J. Chem. Research (S),
1999, 596–597
J. Chem. Research (M),
1999, 2546–2551

Hexakis(terthiophenylthio)benzene as a New Class Liquid Crystalline Molecule

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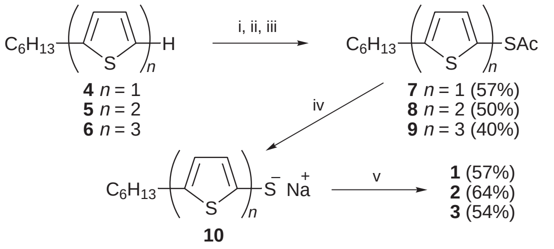
A disk-like molecule, in which six α-linked terthiophenes are connected to a central benzene core *via* a thioether linkage, shows a sequence of calamitic liquid crystalline mesomorphism involving smectic C, smectic A and nematic phases.

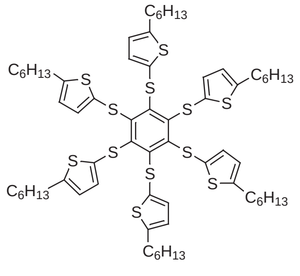
Since the discovery of discotic liquid crystalline materials with high charge-carrier mobilities, disk-like conjugated molecules have been attracting a great deal of current attention as advanced optoelectronic materials.[1] For the design of such molecules with novel architectures, it is desirable to utilize mesogenic extensive π-conjugated systems. Oligothiophenes are expected to be a promising candidate for such conjugated systems, because they can act as a potential charge-carrier with self organization.[2] From this standpoint, we have been interested in hexagonal-shaped (asterisk) molecules arranged by six oligothiophene chromophores around the periphery of a core benzene.[3] As the first example of this type, we here would like to report the construction of a series of substituted benzenes **1**–**3** incorporating mono-, bi- and terthiophenes *via* a thioether linkage as well as the calamitic thermotropic mesomorphism of **3**.

The syntheses of **1**–**3** were carried out using the MacNicol reaction[4] illustrated in Scheme 1. The sodium thiolate species **10**, generated *in situ* by treating each of **7**–**9** with sodium ethoxide in ethanol, were reacted with hexafluorobenzene in DMI,[4b] producing the hexasubstituted benzenes **1**–**3** in 54–64% yields.

The differential scanning calorimetry (DSC) measurements of **1** and **2** showed a sharp single peak at −93 and 139 °C, respectively, in the heating process from the crystalline phase, which corresponded to a transition from crystalline phase to isotropic liquid phase. In contrast, the DSC of **3** showed a sharp endothermic peak at 190 °C and three broad peaks around 250 °C, as illustrated in Fig. 1, indicating the involvement of a liquid crystalline mesophase. The detailed polarizing microscopy observation, furthermore, revealed that the mesophase of **3** consists of a



Scheme 1 *Reagents and conditions*: i, Bu^nLi, THF, −30 °C, 1 h; ii, S, rt, 2.5 h; iii, MeCOCl, −78 °C then rt, 1 h; iv, EtONa, EtOH, rt, 1 h; v, C_6F_6, DMI, rt, 3 d.



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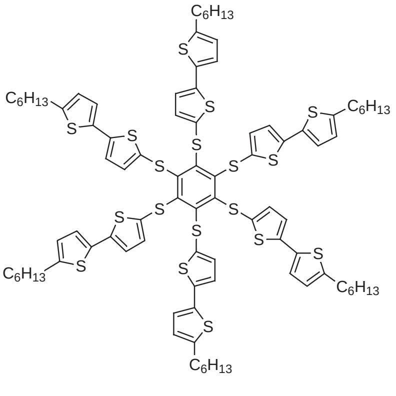

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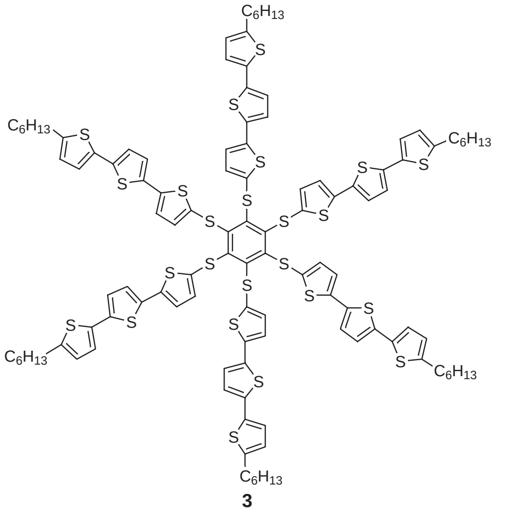

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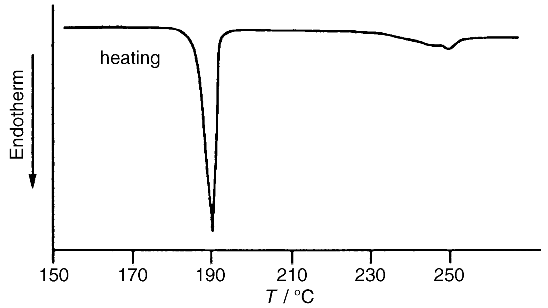

Fig. 1 DSC thermogram **3** (heating rate = 10 K min^{-1})

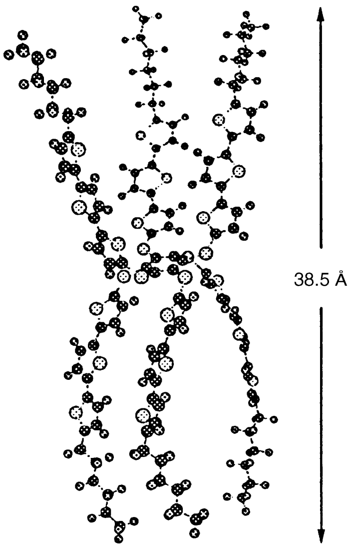

Fig. 2 MM3-calculated molecular conformation of **3**

sequence of three phases with different textures: a smectic C phase between 192 and 232 °C, a smectic A phase between 232 and 236 °C and a nematic phase between 236 and 250 °C. X-Ray diffraction analyses at 210 and 233 °C demonstrated diffraction pattern characteristics of the two smectic phases. From the diffraction peak at 2.42° of the smectic A phase, the interlayer spacing was estimated to be 36.4 Å. This as well as an MM3 calculation[6] has led us to a structural consideration that the molecules adopt, rather than an expected disk type, a cylinder type of conformation, where the six terthiophene segments are alternately folded upward and downward, as illustrated in Fig. 2, and they exist in a homogeneous alignment in the smectic A phase. In addition, the slightly smaller interlayer distance of the smectic C phase (35.7 Å) indicates the arrangement of the molecules with a small slope from the vertical central axis.

References: 6

Fig. 3: Proposed molecular arrangements of **3** in the calamitic mesophases

Received, 28th April 1999; Accepted, 22nd June 1999
Paper E/9/03386F

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