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# Terminal end-group efficiency for the nematic phase using model bicyclo[2.2.2]octanes

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# Terminal end-group efficiency for the nematic phase using model bicyclo[2.2.2]octanes

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The synthesis is reported of new liquid crystals incorporating the 1,4-disubstituted bicyclo[2.2.2]octane ring and a series of substituents in a terminal position on the molecular core. The nature of the terminal substituent is varied from apolar with a small dipole moment to polar with a strong dipole moment. The angle of the dipole moment with respect to the molecular axis is also varied. An updated order of terminal group efficiency for substituents in a terminal position for the nematic phase is provided. The bicyclo[2.2.2]octane ring shields halogen substituents in a lateral position on phenyl rings attached to the bicyclooctane ring to a small degree and reduces the steric efects of these substituents, giving rise to high relative nematic–isotropic transition temperatures.

## 1. Introduction

One of the research challenges in the area of liquid crystal displays (LCDs) is the development of new nematic mixtures of positive dielectric anisotropy for twisted nematic (TN) LCDs [1] with high information content, such as LCD TVs and computer monitors [2–6]. TN-LCDs are driven by thin film transistors at each pixel [2, 3]. This driving method requires nematic mixtures of positive dielectric anisotropy ($\Delta\varepsilon=\varepsilon_{\parallel}-\varepsilon_{\perp}>0$), low viscosity and a high voltage holding ratio (VHR) [4–7]. The latter requirement precludes the use of cyano groups in a terminal position, as they dissolve and solvate ions, e.g. from the alignment layers on the inside of the LCD [8]. The presence of these ions leads to a low voltage holding ratio. The use of aromatic compounds containing one, two or three halogen atoms, especially fluorine and chlorine atoms, has been a highly successful approach adopted to produce LCs of low viscosity and positive dielectric anisotropy [4–7].

A range of liquid crystalline 1,4-disubstituted[2.2.2]octanes have been designed for use as components of nematic mixtures of positive dielectric anisotropy for TN-LCDs [9–20]. A number of these LCs incorporate phenyl rings with a halogen atom in a terminal or lateral position [13–20]. However, the presence of two or three halogen atoms are required to generate a dipole moment large enough to induce a significant magnitude of the dielectric anisotropy [4–7]. 3,4,5-Trifluorobenzene exhibits a dipole moment ($\mu$=3.9 D) almost as large as that of cyanobenzene ($\mu$=4.0 D). This results in very similar values for the dielectric anisotropy ($\Delta\varepsilon\sim 11$) of nematic LCs incorporating these groups at the end of the molecular core [5]. The nematic–isotropic (N–I) transition temperatures of such compounds are usually very low [4–7]. This is due to a combination of steric effects due to the presence of substituents in a lateral position and an absence of molecular interdigitation [4–7]. The 1,4-disubstituted bicyclo[2.2.2]octane ring is large, spherical and symmetrical and has been shown to shield small substituents, such as fluorine atoms, in a lateral position [20]. We now report the synthesis and phase transition temperatures of several 1,4-disubstituted[2.2.2]octanes incorporating phenyl rings with two or three halogen atoms in an attempt to produce LCs of high positive dielectric anisotropy and with relatively high N–I transition temperatures.

An order of terminal group efficiency for substituents in a terminal position for the nematic phase was established in the 1970s by Gray [21]. A series of new terminal polyfluorinated substituents, such as trifluoromethyl and trifluoromethoxy groups, have been used to induce a positive dielectric anisotropy in nematic mixtures for use in LCDs with active matrix addressing. These polyfluorinated end groups do not solvate ions in the boundary layers of LCDs and leach ions from these layers into the nematic mixture [4, 8]. We now report an

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empirically updated order of terminal group efficiency for substituents in a terminal position for the nematic phase including these groups.

The difference in the free energy between the nematic phase and the isotropic phase is attributed in the Maier–Saupe treatment of the nematic phase to (attractive) dispersion forces [22]. Repulsive forces and interactions between permanent dipoles are discounted. The molecular free energy difference in a mean field approximation is defined as

$$\Delta F = -\frac{A\eta^2}{V^2} - T\Delta S(\eta), \qquad (1)$$

where $\eta$ is the order parameter (normally defined by the symbol S, but used here for entropy) defined as

$$\eta = 1 - \frac{3}{2}\sin^2\theta. \qquad (2)$$

$A$ is a factor proportional to the anisotropy of the molecular polarizability ($\Delta\alpha$), $V$ is the molecular volume and $\Delta S(\eta)$ is the difference in the orientational entropy. Excluded volume effects were introduced to account for changes in the clearing point as homologous series are ascended [23, 24]. Hard-rod theories discount dispersion forces and invoke repulsive forces due to steric effects to explain the formation of the nematic phase [25–29]. This short series of compounds differing only in the nature of the terminal substituent with respect to size and shape, dipole moment and polarizability, will also allow the experimental dependence of the nematic clearing point on various molecular physical parameters, such as anisotropy of polarizability, shape anisotropy and permanent dipole moments, to be used to test the compatibility with theories of the nematic phase.

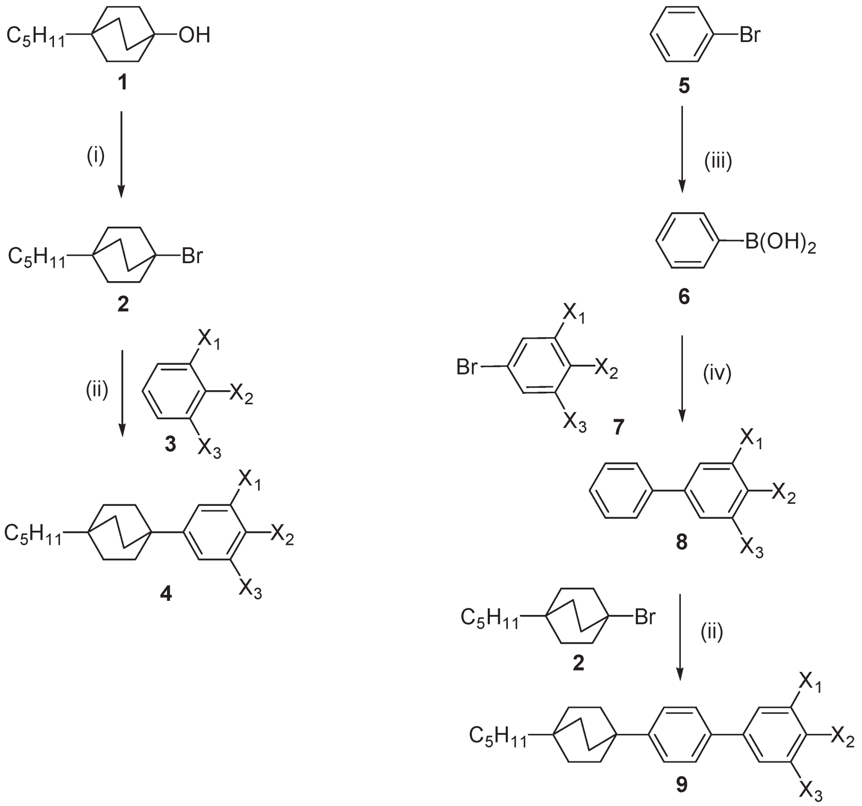
## 2. Experimental

### 2.1. *Instrumentation*

All commercially-available starting materials, reagents and solvents were used as supplied and were obtained from Aldrich, Strem Chem. Inc, Acros or Lancaster Synthesis. All reactions were carried out using a dry nitrogen atmosphere and the temperatures were measured internally. Mass spectra were recorded using a gas chromatography/mass spectrometer (GC/MS)-QP5050A Schimadzu with electron impact (EI) at a source temperature of 200°C. The mass ion of the material is identified by $M^+$. $^1H$ NMR spectra were recorded using a JEOL Lambda 400 spectrometer with an internal standard of tetramethylsilane (TMS). Purification of intermediates and final products was achieved by column chromatography, using silica gel (40–63 μm, 60 A) obtained from Fluorochem, and recrystallization from appropriate solvents. The melting point and other phase transition temperatures were measured using a Linkam 350 hot-stage and control unit in conjunction with a Nikon E400 polarizing microscope. The phase transition temperatures of the final products **4** and **9** were also determined using a Perkin-Elmer DSC-7 and in conjunction with a TAC 7/3 instrument controller, using the peak measurement for the value of the transition temperatures reported. The purity of the final compounds **4** and **9** was determined by elemental analysis using a Chromopack CP3800 gas chromatograph equipped with a 10 m CP-SIL 5CB column. AM1 calculations were carried out with MOPAC 2000. HF and DFT (B3LYP) calculations were carried out with Gaussian 03 [30].

### 2.2. *Synthesis*

The LCs **4** and **9** were initially synthesised using literature methods (see scheme 1) [11, 20]. The commercially-available 1-hydroxy-4-pentylbicyclo[2.2.2]octane **1** was converted into the corresponding bromide **2** using hydrobromic acid [11]. The 1-bromo-4-pentylbicyclo[2.2.2]octane **2** was reacted with commercially available 4-fluorobenzene, 4-chlorobenzene and 3,4,5-trifluorobenzene **3** ($X_1=X_3=H$; $X_2=F$, Cl and $X_{1\text{–}3}=F$) in a Friedel–Crafts alkylation reaction using iron(III) chloride as the catalyst in nitrobenzene as the solvent to yield the desired final compounds **4** ($X_1=X_3=H$; $X_2=F$, Cl and $X_{1\text{–}3}=F$) [20]. Bromobenzene **5** was converted to phenylboronic acid **6** in the usual way [31] and was reacted with commercially available 1-bromo-4-fluorobenzene, 1-bromo-4-chlorobenzene, 1-bromo-4-(trifluoromethoxy)benzene and 1-bromo-3,5-dichlorobenzene **7** ($X_1=X_3=H$; $X_2=F$, Cl, $OCF_3$; $X_1=X_3=Cl$; $X_2=H$ and $X_{1\text{–}3}=F$) in a Suzuki reaction to produce the biphenyls **8** ($X_1=X_3=H$; $X_2=F$, Cl, $OCF_3$; $X_1=X_3=Cl$; $X_2=H$ and $X_{1\text{–}3}=F$) [32]. Reaction of 1-bromo-4-pentylbicyclo[2.2.2]octane **2** with the biphenyls **8** in a Friedel–Crafts alkylation reaction yielded the final products **9** ($X_1=X_3=H$; $X_2=F$, Cl, $OCF_3$; $X_1=X_3=Cl$; $X_2=H$ and $X_{1\text{–}3}=F$). A simpler and more efficient reaction scheme was subsequently used whereby 1-hydroxy-4-pentylbicyclo[2.2.2]octane **1** was reacted directly with bromobenzene in an acid-catalysed alkylation reaction with the bromobenzene serving as reagent and solvent [33]. The resultant 1-pentyl-4-(4-bromophenyl)bicyclo[2.2.2]octane **4** ($X_1=X_3=H$; $X_2=Br$) was then converted into the desired final biphenyl products **9** ($X_{1\text{–}3}=H$ and $X_1=X_3=H$; $X_2=CH_3$, $OCH_3$, $CF_3$) by a Suzuki aryl–aryl coupling reaction with the appropriate commercially available phenyl boronic acids [32].



Scheme 1. Synthesis of compounds **4** and **9**. Reagents and conditions: (i) $ZnBr_2$, $CH_3CO_2H$, 90°C; (ii) $FeCl_3$, $PhNO_2$, 80°C; (iii) (a) Mg, THF, 25°C, (b) trimethyl borate, (c) $HCl_{aq}$; (iv) $Pd(PPh_3)_4$, $K_3PO_4$, DMF, 90°C.

### 2.2.1. 1-Bromo-4-pentylbicyclo[2.2.2]octane (2).

A mixture of 1-hydroxy-4-pentylbicyclo[2.2.2]octane (**1**) (5.00 g, 25 mol), anhydrous zinc bromide (25 g, 0.11 mol) and hydrobromic acid (50 cm$^3$) was heated at 60–70°C for 24 h. The cooled mixture was added to water (100 cm$^3$) and shaken with ether ($3 \times 80$ cm$^3$). The combined organic extracts were washed with brine ($2 \times 500$ cm$^3$) and dried ($MgSO_4$). The crude product was distilled under reduced pressure to give a colourless liquid. Boiling point: 103–105°C, purity: >99% (GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 2.21 (6H, m), 1.54 (6H, m), 1.28–1.00 (8H, m), 0.88 (3H, t, $J$=6.7 Hz). MS ($m/z$): 258 (M$^+$).

### 2.2.2. 1-(4-Fluorophenyl)-4-pentylbicyclo[2.2.2]octane (4; $X_1$=$X_3$=H; $X_2$=F).

A solution of 1-bromo-4-pentylbicyclo[2.2.2]octane (0.6 g, 2.3 mmol) in sieve-dried nitrobenzene (2 cm$^3$) was added dropwise to a stirred solution of 4-fluorobenzene (**3**) (5.2 g, 0.5 mmol) and anhydrous iron(III) chloride (0.6 g, 3.7 mmol) in sieve dried nitrobenzene (2 cm$^3$) maintained at 80°C throughout the addition and overnight. The cooled solution was added to a small volume of hydrochloric acid (15%) stirred for 20 min and extracted with DCM. The remaining organic layer was separated off and distilled to yield a solid residue, which was purified *via* column chromatography using hexane. Purity: >99% (GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 7.32 (2H, d), 6.95 (2H, d), 1.84 (6H, m), 1.52 (6H, m), 1.23 (8H, m), 0.88 (3H, t, $J$=6.7 Hz). MS ($m/z$): 249 (M$^+$).

### 2.2.3. 1-(4-Chlorophenyl)-4-pentylbicyclo[2.2.2]octane (4; $X_1$=$X_3$=H; $X_2$=Cl).

Purity: >99% (GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 7.28 (4H, d), 1.83 (6H, m), 1.54 (6H, m), 1.23 (8H, m), 0.88 (3H, t, $J$=6.7 Hz). MS ($m/z$): 289 (M$^+$).

### 2.2.4. 1-(4-Trifluoromethylphenyl)-4-pentylbicyclo[2.2.2]octane (4; $X_1$=$X_3$=H; $X_2$=$CF_3$).

Purity: >99% (GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 7.50 (2H, d, $J$=7.3 Hz), 7.39 (2H, d, $J$=7.3 Hz), 1.79–1.83 (6H, m), 1.48–1.53 (6H, m), 1.11–1.34 (8H, m), 0.89 (3H, t, $J$=7 Hz). MS ($m/z$): 325, 324 (M$^+$).

### 2.2.5. 1-(4-Trifluoromethoxyphenyl)-4-pentylbicyclo[2.2.2]octane (4; $X_1$=$X_3$=H; $X_2$=$OCF_3$).

Purity: >99% (GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 7.32 (2H, d, $J$=9 Hz), 7.11 (2H, d, $J$=9 Hz), 1.76–1.80 (6H, m), 1.46–1.50 (6H, m), 1.11–1.32 (8H, m), 0.88 (3H, t, $J$=7 Hz). MS ($m/z$): 341, 340 (M$^+$).

**2.2.6. 1-Pentyl-4-(3,4,5-trifluorophenyl)bicyclo[2.2.2]octane (4; $X_{1-3}$=F).** Purity: >99% (GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 6.84 (2H, m), 1.85 (6H, m), 1.54 (6H, m), 1.23 (8H, m), 0.88 (3H, t, $J$=6.7 Hz), MS ($m/z$): 309 ($M^+$).

**2.2.7. Phenylboronic acid (6).** Bromobenzene (**5**) (10 g, 0.0637 mol), was added dropwise to a mixture of magnesium turnings (1.42 g, 58.37 mmol) in THF (400 cm$^3$). The temperature was cooled down to −78°C after completion of the reaction. Then trimethyl borate (9.93 g, 95.95 mmol) was added dropwise over 30 min. The reaction mixture was stirred and allowed to reach room temperature overnight. The reaction mixture was then stirred with hydrochloric acid (300 cm$^3$, 20%) before being extracted with diethyl ether ($2 \times 200$ cm$^3$). The combined extracts were washed with water ($2 \times 200$ cm$^3$) and dried over $MgSO_4$. The solvent was removed under reduced pressure and washed with hexane to yield 4.5 g (58.4%) of the desired white solid. M.p. 218°C.

**2.2.8. 4-Fluorobiphenyl (8; $X_1$=$X_3$=H; $X_2$=F).** A mixture of tetrakis(triphenylphosphine)palladium(0) (0.24 g, 0.21 mol), phenylboronic acid (0.51 g, 4.22 mmol), 1-bromo-4-fluorobenzene (0.93 g, 0.21 mmol), aqueous 2M sodium carbonate solution (3.5 cm$^3$) and 1,2-dimethoxyethane (30 cm$^3$) was heated under reflux overnight. The solution was allowed to cool to room temperature and then poured into water. The organic phase was extracted with diethyl ether and the combined extracts were then washed with brine and dried with $MgSO_4$. The solvent was removed and the residue purified by column chromatography using hexane as a solvent to yield 0.57 g (78.6%) of the desired product. M.p. 58°C, purity: >99% (GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 7.13 (2H, d, $J$=8.7 Hz), 7.34 (1H, t, $J$=7.3 Hz), 7.43 (2H, t, $J$=7.3 Hz), 7.55 (2H, d, $J$=8.7 Hz), 7.57 (2H, d, $J$=7.3 Hz). MS ($m/z$): 172 ($M^+$), 149 (M100), 85, 71, 57.

**2.2.9. 4-Chlorobiphenyl (8; $X_1$=$X_3$=H; $X_2$=Cl).** M.p. 74°C, purity: >99% (GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 7.35 (1H, t, $J$=7.3 Hz), 7.41 (2H, d, $J$=8.7 Hz), 7.44 (2H, t, $J$=7.3 Hz), 7.51 (2H, d, $J$=8.7 Hz), 7.55 (2H, d, $J$=7.3 Hz). MS ($m/z$): 187 ($M^+$).

**2.2.10. 4-Trifluoromethoxybiphenyl (8; $X_1$=$X_3$=H; $X_2$=$OCF_3$).** M.p. 58°C, purity: >99% (GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 7.30 (2H, d, $J$=8.7 Hz), 7.37 (1H, t, $J$=7.3 Hz), 7.45 (2H, d, $J$=7.3 Hz), 7.55 (2H, d, $J$=8.7 Hz), 7.60 (2H, d, $J$=7.3 Hz). MS ($m/z$): 238 ($M^+$), 169, 141, 115, 84 (M100), 69, 51.

**2.2.11. 3,5-Dichlorobiphenyl (8; $X_1$=$X_3$=Cl; $X_2$=H).** M.p. 62°C, purity: >99% (GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 7.35 (1H, t, $J$=7.3 Hz), 7.41 (1H, d, $J$=2.0 Hz), 7.44 (2H, t, $J$=7.3 Hz), 7.52 (2H, d, $J$=7.3 Hz), 7.66 (2H, d, $J$=2.0 Hz), MS ($m/z$): 222 ($M^+$).

**2.2.12. 3,4,5-Trifluorobiphenyl (8; $X_1$=$X_2$=$X_3$=F).** M.p. 56°C, purity: >99% (GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 6.90 (2H, s), 7.34 (1H, t, $J$=7.3 Hz), 7.43 (2H, t, $J$=7.3 Hz), 7.55 (2H, d, $J$=8.7 Hz), 7.57 (2H, d, $J$=7.3 Hz). MS ($m/z$): 207 ($M^+$).

**2.2.13. 1-(4-Fluorobiphenyl-4′-yl)-4-pentylbicyclo[2.2.2]-octane (9; $X_1$=$X_3$=H; $X_2$=F).** A solution of 1-bromo-4-pentylbicyclo[222]octane (0.4 g, 1.54 mmol) in sieve-dried nitrobenzene (2 cm$^3$) was added dropwise to a stirred solution of 4-fluorobiphenyl (**8**) (0.27 g, 1.54 mmol) and anhydrous iron(III) chloride (0.6 g, 3.7 mmol) in sieve dried nitrobenzene (2 cm$^3$) maintained at 80°C throughout the addition and overnight. The cooled solution was added to a small volume of hydrochloric acid (15%) stirred for 20 min and extracted with DCM. The remaining organic layer was separated off and steam distilled to yield a solid residue. This crude solid was purified *via* column chromatography using hexane to give g of a white solid. $^1$H NMR (DMSO-$d_6$, $CDCl_3$) $\delta_H$: 7.58 (2H, d, $J$=8.7 Hz), 7.48 (2H, d, $J$=8.7 Hz), 7.40 (2H, d, $J$=8.7 Hz), 7.29 (2H, d, $J$=8.7 Hz), 1.84 (6H, m), 1.52 (6H, m), 1.27 (8H, m), 0.88 (3H, t, $J$=6.7 Hz). MS ($m/z$): 349 ($M^+$).

**2.2.14. 1-(4-Chlorobiphenyl-4′-yl)-4-pentylbicyclo[2.2.2]-octane (9; $X_1$=$X_3$=H; $X_2$=Cl).** $^1$H NMR (DMSO-$d_6$, $CDCl_3$) $\delta_H$: 7.61 (2H, d, $J$=8.7 Hz), 7.52 (2H, d, $J$=8.7 Hz), 7.53 (2H, d, $J$=8.7 Hz), 7.42 (2H, s), 7.38 (2H, d, $J$=8.7 Hz), 1.82 (6H, m), 1.52 (6H, m), 1.23 (8H, m), 0.88 (3H, t, $J$=6.7 Hz). MS ($m/z$): 366 ($M^+$).

**2.2.15. 1-Pentyl-4-(4-trifluoromethoxybiphenyl-4′-yl)bicyclo[2.2.2]octane (9; $X_1$=$X_3$=H; $X_2$=$OCF_3$).** $^1$H NMR (DMSO-$d_6$, $CDCl_3$) $\delta_H$: 7.72 (2H, d, $J$=8.7 Hz), 7.58 (2H, d, J=4 Hz), 7.44 (2H, d, $J$=8.7 Hz), 7.40 (2H, d, $J$=8.7 Hz), 1.85 (6H, m), 1.52 (6H, m), 1.25 (8H, m), 0.88 (3H, t, $J$=6.7 Hz). MS ($m/z$): 415 ($M^+$).

**2.2.16. 1-(3,5-Dichlorobiphenyl-4′-yl)-4-pentylbicyclo-[2.2.2]octane (9; $X_1$=$X_3$=Cl; $X_2$=H).** $^1$H NMR (DMSO-$d_6$, $CDCl_3$) $\delta_H$: 7.64 (2H, d, $J$=8.7 Hz, $J$=2.1 Hz), 7.46 (2H, d, $J$=8.1 Hz), 7.38 (2H, d, $J$=8.1 Hz), 7.35 (1H, t, $J$=7.3 Hz), 1.85 (6H, m), 1.52 (6H, m), 1.25 (8H, m), 0.88 (3H, t, $J$=6.7 Hz), MS ($m/z$): 400 ($M^+$).

**2.2.17. 1-Pentyl-4-(3,4,5-trifluorobiphenyl-4′-yl)bicyclo-[2.2.2]octane (9; $X_1$=$X_3$=H; $X_2$=$CF_3$).** $^1$H NMR

(DMSO-$d_6$, $CDCl_3$) $\delta_H$: 7.62 (2H, d, $J$=8.1 Hz), 7.58 (2H, d, $J$=8.1 Hz), 7.42 (2H, t, $J$=8.1 Hz), 1.81 (6H, m), 1.50 (6H, m), 1.25 (8H, m), 0.88 (3H, t, $J$=6.7 Hz). MS (*m*/*z*): 385 ($M^+$).

**2.2.18. 1-(4-Bromophenyl)-4-pentylbicyclo[2.2.2]octane (4; $X_1$=$X_3$=H; $X_2$=Br).** Concentrated $H_2SO_4$ (2.5 $cm^3$), was slowly added to a warmed (60°C) solution of 1-hydroxy-4-pentylbicyclo[2.2.2]octane (2.50 g, 0.0127 mol), and bromobenzene (10.00 g, 0.0637 mol). The reaction temperature was increased to 80°C and the solution stirred for 2 h. The cooled mixture was added to water (300 $cm^3$) and the crude product extracted into hexane ($3 \times 200\,cm^3$). The combined organic extracts were washed with brine ($2 \times 200\,cm^3$), dried ($MgSO_4$), filtered and concentrated under reduced pressure. Purification was carried out by recrystallization from EtOH to yield (3.20 g, 75%) white crystalline needles. M.p. 96°C, purity: >99% (GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 7.39 (2H, d, $J$=8.8 Hz), 7.18 (2H, d, $J$=8.8 Hz), 1.74–1.78 (6H, m), 1.45–1.49 (6H, m), 1.10–1.32 (8H, m), 0.88 (3H, t, $J$=7 Hz). MS (*m*/*z*): 334 ($M^+$).

**2.2.19. 1-(Biphenyl-4-yl)-4-pentylbicyclo[2.2.2]octane (9; $X_1$=$X_3$=H; $X_2$=H).** Purity: >99%(GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 7.58 (2H, dd, $J$=8.3, 1.3 Hz), 7.52 (2H, d, $J$=8.6 Hz), 7.38–7.43 (4H, m), 7.29–7.33 (1H, m), 1.83–1.87 (6H, m), 1.48–1.52 (6H, m), 1.11–1.33 (8H, m), 0.89 (3H, t, $J$=7 Hz). MS (*m*/*z*): 334, 333, 332 ($M^+$).

**2.2.20. 1-(4-Methylbiphenyl-4′-yl)-4-pentylbicyclo[2.2.2]-octane (9; $X_1$=$X_3$=H; $X_2$=$CH_3$).** Purity: >99%(GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 7.50 (2H, d, $J$=8.6 Hz), 7.48 (2H, d, $J$=8.2 Hz), 7.38 (2H, d, $J$=8.8 Hz), 7.22 (2H, d, $J$=7.9 Hz), 2.38 (3H, s), 1.82–1.86 (6H, m), 1.48–1.52 (6H, m), 1.10–1.34 (8H, m), 0.89 (3H, t, $J$=7 Hz). MS (*m*/*z*): 348, 347, 346 ($M^+$).

**2.2.21. 1-(4-Methoxybiphenyl-4′-yl)-4-pentylbicyclo[2.2.2]-octane (9; $X_1$=$X_3$=H; $X_2$=$OCH_3$).** Purity: >99%(GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 7.46–7.52 (4H, m), 7.37 (2H, d, $J$=8.6 Hz), 6.96 (2H, d, $J$=8.8 Hz), 3.84 (3H, s), 1.82–1.86 (6H, m), 1.48–1.52 (6H, m), 1.11–1.33 (8H, m), 0.89 (3H, t, $J$=7 Hz). MS (*m*/*z*): 364, 363, 362 ($M^+$).

**2.2.22. 1-Pentyl-4-(4-trifluoromethylbiphenyl-4′-yl)bicyclo[2.2.2]octane (9; $X_1$=$X_3$=H; $X_2$=$CF_3$).** Purity: >99%(GC). $^1$H NMR ($CDCl_3$) $\delta_H$: 7.67 (4H, s), 7.53 (2H, d, $J$=8.6 Hz), 7.43 (2H, d, $J$=8.8 Hz), 1.83–1.87 (6H, m), 1.49–1.53 (6H, m), 1.11–1.33 (8H, m), 0.89 (3H, t, $J$=7 Hz). MS (*m*/*z*): 402, 401, 400 ($M^+$).

### 2.3. *Mesomorphic properties*

The mesomorphic behaviour of compounds **4** and **9** was investigated between cross polarizers using optical microscopy. A nematic (N) phase was observed for many of the compounds prepared. A Schlieren texture with 2-brush and 4-brush disclinations is seen for the nematic phase between crossed polarizers in an optical microscope (see figure 1). Small droplets are seen on cooling slowly from the isotropic phase, which then coalesce to form the Schlieren texture of the nematic phase (see figures 1–2). Only one compound **9** ($X_1$=$X_3$=H; $X_2$=$OCH_3$) exhibits an observable (enantiotropic) smectic A (SmA) phase on cooling from the nematic phase. The SmA phase exhibits a typical focal conic texture as well as optically extinct areas in the same sample, which is characteristic of the (uniaxial) SmA phase. Elliptical and hyperbolic lines of optical discontinuity typical of focal conic defects are also observed as usual.

The transition temperatures of **4** and **9** observed using optical microscopy were confirmed by differential scanning calorimetry (DSC). The base line of the

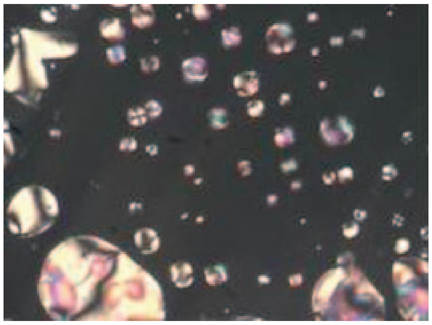


Figure 1. Droplet texture of 1-(4-fluorobiphenyl-4′-yl)-4-pentylbicyclo[2.2.2]octane (**9**, $X_1$=$X_3$=H; $X_2$=F) formed by slow cooling (1°C $min^{-1}$) from the clearing point to the onset of the nematic phase.

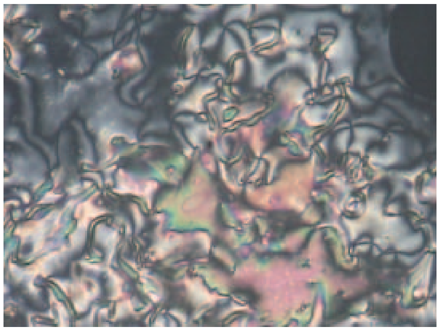


Figure 2. The Schlieren texture of the nematic phase of 1-(4-fluorobiphenyl-4′-yl)-4-pentylbicyclo[2.2.2]octane (**9**, $X_1$=$X_3$=H; $X_2$=F) at 135°C.

spectra is relatively flat and sharp transition peaks are observed with no thermal degradation. Large melting transition peaks and relatively small nematic-isotropic peaks, characteristic of a nematic liquid crystal, were observed. Extrapolated (virtual) N–I transition temperatures were obtained in the usual way using nematic mixtures prepared with BC037 as the nematic host (see figure 3).

## 3. Results and discussion

The 1,4-disubstituted bicyclo[2.2.2]octanes (**4**, $X_1=X_3=H$; $X_2=H$, F, Cl, Br, CN, $CH_3$, $OCH_3$, $CF_3$, $OCF_3$) differ only in the nature of the substituent X in a terminal position on the phenyl ring (see table 1). The nitrile (**4**, $X_1=X_3=H$; $X_2=CN$) and the methoxy ether (**4**, $X_1=X_3=H$; $X_2=OCH_3$) are the only members of the series to exhibit an observable, enantiotropic nematic phase. The large dipole moment of the cyano group ($\mu=4\,D$) [34] in a terminal position on the phenyl ring induces the formation of molecular dimers [35, 36]. The higher length-to-breadth ratio of the effective molecular dimers is responsible for the high N–I transition temperature [21]. The dipole moment of the methoxy ether (**4**, $X_1=X_3=H$; $X_2=OCH_3$) is much lower ($\mu=1.28\,D$) and with a major component orthogonal to the long molecular axis ($\theta=72°$) (see figure 4) [34]. Consequently there is no appreciable dimer formation and the high clearing point may be attributed to the contribution of the polar and polarizable methoxyphenyl group to a high magnitude and anisotropy of the molecular polarizability. This is consistent with the much lower clearing point (difference 49°C) of the methyl-substituted compound (**4**, $X=CH_3$), which differs in molecular structure only in the absence of the oxygen atom compared to the methoxy ether (**4**, $X=OCH_3$). Therefore, the magnitude and anisotropy of the molecular polarizability of the methyl-substituted compound (**4**, $X=CH_3$) will be lower than that of the methoxy-substituted analogue (**4**, $X=OCH_3$). The dipole moments listed in table 1 are literature values [34] for the analogous substituted benzene derivatives (see figure 4). However, the differences in the magnitude of the dipole moments and their direction for the substituted benzenes and the 1-(4-pentylbicyclo[2.2.2]octyl)-4-substituted benzenes **4** should not be significant. Any difference will be a constant across the series of bicyclo[2.2.2]octanes **4**, so that at least the general trends should be valid.

The three-ring bicyclo[2.2.2]octanes (**9**, $X_1=X_3=H$; $X_2=H$, F, Cl, Br, CN, $CH_3$, $OCH_3$, $CF_3$, $OCF_3$) are listed in table 2 in order of increasing nematic clearing point. The presence of an additional 1,4-disubstituted phenyl ring in the biphenyls (**9**, $X_1=X_3=H$; $X_2=H$, F, Cl, Br, CN, $CH_3$, $OCH_3$, $CF_3$, $OCF_3$) compared to the phenyl compounds (**4**, $X_1=X_3=H$; $X_2=H$; $X_2=H$, F, Cl, Br, CN, $CH_3$, $OCH_3$, $CF_3$, $OCF_3$) results in much higher melting points (+89°C on average) and clearing points (+185°C on average comparing values for the four homologues with measured or extrapolated clearing points) as well as the presence of enantiotropic nematic phases for most of the materials studied (see tables 1–2).

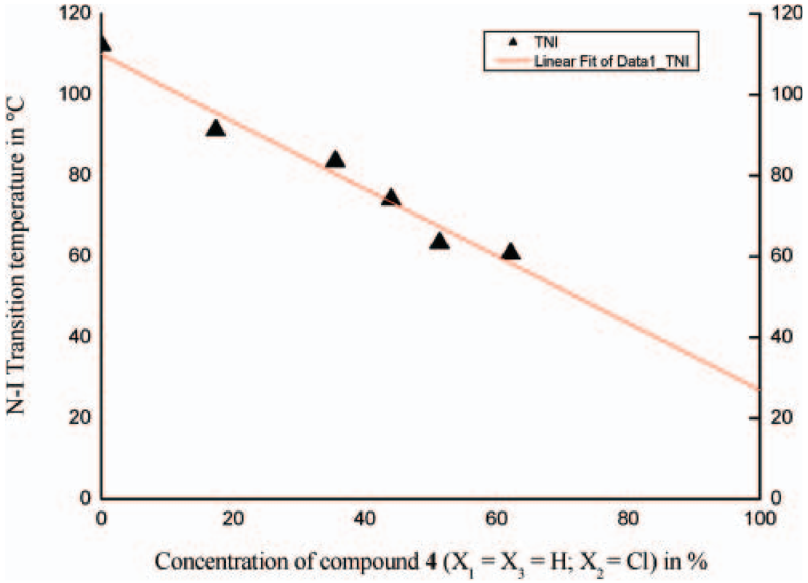
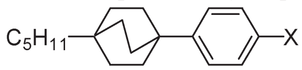


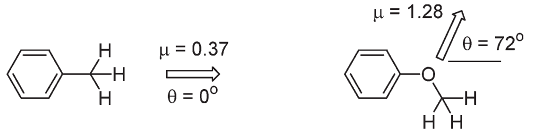
Figure 3. Plot of the nematic–isotropic transition temperature of the mixtures of compound **4** ($X_1=X_3=H$; $X_2=Cl$) and the nematic mixture BC037. The virtual value for the clearing point of the nematic phase extrapolated to 100% of the compound **4** ($X_1=X_3=H$; $X_2=Cl$) is 28°C.

Table 1. Phase transition temperatures (°C) of the 1-pentyl-4-(4-substituted-phenyl)bicyclo[2.2.2]octanes (**4**, $X_1$=$X_3$=H; $X_2$=H, F, Cl, Br, CN, $CH_3$, $OCH_3$, $CF_3$, $OCF_3$). The dipole moments listed are literature values for the corresponding substituted benzene derivatives [34]. The angle $\theta$ is >90° for compounds with negative group moments and <90° for compounds with positive group moments [34].

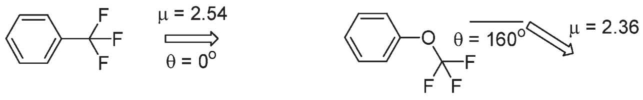


| X | Cr | | N | | I | $\mu$ | $\theta$ |
|---|---|---|---|---|---|---|---|
| H | • | $37^a$ | | – | • | 0 | 0 |
| F | • | 40 | • | – | • | −1.47 | 0 |
| Cl | • | 75 | • | [28] | • | −1.59 | 0 |
| Br | • | 98 | | – | • | −1.57 | 0 |
| CN | • | $62^b$ | • | $100^b$ | • | −4.05 | 0 |
| $CH_3$ | • | $64^c$ | • | $[19]^c$ | • | 0.37 | 0 |
| $CF_3$ | • | 34 | | – | • | −2.54 | 0 |
| $OCH_3$ | • | $64^c$ | • | $70^c$ | • | 1.28 | 72 |
| $OCF_3$ | • | 21 | | – | • | −2.36 | 160 |

[a]Literature value [10]; [b]Literature value [11]; [c]Literature value [20]; [ ] indicates an extrapolated virtual transition.



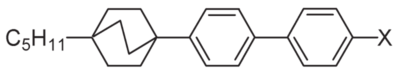
(*a*) toluene [methylbenzene] (*b*) anisole [methoxybenzene]



(*c*) trifluoromethylbenzene (*d*) trifluoromethoxybenzene

Figure 4. Dipole moments of (a) toluene, (b) anisole, (c) trifluoromethylbenzene and (d) trifluoromethoxybenzene. The angle $\theta$ is >90° for compounds with negative group moments and <90° for compounds with positive group moments [34].

Table 2. Phase transition temperatures (°C) of the 1-pentyl-4-(4-substituted-biphenyl-4′-yl)bicyclo[2.2.2]octanes (**9**, $X_1$=$X_3$=H; $X_2$=H, F, Cl, Br, CN, $CH_3$, $OCH_3$, $CF_3$, $OCF_3$).



| X | Cr | | SmA | | N | | I |
|---|---|---|---|---|---|---|---|
| H | • | 125 | | – | • | 141 | • |
| $OCF_3$ | • | 97 | | – | • | 141 | • |
| $CF_3$ | • | 154 | | – | • | 163 | • |
| F | • | 136 | | – | • | 186 | • |
| Cl | • | 172 | | – | • | 215 | • |
| $CH_3$ | • | 146 | | – | • | 221 | • |
| Br | • | $192^a$ | | – | • | $233^a$ | • |
| $OCH_3$ | • | 116 | • | 122 | • | 251 | • |
| CN | • | $159^a$ | | – | • | $269^a$ | • |

[a]Literature value [11].

The melting and clearing points of a subset of the biphenyl bicyclo[2.2.2]octanes (**9**, $X_1$=$X_3$=H; $X_2$=H, F, Cl, Br and CN) increases with increasing polarizability of the terminal $X_2$-group. The presence of molecular dimers [35, 36] for the nitrile (**4**, $X_1$=$X_3$=H; $X_2$=CN) explains the very high clearing point for this derivative [21]. The replacement of the hydrogen atom in a terminal position in the compound **9** ($X_{1–3}$=H) by a fluorine atom in the compound **9** ($X_{1–3}$=H) results in an increase in clearing point of the nematic phase. This increase is consistent with an increase in both the magnitude and anisotropy of polarizability on replacing H with F. The size and shape of the molecule are almost identical, since the lengths of the C–H bond and the C–F bond are almost the same and the van der Waals radius of fluorine is only 12.5% larger than that of hydrogen, although it should be noted that the volume of the fluorine atom is nearly twice as large as that of a hydrogen atom. However, this result is consistent with the Maier–Saupe model of the nematic phase. [22] However, a similar replacement of a hydrogen atom in the methyl- and methoxy-substituted compounds (**9**, $X_1$=$X_3$=H; $X_2$=$CH_3$, $OCH_3$) to produce the corresponding compounds (**9**, $X_1$=$X_3$=H; $X_2$=$CF_3$, $OCF_3$) with a trifluoromethyl group or a trifluoromethoxy group as the terminal substituent, results in much lower clearing points for the two trifluoro-substituted compounds. This behaviour is significant and clearly requires a different explanation.

It is clear from the phase transition temperatures collated in table 2 and the dipole moments and molecular polarizabilities collated in tables 3–4 for the methyl- and methoxy-substituted compounds (**9**, $X_1$=$X_3$=H; $X_2$=$CH_3$, $OCH_3$) and the corresponding trifluoromethyl- or a trifluoromethoxy-substituted compounds (**9**, $X_1$=$X_3$=H; $X_2$=$CF_3$, $OCF_3$) that there is no direct correlation between the magnitude of the nematic clearing point and any of the parameters considered, i.e. molecular shape, dipole moment or molecular polarizability. There is no apparent correlation between the magnitude of the dipole moment and the direction of

Table 3. Gas phase calculations for dipole moment (in Debye) of the 1-pentyl-4-(4-substituted-biphenyl-4′-yl)bicyclo[2.2.2]octanes (**9**, $X_1$=$X_3$=H; $X_2$=$CH_3$, $CF_3$, $OCH_3$, $OCF_3$).

| $X_2$ | AM1 | HF/ 6-31G* | B3LYP/ 3-21G | B3LYP/ 6-31G* |
|---|---|---|---|---|
| $CH_3$ | 0.12 | 0.11 | 0.18 | 0.19 |
| $CF_3$ | 4.13 | 3.95 | 4.21 | 3.88 |
| $OCH_3$ | 1.27 | 1.35 | 1.50 | 1.28 |
| $OCF_3$ | 2.74 | 3.55 | 3.42 | 2.90 |

Table 4. Gas phase calculations for the polarizability (in Å$^3$) of the 1-pentyl-4-(4-substituted-biphenyl-4′-yl)bicyclo[2.2.2]octanes (**9**, $X_1=X_3=H$; $X_2=CH_3$, $CF_3$, $OCH_3$, $OCF_3$).

| $X_2$ | AM1 | HF/ 6-31G* | B3LYP/ 3-21G | B3LYP/ 6-31G* |
|---|---|---|---|---|
| $CH_3$ | 33.8 | 38.5 | 39.4 | 41.9 |
| $CF_3$ | 34.0 | 38.2 | 39.0 | 41.9 |
| $OCH_3$ | 34.9 | 39.0 | 40.4 | 42.9 |
| $OCF_3$ | 35.1 | 38.6 | 39.6 | 42.6 |

the dipole moment either parallel to the long molecular axis or across it. The polarizability of the compounds (**9**, $X_1=X_3=H$, $X_2=CH_3$, $CF_3$, $OCH_3$, $OCF_3$) appears to be almost independent of the nature of the end-group. There is some indication that the anisotropy of polarizabilty is greater for the ethers (**9**, $X_1=X_3=H$, $X_2=OCH_3$, $OCF_3$), rather than the methyl-substituted and trifluoromethyl-substituted analogues (**9**, $X_1=X_3=H$, $X_2=CH_3$, $CF_3$), but the difference does not appear to be significant. The very large differences (~80–110°C) between the nematic clearing point of the compounds (**9**, $X_1=X_3=H$, $X_2=CH_3$, $OCH_3$) with methyl and methoxy terminal end groups and those of the corresponding materials (**9**, $X_1=X_3=H$, $X_2=CF_3$, $OCF_3$) with fluorine atoms in place of the hydrogen atoms in the terminal end group cannot be explained by shape anisotropy as their shapes are almost identical, since the lengths of the C–H bond and the C–F bond are almost the same and the nature of the bonding is the same (*sp*$^3$). Steric effects cannot be completely ruled out, since, although the radius of the fluorine atom is only 12.5% larger than that of the hydrogen atom, the volume is nearly twice as large. This may result in differences in the packing density of molecules with fluorine atoms in place of the hydrogen atoms in the terminal end group.

Alternatively, it may be that the more symmetrical ground state energy level (HOMO) of the methyl- and methoxy-substituted compounds (**9**, $X_1=X_3=H$; $X_2=CH_3$, $OCH_3$) shown in figure 5 may allow a greater degree of overlap of the molecular orbitals of neighbouring molecules aligned parallel to each other in dimer conformations than is possible for the less symmetrical HOMOs of the corresponding materials (**9**, $X_1=X_3=H$, $X_2=CF_3$, $OCF_3$) with fluorine atoms in place of the hydrogen atoms in the terminal end group. The molecular association of pairs of molecules in loosely-bound molecular dimers is known to be an important contributory factor to the high clearing point of the nematic phase of cyano-substituted LCs, such as compound **9** ($X_1=X_3=H$, $X_2=CN$) [35, 36]. This higher degree of overlap of electron density would lower the HOMO energy level of each of the dimer molecules. This would in turn lead to an overall lower free energy of the molecular ensemble making up the nematic phase. The higher order parameter induced by a greater degree of molecular orbital overlap between adjacent molecules in such a parallel arrangement would explain the very high clearing points of the methyl- and methoxy-substitued compounds (**9**, $X_1=X_3=H$; $X_2=CH_3$, $OCH_3$). Attractive dispersion forces would be increased and repulsive forces and interactions would be minimised in this molecular configuration. The low degree of symmetry of the HOMOs of the corresponding trifluoromethyl- or a trifluoromethoxy-substituted compounds (**9**, $X_1=X_3=H$; $X_2=CF_3$, $OCF_3$) would explain their very low nematic clearing points in an analogous fashion. This explanation of the differences in the nematic clearing point of a series of compounds differing only in the nature of the terminal substituent could be tested by determining the Kirkwood–Fröhlich correlation factor, *g*, using measured values of the refractive indices and dielectric constants of the nematic phase and the isotropic liquid of representative members of the series [37]. Another, as yet unidentified, intermolecular interaction may be responsible for these very large differences. The nature of this interaction is not apparent considering the main theories of the nematic phase [22–29]. However, it is consistent with the very large differences in the clearing point of the nematic phase for compounds with very similar structures, including molecular isomers, but differing only in the presence or absence of conjugated and/or non-conjugated heteroatoms, such as oxygen and nitrogen [21, 38]. The symmetry of the HOMOs of these very similar molecules will be substantially different.

The empirical, experimentally-determined order of terminal group efficiency for substituents in a terminal position for the nematic phase is:

$$CN > OCH_3 > Br > CH_3 > Cl > F > CF_3 > OCF_3 \sim H.$$

The order is consistent with that determined previously [21], but contains the two additional trifluoro-substituted groups. It is remarkable that the trifluoromethoxy group is not more efficient in inducing a nematic phase in the model compounds **4** and **9** than a hydrogen atom in the same position taking into account the highly polar nature of the former, cf. the very polar cyano group. Even the polar trifluoromethyl group with a dipole moment parallel to the molecular long axis, like the cyano group, is not much more efficient than a hydrogen atom in contributing to the formation of a nematic phase with a high clearing point.

The 1-pentyl-4-(3,45-trifluorophenyl)bicyclo[2.2.2]octane (**4**, $X_{1-3}=F$) with three fluorine atoms exhibits an

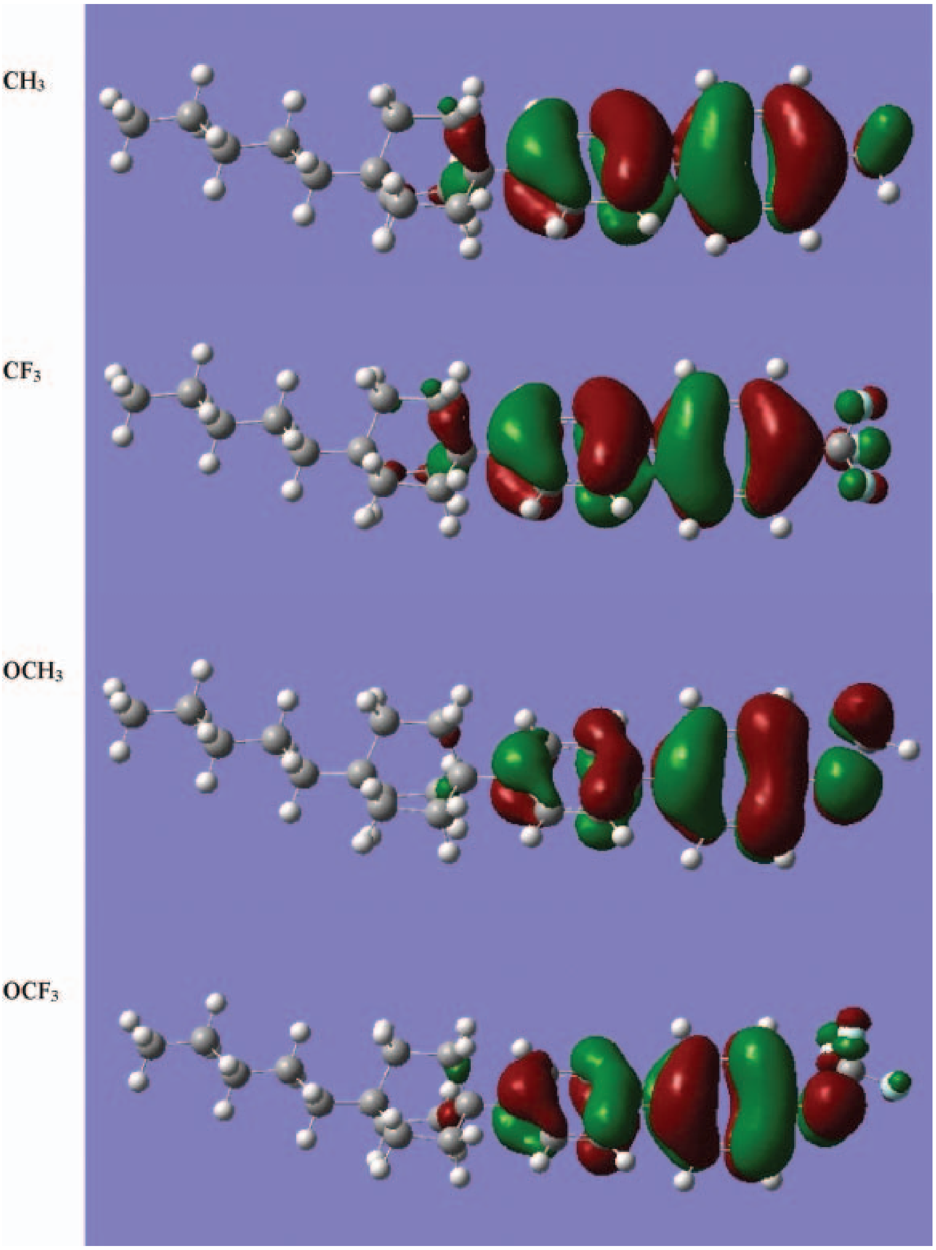
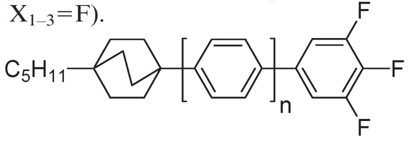


Figure 5. B3LYP/6-31G* calculation of the HOMO of the 1-pentyl-4-(4-substituted-biphenyl-4′-yl)bicyclo[2.2.2]octanes (**9**, $X_1=X_3=H$; $X_2=CH_3$, $CF_3$, $OCH_3$, $OCF_3$).

Table 5. Phase transition temperatures (°C) of the 1-pentyl-4-(3,4,5-trifluorophenyl)bicyclo[2.2.2]octane (**4**, $X_{1\text{–}3}=F$) and the 1-pentyl-4-(3,4,5-trifluorobiphenyl-4′-yl)bicyclo[2.2.2]octane (**9**, $X_{1\text{–}3}=F$).



| *n* | Cr | | N | | I |
|---|---|---|---|---|---|
| 0 | | <−50 | | −11 | |
| 1 | • | 67 | • | 78 | • |

enantiotropic liquid crystalline phase at a temperature much below room temperature (see table 5). The low melting point (<−50°C) and clearing point (−11°C) is most probably attributable to molecular broadening due to the presence of two fluorine atoms in lateral positions. The shielding effect of the 1,4-bicyclo[2.2.2]octane ring [13, 14, 30] is apparently insufficient to generate a higher clearing point.

Molecular modelling shows that there should be a degree of shielding of the lateral fluorine substituents by the 1,4-disubstituted bicyclo[2.2.2]octane ring in

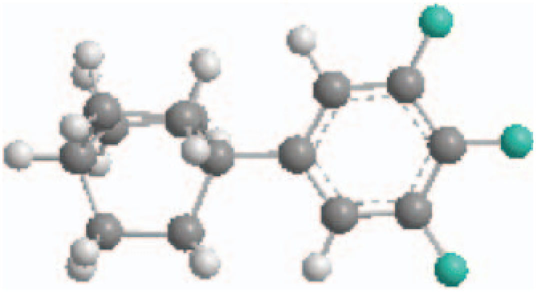


Figure 6. Molecular model of the compound **4** ($X_{1-3}$=F) showing the shielding effect of the 1,4-disubstituted bicyclo[2.2.2]octane ring.

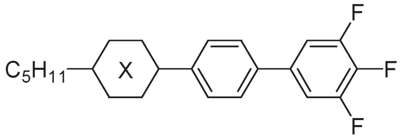
compounds **4** and **9** (see figure 6). The spherical and symmetrical shape of the 1,4-disubstituted bicyclo[2.2.2]octane ring allows the phenyl ring to rotate freely about the bond joining it to the bicyclo[2.2.2]octane ring without leading to very significant broadening of the molecule. However, it has been shown that fluorine atoms in the 3-position (*meta*-substitution]) are less shielded than in the 2-position (*ortho*-substitution) with respect to the bond between the phenyl and bicyclo[2.2.2]octane rings [13, 14, 30]. The longer length-to-breadth ratio of the 1-pentyl-4-(3,4,5-trifluorobiphenyl-4′-yl)bicyclo[2.2.2]octane (**9**, $X_{1-3}$=F) with three rings in the molecular core and the resultant higher degree of shape anisotropy and molecular polarizability leads to much higher melting point (+<117°C) and clearing point (+67°C) compared to those of the 1-pentyl-4-(3,4,5-trifluorophenyl)bicyclo[2.2.2]octane (**4**, $X_{1-3}$=F) with only two rings in the molecular core. The 1-(3,5-dichlorobiphenyl-4′-yl)-4-pentylbicyclo[2.2.2]octane (**9**, $X_1$=$X_3$=Cl, $X_2$=H) with two chlorine substituents in lateral (*meta*-substituted) positions exhibits an enantiotropic nematic phase. It also possesses a low melting point (Cr–N=112°C) and clearing point (N–I=123°C) for the same steric reasons, although a significant lowering of the shape anisotropy is to be expected.

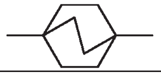
The data collated in table 6 allow a comparison of the 1-pentyl-4-(3,4,5-trifluorobiphenyl-4′-yl)bicyclo[2.2.2]-octane (**9**, $X_{1-3}$=F) with the 4′-pentyl-3,4,5-trifluoroterphenyl (**10**) [39] and the 1-(4-[*trans*-4-pentylcyclohexyl]phenyl)-3,4,5-trifluorobenzene (**11**) [5] differing only in the presence of a 1,4-disubstituted phenyl, cyclohexyl and bicyclo[2.2.2]octyl rings. The terphenyl **10** showed the highest melting point and clearing point. The lowest values for phase transition temperatures were observed for the compound **11** containing the *trans*-1,4-disubstituted cyclohexane ring. Unusually the bicylcooctane derivative (**9**, $X_{1-3}$=F) exhibits an intermediate value of the nematic clearing point between that of the analogous phenyl and cyclohexane derivatives **10** and **11**, respectively. Such bicyclcooctane derivatives usually exhibit the highest nematic clearing points of such series differing only in the nature in the presence of a 1,4-disubstituted phenyl, cyclohexyl and bicyclo[2.2.2]octyl rings [11, 20].

## 4. Conclusion

An updated order of terminal group efficiency for the nematic phase has been established for liquid crystals with substituents in a terminal position of incorporating the trifluoromethyl and trifluoromethoxy groups. These polyfluorinated groups induce a low value of the clearing point of the nematic phase. This may be due to a low degree of symmetry of the HOMO of these molecules incorporating these groups. It is suggested that the spatial distribution of charge should be taken into account, along with molecular properties such as the anisotropy of polarizability and shape, in theories of the nematic phase.

Table 6. Phase transition temperatures (°C) of the terphenyl **10**, cyclohexane **11** and bicyclo[2.2.2]octane **9** ($X_{1-3}$=F) with the same fluorine substituents, but with different 1,4-disubstituted rings X attached to the pentyl chain.



| Compound | Ring X | Cr | | N | | I |
|---|---|---|---|---|---|---|
| **10** |  | • | 94$^a$ | • | 97$^a$ | • |
| **11** |  | • | 31$^b$ | • | 58$^b$ | • |
| **9** |  | • | 67 | • | 78 | • |

$^a$Literature value [38]; $^b$literature value [5].

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