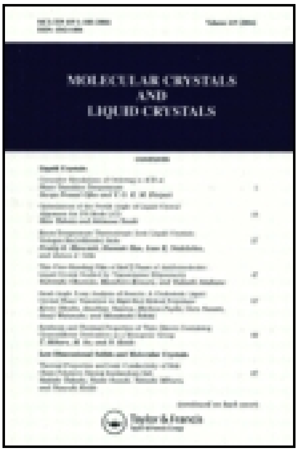

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Phase Diagram of Hexa-N-Alkylthiotriphenylenes

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Phase Diagram of Hexa-*N*-Alkylthiotriphenylenes

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We have used x-ray diffraction and differential scanning calorimetry to establish the phase diagram, liquid crystalline structure, and crystalline structure of a series of hexa-*n*-alkylthiotriphenylenes. At least nine crystal phases are observed. The helical pitch seen in the helical phase is incommensurate with the molecular spacing when measured in single-orientation strands, while commensurate in powder samples.

Keywords: liquid crystal, discotic, incommensurate, helical

INTRODUCTION

The nature of the transition between a columnar liquid crystal and a three-dimensional columnar crystal, and of helical order in columnar liquid crystals, have recently been explored theoretically[1–3] and experimentally.[4,5] Hexahexylthiotriphenylene[4,6] (C_6, Figure 1) represents an intriguing example of a discotic liquid crystal with both a hexagonal disordered (D_{hd}) columnar phase and a closely related helical columnar (H) crystalline phase.

The high temperature D_{hd} phase consists of a perfect hexagonal array of columns, with liquid-like intracolumnar order. Detailed analysis[4] of the diffraction pattern seen in the lower temperature H phase in C_6 indicates the following features: 1) The appearance of (HKL) diffraction peaks, with nonzero H, K, and L, demonstrates that in fact this is a three-dimensionally ordered crystal, which is however closely related in structure to the D_{hd} phase. 2) The molecules in each column are

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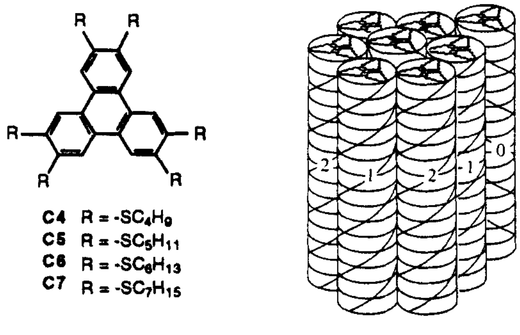

FIGURE 1 Left: Hexa-*n*-alkylthiotriphenylene molecules studied. Right: Schematic illustration of the structure of the H phase (from [4]). Column 0 is displaced by ½ of a molecular spacing from columns 1 and 2, which have the opposite sign of helicity from column 0.

ordered helically; adjacent molecules are rotated to minimize the steric energy. Careful measurements of peak spacings, using x-ray diffraction from single-orientation strands,[7] established the remarkable fact that the helical repeat length is 7.92 rather than 8 molecules, i.e. incommensurate with the positional intracolumnar order. This corresponds to a relative molecular rotation of 45.5°. 3) Formation of the H phase is accompanied by the formation of a 3-column superlattice. The superlattice involves both the *phases* of the helices and the *heights* of the molecules. The model which best describes the data for the H phase is illustrated in Figure 1. The three-column superlattice structure can be thought of as a solution to the frustration inherent in packing disk-like gears tightly in a triangular lattice.

To further clarify the origins of the unusual structure described above, and to establish the effect of tail length on helical phase formation, stability, and pitch, we have carried out a systematic study of the structures of mixtures of hexa-*n*-alkylthiotriphenylenes with a variety of tail lengths.[8]

DESCRIPTION OF THE PHASE DIAGRAM

Figure 2 shows the phase diagram obtained from the study of mixtures of C_n + C_{n-1}, $n = 5, 6, 7$. The effective tail lengths are calculated as the weighted average of the tail lengths of the two parent compounds. Thirty-three mixtures were made by carefully weighing out roughly 10 mg of each compound. The samples were mixed by adding approximately 2 mL of clean methylene chloride, and then allowing the solvent to evaporate in air. Residual moisture was removed by exposing the samples to Drierite. The uncertainty in the effective tail length of each mixture is approximately ± 0.03 carbons. Each sample was characterized by three heating cycles from room temperature to 140°C in a Differential Scanning Calorimetry (DSC) apparatus (Dupont 910 cell with a Dupont 2100 thermal analyzer). The first two heating cycles, designed to ensure that no solvent or water remained in the sample, were performed at 5°C/min, while the third heating and cooling sequence was done at 1°C/min. The transition temperature for tail lengths greater than 4.5 carbons were measured to within 1.0°C.

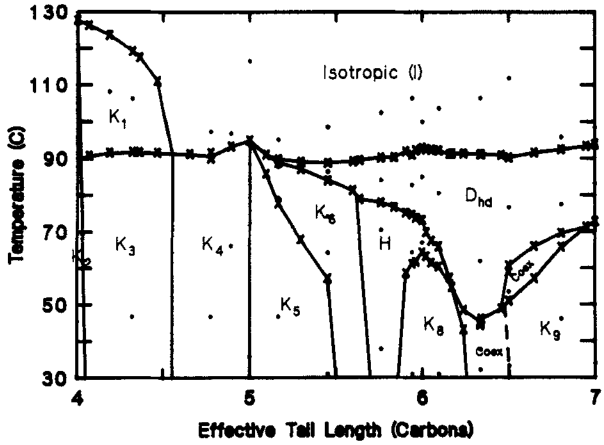

FIGURE 2 Phase diagram for mixtures of hexa-*n*-alkylthiotriphenylenes. Points labeled 'X' are the transition temperatures derived from DSC measurements. Dots represent points where low-resolution powder XRD measurements were made. The K_i refer to different crystalline phases; only the K_5, K_8, and K_9 phases were identified. H is the helical phase.

TABLE I

Space groups and lattice parameters

Phase	K_5	K_8	K_9
Compound Measured	C_5	C_6	C_7
Space Group	$P2_1/n$	C2/c	$P\bar{1}$
a (Å)	8.064(1)	28.688(5)	8.023(1)
b (Å)	19.174(2)	25.016(2)	19.361(3)
c (Å)	32.273(2)	7.875(3)	20.070(3)
α	-	-	95.78(1)°
β	96.84(1)°	97.85(3)°	89.85(1)°
γ	-	-	91.21(1)°

Low resolution powder x-ray diffraction (XRD) measurements employed an INEL fixed target x-ray diffractometer with a curved 120° linear detector. Two or more samples in each phase were measured to confirm consistency with the DSC measurements. No evidence was ever seen of thermal decomposition when samples were heated into the isotropic phase. At least nine different crystal phases, K_i, as well as the crystalline helical H phase, were observed. Further information on the crystal structure of three of the K_i phases was obtained from XRD measurements; Table I gives the lattice parameters of the K_5, K_8, and K_9 phases, all measured at room temperature on single-crystal samples of pure C_5, C_6, and C_7, respectively, with a CAD-4 automated diffractometer using graphite monochromated Cu-K_α radiation. Samples with effective tail length around 4.5 carbons were difficult to characterize, due to history- and container-dependent effects. DSC scans in this region sometimes showed weak features which we believe are most likely due to additional metastable crystalline phases. The D_{hd} phase is observed in all samples with tail length greater than 5 carbons; pure C_5 does not form a D_{hd} phase. The crystal phase below the D_{hd} eutectic point at tail length 6.4 appears to be a mixture of K_8 and K_9; the D_{hd} and K_9 phases were also observed to coexist.

HELICAL PITCH IN STRAND *VS.* BULK

To further characterize the H phase, which extends from tail length 5.65 to 6.10, high resolution powder XRD measurements[9] on two different samples of pure C_6 were performed at the National Synchrotron Light Source, Brookhaven National Laboratory, Beamline X9a. To mitigate the effects of radiation damage, the time each sample spent in the highly intense synchrotron x-ray beam was minimized.[10] In order to determine the ratio of helical pitch to intracolumnar spacing, it was sufficient to measure the positions of only three strong peaks.[4] The fundamental (100) peak establishes the spacing between adjacent columns. The position of the $\frac{1}{3}\frac{1}{3}1$) peak, which arises from the 3-column superlattice, is determined by both the intracolumnar and the intercolumnar spacing, and thus in conjunction with the (100) peak determines the spacing between molecules within one column. The position of the $(20\frac{3}{8})$ peak, which arises from the three-dimensional correlations of the helical order, is determined by the intercolumnar spacing and the helical pitch; in conjunction with the other two peaks it thus allows us to determine the ratio of the helical repeat distance to the intermolecular spacing, which we will refer to as the helical pitch (in units of number of molecules).

The two different samples of pure C_6, measured during two different experimental runs at NSLS, yielded helical pitches of 7.997 ± 0.014 and 8.002 ± 0.017 respectively, i.e. the same and consistent with 8.000 within experimental error. By contrast, the pitch originally measured[4] in pure C_6 in the *strand* geometry was 7.92 ± 0.05. (The measured peak position differed from the calculated commensurate position by at least one peak full-width, and this difference was clearly visible in the raw data). We have repeated this single-orientation strand diffraction measurement on a new batch of samples, with comparable instrumental resolution, and again obtain a pitch of 7.91. It thus appears that in C_6 the helical pitch depends on the sample morphology. In the strand geometry an incommensurate pitch is reproducibly observed, while in a powder sample a commensurate pitch is reproducibly observed, even though the two samples are chemically identical. Considerable surface tension is required to make a strand self-supporting, and such a macroscopic strain may affect the thermodynamics of the system.[11]

Acknowledgments

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10. The (100) peak was monitored at the beginning and end of each measurement to confirm that the sample had not undergone significant radiation damage. This peak is very sensitive to radiation damage, since with increasing radiation exposure the sample evolves from the H phase into the D_{hd} phase, and these phases have different hexagonal lattice constants [8].
11. The idea that surface tension may affect the stability and thermodynamics of the H phase was suggested to us by T. C. Lubensky in advance of the present experimental observations.