

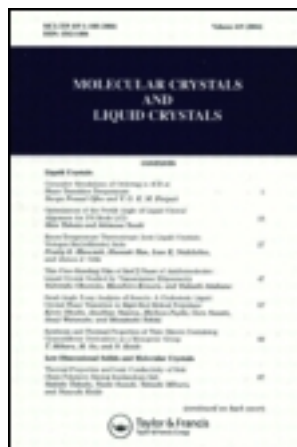
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G. Heppke^a, D. D. Parghi^a & H. Sawade^a

^a Technical University of Berlin, Str. Des 17. Juni 135, 10623, Berlin, Germany

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Investigations on Novel Sulphur-Containing “Banana-Shaped” Liquid Crystals

G. HEPPKE, D. D. PARGHI and H. SAWADE

Technical University of Berlin, Str. Des 17. Juni 135, 10623 Berlin, Germany

This paper details the investigations of a series of novel sulphur-containing “banana-shaped” liquid crystals, B-n(S) ($n = 8-10$). The materials exhibit a B_3 phase and also a phase with a “spiral-domain” texture similar to that of the “ B_7 ” phase. The mesomorphic properties of a series of binary mixtures between the different homologues are reported. Results from current response measurements between pure B-9(S) and a 1:1 binary mixture of B-8(S) and B-10(S) are also presented.

Keywords: “Banana-shaped”; homologous series; antiferroelectric

INTRODUCTION

The first homologous series of bent-core “banana-shaped” liquid crystalline materials was synthesized by Matsunaga in 1993^[1]. Physical measurements carried out by Niori found the materials possessed a spontaneous polarisation which indicated ferroelectric switching^[2]. The very large magnitude of the observed spontaneous polarisation was believed to reflect the highly polar character of the molecules. It is speculated that this polar character is enhanced by the packing of the molecules with their transverse dipoles lying in a common direction (Figure 1) in the “switchable” B_2 phase. The fact that the materials could be “switched” between ferroelectric states by an external electric field, despite the absence of any chiral centres in the molecules, proved to be a curiosity which attracted a number of groups to further investigate these materials^[3]. Recent evidence has suggested that the materials are actually antiferroelectric rather than ferroelectric as initially speculated^[4].



FIGURE 1 Postulated packing arrangement of molecules in the B₂ phase (one smectic layer).

See Color Plate VIII at the back of this issue.

Very recently a new phase, assigned the “B₇”, was discovered by Pelzl *et al.* in a nitro-containing banana-shaped liquid crystal^[5]. The optical texture of the phase is unlike that of any of the known banana phases found in other related materials. The observation of microscopic “spiral domains” in the “B₇” phase is believed to suggest the presence of a helical superstructure^[6]. A new homologous series of materials we reported recently, B-8(S) to B-10(S) (Figure 2), were also found to possess a phase similar in appearance to the “B₇”^[7]. The materials were found to switch electrooptically in this phase; textural observations and current response measurements clearly indicated the switching was antiferroelectric.

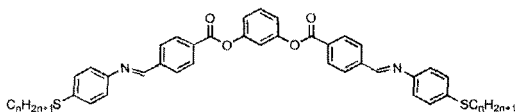


FIGURE 2 Structure of the new sulphur-containing compounds reported recently (B-n(S); n = 8, 9, 10).

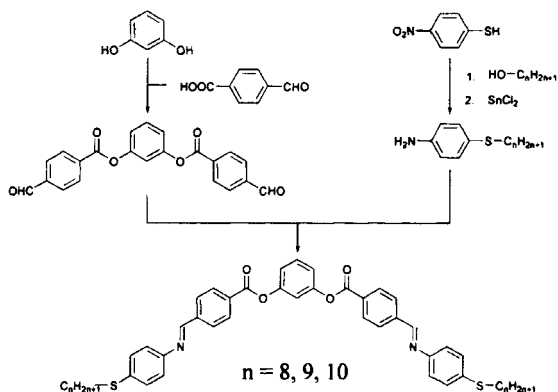
One of the homologues, B-8(S), also exhibited domains of opposite optical activity^[8], similar to those reported for the B₄ phase of the original materials (of Niori *et al.*)^[9].

In this paper we report the synthesis and mesomorphic properties of the sulphur-containing materials together with the mesomorphic and physical properties of a series of binary mixtures of the materials. It is hoped that by studying mixtures an insight into the physical nature of the materials themselves can be gained.

RESULTS AND DISCUSSION

Synthesis

The materials, B-8(S) to B-9(S) were prepared according to the synthesis outlined in Scheme 1.

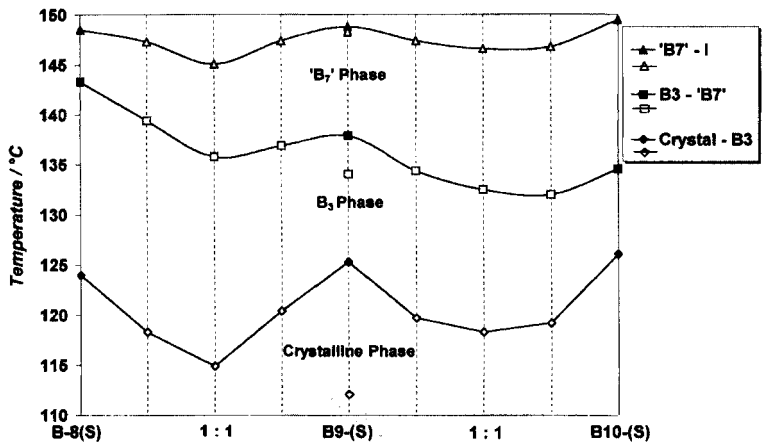


SCHEME 1

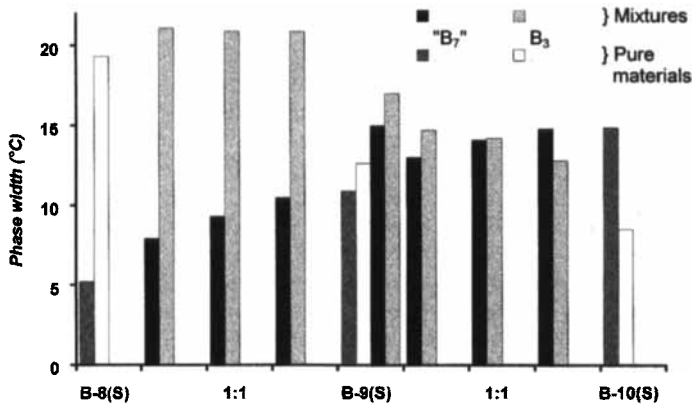
Mesomorphic Properties

Graph 1 shows the transition temperature trends for the pure compounds together with a series of binary mixtures composed of different percentages (by weight) of the compounds (determined by microscopy and DSC). The melting points (crystal – B₃ transitions) of the pure materials increase in temperature with increasing terminal chain length ($n = 8$ to $n = 10$). Conversely, the B₃ – speculated “B₇” transition shows a decrease in temperature, whereas the “B₇” – Isotropic transition is relatively unaffected. A 1:1 binary mixture of B-8(S) and B-10(S) showed lower temperatures for all three transitions in comparison with pure B-9(S). The binary mixtures *between* the pure compounds show a general decline in all transition temperatures on approaching a 1:1 concentration. The fact that the clearing point is also affected in this manner is rather unusual when compared with binary mixtures between “regular” calamitic ferroelectric liquid crystals; in these materials a linear change in the clearing point is most often observed.

Graph 2 shows the change in the widths of the B₃ and speculated “B₇” phases for both the pure materials and the binary mixtures. The phase width for the “B₇” appears to increase in the pure materials with increasing terminal chain length; the B₃ phase does not appear to follow this trend. For the binary mixtures an increase in the proportion of a component with a chain one carbon longer appears to widen the “B₇” phase.



GRAPH 1 Transition temperatures of the pure materials and the binary mixtures (open points = mixtures, closed points = pure materials).



GRAPH 2 Phase widths of the "B7" and B3 phases of the pure materials and binary mixtures.

The characteristic spiral-domain texture of the "B7" phase is observed in all of the pure materials and mixtures; examples of these spiral domains are shown in figures 3a and 3b.

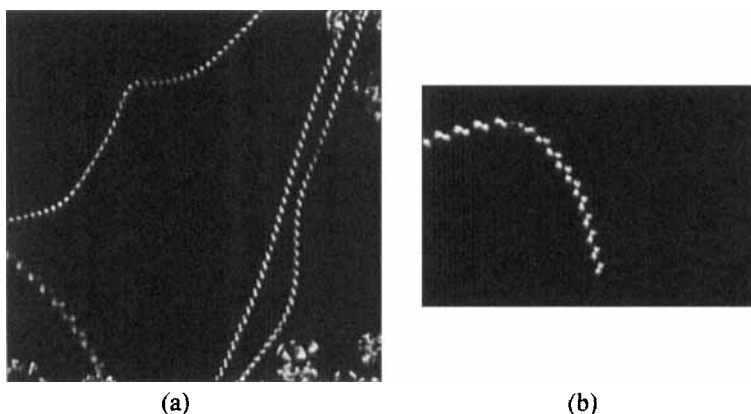


Figure 3(a) Photomicrograph of the speculated " B_7 " phase of the B9(S):B10(S) binary mixture (146 °C); (b) high magnification photomicrograph of a single spiral domain of the " B_7 " phase *growing* out of the isotropic phase of B-8(S). See Color Plate IX at the back of this issue.

By closely examining the propagation of the spirals throughout the sample two directions of growth could be observed; apparent "left-handed" and "right-handed" helical patterns were discernible.

The DSC trace of the 1:1 B-8(S):B-10(S) mixture is shown in Figure 4. The enthalpy values for the phase transitions of this mixture are found to be slightly higher than those of pure B-9(S) (Table 1).

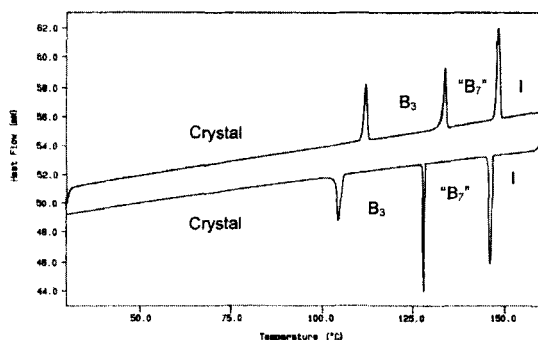


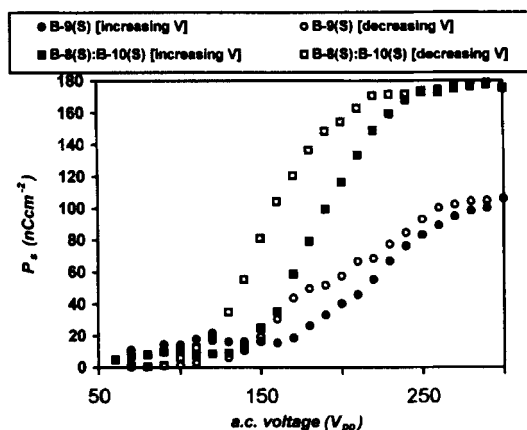
FIGURE 4 DSC trace of the 1:1 B-8(S):B-10(S) mixture (heating and cooling rate: 3.0 °Kmin⁻¹)

Material / Mixture	Cr	$^{\circ}\text{C}$ (kJmol^{-1})	B ₃	$^{\circ}\text{C}$ (kJmol^{-1})	"B ₇ "	$^{\circ}\text{C}$ (kJmol^{-1})	I
B-9(S)	•	125.3 (15.11)	•	137.9 (13.73)	•	148.8 (21.11)	•
1:1 B-8(S):B-10(S)	•	112.0 (15.21)	•	133.7 (14.66)	•	148.3 (24.87)	•

TABLE 1 Transition temperatures and enthalpy values of pure B-9(S) in comparison to the 1:1 B-8(S):B-10(S) mixture.

Physical Properties

Graph 3 shows the spontaneous polarisation hysteresis of the 1:1 B-8(S):B-10(S) mixture in comparison with that of pure B-9(S) taken at 137.7 °C and 142.9 °C respectively (5 °C above the transition to the B₃ phase for each sample). The test cells used for these measurements were standard ITO / PI-coated 5µm Linkam cells with antiparallel rubbing. The measurements were taken at a frequency of 170Hz in order to avoid the contribution of ions to the overall values of the spontaneous polarisation.



GRAPH 3 Spontaneous polarisation hystereses for the materials.

The values of the spontaneous polarisation observed for the B8(S):B-10(S) mixture are generally higher than those of pure B-9(S) under applied fields of identical magnitude. We could speculate this may be due to enhanced packing of the molecules in the *switchable* "B₇" phase of the mixture in comparison with that of pure B-9(S). This may favour the

orientation of the dipole moments within the smectic layers in a common direction that may account for the larger spontaneous polarisation. Further work must of course be undertaken in order to investigate this. A second difference between the two hystereses is that the spontaneous polarisation in the mixture appears to reach saturation (indicated by the levelling of the values on increasing and decreasing field strength). In the case of pure B-9(S) the spontaneous polarisation does not reach saturation at the maximum field strength. This may account for the irregular trend on decreasing the field strength.

The figures below show the increase in the size of the observed current response with increasing field strength ($50V_{pp}$ to $300V_{pp}$), for both the pure material and the mixture, at frequencies of 170Hz, 90Hz and 45Hz (figures 5a to c, and 6a to c respectively).

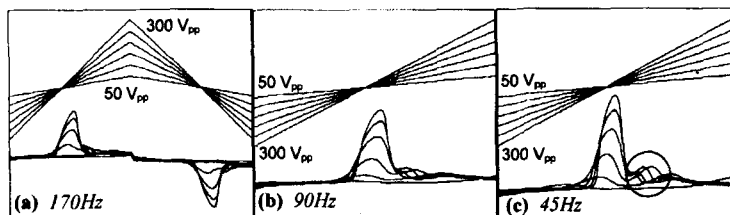


FIGURE 5 Current response of pure B-9(S)

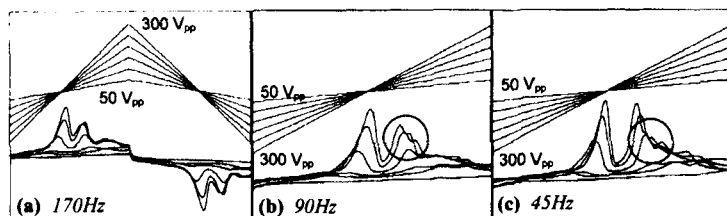


FIGURE 6 Current response of 1:1 B-8(S):B-10(S)

The current responses for the two samples also appear to be dissimilar. For pure B-9(S) at 170Hz a "shoulder" on the main current response peak, implying antiferroelectric switching, is visible at lower field strengths. On increasing the field strength this shoulder appears to merge with the main peak which itself becomes sharper. This behaviour is typical for "regular" antiferroelectric calamitic liquid crystals. By reducing the frequency first to 90Hz then 45Hz this shoulder becomes more pronounced (circled). For

the B-8(S):B-10(S) mixture two peaks on the current response are clearly visible at 170Hz. At 90Hz the second peak itself appears to possess a shoulder (circled); by 45Hz this shoulder becomes resolved as an apparent third peak close to, but distinguishable from, the second peak. The observation of two peaks on the current response of the binary mixture is believed to provide a clear indication of antiferroelectric switching. The observation and indeed the significance of the apparent third peak is not understood although the influence of ions cannot be ruled out at this time

CONCLUSIONS

We have studied the mesomorphic properties of a series of novel sulphur-containing "banana-shaped" liquid crystals and their binary mixtures. The mixtures, as with the pure materials, exhibit the unique "spiral domain" texture similar to that observed in the "B₇" phase, and show an unusual trend in the transition temperatures for both the speculated "B₇" and B₃ phases. The physical properties of a 1:1 B-8(S):B-10(S) mixture, in comparison with pure B-9(S) were also investigated; the two samples were found to behave differently under similar conditions.

Acknowledgements

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References

- [1] Y. Matsunaga, S. Miyamoto, *Mol. Cryst. Liq. Cryst.*, **237**, 311 (1993).
- [2] T. Niori, T. Sekine, H. Takezoe, *J. Mater. Chem.*, **6**, 1231 (1996).
- [3] International Workshop on Banana-Shaped Liquid Crystals: "Chirality by Achiral Molecules" TU-Berlin, Germany (1997).
- [4] D. R. Link, G. Natale, R. Shao, J. E. MacLennan, N. A. Clark, E. Körblova, D. M. Walba, *Science*, **278**, 1924 (1997); G. Heppke, D. Moro, *Science*, **279**, 1872 (1998).
- [5] G. Pelzl, S. Diele, Ch. Lischka, I. Wirth, W. Weissflog, *Liq. Cryst.*, **26**, 135 (1998).
- [6] G. Pelzl, S. Diele, Ch. Lischka, I. Wirth, W. Weissflog, *proceedings of the 28th Freiburger Arbeitstagung Flüssigkristalle*, Freiburg, Germany (1999).
- [7] G. Heppke, D. D. Parghi, H. Sawade, *proceedings of the 28th Freiburger Arbeitstagung Flüssigkristalle*, Freiburg, Germany (1999).
- [8] G. Heppke, D. D. Parghi, H. Sawade, *Liq. Cryst.*, in press.
- [9] G. Heppke, D. Krücker, C. Löhning, D. Löttsch, P. J. Collings, *in preparation*.