PRELIMINARY COMMUNICATIONS

X-ray investigation of discotic mesophases of alkylthio substituted triphenylenes

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Power samples of three alkylthio substituted triphenylenes have been investigated by X-ray diffraction. All have a hexagonal columnar D_{hd} phase. In one compound, a phase transition $D_{ho} \leftrightarrow D_{hd}$ is found, in which the hexagonal lattice of columns remains unaffected by the order–disorder transition within the columns.

It has been recognized for a number of years [1] that disc-like molecules can exhibit thermotropic mesophases. Apart from the fluid nematic phase [2], all of these so-called discotic phases are columnar phases with the molecules stacked in columns that can slide more or less easily along each other, while the order within each column can be either solid- or liquid-like [3]. We have investigated the structural behaviour of a series of alkylthio substituted triphenylenes [4] which have been synthesized recently. All have a hexagonal columnar D_{hd} phase, while one of the compounds also shows a $D_{ho} \leftrightarrow D_{hd}$ phase transition. In addition a diffuse reflection characteristic of the liquid-like aliphatic regions is observed for the higher homologues.

The general formulae of the compounds studied is
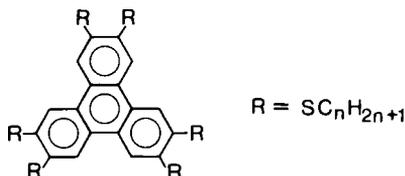
$$R = SC_nH_{2n+1}$$

with $n = 6$, 8 and 10 [4]. The triphenylene core has already proved to be fruitful for building discotic molecules which exhibit mesomorphic behaviour, with end groups R such as $O\text{–}C_nH_{2n+1}$ (HET series) [5, 6], $OCO\text{–}C_nH_{2n+1}$ (HAT series) [6], $OCO\emptyset\text{–}OC_nH_{2n+1}$ [2, 7] and $OCO\emptyset\text{–}C_nH_{2n+1}$ [3]. The transition temperatures of the alkylthio substituted triphenylenes are listed in table 1. The compounds were studied

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by X-ray scattering of powder samples in a glass capillary of 0·3 mm diameter, with a high-temperature Guinier camera using monochromatic $Cu/K_{\alpha 1}$ radiation.

The various columnar phases as determined from the X-ray diffraction pattern are listed in table 1. All three compounds have a D_{hd} phase (hexagonal lattice of liquid-like columns), as inferred by the presence of only one low-angle Bragg peak. The uniaxial symmetry of the phase is confirmed by the observation of homeotropic textures with optical microscopy. The hexyl compound ($n = 6$) shows a second mesophase at a lower temperature, which is essentially a D_{ho} phase (hexagonal lattice of ordered columns). There are, however, a number of weak Bragg reflections that indicate some degree of coupling between the columns. In this sense the phase is rather a crystal than a liquid crystal, albeit with an extreme anisotropy. An analogous situation is that of smectic B phases of rod-like molecules, in which a weak coupling between the solid-like layers can exist. At the $D_{ho} \leftrightarrow D_{hd}$ phase transition, neither the position nor the intensity of the low-angle diffraction peak shows an observable change. This indicates that the hexagonal lattice of columns can be considered to be a constant background for this phase transition. In fact, even in the crystalline phase this lattice of columns is still present with the same lattice spacing. This is a unique feature, and offers one of the purest known examples of melting/condensation of one-dimensional stacks of molecules. It is only the weak coupling between the columns that prevents this phase transition from being effectively one-dimensional. As is well known, general considerations of statistical mechanics imply that phase transitions are impossible in strictly one-dimensional systems [8].

Table 1. Phases of the alkylthio substituted triphenylenes. K = crystalline, D = discotic, I = isotropic liquid, h = hexagonal lattice of columns, o = ordered (solid) columns, d = disordered (liquid) columns. The transition temperatures are in °C.

Alkyl carbon number n	Phases						
	K		D_{ho}		D_{hd}		I
6	x	62	x	70	x	93	x
8	x	55			x	87	x
10	x	67			x	70	x

It is tempting to compare the observed D_{ho} phase with the D_{ho} phase found in the HET series, because the molecules of both series are sterically very similar. In the HET series, the columns were found to be helicoidal with a pitch equal to 13 Å [6]. This structure was also shown to be energetically favourable in a theoretical study [12]. The X-ray pattern of such a structure consists of two diffuse sheets perpendicular to the column axis; these are smeared out over a large angle region in a powder sample. In practice, this can hardly be separated from the background and other contributions. In consequence X-ray data on oriented samples are required to solve this problem.

The distance between neighbouring columns shown in table 2 varies with increasing alkyl chain length from 21·2 Å to 24·8 Å, which is approximately halfway between the diameter of the rigid core including the sulphur atoms (~ 14 Å), and the diameter of the molecule with elongated alkyl chains (~ 26 Å to 30 Å). This implies a large degree of penetration of the alkyl chains into the aliphatic regions of neighbouring columns, and/or a high degree of orientational disorder for the alkyl chains.

At higher Bragg angles, two diffuse reflections occur in the D_{hd} phase: one at 3·6 Å and the other at 4·6 Å (cf. table 2). The first one is only present in the hexyl ($n = 6$)

and octyl ($n = 8$) compounds. It is caused by the stacking of the molecular cores in the columns. The width of the reflection, which is determined by the correlation lengths, $\xi_\parallel$ and $\xi_\perp$, parallel and perpendicular to the column axis, is of the order of $(30\,\text{Å})^{-1}$ full width at half maximum. The location of the reflection along the column axis makes $\xi_\parallel$ dominant in determining the width in a powder sample. If $\xi_\perp$ is assumed to be equal to the core radius it gives a contribution of only a few per cent. Hence we conclude that the in-column correlation length $\xi_\parallel$ is of the order of $30\,\text{Å}$ or about 10 molecules. The intermolecular spacing of $3\cdot6\,\text{Å}$ is close to those found in other triphenylene derivatives [6, 9, 10]. The absence of this reflection in the decyl ($n = C_{10}$) compound is probably due to preferential orientation of the columns along the capillary axis.

Table 2. Bragg spacing d_B of the observed reflections; ‡ diffuse, ( ) very weak.

n	Phase	Hexagonal lattice spacing $(2/\sqrt{3})\,d_B/\text{Å}$	Order within the columns $d_B/\text{Å}$	
6	D_{ho}	21·2	3·61†	
	D_{hd}	21·2	3·6‡	
8	D_{hd}	23·4	3·6‡	4·6‡
10	D_{hd}	24·8		4·6‡

† Additional weak reflections: 3·54; 4·50; 4·59; 4·91; 5·24; (5·71); (6·22); (6·72): (9·36).

The second high-angle reflection ($4\cdot6\,\text{Å}$) is present in the octyl ($n = 8$) and decyl ($n = 10$) compounds. It is much weaker and broader than the first. A similar diffuse reflection is found in many triphenylene derivatives [6, 9–11], and has been identified with the liquid-like order of the alkyl chains [6]. In the hexyl ($n = 6$) compound the alkyl chains are probably just too short for this reflection to gain sufficient intensity. In this context it is interesting to note that the D_{ho} phase of this compound shows a number of weak Bragg reflections around $4\cdot6\,\text{Å}$ with the clearest one at $4\cdot50\,\text{Å}$. We could speculate about a possible relation with the $4\cdot6\,\text{Å}$ diffuse reflection in the other compounds. Then the question arises as to how the order of the alkyl chains is related to the long-range periodicity, which must be described in terms of coupling between the columns. Attempts to identify all the (very weak) reflections in the D_{ho} phase with a specific lattice have failed. A large unit cell is clearly needed to describe the coupling between the columns adequately. To solve the remaining problems experiments on oriented samples are needed.

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