Epitaxygens: Mesophases based on the Triptycene Molecular Subunit†

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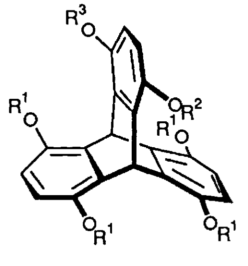
Two examples of triptycene-based epitaxygens, in which aliphatic chains and aromatic cores form symmetry compatible lamellar lattices, have been synthesized and their mesomorphic properties have been studied.

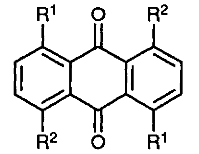
Molecular materials are made of molecular units that are subsequently organized into condensed phases.[1] They are used for making devices mostly in the form of thin films. Langmuir–Blodgett films or lamellar mesophases are particularly attractive for mastering molecular architectures. Aromatic derivatives substituted with aliphatic side chains are routinely used as constitutive molecular units. However, it is always difficult to get defect-free condensed phases from such molecules. This can be reasonably attributed to the different symmetry arrangements of the aliphatic and aromatic moieties.[2] It is proposed to use symmetry compatible aromatic and aliphatic subunits for making new mesogens (Epitaxygens‡) susceptible to formation of ordered lamellar phases. The synthesis of triptycene-based epitaxygens **1** and **2** and their mesomorphic properties are the object of the present publication.

The triptycene derivatives **1** and **2** are synthesized in eight steps starting from commercially available diaminoanthrarufin **3**. This latter is transformed into 1,4,5,8-tetrahydroxyanthraquinone **4** by (i) reaction with $Na_2S_2O_4$ at 100 °C and (ii) oxidation with nitrobenzene.[3] **4** is *O*-alkylated with dodecyl bromide to give **5**. The anthraquinone derivative **5** is reduced with $NaBH_4$[4] to the corresponding diol which is transformed into the corresponding anthracene **6** with phenylhydrazine.[5] Diels–Alder reaction[6–8] of **6** with benzoquinone gives 1,4,5,8-tetradodecyloxy-12,15-dioxo-11,16-dihydro-triptycene **7** which is converted[9] into the corresponding dihydroxy-derivative **8** with AcOH/HBr. The overall yield from **3** to **8** is approximately 25%. The penta-substituted derivative **1** is obtained by treating **8** with dodecanoyl chloride, whereas **2** is obtained with the corresponding acid activated with DCC (1,3-dicyclohexylcarbodiimide).

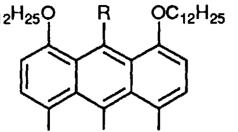


1; $R^1 = C_{12}H_{25}$, $R^2 = H$, $R^3 = \underset{\underset{O}{\|}}{C}C_{11}H_{23}$

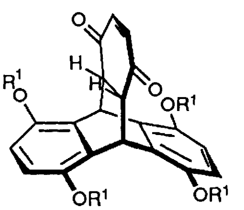
2; $R^1 = C_{12}H_{25}$, $R^2 = R^3 = \underset{\underset{O}{\|}}{C}C_{11}H_{23}$



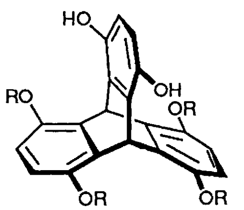
3; $R^1 = NH_2$, $R^2 = OH$
4; $R^1 = R^2 = OH$
5; $R^1 = R^2 = OC_{12}H_{25}$



6; R = H



7; $R^1 = C_{12}H_{25}$



8; $R = C_{12}H_{25}$

Differential scanning calorimetry of compound **1** demonstrates the presence of at least 4 different mesophases, eqn. (1).

$$M_1 \xrightarrow{153\,°C} M_2 \xrightarrow{156\,°C} M_3 \xrightarrow{163\,°C} M_4 \xrightarrow[(22.8\,J\,g^{-1})]{168.8\,°C} I \qquad (1)$$

X-Ray diffraction at small angles shows in all cases a lamellar structure with interplanar distances of 34.9, 29.9, 29.9 and 30.0 Å, respectively. The mesophase M_4 is fluid and its texture is closely related to conventional smectic A phases. In the two-dimensional *P*31*m* symmetry (Fig. 1), the closest packing of the triptycene moieties leads to a unit cell parameter of 8.0 Å; this corresponds to 22.2 Å^2 per paraffinic chain at room temperature. At higher temperatures (M_2, M_3, M_4 mesophases), the interlamellar distance decreases and the inter-triptycene mean distance increases leading to an area of 26.7 Å^2 per paraffinic chain. These values are in agreement with those found in conventional mesophases[1,10] (19.4 Å^2 for hexagonal phases, 23 Å^2 for smectics). The hexa-substituted derivative **2** does not seem to form liquid crystalline phases and melts at 166 °C (27 J g^{-1}). In this case the area per alkyl chain would be only 18.4 Å^2, this value is compatible with

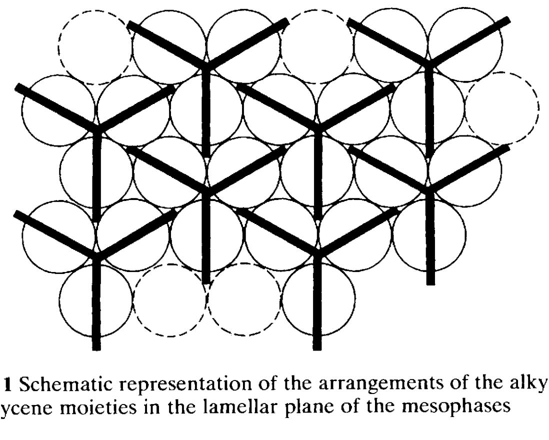


Fig. 1 Schematic representation of the arrangements of the alkyl and triptycene moieties in the lamellar plane of the mesophases

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‡ Epitaxygen: from the Greek epitaksis (order) and genos (generation).

crystallized fully extended paraffinic chains (18.4 Å^2 in the orthorhombic lattice[1,10]). It is worth pointing out that there is a perfect epitaxial fitting between the paraffinic and aromatic moieties, both for the symmetry and for the area of the unit cells.

The possibility of obtaining lamellar mesophases with rigid cores of D_{3h} symmetry has been demonstrated. The use of triptycene subunits allows us to form epitaxial close-packed aliphatic and aromatic lattices of *P*6*mm* and *P*31*m* symmetries. Further studies are in progress to fabricate defect-free thin-film devices.

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