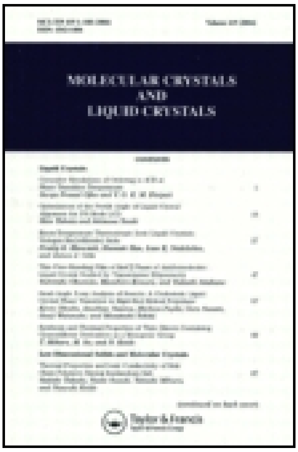

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Molecular Packing in Thermotropic Smectic Phases by Neutron and X-Ray Diffraction

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X-ray and neutron diffraction measurements of the intensity of the 00*l* Bragg reflections from the smectic layers in hydrogenous and partly deuterated isobutyl 4-(4′-phenylbenzylideneamino)cinnamate are reported. A model calculation has been used to deduce from these intensities, the configuration and orientational order of the molecules. The orientations of the long molecular axes are well ordered with $\overline{P}_2 > 0.9$ in S_E, S_B and S_A phases and there is no appreciable interdigitation of the molecules of adjacent layers. These results are compared with those obtained from incoherent quasi-elastic neutron scattering experiments.

Keywords: molecular packing, smectic phases, x-ray diffraction, neutron diffraction

INTRODUCTION

The techniques of X-ray (or neutron) crystallography are able to determine, in detail, the structure of well-ordered molecular crystals. This is done by measuring the intensity of hundreds or thousands of Bragg reflections and then using various sophisticated techniques[1] to derive the structure of a unit cell. Partially disordered materials such as smectic phases generally exhibit a small number, usually less than ten, independent Bragg reflections. This is sufficient to determine the shape and dimensions of the unit cell, but does not permit the application of conventional crystallographic techniques for determining the structure within the unit cell. Many different types of exper-

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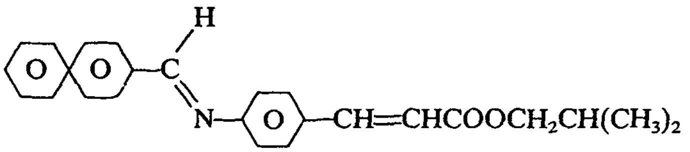
iment have been used to try to deduce something about the structure at a molecular level. In particular, incoherent quasi-elastic neutron scattering (IQENS) has been used to study the geometry and rate of diffusive motion of single molecules in mesophases. It cannot, however, give any information about the relative position of two molecules because incoherent scattering does not involve interference from different atoms. Such information is only given by coherent scattering or diffraction experiments.

In this paper we attempt to deduce as much as possible about the relative positions of different molecules in smectic mesophases. We have done this by measuring the Bragg intensities given by X-ray diffraction and neutron diffraction on normal and partly deuterated versions of a smectic material. The neutron scattering measurements were made in addition to the X-ray measurements in order to increase the number of independent experimental observations. The data has been analysed by comparing them with model calculations. Gross features of the model structure, such as the orientational order of the molecules and the degree of interdigitation between layers, were varied until reasonable agreement between calculated and measured intensities was obtained. In this way the number of structural parameters to be determined was kept to less than the number of experimental observations to be fitted.

The sample chosen for this exploratory work was isobutyl 4-(4′-phenylbenzylideneamino)cinnamate (IBPBAC):



crystal 86°C S_E 114°C S_C 162°C S_A 206°C N 214°C I

It has already been extensively studied by IQENS[2] so the single molecule dynamics are quite well understood.

THEORETICAL BACKGROUND

In a perfect crystal, the integrated intensity I_{hkl} of a Bragg reflection (relative to some standard intensity) depends upon the number of unit cells in the crystal (N) and the square of the modulus of the structure factor of a unit cell at the reciprocal lattice vectors:

$$I_{hkl} = N|F(\tau_{hkl})|^2$$

where τ_{hkl} is a reciprocal lattice vector. If the crystal is not perfect, the unit cell structure factor must be averaged over all unit cells.

$$I_{hkl} = N|\overline{F(\tau_{hkl})}|^2$$

The structure factor of a unit cell is given by summing over the N_c atoms in a unit cell:

$$F(\mathbf{Q}) = \sum_{j=1}^{N_c} a_j(Q)e^{i\mathbf{Q}\cdot\mathbf{r}_j}$$

where **Q** is the scattering vector, $a_j(Q)$ is the atomic scattering factor of atom "j" and $\mathbf{r}_j$ is its position in a unit cell relative to the origin of that unit cell. In a Bragg scattering experiment we only need to calculate $|F(\mathbf{Q})|^2$ for $\mathbf{Q} \equiv \tau_{hkl}$.

The mean structure factor $\overline{F(Q)}$, for a model of the molecular packing in smectic mesophases has been calculated as follows:

i) A reasonable molecular conformation is assumed and the coordinates of the atoms generated from standard tables of bond lengths and angles.[3] In the case of IBPBAC we also have the option of using the configuration found in the crystal phase by conventional X-ray crystallography.[4]

ii) A "long axis" for the molecule is chosen. This was done by finding the principal axis of inertia and then transforming the atomic coordinates so that the centre of mass became the origin and the principal axis of inertia became the "Z" molecular axis. The angle, β, between this axis and the layer normal can then be used to specify the orientation of the molecule.

iii) The amount of interdigitation of the molecules in one layer into the next is then defined. This is done by deciding where the centre of rotation lies on the "Z" molecular axis. The orientational distribution function for the directions of the long molecular axes, $f(\beta)$, must be bipolar so the choice of the centre of rotation determines how spread out along the layer normal the molecule becomes. Figure 1 shows how this choice of centre of rotation determines the distance d, between the positions of the extreme atom on one end of the molecule before and after rotation by π. If the average cosine of the angle between the long molecular axis and the layer normal is given by the formula:

$$\overline{\cos\beta} = \int_0^{\pi/2} f(\beta)\cos\beta\, d(\cos\beta)$$

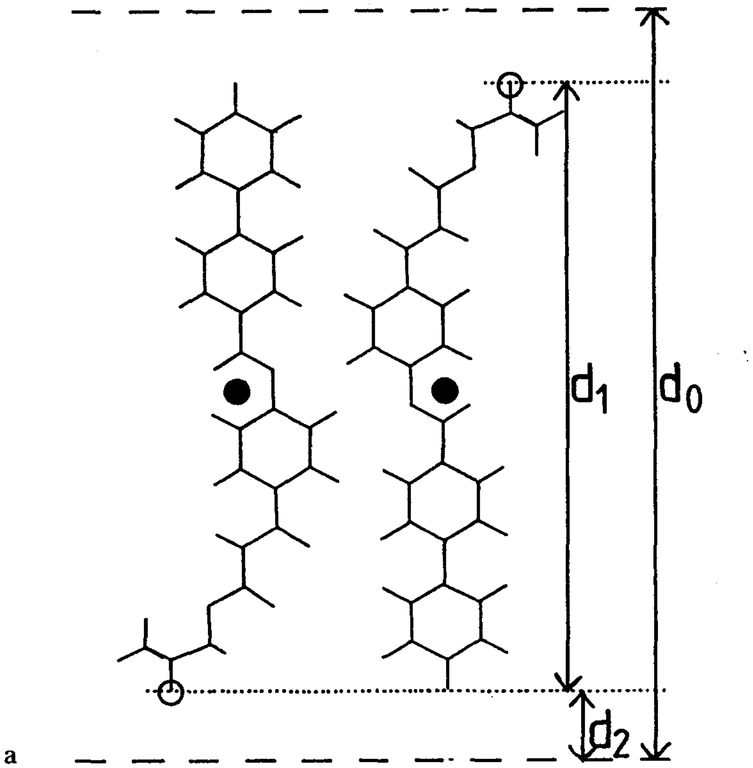


FIGURE 1 Showing how the choice of the centre of rotation (•) affects the interdigitation of neighbouring layers. An open circle marks the extreme atom. (a) Shows a configuration with no interdigitation (d_2 is positive) and (b) shows a large degree of interdigitation (d_2 is negative).

then the average distance along the layer normal between the positions of the extreme atom is given by

$$d_1 = 2|Z_e - Z_r| \overline{\cos \beta}$$

where Z_r and Z_e are the Z coordinates of the centre of rotation and the furthest atom from it in the molecular coordinate system.

We have found it more convenient to discuss the calculation of $\overline{F(Q)}^2$ as a function of d_2 which is the mean distance from the layer boundary of the external atom. The layer boundary is defined by the repeat distance d_0 which has been determined by Bragg's law.

$$d_2 = \frac{1}{2}(d_0 - d_1)$$

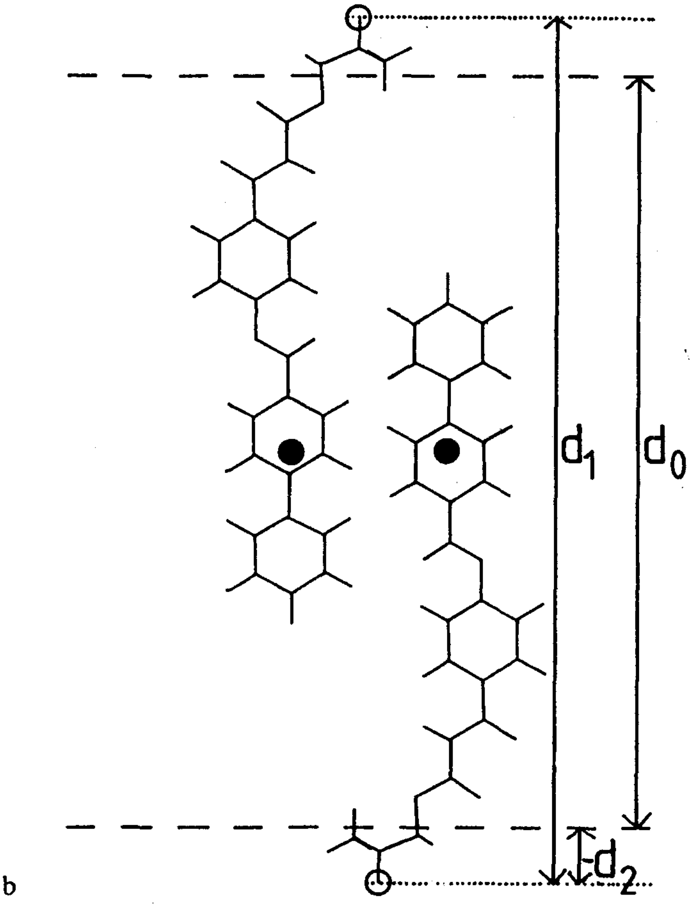


FIGURE 1 (con't.)

A small positive value of d_2Å would indicate that the molecules do not interdigitate into the adjoining layers as shown in Figure 1(a). A negative value would indicate interdigitation as shown in Figure 1(b). A value of d_2 approximately twice the van der Waals radius of the extreme atom would be expected if the molecules filled space efficiently without interdigitation.

iv) The width of the orientational distribution function is defined. We have assumed that the (normalised) distribution function is independent of the azimuthal angle and has the form:

$$f(\beta) = \frac{\delta \cosh(\delta \cos \beta)}{2 \sinh \delta}$$

where δ is the parameter that defines the width of the distribution. We have found it more convenient to discuss the calculation of $\overline{F(Q)}$ as a function of the first nontrivial moment of this distribution, $\overline{P_2}$ (i.e. P_l with $l = 2$) which is the conventional molecular orientational order parameter

$$\overline{P_l} = \int_0^\pi f(\beta)P_2(\cos\beta)\, d(\cos\beta)$$

where P_l $(\cos\beta)$ is the lth Legendre polynomial.

If the molecules in different unit cells in a smectic mesophase have a random orientation about their long axes and the orientations of the long axes are distributed according to the function $f(\beta)$ above, then the modulus squared of the mean structure factor averaged over this orientational distribution is given by:

$$|\overline{F(Q)}^\beta|^2$$

$$= \left[\sum_{j=1}^{M} a_j(Q)\left(\sum_{l=0}^{\infty}(-1)^l(4l+1)j_{2l}(QR_j)\overline{P_{2l}}P_{2l}(\cos\mu_j)P_{2l}(\cos\theta\right.\right]^2$$

where j_l is the lth order spherical Bessel function and θ is the angle between the scattering vector Q, and the layer normal. We will refer to $|\overline{F(Q)}^\beta|^2$ as the molecular form factor. This formula can be derived by a simple extension of the derivation of the formula for the elastic incoherent structure factor.[5,6] In the summation over the M atoms in the molecule, R_j is the distance of the jth atom from the centre of rotation, μ_j is the angle between the "Z" molecular axis and the position vector R_j. The values of the atomic scattering factors can be obtained from standard tables.[7]

Figure 2 shows some examples of molecular form factor calculations for an IBPBAC molecule using the above formula with $\mathbf{Q}$ (a) perpendicular and (b) parallel to the layer normal. The vertical arrows mark the positions of the Bragg peaks (in the S_B) so the value of the molecular form factor, $|\overline{F}(\vec{\mathbf{Q}})^\beta|^2$, at that point represents the Bragg intensity. It can be seen in Figure 2(a) that the intensities for $\mathbf{Q} \perp \mathbf{n}$ do depend upon $\overline{P}_2$ and the intensities for $\mathbf{Q}\|\mathbf{n}$ have also been found to be sensitive to $\overline{P}_2$. This suggests that it should be possible to determine $\overline{P}_2$ accurately from an analysis of intensity data. Figure 2(a) also illustrates how rapidly the form factor decays as Q $(\vec{\mathbf{Q}} \perp \vec{n})$

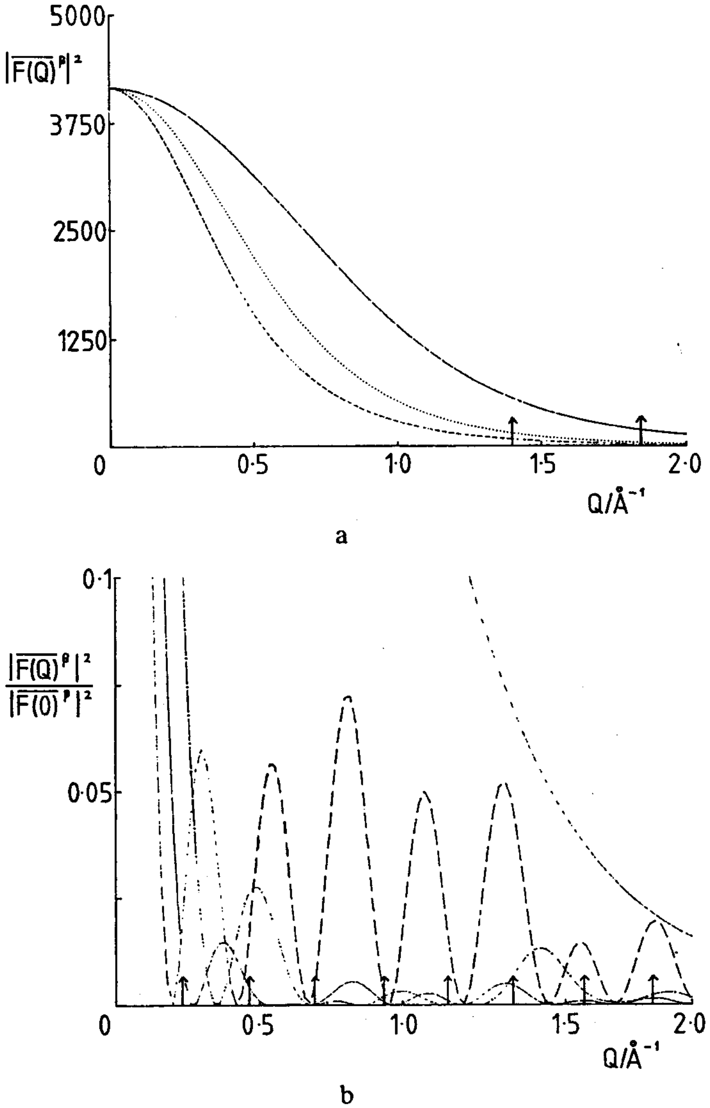


FIGURE 2 a) Molecular form factor for IBPBAC molecules with Q⊥**n** for d_2 = 0.4 Å and $\overline{P}_2$ = 1 (continuous line) $\overline{P}_2$ = 0.9 (dots) and $\overline{P}_2$ = 0.8 (dashes). The arrows mark the positions of the 110 and 210 Bragg reflections.

b) Molecular form factors for IBPBAC molecule with Q parallel to **n** for d_2 = 0.5 Å and $\overline{P}_2$ = 1.0. There have been normalized to their value at Q = 0 so that a comparison can be made between X-ray diffraction (continuous line) and neutron diffraction with a hydrogenous sample (dash-dot) and a partly deuterated sample (dashes). The upper continuous line is the X-ray diffraction form factor for Q perpendicular to **n**.

increase and perhaps explains why *hk*0 peaks at Q higher than the 210 we rarely see in smectic phases. Figure 2(b) illustrates the difference between the molecular form for **Q**||**n** in calculated for X-ray and neutron diffraction.

The molecules in the S_E phase are known to be orientationally ordered about the long axis in a weak two fold potential. In the S_B they rotate in a weak 6 fold potential. We do not believe the approximation of using an isotropic distribution around the long axes introduces any significant error since we are using assumed molecular configurations anyway and are analysing only the 00*l* reflections.

v) The last factor to influence the calculated Bragg intensities is the amplitude of the localized molecule motion perpendicular to the layers. If this gives rise to an independent random displacement of the molecule along the layer normal, the effect on the intensity can be described by a "Debye Waller" factor

$$I_{hkl} = |\overline{F(\bar{\tau}_{hkl})^{\beta,u}}|^2 = |\overline{F(\tau_{hkl})^{\beta}}|^2 \, e^{-\tau_{hkl}^2 \cos^2\theta \, u^2}$$

where u^2 is the mean square amplitude of the displacement.

If we assume that we can make a reasonable guess at the molecular conformation, we are left with three factors, d_2, P_2 and u that influence the calculated intensities of the Bragg reflections. The aim of this work is to determine a set of values for these three parameters that will reproduce the measured Bragg intensities. It is, of course, important to be sure that they are a unique set, and they indicate a physically reasonable packing of the molecules. The strategy used for finding them is discussed later.

EXPERIMENTAL RESULTS

The main problems in measuring the Bragg intensities from smectic mesophases arise from uncertainty in the alignment of the sample into a monodomain and the separation of the diffuse scattering that occurs near some of the Bragg peaks. For the X-ray diffraction two different methods of measurement have been made in order to assess the reliability of the results.

i) An unaligned "powder" sample was prepared by heating crystalline IBPBAC progressively into the S_E, S_B and S_A phases. The intensity of the 001 and 002 rings were measured using a two dimensional position sensitive X-ray detector.[8] The 110/200 rings were also measured, but these have not have been used in the analysis because the peaks with $l \neq 0$ are superimposed on them in powder diffraction.

ii) Smectic samples prepared by magnetic aligning of the nematic phase and subsequent cooling were rocked through the Bragg reflection position and the peak was recorded on a two dimensional position sensitive detector. The 00*l* peaks up to $l = 3$ were recorded in this case since the signal to noise was better. In both cases the illuminated sample volume was approximately 1 mm3.

The neutron scattering was done on normal hydrogenous IBPBAC and a version with deuterated isobutyl chains (D-IBPBAC). We attempted to obtain good "powder" samples by mixing the crystal with glass wool before heating in order to inhibit monodomain growth. A large beam cross section (a few cm^2) was used and then the sample (a 1 cm diameter cylinder) was rotated about an axis perpendicular to the scattering plane during the measurement in order to average out any regions of preferential alignment. These were done on the D1B diffractometer (wavelength 4.8 Å) and repeated on D16 (wavelength 2.5 Å) at the Institut Laue Langevin, Grenoble. Figure 3 shows the neutron scattering from the chain deuterated version of IBPBAC at 100°C in its S_E phase after subtracting an empty can background and correcting for absorption and self shielding using standard programs.[9]

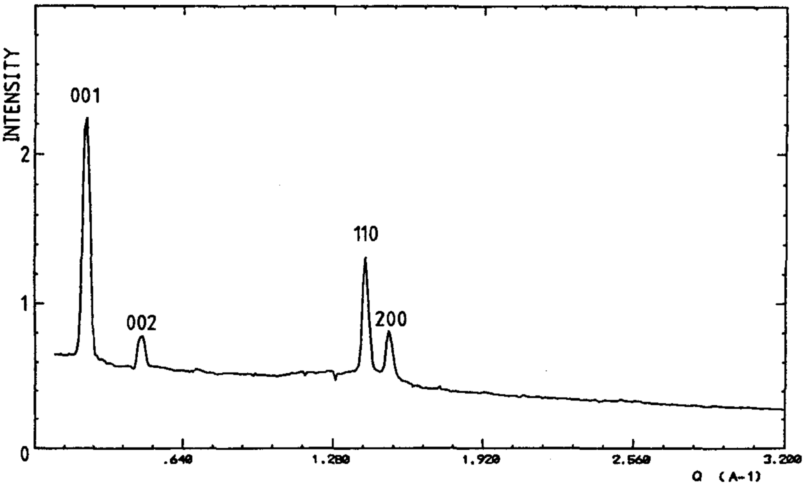


FIGURE 3 Neutron diffraction from a powder sample of D-IBPBAC at 100°C in its S_E phase.

The 00*l* intensities were obtained by subtracting a flat background and integration over the peaks. They were corrected for the Lorentz (and for X-ray, polarization) factors. Table I shows the measured intensities of the 00*l* peaks ratioed to the 001 intensities. Ratios have been used since absolute intensities are not generally very reliable. However, the ratio of the 001 peaks for the two neutron samples should be comparable since the data were measured and treated in the same way. This is confirmed by the ratio of the incoherent background which scales with the number of hydrogen atoms in the molecule. The main source of the uncertainties quoted in the table is the uncertainty in the level of the background under the peak.

Table I shows the results from the two neutron experiments are consistent, but the results for the X-ray experiments on "powder" and aligned samples do not quite agree within the quoted uncertainties. We believe this is due to a systematic error which lies in the presumption of either a perfectly aligned sample or a perfect powder. The aligned sample values shown in Table II were used for the further analysis of the data, but we bear in mind that the quoted uncertainties are likely to be rather optimistic.

STRATEGY FOR ANALYSIS OF RESULTS

Since the dependence of calculated intensity on $\overline{P}_2$, d and u could easily be oscillating, it was thought that a "least squares" analysis would not be very successful since there would be many local minima. Instead the following strategy was adopted:

A computer program was written to calculate $|\overline{F(Q)}^{\beta}|^2$ for the 00*l* reflections ($d_0 = 26.8$ Å) for a wide range of ($\overline{P}_2$, d_2). The calculated $|\overline{F(Q)}^{\beta}|^2$ were then used to correct the observed intensity ratios for the molecular form factor so that the result depended only on the Debye-Waller factor and could be used to calculate a value for the root mean square displacement "u". The program would scan a large ($\overline{P}_2$, d_2) range looking for values that would give consistent values of u for the four different intensity ratios. This was done by finding a "u" range corresponding to the uncertainties in the measured intensities and finding a ($\overline{P}_2$, d_2) pair for which the corresponding four "u" ranges all overlapped. Since the uncertainties in the measured intensities were felt to be underestimates, the procedure was repeated after doubling and tripling the uncertainty estimates. Results for which the corrected ratio of the H to D intensities were outside the uncertainties and were rejected. In this way, a map could be produced of

TABLE I

Showing intensity ratios of 00*l* peaks measured in different experiments.

	S_E, 100°C			S_B, 150°C		S_A, 170°C
	$\frac{I_{002}}{I_{001}}$	$\frac{I_{003}}{I_{001}}$	$\frac{I_{004}}{I_{001}}$	$\frac{I_{002}}{I_{001}}$	$\frac{I_{003}}{I_{001}}$	$\frac{I_{002}}{I_{001}}$
X-rays powder	0.29 ± 0.06	—	—	0.20 ± 0.12	—	—
X-rays monodomain	0.40 ± 0.02	0.02 ± 0.01	≤0.004	0.31 ± 0.02	≤0.003	0.19 ± 0.02
neutrons λ = 4.8Å IBPBAC powder	0.16 ± 0.02	—	—	0.09 ± 0.05	—	—
neutron λ = 2.5Å IBPBAC powder	0.12 ± 0.06	—	—	0.01 ± 0.06	—	0.12 ± 0.06
neutrons λ = 4.8Å D-IBPBAC powder	0.49 ± 0.01	—	—	0.35 ± 0.05	—	—
neutrons λ = 2.5Å D-IBPBC powder	0.49 ± 0.06	—	—	0.45 ± 0.07	—	0.52 ± 0.06

TABLE II

Showing observed intensity ratios used in the analysis and the resulting "u" ranges for the middle of the ($\underset{\sim}{P_2}$, d_2) regions giving self consistent ranges.

	$\frac{I_{002}\,(x)}{I_{001}}$	$\frac{I_{003}\,(x)}{I_{001}}$	$\frac{I_{004}\,(x)}{I_{001}}$	$\frac{I_{002}}{I_{001}}$(HN)	$\frac{I_{002}}{I_{001}}$(DN)	$\frac{I_{002}\,(\mathrm{HN})}{I_{001}(\mathrm{DN})}$
S_E 100°C observed ratio	0.40 ± 0.06	0.02 ± 0.01	<0.008	0.12 ± 0.02	0.49 ± 0.06	0.8 ± 0.3
u/Å calculated for $P_2 = 1.0$ $d_2 = 0.4$Å (from IQENS[2] $u = 0.9 \pm 0.2$Å)	1.0 + 0.8 − 1.0	1.5 + 0.4 − 0.3	1.9 + ∞ − 0.4	2.2 + 0.7 − 0.5	1.8 + 0.5 − 0.4	
S_B 150°C observed ratio	0.31 ± 0.02	0.03 ± 0.01	<0.002	0.14 ± 0.08	0.40 ± 0.07	1.0 ± 0.3
u/Å calculated for $P_2 = 0.97$ $d_2 = 0.4$Å (from IQENS[2] $u = 1.8 \pm 0.2$Å)	0.9 + 1.0 − 0.9	1.7 + 0.4 − 0.3	2.1 + − 0.3	1.7 + ∞ − 1.7	2.2 + 0.5 − 0.4	
S_A 170°C observed ratio	0.19 ± 0.02	<0.06	—	0.12 ± 0.06	0.52 ± 0.06	1.2 ± 0.3
u/Å calculated for $P_2 = 0.95$ $d_2 = 0.4$Å	1.4 + 1.0 − 1.4	—	—	1.7 ± 1.7	2.1 ± 0.3	

the ($\overline{P}_2$, d_2) regions that gave a self consistent set of "u" ranges. Where such regions occurred, the values of "u" would be listed out for inspection.

ANALYSIS OF RESULTS

We have used conformation I of IBPBAC shown in Figure 4 to calculate the results presented here. In fact the procedure was repeated with configuration II and with the configuration found by X-ray crystallography in the crystalline solid. There was no appreciable difference in the results. The assumed configurations I and II are both "planar" molecules. Since we assume an isotropic distribution about the long molecular axis and have not attempted to analyse the *hk*0 reflections, the assumption of planar molecules is not important. The similarity of the results for the three molecular conformations suggests that the details of the assumed conformation are not too important.

Figure 5 shows the regions of ($\overline{P}_2$, d_2) that gave self consistent "u" ranges from the intensities measured from the S_E phase at 100°C with the experimental uncertainties doubled from those shown in Table II. The region around (1.0, 0.4) was examined using a fine grid of ($\overline{P}_2$, d_2) values and the region giving consistent "u" ranges was found

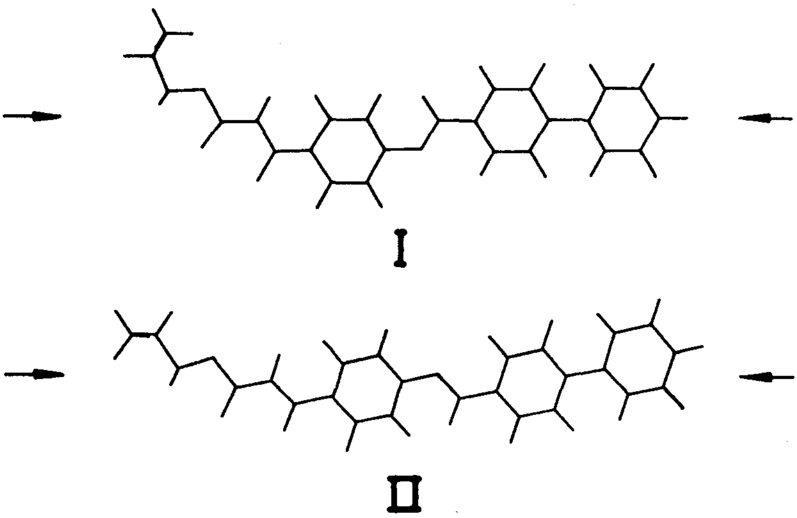


FIGURE 4 Two possible conformations of the IBPBAC molecule.

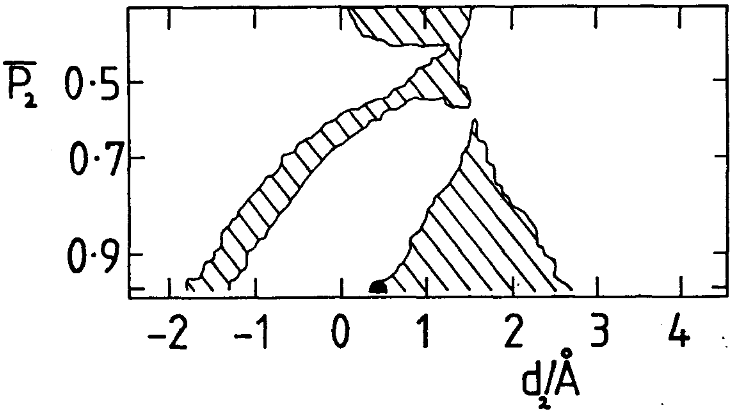


FIGURE 5 Small black area shows the region of the ($\overline{P}_2$, d_2) map that gave self consistent "*u*" ranges for the S_E phase at 100°C. The larger shaded area shows the regions of possible values if the neutron diffraction data are ignored.

to be: $\overline{P}_2 = 0.98^{+0.02}_{-0.01}$, $d_2 = 0.4 \pm 0.02$ Å. The "*u*" ranges calculated from each experimental ratio are also shown in Table II. Although not very precise, they are all consistent with that found by incoherent quasi elastic neutron scattering experiments. Since IQENS only measures motion on a time scale faster than 10^{-10}s it is quite possible that some part of the motion would be too slow to be detected by that technique. The configuration of two molecules with $P_2 = 1.0$ and $d_2 = 0.4$ is shown schematically in Figure 6. It can be seen that efficient filling of space can be achieved using this configuration since the isobutyl group of one molecule fits around the end of the other.

In order to see if the intensities measured by neutron diffraction were actually contributing towards finding a reasonably small ($\overline{P}_2$, d_2) region, the searching procedure was repeated using only the intensities measured by X-ray diffraction. It was found that a very large region in ($\overline{P}_2$, d_2) could give self consistent "*u*" ranges, so no conclusions could be drawn. This demonstrated that it is essential to use neutron intensity data as well as that from X-rays in order to use the method described here successfully.

Figure 7 shows a similar plot for the S_B phase at 150°C. A second region of self consistent "*u*" ranges has appeared but we believe the correct one is still around the point (1.0, 0.4) since no sudden changes in the intensities were observed in measurements every 10° from 100°C to 150°C. Examining this region on a fine grid leads us to $\overline{P}_2 = 0.97 \pm 0.03$, $d_2 = 0.4 \pm 0.2$ Å.

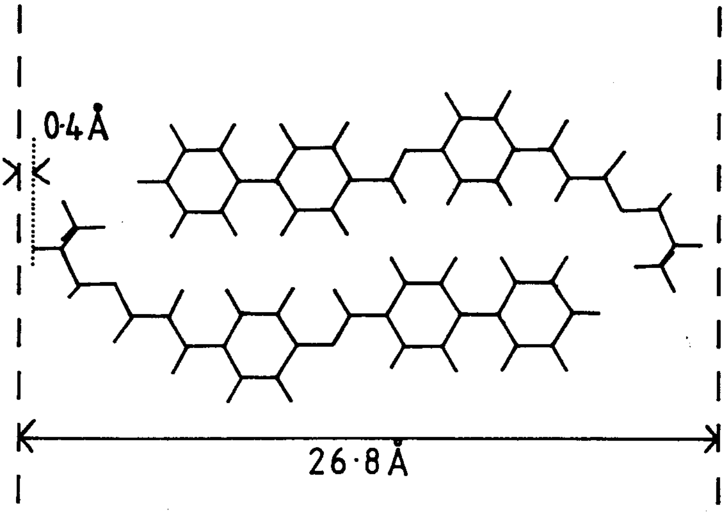


FIGURE 6 Configuration of IBPBAC molecules deduced for the S_E phase.

A value of $\overline{P}_2$ just less than unity has also been found by other techniques. Nuclear quadrupole resonance[10] gives 0.94 at 140°C and quasi elastic neutron scattering[2] estimated ~0.85.

A similar analysis of S_A data is also shown in Figure 7. If we assume the same region to be correct, we obtain $\overline{P}_2 = 0.95 \pm 0.05$ and d_2

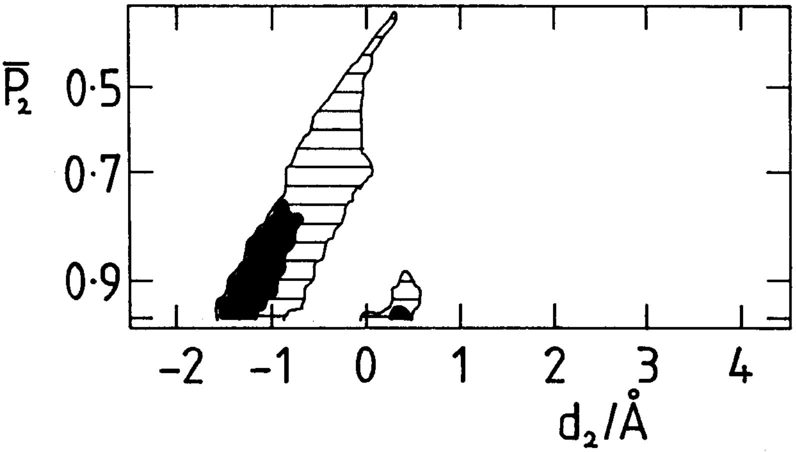


FIGURE 7 The black areas show the ($\overline{P}_2$, d_2) regions that give self consistent "u" ranges for the S_B phase. The shaded areas are the regions for the S_A phase.

= 0.2 ± 0.2 Å. A value of $\overline{P}_2 = 0.6$ was found by IQENS but, on comparing the results for $\overline{P}_2$ with those obtained by IQENS, we must remember that this experiment is a coherent scattering measurement and so measures $\overline{P}_2$ for the angle of inclination of a molecule relative to its neighbours. IQENS measures $\overline{P}_2$ for the dynamic long axis fluctuations of a single molecule. IQENS is therefore measuring $\overline{P}_2$ for the angle of inclination of a molecule relative to a laboratory fixed axis. If molecular reorientations were strongly cooperative we would expect the P_2 measurement by this coherent scattering experiment to be considerably less than found by IQENS as is in fact the case.

CONCLUSIONS

We have shown that it is possible to deduce the gross features of the molecular packing in smectic mesophases by assuming a likely molecular conformation and calculating the mean structure factors for the 00*l* peaks. The fact that a second region of possible solutions is appearing for the S_B and S_A phase, suggests that more independent measurements (e.g. neutron diffraction from differently deuterated samples) would be useful. In future, we intend to concentrate on using monodomain samples where possible since these permit measurements of higher order peaks.

The high values for $\overline{P}_2$ suggest that the molecules are tightly packed in parallel configurations locally and so the dynamic reorientation of the long axes that have been observed using IQENS must be a strongly cooperative phenomenon. The values of d_2 show that for IBPBAC there is no appreciable interdigitation between the molecules of adjacent layers.

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