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Six series of laterally fluorinated liquid crystals containing 1,3,2-dioxaborinane and cyclohexyl units have been synthesized and characterized. Their mesomorphic properties were characterized by polarizing optical microscopy and differential scanning calorimetry. All these compounds are thermotropic liquid crystalline materials. All three-ring compounds (series **A**, **B** and **C**) and most four-ring compounds (series **D**, **E** and **F**) exhibit only a nematic phase, while some four-ring compounds with long terminal alkyl chains show nematic, smectic A and even smectic B phases. In addition, four compounds containing a 1,3-dioxane unit were prepared, and their mesomorphic properties compared with their 1,3,2-dioxaborinane analogues. The dielectric anisotropies of selected target compounds were determined; some showed a negative anisotropy. The relationships between the properties and chemical structures of these new compounds are discussed.

1. Introduction

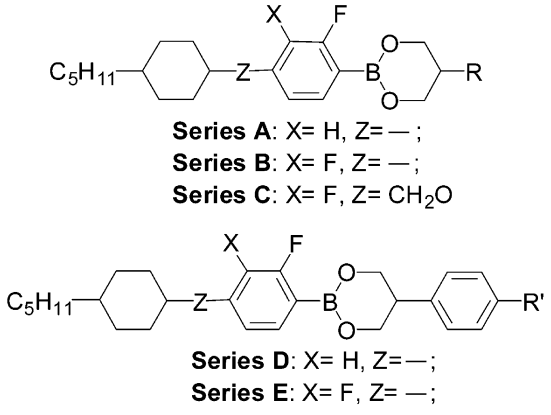
Laterally fluorinated liquid crystals have for many years been a focus of considerable research [1, 2]. One major advantage of such materials is that they may exhibit negative dielectric anisotropy and, at the same time, show low viscosities. Most of these liquid crystals possess phenyl, cyclohexyl or dioxane rings in their core structures.

The 1,3,2-dioxaborinane unit has been studied several times as a liquid crystal core structure [3–8]. These compounds either do not possess lateral fluorine atoms or show positive dielectric anisotropy. Only a few compounds containing 2,3-difluorophenyl and 1,3,2-dioxaborinane units have been reported on previously, and all were based on terphenyl systems [1, 9, 10]. In order to obtain liquid crystal materials with negative dielectric anisotropy, broad nematic temperature ranges and low viscosity, and to establish the relationships between structures and properties in this class of material, we have synthesized six novel series of compounds. The general structures of these systems are shown in scheme 1 (series **A**–**F**).

2. Experimental

2.1. *Characterization*

The structures of the final products and intermediates were confirmed by infrared spectroscopy (Nicolet 560 spectrophotometer), ^{1}H NMR spectroscopy (Bruker 300 spectrometer, where the spectra, unless otherwise stated, were recorded in $CDCl_3$ using Me_4Si as an internal standard; the *J* values are given in Hz), and mass spectrometry (AEIMS-50 SD90 spectrometer). The phase transition temperatures of the target compounds were determined by polarizing optical



Scheme 1. The structures of the target compounds.

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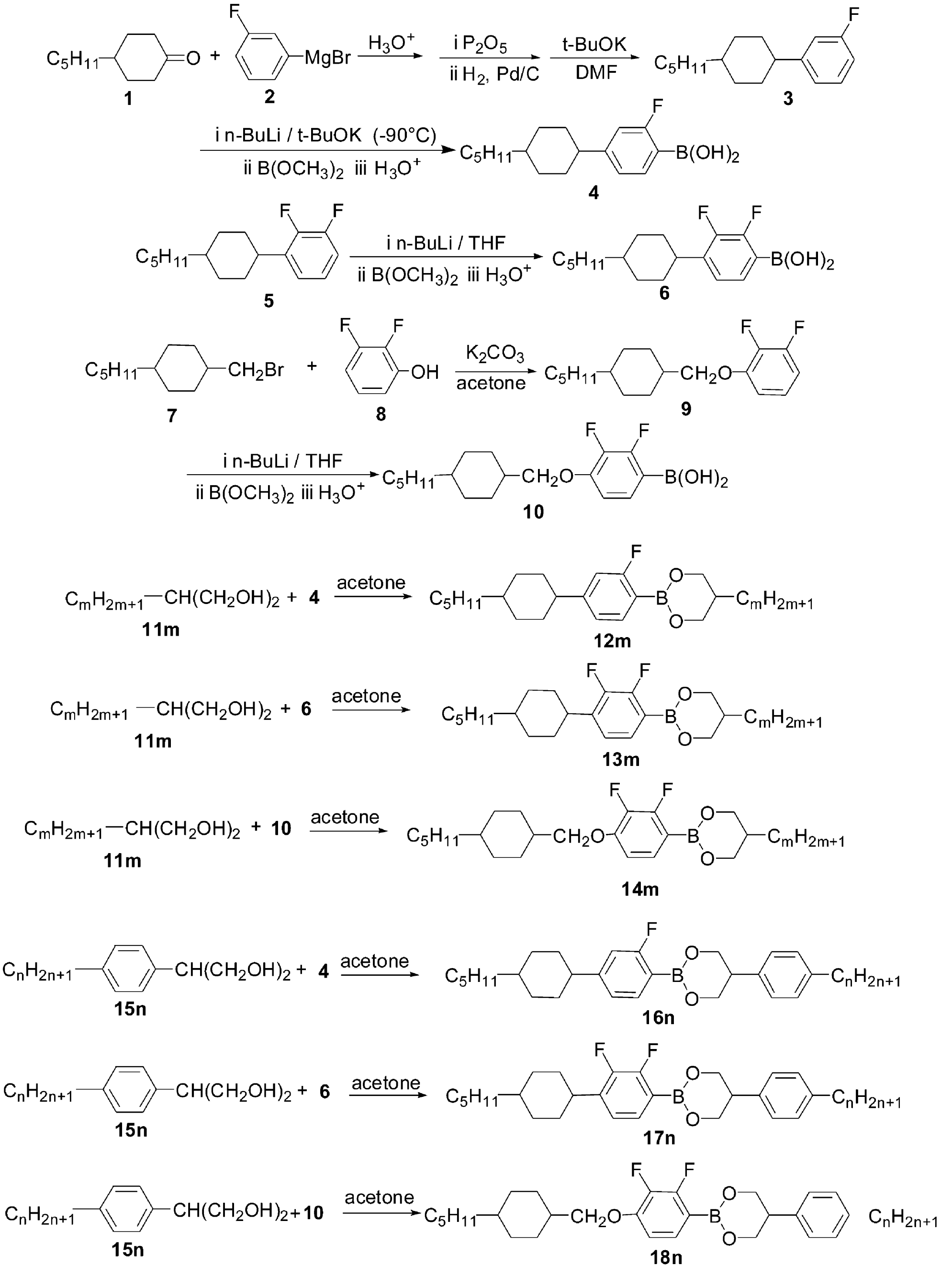
microscopy using a polarizing microscope (Olympus PM-10AD) fitted with a heating stage (Mettler FP-80) and control unit (FP-82), and by differential scanning calorimetry (Mettler DTA TA-2010 DSC heating and cooling rate 10°C min^{-1}). Phase identification was made by comparing the observed textures with those reported in the literature [11, 12]. Elemental analysis for carbon and hydrogen were determined using a Heraeus CHN-O-Rapid elemental analyser. The purity of each final compound was determined by HPLC (Hypersil OD52 C18 Reverse Phase Column 250 × 4.6 mm) and found to be >99%.

2.2. *Synthesis*

The target compounds were prepared according to the procedures detailed in scheme 2. The *trans*-isomer **3** was synthesized by the following procedure. Firstly, the Grignard reagent **2** was quenched with 4-pentylcyclohexone



Scheme 2. Synthetic routes to the target materials.

1, and then hydrolysed with hydrochloric acid; secondly, the resulting benzylic alcohol was dehydrated with phosphorus pentoxide for 10 h in a hexane solution; thirdly, the alkene was hydrogenated using palladium-carbon as catalyst; and finally, the *cis–trans* mixture was treated with a solution of potassium *tert*-butoxide in DMF [13, 14]. The *trans*-isomer **5** was obtained by the published procedures from 2,3-difluorobenzene [13]. The carboxylic acid was directly reduced in excellent yield using lithium aluminium hydride to give the cyclohexylmethanol derivative, and then the bromide **7** was prepared with partial success using a hydrobromic acid and sulphuric acid mixture [15]. Ether **9** was prepared from the crude bromide **7** and 2,3-difluorophenol **8** in an alkylation procedure using potassium carbonate and acetone [15]. The acidic ions of **3**, **5** and **9** were prepared with *n*-butyllithium at $-78°C$ and the lithium salt was quenched with trimethyl borate to give boronic acids **4**, **6** and **10** [13, 16]. Compounds **11**$_m$ were prepared by reported methods from diethyl malonate [17]. Compounds **12**$_n$ were synthesized from 1-(4-alkylphenyl)ethanone via a five-step process, namely Willgerodt reaction, hydrolysis, esterification, condensation reaction and reduction with sodium borohydride [18]. In order to compare the properties of these new materials with those of analogous derivatives of 1,3-dioxane, compounds **20**$_m$ and **21**$_n$ were also synthesized, see scheme 3.

All homologues were prepared using the same methods and therefore general experimental procedures are illustrated for compounds **12**$_5$, **13**$_5$, **14**$_5$, **16**$_5$, **17**$_5$, **18**$_5$, **20**$_5$ and **21**$_5$ as representative examples.

2.2.1. *2,5-Diaryl-1,3,2-dioxaborinanes*

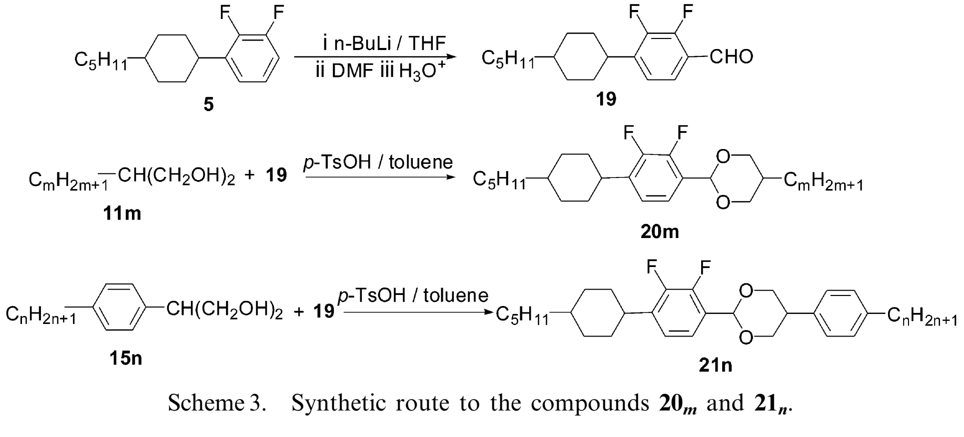
This is a general Procedure. A mixture of substituted phenylboronic acid (**4**, **6** or **10**, 1 mmol), 2-substituted-1, 3-propanediol (**11**$_m$ or **15**$_n$, 1 mmol) in acetone (25 ml) was heated under reflux for 2 h. When the reaction was complete, acetone was distilled away. The resultant residue was purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl ester (5/1) as eluant; this gave white crystals which were recrystallized from petroleum ether (b.p. 60–90°C) to yield white crystals of the corresponding products 12$_m$, **13**$_m$, **14**$_m$, **16**$_n$, **17**$_n$ or **18**$_n$.

2.2.2. *2-[4-(trans-4-n-Pentylcyclohexyl)-2-fluorophenyl]-5-pentyl-1,3,2-dioxaborinane (**12**$_5$)*

Yield 0.22 g, 55%; purity (HPLC) 99.6%; m.p. 85.7°C. Elemental analysis: calculated (found) for $C_{25}H_{40}BFO_2$ C 74.62 (74.73), H 10.02 (9.99). IR (KBr) ν_{max}: 2926, 2870, 1620, 1427, 1306, 1165, 1084, 933, 868, 831 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.89 (6H, t, $J=7.5$), 1.00–1.56 (21H, m), 1.85 (4H, m), 2.09 (1H, m), 2.42 (1H, t, $J=12.5$), 3.77 (2H, t, $J=10.5$), 4.19 (2H, dd, $J=4.5$), 6.84 (1H, d), 6.95 (1H, d), 7.59 (1H, t). MS *m*/*z*: 402 (M^+, 83%), 407, 331, 276 (100%), 263, 135, 81.

2.2.3. *2-[4-(trans-4-n-Pentylcyclohexyl)-2,3-difluorophenyl]-5-pentyl-1,3,2-dioxaborinane (**13**$_5$)*

Yield 0.19 g, 45%; purity (HPLC) 99.0%; m.p. 58.3°C. Elemental analysis: calculated (found) for $C_{25}H_{39}BF_2O_2$ C 71.43 (71.48), H 9.35 (9.29). IR (KBr) ν_{max}: 2926, 2856, 1628, 1448, 1311, 1155, 1055, 947, 868, 825, 671 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.90 (6H, t, $J=7.0$), 1.05–1.58 (19H, m), 1.86 (4H, d, $J=13.5$), 2.09 (2H, m), 2.85 (1H, t, $J=10.5$), 3.32 (1H, m), 3.78 (2H, t, $J=10.5$), 4.20 (2H, dd, $J=4.5$), 6.95 (1H, t), 7.34 (1H, t). MS *m*/*z*: 420 (M^+, 85%), 308, 294 (100%), 281, 153, 81, 55.



Scheme 3. Synthetic route to the compounds **20**$_m$ and **21**$_n$.

2.2.4. *2-[4-(trans-4-n-Pentylcyclohexylmethoxy)-2,3-difluorophenyl]-5-pentyl-1,3,2-dioxaborinane (**14**$_5$)*

Yield 0.24 g, 53.3%; purity (HPLC) 99.5%; m.p. 78.3°C. Elemental analysis: calculated (found) for $C_{26}H_{41}BF_2O_3$ C 69.33 (69.17), H 9.17 (9.03). IR (KBr) ν_{max}: 2920, 2852, 1630, 1458, 1300, 1213, 866, 806, 721, 667 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ: 0.87 (6H, m, $J=7.0$), 0.90–1.57 (22H, m), 1.80 (2H, d, $J=13.5$), 2.00 (2H, d, $J=13.5$), 2.10 (1H, m), 3.80 (4H, m), 4.19 (2H, dd, $J=4.5$), 6.68 (1H, t), 7.35 (1H, t). MS *m*/*z*: 450 (M$^+$, 24%), 284 (100%), 166, 110, 95, 81, 55.

2.2.5. *2-[4-(trans-4-n-Pentylcyclohexyl)-2-fluorophenyl]-5-(4-pentylphenyl)-1,3,2-dioxaborinane (**16**$_5$)*

Yield 0.36 g, 75%; purity (HPLC) 99.7%; m.p. 91.5°C. Elemental analysis: calculated (found) for $C_{31}H_{44}BFO_2$ C 77.81 (77.61), H 9.27 (9.39). IR (KBr) ν_{max}: 2922, 2850, 1620, 1427, 1304, 1159, 1092, 1030, 868, 833 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ: 0.90 (6H, t, $J=7.5$), 1.05–1.61 (19H, m), 1.86 (4H, m), 2.47 (1H, t, $J=13.5$), 2.59 (2H, t, $J=7.5$), 3.31 (1H, m), 4.27 (4H, m, $J=10.5$ and $J=5.0$), 6.85 (1H, d), 6.97 (1H, d), 7.16 (4H, dd), 7.64 (1H, t). MS *m*/*z*: 478 (M$^+$, 70%), 407, 352, 174, 118 (100%), 91.

2.2.6. *2-[4-(trans-4-n-Pentylcyclohexyl)-2,3-difluorophenyl]-5-(4-pentylphenyl)-1,3,2-dioxaborinane (**17**$_5$)*

Yield 0.34 g, 69%; purity (HPLC) 99.1%; m.p. 99.9°C. Elemental analysis: calculated (found) for $C_{31}H_{43}BF_2O_2$ C 75.00 (74.83), H 8.73 (8.64). IR (KBr) ν_{max}: 2924, 2854, 1630, 1448, 1311, 1153, 1039, 949, 883, 827 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ: 0.90 (6H, t, $J=7.0$), 1.06–1.64 (19H, m), 1.87 (4H, d, $J=13.5$), 2.59 (2H, t, $J=7.5$), 2.85 (1H, t, $J=10.5$), 3.32 (1H, m), 4.26 (4H, m, $J=10.5$ and $J=5.0$), 6.96 (1H, t), 7.17 (4H, dd), 7.38 (1H, t). MS *m*/*z*: 496 (M$^+$, 87%), 438, 370, 174, 117 (100%), 91.

2.2.7. *2-[4-(trans-4-n-Pentylcyclohexylmethoxy)-2,3-difluorophenyl]-5-(4-pentylphenyl)-1,3,2-dioxaborinane (**18**$_5$)*

Yield 0.31 g, 59%; purity (HPLC) 99.4%; m.p. 97.7°C. Elemental analysis: calculated (found) for $C_{32}H_{45}BF_2O_3$ C 73.00 (73.13), H 8.61 (8.64). IR (KBr) ν_{max}: 2922, 2850, 1626, 1462, 1298, 1215, 1088, 1034, 885 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ: 0.87 (6H, m, $J=7.0$), 0.90–1.57 (20H, m), 1.87 (4H, dd, $J=13.5$), 2.59 (2H, t, $J=7.5$), 3.32 (1H, m), 3.85 (2H, d, $J=7.5$), 4.26 (4H, m, $J=10.5$ and $J=5.0$), 6.97 (1H, t), 7.16 (4H, dd), 7.37 (1H, t). MS *m*/*z*: 526 (M$^+$, 5%), 360, 174, 117 (100%), 91.

2.2.8. *2,3-Difluoro-4-trans-(4-n-pentyl)cyclohexylbenzaldehyde (**19**)*

n-Butyllithium (70 ml, 2.8 M in hexane, 0.20 mol) was added dropwise to a stirred, cooled (−78°C) solution of compound **5** (43 g, 0.16 mol) in dry THF (400 ml) under an atmosphere of dry nitrogen. The reaction mixture was stirred for 1.5 h, then a previously cooled (−78°C) solution of DMF (16 ml, 0.20 mol) in dry THF (40 ml) was added dropwise at −78°C. The reaction mixture was allowed to warm to room temperature then stirred for 1 h with hydrochloric acid (10%, 250 ml). The product was taken up in ether (2 × 150 ml), and the combined ether extracts were washed with water (2 × 200 ml) and dried (Na$_2$SO$_4$). The solvent was removed *in vacuo* and the pure product isolated by recrystallization from hexane; yield 22.5 g, 48%. ^{1}H NMR (CDCl$_3$) δ: 0.91 (3H, t, $J=6.5$), 1.12 (2H, m), 1.27 (6H, m), 1.52 (2H, m),1.75 (3H, m), 1.90 (4H, m, $J=7.0$), 2.91 (1H, t, $J=12.6$), 7.12 (1H, d), 7.57 (1H, d), 10.21 (1H, s).

2.2.9. *2,5-Diaryl-1,3-dioxanes*

This is a general Procedure. A mixture of 2,3-difluoro-4-*trans*-(4-*n*-pentyl)cyclohexylbenzaldehyde (**19**), 2-substituted-1,3-propanediol (**11**$_m$ or **15**$_n$, 1 mmol), dry toulene (50 ml) and ***p***-toluenesulphonic acid (5 mg) was heated under reflux for 6 h using a Dean and Stark trap to remove water. After cooling to room temperature, the mixture was poured into aqueous sodium hydrogen carbonate (10%, 50 ml). The separated organic layer was washed with water (2 × 50 ml) and dried (Na$_2$SO$_4$). The solvent was removed ***in vacuo*** and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl ether (20/1) as the eluant, to give pale yellow crystals which were recrystallized twice from petroleum ether (b.p. 60–90°C) to yield white crystals of compounds **20**$_m$ or **21**$_n$.

2.2.10. *2-[4-(trans-4-n-Pentylcyclohexyl)-2,3-difluorophenyl]-5-pentyl-1,3-dioxane (**20**$_5$)*

Yield 0.16 g, 38%; purity (HPLC) 99.1%; m.p. 51.2°C. Elemental analysis: calculated (found) for $C_{26}H_{40}F_2O_2$ C 73.90 (73.73), H 9.54 (9.69). IR (KBr) ν_{max}: 2926, 2850, 1637, 1468, 1400, 1126, 1018, 897, 818 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ: 0.89 (6H, t, $J=7.5$), 1.03–1.57 (21H, m), 1.86 (4H, m), 2.14 (1H, m), 2.79 (1H, t, $J=12.0$), 3.55 (2H, t, $J=10.5$), 4.22 (2H, dd,

$J=4.5$), 5.67 (1H, s), 7.00 (1H, t), 7.31 (1H, t). MS *m*/*z*: 422 (M^+, 68%), 295 (100%), 167, 153, 127, 81, 55.

2.2.11. *2-[4-(trans-4-n-Pentylcyclohexyl)-2,3-difluorophenyl]-5-(4-pentylphenyl)-1,3-dioxane (**21$_5$**)*

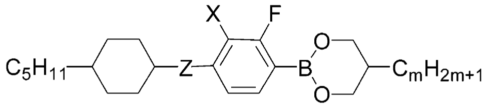
Yield 0.26 g, 52%; purity (HPLC) 99.4%; m.p. 84.3°C. Elemental analysis: calculated (found) for $C_{32}H_{44}F_2O_2$ C 77.07 (77.23), H 8.89 (8.74). IR (KBr) ν_{max}: 2924, 2852, 1637, 1468, 1402, 1144, 1097, 1017, 982, 899, 818 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.91 (6H, t, $J=7.5$), 1.05–1.65 (19H, m), 1.85 (4H, m), 2.60 (2H, t, $J=7.5$), 2.80 (1H, t, $J=12.0$), 3.36 (1H, m), 4.05 (2H, t, $J=10.5$), 4.36 (2H, dd, $J=4.5$), 5.86 (1H, s), 7.04 (1H, t), 7.17 (4H, m), 7.39 (1H, t). MS *m*/*z*: 498 (M^+, 59%), 350, 293, 174 (100%), 117, 91.

3. Results and discussion

Six series of laterally fluorinated liquid crystals containing 1,3,2-dioxaborinane and cyclohexyl units were synthesized. All these compounds exhibit liquid crystalline behaviour. The transition temperatures of series **A**, **B** and **C** are shown in table 1 and represented graphically in figure 1.

It is interesting that there are several similarities in the phase behaviour of series **A**, **B** and **C**. All these compounds show only the nematic phase. On increasing the length of the terminal alkyl chain (*m*) across each series, the melting and the clearing points show a similar trend: specifically they increase initially, then decrease and finally increase again. Compound **12$_5$**, against our expectations, shows the highest melting point and the narrowest nematic temperature range of series **A**, whereas the other two middle ($m=5$) compounds **13$_5$** and **14$_5$** exhibit the broadest nematic temperature ranges in series **B** and **C**, respectively. It is interesting that the compounds with the shortest alkyl chains, **12$_3$**, **13$_3$** and **14$_3$**, have the lowest melting and clearing points in series **A**, **B** and **C**, respectively. This may be because they possess the lowest length/width ratios in their respective series. In all cases, materials with equivalent alkyl chains were compared. Table 1 and figure 1 clearly show that the melting and clearing points of series **B** are lower than those of series **A**, and that temperature ranges of the nematic phase of series **B** are narrower than those of series **A** except for compounds **12$_5$** and **13$_5$**. This is the result of an increase in the number of lateral fluoro-substituents. Although the two fluorines are on the same side of one phenyl ring and the width of the molecule does not obviously increase, the intermolecular distances and forces may have changed. The melting points of series **C** are clearly higher than those of series **B**, whereas the clearing

Table 1. Transition temperatures of series **A**, **B** and **C** compounds. Cr = crystal; N = nematic phase; I = isotropic liquid.



Compound				Transition temperatures/°C				
No.	*m*	*X*	*Z*	Cr		N		I
12$_3$	3	H	—	●	61.5	●	95.8	●
12$_4$	4	H	—	●	67.7	●	110.4	●
12$_5$	5	H	—	●	85.7	●	116.9	●
12$_6$	6	H	—	●	69.0	●	110.6	●
12$_7$	7	H	—	●	72.3	●	115.1	●
13$_3$	3	F	—	●	54.6	●	79.4	●
13$_4$	4	F	—	●	68.0	●	97.1	●
13$_5$	5	F	—	●	58.3	●	106.0	●
13$_6$	6	F	—	●	57.9	●	92.9	●
13$_7$	7	F	—	●	68.6	●	100.9	●
14$_3$	3	F	CH_2O	●	69.7	●	80.8	●
14$_4$	4	F	CH_2O	●	80.8	●	92.5	●
14$_5$	5	F	CH_2O	●	78.3	●	102.8	●
14$_6$	6	F	CH_2O	●	77.0	●	96.2	●
14$_7$	7	F	CH_2O	●	79.9	●	102.1	●

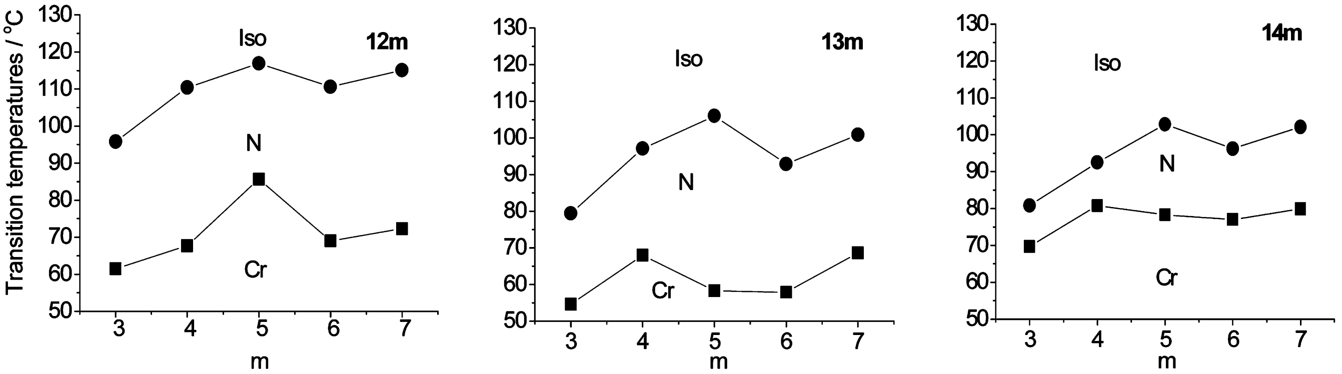
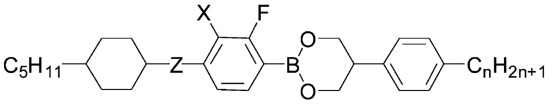


Figure 1. Transition temperature vs. *m* for compounds **12$_m$**, **13$_m$** and **14$_m$**.

Table 2. Transition temperatures of series **D**, **E** and **F** compounds. Cr = crystal; SmB = smectic B phase; SmA = smectic A phase; N = nematic phase; I = isotropic liquid.



No.	*n*	*X*	*Z*	Cr		SmB		SmA		N		I
16$_2$	2	H	—	•	138.7	—		—		•	210.7	•
16$_3$	3	H	—	•	133.3	—		—		•	222.7	•
16$_4$	4	H	—	•	99.7	—		—		•	210.0	•
16$_5$	5	H	—	•	91.5	—		—		•	209.2	•
16$_7$	7	H	—	•	97.6	—		•	137.2	•	194.1	•
16$_9$	9	H	—	•	89.3	•	120.7	•	159.1	•	182.7	•
17$_2$	2	F	—	•	116.8	—		—		•	198.6	•
17$_3$	3	F	—	•	115.9	—		—		•	208.2	•
17$_4$	4	F	—	•	84.7	—		—		•	191.6	•
17$_5$	5	F	—	•	99.9	—		—		•	196.1	•
17$_7$	7	F	—	•	76.0	—		•	141.3	•	184.1	•
17$_9$	9	F	—	•	66.7	—		•	148.7	•	180.6	•
18$_2$	2	F	CH_2O	•	110.6	—		—		•	179.2	•
18$_3$	3	F	CH_2O	•	118.9	—		—		•	187.0	•
18$_4$	4	F	CH_2O	•	94.6	—		—		•	174.7	•
18$_5$	5	F	CH_2O	•	97.7	—		—		•	177.5	•
18$_7$	7	F	CH_2O	•	98.1	—		•	144.9	•	170.4	•
18$_9$	9	F	CH_2O	•	106.0	—		•	157.3	•	164.6	•

points of these two series are very close. This may be explained by the fact that the three-ring core structure has been broken by the methoxy unit, which decreases the liquid crystal stability.

In order to obtain liquid crystals with wide mesomorphic temperature ranges, the four-ring series **D**, **E** and **F** were synthesized. Their transition temperatures are shown in table 2 and represented graphically in figure 2.

There are also several similarities in the phase behaviour of series **D**, **E** and **F**. On increasing the length of the terminal alkyl chain (*n*) across each series, the clearing points decrease steadily and exhibit a clear odd–even effect, while the width of the nematic temperature range first increases and then decreases. In addition, when the alkyl chain length is short ($n \leqslant 5$), the melting points of each series also decrease steadily and exhibit a clear odd–even effect. However, on increasing the alkyl chain length ($n \geqslant 5$), the trends in melting points of these three series of compounds are obviously different: for series **D**, the melting point first increases and then decreases; for series **E**, it decreases steadily; while for series **F**, it increases steadily. As far as the phase behaviour is concerned, when the alkyl chain length is short, only a nematic phase is observed; while on increasing, the alkyl chain length smectic phases appear. This is due to the greater lateral intermolecular attractive forces and the smaller terminal intermolecular attractions. It is well known that lateral fluoro-substitution not only depresses the clearing points but also suppresses the formation of more ordered mesophases. Thus the clearing points of series **E** are lower than those of series **D** and no smectic B phase is seen in series **E** [19]. Comparing the mesomorphic properties of series **E** and **F**, it is easy to see that the clearing points of series **F** are lower than those of series **E** and also the liquid crystal temperature ranges of series **F** are narrower than those of series **E**. As discussed previously, the disruption of the four-ring core structure by the methoxy unit, caused the liquid crystal stability to decrease. Figures 1 and 2 clearly show that the liquid crystal temperature ranges of the four-ring compounds are much wider than those of the corresponding members of series **A**, **B** and **C**, and that their melting and clearing points are also clearly higher. In addition, the mesomorphic behaviour of series **D**, **E** and **F** is considerably more complex than that of series **A**, **B** and **C**. As stated previously, only the nematic phase is shown by the three-ring compounds, whereas

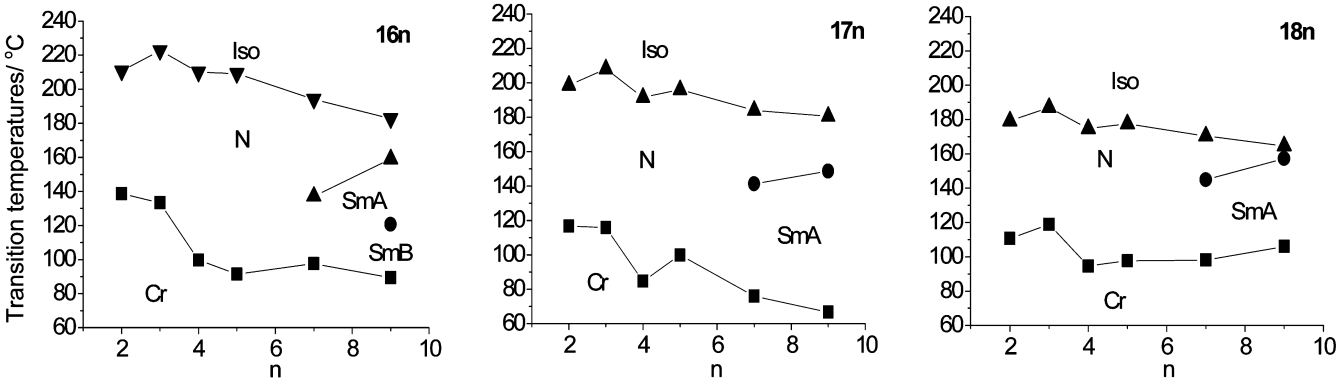
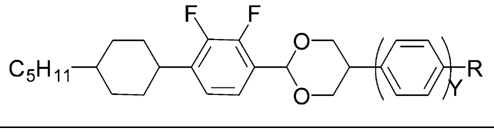


Figure 2. Transition temperature vs. *n* for compounds **16**$_n$, **17**$_n$ and **18**$_n$.

Table 3. Transition temperatures of compounds **20_m** and **21_n**. Cr = crystal; N = nematic phase; I = isotropic liquid.



Compound			Transition temperatures/°C				
No.	*Y*	*R*	Cr		N		I
20_4	0	C_4H_9	●	64.8	●	95.6	●
20_5	0	C_5H_{11}	●	51.2	●	103.1	●
21_4	1	C_4H_9	●	85.6	●	211.2	●
21_5	1	C_5H_{11}	●	84.3	●	208.8	●

smectic A and even smectic B phases are exhibited by some four-ring compounds.

The transition temperatures of compounds **20_m** and **21_n** are shown in table 3. These four compounds were synthesized in order to compare the mesomorphic properties of compounds containing 1,3,2-dioxaborinane units with their 1,3-dioxane analogues. From tables 1, 2 and 3, it can be seen that the melting and clearing points of the corresponding compounds are close, especially for three-ring compounds. This is surprising, because there are clear differences in mesomorphic properties between previously reported compounds containing these two heterocyclic units [8]. Generally, the liquid crystal stability of dioxaborinane derivatives is much lower than their corresponding dioxane analogues [8].

In order to determine the other properties of these materials, eight compounds (**12_5**, **13_5**, **14_5**, **16_5**, **17_5**, **18_5**, **20_5** and **21_5**) were selected for the measurement of dielectric anisotropy by a guest–host method [20]. The dielectric constants of TEB-5008 (liquid crystal mixture for TN-LCD, produced by Qinghua Yawang Liquid Crystal Materials Co. Ltd., China), and of a mixture containing TEB-5008 and 10 wt% of each selected compound, were measured at 20°C (HP 4284A Precision LCR Meter, 1 kHz). The extrapolated dielectric anisotropy values of each pure compound are shown in table 4.

Table 4. Dielectric anisotropy ($\Delta\varepsilon$) of some selected compounds.

Compound	$\varepsilon_{/\!/}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
12_5	4.26	4.27	−0.01
13_5	5.73	6.53	−0.80
14_5	7.28	9.44	−2.16
16_5	4.49	3.82	+0.67
17_5	5.34	5.57	−0.23
18_5	6.08	7.79	−1.71
20_5	4.54	4.99	−0.45
21_5	4.97	4.82	+0.15

As the table shows, the dielectric anisotropies values of all these compounds are clearly different. The dielectric anisotropies of three-ring compounds are lower than those of their four-ring analogues, with the perpendicular absolute dipole moments being similar but the axial absolute dipole moments of the four-ring compounds being larger. The $\Delta\varepsilon$ values of lateral fluoro-substituted compounds containing two substituents are lower than those of their monofluoro-substituted analogues. This can also be explained in terms of the absolute dipole moment: on adding the lateral fluoro-substituent, the perpendicular absolute dipole moment will obviously increase. Compound **16_5** has only one lateral fluoro-substituent and has four rings in its core structure, so its dielectric anisotropy value is the highest, and even positive. The dielectric anisotropy values of the other five new compounds containing 1,3,2-dioxaborinane units are all negative. The $\Delta\varepsilon$ of compounds **14_5** and **18_5** are clearly lower than those of **13_5** and **17_5**, respectively, which is due to the methoxy unit. It is interesting to note that the $\Delta\varepsilon$ of compounds **13_5** and **17_5** are lower than those of their dioxane analogues. This may be explained in steric and electronic terms. The boronation has only three electrons in its *p*-orbital, and thus the boron in 2,5-substituted-1,3,2-dioxaborinane has an empty *p*-orbital, which can form a conjugated system with the adjacent phenyl ring and two oxygen heteroatoms and a fixed geometry. This might induce the increase of the perpendicular absolute dipole moment.

4. Conclusions

We have synthesized 37 new compounds belonging to eight homologous series and studied their mesomorphic properties. The effects of alkyl chain length, fluoro substitution, and core structure, i.e. 1,3,2-dioxaborinane or dioxane units, on the thermal behaviour of the compounds are discussed. Series **A**, **B** and **C** compounds exhibit low melting points and only a nematic phase, as well as negative dielectric anisotropies. Series **D**, **E** and **F** compounds exhibit high clearing points and a broad mesomorphic phase. These new materials might be suitable for application in nematic liquid crystal mixtures for use in LCDs.

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