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# Liquid Crystal Compounds Incorporating the Trans-1,4-Substituted Cyclohexane Ring System

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# Liquid Crystal Compounds Incorporating the Trans-1,4-Substituted Cyclohexane Ring System

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A number of esters and other compounds containing a trans-1,4-substituted cyclohexane ring system have been prepared, and the liquid crystal thermal stabilities of these new mesogens are discussed in relation to those of their analogues containing the 1,4-phenylene ring. The observed effects are discussed in terms of a possible thermal energy absorption by the cyclohexane ring in causing minor conformational changes.

Other physical properties of these new mesogens are also discussed with particular reference to their potential in applications. In relation to electro-optical display devices, such properties as birefringence, dielectric anistropy, viscosity etc., are important parameters, and the new materials have been assessed in this context as possible additives to the 4-*n*-alkyl- and 4-*n*-alkyloxy-4′-cyanobiphenyls for producing a favorable combination of physical parameters.

Also reported is a liquid crystal mixture which has a 100°C nematic range and which contains only materials which are aliphatic. This mixture is assessed for its potential application as an anistropic solvent in analytical techniques such as ultra-violet spectroscopy and nuclear magnetic resonance spectroscopy.

## INTRODUCTION

Materials which form nematic liquid crystals are perhaps the best known and the most fully studied of the various types of mesogen, largely because of their application in electro-optical display devices. In general, nematogens developed for display device applications have been compounds whose molecules consist of a central aromatic core made up of 1,4-phenylene groups linked together either directly, as in the biphenyls, or *via* a central, linking group such as —N=CH— or —CO·O— in the case of Schiff's bases and esters. Additionally the molecules contain terminal substituents, such as alkyl, alkyloxy, and/or cyano groups.[1,2]

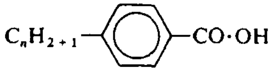
Variations in the physical properties of nematogens containing a central, linking group can be traced to the nature of the central linkage, provided that the terminal substituents are kept the same. As a result certain adverse properties such as colour and chemical/photochemical instability can be associated with these central, linking groups, and the commercial development of electro-optical display devices using the 4-*n*-alkyl-4′-cyanobiphenyls and related nematogens has been successful because these materials contain *no* labile, central linkage. The effect of having only one good aromatic core structure does however restrict considerably the variety which can be achieved in various physical parameters of the nematogens. Yet appreciable variations in these properties are desirable for many of the different applications of nematic liquid crystals in electro-optical display devices. To overcome these limitations, new nematogens emulating the properties of the biphenyls, but having a greater variety of physical properties, are desirable.

Since many of these properties such as viscosity, elastic constants, dielectric anisotropy, nematic range and birefringence must depend appreciably on the structure of the central core of the liquid crystal molecule, we became interested in new mesogens containing a *trans*-1,4-substituted cyclohexane ring.

Apart from the cholesteryl *n*-alkanoates, very few non-aromatic liquid crystals were known until quite recently.[3] An exception was the *trans*-4-*n*-alkylcyclohexane-1-carboxylic acids, first reported in 1967 by Schubert.[4]

TABLE I

Thermodynamic data for the compounds (I)



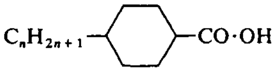
(I)

| *n* | C-N (°C) | N-I (°C) |
|---|---|---|
| 4 | 99.5 | 115.0 |
| 5 | 88.5 | 126.5 |
| 6 | 97.5 | 115.0 |
| 7 | 101.0 | 120.0 |
| 8 | 98.0 | 108.0 |

C = crystal; N = nematic; I = isotropic liquid

TABLE II

Thermodynamic data for the compounds (II)



(II)

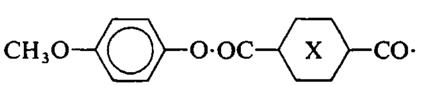
| $n$ | C-$S_B$/N (°C) | $S_B$-N (°C) | N-I (°C) |
|---|---|---|---|
| 4 | 36–40 | - | 86.0 |
| 5 | 53.7 | - | 101.0 |
| 6 | 31.7 | 47.2 | 96.4 |
| 7 | 47.0 | 53.4 | 100.8 |
| 8 | 36.0 | 86.2 | 96.0 |

C = crystal; $S_B$ = smectic B; N = nematic; I = isotropic liquid

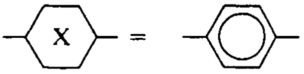
These provided early evidence for the effects of replacing the 1,4-phenylene ring system on the liquid crystal properties of the 4-*n*-alkylbenzoic acids. A comparison of the data in Tables I and II shows that although the cyclohexane acids have much lower melting points and lower nematic to isotropic liquid transition temperatures, their overall nematic temperature ranges are greater.

It must be made clear, however, that the comparisons between Table I and II provide an evaluation of the two ring systems in a liquid crystal system which is of a rather special kind, since the molecules can exist as hydrogen-bonded species of the type shown in Figure I.

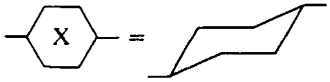
Later work by Dewar, *et al.*[5] compared the effect of the two ring systems in the diester (III).



(III)

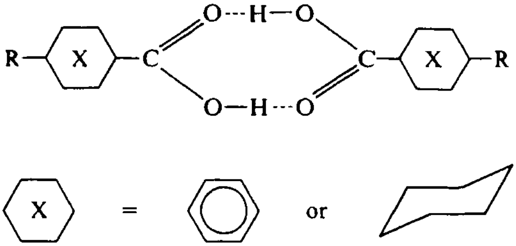


C-N, 209°C; N-I, 285°C (III(a))



C-N, 142°C; N-I, 245°C (III(b))

The higher N-I value for the ester (III(a)) was interpreted in terms of its greater molecular rigidity, linearity, and polarisability, and an enhancement of conjugation *via* the π-electrons. The conclusion was that all four of the above factors made contributions to liquid crystal thermal stability, but that in this particular instance, the effect of having a cyclohexane ring in the *centre* of the molecule greatly emphasised the importance of the rigidity factor.

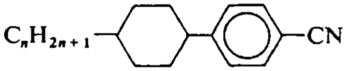


where

FIGURE 1

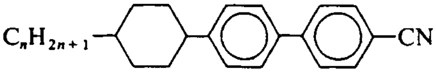
This was however in contrast to the results that Demus[6,7] obtained for the *trans*-4-*n*-alkylcyclohexane-1-carboxylate analogues of some benzoate esters for which the cyclohexane compounds had a considerably enhanced liquid crystal thermal stability (see Results and Discussion). Our current interest in cyclohexane materials was in fact initiated by these results of Demus.

Some time after we had begun the present work on new cyclohexane materials, a further development arose when results were published[8] on the effects of replacing one ring of the 4-*n*-alkyl-4′-cyanobiphenyls and the 4-*n*-alkyl-4″-cyano-*p*-terphenyls by a *trans*-1,4-disubstituted cyclohexane ring. The results related to compounds of the type.



(PCH compounds)

and



(BICH compounds)

The PCH compounds had higher N-I values than the biphenyls, but the BICH compounds had lower N-I transition temperatures than the analogous *p*-terphenyls; further reference will be made to these compounds later.

## RESULTS AND DISCUSSION

As a first step in investigating the effect of replacing a 1,4-phenylene ring by a cyclohexane ring, we decided to investigate a wider range of esters than Demus[6,7] had studied by interacting the trans-4-n-alkylcyclohexane-1-carboxylic acid chlorides with various phenols.

### Trans-4-*n*-alkylcyclohexane-1-carboxylic acids

Highly pure trans-isomers (> 99% by glc) of the required 4-*n*-alkylcyclohexane-1-carboxylic acids (II) are fairly readily prepared, and the data already quoted in Table 2 are for our materials. Very recently, Billard and Mamlok[9] have examined the trans acids with $n = 5$–$7$ and 10 and have established that the smectic phases are orthogonal $S_B$ phases. We agree with this assignment, and that the phases formed by the nematics on cooling are not plastic crystal phases as originally reported.[4] Some discrepancies do exist between the transition temperatures reported by Billard and Mamlok[9] and those we quote in Table 2, and these are as yet unexplained.

These acids as such provide a useful series of reasonably low melting nematogens of a totally aliphatic nature. Their value is contributed to by the fact that quite large melting point depressions are obtained on mixing different homologues; it is noted that a binary mixture will give rise to *three* dimers of the kind shown in Figure 1. For example, a mixture of 30 wt % of the cyclohexane acid (II) with $n = 6$ and 70 wt % of the acid with $n = 4$ cannot be totally frozen. This particular mixture is not a eutectic composition, but the last trace of solid always melts by $-15$°C to give a nematic phase which persists until 82°C. The dielectric anisotropy of the mixture is weakly positive ($+0.3$) and it is readily obtained with a high resistivity ($> 10^{11}\ \Omega$cm); the viscosity is 40 cP at 22°C. The mixture does give a good twisted nematic alignment, with a threshold of 10 V, but the stability of these acids is probably not good enough for them to be considered for display devices.

However, the birefringence of the mixture is very low (0.047–0.051 over the wavelength range 425–600 nm) and Figure 2 shows a plot of the refractive indices for the mixture as a function of wavelength. The mixture is also transparent to visible and ultra-violet light over a wide frequency range.

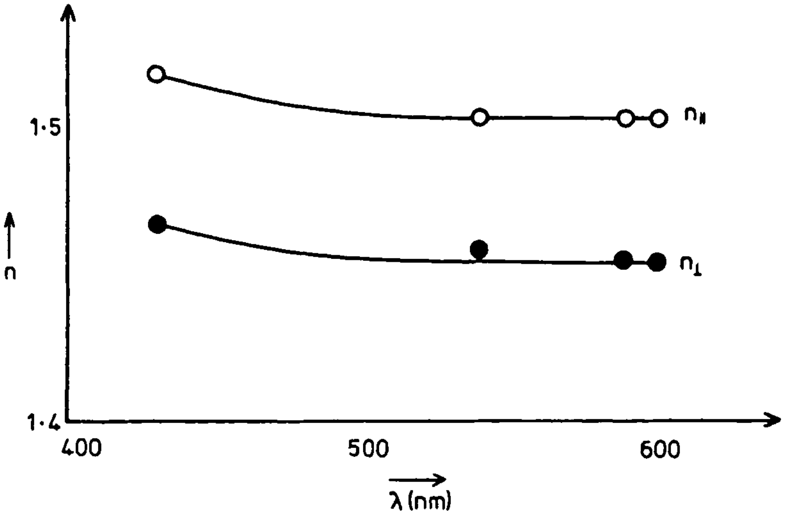


FIGURE 2

Using an unaligned sample in a cell of 27 μ thickness, 80% transmission of light is obtained from 4000 nm down to 285 nm. Thereafter, the absorbance rises (e.g., to 40% at 260 nm), but using carefully compensated cells, it is possible to extend studies of solutes dissolved in such a mixture down to even 220 nm. The ability to align the mixture readily, coupled with its positive dielectric anistropy and its *negative* diamagnetic anistropy[12] therefore make such readily accessible mixtures of interest as solvents for both ultra-violet and visible spectroscopy of oriented solutes and for nmr spectroscopy, i.e., they share the merits of the 4-alkyl-4′-cyanocyclohexylcyclohexanes as spectroscopic solvents.[10] The latter materials do not absorb ultra-violet light above 200 nm, whereas the analogous phenycyclohexanes and biphenyls are transparent down to 285–290 nm and ca. 320 nm, repectively.

### Esters of trans-4-*n*-alkylcyclohexane-1-carboxylic acid

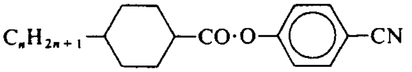
Results for the esters prepared from the acids (II) using 4-cyanophenol, 4-cyano-4′-hydroxybiphenyl and 2-cyano-6-hydroxynaphthalene are given in Tables III, IV, and V respectively.

The relative variations in the properties of the esters (IV), (V), and (VI) caused by the use of different phenol moieties were consistent with those found for the fully aromatic analogues by Coates and Gray.[11] However, it is interesting to note that whilst the N-I transition temperatures of compounds (IV) and (VI) are higher (15–26°C) then those of the analogous benzoate esters, those of the esters (V) are about the same.

In relation to applications in electro-optical display devices, it has already been found[7] that the *trans*-4-*n*-alkylcyclohexane-1-carboxylates have lower viscosities than the analogous benzoate esters. Therefore from the point of view of rise and decay times, the use of compounds (IV), (V), and (VI) in nematic eutectic mixtures for electro-optical devices is advantageous over that of their aromatic analogues.

TABLE III

Thermodynamic data for the esters (IV)



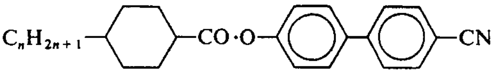
(IV)

| *n* | C-N (°C) | N-I (°C) |
|---|---|---|
| 3 | 55.0 | 68.4 |
| $4^6$ | 44.6 | 68.6 |
| $5^7$ | 48.3 | 79.2 |
| 7 | 54.5 | 80.6 |

C = crystal; N = nematic; I = isotropic liquid

TABLE IV

Thermodynamic data for the esters (V)

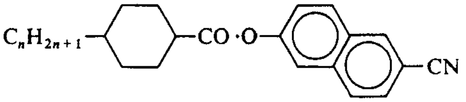

(V)

| $n$ | C-$S_A$/N (°C) | $S_A$-N (°C) | N-I (°C) |
|---|---|---|---|
| 1 | 102.0 | - | 213.3 |
| 2 | 84.4 | - | 229.8 |
| 3 | 94.3 | - | 248.6 |
| 4 | 79.8 | - | 241.9 |
| 5 | 85.2 | - | 240.8 |
| 6 | 83.6 | 143.2 | 226.7 |
| 7 | 91.2 | 179.0 | 227.5 |

C = crystal; N = nematic; $S_A$ = smectic A; I = isotropic liquid

TABLE V

Thermodynamic data for the esters (VI)


(VI)

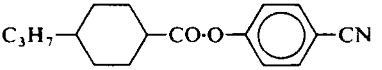
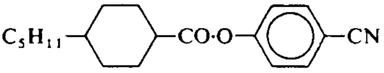
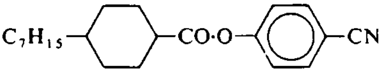
| $n$ | C-$S_A$/N (°C) | $S_A$-N (°C) | N-I (°C) |
|---|---|---|---|
| 1 | 113.5 | - | 118.6 |
| 2 | 76.0 | - | 144.3 |
| 3 | 106.2 | - | 172.6 |
| 4 | 85.0 | - | 166.8 |
| 5 | 86.5 | - | 168.8 |
| 6 | 72.6 | - | 160.5 |
| 7 | 80.0 | 106 | 161 |

C = crystal; $S_A$ = smectic A; N = nematic; I = isotropic liquid

In order to assess other physical properties relevant to display applications, a non-eutectic, but room temperature mixture of three of the esters (IV) (Mixture 1) was prepared.

Although the dielectric anisotropy is much less than that of their benzoate analogues, the lower viscosity of the cyclohexyl derivatives and their lower birefringence still combine to give these materials some advantages over their aromatic counterparts for certain functions and types of electro-optical display.

MIXTURE I

| Components | wt % | C-N (°C) | N-I (°C) |
|---|---|---|---|
|  | 32 | 12-16 | 74.6 |
|  | 38 | | |
|  | 30 | | |

Birefringence ($\Delta n$) = 0.12 at 22°C
Dielectric anisotropy ($\Delta \varepsilon$) = 8.1 at 0.95 × N-I (57.2°)
Threshold voltage ($V_{10}$) in a 6 $\mu$m, PVA aligned, twisted nematic cell = 1.4 V

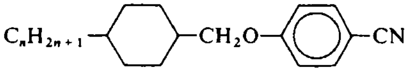
### Cyclohexylmethyl ethers

Although these cyclohexane esters, like the aromatic esters, provide a convenient source of nematogenic compounds, they are naturally not as chemically stable as materials such as the cyanobiphenyls and the PCH compounds. Therefore we prepared the compounds (VII), (VIII), and (IX) in which the ester linkage has been replaced by the —$CH_2O$— linkage. The relevant reaction scheme is shown in Figure 3.

In this case, the analogous fully aromatic materials are labile benzyl ethers which we have not examined. However, a comparison of the thermodynamic data for the compounds in Tables VI, VII, and VIII with those for the analogous esters (Tables III, IV, and V) shows that the N-I transition temperatures have been reduced by 30–60°C, while the melting points have in most cases been increased. Also, the smectic properties for the series

TABLE VI

Thermodynamic data for the compounds (VII)


(VII)

| n | C-N/I (°C) | N-I (°C) | $\Delta H$ kcal mole$^{-1}$ |
|---|---|---|---|
| 3 | 61.6 | (36.3) | 8.0 |
| 4 | 70.0 | (36.0) | 6.7 |
| 5 | 74.3 | (48.6) | 5.6 |
| 7 | 48.0 | 53.5 | 9.6 |

C = crystal; N = nematic; I = isotropic liquid; $\Delta H$ = enthalpy of fusion for the most stable crystal form.

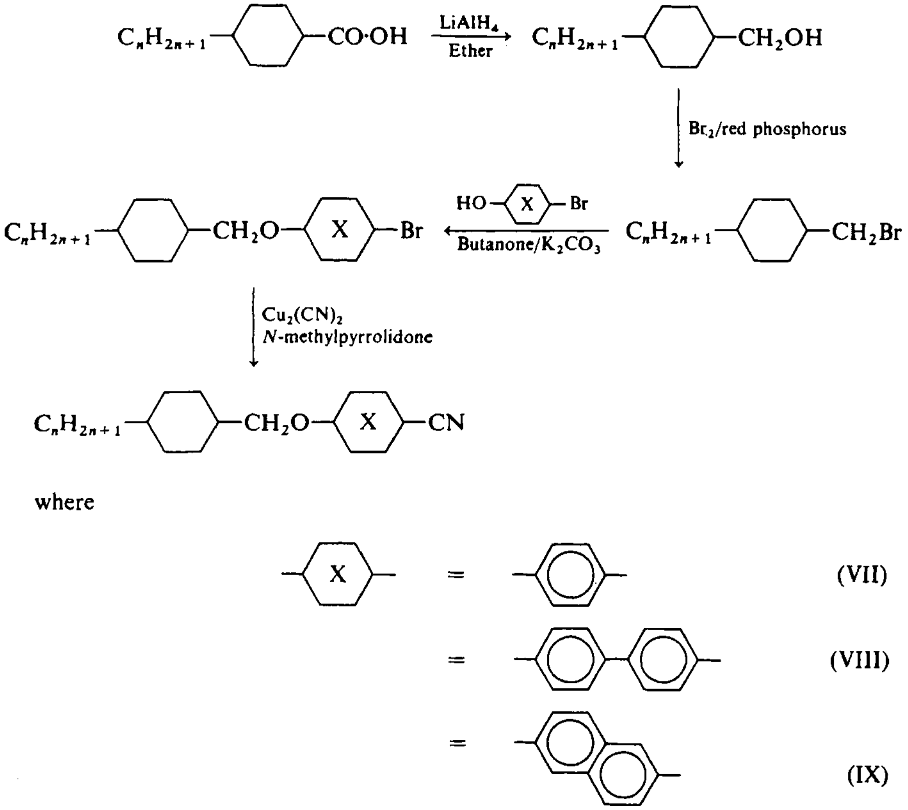
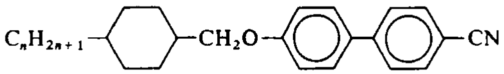


FIGURE 3

## TABLE VII

Thermodynamic data for the compounds (VIII)

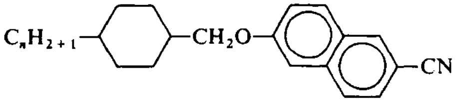


| *n* | C-$S_A$/N (°C) | $S_A$-N (°C) | N-I (°C) | Δ*H* kcal mole$^{-1}$ |
|---|---|---|---|---|
| 3 | 124.0 | - | 198.8 | 4.8 |
| 4 | 93.0 | - | 193.0 | 7.5 |
| 5 | 107.0 | 136.3 | 193.2 | 4.8 |
| 6 | 107.3 | 161.8 | 185.7 | 5.2 |
| 7 | 107.4 | 171.5 | 183.6 | 7.0 |
| 8 | 96.0 | 173.7 | 177.2 | 4.9 |

C = crystal; $S_A$ = smectic A; N = nematic; I = isotropic liquid; Δ*H* = enthalpy of fusion for the most stable crystal form.

TABLE VIII

Thermodynamic data for the compounds (IX)



(IX)

| *n* | C-N (°C) | N-I (°C) | Δ*H* kcal mole$^{-1}$ |
|---|---|---|---|
| 3 | 91.0 | 112.0 | 6.1 |
| 4 | 82.4 | 109.0 | 7.6 |
| 5 | 87.3 | 114.5 | 6.0 |
| 6 | 81.0 | 110.0 | 9.4 |
| 7 | 88.0 | 108.5 | 8.4 |

C = crystal; $S_A$ = smectic A; N = nematic; I = isotropic liquid; Δ*H* = enthalpy of fusion for the most stable crystal form.

(VIII) are more pronounced than those for the series (V). Nonetheless, the use of the cyclohexane ring system with this particular linkage has generated three quite valuable, new sets of mesogens.

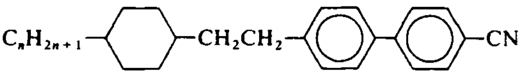
## β-Cyclohexylethyl compounds

Still with the object of obtaining stable materials containing the cyclohexane ring system, the use of the $—CH_2—CH_2—$ linking group between the cyclohexane ring and the aromatic nucleus was next examined. The comparative effects of the $—CH_2O—$ and $—CH_2—CH_2—$ bridging groups on liquid crystal properties can be judged from the data in Tables VII and IX.

The results show that while the N-I transition temperatures have been decreased by only 5–10°, a considerable lowering of the melting points has

TABLE IX

Thermodynamic data for the compounds (X)



(X)

| *n* | C-$S_A$/N (°C) | $S_A$-N (°C) | N-I (°C) | Δ*H* kcal mole$^{-1}$ |
|---|---|---|---|---|
| 3 | 77.2 | - | 193.8 | 5.5 |
| 4 | 71.8 | 74.5 | 182.2 | 6.1 |

C = crystal; $S_A$ = smectic A; N = nematic; I = isotropic liquid; Δ*H* = enthalpy of fusion for the most stable crystal form.

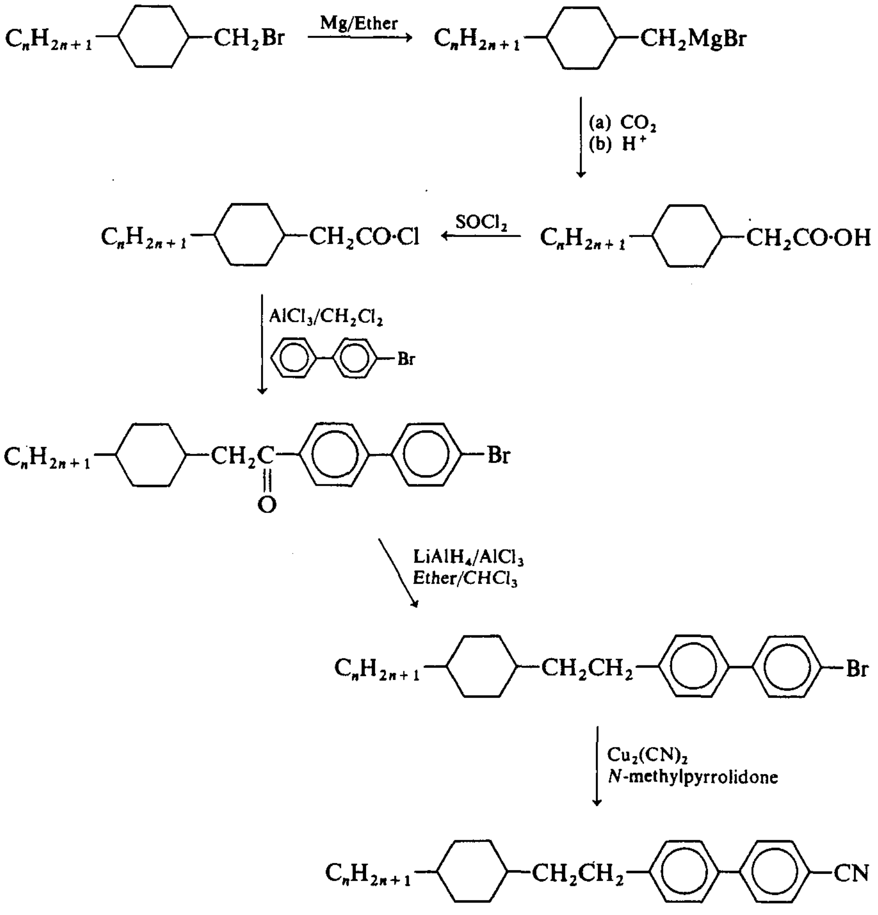


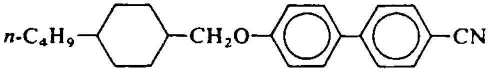
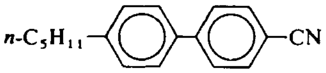
FIGURE 4

occurred as a result of using the —$CH_2$—$CH_2$— group. The N-I values of these materials are also around 30°C higher than those of the corresponding *β*-(4-alkylphenyl)ethyl analogues.

The compounds (X) were prepared from the trans-4-*n*-alkylcyclohexyl-l-methyl bromide (Figure 3) by the reaction scheme in Figure 4.

Since these new materials with —$CH_2O$— and —$CH_2$—$CH_2$— linking groups are closely related structurally to the 4-n-alkyl- and 4-*n*-alkyloxy-4′-cyanobiphenyls, their chemical/photochemical stabilities are equivalent, and they are potentially of interest for display device applications. For example, the use of the compounds (VIII) as additives to increase the clearing point of a low melting nematogen is demonstrated by the binary mixture 2.

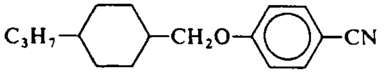
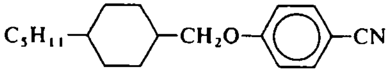
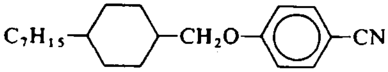
MIXTURE 2

| Components | wt % | C-N (°C) | N-I (°C) |
|---|---|---|---|
|  | 14 | 11 | 58 |
|  | 86 | | |

Birefringence ($\Delta n$) = 0.22 at 23°C.
Dielectric Anistropy ($\Delta\varepsilon$) = 12.2 at 0.95 × N-I (41°C).

In order to establish the physical properties of the compounds (VII) on their own, a mixture (non-eutectic) similar in composition to mixture 1 was prepared.

MIXTURE 3

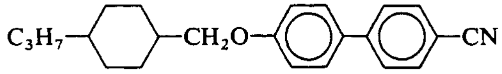
| Components | wt % | C-N[a] (°C) | N-I (°C) |
|---|---|---|---|
|  | 30 | 10–18 | 45 |
|  | 40 | | |
|  | 30 | | |

[a] This is the melting point of a metastable solid which forms on cooling quickly to −30°C. However, after some time the mixture segregates and the components only melt/redissolve completely on heating to 50°C.
Birefringence ($\Delta n$) = 0.11 at 25°C.
Dielectric Anisotropy ($\Delta\varepsilon$) = 10.9 at 0.95 × N-I (29°C).
Threshold voltage ($V_{10}$) in a 6 $\mu$m, PVA aligned, twisted nematic cell = 1.9 V (rms) at 100 Hz.

These materials may therefore be used in admixture with the 4-n-alkyl-4′-cyanobiphenyls to produce variations in birefringence, without adversely affecting the dielectric anisotropy.

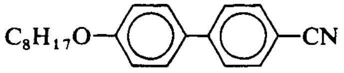
## The relative thermal stabilities of the nematic phases of materials incorporating the 1,4-phenylene and trans-1,4-disubstituted cyclohexane rings

A comparison of the N-I transition temperatures of compounds (XI) and (XII) is of interest.



(XI)

C-N, 124°C; N-I, 198.8°C



(XII)

C-$S_A$, 54.5°C; $S_A$-N, 67°C; N-I, 80°C

The two molecules are of similar length, but the trans-1,4-disubstituted cyclohexane has a very much higher nematic thermal stability. We can infer therefore that the cyclohexane ring system is much more rigid than a unit of 4$CH_2$ groups of the more extended alkyl chain compound (XII), and that because the molecule (XI) is more rigid, the nematic phase will resist the the disorientating effects of thermal energy and persist until a higher temperature.

However, as shown by the work of Dewar, large decreases in N-I transition temperatures occur when the central 1,4-phenylene group of the diester (III) is replaced by a *trans*-1,4-disubstituted cyclohexane ring. Dewar concluded that the loss of rigidity was the main factor causing the decrease of some 40°C in nematic thermal stability, and certainly one would expect the cyclohexane ring to be less rigid than the 1,4-phenylene ring.

The surprising results were those first obtained by Demus[6,7] showing that esters of *trans*-4-alkylcyclohexane-1-carboxylic acid have higher N-I values than the corresponding benzoate esters, and his results are confirmed by our data in Tables III and V. Remember however that the esters in Table IV which have N-I temperatures in the range 213–248°C are of about the *same* nematic thermal stability as the benzoate analogues.

Then the results were published[8] on the PCH and BICH materials. In the case of the PCH materials, increases in the fairly low N-I values of the biphenyls were again found, but for the BICH materials, the rather high N-I values of the terphenyls were reduced, both by changing the 1,4-phenylene ring carrying the alkyl substituent to a *trans*-1,4-disubstituted cyclohexane ring.

These results suggested therefore that the relative nematic thermal stabilities of such systems could not be treated simply by assuming an increase in molecular flexibility on passing from a 1,4-phenylene to a *trans*-1,4-disubstituted cyclohexane system. Indeed it seemed clear that replacement of a 1,4-phenylene ring at the *end* of a reasonably extended, rigid *core structure* in a molecule by a trans-1,4-disubstituted cyclohexane ring could lead to quite large increases in the N-I transition temperatures. The new data reported here on the increased N-I temperatures of the β-cyclohexylethyl compounds compared with their β-phenylethyl analogues also support this conclusion.

FIGURE 5

To try to explain these results, we have considered the generally accepted[13–17] conformational situation which applies to cyclohexane and substituted cyclohexanes. Accordingly, in the *trans*-1,4-disubstituted cyclohexane ring, both substituents prefer to be in equatorial positions, with the ring adopting the chair conformation (Figure 5). This does not mean that the molecule is compelled to behave as if it were *exclusively* in this conformation or rigidly fixed in any way. Therefore in the context of the esters (IV) and (VI), a plausible explanation for their increased liquid crystal thermal stability may be offered in terms of the molecular motions that may occur on heating cycles, compared with those for their fully aromatic analogues.

With the stiff rod-like molecules of the fully aromatic esters, thermal energy may rapidly cause an increase in molecular motions of a type which rapidly break-down the partial order of the nematic phase. On the other hand, with the cyclohexane esters, some of the heat energy may be absorbed by the cyclohexane ring in causing *minor* conformational changes, e.g., chair to twisted chair, and, in this situation it would not be until a higher temperature that the total molecular vibrations would cause the break-up of the nematic order. Such an effect would of course be temperature dependent. Thus at the much higher temperatures involved for the nematic phases of the esters (V), the thermal energy may be sufficiently high to cause more serious conformational changes in the cyclohexane ring system e.g., from the linear diequatorial chair to the non-linear diaxial chair, such that a proportion at least of the molecules adopt a conformation which is not linear. This would then cause a depression in the N-I transition temperatures. Consequently, these esters have similar transition temperatures to their aromatic analogues. A similar situation may also occur with the diester (III), *except* that formation of say the di-axial chair conformer at higher temperatures produces a molecule in which the bulk of the *trans*-1,4-substituents greatly emphasises the nonlinearity of the molecule and causes a greater reduction in the clearing point (N-I).

In agreement with these ideas, is the fact that the PCH compounds (with relatively low N-I values) have higher transition temperatures, whereas the BICH compounds (with rather high N-I values) have lower transition temperatures than their fully aromatic counterparts.

On passing from a 1,4-phenylene to a trans-1,4-disubstituted cyclohexane analogue the extent of the increase in N-I value (when fairly low temperatures are involved) or of the decrease in N-I value (when higher temperatures are involved) is obviously quite variable. This implies, not unnaturally, that the dual role of the cyclohexane ring in acting as an energy sink at lower temperatures and as a centre at which a loss of molecular linearity can occur at higher temperatures varies significantly from system to system. That is, it will depend on whether the cyclohexane ring is centrally or terminally situated, and if terminally situated, on the extent of the rigid core to which it is attached. Factors relating to molecular fit (steric factors) and the strength of the intermolecular interactions will also vary from system to system and determine the importance of these dual roles of the cyclohexane ring.

## CONCLUSION

In conclusion it may be said that the properties of the new nematogens described, together with those of other related materials such as the PCH and BICH compounds reported by other workers,[8] strongly emphasise the importance of derivatives of cyclohexane in this field of study, and suggest that future programmes of research on liquid crystal materials should include investigations of further cyclohexane and related systems.

## EXPERIMENTAL

### Physical measurements and purity of materials

Transition temperatures were measured using a Nikon L-Ke polarising microscope fitted with a Mettler FP52 heating stage and FP5 control unit. The refractive index data were obtained from measurements made using an Abbé refractometer. Dielectric anisotropies were measured by an experimental technique[18] developed by colleagues at the Royal Signals and Radar Establishment, Malvern, England.

The purities of all the final products synthesised and of all those reaction intermediates which were isolated were carefully checked by glc and their structures confirmed by infra-red spectroscopy. In addition, satisfactory elemental analysis results and the correct mass ions were obtained for all the materials, and further structural checks were carried out wherever desirable using a Jeol JNM-4H 100 MHz instrument for nuclear magnetic resonance spectra.

## Preparation of materials

*4-n-alkylbenzoic acids* These known materials were prepared by Friedel-Craft's acetylation[19] of the *n*-alkylbenzenes, followed by hypobromite oxidation[20] of the 4-*n*-alkylacetophenones to the corresponding acids.

*trans-4-n-alkylcyclohexane-1-carboxylic acids* A solution of the 4-*n*-alkylbenzoic acid (0.2 mole) in sodium hydroxide (0.205 mole) dissolved in water (160 ml) was hydrogenated in the presence of Raney nickel catalyst (10 g) in an autoclave (1 l) at 190°C and at a pressure of 170 atm for 30 hr. On cooling, the catalyst was filtered off and the filtrate shaken with ether. The aqueous layer was separated and acidified. The precipitated acids were extracted into ether and the ether extracts washed with water and dried over anhydrous magnesium sulphate. The ether was distilled off giving a mixture of the *cis* and *trans* acids which was dissolved in ethanol (225 ml). Solid thiourea (45 g) was dissolved with heating in the solution obtained. Upon cooling, the inclusion compound of the *trans* 4-*n*-alkylcyclohexane-1-carboxylic acid crystallised from solution in the form of fine white needles. These were filtered off and dried. A further amount of solid thiourea (35 g) was dissolved in the filtrate. Again on cooling, more inclusion compound and some thiourea crystals came out of the solution. These were again filtered off and dried. The filtrate was concentrated to about half its volume and left to cool; again the crystals which formed were filtered off and dried.

The combined crystallisates of inclusion compound and some thiourea were dissolved in 5% aqeuous potassium hydroxide (*ca* 150 ml). The pure *trans* acid liberated upon acidification with concentrated hydrochloric acid was taken up in ether, after which the ethereal solution was dried over anhydrous magnesium sulphate. The ether was distilled off and the crude *trans* acid crystallised from approximately the same volume of acetone (*ca* 30 ml), cooling to −25°C. Yields were somewhat variable (30–53%) for the acids whose transition temperatures are recorded in Table II.

*4-cyano-4′-hydroxybiphenyl* This was prepared by the method of Gray *et al.*[21] by cyanation of 4-bromo-4′-hydroxybiphenyl.

*6-cyano-2-hydroxynaphthalene* This was prepared by a cyanation procedure similar to that used[21] for 4-cyano-4′-hydroxybiphenyl. The starting material was commercially available 6-bromo-2-hydroxynaphthalene. The product (55%) was purified by recrystallisation from toluene containing a little ethanol. The m.p. was 160°C.

*Esters (IV)–(VI)* (Tables III, IV, and V) These were prepared by interacting equimolar amounts of the relevant acid chlorides and phenols in pyridine solution. After evaporating off the solvent under reduced pressure, purification was achieved by dissolving the residue in a minimum volume of chloroform and using chromatography on a column of silica gel which was eluted with chloroform. The combined fractions of ester were then recrystallised until their transition temperatures were constant. Solvents used were either hexane or methanol/ethanol, where appropriate, and yields were of the order 50–65%.

*trans-4-n-alkylcyclohexylmethanols* The *trans*-4-*n*-alkylcyclohexane-1-carboxylic acid (0.14 mole) was dissolved in sodium dried ether (150 ml) and added dropwise to a vigorously stirred suspension of lithium aluminium hydride (0.3 mole) in sodium dried ether (300 ml). When addition was completed the mixture was heated under reflux for 2 hr. On cooling, water was cautiously added to destroy the excess of lithium aluminium hydride. The mixture was then poured into a 20% aqueous solution of hydrochloric acid and stirred until the inorganic salts had dissolved. The product was extracted into ether; the extract was then washed with water and dried ($MgSO_4$). The ether was evaporated off and the residue distilled. Yields were in the range 68–76%.

| | |
|---|---|
| *trans*-4-*n*-propylcyclohexylmethanol | bp 148°C at 25 mm Hg |
| *trans*-4-*n*-butylcyclohexylmethanol | bp 130°C at 20 mm Hg |
| *trans*-4-*n*-pentylcyclohexylmethanol | bp 162°C at 25 mm Hg |
| *trans*-4-*n*-hexylcyclohexylmethanol | bp 157°C at 20 mm Hg |
| *trans*-4-*n*-heptylcyclohexylmethanol | bp 167°C at 20 mm Hg |
| *trans*-4-*n*-octylcyclohexylmethanol | bp 175°C at 20 mm Hg |

*trans-4-n-alkylcyclohexylmethyl bromides* The *trans*-4-*n*-alkylcyclohexylmethanol (0.12 mole) was added to red phosphorus (0.03 g atom) and warmed gently (*ca* 30°C) using an oil bath. Bromine (0.14 mole) was added dropwise to the mixture. When addition was complete (*ca* 0.5 hr), the temperature of the oil bath was raised to 180°C for 1 hr. After this time, the mixture was allowed to cool, shaken with ether and filtered. The filtrate was washed with water, then dried ($Na_2SO_4$). The ether was removed by distillation and the residue distilled. Yields were in the range 52–59%.

| | |
|---|---|
| *trans*-4-*n*-propylcyclohexylmethyl bromide | bp 112°C at 15 mm Hg |
| *trans*-4-*n*-butylcyclohexylmethyl bromide | bp 130°C at 20 mm Hg |
| *trans*-4-*n*-pentylcyclohexylmethyl bromide | bp 165°C at 25 mm Hg |
| *trans*-4-*n*-hexylcyclohexylmethyl bromide | bp 161°C at 20 mm Hg |
| *trans*-4-*n*-heptylcyclohexylmethyl bromide | bp 174°C at 20 mm Hg |
| *trans*-4-*n*-octylcyclohexylmethyl bromide | bp 186°C at 20 mm Hg |

*4-(trans-4′-n-alkylcyclohexylmethoxy)bromobenzenes and 2-(trans-4′-n-alkylcyclohexylmethoxy)-6-bromonaphthalenes* Either 4-bromophenol or 2-bromo-6-hydroxynaphthalene (0.04 mole) potassium carbonate (0.20 mole), and the *trans*-4-*n*-alkylcyclohexylmethyl bromide (0.04 mole) were added to butan-2-one (120 ml). The mixture was stirred and heated under reflux for 48 hr. On cooling, the mixture was poured into water (400 ml) and the mixture shaken with ether (3 × 100 ml). The combined ether extracts were washed with water (2 × 100 ml) and dried ($MgSO_4$). The ether was removed by distillation and the residue crystallised from ethanol. The average yield was about 64%.

| | |
|---|---|
| 4-(*trans*-4′-*n*-propylcyclohexylmethoxy)bromobenzene | mp 58°C |
| 4-(*trans*-4′-*n*-butylcyclohexylmethoxy)bromobenzene | mp 45°C |
| 4-(*trans*-4′-*n*-pentylcyclohexylmethoxy)bromobenzene | mp 56°C |
| 4-(*trans*-4′-*n*-heptylcyclohexylmethoxy)bromobenzene | mp 57°C |
| 2-(*trans*-4′-*n*-propylcyclohexylmethoxy)-6-bromonaphthalene | mp 113°C |
| 2-(*trans*-4′-*n*-butylcyclohexylmethoxy)-6-bromonaphthalene | mp 102.2°C |
| 2-(*trans*-4′-*n*-pentylcyclohexylmethoxy)-6-bromonaphthalene | mp 103°C |
| 2-(*trans*-4′-*n*-hexylcyclohexylmethoxy)-6-bromonaphthalene | mp 99°C |
| 2-(*trans*-4′-*n*-heptylcyclohexylmethoxy)-6-bromonaphthalene | mp 93°C |

*4-(trans-4″-n-alkylcyclohexylmethoxy)-4′-bromobiphenyls* These were prepared by a previously[22] described alkylation procedure. The physical constants for the compounds prepared in this way are given in Table X.

*4-(trans-4′-n-alkylcyclohexylmethoxy)benzonitriles, 2-(trans-4′-n-alkylcyclohexylmethoxy)-6-cyanonphthalenes and 4-(trans-4″-n-alkylcyclohexylmethoxy)-4′-cyanobiphenyls* These were prepared by cyanation of the bromo-compounds by the method described by Gray *et al.*[21] for the 4-*n*-alkoxy-4′-cyanobiphenyls. The physical constants for these compounds are given in Tables VI, VII, and VIII.

*trans-4-n-alkylcyclohexylacetic acids* The *trans*-4-*n*-alkylcyclohexylmethyl bromide (0.08 mole) was converted into the corresponding Grignard reagent and the ethereal solution poured onto a mixture of ether (300 ml) and crushed, solid carbon dioxide. After stirring for 2 hr, the mixture was acidified with concentrated hydrochloric acid. The product was extracted into ether and the combined extracts were washed with water until the washings were neutral to Congo-red indicator. The ether extracts were dried ($Na_2SO_4$) and the ether was removed by distillation. The solid residue was crystallised from *n*-hexane.

| | |
|---|---|
| *trans*-4-*n*-propylcyclohexylacetic acid | mp 51°C; yield 64% |
| *trans*-4-*n*-butycyclohexylacetic acid | mp 56.8°C; yield 61% |

TABLE X

Physical constants for the 4-(*trans*-4″-*n*-alkylcyclohexylmethoxy)-4′-bromobiphenyls

| Alkyl | C-$S_A$ or N (°C) | $S_E$-$S_A$ (°C) | $S_A$-N (°C) | N-I (°C) |
|---|---|---|---|---|
| *n*-propyl | 158.0 | | (154.0) | 178.0 |
| *n*-butyl | 127.2 | (126.0) | 158.4 | 174.9 |
| *n*-pentyl | 140.0 | (122.0) | 161.0 | 176.0 |
| *n*-hexyl | 118.6 | (113.8) | 162.2 | 171.3 |
| *n*-heptyl | 129.0 | (110.0) | 163.5 | 170.3 |
| *n*-octyl | 115.6 | (106.0) | 163.3 | 166.3 |

C = crystal; $S_E$ = smectic E; $S_A$ = smectic A; N = nematic; I = isotropic liquid; transition temperatures in round brackets are for monotropic transitions.

*1-(trans-4′-n-propylcyclohexyl)-2-(4″-[4‴-cyanobiphenylyl]ethane and 1-(trans-4′-n-butylcyclohexyl)-2-(4″-[4‴-cyanobiphenylyl])ethane* These were prepared by first converting the *trans*-4-*n*-alkylcyclohexylacetic acid into the acid chloride which was then used to acylate 4-bromobiphenyl. The resulting ketone was reduced and the product cyanated. The methods employed and the yields obtained were similar to those reported earlier[23] for the fully aromatic analogues. Melting points and other transition temperatures for the intermediates are given below. Data for the cyano compounds are given in Table IX.

*trans*-4-*n*-propylcyclohexylmethyl 4-(4′-bromobiphenylyl) ketone
mp 150°C
*trans*-4-*n*-butylcyclohexylmethyl 4-(4′-bromobiphenylyl) ketone
mp 133°C
1-(*trans*-4′-*n*-propylcyclohexyl)-2-(4″-[4‴-bromobiphenylyl]ethane,
C-N, 128°C; N-I, 162°C
1-(*trans*-4′-*n*-butylcyclohexyl)-2-(4″-[4‴bromobiphenylyl])ethane,
C-N, 103°C; N-I, 143°C

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