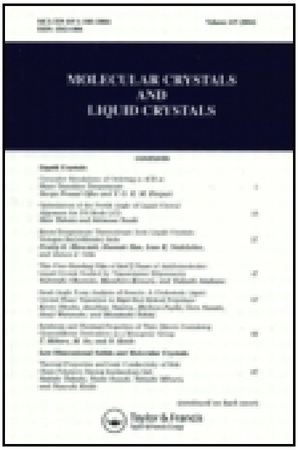

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Synchrotron X-ray Scattering Study of Freely Suspended Discotic Strands

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Synchrotron X-ray Scattering Study of Freely Suspended Discotic Strands

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We report the feasibility of x-ray scattering studies of freely suspended strands of discotic liquid crystals of triphenylene hexa-n-dodecanoate (HAT11) and of hexa-alcoxy derivatives of triphenylene (HET11). With use of a pin and cup configuration, we are able to grow strands, which are stable for days, of diameter > 50 μm with a few single crystal domains. In HAT11, as a function of increasing temperature, the system exhibits two liquid crystal columnar phases labeled D1 and D2. In the columnar phases, the molecules segregate into infinite liquid columns arranged in two-dimensional lattices. We find that the quasi-two-dimensional columnar D2-D1 structural phase transition from hexagonal to centered rectangular (herringbone) is associated with a small lattice distortion consistent with a close-packed model with only the core of the molecule tilted in the D1 phase. By carrying out longitudinal (parallel to column axis) diffuse scattering scans in HAT11 and a series of both small core discotics: benzene-hexa-n-alkanote (BH8), and large core discotics: hexa-alcoxy derivatives of triphenylene (HET11), we are able to unambiguously distinguish that part of the scattering which is associated with intermolecular correlations of only the cores of discotic molecules. Rather surprisingly, we find that *the tilt of the molecular core remains finite in the D2 phase*. We propose that the tilted D1 to tilted D2 transition corre-

sponds to an *orientational* order-disorder transition with the molecular tilt orientation ordered about the column axis in the D1 phase. In a simple model with no orientational short range order, the D2 phase may be thought of as rotationally uncorrelated columns of tilted molecules.

In 1977, S. Chandrasekhar and co-workers[1] reported the discovery of a new columnar liquid crystal phase composed of disk-shaped molecules. Their work has led to the synthesis of numerous similar molecules which exhibit nematic and a new class of columnar liquid crystalline phases[2-5] in which the molecules segregate into infinite columns close packed in various two-dimensional (2D) lattices. To date, optical observations, differential scanning calorimatory, and x-ray studies of polycrystalline preparations have revealed the existence of numerous quasi-two-dimensional hexagonal, rectangular, and oblique lattice phases[4] and also re-entrant nematic phases.[5] Discotics, however, in contrast to liquid crystal phases of rod-shaped molecules which may be readily aligned in moderate magnetic fields, are not aligned in magnetic fields so that a quantitative study of their phase transition behavior has till now not been possible. The Temperature-Concentration phase diagram of rod-shaped liquid crystals which exhibit regions of critical and multicritical behavior, have in fact proven to be ideal testing grounds for the statistical mechanical concepts of phase transitions.[6] Thus, to elucidate the nature of the detailed structure and structural phase transitions in discotics, we have initiated synchrotron x-ray scattering studies of freely suspended strands of such columnar phases. Our x-ray studies demonstrate the single crystal quality of freely suspended strands, which to date, 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 unambiguously disentangle and understand the intermolecular interaction in the 1D columns and the intercolumnar interactions associated with the 2D lattices 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.[9-11]

X-ray scattering studies were carried out on strands of triphenylene hexa-n dodecanoate (HAT11) and of hexa-alcoxy derivatives of triphenylene (HETn,n = 11,7,6). We first discuss the structure and structural phase transition study carried out in HAT11. Previous x-ray work on polycrystalline compounds of HAT11 shows that it exhibits two columnar phases D2 and D1,[2] 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[7] show that the molecules are tilted with respect to the column axis in the D1 phase. Our data indicate that the *molecular tilt remains finite across the transition into the D2 phase*. Thus, we propose that the D1-D2 structural phase transition is an *orientational* order-disorder transition with the molecular tilt orientation ordered about the column axis in the D1 phase. In the simplest model, the D2 phase may be thought of as rotationally uncorrelated columns of tilted molecules.

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-11.[12] With use of horizontal and vertical slits, a pair of asymmetrically cut Ge(111) crystals to monochromatize the incident beam (~7.1 keV), and a LiF(200) crystal to analyze the diffracted beam, we obtain a longitudinal resolution of $1.1 \times 10^{-3}\text{Å}^{-1}$ half-width at half maximum (HWHM). Lower resolution experiments were carried out on thick strands at Exxon with resolution $5.0 \times 10^{-3}\text{Å}^{-1}$ (Figure 4) and $1.8 \times 10^{-2}\ \text{Å}^{-1}$ (Figure 5) HWHM. In these experiments, we studied ~1.5 mm long strands with diameter between 50 μm and 200 μm pulled in an oven with two-stage temperature control to ±0.01°C.

We find that in the D2 (118°C $> T >$ 105°C) and D1 (105°C $> T$ $>$ 70°C) temperature ranges HAT11 exhibits structures with Bragg peaks *only* in the (h,k,O) 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, Figure 3B) with no positional correlations between molecules from different columns along the $\hat{z}$ (strand-axis) direction.[2] Across the D2-D1 transition the system distorts from a hexagonal into a centered rectangular structure with herringbone symmetry. We show in Figure 1 the real and reciprocal lattices of the two phases indexed on a two dimensional rectangular unit cell in the $(x$-$y)$ plane defined $\vec{\tau}\ (h,k) = ha^*\ \hat{x} + kb^*\hat{y}$. We stress that our result on the columnar nature of the D1 phase is contrary to the published work of reference (7) which claims that the D1 phase of HAT11 is a 3-dimensionally ordered crystal. We believe that the discrepancy lies in large temperature gradients across their sample which did not allow them to distinguish between the columnar D1 and lower temperature crystal phase.

In our x-ray studies, strands are prepared in a different manner than the reported work of reference (8). Freely suspended strands

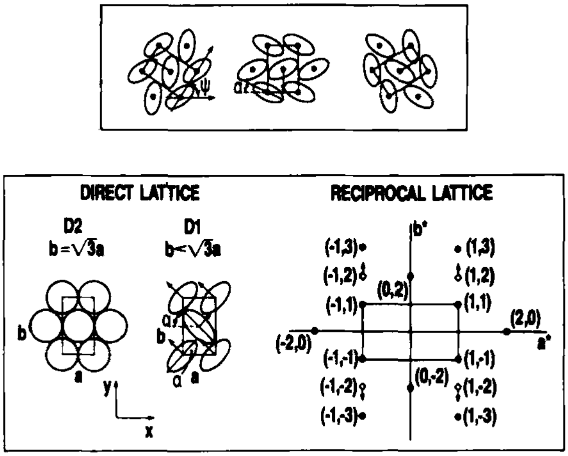

FIGURE 1 Top panel: Three orientationally inequivalent (described by ψ) states (each state also doubly degenerate) of herringbone order on a triangular lattice. Bottom Panel: Direct and reciprocal lattice of the D2 and D1 phases indexed on a (2D) rectangular unit cell. The arrows on the ellipses of the D1 phase indicates the direction of tilt. The herringbone structure of the D1 phase is signaled by the appearance of four new peaks (open diamonds).

are mechanically drawn using a cup and pin configuration as shown in Figure 2. In this set-up, the cup is filled with the liquid crystal compound, and at the desired temperature in the columnar phase, the pin is lowered until contact is made and drawn smoothly to the desired length of between 1 to 2 mm.

We now discuss the structural quality of such freely suspended strands. To determine the degree of the lattice mosaicity, we execute ω (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 (Figure 3B, inset). We show in Figure 3A an ω-scan with $Q_{xy} = |\vec{\tau}_{02}|$ (equivalent to a hexagonal (1,0) peak) over an extended ω-range of about 70 degrees in the D2 phase. The scan shows two narrow bunches of peaks of 1° to 2° mosaic width spaced by 60° 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.[13] Hence, the detailed structure of the two bunches in Figure 3A is not precisely identical because of the structural evolution of the bunches during the scan time of about four minutes. Annealing several hours improves the mosaic quality significantly, a given bunch evolving to a few closely spaced peaks with peaks of

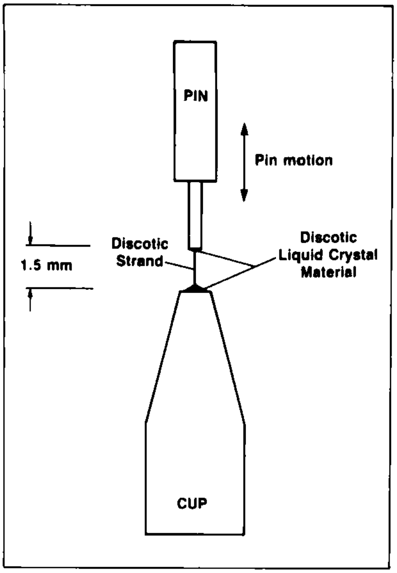

FIGURE 2 Schematic drawing of the pin and cup which sits in a three-stage oven used to mechanically draw freely suspended strands of the columnar phases of discotic compounds. The cup is filled with the material and at the desired temperature, the pin is lowered to contact the fluid and then drawn smoothly to a length of between 1 to 2 mm.

width between 0.15 and 0.3 degrees (Figure 3B; bunch about $\omega = 0$). To accuurately measure $|\vec{\tau}(1,1)|$ and $|\vec{\tau}(0,2)|$, at each momentum transfer $\vec{Q}_{xy}$, we rotationally average with the intensity integrated over ω 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 $|\vec{\tau}(11)| = |\vec{\tau}(0,2)|$; similarly $|\vec{\tau}(1,3) = |\vec{\tau}(2,0)|$ 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 $|\vec{\tau}(11)| \neq |\vec{\tau}(0,2)|$. Figure 3B shows ω scans of the annealed strand in the D1 phase in which the mosaic has evolved to two sets of peaks at $|\vec{\tau}(1,1)| = 0.2749$ Å^{-1} and $|\vec{\tau}(0,2)| = 0.2783$ Å^{-1}. The peaks with different wave vector magnitude Q_{xy} occur closely spaced in ω because the centered rectangular structure of the D1 phase can condense on the triangular column lattice in three orientationally distinct directions (Figure 1). The x-ray beam illuminates sections of the strand with different lattice orientation. Two such distinct regions separated by a soliton type

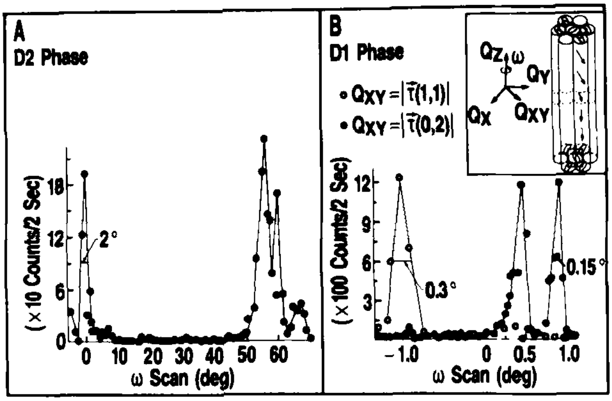

FIGURE 3 Wide range ω-scan (rocking curve) through hexagonal (1,0) peaks in the D2 phase. Figure 3B: Finer ω-scan after annealing in the D1 phase indicates the single crystal quality (mosaic ~0.2°) of discotic strands and as discussed in the text also provides evidence of orientational jumps in strands shown schematically in the inset with the scattering geometry.

defect wall[8] are shown schematically in the inset to Figure 3B. To further test our observations we have used slits to illuminate ≤50 μm sections of the strand to obtain a region with only one lattice orientation. However, the ω scans, while sharp, are usually not single peaked which indicates that 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 = $\sqrt{3a}$ shown in Figure 1. The D2-D1 transition at 105°C, which is first order, is characterized by a lattice distortion and a simultaneous appearance of four 2-fold symmetric diffraction peaks with $Q_{x,y} = |\vec{\tau}(1,2)|$ (Figure 1). The new resolution limited peaks in the D1 phase, with the molecules tilted[8] with respect to the strand axis, signify the onset of long range intercolumn tilt orientational correlations about the column axis with herringbone symmetry. A measurement of the intensity of the peak at $\vec{\tau}(1,2)$ at different temperatures gives the temperature dependence of the square of the orientational order parameter in the D1 phase. However, because of the time dependent dynamics of the different domains in the strand, we find that the intensity is not quantitatively reproducible as a function of temperature near T_C.

To measure the distortion, which is a secondary order parameter of this D2-D1 transition, we carried out rotationally averaged $\tilde{Q}_{xy}$ 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 Figure 4, $\Delta b/b \equiv (b_2 - b_1)/b_1$ 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 $\Delta b/b \simeq 0.015\%$, and $(\Delta a/a)/(\Delta b/b) \sim 0.04 \pm 0.02$ across the transition in the D1 phase. We show in the lower panel of Figure 4 the angle between the optic axis tilt and the strand axis as a function of temperature measured by optical microscopy techniques.[8] The optic axis tilt angle is 28° below the D1-D2 transition and drops abruptly to zero at the transition.

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. Using a close packed hard ellipse model[13] one has $\Delta b/b \sim [1\text{-}(r(60° + \alpha) + r(60° - \alpha))/D] \simeq 0.092$ with herringbone angle $\alpha \sim 7° \pm 4°$ given by $r(\alpha) = 0.5\, D\, (1 - \Delta a/a)$. Here, $r(\theta) = 0.5\, D/(\cos^2\theta + (1/e)^2 \sin^2\theta)^{1/2}$ is the equation for an ellipse in polar coordinates with eccentricity $e = \cos 28° = 0.883$, and D = diameter of molecule ~ 26.5 Å. The optical data measure only the tilt of the central core of the molecules with anisotropic polarizability. The flexible aliphatic

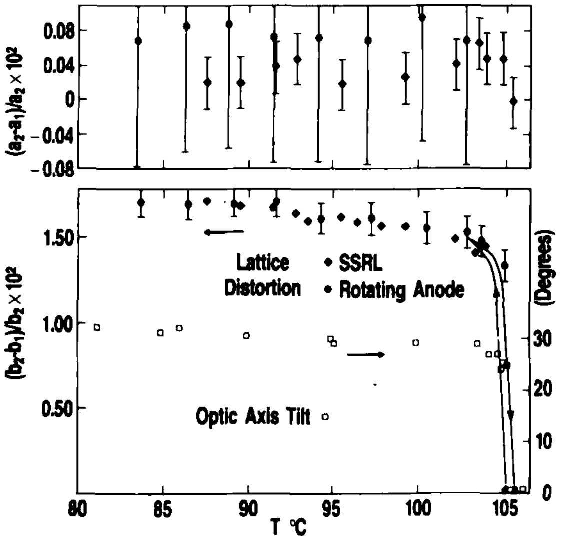

FIGURE 4 Top Panel: Lattice distortion along the a-axis in the D1 phase (a_2 = 26.512 Å). Bottom Panel: Lattice distortion along the b-axis and optic axis tilt angle (open square) in the D1 phase. The lattice constants were measured to an accuracy of about ± 0.008 Å at SSRL and ± 0.035 Å at Exxon (rotating anode). The small lattice distortion is consistent with a close packed hard ellipse model with only the core of the molecules tilted as discussed in the text.

tails need not be tilted. The rigid core has a diameter of about 7 Å; hence, a tilt of 28° of only the core of the molecules (inset Figure 4B) gives a larger eccentricity $e = (1 + 7/26.5 \times (\cos 28° - 1)) = 0.969$ and consequently a smaller distortion $\Delta b/b \sim 0.022$. The sources of error in our model arise from (*i*) the estimation of the fraction of the molecule that is tilted (e.g., a 2 Å error in the size of the tilted core changes $\Delta b/b$ by 0.007), although the triphenylene core is rather rigid and planar which should minimize the uncertainty and (*ii*) the model assumes a close packing of hard ellipses which is clearly not the case for discotic molecules; the entropy associated with the flexible tails favors a larger area per molecule and so a smaller distortion. In any case, the fact that a reasonably simple packing model gives a distortion that is within a percent of what is measured (0.022 compared to 0.015) and almost certainly within the bounds of errors associated with a hard packing model 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 shown in Figure 5A (O,O,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 $\sum_{i=1,2} A\xi^2/(1 + \xi^2(Q_z - Q_{iz})^2)$ centered at $Q_{1z} = 1.35\ \text{Å}^{-1}$ and $Q_{2z} = 1.65\ \text{Å}^{-1}$ (indicated by arrows in Figure 5A) to the data. In these fits, the background is fixed at a value determined from low $(Q_z < Q_{1z})$ and

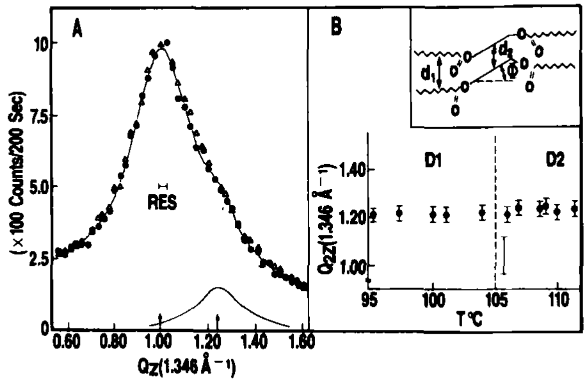

FIGURE 5A (O,O,Q_z) scans along the strand axis through the double profile liquid peak (due to the spacings d_1 and d_2 shown in insert) in the D1 (closed circle) and D2 (open triangle) phases. Figure 4B. The high Q_z peak position versus temperature shows no shift in peak position which indicates that the molecular tilt remains finite in the D2 phase.

high ($Q_z > Q_{1z}$) scattering points away from the diffuse sheet. The first peak is due to the liquid structure of the aliphatic tails, while as we discuss presently, the second peak at $Q_{2z} = 2\pi/d_2 = 1.65\text{Å}^{-1}$ (separately shown as solid line) arises from short range correlations ($\xi \sim 3$ to 4 molecules) of the large aromatic core with spacing d_2 (inset to Figure 5B).

To further elucidate the origin of the observed high Qz peak, we carried out identical (O,O,Qz) scans through columnar phases of a small core discotic: benzene-hexa-n-alkanoate (BH8) with the same ester linkage as HAT11. As shown in Figure 6A the (O,O,Qz) scan shows a *single* peaked profile characteristic of a paraffinic peak at $Q_z = 1.35$ Å^{-1} similar to that found in HAT11 and numerous other systems such as the smectic-A and C phases of rod-shaped liquid crystals and the L_α phases of Lyotropic liquid crystals. The amplitude of the high Qz peak is too small in a discotic compound with a single ring core. HAT11 with a considerably larger triphenylene core exhibits the additional high Q_z scattering. The amplitude of the high Qz peak is further enhanced in a triphenylene core compound with *ether* rather than *ester* linkages. We show in Figure 6C a (O,O,Qz) scan in the columnar phase of the hexa-alcoxy derivative of triphenylene (HET11). Presumably in going from an ester to an ether linkage, the Van der Waals interations between cores is increased. Thus, the high Qz peak in HAT11 Figure 5A and 6B is clearly due to intermolecular correlations between the large aromatic cores. 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 Φ (~28 degrees) drops to zero across the transition, one would expect from a Debye-Scherrer analysis[13] a significant shift in the peak position $dQ_{2z} \sim (Q_{2z}/\cos(28°) - Q_{2z}) = 0.13\ Q_z = 0.18$ Å^{-1} (shown as solid bar in Figure 5B) comparable to the width $\Delta Q_z = 0.20$ Å^{-1} of the scattering. The (O,O,Q_z) scan in the D2 phase is shown as open triangles in Figure 5. We also show the Q_{2z} peak position versus temperature in Figure 5B 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 (top panel Figure 7). However, there are three different ori-

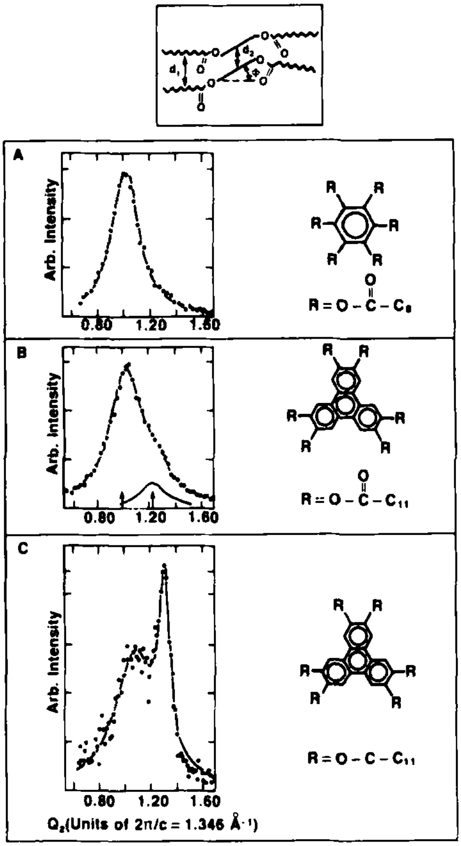

FIGURE 6 (*O,O,Qz*) scans along the strand axis through the liquid sheet in the columnar phases of three discotic compounds with different chemical structure. Figure 6A shows the scattering due to a small core (BH8) compound which exhibits a single peaked profile due to the paraffinic tails. Figure 6B with a larger core (HAT11) shows an additional high *Qz* scattering associated with short-range order of the cores of the molecule. Figure 6C shows an increased amplitude of the high *Qz* scattering; the ester linkage of the molecular in Figure B has been replaced by ether linkages which allow for a larger Van der Waals interaction between cores. The sequence of scans clearly indicate that the high *Qz* scattering is associated only with the core-core correlations as discussed in the text.

entationally inequivalent states of herringbone order on a triangular lattice (Figure 1) and each of these can sit on the lattice in two ways (an example is shown in the bottom panel). In the *tilted D2 phase*, random fluctuations between these six states results in an orientationally disordered hexagonal structure with an optic axis along the strand axis[8] as shown in the bottom panel of Figure 7.

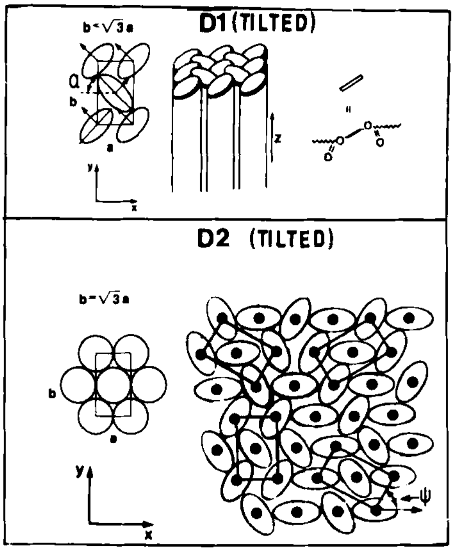

FIGURE 7 Schematic drawing of the D1 and D2 phases. Top panel: The D1 phase with the tilted molecular core arranged in a rectangular cell with herringbone symmetry. The arrows on the ellipse give the azimuthal direction of molecular tilt. *The D1 phase has long-range molecular tilt orientational order.* Bottom panel: The proposed structure of the D2 phase is one with the molecular tilt finite but with *no orientational order of the molecular tilt direction about the column axis.* Local short-range orientational order is associated with random fluctuations between the six orientationally distinct herringbone (four of these states shown in Figure) states possible on a triangular lattice as discussed in the text and shown in the top panel of Figure 1. In the limit of no orientational short range order, the D2 phase may be thought of as rotationally uncorrelated columns of tilted molecules.

In the orientationally disordered tilted D2 phase, one expects a diffuse scattering ring at $|Q_{xy}| = |\vec{\tau}(1,2)|$ due to local short-range herringbone order. However, because the D2-D1 transition is first order in HAT11, the amplitude for such local fluctuations is expected to be extremely weak. In this limit of very small amplitude fluctuations with no orientational short range order, the proposed model for the D2 phase is composed of *rotationally uncorrelated* columns of tilted molecules.

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