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Apolar 2-alkoxyalkoxy-substituted nematic liquid crystals

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The synthesis is reported of a series of apolar nematic liquid crystals incorporating an alkoxyalkoxy chain attached in a terminal position to the molecular core. The dependence of the mesomorphism and phase transition temperatures on the nature of the terminal chain with one, two or three oxygen atoms was studied. Some compounds with a completely alicyclic molecular core and a terminal 2-methoxyethoxy chain exhibit a nematic phase with a low melting point, birefringence and viscosity and a relatively high clearing point in the absence of smectic phases. They do not to absorb light in the near UV and may be useful as components of UV-stable nematic mixtures for use in photoluminescent liquid crystal displays. The presence of the methoxyethoxy chain leads to a relatively large dipole moment perpendicular to the molecular long axis.

1. Introduction

Apolar nematic liquid crystals of low birefringence and low viscosity are required as components of nematic mixtures for liquid crystal displays (LCDs) with high information content and short switching times [1–6]. The twisted-nematic LCD (TN-LCD) [1] with even modest information content uses a multiplexed addressing scheme. A steep voltage/transmission curve is required to achieve this, which requires a nematic mixture with a low k_{33}/k_{11} ratio and a low $\Delta\varepsilon/\varepsilon_\perp$ ratio [7–11]. Nematic LCs with a large positive value of $\Delta\varepsilon$ are also needed to induce a low threshold voltage (V_{10}), which should be as low as possible for battery operation and low power consumption. Therefore, nematic mixtures are required that combine a large positive value of $\Delta\varepsilon$ with a large value of $\varepsilon_\perp$. The addition of apolar compounds with intrinsically low k_{33}/k_{11} and $\Delta\varepsilon/\varepsilon_\perp$ ratios to mixtures of polar nematic LCs with a cyano group in a terminal position induces low values of these ratios for the resultant nematic mixture *and* a high $\Delta\varepsilon$ [11] due to the fact that nematic LCs tend to associate as molecular dimers in the nematic phase [12]. The addition of apolar compounds reduces the degree of pair formation, which results in an increase in $\Delta\varepsilon$ *and* low k_{33}/k_{11} and $\Delta\varepsilon/\varepsilon_\perp$ ratios [11]. Up to 50% of a non-polar material may be added without significantly reducing $\Delta\varepsilon$ [10, 11]. Unfortunately, a consequence of mixing compounds of low and high $\Delta\varepsilon$ is that a smectic phase can be induced in the mixture even when none of the individual components exhibits an observable smectic phase [11]. It is undesirable to have a smectic phase within the required operating range of the mixture as switching times are increased and the effective operating range reduced. Apolar components are also present in nematic mixtures used in LCDs with active matrix addressing in order to induce a low melting point/recrystallization temperature, a low viscosity and short switching times.

Apolar nematic LCs of very low birefringence and low viscosity are also required as components of nematic mixtures for the photoluminescent LCD (PL-LCD), where a high-powered UV backlight is used to address a phosphorescent screen [13–15]. The dependence of the contrast on the viewing angle is very low due to the Lambertian emission and the use of monochromatic beam of UV light with a narrow band-width with orthogonal incidence on the phosphor screen. The LC mixtures used in this device must be stable towards photochemical degradation under illumination with UV light at 365 nm and 390 nm, i.e. show minimal absorption in the near UV. The PL-LCD operates in the TN-LCD or STN-LCD modes with multiplex addressing and requires multiplexable nematic mixtures with low absorption in the near UV.

LCs with two 1,4-disubstituted *trans*-cyclohexane rings in the molecular core and an aliphatic chain in each of the 4,4′-positions of the molecular core, such as those shown in table 1, often possess a low viscosity and a low birefringence. Unfortunately, these aliphatic compounds often exhibit smectic phases, often the highly-ordered smectic B (SmB) phase (see table 1).

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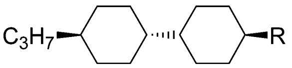
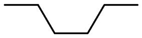
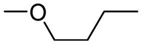
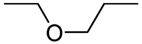
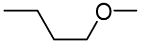
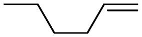
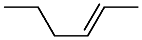
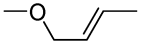
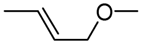
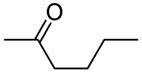
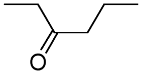
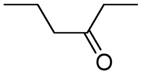
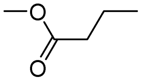
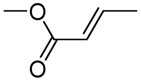
Table 1. Transition temperatures (°C) for the compounds **1**–**13**.



Compound	R	Cr		SmB		N		I	Ref.
1		•	23	•	96		–	•	[16]
2		•	32	•	74		–	•	[17]
3		•	15	•	42		–	•	[16]
4		•	25	•	85		–	•	[18]
5		•	−16	•	89		–	•	[2]
6		•	44	•	75	•	96	•	[16]
7		•	60		–	(•	47	•)	[16, 18]
8		•	30	•	70	•	73	•	[16]
9		•	55	•	96		–	•	[19]
10		•	56	•	92		–	•	[16]
11		•	65	•	84		–	•	[16]
12		•	41	•	69	•	73	•	[16]
13		•	77		–	•	172	•	[15]

However, the presence of an oxygen atom in the form of a *keto*-function in compounds **12** and **13** can lead to the presence of a nematic phase. Therefore, we speculated that the presence of a second oxygen atom in the terminal chain as an *ether* could also lead to the induction of a nematic phase based on the data collated in table 1.

There are many nematic LCs with one non-conjugated oxygen atom either situated between a terminal chain and an alicyclic ring or within the chain itself (see table 1) [20–23]. Unfortunately, the presence of the second oxygen atom in the chain usually results in a low nematic clearing point [24–26]. However, nematic LCs with two 1,4-disubstituted *trans*-cyclohexane rings in the molecular core often exhibit a high clearing point [2–5]. Therefore, such LCs incorporating an alkoxyalkoxy chain may be expected to induce a nematic phase with a reasonably high clearing point as well as low values of the viscosity and the birefringence with advantageous values of the elastic and dielectric constants. LCs with two 1,4-disubstituted *trans*-cyclohexane rings in the molecular core and an aliphatic chain in each of the 4,4′-positions should not absorb UV light at 365 nm or 390 nm. Compounds containing a 1,4-disubstituted *trans*-cyclohexane ring and one 1,4-disubstituted phenyl ring should also have a very low absorption in the near UV and should be suitable for use in PL-LCDs [15].

2. Experimental

2.1. *Instrumentation*

All commercially available starting materials, reagents and solvents were used as supplied and were obtained from Aldrich, Strem Chem. Inc, Acros or Lancaster Synthesis. All reactions were carried out under an atmosphere of dry nitrogen. Reaction temperatures were measured internally. Mass spectra were recorded using a gas chromatography/mass spectrometer GC/MS-QP5050A) Schimadzu with electron impact (EI) at a source temperature of 200°C. Compounds with an RMM>800 g mol^{-1} were analysed using a Bruker, reflex IV, matrix-assisted laser desorption/ionization (MALDI), time of flight (TOF) MS. A 384 well microlitre plate format was used with a scout target. Samples were dissolved in DCM with HABA (2,4-hydroxyphenylazobenzoic acid) matrix (1:10, respectively). The mass ion of the material is identified by M$^+$. ^{1}H NMR spectra were recorded using a JEOL Lambda 400 spectrometer with an internal standard of tetramethylsilane TMS. GC was carried out using a Chromopack CP3800 gas chromatograph equipped with a 10 m CP-SIL 5CB column. Purification of intermediates and final products was achieved by column chromatography, using silica gel (40–63 μm, 60A) obtained from Fluorochem and recrystallization. The purity of the final compounds was determined either by elemental analysis using a Fisons EA 1108 CHN analyser or by GC analysis. The melting point and the other phase transition temperatures were determined using a Linkam 350 hot-stage and control unit in conjunction with a Nikon E400 polarizing microscope. The phase transition temperatures of the final products were confirmed using a Perkin-Elmer DSC-7 and in conjunction with a TAC 7/3 instrument controller using the peak measurement for the transition temperatures. Molecular modelling was used to estimate the dipole moment of such materials as well as those of commercially-available materials with known dipole moments. The dipole moments were predicted using an energy-minimized structure using Cerius^2 MOPAC program [27]. The switching voltages of the nematic mixtures M7–M9 were tested in a standard 6 μm parallel TN-LCD cell at 25°C. The bulk shear viscosity was determined by extrapolation by measuring the viscosity of a solution of PCH32 doped with compound **23** in concentrations of 4, 6, 8 and 10 wt%. The dipole moment of compound **23** was extrapolated from measurements of the dielectric constants of the same mixtures at 25°C.

2.2. *Synthesis*

The aromatic alkoxyalkoxy-substituted ethers were prepared by alkylation using the Williamson ether synthesis [28] of phenols, which were commercially available, supplied by Merck NBSC Southampton, or available from other programmes [24]. The appropriate 2-alkoxyethyl bromides were prepared from the corresponding commercially-available 2-alkoxyethanols and carbon tetrabromide [29, 30]. The aliphatic alkoxyalkoxy-substituted ethers were prepared by alkylation using appropriate 2-alkoxyethyl bromides of cyclohexanols available from other programmes or Merck NBSC Southampton in the usual Williamson ether synthesis [28] using sodium hydride to form the required sodium alkanoates.

2.2.1. *trans*,*trans*-4-(2-Methoxyethoxy)-4′-propyl-1,1′-bicyclohexane (14). A solution of *trans*-4-(*trans*-4-propylcyclohexyl)cyclohexan-1-ol (1.00 g, 4.59 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a suspension of sodium hydride (0.13 g, 5.50 mmol) in tetrahydrofuran (15 cm^3) under nitrogen and at room temperature. The solution was then left to stir (2 h) before a solution of 1-bromo-2-methoxyethane (0.76 g, 5.50 mmol) and potassium iodide (0.08 g, 4.59×10^{-4} mol) was added and the reaction mixture then heated under reflux (48 h). Methanol (20 cm^3) was then added to the reaction mixture followed by water (75 cm^3). The product was then extracted into diethyl ether (3 × 30 cm^3) and then the combined organic layers were washed with brine (2 × 20 cm^3) and dried ($MgSO_4$). The solution was then filtered, the solvent removed under reduced pressure and the crude product purified by column chromatography on silica gel using a 3:7 ethyl acetate-hexane mixture as eluent and recrystallization from cold propanone to yield the desired product as a white crystalline solid. Yield 0.29 g (22%), GC purity (100%). ^{1}H NMR ($CDCl_3$) δ_{400}: 0.86 (3H, t), 0.89–1.10 (2H, m), 1.11–1.32 (13H, m), 1.67–1.76 (6H, m), 2.04–2.08 (2H, m), 3.17 (1H, quintet), 3.38 (3H, s), 3.53 (2H, t), 3.62 (2H, t). IR ν_{max}/cm^{-1}: 2925, 2858, 1454, 1207, 1125, 941. MS m/z: 282 (M$^+$), 206 (M100, $C_{16}H_{22}O_2{}^+$).

2.2.2. 1-(2-Methoxyethoxy)-4-(*trans*-4-propylcyclohexyl)-benzene (23). A mixture of 4-(*trans*-4-propylcyclohexyl)phenol (2.00 g, 9.17 mmol), 1-bromo-2-methoxyethane (1.53 g, 1.10×10^{-2} mol), potassium iodide (0.15 g, 9.17×10^{-4} mol), potassium carbonate (5.06 g, 3.67×10^{-2} mol) and butanone (50 cm^3) was heated under reflux overnight. The crude mixture was filtered through hyflo supercel, which was washed through with copious amounts of propanone. The filtrate was evaporated down under reduced pressure and the crude product purified by column chromatography on silica gel using dichloromethane as the eluent and then by short path distillation to give the desired clear liquid product, which crystallized on cooling. Yield 2.07 g (82%), GC purity (99.9%). ^{1}H NMR ($CDCl_3$) δ_{400}: 0.90 (3H, t), 1.03 (2H, sextet), 1.17–1.45 (7H, m), 1.83–1.88 (4H, m), 2.40 (1H, quintet), 3.44 (3H, s), 3.74 (2H, t), 4.10 (2H, t), 6.86 (2H, d, J=8.5 Hz), 7.11 (2H, d, J=8.5 Hz). IR ν_{max}/cm^{-1}: 2933, 2855, 1617, 1520, 1456, 1367, 1252, 1198, 1129, 1066, 1038, 928, 811. MS *m*/*z*: 276 (M$^+$, M100), 216 ($C_{15}H_{20}O^+$).

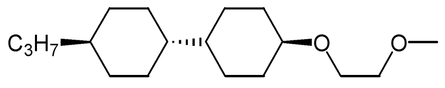
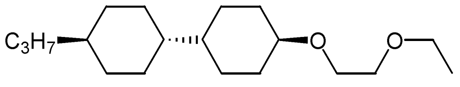
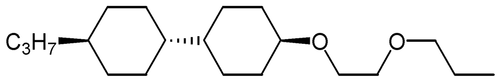
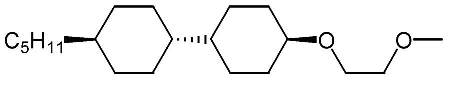
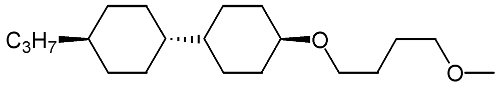
2.3. *Mesomorphic properties*

A nematic (N) phase was observed for some of the compounds prepared, e.g. compound **14**. A Schlieren texture with 2-brush and 4-brush disclinations are observed for the nematic phase observed between crossed polarizers. Small droplets are seen on cooling slowly from the isotropic phase on forming the nematic phase. These droplets then coalesced quickly to form the Schlieren texture. Several compounds exhibit a SmB phase, e.g. compound **19**. On cooling from the isotropic liquid H-shaped platelets were formed, which coalesced to form a typical mosaic texture for a SmB phase. Optically-extinct areas are also present in the same sample, which is consistent with the uniaxial nature of the SmB phase. Several compounds exhibit a smectic E (CrE) phase, e.g. compound **21**, which also exhibits a mosaic texture and homeotropic areas. However, when the mosaic texture of the CrE phase forms directly from the isotropic liquid on cooling no H-shaped platelets are observed. No droplets are seen on cooling slowly from the isotropic (I) phase on forming either the SmB phase or the CrE phase and neither phase exhibits a Schlieren texture. The transitions observed using optical microscopy were confirmed using differential scanning calorimetry (DSC). Where the liquid crystal transition temperatures could not be obtained directly by optical microscopy then the values from DSC analysis corresponding to the onset peak are used.

3. Results and discussion

Compound **14** is a short apolar LC consisting of two 1,4-disubstituted *trans*-cyclohexane rings in the molecular core, a propyl group as one terminal substituent in position 4 on one cyclohexane ring and a methoxyethoxy end group as the second terminal substituent in the same position on the second cyclohexane ring. Compound **14** exhibits a relatively low melting point and a monotropic nematic phase just below the melting point (see table 2). A SmB phase could not be observed. The analogous compound **1** with no oxygen atom in either of the terminal chains and compounds **2**–**4** with one oxygen atom in the terminal chain all exhibit a SmB phase (see table 1). Therefore, the presence of two oxygen atoms in position 1 and 4 of the terminal end chain has resulted in the replacement of the SmB phase with a nematic phase with a relatively high clearing point. Compounds **15** and **16** with an ethoxyethoxy and a propoxyethoxy chain exhibit either a monotropic or a virtual (extrapolated) nematic phase. The clearing point of compound **15** is lower than that of the methoxy homologue **14** as expected taking into account the usual odd–even effect [20]. The melting point of compound **15** is just below room temperature. Compound **16** does not exhibit an observable LC mesophase. However, the virtual nematic clearing point is very low. Therefore, the clearing point of the nematic phase is seen to decrease as the length of the alkoxy chain attached to the second oxygen atom in the chain increases, i.e. longer chains appear to reduce the tendency for mesophase formation. This is consistent

Table 2. Transition temperatures (°C) for the compounds **14**–**18**.

Compound	Structure	Cr		SmB		N		I
14		•	47		–	(•	44	•)
15		•	20		–	(•	7	•)
16		•	90		–	[•	−1	•]
17		•	65	•	64		–	•
18		•	70		–		–	•

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

with previous results [24–26]. Increasing the length of the alkyl chain, from propyl in compound **14** to pentyl in compound **17**, leads to the formation of SmB phase in place of a nematic phase, which is often observed behaviour [20]. The methoxybutyloxy derivative **18** with the second oxygen atom in position 6 instead of position 4 does not exhibit an observable LC phase. This may be due to the high melting point and limited amount of supercooling below the melting point of compound **18**.

Table 3 incorporates three sets of compounds differing only in the nature of one of the terminal chains, i.e. compounds **19**–**22** possess a pentyl chain, compounds **14** and **23**–**25** a methoxyethoxy chain and compounds **15** and **26**–**28** an ethoxyethoxy chain. The core structure differs in each set of four compounds. Compounds **19**–**21**, which have a propyl chain and a pentyl chain in terminal positions, act as reference compounds. The replacement of one of the *trans*-1,4-disubstituted cyclohexane rings in the *trans*,*trans*-1,1′-bicyclohexyl compound **14** with a 1,4-disubstituted phenyl ring to form compound **23** results in the formation of a monotropic nematic phase with a much lower clearing point (−31°C). The replacement of both *trans*-1,4-disubstituted cyclohexane rings in compound **14** with 1,4-disubstituted phenyl rings to form biphenyl **24** results in the loss of an observable nematic phase and a high melting point to be observed. However, the virtual nematic clearing point of the fully-aromatic compound **24** is almost the same as that of the fully-alicyclic compound **14**. The fully-aromatic tolane analogue **25** has a greater length-to-breadth ratio compared to that of the biphenyl analogue **24** and therefore the nematic phase has a higher clearing point. Except for compound **24**, where different phases are compared, the clearing point of the compounds **23**–**25** with a methoxyethoxy chain is generally higher than those of the corresponding compounds **20**–**22** with a pentyl chain instead of a methoxyethoxy chain. Increasing the length of the terminal chain, from methoxy in compounds **23**–**25** to ethoxy in compounds **15** and **26**–**28**, leads to a low value for the clearing point in each case due to the usual odd-even effect.

The replacement of the propyl chain in compounds **14**, **15** and **19**–**28** collated in table 3 by a pentyl chain produces the analogous compounds **17** and **29**–**35** shown in table 4. The clearing point of the compounds shown in table 4 are higher than those of the analogous compounds collated in table 3, where the same phase is exhibited and comparisons are valid. This is clearly due to the replacement of a short alkyl chain with a longer one and is a common phenomenon for homologous series of LCs [20]. The type of mesomorphism does not vary much for the compounds collated in tables 3 and 4.

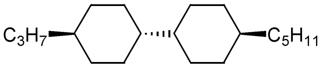
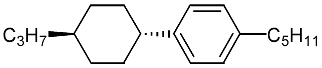
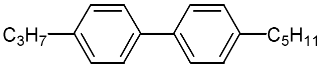
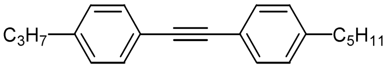
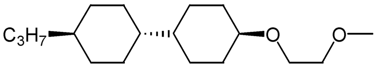
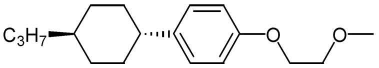
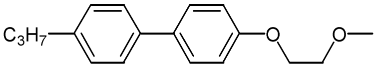
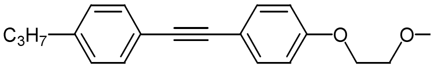
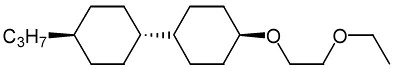
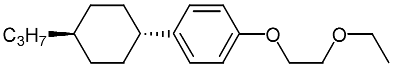
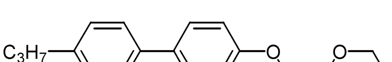
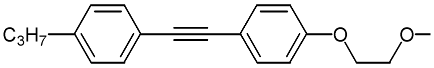
Compound **14** shows that a monotropic nematic phase is produced when a second polar and electron-rich (oxygen) atom is situated in the terminal end chain in position 4. Therefore, a series of compounds with a polar group in position 4 of the terminal end chain was prepared and their transition temperatures determined (table 5). The fluoro-substituted compound **36** does not exhibit a LC mesophase. However, the bromo analogue **37** shows a monotropic nematic phase at a relatively high temperature. The hydroxy analogue **38** exhibits a SmB phase. The formation of the highly-ordered SmB phase may be due to hydrogen bonding between neighbouring molecules. When the hydroxy group is replaced by a methoxy group to produce compound **14**, there is no possibility for hydrogen bonding and a nematic phase is observed. Compound **39** contains a terminal carbon–carbon double bond, but no LC mesophase was observed, despite the presence of an alkenyl chain often leading to high nematic clearing points [2, 3]. The presence of a third oxygen in position seven in the terminal chain of compound **40** produces a monotropic nematic LC with a melting point below room temperature. The presence of three oxygen atoms in such a long chain will result in a high viscosity that will limit their suitability for use in commercial nematic mixtures.

The position and number of oxygen atoms in the terminal end chain attached to a *trans*-4-propylcyclohexylphenyl core was studied and their effects on LC mesophase formation shown in table 6. The end group in compound **41** contains an oxygen atom in the position 3, rather than position 4, and a LC mesophase could be observed despite the low melting point. Compound **42** incorporates a methoxybutoxy end group and a LC phase could not be observed directly. The melting point of compound **42** is low, but the virtual clearing point is very low. The presence of a third oxygen atom in the end chain in compounds **43** and **44** also induces low extrapolated virtual clearing points.

3.2. *Physical properties*

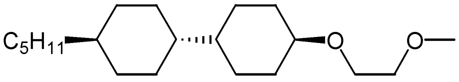
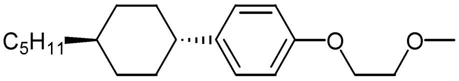
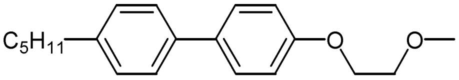
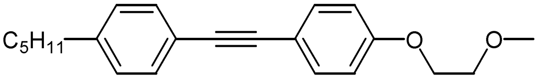
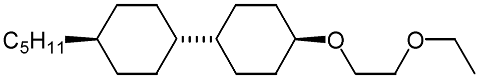
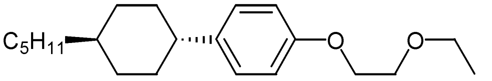
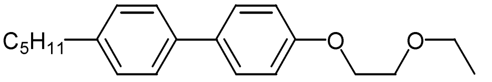
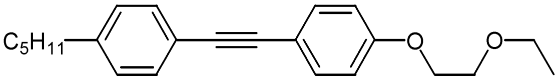
The bulk viscosity of compound **23** (see table 3) was determined by extrapolation from measurements of the viscosity of binary mixtures of the Merck mixture component PCH32 [1-(*trans*-4-propylcyclohexyl)-1-ethylbenzene] doped with compound **23** in concentrations of 4, 6, 8 and 10 wt%. The extrapolated value for the viscosity of this material is relatively low ($12.4\,\mathrm{mP\,s^{-1}}$ at 25°C), although care must be taken when considering values from extrapolations using such low concentrations. The dipole moment (μ) of compound **23** was extrapolated from measurements of the

Table 3. Transition temperatures (°C) for the compounds **14**, **15** and **19**–**28**.

Compound	Structure	Cr		SmE		SmB		N		I
19		•	23		–	•	96		–	•
20		•	−9		–		–	(•	−30	•)
21		•	−18	•	48		–		–	•
22		•	39		–		–	(•	36	•)
14		•	47		–		–	(•	44	•)
23		•	41		–		–	(•	13	•)
24		•	97		–		–	[•	45	•]
25		•	68		–		–	•	67	•
15		•	20		–		–	(•	7	•)
26		•	13		–		–	(•	<−20	•)
27		•	79		–		–	[•	29	•]
28		•	54		–		–	[•	32	•]

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

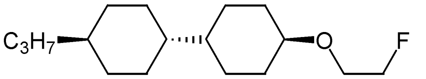
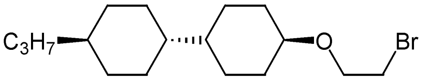
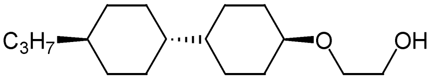
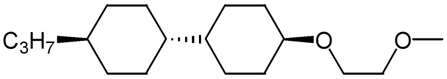
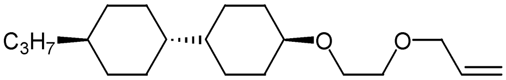
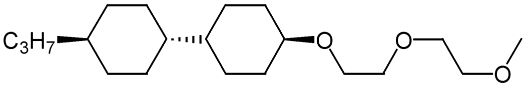
Table 4. Transition temperatures (°C) for the compounds **17** and **29–35**.

Compound	Structure	Cr		SmB		N		I
17		•	65	(•	64	•)	–	•
29		•	45		–	(•	32	•)
30		•	122		–	[•	68	•]
31		•	61		–	•	69	•
32		•	25		–		•	
33		•	22		–	(•	9	•)
34		•	107		–	[•	53	•]
35		•	48		–	[•	36	•]

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

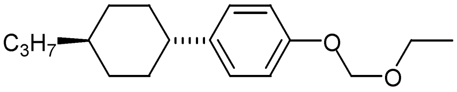
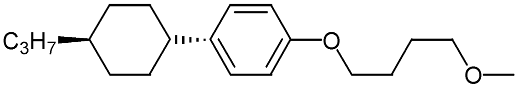
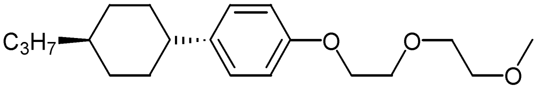
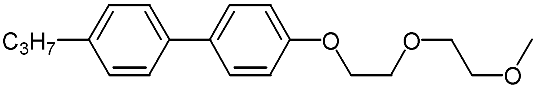
dielectric constants of the same nematic mixtures and was found to be low (2.26 D) and orthogonal to the long molecular axis. This is due to the position of two non-conjugated oxygen atoms in the methoxyethoxy chain (see figure 1 d), and is consistent with the value (2.1 D) predicted by molecular modelling. Therefore, this suggested that the alkoxyethoxy compounds exhibit a low enough value of the viscosity and a relatively high value of the dielectric constant orthogonal to the nematic director ($\varepsilon_{\perp}$) for them to be considered as potential components of nematic mixtures for use in TN-LCDs with multiplex addressing. Consequently, a series of nematic mixtures of consisting of a standard host nematic mixture DOP-017 doped with ~10 wt% of selected examples of the alkoxyethoxy-substituted compounds were prepared and the phase behaviour, dielectric anisotropy $\Delta\varepsilon$ and birefringence Δn determined in order to determine their suitability as components of nematic mixtures for TN-LCDs with multiplex addressing. The mixtures, clearing point of the nematic phase and the structure of the mixture dopants are listed in table 7. None of the mixtures exhibits an observable smectic phase, even mixture M1 that contains 10 wt% of the compound **17**, which

Table 5. Transition temperatures (°C) for the compound **14** and **36**–**40**.

Compound	Structure	Cr		SmB		N		I
36		•	61		–		–	•
37		•	45		–	(•	34	•)
38		•	86	•	83		–	•
14		•	47		–	(•	44	•)
39		•	87		–		–	•
40		•	16		–	(•	8	•)

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

Table 6. Transition temperatures (°C) for the compounds **41**–**44**.

Compound	Structure	Cr		N		I
41		•	−16		–	•
42		•	20	[•	−49	•]
43		•	−7	[•	−37	•]
44		•	47	[•	13	•]

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

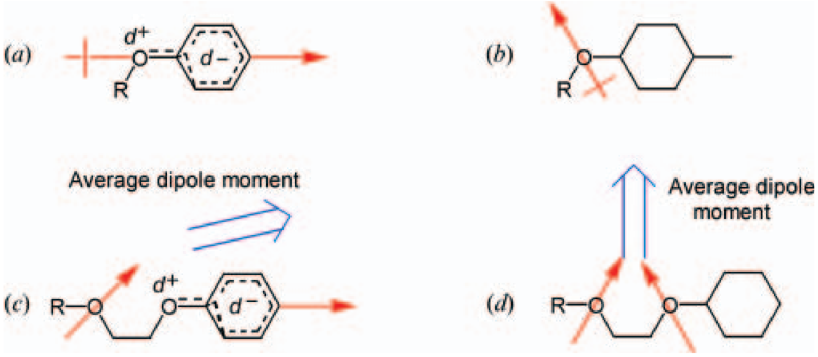
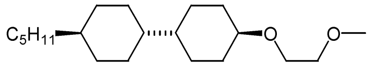
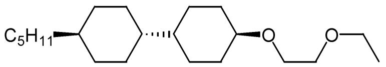
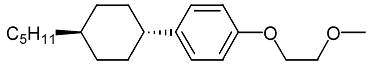
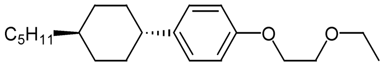
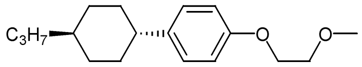
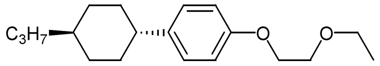
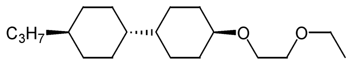
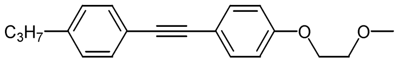
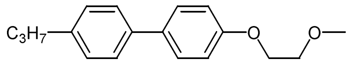


Figure 1. Idealized resonance diagrams showing the possible contribution of oxygen atoms to the dipole moment of the molecule for an aromatic ether (a), alicyclic ether (b), aromatic diether (c) and alicyclic diether (d).

Table 7. The clearing point of the host nematic mixture DOP-017 and the composition and concentration of the doped nematic mixtures M1–M9.

Mixture	%		Structure	N–I
DOP-017	–	–	–	45.2
M1	9.75	**17**		49.9
M2	9.94	**32**		46.5
M3	10.10	**29**		49.3
M4	9.97	**33**		47.2
M5	10.07	**23**		48.0
M6	9.93	**26**		45.1
M7	9.99	**15**		50.3
M8	10.02	**25**		53.6
M9	9.98	**24**		51.1

exhibits a SmB phase at a high temperature. The presence of ~10 wt% of the dopants leads to an increase in the clearing point of the host nematic mixture DOP-017 or leaves it unchanged within the limits of experimental error (cf. compound **26**). Therefore, all the compounds listed in table 7 appear, at least initially, to be potentially suitable as components of nematic mixtures for use in LCDs.

The refractive indices of the mixtures M1–M9 were measured at a fixed absolute temperature of 25°C and a fixed reduced temperature 30°C below the clearing point of the mixture (see table 8). The birefringence (Δn) of all of the doped mixtures is lower than that of the host nematic mixture DOP-017. Mixture M2 is doped with compound **32**, which does not contain any carbon–carbon double bonds, and therefore the resultant mixture exhibits the lowest value of the birefringence of the mixtures studied.

The values of the dielectric permittivity and the dielectric anisotropy ($\Delta\varepsilon$) of the mixtures were determined at 20°C and their values are listed in table 9. The presence of 10% of the new materials lowers the dielectric anisotropy of all of the mixtures compared with that of the host DOP-017 nematic mixture. This is consistent with a large resultant dipole moment orthogonal to the long molecular axis, due to the presence of the two oxygen atoms in the terminal alkoxyethoxy chain (see figure 1 d). The dielectric anisotropy of all of the dopants of the mixtures is expected to be negative for these reasons. All the values for the dielectric constants of these materials are quite similar, which is most probably due to the similarity in molecular structure of these essentially apolar components.

Table 8. The values of the refractive indices and birefringence of the host nematic mixture DOP-017 and the doped nematic mixtures M1–M9.

Mixture	T/°C	n_e	n_o	Δn
DOP-017	25.0	–	–	0.0940
M1	25.0	1.5713	1.4833	0.0880
	19.9	1.5755	1.4841	0.0910
M2	25.0	1.5683	1.4841	0.0840
	16.5	1.5750	1.4853	0.0897
M3	25.0	1.5767	1.4851	0.0916
	19.3	1.5812	1.4865	0.0947
M4	25.0	1.5740	1.4854	0.0886
	17.2	1.5805	1.4871	0.0935
M5	25.0	1.5764	1.4859	0.0905
	18.0	1.5823	1.4872	0.0951
M6	25.0	1.5738	1.4865	0.0873
	15.1	1.5822	1.4880	0.0943
M7	25.0	1.5709	1.4836	0.0873
	20.3	1.5747	1.4847	0.0901
M8	25.0	1.5967	1.4890	0.1077
M9	31.0	1.5821	1.4881	0.0939
	25.0	1.5870	1.4888	0.0982

Table 9. The values of the dielectric constants and the dielectric anisotropy of the host nematic mixture DOP-017 and the doped nematic mixtures M1–M4 and M6–M8.

Mixture	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
DOP-017	12.95	5.13	7.82
M1	11.87	5.12	6.75
M2	11.66	5.15	6.51
M3	11.96	5.18	6.78
M4	11.82	5.21	6.61
M6	12.04	5.35	6.68
M7	11.89	5.14	6.75
M8	12.33	5.24	7.09

TN-LCDs incorporating the mixtures M7–M9 exhibit relatively low threshold voltages (V_{10}=3.1–3.9 V) under standard conditions [24]. These preliminary results serve to illustrate the potential of these materials to serve as components of nematic mixtures for TN-LCDs and especially those for use in the PL-LCD operating in the near UV.

4. Conclusions

We have prepared a range of apolar alkoxyalkoxy-substituted materials with a range of molecular cores. Some of these compounds with an alicyclic molecular core and a terminal 2-methoxyethoxy chain exhibit a nematic phase with a low melting point, birefringence and viscosity and a relatively high clearing point in the absence of smectic phases, e.g. *trans*,*trans*-4-(2-methoxyethoxy)-4′-propyl-1,1′-bicyclohexane. This material does not absorb light in the near UV and may be useful as a component of UV-stable nematic mixtures for use in the PL-LCD using a TN-LCD as the optical shutter. Increasing the length of the alkoxyethoxy chain, placing the second oxygen atom in different positions or introducing a third oxygen atom in the terminal chain leads to a lower nematic clearing point than that of the corresponding 2-methoxyethoxy-substituted analogues.

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