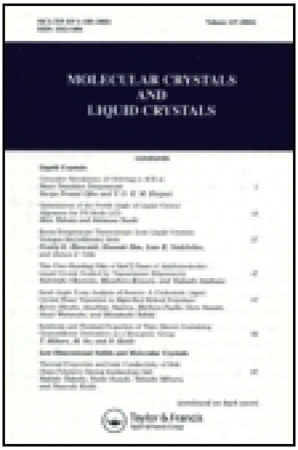

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Dibenzo[g,p]chrysene, a Novel Core for Discotic Liquid Crystals

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Dibenzo[g,p]chrysene, a new π-conjugated polycyclic aromatic hydrocarbon, has been found to function as the core fragment for the preparation of discotic liquid crystals. First two derivatives of this novel core were prepared by a palladium-catalyzed annulation reaction of diphenylacetylenes with 2-iodobiaryls, followed by oxidative coupling. Charge-transfer interactions that induced columnar mesophase formation was observed in both the compounds. Their mesomorphic behavior was studied by polarizing microscopy and differential scanning calorimetry.

Keywords: dibenzo[g,p]chrysene, discotic liquid crystals, columnar mesophase

Liquid crystals formed by disc-shaped molecules, now commonly referred to as discotic liquid crystals, have been of interest since their discovery in 1977 [1]. Most of these compounds possess a flat or nearly flat rigid core surrounded by plural number of peripheral long alkyl chains. Several types of mesophases, such as nematic, smectic, columnar, lamellar, cubic, etc., formed by these discotic molecules have been identified, but a majority of these compounds form columnar mesophases in which the discs are stacked one on top of the other to form columns. A parallel alignment of the columns results in columnar phases with a two-dimensional lattice symmetry such as columnar hexagonal ($\mathrm{Col_h}$), rectangular ($\mathrm{Col_r}$), etc. [2].

π-Conjugated polycyclic aromatic hydrocarbons are attractive building units for the formation of ordered columnar mesophases, as attractive intermolecular interactions between the aromatic cores are primarily responsible for the stacking of cores. A number of polycondensed aromatics such as benzene, naphthalene, anthracene, phenanthrene, triphenylene, perylene, dibenzopyrene, etc. are known to form a variety of columnar

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phases [3]. There is a wide spectrum of potential commercial applications for discotic liquid crystals [4]. Current attention is focused on their use as one-dimensional conductors, photoconductors, light emitting diodes, photovoltaic solar cells, gas sensors, etc. [4,5]. In contrast to thousands of calamitic liquid crystals, far fewer discotic liquid crystals have been synthesized. To explore further their potential applications and to investigate structure-property relationship, newer materials are required. In this communication we report the synthesis of a novel polycyclic aromatic core-dibenzochrysene for the preparation of discotic liquid crystals.

The diameter of the dibenzo[g,p]chrysene core (~9 Å) lies in between the diameter of two well-known discotic cores, triphenylene (~7 Å) and dibenzopyrene (~10 Å). A MM2 energy-minimized structure of octapentyloxy dibenzochrysene (Figure 1) displays a perfectly flat, rigid system, and therefore it is likely to be a good candidate for discotic liquid crystals.

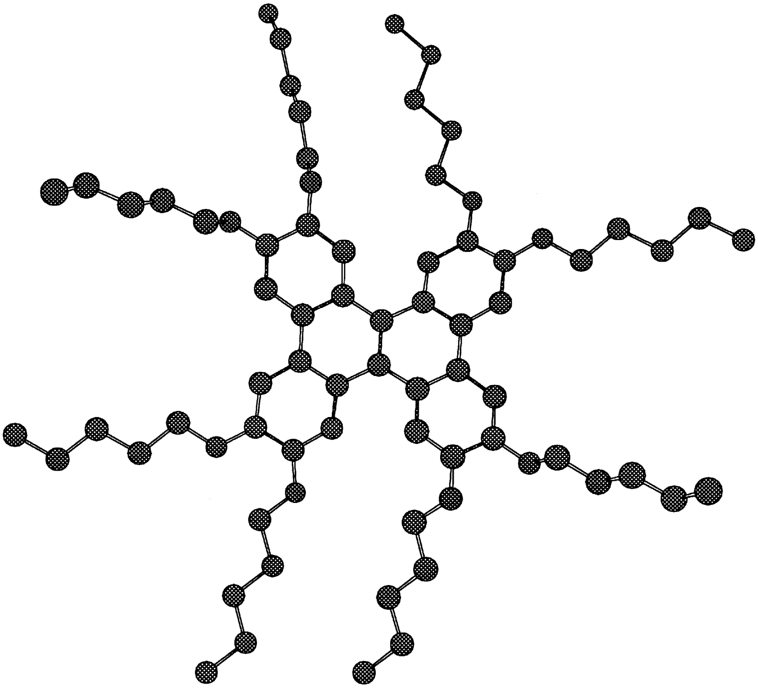
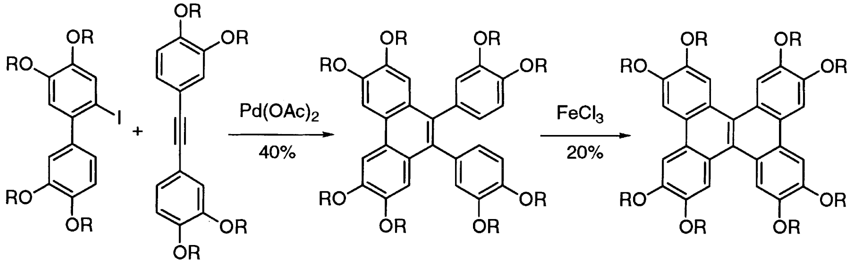


FIGURE 1 MM2 Energy-minimized structures of octapentyloxydibenzo[g,p]chrysene molecule. Calculated core diameter (without chains) is 9.4 Å and with pentyloxy chains (disc diameter) is 25.5 Å.



a: R = C_5H_{11}
b: R = C_8H_{17}

1 **2** **3** **4**

SCHEME 1 Synthesis of octaalkoxydibenzo[g,p]chrysene derivatives.

For the synthesis of dibenzo[g,p]chrysene derivatives **4a** and **4b** the strategy outlined in Scheme 1 was envisaged. The key precursor 9,10-disubstituted phenanthrene **3** is prepared by a palladium-catalyzed annulation reaction of diphenylacetylenes with 2-iodobiaryls [6]. One of the starting materials, 2-iodo-4,4′,5,5′-tetraalkoxybiphenyl **1**, was prepared by the iodination of 3,3′4,4′-tetraalkoxybiphenyl (prepared by classical Ullman coupling of dialkoxymonoiodobenzene) [7]. The second starting material, tetraalkoxydiphenylacetylene **2**, was prepared closely following the literature method [8]. The cyclization of 9,10-disubstituted phenanthrene **3** to prepare dibenzochrysene derivatives **4** was achieved by oxidative coupling using $FeCl_3$ as an oxidizing agent. The use of $FeCl_3$ for the synthesis of various triphenylene derivatives is well documented [9]. Both the compounds were fully characterized from their ^{1}H NMR, ^{13}C NMR, and Mass spectral analysis.*

The thermal behavior of both of the new materials was investigated using a Mettler FP82HT hot stage and central processor in conjunction with Leitz DMRXP polarizing microscope, as well as by differential scanning calorimetry (DSC7 Perkin-Elmer). Virgin compounds **4a** and **4b** are not mesomorphic. The crystalline compound **4a** melts at 165°C and **4b** at 139°C. However, the 2:1 molar charge transfer (C-T) complexes of both the compounds with trinitrofluorenone (TNF) were found to be liquid crystalline

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*Spectral data for **4a**: MS: m/z (FAB) 1016.7; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.18 (s, 4H), 7.88 (s, 4H), 4.28 (t, $J = 6.5$, 8H), 4.09 (t, $J = 6.5$, 8H), 1.97 (m, 16H), 1.5 (m, 32H), and 0.97 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 148.5, 125.4, 124.8, 123.9, 112.0, 107.5, 69.8, 69.5, 29.2, 28.4, 22.5, and 14.0. Spectral data for **4b**: MS: m/z (FAB) 1354.1; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.18 (s, 4H), 7.88 (s, 4H), 4.24 (t, $J = 6.5$, 8H), 4.08 (*t*, $J = 6.5$, 8H), 1.9 (m, 16H), 1.5 (m, 80H), and 0.9 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 148.5, 125.4, 124.8, 123.9, 112.0, 107.5, 69.9, 69.5, 31.8, 29.5, 29.4, 29.3, 26.2, 22.7, and 14.0.

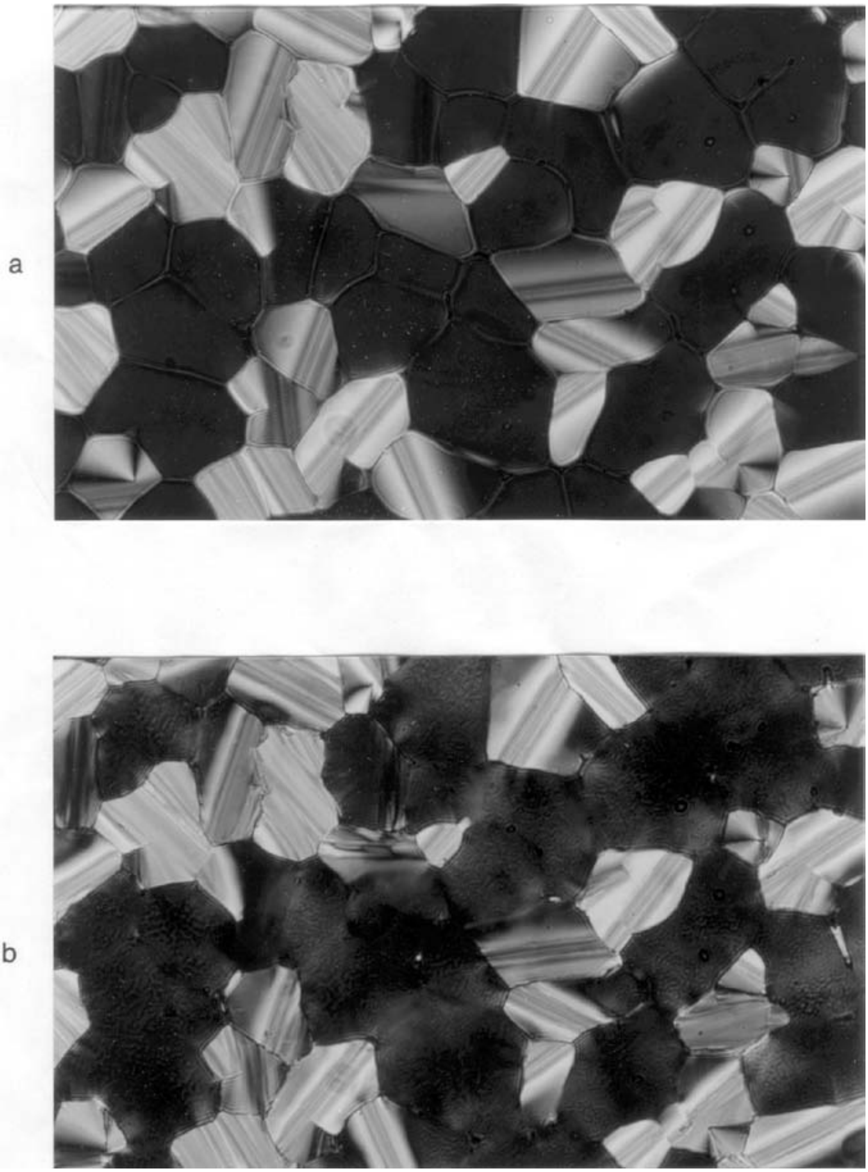

FIGURE 2 (a) Optical textures of **4a** obtained on cooling from the isotropic liquid at 150°C (crossed polarizer, magnification ×200). (b) Optical textures of **4a** obtained on cooling from the isotropic liquid at room temperature (crossed polarizer, magnification ×200). These textures resemble the usual texture of columnar phase.

at room temperature. Mesophase induction and stabilization due to charge-transfer interactions is well known in the literature [10]. Upon heating, the mesophase of the C-T complex of **4a** and **4b** transforms into the isotropic phase at 182.9°C (ΔH, 9.0 J g^{-1}) and 157°C (ΔH, 9.7 J g^{-1}), respectively. On cooling, the columnar phase appears with 2–3°C supercooling in both the cases and remains down to room temperature. Although no textural change was observed at lower temperature (near room temperature), the material becomes very viscous and not shearable. It is possible that it has formed a glass, but no clear glass transition was observed in the DSC run. Textures obtained upon cooling from the isotropic liquid of **4a** at 150°C and 30°C are shown in Figure 2. These textures are very similar to known textures for Col_h phase.

In conclusion, we have prepared the first two derivatives of a novel core, namely dibenzochrysene. The molecular architecture of these two particular compounds is not perfect to display columnar mesophases in the virgin state. However, charge-transfer interactions with TNF, an electron acceptor, spontaneously induce supramolecular order. Synthesis and characterization of several other octaethers, esters, and benzoates of this novel core to investigate structure-property relationship is in progress.

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