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Nematic Liquid Crystals with a Trifluoromethyl Group

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We have synthesised a new class of compounds incorporating a trifluoromethyl group in the terminal alkoxy or alkenyloxy chain. Compounds containing several aromatic rings were synthesised with a view to producing compounds of high birefringence. This also included the synthesis of compounds containing a carbon-carbon triple bond. Compounds with three 1,4-disubstituted rings were synthesised in order to produce materials with a high nematic clearing point and as low a melting point as possible. Laterally fluoro-substituted compounds were prepared to generate a high positive value of the dielectric anisotropy, a low melting point and no smectic mesophases. Substances containing a cyclohexyl ring, which tend to induce a lower viscosity and compounds incorporating a bicyclo[2.2.2]octane ring were also synthesised in order to produce a high nematic clearing point and to influence the elastic constants. The (*E*)-trifluorobut-2-enyloxy-compounds were prepared in attempts to produce compounds with appropriate elastic constants and a high birefringence.

Keywords: nematics; poly-fluorinated; AA-LCDs

INTRODUCTION

Most commercially available liquid crystal displays (LCDs) with high information content utilise the Twisted Nematic device (TN-LCDs)[1,2] or In-Plane Switching (IPS-LCDs)[3,4] with active matrix addressing.[5] These electro-optical effects using nematic liquid crystals can be used to produce large-area, light, flat-panel displays with a high contrast ratio, grey-scale (full colour), fast response times, wide operating temperatures and almost complete absence of cross-talk. The TN-LCD requires nematic liquid

crystals of high positive dielectric anisotropy in order to produce a low threshold voltage and short response times. Furthermore, they should also exhibit a low viscosity and appropriate values of the elastic constants (especially k_{11} and k_{33}) in order to further reduce the response times. A wide operating temperature range requires a low melting point (T_m < -50 °C) and a high clearing point (T_{N-I} > 80 °C -120 °C). The product of the birefringence and the cell gap (Δnd) is fixed for operation in the first or second transmission minimum. Therefore, nematic mixtures of high birefringence enable thin cells to be used. Since both the switch-on and switch-off times are directly proportional to the square of the cell gap, a high birefringence can also give rise to short switching times. The nematic mixtures used in LCDs with active matrix addressing should also exhibit a very high initial value for the resistivity, which should stay as constant as possible over the life-time of the display, in order to maintain the optical performance. Nematic liquid crystals containing several halogen atoms, especially fluorine atoms were found to exhibit a stable holding ratio and an acceptable high value of the dielectric anisotropy.[6-13] The value for the permanent dipole moments of several carbon-fluorine bonds were found to be additive, which results in a high value for the dielectric anisotropy. This does not lead to the solvation of ions from the alignment layers, as happens for nematic mixtures of similar dielectric anisotropy incorporating compounds with a cyano group. This is probably due to the low dipole moment of the fluorine-carbon bond and the spatial distribution of the fluorine atoms in poly-fluorinated nematic liquid crystals.

We have synthesised a new class of compounds suitable for LCD applications, incorporating a trifluoromethyl group situated at the end of a terminal alkoxy or alkenyloxy chain. These compounds fulfil many of the specifications for use in TN-LCDs. These materials were designed so that the resultant dipole moment due to three carbon-fluorine bonds on the same carbon atom is parallel to the molecular long axis, i.e. the nematic director. Although the 4,4,4-trifluorobutyloxy-chain chosen for initial study may adopt non-linear conformations, which would reduce the component of the dipole moment parallel to the director, this is not possible for the (*E*)-4,4,4-trifluorobut-2-enyloxy-chain.

SYNTHESIS

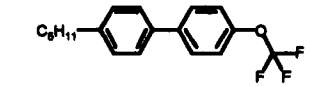
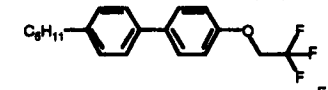
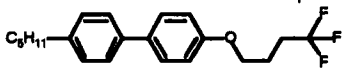
The ethers shown in the tables were prepared from the appropriate alkyl bromide or tosylate and a range of phenols *via* the Williamson Ether Synthesis. The aryl 4,4,4-trifluorobutyl ethers and (*E*)-4,4,4-trifluorobut-2-enyl ethers were synthesised by the reaction of the appropriate phenol with commercially available 1-bromo-4,4,4-trifluorobutane or toluene-4-sulfonic acid (*E*)-4,4,4-trifluorobutenyl ester. This tosylate was produced in the normal way from (*E*)-4,4,4-trifluorobut-2-en-1-ol and 4-methylbenzenesulphonyl chloride. The corresponding non-fluorinated butyloxy-compounds and (*E*)-but-2-enyloxy-materials were prepared in a

similar fashion using commercially available 1-bromobutane or (*E*)-1-chloro-but-2-ene and the appropriate phenol. The 4-*n*-alkyl-4'-hydroxybiphenyls were commercially available. The 3-fluoro-4-hydroxy-4'-pentylbiphenyl was prepared by the aryl-aryl cross coupling of 4'-bromo-4-heptylphenyl and 4-benzyloxy-3-fluorophenylboronic acid in a Suzuki reaction to yield 4-benzyloxy-3-fluoro-4'-pentylbiphenyl followed by deprotection by catalytic hydrogenolysis. The corresponding 4-*n*-alkyl-4'-hydroxytolanes with an additional carbon-carbon triple bond were prepared by cross coupling commercially available 4-*n*-alkylacetylenes with 4-iodophenol using a palladium catalyst. The 4-(*trans*-4-pentylcyclohexyl)phenol was converted into the corresponding triflate, i.e., 4-(*trans*-4-pentylcyclohexyl)phenyl 1,1,1-trifluoromethanesulphonic acid ester, which was subsequently coupled with 4-benzyloxyphenylboronic acid and 4-benzyloxy-3-fluorophenylboronic acid to yield 4-benzyloxy-4'-(*trans*-4-pentylcyclohexyl)biphenyl and 4-benzyloxy-3-fluoro-4'-(*trans*-4-pentylcyclohexyl)biphenyl, respectively. Deprotection of which by catalytic hydrogenolysis led to the desired phenols. The synthesis of 1-(4-hydroxyphenyl)-4-pentylbicylco[2.2.2]octane was achieved through a Friedel Crafts reaction between 1-bromo-4-pentylbicyclo[2.2.2]octane and anisole followed by demethylation of the intermediate formed 1-(4-methoxyphenyl)-4-pentylbicylco[2.2.2]octane. The synthesis of 4-hydroxy-4"-pentylterphenyl produced *via* the aryl-aryl coupling of 4-pentylphenyl boronic acid and 4-bromo-4'-pentylbiphenyl and the subsequent deprotection of the intermediate 4"-benzyloxy-4-pentylterphenyl by hydrogenolysis. A Friedel Crafts reaction between 1-bromo-4-pentylbicyclo[2.2.2]octane and 4-methoxybiphenyl yielded 1-(4-methoxybiphenyl-4'yl)-4-pentylbicylco[2.2.2]octane, which was demethylated to give the desired 1-(4-hydroxybiphenyl-4'-yl)-4-pentylbicylco[2.2.2]octane.

RESULTS AND DISCUSSION

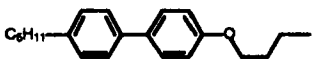
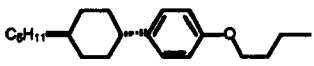
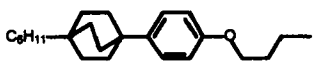
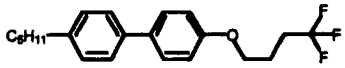
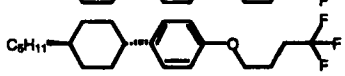
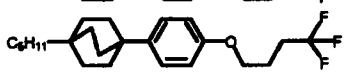
Table 1 contains a comparison of the liquid crystal transition temperatures of compounds, which differ only in the length of their ω,ω,ω-trifluoroalkoxy-chain. Only the 4,4,4-trifluorobutyloxy-compound is mesomorphic. The extrapolated nematic-isotropic transition temperature of 4,4,4-trifluorobutyloxy-compound is also much higher than that of the 2,2,2-trifluooroethoxy-compound. The thermal data collated in Table 2 allows a comparison of the effect of the presence of various co-axial 1,4-disubstituted rings in similar materials differing only in the presence or absence of three fluorine atoms at the end of the terminal chain.

TABLE 1. Transition temperatures for the compounds shown below.

Structure	Cr	SmB	SmA	N-I
	67	-	-	-
	107	-	-	[-30]
	63	99	103	[63]

[ ] Represents an extrapolated 'virtual' transition temperature

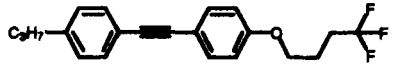
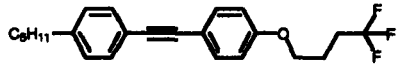
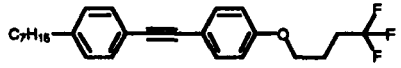
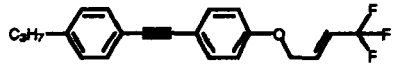
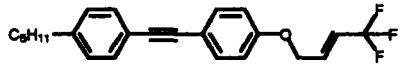
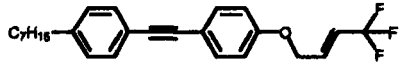
TABLE 2. Transition temperatures for the compounds shown below.

Structure	Cr	SmB	SmA	N-I
	63	81	89	[86]
	34	-	-	46
	65	-	-	77
	63	99	103	[63]
	49	-	-	[21]
	65	-	-	(51)

( ) Represents a monotropic transition temperature
[ ] Represents an extrapolated 'virtual' transition temperature

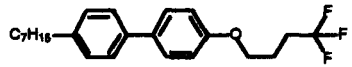
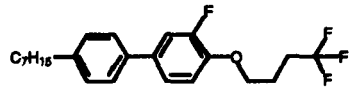
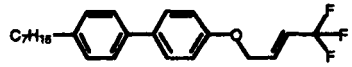
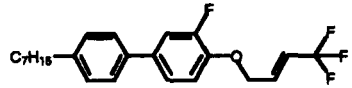
The extrapolated nematic clearing points of the 4,4,4-trifluorobutyloxy-ethers are some 20 °C lower than those of the corresponding butyloxy-substituted analogues. This may well be the result of steric interactions due to fluorine atoms or unfavourable intermolecular dipole-dipole interactions. The two cyclohexane derivatives exhibit the lowest nematic clearing points. However, the smectic phases observed for the 4,4,4-trifluorobutyloxy-substituted ethers occur at higher temperatures than those of the corresponding butyloxy-ether. This appears to confirm a general trend that 4,4,4-trifluorobutyloxy-substituted ethers generally exhibit higher smectic transition temperatures, but a lower nematic clearing point, than those of their non-fluorinated analogues. Table 3 contains thermal data for three homologues of 4,4,4-trifluorobutyloxy-substituted tolanes. The propyl compound is not mesomorphic. However the other homologues exhibit an ordered smectic phase. The tendency to form the smectic X phase increases with increasing chain length. Although the clearing point decreases as alkyl chain length increases, the extrapolated nematic-isotropic transition temperature is remarkably similar for all three homologues. The high extrapolated nematic-isotropic transition temperature of the tolanes is almost certainly due to the high length-to-breadth ratio and the degree of anisotropy of the molecular polarisability. The (*E*)-4,4,4-trifluorobut-2-enyloxy-compounds exhibit higher transition temperatures than the analogous 4,4,4-trifluorobutyloxy-compounds. However, the extrapolated nematic clearing points are lower (12 °C, on average) than those determined for the analogous 4,4,4-trifluorobutyloxy-compounds. This is very unusual and may be attributable in part to the inexactitude of the extrapolation procedure. Data for the dipole moment and the extrapolated nematic-isotropic transition temperatures for some of the new compounds are collated in Table 4. Molecular modelling suggests that the dipole moment of the trifluoromethyl group at the end of the terminal chain of the ethers is almost parallel to the long molecular axis. This appears to be confirmed by the data collated in Table 4, which shows a large dipole moment for these materials. The inclusion of a fluorine atom in a lateral position greatly increases the dipole moment. Unfortunately, a consequence of the incorporation of a fluorine atom in a lateral position is a much lower clearing point. These effects are often additive for poly-fluorinated compounds.[6-13] Interestingly, the inclusion of a *trans*-carbon-carbon double bond into the core system increases the dipole almost to the same extent as the inclusion of a lateral fluorine substituent. This may be attributable to the absence of non-linear conformations of this terminal unit,. This is consistent with the high value for the extrapolated nematic clearing point. Therefore, it is not surprising that the compound which combines a *trans*-carbon-carbon double bond and a fluorine atom in a lateral position *ortho* to the (*E*)-4,4,4-trifluorobut-2-enyloxy-chain, should possess the highest dipole moment and clearing point.

TABLE 3. Transition temperatures for the compounds shown below.

Structure	Cr	SmX	N-I
	106	-	[83]
	98	(86)	[85]
	76	91	[85]
	130	-	[67]
	106	120	[74]
	87	121	[76]

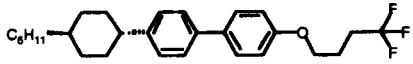
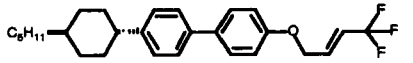
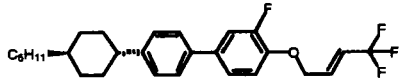
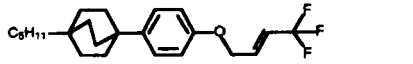
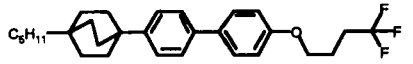
( ) Represents a monotropic transition temperature
[ ] Represents an extrapolated 'virtual' transition temperature

TABLE 4. Dipole moment (D) and T_{N-I} (°C) for the compounds shown below.

Structure	μ	T_{NI}
	9.73	[63]
	17.8	[-5]
	15.4	[48]
	18.2	[20]

[ ] Represents an extrapolated 'virtual' transition temperature

TABLE 5. Physical data measured for 10 % mixtures for the compounds shown below in the host nematic mixture DOP017.

Structure	T_{N-I}	Δn^a	$\Delta\varepsilon$	T^b
Mixture DOP017	45.2	0.094	7.0	-
	64.5	0.095	7.1	24.8
	63.1	0.101	7.5	26.5
	62.2	0.095	7.3	28.8
	53.5	0.093	6.5	31.2
	67.8	0.100	7.3	43.6

a: Measured at T_{N-I} -T = 30 °C
b: $T = T_{on} + T_{off}$ measured at 25 °C.

The nematic clearing point of all of the doped mixtures, shown in Table 5, is significantly higher than that of the host mixture. The clearing point of the mixture containing 1-pentyl-4-[4-(4,4,4-trifluorobutyloxy)biphenyl-4'-yl]bicyclo[2.2.2]octane is especially high. The lowest value is seen for the mixture containing the two-ring bicyclo[2,2,2]octane. This order is to be expected, since the three-ring compounds all possess high clearing points. The birefringence (Δn) also increases for all of the mixtures, with the exception of the mixture containing the bicyclo[2,2,2]octane. This may be attributable to the other compounds in the data set possessing two aromatic rings in their core structures. The order parameter of the mixtures containing the dopants three-ring compounds will also be higher at room temperatures due to the higher clearing pint of these mixtures. This will also result in a higher value for the birefringence at room temperature, since the reduced temperature is greater than that of the host nematic mixture DOP017. The dielectric anisotropy ($\Delta\varepsilon$) of the mixtures is also increased with the

exception of the mixture containing the bicyclo[2.2.2]octane. The resultant dipole moment of the trifluoromethyl group parallel to the molecular long axis is responsible for the high value of dielectric anisotropy ($\Delta\varepsilon$) for these 4,4,4-trifluorobutyloxy compounds. The higher order parameter will also contribute to a higher observed value of the dielectric anisotropy at room temperature. The switching times of the mixtures are as expected, i.e., the inclusion of the viscous bicyclo[2.2.2]octane compounds leads to the longest switching time. The next slowest mixture is that containing contains a three-ring component with a lateral fluoro-substituent. The steric effect of the fluorine atom in a lateral position will also increase the viscosity of the nematic mixture. The fastest switching mixtures contain compounds which do not have any of the unfavourable attributes of the aforementioned compounds.

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