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Molecular disorder in columnar-phase discotic liquid-crystal strands

Ernest Fontes and Paul A. Heiney
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Masashi Ohba,* John N. Haseltine, and Amos B. Smith III
Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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We present x-ray diffraction measurements of freely suspended single-orientation columnar-phase strands of 2,3,7,8,12,13-hexa(-*n*-tetradecanoyloxy)truxene [$(C_{13}H_{27}COO)_6$-TX] which show a dramatic difference between the ordering of the rigid, planar central cores and the flexible hydrocarbon chain tails of the molecules. Diffraction from the strands reveals two types of behavior: the tails are highly disordered, producing a nearly isotropic scattering pattern, whereas the rigid cores are orientationally ordered and translationally disordered within the columns. High-resolution diffraction measurements show that the hexagonal lattice correlation length is greater than 4000 Å, corresponding to more than 200 columns.

I. INTRODUCTION

Since their first realization by Chandrasekhar *et al.*,[1] many classes of materials have been found which exhibit columnar phases.[2] These share a common feature in that the constituent molecules have rigid, planar central "cores" — which could be as simple as a single benzene ring — around which are attached many (typically 6–8) long hydrocarbon chain "tails." In contrast with smectic liquid crystals, which are layered mesophases of rod-shaped molecules having one solidlike and two liquidlike dimensions, discotic columnar phases are liquidlike in the one spatial direction along the columns and solidlike in the two-dimensional array of columns. There appear to be no intercolumn correlations, i.e., the columns slide freely over one another in the column axis direction. The morphology of known columnar phases can be summarized by a two stage process of construction. First, the molecules within each column can form either an ordered (*o*) or disordered (*d*) 1D array. (However, if there are truly no intercolumn interactions elementary statistical-mechanical considerations show that there can be no true *long-range* order within the individual columns.) Second, the columns themselves can be packed into a hexagonal (*h*) or rectangular (*r*) lattice. The four resulting phases are abbreviated[3] D_{ho} (hexagonal and ordered), D_{hd} (hexagonal and disordered), and likewise D_{ro} and D_{rd}. Note that there are many more than four possible space groups with 2D hexagonal or rectangular symmetry, but other such liquid crystalline phases have not yet been identified experimentally.

X-ray scattering has provided valuable information about the structure of columnar phases. From diffuse-scattering profiles of bulk columnar samples, Levelut was able to distinguish the intracolumn order of the cores from a more liquidlike order of the tails, showing that the core behavior is sensitive to the chemical composition of the tails and that the diffuse scattering of the paraffinic tails makes an "octopus" a more appropriate model of the discotic molecules than a rigid disk.[4–6] Safinya *et al.*[7] have measured the x-ray scattering intensity with the momentum transfer parallel to the column axis of freely suspended strands[8] and have observed a scattering profile with two peaks which they attribute to a competition between molecular stacking at two different nearest neighbor distances: a favored tail-tail packing distance and a shorter core-core nearest approach distance. In this model, the disordered structure along the columns is characterized by fluctuations between small domains in which the cores are close packed and tails are compressed, and domains in which the tails are freely packed but the cores are separated. Note that different mean tail-tail and core-core distances are *only* possible in a disordered structure.

A careful study of these two experimentally resolvable diffraction peaks allows a direct comparison of the translational and orientational ordering between the cores and tails of the columnar-phase molecules. Information about the long-range order of constituent parts of molecules should prove useful in trying to understand the structural phase transitions between columnar phases, reentrant phase transitions in single-component systems, as well as the general physical properties of dimensionally anisotropic liquid-crystalline and lamellar systems. In the field of biophysics, for example, knowledge of the melting of the hydrocarbon chains in phospholipid molecules has helped to further understanding of the structure and function of biological membranes.[9]

In this paper we present x-ray measurements of well-oriented, free-standing single orientation columnar phase strands of 2,3,7,8,12,13-hexa(*n*-tetradecanoyloxy)truxene [$(C_{13}H_{27}COO)_6$-TX] which show a dramatic difference in the ordering of the cores versus tails. We show that the x-ray signature of the $(C_{13}H_{27}COO)_6$-TX molecules has two components: the hydrocarbon tail chains are disordered, producing a nearly isotropic distribution of scattering, whereas the rigid cores of the molecules are oriented as in a nematic or smectic phase, with scattering intensity confined to within 30° of the strand axis. The "melted" nature of the aliphatic tail chains implies that theoretical models for discotic mesophases based on hard, flat disk constituent particles should be treated with some caution.

II. EXPERIMENTS

$(C_{13}H_{27}COO)_6$-TX was prepared according to the method of Destrade *et al.*[10] Purification was achieved by successive recrystallization from ethanol/chloroform (2:1, v/v). The purity was determined to be better than 99.98% by high-performance liquid chromatography, using hexane/ethyl acetate (99.5:3.5, v/v) as solvent. The phase sequence of the pure material is[11]

$$K \underset{61}{\rightarrow} (D_{ho} \underset{56}{\leftrightarrow})\, N_d \underset{84}{\leftrightarrow} D_{rd} \underset{112}{\leftrightarrow} D_{ho} \underset{241}{\leftrightarrow} I .$$

Freely suspended strands of the hexagonal phase of $(C_{13}H_{27}COO)_6$-TX (Refs. 10–12) were grown using a technique developed by Safinya *et al.*[7] Material was placed into a cup reservoir in a temperature-controlled oven containing an inert atmosphere (see Fig. 1). As a pin was inserted and then slowly pulled out of the reservoir, a fiber or strand of approximately 150–200 μm in diameter was drawn to a length of 1.5–2 mm. The oven had cylindrical beryllium walls, permitting 360° x-ray access. Rotating the strand through angle ϕ with a scattering vector fixed at the primary hexagonal position showed groups of peaks separated by $\Delta\phi = 60°$, indicative of a multicrystalline sample with domains of hexagonal symmetry. Over time, the sample annealed into several large, well-defined and easily discernible crystalline domains. Thus, it was possible for us to study well oriented *single-orientation* columnar domains.

The x-ray experiments employed an Elliott GX-13 rotating anode generator with an apparent source diameter of 100 μm. Most of the data were collected using a vertically focused LiF(200) monochromator crystal which produced an incident flux of approximately 10^7 Cu$K\alpha_1$ photons/sec in a 400 μm diameter spot at the sample position. With a LiF(200) analyzing crystal this configuration yielded an in-plane longitudinal resolution of $\Delta|\mathbf{q}| = 0.005$ Å^{-1} full width at half maximum (FWHM), an in-plane transverse resolution of $\Delta q_\perp = 0.0005$ Å^{-1} FWHM, and an out-of-plane vertical resolution of $\Delta q_{\text{vert}} = 0.07$ Å^{-1} FWHM. To achieve higher resolution, a Ge(111) monochromator and analyzer in some cases provided 10^5 Cu$K\alpha_1$ photons/sec in a 200 μm$\times$700 μm spot with $\Delta|\mathbf{q}| = 0.0005$ Å^{-1} FWHM, $\Delta q_\perp < 0.0001$ Å^{-1} FWHM, and $\Delta q_{\text{vert}} = 0.007$ Å^{-1} FWHM.

In this paper, the long axis of the strand (and molecular columns) is designated the z-axis direction. The orthogonal x-y plane is the plane of hexagonal symmetry of the columns, and is referred to as the hexagonal basal plane. The scattering space basis is labeled Q_x, Q_y, and

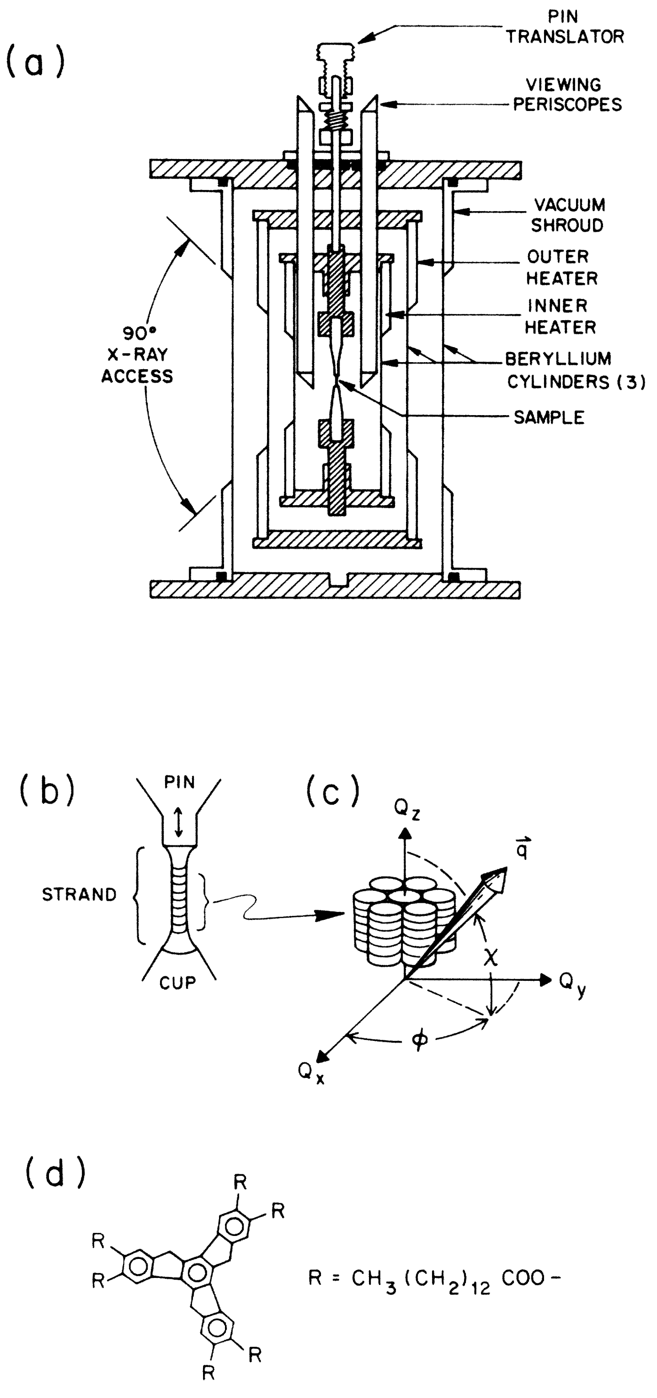

FIG. 1. (a) The temperature-controlled oven used to grow and anneal discotic strands *in situ*, under an inert atmosphere. Retractable periscopes permit visual examination of the strand. Thin cylindrical beryllium walls allow x-ray scattering observations which are unobstructed in the plane normal to the strand (the hexagonal basal plane), and allow for 90° of scattering access in the strand axis plane. Cylindrical inner and outer heating stages provide a uniform thermal environment for the strand. (b) The pin is drawn slowly from the bulk material in the cup to produce a strand. (c) The strand fixed reciprocal lattice is defined with column axis parallel to Q_z. With scattering vector $\mathbf{q}$ defined, ϕ and χ are used as azimuth and polar angles, respectively. (d) Structure of the $(C_{13}H_{27}COO)_6$-TX molecule.

Q_z. Q_b refers to an arbitrary direction in the hexagonal basal plane. q_x, q_y, q_z, and q_b refer to measured diffraction vector components in the above directions.

III. RESULTS

Figure 2(a) shows the scattered intensity, at 120 °C (D_{ho} phase), at the wave vector of the primary hexagonal peak as the strand is rotated about its long axis. Single orientation domains are well isolated, with a signal-to-background intensity ratio in the vicinity of the hexagonal peaks of roughly 10^3. (Background scattering at the hexagonal peak position is mainly due to unoriented bulk discotic material that is simultaneously illuminated by the x-ray beam.) The hexagonal peaks were resolution limited in all dimensions. The 0.0005 Å^{-1} FWHM longitudinal peak width [Fig. 2(b)] sets a lower limit on the hexagonal lattice correlation length of approximately 4000 Å, or approximately 200 columns. The out-of-plane mosaic of the lattice, which is the angular deviation of the hexagonal peaks out of the plane orthogonal to the long axis of the strand, was better than $\Delta X = 1.6°$ FWHM. The azimuthal mosaic of the lattice, measured by rotating the strand about its long axis, was better than $\Delta\phi = 0.03°$ FWHM ($\Delta q_{\perp} = 0.0001$ Å^{-1}). Thus, the 2D hexagonal columnar lattice appears to have long-range order to within instrumental resolution, although our measurements would not have been sensitive to algebraic decay of positional order.

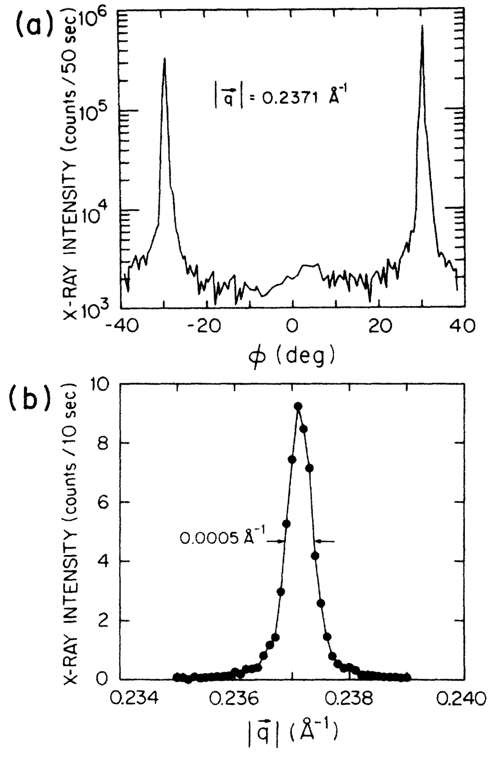

FIG. 2. (a) A plot of scattered intensity, at 120 °C, at the wave vector of the primary hexagonal peak $|\mathbf{q}| = 0.2371$ Å^{-1} as the strand is rotated about its long axis. The hexagonal symmetry peaks are separated by $\Delta\phi = 60°$. The intensities of the resolution limited peaks are not exactly equal due to the coarseness of the step size used in the data collection. (b) High resolution x-ray scattering radial profile of a primary hexagonal peak. Solid line is a guide to the eye.

The long-range order of the two-dimensional lattice of columns is in sharp contrast with the liquidlike structure of the individual columns. X-ray scans with scattering vectors along Q_z (parallel to the columns) measured a double-peaked profile as previously reported for free-standing columnar strands [Fig. 3(b)]. The appearance of two peaks has been attributed[7] to the existence of two unequal nearest-neighbor molecule-molecule stacking distances, a short core-core distance and a somewhat longer tail-tail distance. As a result, the proposed structure along the column has small domains in which the cores are close packed with the tails compressed, and other domains in which the tails are freely packed but the cores do not touch. The broadness of these peaks indicates a short liquidlike translational correlation length and suggests that an appropriate functional form to characterize the scattering intensity is the sum of two Lorentzian peaks:

$$I(q) = I_0 + I_1 \frac{\kappa_1^2}{(q - q_1^2) + \kappa_1^2} + I_2 \frac{\kappa_2^2}{(q - q_2^2) + \kappa_2^2},$$

where $q = (4\pi/\lambda)\sin(\theta)$. Using this form to fit the data in Fig. 3(b) yields $X^2 = 1.017$ for values $I_0 = 255$ counts/300 sec, $q_1 = 1.337$ Å^{-1}, $\kappa_1 = 0.227$ Å^{-1}, $I_1 = 2550$ counts/300 sec, $q_2 = 1.712$ Å^{-1}, $\kappa_2 = 0.129$ Å^{-1}, and $I_2 = 1042$ counts/300 sec. The correlation lengths $\xi = 1/\kappa$ of the tail-tail and core-core interactions are 4.4 Å and 7.8 Å, respectively, corresponding to a single nearest-neighbor chain-chain packing distance for the tails and two parallel nearest neighbors for the cores. Thus, although the structure of $(C_{13}H_{27}COO)_6$-TX at 120 °C has previously been characterized as D_{ho}, "hexagonal ordered,"[12] the positional order along the columns is best described as liquidlike. The degree to which extended order can exist within uncorrelated columns, and the nature of an intracolumn ordering transition $D_{ho} - D_{hd}$,[13] will be the subject of future investigations.

The appearance and relative scattering weights of the two Q_z peaks are sensitive to the chemical composition of the cores and tails. At one extreme is the behavior found in systems of discotic molecules having very small core size relative to the length of the tails. Strands of the hex-*n*-alkanoate BH8, having molecules with a single benzene ring core and six tail chains of eight carbon length, display Q_z x-ray scans[7] with only a single paraffinic tail peak. In this case, the cores are too small for steric core-core alignment to play an important role. The cores follow the liquidlike ordering of the tails and, therefore, all of the scattering weight is found in a single peak. At the other extreme, Safinya *et al.* studied[7] a series of triphenylene compounds and found that certain tail linkages enhanced the intensity and sharpened the core peak dramatically while leaving the tail peak unchanged.

Measurements of the positions and intensities of the core-core and tail-tail peaks as a function of polar angle

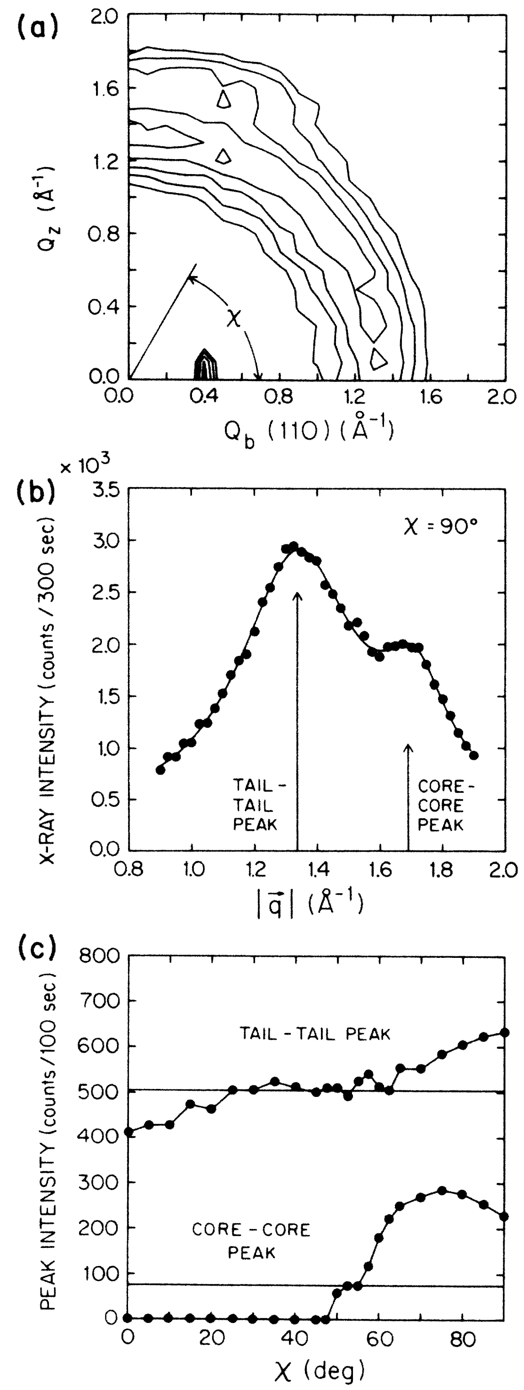

FIG. 3. (a) Equal intensity contours of scattering data at 120 °C in the $Q_z - Q_B$ plane. The plane is defined such that the column axis is along Q_z and the (110) hexagonal peak at 0.411 Å^{-1} is along Q_b. Contours are drawn at 681, 562, 464, 383, and 316 counts/200 sec. The 681-count contour surrounds a peak of 735 counts/200 sec at $q_b = 0$, $q_z = 1.35$ Å^{-1}. (b) X-ray scattering profile along the strand long axis [$\chi = 90°$ in Fig. 3(a)]. The solid line through the data points is a sum of two Lorentzian peaks (described in the text), whose amplitudes and positions are shown by the heights and positions of indicating arrows. (c) The amplitudes of the two peaks shown in Fig. 3(b) are plotted as a function of polar angle χ. The horizontal lines through the two sets of data show the polar average of scattering at that momentum transfer.

away from the column long axis reveal a dramatic difference in the core versus tail behavior. Figure 3(a) shows x-ray equal-intensity contours in the $Q_z - Q_b$ plane. [The Q_b axis is oriented in the hexagonal basal plane along the direction of a secondary hexagonal (110) peak at 0.411 Å^{-1}. However, the core and tail scattering patterns discussed here appear to be independent of the orientation of the Q_b axis in the hexagonal basal plane.] The contour plot shows a ring of scattering (which is a cross-section of a spherical shell) at $|\mathbf{q}| = 1.35$ Å^{-1} resulting from the liquidlike tail-tail correlations. The peak resulting from core-core correlations appears as a shoulder (towards high $|\mathbf{q}|$) on the tail-tail ring, located within 30° of the Q_z axis.

To compare the behavior of the cores and tails we plot [Fig. 3(c)] the intensities of the tail-tail and core-core peaks as a function of polar angle. The intensities are obtained from fits of the function I(q) to data along a line of constant polar angle χ, as indicated in Fig. 3(a). The core-core peak intensity falls off rapidly at $\chi \approx 60°$, and below $\chi = 50°$ the intensity was set equal to zero to produce convergent fits. The tail-tail peak intensity is a slowly varying function of χ, indicating an almost isotropic distribution of C-C links in the tails, analogous to a hydrocarbon liquid. This is in contrast to the behavior of the tails in bulk samples of the hexapentyloxy derivative of triphenylene reported by Levelut.[4] In that system, the diffuse ring due to the aliphatic chains is strongly modulated; the peak in the intensity is about 20° from the column axis, implying that the mean direction of the chains is out of the plane orthogonal to the column axis. Thus, a variety of tail-chain behaviors have been found. Furthermore, temperature dependent behavior will be discussed below.

The shape of the peak due to core-core correlations could be interpreted in one of several ways. First, either an angular mosaic average, due to a misoriented, multidomain sample, or a long-wavelength column undulatory instability which was correlated from column to column, would spread the peak at $q_z = 2\pi/d_{\text{C-C}}$ over a spherical polar cap. (Here $d_{\text{C-C}}$ is the energetically favored core-core nearest-neighbor distance.) However, the small out-of-plane angular width of the Q_b hexagonal peaks indicates that the crystal misorientation mosaic is small ($\Delta\chi < 1.6°$ FWHM), and rules out either of these models.

Second, since the liquidlike nature of the core and tail interactions appears to destroy any correlation between the two parts of the molecules, the shape of the core-core peak might be due to the one-dimensional nature of the cores within the columns. If the translational order of the cores were like that of a true 1D liquid, the core-core peak would define a planar Bragg sheet at fixed q_z. The limited angular extent of the core peak would then be the result of the intensity decay length of the molecular form factor for the approximately circular disk of charge (the core), which yields a finite disk of scattering in the $q_z = 2\pi/d_{\text{C-C}}$ sheet centered about the Q_z axis. A similar description of the diffraction was presented by Levelut.[4]

However, the cores are not expected to exhibit true one-dimensional behavior. Although the translational order of the cores is one-dimensional in the sense that the dominant interaction between the cores is a steric repulsion which favors parallel plane-to-plane core alignment, large fluctuations in both tilt angle and position result in a core-core correlation function which is three dimensional. Column undulatory instabilities can produce similar behavior, although the undulations must be uncorrelated from column to column in order to explain the small vertical mosaic of the Q_b hexagonal peak.[14] Thus we expect to see a scattering pattern which is not completely described by either a diffuse sheet or by a diffuse spherical shell. The core-core peak that we measured was sufficiently diffuse that the detailed shape in the $Q_z - Q_b$ plane was difficult to establish. The columnar phases are perhaps best described as one-dimensional analogs of the two-dimensional liquidlike planes in smectic mesophases. The diffuse nature of the core peak is then due to the same liquidlike motion which characterizes the side-by-side interaction of the rod-shaped smectic molecules and produces a diffuse peak in the scattering plane parallel to the smectic layers.

A previous report[11] indicated that bulk samples of $(C_{13}H_{27}COO)_6$-TX undergo a phase transition $D_{ho} \rightarrow D_{rd}$ at 112 °C. We have been unable to find rectangular order of the column lattice in freely suspended strands. If this order does exist, our data set the following limits: the intensities of those rectangular symmetry peaks which are forbidden in the hexagonal phase are reduced from the hexagonal symmetry peaks by a factor of at least 10^4, and the distortion of the column two-dimensional lattice, which breaks the hexagonal symmetry, is determined by our resolution to be less than 0.5%.

An analysis of the intracolumn and orientational ordering of the D_{rd} phase at 99 °C was carried out with data similar to those collected for 120 °C. The qualitative features at 99 °C are the same as those at 120 °C. Quantitatively, the correlation lengths of the core-core and tail-tail ordering change from 7.8 to 7.0 Å and 4.4 to 4.8 Å, respectively. However, due to the liquid-like nature of the intracolumn ordering, these shifts are not large enough in magnitude to be significant. The change in the orientational order of the tails is more pronounced. The tail-tail peak intensity, which is nearly isotropic in polar angle χ at 120 °C, acquires a more noticeable angular dependence at 99 °C; a least-squares fit to an entire scattering profile yields an angular width of $\Delta\chi = 90° \pm 20°$ FWHM at 120 °C and $\Delta\chi = 40° \pm 12°$ FWHM at 99 °C. The core-core peak angular profile is essentially unchanged over the same temperature range. Levelut has reported[4] similar behavior in bulk samples: upon decreasing temperature, the core peak remains unaffected while the modulation of intensity in the diffuse paraffinic tail ring changes noticeably. The orientational ordering of the cores is insensitive to temperature variation, similar to the behavior of rod-shaped molecules in smectic and nematic phases. The orientational ordering of the tails changes substantially, most probably due to a strong temperature dependence of the conformational degrees of freedom of the hydrocarbon chain tails. Future experiments, with more detailed thermal analysis, might improve our understanding of the role of tail chain freedom in determining the thermodynamics of columnar phase diagrams.

The lack of any observed hexagonal symmetry peaks out of the basal plane $(q_z = 0)$ indicates that column-column correlations are weak or nonexistent. This supports the picture of a columnar phase as a two-dimensional array of one-dimensional liquid columns. However, it is worth noting that the intensity of such a peak, if it existed, might be very small due to the liquid-like disorder of the columns. For example, in our measurements the ratio of the intensity of the primary hexagonal peak to the intensity of the liquidlike Q_z peak is approximately 10^4. Since we expect any hexagonal peak with $q_z \neq 0$ to be even less intense than the core and tail Q_z peaks, they may not be experimentally resolvable above diffuse scattering.

IV. DISCUSSION

It is generally understood that the presence of both rigid central sections and flexible tails is essential to the development of mesomorphic order in both rodlike and discotic liquid crystals. However, despite a number of diffraction and magnetic resonance studies, the details of core versus tail ordering are poorly understood. In this paper we have shown that it is possible to distinguish between ordering of the cores and tails of discotic molecules in free-standing strands: the behavior of the tails and cores of the $(C_{13}H_{27}COO)_6$-TX molecules in a hexagonal columnar phase is dramatically different. We find that the tails are "melted" hydrocarbon chains: a large degree of conformational freedom effectively decouples the ordering of the tails from the cores. Similar behavior is also seen in liquid crystal side-chain polymer systems. The side chains appear decoupled from the long semirigid polymer backbone, revealing the same temperature dependence and order parameter magnitude[15] in a comparison of the orientational long-range order of attached and unattached rod-shaped liquid-crystalline monomers. The orientational order of the discotic tails increases noticeably upon decreasing temperature, suggesting that the temperature dependence of the conformational degrees of freedom to the hydrocarbon chains might play an important role in the statistical mechanics and thermodynamics of the columnar phases.

In sharp contrast with the long-range order of the two-dimensional lattice of columns, within the individual columns the cores behave like an oriented, one-dimensional liquid. The liquidlike nature of the core ordering produces diffuse peaks with a finite azimuthal range which can have both Bragg-sheet and spherical components. In future work we plan to examine the nature of the intracolumn order and to study the order-disorder intracolumn phase transition.

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[*] Present address: Faculty of Pharmaceutical Science, Kanazawa University, Takara-Machi, Kanazawa, Japan.

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