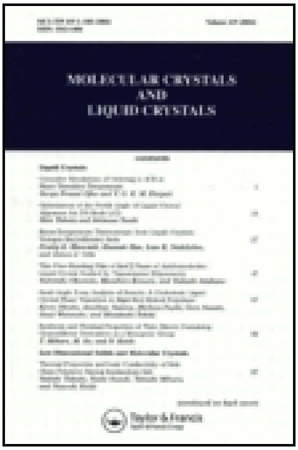

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The 1-(trans-4′-n-Alkylcyclohexyl)-2-(4″-cyanophenyl)ethanes— A New Series of Stable Nematogens of Positive Dielectric Anisotropy

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To cite this article: N. Carr , G. W. Gray & D. G. Mcdonnell (1983): The 1-(trans-4′-n-Alkylcyclohexyl)-2-(4″-cyanophenyl)ethanes— A New Series of Stable Nematogens of Positive Dielectric Anisotropy, Molecular Crystals and Liquid Crystals, 97:1, 13-28

To link to this article: http://dx.doi.org/10.1080/00268948308073138

Mol. Cryst. Liq. Cryst., 1983, vol. 97, pp. 13–28
0026-8941/83/9704–0013/$18.50/0

The 1-(*trans*-4′-*n*-Alkylcyclohexyl)-2-(4″-cyanophenyl)ethanes— A New Series of Stable Nematogens of Positive Dielectric Anisotropy[†]

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(Received February 14, 1983)

The synthesis and some important properties of the 1-(*trans*-4′-*n*-alkylcyclohexyl)-2-(4″-cyanophenyl)ethanes—where *n*-alkyl = C_1 to C_7—are described. These stable low melting materials have excellent properties comparable in many ways with those of the PCH materials wherein the cyclohexyl and phenyl rings are directly linked. The properties of the new series of materials, which we propose should be called the PECH compounds, are further elaborated in a companion paper by Raynes, *et al.*, also presented at the Bangalore conference. In that paper it is made clear that the PECH materials have in fact higher order parameters and give superior order parameters for dissolved dyes compared with the PCH materials. The PECH compounds are therefore significant new nematogens to be considered for use in both twisted nematic and cholesteric-nematic dyed phase change displays.

INTRODUCTION

Following the conception of the twisted nematic electro-optical display mode and the early demonstration of its commercial potential using mixtures of colored and unstable cyano Schiff's bases, a strong demand arose for colorless, stable, room temperature nematic systems of positive dielectric anisotropy. This need was first met[1] by the discovery of the now well known 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls and the related de-

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rivatives of *p*-terphenyl. These materials came on the scene in 1972/73, were highly successful, and are extensively exploited commercially for the manufacture of a wide range of electro-optical display devices using the twisted nematic mode.

However, the liquid crystal field is a very active one, and as expected, other nematogens of positive dielectric anisotropy with related electro-optical and stability characteristics were quickly developed and came on the commercial scene.

The sequence of events is shown in Table I.

The properties of these materials (viscosity, birefringence, elastic constants, dielectric anisotropy, etc.) naturally differ appreciably, and each system has its own particular strengths and weaknesses in relation to different display applications. Despite the range of materials available for use, an interest still exists in new materials of this general type which may have some superior property that renders them advantageous.

This paper now describes a new series of such compounds of the general structure

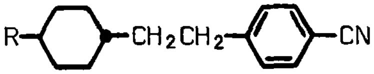
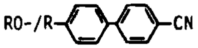
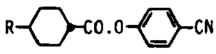
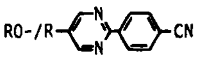
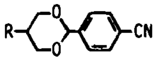


TABLE I

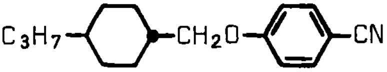
Historical sequence of development of nematogens of positive dielectric anisotropy (R = Alkyl)

Date	Nematogen	Type	Source
1972/73		CB; K	Hull/BDH Chemicals
1973		Cyclohexane esters	Halle, E Germany
1973/74		Pyrimidines	Hoffmann-La Roche
1976/77		PCH	Merck, W Germany
		CCH	
1980		PDX	Halle, E Germany

These compounds, developed over a period of time at the University of Hull, are strictly named the 1-(*trans*-4′-*n*-alkylcyclohexyl)-2-(4″-cyanophenyl)ethanes; effectively however, they are phenethylcyclohexanes, and so it is convenient to designate them as the PECH materials by analogy with the PCH materials of Merck.

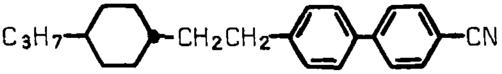
RESULTS AND DISCUSSION

In 1979, Gray and McDonnell[2] published some work on preliminary explorations of the use of more flexible linking groups between the ring systems of typical nematogens. We used one *trans*-1,4-disubstituted cyclohexane ring to compensate for the anticipated lowering of T_{N-I} that would be associated with the increased molecular flexibility. An example of the use of the —CH_2O— linkage in a PCH environment[3] is given below



Despite the reduction in T_{N-I}, such compounds were quite interesting, although they did not give a good temperature dependence of the threshold voltage on twisted nematic display operation.

We then went on to examine the use of the —CH_2CH_2— (dimethylene) linkage, and expecting this to give rather low T_{N-I} values, we explored three-ring structures such as



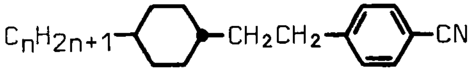
C-N, 77.2°C; N-I, 193.8°C

The analogous compound with a —CH_2O— linkage between the cyclohexyl and biphenylyl rings had

C-N, 124°C; *N-I*, 198.8°C

The T_{N-I} value was therefore only 5°C lower than that of the ether linked material, and compared quite well with that of the BICH analogue[3] where the cyclohexyl and biphenylyl groups are directly linked.

A study of the compounds



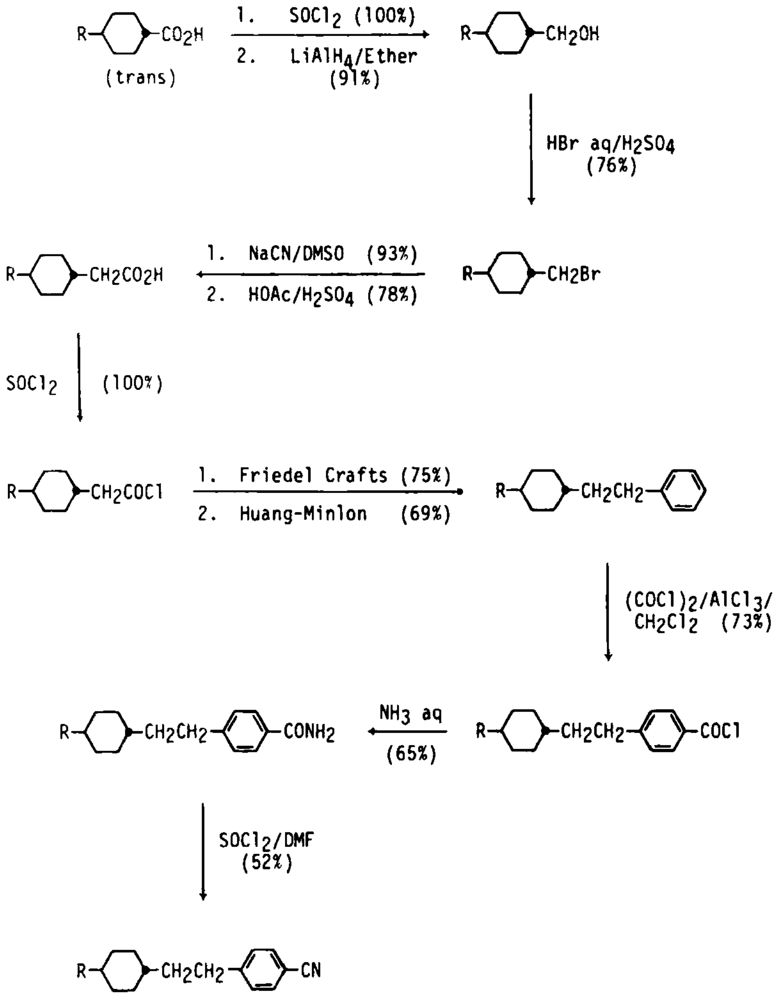
therefore seemed worthwhile, even if we were to obtain $T_{N\text{-}I}$ values that were—by analogy with the corresponding ethers—in the region of 30°C.

We now report some results for the series of PECH compounds with values of *n* from 1 to 7.

The synthetic route employed is shown in the scheme headed Synthesis.

Synthesis

(R = n-alkyl)



NOTE: Yields are average for R = C_1-C_7

Overall yield (11 steps) is 6%

The first compound that we made by this route had $n = 3$, and as the initial data contained in Table II show, the results were very encouraging, and urged us to complete the series by the synthesis of the remaining six homologues.

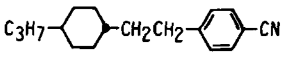
As can be seen from the data in Table II, the propyl homologue had a reasonable melting point, and the T_{N-I} value was significantly better than that which would have been predicted on the basis of the —CH_2O—linked analogue and three-ring mesogens with —CH_2O— and —CH_2CH_2— linking groups. Additionally, the birefringence was low as anticipated, and the viscosity was very good (low and about the same as that for a comparable PCH); the activation energy (E_a) was also reasonable, and the dielectric anisotropy was good.

Completion of the series ($n = 1$ to 7) and measurement of the transition temperatures gave the results in Table III.

As can be seen from Table III, very acceptable melting points were obtained, that for the C_4 homologue being particularly low. Five of the T_{N-I} transitions were enantiotropic; the two monotropic transitions for $n = 1$ and 2 were however observed directly, and are not virtual values.

TABLE II

Initial results

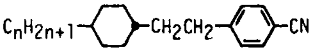


C-N	38°C
N-I	44.5°C
Δn ($0.98 \times T_{N-I}$) using 589.6 nm	0.11
η_{20° (nem ext)	19.5 cP
η_{0° (nem ext)	44 cP
E_a (nem)	6.5 kcal mol^{-1}
η_{20° (iso ext)	33 cP
η_{0° (iso ext)	72 cP
$\varepsilon_\parallel$	16.8
$\varepsilon_\perp$	5.4
$\Delta\Sigma$	11.4

NOTE: Viscosity data from log η versus $^1/T$ plot in the range 38 to 75°C

TABLE III

Transition temperatures for



n	C-N or Iso (°C)	N-I (°C)
1	51	(-10)
2	43.5	(12)
3	38	44.5
4	27	38.5
5	30	51
6	35	47
7	45	54.5

( ) = monotropic transition

Figure 1 shows a plot of the melting points and the $T_{N\text{-}I}$ values as a function of the length of the terminal alkyl chain. Two curves are obtained because of the usual odd-even alternation effect.

Both curves rise initially very steeply and then much more gently as *n* is increased. The melting points show a decrease from *n* = 1 to *n* = 4, and then increase up to *n* = 7.

It is noted that the shapes of the $T_{N\text{-}I}$ curves shown in Figure 1 are very similar to those given when a similar plot is made for the series of PCH compounds.[3] The initial rise from *n* = 1 to *n* = 3 and from *n* = 2 to *n* = 4 is steeper for the PCH series for which the homologues with *n* = 1 and *n* = 2 have considerably lower $T_{N\text{-}I}$ values than those for the corresponding PECH homologues. Thereafter, the $T_{N\text{-}I}$ values for the two series are very similar.

The shapes of the $T_{N\text{-}I}$ curves for the PCH and PECH series are therefore quite different from those for the 4-alkyl-4′-cyanobiphenyls[1] (see Figure 2).

The biphenyl series (Figure 2) shows the now well accepted fall in the $T_{N\text{-}I}$ curves from *n* = 1 to *n* = 3 and from *n* = 2 to *n* = 4, followed by a rise in both curves. In Figure 2, the data have been included for *n* = 8 to remind readers of the onset of smectic properties at this stage in the series of biphenyls. For the PCH series, no smectic properties are evident at *n* = 8 or 9. The point of onset of smectic properties for the PECH series

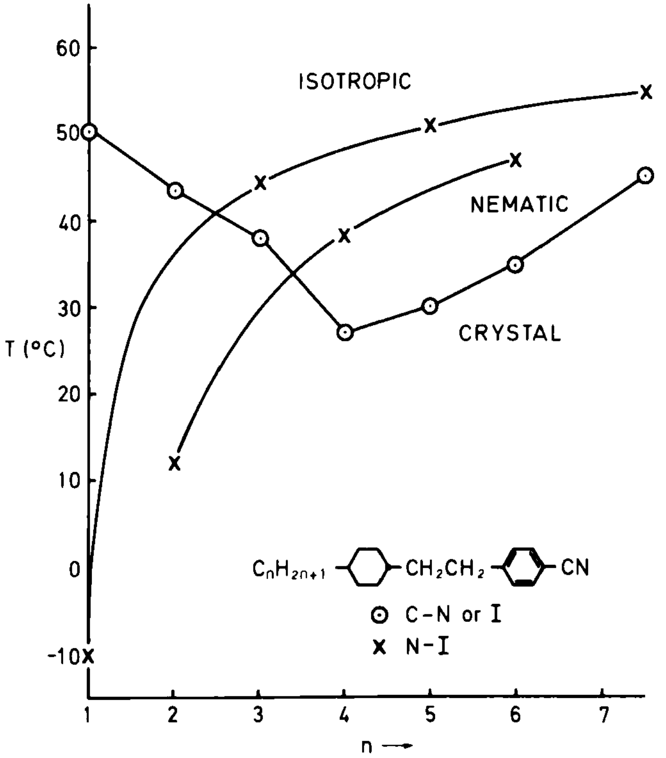


FIGURE 1 Plot of transition temperatures against number of carbon atoms in the *n*-alkyl chain for the series of 1-(*trans*-4′-*n*-alkylcyclohexyl)-2-(4″-cyanophenyl)ethanes.

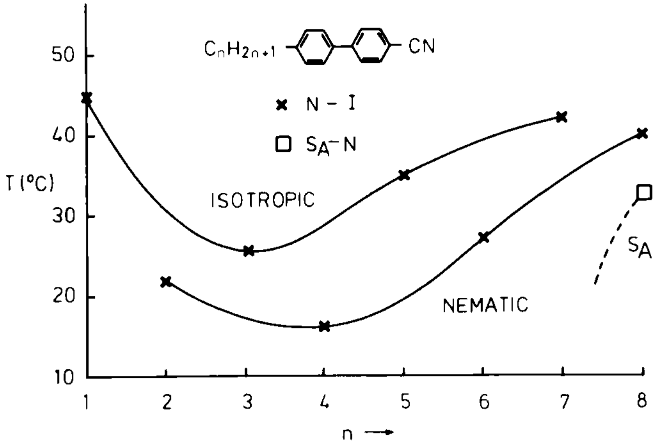


FIGURE 2 Plot of transition temperatures against number of carbon atoms in the *n*-alkyl chain for the series of 4-*n*-alkyl-4′-cyanobiphenyls.

has yet to be established, no sign of smectic behavior having been detected for any of the seven homologues so far investigated, even upon quite extensive supercooling of the nematic phases.

For the purposes of comparison, the melting points for the PCH series, the series of 4-alkyl-4′-cyanobiphenyls, and the new PECH series are given in Table IV. Table V makes a similar comparison possible for the T_{N-I} values for the three series.

Table IV shows that the biphenyl series contains the extremes of the lowest (n = 6) and the highest (n = 1) melting points. The melting points for the PCH and PECH series are broadly similar, but present no consistent pattern or trends.

TABLE IV

Comparison of melting points (°C)

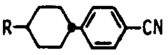
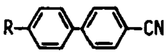
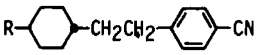
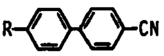
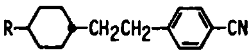
n-R			
Me	38	109	51
Et	40	75	43.5
Pr	42	68	38
Bu	41	46.5	27
Pn	30	22.5	30
Hx	42	13.5	35
Hp	30	28.5	45

TABLE V

Comparison of T_{N-I} (°C) values

n-R			
Me	(-25)	[45 ± 3]	(-10)
Et	(4)	[22 ± 1]	(12)
Pr	46	(25.5)	44.5
Bu	41	(16.5)	38.5
Pn	55	35	51
Hx	47	27	47
Hp	57	42	54.5

( ) = monotropic transition

[ ] = virtual transition

From the $T_{N\text{-}I}$ values given in Table V, the effect of the different shapes of the $T_{N\text{-}I}$ curves for the biphenyl series is evident in the relatively high (but virtual) values for the homologues with $n = 1$ and 2. The very similar values of $T_{N\text{-}I}$ for the series of PCH and PECH compounds when $n = 3$ to 7 are very obvious from the Table, as are the lower values mentioned earlier for the $T_{N\text{-}I}$ values of the PCH homologues with $n = 1$ and $n = 2$.

If we now attempt to put the three series of compounds into an order of decreasing $T_{N\text{-}I}$, we have of course got to allow for the initially high $T_{N\text{-}I}$ values for the methyl and ethyl homologues of the biphenyl series (denoted by *K*). The order of decreasing $T_{N\text{-}I}$ for the methyl and ethyl homologues is therefore

$$K > \mathrm{PECH} > \mathrm{PCH}$$

where the inequality between the PECH and the PCH homologues is 15°C and 8°C respectively for $n = 1$ and 2.

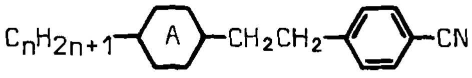
The order for the remaining homologues ($n = 3$ to 7) is however

$$\mathrm{PCH} \geqslant \mathrm{PECH} > K$$

where the inequality between the PCH and the PECH series is now very small (between 1.5°C and 4°C). This reflects the very similar $T_{N\text{-}I}$ values of the higher homologues of the two series; for $n = 6$, both series have $T_{N\text{-}I}$ values of 47°C.

Two related systems were prepared next by a similar synthetic route. In these compounds, the cyclohexane ring (CH) was replaced by a benzene ring (BZ) and by a bicyclo(2.2.2)octane ring (BCO). Results (°C) for the compounds with alkyl = C_5 are given in Table VI, together with those for the corresponding homologue from the PECH series.

From the clearing temperatures given in Table VI, it is obvious that these dimethylene linked materials provide a further[4] family (1)



(1)

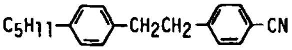
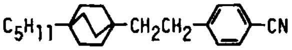
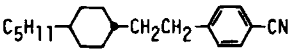
for which the order of decreasing $T_{N\text{-}I}$ value in terms of ring A is

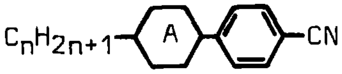
$$\mathrm{BCO} \underset{62^{\circ}\mathrm{C}}{>} \mathrm{CH} \underset{75^{\circ}\mathrm{C}}{>} \mathrm{BZ}$$

The figures under the inequality signs represent the differences between the neighboring pairs of $T_{N\text{-}I}$ values, and by comparison with the corresponding figures for the system

TABLE VI

Related systems

	C-N/I (°)	N-I (°)
	62	[-24]
	76	113
	30	51



BCO $\underset{45^\circ C}{>}$ CH $\underset{20^\circ C}{>}$ BZ

they show that the $T_{N\text{-}I}$ value for system (I) with A = BZ is surprisingly low (virtual $T_{N\text{-}I}$ = [−24°C]) compared with that for the PECH compound ($T_{N\text{-}I}$ = 51°C).

This large difference of 75°C is in fact similar to that obtained if we change the dimethylene bridge in system (*I*) to —CH_2O—.[5] Then,

for *A* = cyclohexane, $T_{N\text{-}I}$ is (48.8°C), mp 74.3°C, for *n* = 5
and for *A* = benzene, $T_{N\text{-}I}$ is (−20°C), mp 48.7°C, for *n* = 5

5PECH therefore shows a slight *gain* in $T_{N\text{-}I}$ relative to the analogous ether linked material. However, the main point is that for the ethers, a large fall (68.8°C) in $T_{N\text{-}I}$ again occurs on passing from ring A = CH to BZ.

One can therefore conclude that the —CH_2CH_2— linkage in system (*I*) gives good $T_{N\text{-}I}$ values relative to the compounds wherein the two rings are directly linked, provided that ring A is BCO or CH, but that this linkage (or —CH_2O—) is an adverse structural factor relative to a direct bond when ring A = BZ. The possibility therefore exists that some structural aspect of the likely anti-parallel correlation of the molecules partly or completely off-sets the flexible nature of the —CH_2CH_2— linkage when ring A = BZ.

As yet, nothing definite has been established about the anti-parallel correlation in the PECH system and the related materials with the CH ring replaced by BZ or BCO. However, three pieces of information about the PECH compounds have been established. Data relating to point (1) below appear in a later Table, and the evidence for points (2) and (3) is given in the companion paper to this one presented by Raynes, *et al.*

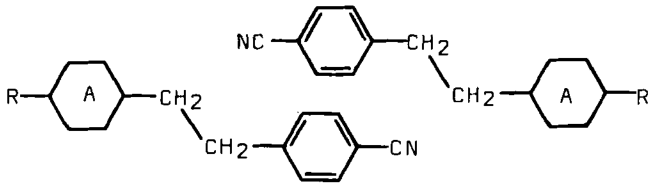
(1) The N–I transitions for the PECH materials are associated with higher enthalpies (ΔH) than those normally observed for N–I transitions.

(2) Order parameters for the PECH materials, and for their mixtures with one another, and for solutions of dyes in such mixtures are generally higher than those for the PCH analogues.

(3) There is a considerable step in the plot of $\bar{\varepsilon}$ against temperature at the T_{N-I} value for the PECH materials.

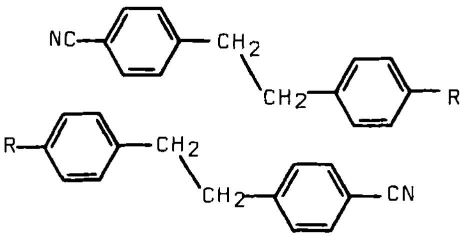
Together, these facts suggest that the PECH compounds form well-ordered, nematic phases which almost certainly involve anti-parallel correlation of the general kind known to exist in the PCH systems.

If we assume that like the PCH materials, the anti-parallel correlation involves overlap just of the cyanophenyl groups, then the molecular pairing for the PECH systems may be considered as that shown below



If this is correct, then the "dimer" does have an enhanced length : breadth ratio compared with the corresponding PCH "dimer", and the position of the cyano groups may reduce the flexibility of the —CH_2CH_2— linkage. Considered together, these factors may explain the rather comparable T_{N-I} values for the PCH and PECH systems. Moreover, when ring A = BCO, there will be an improved occupancy of space that will help to stabilize the nematic order further.

By analogy with the CB series where-in complete overlap of the cyanobiphenylyl cores of the molecules occurs, the "dimer" pairing for system (I) with ring A = BZ *may* be represented as shown below.



Relative to the CB compound, there is less enhancement of the length : breadth ratio, but more significantly, the flexible parts of the molecules are not buttressed and indeed are localized in the center of the molecular pair. While these considerations may possibly explain the low

$T_{N\text{-}I}$ value of the fully aromatic PECH analogue, further comment on these relative $T_{N\text{-}I}$ effects should certainly await experimental evidence relating to the exact nature of the anti-parallel correlation in these systems.

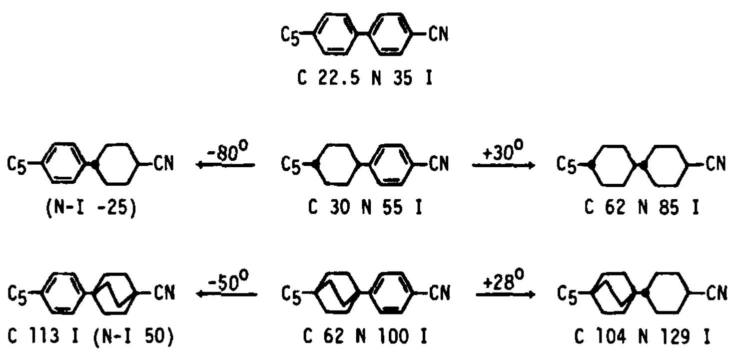
The pitfalls involved in speculating about molecular structural effects on $T_{N\text{-}I}$ values are in fact nicely illustrated by the data in Table VII which gathers together results on structural variants of the biphenyl and PCH compounds and their bicyclo-octane analogues. These results have been drawn from work done at E Merck, Darmstadt and at the University of Hull.

The central column of three structures in Table VII simply show the now accepted increase in $T_{N\text{-}I}$ as the rings are changed from BZ to CH to BCO. Comparison of the PCH compound with the CCH analogue show a considerable increase in $T_{N\text{-}I}$, and it is comforting to see that a similar increase occurs on changing the BZ ring of the bicyclo-octane analogue of PCH to a CH ring. Thus we might conclude that a cyano group attached to an alicyclic ring strongly promotes $T_{N\text{-}I}$. However, the reversed ring structure of PCH, with a cyano-group so attached to a CH ring, shows a dramatic *fall* of 80° to (−25°C) compared with the PCH compound. A large, but smaller decrease of 50° in $T_{N\text{-}I}$ also occurs when we compare the central BCO compound with its reversed ring variant on the left. Despite the cyano-alicyclic structure, this compound has a monotropic $T_{N\text{-}I}$ at 50°C. Such effects tend to make one rather cautious about predicting the effects of structural modifications to molecules.

Finally, in relation to an assessment of the value of these new PECH materials for applications in display devices, information relating to the potential of these materials to form lower melting and broader nematic

TABLE VII

Structural variants (transition temperatures in °C)



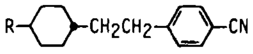
range mixtures was required. As a first step to evaluating eutectic mixtures of some of the homologues, the homologues with $n = 3$, 5, and 7 were separately examined by differential scanning calorimetry. Data relating to the temperatures at onset and at peak maximum for the C–N and N–I transitions, together with the enthalpies of the transitions are given in Table VIII; the temperatures in brackets were those obtained by optical microscopy.

The rather high enthalpies of the T_{N-I} transitions referred to earlier are obvious from the tabulated data. Assuming ideal behavior for the systems, it will be possible now to calculate eutectic compositions for these homologues and obtain mixtures with even lower melting points than that indicated at the foot of Table VIII for the non-eutectic mixture of three homologues.

In this context, it is noted that the PECH materials and their mixtures with one another have good solvent properties, and that good concen-

TABLE VIII

Enthalpy data (Perkin Elmer DSC 2C), at +2.5° min^{-1}



R	C-N Onset °C	C-N Max °C	C-N ΔH kcal mol^{-1}	N-I Onset °C	N-I Max °C	N-I ΔH kcal mol^{-1}
C_3H_7	40.1 (38)	41.6	3.9	46.1 (44.5)	46.6	0.44
C_5H_{11}	29.9 (30)	32.3	3.5	51.8 (51)	53	0.47
C_7H_{15}	43.4 (45)	45.1	5.8	54.3 (54.5)	54.9	0.50

NOTE: (1) Figures in ( ) were obtained by optical microscopy

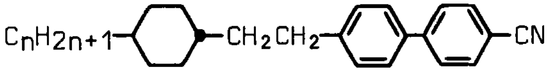
(2) Low enthalpies of fusion (C_3, C_5)

NON-EUTECTIC MIXTURE

C_3:C_5:C_7 30:40:30 (wt %)

C-N, 0° N-I, 49°

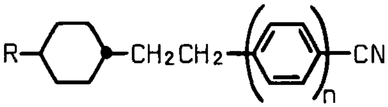
(see paper by EP Raynes et al. - this conference) trations of materials such as the dimethylene bridged, three ring analogues (BECH)



can be obtained. Such mixtures then give appreciably higher T_{N-I} values than that for the three component, non-eutectic mixture given in the Table. Further information on such mixtures will be presented in the paper by Raynes, *et al.*

SUMMARY OF MAIN CONCLUSIONS

The new series of compounds, the PECH systems, of general structure



(where *n* = 1) provide a further range of interesting, stable nematogens. The melting points are quite low, and mixtures containing biphenylyl analogues—the BECH materials—(*n* = 2), have melting points <0°C and provide broad range nematic phases. These nematic phases are of low viscosity, low birefringence and high dielectric anisotropy. Bearing these points in mind, together with the ability of the nematic phases to give well ordered solutions of commercially useful dyes, the PECH and BECH materials should prove to be of real value for display device technology, particularly in the context of dyed cholesteric-nematic phase change displays.

EXPERIMENTAL

Materials

It is not appropriate in a conference paper of this kind to elaborate the experimental details of the preparation of the seven new PECH compounds. As can be seen from the synthetic scheme presented earlier in this paper, the synthesis of each homologue had eleven steps, but individually these involved fairly standard methods.

Commencing with the available *trans*-4-*n*-alkylcyclohexane-1-carboxylic acid, formation of the acid chloride, followed by reduction, formation of the bromide from the alcohol, cyanation, and hydrolysis produced the homologous *trans*-4-*n*-alkylcyclohexyl-1-acetic acid. The acid chloride was then made and used to acylate benzene. On reduction of the ketone, the 1-(*trans*-4′-*n*-alkylcyclohexyl)-2-phenylethane was obtained. Using the method of Neubert, *et al.*,[6] the —COCl group was introduced into the *p*-position of the phenyl group. Conversion to the amide and dehydration of the amide yielded the appropriate PECH product.

The corresponding materials wherein the cyclohexane ring was replaced by a benzene ring or a bicyclo(2.2.2)octane ring were made by the same route, starting with the appropriate 4-alkylbenzoic acid or 4-alkylbicyclo(2.2.2)octane-1-carboxylic acid.

All the final products, and where necessary the intermediates in the various steps in the syntheses, were shown to be pure by various techniques (tlc, glc, hplc) and confirmation of structure was obtained, where appropriate, by nmr, mass spectrometry, elemental analysis and infra-red spectroscopy.

Full experimental details of these procedures will appear in a later publication and in the PhD Thesis of N Carr.

Physical Measurements

Transition temperatures ($T_{C-N \text{ or } I}$, T_{N-I}) for all the PECH materials were measured by optical microscopy using a Nikon L–Ke polarizing microscope in conjunction with a Mettler heating stage (FP 52) and control unit (FP 5).

Transition temperatures and enthalpies of transition for the PECH homologues with $n = 3$, 5 and 7 were obtained by differential scanning calorimetry (Perkin Elmer DSC-2C) using a heating rate of 2.5° min^{-1}.

The birefringence of the nematic phase of the propyl homologue, was determined using an Abbé refractometer and with an aligned sample maintained at $0.98 \times T_{N-I}$.

Viscosities for the propyl homologue were determined at a range of temperatures between 38 and 75°C. A standardized capillary flow viscometer was used. From the plot of log η against reciprocal temperature, the values recorded in Table II for the extrapolated nematic and extrapolated isotropic viscosities at 20°C and 0°C were obtained.

The permittivity values and the dielectric anisotropy for the nematic phase of the propyl homologue were measured at RSRE, Malvern.

Acknowledgments

This paper is published by permission of the Director HMSO. The authors thank the UK Ministry of Defence for a research grant. The authors also thank BDH Chemicals Limited

(Poole) for the supply of the *trans*-4-*n*-alkylcyclohexane-1-carboxylic acids and of 4-*n*-pentylbicyclo(2.2.2)octane-1-carboxylic acid. They also gratefully acknowledge the help of Mrs. C. Hogg with the synthesis of certain intermediates.

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