88. The Synthesis and Some Physical Properties of New Laterally Substituted Phenyl Ethers Containing a *trans*-1,4-Disubstituted Cyclohexane Ring

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The synthesis, liquid-crystal transition temperatures, and some physical properties of a variety of substituted phenyl ethers, most of which incorporate a lateral substituent, are reported. Many of the liquid crystals described exhibit nematic phases with negative dielectric anisotropy at elevated temperatures. The relationship between the nature of the lateral substituents and the observed liquid crystal phases and transition temperatures is discussed.

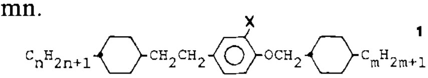
Introduction. – Compounds of moderate-to-strong negative dielectric anisotropy are required for electro-optic display devices based on the deformation of a homeotropically aligned nematic layer [1], and for 'guest-host' displays with positive contrast [2] [3]. The majority of known liquid crystals of negative dielectric anisotropy are mono- or dicyano-laterally substituted *esters* [4]. The stability (thermal, and/or photochemical) of these esters is not high enough for display applications. Nematic mixtures incorporating a recently reported laterally substituted cyclohexyl, (*dicyano*phenyl)*ethane* (*i.e.*, the ester linkage has been replaced by a CH_2CH_2 linking unit) show much improved stability [5]. However, the nematic-isotropic transition temperature of the dicyano-substituted ethane is very low (−55°), and limits the amount of this component that can be incorporated in a mixture. To produce a nematic liquid crystal of negative dielectric anisotropy of equal stability, but with a much higher nematic-isotropic transition temperature, we first synthesised a *mono-cyano*phenylethane with an additional cyclohexane ring [4]. However, this compound only possessed a smectic phase (S_A) and a value for the nematic-isotropic transition temperature (N–I = [90°]) was extrapolated from nematic binary mixtures with the corresponding bromo-compound (N–I, 85.5°) [4].

To produce compounds of moderately strong negative dielectric anisotropy, which *also* exhibit enantiotropic *nematic* phases, similar three-ring, monocyano-substituted compounds were synthesised, which either did not contain a linking unit at all and/or contained a benzene ring in place of one of the cyclohexane rings.

The corresponding non-laterally substituted ethers (required for comparison) were produced *via* alkylation of the appropriate phenol with 4-methylbenzyl bromide (commercially available) or the required (*trans*-4-alkylcyclohexyl)methyl bromide prepared according to known methods [4]. The required phenols were prepared according to modified methods previously described [4]. The desired bromo-substituted ethers were produced *via* alkylation of the appropriate bromo-phenol, prepared from the corresponding phenol by direct bromination using Br_2 (modified known method [4]). The required nitriles were obtained by cyanation of the analogous bromo-substituted ethers (see *Exper. Part*).

Results and Discussion. – The liquid-crystal transition temperatures (C–S/N, S_B–N, S_A–N, N–I) of various 2-laterally substituted (X = H, F, Cl, CN, Br) (*trans*-4-alkylcyclohexyl)methyl 4-[(*trans*-4-alkylcyclohexyl)ethyl]phenyl ethers **1** are listed in *Table 1*. The differences between the clearing points (N–I) of the laterally substituted ethers (X = F, Cl, CN, Br) and those of the corresponding ether (X = H) with an H-atom in place of the lateral substituent are recorded in the eighth column.

Table 1. *Transition Temperatures* (°C) *for Compounds* **1**



1

C_nH_{2n+1}	C_mH_{2m+1}	X	C–S/N	S_B–N	S_A–N/I[a])	N–I[a])	ΔT_{N-I}(H→X)
C_3H_7	C_3H_7	H	97	–	–	124	–
C_3H_7	C_5H_{11}	H	81.5	105	–	125.5	–
C_7H_{15}	C_3H_7	H	65	118.5	–	123	–
C_7H_{15}	C_3H_7	F	50.5	–	90	110	−13
C_7H_{15}	C_3H_7	Cl	46	–	(41)	96	−27
C_7H_{15}	C_3H_7	CN	57	–	96	[90]	−33
C_7H_{15}	C_3H_7	Br	44	–	(10)	86	−37

[a]) ( ) Represents a monotropic transition temperature; [ ] represents a 'virtual' transition temperature.

The first three ethers (X = H) in *Table 1* possess almost identical nematic-isotropic transition temperatures (N–I). High smectic-nematic transition temperatures (S_B–N) are observed for those homologues with longer alkyl chains (n + m ≥ 8). A narrow nematic range (4.5°) is observed for the ether with the longest combined C-chain lengths (n + m = 10). Homologues with longer alkyl chains (n + m ≥ 10) are expected to be completely smectic.

The effect of lateral substituents (X = F, Cl, CN, Br) of various sizes on the liquid-crystal transition temperatures of one homologue (X = H; n = 7; m = 3) of the ethers **1** is shown in *Table 1* and in the *Figure*. Since the CN-substituted ether (X = CN) only exhibits an enantiotropic smectic phase (S_A) a 'virtual' value for N–I was determined by

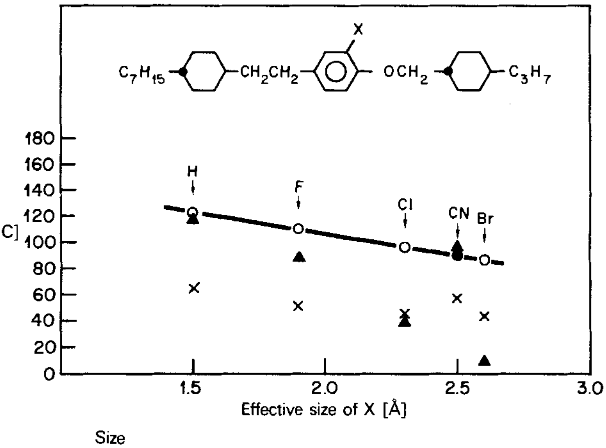
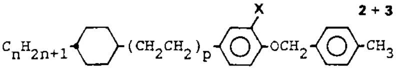


Figure. *Plot of the transition temperatures* vs. *the size of the lateral substituent* (X) *of the ether formulated* (X, crystal-smectic/nematic transition; ▲, smectic-nematic/isotropic liquid transition; ○, enantiotropic nematic-isotropic liquid transition; ●, monotropic nematic-isotropic liquid transition) linear extrapolation from a series of binary mixtures with the bromo-substituted ether (X = Br) [4]. According to the *Figure*, a linear inverse relationship between the N–I and the size of the lateral substituent is observed. The S_B–N also decreases with increasing size of the lateral substituent (with the exception of the CN-substituted compound) but no linear correlation with the size of the lateral substituent exists. It is also interesting to note that the smectic phases exhibited by the laterally substituted ethers (S_A) and the non-laterally substituted ether (S_B) are of different types.

Table 2. *Transition Temperatures* (°C) *for Compounds* **2** *and* **3**



2 + 3

C_nH_{2n+1}	P	X	C–S/N	S_B–N	S_A–N[a])	N–I[a])	$\Delta T_{N\text{-}I}(H \rightarrow X)$
C_7H_{15}	1	H	64	89	–	95	–
C_7H_{15}	1	CN	78	–	(58.5)	(62)	–33
C_7H_{15}	1	Br	79	–	–	(63)	–32
C_3H_7	0	H	121.5	–	–	(110)	–
C_3H_7	0	CN	75	–	–	(40.5)	69.5
C_3H_7	0	Br	66	–	–	(53)	–57

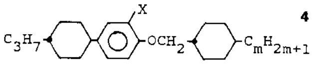
[a]) ( ) Represents a monotropic transition temperature.

The liquid-crystal transition temperatures of two sets of laterally substituted (X = H, CN, Br) benzyl ethers **2** and **3** are given in *Table 2*. Again the differences between the clearing points (N–I) of the ethers with either a CN-group or a Br-atom instead of the H-atom are given in the eighth column.

The trends in the liquid-crystal transition temperatures of the benzyl ethers **2** (P = 1) incorporating an ethyl linkage in addition are similar to those of the analogous cyclohexyl ethers **1** (*Table 1* and *2*). In this case the CN-substituted compound exhibits a narrow-range, monotropic nematic phase (3.5°).

The benzyl ethers **3** with the cyclohexane ring bonded directly to the benzene ring (p = 0) exhibit only nematic phases, although they are all monotropic. This may be due to the small number of C-atoms (4) in the combined alkyl chains. We note that the N–I of the nitrile is considerably lower (–12.5°) than that of the corresponding bromide and very much lower than the parent hydrocarbon (X = H). The clearing point of the bromide (53°) is considerably lower than that (74.5°) of the corresponding Br-substituted 4-*methoxy*benzyl ether (*i.e.*, including an additional O-atom) [6], while the melting points are almost identical.

Table 3. *Transition Temperatures* (°C) *for Compounds* **4**



4

C_mH_{2m+1}	X	C–S_B/N	S_B–N	S_A–N[a])	N–I	$\Delta T_{N\text{-}I}(H \rightarrow X)$
C_3H_7	H	96.5	88.5	–	141.5	–
C_5H_{11}	H	110	111.5	–	142	–
C_7H_{15}	H	121.5	123.5	–	136.5	–
C_3H_7	CN	70.5	–	(60)	85	–56.5
C_5H_{11}	CN	72	–	(71)	91	–51
C_7H_{15}	CN	57.5	–	77	92	–44.5
C_3H_7	Br	42	–	–	85	–56.5
C_5H_{11}	Br	47.5	–	–	90	–52
C_7H_{15}	Br	63.5	–	–	88	–48.5

[a]) ( ) Represents a monotropic transition temperature.

The liquid-crystal transition temperatures of three sets of substituted (X = H, CN, Br) (*trans*-4-alkylcyclohexyl)methyl 4-(*trans*-4-alkylcyclohexyl)phenyl ethers **4** are reported in *Table 3*. The seventh column contains values for the differences in the clearing points (N–I) of the laterally and non-laterally substituted ethers **4**.

The liquid-crystal transition temperatures of the ethers **4** show similar trends to those of the corresponding ethers **1** containing an additional ethyl linkage (*Table 1* and *3*). Where the transition temperatures for the ethers **1** and **4** with identical chain lengths can be compared (m = 3 and 5), the values obtained are somewhat higher for the compounds **4** (with the exception of one melting point). The N–I of the bromides and nitriles **4** are almost identical. As usual, the S_B–N for the nitriles increase with increasing C-chain length, although a wide-range nematic phase can still be observed for the longest chain length studied (m = 7).

Physical Properties. – The values of the dielectric constants and elastic constants, measured at a constant reduced temperature (85° = 0.98 × T_{NI}) of one homologue (m = 7) of the CN-substituted (X = CN) ethers **4** are recorded in *Table 4*. This nitrile is of moderately strong negative dielectric anisotropy (*ca.* –4.5 at r.t.). The ratios of the bend to splay (k_{33}/k_{11}) and the twist to splay (k_{22}/k_{11}) elastic constants are low. These results bear a strong similarity to those obtained for similar two- and three-ring laterally substituted ethanes previously reported [4].

Table 4. *Some Physical Data for One Homologue* (m = 7) *of the Compounds* [4] *Measured at 0.98* × T_{N-I}

Property	Value	Units
$\varepsilon_\parallel$	7.64	
$\varepsilon_\perp$	10.53	
$\Delta\varepsilon$	–2.89	
k_{11}	6.19	10^{-7} dyne
k_{22}	2.85	10^{-7} dyne
k_{33}	6.99	10^{-7} dyne
k_{33}/k_{11}	1.13	
k_{22}/k_{11}	0.46	

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Experimental Part

General. The liquid-crystal transition temp. of the ethers **1–3** were determined by optical microscopy using a *Leitz-Orthoplan* microscope, in conjunction with a *Mettler FP52* heating stage and *FP5* control unit. The 'virtual' N–I given in *Table 1* was determined in the usual manner [4]. The S_A phases were identified from the focal conic fan texture, whereas the S_B phases formed a mosaic texture. Homeotropic areas were observed for both phase types.

The physical properties of the nitrile reported in *Table 4* and in the text were determined using instruments and methods described in [4].

The purity of the final products and reaction intermediates was determined by *TLC* and *GLC*. A *Perkin Elmer Sigma 1* GC system and also a *Perkin Elmer 3920B* gas chromatograph with a *Hewlett Packard 3380A* integrator were used. The structures of the compounds were checked by analysis of their IR, H-NMR, and mass spectra; the instruments used were a *Perkin Elmer PE683 IR* spectrometer with model *3600* data station, a *Brucker WP 200 NMR* spectrometer, and a *Hitachi RMU 6L* mass spectrometer, respectively.

*4-(*trans*-4-Propylcyclohexyl)phenol.* A soln. of BBr_3 (14.5 g, 0.058 mol) and anh. CH_2Cl_2 (15 ml) was added dropwise to a soln. of butyl 4-(*trans*-4-propylcyclohexyl)phenyl ether (10 g, 0.037 mol) and anh. CH_2Cl_2 (35 ml) under anh. conditions at 0°. The reaction soln. was stirred for a further 4 h at r.t. and added to water. The org. phase was separated off and the aq. phase was shaken with CH_2Cl_2 (2 × 50 ml). The combined org. layers were washed with 10% Na_2CO_3 soln. (2 × 200 ml) and H_2O (2 × 500 ml) and then dried ($MgSO_4$). The filtered soln. was evaporated under reduced pressure. The residue was crystallised from AcOEt to yield the pure product (7.5 g, 94%), m.p. 137–8°. IR (KBr): 3400 (PhOH), 1600, 1505, 1445 (Ph), 1370 (C–O), 1230 (OH), 820 (Ph). MS: 218 (M^+). Anal. calc. for $C_{15}H_{22}O$ (218.34): C 82.52, H 10.16; found: C 82.44, H 10.33.

*4-[2-(*trans*-4-Propylcylohexyl)ethyl]phenol* was prepared using the same method (74%), m.p. 98–99°. IR (KBr): 3400 (PhOH), 1600, 1510, 1445 (Ph), 1420 (C–O), 1230 (OH), 820 (Ph). MS: 246 (M^+).

*4-[2-(*trans*-Heptylcyclohexyl)ethyl]phenol* was also prepared using the same method (54%), m.p. 95–96°. IR (KBr): 3400 (PhOH), 1600, 1505, 1445 (Ph), 1415 (C–O), 1225 (OH), 820 (Ph). MS: 394 (M^+).

*2-Bromo-4-(*trans*-4-propylcyclohexyl)phenol.* Br_2 (3.69 g, 0.0229 mol) was added dropwise to a soln. of 4-(*trans*-4-propylcyclohexyl)phenol (5.0 g, 0.0229 mol) and CH_2Cl_2 (150 ml) under anh. conditions at 0°. The red colour disappeared immediately on addition and a regular flow of HBr was observed. After the addition the resultant soln. was stirred for 1 h at r.t., then washed with 10% $NaHSO_4$ soln. (2 × 200 ml) and H_2O (2 × 500 ml) and dried ($MgSO_4$). The solvent was removed from the filtered soln. under slightly reduced pressure to yield crude product which was taken up in a small amount of solvent and eluted from a silica-gel column with toluene. Single-spot fractions were collected and evaporated together and the residue crystallised from AcOEt to give the pure product (6.5 g, 95%), m.p. 46°. IR (KBr): 3400 (PhOH), 1580, 1490, 1445 (Ph), 1340 (C–O), 1205, 1180 (OH), 770 (Ph). MS: 296, 298 (M^+). Anal. calc. for $C_{15}H_{21}BrO$ (297.24): C 60.61, H 7.12, Br 26.88; found: C 60.65, H 7.23, Br 26.58.

*(4-Heptylcyclohexyl)methyl 2-Bromo-4-(*trans*-4-propylcyclohexyl)phenyl Ether.* A mixture of 2-bromo-4-(*trans*-4-propylcyclohexyl)phenol (2.5 g, 0.0085 mol), (*trans*-4-heptylcyclohexyl)methyl bromide (2.8 g, 0.0102 mol) anh. K_2CO_3 (4.7 g, 0.0339 mol) and anh. DMF (50 ml) was heated at an oil-bath temp. of 120° overnight under anh. conditions. The cooled mixture was added to H_2O (500 ml) and shaken with $CHCl_3$ (3 × 50 ml). The combined org. extracts were washed with H_2O (2 × 500 ml) and then dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was taken up in a small amount of solvent and eluted from a silica-gel column with hexane. Single-spot fractions were collected and evaporated together and the residue was crystallised from AcOEt until constant transition temp. were obtained for the *ether* (see *Table 1–3* for the liquid-crystal transition temp. of this ether and the other ethers prepared by this procedure). The yield of pure ether was 4.0 g (96%). IR (KBr): 1600, 1500, 1455 (Ph), 1255 (C–O), 810 (Ph). MS: 490, 492 (M^+). Anal. calc. for $C_{29}H_{47}BrO$ (491.60): C 70.85, H 9.64, Br 16.25; found: C 70.64, H 9.76, Br 16.67.

*2-[(*trans*-4-Heptylcyclohexyl)methoxy]-5-(*trans*-4-propylcyclohexyl)benzonitrile.* A soln. of (*trans*-4-heptylcyclohexyl)methyl 2-bromo-4-(*trans*-4-propylcyclohexyl)phenyl ether (4.0 g, 0.0082 mol), anh. CuCN (1.8 g, 0.020 mol), and anh. 2-methyl-1-pyrrolidinone (50 ml) was heated at an oil-bath temperature of 185° for 3 h under anh. conditions. The cooled mixture was added to a soln. of anh. $FeCl_3$ (2.0 g) and conc. HCl (0.5 ml) in H_2O (20 ml) and stirred for 30 min at 50–60°. The resultant mixture was shaken with Et_2O (4 × 50 ml) and the combined org. layers were washed with brine (2 × 500 ml) and then dried ($MgSO_4$). The filtered soln. was evaporated under slightly reduced pressure to yield a solid residue which was purified as described for the bromo compound to yield pure *nitrile* (see *Table 1–3* for the liquid-crystal transition temp. of this nitrile and the other nitriles prepared by this method). The yield of pure nitrile was 1.6 g (45%). IR (KBr): 2215 (CN), 1260 (C–O), 810 (Ph). MS: 437 (M^+). Anal. calc. for $C_{30}H_{47}NO$ (437.71): C 82.32, H 10.82, N 3.20; found: C 82.49, H 11.01, N 3.22.

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