

## Synchrotron X-Ray Study of the Orientational Ordering $D2$ - $D1$ Structural Phase Transition of Freely Suspended Discotic Strands in Triphenylene Hexa- $n$ -dodecanoate

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We demonstrate the feasibility of x-ray scattering studies of freely suspended strands of discotic liquid crystals (of triphenylene hexa- $n$ -dodecanoate). We are able to grow strands, which are stable for days, of diameter  $> 50 \mu\text{m}$  with a few single-crystal domains. Unexpectedly, we find that the quasi two-dimensional structural phase transition from columnar  $D2$  to columnar  $D1$  corresponds to the orientational ordering of columns of molecules with the molecules tilted at finite angles to the column axis in both phases.

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Recently, disk-shaped molecules have been synthesized that exhibit a new class of columnar liquid-crystalline phases<sup>1,2</sup> in which the molecules segregate into infinite columns close packed in various two-dimensional (2D) lattices. To elucidate their structure and phase transitions, we have initiated synchrotron x-ray scattering studies of freely suspended strands<sup>3</sup> of such columnar phases. Our x-ray studies demonstrate the single-crystal quality of freely suspended strands, which provide the only viable technique for preparation of columnar phase samples suitable for high-resolution x-ray studies. Only high-resolution x-ray studies of such oriented samples allow one to disentangle and understand the intracolumnar 1D interactions and the intercolumnar 2D structure in the columnar phases and at the transitions. We expect these studies will enhance our understanding of collective behavior in lower-dimensional materials, as has been demonstrated for analogously prepared films of rod-shaped molecules.<sup>4,5</sup>

X-ray scattering studies were made on strands of triphenylene hexa- $n$ -dodecanoate (HAT11). Previous x-ray work on HAT11 shows that it exhibits two columnar phases  $D2$  and  $D1$ ,<sup>2</sup> but has left unclear the nature of the  $D2$ - $D1$  structural phase transition from a (2D) hexagonal to a (2D) centered rectangular lattice of columns of molecules. Qualitative optical observations<sup>3</sup> show that the molecules are tilted with respect to the column axis in the  $D1$  phase. Our data lead us to propose a model with the molecular tilt remaining finite across the transi-

tion into the  $D2$  phase. We find that the structural phase transition is associated with the intercolumn ordering of the molecular tilt orientation about the column axis.

The experiments were carried out at the Stanford Synchrotron Radiation Laboratory (SSRL) with use of the x-ray diffraction spectrometer stationed on beam line VII-2.<sup>6</sup> With use of horizontal and vertical slits, a pair of asymmetrically cut Ge(111) crystals to monochromatize the incident beam ( $\sim 7.1 \text{ keV}$ ), and LiF(200) crystal to analyze the diffracted beam, we obtain a longitudinal resolution of  $1.1 \times 10^{-3} \text{ \AA}^{-1}$  half-width at half maximum (HWHM). Lower-resolution experiments were carried out on thick strands at Exxon with resolution  $5.0 \times 10^{-3} \text{ \AA}^{-1}$  (Fig. 3) and  $1.8 \times 10^{-2} \text{ \AA}^{-1}$  (Fig. 4) HWHM. In these experiments, we studied  $\sim 1.5$ -mm-long strands with diameter between 50 and 200  $\mu\text{m}$  pulled in an oven with two-stage temperature control to  $\pm 0.01^\circ\text{C}$ .

We find that in the  $D2$  ( $118^\circ\text{C} > T > 105^\circ\text{C}$ ) and  $D1$  ( $105^\circ\text{C} > T > 70^\circ\text{C}$ ) temperature ranges HAT11 exhibits structures with Bragg peaks *only* in the  $(h, k, 0)$  plane and diffuse sheets at  $(h, k, \pm 2\pi/d)$  with  $d \sim$  molecular spacing within columns, consistent with the previous identification of the structures as two-dimensional lattices of liquid columns [inset, Fig. 1(b)] with no positional correlations between molecules from different columns along the  $\hat{z}$  (strand-axis) direction.<sup>2</sup> Across the  $D2$ - $D1$  transition the system distorts from a hexagonal into a centered rectangular structure with herringbone

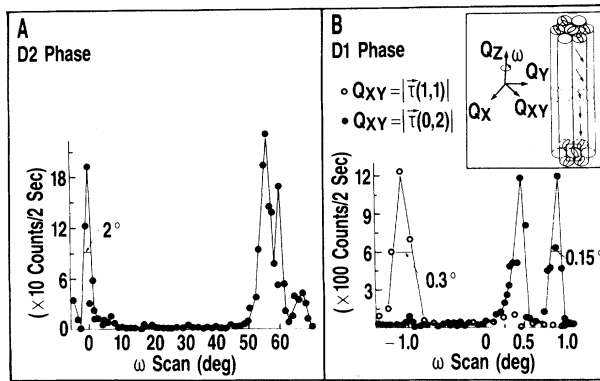


FIG. 1. (a) Wide-range  $\omega$  scan (rocking curve) through hexagonal (1,0) peaks in the  $D2$  phase. (b) Finer  $\omega$  scan after annealing in the  $D1$  phase indicates the single-crystal quality (mosaic  $\sim 0.2^\circ$ ) of discotic strands and as discussed in the text also provides evidence of orientational jumps in strands shown schematically in the inset with the scattering geometry.

symmetry. We show in Fig. 2 the real and reciprocal lattices of the two phases indexed on a two-dimensional rectangular unit cell in the  $x$ - $y$  plane defined as  $\vec{\tau}(h,k) = ha^*\hat{x} + kb^*\hat{y}$ .

We now discuss the structural quality of the free-suspended strands. To determine the degree of the lattice mosaicity, we execute  $\omega$  (rocking curve) scans in the  $D2$  and  $D1$  phases with  $\vec{Q}$  in the  $x$ - $y$  plane. In these scans the amplitude of the momentum transfer is fixed at the peak value of a  $Q_{xy}$  reflection [Fig. 1(b), inset]. We show in Fig. 1(a) an  $\omega$  scan with  $Q_{xy} = |\vec{\tau}(0,2)|$  [equivalent to a hexagonal (1,0) peak] over a  $70^\circ$   $\omega$  range in the  $D2$  phase. The scan shows two narrow bunches of peaks of  $1^\circ$  to  $2^\circ$  mosaic width spaced by  $60^\circ$  and is typical of what is obtained immediately after pulling a strand. The mosaic structure of a particular bunch evolves continuously in time with significant changes occurring in minutes.<sup>7</sup> Hence, the detailed structure of the two bunches in Fig. 1(a) is not precisely identical because of the structural evolution of the bunches during the scan time of four min. Annealing several hours improves the mosaic quality significantly, a given bunch evolving to a few closely spaced peaks with peaks of width between  $0.15^\circ$  and  $0.3^\circ$  [Fig. 1(b); bunch about  $\omega = 0$ ]. To measure  $|\vec{\tau}(1,1)|$  and  $|\vec{\tau}(0,2)|$  accurately, at each momentum transfer  $\vec{Q}_{xy}$ , we rotationally average, with the intensity integrated over  $\omega$ , segments which contain evolving peaks. In the  $D2$  phase at a given temperature, all such rotationally averaged longitudinal scans result in a peak at the same  $Q_{xy}$  indicating that  $|\vec{\tau}(1,1)| = |\vec{\tau}(0,2)|$ ; similarly,  $|\vec{\tau}(1,3)| = |\vec{\tau}(2,$

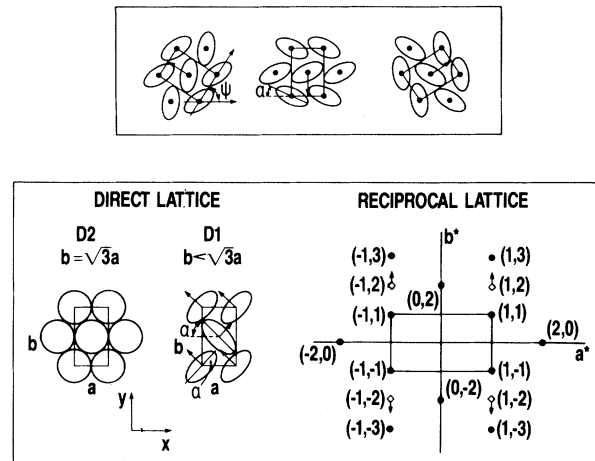


FIG. 2. Top panel: Three orientationally inequivalent (described by  $\psi$ ) states (each state also doubly degenerate) of herringbone order on a triangular lattice. Bottom panel: Direct and reciprocal lattice of the  $D2$  and  $D1$  phases indexed on a (2D) rectangular unit cell. The arrows on the ellipses of the  $D1$  phase indicate the direction of tilt. The herringbone structure of the  $D1$  phase is signaled by the appearance of four new peaks (open diamonds).

$0)|$  and thus the lattice is hexagonal. In the  $D1$  phase the system distorts to a centered rectangular lattice with herringbone symmetry, as evidenced by the appearance of the  $\vec{\tau}(1,2)$  peaks and a lattice distortion so that  $|\vec{\tau}(1,1)| \neq |\vec{\tau}(0,2)|$ . Figure 1(b) shows  $\omega$  scans of the annealed strand in the  $D1$  phase in which the mosaic has evolved to two sets of peaks at  $|\vec{\tau}(1,1)| = 0.2749 \text{ \AA}^{-1}$  and  $|\vec{\tau}(0,2)| = 0.2783 \text{ \AA}^{-1}$ .

The peaks with different wave-vector magnitude  $Q_{xy}$  occur closely spaced in  $\omega$  because the centered rectangular structure of the  $D1$  phase can condense on the triangular column lattice in three orientationally distinct directions (Fig. 2). The x-ray beam illuminates sections of the strand with different lattice orientation. Two such distinct regions separated by a soliton-type defect wall<sup>3</sup> are shown schematically in the inset to Fig. 1(b). To further test our observations we have used slits to illuminate  $\leq 50 \mu\text{m}$  sections of the strand to obtain a region with only one lattice orientation. However, the  $\omega$  scans, while sharp, are usually not single peaked and the in-plane structure contains a few single-column lattice domains separated by a few degrees.

We now discuss the  $D2$ - $D1$  structural phase transition. For clarity, we describe the hexagonal  $D2$  phase by a (2D) centered rectangular structure with  $b = \sqrt{3}a$  shown in Fig. 2. The  $D2$ - $D1$  transition at  $105^\circ\text{C}$ , which is first order, is characterized by a lat-

tice distortion and a simultaneous appearance of four twofold symmetric peaks with  $Q_{xy} = |\vec{\tau}(1, 2)|$  (Fig. 2). The new resolution-limited peaks in the  $D1$  phase signify the onset of long-range intercolumn molecular tilt orientational correlations about the column axis with herringbone symmetry. The intensity of the peak at  $\vec{\tau}(1, 2)$  as a function of temperature in the  $D1$  phase yields the square of the orientational order parameter. However, because of the time-dependent dynamics of the different domains in the strand, we find that the intensity is not quantitatively reproducible near  $T_C$ .

To measure the distortion, which is a secondary order parameter of this  $D2$ - $D1$  transition, we carried out rotationally averaged  $\bar{Q}_{xy}$  scans through the inplane peaks at  $\vec{\tau}(1, 1)$ ,  $\vec{\tau}(0, 2)$ , and  $\vec{\tau}(1, 3)$  in both phases for each temperature. We plot in Fig. 3  $\Delta b/b \equiv (b_2 - b_1)/b_1$  and  $\Delta a/a \equiv (a_2 - a_1)/a_1$  as a function of temperature. We find that the lattice contraction is primarily along the  $b$  axis with  $\Delta b/b \approx 0.015$ , and  $(\Delta a/a)/(\Delta b/b) \approx 0.04 \pm 0.02$  across the transition in the  $D1$  phase. We show in the lower panel of Fig. 3 the angle between the optic axis tilt and the strand axis as a function of temperature measured by optical microscopy techniques.<sup>3</sup> The optic axis tilt angle is  $28^\circ$  below the  $D1$ - $D2$  transition and drops abruptly to zero at the transition.

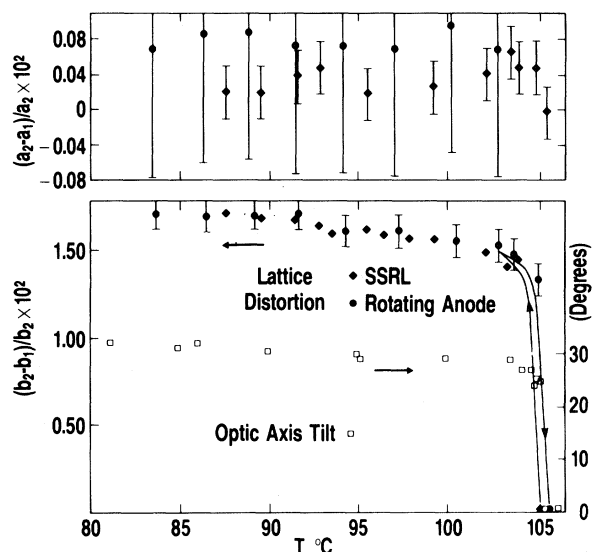


FIG. 3. Top panel: Lattice distortion along the  $a$  axis in the  $D1$  phase ( $a_2 = 26.512 \text{ \AA}$ ). Bottom panel: Lattice distortion along the  $b$  axis and optic axis tilt angle (open square) in the  $D1$  phase. The lattice constants were measured to an accuracy of about  $\pm 0.008 \text{ \AA}$  at SSRL and  $\pm 0.035 \text{ \AA}$  at Exxon.

The small distortion  $\Delta b/b \sim 0.015$  rules out a herringbone close packing of ellipses resulting from a tilt of the entire molecule; this would yield a significantly larger distortion of the hexagonal lattice.<sup>7</sup> With use of a close-packed hard-ellipse model one has  $\Delta b/b \sim 1 - [r(60^\circ + \alpha) + r(60^\circ - \alpha)]/D \approx 0.092$  with herringbone angle  $\alpha \sim 7^\circ \pm 4^\circ$  given by  $r(\alpha) = 0.5D(1 - \Delta a/a)$ . Here,  $r(\theta) = 0.5D/[\cos^2\theta + (1/e)^2 \sin^2\theta]^{1/2}$  is the equation for an ellipse in polar coordinates with eccentricity  $e = \cos 28^\circ = 0.883$ , and  $D =$  diameter of molecule  $\sim 26.5 \text{ \AA}$ . The optical data measure only the tilt of the central core of the molecules with anisotropic polarizability. The flexible aliphatic tails need not be tilted. The rigid core has a diameter of about  $7 \text{ \AA}$ ; hence, a tilt of  $28^\circ$  of only the core of the molecules [inset to Fig. 4(b)] gives a larger eccentricity  $e = 1 + (7/26.5)(\cos 28^\circ - 1) = 0.969$  and consequently a smaller distortion  $\Delta b/b \sim 0.022$ . A close-packed model is clearly not ideal for discotics; thus, the reasonable agreement (0.022 compared to 0.015) with the experimental data is a persuasive argument that only the core is tilted.

We next consider whether the molecular tilt angle is an order parameter of this phase. We show in Fig. 4(a)  $(0, 0, Q_z)$  scans in both the  $D1$  and  $D2$  phases along the strand axis through the diffuse sheet which probes intermolecular correlations in columns. The scattering is clearly not single peaked. The solid line through the data is the result of least-squares fits of a sum of two Lorentzians  $\sum_{i=1,2} A_i \xi^2/[1 + \xi^2(Q_z - Q_{iz})^2]$  centered at  $Q_{iz} = 1.35 \text{ \AA}^{-1}$  and  $Q_{2z} = 1.68 \text{ \AA}^{-1}$  [indicated by ar-

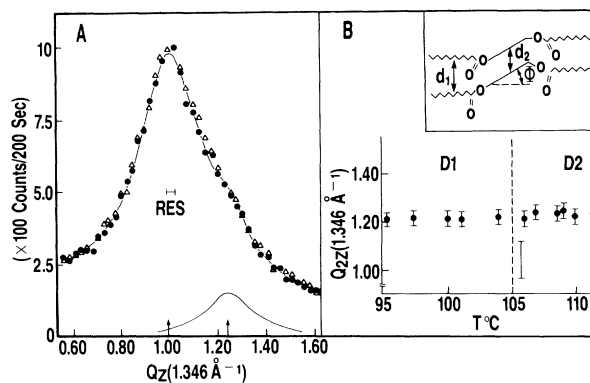


FIG. 4. (a)  $(0, 0, Q_z)$  scans along the strand axis through the double-profile liquid peak (due to the spacings  $d_1$  and  $d_2$  shown in inset) in the  $D1$  (closed circle) and  $D2$  (open triangle) phases. (b) The high- $Q_z$  peak position vs temperature shows no shift in peak position, which indicates that the molecular tilt remains finite in the  $D2$  phase.

rows in Fig. 4(a)] to the data. In these fits, the background is fixed at a value determined from low ( $Q_z < Q_{1z}$ ) and high ( $Q_z > Q_{1z}$ ) scattering points away from the diffuse sheet. As pointed out by Levelut<sup>2</sup> the first peak is due to the liquid structure of the aliphatic tails, while the second peak at  $Q_{2z} = 2\pi/d_2 = 1.68 \text{ \AA}^{-1}$  (separately shown as solid line), which does not appear in small-core discotics,<sup>7</sup> arises from short-range correlations ( $\xi \sim 3$  to 4 molecules) of the large aromatic core with spacing  $d_2$  [inset to Fig. 4(b)]. The tilt behavior across the transition is related to the change of the  $Q_{2z}$  peak position. In the simplest model, where the molecular tilt angle  $\Phi$  ( $\sim 28^\circ$ ) drops to zero across the transition, one would expect a significant shift in the peak position  $dQ_{2z} \sim Q_{2z}/\cos(28^\circ) - Q_{2z} = 0.13Q_z = 0.18 \text{ \AA}^{-1}$  [shown as solid bar in Fig. 4(b)] comparable to the width  $\Delta Q_z = 0.20 \text{ \AA}^{-1}$  of the scattering. The  $(0, 0, Q_z)$  scan in the  $D2$  phase is shown as open triangles in Fig. 4. We also show the  $Q_{2z}$  peak position versus temperature in Fig. 4(b), which indicates no statistically significant shift in the peak position across the transition. This suggests that while the tilt may change by a few degrees across the transition, it remains finite in the  $D2$  phase and consequently rules out the tilt angle as an order parameter of the  $D1$  phase.

We thus propose that the  $D2$ - $D1$  structural phase change is characterized primarily by the onset of the intercolumn ordering of the molecular tilt orientation about the column axis. In the  $D1$  phase, the columns of tilted molecules are close packed with herringbone order. However, there are six ways in which this order can be imposed on a triangular lat-

tice (Fig. 2). In the tilted  $D2$  phase, random fluctuations between these states results in an orientationally disordered hexagonal structure with an optic axis along the strand axis.<sup>3</sup>

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