Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Manickam, M. , Kumar, Sandeep , Preece, Jon A. and Spencer, Neil(2000) 'The first hexagonal columnar discotic liquid crystalline carbazole derivative', Liquid Crystals, 27: 5, 703 — 706

To link to this Article: DOI: 10.1080/026782900202598

URL: http://dx.doi.org/10.1080/026782900202598

LIQUID CRYSTALS, 2000, VOL. 27, NO. 5, 703–706

Preliminary communication

The first hexagonal columnar discotic liquid crystalline carbazole derivative

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(*Received 19 November 1999; accepted 14 January 2000*)

The synthesis of two carbazole derivatives is described by a method in which one and three carbazole moieties are covalently attached to a hexa-alkoxytriphenylene core, respectively. The first of these materials displays hexagonal columnar liquid crystalline behaviour when doped with trinitrofluorenone, at room temperature, as confirmed by the mesophase textures viewed by optical polarizing microscopy and the results from differential scanning calorimetry. These materials may have potential applications in the area of photorefractive materials.

Due to their extensive biological activity, carbazole derivatives and their chemistry have been studied at length [1]. However, it is only recently that they have been examined in terms of their material properties [1, 2] and in particular their photorefractive properties [3]. The interest in photorefractive materials [4] lies in their numerous potential technological applications [5] in, for example, high density optical data storage, optical image processing, phase conjugated mirrors, dynamic holography, optical computing, parallel optical logic, and pattern recognition. Thus, recent studies on carbazole materials have been concerned with electroluminescence [6], non-linear optics [7], and photoconductivity [8]. Amorphous organic photorefractive materials [9] have many advantages over crystalline inorganic [3] and latterly crystalline organic [10] photorefactive materials on which the early research was carried out. These advantages include large optical non-linearities, low dielectric constants, low cost, structural flexibilty, and ease of fabrication. However, the major drawback of amorphous organic photorefractive materials is that a low T_g is required in order that the material can be aligned by a d.c. electric field to induce a degree of anisotropic ordering [11]. The chemical modification of the carbazole moiety to induce liquid crystallinity is attractive as a way to combine the advantages of the amorphous materials with anisotropic ordering. However, to date there are only a few examples in which the carbazole moiety has been incorporated into thermotropic low molecular mass and polymeric liquid crystalline materials [12] and into lyotropic liquid crystals [13]. Furthermore, as far as we are aware there are no examples of low molecular mass, thermotropic, hexagonal columnar discotic liquid crystals which incorporate the carbazole moiety. Thus, one of the approaches that we are adopting to induce hexagonal columnar discotic mesophases in carbazole derivatives is the covalent modification of the carbazole moiety using the well-known [14] discotic triphenylene derivatives. Here we report the synthesis and mesophase behaviour of two carbazole derivatives **1** and **2** (see the scheme), in which one and three carbazole moieties, respectively, have been covalently attached through the nitrogen atom of the carbazole to a mesogenic hexa-alkoxytriphenylene core.

The mono- and tris-hydroxytriphenylenes **3** and **4** were synthesized by reported procedures [15], and the carbazole derivative **5** was synthesized by *N*-alkylation of the carbazole moiety with an excess of 1,6-dibromohexane using NaH as base to deprotonate the carbazole NH group. Compounds **1** and **2** were synthesized by mono- and tris-*O*-alkylation of **3** and **4**, respectively, with the carbazole derivative **5** using potassium carbonate as base to deprotonate the triphenylene OH groups (see the scheme). The table lists analyical data characterizing compounds **1** and **2**.

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
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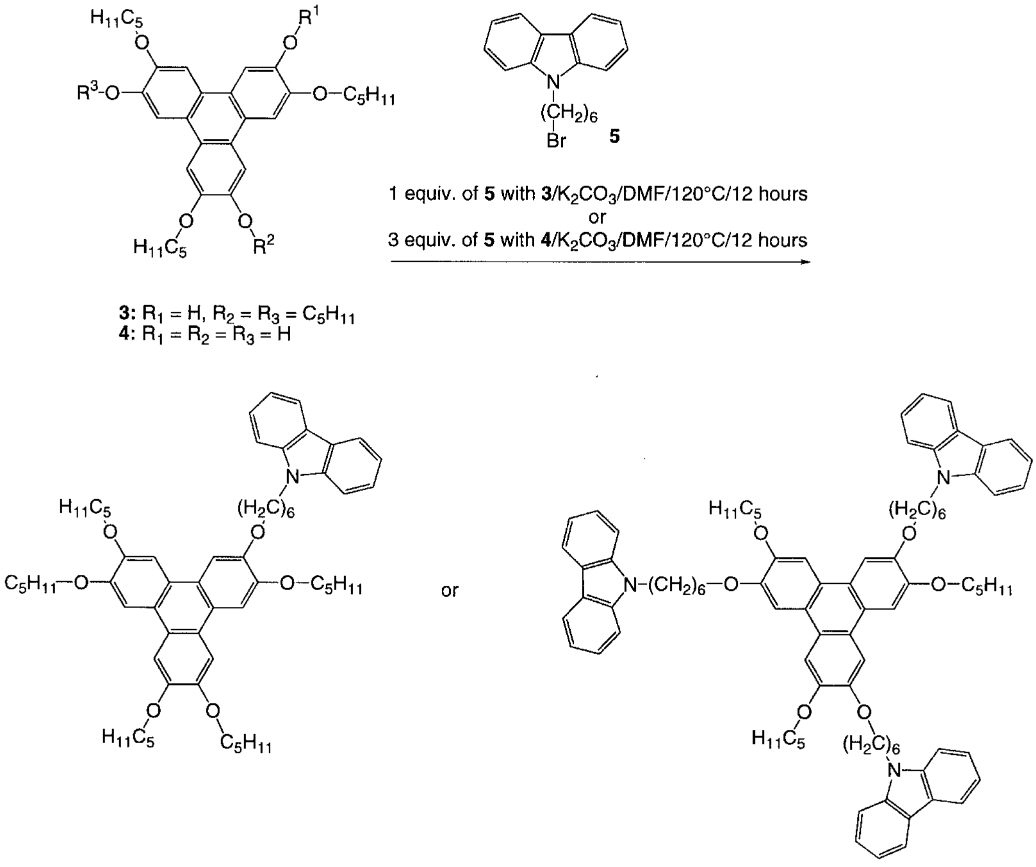

Scheme. Synthesis of the mono- and tris-carbazole-containing triphenylene derivatives **1** and **2**, respectively.

Table. Analytical data for the characterisation of carbazole derivatives **1** and **2**.

Compound 1

^{1}H NMR (300 MHz, CDCl$_3$) δ_H 8.09 (2H, $J = 7.7$ Hz, Ar-H), 7.82, (6H, m, Ar-H), 7.44 (4H, m, Ar-H), 7.21 (2H, m, Ar-H), 4.35 (2H, t, $J = 7.0$ Hz, N–CH$_2$–), 4.20 (12 H, m, 6 × O–CH$_2$–), 1.92 (14H, m, 7 × –CH$_2$–), 1.48 (2H, m, –CH$_2$–), 0.95 (15H, m, 5 × –CH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$) δ_C 149.0, 148.9, 140.4, 125.6, 123.7, 123.6, 122.8, 120.3, 118.9, 108.6, 107.6, 107.5, 107.4, 107.3, 69.8, 69.7, 69.6, 69.4, 43.0, 29.3, 29.1, 29.0, 28.8, 27.1, 26.0, 22.5, 14.0.

FABMS [M$^+$] = 923.

Elemental analysis requires for $C_{61}H_{81}O_6N$: C 79.30, H 8.77, N 1.51; found C 79.30, H 8.58, N 1.46%.

Compound 2

^{1}H NMR (300 MHz, CDCl$_3$) δ_H 8.08 (6H, d, $J = 7.7$ Hz, Ar-H), 7.80 (6H, brs, Ar-H), 7.43 (6H, m, Ar-H), 7.42 (6H, brs, Ar-H), 7.20 (6H, m, Ar-H), 4.33 (6H, t, $J = 6.9$ Hz, 3 × N–CH$_2$–), 4.15 (12H, m, 12 × O–CH$_2$–), 1.92 (18H, m, 9 × –CH$_2$–), 1.53 (24H, m, 12 × –CH$_2$–), 0.9 (9H, t, $J = 7.3$ Hz, 3 × CH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$) δ_C 149.0, 148.9, 140.4, 125.5, 123.7, 123.6, 122.8, 120.3, 118.7, 108.5, 107.5, 107.4, 69.7, 69.4, 42.9, 29.3, 29.0, 28.9, 28.3, 27.1, 25.9, 22.4, 14.0.

FABMS [M$^+$] = 1283.

Elemental analysis requires for $C_{87}H_{99}O_6N_3$: C 81.42, H 7.72, N 3.26; found C 81.42, H 7.83, N 3.26%.

The thermal behaviour of the monocarbazole derivative **1** and its 1 : 1 molar charge transfer complex was investigated by polarizing optical microscopy and differential scanning calorimetry (DSC 7, Perkin Elmer). The monocarbazole derivative **1** was found to be non-mesogenic. DSC shows one broad peak with a peak temperature at 105.8°C for the transition crystal to isotropic phase. It crystallizes again at room temperature on cooling. On subsequent heating, it melts at about 80°C. However, the 1 : 1 molar charge transfer complex of this compound with trinitrofluorenone (TNF) was found to be liquid crystalline at room temperature. Upon heating, the mesophase transforms into the isotropic phase at about 120°C. On cooling, the Col$_h$ phase appears at about 110°C and remains down to room temperature. Textures obtained upon cooling from the isotropic liquid at 100°C and 30°C are shown in the figure. These textures are very similar to known textures for Col$_h$ phases and the columnar phase is miscible with the well characterized Col$_h$ phase of hexapentyloxytriphenylene. DSC of this charge transfer (CT) complex (**1**/TNF, 1 : 1), however, shows only a very weak and broad transition on heating and cooling. CT formation of compound **1** with different molar concentrations of TNF and their thermal behaviour are currently under investigation.

(*a*)

(*b*)

Figure. Mesophase texture of a binary 1:1 mixture of **1** and TNF at (*a*) 100°C, and (*b*) 30°C. As observed in the microscope, the birefringence colours in both cases are predominantly yellow, orange and brown.

The thermal behaviour of the tris-carbazole derivative **2** as investigated by optical polarizing microscopy displayed a crystal/crystal transition at 100°C, followed by isotropic melting at 132°C. Upon cooling and crystallizing at room temperature, followed by reheating, **2** displayed only an isotropic melting transition at 122–135°C. DSC revealed an endotherm at 99.1°C, but no endotherm at 132°C was observed for the first heating run. Additionally, a contact preparation experiment involving compound **2** and TNF did not show any signs of mesophase induction.

We have demonstrated for the first time the induction of a hexagonal columnar mesophase in a material which contains the photorefractive carbazole moiety, by the covalent attachment of one carbazole moiety, through the nitrogen atom to one chain of a hexa-alkoxytriphenylene unit, followed by doping with TNF to generate the CT mesophase. It should be noted that the introduction of three carbazole moieties to the triphenylene core resulted in a material that could not be induced to display a mesophase when TNF was doped into the material. Reasons for the lack of liquid crystallinity in this case may be (i) the increase in the π-surface area affording a material with much higher intermolecular interactions, and (ii) steric crowding around the triphenylene core which will not facilitate a planar disc structure. Currently, we are synthesizing and characterizing a series of mono-, bis-, tris- and hexakis-carbazole triphenylene derivatives and investigating their thermal behaviour alone and as CT complexes with TNF.

This project is supported by the EPSRC and Perkin-Elmer in the UK.

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