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The Synthesis and Mesomorphic Properties of Some Novel Antiferroelectric Liquid Crystals

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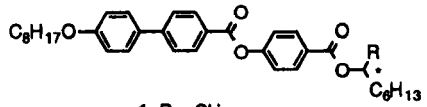
Several esters have been synthesised that exhibit the antiferroelectric smectic C phase. The core structures, like virtually all antiferroelectric materials, are very similar to that of MHPOBC. Lateral fluoro substituents have been used to reduce melting points and to investigate their effect on mesomorphic properties, spontaneous polarisation and tilt angle. A new device format reported by Lagerwall requires antiferroelectric liquid crystals with a 45° tilt angle. Novel antiferroelectric materials were prepared with fluoro substituents in lateral positions and in a terminal chain to provide low melting points, high antiferroelectric phase stability, high spontaneous polarisation and tilt angles of up to 45°. The synthetic routes to the novel materials are discussed, and the transition temperatures, tilt angles and spontaneous polarisations are compared to those of known materials.

Keywords: liquid crystals; synthesis; antiferroelectric; tilt angle

INTRODUCTION

The antiferroelectric smectic C liquid crystal phase is identical to the ferroelectric analogue except that the tilt direction of the molecules alternates from layer to layer in the phase structure. This interesting phase is a relatively recent discovery,[1] but already promising display

devices have been constructed.[2] Such display devices offer significant advantages over displays based on nematic liquid crystals. The switching is much faster and high-level multiplex addressing is possible. The inherent in-plane switching of the molecules provides excellent angles of viewing. Ferroelectric displays also have such advantages, but antiferroelectric displays have much better grey scale capability due to the special dependence of switching on applied field, and have a greater resistance to shock. Fundamental work is still on-going to provide a better understanding of the antiferroelectric liquid crystal phase and the associated physical properties,[2-7] however, displays using antiferroelectric materials are close to commercial availability; a clear demonstration of the importance of such devices.



1, R = CH_3

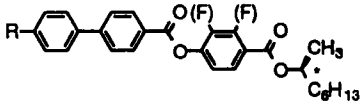
C 73.5 $S_C^*{}_{anti}$ 118.8 $S_C^*{}_{ferri}$ 119.8 $S_C^*{}_{ferro}$ 121.6 $S_C^*{}_{alpha}$ 122.6 S_A^* 147.7 I

2, R = CF_3

C 84.3 $S_C^*{}_{anti}$ 108.0 $S_C^*{}_{ferro}$ 109.0 S_A^* 121.0 I

Materials that exhibit the antiferroelectric phase are fairly common, but they all tend to have structures that are very similar to the well known MHPOBC (**1**) and the trifluoromethyl analogue (**2**).[1,2] A greater range of materials is required to facilitate fundamental studies, and to improve material properties for greater suitability for displays devices. Very recently, Lagerwall has reported a new device format based on antiferroelectric materials with a 45° tilt angle, this format provides two bright scattered states and a complete black state between crossed polarisers, and does not require any molecular alignment.[8]

The aim of this work was to synthesise antiferroelectric liquid crystals with low melting point, high antiferroelectric phase stability, high spontaneous polarisation and high tilt angle. In order to achieve these aims structures of type **I** and **II** were prepared and evaluated.



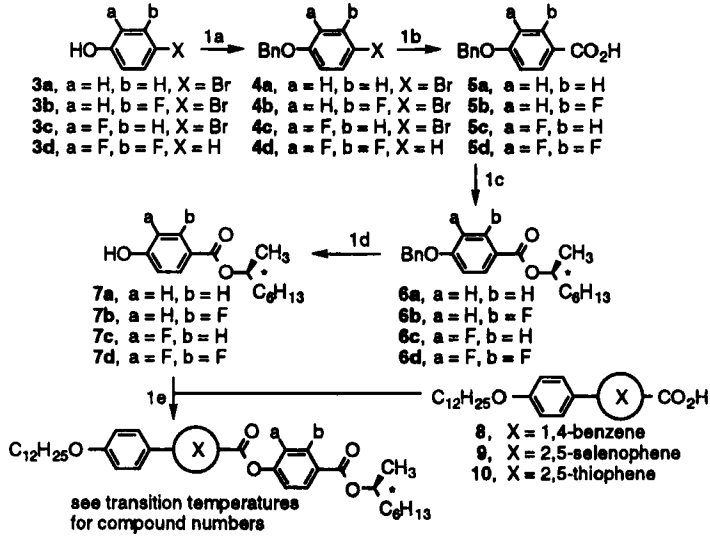
I, $R = CH_3(CH_2)_nO$
II, $R = CF_3(CF_2)_mCO_2(CH_2)_nO$

Lateral fluoro substituents are well known to reduce melting point, yet maintain liquid crystal phase stability, additionally the lateral dipole generated can aid molecular tilting.[9] The fluoro substituents in the terminal chain (Structure **II**) are known to produce a high tilt angle,[10,11] and when combined with lateral fluoro substituents low melting points will be achieved and hopefully a higher tilt angle.

SYNTHESIS

In principle the synthesis of antiferroelectric liquid crystals is relatively straightforward due to the sectional nature of the ester structures. Of course, in reality such syntheses are time-consuming and ultimately very low-yielding due to the number of steps (including protection and deprotection) and essential purification procedures required for multi-ester structures. The number of steps and the expense of chiral starting materials means that special considerations of efficiency are required.

Scheme 1 shows a general synthetic route to a wide range of antiferroelectric esters. Phenols (**3**) are protected with a benzyl group which then allows low-temperature lithiation to facilitate the generation of the desired carboxylic acids (**5**) through the exploitation of the bromo substituent or, in the case of **4d**, an acidic proton. A Mitsunobu esterification enables the efficient introduction of the chiral centre through a stereogenic inversion process which maintains the high enantiomeric excess of the chiral alcohol. Removal of the benzyl protecting group then allows for the convenient DCC-DMAP esterification with the known biaryl carboxylic acids (**8-10**)[4] to provide a wide range of antiferroelectric esters (**11-13**).

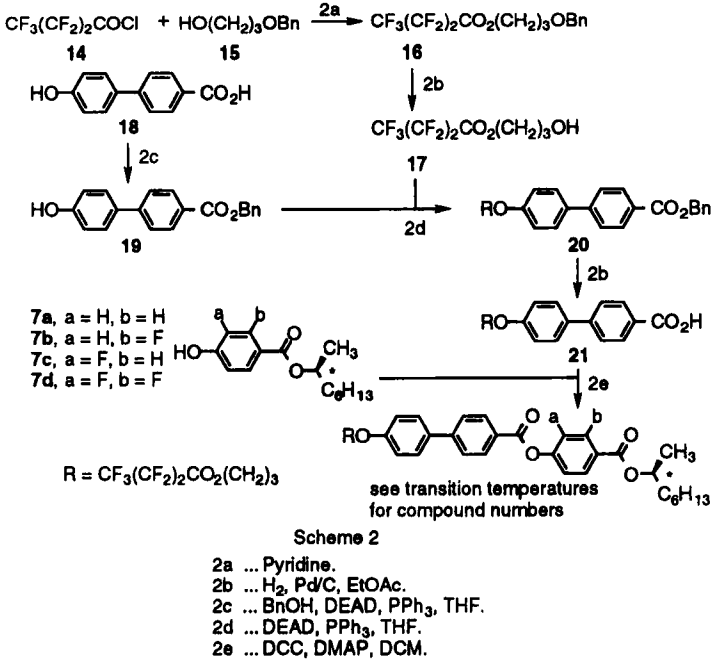


Scheme 1

1a ... BnBr, K_2CO_3, butanone.
1b ... (i) *n*-BuLi, THF; (ii) CO_2(solid), THF; (iii) HOAc.
1c ... (*R*)-(−)-2-Octanol, DEAD, PPh_3, THF.
1d ... H_2, Pd/C, EtOAc.
1e ... DCC, DMAP, DCM.

Scheme 2 shows the additional synthetic complexity involved in the introduction of a semi-fluorinated terminal chain. The sequence of the synthetic routes is crucial for the efficient generation of antiferroelectric ester in high purity as the perfluoro carbonyl unit is highly susceptible towards nucleophilic attack. Compound **16** was easily obtained, and the removal of the benzyl protecting group gave alcohol **17**. The Mitsunobu etherification to yield **20** is particularly low-yielding (as expected) and so is best performed early in the sequence before the chiral unit is involved. Debenzylation of **20** enabled convenient DCC-DMAP processes to generate the antiferroelectric liquid crystals (**22**) in good overall yield. The purification of the esters (**22**) was relatively simple due to the significant difference of the two starting materials. The route used by

Drzewinski *et al.* in the synthesis of **22a** does not offer such advantages of efficiency and purification, and yields a material with significantly lower transition temperatures (see later).[11]



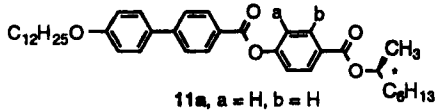
Scheme 2

2a ... Pyridine.
2b ... H_2, Pd/C, EtOAc.
2c ... BnOH, DEAD, PPh_3, THF.
2d ... DEAD, PPh_3, THF.
2e ... DCC, DMAP, DCM.

RESULTS AND DISCUSSION

In comparison with parent system **11a**,[4] the use of lateral fluoro substituents has significantly reduced the melting point in all cases (**11b-d**). In the case of the outer-edge fluoro substituent (**11b**) the melting point is very low, and the antiferroelectric phase stability has actually been increased by nearly 10 °C to give a very wide temperature range (70 °C), yet the ferroelectric phase stability is virtually unchanged and the smectic A phase stability is 6 °C lower. Such results may lead to the conclusion that lateral fluoro substitution

can favour the antiferroelectric phase, however, other locations of lateral fluoro substituents (**11c** and **11d**) do not support a generality, but they do allow the generation of the antiferroelectric phase.



11a, a = H, b = H

C 72.9 S_C^* anti 99.9 S_C^* ferri 103.5 S_C^* ferro 117.0 S_C^* alpha 122.2 S_A^* 132.7 I

11b, a = H, b = F

C 39.6 S_C^* anti 108.4 S_C^* ferro 118.6 S_A^* 126.7 I

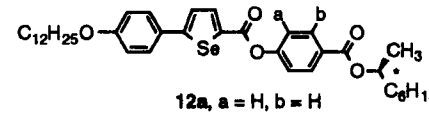
11c, a = F, b = H

C 53.3 S_C^* anti 78.3 S_C^* ferri 82.0 S_C^* ferro 90.7 S_A^* 105.7 I

11d, a = F, b = F

C 52.8 S_C^* anti 94.0 S_C^* ferri 95.2 S_C^* ferro 99.5 S_A^* 110.0 I

The selenophene confers a slight bend in structures, and compounds **12**, and **12a** was prepared to investigate reports that a bent structure favours the antiferroelectric phase above other mesophases.[4]



12a, a = H, b = H

C 67.7 S_C^* anti 97.8 S_C^* ferri 99.0 S_C^* ferro 109.4 S_A^* 116.6 I

12b, a = H, b = F

C 75.5 S_C^* anti 91.8 S_C^* ferri 92.1 S_C^* ferro 98.9 S_A^* 109.1 I

12c, a = F, b = H

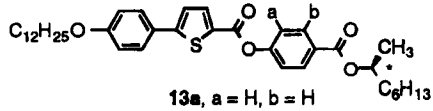
C 48.0 S_A^* 79.3 I

12d, a = F, b = F

C 46.3 S_C^* anti 79.9 S_C^* ferri 83.3 S_C^* ferro 84.3 S_A^* 93.7 I

The fluoro substituted analogues (**12b-d**) emphasise the significance of the location with the inner-core position (**12c**) eliminating all tilted smectic mesophases, despite a very low melting point. Whereas those compounds with an outer-edge fluoro substituent (**12b** and **12d**) exhibit the antiferroelectric and ferroelectric phases to high temperature. Lateral fluoro substitution appears to be less tolerated in

the selenophene core than in the comparable phenyl core systems resulting in comparatively lower liquid crystal phase stability.



13a, a = H, b = H

C 64.2 $S_C^*{}_{anti}$ 80.2 $S_C^*{}_{ferri}$ 82.8 $S_C^*{}_{ferro}$ 92.6 S_A^* 97.9 I

13b, a = H, b = F

C 58.8 ($S_C^*{}_{anti}$ 58.3) $S_C^*{}_{ferri}$ 64.6 $S_C^*{}_{ferro}$ 70.4 S_A^* 81.8 I

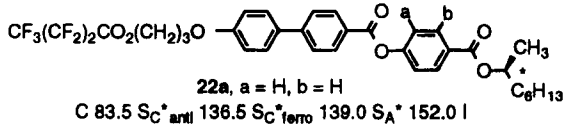
13c, a = F, b = H

C 41.4 $S_C^*{}_{ferro}$ 56.5 S_A^* 67.4 I

13d, a = F, b = F

C 57.4 $S_C^*{}_{anti}$ 64.0 $S_C^*{}_{ferri}$ 68.5 $S_C^*{}_{ferro}$ 69.5 S_A^* 74.5 I

The thiophene analogues (compounds **13**) have a greater bend than the selenophene systems (**12**) and accordingly the transition temperatures are lower, however, the phase morphology is similar. Lateral fluoro substituents in the thiophene systems are now even less tolerated than for the selenophene systems, thus the effect of the lateral fluoro substituents becomes increasingly dramatic as the bend in the core increases.



22a, a = H, b = H

C 83.5 $S_C^*{}_{anti}$ 136.5 $S_C^*{}_{ferro}$ 139.0 S_A^* 152.0 I

22b, a = H, b = F

C 61.5 $S_C^*{}_{anti}$ 103.0 $S_C^*{}_{ferro}$ 109.0 S_A^* 120.0 I

22c, a = F, b = H

C 57.0 $S_C^*{}_{anti}$ 104.0 $S_C^*{}_{ferro}$ 105.0 I

22d, a = F, b = F

C 66.0 $S_C^*{}_{anti}$ 95.0 $S_C^*{}_{ferro}$ 99.0 S_A^* 104.0 I

The introduction of a perfluorocarboxy unit into the terminal chain (compounds **22**) generally leads to increased transition temperatures. In the case of **22a** the antiferroelectric phase stability has increased by far more (37 °C) than the ferroelectric and smectic A phase stabilities

(around 20 °C) when compared with compound **11a** (compound **22a** has been reported previously[11] with significantly lower transition temperatures). Lateral fluoro-substituted analogues (**22b-d**) have much lower melting points than **22a**, and their antiferroelectric phase stabilities are reduced by as much as other phases which contrasts with the situation seen for compounds **11**.

The spontaneous polarisation values of compounds **11** are all around 150 nC cm^{-2} and the tilt angles are all around 25-30°.[5] Compound **22a** with the fluoro-substituted terminal chain has a spontaneous polarisation of 500 nC cm^{-2} and a tilt angle of 40°, whereas the lateral fluoro-substituted analogue (**22b**) has a lower spontaneous polarisation (400 nC cm^{-2}), but has a tilt angle of 45°.

ACKNOWLEDGEMENTS

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