Interfacial layer interactions: their effects on synclinic and anticlinic smectic mesophase behaviour in liquid crystals†

Stephen J. Cowling* and John W. Goodby

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Through the use of bulky cyclic terminal groups, anticlinic smectic C phases have been observed in 2-methylbutyl materials based on the MHPOBC motif.

Since the first discovery by Meyer *et al.*[1] of a liquid crystal which exhibited ferroelectric behaviour where the lath-like molecules are tilted in the same direction in layers (synclinic), research into ferroelectric liquid crystals has predominantly concentrated on investigations involving changes to the central core geometries of mesogenic materials or by varying the length of the terminal aliphatic or chiral aliphatic chain (tail), resulting in a number of detailed reviews of ferroelectric LCs being reported.[2] Classical investigations of ferroelectric LCs have led to a number of interesting phenomena being discovered including spontaneous polarisation inversion[3] as a function of temperature and the discovery of novel mesophases such as the Twist Grain Boundary (TGB) phase,[4] and antiferroelectric and ferrielectric subphases of the smectic C phase.[5] Extensive research in the area of ferro- and anti-ferroelectric LCs has provided for a number of property–structure–activity relationships to be developed for materials based on the central core structures, shown in Fig. 1.

Typically these cores were substituted with chiral end-groups such as 1-methylalkyl[6] and 1-trifluoromethylalkyl.[7] In some cases a methoxy or an ethoxy group was located at the terminal position of the chiral tail.[8] The 1-methylheptyl substituted systems predominantly exhibit antiferroelectric (anticlinic) phases, with many materials also exhibiting novel "V"-shaped switching in electrooptic experiments, which have been used in prototype display devices.

There have not been many studies which examine the effects of the interfaces between the smectic layers. In order for the formation of various types of smectic phase behaviour there has to be a transfer of structural information[9] across the interlayer interface between the diffuse smectic layers. In a recent publication[10] we demonstrated that through the inclusion of bulky alicyclic rings at the ends of the molecules it was possible to weaken the interlayer interactions and induce TGB phases. We have also demonstrated that it is possible to generate high tilt anticlinic phases *via* the inclusion of polar fluorinated end groups, and we have shown how the inclusion of a single hydrogen atom in a fluorinated chain causes extreme disruption to the mesophase formation[11] compared to their purely perfluorinated analogues.

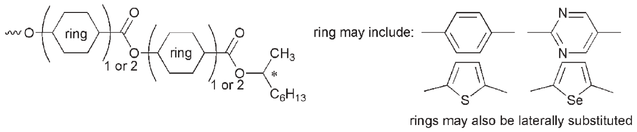


Fig. 1 General structure of ferroelectric/antiferroelectric liquid crystals.

In this article we demonstrate that through the inclusion of an ether-linked cyclobutane or oxetane ring at the terminal position of a terminal chain, see Fig. 2, it is possible to promote the formation of anticlinic behaviour in compounds containing the weakly polar and less sterically hindered chiral 2-methylbutyl moiety. We also show that there is a marked odd/even effect which either promotes synclinic or anticlinic behaviour. As a basis of reference it was also necessary to prepare conventional materials of equivalent structure and chain length to those with terminal ring structures. For this purpose compounds of series **1** were prepared. In all of the series presented we also incorporated lateral fluoro substituents in the core in order to moderate the lateral molecular interactions.

The synthetic route for the preparation of compounds from series 1 is shown in Scheme 1 and the synthetic route for the preparation of compounds from series 2 and 3 is shown in Scheme 2. For the sake of brevity, the full synthetic details are given in the ESI.†

Compound **1** was alkylated using an alkyl bromide with potassium carbonate as the base in butanone. The methyl protecting group was removed by hydrolysis to give carboxylic acid **3**. The final step to give compounds **1.1–1.6** was an esterification with compound **4** using dicyclohexylcarbodiimide (DCC) and *N*, *N*′-dimethylaminopyridine (DMAP). The synthesis of compound **4** has been reported previously.[12] The synthesis of compounds **2.1–2.6** required the preparation of 1-methylcyclobutanemethanol (**7**). This was achieved by derivatisation using methyl iodide and LDA to give **6** followed by reduction of the carboxylic acid using lithium aluminium hydride to give alcohol **7**. From this point, the preparation of compounds **2.1–2.6** and **3.1–3.6** followed the same synthetic pathway. Compounds **9** and **10**

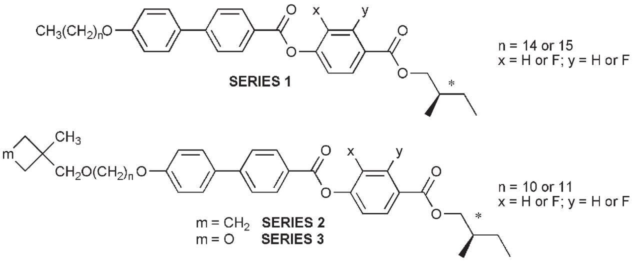
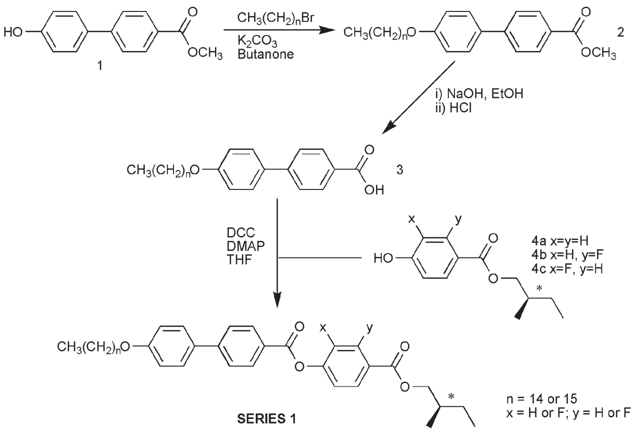


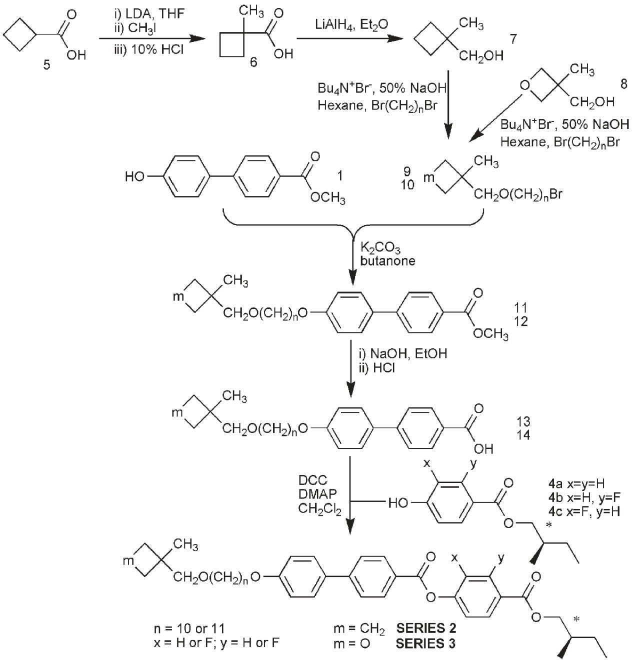
Fig. 2 Structures of compounds of series **1–3**.

Department of Chemistry, University of York, Heslington Road, York, UK YO10 5DD. E-mail: sc520@york.ac.uk; jwg500@york.ac.uk; Fax: +44 (0)1904 432592; Tel: +44 (0)1904 432539

† Electronic supplementary information (ESI) available: Full synthetic details for the synthesis of compounds of series **1**, **2** and **3**. See DOI: 10.1039/b610154b

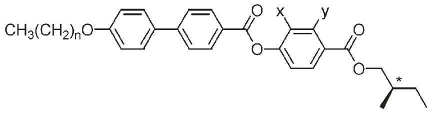


Scheme 1 Preparation of alkoxy compounds of series **1**.



Scheme 2 Preparation of compounds of series **2** and **3**.

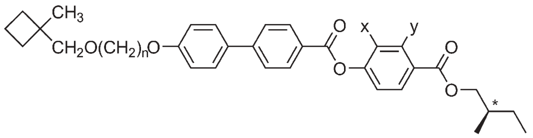
Table 1 Structure and transition temperature of series **1**



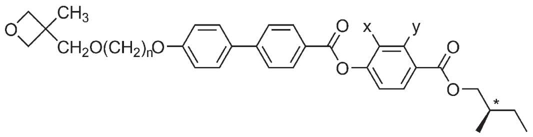
Compd	*n*	x	y	Transition temperatures[a]/°C
1.1	14	H	H	K 82.2 C* 127.4 A 168.2 Iso
1.2	14	H	F	K 60.7 C* 123.7 A 165.8 Iso
1.3	14	F	H	K 72.7 C* 99.9 A 139.3 Iso
1.4	15	H	H	K 73.7 C* 127.6 A 167.3 Iso
1.5	15	H	F	K 53.1 C* 122.5 A 164.8 Iso
1.6	15	F	H	K 71.0 C* 98.1 A 138.5 Iso

[a] In the table A is smectic A, C* is smectic C*.

Table 2 Structure and transition temperature of series **2** and **3**



Compd	*n*	x	y	Transition temperatures[a]/°C
2.1	10	H	H	K 32.8 C* 125.7 A 146.7 Iso
2.2	10	H	F	K 41.8 C* 123.9 A 147.6 Iso
2.3	10	F	H	K 36.1 C* 101.5 A 115.7 Iso
2.4	11	H	H	K 59.4 C_A* 88.9 C* 124.0 A 146.8 Iso
2.5	11	H	F	K 38.2 C_A* 89.8 C* 119.3 A 145.7 Iso
2.6	11	F	H	K 68.1 C* 101.2 A 117.1 Iso



Compd	n	X	y	Transition temperatures[a]/°C
3.1	10	H	H	K −5.6 C* 101.3 A 135.3 Iso
3.2	10	H	F	K −20.1 C* 98.9 A 143.7 Iso
3.3	10	F	H	K 31.3 C* 54.7 A 108.0 BP 111.2 Iso
3.4	11	H	H	K 52.0 C_A* 70.0 C* 104.5 A 130.5 Iso
3.5	11	H	F	K 32.4 C_A* 65.0 C* 112.3 A 124.9 Iso
3.6	11	F	H	K 73.4 C* 74.8 A 102.6 Iso

[a] In the table A is smectic A, C* is smectic C* and C_A* is antiferroelectric smectic C*.

were prepared by reacting compound **7** or **8** with the appropriate dibromoalkane. The final synthetic steps were identical to the preparation of compound **1.1–1.6**.

The compounds were all characterised by polarised optical microscopy, differential scanning calorimetry and electrooptical analysis.[10] The transition temperatures for compounds of series **1** are given in Table 1 and the transition temperatures for compounds of series **2** and **3** are given in Table 2.

Compounds of series **1**, which are of conventional structure, all exhibit smectic A and smectic C* phases. There is clearly a strong effect of the position of the lateral fluoro substituent on mesophase stability where transition temperatures are significantly lower when the fluoro substituent is in the 2-position, compounds **1.3** and **1.6**. The combination of the 2-methylbutyl and the long alkoxy chains at the smectic layer interfaces strongly promote synclinic behaviour, which is expected from the current structure–property relationships based on the fact that for anticlinic behaviour a terminal branched chain, typically a 1-methylheptyl unit is required. Examination of cyclobutane (series **2**) and oxetane (series **3**) reveals much more varied behaviour. For the compounds with a decylmethylene spacer (**2.1–2.3** and **3.1–3.3**) the mesophase behaviour is similar to that of the alkoxy compounds in series **1**. However, by POM an antiferroelectric phase was also observed in **2.4, 2.5, 3.4** and **3.5**. Confirmation was obtained *via* electrooptic studies. Thus, each material was flow-filled into 4 μm antiparallel buffed polyimide cells (Linkam) and the direction and magnitude of spontaneous polarisation was determined using a current reversal technique. Compounds **2.6** and **3.6** do not show any evidence of anticlinic ordering and there was a reduction in mesophase stability, which is associated with the position of the fluoro substituent. The interaction of the fluoro substituent with the adjacent carbonyl effectively causes an internal rotation of the terminal phenyl ring which in turn reduces the ability of the

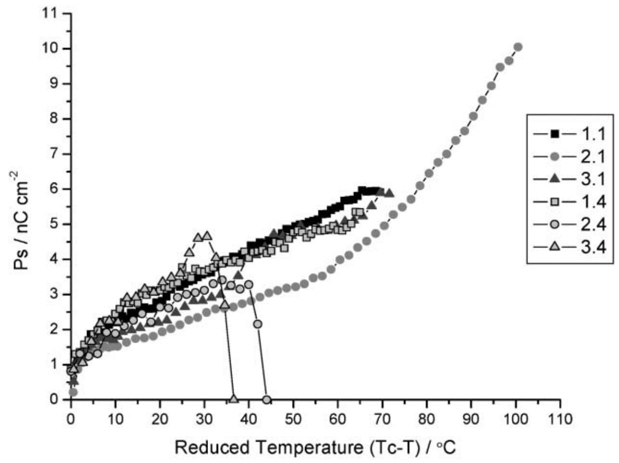


Fig. 3 Spontaneous polarisation as a function of reduced temperature for compounds **1.1**, **2.1**, **3.1**, **1.4**, **2.4** and **3.4**.

molecules to pack efficiently laterally for mesophase formation. This change in core conformation is sufficient to prevent the formation of anticlinic organisation in these homologues.

Fig. 3 shows the spontaneous polarisation as a function of reduced temperature for compounds **1.1, 2.1, 3.1, 1.4, 2.4** and **3.4**. It was clear that the alkoxy compounds from series **1** switched solely in a ferroelectric manner, giving rise to a single current peak which is associated with a ferroelectric response. Identical behaviour was also observed for **2.1** and **3.1**. Most interestingly, compounds **2.4** and **3.4** began switching in a ferroelectric mode but when they approached the transition to the anticlinic phase, the spontaneous polarisation fell rapidly towards zero. A threshold voltage was observed which was too large for further switching to occur. This behaviour indicated that the transition to the antiferroelectric state results in an apparent threshold to switching indicating strong interlayer interactions. The direction of polarisation for all of the materials reported was negative and there was no evidence to suggest that the sign of polarisation for compounds **2.4, 2.5, 3.4** and **3.5** was undergoing polarisation inversion.

To confirm if this mesophase was an antiferroelectric phase, mixture studies with 1-methylheptyloxycarbonylphenyl octyloxybiphenyl carboxylate (MHPOBC) were carried out. The materials were found to be completely miscible with MHPOBC throughout the concentration range. Fig. 4 shows a binary phase diagram for **3.4** mixed with MHPOBC. Clearly the smectic A–isotropic liquid, smectic C*–smectic A and anticlinic smectic C–smectic C* show linear behaviour over the whole mixture range. Only the ferrielectric smectic Cγ phase and the hexatic stacked smectic I phase are suppressed at approximately 60 wt% **3.4** in MHPOBC. The bulky cyclic group does not support the formation of a higher order smectic phase and to date none have been observed with this type of end group. This provides further evidence that this type of group may interfere with the organisation of the molecules at the interface *via* reduction of the interlayer interactions through steric crowding.

It has been shown that the inclusion of a small bulky group at the terminus of an alkyl chain in a typical ferroelectric liquid crystal can alter the interactions at the smectic layer interfaces sufficiently to promote anticlinic phase behaviour. Indeed, one of the major problems for commercialisation of antiferroelectric (AF) LCDs is the need for pitch compensation. Although these materials exhibit extremely high switching thresholds, a 2-methylbutyl group provides a longer pitch than a 1-methylheptyl. Most antiferroelectric liquid crystals have very short pitches, typically <2 μm and these new materials, due to their miscibility, may provide a way to provide pitch compensation in AFLC mixture to facilitate alignment in future devices.

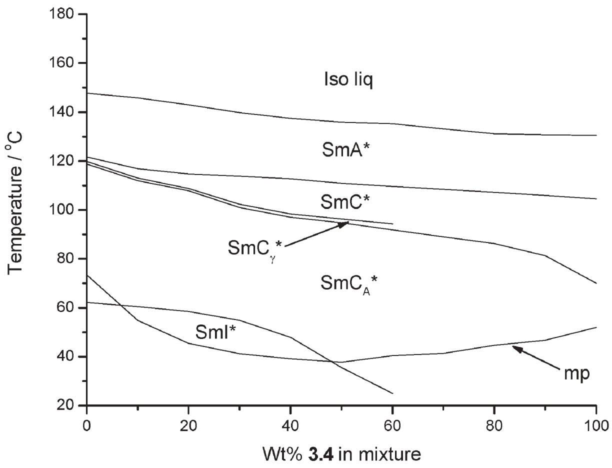


Fig. 4 Binary phase diagram of **3.4** with MHPOBC.

In conclusion we have demonstrated that it is possible to investigate the layer packing and interlayer interactions in lamellar smectic phases *via* the use of electrical field studies. Property–structure correlations obtained from such studies should be useful in the design of future materials for display and projector devices where grey scale and rapid response times are required.

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