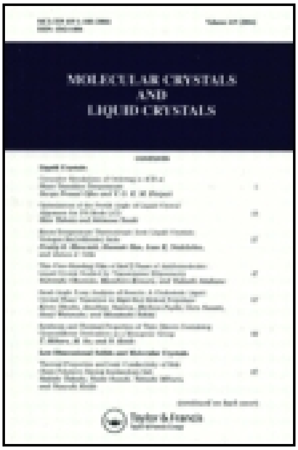


Molecular Crystals and Liquid Crystals

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

The Properties of Liquid Crystal Materials Incorporating the $-CH_2O-$Inter-ring Linkage

N. Carr [a] & G. W. Gray [a]

[a] Department of Chemistry, The University, Hull, HU6 7RX, England

To cite this article: N. Carr & G. W. Gray (1985): The Properties of Liquid Crystal Materials Incorporating the $-CH_2O-$Inter-ring Linkage, Molecular Crystals and Liquid Crystals, 124:1, 27-43

To link to this article: http://dx.doi.org/10.1080/00268948508079463

Mol. Cryst. Liq. Cryst., 1985, Vol. 124, pp. 27–43
0026-8941/85/1244–027/\$20.00/0

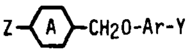
Printed in the United States of America

The Properties of Liquid Crystal Materials Incorporating the —CH_2O— Inter-ring Linkage†

N. CARR and G. W. GRAY
Department of Chemistry, The University, Hull, HU6 7RX, England

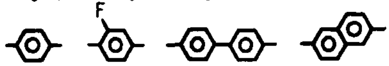
(*Received October 23, 1984*)

To establish more securely the influence of the —CH_2O— inter-ring linkage upon the properties of mesogens of both high and low dielectric anisotropy, a range of ethers with the following general structure has been prepared and their properties examined.



where Z = alkyl when A = cyclohexane or BCO
Z = alkyl or alkoxy when A = benzene
Y = alkyl, alkoxy, or cyano

Ar =



The thermal and electro-optic properties of the compounds are discussed, and comparisons made where possible with analogous materials incorporating the —CH_2CH_2— linkage.

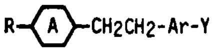
INTRODUCTION

Liquid crystal materials with flexible inter-ring linkages are attracting growing attention for applications since first reports[1,2] were made of the use of the —CH_2CH_2— linkage in compounds of general structure

---

†Presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.

(I), of which some examples with transition temperatures are given below.



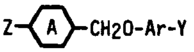
(I)

R	A	Ar	Y	C-N/I	S_B-N	N-I (°C)
C_5H_{11}	cyclohexane	benzene	OC_2H_5	18	(8)	47
C_3H_7	cyclohexane	biphenyl	CN	77.2	-	193.8
C_5H_{11}	BCO	benzene	CN	76	-	113
C_5H_{11}	cyclohexane	benzene	CN	30	-	51
C_5H_{11}	benzene	benzene	CN	62	-	[-24]*

[ ] virtual transition

* Note that separation of polarisable aromatic centres by $-CH_2CH_2-$ strongly depresses nematic properties

By contrast, less attention has been paid[3,4] to the $—CH_2O—$ inter-ring linkage, and the results on such systems tend to be somewhat scattered in the literature. To remedy this situation, we have prepared and examined a range of ethers of general structure (II).



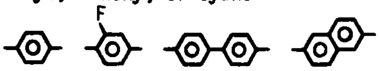
(II)

where Z = alkyl when A = cyclohexane or BCO

Z = alkyl or alkoxy when A = benzene

Y = alkyl, alkoxy, or cyano

Ar =



RESULTS AND DISCUSSION

Ethers of highly positive Δε

Table I summarises the thermal data for materials of general structure (II) where the terminal substituent Y is cyano.

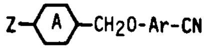
Some general comments may be made about the transition temperatures given below in Table I.

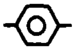
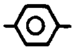
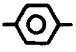
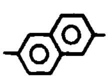
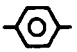
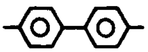
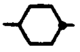
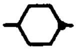
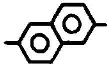
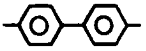
(1) For ring A = benzene, the order of decreasing T_{N-I} with respect to varying Ar is

biphenyl > naphthalene > benzene
85°C 82°C (for C_5H_{11})

TABLE I

Ethers of highly positive Δε



A	Ar	Z	$C-S_A/N/I$	S_A-N/I	N-I (°C)
		C_5H_{11}	49	-	[-20]
		C_6H_{13}	48	-	[-3]
		C_9H_{19}	60	-	[5]
		CH_3	89	-	[-44]
		C_4H_9	79	-	(57)
		C_5H_{11}	72	-	73.5
		C_5H_{11}	82	-	(62)
		C_6H_{13}	82	-	(56)
		C_9H_{19}	74	-	(71)
		C_5H_{11}	91	-	147
		C_6H_{13}	85	129	142
		C_9H_{19}	60	142	-
		C_5H_{11}	74.3	-	(48.6)*
		C_5H_{11}	87.3	-	114.5*
		C_5H_{11}	107.0	136.3	193.2*

( ) monotropic and [ ] virtual transitions.
*see ref 1.
C, crystal; $S_{A,B---}$, smectic A, B---; N, nematic; I, isotropic.

Corresponding inequalities[1] for ring A = cyclohexane are

$$78.7°C \text{ and } 65.9°C \text{ (for } C_5H_{11})$$

(2) For ring A = benzene, the T_{N-I} values are much lower than those for A = cyclohexane, for each Ar. When A = benzene, two polarisable aromatic centres are electronically isolated by the —CH_2O— linkage and the low T_{N-I} of [−20°C] for Ar = benzene and R = C_5H_{11}, reminds us of the T_{N-I} of [−24°C] for the analogous system when the isolating linkage is —CH_2CH_2—.

(3) For Ar = benzene, the highest T_{N-I} values are for ring A = BCO, and the now familiar order of decreasing T_{N-I} is

BCO > cyclohexane > benzene
24.9°C 68.6°C† (for C_5H_{11})

(4) For both A = benzene and cyclohexane, smectic properties occur when Ar = biphenyl—

at R = C_5H_{11} for A = cyclohexane

and at R = C_6H_{13} for A = benzene

Ethers of low $\Delta\epsilon$

Ethers of low dielectric anisotropy were of interest to establish the potential of such materials as replacements for esters commonly used for disrupting the anti-parallel correlations of cyano-substituted nematic materials to make them more suitable for multiplex addressed electro-optic displays.

Di-alkyl substituted ethers

Some examples of materials of general structure (II) carrying terminal alkyl groups, i.e., Z and Y = alkyl groups (R and R′), are recorded in Table II.

The results in Table II emphasise the strong S_B character of these di-alkyl substituted ethers. Only two of the ethers studied exhibit nematic phases (3.5 and 5.2) and these are monotropic ( ). The ether 5.1 exhibits no phase, and the transition temperature of 17°C in [ ] indicates that the transition is virtual in nature. The transition temperature was determined by extrapolation of transition temperature data for a range of mixtures of 5.1 in the commercial nematic host E7 (B.D.H. Chemicals Limited, Poole, Dorset).

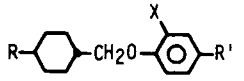
The nematic properties of these ethers are depressed strongly by a lateral fluoro-substituent, as shown by the last material listed in Table II. The difference in the virtual T_{N-I} values is 31°C on passing from parent 5.5 to the 2-fluoro-analogue. This clearly restricts the

---

†This large decrease further emphasises comment 2 above—eg, the decrease is only 20°C from 5PCH to 5CB.

TABLE II

Ethers of low Δε



(*cf* also ref 4)

R	R'	X	C-S_B/I	S_B-I	N-I (°C)
C_3H_7	C_5H_{11}	H	24	-	(4)
C_5H_{11}	CH_3	H	47	-	[17]
C_5H_{11}	C_2H_5	H	30	-	(5.5)
C_5H_{11}	C_3H_7	H	32	(10)	[4]
C_5H_{11}	C_4H_9	H	23	(21)	[-4]
C_5H_{11}	C_5H_{11}	H	35	(31)	[21]
C_5H_{11}	C_6H_{13}	H	30	36	[18]
C_5H_{11}	C_7H_{15}	H	34	38	[26]
C_5H_{11}	C_5H_{11}	F	43	-	[-10]

use of the introduction of a lateral fluoro-substituent to control the smectic properties of such ethers. When the inter-ring linkage is —CO.O—, a fluoro-substituent in this position depresses T_{N-I} by a much smaller effect—around 11°C. This may reflect the different flexibility and conjugative interactions for the —CH_2O— linked materials.

For the 5.3 to 5.7 ethers in Table II, it will be noted that the T_{N-I} values are virtual values (again obtained using data for solutions in E7) and lie *below* the T_{S_B-I} values (monotropic or enantiotropic). These T_{N-I} values therefore represent the potential of the materials to exhibit nematic properties if their inherent smectic (B) characteristics were sufficiently strongly repressed—as in the case of mixtures in E7.

The various transition temperatures for the materials with R = C_5H_{11} listed in Table II are plotted against the number of carbon atoms in the other terminal alkyl group in Figure 1. The strongly monotropic mesogenic characteristics of the series are emphasised by the graphical presentation. The T_{S_B-I} values lie on a rising and levelling curve without any obvious alternation effect. The T_{N-I} values lie on two curves whose shape is reminiscent of the T_{N-I} curves for series such as the 4-alkyl- and 4-alkoxy-4'-cyanobiphenyls, i.e., falling to early minima and then rising and leveling off. The alternation

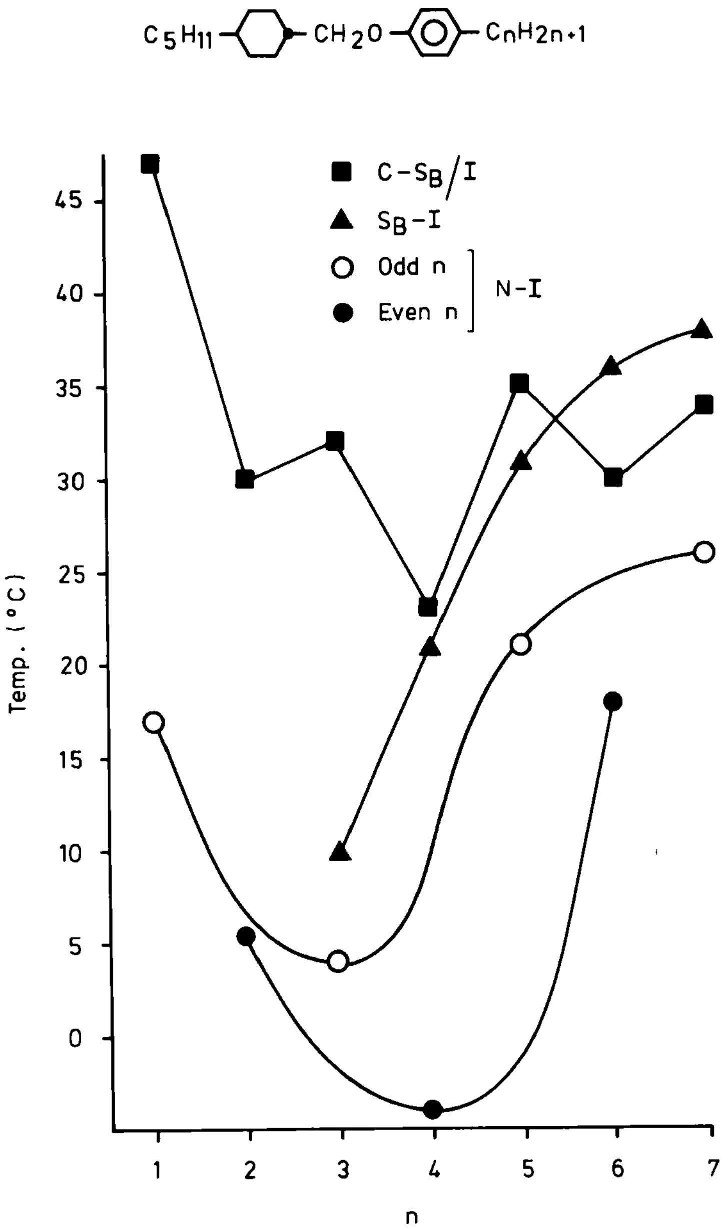


FIGURE 1 Plot of the transition temperatures for the di-alkyl substituted ethers (incorporating a n-pentyl group on the left) against n, the number of carbon atoms in the right hand alkyl group.

effect is obviously marked, with the odd carbon members forming, as normal, the upper curve. Bearing in mind that all but two of the T_{N-I} values are virtual and therefore subject to some uncertainties because of the extrapolation procedure used in obtaining the values, the trends in these T_{N-I} curves seem reasonable and suggest that the virtual values are meaningful.

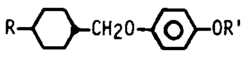
Alkyl/alkoxy substituted ethers

Attention was then paid to ethers analogous to those discussed in the above section, but in which the right hand alkyl group (R′) was replaced by an alkoxy group (OR′). The results for some ethers of this class, again materials of low $\Delta\epsilon$, are recorded in Table III.

The transition temperatures are of course higher for the alkoxy derivatives. Smectic B properties are again quite marked; the S_B-N transitions are all monotropic, as are the succeeding T_{N-I} values. Compound 3.07 gives an enantiotropic S_B-I transition, and four of the ethers listed in the Table give only monotropic nematic phases, without any detectable S_B phase before onset of crystallisation. For

TABLE III

Transition temperatures for:



(*cf* also ref 4)

R	R'	C-S_B/I	S_B-N/I	N-I (°C)
CH_3	C_4H_9	55	-	[18]
C_3H_7	CH_3	42	-	[23]
C_3H_7	C_2H_5	73	-	(44)
C_3H_7	C_3H_7	53	-	(34)
C_3H_7	C_4H_9	55	(25)	(46)
C_3H_7	C_5H_{11}	54	(30)	(42)
C_3H_7	C_6H_{13}	52	(49)	[48]
C_3H_7	C_7H_{15}	42	60	[50]
C_5H_{11}	CH_3	46	-	(38)
C_5H_{11}	C_4H_9	55	(47)	(53)
C_6H_{13}	CH_3	45	-	(36)
C_6H_{13}	C_4H_9	54	(50)	-

Virtual T_{N-I} values [ ] were determined by extrapolation of data obtained for a range of mixtures in a nematic host (E7).

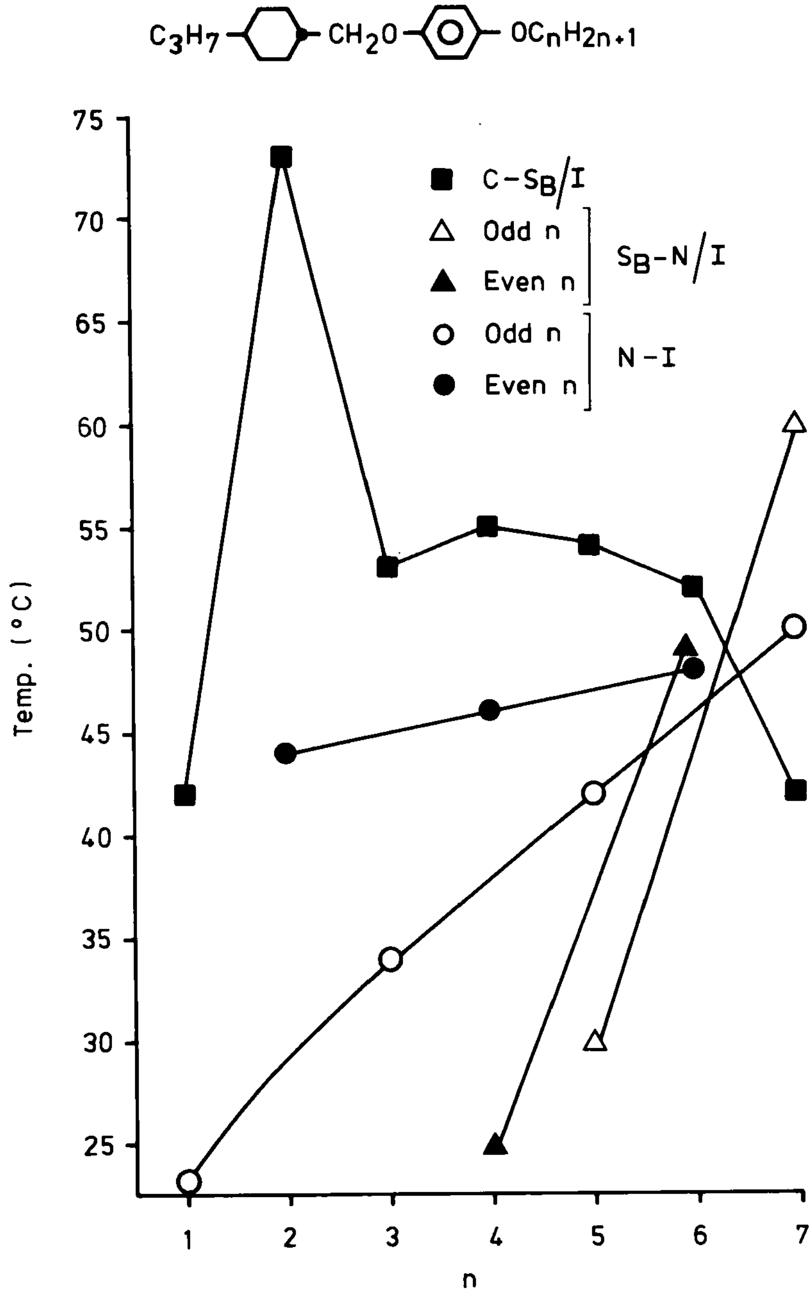


FIGURE 2 Plot of the transition temperatures for the *trans*-4-propylcyclohexylmethyl 4-alkoxyphenyl ethers against n, the number of carbon atoms in the alkoxy group.

those members exhibiting either no phase or an enantiotropic or a monotropic S_B-I transition, virtual T_{N-I} values were determined, as discussed in the previous section. Comparison of compound 5.04 with compound 5.5 (Table II) shows that the alkoxy compound has an increased thermal stability of its S_B phase by 16°C, but it now shows a nematic phase above this smectic phase. The dialkyl compound does not, and the change from alkyl to alkoxy has increased T_{N-I} by 32°C, favouring nematic more than S_B behaviour.

Figure 2 expresses graphically the trend in the various transition temperatures for the *trans*-4-propylcyclohexylmethyl 4-alkoxyphenyl ethers with increasing length of the carbon chain in the alkoxy group. The two virtual T_{N-I} values relate well to the other monotropic T_{N-I} values and this gives us confidence in these values. The T_{N-I} values alternate quite markedly and the upper of the two rising T_{N-I} lines relates, as expected, to even values of n. The even S_B-N/I curve also lies above that for odd n values. In several cases,[5] the S_B-N/I alternation has been found to be opposite in sense to that of T_{N-I} values, but exceptions such as this are not unknown.

Bicyclo(2.2.2)octylmethyl ethers

Several 4-alkylbicyclo(2.2.2)octylmethyl 4-alkyl- or -alkoxy-phenyl ethers, two carrying a fluoro-substituent in the 2-position of the phenyl ring were prepared. The structure of these esters is represented in Table IV which lists the various transition temperatures for these materials.

The following comments are made about the results in Table IV.

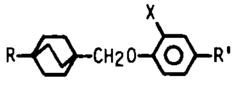
(1) The two laterally fluoro-substituted ethers again have T_{N-I} values substantially lower (*ca.* 20°C) than those of their unfluorinated counterparts. The effect is smaller than for the cyclohexane analogues (see comments following Table II), possibly due to the shielding effect of the BCO ring, but is again much greater than the effect in BCO esters for which a similarly positioned fluoro-substituent may even enhance T_{N-I} by *ca.* 2°C.

(2) Smectic B properties still occur both in the dialkyl and alkyl/alkoxy systems. No assessment can be made of the effect of the 2-fluoro-substituent on the S_B properties, as neither of the unfluorinated parent ethers gave a S_B phase.

(3) All the phases were monotropic, and in three cases virtual T_{N-I} values had to be obtained from results obtained with mixtures in E7. All the N–I transition temperatures are higher for the BCO ethers than for the cyclohexyl analogues, an effect which is now well

TABLE IV

Transition temperatures for:



and -OR'

R	R'/OR'	X	C-I	S_B-N/I	N-I (°C)
C_3H_7	C_5H_{11}	H	51	-	[21]
C_5H_{11}	CH_3	H	69	-	(33.5)
C_5H_{11}	C_2H_5	H	58	-	(20)
C_5H_{11}	C_3H_7	H	56	-	(30)
C_5H_{11}	C_4H_9	H	56	-	(19)
C_5H_{11}	C_5H_{11}	H	47	-	(32)
C_5H_{11}	C_6H_{13}	H	43	(30)	[27]
C_5H_{11}	C_7H_{15}	H	47	(35.5)	(36)
C_5H_{11}	C_4H_9O	H	74	(61)	(68)
C_3H_7	C_5H_{11}	F	41	-	[2]
C_5H_{11}	C_5H_{11}	F	38	-	(11.5)

( ) monotropic.
[ ] virtual values obtained by extrapolation.

established for many series of materials. Taking the 5.2 compounds as examples, the monotropic T_{N-I} values rise by 14.5°C from cyclohexane to BCO ether. For the 3.5 systems, where a monotropic T_{N-I} value is available for the cyclohexane ether, but not for the BCO ether, the increase is 17°C.

The 5.6 and 5.7 ethers also give T_{N-I} increases of 9° and 10°C respectively, but interestingly these increases are accompanied by decreases in the transition temperatures for the S_B phase (6° and 2.5°C repectively). This indicates a lower tendency of the BCO dialkyl ethers to be S_B.

However, the one alkyl/alkoxy BCO ether prepared, 5.04 in Table IV, has both a higher T_{N-I} value (by 15°C) and a higher T_{S_B-N} value (by 14°C)—but notably a higher m.p.—than the 5.04 member of the cyclohexane series (see Table III). For the alkyl/alkoxy systems, S_B and N thermal stability therefore seem to be similarly affected by the change from a cyclohexane to a BCO ring.

In Figure 3 are plotted the S_B–N or I and N–I transition temperatures for the 4-pentylbicyclo(2.2.2)octylmethyl 4-alkylphenyl ethers.

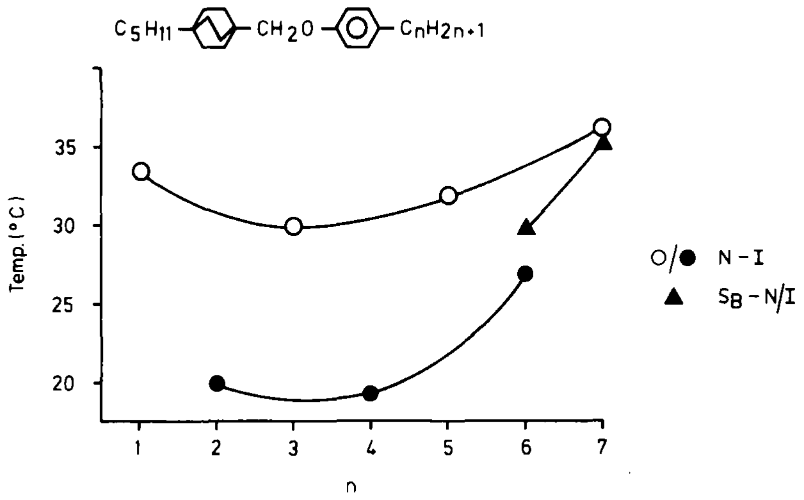
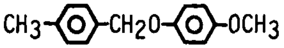
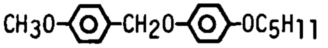
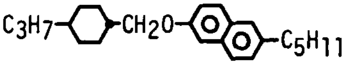
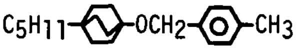


FIGURE 3 Plot of the monotropic and virtual transition temperatures for the 4-pentylbicyclo(2.2.2)octylmethyl 4-alkylphenyl ethers against n, the number of carbon atoms in the alkyl group.

Since all these transitions are monotropic or virtual, the m.p.s have not been included in the diagram. The T_{N-I} point for 5.6 lies below the T_{S_B-I} point because the former represents a virtual transition (the only one in the figure). Attention is drawn only to the quite marked, but otherwise normal alternation effect.

Miscellaneous ethers of low Δε

Further miscellaneous materials with a —CH$_2$O— inter-ring linkage were prepared and of those four examples are listed for comment.

No	Structure	C-I (°C)	N-I (°C)
1		82	[-6]
2		93	[38]
3		99	(78)
4		63	[-210]

From the observed trend in T_{N-I} on changing from a BCO ring to a cyclohexane ring, and from the generally accepted order of decreasing T_{N-I} established for many systems as

BCO > cyclohexane > benzene

it was clear that terminally dialkyl substituted benzyl phenyl ethers would have very low transition temperatures. Moreover, such materials fall into the same category as the first three examples in Table I. For these compounds, the transition temperatures (T_{N-I}) are abnormally low because of the alternation of highly polarisable and weakly polarisable parts of the molecule. That is, in the benzyl ethers, two aromatic rings are isolated from each other by a linkage involving saturated carbon. For these reasons, no examples of such ethers were made, but the first two benzyl phenyl ethers in the above list, one carrying one alkoxy and the other two alkoxy terminal groups emphasise the above points. Despite the terminal alkoxy functions, the T_{N-I} values are both vitual and low for the structures involved.

The fourth ether in this miscellaneous group involves an inversion of the central linkage with respect to that in compound 5.1 in Table IV. An extraordinary drop in T_{N-I} is associated with this structural change—243.5°C in fact, as a consequence of the very low virtual T_{N-I} of [−210°C] for the ether with a linkage inversion. Obviously such a low T_{N-I} is associated with a long extrapolation in the procedure to determine the virtual value, and there must be uncertainties about the value determined. Even bearing this in mind however, it is clear that a very large fall in T_{N-I} is associated with the reversal of the inter-ring linkage. This can only be interpreted in terms of the separation in the —OCH_2— linked molecule of two distinct regions of high polarisability by a region of low polarisability—a situation which is known to have an adverse effect on T_{N-I} values, see reference 6, i.e., the ether oxygen is now isolated and unable to conjugate with the aromatic ring because of the intervening CH_2 group.

The behaviours of ethers 1, 2, and 4 in the above list are therefore associated with a related structural phenomenon.

The third ether in the above list was made simply to establish the behaviour of a *trans*-4-alkylcyclohexylmethyl 6-alkyl-2-naphthyl ether.

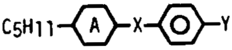
Comparisons of —CH_2CH_2— and —CH_2O— linked materials

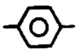
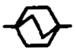
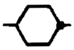
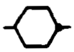
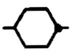
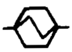
The results contained in Table V allow a comparison to be made of the transition temperatures for several pairs of materials differing only in the nature of the inter-ring linkage (—CH_2O— or —CH_2CH_2—). When A is benzene or cyclohexane, the different central linkages give very comparable $T_{S_B-N/I}$ and T_{N-I} transition temperatures irrespective of whether $\Delta\epsilon$ is strongly positive (Y = CN) or low (Y = OAlkyl or Alkyl). The transition temperatures for the 4-cyanobiphenylyl compounds with A = cyclohexane and X = —CH_2CH_2— or —CH_2O— are also very similar.[1]

It is noted however that when A is bicyclo-octane, the dimethylene bridge gives significantly higher stabilities to both the smectic B and nematic phases for both Y = CN and Alkyl.

TABLE V

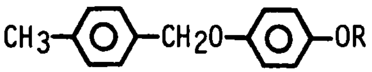
Transition temperatures for:



			Transition temperatures (^{o}C)		
A		Y	C-N/S_B/I	S_B-N/I	N-I
	CH_2CH_2	CN	62		[-24]
	CH_2O	CN	49		[-20]
	CH_2CH_2	CN	30		51
	CH_2O	CN	74.3		(48.8)
	CH_2CH_2	CN	76		113
	CH_2O	CN	72		73
	CH_2CH_2	OCH_3	30		34
	CH_2O	OCH_3	46		(38)
	CH_2CH_2	OC_4H_9	26	44.5	45.5
	CH_2O	OC_4H_9	55	(47)	(53)
	CH_2CH_2	C_3H_7	3	16	[3]
	CH_2O	C_3H_7	32	(10)	[4]
	CH_2CH_2	C_3H_7	60		62
	CH_2O	C_3H_7	56		(30)
	CH_2CH_2	C_5H_{11}	45	58	62
	CH_2O	C_5H_{11}	47		(32)

Electro-optic data

Assessments of the potential of a number of the ethers of low $\Delta\epsilon$ for use as additives to hosts of highly positive $\Delta\epsilon$ in electro-optic displays have been made at RSRE, Malvern. As examples of the results obtained, we quote the following data on three of the ethers.



R = $-CH_3$, 12.5 wt % + R = $-C_4H_9$, 12.5 wt %

T_{N-I} = 45^oC

M_{20^oC} = 1.71; M'_{20^oC} = 1.30

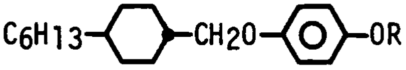
Δn (20^oC, 589 nm) = 0.175

$\Delta\varepsilon$ ($0.95 \times T_{N-I}$) = 9.8

Rise time (20^oC, 3 V) = 53 ms

Decay time (20^oC, 3 V) = 65 ms

V_{10} (0^o) = 1.68 V at 20^oC



R = $-CH_3$, 25 wt % + R = $-C_4H_9$, 20 wt %

T_{N-I} = 57^oC

M_{20^oC} = 1.70; M'_{20^oC} = 1.31

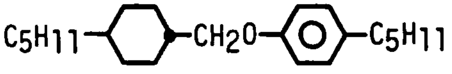
$\Delta\varepsilon$ ($0.95 \times T_{N-I}$) = 7.5

Rise time (20^oC, 3 V) = 100 ms

Decay time (20^oC, 3 V) = 86 ms

V_{10} (0^o) = 1.90 V at 20^oC

$$\frac{-1}{V}\left(\frac{dV}{dT}\right)\%\ {}^{o}C^{-1}\ \left[\begin{array}{lcl} \text{at } V_{90}\ (45^o) & = & 0.51 \\ \text{at } V_{50}\ (10^o) & = & 0.65 \\ \text{at } V_{10}\ \ (0^o) & = & 0.68 \end{array}\right.$$



40 wt %

T_{N-I} = 54°C

$M_{20^{\circ}C}$ = 1.68; $M'_{20^{\circ}C}$ = 1.31

Δn (20°C, 589 nm) = 0.152

Rise time (20°C, 3 V) = 83 ms

Decay time (20°C, 3 V) = 59 ms

V_{10} (0°) = 1.97 V at 20°C

$$\frac{-1}{V}\left(\frac{dV}{dT}\right)\ \%\ {}^{\circ}C^{-1}\left[\begin{array}{lll}\text{at } V_{90}\ (45^{\circ}) & = & 0.83\\ \text{at } V_{50}\ (10^{\circ}) & = & 0.87\\ \text{at } V_{10}\ (0^{\circ}) & = & 0.86\end{array}\right.$$

Summarising the situation in the light of the above electro-optic results, we may make the following points.

(1) The 4-alkoxyphenyl 4-alkylbenzyl ethers provide a novel series of relatively stable mesogens that have some properties—see first example quoted above—that are quite acceptable for display device applications (low smectic tendencies; reasonable figures of merit and viscosities—as judged by the response times—when incorporated in a nematic host). The low transition temperatures of the materials and their low solubilities in nematic hosts (a problem which increases on passing from alkyl/alkoxy to dialkoxy ether) are however serious disadvantages. The low T_{N-I} values of the terminally cyano-substituted benzyl ethers are also a disadvantage.

(2) The cyclohexylmethyl ethers of low Δε are stable, and relative to the corresponding benzyl ethers have superior T_{N-I} values. These ethers—see above—have comparable figures of merit to the benzyl ethers when incorporated in suitable mixtures, but the switch-on voltages and temperature dependencies of V_{th} are high for such mixtures, and the strong smectic characteristics of the materials are a further disadvantage.

(3) Although the bicyclo-octyl ethers of low Δε have the best T_{N-I} values, again the smectic tendencies are high, and the viscosity coefficients are poor. Addition of just 10 wt % of a dialkyl substituted BCO ether to a host consisting of esters gave very considerable increases in viscosity. The fairly high m.p.s, low solubilities and high

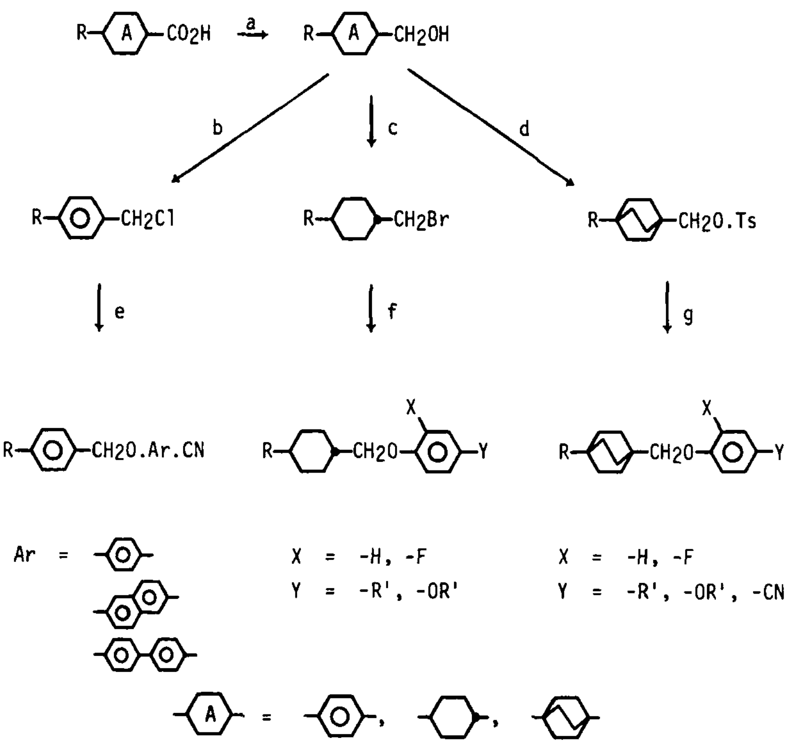
viscosities of the cyano substituted BCO ethers are likewise disadvantageous.

EXPERIMENTAL

Materials

The various ethers were prepared by fairly standard procedures, and full details are available in the thesis of N. Carr.[7] The synthetic routes employed are however recorded in the reaction scheme below.

SYNTHETIC ROUTES FOR ETHERS



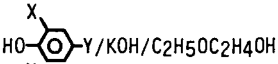
(a) ... $SOCl_2$; $LiAlH_4$/ether

(b) ... $SOCl_2/CHCl_3$

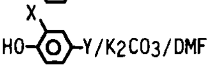
(c) ... aq HBr/H_2SO_4

(d) ... Tosyl chloride/pyridine

(e) ... $HO.Ar.CN/Na_2CO_3/EtOH$

(f) ... 

$HO\text{-}C_6H_3(X)\text{-}Y/KOH/C_2H_5OC_2H_4OH$

(g) ... 

$HO\text{-}C_6H_3(X)\text{-}Y/K_2CO_3/DMF$

All final products were shown to be pure by t.l.c., g.l.c. and/or h.p.l.c. Confirmation of the structures of the products (and, where necessary, for any synthetic intermediates) was obtained by ^{1}H n.m.r. spectroscopy (Jeol J.N.M.-P.M. × 60 spectrometer), infra-red spectroscopy (Perkin-Elmer 457 grating spectrophotometer) and mass spectrometry (A.E.I.M.S. 902).

Transition temperatures were measured using a Mettler FP5 hot stage and control unit, in conjuction with a Nikon LKe polarising microscope. Products were also checked when necessary by differential scanning calorimetry (Perkin-Elmer DSC 2C with Data Station).

Acknowledgments

This paper is published by permission of the Director HMSO and the authors thank the U.K. Ministry of Defence for a research grant to N.C. They also thank Dr. E. P. Raynes and his colleagues at R.S.R.E., Malvern, U.K. for their electro-optic assessment work on some of the products.

References

1. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.*, **53**, 147 (1979); N. Carr, G. W. Gray and D. G. McDonnell, *loc. cit.*, **97**, 13 (1983).
2. M. Petrzilka and M. Schadt, U. K. Patent 2 107 733 (1982).
3. G. W Gray, *Mol. Cryst. Liq. Cryst.*, **63**, 3 (1981).
4. M. Osman, *Mol. Cryst. Liq. Cryst. Lett.*, **72**, 291 (1982); **82**, 47 (1982).
5. D. Coates and G. W. Gray, *J. Phys. (Paris)*, **36**, 365 (1975).
6. R. Eidenschink, *Kontakte*, **3**, 12 (1980).
7. N. Carr, Ph.D. Thesis, University of Hull (1984).