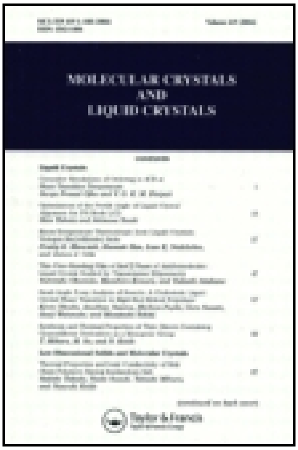

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The Physical Properties of the Cyanophenylcyclohexyl Ethanes (PECH)

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The Physical Properties of the Cyanophenylcyclohexyl Ethanes (PECH)*

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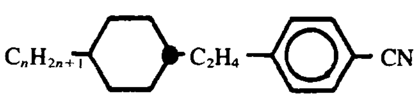
The physical properties of a new homologous series of stable, low-melting nematic materials, the cyanophenylcyclohexyl ethanes (PECH) are reported and compared with those of other stable, nematic materials. A broad range mixture is reported with a low viscosity, medium birefringence and large positive dielectric anisotropy. This mixture shows a high order parameter which increases the contrast of displays using dissolved pleochroic dyes. A comparison is also made between the structural isomers of PECH and PCH which questions the validity of molecular theories of elastic constants.

INTRODUCTION

Carr, Gray and McDonnell have recently described a new homologous series of stable, low-melting nematic materials called the phenylcyclohexyl ethanes[1] (PECH), which have the structure:

*n*PECH 

In this paper we present information on the physical properties of these new materials and their performance in display devices. The properties of the propyl, pentyl and heptyl homologues and their ternary mixture are re-

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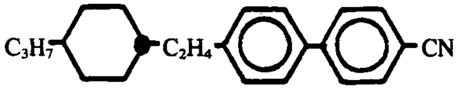
ported. A comparison of the properties of this mixture is made with similar mixtures of existing stable nematic materials. The properties of a broad range mixture, formed by adding the three ring biphenylylcyclohexyl ethane[2]

3BECH 

Nematic Range
74°C → 188°C

to the PECHs, are described. This mixture is found to be particularly useful in both twisted nematic devices and pleochroic dye devices, where the high order parameter of the ethanes produces a contrast higher than that obtained using other nematic materials.

EXPERIMENTAL

The bulk viscosities were measured to an accuracy of 3% using a Brookfield rotating cone viscometer whose temperature was controlled over the range −15°C to +85°C by a circulating, thermostated liquid.

The ordinary, extraordinary and isotropic refractive indices (n_0, n_e and n_{is}) were measured to an accuracy of 0.01% at 589.6 nm (D_1 sodium line) using an Abbé refractometer with prisms coated with lecithin to induce homeotropic alignment of the liquid crystal. The temperature was controlled to within 0.3°C over the range −15°C to +80°C by a circulating thermostated liquid. The nematic order parameter S was obtained from the refractive indices by using the Vuk's relation

$$S(\Delta\alpha/\overline{\alpha}) = (n_e^2 - n_0^2)/(\overline{n}^2 - 1)$$

where

$$\overline{n}^2 = (n_e^2 + 2n_0^2)/3$$

together with a novel extrapolation procedure, recently described by Tough and Bradshaw[3] which determines the polarizabilities $\Delta\alpha/\overline{\alpha}$.

The dielectric permittivities parallel ($\varepsilon_\parallel$) and perpendicular ($\varepsilon_\perp$) to the director in the nematic phase and in the isotropic phase (ε_{is}) were determined to an absolute accuracy of 1% from the capacitance of a parallel plate capacitor, surrounded by a "guard" electrode and measured empty and full of liquid crystal. The electrodes were coated with about 100 Å of SiO_x, evaporated at 60° to the plate normal in order to induce homogeneous alignment of the liquid crystal with a zero tilt angle. $\varepsilon_\perp$ was determined from low voltage data and $\varepsilon_\parallel$ by extrapolating the high voltage data to infinite voltage.[4] The temperature was controlled to within 0.1°C over the range 0°C to 100°C using thermostated dry nitrogen gas. An HP 9825A desk-top calculator controlled the measurement and recorded the data.

Splay and bend elastic constants (K_{11} and K_{33}) were calculated by fitting the detailed capacitance-voltage data from the permittivity determination to the continuum theory, using a three parameter nonlinear least-squares fitting program. The estimated accuracy of this determination is 2% for K_{11} and 5% for K_{33}.[5]

The order parameters (S) of pleochroic dyes dissolved in the liquid crystal were measured using thermostated cells fitted to a Perkin-Elmer 554 double beam spectrometer. The sample beam contained a cell filled with the dye-host mixture and an identical cell filled with the host alone was placed in the reference beam. The beams were polarized vertically using HN32 linear polarizers and both cells were rotated through 90° to obtain the spectra for $A_\parallel$ and $A_\perp$, from which S was determined using the expression

$$S = (A_\parallel - A_\perp)/(A_\parallel + 2A_\perp)$$

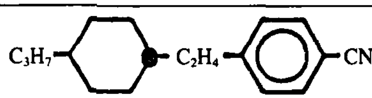
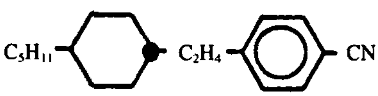
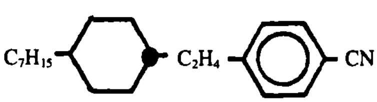
The solubilities of the dyes were obtained spectroscopically using standard and saturated solutions.

PROPERTIES OF THE ETHANE HOMOLOGUES

Table I gives the nematic ranges of the 3PECH, 5PECH and 7PECH.[1] Their refractive indices (n_e and n_0) are shown in Figure 1 and their birefringence of ≈0.11 is consistent with the presence of a saturated cyclohexane ring and

TABLE I

Cyanophenylcyclohexyl ethanes (PECH)

		Nematic Range (°C)
3PECH		38 → 44
5PECH		30 → 51
7PECH		45 → 54

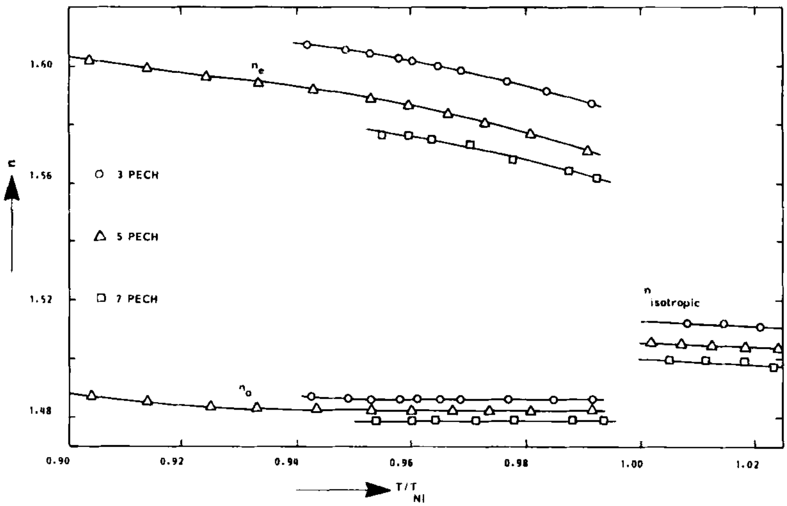


FIGURE 1 Refractive indices of the PECH homologues.

an aromatic phenyl ring in the molecule. With the possible exception of 5PECH the nematic ranges are too narrow for a reliable determination of a nematic order parameter.

The dielectric permittivities are shown in Figure 2 and show that the PECHs possess the strong positive dielectric anisotropy ($\Delta\varepsilon \approx +11$) ex-

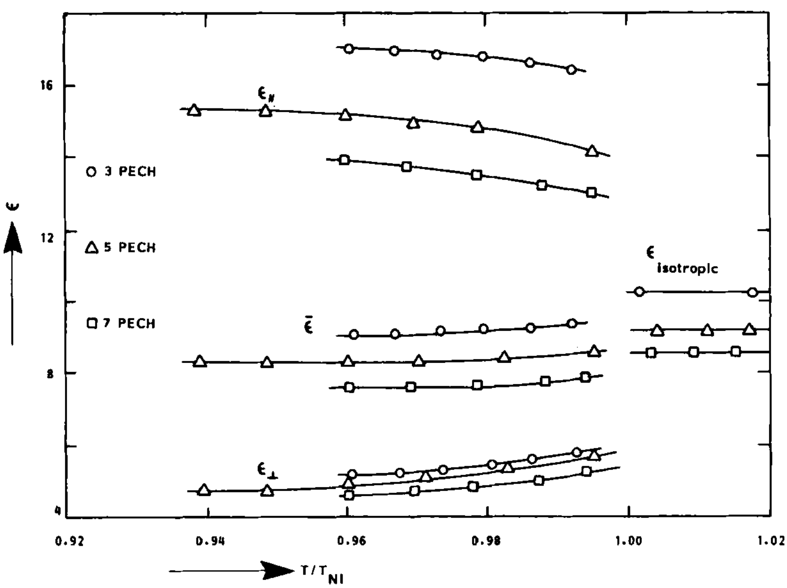


FIGURE 2 Dielectric permittivities of the PECH homologues.

pected from the large dipole moment of a cyanophenyl group. At T_{NI} there is a noticeable jump from $\bar{\varepsilon}$ ($\frac{1}{3}[\varepsilon_{\parallel} + 2\varepsilon_{\perp}]$) to ε_{is} suggesting that there is the significant antiparallel ordering[6] which is typical of other terminal cyano-substituted nematic materials. The magnitude of the jump is actually larger than in other materials (discussed in a later section).

Figure 3 presents the splay elastic constants (K_{11}). The relative trend with increasing alkyl chain length has been observed in many other systems. However the absolute values are higher (≈40%) than in other nematic series. We will return to this point later in the paper. The ratios of the splay and bend constants (K_{33}/K_{11}) in Figure 4 show a decrease with increasing length of alkyl chain which is typical of other series of nematic materials. The magnitudes of (K_{33}/K_{11}) in the PECH are similar to those found in other materials containing a *trans*-1,4-disubstituted cyclohexane ring.[7]

COMPARISON OF 3/5/7 MIXTURES

This section continues the philosophy started by Bradshaw *et al.*[8] of using a standard mixture with a wide nematic range for making comparisons between different nematic families. The mixture they chose uses the propyl, pentyl and heptyl homologues in the ratio of 30%, 40% and 30% by

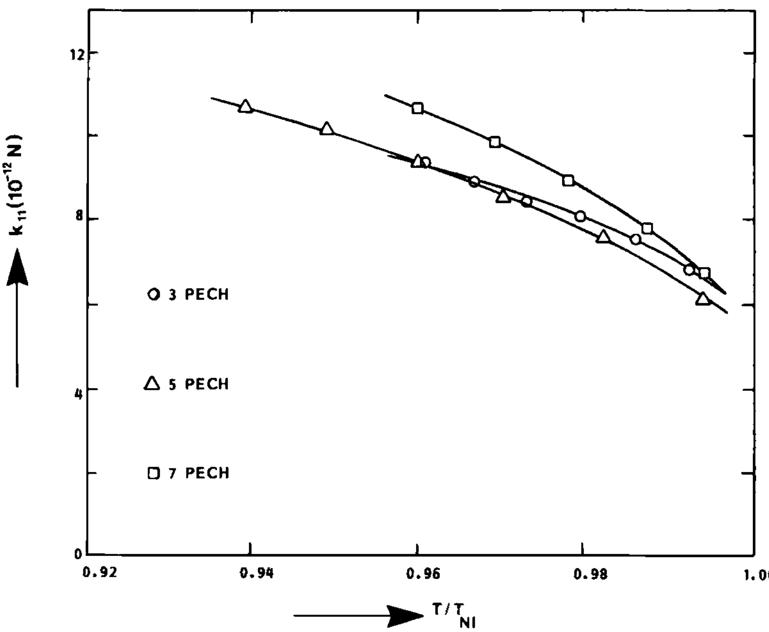


FIGURE 3 Splay elastic constants (K_{11}) of the PECH homologues.

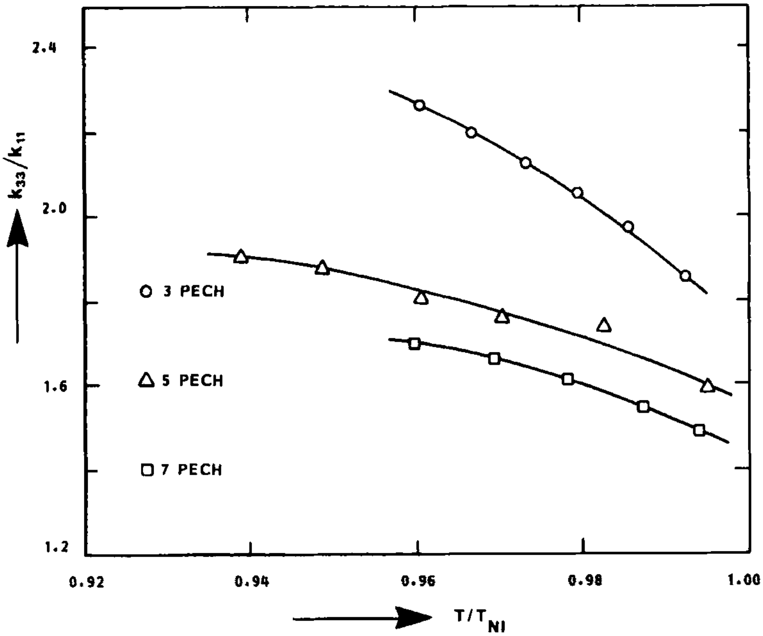


FIGURE 4 Ratio of bend/splay elastic constants (K_{33}/K_{11}) of the PECH homologues.

weight. Although this combination is rarely close to the eutectic composition, it does provide a wide range mixture which can be supercooled to the eutectic temperature or below.

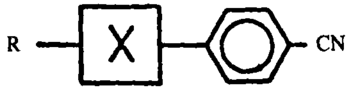
The materials examined are shown in Table II with their names and acronyms. The main properties of the various 3/5/7 mixtures are summarized in Table III and the general trends in Table IV. The melting points, quoted in Table III, represent the temperature of initial melting of the mixtures, and should be representative of the melting points of the eutectic mixtures. In most cases the mixtures showed significant supercooling.

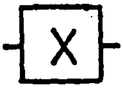
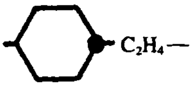
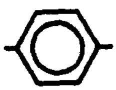
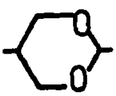
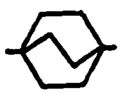
The bulk viscosities, summarized in Table III, are shown in detail in Figure 5. As seen from the trends in Table IV, the viscosities of the PCH and PECH are virtually identical. The insertion of the $-C_2H_4-$ linkage between the two rings has no effect on the bulk viscosity. This is rather surprising because the linkage introduces some flexibility into the molecule, and increasing the number of $-CH_2-$ groups in a molecule normally increases the viscosity.[9]

The refractive indices, shown in Figures 6 and 7, are presented as Δn and $\bar{n}$ rather than the more conventional pairing of n_e and n_0. There are marked

TABLE II

Materials examined



	Nomenclature	Acronym
	1-(4′-cyanophenyl), 2-(trans-4″-*n*-alkyl-cyclohexyl) ethane	PECH
	Trans-1-*n*-alkyl-4-(4′-cyanophenyl)-cyclohexane	PCH
	4-n-Alkyl-4′-cyanobiphenyl	CB
	5-*n*-Alkyl-2-(4-cyanophenyl)-1, 3-dioxan	PDX
	1-*n*-Alkyl-4-(4′-cyanophenyl) bicyclo-(2, 2, 2) octane	BCO

differences in Δn which are attributed to the different values of $\Delta\alpha/\bar{\alpha}$ shown in Table III. Materials containing saturated rings show fairly similar values ($\Delta\alpha/\bar{\alpha} \approx 0.43$ and $\Delta n \approx 0.12$), whereas the CB mixture which contains only unsaturated rings is approximately twice as anisotropic.

Again we note very little effect of introducing the $—C_2H_4—$ linkage into PCH (Table IV). The slightly lower values of PECH probably reflect the increased molecular weight. These detailed refractive indices were also analyzed to give $\Delta\alpha/\bar{\alpha}$ and S using the Vuk's relation and the novel extrapolation procedure.[3] Figure 8 gives the order parameters (S), and we see that apart from the trends between different rings observed previously,[8] there is also the first significant consequence of inserting the $—C_2H_4—$ linkage. The order parameter has been increased so that the PECH is now similar to BCO, the previous best (Table IV).

It is also noticeable that the shape of the order parameter curve with temperature varies between materials. The order parameter close to the

TABLE III

Properties of 30:40:30 mixtures of propyl/pentyl/heptyl homologues

	PECH	PCH	CB	PDX	BCO
Nematic range	0°C → 49°C	0°C → 50°C	−10°C → 35°C	5°C → 45°C	20°C → 90°C
Viscosity (cP) 20°C	25	26	34	41	96
Viscosity (cP) 0°C	86	85	100	148	—
Birefringence (20°C)	0.12	0.12	0.22	0.11	0.13
Polarizability ($\Delta\alpha/\bar{\alpha}$)	0.41	0.44	0.75	0.43	0.43
Order parameter ($0.9T_{NI}$)	0.67	0.65	0.62	0.62	0.67
Dielectric permittivities ($0.9T_{NI}$) $\varepsilon_{\perp}$	4.4	4.9	5.7	8.5	4.5
Dielectric permittivities ($0.9T_{NI}$) $\varepsilon_{\parallel}$	16.3	17.6	22.3	27.6	16.0
Permittivity jump at T_{NI} $\left[\frac{2(\varepsilon_{is} - \bar{\varepsilon})}{(\varepsilon_{is} + \bar{\varepsilon})}\right]_{T_{NI}}$ (%)	10	7	4	4	4
Elastic constants ($0.9T_{NI}$) $K_{11}(10^{-12}$ N)	13.0	9.6	9.8	8.3	8.6
Elastic constants ($0.9T_{NI}$) $\frac{K_{33}}{K_{11}}$	2.08	2.17	1.55	1.55	2.48

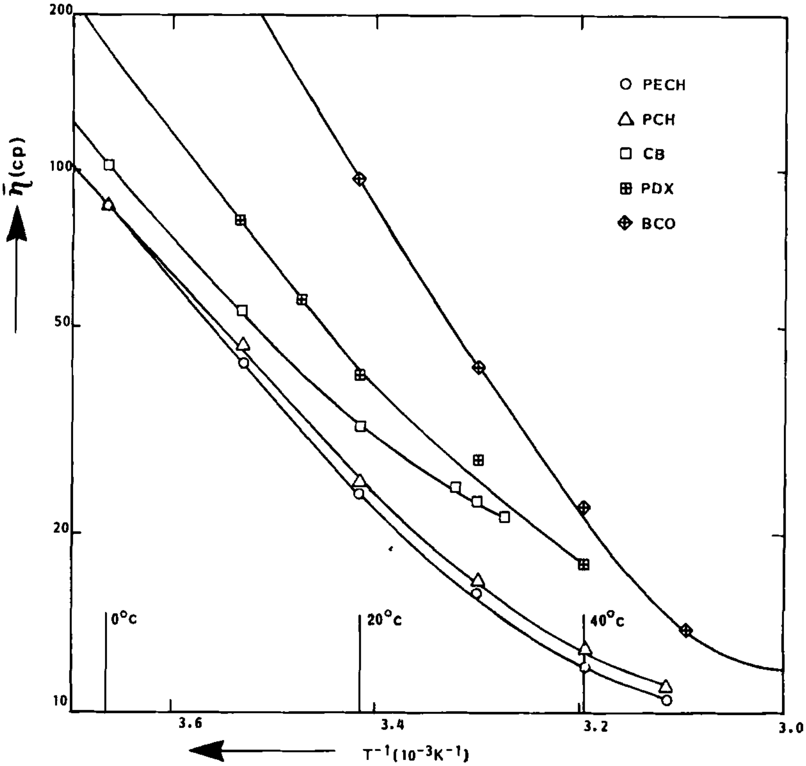


FIGURE 5 Bulk viscosities of the 3/5/7 mixtures.

clearing temperature is higher for PECH and to a lesser extent PCH than the other materials (BCO could not be measured close to T_{NI}).

The dielectric permittivities are presented in Figures 9 and 10. The molecular dipole moments are expected to be highest in the compounds containing a heterocyclic ring and lowest in those containing alicyclic rings. The trend for increasing $\Delta\varepsilon$ is shown in Table IV, and again there is virtually no difference between PCH and PECH. All the mixtures show the marked discontinuity between $\bar{\varepsilon}$ and ε_{is} at T_{NI} caused by antiparallel local ordering;[6] however the actual magnitude of this discontinuity varies (Table III) from 10% for PECH down to 4% for CB, PDX and BCO. PECH and to a lesser extent PCH show a larger order parameter close to the clearing point (Figure 8), and this may be the explanation for the larger permittivity discontinuities. The same explanation may apply to the large enthalpy observed for the nematic-isotropic transition of PECH.[1]

TABLE IV

Trends exhibited by the 3/5/7 mixtures

Viscosity	PECH < CB < PDX ≪ BCO PCH
Birefringence	PECH BCO ≈ ≪ CB PCH PDX
Order parameter	CB PECH < PCH < PDX BCO
Dielectric anisotropy	PECH ≈ BCO < CB < PDX PCH
K_{33}/K_{11}	CB PECH < < BCO PDX PCH

The splay elastic constants (K_{11}) are given in Figure 11 and the ratio of splay to bend constants (K_{33}/K_{11}) in Figure 12; these show a second important characteristic of the PECHs. All the other materials show rather similar values; however, the elastic constants for the PECH are at least 40% higher. The large increase caused by inserting the $—C_2H_4—$ linkage is only partially accounted for by the increase in order parameter. The ratio (K_{33}/K_{11}) varies markedly between materials and shows a strong dependence on the type of ring used (Figure 12). There is virtually no effect on K_{33}/K_{11} of inserting a $—C_2H_4—$ linkage (PECH gives a ratio very similar to PCH). The effect of different rings on K_{33}/K_{11} is summarized in Table IV.

COMPARISON OF PECH AND PCH STRUCTURAL ISOMERS

A consistent theme of the previous section was the extreme similarity between the PECH and PCH materials. The only significant differences caused by inserting the $—C_2H_4—$ linkage between the two rings are an increase of ≈4% in order parameter and at least 40% in the elastic constants. The similarity between PECH and PCH is even closer between structural isomers, for example comparing 3PECH with 5PCH or 5PECH

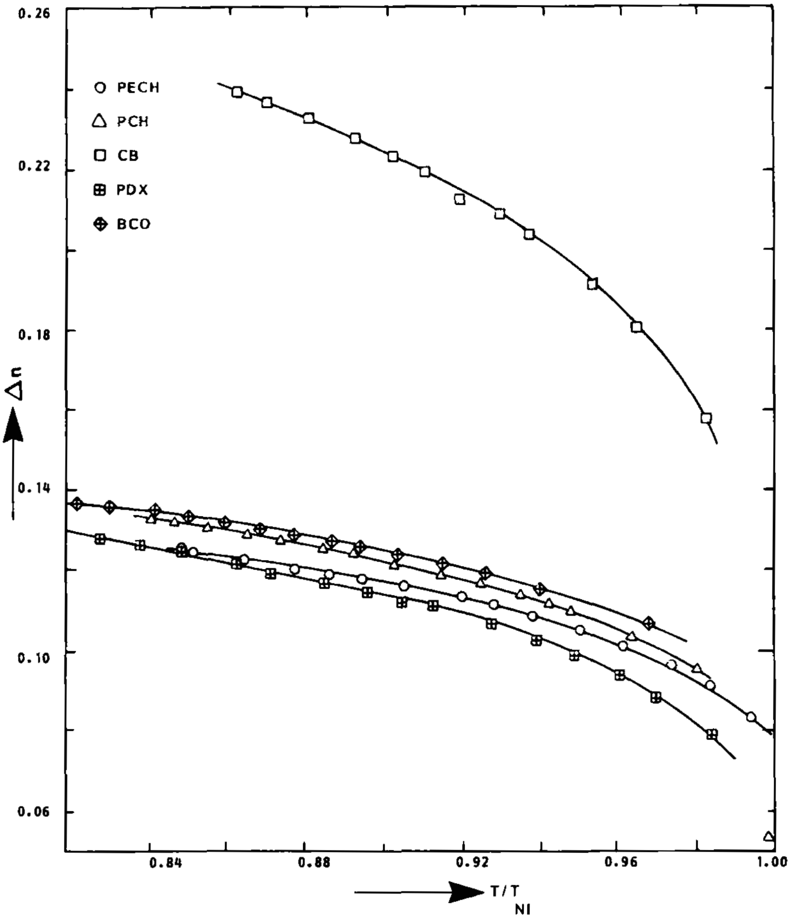


FIGURE 6 Birefringences (Δn) of the 3/5/7 mixtures.

with 7PCH. Apart from having the same molecular weight the structural isomers have the same length and breadth, and should possess similar dipole moments and polarizabilities. The properties of the structural isomers in Table V show that the clearing points, refractive indices and dielectric permittivities are indeed very similar. The small differences in the last two properties probably arise from the slightly higher order parameter of the PECH. These molecular properties are therefore consistent with the similarity between the molecules themselves, and the equivalence of the

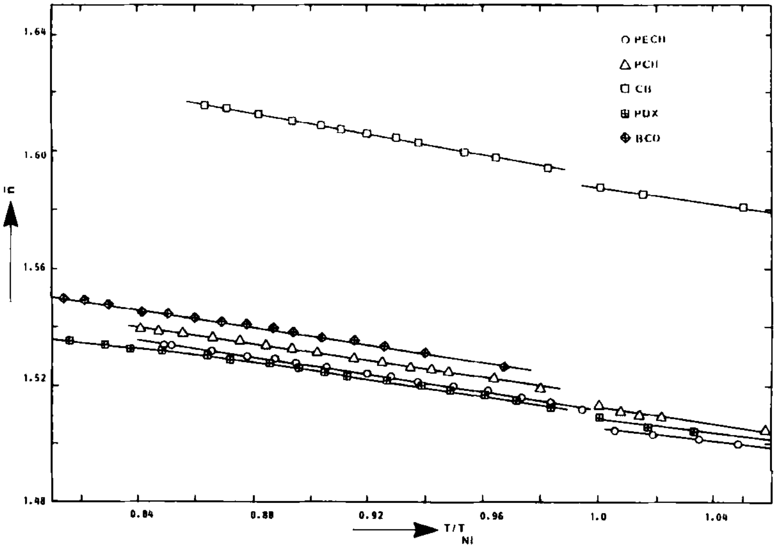


FIGURE 7 Mean refractive indices ($\bar{n}$) of the 3/5/7 mixtures.

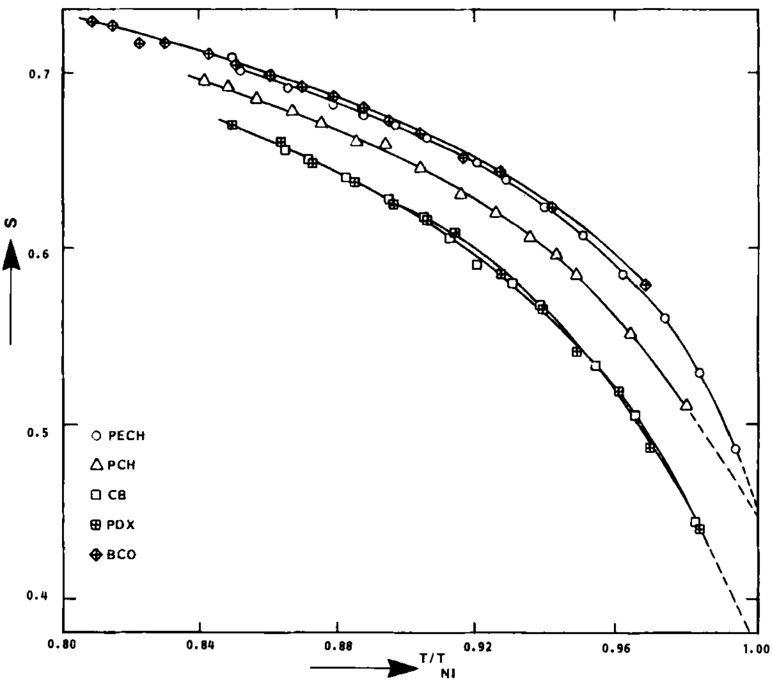


FIGURE 8 Order parameters of the 3/5/7 mixtures.

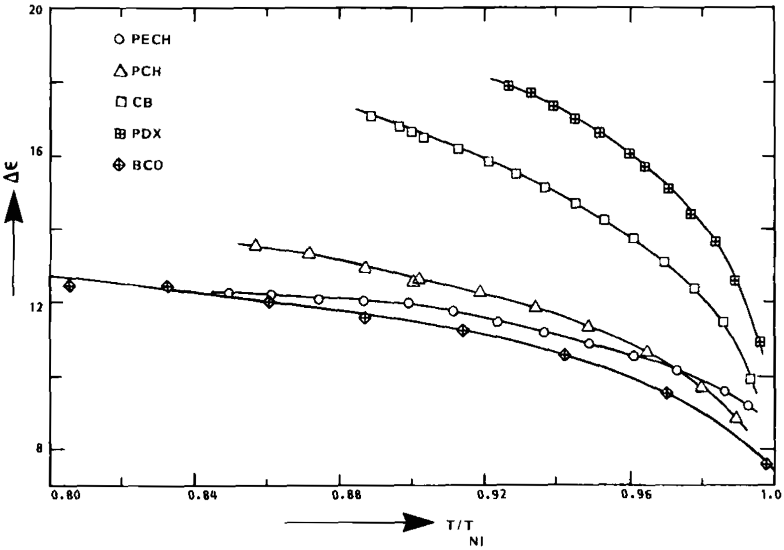


FIGURE 9 Permittivity anisotropies (Δε) of the 3/5/7 mixtures.

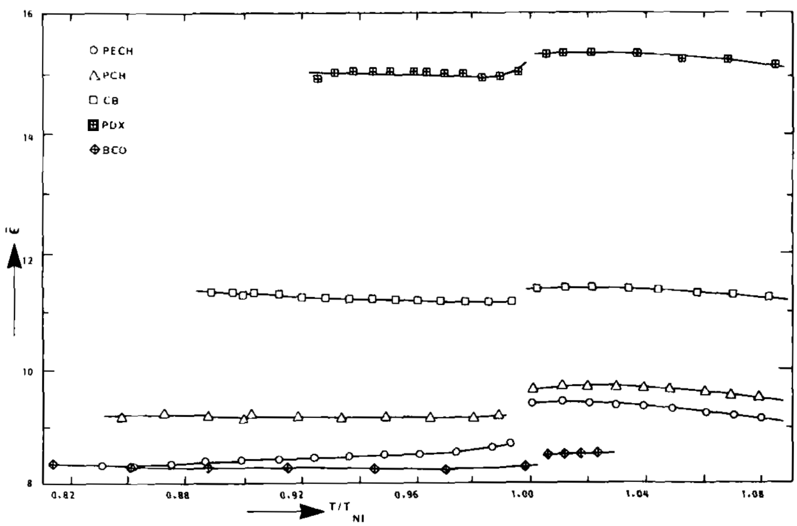


FIGURE 10 Mean permittivities ($\bar{\varepsilon}$) of the 3/5/7 mixtures.

dielectric permittivities also suggests that the antiparallel local order is similar in both magnitude and form in PECH and PCH.

The elastic constants present a completely different picture. In PECH, K_{11} is $\approx$ 50% higher and $K_{33} \approx$ 100% larger than in the equivalent PCH

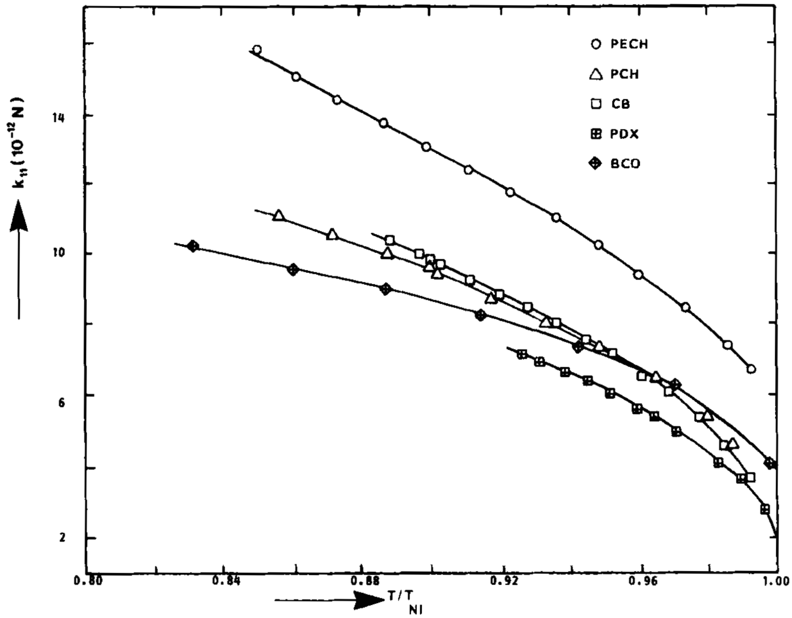


FIGURE 11 Splay elastic constants (K_{11}) of the 3/5/7 mixtures.

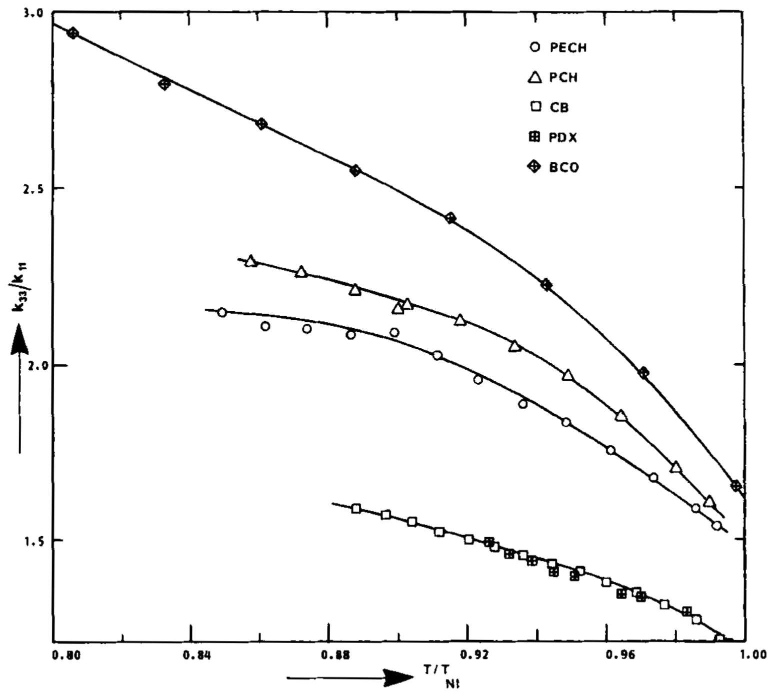


FIGURE 12 Ratio of bend/splay elastic constants (K_{33}/K_{11}) of the 3/5/7 mixtures.

TABLE V

Comparison of PECH and PCH structural isomers

Properties at 0.96 T_{NI}		3PECH	5PCH	5PECH	7PCH
Order parameter S		0.59	0.57	0.60	0.57
Birefringence Δn		0.116	0.104	0.103	0.098
Dielectric permittivities	$\Delta\varepsilon$	12.0	10.7	10.2	9.6
	$\bar{\varepsilon}$	9.1	9.0	8.3	8.2
	ε_{is}(80°C)	9.8	9.3	8.8	8.5
Elastic constants	$K_{11}(10^{-12}$ N)	9.4	6.5	9.4	7.2
	$K_{33}(10^{-12}$ N)	21.2	11.5	17.0	10.6

material. These very large differences in the elastic constants of molecules, which in every other respect are virtually identical, must cast serious doubts on theoretical attempts to explain elastic constants by reference to only molecular aspects; the more subtle long-range effects must also play a significant role.

BROAD RANGE ETHANE MIXTURES

The nematic range of the mixture of 3PECH, 5PECH and 7PECH was increased using 3BECH. The composition of the mixture was adjusted to give a narrow range of melting, and the mixture JC10 given in Table VI was finally formulated. Table VII shows that JC10 is a useful broad range

TABLE VI

Composition of PECH broad range mixture JC10

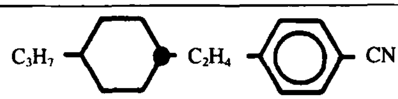
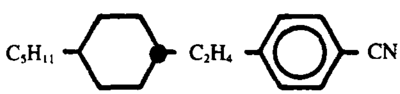
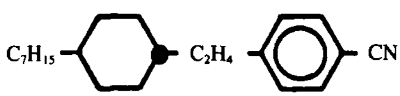
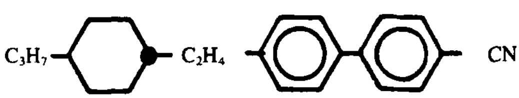
	wt %
	32
	30
	19
	19

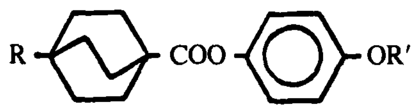
TABLE VII

Properties of PECH broad range mixture JC10

Nematic range		−10°C → +70°C
Viscosity	20°C	30 cP
	0°C	120 cP
Birefringence Δn (20°C)		0.138
Order parameter S (20°C)		0.71
Dielectric constants (20°C)		
	$\varepsilon_{\perp}$	4.2
	$\varepsilon_{\parallel}$	16.2
	$\Delta\varepsilon$	12.0
Elastic constants (20°C)		
	K_{11}	14.7×10^{-12} N
	(K_{22}/K_{11})	0.54
	(K_{33}/K_{11})	2.32

(−10°C to +70°C) nematic mixture with low viscosity (30 cP), medium birefringence (0.14) and a strong positive dielectric anisotropy (+12.0). The twist elastic constant (K_{22}) was measured using a light scattering technique,[10] and the ratio K_{22}/K_{11} is typical of other nematic materials.

The electro-optic properties in standard 8 μm, low-tilt, twisted nematic devices are shown in Table VIII. The nomenclature and experimental details have been summarized by Raynes.[11] In common with other terminal cyano-substituted materials the multiplexing performance is improved (both M_{20} and $(1/V)(dV/dT)$ are lowered and the margin is increased) by the addition of a noncyano material.[5] Table VIII shows the improved multiplexing performance obtained when 30% by weight of the alkyl-alkoxy BCO ester[12] (see structure below) was added to JC10.



The properties of pleochroic dyes dissolved in JC10 were examined to see if the increased nematic order parameter (Figure 8) is transferred to the ordering of the dyes. Three recently developed anthraquinone dyes[13] were used and their order parameters and solubilities examined in JC10 and compared with two standard hosts, E43 a CB mixture from BDH, and ZLI 1132 a PCH mixture from E. Merck. Table IX shows that the blue and yellow dyes do show higher order parameters in JC10 (producing higher contrast in dye displays). Although the solubilities are slightly lower in JC10, they are quite acceptable for most types of dye displays.

TABLE VIII

Twisted nematic multiplexing properties of PECH mixtures

	JC10	JC10 +(R-OR)BCO Ester (30 wt.%)
T_{NI}	70°C	72°C
V_{90} (45°) (20°C)	1.42 V	1.45 V
M'_{20}	1.46	1.40
M_{20}	1.97	1.85
$\frac{1}{V}\left(\frac{dV}{dT}\right)$	0.7%/°C	0.5%/°C
Margin	0	6%

TABLE IX

Properties of dyes in broad range mixtures at 20°C

		CB (E43)	PCH (ZLI 1132)	PECH (JC10)
Nematic range		−10°C → 80°C	−6°C → +70°C	−10°C → +70°C
Blue dye	S	0.77	0.78	0.80
	Sol	7.0%	10.0%	3.7%
Yellow dye	S	0.79	0.80	0.82
	Sol	7.8%	4.0%	2.9%
Red dye	S	0.80	0.80	0.77
	Sol	15%	5%	4%

CONCLUSIONS

The PECHs represent a very useful new homologous series of stable, low-melting, nematic materials for use in display devices. Broad range mixtures have been formulated with a low viscosity, medium birefringence and a large positive dielectric anisotropy. Their performance in a variety of twisted nematic devices is excellent. The PECHs are particularly well suited for use with pleochroic dyes in displays, since their higher order parameters increase the contrast of the display. Finally, a comparison of properties between the structural isomers PECH and PCH questions the validity of molecular theories of elastic constants.

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