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Novel dibenzo[*fg*,*op*]naphthacene discotic liquid crystals: a versatile rational synthesis

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A rational synthesis for dibenzo[*fg*,*op*]naphthacene derivatives (also named as dibenzopyrene) is described. The methodology involves the preparation of a quaterphenyl using a palladium-catalysed cross-coupling of arylboronic acids followed by chemical or photochemical cyclization. The versatility of the process is shown by the formation of various dibenzo[*fg*,*op*]naphthacene derivatives having identical or non-identical peripheral chains. All the new compounds exhibit a single mesophase, which has been identified by X-ray diffractometry and optical microscopy as hexagonal columnar (Col$_h$). X-Ray results confirm that hexasubstituted dibenzonaphthacenes are more ordered than octasubstituted derivatives.

Introduction

The discovery of discotic liquid crystals by Chandrasekhar in 1977 has opened up a whole new field of liquid crystal research.[1] In general, these mesogens have flat or nearly flat aromatic cores surrounded by more than one long aliphatic chain. The mesophases of these compounds usually have a columnar structure in which the disks are stacked one on top of the other to form columns. Attractive intermolecular interactions between the aromatic cores are primarily responsible for the stacking of cores. One may expect that, up to some extent, increasing the core–core attractive interactions (for example by large polycyclic aromatic cores) while maintaining some minimal constraints on the number, size, and nature of the side chains, would enhance molecular stacking and lead to the formation of novel liquid crystalline mesophases. This prompted researchers around the world to explore several polycondensed aromatics for the formation of discotic liquid crystals. A number of liquid crystals based on naphthalene, anthracene, phenanthrene, triphenylene, perylene, dibenzopyrene, *etc.*, have been prepared and extensively studied.[2]

These materials are of increasing interest as self-organizing molecular wires through which charge or excitons can migrate rapidly.[3] Conductivity along the molecular columns was reported to be several orders of magnitude higher than that observed for organic polymers.[4] Very high charge carrier mobility has been observed in the highly ordered columnar phases of various discotic liquid crystals.[4,5] Because of these properties, their potential applications in conducting, photoconducting systems, optical data storage, light emitting diodes, photovoltaic solar cells, gas sensors, and other devices have been envisaged.[3,4] It has recently been demonstrated that the degree of order determines charge mobility in columnar liquid crystalline materials.[5b,c] It is expected that an increase in the orbital overlap area will lead to higher charge mobility. Van de Craats has very recently observed a positive effect of increasing the macrocyclic core size on the intracolumnar charge carrier mobility. Hexabenzocoronenes show remarkably high charge carrier mobility (up to 0.38 cm^2 V^{-1} s^{-1}) in the liquid crystalline phase.[6] Schmidt-Mende *et al.* recently used hexabenzocoronene based discotic liquid crystals as a hole transporting layer to construct an efficient organic photovoltaic solar cell.[7]

Discotic liquid crystals based on dibenzo[*fg*,*op*]naphthacene, also named as dibenzopyrene (DBP), have been the subject of many recent publications. Bock and Helfrich have demonstrated for the first time the existence of ferroelectricity in the columnar liquid crystals of 1,2,5,6,8,9,12,13-octakis[(*S*)-2-heptyloxypropanoyloxy)dibenzopyrene.[8,9] Synthesis of various octaalkoxy-substituted DBP and their photophysical properties have been reported by the Ringsdorf and Markovitsi groups.[10,11] Mesomorphic properties of five homologues of the 1,2,5,6,8,9,12,13-octaalkoxy-DBP (Fig. 1) and their charge transfer complexes with 2,4,7-trinitrofluoren-9-one are reported by Zamir *et al.*[12] The electro-optical and electromechanical effects in these materials were also reported very recently.[13,14]

Because of the larger core having more delocalized π electrons than triphenylene, a greater degree of π–π interaction and hence higher charge carrier mobility was expected in these derivatives.[10] However, the charge carrier mobility in the octasubstituted DBP derivatives was found to be one order of magnitude lower than in the columnar phase of hexaalkoxytriphenylenes.[15] This could be because of less ordered columnar packing due to the steric hindrance caused by the 'bay region' alkoxy chains and this results in lower charge carrier mobility. It is anticipated that the removal of these alkoxy chains from the 1 and 8 positions will give a better core–core interaction and, therefore, high charge carrier mobility. Energy minimized structures of an octasubstituted DBP (Fig. 2a) and hexasubstituted DBP (Fig. 2b) clearly suggest that hexasubstituted DBP derivatives should form more ordered columnar mesophase due to less steric hindrance of the bay region side chains.

All the dibenzo[*fg*,*op*]naphthacene discotic liquid crystals prepared so far are octasubstituted. These derivatives were synthesized following the method of Musgrave and Webster[16] which involves the oxidation of 3,3′,4,4′-tetramethoxybiphenyl

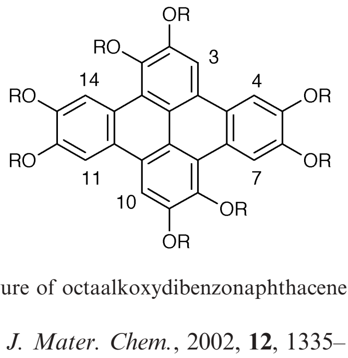


Fig. 1 Structure of octaalkoxydibenzonaphthacene derivatives.

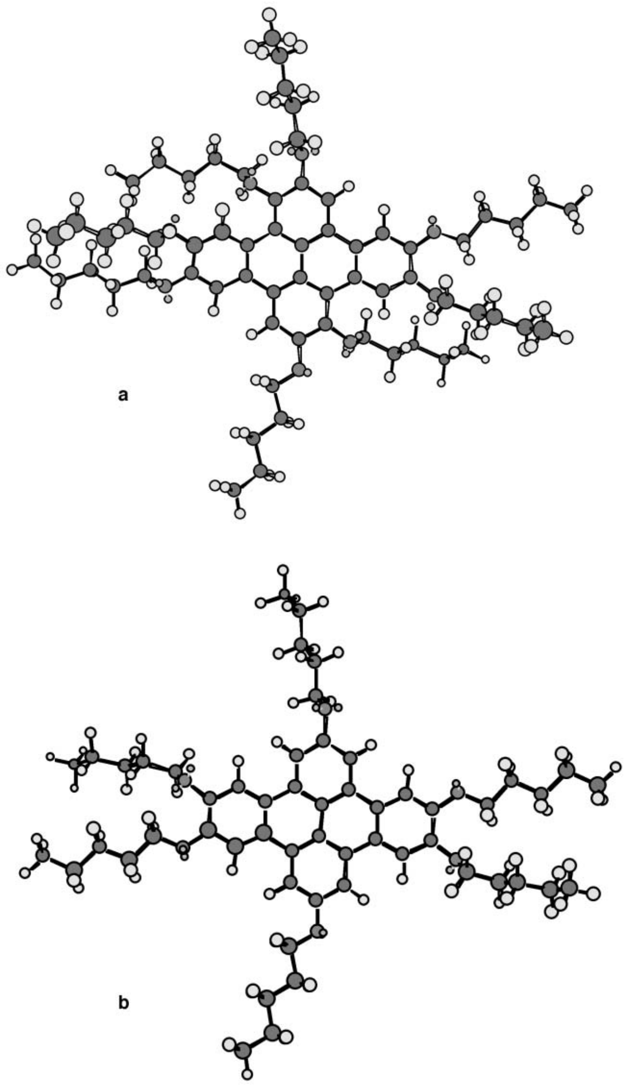


Fig. 2 MM2 Energy minimised structures of (a) octaalkoxydibenzonaphthacene and (b) hexaalkoxydibenzonaphthacene derivatives.

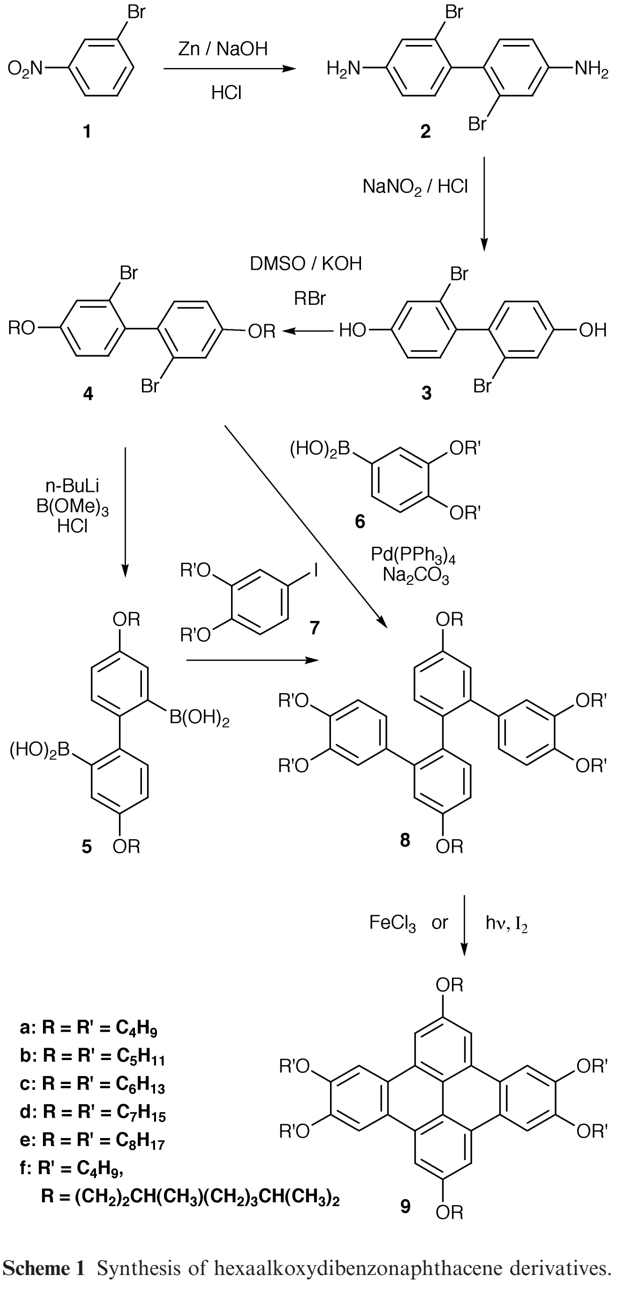
by chloranil in 70% sulfuric acid to 2,5,6,9,12,13-hexamethoxydibenzo[*fg*,*op*]naphthacene-1,8-quinone and its 1,10-quinone isomer. Reductive acetylation followed by alkylation resulted in the synthesis of octasubstituted-DBP liquid crystals. Direct oxidation of tetrakis(pentyloxy)biphenyl by chloranil to hexakis(pentyloxy)dibenzo[*fg*,*op*]naphthacene-1,8-quinone and its conversion to octakis(pentyloxy)-DBP by the above mentioned procedure has also been reported by the Ringsdorf group.[10] We have recently reported that VOCl$_3$ can be efficiently utilized under very mild reaction conditions for the preparation of two quinones.[17]

Hitherto, the synthesis of any low degree substituted DBP discotic liquid crystal is not known. In a preliminary communication, we have recently reported a novel, regiospecific synthesis of variable degree substituted dibenzo[*fg*,*op*]naphthacene derivatives.[18] The versatility of the process is now examined by applying it to the synthesis of various dibenzo[*fg*,*op*]naphthacene derivatives having identical and non-identical peripheral chains.

Experimental

General information

Chemicals and solvents (AR quality) were used without any purification. Column chromatographic separations were performed on silica gel (230–400 mesh) and neutral aluminium oxide. Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). HPLC analysis was performed on a Merck-Hitachi LaChrom 2000 machine using an UV detector and Merck LiChrospher Si 60 (5μm) column. Mass spectra were recorded on a JEOL J600H spectrometer in FAB$^+$ mode using *m*-nitrobenzyl alcohol (NBA) matrix. NMR spectra were recorded on a 200 or 400 MHz machine (Bruker). All chemical shifts are reported in δ units downfield from Me$_4$Si, and J values are given in Hz. Transition temperatures were measured using a Mettler FP82HT hot stage and central processor in conjunction with a Leitz DMRXP polarizing microscope as well as by differential scanning calorimetry (DSC7 Perkin-Elmer). X-Ray studies were performed using an image plate detector (MAC Science DIP1030). Unoriented samples contained in sealed Lindemann glass capillaries were irradiated with Cu Kα rays obtained from a sealed-tube generator (Enraf-Nonius FR 590) in conjunction with double mirror focusing optics. The synthesis of different hexaalkoxy-DBN derivatives is outlined in Scheme 1. The 2,2′-dibromo-4,4′-dihydroxybiphenyl **3** was prepared as reported.[19]



Scheme 1 Synthesis of hexaalkoxydibenzonaphthacene derivatives.

Synthesis of 2,2′-dibromo-4,4′-dialkoxybiphenyls 4a–f; general procedure:

Powdered KOH (448 mg, 8 mmol) was mixed with DMSO (2 ml) at room temperature and stirred for 10 min. 2,2′-Dibromo-4,4′-dihydroxybiphenyl (344 mg, 1 mmol) followed by appropriate alkyl bromide (4 mmol) was added and the reaction mixture was stirred at 60 °C for 12 h and then worked up by adding ice–water and extracting with hexane. The combined extracts were washed with water followed by brine and dried over anhydrous sodium sulfate. Solvent was removed under vacuum and the crude product was purified by column chromatography over silica gel. Elution of the column with hexane yielded 2,2′-dibromo-4,4′-dialkoxybiphenyls **4a–f** in 60–80% yield.

4a. δ_H (200 MHz, $CDCl_3$): 7.19 (2H, d, *J* 2.5), 7.12 (2H, d, *J* 8.5), 6.88 (2H, dd, *J* 2.5, 8.5), 3.98 (4H, t, *J* 6.4), 1.8 (4H, m), 1.52 (4H, m), 0.99 (6H, t, *J* 7.2).

4b. δ_H (200 MHz, $CDCl_3$): 7.19 (2H, d, *J* 2.5), 7.12 (2H, d, *J* 8.5), 6.88 (2H, dd, *J* 2.5, 8.5), 3.97 (4H, t, *J* 6.5), 1.8 (4H, m), 1.52 (8H, m), 0.94 (6H, t, *J* 7.2); *m*/*z* 484 (M^+, 100%).

4c. δ_H (200 MHz, $CDCl_3$): 7.19 (2H, d, *J* 2.5), 7.12 (2H, d, *J* 8.5), 6.88 (2H, dd, *J* 2.5, 8.5), 3.98 (4H, t, *J* 6.4), 1.8–1.3 (16H, m), 0.92 (6H, m); *m*/*z* 512.3 (M^+, 100%).

4d. δ_H (200 MHz, $CDCl_3$): 7.19 (2H, d, *J* 2.5), 7.12 (2H, d, *J* 8.5), 6.88 (2H, dd, *J* 2.5, 8.5), 3.97 (4H, t, *J* 6.4), 1.8–1.3 (20H, m), 0.88 (6H, m); *m*/*z* 540.4 (M^+, 100%).

4e. δ_H (200 MHz, $CDCl_3$): 7.19 (2H, d, *J* 2.5), 7.12 (2H, d, *J* 8.5), 6.88 (2H, dd, *J* 2.5, 8.5), 3.97 (4H, t, *J* 6.4), 1.8–1.3 (24H, m), 0.88 (6H, m); *m*/*z* 568.4 (M^+, 30%).

4f. δ_H (200 MHz, $CDCl_3$): 7.19 (2H, d, *J* 2.5), 7.12 (2H, d, *J* 8.5), 6.88 (2H, dd, *J* 2.5, 8.5), 4.0 (4H, t, *J* 6.9), 1.8–1.3 (20H, m), 0.95 (6H, d, *J* 6.3), 0.88 (12H, d, *J* 6.5); *m*/*z* 624.2 (M^+, 25%).

Synthesis of diboronic acids 5b and 5d; general procedure:

To a solution of 2,2′-dibromo-4,4′-dialkoxybiphenyl (1 mmol) in dry THF (20 ml), a 2.5 M solution of *n*-butyllithium in hexane (2.2 mmol) was added dropwise at −78 °C. The reaction mixture was stirred at this temperature for 1 h under argon. A solution of trimethyl borate (4.4 mmol) in dry THF was added dropwise at the same temperature. The reaction mixture was allowed to warm to room temperature overnight and then stirred with 10% aqueous HCl (20 ml) for 2 h. The product was extracted with ethyl acetate. Combined extracts were dried over anhydrous sodium sulfate. Solvent was removed under vacuum and the crude product was purified by column chromatography over silica gel. Elution of the column with ethyl acetate yielded the diboronic acid in 20% yield.

5b. δ_H (200 MHz, $CDCl_3$): 7.51 (2H, d, *J* 8.7), 7.35 (2H, d, *J* 2.8), 7.05 (2H, dd, *J* 8.7, 2.8), 4.82 (2H, s), 4.01 (4H, t, *J* 6.5), 1.8 (4H, m), 1.6–1.3 (8H, m), 0.93 (6H, t, *J* 6.8).

5d. δ_H (200 MHz, $CDCl_3$): 7.51 (2H, d, *J* 8.7), 7.35 (2H, d, *J* 2.8), 7.04 (2H, dd, *J* 8.7, 2.8), 4.78 (2H, s), 4.01 (4H, t, *J* 6.5), 1.8 (4H, m), 1.6–1.3 (16H, m), 0.93 (6H, t, *J* 6.8).

Synthesis of 3,4-dialkoxyphenylboronic acids 6a–f

3,4-Dialkoxyphenylboronic acids **6a–f** were prepared following literature methods.[20,21]

Synthesis of quaterphenyls 8a–f; general procedure I

A mixture of 3,4-dialkoxyphenylboronic acid **6a–f** (4 mmol) in ethanol–ether (2 : 1, ~5 ml) was added to a stirred mixture of 2,2′-dibromo-4,4′-dialkoxybiphenyl **4a–f** (1 mmol), tetrakis-(triphenylphosphine)palladium(0) (0.04 mmol) and 2 M aqueous sodium carbonate (10 ml) in degassed THF (15 ml). The reaction mixture was refluxed for 20 h under nitrogen. After cooling to room temperature, it was poured over water and extracted with diethyl ether (4 × 30 ml). The combined extracts were washed with water followed by brine and dried over anhydrous sodium sulfate. Solvent was removed under vacuum and the crude product was purified by column chromatography over silica gel. Elution of the column with hexane–dichloromethane yielded quaterphenyls **8a–f** in 25–30% yield.

General procedure II

A mixture of diboronic acid **5b** or **5d** (1 mmol), 3,4-dialkoxyiodobenzene **7** (2.2 mmol), tetrakis(triphenylphosphine)palladium(0) (0.03 mmol) and 2 M aqueous sodium carbonate (10 ml) in degassed DME (50 ml) was refluxed for 15 h under nitrogen. Work-up and purification as mentioned above yielded quaterphenyls **8b** or **8d** in about 20% yield.

8a–f. All the quaterphenyls give similar ^1H NMR spectra differing in only the number of alkyl chain CH_2 protons. δ_H (200 MHz, $CDCl_3$): 7.27 (2H, d, *J* 8.4), 6.84 (2H, dd, *J* 2.6, 8.4), 6.69 (2H, d, *J* 2.6), 6.52 (2H, d, *J* 8.1), 6.17 (2H, br s), 6.17 (2H, br s), 3.94 (8H, m), 3.54 (4H, m), 1.8–1.3 (alkyl chain CH_2, m), 0.86 (18H, t, *J* 6.7).

Mass spectra of all the compounds give correct molecular ion peaks.

Synthesis of hexaalkoxydibenzo[*fg*,*op*]naphthacenes 9a–f; general procedure

Photocyclization method. An Ace Glass Incorporated photochemical reaction assembly (catalog no. 7840) was used for the photochemical cyclization reactions. An equimolar mixture of quaterphenyl **8a–f** and iodine in dry benzene (200 ml) was irradiated for 48 h in argon atmosphere. Aqueous sodium thiosulfate solution (20%, 100 ml) was added in the reaction mixture and it was extracted with dichloromethane. The combined extracts were washed with water and dried over anhydrous sodium sulfate. Solvent was removed under vacuum and the crude product was purified by repeated column chromatography over silica gel and neutral alumina. Elution of the column with hexane–dichloromethane yielded hexaalkoxydibenzo[*fg*,*op*]naphthacene **9a–f** in 10–15% yield.

Chemical cyclization method. To a solution of quaterphenyl **8b** (1 mol) in dry dichloromethane (10 ml), anhydrous $FeCl_3$ (4 mmol) was added. The reaction mixture was stirred at room temperature for 30 min under N_2 atmosphere. The reaction was quenched with methanol (5 ml) and after that it was poured over ice–water (20 ml) and extracted with CH_2Cl_2 (4 × 20 ml). Purification of the crude product as mentioned above furnished the hexakis(pentyloxy)-DBN **9b** in 10% yield.

9a. ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (4H, s), 8.02 (4H, s), 4.31 (4H, t, *J* 6.4), 4.24 (8H, t, *J* 6.5), 1.9 (12H, m), 1.5 (12H, m), 1.0 (18H, m); ^{13}C NMR (50 MHz, $CDCl_3$): δ 157.0, 150.0, 130.2, 124.8, 118.0, 107.7, 106.6, 69.3, 68.3, 31.7, 31.5, 19.4, 14.0; HPLC: 99.0% (silica, hexane–dichloromethane: 7 : 3, flow 1.0 ml min^{-1}, retention time 14.36 min); MS: *m*/*z* 734.3 (100%); elemental anal: calcd for $C_{48}H_{62}O_6$, C 78.44, H 8.50: found, C 78.26, H 8.65%.

IR data: the same spectrum is observed for all compounds **9a–f**: ν_{max}/cm^{-1} 2934, 1604, 1532, 1408, 1381, 1263, 1177, 1075.

UV–vis data: all samples were measured in dichloromethane and similar spectrum is observed for all the compounds. λ_{max}/nm 268, 286, 307, 337, 354, 377, 398.

9b. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.18 (4H, s), 8.09 (4H, s), 4.37 (4H, t, *J* 6.4), 4.30 (8H, t, *J* 6.5), 2.0 (12H, m), 1.57 (24H, m), 1.0 (18H, m); ^{13}C NMR (50 MHz, CDCl$_3$): δ 157.0, 149.9, 130.1, 124.7, 107.5, 106.5, 69.5, 68.6, 29.1, 28.4, 22.6, 14.1; HPLC: 99.9% (silica, hexane–dichloromethane: 7 : 3, flow 1.0 ml min^{-1}, retention time 8.31 min); MS: *m*/*z* 819.4 (40%); elemental anal: calcd for $C_{54}H_{74}O_6$, C 79.18, H 9.11: found, C 79.30, H 9.32%.

9c. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.18 (4H, s), 8.02 (4H, s), 4.29 (4H, t, *J* 6.5), 4.23 (8H, t, *J* 6.5), 1.91 (12H, m), 1.5 (36H, m), 1.0 (18H, m); HPLC: 98% (silica, hexane–dichloromethane: 8 : 2, flow 1.0 ml min^{-1}, retention time 12.63 min); other spectral data could not be obtained because of the paucity of the material.

9d. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.10 (4H, s), 8.01 (4H, s), 4.30 (4H, t, *J* 6.3), 4.23 (8H, t, *J* 6.3), 1.92 (12H, m), 1.5 (48H, m), 0.85 (18H, brs); ^{13}C NMR (100 MHz, CDCl$_3$): δ 157.2, 150.1, 130.4, 124.9, 118.2, 107.8, 106.7, 69.8, 68.8, 32.1, 29.9, 29.7, 29.4, 26.5, 22.9, 14.3; HPLC: 99.6% (silica, hexane–dichloromethane: 7 : 3, flow 1.0 ml min^{-1}, retention time 11.50 min); elemental anal: calcd for $C_{66}H_{98}O_6$, C 80.28, H 10.00: found, C 80.34, H 10.28%.

9e. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.18 (4H, s), 8.09 (4H, s), 4.37 (4H, t, *J* 6.6), 4.30 (8H, t, *J* 6.6), 1.99 (12H, m), 1.5 (60H, m), 0.90 (18H, t, *J* 6.6).); HPLC: 98.5% (silica, hexane–dichloromethane: 8.5 : 1.5, flow 1.0 ml min^{-1}, retention time 11.50 min). Other spectral data could not be obtained because of the paucity of the material.

9f. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.18 (s, 4H), 8.09 (s, 4H), 4.41 (t, *J* 6.6, 4H), 4.31 (t, *J* 6.6, 8H), 2.0–1.3 (m, 42H), 1.07 (m, 18H), 0.89 (d, *J* 6.5, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 156.9, 150.0, 130.1, 124.8, 118.2, 107.8, 106.5, 69.3, 66.9, 39.3, 37.4, 36.6, 31.5, 30.0, 27.9, 24.7, 22.7, 19.8, 19.3, 13.9; HPLC: 99.9% (silica, hexane–dichloromethane: 7 : 3, flow 1.0 ml min^{-1}, retention time 7.58 min); MS: *m*/*z* 902.2 (100%); elemental anal: calcd for $C_{60}H_{86}O_6$, C 79.78, H 9.60: found, C 79.69, H 9.82%.

Results and discussion

Synthesis

For the synthesis of various dibenzo[*fg*,*op*]naphthacene (DBN) derivatives **9a–f** the strategy outlined in Scheme 1 was envisaged. The synthesis is based on the preparation of key intermediate quaterphenyl **8** starting from 3-nitrobromobenzene **1**. The 2,2′-dibromo-4,4′-dihydroxybiphenyl **3** was prepared as reported by Cornforth.[19] Alkylation of the diphenol with the appropriate 1-bromoalkane yielded 2,2′-dibromo-4,4′-dialkoxybiphenyls **4**. The quaterphenyls **8** were prepared either by coupling **4** with dialkoxyboronic acids **6** or by first converting the dibromobiphenyls **4** to diboronic acids **5** and then reacting with dialkoxyiodobenzenes **7**. Photocyclodehydrogenation of the quaterphenyls **8** in the presence of an excess of iodine furnished the desired 2,5,6,9,12,13-hexaalkoxy-DBN derivatives **9a–f**. The cyclization can also be achieved by oxidative coupling using FeCl$_3$ as oxidizing agent. The use of FeCl$_3$ for the synthesis of various triphenylene derivatives is well documented.[20,22] Final compounds were characterized from their ^{1}H NMR, ^{13}C NMR, IR, UV–vis, mass and elemental analysis.

Thermal behavior

All the DBN derivatives **9a–f** were found to be liquid crystalline with a very broad mesophase temperature range. The nature of these new liquid crystals was studied by differential scanning calorimetry (DSC) and by optical microscopy with polarized light. Transition temperatures and transition enthalpies were determined by DSC. Data obtained from the heating and cooling cycles of DSC are collected in Table 1. The peak temperatures are given in °C and the numbers in parentheses indicate the transition enthalpy (ΔH) in kJ mol^{-1}.

As may be seen from the data, all compounds exhibit a very similar behaviour, *viz.* they form a single enantiotropic mesophase with a broad mesophase range. Isotropic temperature decreases on increasing number of carbon atoms in the peripheral chains. For the crystalline to mesophase transition, ΔH increases with increasing number of carbon atoms in side chains. This may reflect selective melting of the side chains. Conversely, the enthalpy difference associated with the transition from mesophase to isotropic liquid is approximately constant, reflecting unstacking of the aromatic cores. This behavior is typical of discotic mesophases. The degree of supercooling observed for columnar mesophase to isotropic temperature is not significant compared with that found for crystalline to columnar phase temperature. Similar behaviour has been shown for many triphenylene based discotic liquid crystals.[20] It is interesting to compare the thermal behaviour of these hexaalkoxy-DBP derivatives with octaalkoxy-DBP derivatives.[12] All the hexasubstituted derivatives are thermally more stable (having higher isotropic temperature) than the octasubstituted dibenzopyrenes. The lower melting and clearing temperatures of octaalkoxy-DBP could be due to the presence of two extra alkoxy chains and the steric hindrance caused by these chains. Triphenylene based discotic liquid crystals having an extra alkoxy chain in the bay region also exhibit similar effects. 1,2,3,6,7,10,11-Heptaalkoxytriphenylenes have much lower melting and isotropic temperatures compared to symmetrically substituted 2,3,6,7,10,11-hexaalkoxytriphenylenes.[23] Seven-tail triphenylene discotic liquid crystals in which one of the peripheral chains is attached to the core *via* an amide linkage show very high clearing temperatures.[24] This is due to the H-bonding of the amide group and, therefore, can not be compared with the normal alkoxy triphenylene derivatives. The use of branched chains often reduces melting and isotropic temperatures.[25] Some effects of the introduction of branched-chains into mesogens on the mesomorphism have been summarised by Ohta and co-workers.[25b] On replacing two *n*-butyloxy tails in compound **9a** by branched chains, both melting and clearing temperatures were lowered. The resulting compound **9f** exhibits an isotropic temperature about 71 °C lower than **9a**. The results are in accordance with the

Table 1 Phase transition temperatures (peak temp.) and enthalpies of hexasubstituted dibenzopyrene derivatives. Cr = crystal, Col$_h$ = hexagonal columnar liquid crystalline phase, I = isotropic

	Thermal transitions/°C and enthalpy changes/kJ mol^{-1} in parentheses	
Compound	Heating scan	Cooling scan
9a	Cr 147.7 (27.7) Col$_h$ 236.9 (2.9) I	I 234.4 (2.6) Col$_h$ 117.0 (29.4) Cr
9b	Cr 120.5 (52.1) Col$_h$ 223.1 (4.1) I	I 219.9 (3.7) Col$_h$ 96.3 (54.0) Cr
9c[a]	Cr 143 Col$_h$ 188 I	I 187 Col$_h$ 102 Cr
9d	Cr 143.4 (86.2) Col$_h$ 179.7 (2.8) I	I 178.2 (2.6) Col$_h$ 103.4 (85.8) Cr
9e[a]	Cr 134 Col$_h$ 161 I	I 159 Col$_h$ 96 Cr
9f	Cr 118.7 (63.8) Col$_h$ 165.5 (2.8) I	I 161.4 (4.3) Col$_h$ 87.8 (63.6) Cr

[a] Based on polarizing microscopy.

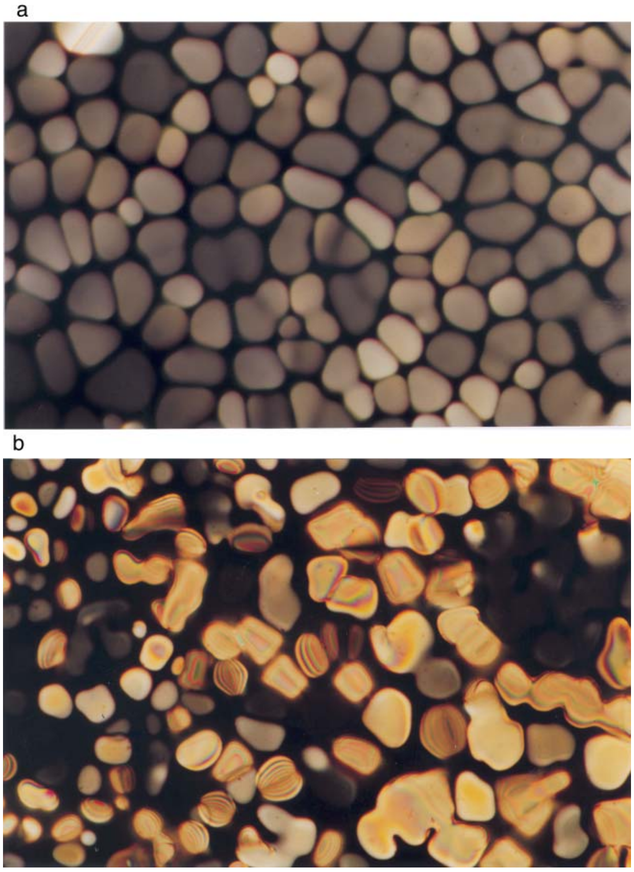


Fig. 3 (a) Optical textures of **9a** obtained on cooling from the isotropic liquid at 226 °C (crossed polarizer, magnification × 200). (b) Optical textures of **9d** obtained on cooling from the isotropic liquid at 150 °C (crossed polarizer, magnification × 200). These textures resemble the usual texture of columnar phase.

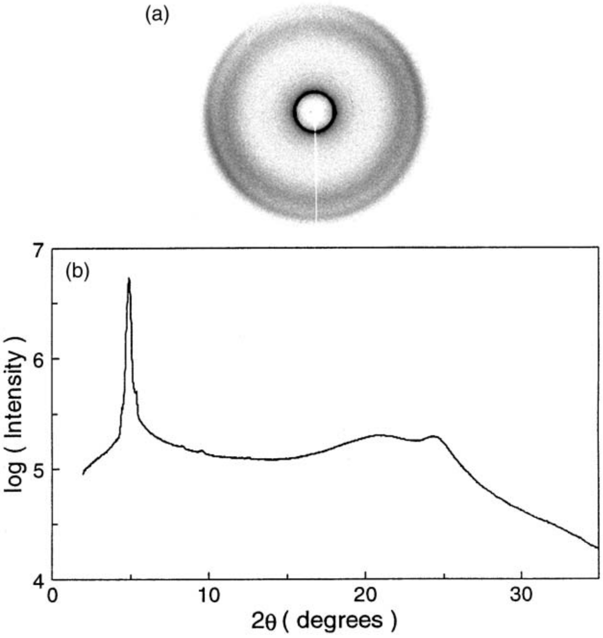


Fig. 4 (a) X-Ray diffraction pattern obtained for compound **O5DBP** at 27 °C; (b) χ-averaged one-dimensional intensity *vs.* 2θ profile. The sharp peak at low angle ($2\theta \approx 5°$) corresponds to the disc diameter. Whereas the first diffuse peak at $2\theta \approx 18°$ is from the aliphatic chains, the fairly sharp peak at higher angles ($\sim 25°$) is due to the stacking of the rigid cores within a column giving a core–core separation of 3.63 Å.

observations reported by Cross *et al.* for various unsymmetrical triphenylene derivatives. In a number of unsymmetrical triphenylene derivatives a maximum in the columnar phase–isotropic clearing point is found for the most symmetrical triphenylene, *i.e.* when all the six alkoxy chains are of equal length.[20] The lower melting and clearing temperatures of the compound **9f** could be due to the unsymmetrical nature (by virtue of non-identical peripheral chains) and the presence of two branched chains in the molecule. The decrease in the transition temperature due to the disorder and stereoheterogeneity caused by branched chains is well documented.[25,26]

Microscopy with polarized light suggested that all compounds **9a–f** form hexagonal columnar mesophases. Classical textures of columnar mesophases appeared upon cooling from the isotropic liquid. These textures are very similar to the known textures for the $\mathrm{Col_h}$ phases shown by several well characterized discotic liquid crystals.[27] Fig. 3 shows two representative examples of such photomicroscopic pictures of compound **9a** and **9d** obtained on cooling from the isotropic liquid.

X-Ray diffraction studies

To verify our hypothesis that the hexaalkoxydibenzo[*fg*,*op*]-naphthacene derivatives should form more ordered columnar phases than octasubstituted derivatives, we prepared octakis-(pentyloxy)dibenzo[*fg*,*op*]naphthacene (O5DBP, Fig. 1, R = C_5H_{11})[10] and performed X-ray investigations on both the octakis(pentyloxy) (**O5DBP**) and hexakis(pentyloxy)dibenzo-[*fg*,*op*]naphthacene (**9b**) derivatives under similar conditions. Diffraction patterns for compound **O5DBP** with eight alkoxy substituents and **9b** with six alkoxy substituents were recorded at fixed intervals from the isotropic phase, *viz.*, ~10 °C, 30 °C and 70 °C. Fig. 4a and 4b show a representative diffraction pattern and the derived one-dimensional intensity *vs.* 2θ profile obtained at 27 °C for **O5DBP**; Fig. 5a and 5b show the same for the compound **9b** at 120 °C. In the low-angle region, four sharp peaks—one strong and three weak reflections—are seen whose *d*-spacings are in the ratio of $1 : 1/\sqrt{3} : 1/\sqrt{4} : 1/\sqrt{7}$. Identifying the first peak with the Miller index 100, the ratios conform to the expected values from a two-dimensional hexagonal lattice. In the wide-angle region two diffuse

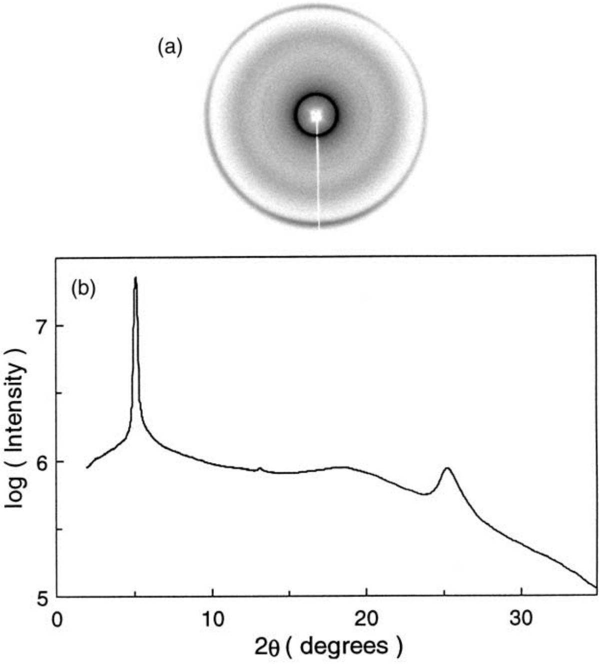


Fig. 5 (a) X-Ray diffraction pattern obtained for compound **9b** at 120 °C; (b) χ-averaged one-dimensional intensity *vs.* 2θ profile. The peaks at $2\theta \approx 5°$, 19° and 25° are from the disc diameter, aliphatic chains and due to the packing of rigid cores within a column.

Table 2 X-Ray diffraction data for octa- and hexa-substituted dibenzonaphthacene derivatives giving the disc diameter d_{100}, the core–core separation ($d_{\text{core–core}}$), and the correlation length for the intracolumnar order

		d-Spacing numbers/Å			
Compound	Temp./°C	d_{100}	$d_{\text{core–core}}$	d_{alkyl} chain	Correlation length/Å
O5DBP	87	21.19	3.89	4.51	37.84
O5DBP	67	21.20	3.81	4.43	41.83
O5DBP	27	21.87	3.63	4.23	82.12
9b	210	21.17	3.60	4.84	93.78
9b	190	21.17	3.59	4.80	113.86
9b	150	21.08	3.55	4.75	123.32
9b	120	20.98	3.53	4.70	143.82

reflections are seen. The broad one centered at ~4.6 Å corresponds to the liquid-like order of the aliphatic chains. The relatively sharper one seen at higher 2θ-values is due to the stacking of the molecular cores one on top of another. The diffuse nature of the peak suggests that the stacking of discs within each column is correlated over short distances only. All these features are characteristics of the Col_h phase.

Table 2 summarizes the different spacings extracted by fitting each of the peaks in the one-dimensional profile to a Lorentzian form. Also shown is the correlation length for the intracolumnar packing arising out of the core–core interaction. The correlation length is calculated using the FWHM of the sharper peak at higher angles and the Scherrer expression.[28] As can be noted from the table the disc diameter remains the same at ~21 Å for both **O5DBP** and **9b** irrespective of the number of alkoxy chain substituents, *i.e.*, whether it is 8 or 6. Also the disc diameter remains constant with varying temperature for both the compounds.

Fig. 6 and 7 show plots of the average stacking distance (or core–core separation) and core–core correlation length as a function of $T_\text{iso} - T$, T_iso being the isotropic temperature. The core–core distance shows a strong temperature dependence for **O5DBP** but has a smaller variation for **9b**. It should be noted here that the value of the core–core distance is smaller for a compound with six alkoxy substituents to the core (**9b**) than that for one with eight alkoxy substituents (**O5DBP**). The core–core correlation length is higher for the compound with six alkoxy substituents (**9b**) than for the compound **O5DBP** with eight alkoxy substituents. A probable reason is that the density of the core–core packing increases as the number of alkoxy substituents on the central core decreases. We have observed a similar behaviour in a triphenylene based system also.[23]

In conclusion, the methodology outlined above has given us a great deal of control in the modification of the dibenzo[*fg*,*op*]naphthacene discotic core. Whereas the synthesis of octasubstituted dibenzo[*fg*,*op*]naphthacene to give low molar mass discotic liquid crystals is fairly easy, the synthesis of any low degree substituted dibenzo[*fg*,*op*]naphthacene has so far not been achieved. A variety of dibenzo[*fg*,*op*]naphthacene discotics can now be designed and created using the above methodology. A comparison of the X-ray results for octasubstituted and hexasubstituted-dibenzo[*fg*,*op*]naphthacene clearly indicate, as predicted, that hexasubstituted dibenzo[*fg*,*op*]-naphthacene derivatives are more ordered than octasubstituted derivatives and, therefore, are better candidates for charge migration studies.

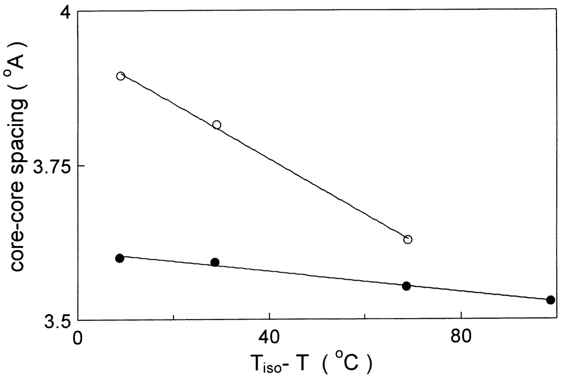


Fig. 6 Plot of core–core spacing as a function $T_\text{iso} - T$ for **O5DBP** (open circle) and for the compound **9b** (solid circle). T_iso being the clearing point temperature. Notice the smaller core–core spacing for the compound **9b** than for the compound **O5DBP** indicating better core–core packing in the compound **9b**.

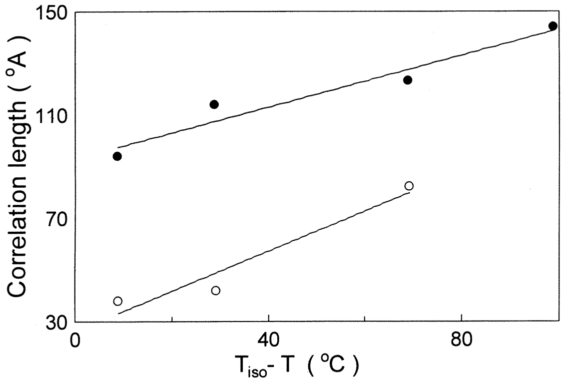


Fig. 7 Plot of correlation length *vs.* $T_\text{iso} - T$ for **O5DBP** (open circle) and for **9b** (solid circle). Higher values for the correlation length in the case of compound **9b** than for the compound **O5DBP** indicate that the phase is more ordered in compound **9b**.

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