Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

The preparation and liquid crystal properties of materials incorporating a mono-substituted ring system

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To cite this Article Carrt, N. and Gray, G. W.(1989) 'The preparation and liquid crystal properties of materials incorporating a mono-substituted ring system', Liquid Crystals, 6: 4, 467 — 480
To link to this Article: DOI: 10.1080/02678298908034191
URL: http://dx.doi.org/10.1080/02678298908034191

LIQUID CRYSTALS, 1989, VOL. 6, NO. 4, 467–480

The preparation and liquid crystal properties of materials incorporating a mono-substituted ring system

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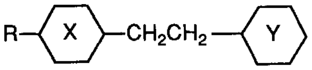
The liquid crystal properties of a homologous series from methyl to heptyl of novel 1-(*trans*-4-alkylcyclohexyl)-2-phenylethanes (PECH) are presented. These compounds are stable materials of low viscosity and low dielectric anisotropy incorporating the $-CH_2CH_2-$ inter-ring linkage. Comparisons are made between the propyl homologue, PECH 3.H, and the commercial isomeric material PCH 3.2. The effect of replacing the *trans*-cyclohexane ring with a bicyclo(2.2.2)octane ring is discussed. A reversed PECH system, in which the alkyl chain is attached to the aromatic moiety (mono-substituted cyclohexane ring), was prepared. An analogous mono-substituted cyclopentane system was also investigated. The separation of two polar/highly polarisable functions in a molecule by a non-polar, non-conjugated group is known to have a detrimental effect on the liquid crystal thermal stability. A collection of data exemplifies this effect which is discussed simply in terms of molecular bonding principles.

1. Introduction

The use of nematic liquid crystals with a low viscosity and high dielectric anisotropy ($\Delta\varepsilon$) for display applications is now well established. It is generally found that device performance is optimized when a mixture of low and high $\Delta\varepsilon$ materials is used rather than just high $\Delta\varepsilon$ materials alone, e.g., materials with terminal cyano-groups. This is due to the low $\Delta\varepsilon$ material breaking up the molecular anti-parallel dipole correlations that occur with such high $\Delta\varepsilon$ materials, thereby increasing the device sharpness [1]. Approximate concentrations of high $\Delta\varepsilon$: low $\Delta\varepsilon$ material of 2:1 have been found to produce the best results. Thus, the development of new materials of both low viscosity and low $\Delta\varepsilon$ is essential if device performances are to be improved.

This work describes the investigation of some low viscosity, low dielectric anisotropy systems incorporating a mono-substituted ring and the $-CH_2CH_2-$ inter-ring linkage, according to the general formula (1)



(1)

where *R*, ring *X* and *Y* are selected from the following: R = *n*-alkyl; X = 1,4-disubstituted benzene, *trans*-1,4-disubstituted cyclohexane or 1,4-disubstituted bicyclo-(2.2.2)octane; and Y = phenyl, cyclohexyl or cyclopentyl. These materials contain no functional groups of high polarity within the molecules. As such groups often tend to increase the viscosity (and possibly $\Delta\varepsilon$), due to increased intermolecular attractions via dipole–dipole interactions, it was anticipated that compounds of usefully low viscosity and $\Delta\varepsilon$ would be obtained. In addition, as the molecular structures are

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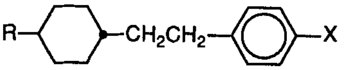
hydrocarbon based (no reactive centres present), a highly stable family of materials should be produced.

2. Results and discussion

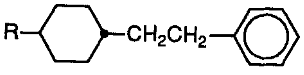
Useful liquid crystal properties have been reported [2–5] for phenethylcyclohexyl (PECH) materials of structure (2)



(2)

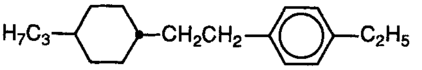
where X = –CN, –OR' or –R'. Room temperature liquid crystal phases have been found for all three series of these compounds and in each case, the measured viscosity is amongst the lowest observed for such mesogens. Furthermore, it can be seen that materials of either low or high $\Delta\varepsilon$ are produced depending on the choice of the terminal substituent, –X.

It seemed attractive therefore to investigate compounds of structure (3), whereby the PECH core structure of (2) is retained, but the aromatic ring is only monosubstituted (i.e. –X = –H in type (2) materials). These compounds are in fact produced *en route* to some type (2) materials [4], and are envisaged



(3)

as low viscosity, low $\Delta\varepsilon$ materials for use as mixture additives. Transition temperatures and viscosity data for these PECH R. H compounds are listed in table 1 for the first seven members of the series. None of these compounds exhibits a liquid crystal phase, but given that the dialkyl compound [6] (4)

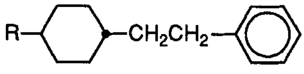


(4)

$T_{CI} = -5°C,\ T_{NI} = [-28°C]$

has a low virtual T_{NI} value, coupled with the knowledge that almost any terminal substituent raises T_{NI} relative to the unsubstituted material, it had not been anticipated that the PECH R. H. materials would exhibit high temperature liquid crystal phases. A plot of the transition temperatures against alkyl chain length is shown in figure 1.

Table 1. Physical data for some compounds of structure



R	T_{CI}/°C	T_{NI}/°C	$\eta_{20°C}$(I)/cP
CH_3–	–5	[–83]	5·3
C_2H_5–	1	[–75]	6·7
C_3H_7–	3	[–55]	8·5
C_4H_9–	–11	[–66]	10·8
C_5H_{11}–	–1·5	[–30]	13·4
C_6H_{13}–	9	[–40]	15·6
C_7H_{15}–	7	[–25]	18·6

[ ] denotes a virtual transition temperature; the host is in all cases E7 (BDH Ltd, Poole, Dorset).

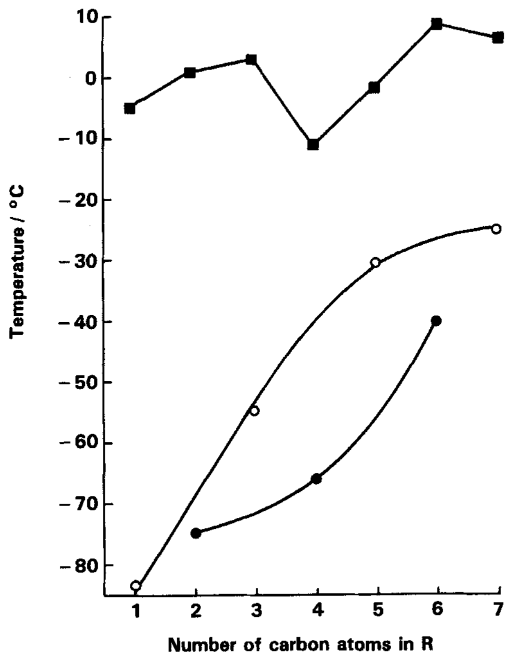
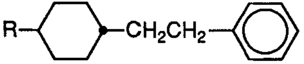


Figure 1. The dependence of the transition temperatures on the number of carbon atoms in *R* for the series  ■ indicates the crystal-isotropic transition temperature; ○ denotes the nematic-isotropic transition temperature for odd values of *R* while ● represents this for even values of *R*.

Whilst no detailed analysis of the T_{NI} values is undertaken, due to their virtual nature, these values appear to be reasonably self-consistent in that they increase for both the odd and even homologues as the series is ascended. A minimum value in the melting points is observed for the butyl homologue, a common feature for many series of compounds.

Figure 2 contains a plot of the isotropic viscosity against the alkyl chain length and shows that a smooth increase in viscosity occurs for successive homologues. This may be interpreted in terms of the greater intermolecular attractive (van der Waals) forces resisting the flow of the molecules past one another. The viscosities of these materials are relatively low and, in general terms, as a nematic viscosity is usually lower than an isotropic viscosity (extrapolated to the same temperature), it would be expected that the effective viscosity of these materials in nematic mixtures would be lower still.

Table 2 contains comparative data for PECH 3.H and compound PCH 3.2, (E. Merck, Darmstadt, F.R. Germany) which is one of the best materials available for use as a low viscosity, low $\Delta\varepsilon$ mixture additive. These materials are, in fact, structural isomers and so provide a direct comparison between the two different core structures. The viscosity of PECH 3.H is only slightly higher than that of PCH 3.2, whilst T_{NI} for PECH 3.H *appears* to be much more favourable. However, such low T_{NI} values may not be too accurate due to the necessity for a relatively long extrapolation across the diagram of state and the fact that these values are often found to be host dependent.

Table 3 contains further data for comparative mixtures incorporating these materials. These results shows that a small advantage has been gained in terms of the

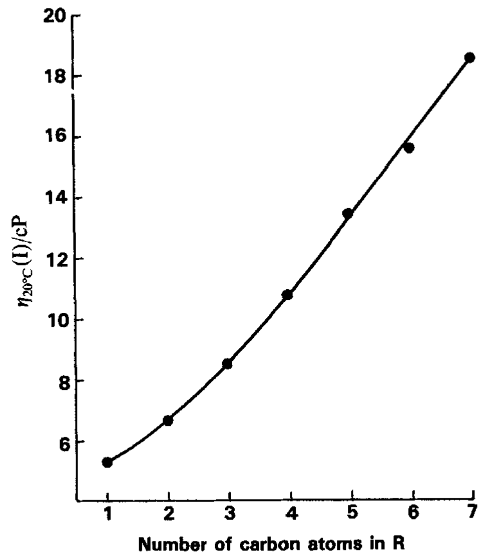


Figure 2. The dependence of viscosity on the number of carbon atoms in R for the series

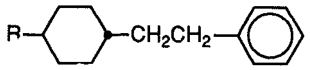
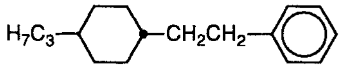
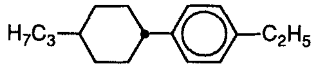


Table 2. Physical data for the compounds of structure



(PECH 3.H)



(PCH 3.2)

	PECH 3.H	PCH 3.2
$T_{CI}/°C$	3	−1·5
$T_{NI}/°C$	[−55]	[−75]
$\eta_{20°C}(I)/cP$	8·5	7·5

[ ] denotes a virtual transition temperature; host is E7.

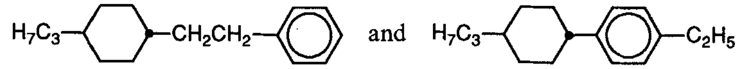
dielectric anisotropy for the mixture containing PECH 3.H, whilst the T_{NI} value is lower, relative to the PCH 3.2 mixture; despite the higher virtual T_{NI} obtained using E7 as host.

The viscosity of the PECH 3.H mixture is slightly higher than that of the PCH 3.2 mixture. However, as the viscosity of any mixture is most important at very low temperatures, due to slower device response times, materials are best compared by their activation energy, E_a (see equation (1)). This is a measure of the energy required for the molecules to flow past one another and is therefore related to the orientational changes of the molecules when switching between the ON and OFF states.

$$\eta = \eta_0 \exp\left(\frac{-E_a}{RT}\right), \qquad (1)$$

where η is the flow aligned viscosity at temperature T and η_0 is the flow aligned viscosity at absolute zero. Low values of E_a are therefore desirable, and whilst that for the PCH mixture is the lower of the two, the value for the PECH mixture is only

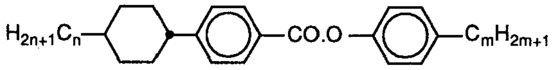
Table 3. Physical and electro-optic data for 27 wt % of the compounds of structure



when incorporated into a nematic host†.

		HOST + 27 wt % of PECH 3.H	HOST + 27 wt % of PCH 3.2
$T_{NI}/°C$		72	86·5
$\eta_{20°C}(N)/cP$		22	18·5
$\eta_{10°C}(N)/cP$		36	30
$\eta_{0°C}(N)/cP$		64	53
$\eta_{-10°C}(N)/cP$		135	103
$E_a(N)/kJ\ mole^{-1}$		16·8	15·9
$T = 0{\cdot}85 \times T_{NI}$	$\varepsilon_{\parallel}$	7·66	7·36
	$\varepsilon_{\perp}$	3·45	3·35
	$\Delta\varepsilon$	4·21	4·01

† The composition of the additive plus the host is: low viscosity additive, 27 wt %; PCH 3, 10 wt %; PCH 5, 5 wt %; PCH 3·02, 10 wt %; BCH 5, 7 wt %; BCH 5·2, 17 wt %; CBC 5·3, 10 wt %; HP 3·3, 8 wt %; HP 5·3, 6 wt %; where HP nm is

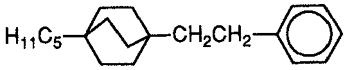
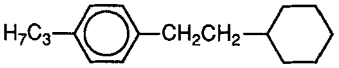
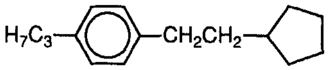


greater by approximately 5 per cent. Consequently, the PECH R. H materials are comparable with PCH dialkyl compounds and thus represent a novel family of useful low viscosity, low dielectric anisotropy mixture additives.

Further work by colleagues at RSRE Malvern has shown that incorporation of the PECH R. H. materials into mixtures is efficient at breaking up the anti-parallel correlations that exist in high $\Delta\varepsilon$ materials. A reduction in the elastic constant ratio, K_{33}/K_{11}, is observed which produces improved display sharpness. In addition, the temperature dependence of the elastic constant ratio has been found to be relatively low. These points further emphasise the usefulness of the PECH R. H materials, and it is worth noting that some closely related PECH materials have also been shown to produce enhanced solubility for some high T_{NI} liquid crystal materials, whilst others have produced high order parameters of dissolved dyes [7], i.e. structure (2), X = $-OR'$ and –CN respectively.

The effect of various ring systems on the properties of type (3) materials was assessed by replacing the cyclohexane ring with a bicyclo(2.2.2)octane ring, reversing the cyclohexane and phenyl rings, and replacing the phenyl ring with a cyclopentyl ring. Table 4 contains transition temperatures and viscosity data for these systems. The effect of replacing the *trans*-cyclohexane ring by the bicyclo(2.2.2)octane ring can be assessed by comparing PEBCO 5.H with PECH 5.H (table 1). The melting point, T_{NI} and isotropic viscosity have all increased (+25.5°C, +38.5°C and +25.1 cP respectively) relative to PECH 5.H. The increases in the transition temperatures are similar to those found when such a structural change is made in other systems and therefore supports the estimate for the virtual T_{NI} of PECH 5.H. The large viscosity increase serves to underline the difference between the relatively sleek, free-moving nature of the cyclohexane ring and the bulky, more spherical geometry of the bicyclo(2.2.2)octane ring. It should be noted that the monotropic nematic phase of PEBCO 5.H is the first liquid crystal phase to be observed directly for any mono-substituted, $-CH_2CH_2-$ linked material of this type.

Table 4. Physical data for some further novel mono-substituted systems incorporating the $-CH_2CH_2-$ inter-ring linkage.

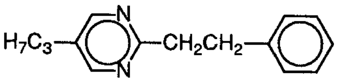
Structure	Code	$T_{CI}/°C$	$T_{NI}/°C$	$\eta_{20°C}(I)/cP$
	PEBCO 5.H	24	(8·5)	38·5
	CHEB 3.H	<0	$[-110]$	9·7
	CPEB 3.H	<0	$[-200]$	5·8

[ ] denotes a virtual transition temperature; host is E7.
( ) denotes a monotropic transition temperature.

Reversal of the ring systems in PECH 3.H to produce CHEB 3.H serves only to worsen the liquid crystal thermal stability as T_{NI} is estimated to have fallen by 55°C. It is envisaged that the mono-substituted cyclohexane ring in CHEB R. H systems is able to undergo conformational changes more easily than when restrained by an additional substituent as for the PECH R. H materials. As a result, a greater proportion of conformations that are disruptive to the one dimensional ordering of the fluid will be present, and these will serve to reduce T_{NI}.

When the mono-substituted aliphatic ring is cyclopentane (CPEB), the system has little or no tendency towards forming a liquid crystal phase. Such a system must have a highly non-linear structure and apparently offers little advantage relative to simple organic materials (e.g., hydrocarbons, solvents, etc.) normally considered incompatible with liquid crystal behaviour.

It is also possible to compare the effect of the heterocyclic 1,3-disubstituted pyrimidine ring in the known [8] compound (5) with PECH 3.H (cf. table 1). Such a change combines the effects of separation of two regions of high polarisability by the $-CH_2CH_2-$ inter-ring linkage, and the introduction of the dipole associated with the heterocyclic ring.

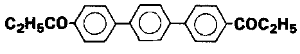
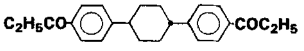
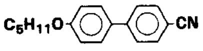
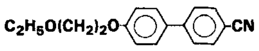
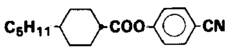
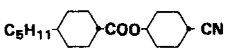
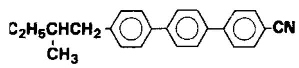
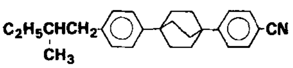
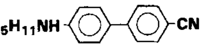
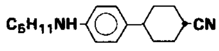
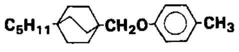
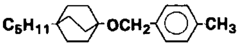
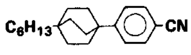
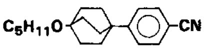
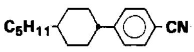
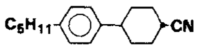
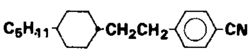
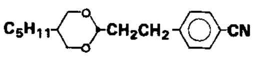


(5)

$$T_{CI} = 22°C,\ T_{NI} = [-85°C],\ \eta_{20°C}(I) = 13{\cdot}3cP$$

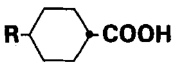
With respect to the melting point, T_{NI} and the viscosity the PECH 3.H material is better off in all cases. These results are consistant with the observations of other aromatic [4] and heterocyclic [5, 8] rings being separated from a second aromatic ring by the $-CH_2CH_2-$ inter-ring linkage. In general, it has been found that the separation of two aromatic rings by a non-conjugated linkage is unfavourable from the point of view of liquid crystal (nematic) thermal stability. A search of the general literature on liquid crystal materials has revealed that there are many examples of compounds having good liquid crystal thermal stability where a structurally related compound has poor thermal stability. Examples of such compounds are given in table 5, and it can be seen that the materials and groups involved cover many different types. Furthermore, there are many examples (see table 6) of known, useful liquid crystal

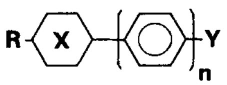
Table 5. Comparitive thermal data for some liquid crystal materials with structurally related materials of relatively low thermal stability.

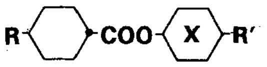
Compound	T_{NI}/°C	Ref.	Comparison	T_{NI}/°C	Ref.
	314	[9]		237	[10]
	68	[11]		[−15]	[12]
	79	[13]		[16]	[14]
	208	[15]		156	[15]
	91	[16]		(17)	[16]
	(33·5)	[17]		[−210]	[17]
	86	[18]		< 20	[15]
	55	[19]		[−25]	[20]
	51	[4]		(19)	[8]

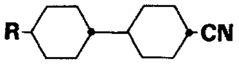
[ ] denotes a virtual transition temperature
( ) denotes a monotropic transition temperature

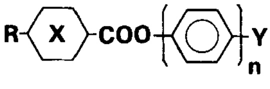
Table 6. A list of some useful liquid crystal materials containing alkyl-alicyclic ring functions for which no reports of liquid crystal properties for the corresponding materials containing alkoxy-alicyclic ring functions have appeared.

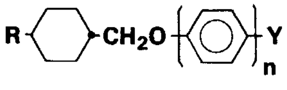


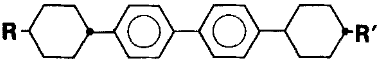


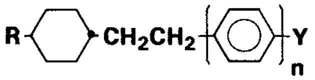












Y = −R′, −OR′, −CN

n = 1 , 2

X = 

materials involving alkyl-alicyclic rings for which no reports on the corresponding alkoxy-alicylic ring materials have appeared. It is now widely accepted that these latter compounds have extremely poor liquid crystal thermal stability.

Earlier explanations of such effects have considered the molecules either;

(*a*) to be made up of certain highly polar/polarizable regions [5, 8, 17, 21], the separation of which, by regions of low polarity/polarizability, appears to be detrimental to the liquid crystal thermal stability, or
(*b*) to contain different regions which function as energy emitters and receivers [20].

It is perhaps simpler to consider these effects in terms of the different types of bonding within the molecules. Almost without exception, all of the known examples of materials that exhibit unexpectedly low liquid crystal thermal stability contain within the molecules two distinct regions of non-bonded or relatively weakly bonded electrons separated by regions of essentially inert, strongly bonded electrons. The non-bonded electrons are usually lone electron pairs, whilst the weakly bonded electrons are usually in *p*-orbitals that can interact to form conjugated π-electron systems (sp or sp^2 systems). Lone pair electrons on oxygen or nitrogen atoms isolated from aromatic rings, and interacting *p*-orbitals in aromatic systems, nitrile groups, ester functions, etc., provide examples of non-bonded and weakly-bonded electron systems respectively. When a single such region is present within a molecule the system often tolerates this well, and indeed, such a region may in fact be a contributory factor to the reasonably good thermal stability of the mesophase observed for many such materials. However, in a molecule where two such regions are present, but isolated from one another, it seems that such interactions become disadvantageous for mesophase formation, as a result of disruptive (repulsive) intermolecular intractions. Note that the explanation given here for the instability of such materials is based upon electronic properties of the molecules and can be contrasted with the reasons for the properties of the mono-substituted cyclohexane and cyclopentane compounds discussed previously, where instability is associated with molecular deformations. The incidence of observable liquid crystal properties in systems involving separation of two regions of non-bonded or weakly bonded electrons is only likely to occur with molecules of quite extended molecular structures. The strongly bonded electron systems involve σ-bonds that result from direct orbital interactions, such as those found in carbon–carbon and carbon–hydrogen bonds (sp^3 systems). On this basis, it is possible to inspect a structure and predict whether it represents a mesogen of high thermal stability, or one of exceptionally poor liquid crystal behaviour.

3. Experimental

3.1. *Structure and purity of materials*

Infra-red, H.N.M.R. and mass spectra were obtained for the compounds synthesized and found to be consistent with the required structures. Infra-red spectra were determined using a Perkin–Elmer 457 spectometer, H.N.M.R. spectra using a JEOL JNM-4HX60 spectometer and mass spectra using a AEI MS 902 mass spectrometer. Each final product gave a single spot on thin layer chromatography (TLC) and was at least 99·7 per cent pure as determined by gas-liquid chromatography (GLC) and values of 99·9 per cent were common. All final products were assessed either by high resolution MS or gave satisfactory elemental analyses.

3.2. *Transition temperatures*

Melting points were determined by the standard capillary method. Whenever this was below ambient temperature, a combination of low temperature microscopy and differential scanning calorimetry (DSC) was used. The low temperature microscopy and liquid crystal transition temperatures were measured using a Nikon L-Ke or Vickers M72C polarising microscope equipped with a Mettler FP52 heating/cooling stage coupled to a Mettler FP5 temperature control unit. DSC measurements were made using a Perkin Elmer DSC-2C system. When the material under test did not exhibit a nematic phase, a virtual T_{NI} was determined. This was done by making mixtures of the test material with the nematic eutectic E7 (BDH Ltd, Broom Road, Poole, Dorset) and measuring the N–I transition temperatures. By extrapolating the mixture T_{NI} versus composition plot to 100 per cent composition for the test material, T_{NI} of the test material was determined.

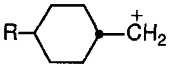
3.3. *Viscosity measurements*

The nematic viscosity, $\eta(N)$, or the isotropic viscosity, $\eta(I)$, of a material was measured using a Poulten, Selfe and Lee (Model 250) semi-micro capillary viscometer.

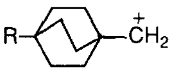
3.4. *Preparation of materials*

Each general experimental procedure is outlined by particular reference to a representative homologue, and the overall synthetic route is illustrated in figure 3.

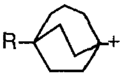
Although the *trans*-cyclohexane and bicyclo(2.2.2)octane rings are closely related aliphatic ring systems their chemistry can be quite different. In relation to this work the main difference is the formation of the substituted acetonitriles. The substituted *trans*-cyclohexylacetonitriles were prepared by bromination of the substituted *trans*-cyclohexylmethanols followed by cyanation of the bromides (steps c and e). However, bromination of the corresponding substituted-bicyclo(2.2.2)octylmethanols by the same procedure produced a mixture of products with no substantial formation of the required bromide. The most likely kinetics for this reaction are first order (S_N1 mechanism) and produce the intermediate (6) in the case of cyclohexane:



(6)



(7)



(8)

This primary carbocation will combine rapidly with a bromide anion to form the product. However, the byclo(2.2.2)octyl carbocation (7) is capable of rearrangement by C–C bond cleavage to produce the tertiary carbocation (8). This process is not as favourable for (6) as only a secondary carbocation can result. The resulting substituted-bicyclo(3.2.2.)nonyl carbocation (8) is capable of further change by way of hydride shifts etc., and can produce a complicated mixture of bromination products. Consequently, the substituted-bicyclo(2.2.2)octylacetonitriles were prepared by tosylation (S_N2 mechanism) of the corresponding substituted-methanols (steps d and f).

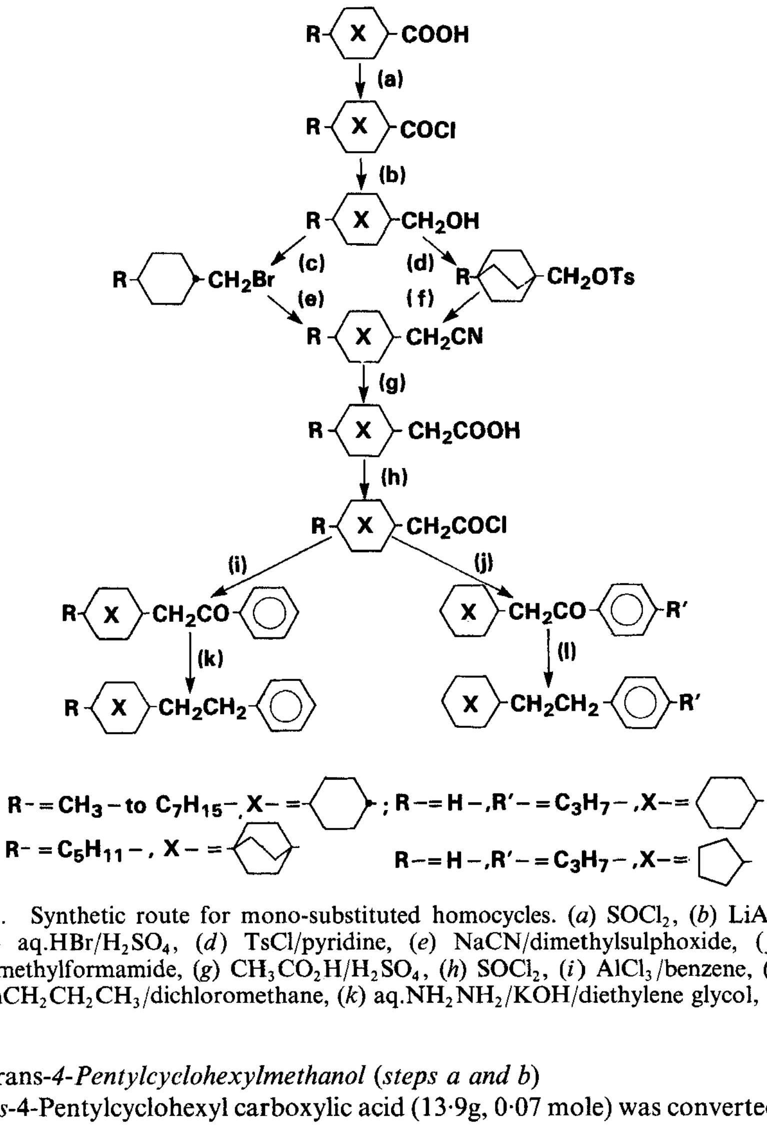


Figure 3. Synthetic route for mono-substituted homocycles. (*a*) $SOCl_2$, (*b*) $LiAlH_4$/ether, (*c*) aq.HBr/H_2SO_4, (*d*) TsCl/pyridine, (*e*) NaCN/dimethylsulphoxide, (*f*) KCN/dimethylformamide, (*g*) CH_3CO_2H/H_2SO_4, (*h*) $SOCl_2$, (*i*) $AlCl_3$/benzene, (*j*) $AlCl_3$/$PhCH_2CH_2CH_3$/dichloromethane, (*k*) aq.NH_2NH_2/KOH/diethylene glycol, (*l*) as (K).

3.4.1. trans-*4-Pentylcyclohexylmethanol* (*steps a and b*)

trans-4-Pentylcyclohexyl carboxylic acid (13·9g, 0·07 mole) was converted into the acid chloride using thionyl chloride (120 cm^3). A solution of the acid chloride in dry ether (80 cm^3) was added to a solution of lithium aluminium hydride (5·3 g, 0·14 mole) in dry ether (100 cm^3) at such a rate as to maintain gentle reflux for 30 min. Water and then dilute hydrochloric acid were added to destroy the excess of lithium aluminium hydride. The ethereal layer was decanted off and the remaining inorganic salts were washed with ether. The combined extracts were washed with water and dried (Na_2SO_4). Distillation yielded the product as a colourless liquid, 12·0 g (93 per cent), b.p. 99°C at 0·1 mm Hg.

The following alcohols were prepared similarly in yields of 88–99 per cent:

trans-4-methylcyclohexylmethanol,	b.p. 90°C at 5 mm Hg,
trans-4-ethylcyclohexylmethanol,	b.p. 143°C at 3 mm Hg,
trans-4-propylcyclohexylmethanol,	b.p. 155°C at 3 mm Hg,
trans-4-butylcyclohexylmethanol,	b.p. 150°C at 1 mm Hg,

trans-4-hexylcyclohexylmethanol,	b.p. 111°C at 0·2 mm Hg,
trans-4-heptylcyclohexylmethanol,	b.p. 116°C at 0·1 mm Hg,
4-pentylbicyclo(2.2.2)octylmethanol,	b.p. 150°C at 0·05 mm Hg,

3.4.2. trans-*4-Pentylcyclohexylmethyl bromide* (*step c*)

To an efficiently stirred mixture of 48–50 per cent hydrobromic acid solution (15 cm^3), concentrated sulphuric acid (4 cm^3) and *trans*-4-pentylcyclohexylmethanol (12·7 g, 0·069 mole) was added dropwise an additional amount of concentrated sulphuric acid (2·5 cm^3). The mixture was then heated under reflux for 3 h. The cooled solution was poured onto ice and then shaken with ether. The combined extracts were washed with brine and dried (Na_2SO_4). The product was obtained by distillation under reduced pressure which yielded a pale yellow liquid, 14·0 g (82 per cent), b.p. 155°C at 15 mm Hg.

The following alkyl bromides were prepared similarly in yields of 69–81 per cent:

trans-4-methylcyclohexylmethyl bromide,	b.p. 61°C at 3 mm Hg,
trans-4-ethylcyclohexylmethyl bromide,	b.p. 66°C at 2 mm Hg,
trans-4-propylcyclohexylmethyl bromide,	b.p. 96°C at 4 mm Hg,
trans-4-butylcyclohexylmethyl bromide,	b.p. 151°C at 15 mm Hg,
trans-4-hexylcyclohexylmethyl bromide,	b.p. 166°C at 15 mm Hg,
trans-4-heptylcyclohexylmethyl bromide,	b.p. 98°C at 0·2 mm Hg

3.4.3. *4-Pentylbicyclo(2.2.2)octylmethyl toluene-4-sulphonate* (*step d*)

A solution of 4-pentylbicyclo(2.2.2)octylmethanol (2·5 g, 0·012 mole) and toluene-4-sulphonyl chloride (3·4 g, 0·018 mole) in dry pyridine (33 cm^3) was stirred and heated at 40°C for 60 h. The cooled reaction mxiture was poured into ice-water (60 g) and shaken with ether. The combined extracts were washed with dilute hydrochloric acid, water, then dried (Na_2SO_4). The tosylate was isolated and crystallized from light petroleum (b.p. 40–60°C). The yield of colourless crystals was 3·1 g (71 per cent), m.p. 67°C.

3.4.4. trans-*4-Pentylcyclohexylacetonitrile* (*step e*)

Sodium cyanide (8·0 g, 0·163 mole) was dissolved in dry dimethyl sulphoxide (90 cm^3) by stirring at 150°C for several minutes. To this solution was added a solution of *trans*-4-pentylcyclohexylmethyl bromide (30·0 g, 0·122 mole) in dry dimethyl sulphoxide (60 cm^3) and the temperature kept at 150°C for 90 min. The cooled reaction mixture was poured into ice-water and shaken with cyclohexane. The extracts were washed with brine and dried (Na_2SO_4). The nitrile, a pale yellow oil, gave a purity of 98·5 per cent by GLC and was used in the hydrolysis step without purification. The yield was 22·5 g (86 per cent).

The *trans*-4-methyl-, ethyl-, propyl-, butyl-, hexyl-, and heptyl- cyclohexylacetonitriles were prepared similarly in yields >87 per cent and of purity >98 per cent.

3.4.5. *4-Pentylbicyclo(2.2.2)octylacetonitrile* (*step f*)

4-Pentylbicyclo(2.2.2)octylmethyl toluene-4-sulphonate (2·1 g, 0·0057 mole) was heated under reflux in dry dimethylformamide (20 cm^3) with potassium cyanide (0·44 g, 0·0068 mole) for 18 h. A solution of iron (III) chloride (1·4 g, 0·0066 mole) in water (80 cm^3) and concentrated hydrochloric acid (56 cm^3) was added and the mixture was stirred at 50–60°C for 20 min.

The cooled solution was poured into water and shaken with ether. The extracts were washed with brine and dried (Na_2SO_4). The product, an oil, was purified by distillation under reduced pressure yielding 1·1 g (90 per cent), b.p. 130°C at 2 mm Hg.

3.4.6. trans-*4-Pentylcyclohexylacetic acid* (*step g*)

trans-4-Pentylcyclohexylacetonitrile (22·5 g, 0·117 mole) was heated under gentle reflux for 18 h in a mixture of 50 percent (w : w) aqueous sulphuric acid (100 cm^3) and glacial acetic acid (250 cm^3). The excess of acetic acid was then removed *in vacuo* and the residue was shaken with dichloromethane. The extracts were washed with water and dried ($CaCl_2$). The product was crystallised twice from light petroleum (b.p. 40–60°C). The yield was 20·7 g (84 per cent), m.p. 59°C.

The following acids were prepared similarly in yields between 74 and 82 per cent

trans-4-methylcyclohexylacetic acid,	m.p. 74°C,
trans-4-ethylcyclohexylacetic acid,	m.p. 45°C,
trans-4-propylcyclohexylacetic acid,	m.p. 51°C,
trans-4-butylcyclohexylacetic acid,	m.p. 60°C,
trans-4-hexylcyclohexylacetic acid,	m.p. 66°C,
trans-4-heptylcyclohexylacetic acid,	m.p. 68°C,
4-pentylbicyclo(2.2.2)octylacetic acid,	m.p. 70°C.

3.4.7. trans-*4-Pentylcyclohexylmethyl phenyl ketone* (*steps h and i*)

A solution of trans-4-pentylcyclohexylacetic acid (7·0 g, 0·033 mole), converted to the acid chloride, in dry benzene (80 cm^3) was added to a stirred solution of crushed anhydrous aluminium chloride (5·3 g, 0·04 mole) in dry benzene (70 cm^3) at a rate such that the reaction temperature was maintained between 5–10°C. The mixture was then allowed to warm to room temperature and stirred for 18 h. It was then warmed at 50°C for one hour. The cooled solution was then acidified (dilute hydrochloric acid), poured into water and shaken with ether. The extracts were washed with water and dried (Na_2SO_4). The crude product was distilled (b.p. 130°C at 2·5 mm Hg) to yield a white solid which was crystallized from light petroleum (b.p. 40–60°C); the yield was 8·0 g (89 per cent), m.p. 43°C.

The following ketones were prepared similarly in yields ranging from 50-90 per cent

trans-4-methylcyclohexymethyl phenyl ketone, m.p. 55°C,
trans-4-ethylcyclohexylmethyl phenyl ketone, m.p. 43·5°C,
trans-4-propylcyclohexylmethyl phenyl ketone, m.p. 46°C,
trans-4-butylcyclohexylmethyl phenyl ketone, m.p. 26°C,
trans-4-hexylcyclohexylmethyl phenyl ketone, m.p. 27°C,
trans-4-heptylcyclohexylmethyl phenyl ketone, m.p. 51°C,
4-pentylbicyclo(2.2.2)octylmethyl phenyl ketone, m.p. 44°C.

3.4.8. *Cyclohexylmethyl 4-propylphenyl ketone* (*steps h and j*)

A solution of propylbenzene (3·2 g, 0·027 mole) and cyclohexylacetic acid (2·0 g, 0·014 mole), converted to the acid chloride, in dry dichloromethane (100 cm^3) was added to a suspension of crushed anhydrous aluminium chloride (2·3 g, 0·017 mole) in dry dichloromethane (80 cm^3) at a rate such that the reaction temperature did not rise above 10°C. After the addition, the solution was allowed to warm to room temperature and stirred for a further 18 h. The reaction mixture was heated under gentle reflux for 45 min, acidified (dilute hydrochloric acid), diluted and shaken with chloroform. The extracts were washed with water and dried ($CaCl_2$). The dark brown solid was purified by crystallization from a 10 : 1 (v : v) mixture of light petroleum (b.p. 40–60°C). This yielded the ketone as pale yellow crystals, 2·1 g, (62 per cent), b.p. 102°C at 0·04 mm Hg.

Cyclopentylmethyl 4-propylphenyl ketone was prepared similarly (63 per cent), b.p. 100°C at 0·05 mm Hg.

3.4.9. *1-(*trans*-4-Pentylcyclohexyl)-2-phenylethane (steps k and l)*

A solution of phenyl *trans*-4-pentylcyclohexylmethyl ketone (2·2 g, 0·008 mole), potassium hydroxide (2·3 g, 0·040 mole), 98–100 per cent hydrazine hydrate (4·6 g, 0·093 mole) and water (0·9 g, 0·050 mole) in diethylene glycol (175 cm^3) was heated at 130°C for 1·5 h with stirring. The temperature was then raised to 205°C to drive off the excess of water and hydrazine hydrate. The mixture was then kept at 205° C for 4 h. It was then poured into ice-water and shaken with cyclohexane. The extracts were washed with water and dried (Na_2SO_4). The product was obtained as a colourless liquid by distillation (b.p. 120°C at 2 mm Hg). The yield was 1·1 g (54 per cent), m.p. 1·5°C.

The following hydrocarbons were prepared similarly in yields of 50–85 per cent

1-(*trans*-4-methylcyclohexyl)-2-phenylethane, b.p. 85°C at 0·05 mm Hg, m.p. – 5°C,
1-(*trans*-4-ethylcyclohexyl)-2-phenylethane, b.p. 100°C at 0·05 mm Hg, m. p. 1°C,
1-(*trans*-4-propylcyclohexyl)-2-phenylethane, b.p. 113°C at 0·5 mm Hg, m.p. 3°C,
1-(*trans*-4-butylcyclohexyl)-2-phenylethane, b.p. 120°C at 1 mm Hg, m.p. – 11°C,
1-(*trans*-4-hexylcyclohexyl)-2-phenylethane, b.p. 125°C at 0·07 mm Hg, m.p. 9°C,
1-(*trans*-4-heptylcyclohexyl)-2-phenylethane, b.p. 150°C at 4·0 mm Hg, m.p. 7°C,
1-cyclohexyl-2-(4-propylphenyl)ethane, b.p. 100°C at 0·06.mm Hg,
1-cyclopentyl-2-(4-propylphenyl)ethane, b.p. 94°C at 0·05 mm Hg,
1-(4-pentylbicyclo(2.2.2)octyl)-2-phenylethane, m.p. 24°C, T_{NI} 8·5°C (monotropic).

4. Conclusion

The PECH R.H compounds represent a family of stable, low viscosity, low dielectric anisotropy materials that are comparable with the best liquid crystal additives currently available, and illustrate that useful liquid crystal properties can be obtained from mono-substituted compounds. The incorportation of the bicyclo(2.2.2)octane ring into the base structure produces a similar effect to that obtained for the same structural change in many other liquid crystal systems, i.e. higher T_{NI}, viscosity, etc. However, the use of mono-substituted cyclohexane and cyclopentane ring systems has been found to be unfavourable, particularly with respect to liquid crystal thermal stability. By comparing the mono-substituted materials prepared in this work with other known materials, along with other examples from the literature, it has been possible to interpret the principles of liquid crystal instability (see also [22]) often associated with molecular polarity/polarizability at a more fundamental level, i.e. in terms of the nature of the bonding present in the molecule.

The authors gratefully acknowledge the U.K. Ministry of Defence for a research grant. Colleagues at RSRE, Malvern are thanked for permission to publish the electro-optic data. This paper is published by permission of the Director, HMSO.

References

[1] Bradshaw, M. J., and Raynes, E. P., 1983, *Molec. Crystals liq. Crystals*, **91**, 145.
[2] Gray, G. W., 1982, *Polymer Liquid Crystals*, edited by A. Ciferri, W. R. Krigbaum and R. B. Meyer (Academic Press), Chap. 1.
[3] Schadt, M., Petrzilka, M., Gerber, P. R., Villiger, A., and Trickes, G., 1983, *Molec. Crystals liq. Crystals*, **94**, 139.
[4] Carr, N., Gray, G. W., and McDonnell, D. G., 1983, *Molec. Crystals liq. Crystals*, **97**, 13.
[5] Carr, N., Gray, G. W., and Nicholas, B. M., 1986, Paper presented at the 11th International Liquid Crystal Conference, Berkley, California, U.S.A.
[6] Carr, N., and Gray, G. W. (unpublished results).
[7] Bradshaw, M. J., Constant, J., McDonnell, D. G., and Raynes, E. P., 1983, *Molec. Crystals liq. Crystals*, **97**, 177.
[8] Andrews, B. M., Gray, G. W., and Bradshaw, M. J., 1985, *Molec. Crystals liq. Crystals*, **123**, 257.
[9] Schubert, H., Lorenz, H-J., Hoffmann, R., and Franke, F., 1966, *Z. Chem.*, **6**, 337.
[10] Schubert, H., Schulze, W., Deutscher, H. J., Uhlig, V., and Kuppe, R., 1975, *J. Phys., Paris*, **36**, 379.
[11] Gray, G. W., Harrison, K. J., and Nash, J. A., 1973, *Electron Lett.*, **9**, 130.
[12] Gray, G. W., and Mosley, A. (unpublished results).
[13] Deutscher, H-J., Kuschel, F., Schubert, H., and Demus, D., 1974, D.D.R. Patent 105701.
[14] Osman, M. A., and Revesz, L., 1979, *Molec. Crystals liq. Crystals Lett.*, **56**, 105.
[15] Gray, G. W., 1978 *Advances in Liquid Crystal Materials for Applications* (special publication by BDH Ltd., Poole, Dorset).
[16] Osman, M. A., and Reversz, L., 1980, *Molec. Crystals liq. Crystals Lett.*, **56**, 133.
[17] Carr, N., and Gray, G. W., 1985, *Molec. Crystals liq. Crystals*, **124**, 27.
[18] Gray, G. W., and Kelly, S. M., 1981, *Angew. Chem. Int. Ed. Engl.*, **20**, 393.
[19] Eidenschinck, R., Erdmann, D., Krause, J., and Pohl, L., 1977, *Angew. Chem. Int. Ed. Engl.*, **16**, 100.
[20] Eidenschinck, R., 1980, *Kontakte* (E. Merck), **3**, 12.
[21] Carr, N., Gray, G. W., and Kelly, S. M., 1985, *Molec. Crystals liq. Crystals*, **129**, 301.
[22] Toyne, K. J., 1987, *Thermotropic Liquid Crystals* (C.R.A.C. Vol. 22) edited by G. W. Gray (John Wiley & Sons), Chap. 2.