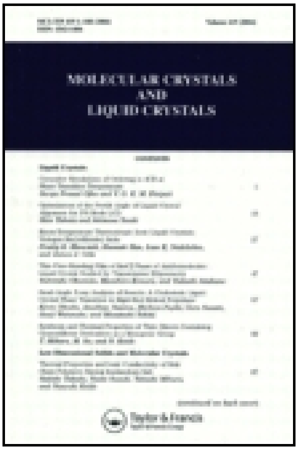

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Structure and Correlations in Smectic B, F and I Phases

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Structure and Correlations in Smectic B, F and I Phases†

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The question of which of the known smectic phases exhibits long range 3 dimensional order is first discussed briefly. The major theme of the paper is the nature of the structure and correlations in S_B, S_F, and S_I phases. Results are presented about the temperature dependence of the interlayer stacking arrangement and the existence of strong layer undulations in crystalline S_B phases and about the existence of a S_B phase with very weak positional correlations between layers and short range order within the layers.

The relation between the S_I and S_F structures is established for the first time: both consist of uncorrelated layers in which the molecules are tilted relative to the layer normal and have limited positional correlations within layers. Both have 3-d long range bond orientational order of the *C*-centred monoclinic lattices. They differ in the direction of tilt of the molecules relative to the pseudo-hexagonal packing in the plane normal to the long axes: in S_F the tilt is directed towards an edge of the hexagon, while in S_I it is directed towards an apex. These results enable previously described phases to be classified (or reclassified) as S_I phases and emphasise the existence of more ordered phases with similar tilt to the S_I phase but otherwise analagous to S_G and S_H—we call these S'_G and S'_H. Finally a preliminary report is given of X-ray structural work which shows that the recently postulated S_J and S_K phases do not exist.

INTRODUCTION

The liquid crystal phases which have so far been reported are shown in Figure 1. In the orthogonal smectic phases, the molecular long axes have an orientational distribution function $f(\beta)$ which is peaked along the layer normal ($\beta = 0$), whereas in the tilted phases, $f(\beta)$ peaks at a finite tilt angle

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† This paper describes work carried out as part of a long-term collaborative programme with Professor G. W. Gray, University of Hull. All of the samples used in the experiments were prepared, purified and characterised in his laboratory.

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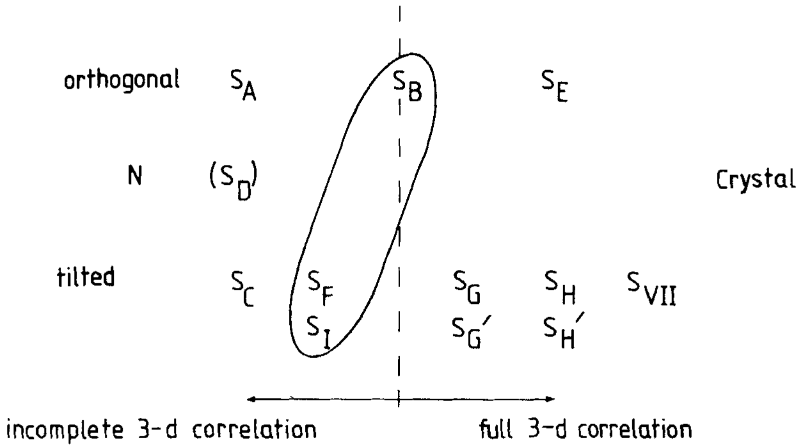

FIGURE 1 Summary of liquid crystal phases. The nomenclature used is that recommended by Demus, Goodby, Gray, and Sackmann[3]; for S_G' and S_H' see text. The dashed line separates those phases which have full crystal-like 3-d correlations from those which do not, and the three phases which are the main subject of this paper are enclosed in the heavy solid line.

β_t. The S_D phase is a pathological cubic phase which has been found to occur in a number of compounds above S_C and sometimes below S_A^1; we will not discuss this phase here. S_J and S_K phases were postulated recently by Barrall *et al.*,[2] but we will indicate later that these are not in fact new smectic phases. The dashed line in the figure divides those phases which have long range 3-d order from those which do not. The existence of such order in S_E, S_G, and S_H phases is now well-established because all show several *hkl* reflections, although considerable (dynamic) disorder exists, and only relatively low Q reflections are observed[4] ($Q = 4\pi \sin \theta/\lambda$). The S_G phase has a *C*-centred monoclinic cell with pseudo-hexagonal molecular packing of molecules tilted towards an edge of the hexagon ($a > b$) (see Figure 8) while for S_H the hexagon becomes more distorted and the cell is no longer *C*-centred as a result of a quenching of the 6-fold rotational disorder of the molecules which exists in S_G. S_G' and S_H' are very similar except that the tilt direction is towards an apex of the pseudo-hexagonal molecular packing ($b > a$) (see below). These phases (S_G' and S_H') have so far only been observed for a few compounds having a chiral centre within the molecules. The monoclinic structure of S_{VII}, so far known only for TBBA,[5] has not yet been determined in detail. S_G and S_H, S_G' and S_H' are all monolayer structures, while S_{VII} is a bilayer,[5] and orthorhombic S_E structures have been found with both monolayer and bilayer arrangements for different substances. The S_G phase certainly has rotational disorder in which the molecules reorientate about their long axes on a time scale of 10^{-11} s,[6] while this is partially quenched in S_H (and S_E) phases.[7,8] Nevertheless it seems clear that those phases to the right of the dashed line in Figure 1 are crystalline. In no case has a high resolution study of the peak profiles shown positively that the 3-d order is truly infinite, but there seems no reason to doubt this, especially in view of the recent proofs of 3-d long range order for a smectic B phase.[9,10] It should not therefore be surprising if apparently more "smectic" phases are reported, since there must exist the possibility of a variety of other crystal structures for long non-rigid molecules. The criteria usually used for distinguishing so called "true crystal" from liquid crystal phases—absence of temperature hysteresis in transitions between liquid crystal phases, flow, miscibility, and optical texture are certainly arbitrary. On the other hand, the hysteresis observed at the "crystal" to smectic (S_B, S_E, S_G, S_H etc.) transitions arises because these are strong first order transitions which implies that the (crystalline) S_E, S_G, S_H phases have considerable disorder.

The truly liquid crystalline phases S_A and S_C are now quite well understood. They are characterised by 1-d density waves with algebraic decay of positional correlations along the density wave (at least for S_A). It is worth emphasizing that the molecular tilt in S_C phases in fact has long range 3-d order as shown by X-ray diffraction patterns of monodomain samples. However for both S_A and N phases remarkable new results have emerged in the last year or two concerning the existence of re-entrant phases, bilayer–monolayer transitions, undulation structures and coexistent density waves of incommensurate wavelengths.[11–15]

This paper is concerned primarily with examples of the "intermediate" phases S_B, S_I and S_F (and briefly "S_J" and "S_K") which are interesting for a variety of reasons. Firstly, although one example (40.8 :$C_4H_9OPhCHNPhC_8H_{17}$) of an S_B phase has now been positively shown to be crystalline,[9,10] and many examples are now known which certainly possess extensive 3-d correlations, these phases have some very unusual properties. Furthermore, there remains the possibility of S_B phases without long range 3-d correlation which have been the subject of much theoretical speculation.[16,17] Secondly, the S_F phase has already been shown to be essentially a 2-d phase with very weak interlayer correlations, long range (3-d) bond orientational order and short range positional order in the layers.[6,18–20] (as suggested by Birgeneau and Litster[17] for the S_B phase). Here we comment further on the existing S_F results and relate the S_F structure to that of the newly discovered S_I phase. The X-ray diffraction pattern of this phase[21,22] shows only the lowest order (monoclinic) *hk*0 reflections (a single ring in the powder pattern), in addition to 00*l* layer reflections; it is a tilted phase and its diffraction pattern is closely similar to that of S_F and/or S_B depending on sample or type of experiment.

Smectic B phases

Introduction: The smectic B phase has been extensively studied over the last decade (note that here we consider only orthogonal, uniaxial structures as S_B phases). The average structure has hexagonal symmetry with long range bond orientational order as shown by the existence of six reflections of types† (100, 110, etc.).[23] In general the local structure is a herringbone packing and the average hexagonal symmetry is obtained by superposition of three different orientations of the local orthorhombic cells.[24] The situation is dynamic and individual molecules rotate[6, 7, 25] among six equivalent sites on a time scale of 10^{-11} s. However, until recently only *hk*0 reflections had been observed (and usually only those for $h, k \leqslant 1$) which led to considerable interest and theoretical speculation on the nature of this phase, centred on the question of order within and coupling between the layers. About two years ago,[26, 27] we discovered that the preparation of very well aligned samples by slow cooling in magnetic fields of $\sim$2T (which generally gave 2-d powder samples with smectic layers perpendicular to the field) enabled *hkl* reflections to be observed showing the existence of 3-d correlations. A variety of compounds were examined, and it was found that the hexagonal layers could stack with an *ABAB* .. (bilayer) or, *ABCA* .. (trilayer) configuration as well as random *ABC* packing or no interlayer correlations; later a single highly disordered example of a monolayer *AA* .. packing was found.[6] At the same time high resolution X-ray diffraction experiments were being performed on 40.8 by two groups: Moncton and Pindak[9] studied free thin films and Pershan *et al.*[10] studied magnetically aligned samples. Both groups found that the shape of the reflections is resolution-limited showing the phase to be truly crystalline—although strong diffuse scattering shows the presence of considerable disorder, probably associated with very soft transverse modes involving relative displacement of layers. Diffuse scattering can also arise from statically disordered regions in imperfect samples.

In this paper we consider two aspects of S_B structures: first some quite novel properties of crystalline (and to some extent of uncorrelated) specimens, and secondly the question of the existence of S_B structures with essentially zero correlation between layers.

Temperature-dependent interlayer correlations

We have studied a number of compounds of the n0.m series[6] (C_nH_{2n+1}OPh-CHNPhC_mH_{2m+1}) which display a rich smectic polymorphism. In the S_B phase of many of these compounds, the layer packing changes reversibly with temperature between *ABA* .. and *ABCA* .. types. This is illustrated in Figure

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† Hexagonal indexing is used for S_B.

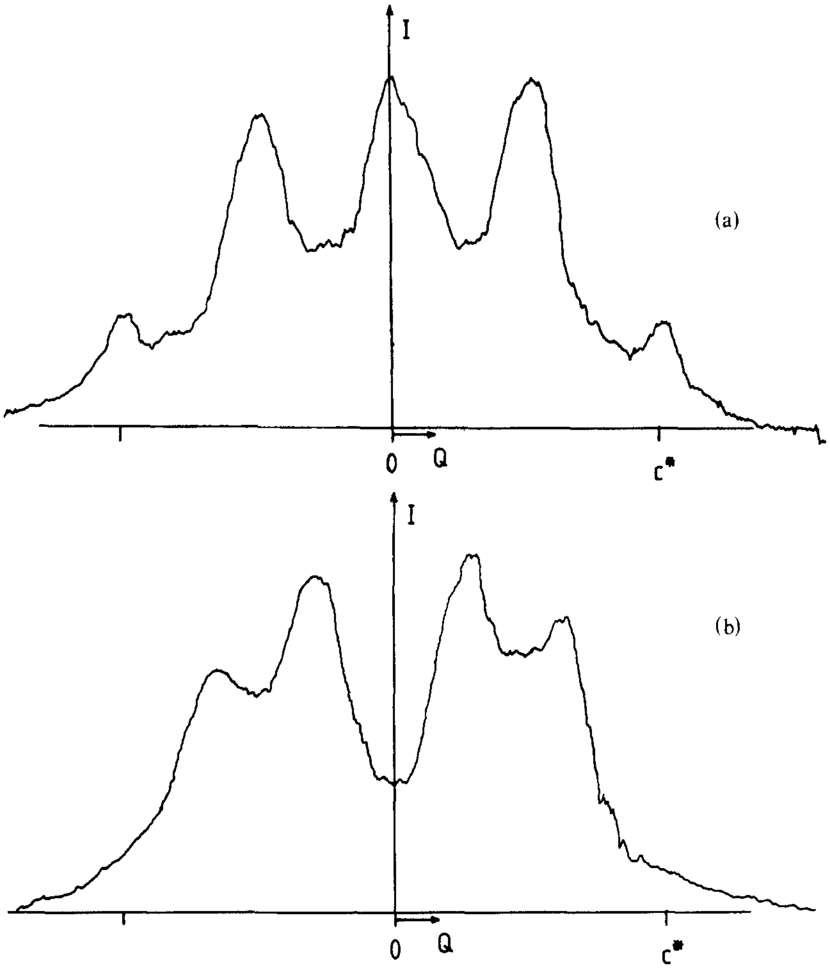


FIGURE 2 Microdensitometer traces from X-ray photographs of the S_B phase of 50.7 along the **c*** ($<00l>$) direction centred at $\mathbf{Q} = |\mathbf{a}^*|$ a) $T = 38°\mathrm{C}$; peaks at 0, $\pm\frac{1}{2}$, ± 1 showing an *ABA* ... stacking sequence b) $T = 40°\mathrm{C}$ peaks at $\pm\frac{1}{3} \pm \frac{2}{3}$ showing an *ABCA* ... stacking sequence.

2 by microdensitometer traces of X-ray photographs of 50.7 along the $\langle 00l \rangle$ (**c***) direction for the first (100, $1\bar{1}0$, etc.) ring in the reciprocal space of the 2-d powder sample. These show clearly the two types of packing, but the really remarkable result is that in several cases the layer stacking changes twice, e.g., for 50.7 the following sequence is found S_G 36°C *ABA* ... 39°C *ABCA* ... 42°C *ABA* ... 52°C S_C. We have failed to find any thermal effects associated with these changes nor do we observe any qualitative difference between the structures of the high and low temperature bilayers. These

changes clearly reflect the very weak elastic constants for shear of the layers, but the driving mechanism for the changes is not understood.

Layer undulations

In the S_B phases of all the n0.m compounds examined which give an S_G phase on cooling, satellite reflections have been observed[6, 27] having wave vectors $\pm Q^s_{xy}$ parallel to the layers; no satellites are observed for *hk*0 reflections. A similar result has also been found for 80.05 ($C_8H_{17}OPhPhCO_2PhOC_5H_{11}$) which has essentially zero interlayer correlation (see below) and gives only a crystal (or monotropic S_E) phase on cooling. In all cases, $18Q^s_{xy} \sim 2\pi/d_{100}$, ($2\pi/Q^s_{xy} \sim 80$Å) and the satellites increase in intensity with decreasing *T*. Sometimes very weak higher order satellites have also been observed with $Q'_{xy} = \frac{3}{2}Q^s_{xy}$. These results show that the smectic layers are not flat, but have undulations of very well-defined wavelength whose amplitude increases with decreasing temperature. The molecular displacements in these undulations are longitudinal motions parallel to the molecular long axes.

The satellites are most intense for the 001 reflection and typical results are shown in Figure 3 for 50.7. These were obtained by neutron scattering using an area detector on the D17 spectrometer at ILL Grenoble. They show clearly the sharp satellites and also the transition to the S_G phase which clearly also involves longitudinal molecular displacements resulting in a tilted structure. It appears that the transition occurs when the S_B structure becomes unstable to the undulations. We are currently attempting to determine the dynamics of these undulations in the S_B phase.

Uncorrelated S_B phases

At the same time that the existence of 3-d correlations in S_B phases was first reported a number of examples were given where no correlations between layers were found.[26] This is revealed by the existence of continuous bars of scattering parallel to **c*** and of length $\sim \pm \mathbf{c}^*$, centred on the lowest order *hk*0 reciprocal lattice nodes (100, $1\bar{1}0$, etc.). For the case where molecular positions are completely uncorrelated between layers, the scattering intensity along the bar is determined bythe molecular structure factor: $I \sim \langle F_m(00l)\rangle^2$. This has roughly the same *Q*-dependence for all typical liquid crystal molecules, falling from a maximum at $Q_z = 0$ to relatively small values for $Q_z \gtrsim (\mathbf{c}^*)$. The observed profiles are at least qualitatively of this form and certainly show no structure. It is important to establish whether structures with intrinsically uncorrelated layers exist and if so the nature and extent of the *intra*layer correlations: are these infinite (crystal-like) or short range ($\sim e^{-r/\xi}$)? A third

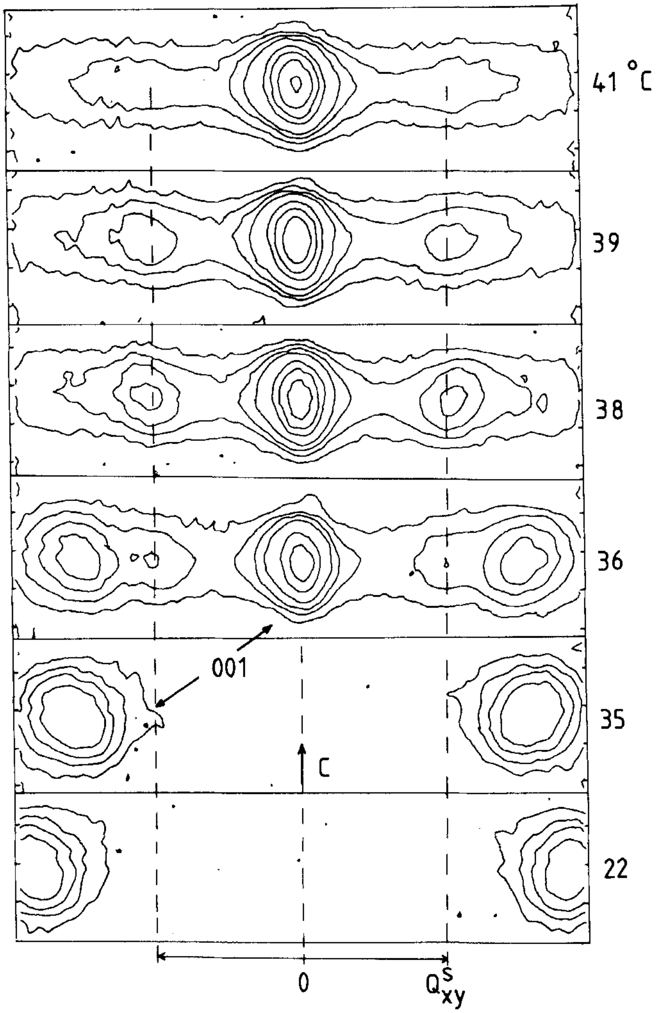


FIGURE 3 Neutron diffraction results for 50.7 showing the development of satellite reflections associated with the first layer reflection (001) in the S_B phase, and the S_B–S_G transition.

possibility is the existence of algebraic decay, but Birgeneau and Litster have pointed out that this should be accompanied by infinite susceptibility so that even very weak interlayer correlations should convert it to true LRO. The difficulty in trying to answer these questions is essentially that of attempting to prove a negative. It is certain that S_B *samples* can be obtained in which there is no interlayer correlation, but it is hard to determine whether this is the most stable structure, since the S_B phase is certainly very soft with respect to interlayer shear.

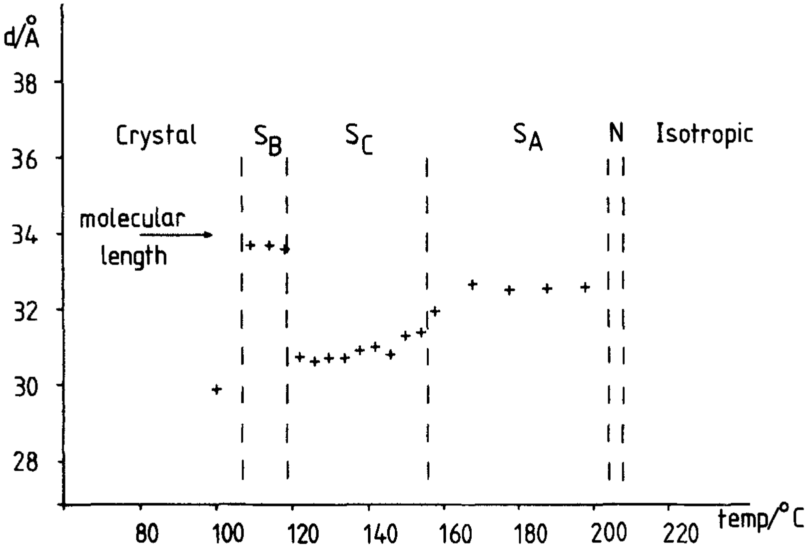


FIGURE 4 Layer spacings as a function of temperature for 80.05.

From our previous work, we therefore selected for reexamination the example which showed most clearly a lack of interlayer correlation. This was 80.05 which has an interesting phase behaviour Cr, 107°, S_B, 119°, S_C, 156°, S_A, 204°, N, 208°, Iso. The smectic layer spacings are shown as a function of temperature in Figure 4. A sample was prepared in a flat plate holder with aluminium windows and of thickness ~1 mm. This was cooled at ~0.3°C/min from the isotropic phase in a field of ~2T. The diffraction pattern from this sample is shown in Figure 5a. This shows the satellite reflections associated with $00l$ and also the bars of scattering parallel to **c*** centred on the primary (100, $1\bar{1}0$, etc.) hexagonal reciprocal lattice points. No *hkl* reflections have been observed in any of several experiments. However, the microdensitometer profile parallel to **c*** (Figure 6) shows that the intensity has weak maxima near $l = \pm\frac{1}{2}$. This suggests[28] a random packing of *A*, *B*, *C* type layers for which

$$I \sim \langle F_m(00l)\rangle^2 \langle F^g_{abc}\rangle^2$$

where $\langle F_m\rangle$ is the molecular structure factor and $\langle F^g_{abc}\rangle$ the geometric structure factor for the random layer stacking. The former was calculated for the molecule assuming 2 fold head-to-tail disorder and standard bond lengths and angles, while the latter is given by Guinier.[28] The calculated profile is shown in Figure 6 and is not in good agreement with experiment, which gives a much broader profile. In fact, no simple rigid-molecule, static-layer

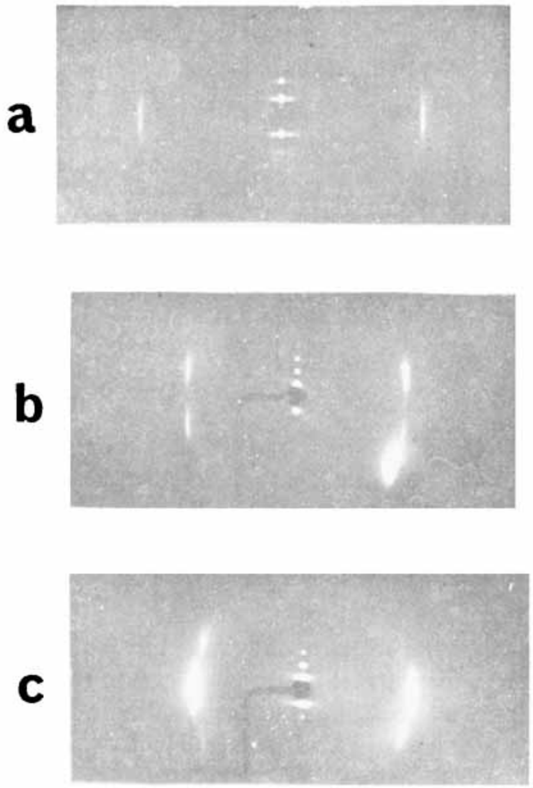


FIGURE 5 X-ray diffraction photographs taken with the incident beam parallel to the smectic layers on aligned samples which are partially disordered about the C* direction a) S_B phase of 80.05 b) S_F phase of TBDA c) S_I phase of TBDA.

model can give such a broad profile because the limit of no correlation is simply $I = \langle F_m(00l)\rangle^2$ which is too narrow. This suggests that an important component of the scattering is associated with molecular motions (e.g. tail disorder or transverse motions of the layers), and indeed the profile roughly resembles that of the diffuse scattering under the $h0l$ Bragg peaks for the soft crystal S_B phases of 50.7 and 40.8 as shown in Figure 6. More detailed modelling is clearly required, but the above qualitative comparisons suggest that the interlayer coupling in the S_B phase of 80.05 is very weak giving very weak positional correlations between layers—with a tendency to random *ABC* packing and strong diffuse scattering associated with molecular motions.

The intensity profile perpendicular to **c*** at $l \sim \frac{1}{2}$ is shown in Figure 7 compared with the (Gaussian) experimental resolution function. The result of folding with a Lorentzian peak shape gives a reasonable agreement with

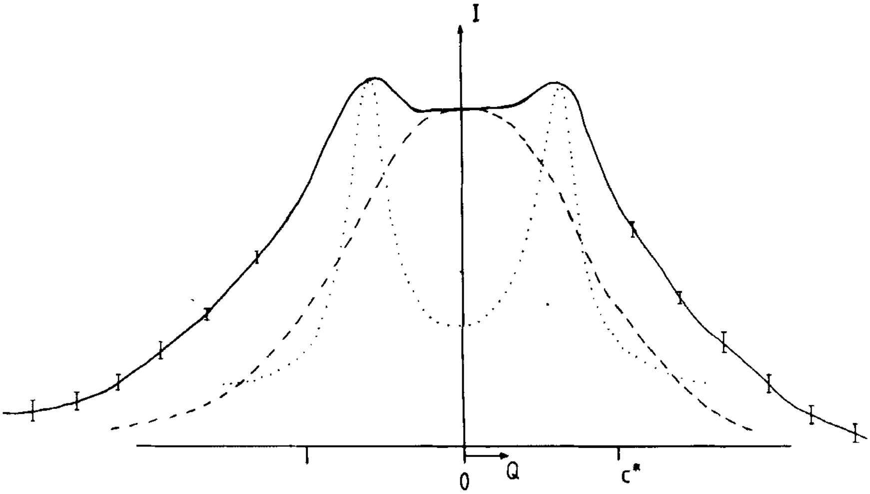


FIGURE 6 Intensity profile parallel to **c*** of the 100 scattering ring of the S_B phase of 80.05. Solid line: experimental result taken from Figure 5a; dotted line: calculated for random *ABC*... packing: $I \sim \langle F_m \rangle^2 \langle F^g_{abc} \rangle^2$; dashed line: diffuse scattering from S_B phase of n0.m compounds scaled according to **c*** values and arbitrarily in intensity (*cf* Figure 2).

experiment except for the wings of the peak, but the broadening is small compared with the experimental resolution. Because there are no "Bragg" peaks it is not possible to make a direct separation between elastic and diffuse (elastic and "inelastic") scattering, and hence operationally to define a true time-averaged structure, and it would be of interest to examine this by neutron scattering where an energy analysis can be performed. We must therefore analyse the peak profile as a whole, and the approximately Lorentzian profile suggests an overall correlation function which is exponential ($e^{-r/\xi_\perp}$) giving $\xi_\perp \sim 350$ Å, but the scattering profile appears to have stronger wings than a single Lorentzian. If these were used to determine and subtract off a "diffuse background", then $\xi_\perp$ would be markedly increased, so that the above value should be regarded as a lower limit.

In summary, it appears that in the S_B phase of 80.05 the layers are very weakly coupled resulting in weak interlayer correlations. The existence of long range bond orientational order could not be determined because the sample was a 2-d powder, but work on other S_B phases suggests that it is present. The correlation length within a layer $\xi_\perp^{\sim} \gtrsim 350$ Å suggests that this is an S_B phase with only SRO in the layers although higher resolution studies are required in order to check this. If such phases exist, then the question arises as to whether correlated and uncorrelated S_B phases are distinct as they are for the tilted versions S_G and S_F (see below).

A final point worth emphasizing is that most of the S_B phases examined

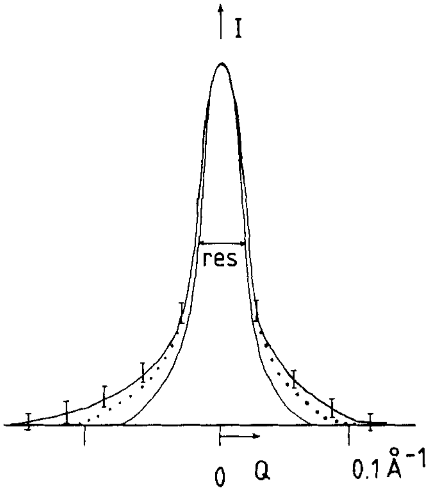


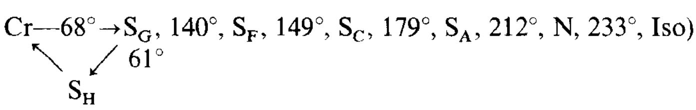
FIGURE 7 Intensity profile perpendicular to c* of the 100 ring of 80.05 in the S_B phase at $l = \frac{1}{2}$. Outer line: experimental result from Figure 5a; Inner line: experimental resolution function; Dotted line: Lorentzian with $\xi_\perp = 350$Å folded with resolution function.

only show two or three orders of 00*l* reflections so that the layer distribution function $f(Z)$ is not sharp and $\langle Z^2 \rangle^{1/2} \gtrsim 3$ Å. Indeed quasi-elastic neutron scattering measurements have shown[6,7,25] that the molecules undergo a localized diffusive motion with an amplitude of ~2Å on a time scale of $\sim 10^{-11}$ s.

S_F and S_I phases

Introduction: The essential features of the S_F structure were first established in our laboratory two years ago[18] and these have been confirmed and amplified by subsequent work on a variety of compounds.[6,19,20] The most extensively studied example is

TBPA ($C_5H_{11}PhNCHPhCHNPhC_5H_{11}$;



$$\begin{tikzcd} \text{Cr} \arrow[r, "68^\circ"] & S_G, 140^\circ, S_F, 149^\circ, S_C, 179^\circ, S_A, 212^\circ, N, 233^\circ, \text{Iso)} \arrow[dl, "61^\circ"] \\ S_H \arrow[u] & \end{tikzcd}$$

The molecular long axes have a pseudo-hexagonal packing tilted relative to the layer normal to give a *C*-centred monoclinic cell. Only the lowest order zero level (200, 110, etc.) reciprocal lattice ring is observed, but monodomain samples can be prepared in which this has six maxima showing that S_F has 3-d long range bond orientational order. The 00*l* layer reflections have resolution-limited width (so far only low resolution experiments) but the *hk*0 reflections have the form of diffuse bars parallel to **c*** (except for 50.6[20] see below) and of length ~ ±**c*** showing that the layers are almost uncorrelated—they can thus slide readily relative to each other (but not rotate), while preserving the crystal axes. The profile of the scattering bars perpendicular to **c*** is approximately Lorentzian and indicates a correlation length for the regular packing within a layer of >50 Å depending on the sample. Thus the layers have long range bond orientational order but the molecular positions within the layers have short range order (SRO) only and this was the first experimental example of this type of phase predicted by Birgeneau and Litster (for the S_B phase) following the work of Halperin and Nelson.[29]

The existence of the S_I phase has only been confirmed very recently. It is a tilted biaxial phase, powder diffraction photographs of which show only a single outer ring, similar to that in S_B phases and apparently sharper than for S_F.[21,22] Diele *et al.*[21] have just published the first diffraction photographs of an aligned specimen using PDOBAC($C_{12}H_{25}OPhCHNPhCH{=}CH\text{-}COOC_5H_{11}$). These show a ring with six maxima when looking down the molecular long axes and bars of scattering for the beam parallel to the layers. In other words the diffraction photographs appear closely similar to those of S_F phases.

Symmetry

In order to try to clarify the relationship of S_I and S_F structures we have investigated the compound TBDA ($C_{10}H_{21}PhNCHPhCHNPhC_{10}H_{21}$; Cr, 73°, S_G, 120°, S_F, 150°, S_I, 156.1°, S_C, 190.8°, S_A, 192.4°, Iso) which has both S_F and S_I phases.

Powder photographs confirm the existence of a single outer ring in both phases, but somewhat sharper for S_I. Many experiments were carried out, but it was difficult to prepare aligned samples. However, by using a flat 1 mm thick sample and cooling slowly from the isotropic phase in a field of ~2T directly into S_F or S_I phases, well-aligned specimens were eventually prepared. The diffraction patterns then changed reversibly at the S_F–S_I transition and examples are shown in Figure 5b and c. Noting that these are for specimens partially disordered about **c***, the difference in the structures is readily apparent. In some samples with the beam approximately parallel to the long axes, a weak hexagonal intensity modulation of the rings was found for both phases. The situation is summarized in Figure 8 which shows how the two types of pattern of Figure 5b and c arise from tilted pseudo-hexagonal packings of the molecules having different tilt directions. For the S_F, the hexagon is tilted towards an edge (or alternatively adjacent 100 rows are uniformly displaced), while for S_I the tilt is toward an apex of the

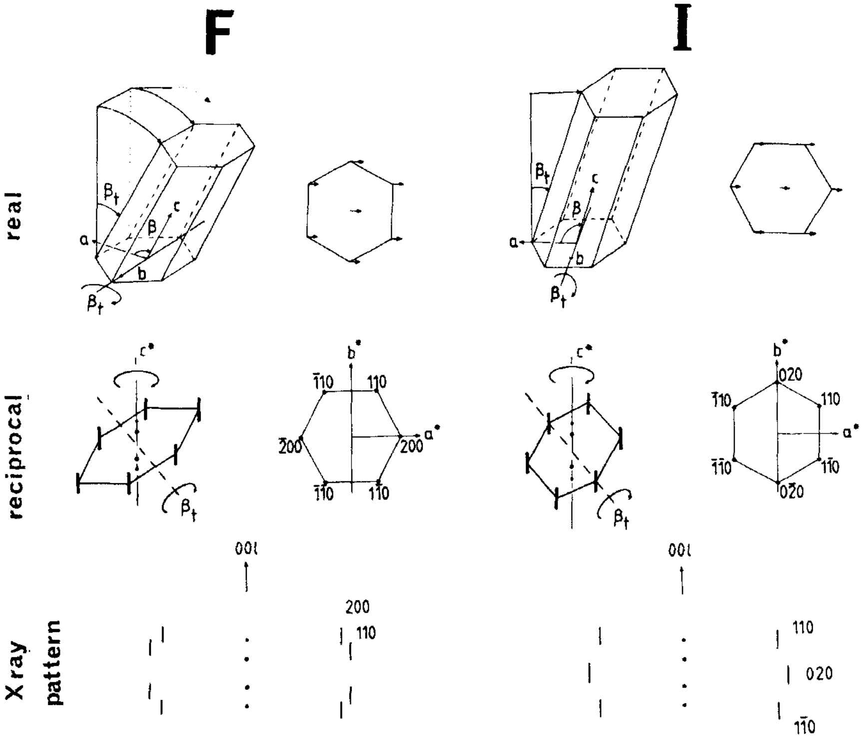


FIGURE 8 Representations of real and reciprocal lattices for S_F and S_I phases and the resultant diffraction pattern as shown in Figure 5b and 5c. The molecules are parallel to **c** and the pseudo-hexagonal packing of the molecules in the plane perpendicular to **c** is shown, with arrows indicating the direction of tilt. The hexagonal *hk*0 net is shown together with a perspective view depicting the tilt geometry and the diffuse bars of scattering parallel to **c***. A schematic representation is given of the X-ray diffraction pattern with the beam parallel to the layers for a sample with disorder about **c***.

hexagon. In both cases there is no significant distortion from hexagonal packing in the plane perpendicular to the molecules (the *hk*0 plane of the reciprocal lattice has ~hexagonal symmetry) and the unit cell is C-centred monoclinic with parameters as follows

$$S_F \quad a = 9.9\,\text{Å} \quad b = 5.4\,\text{Å} \quad c = 41.6\,\text{Å} \quad \beta = 112^\circ$$

$$S_I \quad a = 5.8\,\text{Å} \quad b = 9.2\,\text{Å} \quad c = 41.7\,\text{Å} \quad \beta = 114^\circ$$

The scattering centred on the zero level reciprocal lattice nodes in both cases consists of diffuse bars and the profiles are shown in Figure 9 and Figure 10. These are qualitatively similar for the two phases, showing that both consist

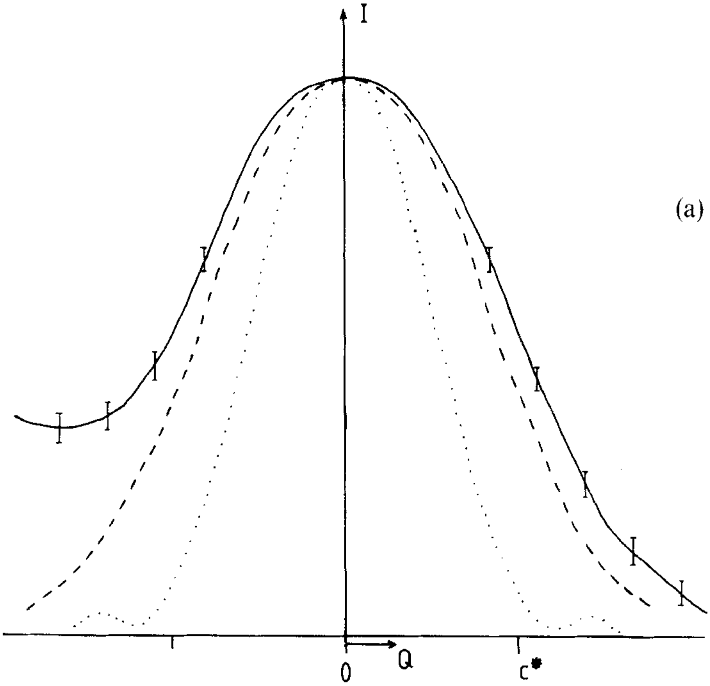


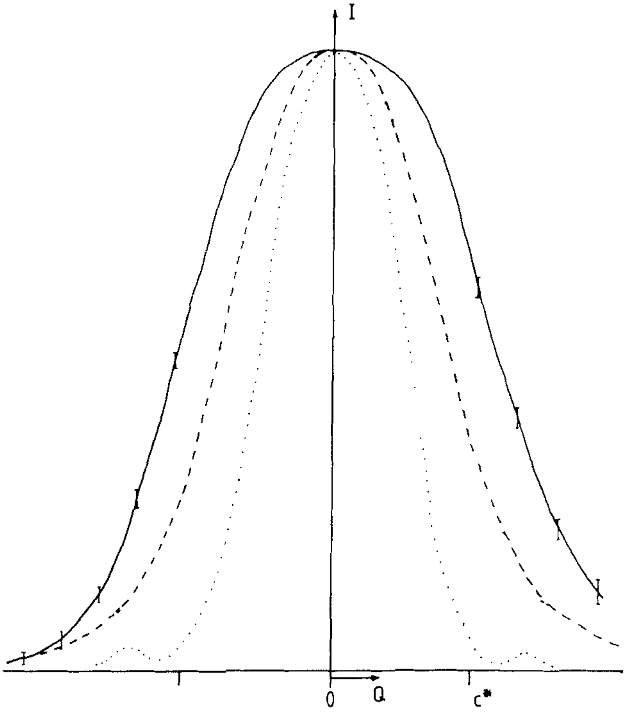
FIGURE 9 Intensity profiles parallel to c* of a) the 110 ring of the S_F phase TBDA and b) the 020 ring of the S_I phase (*cf.* Figure 8). Solid lines: Experimental results from Figures 5b and c; Dotted lines: Molecular structure factor $\langle F_m(00l)\rangle^2$; Dashed lines: Diffuse background from S_B phase of n0.m compounds as for Figure 6.

of uncorrelated layers (but with long range 3-d bond orientational order), and have limited positional correlations in the layers (see below).

These results show that for TBDA the essential difference between S_F and S_I phases lies in the *direction* of tilt of the pseudo-hexagonal molecular packing. There may also be quantitative differences in correlation lengths, but the important difference is in the molecular arrangement in a layer.

The very small transition enthalpy[30] $\Delta H \sim 3 J mol^{-1}$ is consistent with the close similarity of the two phases.

The symmetry of the S_I phase established above was in fact determined by Diele *et al.*[21] for PDOBAC, but its relation with the S_F structure was not then clear. Indeed in the first paper which established the structure of the S_F phase[18] two compounds were examined: TBPA (above) and 80SF $C_8H_{17}O$-$PhPhCOOPhCH_2CH(CH_3)C_2H_5$). These were both characterized as S_F by texture and miscibility, but TBPA has a tilt like the S_F phase of TBDA ($a > b$) while 80SF tilts as for the S_I of TBDA ($b > a$). Since these structures are clearly different, they should in fact be different phases, so the uncorre-



lated smectic phase of 80SF, previously classified as S_F, must in fact be an S_I phase. This requires that the miscibility situation be reexamined more carefully, but it is reminiscent of that for S_B–S_G (tilted S_B) phases which were for long thought to be miscible until the very careful experiments of Goodby and Gray.[31] Immiscibility might be even harder to detect for S_F/S_I mixtures, because of the possibility of microphase separation alternately into a few layers of each type.

In the light of the above discussion it now seems clear that the smectic III phase of the ferroelectric liquid crystal HOBACPC($C_6H_{13}OPhCH{=}NPhCH{=}CHCO_2CH_2(Cl)CHCH_3$) and related compounds studied by Doucet *et al.*[32] is in fact an S_I phase as it has precisely the characteristics described above.

Correlations

The profiles of the scattering bars (in fact cylinders) associated with the first *hk*0 reflections (Figure 5b, c) are shown for both S_F and S_I phases of TBDA in

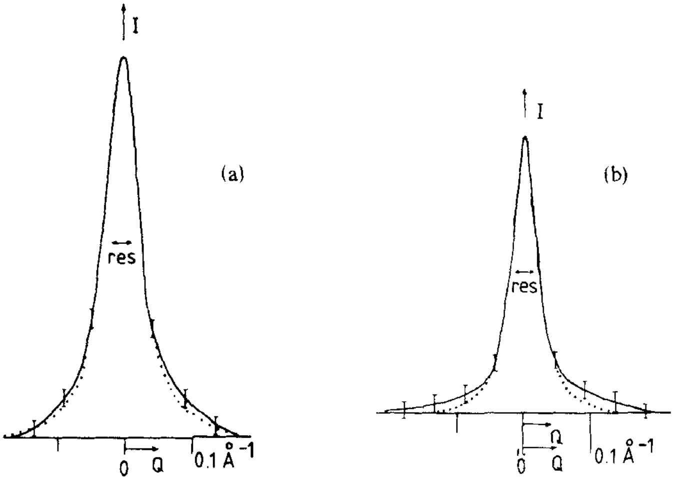


FIGURE 10 Intensity profiles perpendicular to **c*** at $l = 0$ of a) the 110 ring of the S_F phase of TBDA and b) the 020 ring of the S_I phase. Experimental results (solid lines) taken from Figure 5b and 5c are compared with calculated curves obtained by folding the instrumental resolution function with Lorentzians of width $\xi_{\perp}^{-1}$ (dotted curve).

Figures 9 and 10. For completely uncorrelated layers, the elastic scattering for **Q** parallel to **c*** should be determined by the molecular structure factors ($I \sim \langle F_m(00l)\rangle^2$). This has been calculated for molecules in their most extended conformation (and appropriate tilt angle) and is shown in Figure 9. Even making maximum allowance for mosaic effects in the sample (imperfect alignment), the actual profile is broader than $\langle F_m\rangle^2$ in both phases. A similar result was found for the uncorrelated S_B phase and in the same way we here compare experiment with the scaled diffuse scattering found for the S_B phases of nO.m compounds. The improved agreement again strongly suggests that the diffuse bars of scattering have a similar origin in both cases and probably contain a major component associated with molecular motions. This must in any case be expected because of the very weak interlayer coupling and at least partially melted tails.

The profile for $\mathbf{Q} \perp \mathbf{c}^*$ (Figure 10) is Lorentzian for S_F but has more pronounced wings for S_I. The best fit Lorentzians (Figure 10) give correlation lengths as follows: $S_F; \xi > 50$ Å; $S_I: \xi > 180$ Å. The figures can be regarded only as lower limits because of mosaic effects and, at least for S_I, because of the complex form of the profile. More accurate experiments of higher resolution are required for a proper analysis of the true shape of the scattering profile for $\mathbf{Q} \perp \mathbf{c}^*$ and neutron scattering is required for an energy analysis of the scattering.

The above discussion applies to all the S_F and S_I phases which have been examined. The S_F phase of 50.6,[20] however, shows a slightly different pattern in that the *hk*0 scattering bar is parallel to **c** and not to **c***. Although there might well be complications in this case due to mosaic effects, the profile is certainly different from that of the other S_F (and S_I) phases. We suggest that this is connected with the weaker layers in 50.6 (as in most of the n0.ms) which are more like the density wave of the S_C phase in this compound, rather than well-defined smectic layers. The scattering profile is more related therefore to individual molecules rather than individual layers.

S'_G and S'_H phases

Having established the difference between S_I and S_F phases and suggested that 80SF and HOBACBC have an S_I phase the question arises as to the existence of more ordered smectic phases analogous to S_G and S_H (monoclinic with $a > b$), but with the alternative tilt direction of the S_I phase ($b > a$). Such phases indeed exist: that analogous to S_G was first described by Doucet *et al.* for HOBACBC[32] and both were found for 80SF.[18] Both these compounds have a chiral centre, but the same results were found for 80SF on a pure isomer and on the racemate. As stated earlier, the existence of other ordered structures is not surprising, and it is not appropriate to give here any details. However, for completeness, we give below the unit cell parameters for TBPA and 80SF respectively for S_F, S_G, S_H and S_I, S'_G, S'_H phases.†

	TBPA		80SF
S_F	$a \sim 9.8$ Å	S_I	$a \sim 5.6$ Å
	$b \sim 5.2$ Å		$b \sim 9.1$ Å
	$c = 31.5$ Å		$c = 30.6$ Å
	$\beta = 113°$		$\beta = 113°$
S_G	$a = 9.82$ Å	S'_G	$a = 5.7$ Å
	$b = 5.25$ Å		$b = 9.0$ Å
	$c = 31.6$ Å		$c = 31.0$ Å
	$\beta = 115°$		$\beta = 114°$
S_H	$a = 10.0$ Å	S'_H	$a = 5.4$ Å
	$b = 5.3$ Å		$b = 9.1$ Å
	$c = 30.9$ Å		$c = 31.0$ Å
	$\beta = 118°$		$\beta = 114°$

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† In view of the accepted nomenclature of S_F and S_I there would be logic in naming S'_G and S'_H as S_J and S_K respectively. However, we believe that at the present time this might be premature and would certainly be confusing.

The smectic phases of HEPTOBPD($C_7H_{15}OPhCH{=}NPhN{=}CHPhOC_7H_{15}$)^{KJ}($S_J$ and S_K)

Full details of this investigation will be published elsewhere, but we believe a brief statement of results in this system is appropriate here because of the earlier report of two possible new smectic phases. The following phase behaviour was suggested on the basis of microscopic and DSC investigation

Crys, 127°, S_K, 130°, S_H, 146°, S_G, 154°, S_J, 157°, S_F, 164°, S_C, 197°, N, 241°, Iso

Detailed X-ray measurements on both powder and aligned samples have been completed and establish the following sequence of phases

Crys, 127°, Crys, 130°, Crys, 146°, S'_H, 154°,
S'_G, 157°, S_I, 164°, S_C, 197°, N, 241°, Iso

The existence of the S_I phase was established from X-ray measurements on aligned samples on the basis of tilt direction as for TBDA. A re-examination of the microscopic texture also now suggests S_I in place of S_F.[33] The existence of the S'_G and S'_H phases was established from the symmetry of the X-ray photographs (although alignment tends to be lost on cooling below S_I) and by indexing of powder photographs. This substance also exhibits rich crystalline polymorphism.

CONCLUSIONS

For certain crystalline S_B structures we have demonstrated the existence of two novel structural features

i) a change in the symmetry of the interlayer correlations with temperature.

ii) the presence of strong undulations of the layers of well-defined wavelength.

We have established also that three liquid crystal phases exist in which the molecular positions in different layers are essentially uncorrelated, but there exists long range bond orientational order of the lattice. The three phases are distinguished by the symmetry of this lattice

S_B–hexagonal
S_F–*C*-centred monoclinic, $a > b$
S_I–*C*-centred monoclinic, $a < b$

It seems likely that in all cases there exists only short range order of molecular positions within the layers with $\xi_\perp \gtrsim 100$ Å but there appears to be a strong "inelastic" component in the scattering and higher resolution and neutron scattering experiments are required to clarify this.

A number of other questions are also raised by this work *viz*:

1) There appear to be at least three distinct crystal S_B phases, all hexagonal and distinguished by the layer stacking (*AA* .. ; *ABA* .. ; *ABCA* ..). What other information can be obtained about these phases and the transitions between them?

2) Are correlated and uncorrelated S_B structures distinct phases as the equivalent tilted phases S_F and S_G (or S_I and S'_G) undoubtedly are?

3) What is the phase diagram for mixtures involving compounds having S_F and S_I, S_G and S'_G, and S_H and S'_H phases and how useful is the miscibility criterion for identifying these phases?

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