0.006 mole), and anhydrous potassium carbonate (6.9 g, 0.05 mole) in dry butanone (60 cm^3); the mixture was then stirred and heated under reflux for 48 hr. Upon cooling, the mixture was poured into water (60 cm^3) and then shaken with ether (3 x 60 cm^3). The combined ethereal extracts were washed with water (3 x 40 cm^3), dried (Na_2SO_4), and filtered, and the solvent was removed *in vacuo*. The crude product was purified by column chromatography using silica gel as the stationary phase and chloroform as the eluant. The final product was obtained by crystallisation from a small volume of light petroleum (bp 40-60°C). The yield was 0.7 g (42%), C-I 49°C.

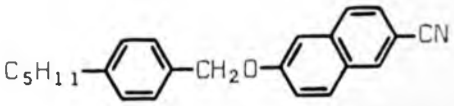
Similarly prepared in yields of 30-40% were the cyano-substituted ethers:



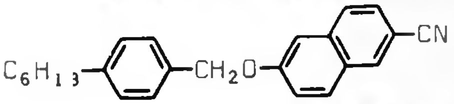
C-I 48°C;



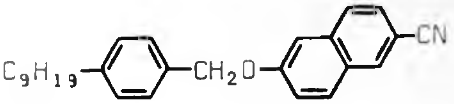
C-I 60°C;



C-I 82°C, N-I (62°C);



C-I 82°C, N-I (56°C);



C-I 74°C, N-I (71°C);

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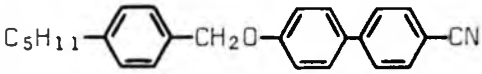
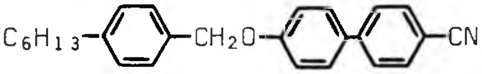
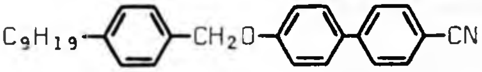
† or 6-cyano-2-naphthol or 4-cyano-4'-hydroxybiphenyl, as appropriate


C-N 91°C, N-I 147°C;


C-S_A 85°C, S_A-N 129°C, N-I 142°C;


C-S_A 60°C, S_A-I 142°C.

Further data relating to transition temperatures for these compounds are given in Table 2, page 123.

4-(4'-Methylbenzyloxy)methoxybenzene

The sodium salt of 4-methoxyphenol was formed by adding a solution of the phenol (6.2 g, 0.05 mole) in super-dry ethanol (30 cm^3) to a solution of sodium ethoxide (prepared from sodium (1.2 g, 0.05 g atom) and super-dry ethanol (100 cm^3)). The excess of ethanol was removed by distillation and the salt dried *in vacuo*. The salt was taken up in 1,2-dimethoxyethane (60 cm^3); 4-methylbenzyl chloride (5.6 g, 0.04 mole) was then added, and the whole heated under reflux for 6 hr. The reaction mixture was poured into water (120 cm^3) and the resulting brown precipitate was filtered off and taken up in ether (100 cm^3). The solution was dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo*. The pure material, 2.9 g (32%), C-I 82°C, was obtained after two crystallisations from light petroleum (bp 40-60°C).

4-(4'-Methylbenzyloxy)butyloxybenzene

4-Butyloxyphenol (2.5 g, 0.015 mole) was added to 0.30M potassium hydroxide solution (50 cm^3) and the suspension heated under reflux for 1 hr. 4-Methylbenzyl chloride (2.1 g, 0.015 mole) in dioxan (34 cm^3) was added over 40 min, and the reaction mixture heated under reflux for 18 hr. The cooled mixture was poured into water (100 cm^3) and the whole shaken with ether (3 x 80 cm^3). The combined ethereal extracts were washed successively with 20% potassium hydroxide solution (3 x 50 cm^3) and water (3 x 80 cm^3). The solution was dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo* to yield the crude product, which was crystallised from light petroleum (bp 40-60°C). The final product, 0.8 g (21%), C-I 76°C, was obtained by a further crystallisation from the same solvent.

trans-*4-n-Alkylcyclohexylmethanols*

These alcohols were prepared in yields of 87-99% by the above lithium aluminium hydride reduction procedure starting with the *trans*-4-n-alkylcyclohexane-1-carboxylic acids.

trans-4-methylcyclohexylmethanol,	bp 90°C at 5 mm Hg
trans-4-ethylcyclohexylmethanol,	bp 143°C at 3 mm Hg
trans-4-propylcyclohexylmethanol,	bp 155°C at 3 mm Hg
trans-4-butylcyclohexylmethanol,	bp 150°C at 1 mm Hg
trans-4-pentylcyclohexylmethanol,	bp 99°C at 0.1 mm Hg
trans-4-hexylcyclohexylmethanol,	bp 111°C at 0.2 mm Hg
trans-4-heptylcyclohexylmethanol,	bp 116°C at 0.1 mm Hg

trans-*4-n-Alkylcyclohexylmethyl bromides*

To an efficiently stirred mixture of 48-50% hydrobromic acid solution (15 cm^3), concentrated sulphuric acid (4 cm^3), and *trans*-4-pentylcyclohexylmethanol (12.7 g, 0.069 mole) was added dropwise an additional amount of concentrated sulphuric acid (2.5 cm^3). The mixture was then heated under reflux for 3 hr. The cooled solution was poured onto ice (60 g) and then shaken with ether (3 x 60 cm^3). The combined ethereal extracts were washed with brine (3 x 50 cm^3), dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo* to leave the product as a brown oil. This was purified by distillation under reduced pressure which yielded a pale yellow liquid, 14.0 g (82%), bp 155^{o}C at 15 mm Hg.

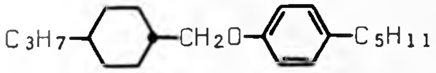
Similarly prepared in yields of 69-81% were the alkyl bromides:

trans-4-methylcyclohexylmethyl bromide, bp 61^{o}C at 3 mm Hg;
trans-4-ethylcyclohexylmethyl bromide, bp 66^{o}C at 2 mm Hg;
trans-4-propylcyclohexylmethyl bromide, bp 96^{o}C at 4 mm Hg;
trans-4-butylcyclohexylmethyl bromide, bp 151^{o}C at 15 mm Hg;
trans-4-hexylcyclohexylmethyl bromide, bp 166^{o}C at 15 mm Hg;
trans-4-heptylcyclohexylmethyl bromide, bp 98^{o}C at 0.2 mm Hg;

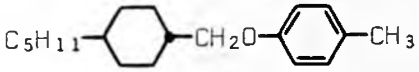
*4-(*trans*-4'-n-Alkylcyclohexylmethoxy)-n-alkylbenzenes*

trans-4-Pentylcyclohexylmethyl bromide (2.5 g, 0.01 mole) was added to a mixture of 4-pentylphenol (2.5 g, 0.015 mole) and potassium hydroxide (0.98 g, 0.0175 mole) in solution in 95% 2-ethoxyethanol (5 cm^3). The mixture was heated under reflux for 2 hr, whereupon a further portion of potassium hydroxide (0.14 g, 0.0025 mole) was added, and the mixture was again heated under reflux for 2 hr. The cooled reaction mixture was poured into water (100 cm^3) and then shaken with ether (3 x 80 cm^3). The combined ethereal extracts were washed with 20% sodium hydroxide solution (3 x 60 cm^3), water (3 x 60 cm^3) and then dried (Na_2SO_4). The solution was filtered and the solvent was removed *in vacuo*. The crude material was purified by column chromatography using silica gel as the stationary phase and a 2:1 (v:v) mixture of chloroform: light petroleum (bp 40-60°C) as the eluant. The final product was obtained by distillation under reduced pressure (bp 150°C at 0.2 mm Hg) and crystallisation from light petroleum (bp 40-60°C). The yield was 1.6 g (48%), C-I 35°C, S_B-I (31°C).

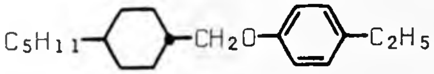
Similarly prepared in yields of 40-60% were the ethers:



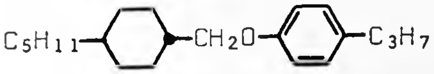
C-I 24°C, N-I (4°C);



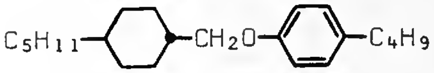
C-I 47°C;



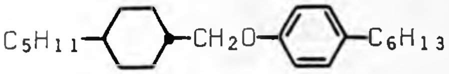
C-I 30°C, N-I (5.5°C);



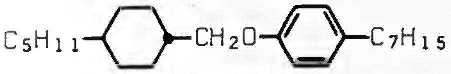
C-I 32°C, S_B-I (10°C);



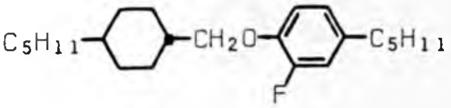
C-I 23°C, S_B-I (21°C);



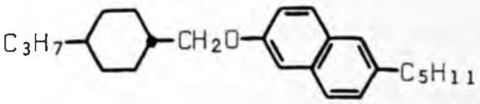
C-S_B 30°C, S_B-I 36°C;



C-S_B 34°C, S_B-I 38°C;



C-I 43°C;



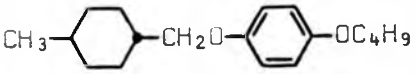
C-I 99°C, N-I (78°C).

Further data relating to transition temperatures for these compounds are given in Table 8, page 140.

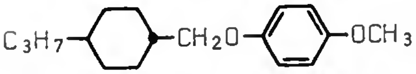
*4-(*trans*-4'-n-Alkylcyclohexylmethoxy)-n-alkoxybenzenes*

These materials were prepared in variable yields (30-65%) in a similar way to that described above for the corresponding dialkyl materials, but using the appropriate 4-n-alkoxyphenol.

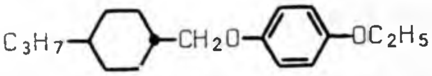
The ethers prepared in this way were:



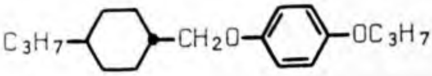
C-I 55°C;



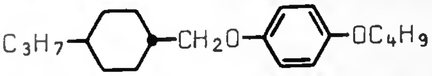
C-I 42°C;



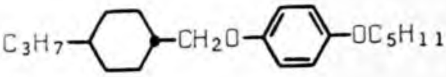
C-I 73°C, N-I (44°C);



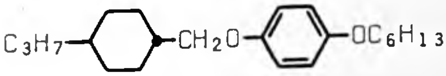
C-I 53°C, N-I (34°C);



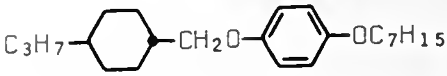
C-I 55°C, S_B-N (25°C), N-I (46°C);



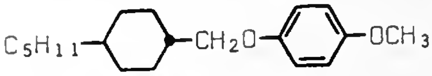
C-I 54°C, S_B-N (30°C), N-I (42°C);



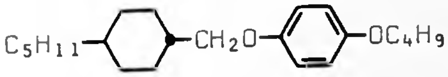
C-I 52°C, S_B-I (49°C);



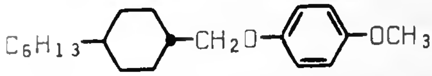
C-S_B 42°C, S_B-I 60°C;



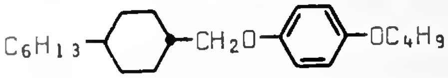
C-I 46°C, N-I (38°C);



C-I 55°C, S_B-N (47°C), N-I (53°C);



C-I 45°C, N-I (36°C);



C-I 54°C, S_B-I (50°C).

Further data relating to transition temperatures for these compounds are given in Table 6, page 134.

1-n-Alkyl-4-bromobicyclo(2.2.2)octanes

A mixture of 4-pentylbicyclo(2.2.2)octanol (17.6 g, 0.09 mole), zinc bromide (89.4 g, 0.397 mole), and 48-50% hydrobromic acid solution (177 cm^3) was heated at 75°C for 24 hr. The cooled reaction mixture was poured into water (500 cm^3) and the mixture shaken with chloroform (3 x 100 cm^3). The combined organic extracts were washed with water (2 x 500 cm^3), dried ($CaCl_2$), filtered, and the solvent was removed *in vacuo*. This yielded the product as a pale yellow oil, 22.6 g (97%), which was used without purification.

Similarly prepared were the bromides:

1-bromo-4-methylbicyclo(2.2.2)octane (90%);
1-bromo-4-propylbicyclo(2.2.2)octane (93%);
1-bromo-4-butylbicyclo(2.2.2)octane (95%).

4-n-Alkylbicyclo(2.2.2)octane-1-carboxylic acids

1-Bromo-4-pentylbicyclo(2.2.2)octane (15.6 g, 0.06 mole), was added dropwise over 20 min, at the same time as formic acid (64.2 cm^3) was added - but in this case over a more extended period of 6 hr - to a vigorously stirred mixture of concentrated sulphuric acid (918 cm^3) and silver (I) sulphate (18.7 g, 0.06 mole) at 0°C. The mixture was stirred for a total of 7 hr, then cautiously added to ice (800 g) and stirred for 30 min. The whole was shaken with chloroform (4 x 200 cm^3) and the combined organic extracts were washed with water (2 x 1 ℓ). The solution was dried ($CaCl_2$), filtered, and the solvent was removed *in vacuo* to yield the crude acid as a pale yellow solid. The final product was obtained by crystallisation from methanol. The yield was 11.5 g (85%), mp 159°C.

Similarly prepared were the acids:

4-methylbicyclo(2.2.2)octane-1-carboxylic acid (79%), mp 188°C;
4-propylbicyclo(2.2.2)octane-1-carboxylic acid (74%), mp 215°C;
4-butylbicyclo(2.2.2)octane-1-carboxylic acid (82%), mp 157°C.

4-n-Alkylbicyclo(2.2.2)octylmethanols

These were prepared by the above lithium aluminium hydride reduction procedure from the corresponding 4-n-alkylbicyclo(2.2.2)-octane-1-carboxylic acids, and the pale yellow oils used without purification.

4-methylbicyclo(2.2.2)octylmethanol	(90%);
4-propylbicyclo(2.2.2)octylmethanol	(94%);
4-butylbicyclo(2.2.2)octylmethanol	(96%);
4-pentylbicyclo(2.2.2)octylmethanol	(95%).

4-n-Alkylbicyclo(2.2.2)octylmethyl toluene-4-sulphonates

A solution of 4-pentylbicyclo(2.2.2)octylmethanol (2.5 g, 0.012 mole) and toluene-4-sulphonyl chloride (3.4 g, 0.018 mole) in dry pyridine (33 cm^3) was stirred and heated at 40^{o}C for 60 hr. The cooled reaction mixture was poured into ice-water (60 g) and the organic products were extracted into ether (3 x 50 cm^3). The combined ethereal extracts were washed with dilute hydrochloric acid (50 cm^3), water (3 x 50 cm^3), and dried (Na_2SO_4). The solution was filtered and the solvent was removed *in vacuo* to yield the crude tosylate as a pale yellow solid. The final product was obtained by crystallisation from light petroleum (bp 40-60^{o}C). The yield of colourless crystals was 3.1 g (71%), mp 67^{o}C.

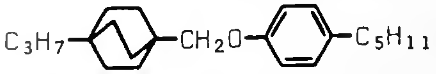
Similarly prepared were the tosylates:

4-methylbicyclo(2.2.2)octylmethyl toluene-4-sulphonate	(82%),	mp 127^{o}C;
4-propylbicyclo(2.2.2)octylmethyl toluene-4-sulphonate	(76%),	mp 97^{o}C;
4-butylbicyclo(2.2.2)octylmethyl toluene-4-sulphonate	(72%),	mp 65^{o}C.

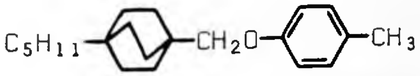
4-(4'-n-Alkylbicyclo(2'.2'.2')octylmethoxy)-n-alkylbenzenes

4-Pentylbicyclo(2.2.2)octylmethyl toluene-4-sulphonate (2.5 g, 0.007 mole) and 4-pentylphenol (3.4 g, 0.021 mole) were stirred and heated under reflux in dry dimethylformamide (12.5 cm^3) for 18 hr in the presence of potassium carbonate (2.9 g, 0.021 mole). The cooled reaction mixture was poured into water (60 cm^3) and the organic products were extracted into ether (3 x 60 cm^3). The combined ethereal extracts were washed with 20% sodium hydroxide solution (3 x 60 cm^3), water (3 x 60 cm^3), then dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo*. The crude product was purified by column chromatography using silica gel as the stationary phase and a 2:1 (v:v) mixture of chloroform:light petroleum (bp 40-60^oC) as the eluant. The final product was obtained by distillation under reduced pressure (bp 190^oC at 4 mm Hg) and crystallisation from light petroleum (bp 40-60^oC). The yield was 1.4 g (55%), C-I 47^oC, N-I (32^oC).

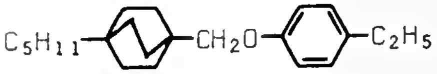
Similarly prepared in variable yields (30-60%) were the ethers:



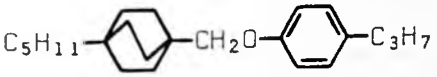
C-I 51^oC;



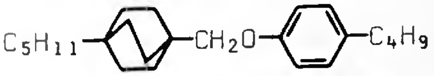
C-I 69^oC, N-I (33.5^oC);



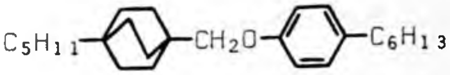
C-I 58^oC, N-I (20^oC);



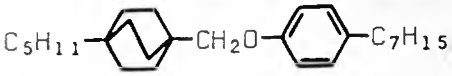
C-I 56^oC, N-I (30^oC);



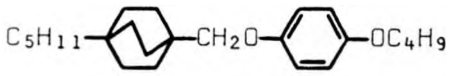
C-I 56^oC, N-I (19^oC);

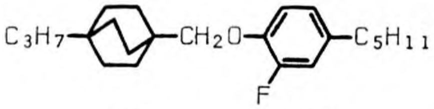


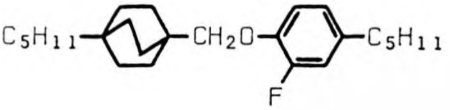
C-I 43^oC, S_B-I (30^oC);



C-I 47^oC, S_B-N (35.5^oC), N-I (36^oC);


C-I 74°C, S_B-N (61°C), N-I (68°C);


C-I 41°C;


C-I 38°C, N-I (11.5°C)

Further data relating to transition temperatures for these compounds are given in Table 11, page 160.

4-(4'-n-Alkylbicyclo(2'.2'.2')octylmethoxy)cyanobenzenes

These compounds were prepared by the above procedure for the dialkyl and alkyl-alkoxy analogues using 4-cyanophenol.

The compounds prepared were:

4-(4'-methylbicyclo(2'.2'.2')octylmethoxy)cyanobenzene, (46%), C-I 89°C;

4-(4'-butylbicyclo(2'.2'.2')octylmethoxy)cyanobenzene, (49%), C-I 79°C, N-I (57°C);

4-(4'-pentylbicyclo(2'.2'.2')octylmethoxy)cyanobenzene, (41%), C-N 72°C, N-I 73.5°C.

4-(4'-Methylbenzyloxy)-1-pentylbicyclo(2.2.2)octane

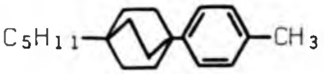
4-Methylbenzyl chloride (2.5 g, 0.018 mole), 4-pentylbicyclo-(2.2.2)octanol (3.0 g, 0.015 mole), and potassium hydroxide (12.6 g, 0.225 mole) were stirred and heated at 215°C for 6 hr. The cooled reaction mixture was poured into ice-water (100 g) and the whole shaken with ether (3 x 60 cm^3). The combined ethereal extracts were washed with water (3 x 40 cm^3), dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo* to yield a yellow solid which was crystallised from light petroleum (bp 40-60°C). The final product was obtained as a white powder by recrystallisation (twice) from the same solvent. The yield was 0.3 g (7%), C-I 63°C.

5.2.2 Derivatives of Phenylbicyclo(2.2.2)octane

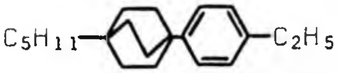
1-n-Alkyl-4-(4'-n-alkylphenyl)bicyclo(2.2.2)octanes

A solution of 1-bromo-4-pentylbicyclo(2.2.2)octane (14.0 g, 0.058 mole) in sieve-dried nitrobenzene (200 cm^3) was added dropwise to a well-stirred solution of freshly crushed, anhydrous aluminium chloride (3.1 g, 0.023 mole) and pentylbenzene (85.8 g, 0.580 mole) in sieve-dried nitrobenzene (350 cm^3) maintained at 80°C. The solution was stirred and heated at this temperature for 18 hr. Enough dilute hydrochloric acid was added to the cooled solution to destroy the Friedel-Crafts complex, and the mixture was stirred for 30 min. The organic layer was separated off and steam distilled to remove the nitrobenzene and residual pentylbenzene. The residue was taken up in chloroform, dried ($CaCl_2$), filtered, and the solvent was removed *in vacuo*. The crude product was purified by column chromatography using silica gel as the stationary phase and a 3:2 (v:v) mixture of chloroform:light petroleum (bp 40-60°C) as the eluant. The final product was obtained by crystallisation from light petroleum (bp 40-60°C). The yield was 7.5 g (57%), C-I 52°C, N-I (33°C).

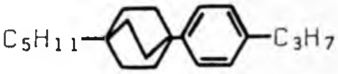
Similarly prepared, in yields normally in the range 45-65%, were the following compounds, which include three of the lower homologues of the alkoxyphenyl series which could be prepared by this route:



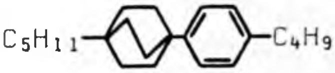
C-I 64°C;



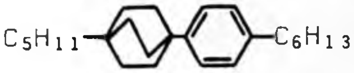
C-I 44°C;



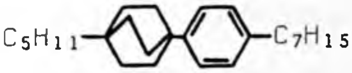
C-I 50°C;



C-I 34°C;



C-I 47°C, S_B-I (30°C);

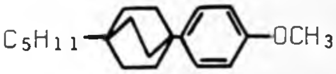


C-I 52°C, S_B-I (44°C);

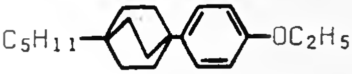
C-I 57°C;

C-I 49°C;

C-I 81°C, N-I (74°C);



C-N 64°C, N-I 70°C;



C-N 73°C, N-I 86°C.

Further data relating to the transition temperatures for these compounds are given in Table 16, page 178.

1-(4'-Hydroxyphenyl)-4-pentylbicyclo(2.2.2)octane

48-50% Hydrobromic acid solution (50 cm^3) was added to 1-(4'-methoxyphenyl)-4-pentylbicyclo(2.2.2)octane (6.8 g, 0.024 mole) prepared by the above method. Enough of a solution of hydrogen bromide in glacial acetic acid (45% w:v) was then added to produce a homogeneous solution. The mixture was heated under reflux for 72 hr and the solid formed on cooling was filtered off. The product was decolourised with the aid of decolourising charcoal by heating under reflux in ethanol and purified by crystallisation from the same solvent. The yield was 3.9 g (60%), mp 123°C.

1-(4'-n-Alkoxyphenyl)-4-pentylbicyclo(2.2.2)octanes

A solution of pentyl iodide (2.0 g, 0.01 mole) in dry butanone (30 cm^3) was added dropwise to a stirred mixture of 1-(4'-hydroxyphenyl)-4-pentylbicyclo(2.2.2)octane (2.7 g, 0.01 mole) and anhydrous potassium carbonate (7.6 g, 0.055 mole) in dry butanone (40 cm^3). The mixture was then stirred and heated under reflux for 64 hr. The cooled mixture was poured into water (150 cm^3) and the whole was then shaken with ether (3 x 70 cm^3). The combined ethereal extracts were washed with water (3 x 40 cm^3), dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo*. The product was crystallised from light petroleum (bp 40-60°C) and obtained pure by crystallisation from the same solvent. The yield was 1.7 g (50%), C-I 75°C, S_B-N (50°C), N-I (70.5°C).

Similarly prepared were the compounds:†

1-pentyl-4-(4'-n-propyloxyphenyl)bicyclo(2.2.2)octane
(61%), C-I 72°C, N-I (65°C);

1-(4'-butyloxyphenyl)-4-n-pentylbicyclo(2.2.2)octane
(42%), C-N 65°C, N-I 77°C

1-(4'-hexyloxyphenyl)-4-n-pentylbicyclo(2.2.2)octane
(39%), C-N 66°C, S_B-N (54°C), N-I 79°C.

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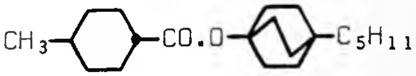
† Note that three related compounds containing shorter chain alkyloxy groups were also prepared by the method given previously for the terminally dialkyl substituted systems.

5.2.3 *Esters of Bicyclo(2.2.2)octane- and Cyclohexane-1-carboxylic Acids*

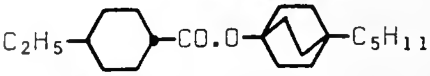
4-Pentylbicyclo(2.2.2)octane trans-*4-pentylcyclohexane-1-carboxylate*

A solution of 4-pentylbicyclo(2.2.2)octanol (2.0 g, 0.01 mole) in freshly distilled, dry pyridine (15 cm^3) was added dropwise to a boiling solution of *trans*-4-pentylcyclohexane-1-carboxylic acid chloride (2.2 g, 0.01 mole) in dry toluene (35 cm^3). The mixture was heated under reflux for 64 hr, and the excess of pyridine and toluene were removed *in vacuo*. The crude product was column chromatographed using silica gel as the stationary phase and a mixture of 2:1 (v:v) chloroform:light petroleun (bp 40-60°C) as the eluant. The final product was obtained by distillation (bp 185°C at 0.4 mm Hg) to give a room temperature smectic liquid crystal. The yield was 2.1 g (56%), C-S_B -3°C, S_B-I 107°C.

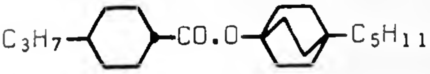
Similarly prepared in yields of 45-80% were the following esters:



C-S_B 22°C, S_B-I 49°C;

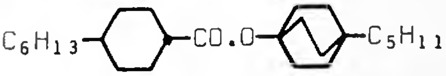


C-S_B 4°C, S_B-I 73°C;

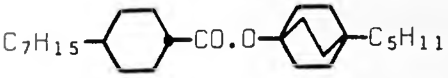


C-S_B 1°C, S_B-I 88°C;

C-S_B 9°C, S_B-I 104.5°C;

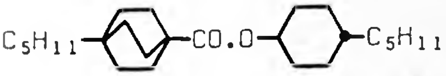


C-S_B 19°C, S_B-I 115°C;

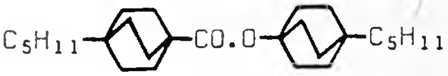


C-S_B 11°C, S_B-I 114°C;

C-S_B 18°C, S_B-N 79°C, N-I 92°C;



C-S_B 17°C, S_B-I 96°C



C-S_B, 40°C, S_B-I 191.5°C

Further data relating to the transition temperatures for these compounds are given in Table 18, page 186.

5.2.4 Compounds Incorporating the $-CH_2CH_2-$ Inter-Ring Linkage

1-(4'-Pentylphenyl)-2-(4"-pentylphenyl)ethane

A solution of 4-pentylbenzyl chloride (4.0 g, 0.02 mole) (prepared as described in Section 5.2.1) in dry ether (10 cm^3) was added dropwise to freshly cut sodium (0.9 g, 0.04 g atom) covered with dry ether (15 cm^3) and warmed, as necessary, to initiate the reaction. The mixture was then heated under reflux for 18 hr. To the cooled reaction mixture was added firstly methanol (15 cm^3), then 50% (v:v) aqueous ethanol (15 cm^3), and finally water (15 cm^3). The mixture was again heated under reflux for 1 hr, and then the cooled solution was poured into water and the whole shaken with ether (3 x 60 cm^3). The combined ethereal extracts were shaken with concentrated sulphuric acid (2 x 40 cm^3), 10% sodium bicarbonate solution (2 x 50 cm^3), and water (3 x 50 cm^3). The solution was dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo*. The product was crystallised from light petroleum (bp 40-60°C) and recrystallised from the same solvent. The yield was 0.74 g (23%), C-I 42°C.

*1-(*trans*-4'-n-Alkylcyclohexyl)-2-(*trans*-4"-n-alkylcyclohexyl)-ethanes*

These compounds were prepared by the above coupling procedure using the appropriate *trans*-4-n-alkylcyclohexylmethyl bromide (prepared as described in Section 5.2.1):

1-(*trans*-4'-propylcyclohexyl)-2-(*trans*-4"-propylcyclohexyl)ethane (22%), C-S_B 36°C, S_B-I 71.5°C;†

1-(*trans*-4'-pentylcyclohexyl)-2-(*trans*-4"-pentylcyclohexyl)ethane (18%), C-S_B 46°C, S_B-I 108°C;††

1-(*trans*-4'-hexylcyclohexyl)-2-(*trans*-4"-hexylcyclohexyl)ethane (28%), C-S_B 46°C, S_B-I 113°C.

trans-*4-n-Alkylcyclohexylacetonitriles*

Sodium cyanide (8.0 g, 0.163 mole) was dissolved in dry dimethyl sulphoxide (90 cm^3) by stirring at 150°C for several minutes. To this solution was added a solution of *trans*-4-pentylcyclohexylmethyl bromide (30.0 g, 0.122 mole) - prepared as described in Section 5.2.1 - in dry dimethyl sulphoxide (60 cm^3) and the temperature kept at 150°C for 90 min. The cooled reaction mixture was poured into ice-water (250 g) and the whole shaken with cyclohexane (3 x 70 cm^3). The combined organic extracts were washed with brine (3 x 50 cm^3), dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo* to yield the nitrile as a pale yellow oil. Since glc analysis gave a purity of 98.5%, the product was used in the hydrolysis step without purification. The yield was 22.5 g (96%).

Similarly prepared in yields >87% and of purity >98% were the nitriles:

trans-4-methylcyclohexylacetronitrile;
trans-4-ethylcyclohexylacetronitrile;
trans-4-propylcyclohexylacetronitrile;

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† Literature value,[111] C 35 S 73 I

†† Literature values, C 46 S 109 I,[112] C 49 S 108 I[111]

trans-4-butylcyclohexylacetronitrile;
trans-4-hexylcyclohexylacetronitrile;
trans-4-heptylcyclohexylacetronitrile, mp 35°C.

trans-*4-n-Alkylcyclohexylacetic acids*

trans-4-pentylcyclohexylacetronitrile (22.5 g, 0.117 mole) was heated under gentle reflux for 18 hr in a mixture of 50% (w:w) aqueous sulphuric acid (100 cm^3) and glacial acetic acid (250 cm^3). The excess of acetic acid was then removed *in vacuo* and the residue was shaken with dichloromethane (4 x 80 cm^3). The combined organic extracts were washed with water (3 x 60 cm^3), dried ($CaCl_2$), filtered, and the solvent was removed *in vacuo*. The product was crystallised from light petroleum (bp 40-60°C) and recrystallised from the same solvent. The yield was 20.7 g (84%), mp 59°C.

Similarly prepared in yields between 74 and 82% were the acids:

trans-4-methylcyclohexylacetic acid, mp 74°C;
trans-4-ethylcyclohexylacetic acid, mp 45°C;
trans-4-propylcyclohexylacetic acid, mp 51°C;
trans-4-butylcyclohexylacetic acid, mp 60°C;
trans-4-hexylcyclohexylacetic acid, mp 66°C;
trans-4-heptylcyclohexylacetic acid, mp 68°C.

4-Ethoxyphenyl trans-*4-pentylcyclohexylmethyl ketone*

A solution of ethoxybenzene (3.3 g, 0.027 mole) and *trans*-4-pentylcyclohexylacetic acid (3.0 g, 0.014 mole) - converted to the acid chloride - in dry dichloromethane (100 cm^3) was added to a suspension of crushed anhydrous aluminium chloride (2.3 g, 0.017 mole) in dry dichloromethane (80 cm^3) at a rate such that the reaction temperature did not rise above 10°C. After the addition, the solution was allowed to warm to room temperature and stirred for a further 18 hr. The reaction mixture was heated under gentle reflux for 45 min and then cooled. The solution was acidified with dilute hydrochloric acid, then poured into water (100 cm^3), and the whole shaken with chloroform (3 x 100 cm^3). The combined organic extracts were washed with water (2 x 60 cm^3), dried ($CaCl_2$), filtered, and the solvent was removed *in vacuo*. The dark brown solid was purified by crystallisation from a 10:1 (v:v) mixture of light petroleum (bp 40-60°C):methanol, followed by recrystallisation from light petroleum (bp 40-60°C). This procedure yielded the ketone as pale yellow crystals, 2.8 g (62%), mp 68°C.

Similarly prepared were the ketones:

trans-4-pentylcyclohexylmethyl 4-propylphenyl ketone
(65%), mp 45°C;

4-methoxyphenyl *trans*-4-pentylcyclohexylmethyl ketone
(71%), mp 58°C.

*1-(4'-Ethoxyphenyl)-2-(*trans*-4"-pentylcyclohexyl)ethane*

A solution of crushed anhydrous aluminium chloride (3.4 g, 0.025 mole) in dry ether (60 cm^3) was added dropwise to a suspension of lithium aluminium hydride (0.5 g, 0.013 mole) in dry ether (100 cm^3). To this was added dropwise, with stirring, a solution of 4-ethoxyphenyl *trans*-4-pentylcyclohexylmethyl ketone (2.0 g, 0.006 mole) in dry chloroform (20 cm^3) and the mixture was heated under reflux for 18 hr. Water (5 cm^3) was then cautiously added, followed by enough dilute hydrochloric acid to coagulate the inorganic salts. The ethereal layer was decanted off, the residual salts were rinsed several times with more ether, and the ethereal layers again decanted. The combined ethereal extracts were washed with water (2 x 100 cm^3), dried, filtered, and the solvent was removed *in vacuo*. The crude product was purified by column chromatography using silica gel as the stationary phase and a 2:1 (v:v) mixture of chloroform:light petroleum (bp 40-60°C) as the eluant. The pure material was obtained as a room temperature nematic liquid crystal by distillation (bp 150°C at 0.7 mm Hg); the yield was 1.4 g (74%), C-N 18°C, S_B-N (8°C), N-I 47°C.†

Similarly prepared were the compounds:

1-(4'-methoxyphenyl)-2-(*trans*-4"-pentylcyclohexyl)ethane (62%), C-N 30°C, N-I 34°C;

1-(*trans*-4'-pentylcyclohexyl)-2-(4"-propylphenyl)ethane (29%), C-S_B 3°C, S_B-I 16°C.††

<u>trans-*4-n-Alkylcyclohexylmethyl phenyl ketones*</u>

A solution of *trans*-4-propylcyclohexylacetic acid (6.0 g, 0.033 mole) - converted to the acid chloride - in dry benzene (80 cm^3) was added to a stirred solution of crushed anhydrous aluminium chloride (5.3 g, 0.04 mole) in dry benzene at a rate such that the reaction temperature was maintained between 5-10°C. The mixture was then allowed to warm to room temperature and stirred for 18 hr. It

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† Literature value,[114] C 18 N 46 I (no smectic phase quoted)

†† Literature value,[114] C 4 S_B 18 I

was then warmed at 50°C for 1 hr. The cooled solution was acidified with dilute hydrochloric acid, stirred for 30 min, and then poured into water (150 cm^3). The aqueous phase was separated off and shaken with ether (3 x 50 cm^3). The combined organic extracts were washed with water (2 x 80 cm^3), dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo*. The crude product was distilled (bp 130°C at 2.5 mm Hg) to yield a white solid which was crystallised from light petroleum (bp 40-60°C); the yield was 7.1 g (89%), mp 46°C.

Similarly prepared in yields ranging from 50-90% were the ketones:

trans-4-methylcyclohexylmethyl phenyl ketone, mp 55°C;
trans-4-ethylcyclohexylmethyl phenyl ketone, mp 43.5°C;
trans-4-butylcyclohexylmethyl phenyl ketone, mp 26°C;
trans-4-pentylcyclohexylmethyl phenyl ketone, mp 43°C;
trans-4-hexylcyclohexylmethyl phenyl ketone, mp 27°C;
trans-4-heptylcyclohexylmethyl phenyl ketone, mp 51°C.

*1-(*trans*-4'-n-Alkylcyclohexyl)-2-phenylethanes*

A solution of phenyl *trans*-4-propylcyclohexylmethyl ketone (2.0 g, 0.008 mole), potassium hydroxide (2.3 g, 0.040 mole), 98-100% hydrazine hydrate (4.6 g, 0.093 mole), and water (0.9 g, 0.050 mole) in diethylene glycol (175 cm^3) was heated at 130°C for 1.5 hr with stirring. The apparatus was adapted for distillation and the temperature raised to 205°C to drive off the excess of water and hydrazine hydrate. The apparatus was then changed back for heating under reflux and the mixture kept at 205°C for 4 hr. The cooled mixture was poured into ice-water (600 g) and the whole shaken with cyclohexane (4 x 80 cm^3). The combined organic extracts were washed with water (3 x 60 cm^3), dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo*. The pure material was obtained as a colourless liquid by distillation (bp 113^{0}C at 0.5 mm Hg); the yield was 1.0 g (54%), C-I 3^{0}C.

Similarly prepared in yields of 50-85% were the hydrocarbons:

1-(*trans*-4'-methylcyclohexyl)-2-phenylethane,
bp 85^{0}C at 0.05 mm Hg, C-I -5^{0}C;

1-(*trans*-4'-ethylcyclohexyl)-2-phenylethane,
bp 100^{0}C at 0.05 mm Hg, C-I 1^{0}C;

1-(*trans*-4'-butylcyclohexyl)-2-phenylethane,
bp 120^{0}C at 1 mm Hg, C-I -11^{0}C

1-(*trans*-4'-pentylcyclohexyl)-2-phenylethane,
bp 120^{0}C at 2 mm Hg, C-I -1.5^{0}C;

1-(*trans*-4'-hexylcyclohexyl)-2-phenylethane,
bp 125^{0}C at 0.07 mm Hg, C-I 9^{0}C;

1-(*trans*-4'-heptylcyclohexyl)-2-phenylethane,
bp 150^{0}C at 4.0 mm Hg, C-I 7^{0}C.

Further data relating to the transition temperatures for these compounds are given in Table 30, page 215.

*Methyl 4-(*trans*-4'-propylcyclohexylethyl)phenyl ketone*

This compound was prepared by the method described earlier for the preparation of 4-ethoxyphenyl *trans*-4-pentylcyclohexylmethyl ketone using acetyl chloride (0.8 g, 0.01 mole) and 1-phenyl-2-(*trans*-4'-propylcyclohexyl)ethane (2.3 g, 0.01 mole). The yield was 2.1 g (79%), mp 58^{0}C.

*1-(4'-Ethylphenyl)-2-(*trans*-4"-propylcyclohexyl)ethane*

This compound was prepared by the method used above for the preparation of 1-(*trans*-4'-n-alkylcyclohexyl)-2-phenylethanes, using

4-(*trans*-4'-propylcyclohexylethyl)phenyl methyl ketone (2.0 g, 0.007 mole). The yield was 0.7 g (37%), C-I -5°C. Further data relating to the transition temperatures for this compound are given on page 214.

*4-[2'-(*trans*-4"-n-Alkylcyclohexyl)ethyl]benzoyl chlorides*

Oxalyl chloride (2.8 g, 0.022 mole) was added over 5 min to a stirred suspension of aluminium chloride (1.5 g, 0.011 mole) in dry dichloromethane (27 cm^3) at 5°C. 1-Phenyl-2-(*trans*-4'-propylcyclohexyl)ethane (2.5 g, 0.011 mole) in dry dichloromethane (40 cm^3) was added dropwise over 1 hr to the stirred mixture at 5°C. Unused oxalyl chloride and phosgene were removed *in vacuo*; fresh, dry dichloromethane (40 cm^3) was then added to the mixture and the whole cooled to 0°C. The mixture was poured into an efficiently stirred mixture of calcium chloride (1.9 g) and crushed ice (34 g) such that the temperature was kept below 5°C. The organic layer was quickly separated and dried ($CaCl_2$), and the residual yellow liquid taken up in dry ether (50 cm^3), cooled to 0°C, and shaken successively with an ice-cooled 5% potassium hydroxide solution (50 cm^3) and ice-cooled water (50 cm^3). The extract was then dried (Na_2SO_4). After filtration, the solvent was removed *in vacuo* to yield the acid chloride as a pale yellow oil which was used immediately after distillation; the yield was 2.4 g (75%), bp 138°C at 0.02 mm Hg.

Similarly prepared in yields between 68 and 78% were the acid chlorides:

4-[2'-(*trans*-4"-methylcyclohexyl)ethyl]benzoyl chloride,
bp 120°C at 0.2 mm Hg

4-[2'-(*trans*-4"-ethylcyclohexyl)ethyl]benzoyl chloride,
bp 130°C at 0.01 mm Hg;

4-[2'-(*trans*-4"-butylcyclohexyl)ethyl]benzoyl chloride,
bp 150°C at 0.1 mm Hg;

4-[2'-(*trans*-4"-pentylcyclohexyl)ethyl]benzoyl chloride,
bp 155°C at 0.02 mm Hg;

4-[2'-(*trans*-4"-hexylcyclohexyl)ethyl]benzoyl chloride,
bp 160°C at 0.01 mm Hg;

4-[2'-(*trans*-4"-heptylcyclohexyl)ethyl]benzoyl chloride,
bp 170°C at 0.05 mm Hg

*4-[2'-(*trans*-4"-n-Alkylcyclohexyl)ethyl]benzamides*

A solution of 4-[2'-(*trans*-4"-propylcyclohexyl)ethyl]benzoyl chloride (2.4 g, 0.008 mole) in ethylene glycol dimethyl ether (30 cm^3) was added dropwise to a vigorously stirred solution of aqueous ammonia (d = 0.88, 125 cm^3) at 0°C. The mixture was shaken with ether (3 x 50 cm^3), and the combined ethereal extracts were washed with water (2 x 50 cm^3), dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo*. The product was obtained by crystallisation from ethanol and recrystallisation from a 1:1 (v:v) mixture of light petroleum (bp 40-60°C):ethanol; the yield was 1.6 g (72%), mp 215°C.

Similarly prepared in yields between 60 and 65% were the amides:

4-[2'-(*trans*-4"-methylcyclohexyl)ethyl]benzamide, mp 202°C;
4-[2'-(*trans*-4"-ethylcyclohexyl)ethyl]benzamide, mp 206°C;
4-[2'-(*trans*-4"-butylcyclohexyl)ethyl]benzamide, mp 192°C;
4-[2'-(*trans*-4"-pentylcyclohexyl)ethyl]benzamide, mp 210.5°C;
4-[2'-(*trans*-4"-hexylcyclohexyl)ethyl]benzamide, mp 202°C;
4-[2'-(*trans*-4"-heptylcyclohexyl)ethyl]benzamide, mp 198°C.

*1-(*trans*-4'-n-Alkylcyclohexyl)-2-(4"-cyanophenyl)ethanes*

Dry, redistilled thionyl chloride (2.8 g, 0.024 mole) was added dropwise to a stirred solution of 4-[2'-(*trans*-4"-propylcyclohexyl)-ethyl]benzamide (1.6 g, 0.006 mole) in dry dimethylformamide (100 cm^3) at room temperature. The mixture was stirred for 15 hr. Dilute hyrochloric acid was added to destroy the excess of thionyl chloride, and the whole was then poured into ice-water (200 g) and shaken with ether (3 x 100 cm^3). The combined ethereal extracts were washed with water (3 x 80 cm^3), dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo*. The crude solid was purified by column chromatography using silica gel as the stationary phase and chloroform as the eluant, followed by distillation under reduced pressure (bp 150°C at 1 mm Hg). The pure material was obtained by crystallisation from light petroleum (bp 40-60°C); the yield was 0.6 g (42%), C-N 38°C, N-I 44.5°C.

Similarly prepared in yields of 40-65% were the nitriles:

1-(4'-cyanophenyl)-2-(*trans*-4"-methylcyclohexyl)ethane,
C-I 51°C, N-I (-10°C);

1-(4'-cyanophenyl)-2-(*trans*-4"-ethylcyclohexyl)ethane,
C-I 43.5°C, N-I (12°C);

1-(*trans*-4-butylcyclohexyl)-2-(4"-cyanophenyl)ethane,
C-N 27°C, N-I 38.5°C;

1-(4'-cyanophenyl)-2-(*trans*-4"-pentylcyclohexyl)ethane,
C-N 30°C, N-I 51°C;

1-(4'-cyanophenyl)-2-(*trans*-4"-hexylcyclohexyl)ethane,
C-N 35°C, N-I 47°C

1-(4'-cyanophenyl)-2-(*trans*-4"-heptylcyclohexyl)ethane,
C-N 45°C, N-I 54.5°C.

*1-(4'-Hydroxyphenyl)-2-(*trans*-4"-pentylcyclohexyl)ethane*

This compound was prepared from the methyl ether (1.3 g, 0.0045 mole) by the demethylation procedure used on 1-(4'-methoxyphenyl)-4-pentylbicyclo(2.2.2)octane (see Section 5.2.2).

The product, 0.9 g (75%), mp 102.5°C, was crystallised from light petroleum (bp 40-60°C).

*1-(4'-n-Alkoxyphenyl)-2-(*trans*-4"-n-alkylcyclohexyl)ethane*

These compounds were prepared from the above phenol by the alkylation procedure used on 1-(4'-hydroxyphenyl)-4-pentylbicyclo(2.2.2)octane (see Section 5.2.2).

The following ethers were prepared in yields between 42 and 63% by this method:

1-(*trans*-4'-pentylcyclohexyl)-2-(4"-propyloxyphenyl)ethane,
C-S_B 24°C, S_B-N 31$\overset{\circ}{.}$5 C, N-I 33°C;

1-(4'-butyloxyphenyl)-2-(*trans*-4"-pentylcyclohexyl)ethane,
C-S_B 26°C, S_B-N 44.5°C, N-I 45.5°C;

1-(*trans*-4'-pentylcyclohexyl)-2-(4"-pentyloxyphenyl)ethane,
C-S_B 16°C, S_B-I 44°C;

1-(4'-hexyloxyphenyl)-2-(*trans*-4"-pentylcyclohexyl)ethane,
C-S_B 18°C, S_B-I 49.5°C.

4-Butylbicyclo(2.2.2)octylacetonitrile

4-Butylbicyclo(2.2.2)octylmethyl toluene-4-sulphonate (2.0 g, 0.0057 mole) was heated under reflux in dry dimethylformamide (20 cm^3) with potassium cyanide (0.44 g, 0.0068 mole) for 18 hr. A solution of iron (III) chloride (1.4 g, 0.0066 mole) in water (80 cm^3) and concentrated hydrochloric acid (5.6 cm^3) was added and the mixture was stirred at 50-60°C for 20 min. The cooled solution was poured into water (50 cm^3) and the whole shaken with ether

(3 x 80 cm^3). The combined ethereal extracts were washed with brine (2 x 60 cm^3), dried (Na_2SO_4), filtered, and the solvent was removed *in vacuo* to yield the crude nitrile as a brown oil. The product was purified by distillation under reduced pressure, yielding 1.0 g (90%), bp 135°C at 3 mm Hg.

4-Butylbicyclo(2.2.2)octylacetic acid

This compound was prepared from the substituted acetonitrile (1.0 g, 0.005 mole) by the acidic hydrolysis procedure used for preparing the *trans*-4-n-alkylcyclohexylacetic acids (see above). The yield was 0.67 g (61%), mp 85°C.

4-Butylbicyclo(2.2.2)octylmethyl 4-ethoxyphenyl ketone

This compound was prepared by the Friedel-Crafts acylation procedure used for the preparation of 4-ethoxyphenyl *trans*-4-pentylcyclohexylmethyl ketone (see above) using 4-butylbicyclo(2.2.2)octylacetic acid (0.67 g, 0.003 mole) - converted into the acid chloride - and ethoxybenzene. The product was crystallised from a 10:1 (v:v) mixture of light petroleum (bp 40-60°C):methanol, the yield was 0.40 g (40%), mp 67°C.

1-(4'-Butylbicyclo(2'.2'.2')octyl)-2-(4"-ethoxyphenyl)ethane

This compound was prepared by the reduction procedure used for the preparation of 1-(4'-ethoxyphenyl)-2-(*trans*-4"-pentylcyclohexyl)-ethane (see page 264), using 4-butylbicyclo(2.2.2)octylmethyl 4-ethoxyphenyl ketone (0.40 g, 0.0012 mole). The pure material was purified by column chromatography using silica gel as the stationary phase and a 2:1 (v:v) mixture of chloroform:light petroleum (bp 40-60°C) as the eluant. The final product was obtained by crystallisation from light petroleum (bp 40-60°C); the yield was 0.33 g (87%), C-N 57°C, N-I 87°C.

4-Pentylbicyclo(2.2.2)octylmethyl phenyl ketone

This compound was prepared by the Friedel-Crafts acylation procedure used for the analogous *trans*-4-n-alkylcyclohexylmethyl phenyl ketones using 4-pentylbicyclo(2.2.2)octylacetic acid (5.0 g, 0.021 mole) - a gift from BDH Chemicals Limited, Poole, Dorset. The product was purified by column chromatography using silica gel as the stationary phase and chloroform as the eluant, followed by crystallisation from light petroleum (bp 40-60°C) using cardice as the refrigerant. The yield was 3.55 g (56%), mp 44°C.

1-(4'-Pentylbicyclo(2'.2'.2')octyl)-2-phenylethane

This compound was prepared by the Huang-Minlon reduction procedure used for the analogous 1-(*trans*-4'-n-alkylcyclohexyl)-2-phenylethanes using 4-pentylbicyclo(2.2.2)octylmethyl phenyl ketone (3.4 g, 0.011 mole). The pure material was obtained as a colourless, low melting solid by distillation (bp 120°C at 4 mm Hg). The yield was 3.0 g (91%), C-I 24°C, N-I (8.5°C).

4-[2'-(4"-Pentylbicyclo(2".2".2")octyl)ethyl]benzoyl chloride

This compound was prepared from 1-(4'-pentylbicyclo(2'.2'.2')-octyl)-2-phenylethane (3.0 g, 0.011 mole) by the modified Friedel-Crafts procedure, employing oxalyl chloride, used for the analogous 4-[2'-(*trans*-4"-n-alkylcyclohexyl)ethyl]benzoyl chlorides. The product was purified by distillation to yield the acid chloride as a pale yellow oil. The yield was 2.3 g (62%), bp 160°C at 0.1 mm Hg.

4-[2'-(4"-Pentylbicyclo(2".2".2")octyl)ethyl]benzamide

This compound was prepared by the ammonolysis procedure used for the analogous 4-[2'-(*trans*-4"-n-alkylcyclohexyl)ethyl]benzamides using 4-[2'-(4"-pentylbicyclo(2".2".2")octyl)ethyl]benzoyl chloride (2.25 g, 0.007 mole). The product was crystallised from a 6:1 (v:v) mixture of light petroleum (bp 40-60°C):ethanol to yield the amide as a white powder 1.30 g (61%), mp 245°C.

1-(4'-Cyanophenyl)-2-(4"-pentylbicyclo(2".2".2")octyl)ethane

This compound was prepared by the dehydration procedure used for the analogous 1-(*trans*-4'-n-alkylcyclohexyl)-2-(4"-cyanophenyl)-ethanes using 4-[2'-(4"-pentylbicyclo(2".2".2")octyl)ethyl]benzamide (1.2 g, 0.004 mole). The pure nitrile was obtained by crystallisation twice from light petroleum (bp 40-60°C), using cardice as refrigerant. The yield was 0.59 g (52%), C-N 76°C, N-I 113°C.

CONCLUSION

The reader is referred to the end of each individual section, giving the results for a particular system that has been studied, for a more detailed summary of the results.

In total over one hundred liquid crystal materials and additives have been synthesised; these represent nearly thirty different structural types, which in some cases required over ten experimental steps to produce. Overall, the chemistry involved was interesting and varied, and centred around the widely different properties of the ring systems (benzene, *trans*-cyclohexane and bicyclo(2.2.2)octane) and the inter-ring linking groups ($-CH_2O-$, single bond, -CO.O-, and $-CH_2CH_2-$) used.

The compounds produced illustrate the importance of molecular structure with respect to the potential of the material for liquid crystal formation. For example, the choice of the ring systems, inter-ring linkage (if any), terminal and lateral substituents incorporated into the molecule are shown to be critical to the liquid crystal properties exhibited by the material.

Useful properties are observed for many of these novel materials, from the points of view of chemical stability, mesophase range, and general physical and electro-optic properties. Consequently, several different types of material investigated here compare very favourably with the various liquid crystal compounds used commercially. These materials therefore appear to be well suited for use in electro-optic displays.

By carrying out this programme of work in a relatively systematic manner, not only have useful materials for liquid crystal applications been developed, but also it has been possible to relate some of the properties, including some of the less well understood physical and electro-optic parameters of liquid crystals, to the molecular structure of the material involved. Although many of these parameters still defy rationalisation in molecular structural terms, only by pursuing such relationships will the underlying principles governing such parameters ever be adequately understood.

This work emphasises the fact that none of the currently available theories relating to the liquid crystal state is able to account satisfactorily for all of the experimental data, and it would seem that some unified approach involving the more relevant aspects of the most realistic models may provide a better description of this state of matter.

Finally, this work illustrates the point that academic and applied research are not mutually exclusive, and that they can be carried out in an integrated manner to produce more meaningful results than those that would have arisen if either single approach had been adopted.

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