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# Synthesis and Properties of Some 2- n-Alkyl-6-(4′-cyanophenyl)-naphthalenes -3,4-dihydronaphthalenes, and -1, 2, 3, 4-tetra-hydronaphthalenes

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# Synthesis and Properties of Some 2-*n*-Alkyl-6-(4′-cyanophenyl)-naphthalenes -3,4-dihydronaphthalenes, and -1,2,3,4-tetra-hydronaphthalenes†

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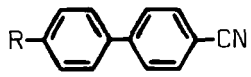
Five (ethyl to *n*-hexyl) of each of the series of 2-*n*-alkyl-6-(4′-cyanophenyl)-naphthalenes and -3,4-dihydronaphthalenes, and three (ethyl, *n*-butyl, and *n*-hexyl) of the corresponding series of -1,2,3,4-tetrahydronaphthalenes were prepared.

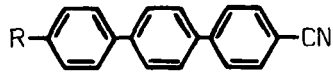
All these compounds exhibit nematic phases (no smectic phases were found) and the nematic-isotropic transition temperatures of these compounds are compared with those of the corresponding 4-*n*-alkyl-4′-cyano biphenyls and 4-*n*-alkyl-4″-cyano-*p*-terphenyls. Some explanation is given for the observed nematic thermal stabilities of the titled compounds. Assessments of the viscosities of the titled compounds have been carried out, and the effects on viscosity of substituting 2-*n*-pentyl-6-(4′-cyanophenyl) naphthalene for 4-*n*-pentyl-4″-cyano-*p*-terphenyl in commercially available mixtures have also been investigated.

## INTRODUCTION

The 4-*n*-alkyl-4′-cyanobiphenyls and 4-*n*-alkyl-4″-cyano-*p*-terphenyls [(I) and (II)] discovered by Gray[1] and his group at Hull University in the early 1970's have had enormous success in their application in twisted nematic display devices.




(I)



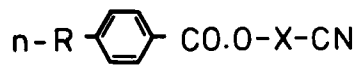

(II)

R = n-alkyl

†Presented at the Ninth International Liquid Crystal Conference, Bangalore, India, December 6–10, 1982.

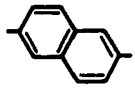
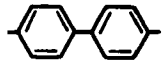
TABLE I

Comparison of the thermal data for the cyano-substituted esters of structure (III)[3]




(III)

Transition temperatures (°C)

| |  | |  | |  | |
|---|---|---|---|---|---|---|
| X | | | | | | |
| n—R | C—N/I | N—I | C—N | N—I | C—N | N—I |
| $C_4H_9$ | 67.0° | 42.6° | 81.0° | 142.3° | 110.0° | 242.0° |
| $C_5H_{11}$ | 64.5° | (57.8) | 96.5° | 154.3° | 109.0° | 237.5° |
| $C_6H_{13}$ | 44.5° | 47.0° | 73.0° | 138.4° | 91.0° | 229.6° |
| $C_7H_{15}$ | 44.0° | 57.0° | 69.5° | 135.3° | 92.0° | 224.4° |

( ) Indicates a monotropic transition temperature.

The innovative feature of these materials was the omission from the molecular structures of a central linking group between the rings. In many other mesogenic systems, such groups have led to chemical or photochemical instability, but the advent of the cyano-biphenyls and -*p*-terphenyls proved that the central linking group was not essential for the formation of liquid crystal phases.

Comparison of the nematic-isotropic liquid transition temperatures ($T_{N-I}$ values) of various mesogens[1,2,3] which have the general structure (III) in Table I, illustrates the fact that the 2,6-naphthyl group lies intermediate between the phenyl and biphenylyl groups in promoting nematic thermal stability, and that these compounds can also have lower melting points than their biphenylyl analogues. Although the 4-*n*-alkyl-4″-cyano-*p*-terphenyls (II) have very high $T_{N-I}$ values and are excellent additives for increasing the clearing points of mesogenic mixtures, these compounds also have high melting points and rather low solubilities, and these are less than desirable features.

We therefore decided to examine some naphthalene analogues of the biphenyl system (I), together with certain related dihydro- and tetrahydro-systems, in the hope that, although the $T_{N-I}$ values might be lower than the terphenyls (II), overall advantage might be gained as a result of lowering the melting points. The compounds selected for study were the 2-*n*-alkyl-6-(4′-cyanophenyl)-naphthalenes, -3,4-dihydronaphthalenes and -1,2,3,4-tetrahydronaphthalenes.

It was, of course, recognized that thermal information relating to a new mesogenic system is only one of many considerations which must be taken into account in any evaluation of the usefulness of that system in its application to electro-optical display devices. If the naphthalene analogues of the biphenyls (I) seemed interesting, a more comprehensive assessment of certain other of their physical properties was palnned.

In this connection, it is worth noting that the reaction pathway (Figure 1) chosen to prepare the 2,6-disubstituted phenylnaphthalenes can also be used to prepare both the dihydro- and tetrahydro-analogues (see experi-

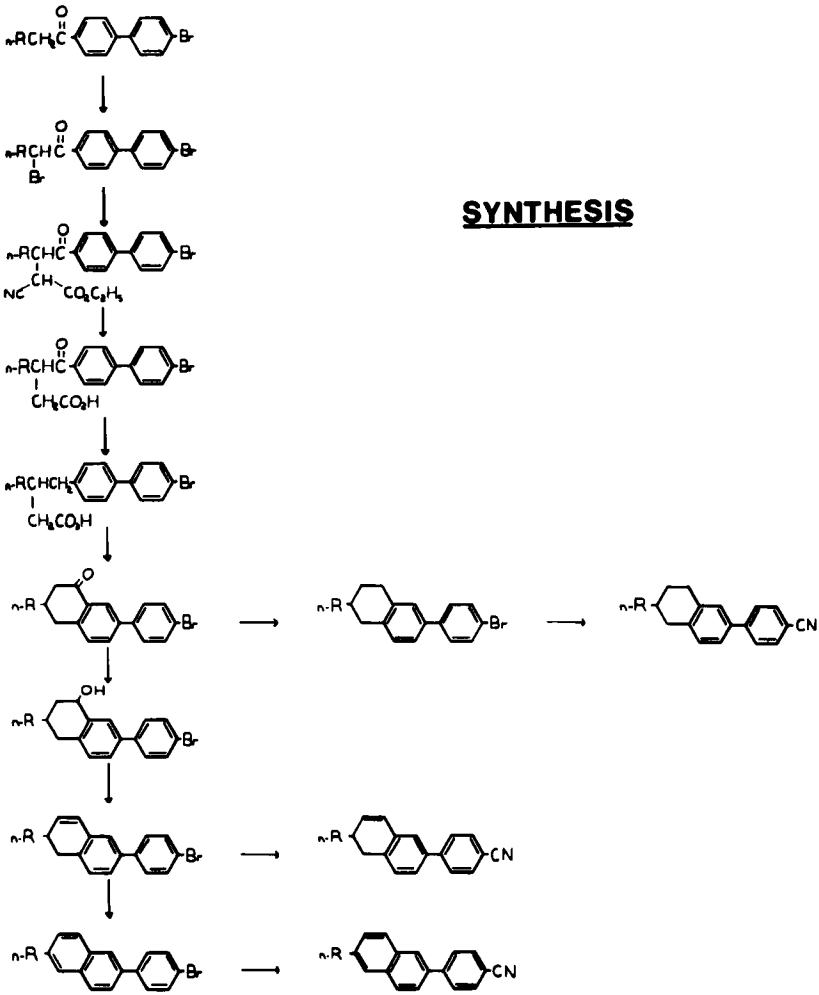



FIGURE 1 Reaction pathway for the synthesis of the phenylnaphthalenes and related compounds.

mental section for further details). These partially hydrogenated compounds would also be mesogenic in their own right, and their viscosities (for a given *R* group) could be lower than that of the corresponding fully aromatic compound. This effect has been demonstrated clearly by the introduction of a *trans*-cyclohexyl ring in place of a phenyl ring in the carboxylic acid moiety of the 4-*n*-alkylphenyl 4-alkylbenzoates.[4] Also reduction in the aromaticity of the system allows the birefringence to be reduced — an advantageous effect in phase change displays.

## RESULTS AND DISCUSSION

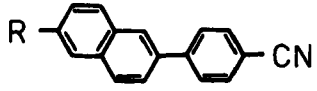
### Transition temperatures

Altogether five (ethyl to *n*-hexyl) of each of the 2-alkyl-6-(4′-cyanophenyl)-naphthalenes and -3,4-dihydronaphthalenes and three (ethyl, *n*-butyl and *n*-hexyl) of the -1,2,3,4-tetrahydronaphthalenes were prepared. The melting points, enthalpies of fusion and $T_{N-I}$ values of the above compounds are given in Tables II, III and IV respectively.

Plots of the *N-I* transition temperatures against the number of carbon atoms in the *n*-alkyl chain for the 2-*n*-alkyl-6-(4′-cyanophenyl)-naphthalenes and 2-*n*-alkyl-6-(4′-cyanophenyl)-3,4-dihydronaphthalenes are given in Figures 2 and 3 respectively. The plots show the usual odd-even alternation of the *N-I* transition temperature; two falling curves may be drawn through the points for the 2-*n*-alkyl-6-(4′-cyano-phenyl)-naphthalenes, but for the -3,4-dihydronaphthalenes, we have two ascending

TABLE II

Thermal data for the 2-*n*-alkyl-6-(4′-cyanophenyl)-naphthalenes

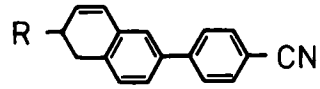



| n—R | Transition Temperature (°C) C—N | N—I | Enthalpy of fusion[a] (kJ mol$^{-1}$) |
|---|---|---|---|
| $C_2H_5$ | 119.5° | 135.3° | 23.4 |
| $C_3H_7$ | 107.5° | 144.5° | 18.8 |
| $C_4H_9$ | 74.5° | 129.3° | 20.9 |
| $C_5H_{11}$ | 85.5° | 128.0° | 26.0 |
| $C_6H_{13}$ | 59.0° | 117.0° | — |

[a]See footnote, Table IV.

TABLE III

Thermal data for the 2-*n*-alkyl-6-(4′-cyanophenyl)-3,4-dihydronaphthalenes




| n—R | Transition temperature (°C) C—N/C—I | N—I | Enthalpy of fusion[a] (kJ mol$^{-1}$) |
|---|---|---|---|
| $C_2H_5$ | 60.5° | (54.5°) | 23.0 |
| $C_3H_7$ | 72.0° | 82.5° | 25.1 |
| $C_4H_9$ | 39.0° | 74.6° | 20.9 |
| $C_5H_{11}$ | 87.0° | (84.5)° | 33.5 |
| $C_6H_{13}$ | 49.5° | 79.7° | 24.2 |

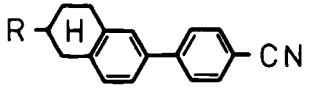
[a]See footnote, Table IV.

curves. In both graphs, the lower curve represents the homologues with an even number of carbon atoms in the *n*-alkyl chain.

The melting points for these two series of compounds do not show any regular trends with increasing alkyl chain length, but in both series, the compounds contained an even number of carbon atoms in the alkyl chain, i.e., the butyl and hexyl homologues, have relatively low melting points, and hence have wide nematic ranges.

TABLE IV

Thermal data for the 2-*n*-alkyl-6-(4′-cyanophenyl)-1,2,3,4-tetrahydronaphthalenes




| n—R | Transition temperature (°C) C—N/C—I | N—I | Enthalpy of fusion[a] (kJ mol$^{-1}$) |
|---|---|---|---|
| $C_2H_5$ | 82.5° | (81.6°) | 24.3 |
| $C_4H_9$ | 72.0° | 98.6° | — |
| $C_6H_{13}$ | 75.5° | 102.4° | — |

( ) Indicates a monotropic transition.

[a]The enthalpies of fusion were measured using a Stanton-Redcroft Differential Thermal Analyzer (model 671), using pure indium as the standard. The $\Delta H$ values for the $T_{N-I}$ were in the range 0.6–1.0 kJ mol$^{-1}$.

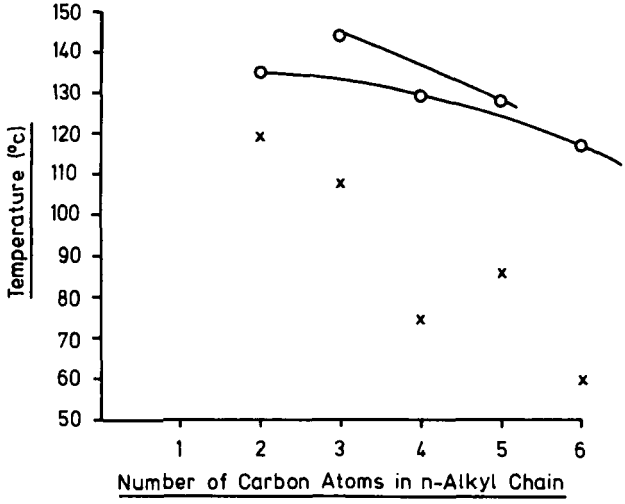



FIGURE 2 Graph of $T_{C-N}$ and $T_{N-I}$ against number of carbon atoms in the *n*-alkyl chain for the 2-*n*-alkyl-6-(4′-cyanophenyl) naphthalenes.
(*X* = *C-N*; *O* = *N-I*)

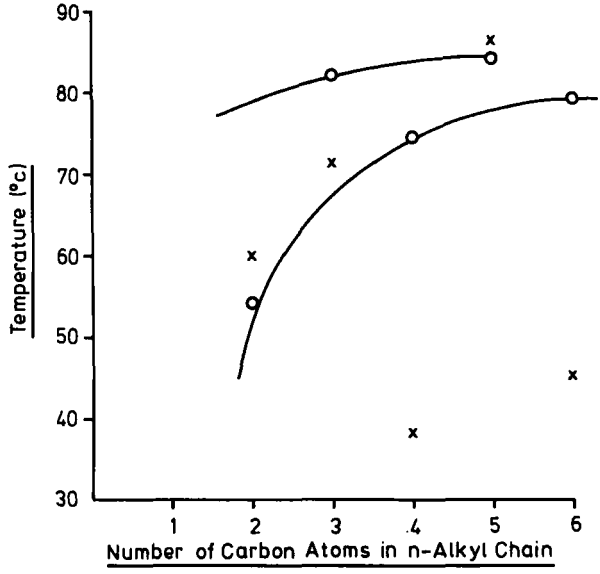



FIGURE 3 Graph of $T_{N-I}$, $T_{C-N}$ and $T_{C-I}$ against number of carbon atoms in the *n*-alkyl chain for the 2-*n*-alkyl-6-(4′-cyano-phenyl)-3,4-dihydronaphthalenes.
(*X* = *C-N* or *C-I*; *O* = *N-I*)

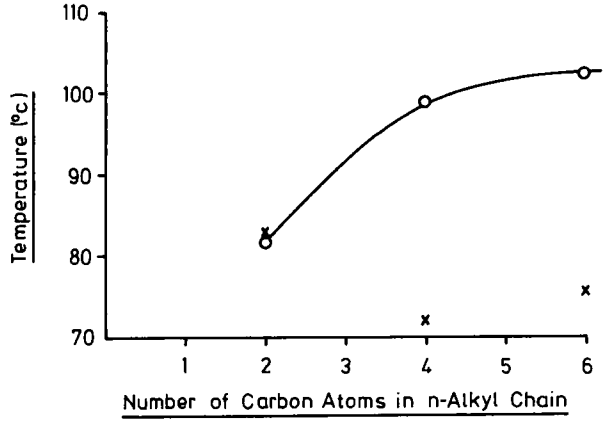
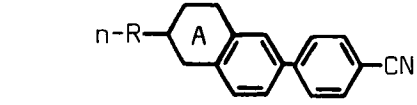



FIGURE 4 Graph of $T_{N-I}$, $T_{C-N}$ and $T_{C-I}$ against the number of carbon atoms in the *n*-alkyl chain for 2-*n*-alkyl-6-(4′-cyanophenyl)-1,2,3,4-tetrahydronaphthalenes. ($X$ = *C-N* or *C-I*; $O$ = *N-I*)

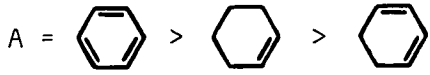
The $T_{N-I}$ curve for the three 2-*n*-alkyl-6-(4′-cyanophenyl)-1,2,3,4-tetrahydronaphthalenes is similar in shape to that for the even members of the 2-*n*-alkyl-6-(4′-cyanophenyl)-3,4-dihydronaphthalenes (Figure 4).

The following conclusions can be drawn by comparing the thermal data given in Tables II, III, and IV.

1. From the $T_{N-I}$ values for the ethyl, *n*-butyl and *n*-hexyl homologues of the three different series, the following nematic thermal efficiency order can be compiled.




(IV)




The difference between the $T_{N-I}$ values obtained by averaging the transition temperatures for the three homologues of the 2-*n*-alkyl-6-(4′-cyanophenyl)-naphthalenes and the -tetrahydronaphthalenes was 33.0°, while that between the former compounds and the dihydronaphthalenes was 57.6°.

2. In general, the trend of the melting points for the three series mirror the above nematic thermal efficiency order, with the dihydronaphthalenes usually having the lowest melting points. The exception to this is for the

hexyl homologues, for which the tetrahydronaphthalene has the highest melting point.

3. The 2-alkyl-6-(4′-cyanophenyl)naphalenes gave the widest nematic ranges (for the butyl homologue, 54.8°; for the hexyl homologue, 58.0°).

4. In both the phenyl- and dihydro-naphthalene series, the butyl and hexyl homologues had very low melting points.

5. No smectic phases were observed for any of the three series of compounds.

6. When the $T_{N-I}$ values for the three series of naphthalene compounds (Tables II, III, and IV) are compared with those for the 4-*n*-alkyl-4′-cyanobiphenyls and the related *p*-terphenyls,[1,2,3] the following nematic thermal efficiency order is obtained.

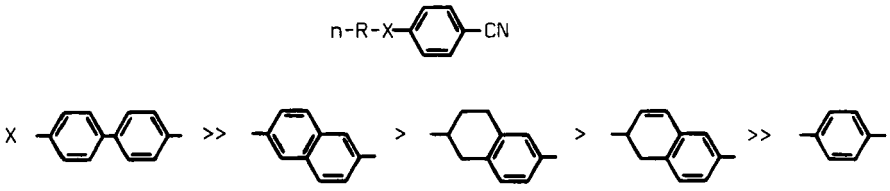
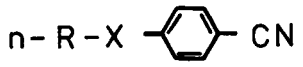
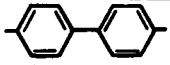
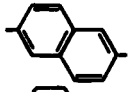
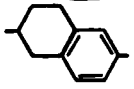
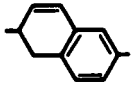



TABLE V

The thermal data from which the Nematic Thermal Efficiency Order has been compiled




| X | n—R | Average N—I transition temperature (°C) | |
|---|---|---|---|
|  | $C_5H_{11}$, $C_6H_{13}$ | 233.5° | |
| | | | 108.7° |
|  | $C_4H_9$, $C_5H_{11}$, $C_6H_{13}$ | 128.8° | |
| | | | 20.3° |
|  | $C_4H_9$, $C_6H_{13}$ | 100.5° | |
| | | | 20.9° |
|  | $C_4H_9$, $C_5H_{11}$, $C_6H_{13}$ | 79.6° | |
| | | | 53.4° |
|  | $C_4H_9$, $C_5H_{11}$, $C_6H_{13}$ | 26.2° | |

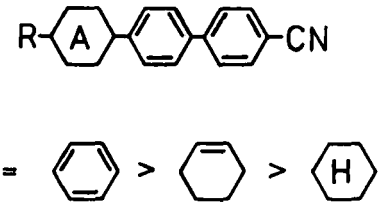


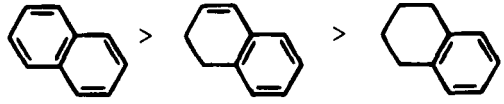

FIGURE 5 The nematic thermal stability order in terms of ring A for the cyano-compounds formulated.

It must be emphasized that this nematic thermal efficiency order has been compiled using a rather limited number of homologues (see Table V) but the order should reflect the underlying trends.

The observed nematic thermal stability order for the phenyl-naphthalenes and the related compounds may be discussed in the following terms. In the 4-*n*-alkyl-4″-cyano-*p*-terphenyls, as the aromatic ring A is progressively hydrogenated to give the tetrahydro- and *trans*-cyclohexyl compounds, the fall in nematic thermal stability mirrors the decrease in molecular polarizability[5] (Figure 5).

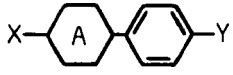
The sequence is observed, despite the fact that in a biphenyl type system only one third of the electronic effect is transmitted from one aromatic ring to another across the 1—1′ bond.[6]

In the case of the naphthyl moiety, very little loss of electronic transmission is observed, because of the fused-ring nature of the naphthyl moiety. Consequently, it is more efficient in dissipating electronic charge than the biphenyl system. On this basis, therefore, we would have expected a fall in the nematic thermal stability as ring A in Figure 5 was hydrogenated, i.e.

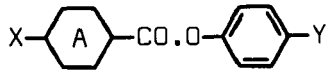



The fact that the positions of the dihydro- and tetrahydro- naphthalene compounds is reversed in the above sequence suggests that the nematic thermal stability in this series of compounds is not based solely on molecular polarizability considerations.

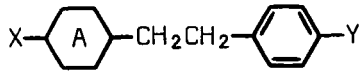
This situation is already well known for a variety of mesogenic materials for which the $T_{N-I}$ values are not too elevated.[7,8] Thus, for compounds of structure



or




or




it is established that the $T_{N-I}$ values fall as ring A is changed from cyclohexane to benzene, i.e. not in the order of decreasing anisotropy of the molecular polarisability ($\Delta\alpha$). It is argued that at low temperatures, the greater flexibility and volume of the cyclohexane ring are advantageous in terms of space filling and close molecular packing, and thereby enhance the nematic order. When higher temperatures are involved however, as in the case of the three ring mesogens in Figure 5, the flexibility of the cyclohexane ring may become disadvantageous, thermal effects causing the adoption of non-linear arrangements of the 1,4-bonds from the cyclohexane ring. The order is then reversed, and the aromatic *p*-terphenyl has the highest $T_{N-I}$.

In the systems under study here, the flexibility of the *fused* dihydro- and tetrahydro-rings will be reduced. Moreover, because broader molecules are involved, we are dealing with lower $T_{N-I}$ systems. We now have the phenylnaphthalene with the highest $T_{N-I}$, suggesting that the high $\Delta\alpha$ value is the important factor. However, the reversal of the order of the tetrahydro- and dihydro-systems from that expected on the grounds of $\Delta\alpha$ does suggest that even the somewhat limited flexibility of the fused tetrahydro-ring makes a contribution to the the packing efficiency and promotes $T_{N-I}$ above that of the more polarisable dihydro-system.

To summarize, the fact that the compounds containing a fully aromatic naphthyl moiety have the highest nematic thermal stability may be attributed to the high molecular polarizability stemming from the fact that these molecules contain a fused ring system. The position of the partly saturated compounds in the nematic efficiency order may, however, result from the importance of flexibility in relation to the nematic thermal stability.

## Viscosity

Since the Twisted Nematic mode of display device operation[9] is based upon a field effect, then the rise and decay times for such a device are dependent

upon the fluid properties of the materials used. To achieve fast rise and decay times, the viscosity of the materials used should be as low as possible.

To obtain a comparison of the viscosities of the phenylnaphthalenes and their dihydro-analogues with those of the 4-*n*-alkyl-4′-cyanobiphenyls, a graph of log viscosity against $1/T$ ($10^{-3}K^{-1}$) was plotted (see Figure 6) to obtain an extrapolated value at 20°C for each of the new compounds. These values could then be compared with the viscosity of 4-*n*-hexyl-4′-cyanobiphenyl at 20°C. The viscosity data is given in Table VI.

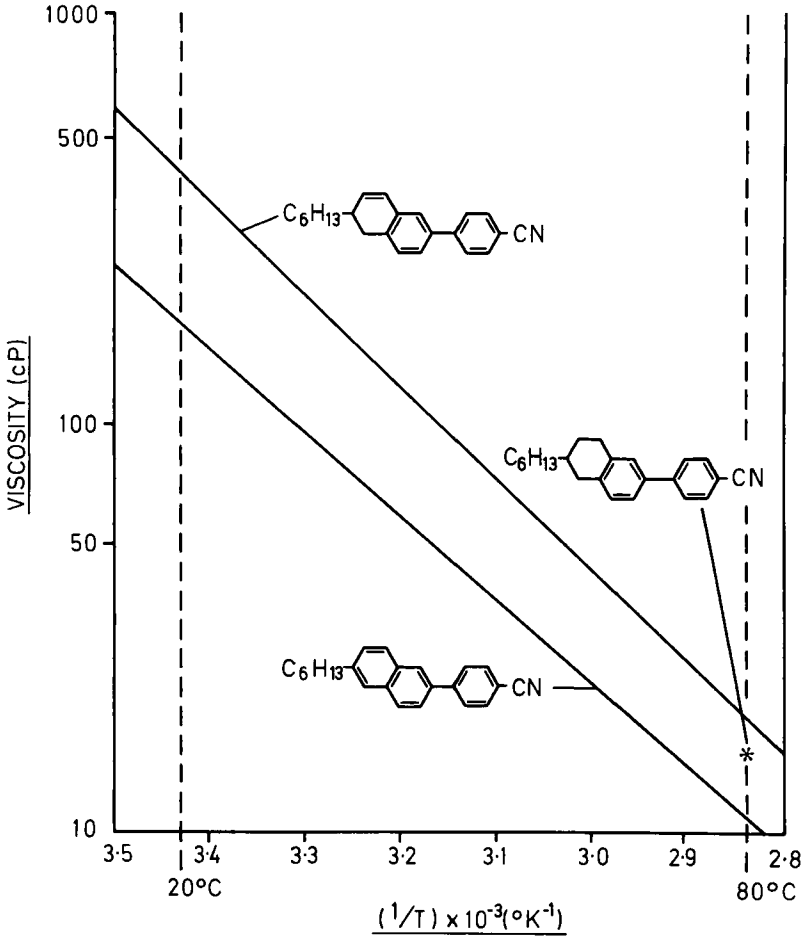
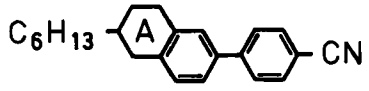



FIGURE 6 Graph of log viscosity against $1/T$ for the phenylnaphthalenes and related compounds.

TABLE VI

Viscosity data for the 2,6-disubstituted phenylnaphthalenes and related compounds, and a comparison with results obtained for 4-*n*-hexyl 4′-cyanobiphenyl




| °C | $1/T(K^{-1})$ $\times 10^{-3}$ | A | A | A | $C_6H_{13}$ A CN |
|---|---|---|---|---|---|
| | | Viscosity (cP) | | | Viscosity (cP) |
| 80 | 2.833 | 11.0 | — | 16.6 | — |
| 75 | 2.874 | 12.8 | 23.0 | — | — |
| 70 | 2.915 | 15.0 | 28.5 | — | — |
| 65 | 2.959 | 18.8 | 36.0 | — | — |
| 60 | 3.003 | 24.25 | 44.5 | — | — |
| 55 | 3.049 | — | 57.5 | — | — |
| 20 | | 176* | 410* | | 43.5 |

*Extrapolated from Figure 6.

From both Figure 6 and Table VI, it can be seen that the extrapolated nematic viscosities at 20°C for the phenylnaphthalenes and the dihydro-analogues are approximately four times and ten times greater respectively than the viscosity of the 4-*n*-alkyl-4′-cyanobiphenyl. By comparing the viscosities of the phenylnaphthalene and the tetrahydro-naphthalene at 80°C, one can estimate that the viscosity for the tetrahydro-naphthalene at 20°C would lie between those for the phenylnaphthalene and the dihydro-naphthalene. These data suggest that the phenylnaphthalenes and their partly hydrogenated analogues are too viscous to be used as the host material in a conventional twisted nematic device.

The fact that the partly hydrogenated systems are more viscous than the phenylnaphthalene implies that the reduced flexibility of the fused alicyclic rings does not contribute to reducing viscosity as a 1,4-disubstituted cyclohexane ring does.

Despite this, the low m.p.s. and the fairly high $T_{N-I}$ values of the phenylnaphthalenes may make them worthy of consideration as high $T_{N-I}$ additives, i.e. in a role similar to that in which the 4-*n*-alkyl-4″-cyano-*p*-terphenyls have been used successfully for many years.

In order to evaluate this possibility for the phenylnaphthalenes, their performance, in relation to their viscosity, was compared with that of an

TABLE VII

Viscosity data and $T_{N-I}$ values for mixtures A and B, E7 and E9

| | Viscosity at 20°C (cP) | N—I transition temperature (°C) |
|---|---|---|
| E7 | 40.0 | 60.5 |
| E9 | 96.0 | 83.5 |
| Mixture A | 44.7 | 50.9 |
| Mixture B | 52.7 | 59.4 |

equivalent system which contained a terphenyl additive. The commercial mixture E7 consists of alkyl- and alkoxy-cyanobiphenyls with 4-*n*-pentyl-4″-cyano-*p*-terphenyl as the high $T_{N-I}$ additive. We made up two mixtures, A and B, which contained the same biphenyl matrix as that in E7, but excluded the terphenyl component. To mixture A we added 2-*n*-pentyl-6-(4′-cyanophenyl)naphthalene at an equivalent concentration to that of 4-*n*-pentyl-4″-cyano-*p*-terphenyl in E7. In mixture B, because of the lower $T_{N-I}$ value of 2-*n*-pentyl-6-(4′-cyanophenyl)naphthalene, we added a higher concentration of this compound so that the $T_{N-I}$ values of mixture B and E7 were comparable.

The viscosities (measured at 20°C), and the $T_{N-I}$ values of E7, E9,[‡] and mixtures A and B, are given in Table VII.

From the plot of decay times against temperature for twisted nematic devices containing E7 and E9 (Figure 7), the inference can be drawn that the decay times for mixtures A and B will be slightly higher than that for E7. The decay times for mixtures A and B should however be much better than that of E9.

## CONCLUSION

From this study, $T_{N-I}$ values intermediate between those for the 4-*n*-alkyl-4′-cyanobiphenyls and the 4-*n*-alkyl-4″-cyano-*p*-terphenyls have been established for the 2-*n*-alkyl-6-(4′-cyanophenyl)naphthalenes. This result was as expected. However, the analogous systems with dihydro- and tetrahydro-naphthalene rings have lower $T_{N-I}$ values and higher viscosities.

[‡]E9 is also a commercially available twisted nematic mixture and is very similar to E7, except that E9 contains larger amounts of alkoxycyanobiphenyls. Both materials can be purchased from BDH Chemicals Limited, Poole, BH12 4NN, England.

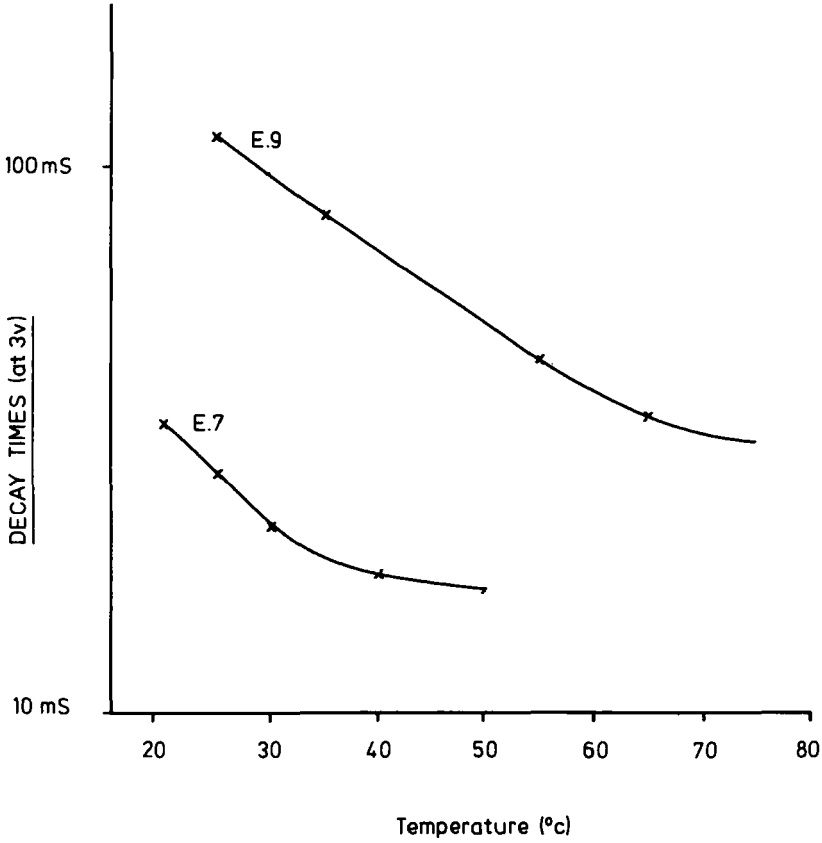



FIGURE 7 Graph of log decay time against temperature for commercial mixtures E7 and E9.

This unexpected result shows the role of molecular polarizability and the flexibility of the substituted rings in the molecules of mesogens upon physical properties and this must be assessed rather carefully in the context of molecular environment.

The fully aromatic phenylnaphthalenes could be of interest as high $T_{N-I}$ additives that do not enhance the host viscosity too greatly.

## EXPERIMENTAL

### Materials

The reaction pathway used in the preparation of the 2,6-disubstituted phenylnaphthalenes and related compounds (see Figure 1) involved a con-

siderable number of synthetic steps, but many entailed fairly standard methods. It is not thought appropriate, in a conference paper of this kind, to elaborate all the experimental details; these will appear in another publication.

We will simply consider the synthetic scheme briefly, starting with the appropriate 4-*n*-alkanoyl-4′-bromobiphenyl. Bromination at the $\alpha$-$CH_2$ to the carbonyl group, followed by nucleophilic substitution using ethyl cyanoacetate, afforded the cyano-esters, which on subsequent hydrolysis and decarboxylation gave the 3-*n*-alkyl-$\gamma$-ketonic acids. Reduction of the carbonyl group using the Huang-Minlon reaction prior to cyclization of the disubstituted butanoic acids, afforded the disubstituted tetralones. At this point in the reaction pathway, the disubstituted tetralones can be used in two different ways. If the carbonyl moiety of the tetralone was fully reduced and the resulting product cyanated, then the 2-*n*-alkyl-6-(4′-cyanophenyl)-1,2,3,4-tetrahydronaphthalenes were formed. However, if the carbonyl moiety was partly reduced and the resulting alcohol dehydrated with phosphorous pentoxide, the precursor (A) to the required dihydro-compounds was formed, and cyanation of this afforded the 2-*n*-alkyl-6-(4′-cyano phenyl)-3,4-dihydronaphthalenes. On aromatising this precursor (A) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and cyanating the product, the 2-*n*-alkyl-6-(4′-cyanophenyl)naphthalenes were obtained.

## Physical Measurements

All the final products were shown to be pure by microanalysis and by various standard techniques (t.l.c., g.l.c. and h.p.l.c.). Structural confirmation for these (and, where necessary, for any of the intermediates) was obtained by $^1$H n.m.r. spectroscopy (Jeol J.N.M.-P.M.X 60 spectrometer), infra-red spectroscopy (Perkin-Elmer 457 grating spectrophotometer) and mass spectrometry (A.E.I. M.S. 902 mass spectrometer).

The viscosities of the *n*-hexyl homologues were determined at various temperatures using a standardized capillary flow viscometer.

## Acknowledgments

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