Liquid-Crystalline and Helical Order in a Discotic Mesophase

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We have used x-ray diffraction to study oriented strands of hexa-hexylthiotriphenylene discotic liquid crystals. The low-temperature D_{ho} phase consists of a triangular array of columns with periodic positional and incommensurate helical intracolumn order. A three-column superlattice results from the frustration imposed by molecular interdigitation in triangular symmetry. We suggest that the $D_{\text{hd}} \rightarrow D_{\text{ho}}$ transition is driven by the increase in hydrocarbon tail stiffness and length with decreasing temperature.

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Liquid crystals have provided us with unique models for phase transitions in systems with less than perfect structural order.[1] Discotic liquid crystals[2] are composed of disk-shaped molecules with rigid planar central cores and 6–8 flexible hydrocarbon chain tails. They form nematic phases, and also more highly ordered columnar mesophases, which have been classified according to the symmetry of the columns and the nature of the intracolumn order. The most commonly observed hexagonal and rectangular disordered phases, D_{hd} and D_{rd}, consist of triangular or rectangular arrays of columns with only fluidlike intracolumn order and consequently no long-range column-column correlation of the molecular heights. Additionally, the molecules within each column can order to form the hexagonal ordered phase, D_{ho}. However, since true long-range order cannot exist in one dimension, if long-range intracolumn order develops then the columns must be correlated. Ordered columnar phases may thus be analogs of higher smectic phases seen in rodlike mesogens, which are three-dimensional crystals with local structures close to those of true smectic phases.

A D_{hd}-D_{ho} transition has so far only been observed in hexa-hexylthiotriphenylene[3] [HHTT, Fig. 1(a)]. In this Letter we describe single-crystal-geometry x-ray diffraction measurements of the columnar phases of HHTT. We find that in the D_{ho} phase helical molecular orientational order develops within the columns. The helical period is incommensurate with the intermolecular spacing. Additionally, a three-column superlattice develops, associated with both the helical phase and the vertical displacement of three columns.

For the x-ray experiments, the HHTT liquid crystal was drawn into free-standing, single-orientation strands[4,5] and measured in a focusing geometry as described previously.[5] The strands were typically 200 μm in diameter and 1.5–2 mm long. The longitudinal resolution was $\Delta q_{\parallel} = 0.0050$ Å^{-1} full width at half maximum (FWHM). In the discussion that follows, q_z refers to the component of the diffraction vector along the molecular column direction, while q_x, q_y, and $q_b \equiv (q_x^2 + q_y^2)^{1/2}$ refer to components in the equatorial plane.

Our measurements are consistent with previous work[3]

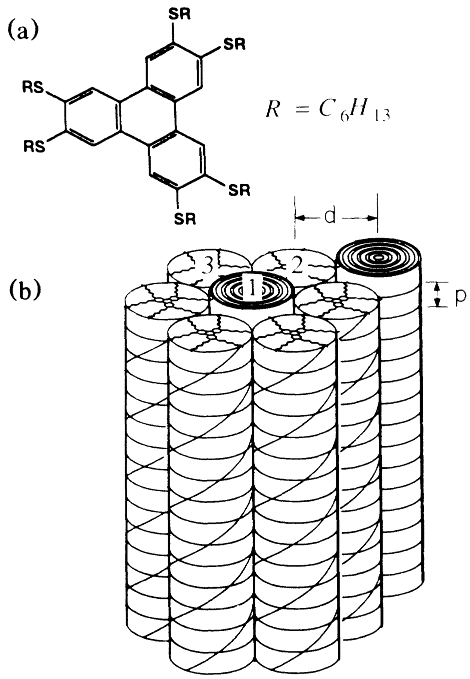

FIG. 1. (a) Hexa-hexylthiotriphenylene (HHTT). (b) Proposed structure of three-column superlattice (not to scale). Column 1 has random average helical phase, and is displaced by $p/2$ from columns 2 and 3, which have correlated phases.

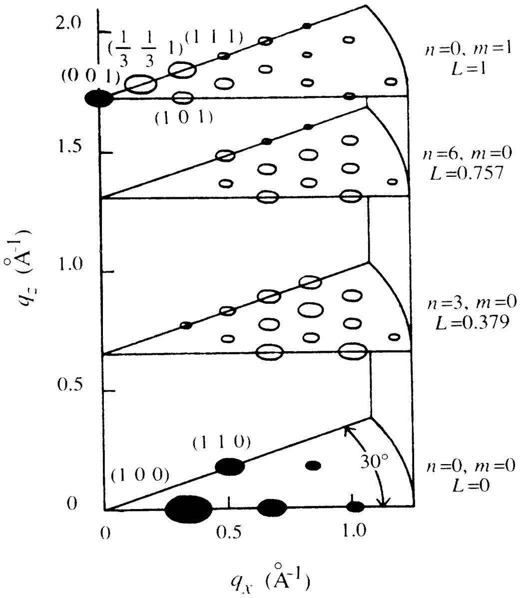

FIG. 2. Perspective schematic of diffraction pattern. Circle sizes are proportional to log(I); we measured 14700 and 1.7 counts/s in the (100) and (300) peaks, respectively. Open circles indicate peaks observed in the $D_{\rm ho}$ phase only; filled circles, those found in both $D_{\rm ho}$ and $D_{\rm hd}$ phases.

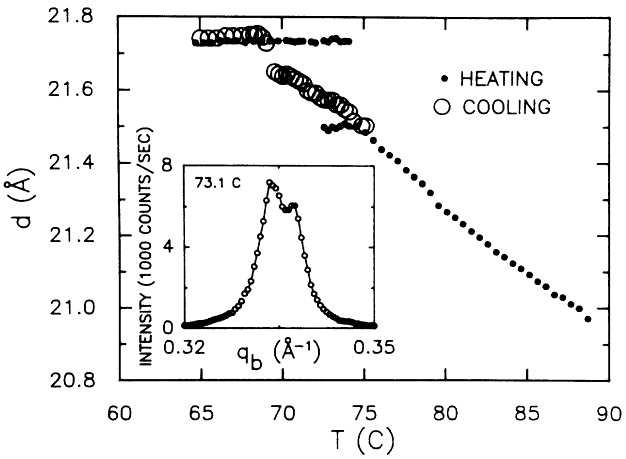

FIG. 3. Intercolumn distance d vs temperature. Filled circles indicate measurements made on warming; open circles, measurements on cooling. Inset: a typical coexistence profile of the (100) peak, at 73.1 C.

on HHTT, which has shown the phase sequence

$$K \xrightarrow[62C]{} D_{\rm ho} \xleftrightarrow[70\,C]{} D_{\rm hd} \xleftrightarrow[93\,C]{} I,$$

where I refers to the isotropic phase. Our differential-scanning-calorimetry measurements indicate that both the $D_{\rm ho} \leftrightarrow D_{\rm hd}$ and $K \leftrightarrow D_{\rm ho}$ transitions are first order. This is confirmed by our x-ray measurements: The $D_{\rm ho} \leftrightarrow D_{\rm hd}$ transition shows hysteresis and coexistence over a 2–5 C range. The $D_{\rm ho}$ phase can be supercooled deep ($\sim$10–20 C) into the K phase.

The diffraction pattern in the $D_{\rm hd}$ phase (Fig. 2, filled circles) is qualitatively very similar to that previously observed in a hexa-substituted truxene mesogen.[5] In the equatorial plane, a triangular array of sharp ($HK0$)-type reflections is observed, corresponding to long-range (correlation length $\xi \geq 800$ Å) hexagonal ordering of the columns. The only additional reflection is a diffuse meridional (001) peak at $q_z = 1.727$ Å^{-1}, due to intracolumn liquidlike ordering of the disks. All the reflections observed in the $D_{\rm hd}$ phase are also observed in the $D_{\rm ho}$ phase. The integrated intensities do not change appreciably through the transition, although the (001) peak sharpens to become resolution limited. Figure 3 shows the intercolumnar distance d as a function of temperature. The dramatic negative thermal coefficient of expansion in the $D_{\rm hd}$ phase is most likely the consequence of the hydrocarbon tails becoming stiffer and therefore longer with decreasing temperature. Indeed, the same effect may provide the driving mechanism for the $D_{\rm hd} \rightarrow D_{\rm ho}$ transition: As tail conformational degrees of freedom are "frozen out," steric hindrance between tails in adjacent columns should become more important, resulting in enhanced column-column coupling. Extrapolation of d vs T from the $D_{\rm hd}$ phase to the constant value measured in the $D_{\rm ho}$ phase indicates that we may be close to a second-order transition, which is, however, preempted by a first-order jump. (However, a superlattice peak intensity would be a better choice for an order parameter than d.) All peak positions, including those of the new peaks discussed below, are essentially temperature independent in the $D_{\rm ho}$ phase; the length of the fundamental (100) vector is $|\mathbf{q}| = 0.334$ Å^{-1}.

Upon formation of the $D_{\rm ho}$ phase, a number of new reflections appear, as indicated by the open circles in Fig. 2. All the reflections in the $D_{\rm ho}$ phase are resolution limited ($\xi \geq 800$ Å). We will continue to use the Bragg indices of the $D_{\rm hd}$ phase to describe these reflections. New reflections in planes at $q_z = 0.654$, 1.309, and 1.727 Å^{-1} correspond to $L = 0.379$, $L = 0.758$, and $L = 1$. The first two values are very close to $L = \frac{3}{8}$ and $L = \frac{6}{8}$, but careful measurements of vector *differences* associated with reflection through the $q_z = 0$ plane have verified that the peaks consistently deviate from these commensurate positions by at least one FWHM (Fig. 4). The structure is thus crystalline, with an incommensurate modulation along the columnar axis. No new peaks are seen along the ($00L$) meridional axis. In the q_x and q_y directions, the new reflections correspond to a $\sqrt{3}\times\sqrt{3}R30°$ superlattice; i.e., the new fundamental is indexed as $(\frac{1}{3}\,\frac{1}{3}\,0)$. The new unit cell therefore consists of three columns.

The $D_{\rm ho}$ diffraction pattern is consistent with a helical arrangement of molecules within the columns. Indeed, helical order has previously been observed in columnar phases of discotic and cone-shaped molecules.[6] Semiempirical conformational analyses[7] of triphenylene derivatives similar to HHTT have indicated that adja-

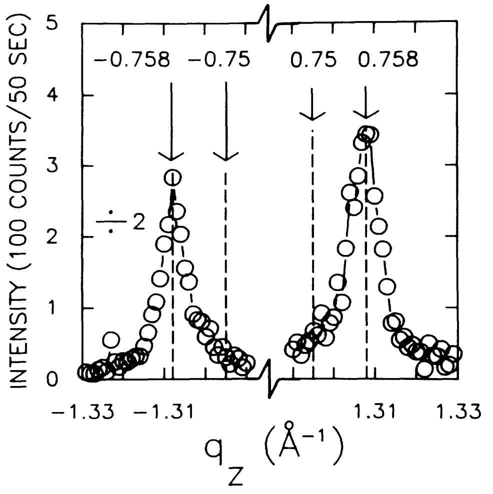

FIG. 4. (20L) peaks in the D_{ho} phase. Here $q_x=0.668$ Å^{-1}, $q_y=0$, and $L\equiv q_z/1.727$ Å^{-1}. Arrows indicate fitted peak positions and commensurate $L=\pm\frac{6}{8}$ positions.

cent molecules along a column minimize steric hindrance via a relative rotation of roughly 45°. Alternate tails around the circumference of each molecule tilt above and below the plane of the core, so that once the initial clockwise-counterclockwise symmetry is broken the helical order can extend to large distances. The diffraction pattern for a group of atoms repeated along the z axis by the operation of an noninteger screw is well known[8]: Diffraction maxima are found at $q_z=2\pi(n/P+m/p)$. m and n are integers; n must be a multiple of 3 because of the threefold symmetry of the HHTT molecule. p is the intracolumn molecular spacing, and is determined from the position of the (001) peak: $p=2\pi/1.727$ Å^{-1} $=3.638$ Å. P is the pitch of the helix, and is determined from the $n=3$ helical peaks at 0.654 Å^{-1}: $P=6\pi/0.654$ Å$^{-1}=28.82$ Å$=7.92p$. This corresponds to a 45.5° rotation between adjacent molecules. We can model a single helical column of molecules by N coaxial discontinuous helices, where N is the number of atoms per molecule. If the position of the jth atom in the molecule is given, in cylindrical coordinates, by (ρ_j,ϕ_j,z_j), then the scattered intensity for a given (n,m) reflection is given by

$$I(\mathbf{q})=C(q)\,|S(\mathbf{q})|^2,$$
$$S(\mathbf{q})=\sum_{j=1}^{N} f_j(q)J_n(q_b\rho_j)e^{i[n(\psi+\phi_j+\pi/2)+q_z z_j]}. \tag{1}$$

Here $C(q)$ includes polarization and other slowly varying terms, ψ relates to the absolute phase of the helix, f_j is an atomic form factor, and J_n is the nth order Bessel function. The D_{ho} phase can be modeled by packing such columns in a triangular lattice. The superlattice order is associated with groups of three columns forming triangles. Within each group of three columns, we assign the molecules in column k overall equatorial and vertical displacements $\mathbf{r}_k$ and $\Delta_k\hat{\mathbf{z}}$, and helical phase Φ_k. (The $\mathbf{r}_k$'s are generated by triangular lattice vectors $\mathbf{a}$ and $\mathbf{b}$; the vertical translation is defined such that it preserves helical phase.) In Eq. (1), $S(\mathbf{q})$ is then multiplied by

$$\sum_{k=1}^{3}\exp[i(\mathbf{q}_b\cdot\mathbf{r}_k+2\pi m\Delta_k/p+n\Phi_k)].$$

In the discussion that follows, we have assumed a symmetric unit cell: $\mathbf{r}_1=0$, $\Delta_1=0$, $\Phi_1=0$ or is random, $\mathbf{r}_2=\mathbf{a}$, $\Delta_2=p\delta$, $\Phi_2=\beta$, $\mathbf{r}_3=\mathbf{b}$, $\Delta_3=-p\delta$, and $\Phi_3=-\beta$.

A careful structural analysis depends sensitively on the details of the molecular conformations. Certain conclusions, however, are quite insensitive to these details. First, the superlattice ordering must involve both helical phase differences Φ_k and vertical displacements Δ_k, since superlattice peaks are seen in both the ($n=0$, $m=1$) plane and the ($n=3,6$, $m=0$) planes. Second, the nonzero intensities of the (001) and ($\frac{1}{3}\,\frac{1}{3}\,1$) peaks rigorously exclude $\delta=0$ or $\delta=\frac{1}{3}$. Fits to the entire diffraction profile (Fig. 2) consistently give $0.45\le\delta\le0.55$; δ is probably exactly equal to $\frac{1}{2}$. This implies that columns 2 and 3 are at the same height. The intercolumn separation in the D_{ho} phase is 5%–15% smaller than the diameter of the HHTT molecule with the tails fully extended. This implies that either the molecules must be at different heights, forming an interdigitated structure, or that if the molecules are at the same height, the tails must interlock in a gearlike fashion. Molecular interdigitation in a triangular lattice is frustrated, and further frustration is introduced by the rotational degrees of freedom: While it is possible to construct an interlocking triangular mesh of gears, they cannot rotate. A plausible solution to both of these frustration problems, which also provides a good fit to the data[9,10] is shown in Fig. 1(b). Columns 2 and 3 form part of a sublattice of molecules, all at the same height, which have a single rotational degree of freedom. Column 1 forms part of a second sublattice of molecules which have random helical phases, and are displaced vertically by $p/2$. The $\sqrt{3}\times\sqrt{3}R30°$ superlattice in both displacements and helical phase is thus seen to arise naturally from the frustration automatically present in a triangular lattice of interdigitated disks.

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