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Preliminary communication

Intermolecular organization of triphenylene-based discotic mesogens by interdigitation of alkyl chains

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Two homologous series of 2,3,6,7,10,11-hexa-alkyloxy-substituted triphenylenes have been synthesized, such that alkyl chains of two different lengths alternate around the rigid triphenylene core in order to allow interdigitation of the chains between neighbouring columns in a hexagonal columnar mesophase. We report here the dependence of structural and thermal properties on the extent of interdigitation, as investigated by X-ray diffraction, polarized optical microscopy and differential scanning calorimetry.

Discotic mesogens can form a number of different types of liquid crystalline phase [1], including hexagonal columnar (Col_h) [2], rectangular columnar (Col_r) [3] and nematic discotic (N_D) phases [4]. Triphenylene-based mesogens exhibit hexagonal columnar mesophases [1] and it is the properties of this phase that promise to be exploited in potential applications of these materials, such as photoconductivity [5], which is the main focus at present. Generally, the properties of Col_h mesophases are influenced by the degree of order of the molecules within a column. Hexahexylthiotriphenylene (HHTT) [6] exhibits a helical Col_h mesophase with a charge mobility of 0.1 $V\,cm^{-1}\,s^{-1}$, the highest observed for a triphenylene-based mesogen. Various methods for increasing the extent of ordering have been employed, including variation of the lengths of the alkyl chains as well as the formation of oligomers and polymers [7]. In the present study, a novel approach has been employed, based on *interdigitation* of the peripheral alkyl chains [8].

In order to achieve interdigitation, we focus on the molecular structures shown in figure 1 (*a*,*b*), involving two different lengths of alkyl chain (denoted $\mathbf{C}_m\mathbf{C}_n$ for a compound containing *n*-alkyl chains C_mH_{2m+1} and C_nH_{2n+1}) alternating around the periphery of the triphenylene core. These compounds fall into two series:

Series I: the compounds are of the type $\mathbf{C}_5\mathbf{C}_n$, which were investigated to probe systematically the effect of changing the difference (*m-n*) between the lengths of the two types of alkyl chain on the mesophase properties and structural properties, in comparison with $\mathbf{C}_n\mathbf{C}_n$ triphenylenes in which all alkyl chains have the same length [6 (*b*), 9].
Series II: the compounds are of the type $\mathbf{C}_{10-n}\mathbf{C}_n$, representing a set of constitutional isomers, with varying differences between the lengths of the two types of alkyl chain. We note that the compound $\mathbf{C}_5\mathbf{C}_5$ is a member of both Series I and II and provides a central reference point for our comparative studies.

Series I compounds were synthesized by alkylation of catechol to form 1,2-dipentyloxybenzene, which was

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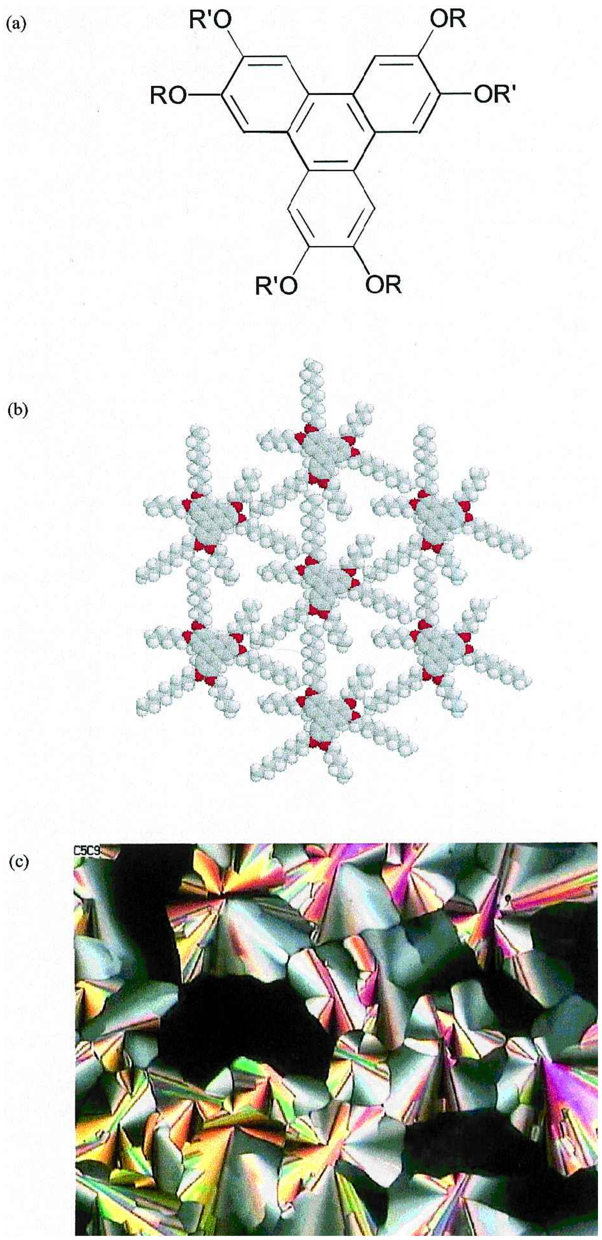

Figure 1. (*a*) The general molecular structure of the triphenylene derivatives. Series I—$\mathbf{C_5C_n}$: $R = C_5H_{11}$, $R' = C_nH_{2n+1}$ ($n = 0$–9) Series II—$\mathbf{C_{10-n}C_n}$: $R = C_{(10-n)}H_{2(10-n)+1}$, $R' = C_nH_{2n+1}$ ($n = 2$–4). (*b*) Idealized illustration of interdigitation of the alkyl chains between neighbouring $\mathbf{C_5C_9}$ molecules in a hexagonal packing arrangement, based on an intercolumnar spacing of 24.2 Å. This is a greater distance than the observed experimental value, but this can be accounted for by the fully-*trans*-conformation used for the alkyl chains. In practice, some degree of disorder in the alkyl chains is expected and the alkyl chains will not be fully extended. (*c*) Mesophase texture of $\mathbf{C_5C_9}$ at 55°C on cooling slowly from the isotropic liquid. This texture is typical of the mesophases of Series I and II liquid crystalline materials.

subsequently trimerized using ferric chloride [10] or molybdenum pentachloride [11] yielding hexapentyloxytriphenylene ($\mathbf{C_5C_5}$). Selective dealkylation using 9-Br-BBN [12] or bromocatechol borane [13] yielded two isomers of tripentyloxy-trihydroxytriphenylene: symmetrical (with hydroxyl groups at the 3-, 7- and 11-positions) and unsymmetrical (with hydroxyl groups at the 3-, 6- and 11-positions). The symmetrical isomer was isolated by silica gel chromatography. Subsequent re-alkylation of 2,6,10-tripentyloxy-3,7,11-trihydroxy-triphenylene yielded the Series I compounds.

Series II compounds were synthesized in a similar manner: catechol was alkylated with *R*-Br and the alkylation of the symmetrical trihydroxytriphenylene was carried out with *R*′-Br, such that the total number of carbon atoms in *R* and *R*′ is 10. The thermal properties of all compounds synthesized were characterized by differential scanning calorimetry (DSC) and variable temperature polarized optical microscopy (POM). The transition temperatures and other thermodynamic data for the transition from the mesophase to the isotropic liquid are reported in the table.

We now discuss the transition temperatures for the materials studied. Series I compounds from $\mathbf{C_5C_3}$ to $\mathbf{C_5C_9}$ exhibit mesophases, with the highest clearing temperature observed for $\mathbf{C_5C_4}$ (129°C). This behaviour is similar to that in $\mathbf{C_nC_n}$ compounds [1 (*a*)] for which the highest clearing temperature (146°C) is observed for $\mathbf{C_4C_4}$. Note that the clearing temperature for $\mathbf{C_5C_4}$ (129°C) is intermediate between those for $\mathbf{C_4C_4}$ (146°C) and $\mathbf{C_5C_5}$ (122°C). Optical textures, viewed using crossed polarizers are broken focal-conic textures, typical of hexagonal columnar mesophases, see figure 1 (*c*). The enthalpy and entropy changes associated with the transitions from the mesophase to the isotropic liquid apparently exhibit regular trends, with maximum values observed for $\mathbf{C_5C_4}$. Rationalization of these trends requires the development of models to understand the structural properties of both the mesophases and the isotropic liquid phases of each compound. Of the Series II materials, only $\mathbf{C_6C_4}$ and $\mathbf{C_5C_5}$ exhibit a mesophase. The mesophase range of $\mathbf{C_6C_4}$ is narrower than that for $\mathbf{C_5C_5}$, and the clearing temperature of $\mathbf{C_6C_4}$ (96°C) is lower than that for $\mathbf{C_5C_5}$ (122°C).

Analysis of the Series I materials ($\mathbf{C_5C_n}$) by X-ray diffraction (XRD) shows interesting structural differences across the series, both in the crystalline and liquid crystalline phases. The materials $\mathbf{C_5C_3}$ to $\mathbf{C_5C_9}$ exhibit $\mathrm{Col_h}$ mesophases, figure 1 (*c*), and the intercolumnar spacing—calculated from the *d*-spacing of the (1 0 0) reflection—for the mesophase increases as the alkyl chain length *n* increases (figure 2), consistent with the idealized self-filling, interdigitated structure shown in figure 1 (*b*). Further evidence for the interdigitation

Table. Mesophase to isotropic liquid transition temperatures, and the corresponding enthalpy and entropy changes for selected materials in Series I and Series II. All data are from DSC measurements, from the heating cycles at a rate of 10°C min^{-1}. The estimated errors in the measurement of ΔH and ΔS are ± 5%. I = isotropic liquid.

Compound(a)	Transition	Transition temp./°C	ΔH/kJ mol^{-1}	ΔS/J $\mathrm{K}^{-1}\,\mathrm{mol}^{-1}$
C_5C_3	$\mathrm{Col_h} \rightarrow \mathrm{I}$	105	5.4	14.4
C_5C_4	$\mathrm{Col_h} \rightarrow \mathrm{I}$	129	9.9	24.6
C_5C_5	$\mathrm{Col_h} \rightarrow \mathrm{I}$	122	8.2	20.8
C_5C_6	$\mathrm{Col_h} \rightarrow \mathrm{I}$	106	5.8	15.2
C_5C_7	$\mathrm{Col_h} \rightarrow \mathrm{I}$	91	4.9	13.3
C_5C_8	$\mathrm{Col_h} \rightarrow \mathrm{I}$	68	1.7(b)	4.8(b)
C_5C_9	$\mathrm{Col_h} \rightarrow \mathrm{I}$	59	3.2	9.4
C_6C_4	$\mathrm{Col_h} \rightarrow \mathrm{I}$	96	1.2	3.2

(a) **C_5C_1**, **C_5C_2**, **C_7C_3**, **C_8C_2** and **C_9C_1** do not exhibit mesophases.
(b) Data recorded on cooling cycle at 10°C min^{-1}.

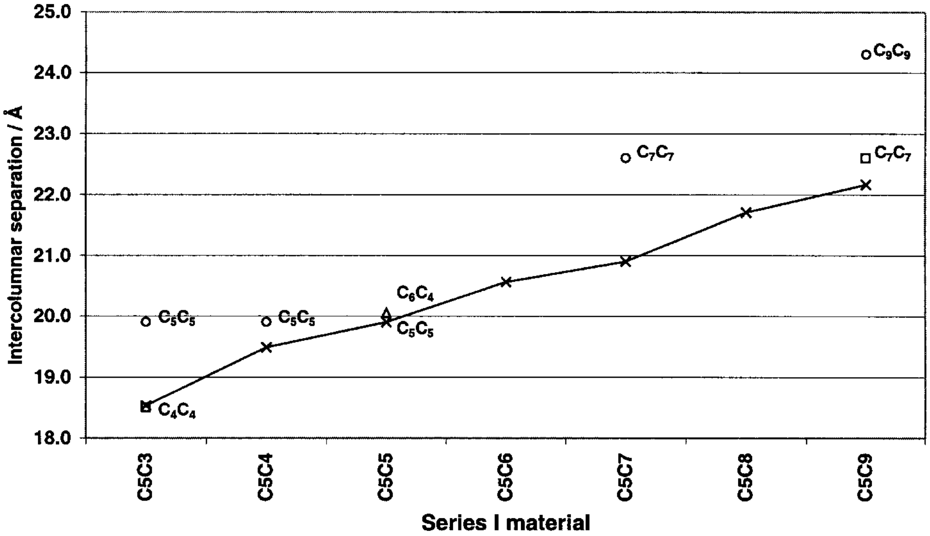

Figure 2. Intercolumnar spacings for **C_5C_n** (Series I) materials (×), **$C_{10-n}C_n$** (Series II) materials (Δ), the **$C_{(5+n)/2}C_{(5+n)/2}$** materials corresponding to the average chain length of a given **C_5C_n** material (□) and the **C_nC_n** material corresponding to the longer chain length of a given **C_5C_n** material (○).

model comes from comparison between the **C_5C_n** and **C_nC_n** materials, for which the intercolumnar spacings for pairs of constitutional isomers are virtually identical [14] (e.g. **C_5C_3** and **C_4C_4**, **C_5C_9** and **C_7C_7**). Similarly, the intercolumnar spacings for **C_5C_5** and **C_6C_4** are virtually identical. Note that in [14] it would appear that the conversion from a d_{100} spacing to an intercolumnar spacing for **C_4C_4** does not seem to have been made.

The intercolumnar spacings (figure 2) for the Series I materials **C_5C_3** (18.5 Å) and **C_5C_9** (22.2 Å) correspond closely to the intercolumnar spacings of their constitutional isomers in the **C_nC_n** series (**C_4C_4** (18.5 Å) [6(*b*)] and **C_7C_7** (22.6 Å) [9]), providing a strong indication that interdigitation of the alkyl chains occurs in the mesophase. Further support for this model comes from comparing the intercolumnar spacings of **C_5C_3** versus **C_5C_5**, and **C_5C_9** versus **C_9C_9** (figure 2), which clearly shows that the intercolumnar spacing in the **C_5C_n** materials is not governed simply by the length of the longer chain. Likewise, for Series II materials **C_6C_4** and **C_5C_5**, XRD patterns of the mesophases indicate the formation of the $\mathrm{Col_h}$ phase with an intercolumnar spacing that is virtually identical in each case: **C_5C_5** (19.8 Å), **C_6C_4** (19.9 Å).

We are currently utilizing a combination of variable temperature solid state ^{2}H NMR spectroscopy, variable temperature XRD and molecular modelling to probe further the interdigitation of the alkyl chains of the triphenylene liquid crystals described here and to assess further the extent to which the molecular structure dictates the bulk behaviour.

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