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THE PHYSICAL PROPERTIES OF A SERIES OF ANTIFERROELECTRIC HETROCYCLIC ESTERS.

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Abstract A series of highly chiral hetrocyclic esters have been studied. The effect that the choice of hetroatom has on the linearity of the molecules and hence the mesomophism of the materials has been investigated. Measurements of the spontaneous polarisation, tilt angle, current response time and rotational viscosities of the materials are reported. At 30°C below the transition from the SmA phase all members of the series show a Ps of ~100nCcm^{-2} and a high tilt angle of about 30°. These physical measurements confirm the presence of a higher order antiferroelectric phase in the selenophene derivative in this series.

INTRODUCTION

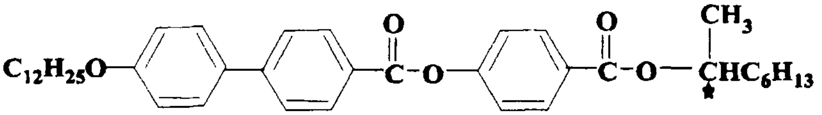
The technological importance of ferroelectric liquid crystals was realised when, in 1980, Clark and Lagerwall developed the first electro-optic device based on the ferroelectric SmC* cell[1]. In 1989, Chandani *et al.* reported a new chiral compound that possessed 3 tilted smectic phases in addition to the ferroelectric SmC* [2]. In one of these phases, the antiferroelectric smectic C (SmC^*_A) phase, the molecules in neighbouring layers tilt to the same degree but in the opposite direction. Previous work has shown that all molecules exhibiting a SmC^*_A phase have a relatively large transverse permanent electric dipole and the formation of the SmC^*_A phase is thought to be driven by the pairing of these dipole moments between neighbouring layers[3]. The SmC^*_γ phase is ferrielectric[4] and its structure is thought to be made up from periodically repeated blocks of ferroelectric and antiferrolelectric ordering. As such the SmC^*_γ phase exhibits a finite tilt angle and spontaneous polarisation weaker than that in the ferroelectric SmC* phase. The structure of the SmC*α phase is not yet clear but it is thought to be a tilted smectic phase where the correlation between the molecular tilt in neighbouring layers is greatly reduced. Both the SmC*γ and SmC*α phase are thought to appear as a result of competition between the driving forces that stabilise the ferroelectric and antiferroelectric phases.

An applied field of sufficient strength is observed to induce a transition from the antiferroelectric and ferrielectric phases to a ferroelectric state. These field induced transitions are observed as tristable switching in the antiferroelectric case and tetrastable switching in the ferrielectric case. Field induced transitions are utilised in antiferroelectric liquid crystal displays (AFLCDs) the advent of which has increased the need to understand more about the nature of these antiferroelectric phases, their structures, how they are stabilised and how their mesomorphism can be "tailored" to suit different applications. AFLCDs have been produced which exhibit high contrast ratios, fast response times (video rate) and wide viewing angles. Prototype AFLCDs exhibiting grey scale and hence full colour have been demonstrated[5-9].

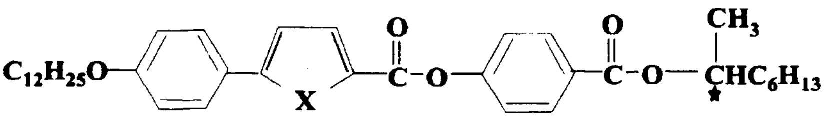
This paper reports the effect of substitution on the molecular packing and hence the ferroelectric, ferrielectric and antiferroelectric polymorphism of a series of hetrocyclic esters and how these effect the physical switching properties observed.

MESOMORPHIC PROPERTIES

The materials investigated were a series of substituted hetrocyclic esters and the parent phenyl compound as shown below in figure 1.



Compound 1



Compound **2** (X = Se), **3** (X = S), **4** (X = O)

FIGURE 1, The general structures of the compounds studied.

For convenience the phenyl compound will be referred to as compound **1** and the hetrocyclic compounds will be designated as compounds **2**, **3** and **4** for X = Se, S and O respectively. The different substituents are of different sizes as such cause different amounts of ring strain. This in turn leads to different degrees of linearity of the rigid molecular cores as depicted in the molecular models in figure 2, which were generated using Cerius^2 on an Iris Indigo silicon graphics workstation. Obviously, the degree of bend in the molecule affects the packing of the molecules giving rise to the enhancement of different frustrated smectic phases as illustrated by the mesomorphic transition temperatures depicted in figure 3 it can be seen that:

- as would be expected, the more linear the molecular core the higher the melting and clearing points;
- the overall liquid crystal range is enhanced in the more linear molecules;
- increasing the degree of bend by introducing a furan ring to give compound **4** results in a lack of mesophases;
- all the compounds, except the furan derivative, exhibit enantiotropic frustrated smectic phases.
- only compound **2**, the selenophene derivative, exhibits smectic I* phases.

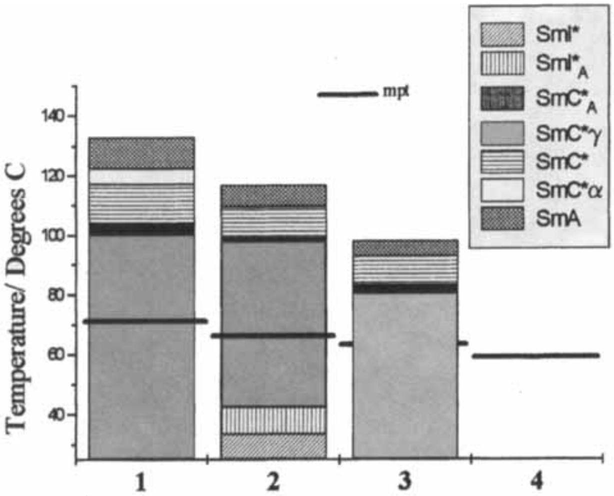


FIGURE 3, Mesomorphic transition temperatures.

EXPERIMENTAL DETAIL

The liquid crystalline samples were contained in 7.5μm thick ITO coated glass cells for all the physical measurements. The inner surfaces of the cells were coated with a rubbed polyimide layer to give homogeneous alignment. The cells were maintained in a

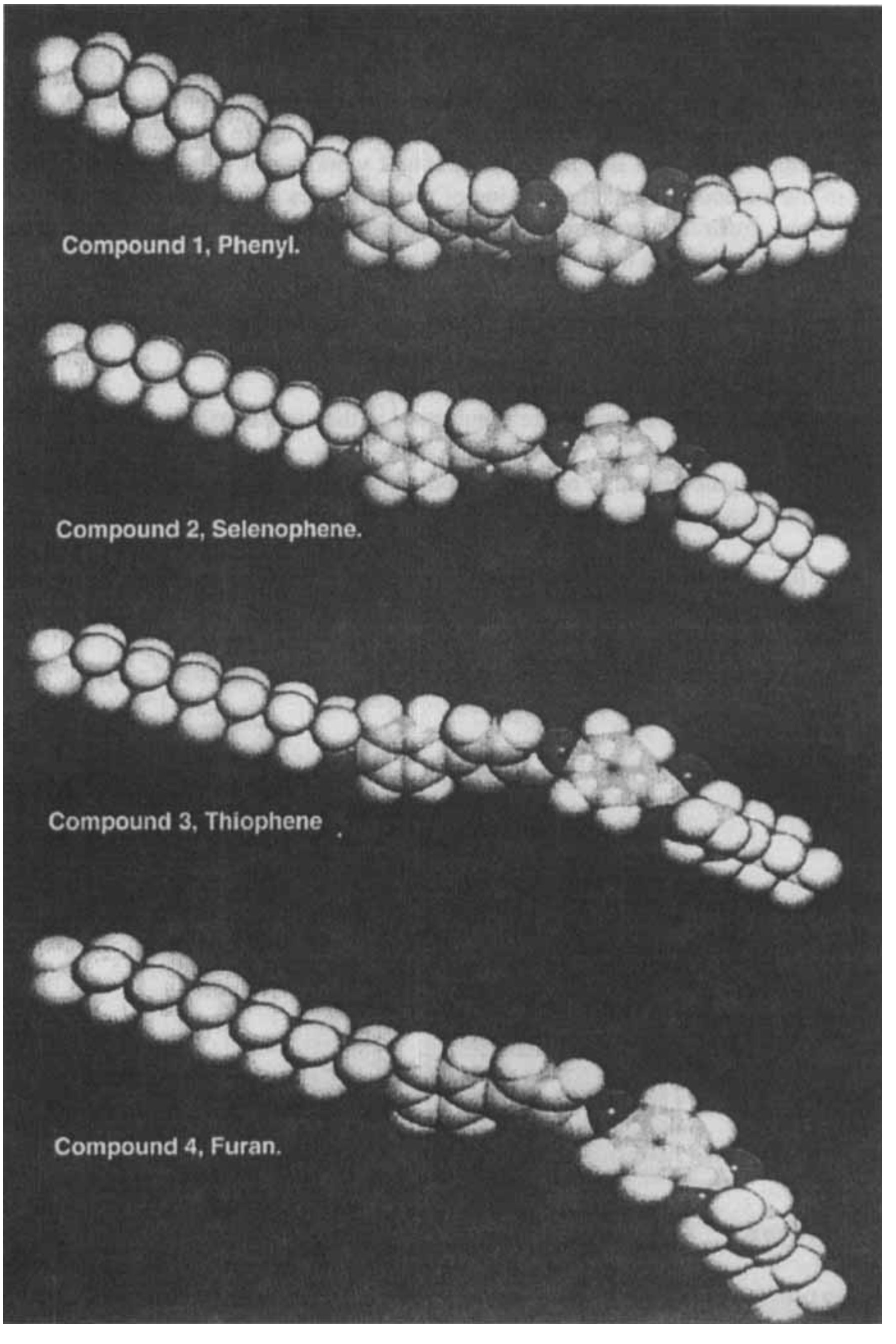


FIGURE 2. Molecular models of compounds used.

temperature controlled environment using a Linkam hot stage and temperature controller with an accuracy of ±0.1 °C. The phase transitions were detected by DSC and confirmed using polarising optical microscopy.

The spontaneous polarisation (Ps) was evaluated using the current pulse technique[10] to an accuracy of $\pm 2\mathrm{nC/cm^2}$. Current response times were measured as the time between field reversal and the peak of the current pulse on application of a square wave driving signal. Tilt angles were measured optically as half the angle between two extinction positions when the sample was switched between crossed polarisers to an accuracy of ±1°. The rotational viscosities were calculated using information from the profile of the current pulse and a knowledge of the tilt angle and Ps[11].

The saturated Ps, tilt angles, current response times and rotational viscosities of the compounds were determined on application of an electric field high enough to ensure saturated ferroelectric switching ($\pm 10\mathrm{V}\mu\mathrm{m}^{-1}$ at a frequency of 200 Hz).

FERROELECTRIC PROPERTIES

The Ps as a function of reduced temperature can be seen in figure 4 a). It is observed that the Ps is relatively large for all the liquid crystalline compounds, in all cases saturating between 120 - 150 $\mathrm{nCcm^{-2}}$. That the Ps curves are very similar is not surprising; the molecules are of similar size and dipole moment. All curves also show some degree of deviation from the expected Curie-Weiss behaviour. The Ps of compound **2** is observed to be continuous across the transition from $\mathrm{SmC_A^*}$ to $\mathrm{SmI_A^*}$.

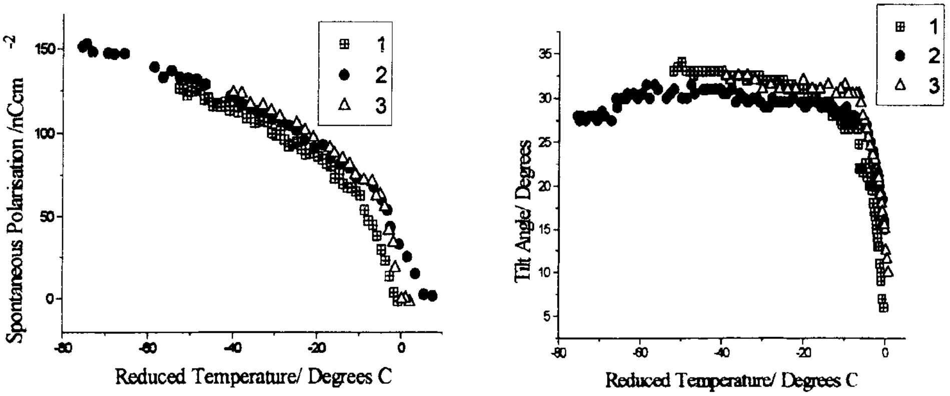


FIGURE 4 a.)

FIGURE 4 b.)

FIGURE 4, a) The spontaneous polarisation; b) the tilt angle as functions of reduced temperature. Applied field $\pm 10\mathrm{V}\mu\mathrm{m}^{-1}$ at 200 Hz.

The variation of the tilt angle as a function of reduced temperature can be seen in figure 4 b). The tilt angles of the compounds are also relatively high reaching values of about 30°. All the tilt angles are very steep in the high temperature region of the graph indicating the possibility of a strongly first order phase transition. In the case of compound **1** this is due to the presence of a SmC_{α}^{*} phase. It may be that compounds **2** and **3** also possess such a phase but if so it is relatively narrow and as such has not yet been detected. In this situation it can be expected that Curie-Weiss behaviour[12] will not be observed. Another possibility lies in the nature of the ferroelectric SmC* phase found in these antiferroelectric compounds (hereafter denoted SmC^{*}_{β}). Recent work has shown that the SmC^{*}_{β} phase is distinct from the ferroelectric SmC* phase[13] and exhibits some degree of ferrielectric-like ordering[14]. In this case non Curie-Weiss behaviour would also be expected. In compound **2** the tilt angle decreases at the SmC_{A}^{*} to SmI_{A}^{*} transition, indicating an increase in layer spacing in the SmI* phases. The evolution of the current response time with temperature is depicted in figure 5 a) and the response time of compound **2** can be seen to increase dramatically at the phase transition from SmC_{A}^{*} to SmI_{A}^{*} while the rotational viscosity (figure 5 b)) increases discontinuously by an order of magnitude. These dramatic increases are both consistent with a significant increase in order of the system.

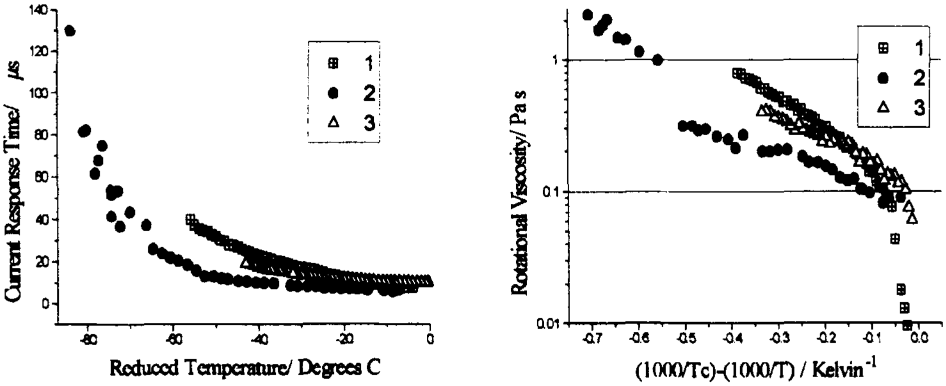


FIGURE 5 a.) FIGURE 5 b.)

FIGURE 5, a) The current response time and b) the rotational viscosity as functions of reduced temperature. Applied field $\pm 10 V\mu m^{-1}$ at 200 Hz.

CONCLUSIONS

We have found that the basic structure of this series of compounds is very good for producing enantiotropic frustrated smectic phases. Obviously, the more linear the molecules the better they are at packing into liquid crystal phases and the overall mesomorphic range is enhanced. Introducing more bend in the molecule lowers the melting and clearing points of the materials as would be expected. A small amount of bend is found to optimise the range of antiferroelectric and ferrielectric behaviour (greater than 30°C wide in the selenophene derived compound **2**). This type of modification of the linearity of the molecules may be a useful way of tailoring the polymesomorphism of the materials while not significantly changing the size, dipole and hence switching properties of the molecules involved allowing all aspects of the materials' properties to be optimised.

The slightly bent "banana shaped" molecules of compound **2** (Se) give rise to more than one each of ferroelectric and antiferroelectric phases. The physical measurements are consistent with there being a transition to a more ordered smectic phase below the $\mathrm{SmC*}_A$ phase. Observation of the optical hysteresis and current pulse traces in this region (to appear in a future paper) lead us to believe this phase is that tentatively designated the $\mathrm{SmI*}_A$ by Chandani *et al.*[15] with a ferroelectric SmI* phase below. Miscibility studies are needed to confirm that the higher ordered smectic phases observed are indeed smectic I* phases, such measurements will be reported in a future paper.

This work also shows further evidence that the nature of the $\mathrm{SmC*}_\beta$ is not yet fully understood. Li *et al.*[13] found that the ferrielectric-like ordering in this phase was dependant on cell thickness, being stabilised in thinner cells, while Sako *et al.*[14] found that observation of this phase was dependant on the optical purity of the material. Further investigations into the physical switching properties of the $\mathrm{SmC*}_\beta$ phase and how they vary with both optical purity and cell thickness will be reported in a future paper.

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