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Novel sulphur-containing banana-shaped liquid crystal molecules

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In this preliminary report we present the mesomorphic properties and electro-optic investigations of three new 'banana-shaped' mesogens. The materials are structurally similar to Niori's the original bent-core materials but possess alkylthio substituents in place of alkoxy substituents. Microscopic investigations revealed an unusual 'spiral-domain texture', similar to that observed in the 'B_7' phase of related materials. Further investigations support our earlier observations that the materials display antiferroelectric switching in this phase, in two of the new materials studied. The nature of this phase, in comparison with the 'switchable' (B_2) and 'chiral-domain' (B_4) phases of the original materials, is discussed.

1. Introduction

In 1974 Meyer *et al.* showed that tilted smectic liquid crystalline phases composed of chiral molecules (such as the SmC*, SmI* and SmF* phases) can exhibit a net spontaneous polarization [1]. The fact that this spontaneous polarization ($\mathbf{P}_s$) could be reversed by the application of an external electric field placed the materials into a new class of ferroelectrics. Ferrielectric and antiferroelectric properties were also found to exist in liquid crystals towards the end of the following decade [2]. Subsequent to these discoveries a vast number of new liquid crystalline substances with these properties has been synthesized [3].

It was generally recognized that the reduced symmetry, which is responsible for the origin of both ferroelectricity and antiferroelectricity in liquid crystalline substances, is partially a consequence of the chiral structure of the constituent molecules [1, 4]. However, a number of molecules have been reported recently which do not possess a chiral structure and nevertheless display ferroelectric properties in the bulk material [5]. One such group of materials consists of the bent-core 'banana-shaped' liquid crystal molecules originally synthesized by Matsunaga *et al.* [6] and reported to be ferroelectric by Niori *et al.* [7].

The origin of the spontaneous polarization in these novel systems is believed to be a combination of three factors: (i) the highly polar character of the molecules, (ii) the packing arrangement of the molecules in smectic layers (with the dipoles facing in a common direction within the layers), and (iii) the tilt of the molecules with respect to the smectic layer normal [8]. All three factors together can lead to a chiral layer symmetry, although the molecules themselves are not chiral. Recent investigations on the switching properties of the original materials, initially speculated as being ferroelectric by Niori *et al.* [7], have provided strong evidence to support the postulation that the materials are actually antiferroelectric in nature [8–10].

In fact the chiral character exhibited by these materials has been indicated by the appearance, between uncrossed polarizers, of domains of opposite optical activity in the B_4 † phase of the original materials [11]. Very recently a microscopic 'spiral-domain' or 'telephone wire-like' texture in the newly discovered 'B_7' phase of some nitro substituted homologues has also been reported [12]. The existence of helical ordering in mesophases formed by 'banana-shaped' molecules is believed to be a consequence of the chiral layer structure [13].

2. Results and discussion

2.1. *Mesomorphic properties*

In order to study the structural factors necessary for the formation of the 'switchable' B_2 phase by banana-shaped liquid crystal molecules, a new homologous series of materials was synthesized recently [14]. The materials differ from the original materials only by the presence of alkylthio substituents in place of the alkyloxy substituents (figure 1). The transition temperatures (°C) and phase sequence of the new materials, in comparison with those of the original materials, are listed in the table.

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† Note that the notation used to describe these phases ('B_x') is based on the system approved at the International Workshop on Banana-Shaped Liquid Crystals: 'Chirality by Achiral Molecules' (TU Berlin, 1997).

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Table. Transition temperatures (°C) of the new materials (**B-*n*(S)**; $n = 8$–10) in comparison with the alkoxy analogues (**B-*n*(O)**; $n = 8$–10), obtained by polarizing optical microscopy and DSC.

Compound	*n*	Cr		B_4		B_3		B_2		'B_7'		I
B-8(O)	8	•	105.0	•	155.2	•	162.0	•	—	—	175.3	•
B-8(S)	8	•	124.4	—	—	•	—	—	143.4	•	148.8	•
B-9(O)	9	•	106.2	•	152.5	•	154.5	•	—	—	174.9	•
B-9(S)	9	•	125.3	—	—	•	—	—	137.9	•	148.8	•
B-10(O)	10	•	103.7	•	150.6	•	153.0	•	—	—	174.0	•
B-10(S)	10	•	126.0	—	—	•	—	—	134.6	•	149.4	•

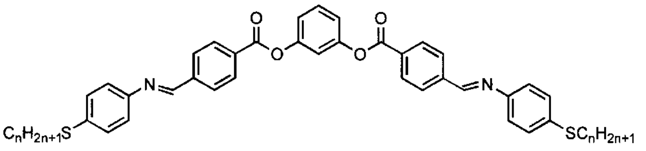


Figure 1. Structure of the new sulphur-containing banana-shaped molecules, **B-*n*(S)** ($n = 8$–10).

The phases were identified by textural observations on thin films between glass slides using a microscope fitted with crossed polarizers.

The data in the table show that replacing the alkoxy terminal chains in the original materials by the corresponding alkylthio chains maintains the occurrence of mesophases in the new materials. The transition temperatures of the new materials—**B-8(S)** to **B-10(S)**—are generally lower than those of the original materials—**B-8(O)** to **B-10(O)**—and the phase morphology is quite considerably altered. The B_2 phase was not observed in any of the materials, but they did possess a phase with a similar optical texture to that of the 'B_7' phase reported by Pelzl *et al.* [12]. The growth of the spiral domain texture of this phase in two of the materials, **B-9(S)** and **B-8(S)**, is shown in figures 2 and 3, respectively. The enthalpy values for all the materials are comparable with those obtained for the same phases in other banana-shaped mesogens [12, 13]; figure 4 shows the DSC heating and cooling cycles for one of the materials, **B-9(S)**. The only phase in common in both series of materials is the B_3 phase. In the original materials this phase lies between the B_4 and B_2 phases, whereas in the alkythio materials the B_3 phase is found below the 'B_7' phase. A contact preparation between a member of the new series, **B-9(S)**, and a standard 'switchable' banana-shaped

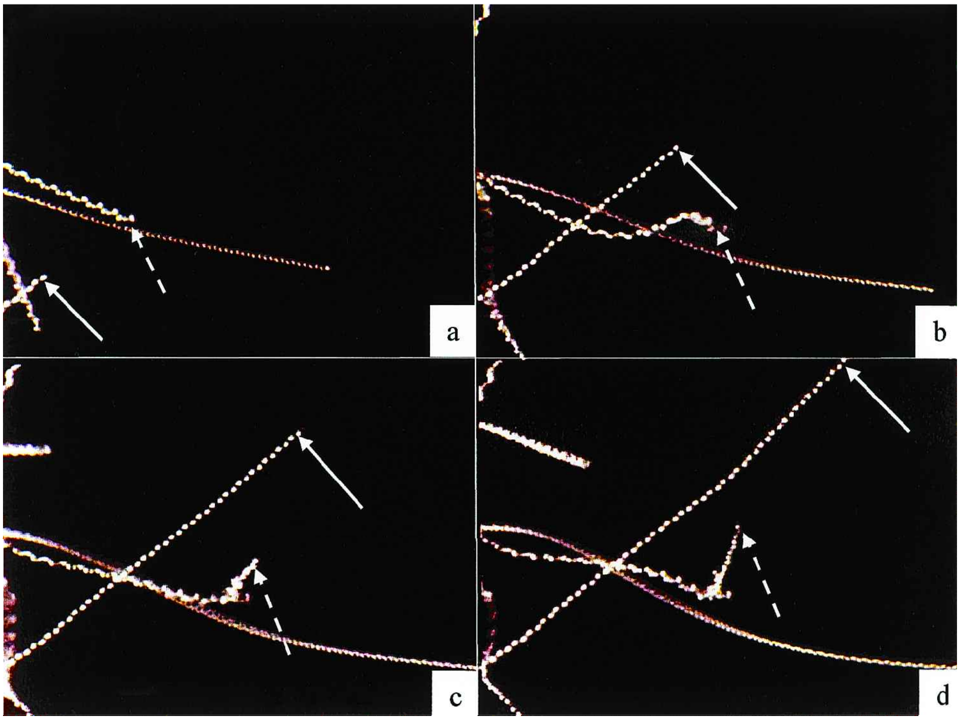


Figure 2(*a*–*d*). Growth of two 'spiral domains' (indicated by arrows) in the microscopic texture of the 'B_7' phase of **B-9(S)** (glass slide, ×25 magnification). The photographs were taken at intervals of 2 s at 147.5°C.

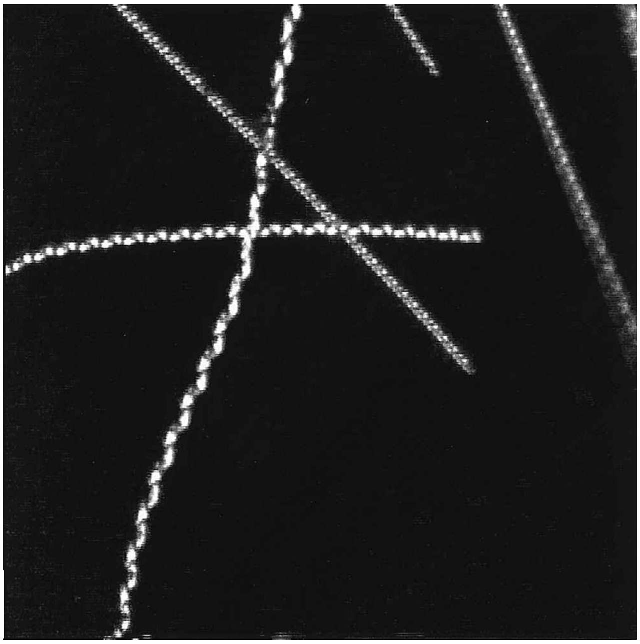


Figure 3. Individual spiral domains in the microscopic texture of the ‘B_7’ phase of **B-8(S)** at 147.2°C (glass slide, × 32 magnification).

mesogen, **B-14**, in which the B_2 phase was found to be miscible with that of the first ‘switchable’ example, **B-(8)** implied (albeit rather crudely) that the phases were immiscible with each other, see figures 5 (*a*) and 5 (*b*). This partially supports the speculation that the two phases are not identical in structure. More detailed investigations of the miscibility of the ‘B_7’ phase, in combination with X-ray studies, are presently being undertaken in order to ascertain the actual differences in structure and nature between the ‘B_7’ and B_2 phases [15].

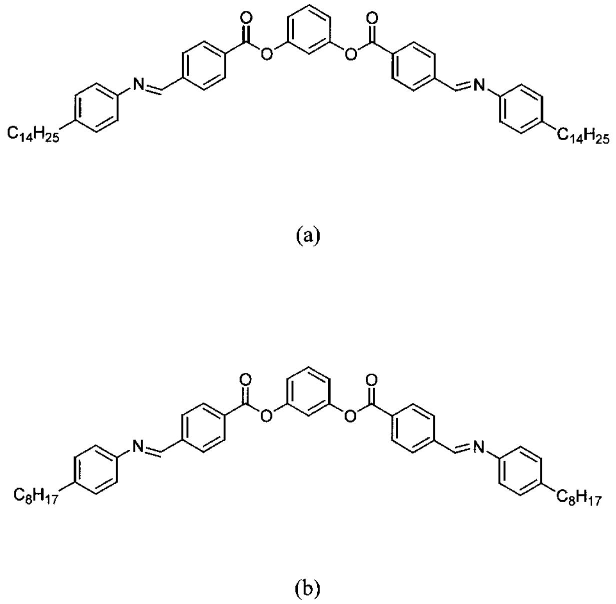


Figure 5. (*a*) **B-14**, a ‘standard’ B_2-forming banana-shaped mesogen; (*b*) **B-8**, the first banana-shaped molecule to form a ‘switchable’ B_2 phase.

As with the alkoxy materials, an increase in the length of the terminal chains, from 8 carbons to 10 carbons, compounds **B-8(S)** to **B-10(S)**, has little effect on the observed transition temperatures.

2.2. *Electro-optic investigations*

The electro-optic properties of two of the new materials, **B-8(S)** and **B-10(S)** were investigated by the current pulse method [16]. The first measurements were carried out in a commercially available ITO-coated (EHC) test cell without alignment layers. The thickness of the

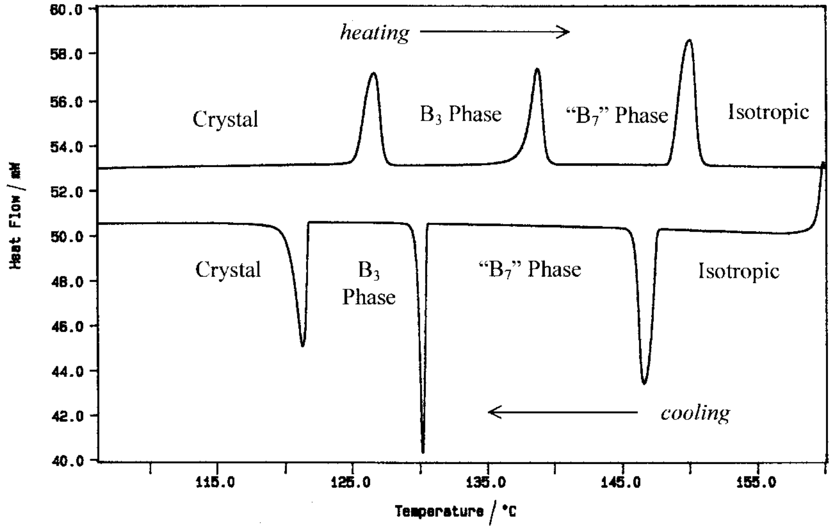


Figure 4. DSC trace of **B-9(S)** on heating and cooling cycles (3.0°C $\min^{-1}$). The B_3 and ‘B_7’ phases arise via clear first order transitions.

cell was found to be 2.7 µm by measurement of its capacitance before filling. A small quantity of **B-10(S)** was filled into the cell by capillary action, with care taken to exclude air bubbles from the 16 mm^2 electrode ('active') area. The liquid crystal was heated to the isotropic phase and allowed to cool slowly (1 K min^{-1}) into the 'B_7' phase. The micrographs in figure 6 show the textures of the 'B_7' phase of the material in the cell between crossed polarizers, at 149°C, under an applied triangular-wave electric field of 100 V_{pp} (± 18.4 V µm^{-1}). A fairly low frequency of 0.5 Hz was applied to allow the textures of the ferroelectric states to be photographed. Domains in which the molecules are aligned in opposite ferroelectric states are clearly observable in figure 6 (*a*). These domains were found to 'switch' to the opposite ferroelectric states on reversing the direction of applied field, figure 6 (*b*), so that the 'dark' domains appeared 'bright', and *vice versa* [11].

A few degrees below the transition to the isotropic phase, the switching appeared to be bistate since the intermediate antiferroelectric state could not be observed, even on removal of the electric field. On cooling to several degrees above the transition to the B_3 phase, a third green-coloured 'striped' texture became

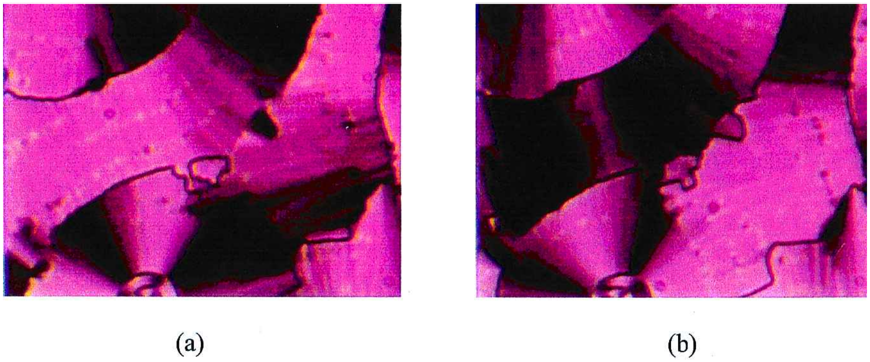

(a) (b)

Figure 6 (*a*, *b*). Photomicrographs of the optical textures of the two ferroelectric states in the 'B_7' phase of **B-10(S)** (149°C).

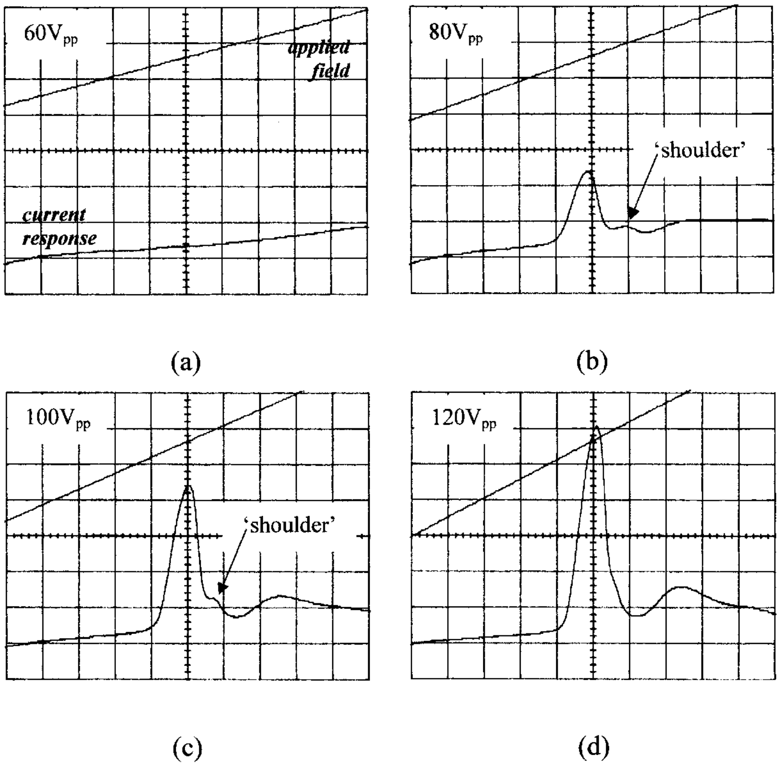
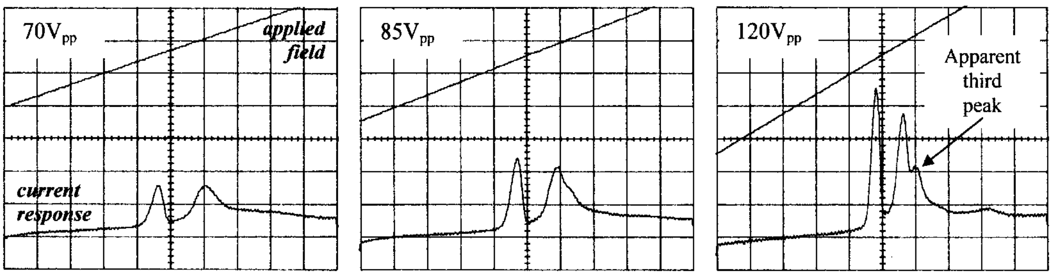


Figure 7 (*a*–*d*). Increase in the observed current response on increasing the amplitude of the applied field (60–120 V_{pp}, 90 Hz) in the 'B_7' phase of **B-10(S)** (149°C). The 'shoulder' (labelled) indicates that a contribution from antiferroelectric switching may be present.



(a) (b) (c)

Figure 8 (*a*–*c*). Current response of the ‘B$_7$’ phase of **B-10(S)** with increasing field strength (149°C, 40 Hz).

clearly distinguishable. This apparent change between bistate and tristate switching behaviour will be the subject of future investigations [17]. On cooling further into the B$_3$ phase, switching could no longer be observed; this is no doubt due to the crystalline nature of this phase [18].

Figure 7 shows the effect of increasing the applied voltage from 60 to 120 V$_{pp}$ on the observed current response. A single polarization peak indicated that ferroelectric switching was occurring in the material. A contribution from antiferroelectric (‘tristate’) switching to the overall switching is tentatively speculated as being present from the observation of an apparent ‘shoulder’ on this peak (labelled in figure 7).

On decreasing the frequency from 90 to 40 Hz, two peaks became clearly discernible on the current response trace at applied voltages of 70 and 85 V$_{pp}$, figures 8 (*a*) and 8 (*b*). This ‘double-flow’ of charge is characteristic for ‘tristate’ antiferroelectric switching and supports our initial speculations that the ‘B$_7$’ phase, as with the B$_2$ phase, is antiferroelectric in nature. This behaviour is comparable to the SmC$^*_A$ phase of ‘standard’ chiral antiferroelectric liquid crystal such as (*R*)- or (*S*)-MHPOBC; at lower frequencies the single current response peak (denoting direct switching between the ferroelectric states) can be resolved into two peaks (denoting switching between the ferroelectric states via the antiferroelectric state) [2]. At 120 V$_{pp}$ an apparent third peak, which follows the two postulated antiferroelectric peaks, is observed, figure 8 (*c*). This may suggest that in addition to the bistate and tristate switching, a combination of switching through the two different types of antiferroelectric phases (homochiral and racemic) [8, 9] is occurring in this sample. This is, at the present time, of course purely speculative as further detailed work must be undertaken to investigate the nature of the antiferroelectric switching which takes place in this phase.

The corresponding **P**$_s$ values of the material as a function of increasing field strength, measured at 90 Hz, are shown in figure 9. The magnitude of the observed **P**$_s$ increased with the applied field; the maximum value of the **P**$_s$ was found to be 94 nC cm^{-2}. This is much lower than values obtained for the original ‘banana-shaped’ (alkoxy) homologues. At the transition to the B$_3$ phase, the current response peaks decreased in intensity, despite increasing the strength of the applied field, until the peaks could no longer be observed. The absence of any observable switching in the B$_3$ phase is consistent with recent observations [18].

The electro-optic switching observed in the ‘B$_7$’ phase of **B-10(S)** was also found in the same phase of the nonylthio homologue, **B-9(S)**, in a 5.2 µm-thick test cell. As before, the cell did not possess any alignment layers. Similar electro-optic switching, between two ferroelectric states with identical *overall* transmittance, was observed in this cell at a frequency of 0.5 Hz (100 V$_{pp}$). On cooling to several degrees above the transition to the B$_3$ phase, the third ‘antiferroelectric’ state became clearly visible. The micrographs in figure 10 show the optical textures

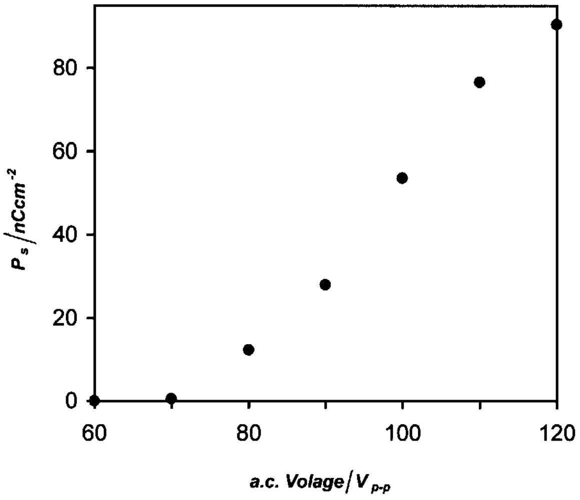


Figure 9. Observed **P**$_s$ for **B-10(S)** on increasing the applied field.

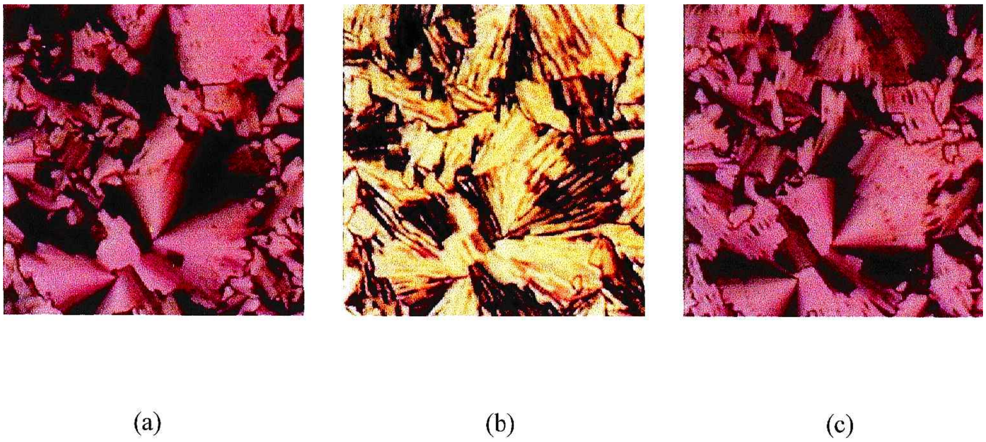
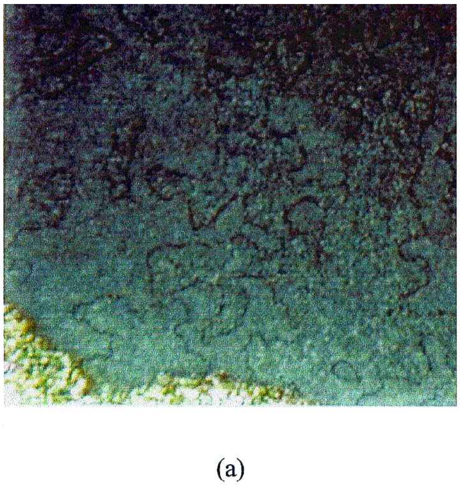

(a) (b) (c)

Figure 10. Optical textures of the two observed ferroelectric states (*a*) and (*c*) and the speculative antiferroelectric state (*b*), in a 5.2 μm-thick cell, **B-9(S)**.


(a)

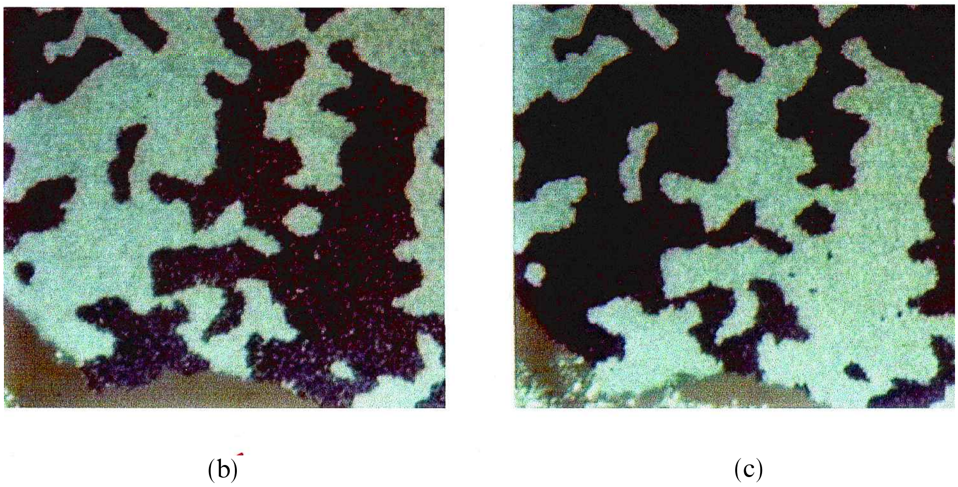

(b) (c)

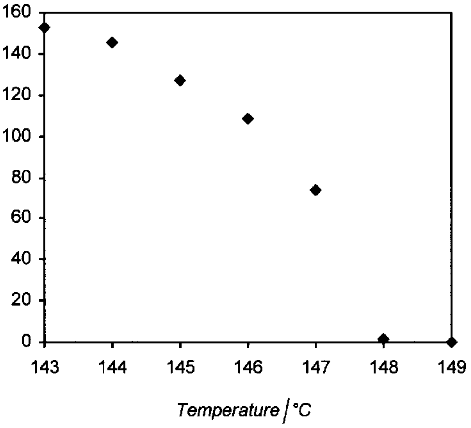
Figure 11. (*a*) Unusual texture of the 'B_7' phase in a 4.1 μm-thick **B-8(S)** cell (after removal of the applied field). (*b*, *c*) Domains of 'opposite optical activity' observed in the 'B_7' texture of **B-8(S)** by rotating the lower polariser first 10° *clockwise* (*b*), then 10° *anticlockwise* (*c*) from the 'crossed' position, in the same region of the cell as shown in figure 10(*a*).

of the two ferroelectric states, (*a*) and (*c*), and the 'middle' antiferroelectric state (*b*).

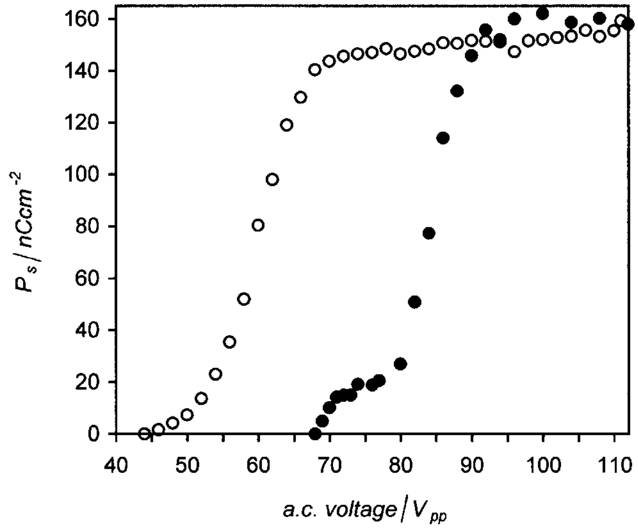
Electro-optic measurements were also carried out on **B-8(S)**, the octyl homologue of **B-10(S)**. The EHC cell used for these measurements was 4.1 µm thick and possessed polyimide alignment layers. On cooling slowly (1.0 K min^{-1}) from the isotropic liquid into the 'B_7' phase, with an applied triangular-wave field of 100 V_{pp} (± 12.2 V $\mu\mathrm{m}^{-1}$) at 40 Hz, a different texture from those of the 'B_7' phases in the cells of **B-10(S)** became visible, figure 11 (*a*). The fact that the cell possessed alignment layers, whereas the cells used for investigating **B-10(S)** did not, may have contributed to the difference in the texture, although this may not account for such a large difference. Rotating the lower polarizer of the microscope *clockwise* by 10°, so that it was no longer 'crossed' at 90° with the upper polarizer, revealed that the texture of this phase (in the cell) was composed of 'dark' and 'light' domains, figure 11 (*b*). Rotating the lower polarizer *anticlockwise* by 20° from this position (so that it was 10° away from 'crossed' in the opposite direction) had the effect of reversing the transmittance of light within these domains; the 'dark' domains now appeared 'light' and *vice versa*, figure 11 (*c*). These textures and this behaviour bear close resemblance to those observed by Heppke *et al.* in the B_4 phase of **B-10**, one of the original alkoxy-substituted 'banana-shaped' mesogens [11]. In the original material, similar domains which were found to possess 'opposite optical activity' were postulated as resulting from the spontaneous optical resolution of the phase on cooling from the B_2 phase. This microseparation, between *like* and *unlike* chiral domains, provided further evidence to support the hypothesis that smectic phases formed by achiral banana-shaped molecules are in fact chiral by nature.

Conversely, by cooling **B-8(S)** at a faster rate (5°C min^{-1}), and without applying an electric field, the texture of the 'B_7' phase appeared to resemble those of the phases in the **B-10(S)** cell. On application of a field of 90 V_{pp} (± 10.1 V $\mu\mathrm{m}^{-1}$, 10 Hz) the focal-conic-like texture began to 'switch' in a similar manner to that in the previous cells. This switching was also accompanied by a measurable $\mathbf{P}_s$ peak on the current response: figure 12 (*a*) shows the increase in the observed $\mathbf{P}_s$, on cooling the material from the isotropic liquid, measured with an applied field of 100 V_{pp} (± 12.2 V $\mu\mathrm{m}^{-1}$) at a frequency of 200 Hz. The $\mathbf{P}_s$ hysteresis against field strength of the material in the 'B_7' phase at 143°C, is shown in figure 12 (*b*).

The maximum value of the $\mathbf{P}_s$ from the hysteresis measurement was found to be 160.2 nC cm^{-2}. This value is greater than that obtained for **B-10(S)**, but still smaller than the $\mathbf{P}_s$ values of the original banana-shaped mesogens [7].



(a)



(b)

Figure 12. (*a*) Increase in the observed $\mathbf{P}_s$ on cooling from the isotropic liquid; (*b*) measured $\mathbf{P}_s$ hysteresis (on increasing and decreasing applied field) in the 'B_7' phase for **B-8(S)** (143.0°C).

3. Conclusions

A series of new sulphur-containing LC materials with banana-shaped molecules has been prepared and characterized. The materials exhibit the unusual 'spiral-domain' texture in the novel 'B_7' phase, which is believed to provide evidence to indicate the helical character, and consequently chiral nature, of the phase. In addition one of the materials, **B-8(S)**, exhibited a texture with domains of 'opposite optical activity' in an aligned cell. Two of the materials investigated, **B-8(S)** and **B-10(S)**, displayed an electro-optic response in the 'B_7' phase, together with a measurable spontaneous polarization; preliminary results indicate that the phase is antiferroelectric in nature. Further detailed investigations of these materials will be presented in the near future [14, 15, 17].

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