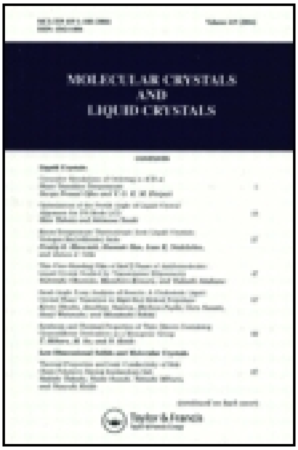

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A Compound Exhibiting a Crystal b to Hexatic b Phase Change

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A COMPOUND EXHIBITING A CRYSTAL B TO HEXATIC B PHASE CHANGE

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Abstract: Recent studies have shown that the smectic B phase can exhibit two basic structural forms, namely the hexatic B and the crystal B modifications. Furthermore, a transition between the two phases has been shown to occur in certain binary mixtures. This present study demonstrates that a pure compound is also capable of exhibiting such a phase transition, thus indicating that the two B modifications have separate identities.

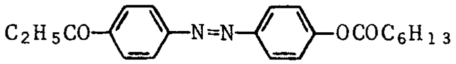
Introduction

The smectic B phase has been shown to exhibit two basic structural forms,[1,2,3] the hexatic B and crystal B phases. In the crystal B phase the ordering of the molecules within the layers (hexagonal) and between the layers is long-range, whilst in the hexatic B phase there is very little layer correlation and the in-plane hexagonal, positional ordering extends only over a distance of 100-200 Å. Miscibility studies involving hexatic B and crystal B phases have revealed that a transition, observable by X-ray diffraction, can occur between the two phases in certain binary mixtures.[4] This fact indicates that the two phases have separate identities and therefore should be of different miscibility groups.

However, in a recent study by Poeti *et al.*[5] a material was disclosed that exhibited four smectic phases and a nematic phase. The authors although declining to categorise the smectic phases, indicated that there were no appreciable changes in the microscopic textures at the phase transitions between the three higher temperature smectic phases. As these three phases exhibit only focal-conic and homeotropic textures the material, 4-propionyl-4'-n-heptanoyloxyazobenzene, warranted further investigation in order to ascertain the relationship between these phases and the hexatic B-crystal B phenomenon.

Results and Discussion

The compound 4-propionyl-4'-n-heptanoyloxyazobenzene



was synthesised and found to have the following transition temperatures

$$\mathrm{I} \xrightarrow[142.5]{} \mathrm{N} \xrightarrow[141.7]{} \mathrm{S_A} \xrightarrow[90.3]{} \mathrm{S_1} \xrightarrow[86]{} \mathrm{S_2} \xrightarrow[76.5]{} \text{crystal } (\mathrm{S_3}) \quad \underset{92}{\text{mp}}$$

in agreement with those reported previously. The last phase indicated by Poeti *et al.* as S_3 is in fact recrystallisation occurring. The microscopic textural pattern of the crystal retains some characteristics of the preceding phase S_2, ie, a broken focal-conic texture appears to be adopted by the crystal. Thus, the ester only exhibits three smectic mesophases; however, all of these phases show unbroken focal-conic fan and homeotropic textures. The three phases also exhibited positive uniaxial interference figures indicating that the phases could only be of the A, hexatic B or crystal B types.

Microscopic observations of the textures formed by this compound show that a nematic phase separates in its schlieren texture on cooling the isotropic liquid. Further cooling produces a transition to a smectic A phase characterised by its focal-conic and homeotropic textures. The homeotropic texture is retained on subsequent cooling through to the S_1 and S_2 phases. The focal-conic texture, however, does show some very small and ill-defined changes at the transitions from the A phase to S_1 and from S_1 to S_2. The fan texture becomes less lined at each transition with the radial lines and parabolic focal-conic defects associated with the focal-conic domains of the A phase being reduced in number at each transition. Thus S_3 exhibits a very clear, unblemished focal-conic fan texture with few defects, whilst the S_A phase has a larger number of these defects. However, cooling and reheating of the sample gives more pronounced changes in the defects particularly for the A phase, which shows a greater number of defects on reheating due to the paramorphic constraints of the previous phase.

Differential scanning calorimetry confirms the microscopic observation that five transitions do occur on cooling; Figure 1 shows the heating and cooling traces for the azo-ester. The upper trace shows the first heating cycle; the largest peak indicates the melting of the material directly to the S_A phase. The cooling cycle shown below depicts five enthalpy changes, with two extra phase transitions occurring below the original melting point. These changes are for the S_A to S_1 and S_1 to S_2 transitions.

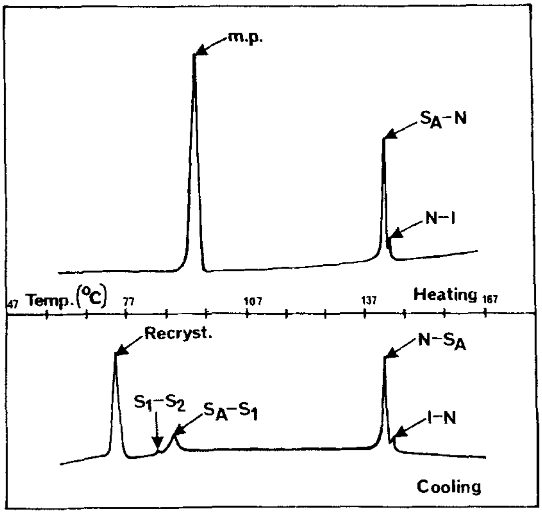


FIGURE 1: The DSC heating and cooling cycles for 4-propionyl-4'-n-heptanoyloxyazobenzene

In order to ascertain the nature of the phase types of the azo-ester miscibility studies were carried out using standard materials. As no material is available that exhibits both hexatic and crystal B phases, two miscibility studies were carried out using two standard materials which exhibit different B modifications, n-hexyl 4'-n-pentyloxybiphenyl-4-carboxylate

(65OBC, A, hexatic B, and E phases)[2] and *N*-(4'-n-butyloxybenzylidene)-4-n-octylaniline (40.8, N, A, and crystal B phases).[3] The miscibility diagrams of state for binary mixtures involving the azo-ester and the two reference compounds are shown back-to-back in Figure 2. The left-hand miscibility figure clearly shows that the crystal B phase of 40.8 is miscible with the S_2 phase of the azo-ester. The azo-compound is also shown to exhibit nematic and smectic A phases as well. The right-hand miscibility figure involving mixtures of the azo-ester and 65OBC shows that the S_1 phase is of the hexatic type. The S_1 to S_2 phase transition temperatures fall away with an increasing proportion of 65OBC in the mixture. The S_B to S_E transition temperatures also fall away on increasing the proportion of the azo-ester in the mixture with 65OBC indicating that the ester is unlikely to exhibit S_E properties.

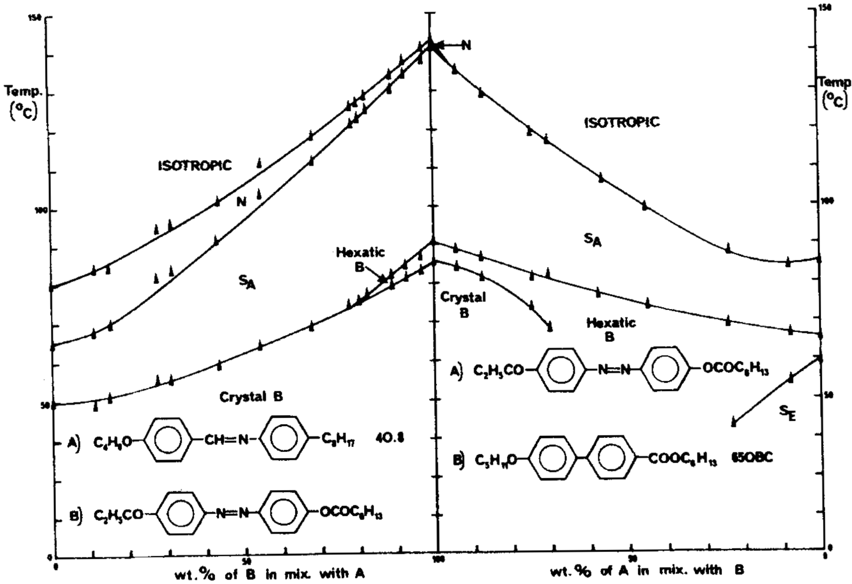


FIGURE 2: Miscibility diagrams of state for 4-propionyl-4'-n-heptanoyloxyazobenzene with 40.8 (left-hand side) and 65OBC (right-hand side)

The clear band of hexatic B phase occurring through the central portion of the combined figures plus the crystal B phase being formed on cooling this phase indicates that the azo-ester exhibits N, A, hexatic B, and crystal B phases.

Attempts to confirm these observations by structural analysis using X-ray diffraction techniques failed because of recrystallisation of the sample. However, the oxidised compound, 4-propionyl-4'-n-heptanoyloxyazoxybenzene was found to exhibit a similar phase sequence to the azo compound, but it also exhibits a smectic E phase below S_2 on cooling.

Conclusion

The compound 4-propionyl-4'-n-heptanoyloxyazobenzene was found to exhibit a N, A, hexatic B, crystal B phase sequence indicating that the two B phases have separate identities and should not share the same miscibility code-letter.

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