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Preliminary communication

Synthesis and characterization of a trefoil-shaped liquid crystal based on 1,3,5-triazine with carbazole groups

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A trefoil-shaped liquid crystal containing an aromatic hetero-nucleus has been synthesized by the reaction of cyanuric chloride with 3,6-didecanoyl carbazole (DDC). The molecular structure was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectroscopy and elemental analysis. The core consists of 1,3,5-triazine directly linked to three carbazole groups. The trefoil-shaped conformation is suggested by molecular modelling. The mesophase was investigated using DSC, X-ray diffraction and polarizing optical microscopy. The X-ray diffraction pattern of a sample cooled slowly from the isotropic state showed sharp peaks in the small angle and wide angle regions implying the existence of a columnar phase with inter- and intra-columnar ordering. An unusual reticular texture similar to a cholesteric texture was observed.

There is increasing interest in discotic liquid crystalline materials because of their application potential in, for example, xerography, electrophotography and molecular electronic devices. Since Chandrasekhar [1] first prepared disc-like liquid crystals in 1977, more than 1500 discotic mesogens have been synthesized [2]. A typical molecular structure of a discotic liquid crystal consists of a planar, macrocycle aromatic core surrounded by several long alkyl chains; such structures with strong π-π interactions generally form columnar phases. A variety of disc-shaped molecules with electron-rich cores, such as porphyrins [3–5], phthalocyanines [6, 7], triphenylenes [8–12], hexabenzocoronenes [13–18], and various planar transition metal coordinating complexes have been extensively investigated [19–23]. However, columnar phases are also formed when the planar core of the molecule is replaced by one that is conical or pyramidal-shaped [24, 25] and, in rare cases, even when the central core is absent, as in some macrocyclic molecules [26].

A number of discotic liquid crystalline (DLC) materials based on aromatic hydrocarbon nuclei have been widely investigated, but DLCs based on aromatic hetero-nuclei, which are promising opto-electronic materials, have been less well studied. Derivatives of triarylamino-1,3,5-triazine were reported to be discotic liquid crystals forming columnar mesophases [27, 28].

In an attempt to obtain a new photoconductive material, we have designed and synthesized a new aromatic hetero-nucleus molecule based on 1,3,5-triazine substituted by three carbazole groups with long alkyl side chains. We note that Preece *et al.* have reported discotic liquid crystalline carbazole derivatives [29]. However in their case the carbazole groups are situated at the end of the side chains surrounding a discotic triphenylene core. In our case the carbazole groups connect directly with the central triazine ring giving a trefoil-shaped core. Molecular modelling provides the molecular shape shown as figure 1. The twist angle between the 3,6-didecanoylcarbazolyl units, the lobes of the trefoil-shape and the central 1,3,5-triazine is about 20°–25°.

The synthetic route used to obtain, 2,4,6-tris-(3,6-didecanoylcarbazolyl)-1,3,5-triazine (DCT), is shown in figure 2.

Decanoyl chloride was first synthesized in a conventional manner. A mixture of decanoic acid (20 ml,

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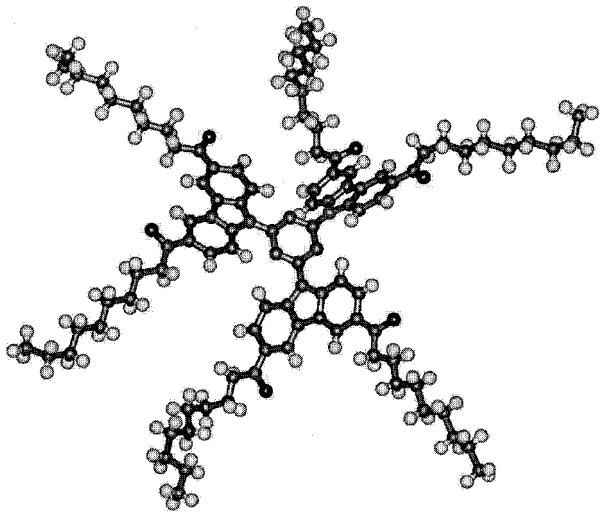

Figure 1. Trefoil-shaped conformation of DCT.

101.1 mmol), thionyl chloride (22 ml, 303.2 mmol) and DMF (3 drops) was heated at reflux for 5 h. The excess $SOCl_2$ was removed and the decanoyl chloride distilled under reduced pressure.

3,6-Didecanoylcarbazole (DDC) was prepared by the method described by Evsyukov *et al.* [30]. To a suspension of $AlCl_3$ (3.00 g, 22.5 mmol) in dichloroethane (DCE) (10 ml) stirred at 0°C under a nitrogen atmosphere, decanoyl chloride (4.20 g, 22.0 mmol) was added dropwise via a syringe. After stirring for 10 min, carbazole (1.67 g, 10.0 mmol) was added and the reaction proceeded for 1 h at 0°C. Then the cooling bath was removed and the deep brown mixture was stirred for 2 h to allow slow warming to room temperature. When the mixture was poured onto crushed ice, the brown colour disappeared instantly. After acidifying with hydrochloric acid and washing with water, the organic layer was

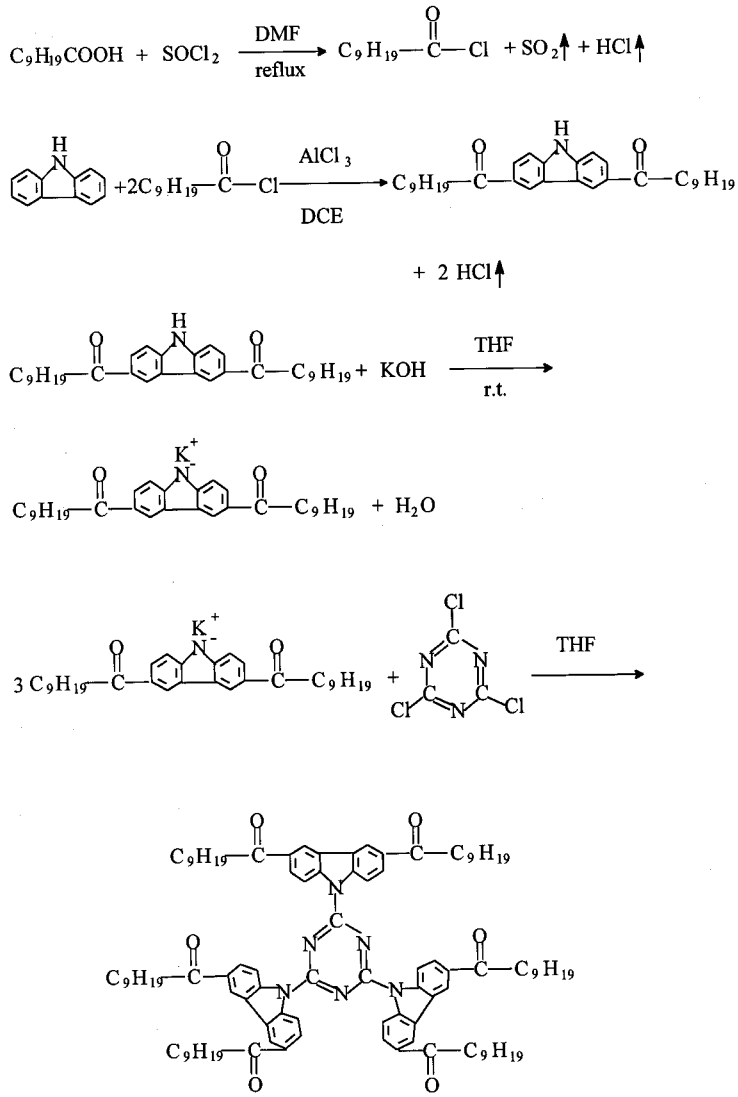

Figure 2. Synthetic route used to obtain DCT.

distilled under reduced pressure to remove DCE. The solid crude product was dissolved in THF and precipitated with petroleum ether. Pure DDC (4.04 g, 84.9% yield) was obtained by recrystallization from acetone. ^{1}H NMR (500 MHz, CF_3COOD, ppm): $\delta = 0.88$–1.91 (m, 34H, $-C_8H_{17}$), 3.30 (t, 4H, $-CH_2-C=O$), 7.64 (d, 2H, $H_{1,8}$-carbazole), 8.26 (d, 2H, $H_{2,7}$-carbazole), 8.97 (s, 2H, $H_{4,5}$-carbazole), 9.18 (s, 1H, NH-carbazole).

2,4,6-Tris(3,6-didecanoylcarbazolyl)-1,3,5-triazine (DCT) was finally synthesized. In a round bottom 50 ml flask potassium hydroxide (0.43 g, 6.0 mmol) was added to 3,6-didecanoylcarbazole (3.00 g, 6.0 mmol) dissolved in THF (20 ml). The pale brown solution was stirred at room temperature for 12 h and the brown product, potassium 3,6-didecanoyl carbazole, was obtained after removing the solvent and drying in vacuum. This intermediate was dissolved in dried THF, and cyanuric chloride (0.39 g, 2.1 mmol) was added under a nitrogen atmosphere. The pale brown colour disappeared instantly with the addition of cyanuric chloride. The mixture was stirred at room temperature for 1 h, then heated under reflux for 6 h. After the solvent was evaporated, a pale yellow solid was obtained which was re-dissolved in petroleum ether and the solution was filtered. Crude DCT was obtained by filtration and precipitation with acetone. Pure DCT (2.37 g, 75.0% yield) was obtained by chromatography on silica gel (100–200 mesh) using $CHCl_3$ as eluent. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): $\delta =$ 0.87–1.87 (m, 102H, $-C_8H_{17}$), 3.16 (t, 12H, $-CH_2-C=O$), 8.12 (d, 6H, $H_{1,8}$-carbazole), 8.82 (s, 6H, $H_{4,5}$-carbazole), 8.93 (d, 6H, $H_{2,7}$-carbazole). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): $\delta = 14.37$, 22.96, 24.22, 29.67, 29.74, 29.88, 30.08, 32.21, 39.00, 116.23, 120.02, 125.77, 126.83, 133.36, 140.46, 163.55, 198.83. FABMS $[M^+] = 1501.97$. Elemental analysis: calc. for $C_{99}H_{132}N_6O_6$ (1502), C 79.16, H 8.86, N 5.59; found C 78.80, H 8.94, N 5.15%.

The DSC traces of DCT, measured using a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 20°C min^{-1}, are shown in figure 3. It can be seen that during the first heating run, DCT melts into a mesophase at about 108°C, and clears at about 166°C. In the second heating run, the peaks remain almost in the same position but become sharper, which means that after the first heating run the structural ordering has been improved. It should be noted that the peaks occur about 30°C lower on cooling. This suggests that the phases undergo supercooling.

The X-ray diffraction pattern of the mesophase is shown in figure 4, and was measured using a MXP18AHF. The sample was heated and held at 240°C for an hour, then cooled to about 145°C for half an hour, and the X-ray pattern was measured at 150°C. A strong diffraction peak with a value of 2θ of 3.8° in the small angle region corresponds to a columnar superstructure with a column–column spacing of 23.2 Å; while a peak at $2\theta = 23.2°$ in the wide angle region corresponds to an intracolumnar stacking with a core–core spacing of 3.82 Å. Other diffuse diffraction peaks in the wide angle region correspond to random arrangements of the surrounding side chains.

The optical texture obtained using polarizing optical microscopy for the mesophase is shown in figure 5. The thin film sample was annealed for 3 days at 150–160°C. A recticular texture similar to a cholesteric texture was observed, which it is suggested arises from a highly ordered columnar mesophase in which optical fluctuations between different domains are small. Further study is in progress.

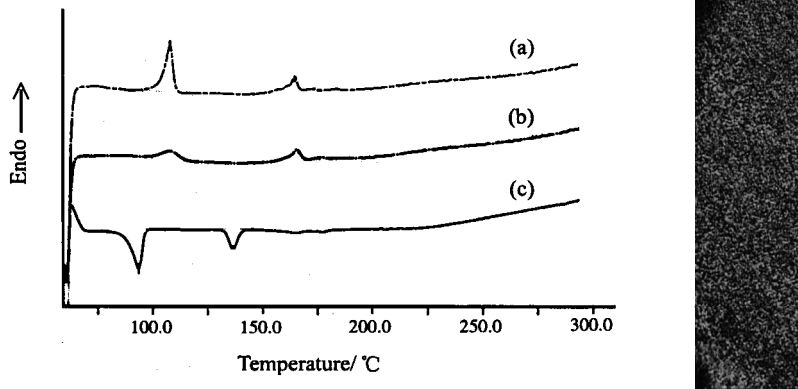

Figure 3. DSC traces of DCT: (*a*) second heating run, (*b*) first heating run, (*c*) first cooling run.

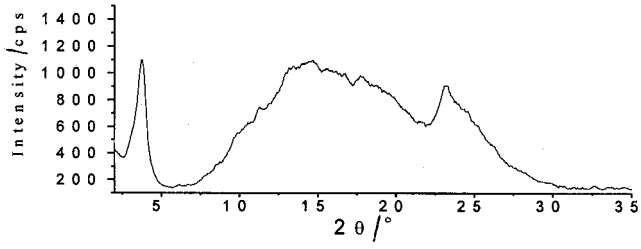

Figure 4. X-ray diffraction pattern of DCT at 150°C.

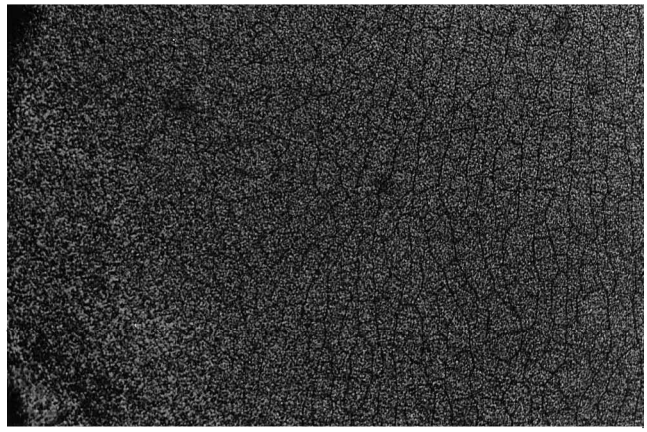

Figure 5. Optical texture of DCT at 150°C (100× magnification).

In conclusion, a novel trefoil-shaped molecule, 2,4,6-tris(3,6-didecanoylcarbazolyl)-1,3,5-triazine (DCT) has been synthesized by the reaction of cyanuric chloride and 3,6-didecanoylcarbazole. DSC measurements, X-ray diffraction pattern and optical texture suggest the existence of a highly ordered columnar mesophase.

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