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

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To cite this Article Campbell, Neil L. , Kelly, Stephen M. and Tuffin, Rachel P.(2007) 'Polar 2-alkoxyethoxy-substituted nematic liquid crystals', Liquid Crystals, 34: 12, 1415 — 1424

To link to this Article: DOI: 10.1080/02678290701742912

URL: http://dx.doi.org/10.1080/02678290701742912

Liquid Crystals, Vol. 34, No. 12, December 2007, 1415–1424

Polar 2-alkoxyethoxy-substituted nematic liquid crystals

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(*Received 22 June 2007; accepted 3 September 2007*)

The synthesis is reported of a series of polar nematic liquid crystals incorporating an alkoxyalkoxy chain attached in a terminal position to a molecular core consisting of two aromatic rings. The dependence of the mesomorphism and phase transition temperatures on the nature of this terminal chain was studied. The shape anisotropy of the core is increased by the presence of an additional 1,4-disubstituted phenyl unit in a number of *p*-terphenyls. A number of highly polar esters with a terminal methoxyethoxy chain have been prepared as dopants to lower the threshold voltage of LCDs. The presence of the methoxyethoxy chain leads to an increase in the molecular dipole moment, the dielectric anisotropy and the dielectric constant perpendicular to the molecular long axis. Several compounds with a four-unit diether central linkage were also prepared.

1. Introduction

The twisted-nematic liquid crystal display (TN-LCD) [1] is still the most common commercial LCD more than thirty years after its invention [1–6]. It is necessary to use a multiplexed addressing scheme for TN-LCDs with even modest information content, e.g. simple calculators, and a steep voltage/transmission curve is required to achieve this [7–11]. A low k_{33}/k_{11} ratio and a low $\Delta\varepsilon/\varepsilon_{\perp}$ ratio are required to induce a steep voltage/transmission curve [7–11]. Nematic LCs with a large positive value of $\Delta\varepsilon$ are also needed to induce a low threshold voltage (V_{10}). V_{10} should be as low as possible for battery operation and low power consumption. Therefore, nematic mixtures are required combining a large positive value of $\Delta\varepsilon$ with a large value of $\varepsilon_{\perp}$. Aromatic materials with a strong polar terminal group, e.g. a cyano group, usually exhibit a large value $\Delta\varepsilon$ in the nematic phase due to the large dipole moment (μ=4 D) and therefore induce low threshold voltages in TN-LCDs. Unfortunately, the value of $\varepsilon_{\perp}$ is correspondingly low ($\Delta\varepsilon=\varepsilon_{\parallel} - \varepsilon_{\perp}$) and the steepness of the voltage/transmission curve of TN-LCDS using mixtures of polar LCs is insufficient for multiplex addressing. Fortunately, it was found that 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 led to sufficiently low values of these ratios for the resultant nematic mixture *and* a high $\Delta\varepsilon$ [11]. This is due to the fact that nematic LCs tend to associate as molecular dimers in the nematic phase [12]. The degree of pair formation is reduced by the addition of apolar compounds, which results in an increase in $\Delta\varepsilon$ *and* low k_{33}/k_{11} and $\Delta\varepsilon/\varepsilon_{\perp}$ ratios [11]. In some cases up to 50% of a non-polar material can 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 produced in the mixture, although none of the individual components exhibits a smectic phase [11]. This phenomenon is difficult to predict and, although it is undesirable to have a smectic phase within the required operating range of the mixture, the presence of a smectic phase at lower temperatures can produce advantageous values and ratios of the elastic constants [11]. Apolar components are also added to polar polyfluorinated LCs used in TN-LCDs with active matrix addressing and that do not associate to form molecular dimers, in order to lower both the melting point/recrystallization temperature and the viscosity, and hence the switching times, of the mixture.

The presence of a conjugated oxygen atom in an alkyl aryl ether (R–O–Ar) leads to a larger molecular dipole moment (μ) than that of the corresponding material with an alkyl chain in place of the alkoxy chain, or that of a non-conjugated alkyl alkyl ether, due to a longer effective molecular core and a higher degree of molecular delocalization and polarization (see figures 1 a and 1 b), respectively [13, 14]. For example, the magnitude of the dielectric anisotropy of the 4-alkoxy-4′-cyanobiphenyls is higher than that of the corresponding 4-alkyl-4′-cyanobiphenyls [14]. We

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290701742912

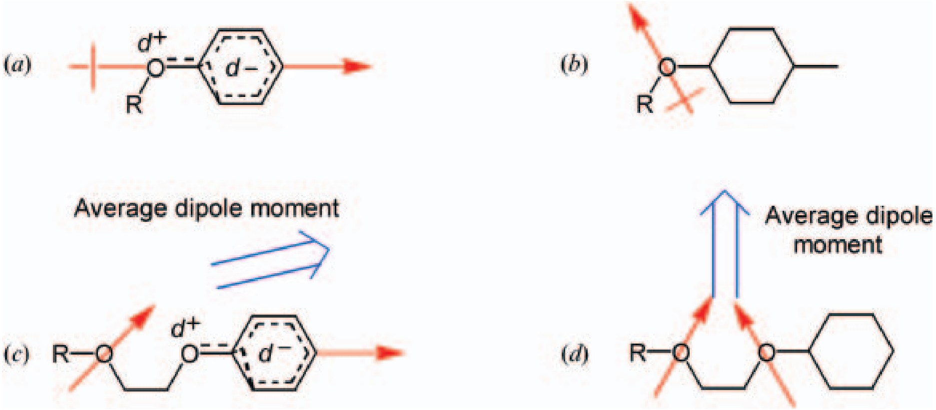


Figure 1. Idealized resonance diagrams showing the possible contribution of oxygen atoms to the dipole moment of the molecule for an aromatic ether (a), alicyclic ether (b), aromatic diether (c) and alicyclic diether (d).

hypothesize that incorporating a second oxygen atom into the end chain in the fourth position in the chain, i.e. using the alkoxyethoxy end group, in *aromatic* nematic LCs, would result in an increase in the magnitude of the orthogonal and parallel components of the molecular dipole (see figure 1 c), rather than in aliphatic diethers (see figure 1 d). The larger values of the dipole moment should lead to higher values in both $\Delta\varepsilon$ and $\varepsilon_\perp$.

LCs of high birefringence are also useful for nematic mixtures, since the product of the birefringence and the cell gap ($\Delta n d$) is fixed for operation in the first or second transmission minimum of TN-LCDs [3, 4, 9, 15, 16]. Therefore, nematic mixtures of high Δn enable thin TN-LCDs to be used. Since both the switch-on and switch-off times are directly proportional to the square of the cell gap, *d*, a high value for Δn can also give rise to short switching times. Therefore, we decided to attempt the synthesis of a range of aromatic alkoxyethoxy-substituted compounds exhibiting an enantiotropic nematic phase of high positive $\Delta\varepsilon$, high Δn and low $\varepsilon_\perp$. We also decided to synthesize a number of 2-methoxyethoxy-substituted benzoate esters of *very* high $\Delta\varepsilon$ to use as dopants to lower V_{10} of TN-LCDs. These simple aromatic esters also incorporate fluoro- and cyano-substituted phenyl rings, which contribute to a very high molecular dipole moment (μ=6–8 D) [17, 18].

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 [14, 19–22]. The presence of a non-conjugated oxygen atom in any position in the molecular structure nearly always leads to low nematic clearing points. There are also a few examples of nematic LCs with two oxygen atoms in the terminal chain attached to the aromatic core [23, 24]. The presence of the second oxygen atom also usually results in a low nematic clearing point. However, it was shown that the incorporation of two oxygen atoms, one of which is directly attached to the aromatic ring and the other in the chain, can result in a clearing point of the nematic phase not very much lower than that of the corresponding compound with a methylene unit (CH_2) in place of the second oxygen atom in the chain (see figure 2). Therefore, we decided to further investigate this class of nematic LCs first and use the knowledge gained from this short study to synthesize further materials.

2. Experimental

2.1. *Instrumentation*

All commercially available starting materials, reagents and solvents were used as supplied (unless otherwise stated) and were obtained from Aldrich, Strem Chem. Inc, Acros or Lancaster Synthesis. All reactions were carried out using a dry nitrogen atmosphere unless water was present as solvent or reagent and the 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

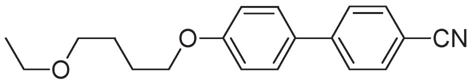


Figure 2. The molecular structure of 4-cyano-4′-(4-ethoxybutoxy)biphenyl (Cr–I=65°C; N–I=50.5°C) with two oxygen atoms in the terminal chain [24]. The clearing point (N–I=50.5°C) is lower than that (Cr–N=53.5°C; N–I=75°C) of 4-cyano-4′-heptyloxybiphenyl with only one oxygen atom between the terminal chain aromatic core and higher than that (Cr–SmA=21°C; SmA–N=32.5°C; N–I=40°C) of 4-cyano-4′-octylbiphenyl with no oxygen atoms in the terminal chain [14].

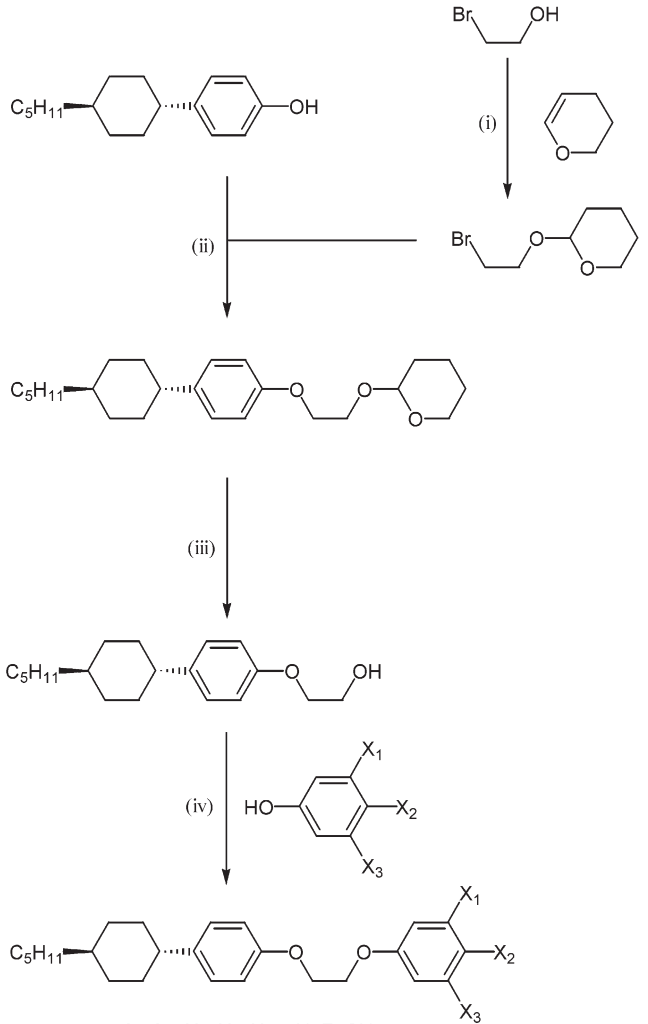
using a Bruker, reflex IV, matrix assisted laser desorption/ionization (MALDI), time of flight (TOF) MS. A 384 well microlitre plate format was used with a scout target. Samples were dissolved in DCM with HABA (2-(4-hydroxyphenylazo)benzoic acid) matrix (1:10, respectively). The mass ion of the material is identified by M^+. ^{1}H NMR spectra were recorded using a JEOL Lambda 400 spectrometer and an internal standard of tetramethylsilane (TMS) was used. 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 mainly accomplished by gravity column chromatography, using silica gel (40–63 µn, 60 A) obtained from Fluorochem. The purity of the final compounds was determined by elemental analysis using a Fisons EA 1108 CHN analyser. The melting point and the other transition temperatures of the solid compounds prepared were measured using a Linkam 350 hot-stage and control unit in conjunction with a Nikon E400 polarizing microscope. The phase transition temperatures of all 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 reported value of the transition temperatures. Molecular modelling was used to estimate the dipole moment of such materials as well as those of commercially available materials whose dipole moments are known. The dipole moments were predicted using an energy-minimized structure using Cerius^2 MOPAC program [25]. It was found that the error of the molecular modelled results and the experimental results were within an acceptable range (± 0.5). The switching voltages of mixtures M1 were tested in a standard 6 µm parallel TN-LCD cell at 25°C.

2.2. *Synthesis*

The three alkoxyethoxy-4′-cyanobiphenyls (**3, 7** and **8**) were prepared by alkylation of commercially available 4-cyanobiphenyl in the usual Williamson ether synthesis [26] and the appropriate 2-alkoxyethyl bromides prepared from the corresponding commercially available 2-alkoxyethanols and carbon tetrabromide [27, 28]. The 4-cyano-4′-[2-(2-methoxyethoxy)ethoxybiphenyl (**9**) was prepared in a similar manner using the appropriate alkyl bromide prepared from the corresponding alcohol in the same way. The 2-methoxyethoxy-substituted aryl ethers (**10**–**17**) were synthesized by alkylation of phenols available from other programmes, prepared as previously described, in the usual Williamson ether synthesis [26] with 2-methoxyethyl bromide prepared from the commercially available 2-methoxyethanol and carbon tetrabromide and triphenylphosphine [27, 28]. The 4-(2-methoxyethoxy)-4″-fluoro-*p*-terphenyl (**18**) and the 4-(2-methoxyethoxy)-4″-trifluoromethoxy-*p*-terphenyl (**19**) were prepared by a Suzuki aryl–aryl coupling reaction [29, 30] between commercially-available 4-fluorophenylboronic acid and 4-trifluoromethoxyphenylboronic acid and 4-bromo-4″-(2-methoxyethoxy)biphenyl prepared by alkylation of 4-bromo-4″-hydroxybiphenyl with 2-methoxyethyl bromide in the usual way. The esters (**22**–**24**) were synthesized by esterification of the appropriate phenols supplied by E. Merck and 4-(2-methoxyethoxy) benzoic acid using DCC/DMAP [31]. The 4-(2-methoxyethoxy)benzoic acid was prepared by alkylation of commercially-available 4-hydroxybenzoic acid using with 2-methoxyethyl bromide in the usual way. The ethers (**25**–**27**) were synthesized as shown in reaction scheme 1. First 2-methoxyethanol was protected as the THP derivative [32] and then used to alkylate 4-(*trans*-4-pentylcyclohexyl)phenol, provided by E. Merck, in the usual way [26]. The THP protecting group was removed using *p*-toluenesulfonic acid [32] to yield the corresponding alcohol, which was reacted with the appropriate phenols in a Mitsunobu reaction [33]. The phenols were either commercially available or provided by E. Merck.

2.2.1. 4-Cyano-4′-(2-propyloxyethoxy)biphenyl (3). A solution of 4-cyano-4′-hydroxybiphenyl (1.00 g, 5.13 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a mixture of 2-propyloxyethanol (0.53 g, 5.13 mmol), triphenylphosphine (1.35 g, 5.13 mmol), diethyl azodicarboxylate (0.89 g, 5.13 mmol) in tetrahydrofuran (10 cm^3) at room temperature. The reaction mixture was then stirred under nitrogen (15 h) and then evaporated down under reduced pressure. The crude product was purified by column chromatography on silica gel using a 1:1 dichloromethane–hexane mixture as eluent. The solvent was then removed under reduced pressure and the product recrystallized from ethanol. Yield 0.23 g (13%), GC purity (99.9%). ^{1}H NMR ($CDCl_3$) δ_{400}: 1.30 (3H, t), 1.69 (2H, quintet), 3.49 (2H, t), 3.79 (2H, t), 4.23 (2H, t), 6.99 (2H, d, $J \approx 8.5$ Hz), 7.51 (2H, d, $J \approx 8.5$ Hz), 7.65 (2H, d, $J \approx 8.5$ Hz), 7.68 (2H, d, $J \approx 8.5$ Hz). IR ν_{max}/cm^{-1}: 2966, 2921, 2208, 1615, 1513, 1489, 1438, 1269, 1209, 1130, 1063, 808, 519. MS *m*/*z*: 281 (M^+, M^{100}), 195 ($C_{13}H_9ON^+$), 71 ($C_4H_7O^+$).

2.2.2. 4-(2-Methoxyethoxy)benzoic acid. 4-Hydroxybenzoic acid (3.00 g, 2.17×10^{-2} mol) was dissolved in a mixture of ethanol (15 cm^3) and potassium hydroxide (3.22 g, 5.64×10^{-2} mol) in water (5 cm^3).



25-27; X_1, X_2, X_3 = H, F, CN

Scheme 1. Reagents and conditions for synthesis of new compounds: (i) PTS, CH_2Cl_2, (ii) K_2CO_3, KI, $CH_3COC_2H_5$, (iii) C_2H_5OH, PTS, (iv) DEAD, TPP, THF.

The solution was then heated gently and stirred before 1-bromo-2-methoxyethane (3.32 g, 2.39×10^{-2} mol) and potassium iodide (0.01 g, 6.02×10^{-5} mol) was added slowly. The resulting reaction mixture was then heated under reflux (15 h) and the solvent evaporated and the resulting solid residue dissolved in water (50 cm^3). The solution was washed with ether and then made strongly acidic with hydrochloric acid. The product was filtered and then recrystallized from ethanol. Yield 1.36 g (32%). M.p. = 154°C. ^{1}H NMR ($CDCl_3$) δ_{400}: 3.45 (3H, s), 3.77 (2H, t), 4.18 (2H, t), 6.94 (2H, d, $J\approx8.5$ Hz), 7.99 (2H, d, $J\approx8.5$ Hz), 11.96 (1H, s). IR ν_{max}/cm^{-1}: 2969, 2913, 1694, 1610, 1515, 1431, 1377, 1303, 1263, 1175, 1132, 1055, 1032, 922, 861, 695. MS *m/z*: 196 (M^+), 164 ($C_9H_8O_3^+$), 138 ($C_7H_6O_3^+$), 121 (M^{100}, $C_7H_5O_2^+$).

2.2.3. 3,4,5-Trifluorophenyl 4-(2-methoxyethoxy)benzoate (24).

A solution of 3,4,5-trifluorophenol (0.38 g, 2.55 mmol) in dichloromethane (10 cm^3) was added to a solution of *N,N*-dicyclohexylcarbodiimide (0.63 g, 3.06 mmol), 4-(3-methoxyethoxy)benzoic acid compound (125) (0.50 g, 2.55 mmol), 4-(dimethylamino) pyridine (0.03 g, 2.55×10^{-4} mol) in dichloromethane (5 cm^3), at 0°C and then left to stirred overnight at room temperature. The solution was then filtered to remove precipitated material (DCU) and the filtrate evaporated down under reduced pressure. The crude product was purified by column chromatography on silica gel using a 1:1 dichloromethane–petroleum ether (40–60°C) mixture as eluent, followed by recrystallization from ethanol. Yield 0.32 g (38%), GC purity (99.8%). CHN: expected C 58.90%, H 4.02%; found C 59.20%, H 3.99%.^{1}H NMR ($CDCl_3$) δ_{400}: 3.45 (3H, s), 3.79 (2H, t), 4.20 (2H, t), 7.00–7.04 (4H, m), 8.07 (2H, d, $J\approx8.7$ Hz). IR ν_{max}/cm^{-1}: 2957, 2931, 1720, 1623, 1577, 1512, 1435, 1255, 1208, 1163, 1135, 1111, 1055, 978, 791, 699. MS *m/z*: 326 (M^+), 179 (M^{100}, $C_{10}H_{11}O_3^+$), 121 ($C_7H_5O_2^+$).

2.2.4. 2-{2-[4-(*trans*-4-Pentylcyclohexyl)phenoxy]ethoxy}-tetrahydropyran.

4-(*trans*-4-Pentylcyclohexyl)phenol (10.00 g, 4.07×10^{-2} mol) was added dropwise to a solution of 2-(2-bromoethoxy)tetrahydro-2*H*-pyran (9.35 g, 4.47 mol), potassium iodide (0.68 g, 4.07 mmol) and potassium carbonate (22.50 g, 1.63×10^{-1} mol) in butanone (200 cm^3) under nitrogen and at room temperature. The reaction mixture was then refluxed (80°C, 24 h). The crude mixture was filtered through hyflo supercel and washed through with propanone. The solvent was then removed under reduced pressure and the crude product purified by column chromatography on silica gel using dichloromethane as the eluent and recrystallization from cold acetone to give the desired product as a white crystalline solid. Yield 4.44 g (29%). M.p. = 34°C. ^{1}H NMR ($CDCl_3$) δ_{400}: 0.87 (3H, t), 0.89–1.34 (8H, m), 1.50–1.85 (6H, m), 2.04–2.06 (4H, m), 3.49–4.06 (3H, m), 4.14 (2H, quartet), 4.51 (1H, quintet), 4.63 (2H, t), 4.68 (2H, t), 5.00 (2H, t), 6.46 (1H, t), 6.83 (2H, d, $J\approx8.4$ Hz), 7.10 (2H, d, $J\approx8.4$ Hz). IR ν_{max}/cm^{-1}: 2928, 2855, 2354, 1617, 1511, 1451, 1373, 1252, 1166, 1111, 1027, 830. MS *m/z*: 374 (M^+), 317 (M^{100}, $C_{20}H_{29}O_3^+$), 232 (M^{100}, $C_{15}H_{20}O_2^+$).

2.2.5. 2-[4-(*trans*-4-Pentylcyclohexyl)phenoxy]ethanol.

2-{2-[4-(*trans*-4-Pentylcyclohexyl)phenoxy]ethoxy}tetrahydropyran (3.93 g, 1.05×10^{-2} mol) was added to a solution of pyridinium *p*-toluenesulfonate (2.64 g, 1.05×10^{-2} mol) in ethanol (25 cm^3). The resulting mixture was then stirred (55°C, 3.5 h), added to water (250 cm^3) and the resultant aqueous layer extracted into diethyl ether (2×100 cm^3). The combined organic layers were washed with brine (2×100 cm^3), dried ($MgSO_4$) and the solvent removed under reduced pressure. The raw product was recrystallized from ethanol. Yield 2.94 g (98%), GC purity (99.8%). M.p.=65°C. ^{1}H NMR ($CDCl_3$) δ_{400}: 0.89 (3H, t), 1.03 (2H, sextet), 1.20–1.46 (11H, m), 1.84–1.87 (4H, m), 2.00 (1H, s), 2.41 (1H, quintet), 3.94 (2H, t), 4.06 (2H, t), 6.85 (2H, d, $J\approx8.4$ Hz), 7.12 (2H, d, $J\approx8.4$ Hz). IR ν_{max}/cm^{-1}: 3426, 2927, 2854, 1617, 1516, 1463, 1387, 1289, 1257, 1178, 1083, 1047, 893, 542. MS *m*/*z*: 290 (M$^+$), 246 (M^{100}, $C_{16}H_{22}O_2^+$).

2.2.6. 1-Fluoro-4-{2-[4-(*trans*-4-pentylcyclohexyl)phenoxy]ethoxy}benzene (25). A solution of 2-[4-(*trans*-4-pentylcyclohexyl)phenoxy]ethanol (0.50 g, 1.72 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a mixture of 4-fluorophenol (0.19 g, 1.72 mmol), triphenylphosphine (0.45 g, 1.72 mmol), diethyl azodicarboxylate (0.30 g, 1.72 mmol) in tetrahydrofuran (10 cm^3) at room temperature. The reaction mixture was stirred under nitrogen (15 h) and then evaporated down under reduced pressure. The crude product was purified by column chromatography on silica gel using a 1:1 dichloromethane–hexane mixture as eluent and recrystallization from toluene. Yield 0.17 g (26%), GC purity (99.9%). CHN: expected C 77.67%, H 9.13%; found C 78.00%, H 8.79%. ^{1}H NMR ($CDCl_3$) δ_{400}: 0.89 (3H, t), 1.03 (2H, sextet), 1.20–1.46 (11H, m), 1.84–1.87 (4H, m), 2.41 (1H, quintet), 4.27 (2H, t), 4.29 (2H, t), 6.87 (2H, d, $J\approx8.5$ Hz), 6.90 (2H, d, $J\approx8.6$ Hz), 7.00 (2H, d, $J\approx8.6$ Hz), 7.13 (2H, d, $J\approx8.5$ Hz). IR ν_{max}/cm^{-1}: 2967, 2925, 2855, 1657, 1616, 1513, 1455, 1380, 1250, 1224, 1186, 1101, 1067, 941, 835, 544. MS *m*/*z*: 384 (M^+, M^{100}), 278 ($C_{19}H_{18}O_2^+$).

2.3. *Mesomorphic properties*

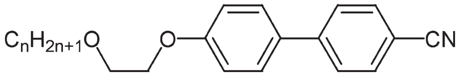
A nematic (N) phase was observed for many of the compounds prepared. A Schlieren texture with 2-brush and 4-brush disclinations are observed for the nematic phase observed between crossed polarizers. Small droplets are seen on cooling slowly from the isotropic (I) phase on forming the nematic phase. The transitions observed using optical microscopy were confirmed using differential scanning calorimetry (DSC). Where the phase transition temperatures could not be obtained directly by optical microscopy then the values from DSC analysis corresponding to the onset peak are used or virtual values were obtained by extrapolation using different concentrations of the final product in a standard nematic mixture (DOP-017).

3. Results and discussion

3.1. *Mesomorphism*

Compounds **3**, **7** and **8** were synthesized to study the effect of increasing the length of the alkoxy chain of the homologous series of the 4-cyano-4′-(2-alkoxyethoxy)-biphenyls **1**–**8** [23] (see table 1), while keeping the position of the oxygen atom constant. There is no observable trend for changes in the melting point with chain length. However, the clearing point decreases from a high value for the shortest chain (*n*=1), reaches a low value for intermediate chain lengths (*n*=2–5) and increases again with increasing chain length. There is a clear odd–even effect in the nematic clearing point as expected. Compound **4** is an example of a nematic material containing the diether end group with a melting point below room temperature. The 4-cyano-4′-[2-(2-methoxyethoxy)ethoxybiphenyl (**9**) with three oxygen atoms in the terminal chain (see figure 3), does not exhibit an observable nematic phase, although the melting point is not that much above room temperature (Cr–I=49°C). The extrapolated nematic clearing point is relatively low (N–I=9°C). However, it is considerably higher than that (−9°C) of the equivalent compound **4** with two oyxgen atoms in the terminal chain of the same length, i.e. with a methylene unit (CH_2) in place of the third oxygen atom. However, it is clear that care

Table 1. The phase transition temperatures (°C) for the new compounds **3, 7, 8** and the literature homologues **1, 2** and **4**–**6** [23].



Compound	*n*	Cr		N		I
1	1	•	99	(•	63)	•
2	2	•	43	(•	−15)	•
3	3	•	34	(•	3)	•
4	4	•	16	(•	−9)	•
5	5	•	47	(•	−2)	•
6	6	•	57	(•	19)	•
7	7	•	34	[•	14]	•
8	8	•	59	[•	8]	•

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

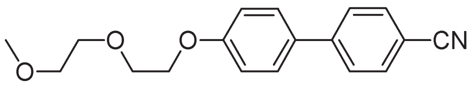


Figure 3. The molecular structure of 4-cyano-4′-[2-(2-methoxyethoxy)ethoxybiphenyl (**9**) with three oxygen atoms in the terminal chain (Cr–I=49°C; N–I=[9°C] extrapolated).

must be taken when comparing and interpreting differences between observable monotropic transitions with those obtained by extrapolation from nematic mixtures.

Since the combination of the 2-methoxyethoxy end group with the polar cyanobiphenyl moiety with two aromatic rings in the molecular core is seen to induce a nematic phase with the highest clearing point, it was decided to study the effect of the combination of the 2-methoxyethoxy group and a range of different aromatic rings and substituents in lateral and terminal positions on the mesomorphic behaviour of these materials. The results of these studies are collated in table 2. None of the materials **10**–**17** with only two aromatic rings in the aromatic core exhibits an observable LC phase, except for the reference 4-cyano-4′-methoxyethoxybiphenyl (**3**), i.e. the nematic clearing points for the two-ring compounds are virtual (extrapolated) values. In the case of compound **10** the presence of the lateral fluoro-substituent can be expected to reduce the formation of molecular dimers with anti-parallel correlations present in the nematic phase of compound **10**, for example, and as a result no nematic phase is observed due to the much shorter effective length-to-breadth ratio. Most of the materials shown in the table below possess a low length-to-breadth ratio, which may be responsible for the lack of liquid crystalline behaviour [14, 34]. The extrapolated nematic clearing points are low except for that of the biphenyl diether **15**, which is probably due to the presence of two oxygen atoms attached to, and conjugated with, the aromatic core, and that of compound **14**, whose clearing point is surprisingly high for a naphthalene compound with a low length-to-breadth ratio.

The *p*-terphenyls **18** and **19**, also shown in table 2, with three 1,4-disubstituted phenyl rings in the molecular core possess a greater shape anisotropy than the two-ring compounds **10**–**17**. Compound **18** contains a single fluoro substituent in a terminal position and, unfortunately, does not exhibit an observable nematic mesophase. However, when a larger polar end group is present, e.g. in the form of a trifluromethoxy end group in compound **19**, an enantiotropic nematic phase is observed. The terphenyls **18** and **19** exhibit much higher melting and clearing points than those of the two ring materials **10**–**19** as a consequence of the greater length-to-breadth ratio and the higher degree of anisotropy of the molecular polarisability [14, 34].

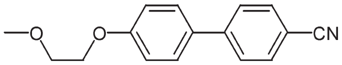
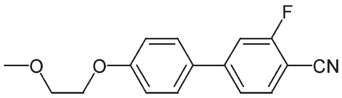
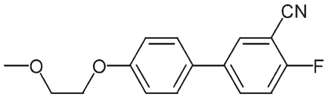
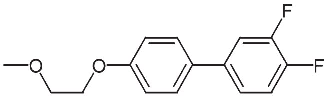
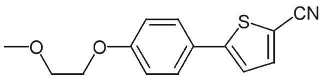
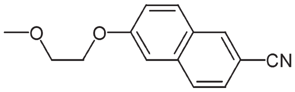
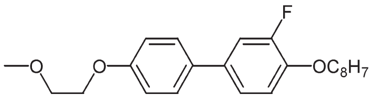
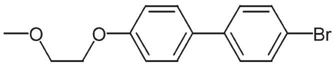
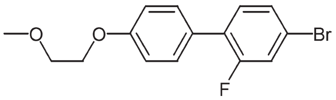
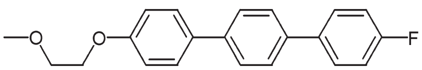
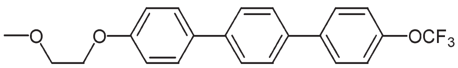
The commercially important esters **20** and **21** are shown in table 3 as reference compounds [35]. The dopants **20** and **21** have a strong dipole moment parallel to the long molecular axis. The strong dipole is a result of the use of a nitrile in a terminal position of the terminal phenyl ring along with the contribution from two fluoro substituents in positions three and five [35]. These fluoro-substituents also help to prevent the formation of antiparallel correlations within the bulk material and, therefore, increase the overall dielectric anisotropy of the material [18]. Both esters **20** and **21** show a monotropic nematic phase with a clearing point below room temperature. The esters **22**–**24** containing the methoxyethoxy terminal group in place of the pentyl chain of the ester **20** or the butoxy-chain of the ester **21** do not exhibit an observable LC mesophase. The presence of the extra oxygen in compound **23** does not increase the melting point in comparison to that of the butoxy ester **21**, but the extrapolated nematic clearing point is much lower than that of the butoxy-substituted ester **21** or the pentyl-substituted ester **20**.

The effect of the diether group on the mesomorphism and liquid crystalline transition temperatures was further studied by changing the position of the group from being in the chain to within the molecular core of the compounds **25**–**27** (see table 4). A third ring in these materials increases the length-to-breadth ratio and the presence of a polar substituent would be expected to induce a nematic phase with a high clearing point. Unfortunately, the diethers **25**–**27** do not exhibit an observable LC phase. This lack of liquid crystalline phase formation is possibly brought about by the separation of the two aromatic systems in the core of the material or to dipole-dipole effects [14]. It may also be attributable to nonlinear conformations of these molecules induced by the presence of a flexible aliphatic central linking unit. The extrapolated values are as expected with the diether **27** exhibiting the lowest clearing point due to the presence of two fluorine atoms in lateral positions on the terminal benzonitrile moiety. The benzonitrile **26** possesses the highest extrapolated value of the nematic clearing point due to the presence of the cyano group in a terminal position.

3.2. *Physical properties*

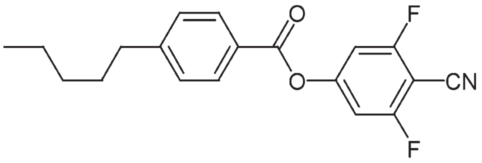
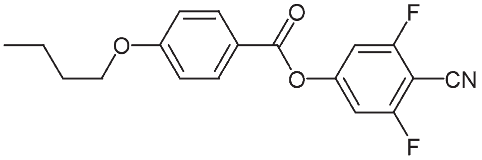
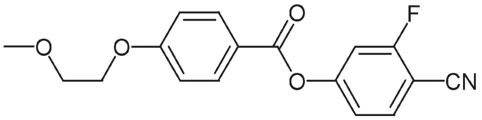
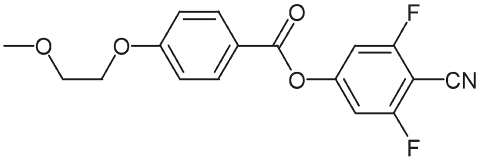
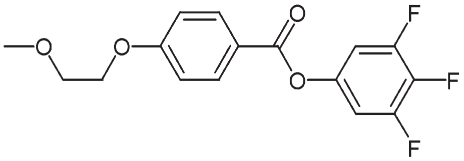
The mixture M1 incorporates 10% of the 4-cyano-3-fluorophenyl 4-(2-methoxyethoxy)benzoate (**22**) in the host nematic mixture DOP-017, as shown in table 5. The mixture M1 exhibits a lower nematic clearing point and a higher value of the birefringence than the corresponding values of the host mixture DOP-017 (see table 6), as expected. The dielectric constants and the dielectric anisotropy of the nematic mixture M1 are greater than those of the of the host mixture. This could have been expected considering the fact that the related esters **20** and **21** are known to exhibit very large values of the dielectric anisotropy ($\Delta\varepsilon > +50$) [35] due to the very large dipole moment produced by the adjacent

Table 2. The phase transition temperatures (°C) for the aromatic two-ring alkyl aryl ethers **3** and **10**–**19**:

Compound	Structure	Cr		N		I
3		•	99	(•	63)	•
10		•	83	[•	17]	•
11		•	94	[•	11]	•
12		•	57	[•	−40]	•
13		•	108	[•	15]	•
14		•	82	[•	28]	•
15		•	75	[•	37]	•
16		•	130		–	•
17		•	57	[•	12]	•
18		•	244		–	•
19		•	273	•	288	•

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

Table 3. The phase transition temperatures (°C) for the phenyl benzoates **20** and **21** [35] and **22**–**24** and the experimentally-determined dipole moment (μ_{exp}) and the dipole moment (Debye) predicted from molecular modelling (μ_{pred}).

Compound	Structure	Cr		N		I	μ_{exp}	μ_{pred}
20		•	30	(•	−8)	•	7.2	7.4
21		•	72	(•	8)	•	7.8	7.8
22		•	97	[•	23]	•		
23		•	72	[•	−27]	•	–	8.5
24		•	75	[•	8]	•		

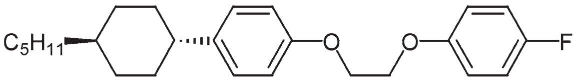
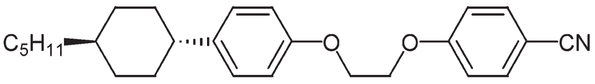
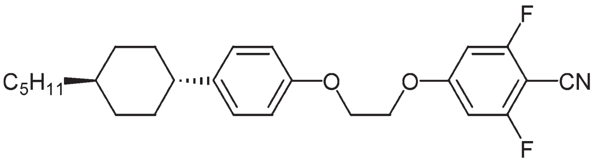
[ ] Represents a virtual transition temperature.

fluorine and cyano groups in the non-associated parent molecules (see table 3) [17, 18]. The mixture M1 exhibits a relatively low switching voltage of 3.0 V as expected considering the very high positive dielectric anisotropy due to the combination of the fluoro and cyano substituents. The presence of the alkoxyethoxy chain in the dopant **22** should induce a higher value of the $\Delta\varepsilon/\varepsilon_{\perp}$ ratio, which should also lead to a steeper electro-optical response curve. Unfortunately, the viscosity of such dopants incorporating alkoxyethoxy chains is expected to be greater than that of the corresponding dopants with alkoxy or alkyl chains. The higher viscosity induced by the presence of such dopants could result in longer response times, despite. Therefore, although such 2-methoxyethoxy-substituted esters may be of use as dopants to reduce the threshold voltage and increase the steepness of the electro-optical response curve of commercial LC mixtures, further studies are necessary to determine their real usefulness in commercial applications.

4. Conclusions

The presence of a 2-alkoxyethoxy chain attached in a terminal position to an aromatic core leads to a low clearing point of the nematic phase. The shortest chain, i.e. the 2-methoxyethoxy chain, leads to the lowest decrease in the nematic clearing point and also leads to

Table 4. The phase transition temperatures (°C) for the three-ring diethers **25**–**27**.

Compound	Structure	Cr		N		I
25		•	145	[•	52]	•
26		•	133	[•	87]	•
27		•	85	[•	28]	•

[ ] Represents a virtual transition temperature.

Table 5. Composition and clearing point (°C) of the host nematic mixture DOP-017 and the doped nematic mixture M1 consisting of 10% of the ester **22** in the nematic mixture DOP-017.

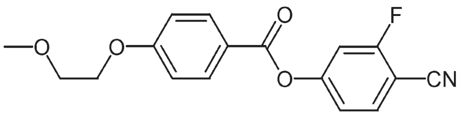
Mixture		Dopant	N–I
DOP-017	–	–	45
M1	**22**		42

Table 6. The refractive indices, birefringence, dielectric constants and the dielectric anisotropy of the host nematic mixture DOP-017 and the doped nematic mixture M1 measured at 25°C and 32°C.

Mixture	T/°C	n_e	n_o	Δn	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
DOP-017	25.0	–	–	0.0940	12.95	5.13	7.82
M1	32.0	1.5778	1.4861	0.0917	13.50	5.51	7.99
	25.0	1.5876	1.4874	0.1002			

an increase in the dielectric anisotropy of the nematic phase and the dielectric constant orthogonal to the nematic director. The presence of a third oxygen atom in the terminal chain leads to an increase in the clearing point of the nematic phase comparing only compounds with the same overall chain length. A four-unit diether linking group leads to low nematic clearing points. Polar 2-methoxyethoxy-substituted *p*-terphenyls can exhibit high nematic clearing points. A number of highly polar esters with a terminal 2-methoxyethoxy-chain have been identified as suitable dopants to lower the threshold voltage of TN-LCDs.

Acknowledgements

We express our thanks to Qinetiq for funding for a postgraduate studentship (NLC) and to Merck-NBSC, Southampton, UK, for the supply of some reaction intermediates. We would also like to thank B. Worthington (^{1}H NMR) and K. Welham (MS) of the

University of Hull for spectroscopic measurements. The referee is thanked for number of constructive and helpful comments.

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