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Terminal trifluoromethyl-alkoxy and -alkenyloxy nematic liquid crystals for LCDs with active matrix addressing

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We have synthesized a new class of compounds suitable for LCD applications, incorporating a trifluoromethyl group in the terminal alkoxy- or alkenyloxy-chain. These compounds appear to fulfil many of the requirements for use in TN-LCDs. Core units containing a cyclohexyl ring, which tend to induce a lower viscosity than that of the analogous aromatic materials, were synthesized. Systems containing several aromatic rings were also prepared with a view to producing compounds of high birefringence. Compounds containing a lateral fluoro-substituent as well as a polar substituent in a terminal position were synthesized in order to generate a high positive value of the dielectric anisotropy. Molecules incorporating a bicyclo[2.2.2]octane ring were also synthesized in order to produce a high nematic clearing point and to influence the elastic constants. Compounds with three 1,4-disubstituted rings were synthesized with a view to producing materials with a high nematic clearing point and as low a melting point as possible. A series of compounds with a carbon–carbon double bond in the terminal chain was prepared in an attempt to produce compounds with appropriate values and ratios of the elastic constants.

1. Introduction

The twisted nematic liquid crystal display (TN-LCD) [1] with multiplex or active matrix addressing [2–12] and the super twisted nematic liquid crystal display (STN-LCD) with multiplex addressing [13–23] are the most common kinds of flat panel displays. TN-LCDs with multiplex addressing and even a moderate information content exhibit low contrast and brightness, and long response times as well as a narrow, asymmetrical viewing angle cone. Therefore, the multiplexed addressed TN-LCD is clearly unsuitable for fast, high information content displays, especially for applications with video-rate addressing. In contrast, large area TN-LCDs with some form of active-matrix addressing possess a high contrast ratio, almost complete absence of cross-talk, grey-scale and relatively fast response times. The few disadvantages still apparent are a direct consequence of the optics and construction of the TN-LCD, i.e. low luminosity or high power consumption. TN-LCDs [12] with active matrix addressing usually utilize either a discrete thin film transistor (TFT-TN-LCDs) [6] or a diode (MIM-TN-LCDs) [7] as the active element at each individual pixel on an amorphous or crystalline silicon substrate [8]. The high production cost associated with the silicon substrate and low production yield due to pixel damage and subsequent repair initially hindered the market acceptance of active-matrix addressed TN-LCDs. However, improved production equipment and processes have reduced the price differential with comparable STN-LCDs substantially. Thus, TN-LCDs with active matrix addressing are increasing their share of the flat panel display market partially at the expense of STN-LCDs.

The TN-LCD requires nematic liquid crystals of positive dielectric anisotropy ($\Delta\varepsilon = \varepsilon - \varepsilon_{\perp} > 0$). The threshold voltage for a twisted nematic cell is then defined [1] by the equation

$$V_{\mathrm{th}} = \pi \left[\frac{1}{\varepsilon_0 \Delta\varepsilon} \left(k_{11} + \frac{k_{33} - 2k_{22}}{4} \right) \right]^{1/2} \qquad (1)$$

where k_{11}, k_{22} and k_{33} are the Frank elastic constants, ε_0 is the dielectric constant of a vacuum and $\Delta\varepsilon$ is the dielectric anisotropy of the nematic mixture. Thus, activated pixels appear dark against a bright background for TN-LCDs with positive contrast. Upon removal of the applied field, surface and elastic forces restore the twist, which allows plane polarized light to be transmitted once more and the display appears bright. The

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response times, t_{on} and t_{off}, are defined [1] by equations

$$t_{on} \propto \frac{\eta d^2}{\Delta\varepsilon \mathbf{E} - \kappa\pi^2}, \quad t_{off} \propto \frac{\eta d^2}{\kappa\pi^2}$$

where $\kappa = k_{11} + (k_{33} - 2k_{22})/4$, η is the rotational viscosity, γ_1, and **E** is the applied field. Therefore, a nematic mixture of high positive dielectric anisotropy is required in order to produce a low threshold voltage for the display. The nematic mixture should also exhibit a low viscosity and a low value of the elastic constant term, κ, in order to produce short response times. The birefringence of the mixture is also an important factor, since the product of the birefringence and the cell gap (Δnd) is fixed for operation in the first or second transmission minimum [3–5]. 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.

Furthermore, TN-LCDs with active matrix addressing require a nematic mixture of very high constant resistivity in order to maintain the optical performance of the display. The holding ratio, *HR*, represents the stability of the resistivity of the liquid crystal mixture over time

$$HR = \left\{[1 - \exp(-2T/\tau)]\left(\frac{\tau}{2T}\right)\right\}^{1/2}$$

where T is the frame time and τ is the time constant for the pixel and storage capacitor. These requirements impose very demanding specifications on the purity, stability (chemical, photochemical and electrochemical), and the resistivity over time of each of the individual mixture components and the nematic mixture itself.

The usual liquid crystals with a terminal cyano group used in nematic mixtures for TN-LCDs and STN-LCDs with multiplex addressing are unsuitable for LCDs with active matrix addressing. The high polarity of the cyano group facilitates the solvation of ions out of the alignment and passivation layers on the inside of an LCD [24]. The resultant large number of inorganic ions in the nematic mixture in the centre of the cell reduces the resistivity of the nematic mixture. This in turn leads to a decrease in the effective holding voltage and, consequently, a lower observed contrast ratio for the display. Liquid crystals containing several halogen atoms, especially fluorine atoms, were found to exhibit a stable holding ratio [24–38]. This is probably attributable to the much lower value for the permanent dipole moment of a carbon–fluorine single bond compared with that of the carbon–nitrogen triple bond of the cyano group. However, the clearing point (N–I) of such compounds, especially the two-ring derivatives, is often low [24]. The structure of a typical two-ring polyfluorinated component (with a trifluoromethoxy group in a terminal position) of nematic mixtures for TN-LCDs with active matrix addressing is shown in figure 1. Such nematic mixtures often contain a high proportion of the corresponding three-ring materials in order to generate a sufficiently high clearing point. The relatively high concentration of components with three rings can give rise to a relatively high viscosity and, consequently, long response times. The presence of ordered smectic phases, especially the smectic B phase, induced at low temperatures can also be a problem in such mixtures.

We now report the synthesis of a new class of compounds suitable for LCD applications, incorporating

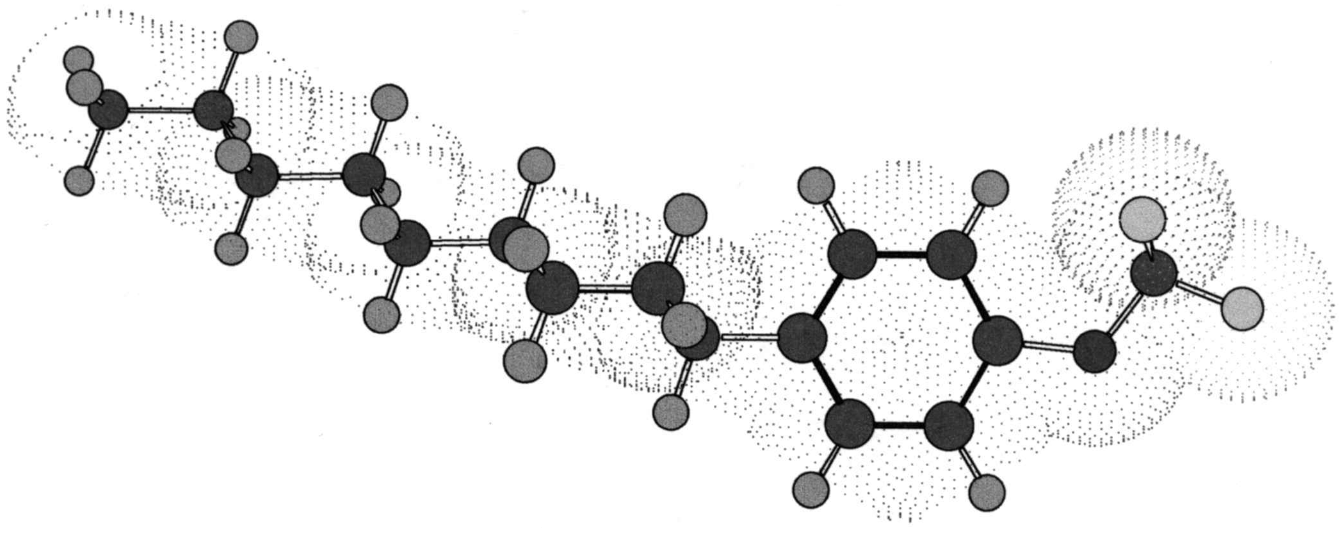


Figure 1. The energy-minimized structure of 1-(*trans*-4-pentylcyclohexyl)-4-trifluoromethoxybenzene (**23**) calculated using the Cerius^2 commercial package. Dipole moment = 2.660 D.

three fluorine atoms attached to the same carbon atom at the end of a terminal butyloxy chain or (*E*)-but-2-enyloxy chain. These new compounds incorporating either a 4,4,4-trifluorobutyloxy unit or a (*E*)-4,4,4-trifluorobut-2-enyloxy group fulfil many of the specifications for use in TN-LCDs with active matrix addressing. These materials were designed so that the resultant dipole moment due to the three carbon–fluorine bonds on the same carbon atom points along the molecular long axis, i.e. parallel to the nematic director, see figure 2. 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 also attached to the same molecular core units. However, the energy-minimized structures also produced using the Cerius^2 package indicate that trifluorobutyloxy compound **3b** possesses a larger dipole (2.903 D) along its molecular axis than that (2.660 D) of the trifluoromethoxy analogue **23**. The larger length-to-breadth ratio of this new class of rod-like compounds should also increase the tendency for mesophase formation, e.g. compare structures **3b** and **23** shown in figures 1 and 2, respectively.

2. Synthesis

Scheme 1 outlines how the aryl 4,4,4-trifluorobutyl ethers **3a–h** and (*E*)-4,4,4-trifluorobut-2-enyl ethers **6a–h** were synthesized. An appropriate phenol **1a–h** was reacted with commercially available 1-bromo-4,4,4-trifluorobutane (**2**) or toluene-4-sulphonic acid (*E*)-4,4,4-trifluorobutenyl ester (**5**) in a Williamson ether synthesis. The tosylate **5** was produced in the normal way from commercially available (*E*)-4,4,4-trifluorobut-2-en-1-ol (**4**) and 4-methylbenzenesulphonyl chloride [39]. Scheme 1 also shows how the corresponding non-fluorinated butyloxy-analogues **8c–h** and (*E*)-but-2-enyloxy-analogues **10c–h**, synthesized for comparison purposes, were prepared in a similar fashion using commercially available 1-bromobutane (**7**) or (*E*)-1-chloro-but-2-ene (**9**) and an appropriate phenol **1a–h**. The 4-(*trans*-4-propylcyclohexyl)phenol (**1a**), 4-(*trans*-4-pentylcyclohexyl)phenol (**1b**) and 4-hydroxy-4′-pentylbiphenyl (**1e**) were commercially available. The other phenols required were synthesized as shown in schemes 2–5. The synthesis of 4-hydroxy-4′-(*trans*-4-pentylcyclohexyl)biphenyl (**1c**) and 3-fluoro-4-hydroxy-4′-(*trans*-4-pentylcyclohexyl)biphenyl (**1d**) is shown in scheme 2. The 4-(*trans*-4-pentylcyclohexyl)phenol (**1a**) was converted into the corresponding triflate, i.e. 4-(*trans*-4-pentylcyclohexyl)phenyl 1,1,1-trifluoromethane sulphonic acid ester (**11**) [40], which was subsequently coupled [41] with 4-benzyloxyphenylboronic acid (**12**) and 4-benzyloxy-3-fluorophenylboronic acid (**13**) to yield 4-benzyloxy-4′-(*trans*-4-pentylcyclohexyl)biphenyl (**14**) and 4-benzyloxy-3-fluoro-4′-(*trans*-4-pentylcyclohexyl)-biphenyl (**15**), respectively. Deprotection of **14** and **15** by catalytic hydrogenolysis [42] led to the desired phenols **1c** and **1d**, respectively. Scheme 3 outlines how the synthesis of 1-(4-hydroxyphenyl)-4-pentylbicyclo-[2.2.2]octane **1f** was achieved through a Friedel Crafts [43] reaction between 1-bromo-4-pentylbicyclo[2.2.2]-octane **16** and anisole **17** followed by demethylation [44] of the intermediate 1-(4-methoxyphenyl)-4-pentyl-bicyclo[2.2.2]octane (**18**). The synthesis of 4-pentyl-4″-hydroxy-*p*-terphenyl (**1g**) produced via the aryl–aryl coupling of 4-pentylphenyl boronic acid (**12**) and 4-bromo-4′-pentylbiphenyl (**19**) and subsequent deprotection of the intermediate 4″-benzyloxy-4-pentyl-*p*-terphenyl **20** by hydrogenolysis is shown in scheme 4. Scheme 5

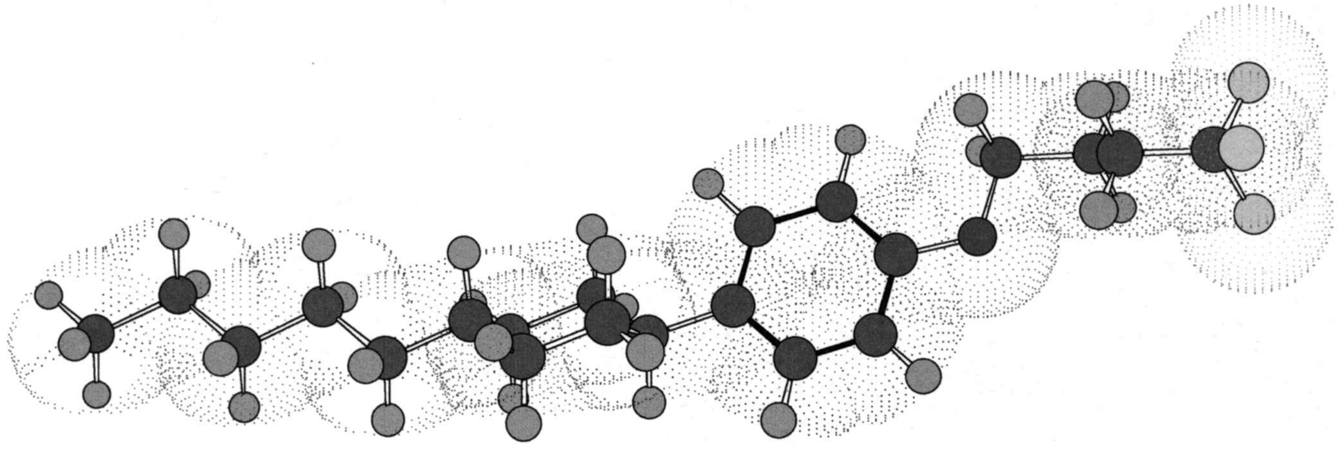
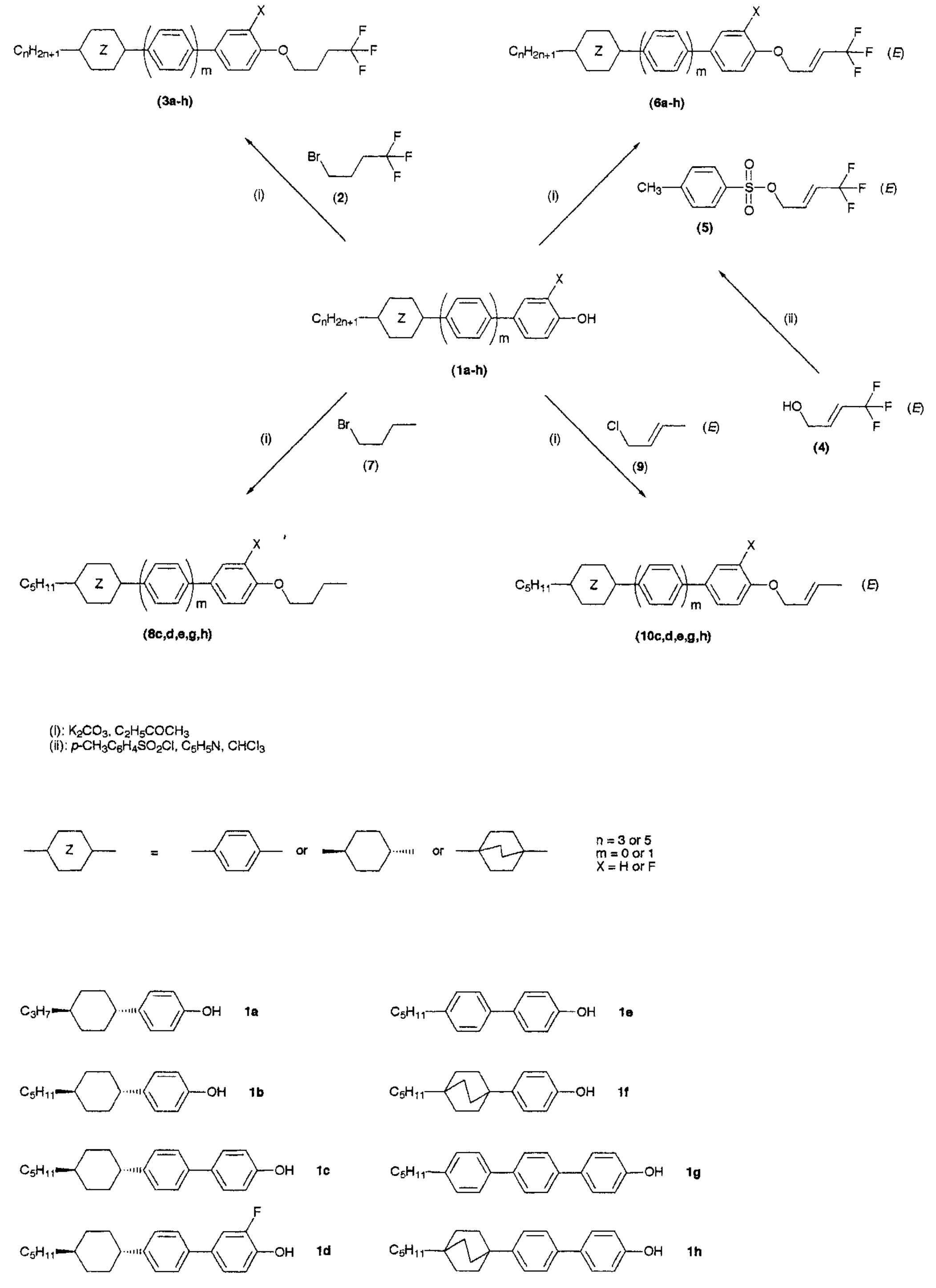


Figure 2. The energy-minimized structure of 1-(*trans*-4-pentylcyclohexyl)-4-(4,4,4-trifluorobutyloxy)benzene (**3b**) calculated using the Cerius^2 commercial package. Dipole moment = 2.903 D.



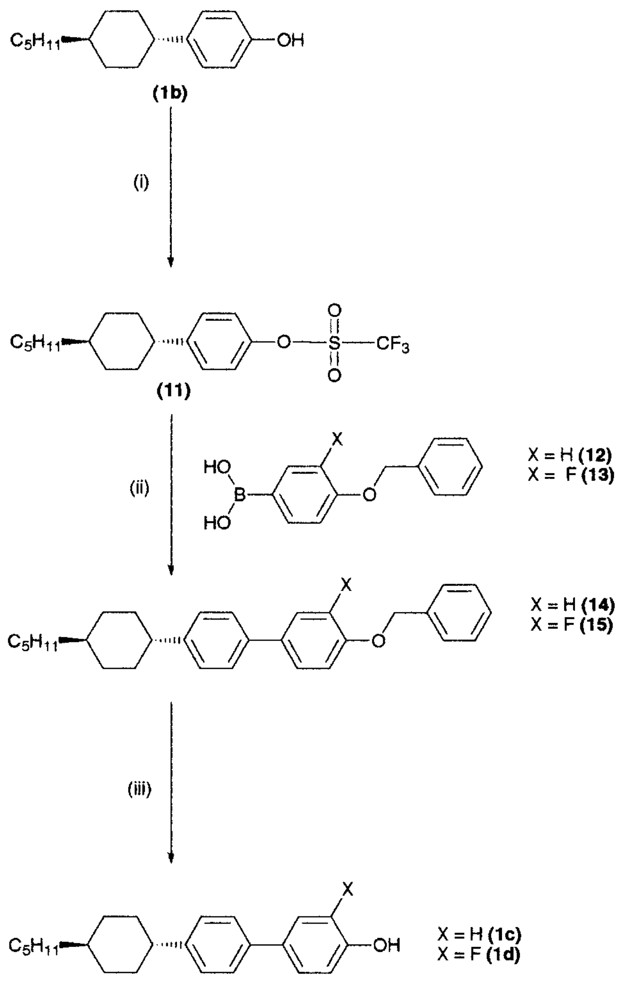
Scheme 1.

illustrates the synthesis of 1-(4-hydroxybiphenyl-4′-yl)-4-pentylbicyclo[2.2.2]octane (**1h**). A Friedel Crafts [43] reaction between 1-bromo-4-pentylbicyclo[2.2.2]octane (**16**) and 4-methoxybiphenyl (**21**) yielded 1-(4-methoxybiphenyl-4′yl)-4-pentylbicyclo[2.2.2]octane (**22**), which was demethylated [44] to give the desired phenol **1h**.

3. Phase characterization

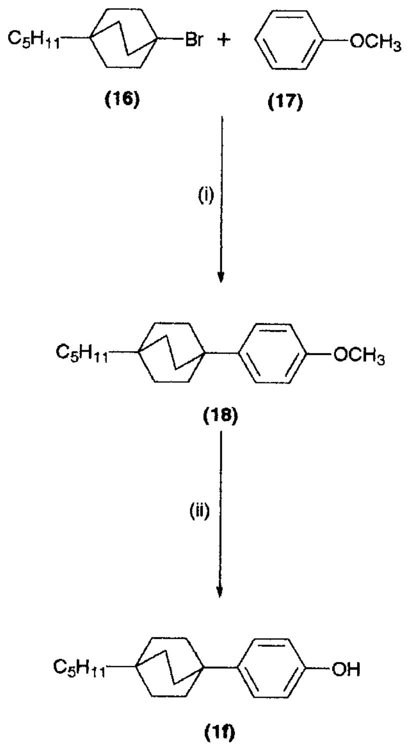
3.1. *Phase characterization by thermal optical microscopy*

The thermotropic mesophases observed for the compounds shown in tables 1–9 were investigated between crossed polarizers using optical microscopy.



(i): Trifluoromethanesulphonic acid anhydride, 2,6-lutidine, dichloromethane
(ii): $Pd(Ph_3)_4$, 2M Na_2CO_3, 1,2-dimethoxymethane
(iii): H_2, Pd/C, ethanol, ethyl acetate

Scheme 2.

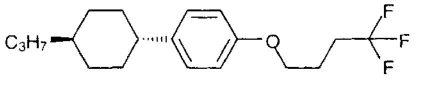
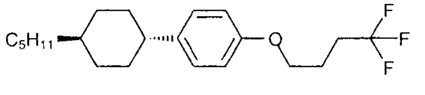


(i): $FeCl_3$, nitrobenzene
(ii): (a) BBr_3, CH_2Cl_2 (b) H^+ / H_2O

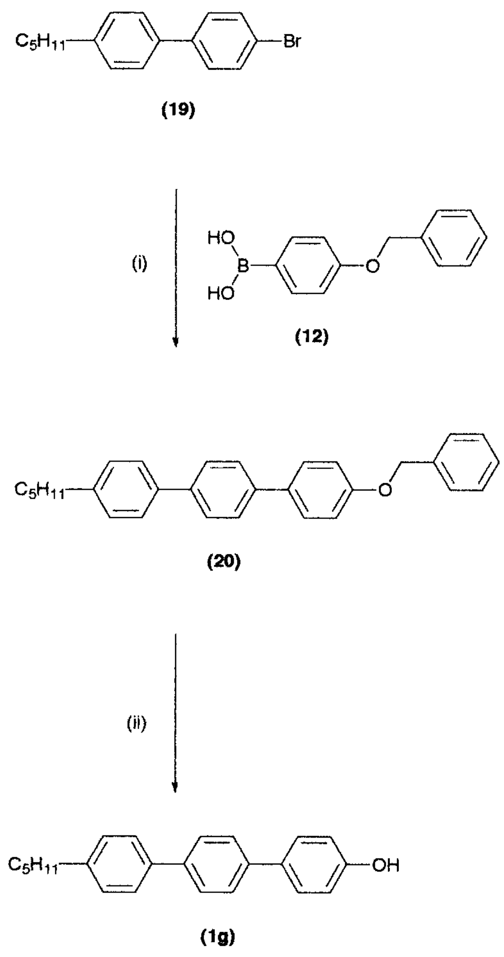
Scheme 3.

The phases observed included the nematic phase, the smectic A phase (SmA), the smectic B phase (SmB) and an unidentified smectic phase (SmX). Some compounds exhibited only the nematic phase, e.g. see table 3, and the nematic phase was often observed above the smectic phases when they occurred, e.g. see table 4. The fluid schlieren texture with two-point and four-point brushes was formed on heating by melting the birefringent crystals (where an enantiotropic nematic phase was formed), e.g. see table 3. Nematic droplets were always apparent on cooling the sample of nematic material from the isotropic liquid formed above the clearing point. These droplets then coalesced quickly to form

Table 1. Transition temperatures (°C) for 1-(*trans*-4-propylcyclohexyl)-4-(4,4,4-trifluorobutoxy)benzene (**3a**) and 1-(*trans*-4-pentylcyclohexyl)-4-(4,4,4-trifluorobutoxy)benzene (**3b**).

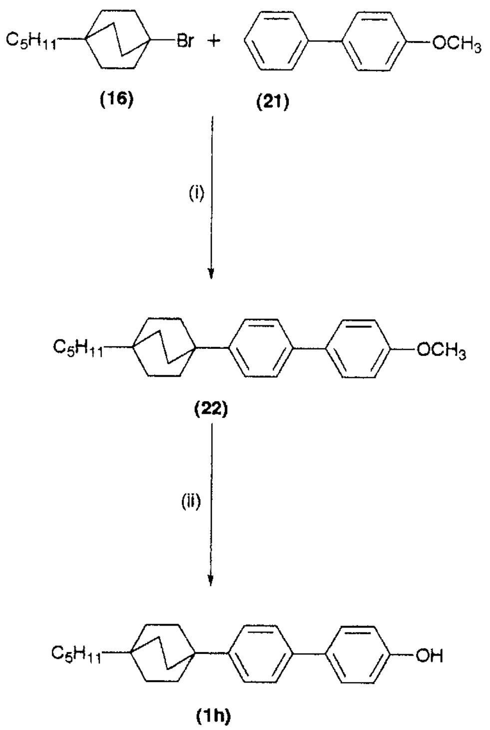
Compound	Structure	Cr		N		I
3a		●	50		—	●
3b		●	49	[●	21][a]	●

[a] [] Represents an extrapolated value.



(i): $Pd(Ph_3)_4$, 2M Na_2CO_3, 1,2-dimethoxymethane
(ii): H_2, Pd/C, ethanol, ethyl acetate

Scheme 4.

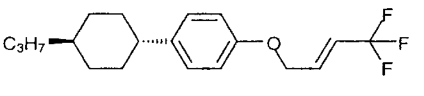
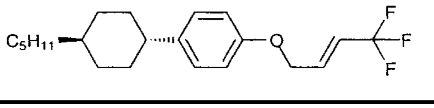


(i): $FeCl_3$, nitrobenzene
(ii): (a) BBr_3, CH_2Cl_2 (b) H^+ / H_2O

Scheme 5.

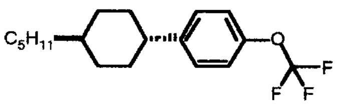
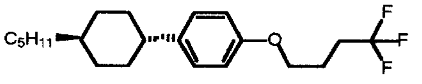
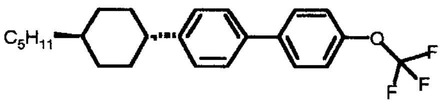
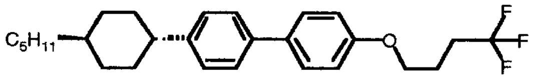
the typical schlieren texture with two-point and four-point brushes. Optically extinct homeotropic areas were also often observed. On heating the nematic phase, a shimmering yellow, very mobile texture with broad disclination lines was observed just below the clearing point. Where an enantiotropic nematic phase could not be observed an extrapolated value was determined in some cases, e.g. see tables 1–3. A linear clearing point relationship across the phase diagram for mixtures of different composition of the test material in the commercial nematic mixture E7 is assumed. Linear extrapolation of the transition temperature line to 100% of the test material gave the value of the virtual, extrapolated nematic clearing point. The extrapolation is made over

Table 2. Transition temperatures (°C) for 1-(*trans*-4-propylcyclohexyl)-4-[(*E*)-4,4,4-trifluorobut-2-enyloxy]benzene (**6a**) and for 1-(*trans*-4-pentylcyclohexyl)-4-[(*E*)-4,4,4-trifluorobut-2-enyloxy]benzene (**6b**).

Compound		Structure	Cr		N		I
6a	(*E*)		•	50		—	•
6b	(*E*)		•	41	[•	15][a]	•

[a] [] Represents an extrapolated value.

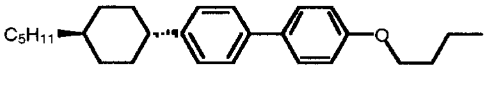
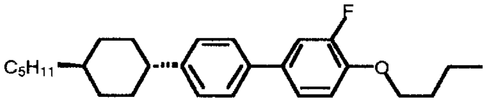
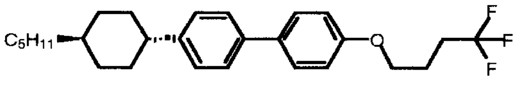
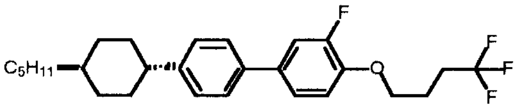
Table 3. Transition temperatures (°C) for 1-(*trans*-4-pentylcyclohexyl)-4-trifluoromethoxybenzene (**23**) [28], 1-(*trans*-4-pentylcyclohexyl)-4-(4,4,4-trifluorobutoxy)benzene (**3b**), 4-(*trans*-4-pentylcyclohexyl)-4′-trifluoromethoxybiphenyl (**24**) [28] and 4-(*trans*-4-pentylcyclohexyl)-4′-(4,4,4-trifluorobutyloxy)biphenyl (**3c**).

Compound	Structure	Cr		SmB		SmA		N		I
23		•	12		—		—	•	—[b]	•
3b		•	49		—		—	[•	21][a]	•
24		•	43	•	128		—	•	148	•
3c		•	72	•	177	•	211	[•	137][a]	•

[a] [] Represents an extrapolated value.

[b] No extrapolated N–I value can be found in the literature.

Table 4. Transition temperatures (°C) and some enthalpies (J g^{-1}) for 4-butyloxy-4′-(*trans*-4-pentylcyclohexyl)biphenyl (**8c**), 4-butoxy-3-fluoro-4′-(*trans*-4-pentylcyclohexyl)biphenyl (**8d**), 4-(*trans*-4-pentylcyclohexyl)-4′-(4,4,4-trifluorobutyloxy)biphenyl (**3c**) and 3-fluoro-4′-(*trans*-4-pentylcycohexyl)-4-(4,4,4-trifluorobutyloxy)biphenyl (**3d**).

Compound	Structure	Cr		SmB		SmA		N		I
8c		•	64 (71.4)	•	176 (9.2)	•	191 (7.4)	•	202 (2.1)	•
8d		•	54 (22.8)	•	114 (3.5)	•	166 (7.0)	•	171 (2.0)	•
3c		•	72 (37.6)	•	176 (96.2)	•	210 (17.6)	•	—	•
3d		•	76 (42.9)	•	119 (3.2)	•	167 (10.5)	•	—	•

as short a composition range as possible in order to be as certain as possible that no curvature of the line occurs.

The focal-conic (fan) texture was always formed on cooling from either the nematic phase or the isotropic liquid in those compounds which exhibited a smectic A phase; this was accompanied by optically extinct homeotropic areas, see tables 4–6, 8 and 9. As the sample was cooled further, the texture often formed more homeotropic areas. These were optically extinct when viewed between crossed polarizers, which indicates that the phase is optically uniaxial. This optical behaviour, i.e. simultaneous presence of both homeotropic and focal-conic textures, indicates that the mesophase observed is a calamitic smectic A phase. The elliptical and hyperbolic

Table 5. Transition temperatures (°C) and some enthalpies (J g^{-1}) for 4-[(*E*)-but-2-enyloxy]-4′-(*trans*-4-pentylcyclohexyl)biphenyl (**10c**), 4-[(*E*)-but-2-enyloxy]-3-fluoro-4′-(*trans*-4-pentylcyclohexyl)biphenyl (**10d**), 4-(*trans*-4-pentylcyclohexyl)-4′-[(*E*)-4,4,4-trifluorobut-2-enyloxy]biphenyl (**6c**) and 3-fluoro-4′-(*trans*-4-pentylcyclohexyl)-4-[(*E*)-4,4,4-trifluorobut-2-enyloxy]biphenyl (**6d**).

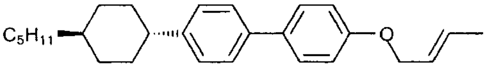
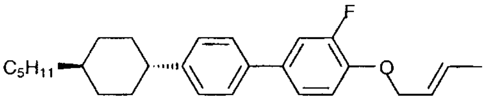
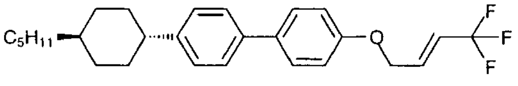
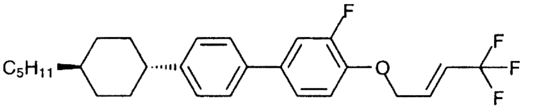
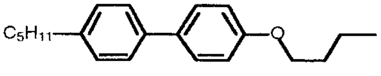
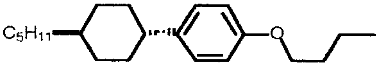
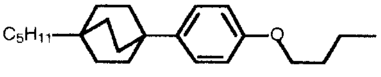
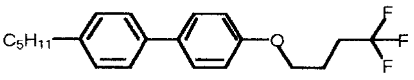
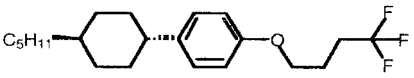
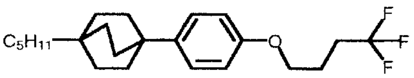
Compound		Structure	Cr		SmB		SmA		N		I
10c	(*E*)		•	81 (67.8)	•	160 (7.0)	•	190 (4.9)	•	208 (1.2)	•
10d	(*E*)		•	70		—	•	156	•	171	•
6c	(*E*)		•	91 (40.7)	•	167 (5.0)	•	209 (18.1)		—	•
6d	(*E*)		•	94 (44.6)	•	110 (2.7)	•	161 (10.2)		—	•

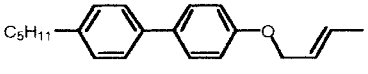
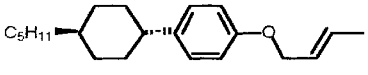
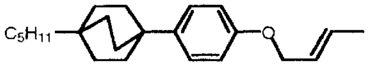
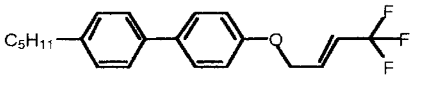
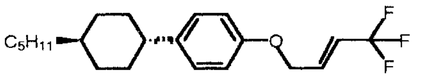
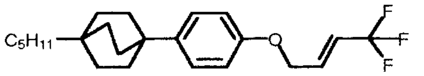
Table 6. Transition temperatures (°C) for 4-butyloxy-4′-pentylbiphenyl (**8e**) [48], 1-butyloxy-4-(*trans*-4-pentylcyclohexyl)benzene (**8b**) [49], 1-butyloxy-4-(4-pentybicylo[2.2.2]octyl)benzene (**8c**) [50], 4-pentyl-4′-(4,4,4-trifluorobutyloxy)biphenyl (**3e**), 1-(*trans*-4-pentylcyclohexyl)-4-(4,4,4-trifluorobutyloxy)benzene (**3b**) and 1-pentyl-4-[4-(4,4,4-trifluorobutyloxy)phenyl]bicyclo-[2.2.2]octane (**3f**).

Compound	Structure	Cr		SmB		SmA		N		I
8e		•	63	•	81	•	89	[•	86][a]	•
8b		•	34		—		—	•	46	•
8f		•	65		—		—	•	77	•
3e		•	63	•	99	•	103	[•	63][a]	•
3b		•	49		—		—	[•	21][a]	•
3f		•	65		—		—	(•	51)[b]	•

[a] [] Represents an extrapolated value.

[b] () Represents a monotropic transition temperature.

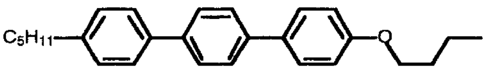
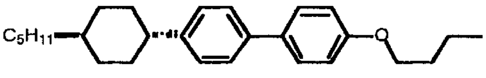
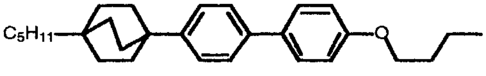
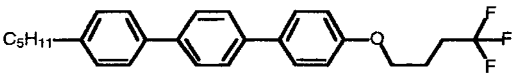
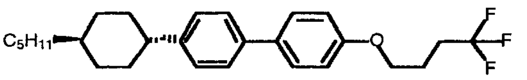
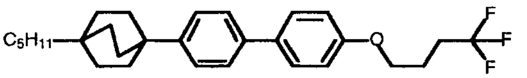
Table 7. Transition temperatures (°C) for 4-[(*E*)-but-2-enyloxy]-4′-pentylbiphenyl (**10e**), 1-[(*E*)-but-2-enyloxy]-4-(*trans*-4-pentylcyclohexyl)benzene (**10b**) [51], 1-(4-[(*E*)-but-2-enyloxy]phenyl)-4-pentylbicyclo[2.2.2]octane (**10f**) [48], 4-pentyl-4′-[(*E*)-4,4,4-trifluorobut-2-enyloxy]biphenyl (**6e**), 1-(*trans*-4-pentylcyclohexyl)-4-[(*E*)-4,4,4-trifluorobut-2-enyloxy]benzene (**6b**) and 1-pentyl-4-{4-[(*E*)-4,4,4-trifluorobut-2-enyloxy]phenyl}bicyclo[2.2.2]octane (**6f**).

Compound		Structure	Cr		SmX		SmB		N		I
10e	(*E*)		●	75		—	●	103	[●	94][a]	●
10b	(*E*)		●	38		—		—	●	67	●
10f	(*E*)		●	62		—		—	●	97	●
6e	(*E*)		●	66	●	116	●	121	[●	53][a]	●
6b	(*E*)		●	41		—		—	[●	15][a]	●
6f	(*E*)		●	68		—		—	(●	42)[b]	●

[a] [] Represents an extrapolated value.

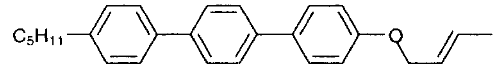
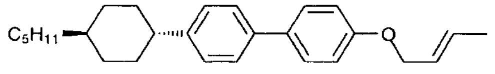
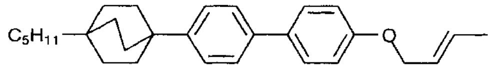
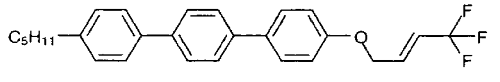
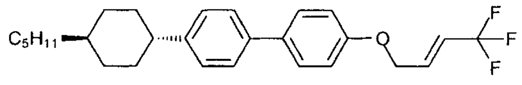
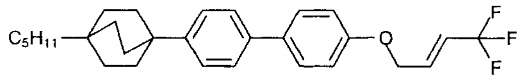
[b] () Represents a monotropic transition temperature.

Table 8. Transition temperatures (°C) for 4-butyloxy-4″-pentylterphenyl (**8g**), 4-butoxy-4′-(*trans*-4-pentylcyclohexyl)biphenyl (**8c**), 1-(4-butoxybiphenyl-4′-yl)-4-pentylbicyclo[2.2.2]octane (**8h**), 4-pentyl-4″-(4,4,4-trifluorobutoxy)terphenyl (**3g**), 4-(*trans*-4-pentylcyclohexyl)4′-(4,4,4-trifluorobutoxy)biphenyl (**3c**) and 1-pentyl-4-[4-(4,4,4-trifluorobutoxy)biphenyl-4′-yl]bicyclo[2.2.2]octane (**3h**).

Compound	Structure	Cr		SmB		SmA		N		I
8g		●	125	●	220	●	240		—	●
8c		●	64	●	176	●	191	●	202	●
8h		●	87	●	199	●	220	●	240	●
3g		●	203		—	●	267		—	●
3c		●	72	●	176	●	210	[●	137][a]	●
3h		●	80	●	205	●	247		—	●

[a] [] Represents an extrapolated value.

Table 9. Transition temperatures (°C) for 4-[(*E*)-but-2-enyloxy]-4″-pentylbiphenyl (**10g**), 4-[(*E*)-but-2-enyloxy]-4′-(*trans*-4-pentylcyclohexyl)benzene (**10c**) 1-{4-[(*E*)-but-2-enyloxy]biphenyl-4′-yl}-4-pentylbicyclo[2.2.2]octane (**10h**), 4-pentyl-4″-[(*E*)-4,4,4-trifluorobut-2-enyloxy]terphenyl (**6g**), 4-(*trans*-4-pentylcyclohexyl)-4′-[(*E*)-4,4,4-trifluorobut-2-enyloxy]biphenyl (**6c**) 1-pentyl-4-{4′-[(*E*)-4,4,4-trifluorobut-2-enyloxy]biphenyl-4-yl}bicyclo[2.2.2]octane (**6h**).

Compound	Cr	Structure	Cr		SmB		SmA		N		I
10g	(*E*)		•	70	•	207	•	220		—	•
10c	(*E*)		•	81	•	160	•	190	•	208	•
10h	(*E*)		•	116	•	170	•	211	•	236	•
6g	(*E*)		•	240	•	246	•	270		—	•
6c	(*E*)		•	91	•	167	•	209		—	•
6h	(*E*)		•	111		—	•	169	•	235	•

lines of optical discontinuity, characteristic of focal-conic defects, were also observed. This optical behaviour classifies the mesophase as smectic A with a layered structure, where the long axes of the molecules are on average orthogonal to the layer planes and the in-plane and out-of-plane positional ordering of the molecules is short range.

Several of the compounds exhibited dark transition bars across the backs of the focal-conics over a short temperature range on both heating and cooling. The homeotropic areas did not appear to change. This behaviour is typical of the transition from/to the smectic B phase. It was not possible to determine from the optical behaviour whether these were hexatic smectic B phases or crystal smectic B phases. In a few cases the smectic B phase was formed directly from the isotropic liquid, see table 7. A mosaic texture was observed after the initial formation of H-shaped patterns from the nematic phase. These coalesced quickly to form a multicoloured mosaic texture. The smectic X phase noted in table 7 could not be identified by optical microscopy; it is almost certainly a tilted crystal smectic phase.

3.2. *Phase characterization by differential scanning calorimetry*

Enthalpy values for the liquid crystal transitions for some compounds typical of those prepared are collated in tables 4 and 5 (shown in brackets). The enthalpy of transition between the nematic phase and the isotropic liquid is relatively small (1.2–2.1 J g^{-1}), as expected. In comparison the enthalpy of fusion (22.8–71.4 J g^{-1}) and the enthalpies of transition from the lamellar smectic A and smectic B phases to either the relatively disordered nematic phase (4.9–7.41 J g^{-1}) or the isotropic liquid (10.2–59.6 J g^{-1}) are large. The enthalpy of transition between the smectic A and the smectic B phase is usually moderate (2.7–17.1 J g^{-1}) as expected, as the change from one lamellar arrangement to another is not very great—from a hexagonal arrangement within the layers of the smectic B phase to a disordered lamellar structure in the smectic A phase. The higher values observed for some of these transitions may indicate that the smectic B phase is a crystal B phase in these cases. The values measured are of a similar magnitude to those found in conventional liquid crystal systems; these were determined twice on heating and cooling cycles on the same sample. The value found on the first heating cycle is quoted in the tables. However, the values obtained on separate samples of the same compounds were reproducible and very little thermal degradation was observed. A typical heating thermogram is shown in figure 3 for compound **3c**. The base line is relatively flat, and sharp transition peaks are observed. A low value for the SmB–SmA transition and a high value for the SmA transition to the isotropic liquid are as expected. The enthalpy of transition from the crystalline state to

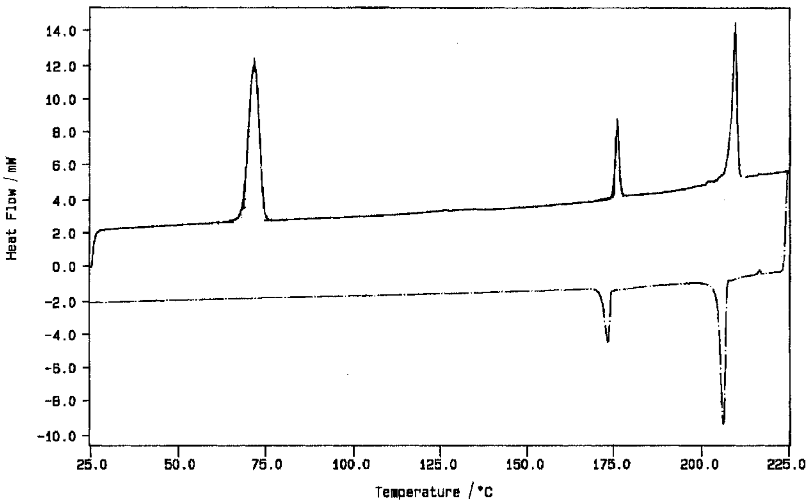


Figure 3. Differential scanning thermogram as a function of temperature for the first heating (full line) and cooling (dot-dash line) cycles for 4-(*trans*-4-pentylcyclohexyl)-4′-(4,4,4-trifluorobutyloxy)biphenyl (**3c**); scan rate 10°C min^{-1}.

the ordered SmB phase is also only moderate due to the relatively small difference in order between these two states. The values for the transition temperatures obtained by optical microscopy agree well (≈1–2°C) with those values determined by differential scanning calorimetry for this material and all of the other compounds prepared.

4. Mesomorphism

The thermal data listed in table 1 for the 4,4,4-trifluorobutyloxy substituted ethers **3a** and **3b** containing two 1,4-disubstituted rings and in table 2 for the corresponding two-ring (*E*)-4,4,4-trifluorobut-2-enyloxy substituted ethers **6a** and **6b** show that these compounds do not exhibit any observable liquid crystalline behaviour as single compounds. They do, however, give virtual extrapolated nematic–isotropic liquid transitions at ambient temperature as constituents of nematic mixtures. The lower clearing point for the compound **6b** containing a carbon–carbon double bond in the terminal chain compared with that of compound **3b** is surprising. The nematic clearing point of alkenyloxy compounds with a *trans*-carbon–carbon double bond in the 2-position are generally higher than those of the corresponding compounds without a double bond. However, this may be attributable to the inexactitude of the extrapolations and a degree of non-ideal behaviour of these compounds in nematic mixtures.

The liquid crystal transition temperatures for a related pair of two-ring and three-ring materials incorporating a trifluoromethoxy- or a 4,4,4-trifluorobutyloxy substituent in a terminal position are collated in table 3 for comparison. The clearing point of the 4,4,4-trifluorobutyloxy substituted compound **3b** appears to be higher than that of the trifluoromethoxy compound **23**, whose clearing point is apparently lower than 12°C. However, an extrapolated value for the nematic clearing point is not available from the literature. The corresponding three-ring material **3c** incorporating a 4,4,4-trifluorobutyloxy group also exhibits a higher clearing point (SmA–I) than that (N–I) of the analogous trifluoromethoxy substituted material **24**. However, compound **3c** exhibits a smectic B and a smectic A phase, whereas compound **24** exhibits a nematic phase. Indeed the extrapolated nematic clearing point of compound **3c** is just below that of the corresponding trifluoromethyl ether **24** [8]. The 4,4,4-trifluorobutyloxy substituted ether **3c** would be expected to exhibit a higher nematic clearing point than that of the trifluoromethoxy ether **24** due to its greater length-to-breadth ratio—compare figures 1 and 2. However, the lower clearing point may be due to a higher number of non-linear conformations for the 4,4,4-trifluorobutyloxy chain at these elevated temperatures. There are no other possible conformations for the trifluoromethyoxy group, since it can only rotate about the carbon–oxygen bond linking it with the phenyl ring. A similar explanation has been used to rationalize the relatively low clearing points of three-ring compounds incorporating the *trans*-1,4-disubstituted cyclohexane ring with respect to that of the corresponding materials incorporating either a 1,4-disubstituted phenyl ring or a 1,4-disubstituted bicyclo[2.2.2]octane ring in place of the cyclohexane ring. The cyclohexane ring has by far the highest degree of conformational flexibility, see also below. However, this possible explanation cannot be invoked to explain the lower nematic–isotropic transition temperature of the analogous (*E*)-4,4,4-trifluorobut-2-enyloxy ethers, e.g. **6b** in table 2. Therefore, the lower clearing point may be attributable to the isolated, non-conjugated nature of the three fluorine atoms in analogy with the known effect for non-conjugated heteroatoms, especially the oxygen atom, in terminal chains [45, 46].

The thermal data collated in table 4 for the three ring ethers **8c**, **8d**, **3c** and **3d** illustrate the influence of the presence of a fluorine atom as a terminal substituent and a lateral substituent. The presence of a fluorine atom in a lateral position in the core of the butyloxy ether **8c** leads to markedly lower transition temperatures than those of the corresponding non-laterally substituted analogue **8d**. However, the presence of three fluorine atoms as part of the 4,4,4-trifluorobutyloxy end group (**3c**) gives rise to higher transition temperatures than those of the corresponding compound **8c** with hydrogen in place of fluorine. The nematic phase has also been suppressed. This may well be due to intermolecular dipole–dipole interactions attributable to the fluorine atoms at the end of the terminal chain. Again the presence of a fluorine atom in a lateral position of the 4,4,4-trifluorobutyloxy compound **3d** gives rise to lower transition temperatures than those of the corresponding non-laterally substituted material **3c**. There appears to be a general tendency for fluorine in a terminal position to favour the formation of smectic phases, especially the smectic A phase. However, a fluorine atom in a lateral position reduces the transition temperatures and tends to suppress smectic phases, i.e. favours the formation of the nematic phase. The suppression of the nematic phase and the promotion of smectic behaviour may also be attributable to microphase separation of the three different constituent parts of this type of molecule, i.e. the alkyl chain, the central core and the fluorinated alkyl chain [47].

The transition temperatures of the analogous ethers **10c**, **10d**, **6c** and **6d** with or without fluorine substituents, but with a *trans*-carbon–carbon double bond in the terminal chain, are collected in table 5. The reference compound **10c** without a fluorine substituent exhibits a smectic B, a smectic A and a nematic phase at elevated temperatures. The presence of a fluorine atom in a lateral position in compound **10d** leads to lower transition temperatures (as expected) than those of compound **10c** with a hydrogen atom in place of the fluorine atom, but also to the suppression of the smectic B phase. The compounds **6c** and **6d** with fluorine substituents at the end of the terminal chain possess only smectic phases. The ether **6d** exhibits a lower clearing point than the non-terminally fluorinated analogue **10d**. These trends in mesomorphism are similar to those observed for the compounds listed in table 4.

The thermal data collated in table 6 allow a comparison of the effect of the presence of different 1,4-disubstituted rings with co-axial substituents in the cores of similar materials differing otherwise only in the presence or absence of three fluorine atoms at the end of the terminal chain. The extrapolated nematic clearing points of the 4,4,4-trifluorobutyloxy ethers **3e**, **3b** and **3f** are some 20°C lower than those of the corresponding butyloxy analogues **8e**, **8b** and **8f** [48–50]. This may well be the result of steric interactions due to the fluorine atoms or unfavourable intermolecular dipole–dipole interactions. The two cyclohexane derivatives **8b** and **3b** exhibit the lowest nematic clearing points. This is unusual, although extrapolation of some of the data from nematic mixtures may be giving erroneous results. However, the smectic phases observed for the 4,4,4-trifluorobutyloxy ethers **3e** occur at higher temperatures than those of the corresponding butyloxy ether **8e**. This appears to confirm a general trend that 4,4,4-trifluorobutyloxy ethers exhibit higher smectic transition temperatures, but a lower nematic clearing point, than those of their non-fluorinated analogues. The same general trends are evident from the transition temperatures collated in table 7 for the analogous series of (*E*)-4,4,4-trifluorobut-2-enyloxy ethers **6e**, **6b** and **6f** and the comparison compounds **10e**, **10b** [51] and **10f**. However, the data are again a mixture of observed transition temperatures and extrapolated values. In spite of this, the data seem to confirm the lower values for the cyclohexane derivatives.

A useful comparison of the clearing points collated in table 8 for the corresponding three-ring materials **8g**, **8c**, **8h**, **3g**, **3c** and **3h** is difficult to develop due to the absence of a nematic phase for the ethers **8g**, **3g** and **3h**. The solubility of some of these three-ring ethers is insufficient in E7 to allow meaningful extrapolated clearing points to be determined. The terphenyl ethers **8g** and **3g** exhibit higher clearing points than those of the corresponding ethers incorporating either an aliphatic bicyclo[2.2.2]octane ring, **8h** and **3h**, or an aliphatic cyclohexyl ring, **8c** and **3c**, in place of the aromatic phenyl ring. This is consistent with previous data which indicate that apolar biphenyls and terphenyls exhibit a higher tendency to form smectic phases with high absolute transition temperatures. However, as usual, the 4,4,4-trifluorobutyloxy ethers **3g**, **3c** and **3h** possess a greater tendency for smectic A phase formation than do the corresponding butyloxy compounds **8g**, **8c** and **8h**.

The thermal data listed in table 9 reveal that the (*E*)-4,4,4-trifluorobut-2-enyloxy ethers **10g**, **10c**, **10h**, **6g**, **6c** and **6h** possess very similar clearing points to those of the corresponding 4,4,4-trifluorobutyl ethers **8g**, **8c**, **8h**, **3g**, **3c** and **3h** shown in table 8. This is in spite of the added rigidity that the double bond confers upon such molecules. This is the reverse of normal behaviour [9]. However, the (*E*)-4,4,4-trifluorobut-2-enyloxy ether **6h** exhibits an enantiotropic nematic phase, whereas the corresponding but-2-enyloxy compound **10h**, while exhibiting a nematic phase with a similar clearing point, also has a smectic A phase.

5. Physical properties

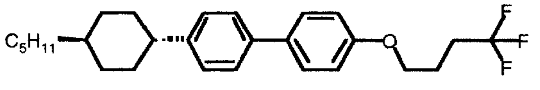
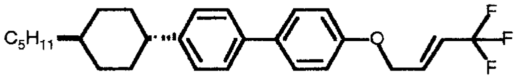
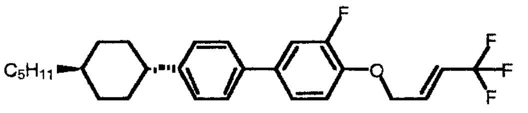
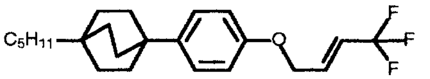
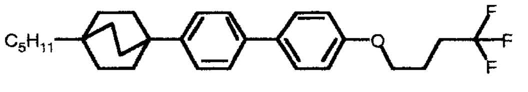
Several representative examples of the new compounds have been evaluated for potential use in nematic mixtures for TN-LCDs with active-matrix addressing. A fixed amount (10 wt %) of the compound to be evaluated was dissolved in a standard nematic mixture DOP017 and the physical properties of the resultant mixture were assessed and compared with those of DOP017. The physical data for the doped nematic mixtures containing representative examples of the new compounds **3c**, **6c**, **6d**, **6f** and **3h** are collated in table 10.

The nematic clearing points of all of the doped mixtures are 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 **3h** is especially high. The lowest value is seen for the mixture containing the two-ring bicyclo[2.2.2]octane **6f**. This order is to be expected, since the three-ring compounds **3c**, **6c**, **6d** and **3h** all possess high clearing points.

The birefringence (Δn) also increases for all of the mixtures, with the exception of the mixture containing compound **6f**. This is because the other compounds in the data set possess two aromatic rings in their core structures. The greater number of delocalized π-electrons will give rise to a higher value for Δn for the biphenyl derivatives. The order parameter of the mixtures containing the dopants **3c**, **6c**, **6d**, **6f** and **3h** will also be higher at room temperature due to the higher clearing point of the 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 compound **6f**. With the exception of this mixture, the dielectric anisotropy is increased on average by 4% for a 10% content of the compounds in the DOP017 mixture. The resultant dipole moment of the trifluoromethyl group should be parallel to the molecular long axis assuming the usual conformation of terminal chains in the nematic phase—see figure 2. This should lead to a high value of the dielectric anisotropy ($\Delta\varepsilon$) for these 4,4,4-trifluorobutyloxy compounds. This is indeed observed to be the case. The higher order parameter will also contribute to a higher observed value of the dielectric anisotropy at room temperature.

Table 10. The clearing point (°C), dielectric anisotropy, birefringence and switching times (s) measured for 10 wt % mixtures of 4-(*trans*-4-pentylcyclohexyl)-4′-(4,4,4-trifluorobutyloxy)biphenyl (**3c**), 4-(*trans*-4-pentylcyclohexyl)-4′-[(*E*)-4,4,4-trifluorobut-2-enyloxy]biphenyl (**6c**), 3-fluoro-4′-(*trans*-4-pentylcyclohexyl)-4-[(*E*)-4,4,4-trifluorobut-2-enyloxy]biphenyl (**6d**), 1-pentyl-4-{4-[(*E*)-4,4,4-trifluorobut-2-enyloxy]phenyl}bicyclo[2.2.2]octane (**6f**), 1-pentyl-4-[4-(4,4,4-trifluorobutoxy)biphenyl-4′-yl]-bicyclo[2.2.2]octane (**3h**), in the host nematic mixture DOP017.

Compound		Structure	$T_{\text{N-I}}$	Δn^{a}	$\Delta\varepsilon$	$t_{\text{on}}{}^{b}$	$t_{\text{off}}{}^{b}$	$t_{\text{on}}+t_{\text{off}}{}^{b}$
DOP017		Host nematic mixture	45.2	0.094	7.0	—	—	—
3c			64.5	0.095	7.1	2.8	22	24.8
6c	(*E*)		63.1	0.101	7.5	3.7	22.8	26.5
6d	(*E*)		62.2	0.095	7.3	3.6	25.2	28.8
6f	(*E*)		53.5	0.093	6.5	3.2	28	31.2
3h			67.8	0.100	7.3	3.4	40.2	43.6

[a] Measured at $T_{\text{N-I}}-T = 30$°C.
[b] Measured at 25°C.

The switching times of the mixtures are as expected, e.g. the inclusion of the most viscous compound **3h** leads to the longest switching time. The presence of the bicyclo[2.2.2]octane ring in compound **6f** also results in a long switching time due to its high viscosity. The next slowest mixture is that containing **6d**, which 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 **3c** and **6c**, which do not have any of the unfavourable attributes of the aforementioned compounds.

6. Experimental

6.1. *Characterization*

The structures of intermediates and final products were confirmed by proton (^{1}H) nuclear magnetic resonance (NMR) spectroscopy (JOEL JMN-GX270 FT nuclear resonance spectrometer), infrared (IR) spectroscopy (Perkin Elmer 783 infrared spectrophotometer) and mass spectrometry (MS) (Finnegan MAT 1020 automated GC/MS). Reaction progress and product purity were checked using a CHROMPACK CP 9001 capillary gas chromatograph fitted with a 10 m CP-SIL 5CB (0.12 µm, 0.25 mm) capillary column. Transition temperatures were determined using an Olympus BH-2 polarizing light microscope together with a Mettler FP52 heating stage and a Mettler FP5 temperature control unit. The analysis of transition temperatures and enthalpies was carried out using a Perkin-Elmer DSC7-PC differential scanning calorimeter.

6.2. *General synthetic procedures*

Tetrahydrofuran was dried by distillation over sodium wire in the presence of benzophenone. Dichloromethane was dried by distillation over phosphorus pentoxide. Chloroform was alumina-filtered to remove residual ethanol. Methanol and ethanol were distilled before use. All of these solvents were then stored over 4 Å molecular sieves; diethyl ether was dried and stored over sodium wire.

6.2.1. *1-(trans-4-Propylcyclohexyl)-4-(4,4,4-trifluorobutyloxy)benzene (3a)*

A solution of 1-bromo-4,4,4-trifluorobutane (0.48 g, 2.23 mmol), 4-(*trans*-4-pentylcyclohexyl)phenol (0.50 g, 2.03 mmol), potassium carbonate (1.12 g, 8.13 mmol) and butanone (40 cm^3) was heated at 80°C overnight. The cooled reaction mixture was filtered and evaporated down. The resultant product was purified by column chromatography on silica gel using a 95:5 (v/v) mixture of light petroleum (b.p. 40–60°C) and ethyl acetate as eluant, and recrystallization from ethanol to yield the desired product (0.35 g, 49%); m.p. 49°C, purity 99.6%. ^{1}H NMR (CDCl$_3$) δ: 0.92 (3H, t), 1.05 (2H, m), 1.32 (7H, m), 1.85 (4H, m), 2.03 (2H, m), 2.34 (3H, m), 3.98 (2H, t), 6.81 (2H, m), 7.11 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1610, 1510, 1450, 1250, 1130, 1020, 820. MS *m*/*z*: 328 (M$^+$), 243.

The analogous ethers **3b–h** were prepared in a similar fashion using 1-bromo-4,4,4-trifluorobutane and the appropriate phenols **1b–h** in a Williamson alkylation reaction.

6.2.2. *1-(trans-4-Pentylcyclohexyl)-4-(4,4,4-trifluorobutyloxy)benzene (3b)*

^{1}H NMR (CDCl$_3$) δ: 0.89 (3H, t), 1.06 (2H, m), 1.29 (11H, m), 1.86 (4H, m), 2.03 (2H, m), 2.33 (3H, m), 3.99 (2H, t), 6.80 (2H, m), 7.15 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 2915, 1610, 1510, 1450, 1240, 1120, 1020, 810. MS *m*/*z*: 356 (M$^+$), 243, 230, 133, 119, 107.

6.2.3. *4-(trans-4-Pentylcyclohexyl)-4′-(4,4,4-trifluorobutyloxy)biphenyl (3c)*

^{1}H NMR (CDCl$_3$) δ: 0.88 (3H, t), 1.05 (2H, m), 1.30 (9H, m), 1.46 (2H, m), 1.90 (4H, m), 2.08 (2H, m), 2.33 (2H, m), 2.49 (1H, tt), 4.05 (2H, t), 6.92 (2H, m), 7.25 (2H, m), 7.48 (4H, m). IR (KBr) ν_{max}/cm^{-1}: 2925, 1610, 1500, 1450, 1250, 1160, 1020, 820. MS *m*/*z*: 432 (M$^+$), 319.

6.2.4. *3-Fluoro-4′-(trans-4-pentylcyclohexyl)-4-(4,4,4-trifluorobutyloxy)biphenyl (3d)*

^{1}H NMR (CDCl$_3$) δ: 0.90 (3H, t), 1.07 (2H, m), 1.29 (10H, m), 1.48 (2H, m), 1.88 (4H, m), 2.08 (2H, m), 3.35 (2H, m), 4.12 (2H, t), 6.98 (1H, m),7.27 (4H, m), 7.43 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1610, 1500, 1450, 1250, 1140, 1020, 810. MS *m*/*z*: 450 (M$^+$), 337.

6.2.5. *4-Pentyl-4′-(4,4,4-trifluorobutyloxy)biphenyl (3e)*

^{1}H NMR (CDCl$_3$) δ: 0.90 (3H, t), 1.35 (4H,), 1.65 (2H, m), 2.05 (2H, m), 2.35 (2H, m), 2.65 (2H, t), 4.06 (2H, t), 6.95 (2H, m), 7.24 (2H, m), 7.48 (4H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1600, 1500, 1450, 1250, 1150, 1030, 800. MS *m*/*z*: 350 (M$^+$), 293, 183.

6.2.6. *1-Pentyl-4-[4-(4,4,4-trifluorobutyloxy)phenyl]-bicyclo[2.2.2]octane (3f)*

^{1}H NMR (CDCl$_3$) δ: 0.88 (3H, t), 1.22 (8H, m), 1.45 (6H, m), 1.75 (6H, m), 2.03 (2H, m), 2.30 (2H, m), 3.98 (2H, t), 6.81 (2H, m), 7.25 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 2930, 1600, 1510, 1460, 1250, 1130, 1030, 826. MS *m*/*z*: 382 (M$^+$), 255, 146, 91.

6.2.7. *4-Pentyl-4″-(4,4,4-trifluorobutyloxy)terphenyl (3g)*

^{1}H NMR (CDCl$_3$) δ: 0.91 (3H, t), 1.36 (4H, m), 1.66 (2H, m), 2.09 (2H, m), 2.35 (2H, m), 2.65 (2H, t), 4.07

(2H, t), 6.98 (2H, m), 7.25 (2H, m), 7.59 (8H, m). IR (KBr) ν_{max}/cm^{-1}: 2930, 1500, 1390, 1250, 1150, 1030, 910, 810. MS *m/z*: 426 (M$^+$), 369, 230.

6.2.8. *1-Pentyl-4-[4′-(4,4,4-trifluorobutyloxy)biphenyl-4-yl]bicyclo[2.2.2]octane (**3h**)*

^{1}H NMR (CDCl$_3$) δ: 0.89 (3H, t), 1.21 (8H, m), 1.51 (6H, m), 1.85 (6H, m), 2.05 (2H, m), 2.35 (2H, m), 4.05 (2H, t), 6.96 (2H, m), 7.38 (2H, m), 7.48 (4H, m). IR (KBr) ν_{max}/cm^{-1}: 2940, 1610, 1500, 1450, 1250, 1150, 1030, 820. MS *m/z*: 458 (M$^+$), 332, 91.

6.2.9. *(E)-4,4,4-Trifluorobut-2-enyl toluene-4-sulphonate (**5**)*

A solution of *p*-toluenesulphonyl chloride (11.37 g, 0.0595 mol) in pyridine (6.27 g, 0.0794 mol) and dichloromethane (40 cm^3) was added dropwise to a solution of (*E*)-4,4,4-trifluorobut-2-en-1-ol (**4**) (5.00 g, 0.379 mol) in dichloromethane (40 cm^3) at 0°C. The reaction mixture was maintained at 0°C overnight, allowed to reach room temperature, stirred for 1 h and then a mixture of ether (20 cm^3) and water (30 cm^3) was added. The organic layer was separated off and the aqueous layer extracted into dichloromethane. The combined organic layers were washed with water (1×100 cm^3), dried (MgSO$_4$) and the solvent removed to yield a liquid. This was purified by column chromatography on silica gel using a 95:5 (v/v) mixture of light petroleum (b.p. 40–60°C) and ethyl acetate as eluent to yield the desired product (5.36 g, 48%); purity 98.2%. ^{1}H NMR (CDCl$_3$) δ: 2.50 (3H, s), 4.65 (2H, m), 5.90 (1H, m, $J_t = 15.8$ Hz), 6.31 (1H, m), 7.43 (2H, m), 7.82 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 2930, 1600, 1320, 1270, 1130, 1050, 960, 810. MS *m/z*: 280 (M$^+$), 235, 91.

6.2.10. *1-(trans-4-Propylcyclohexyl)-4-[(E)-4,4,4-trifluorobut-2-enyloxy]benzene (**6a**)*

A solution of compound **5** (0.70 g, 2.51 mmol), 4-(*trans*-4-propylcyclohexyl)phenol (0.50 g, 2.29 mmol), potassium carbonate (1.12 g, 8.13 mmol) and butanone (40 cm^3) was heated at 80°C overnight. The reaction mixture was worked up and purified as described for the ether **3a** to yield the desired product (0.15 g, 21%). ^{1}H NMR (CDCl$_3$) δ: 0.90 (3H, t), 1.23 (9H, m), 1.85 (4H, m), 2.42 (1H, tt), 4.62 (2H, m), 6.05 (1H, m), 6.55 (1H, m), 6.84 (2H, m), 7.14 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1600, 1500, 1450, 1310, 1250, 1110, 955, 820. MS *m/z*: 326 (M$^+$), 241, 133, 119, 107.

The analogous ethers **6b–h** were prepared in a similar fashion using (*E*)-4,4,4-trifluorobut-2-enyl toluene-4-sulphonic acid ester (**5**) and the appropriate phenols **1b–h** in a Williamson alkylation reaction.

6.2.11. *1-(trans-4-Pentylcyclohexyl)-4-[(E)-4,4,4-trifluorobut-2-enyloxy]benzene (**6b**)*

^{1}H NMR (CDCl$_3$) δ: 0.90 (3H, t), 1.23 (13H, m), 1.85 (4H, m), 2.43 (1H, tt), 4.62 (2H, m), 6.05 (1H, m), 6.56 (1H, m), 6.85 (2H, m), 7.14 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1600, 1500, 1450, 1310, 1240, 1100, 960, 820. MS *m/z*: 354 (M$^+$), 241, 133, 119, 107.

6.2.12. *4-(trans-4-Pentylcyclohexyl)-4′-[(E)-4,4,4-trifluorobut-2-enyloxy]biphenyl (**6c**)*

^{1}H NMR (CDCl$_3$) δ: 0.85 (3H, t), 1.08 (2H, m), 1.37 (11H, m), 1.90 (4H, m), 2.50 (1H, tt), 4.72 (2H, m), 6.10 (1H, m), 6.60 (1H, m), 6.98 (2H, m), 7.28 (2H, m), 7.52 (4H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1600, 1500, 1450, 1310, 1240, 1100, 960, 810. MS *m/z*: 430 (M$^+$), 321, 169.

6.2.13. *3-Fluoro-4′-(trans-4-Pentylcyclohexyl)-4-[(E)-4,4,4-trifluorobut-2-enyloxy]biphenyl (**6d**)*

^{1}H NMR (CDCl$_3$) δ: 0.90 (3H, t), 1.05 (2H, m), 1.42 (11H, m), 1.95 (4H, m), 2.55 (1H, tt), 4.75 (2H, m), 6.12 (1H, m), 6.58 (1H, m), 6.97 (1H, m), 7.27 (4H, m), 7.44 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1600, 1500, 1450, 1310, 1270, 1100, 960, 810. MS *m/z*: 448 (M$^+$), 339.

6.2.14. *4-Pentyl-4′-[(E)-4,4,4-trifluorobut-2-enyloxy]-biphenyl (**6e**)*

^{1}H NMR (CDCl$_3$) δ: 0.91 (3H, t), 1.36 (4H, m), 1.65 (2H, m), 2.32 (2H, t), 4.69 (2H, m), 6.10 (1H, m), 6.57 (1H, m), 6.97 (2H, m), 7.24 (2H, m), 7.50 (4H, m). IR (KBr) ν_{max}/cm^{-1}: 2940, 1610, 1500, 1450, 1310, 1270, 1130, 960, 810. MS *m/z*: 348 (M$^+$), 239, 182.

6.2.15. *1-Pentyl-4-{4-[(E)-4,4,4-trifluorobut-2-enyloxy]phenyl}bicyclo[2.2.2]octane (**6f**)*

^{1}H NMR (CDCl$_3$) δ: 0.90 (3H, t), 1.23.40 (8H, m), 1.49 (6H, m), 1.78 (6H, m), 4.65 (2H, m), 6.06 (1H, m), 6.55 (1H, m), 6.83 (2H, m), 7.24 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 2940, 1610, 1510, 1460, 1310, 1270, 1110, 960, 820. MS *m/z*: 380 (M$^+$), 254, 145.

6.2.16. *4-Pentyl-4″-[(E)-4,4,4-trifluorobut-2-enyloxy]-terphenyl (**6g**)*

^{1}H NMR (CDCl$_3$) δ: 0.90 (3H, t), 1.37 (4H, m), 1.65 (2H, m), 2.65 (2H, t), 4.70 (2H, m), 6.15(1H, m), 6.60 (1H, m), 7.02 (2H, m), 7.27 (2H, m), 7.60 (8H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1220, 1110, 910, 760. MS *m/z*: 424 (M$^+$), 315, 258.

6.2.17. *1-Pentyl-4-{4-[(E)-4,4,4-trifluorobut-2-enyloxy]bipheny-4′-yl}bicylo[2.2.2]octane (**6h**)*

^{1}H NMR (CDCl$_3$) δ: 0.89 (3H, t), 1.24 (8H, m), 1.49 (6H, m), 1.83 (6H, m), 4.68 (2H, m), 6.09 (1H, m), 6.59 (1H, m), 6.96 (2H, m), 7.37 (2H, m), 7.49 (4H, m).

IR (KBr) ν_{max}/cm^{-1}: 2920, 1600, 1500, 1450, 1310, 1250, 1130, 960, 810. MS *m*/*z*: 456 (M^+), 347, 221.

6.2.18. *4-(trans-4-Pentylcyclohexyl)phenyl 1,1,1-trifluoromethanesulphonate (11)*

A solution of trifluoromethanesulphonic acid anhydride (27.51 g, 0.0967 mol) in dichloromethane (125 cm^3) was added dropwise to a stirred solution of 4-(*trans*-4-pentylcyclohexyl)phenol (**1b**) (20.00 g, 0.0813 mol), 2,6-lutidine (10.44 g, 0.0976 mol) and dichloromethane (125 cm^3) at 0°C. The reaction mixture was maintained at 0°C overnight and added to water (500 cm^3); the organic layer was separated off and the aqueous layer shaken with dichloromethane (3×50 cm^3). The combined organic layers were washed with dilute sodium carbonate solution (2×100 cm^3), dried ($MgSO_4$) and filtered. The solvent was removed and the crude product purified by column chromatography (silica gel), using 95 : 5 (v/v) mixture of light petroleum (b.p. 40–60°C) and ethyl acetate as eluent (yield 28.65 g, 87%); purity 99.5%. ^{1}H NMR ($CDCl_3$) δ: 0.88 (3H, m), 1.06 (2H, m) 1.32 (11H, m), 1.88 (4H, m), 2.49 (1H, tt), 7.16 (2H, m), 7.27 (2H, m) IR (KBr) ν_{max}/cm^{-1}2920, 1500, 1430, 1250, 1200, 1090, 1000, 840. MS *m*/*z*: 378 (M^+), 252, 69.

6.2.19. *4-Benzyloxy-4′-(trans-4-pentylcyclohexyl)-biphenyl (14)*

A mixture of compound **11** (15.00 g, 39.68 mmol), 4-benzyloxyphenylboronic acid (**12**) (9.05 g, 39.68 mmol), tetrakis(triphenylphosphine)palladium(0) (0.50 g), 2M sodium carbonate solution (140 cm^3) and 1,2-dimethoxyethane (200 cm^3) was heated under reflux overnight. The cooled reaction mixture was added to water (200 cm^3), the organic layer separated off and the aqueous layer shaken with dichloromethane (3×50 cm^3). The combined organic layers were washed with dilute sodium carbonate solution (2×100 cm^3), dried ($MgSO_4$), filtered and the solvent removed. The resultant crude product was recrystallized from ethanol (yield 9.40 g, 58%). Cr 115°C SmB 194°C SmA 206°C N 218°C I, purity 99.3%. ^{1}H NMR ($CDCl_3$) δ: 0.89 (3H, t), 1.05 (2H, m), 1.28 (9H, m), 1.50 (2H, m), 1.90 (4H, m), 2.50(1H, tt), 5.10 (2H, s), 7.03 (2H, m), 7.25 (2H, m), 7.38 (3H, m), 7.48 (6H, m). IR (KBr) ν_{max}/cm^{-1}: 2940, 1590, 1500, 1450, 1250, 1050, 1000, 820, 740. MS *m*/*z*: 412 (M^+), 321, 91.

6.2.20. *4-Hydroxy-4′-(trans-4-pentylcyclohexyl)-biphenyl (1c)*

10% Palladium-on-charcoal (0.5 g) was added to a solution of 4-benzyloxy-4′-(*trans*-4-pentylcyclohexyl)-biphenyl (**14**) (9.17 g, 22.2 mmol) in terahydrofuran (250 cm^3) and ethanol (30 cm^3). The mixture was stirred under an atmosphere of hydrogen. When GC analysis indicated that the reaction was complete, the catalyst was filtered off, the solvent removed and the crude solid product recrystallized from ethanol (yield 5.45 g, 76%). Cr 209°C I, purity 100.0%. ^{1}H NMR ($CDCl_3$) δ: 0.90 (3H, t), 1.05 (2H, m), 1.28 (9H, m), 1.45 (2H, m), 1.90 (4H, m), 2.50 (1H, tt), 5.10 (1H, s), 6.87 (2H, m), 7.25 (2H, m), 7.45 (4H, m). IR (KBr) ν_{max}/cm^{-1}: 3390, 2920, 1600, 1500, 1450, 1250, 820. MS *m*/*z*: 322 (M^+), 209, 196, 183.

6.2.21. *4-Butyloxy-4′-(trans-4-pentylcyclohexyl)-biphenyl (8c)*

A solution of butyl bromide (**7**) (0.48 g, 2.23 mmol), phenol **1c** (0.25 g, 0.78 mmol), potassium carbonate (0.43 g, 3.10 mmol) and butanone (40 cm^3) was heated at 80°C overnight. The reaction mixture was worked up and purified as described for the ether **3a** to yield the desired product (0.10 g, 34%). ^{1}H NMR ($CDCl_3$) δ: 0.90 (3H, t), 1.02 (3H, t), 1.07 (2H, m), 1.32 (9H, m), 1.50 (4H, m), 1.77 (2H, m), 1.90 (4H, m), 2.50 (1H, tt), 3.98 (2H, t), 6.95 (2H, m), 7.25 (2H, m), 7.48 (4H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1600, 1500, 1450, 1250, 1180, 1030, 820. MS *m*/*z*: 378 (M^+), 138.

The analogous ethers **8d**, **8e**, **8g** and **8h** were prepared in a similar fashion using butyl bromide (**7**) and the appropriate phenols **1d**, **1e**, **1g** and **1h** in a Williamson alkylation reaction.

6.2.22. *4-Butyloxy-3-fluoro-4′-(trans-4-pentylcyclohexyl)-biphenyl (8d)*

^{1}H NMR ($CDCl_3$) δ: 0.88 (3H, t), 0.98 (3H, t), 1.07 (2H, m), 1.28 (10H, m), 1.48 (4H, m), 1.85 (5H, m), 2.50 (1H, tt), 4.06 (2H, t), 7.00 (1H, m), 7.27 (4H, m), 7.45 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1620, 1500, 1450, 1250, 1130, 1000, 810. MS *m*/*z*: 396 (M^+), 340, 138.

6.2.23. *4-Butyloxy-4′-pentylbiphenyl (8e)*

^{1}H NMR ($CDCl_3$) δ: 0.89 (3H, t), 0.97 (3H, t), 1.35 (2H, m), 1.58 (6H, m), 1.85 (2H, m), 2.62 (2H, t), 4.02 (2H, t), 6.94 (2H, m), 7.24 (2H, m), 7.48 (4H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1600, 1480, 1440, 1240, 1100, 1000, 810. MS *m*/*z*: 296 (M^+), 240, 183.

6.2.24. *4-Butyloxy-4″-pentylterphenyl (8g)*

^{1}H NMR ($CDCl_3$) δ: 0.91 (3H, t), 0.99 (3H, t), 1.37 (4H, m), 1.51 (2H, m), 1.67 (2H, m), 1.80 (2H, m), 2.65 (2H, t), 4.01 (2H, t), 6.98 (2H, m), 7.27 (2H, m), 7.58 (8H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1650, 1570, 1460, 1220, 1100, 1080, 760. MS *m*/*z*: 372 (M^+), 315, 259, 230.

6.2.25. *1-(4-Butyloxybiphenyl-4′-yl)-4-pentylbicyclo-[2.2.2]octane (8h)*

^{1}H NMR ($CDCl_3$) δ: 0.89 (3H, t), 0.98 (3H, t), 1.24 (8H, m), 1.49 (8H, m), 1.80 (8H, m), 3.99 (2H, t), 6.94

(2H, m), 7.36 (2H, m), 7.48 (4H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1600, 1500, 1450, 1250, 1040, 810. MS *m/z*: 404 (M^+), 278.

6.2.26. *4-[(E)-But-2-enyloxy]-4′-(trans-4-pentylcyclohexyl)biphenyl (**10c**)*

A solution of (*E*)-but-2-enyl chloride (**9**) (0.08 g, 0.88 mmol), phenol **1c** (0.25 g, 0.78 mmol), potassium carbonate (0.43 g, 3.12 mmol) and butanone (40 cm^3) was heated at 80°C overnight. The reaction mixture was worked up and purified as described for the ether **3a** to yield the desired product (0.11 g, 38%). ^{1}H NMR ($CDCl_3$) δ: 0.89 (3H, t), 1.07 (2H, m), 1.27 (9H, m), 1.48 (2H, m), 1.75 (3H, m), 1.89 (4H, m), 2.48 (1H, tt), 4.49 (2H, m), 5.75 (1H, m $J_t = 15.4$ Hz), 5.87 (1H, m), 6.96 (2H, m), 7.24 (2H, m), 7.48 (4H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1600, 1500, 1450, 1250, 1040, 960, 810. MS *m/z*: 376 (M^+), 322, 209.

The analogous ethers **10d**, **10e**, **10g** and **10h** were prepared in a similar fashion using (*E*)-but-2-enyl chloride (**9**) and the appropriate phenols **1d**, **1e**, **1g** and **1h** in a Williamson alkylation reaction.

6.2.27. *4-[(E)-But-2-enyloxy]-3-fluoro-4′-(trans-4-pentylcyclohexyl)biphenyl (**10d**)*

^{1}H NMR ($CDCl_3$) δ: 0.90 (3H, t), 1.09 (2H, m), 1.30 (9H, m), 1.46 (4H, m), 1.83 (5H, m), 2.49 (1H, tt), 4.72 (2H, m), 6.12 (1H, m), 6.64 (1H, m), 7.00 (1H, m), 7.28 (4H, m), 7.47 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 2930, 1610, 1500, 1450, 1310, 1250, 1100, 960, 820. MS *m/z*: 394 (M^+), 340, 138.

6.2.28. *4-[(E)-But-2-enyloxy]-4′-pentylbiphenyl (**10e**)*

^{1}H NMR ($CDCl_3$) δ: 0.90 (3H, t), 1.35 (4H, m), 1.66 (2H, q), 1.75 (3H, d), 2.62 (2H, t), 4.48 (2H, d), 5.67–5.98 (2H, m), 6.96 (2H, d), 7.24 (2H, t), 7.47 (4H, t). IR (KBr) ν_{max}/cm^{-1}: 2920, 2860, 1600, 1500, 1450, 1380, 1250, 1150, 1000, 970, 810. MS *m/z*: 294 (M^+), 240, 183.

6.2.29. *4-[(E)-But-2-enyloxy]-4″-pentylterphenyl (**10g**)*

^{1}H NMR ($CDCl_3$) δ: 0.91 (3H, t), 1.36 (6H, m), 1.68 (2H, m), 1.78 (3H, m), 4.65 (2H, t), 5.78 (1H, m), 5.90 (1H, m), 7.00 (2H, m), 7.26 (2H, m), 7.58 (8H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1600, 1500, 1450, 1250, 1150, 1000, 970, 820. MS *m/z*: 370 (M^+), 315, 259.

6.2.30. *1-{4-[(E)-But-2-enyloxy]biphenyl-4′-yl}-4-pentylbicyclo[2.2.2]octane (**10h**)*

^{1}H NMR ($CDCl_3$) δ: 0.89 (3H, t), 1.24 (8H, m), 1.50 (7H, m), 1.80 (8H, m), 4.49 (2H, m), 5.76 (1H, m), 5.87 (1H, m), 6.95 (2H, m), 7.36 (2H, m), 7.48 (4H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1700, 1600, 1500, 1250, 1090, 960, 810. MS *m/z*: 402 (M^+), 347, 221.

6.2.31. *4-Benzyloxy-3-fluoro-4′-(trans-4-pentylcyclohexyl)biphenyl (**15**)*

A mixture of 1,1,1-trifluoromethanesulphonic acid, compound **11** (11.82 g, 31.26 mmol), 4-benzyloxy-3-fluorophenylboronic acid (**13**) (7.69 g, 31.26 mmol), tetrakis(triphenylphosphine)palladium(0) (0.50 g), 2M sodium carbonate solution (140 cm^3) and 1,2-dimethoxyethane (200 cm^3) was heated under reflux overnight. The reaction mixture was worked up and purified as described for compound **14** to yield the desired product (8.23 g, 61%). Cr 73°C SmB 130°C SmA 168°C N 187°C I, purity 99.2%. ^{1}H NMR ($CDCl_3$) δ: 0.91 (3H, t), 1.05 (2H, m), 1.28 (9H, m), 1.50 (2H, m), 1.90 (4H, m), 2.50(1H, tt), 5.18 (2H, s), 7.05 (1H, m), 7.38 (11H, m). IR (KBr) ν_{max}/cm^{-1}: 2940, 1500, 1450, 1250, 1090, 1050, 810, 740. MS *m/z*: 430 (M^+), 339, 91.

6.2.32. *3-Fluoro-4-hydroxy-4′-(trans-4-pentylcyclohexyl)biphenyl (**1d**)*

10% Palladium-on-charcoal (0.5 g) was added to a solution of the ether **15** (8.00 g, 18.60 mmol) in terahydrofuran (250 cm^3) and ethanol (30 cm^3). The reaction mixture was worked up and purified as described for compound **1c** to yield the desired product (6.12 g, 97%). Cr 132°C I, purity 99.4%. ^{1}H NMR ($CDCl_3$) δ: 0.90 (3H, t), 1.07 (2H, m), 1.30 (9H, m), 1.48 (2H, m), 1.90 (4H, m), 2.48 (1H, tt), 5.29 (1H, s), 7.03 (1H, m), 7.26 (4H, m), 7.43 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 3400, 2940, 1600, 1500, 1450, 1250, 820. MS *m/z*: 340 (M^+), 240, 227, 214, 200.

6.2.33. *1-(4-Methoxyphenyl)-4-pentylbicyclo[2.2.2]-octane (**18**)*

A solution of 1-bromo-4-pentylbicyclo[2.2.2]octane (**16**) (10.00 g, 0.038 mol), methoxybenzene (**17**) (168 g, 1.55 mol), anhydrous iron chloride (2.24 g, 0.0140 mol) and nitrobenzene (80 cm^3) was heated at an oil bath temperature of 80°C overnight. A small amount of 15% hydrochloric acid was added to the cooled mixture, which was then stirred for 20 min. The organic layer was separated off and steam distilled to yield a black solid residue (12.10 g); this was taken up in dichloromethane and the resultant solution dried ($MgSO_4$), filtered and evaporated down. The crude product was purified by column chromatography on silica gel using a 95:5 (v/v) mixture of light petroleum (b.p. 40–60°C) and ethyl acetate as eluent followed by recrystallization from ethanol to yield the desired product (3.60 g, 33%). Cr 64°C N 70°C I (Lit Cr 64°C N 70°C I [43]), purity 99.8%. ^{1}H NMR ($CDCl_3$) δ: 0.89 (3H, t), 1.21 (8H, m), 1.47 (6H, m), 1.77 (6H, m), 3.78 (3H, s), 6.32 (2H, m), 7.24 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1600, 1510, 1450, 1245, 1040, 810. MS *m/z*: 286 (M^+), 121.

6.2.34. *4-(4-Pentylbicyclo[2.2.2]oct-1-y l)phenol (**1f**)*

A 1.0M solution of boron tribromide (0.0186 mol, 19 cm^3) in dichloromethane (30 cm^3) was added dropwise to a solution of the ether **19** (3.60 g, 0.124 mol) in dichloromethane (20 cm^3) at -20°C. The reaction mixture was stirred overnight at room temperature. The solution was then poured onto an ice/water mixture (200 g). The organic layer was separated off and the aqueous layer extracted with dichloromethane ($3 \times 50\,cm^3$). The combined organic layers were washed with water (200 cm^3), dilute sodium carbonate (100 cm^3), water (200 cm^3), dried ($MgSO_4$), filtered and then evaporated down. The crude product was purified by recrystallization from ethanol (yield 2.78 g, 82%). Cr 124°C I, purity 94.7%. ^{1}H NMR ($CDCl_3$) δ: 0.90 (3H, t), 1.24 (8H, m), 1.46 (6H, m), 1.76 (6H, m), 4.65 (1H, s), 6.75 (2H, m), 7.18 (2H, m). IR (KBr) ν_{max}/cm^{-1}: 3400, 2920, 1600, 1510, 1450, 1250, 1180, 820. MS *m/z*: 272 (M^+), 146, 91.

6.2.35. *4''-Benzyloxy-4-pentylterphenyl (**20**)*

A mixture of 4-bromo-4'-pentylbiphenyl (**19**) (2.41 g, 7.11 mmol), 4-pentylphenylboronic acid (**12**) (1.36 g, 7.11 mmol), tetrakis(triphenylphosphine)palladium(0) (0.50 g), 2M sodium carbonate solution (140 cm^3) and 1,2-dimethoxyethane (200 cm^3) was heated under reflux overnight. The reaction mixture was worked up and purified as described above for compound **14** to yield the desired product (0.63 g, 22%), purity 99.2%. ^{1}H NMR ($CDCl_3$) δ: 0.92 (3H, t), 1.36 (4H, m), 1.65 (2H, m), 2.65 (2H, m), 5.15 (2H, s), 7.07 (2H, m), 7.27 (2H, m), 7.48 (13H, m). IR (KBr) ν_{max}/cm^{-1}: 2930, 1650, 1500, 1445, 1250, 1030, 810, 770. MS *m/z*: 406 (M^+), 315, 91.

6.2.36. *4-Hydroxy-4''-pentylterphenyl (**1g**)*

10% Palladium-on-charcoal (0.5 g) was added to compound **20** (2.42 g, 5.96 mmol) dissolved in terahydrofuran (250 cm^3) and ethanol (30 cm^3). The reaction mixture was worked up and purified as described for the phenol **1c** to yield the desired product (1.04 g, 55%). Cr 255°C I, purity 99.4%. ^{1}H NMR ($CDCl_3$) δ: 0.91 (3H, t), 1.35 (4H, m), 1.64 (2H, m), 2.59 (2H, m), 6.93 (2H, m), 7.26 (2H, m), 7.48 (2H, m), 7.55 (2H, m), 7.61 (4H, m), 8.9 (1H, s). IR (KBr) ν_{max}/cm^{-1}: 3440, 2258, 1670, 1000, 820. MS *m/z*: 316 (M^+), 259, 129, 57.

6.2.37. *1-(4-Methoxybiphenyl)-4-pentylbicyclo-[2.2.2]octane (**22**)*

1-Bromo-4-pentyl bicyclo[2.2.2]octane (**16**) was added to a mixture of aluminium trichloride (2.38 g, 17.83 mmol), 4-methoxybiphenyl (**21**) (1.27 g, 7.60 mmol) and dichloromethane (10 cm^3) at -15°C. The reaction mixture was stirred for 1.5 h and then poured onto ice, acidified with 35% hydrochloric acid, and extracted into diethyl ether ($2 \times 100\,cm^3$). The combined organic layers were washed with water ($2 \times 100\,cm^3$), dried ($MgSO_4$), filtered and the solvent removed. The crude product was purified by column chromatography on silica gel using an 80:20 (v/v) mixture of light petroleum (b.p. 40–60°C) and ethyl acetate as eluent and recrystallization from ethanol, to yield the desired product (1.04 g, 41%). Cr 118°C N 236°C I, purity 95.8%. ^{1}H NMR ($CDCl_3$) δ: 0.89 (3H, t), 1.21 (8H, m), 1.49 (6H, m), 1.85 (6H, m), 3.84 (3H, s), 6.96 (2H, m), 7.37 (2H, m), 7.49 (4H, m). IR (KBr) ν_{max}/cm^{-1}: 2920, 1600, 1500, 1445, 1250, 1180, 1040, 820. MS *m/z*: 362 (M^+), 236, 68.

6.2.38. *1-(4-Hydroxybiphenyl-4'-yl)-4-pentylbicyclo-[2.2.2]octane (**1h**)*

A 1.0M solution of boron tribromide (3.57 mmol, 3.6 cm^3) in dichloromethane (30 cm^3) was added dropwise to a solution of the ether **22** (0.87 g, 2.38 mmol) in dichloromethane (20 cm^3) at -20°C. The reaction mixture was stirred overnight at room temperature and then worked up and purified as described for compound **1f** to yield the desired phenol (0.3 g, 82%), purity 95.5%. ^{1}H NMR ($CDCl_3$) δ: 0.90 (3H, t), 1.22 (8H, m), 1.46 (6H, m), 1.76 (6H, m), 4.62 (1H, s), 6.88 (2H, m), 7.36 (2H, m), 7.46 (4H, m). IR(KBr) ν_{max}/cm^{-1}: 3400, 2920, 1600, 1500, 1450, 1250, 810. MS *m/z*: 348 (M^+), 221, 182.

7. Conclusions

The presence of three fluorine atoms on the same carbon atom in a terminal position in the end chain gives rise to lower nematic clearing points than those of the corresponding materials with hydrogen atoms in place of the fluorine atoms. This may be due to unfavourable intermolecular dipole–dipole effects attributable to the isolated, non-conjugated nature of the three fluorine atoms at the end of the terminal chain. The presence of three fluorine atoms in a terminal position in the chain generally tends to induce smectic phases rather than the nematic phase. The presence of a fluorine atom in a lateral position *ortho*- to the terminal chain gives rise to a lower nematic clearing point than that of the corresponding material with a hydrogen atom in place of the fluorine atom, due to steric effects. Smectic phases are also suppressed for the same reasons. The compounds synthesized appear to be potentially useful components of positive dielectric anisotropy for use in nematic mixtures for TN-LCDs. The synthesis of similar compounds without an oxygen atom between the aromatic core and the terminal chain incorporating the three fluorine atoms should give rise to lower melting points, a lower viscosity and perhaps a higher dielectric anisotropy.

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