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HETEROCYCLIC ESTERS EXHIBITING FRUSTRATED LIQUID CRYSTAL PHASES

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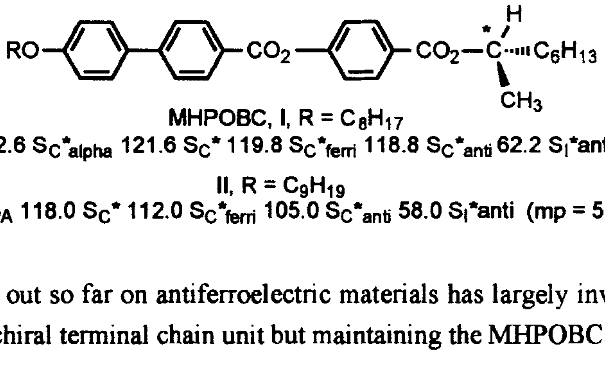
Abstract A series of novel heterocyclic esters has been prepared based on selenophene, thiophene and furan units; for comparison the parent, phenyl analogue was also prepared. All the materials except the least linear furan analogue are mesogenic and exhibit the S_A, S_C*, S_C*_{ferri} and S_C*_{anti} liquid crystalline phases. In addition, the selenophene material exhibits a higher ordered antiferroelectric phase which has been designated the antiferroelectric smectic I (S_I*_{anti}) phase and below this the S_I* phase was generated. The synthesis, mesomorphic behaviour and physical properties of the materials are reported.

INTRODUCTION

Research into ferroelectric liquid crystals has been extremely active over the last twenty years because of the potential in low-powered, fast-switching, bistable devices that can provide high resolution over large and very small display areas. These advantages, combined with simple device construction, make ferroelectric display devices, especially those of small size, superior to TFT nematic display technology. However, ferroelectric display technology has some fairly severe problems such as alignment, grey scale and sensitivity to shock. In 1989, Chandani *et al.* discovered the antiferroelectric smectic C phase.[1] The structure of this phase is analogous to that of the ferroelectric smectic C phase except that the tilt direction alternates through successive 'layers' of the phase. Accordingly, the antiferroelectric phase exhibits tristate switching which provides for excellent multiplexability, but more importantly enables the introduction of grey scale. Other advantages of the antiferroelectric display include better alignment, a better viewing angle and a reduced sensitivity to shock.[2]

The generation of the antiferroelectric phase appears to require a very specific molecular structure that includes ester groups and at least three rings. Indeed, the vast majority of compounds that exhibit the antiferroelectric phase are structurally very similar to MHPOBC (**I**),[1] which was the first material reported to exhibit the antiferroelectric phase, and compound **II**.[3] Such structures are not conducive to fast-switching because of the inherent high viscosity associated with three-ring structures, polar ester groups and branched terminal chain units. Additionally, such structures confer disadvantageously high melting points. Accordingly, much more work needs to be carried out to fully explore the way in which the antiferroelectric phase is generated and thus determine the optimum structures that will best serve commercially-viable antiferroelectric display devices.



MHPOBC, I, R = C_8H_{17}

I 147.7 S_A 122.6 $S_C{}^*{}_{alpha}$ 121.6 $S_C{}^*$ 119.8 $S_C{}^*{}_{ferri}$ 118.8 $S_C{}^*{}_{anti}$ 62.2 $S_I{}^*$anti (mp = ?)

II, R = C_9H_{19}

I 142.2 S_A 118.0 $S_C{}^*$ 112.0 $S_C{}^*{}_{ferri}$ 105.0 $S_C{}^*{}_{anti}$ 58.0 $S_I{}^*$anti (mp = 59.3)

The work carried out so far on antiferroelectric materials has largely involved altering the nature of the chiral terminal chain unit but maintaining the MHPOBC core.[2,4,5] The work reported here represents an investigation of how the generation of the antiferroelectric phase is affected by the structural nature of the core. It has been proposed that the antiferroelectric phase is promoted by a bent molecular structure,[4,6] however, it is recognized that bent structures are generally not conducive towards the generation of liquid crystal phases. The inclusion of the 2,5-disubstituted selenophene (**25**), thiophene (**26**) and furan (**27**) units within the core generates compounds with a degree of bend that increases in the order listed. Accordingly, comparison with the analogous parent phenyl material (**9**) would show how a bent core structure affects the tendency towards the generation of the antiferroelectric phase. The novel compounds reported are shown in Figure 1.

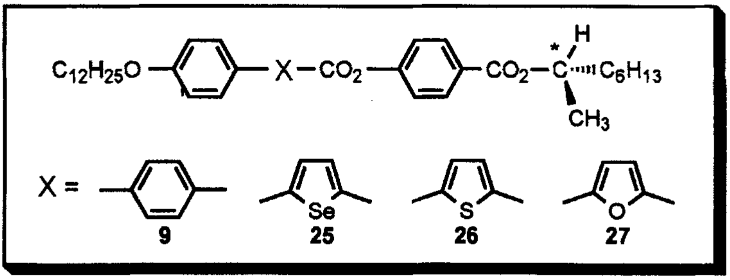
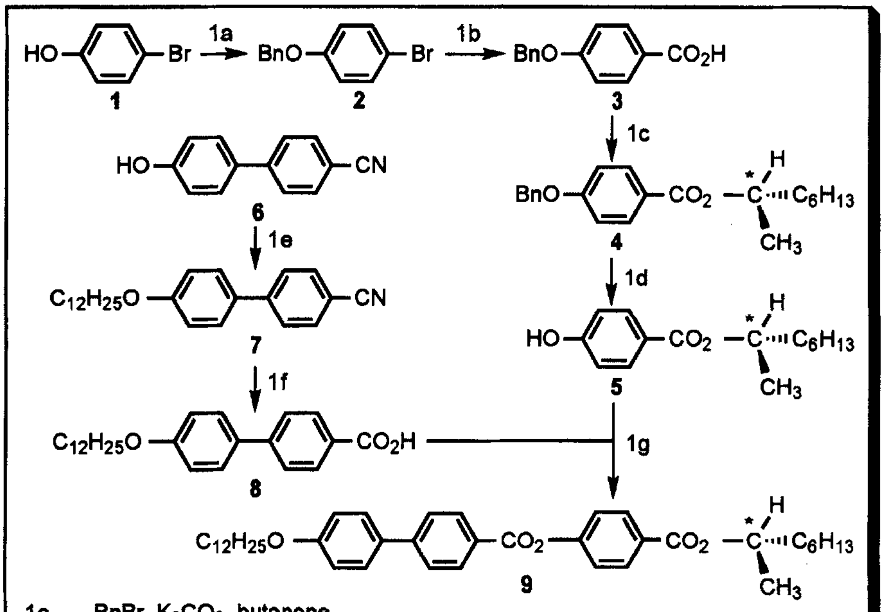


FIGURE 1 The liquid crystalline esters prepared.

SYNTHESIS

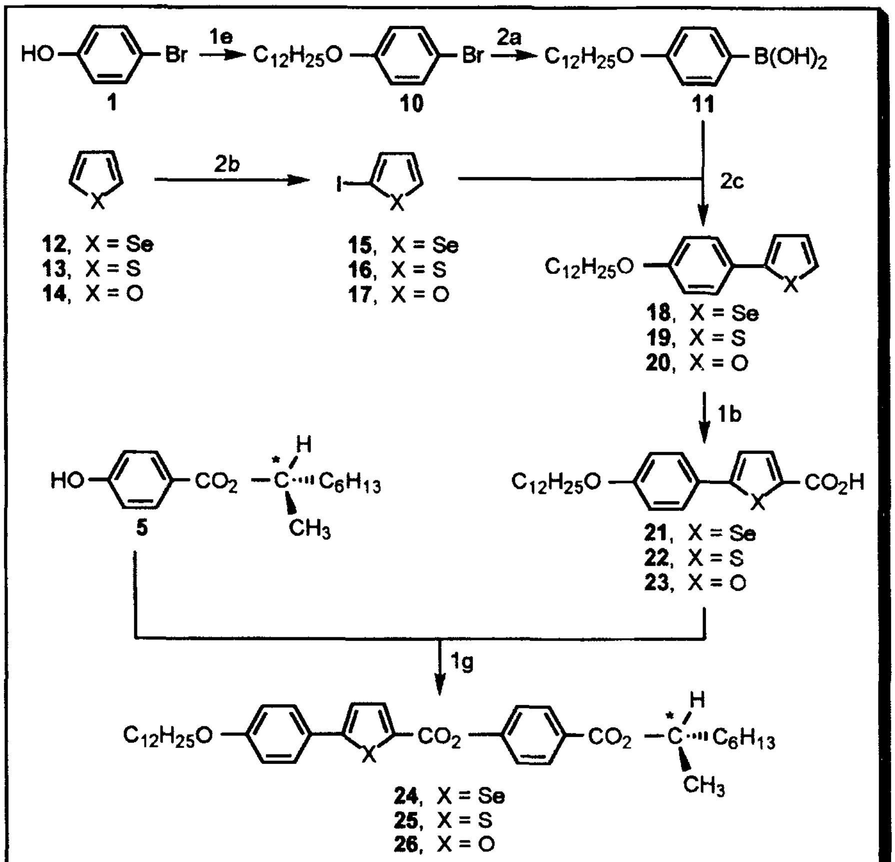
Scheme 1 outlines the synthetic methods used for the preparation of the parent phenyl ester **9**.



1a ... BnBr, K_2CO_3, butanone
1b ... (i) nBuLi, THF; (ii) CO_2(solid), THF; (iii) HOAc
1c ... *(R)-(-)*-2-Octanol, DEAD, PPh_3, THF
1d ... H_2, Pd/C, EtOAc
1e ... $C_{12}H_{25}Br$, K_2CO_3, butanone
1f ... H_2SO_4, H_2O, HOAc
1g ... DCC, DMAP, CH_2Cl_2

Scheme 1

The benzyl-protection of the hydroxyl group of compound **1** enabled a lithiation to be carried out on compound **2**. The lithium salt was quenched using a slurry of solid carbon dioxide in dry THF and subsequent acidification with glacial acetic acid afforded compound **3** in good yield. Carboxylic acid **3** and *(R)-(-)*-2-octanol were involved in an efficient Misunobu esterification which provided ester **4** with an inverted stereochemistry at the chiral centre.[7]



2a ... (i) nBuLi, THF; (ii) MeO_3B, THF; (iii) 10% HCl
2b ... (i) nBuLi, THF; (ii) I_2, THF
2c ... $Pd(PPh_3)_4$, Na_2CO_3, DME

Scheme 2

Debenzylation of compound **4** gave a quantitative yield of the required phenol (**5**). Compound **6** was *O*-alkylated using standard conditions to provide the alkoxycyanobiphenyl (**7**) in excellent yield. Hydrolysis of the nitrile unit to the carboxylic acid (compound **8**) was efficiently effected using a mixture of sulfuric acid and acetic acid. Carboxylic acid **8** and phenol **5** were then esterified using the standard DCC / DMAP method of Hassner and Alexanian[8] to give the desired liquid crystalline ester (**9**) in good yield.

Scheme 2 illustrates the general synthetic route that provided the desired heterocyclic esters (**24-26**). The alkoxyphenyl heterocycles (**18-20**) were efficiently prepared by palladium-catalysed cross-coupling reactions involving boronic acid **11** (easily prepared by a standard method) and heterocyclic iodides (**15-17**).[9] In each case, the heterocyclic iodides were prepared by quenching the lithium salt of the parent heterocycle (**12-14**) with iodine. Bromination of the parent heterocycles with *N*-bromosuccinimide can be successful in the case of selenophene (**12**) and thiophene (**13**), however, small traces of the dibrominated products must be removed. Furan (**14**) is less aromatic in character and undergoes addition rather than substitution and hence bromination is not possible. The acidic proton of each phenyl heterocycle (**18-20**) was exploited with butyllithium; subsequent quenching of the lithium salt with solid carbon dioxide gave the required heterocyclic carboxylic acids (**21-23**) in good yields. Each acid was esterified with phenol **5** (Scheme 1) as described for the preparation of compound **9** (Scheme 1). The purification of compound **26** was limited to column chromatography because attempted recrystallisation resulted in the formation of a gel which could not be filtered, despite the use of a wide variety of recrystallisation solvents including ethanol, hexane, benzene, toluene, ethyl acetate and dimethoxyethane. Many selenium-containing materials are photosensitive and so where possible compounds **15**, **18**, **21** and **24** were handled in the dark, although no decomposition was detected.

RESULTS AND DISCUSSION

Various homologues of compound **9** have been previously reported (*e.g.*, compounds **I** and **II**).[1,3] The octyloxy homologue (**I**) was the first compound reported to generate the antiferroelectric smectic C ($S_C{}^*{}_{anti}$) phase. Accordingly, the phase morphology of compound **9** was as expected in the generation of $S_A{}^*$, $S_C{}^*{}_{alpha}$, $S_C{}^*$, $S_C{}^*{}_{ferri}$, $S_C{}^*{}_{anti}$ liquid crystalline phases and the transition temperatures were consistent with those of other homologues. However, unlike compounds **I** and **II**, compound **9** does not exhibit the higher ordered antiferroelectric smectic I ($S_I{}^*{}_{anti}$) phase probably because of the higher melting point.

The heterocyclic analogues (**24-26**) of compound **9** were prepared to determine how the stability of the antiferroelectric phase is influenced by the bend in the core.

TABLE 1 Transition temperatures (°C) for novel esters.

compound	mp	$S_I{}^*$ to $S_I{}^*{}_{anti}$	$S_I{}^*{}_{anti}$ to $S_C{}^*{}_{anti}$	$S_C{}^*{}_{anti}$ to $S_C{}^*{}_{ferri}$	$S_C{}^*{}_{ferri}$ to $S_C{}^*$	$S_C{}^*$ to S_A	S_A to I
9	72.9	—	—	99.9	103.5	122.2§	132.7
24	67.7	33.3	42.2	97.8	99.0	109.4	116.6
25	64.2	—	—	80.2	82.8	92.6	97.9
26	61.2	—	—	—	—	—	—

§ $S_C{}^*{}_{alpha}$ from 117.0 °C

The selenophene system (**24**) is the closest to the linearity of, and exhibits the same phases as, compound **9**. Interestingly, the $S_C{}^*{}_{anti}$ phase stability is only slightly reduced despite a marked reduction in the stability of the $S_C{}^*$ phase. Despite a similarly high melting point, compound **24** supercools sufficiently to allow the generation of an underlying, ordered antiferroelectric phase which has been designated as the $S_I{}^*{}_{anti}$ phase on the basis of miscibility studies and physical property evaluations. Differential scanning calorimetry reveals a distinct enthalpy change, and a marked change in the optical texture is seen through optical polarising microscopy at the transition. The observation of physical properties with changing temperature reveals the increased order of the lower temperature phase and proves the antiferroelectric nature. On cooling compound **24** from the $S_C{}^*{}_{anti}$ phase, the viscosity increases by an order of magnitude, the tilt angle quickly falls by several degrees and the switching time becomes an order of magnitude longer. However, the double hysteresis, characteristic of antiferroelectric behaviour, remains throughout both mesophases. An ordered ferroelectric mesophase is found at lower temperatures. Optical polarising microscopy and physical property evaluations suggest that this ordered ferroelectric phase is the $S_I{}^*$ phase. The structures of the designated $S_I{}^*{}_{anti}$ and $S_I{}^*$ phases are currently being evaluated by X-ray analysis and the results will be reported in due course.

A more severely bent core is produced by the thiophene analogue (**25**) and yet the same mesophase morphology as the parent system (**9**) is exhibited. However, phase stabilities are considerably reduced in comparison to compound **9** and in comparison to the selenophene system (**24**); the stability of each mesophase has been equally reduced, so the bend is now too severe to give any special support to the antiferroelectric phases.

The furan derivative (**26**) is non-mesogenic, despite a reasonably low melting point of 61.2 °C. The reduction in mesophase stability in going from compound **9** through compounds **24** to **26** appears consistent with the degree of bend in the molecular core which restricts the close association of the molecules. The incorporation of a heterocycle into such a core would thus be expected to reduce the crystalline nature and this is clearly evident as the melting points are seen to decrease with the increase in curvature of the molecule.

CONCLUSIONS

The use of a 2,5-disubstituted heterocyclic unit in place of a phenyl unit introduces a bend into the molecular core which reduces the liquid crystal phase transition temperatures. However, the selenophene and thiophene units both support the ferroelectric, ferrielectric and antiferroelectric smectic C phases. Additionally, the selenophene material generates an antiferroelectric smectic I phase. This ordered antiferroelectric phase can be detected by optical polarising microscopy, differential scanning calorimetry and by observing temperature-dependent physical properties. The furan analogue has the least linear structure and is non-mesogenic.

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