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Long and Short Range Order in the Crystalline and Smectic *B* Phases of Terephthal-Bis-Butylaniline (TBBA)†

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Abstract—*We proposed recently a model for the structure of the smectic B modification of two liquid crystals (EBAC and TBBA). These two compounds only differ by the fact that the molecules are perpendicular to the smectic planes in EBAC and tilted in TBBA.*

The model implies for both phases:

—an hexagonal order within each smectic plane;

—fluctuations of the director of the molecules connected with a correlated longitudinal motion of linear chains of about five molecules for TBBA.

In the case of TBBA further experiments have been performed in order to study the structure of the smectic B phase in the whole stability range: no significant change was found. The tilt angle of the molecules with the normal to the smectic planes decreases with temperature from 32° at $T = 114\,°\mathrm{C}$ to 26° at $T = 142\,°\mathrm{C}$, while the correlation length decreases only slightly.

Using both powder and single crystal X-ray diagrams some gross information on the structure of the solid crystalline phase was obtained: the crystal lattice is monoclinic with $a = 17.54\,\text{Å}$, $b = 5.75\,\text{Å}$, $c = 53.2\,\text{Å}$, $\beta = 115°$ and the space group is probably $A\ 2/a$. The periodicity along the molecular direction is a little smaller (27 Å) than the molecular length measured in the different smectic phases (29 Å). At the transition temperature the molecular orientation changes only slightly. A collective motion of the molecules even exists in the solid phase involving a correlation length of about 7 molecules.

1. Introduction

The smectic B modification of liquid crystals has been observed in about fifty compounds;⁽¹⁾ this phase has many characteristics of the crystalline state: high viscosity, mosaic structure.... Based upon X-ray measurements performed on single domains, we have recently

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proposed a model for the smectic *B* phases of two different compounds:(2) the molecules exist in layers with their long molecular axes perpendicular to the layer (EBAC) or tilted with respect to the direction of the normal to the layer (TBBA). In each layer, the packing of the molecules is pseudohexagonal. The axes of the molecules of different layers are nearly collinear, in spite of slight fluctuations of the director† of the molecules; due to these fluctuations, there is only a three-dimensional short range order which may be considered as a "local lattice". Such a structure (Fig. 1) is very similar to that of certain plastic crystals.

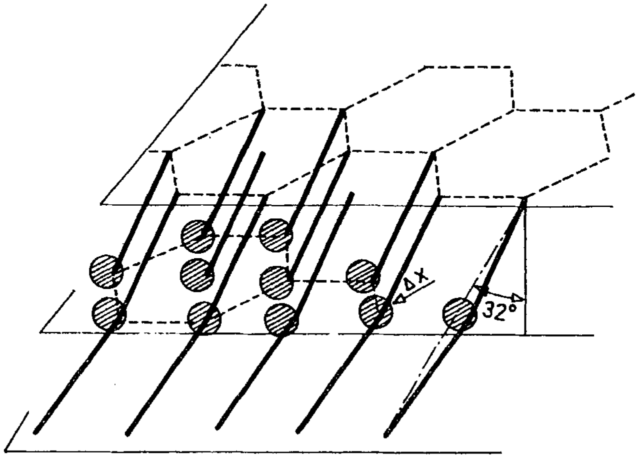

Figure 1. Model for the S_B phase of TBBA: ———, molecular long axes; —·—·—·—, mean direction of the molecular axes; Δx is characteristic of the planar fluctuation related to the director fluctuations.

In order to have a more precise idea about the nature of the smectic *B* phase, we have performed further experiments on the S_B and crystalline phases of TBBA. TBBA presents four mesomorphic phases:

$$\text{Crystal} \overset{113^\circ\text{C}}{\rightleftarrows} S_B \overset{144^\circ\text{C}}{\rightleftarrows} S_C \overset{172\cdot5^\circ\text{C}}{\rightleftarrows} S_A \overset{196\cdot6^\circ\text{C}}{\rightleftarrows} \text{Nematic} \overset{236\cdot5^\circ\text{C}}{\rightleftarrows} \text{Isotropic liquid}$$

i) We review the principal features of the X-ray patterns of a single domain of the *B* phase and our quantitative conclusions from these experiments as given in our first paper. In the present experi-

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† The director of the molecules is a unit vector parallel to their long axes.

ment, we give further information on the temperature dependence of the characteristic parameters of the structure.

ii) A precise determination of the "lattice cell" of the *B* phase from Debye–Scherrer patterns confirms the first results obtained on single domains and gives a better understanding of the structure. In addition, we give the results of measurements of certain other parameters in the three smectic phases of TBBA.

iii) We propose a model for the structure of the crystalline phase in order to understand the differences and the similarities between the solid and S_B phases.

2. Single Domain Studies

X-ray photographs of single domains were made by exposing flat film using a convergent monochromatic beam incident upon a fixed sample. Single domains of the *B* phase are obtained by heating single crystals above the melting point and the temperature of the sample is then held to within ± 0.5 °C. Figure 2 shows the photographs obtained for a sample temperature of 115 °C:

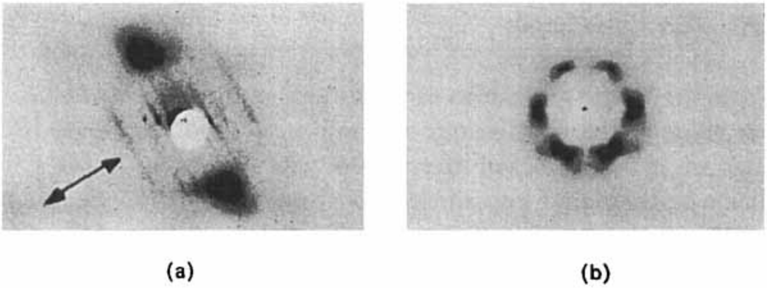

Figure 2. Single domains patterns: ($\lambda = 1.54$ Å) $T = 115$ °C. (a) The incident beam is parallel to the smectic layers (↔ shows the direction of molecules). (b) The incident beam is parallel to the molecules.

a) with the incident beam parallel to the smectic layers, (b) with the incident beam parallel to the axes of the molecules. In Fig. 2b, it is seen that the hexagonal packing of the molecules is very regular, the spots being fairly sharp. In Fig. 2a, the two principal features are:

Parallel equidistant lines from diffuse scattering corresponding to planes in the reciprocal lattice. These planes must originate from uncorrelated periodic linear chains in the direct lattice and it is found that the periodicity of the chains is nearly equal to the length of the molecules. Thus it appears that there are strings of molecules moving independently; the absence of the equatorial planes implies a longitudinal motion of the chains.(3) Furthermore the planes have a finite width and are limited to a nearly cylindrical region of 1/4.5 Å radius. According to Guinier(4) the lateral extent of these planes results from fluctuations of the director of the molecules, while the width of the diffuse lines is inversely proportional to the length of the molecules.

The Bragg reflections from the smectic layers correspond to points of the reciprocal lattice on the "diffuse scattering planes" or "sheets" and we can measure directly on the photograph the angle between the layer planes and the molecules (32° at 115 °C).

TABLE 1

Temperature	115°
Mean angle between the molecular axes and the perpendicular to smectic layer	32°
Mean fluctuations of the director of molecules	2°
Correlation length	7 molecules

From the length and width of the diffuse sheets, we can deduce the mean value of the fluctuations of the director and the length of the strings of molecules. All the results are shown in Table 1. In addition to these first experiments, we have studied the variation of the diffuse sheets with the temperature in order to have some quantitative information concerning the disorder (Fig. 3):

The width of these sheets increases with increasing temperature; that means that the correlation length decreases from seven molecules at the melting point to four at the transition to the S_C phase;

The length of each diffuse sheet is constant over the whole range of temperature, the fluctuations of the director remain unchanged;

The attenuation of the scattering corresponding to the higher order "diffuse planes" is related to the amplitude of longitudinal motions of molecules through a Debye–Waller factor, this amplitude goes from about 1 Å to 2 Å throughout the S_B phase (113 °C–144 °C).

In conclusion, even if there is a slight decrease of the long range order with increasing temperature, the local lattice still remains well defined just below the transition to the smectic *C* modification.

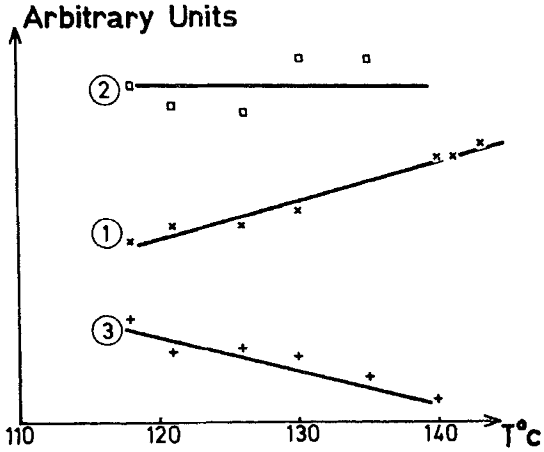

Figure 3. Temperature dependence of the diffuse scattering planes in the S_B phase. (1) Width of the 2nd line; (2) length of the 2nd line; (3) ratio of the scattering intensity of the 6th line over that of the 2nd line.

3. Precise Determination of the "Cell" of the S_B Phase

This determination has been done with Debye–Scherrer patterns taken with a Guinier camera using a monochromatic focusing beam and a heating stage. The temperature was held within ± 2°. In the D.S. pattern (Fig. 4) one can see two rings corresponding to first and second order reflections from smectic layers and 7 rings corresponding

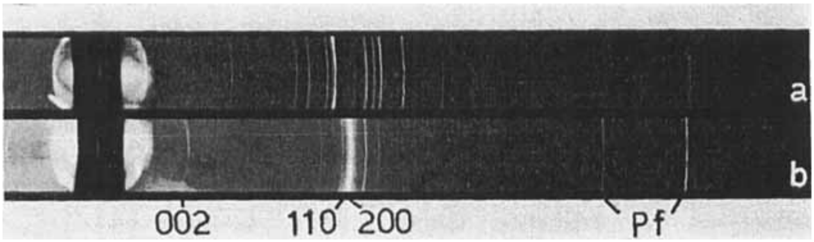

Figure 4. Debye–Scherrer photographs ($\lambda = 1.54$ Å). (a) Crystalline phase 20 °C. (b) Smectic *B* phase 125 °C.

to reflections from planes with reticular distance between 5 and 4 Å. This group of reflections consists of one intense doublet and additional weaker lines. The entire pattern is consistent with a monoclinic cell (Fig. 5) wherein the face (C) is centered.

$T = 125\,^\circ\text{C}$
$a = 10.10 \pm 0.05\,\text{Å}$
$b = 5.18 \pm 0.02\,\text{Å}$
$c = 28.6 \pm 0.2\,\text{Å}$
$\beta = 119.0^\circ \pm 0.5^\circ$

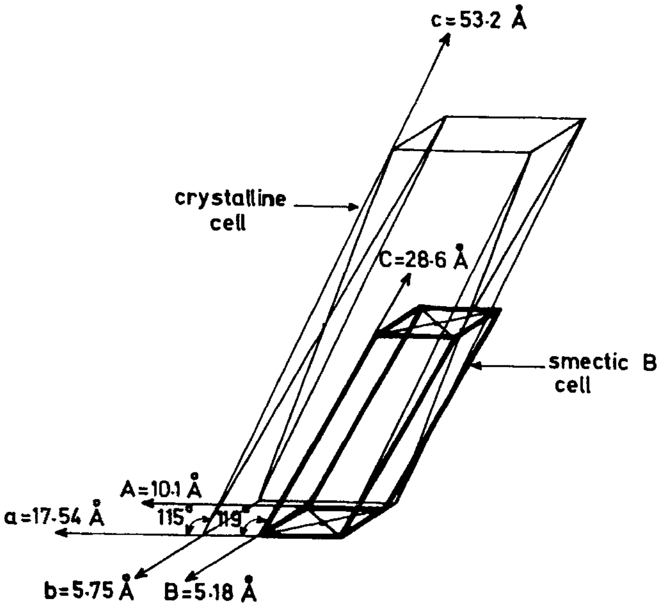

Figure 5. Cells of: crystalline phase 20 °C; smectic B phase 125 °C.

The molecules are parallel to c direction and the smectic layers are parallel to the (0, 0, 1) planes. The lattice is pseudohexagonal in the plane of the layer and the intense doublet is related to the reflections on the two different sets of reticular planes, (200) and (110), parallel to the axes of the molecules. Table 2 gives the indices of the observed reflections. No reflections for h, k, $l > 2$ are observed; this is consistent with the fact that only a local lattice exists. Nevertheless, the rings are very sharp especially for the 200 and 110 reflections.

This sharpness, however. is consistent with a model in which the correlation extends only to a few layers; this corresponds to a correlation length of about 150Å in the c direction.

From the intensity decrease of the $(0\ 0\ l)$ reflections with increasing l one can deduce that the amplitude of the fluctuations of the thickness of the layers is about 2 Å.

Table 2

Indices	Reticular distances (Å)
0 0 1	24.80
0 0 2	12.39
$\bar{2}$ 0 2	5.052
$\bar{1}$ 1 1	4.608
$\bar{1}$ 1 2	4.594
1 1 0	4.467
2 0 0	4.428
1 1 1	4.216
2 0 1	4.024

Looking at the structure, we can point out an interesting feature: the points of intersection of the molecules with a plane perpendicular to their axes form a nearly regular hexagonal lattice (Fig. 6). The small distortion from the regular hexagonal lattice can be characterized by the splitting of the two Debye–Scherrer rings (110) and (200): the two corresponding reticular distances only differ by about 1%. As the TBBA molecules have no cylindrical shape, this nearly hexagonal packing suggests the existence of some motion of the molecules about their axes; in that case, the S_B modification would appear as a particular kind of plastic crystal.

From the "cell" parameters, one can also deduce the tilt angle and the length of the molecules in the S_B phase. This length, 29 Å, corresponds to fully elongated molecules as measured on a model.(11) In the S_A phase one finds a thickness of layers of 29 Å equal to the length of the molecule; this result in the particular case of TBBA is in contradiction with De Vries(12) conclusions which suggest that the layer thickness is smaller than the molecular length in S_A phases. For the case of the S_C phase, we assume that the molecular length has the same value, 29 Å, in absence of any direct experimental determination of this length. From the measurement of the layer spacing on Debye–Scherrer patterns at different temperatures we then deduce the variation of the tilt angle with temperature. This variation within the three smectic phases is reported Fig. 7. Our results are consistent with the results of Taylor *et al.*$^{(5)}$ for the S_C phase. The tilt angle varies from 32° at the melting point to 0° at the $S_C \rightarrow S_A$ transition point.

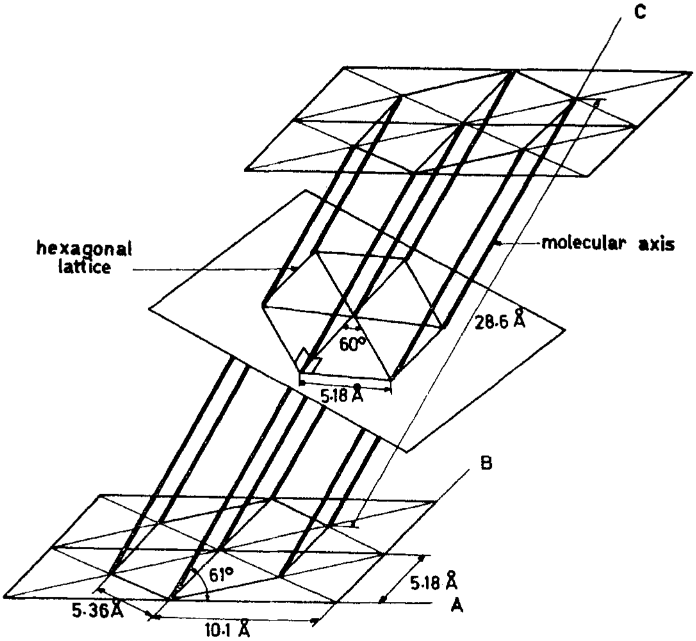

Figure 6. Evidence of a nearly regular hexagonal lattice in a plane perpendicular to the molecules.

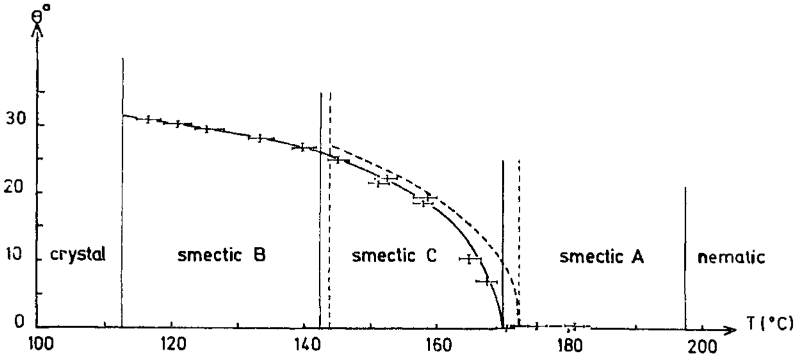

Figure 7. Tilt angle variation of the three smectic phases: ———, from our Debye–Scherrer measurements; - - - - - - -, Taylor *et al.* measurements.

4. A Tentative Model for the Structure of the Crystalline Phase

The parameters and the space group are determined by the precession methods and the method of Weissenberg. The X-ray patterns yield a monoclinic cell with:

$$a = 17.54 \pm 0.03\,\text{Å}$$
$$b = 5.75 \pm 0.01\,\text{Å}$$
$$c = 53.2 \pm 0.2\,\text{Å}$$
$$\beta = 115.0^\circ \pm 0.2^\circ$$

as shown in Fig. 5.

Two kinds of systematic extinctions are found:

$$(h,\ k,\ l)\ k + l = 2n + 1$$
$$(h,\ 0,\ l)\quad h = 2n + 1$$

The first kind implies a centered (A) face; the second implies a glide plane along a. Two space groups, Aa and $A\ 2/a$, correspond to such extinction conditions. In the first case, there are four equivalent positions in a unit cell and eight in the second case. From the measured density: 1.07 g/cm^3, we deduce that there are eight molecules per unit cell with a crystal density of 1.074 g/cm^3. A cell

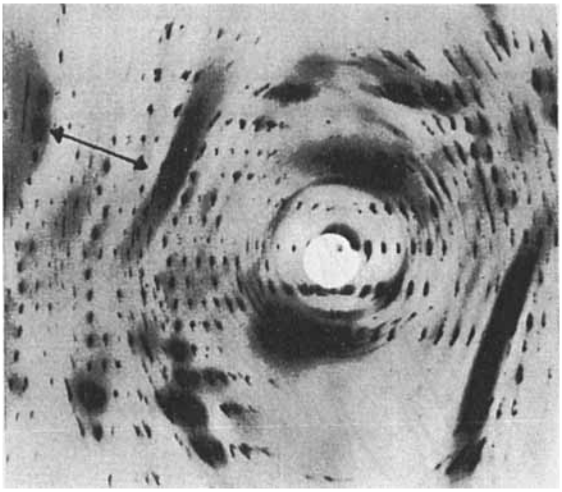

Figure 8. Single crystal pattern of the crystalline phase ($\lambda = 1.54$ Å) fixed crystal, incident beam parallel to the b axis, cylindrical film. ↔ shows the direction of molecules.

of the *Aa* space group would then require an asymmetric unit of two molecules; since such units are seldom found in molecular crystals, it is likely that the space group is *A* 2/*a*.

In order to locate the position of the eight molecules, let us first make an observation about diffuse scattering:

Diffuse lines, perpendicular to the *c* axis, can be seen on oscillating and on Weissenberg photographs (Fig. 8). On heating the crystal in the smectic *B* phase, the location and the width of these lines remain the same, while their number and their length decrease. These diffuse lines were previously described as "diffuse scattering planes" characteristic of the smectic *B* structure: it follows that, even in the solid phase, some longitudinal motion of independent strings of about seven molecules also occurs, but with a much smaller amplitude (about 0.1 Å); nevertheless there is no detectable fluctuation of the molecular direction in the crystalline phase. Furthermore the existence of such diffuse scattering planes gives us some indication about the location of molecules in the cell: just as in the smectic *B* phase, there are strings of molecules parallel to the *c* axis. Since the crystal

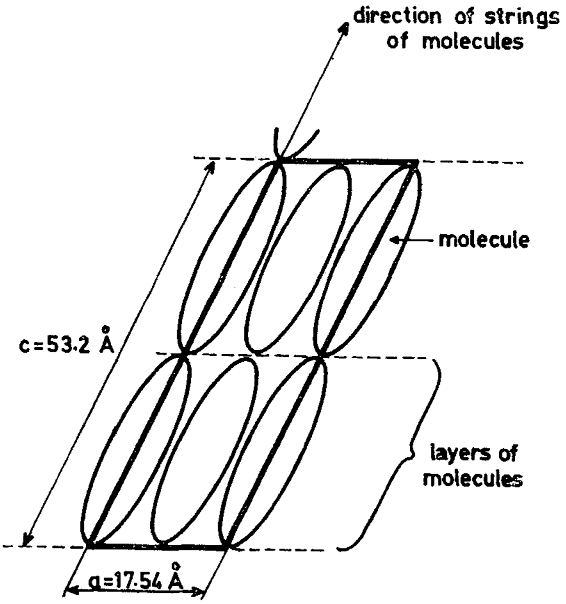

Figure 9. Location of the molecules in the crystalline cell.

parameter c is about 54 Å and each molecule is about 29 Å in length, it seems reasonable to suppose that there are two molecules, lying along the c direction.

From steric considerations it is then possible to construct a model of the crystalline phase which includes both the linear and layer structures (Fig. 9) and which leads to a pseudo-hexagonal packing in the (0 0 1) plane. In such a model the tilt angle seems to be 25°, less than in the S_B phase; the apparent molecular length (half of the periodicity along the c direction) appears smaller (27 Å) and has to be confirmed by the structure determination which is now in progress: such a small value could be explained by assuming either interpretation of molecules belonging to different layers or distortion of the aliphatic chains with some tilting of the axes of the molecules relative to the c direction.

5. Conclusion

The smectic B modification of TBBA is characterized by a stacking of hexagonal layers of molecules. Strings of about five molecules are formed as a result of the correlation of the positions of the molecules through successive layers, yielding only a local three-dimensional order. Each string moves in a longitudinal direction independently of the other strings. With increasing temperature the correlation length decreases, while the mean amplitude of vibration of each string increases. Through the study of the crystalline phase, we were able to show that the essential difference between the two phases concerns the range of the order extent; and the smectic B structure can be described by a paracrystalline lattice.(6) In both phases the molecules are in layers with a pseudo-hexagonal packing in each layer. The strings of molecules are of about the same length but *the amplitude of vibration is one order of magnitude less in the solid phase.* As a result of our experiments, the smectic B phase may be considered the analog of a plastic crystalline phase with a rotational motion of molecules about their long axes.

Another alternative model may be that of Sarma.(7) In this model, the attractive forces are strong between molecules of the same layers and weak between different layers. In such a case a rotational motion of molecules is not obvious, but attractive interactions between the planes of molecules would extend through about five layers in view of the experimental results obtained in the case of TBBA. Let us remark that the extent of the order in the S_B phase varies with the nature of the compound: for example, A. de Vries(8) found a very similar smectic structure which he named smectic *H*, the correlation length of which is about 10 molecules. This smectic *H* shows an uninterrupted miscibility with a smectic *B*(9). Thus this phase must be considered as a smectic *B* modification. On the other hand, in EBAC we found a correlation length of only two molecules. One can think that different cases can exist with differences in the correlation length and that the Sarma model describes a limiting case with the shortest correlation length.

Such differences in the order extent lead to differences in the Debye–Scherrer pattern especially with respect to the number of the outer rings. Therefore, we think that this number cannot be taken as a unique criterion for a classification of smectic modifications.(10) Moreover it is an experimental fact that some Bragg reflections can be seen only on single domain patterns and not on Debye–Scherrer patterns; the characteristics of the Debye–Scherrer Camera could also have an influence on the separation of a doublet and on the visibility of weakest rings.

In conclusion X-ray diffraction studies on single domains are necessary to establish, whether or not, other kinds of order exist in liquid crystals.

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