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A Study of the Transitions Smectic A–Hexatic B and Hexatic B–Crystal B By X-Ray Diffraction†

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The phase transitions Smectic A–hexatic B and hexatic B–crystal B for the pure compound 4-propionyl-4′-*n*-heptanoyloxyazobenzene have been investigated by X-ray diffraction.

Pretransitional effects have been observed in the Smectic A phase.

The temperature dependence of the in-plane positional coherence length $\xi_{\parallel}$ has been determined from the large angle diffusion peak, associated with an in-plane structure factor of Lorentzian shape, as predicted by theory.

$\xi_{\parallel}$ values vary in the hexactic phase from $\xi_{\parallel} \simeq 100$ Å to $\xi_{\parallel} \simeq 40$ Å in the range of temperature from 88.7 °C to 85.6 °C, in very good agreement with previous results of Pindak *et al.* on a single crystal of a compound showing only the hexatic B and no crystal B phase.

INTRODUCTION

A theoretical study of the melting of two dimensional (2D) solids made by Halperin and Nelson[1] predicted the existence of a 2D liquid crystal phase with an exponential decay of translational order, but power-law decay of six-fold orientational order. Birgeneau and Litster[2] suggested that the concepts introduced by Halperin and Nelson for the two-dimensional melting can be carried over to a three-dimen-

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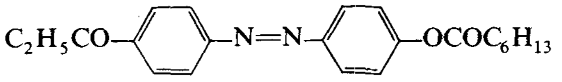
sional (3D) liquid crystal consisting of 2D layers. The existence of such a new mesophase was detected by Pindak *et al.*[3] in the compound 65OBC. A coherence length $\xi_\parallel$ ranging from 60 to 90 Å inside the layers for this phase was found.

A transition between the well known smectic B phase, called the crystal B phase, and the new mesophase, called the hexatic B phase, was detected by Goodby and Pindak[4] in binary mixtures: while conventional miscibility methods could not be used to distinguish between the two B phases, X-ray diffraction clearly indicated that the two phases are thermodynamically distinct and have separate identities.

The existence of both these B modifications in a pure compound was first shown by Goodby,[5] by using miscibility techniques and then by Albertini *et al.*[6] by using X-ray diffraction. The compound used in these two investigations was 4-propionyl-4′-*n*-heptanoyloxyazobenzene, which was first synthesised by Poeti, Fanelli and Braghetti[7] and has the structural formula:



The compound shows the following phase transitions:[5-7]

$$\mathrm{I} \xrightarrow[143.5\,^\circ\mathrm{C}]{} \mathrm{N} \xrightarrow[141.5\,^\circ\mathrm{C}]{} \mathrm{S_A} \xrightarrow[\sim 90\,^\circ\mathrm{C}]{} \mathrm{B_{hex}} \xrightarrow[\sim 85.5\,^\circ\mathrm{C}]{} \mathrm{B_{cryst}} \xrightarrow[76.5\,^\circ\mathrm{C}]{} \underset{92\,^\circ\mathrm{C}}{\text{crystal (mp)}}$$

In ref. 6, the following structural quantities have been obtained at $T = 87\,^\circ\mathrm{C}$: a short range order inside the hexatic layers, with a correlation length of 60 ± 6 Å; an interlayer periodicity $d = 25.8 \pm 0.2$ Å, and a hexagonal lattice parameter $a = 5.01 \pm 0.01$ Å. Moreover a Lorentzian shape of the in-plane structure factor has been found, in agreement with the theoretical predictions for the hexatic phase.

Some other experiments have been performed very recently on the hexatic B mesophase. In particular, the differences between the compound 65OBC, which exhibits a hexatic B phase, and the compound 40.8, which exhibits a crystal B phase, were investigated by Huang *et al.*,[8] and by Cladis and Goodby[9]. The former, in a study of heat capacity, produced evidence for the second order character of the transition hexatic B–smectic A for 65OBC, in contrast to the first order crystal B–smectic A transition of 40.8. The latter found different pressure-temperature diagrams for the two compounds.

The shear mechanical properties of hexatic B have been studied by Pindak *et al.*:[10] no in-plane shear modulus was found in the hexatic phases investigated.

A theoretical explanation of the results of refs. 3 and 8 can be found in the model proposed by Bruinsma and Aeppli[11] for the hexatic phase.

Finally, thermodynamic and dilatometric characteristics of the hexatic B phase for some compounds were obtained by Poeti, Fanelli, and Guillon.[12]

Studies on 2D non-liquid phases were performed on thin films of 40.8 by Moncton and Pindak[13] and on Smectic F and Smectic I phases of TBBA homologous compounds by Benattar *et al.*:[14a,b] a coherence length of a few hundred Å was obtained for smectic F, which might correspond to a tilted hexatic phase.

In the present work we have studied the Smectic A to hexatic B and hexatic B to crystal B transitions of the compound 4-propionyl-4′-*n*-heptanoyloxyazobenzene.

EXPERIMENTAL RESULTS

Experimental details

The X-ray diffraction experiment was carried out by using Ni-filtered Cu$K\alpha$ radiation ($\lambda = 1.54$ Å), provided by a PW1130/90 Philips generator, and a horizontal MZIII Rich. Seifert goniometer.

The sample had a thickness of ~ 1.5 mm and was held by two very thin Al sheets fixed to a circular hole in an Al matrix with a diameter of ~ 1 cm. Heating was achieved by a hot stage containing electrical resistors, providing a temperature control to ±0.1°C.

Results

X-ray diffraction patterns have been recorded at different temperatures starting from 92°C in the S_A phase and progressively cooling the sample through the S_A–hexatic B transition and the hexatic B–crystal B transition to 83°C. Figure 1 presents the patterns obtained for the different mesophases. The low angle peaks corresponding to Bragg diffraction from smectic layers have been omitted from Figure 1 because they remain practically unchanged as a function of temperature, as already noted in ref. 6. However, from their position, the interlayer spacing was obtained and is reported as a function of temperature in Figure 3.

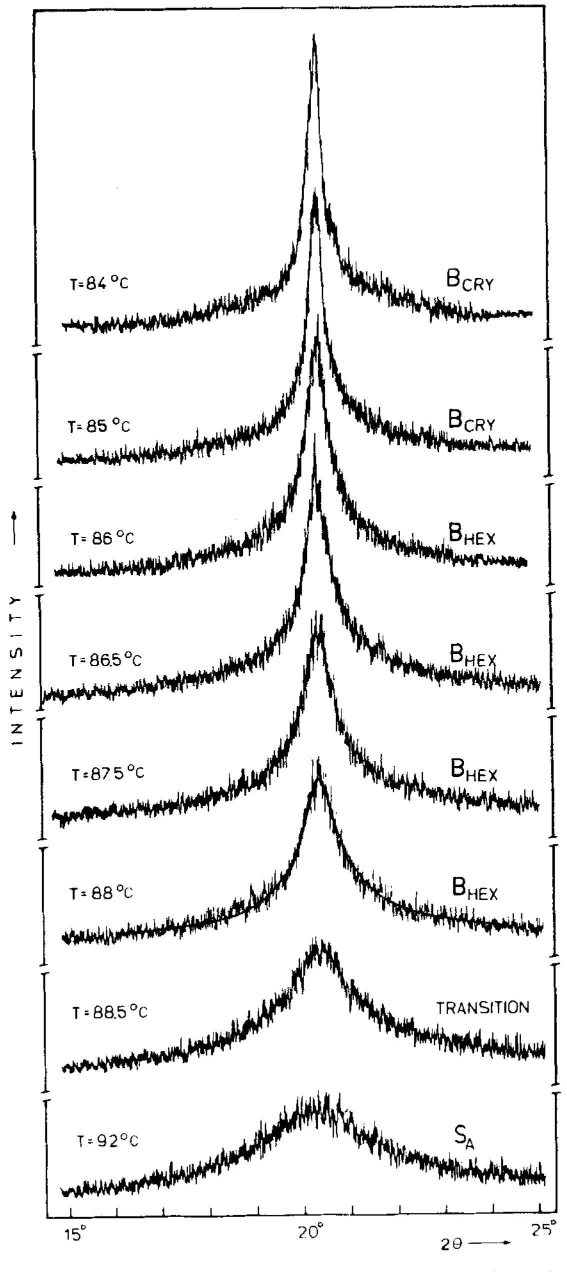


FIGURE 1 X-ray intensity *vs.* diffraction angle 2θ for different values of temperature.

Figure 1 therefore reports only the large angle diffusion peak, which is quite broad at the higher temperatures in the S_A phase and becomes progressively narrower as the temperature is decreased. The narrow peaks obtained at 85 and 84 °C are characteristic of the smectic B phase as discovered[15] a long time ago, and correspond to the (100) hexagonal reflection. Actually if a three-dimensional character for this crystal B phase is assumed, one should also observe the (101) reflection, which however is very near to the (100) reflection, and it is possible that they are not resolved, using the powder method, as already emphasized in ref. 16 and discussed in ref. 6.

For intermediate temperatures (e.g. 87.5 °C), a less narrow peak is observed which corresponds to a shorter range ordering within the layers compared with the long range ordering of the crystal B phase; this is in agreement with the already known characteristics of the hexatic B phase,[3,6] as will be discussed below.

A first semi-quantitative, but pictorial elaboration of the data is reported in Figure 2a, which presents the full width at half maximum as deduced from the data of Figure 1, after correction for the $\Delta Q = 0.014$ Å^{-1} resolution width ($Q = 4 \cdot \pi \cdot \sin\theta/\lambda$, where λ is the X-ray wavelength) obtained from the (100) reflection of α-quartz powder.[6] A curve was fitted by hand to the data and the derivative of this curve was calculated as a function of temperature: from the data reported in Figure 2b, two peaks appear at $T = 88.7$ °C and $T = 85.6$ °C, which show in an unusual way the existence of the phase transitions S_A–hexatic B and hexatic B–crystal B respectively.

From the position of the center of the large angle peak for the crystal B and hexatic B phases, the interplanar distance d_{100} was obtained. The relation between d_{100} and the intermolecular distance d in a hexagonal structure is $d = 2 \cdot d_{100}/\sqrt{3}$.

Figure 4 reports d values as a function of temperature. In the smectic A phase the hexagonal order is destroyed and d was found by using the modified Bragg equation:[17] $1.117\,\lambda = 2 \cdot d \cdot \sin\theta$.

The abrupt increase of the d values at the transition S_A–B_{hex} might not correspond to an actual physical situation, and may be due to an incomplete applicability of the modified Bragg equation to the system under investigation.

From the data reported in Figure 1, the in-plane positional correlation length $\xi_{\parallel}$ was obtained as a function of temperature by using the same procedure adopted in ref. 6. Theory[1,2] predicts that the in-plane structure factor of hexatic and S_A phases should be of Lorentzian shape:

$$f(\mathbf{Q}_p) \propto \left[(\mathbf{Q}_p - \mathbf{Q}_0)^2 + K^2\right]^{-1},$$

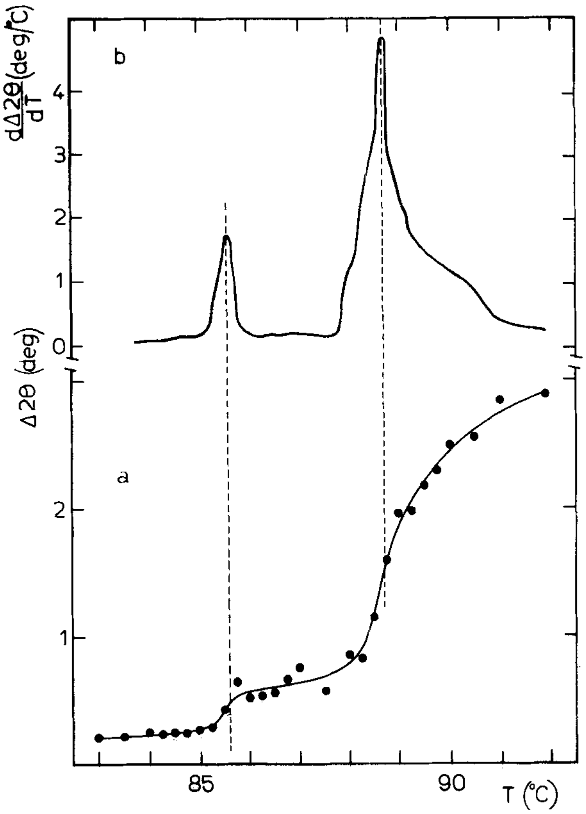


FIGURE 2 Full width at half maximum of the large angle peak *vs.* temperature, (a) after correction for instrumental resolution and (b) its derivative $d\Delta 2\theta/dT$.

Q_0 being the (100) vector in reciprocal space and the width K being related to the in-plane correlation length $\xi_{\parallel}$ by $\xi_{\parallel} = 1/K$. However, the lineshape of a powder ring is not Lorentzian due to the three-dimensional extension of the Bragg spot in reciprocal space. In order to take into account this fact, the intensity distribution $I(Q)$ was obtained by integration of the intensity located around the (100) point of the reciprocal lattice, over a sphere of radius Q, centered at the origin of the reciprocal space, in a way similar to that reported in ref. 14:

$$I(Q) \propto \int_{\text{sphere}} d\omega \cdot Q^2 \cdot f(\mathbf{Q}_p) \cdot g(\mathbf{Q}_y)$$

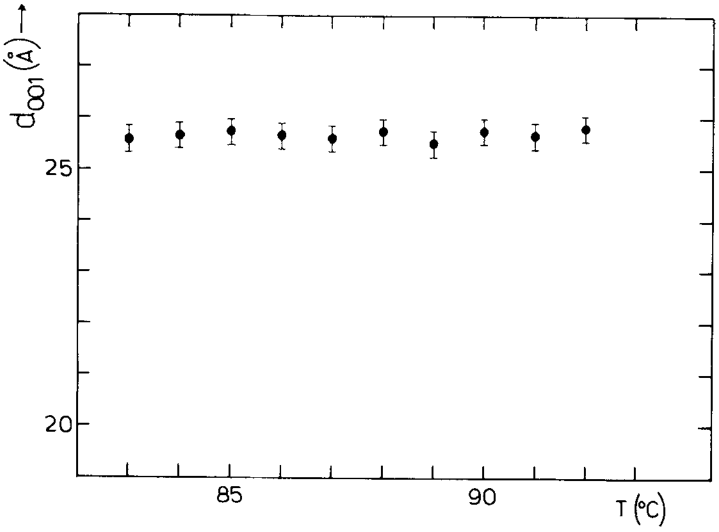


FIGURE 3 Interlayer spacing *vs.* temperature.

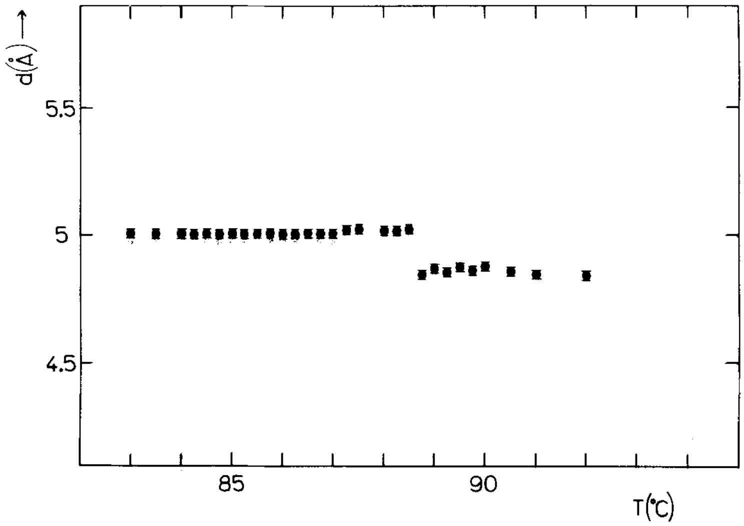


FIGURE 4 Intermolecular distance *d vs.* temperature.

where $\mathbf{Q}_p$ is the in-plane component and $\mathbf{Q}_y$ is the component normal to the smectic plane of the $\mathbf{Q}$ vector; $f(\mathbf{Q}_p)$ is the in-plane structure factor and $g(\mathbf{Q}_y)$ is the square of the Fourier transform of the electronic density along the layer normal.

In order to evaluate the (100) reflection spread in reciprocal space, along bars parallel to c^* (i.e., parallel to the layer normal), the following electronic density ρ along the layer normal direction z was assumed by supposing a molecular organization similar to that obtained in smectic A phases—see ref. 18:

$$\rho(z) \propto 4 \quad \text{for } |z| \leq 8.8\ \text{Å} \qquad \text{(core of the molecules)}$$

$$\rho(z) \propto 3 \quad \text{for } 8.8\ \text{Å} < |z| \leq 12.9\ \text{Å} \qquad \text{(aliphatic chains).}$$

The layers were assumed to be completely uncorrelated, on the basis of experimental results obtained in ref. 3. As a consequence, we

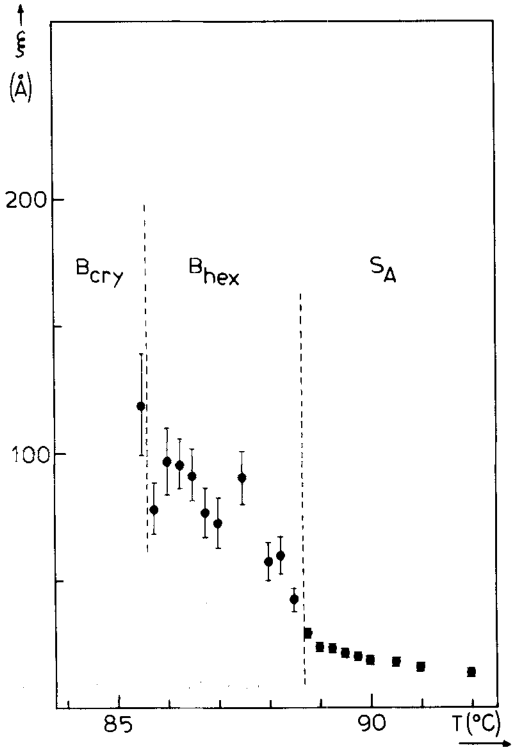


FIGURE 5 In-plane positional coherence length $\xi_{\parallel}$ for the S_A and hexatic phases *vs.* temperature.

obtained:

$$g(\mathbf{Q}_y) \propto \left[3 \cdot \sin(Q_y \cdot 12.9) + \sin(Q_y \cdot 8.8)\right]^2 \cdot Q_y^{-2}.$$

Convolution with the instrumental resolution function was then performed. The best-fit curve so obtained at the temperature $T = 88\,°\mathrm{C}$ for $\xi_{\parallel} = 57$ Å is shown in Figure 1. Similar best fits obtained for each temperature gave the $\xi_{\parallel}$ values reported in Figure 5.

A pretransitional effect in the $\mathrm{S_A}$ mesophase and a progressive increase in $\xi_{\parallel}$ in the hexatic phase as the temperature is decreased are observed.

CONCLUSION

This investigation by X-ray diffraction of 4-propionyl-4′-*n*-heptanoyloxyazobenzene, concerning the phase transitions Smectic A–hexatic B and hexatic B–crystal B, adds new and more complete evidence that this compound possesses two distinct B phases, namely the hexatic B and crystal B mesophases.

In particular the two transitions have been detected in an unusual way, namely through the observation of two peaks in the curve representing the derivative of the large angle diffusion peak width with respect to the temperature.

Moreover the range of values obtained for the in-plane positional coherence length $\xi_{\parallel}$ as a function of temperature is in very good agreement with previous work by Pindak *et al.*[3] on a single crystal of a compound showing only the hexatic B phase and no crystal B phase.

As a general conclusion, the theoretical predictions that the mesophase hexatic B should have a separate identity as compared with the crystal B phase appears to be further confirmed by the new data presented in this work.

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