A novel series of anthraquinone-based discotic liquid crystals with bulky substituents: synthesis and characterization

Veena Prasad[a]; K. Krishnan[a]; V. S. K. Balagurusamy[a]
[a] Centre for Liquid Crystal Research,

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A novel series of anthraquinone-based discotic liquid crystals with bulky substituents: synthesis and characterization

VEENA PRASAD, K. KRISHNAN* and V. S. K. BALAGURUSAMY

Centre for Liquid Crystal Research, P.O. Box. 1329, Jalahalli, Bangalore-560013, India

A novel series of anthraquinone-based discotic liquid crystals with bulky substituents, namely 1,5-dibenzyloxy-2,3,6,7-tetraalkyloxy-9,10-anthraquinones, has been synthesized starting from gallic acid. This is, to our knowledge, the first example of bulky substitution in a discotic C_2-symmetric molecule forming columnar phases. Except for the lowest homologue, all members of this series are found to exhibit columnar mesophases; the low temperature mesophase appears to be three-dimensionally ordered whereas the high temperature mesophase is hexagonal columnar (Col_h). We find that the introduction of benzyl substituents for alkyl chains (in the 1,5-positions) on the anthraquinone hexaalkoxylates stabilizes the three-dimensionally ordered phase, whereas it destabilizes the Col_h phase, compared with the anthraquinone hexaalkoxylates. Interestingly, the three-dimensionally ordered phase extends down to − 50°C, making these new derivatives suitable for device applications.

1. Introduction

Since the discovery of discotic liquid crystals [1], a large number of disc-like organic molecules have been found to form columnar phases. However, only recently has there been increasing activity in designing and synthesizing discotic liquid crystals suitable for various applications such as charge transport [2(*a–e*)], photoconductivity [3], ferroelectric switching [4], optical information storage and retrieval [5] and organic light-emitting diodes [6]. Columnar phases formed by molecules based on disc-shaped rigid polynuclear aromatic cores that have correlation among the neighbours along the column have been shown to possess high electrical conductivity along the columns [2(*a–e*)]. Extensive studies (synthetic as well as physical) have been made of triphenylene-based [2], and phthalocyanine-based [7] discotic liquid crystals. Surprisingly, very limited studies have been carried out on the design and synthesis of discotic liquid crystals based on the C_2-symmetric anthraquinone core, unlike the much studied triphenylene system which is C_3-symmetric [8, 9].

Substitution of certain bulky groups for one of the alkoxy chains attached to the triphenylene core of the hexaalkoxytriphenylenes, through a carbonyloxy linkage which destroys the C_3-symmetry of the triphenylene core, has been found to induce a mesophase with long range

order along the columns resulting in three-dimensional ordering [10]. In continuation of our interest in the design and synthesis of anthraquinone-based discotic liquid crystals, we have introduced bulky benzyl groups for the alkyl groups at the 1,5 positions of the hexaethers of anthraquinone by a synthetic method described by us recently [11], through an ether linkage, without destroying the C_2-symmetry of the molecule. Further, it does not introduce any additional strong dipolar interaction among the molecular cores through any group with a strong permanent dipole moment. We have studied the effect of bulky substituents on the mesomorphic behaviour by polarized light microscopy and differential scanning calorimetry.

2. Experimental methods
2.1. *Synthesis*

C_2-symmetric dibenzyloxytetraalkyl oxyanthraquinone derivatives have been prepared starting from gallic acid according to the scheme depicted below. Thus, acid-mediated dimerization of gallic acid gave rufigallol in 49% yield. The crude rufigallol was selectively tetraalkylated [11] by heating it with the appropriate bromoalkane (4 equiv.) and powdered sodium hydroxide (4 equiv.) in dimethyl sulfoxide at 70°C over a period of 18 h to yield the rufigallol tetraethers (DHT nA, $n = 4 \ldots 10$). The crude products obtained were purified by two recrystallizations from chloroform–methanol to give pure tetraethers as yellow needles in 20–38% yields.

*Author for correspondence; e-mail: uclcr@giasbg01.vsnl.net.in
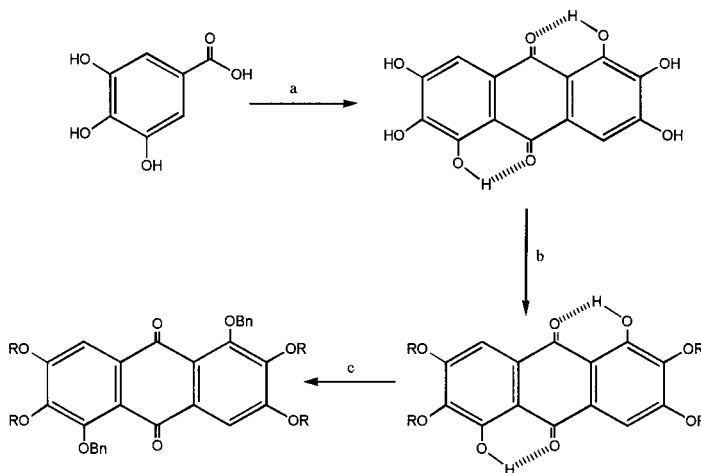
(a) Conc. H_2SO_4, 100°C, 2.5 h, 49%; (b) *R*-Br (4 eq.), NaOH (4 eq.), DMSO, 70°C, 18 h, 20–38%; (c) Bn–Br (12 eq.), K_2CO_3 (16 eq.), *n*-Bu$_4$NI (cat.), DMF, 105°C, 20 h, 83–90%

Scheme.

All the tetraethers were found to have very similar IR and ^{1}H NMR spectral characteristics. IR spectra of the tetraethers exhibit a carbonyl resonance at *c.* 1600 cm^{-1}, which is characteristic of an intramolecularly hydrogen-bonded anthraquinone-carbonyl moiety; ^{1}H NMR spectra exhibit a singlet resonance at *c.* δ 12.8 ppm, the characteristic resonance of an intramolecularly hydrogen-bonded phenolic proton, and another singlet resonance at *c.* δ 7.4 ppm, characteristic of an aromatic proton, see figure 1 (*a*). Due to the C_2-symmetric nature of these tetraethers, only one aromatic proton resonance integrating for two protons, and only one phenolic proton resonance integrating for two protons appeared in the ^{1}H NMR spectra. Moreover, no other aromatic or phenolic proton resonances (not even traces) appeared, suggesting that these tetraethers obtained after two recrystallizations are very pure, see figure 1 (*a*). The ^{13}C NMR spectra of these tetraethers showed six aromatic carbon resonances at *c.* δ 158, 157, 141, 129, 112, and 104 ppm, an intramolecularly hydrogen-bonded quinone-carbonyl carbon resonance at *c.* δ 186 ppm, and importantly only two aryloxymethylene carbon resonances at *c.* δ 73.2 and 68.9 ppm, in addition to the methylene and methyl resonances, figure 1 (*b*). Mass spectra of the ethers exhibited the anticipated molecular ion peaks $[(M + 1)^+]$. These spectral features unambiguously confirmed the structure of the tetraethers (DHT*n*A, *n* = 4 … 10) prepared by the method described above.

The tetraethers (DHT*n*A, *n* = 4 … 10) were successfully dibenzylated by a recently described procedure [11]. Thus, by heating a mixture of tetraether, anhydrous potassium carbonate (16 equiv.) and benzyl bromide (12 equiv.) in dimethyl formamide in the presence of a catalytic amount of tetrabutylammonium iodide at 105°C for 20 h, 1,5-dibenzyloxy-2,3,6,7-tetraalkyloxy-9,10-anthraquinones (DBT*n*A, *n* = 4 … 10) in 83–90% yields were obtained. IR spectra of these 1,5-benzylsubstituted ethers exhibit a carbonyl resonance at *c.* 1660 cm^{-1}, which is characteristic of a non-hydrogen-bonded anthraquinone–carbonyl moiety. The ^{1}H NMR spectra of these derivatives showed a singlet resonance at *c.* δ 5.12 ppm integrating for four protons, characteristic of aryloxybenzylic protons, and two triplets at *c.* δ 4.2 and 4.1 ppm integrating for four protons each and, two multiplets in the aromatic region integrating for six protons each, in addition to the methylene and methyl proton resonances, see figure 2 (*a*). The ^{13}C NMR spectra of these derivatives showed a quinone-carbonyl carbon resonance at *c.* δ 181 ppm, six aromatic carbon resonances at *c.* δ 157, 153, 147, 133, 121 and 107 ppm corresponding to the anthraquinone core, four more aromatic carbon resonances at *c.* δ 137, 128.6, 128.3 and 127.9 ppm corresponding to the aromatic carbons of the benzyl groups, and three aryloxymethylene carbon resonances at *c.* δ 75.6, 74.2 and 69.1 ppm, in addition to the methylene and methyl carbon resonances, see figure 2 (*b*). Mass spectra of these ethers showed the anticipated molecular ion peaks $[(M + 1)^+$ or $(M)^+]$. These spectral features unambiguously confirmed the structure of the 1,5-dibenzylated derivatives (DBT*n*A, *n* = 4 … 10).

2.2. *The compounds synthesized*

The structures and codings for the compounds synthesized are given below.
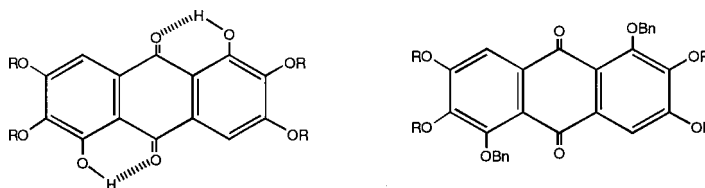
(DHT4A) $R=C_4H_9$; (DHT5A) $R=C_5H_{11}$ (DBT4A) $R=C_4H_9$; (DBT5A) $R=C_5H_{11}$

(DHT6A) $R=C_6H_{13}$; (DHT7A) $R=C_7H_{15}$ (DBT6A) $R=C_6H_{13}$; (DBT7A) $R=C_7H_{15}$

(DHT8A) $R=C_8H_{17}$; (DHT9A) $R=C_9H_{19}$ (DBT8A) $R=C_8H_{17}$; (DBT9A) $R=C_9H_{19}$

(DHT10A) $R=C_{10}H_{21}$ (DBT10A) $R=C_{10}H_{21}$

Structure.

2.3. *General experimental procedures*

Bromoalkanes were received from Merck-Schuchardt. Sulphuric acid, dimethyl sulfoxide, sodium hydroxide, anhydrous potassium carbonate, and tetrabutylammonium iodide were obtained from E Merck (India) Ltd. Gallic acid was obtained locally and dimethyl formamide (HPLC grade) was received from Spectrochem. All these chemicals were used as received. Rufigallol and compound DHT8A were prepared according to the procedures described in [11]. ^{1}H NMR spectra were recorded on a Bruker (Avance DPX) 200 MHz spectrometer using $CDCl_3$ as solvent; ^{13}C NMR spectra were recorded on a Bruker (DRX 500) operating at 125 (^{13}C) MHz spectrometer using $CDCl_3$ as solvent. FTIR spectra were recorded from thin film samples on a Perkin Elmer FTIR (spectrum 1000) spectrometer. Mass spectra were recorded on a JEOL JMS600 instrument. All the new compounds have been characterized by ^{1}H NMR, IR and Mass spectral analyses. Optical observations of the phase behaviours and melting transitions of non-mesogenic compounds were carried out with a Leitz (DMRXP) polarized light microscope attached with a Mettler FP 82 HT hot stage operated by a Mettler FP 90 temperature controller. DSC thermograms were recorded on a Perkin Elmer DSC 7 instrument, at a scanning rate of 5°C min^{-1}, unless otherwise specified.

2.4. *Synthetic procedures*

2.4.1. *1,5-Dihydroxy-2,3,6,7-tetradecyloxy-9,10-anthraquinone (DHT10A)*

A stirred mixture of crude rufigallol (2.5 g, 8.2 mmol), powdered NaOH (1.36 g, 33.9 mmol, 4 equiv.), *n*-bromodecane (7.5 ml, 36.1 mmol, 4.4 equiv.) in DMSO (50 ml) was heated to 70°C and held at that temperature under nitrogen for 18 h. The reaction mixture was cooled in an ice–water bath, diluted with 15 ml of water and filtered. The filter-cake was washed with cold water and dried to give a brown–yellow solid, which was crystallized from chloroform–methanol to give a yellow solid. This was further recrystallized from chloroform–methanol to give DHT10A (2.7 g, 38% yield) as yellow needles (m.p. 109.9–111.2°C). IR: 2922, 2852, 1602, 1466, 1418, 1364, 1327, 1279, 1142, 1091 cm^{-1}; ^{1}H NMR: δ 12.78 (s, 2H), 7.41 (s, 2H), 4.15 (q, 8H, $J = 6.5$ Hz), 2.0–1.75 (m, 8H), 1.65–1.20 (m, 56H), 0.89 (m, 12H) ppm; Mass (FAB): 866.5 $(M + 1)^+$.

The other DHT*n*A compounds were prepared by analogous processes.

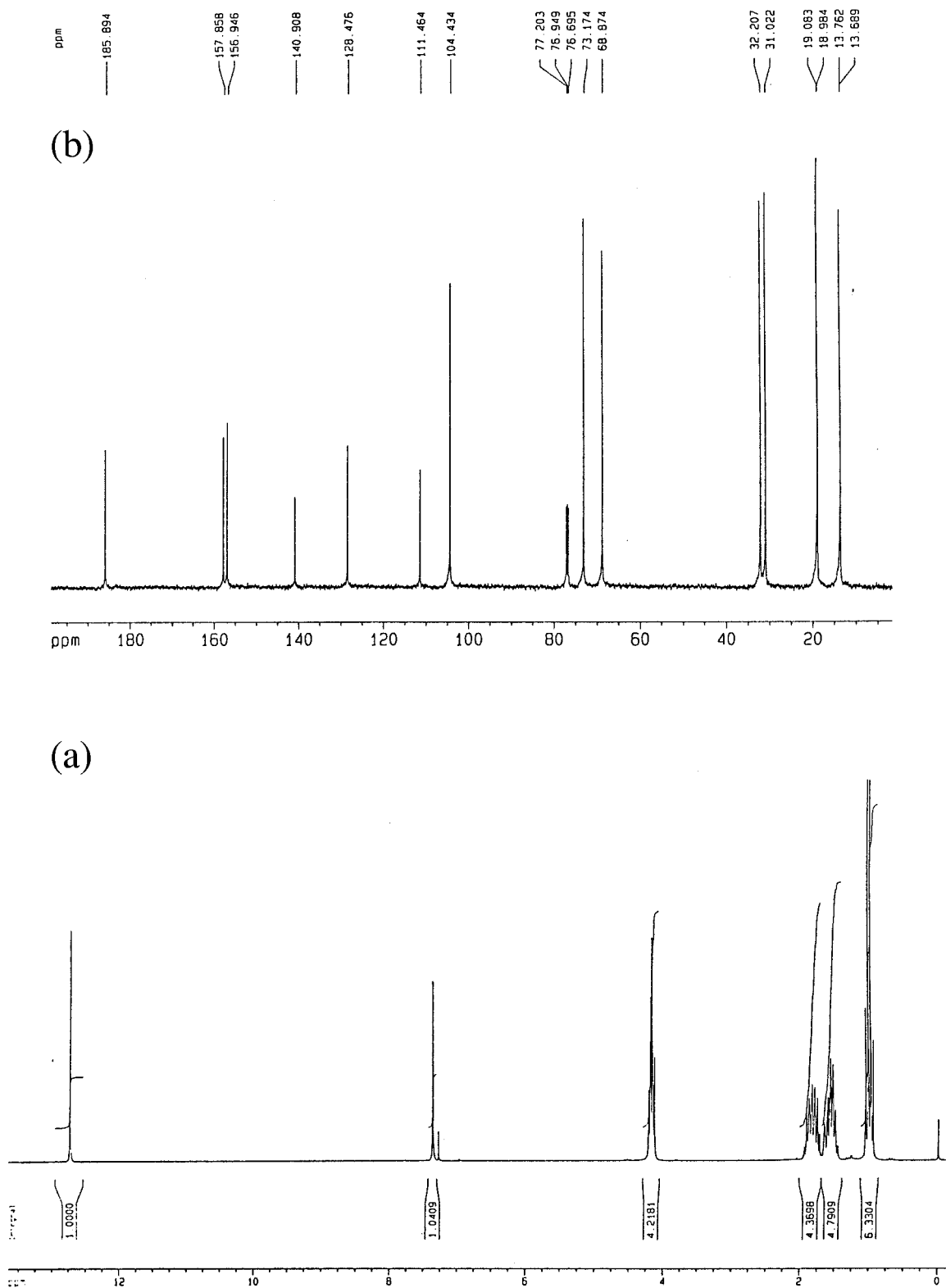### 2.4.2. *1,5-Dihydroxy-2,3,6,7-tetranonyloxy-9,10-anthraquinone (DHT9A)*

Yellow needles (m.p. 109.7–110.8°C) in 38% yield. IR: 2919, 2849, 1600, 1466, 1418, 1364, 1324, 1279, 1141, 1090 cm^{-1}; ^{1}H NMR: δ 12.78 (s, 2H), 7.41 (s, 2H), 4.15 (q, 8H, $J = 6.5$ Hz), 2.0–1.75 (m, 8H), 1.65–1.20 (m, 48H), 0.88 (m, 12H) ppm; Mass (FAB): 809.7 $(M + 1)^+$.

2.4.3. *1,5-Dihydroxy-2,3,6,7-tetraoctyloxy-9,10-anthraquinone (DHT8A)*

The procedure for this compound is given in our earlier paper, [11], but for convenience we give the spectral features of this derivative here also. Elemental analysis: Found C 73.24, H 9.60; $C_{46}H_{72}O_8$ requires C 73.37, H 9.64%; IR: 2923, 2850, 1599, 1466, 1417, 1401, 1362, 1325, 1279, 1140, 1089, 1056 cm^{-1}; ^{1}H NMR: δ 12.78 (s, 2H), 7.41 (s, 2H), 4.16 (quartet, 8H, $J = 6.5$ Hz), 1.90–1.70 (m, 8H), 1.59–1.20 (m, 40H), 0.89 (m, 12H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 186.8, 158.4, 157.6, 141.6, 129.2, 112.2, 105.2, 74.1, 69.8, 32.3, 30.7, 29.8, 29.7, 29.5, 26.4, 26.3, 23.1, 14.5 ppm; Mass (FAB): 754.5 $(M + 1)^+$.

2.4.4. *1,5-Dihydroxy-2,3,6,7-tetraheptyloxy-9,10-anthraquinone (DHT7A)*

Yellow needles (m.p. 108.6–109.8°C) in 29% yield. IR: 2923, 2853, 1600, 1466, 1417, 1401, 1362, 1324, 1279, 1140, 1089 cm^{-1}; ^{1}H NMR: δ 12.78 (s, 2H), 7.41 (s, 2H),
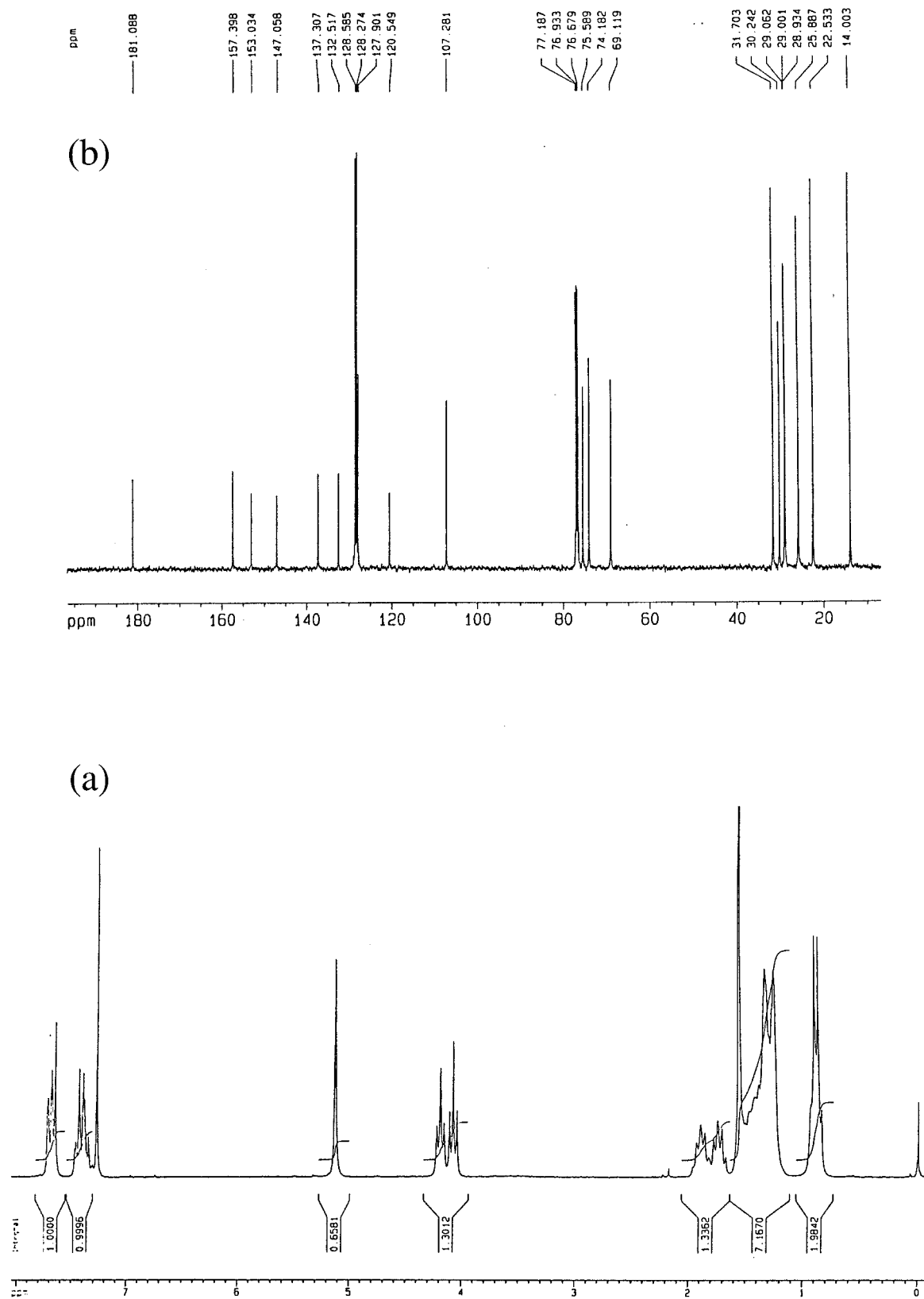
Figure 1. (*a*) ^{1}H NMR (200 MHz, CDCl$_3$) and (*b*) ^{13}C NMR (125 MHz, CDCl$_3$) spectra of DHT4A.

Figure 2. (*a*) ^{1}H NMR (200 MHz, CDCl$_3$) and (*b*) ^{13}C NMR (125 MHz, CDCl$_3$) spectra of DBT7A.

4.16 (q, 8H, $J = 6.5$ Hz), 1.9–1.70 (m, 8H), 1.53–1.20 (m, 32H), 0.89 (m, 12H) ppm; Mass (FAB): 698.2 $(M + 1)^+$.

2.4.5. *1,5-Dihydroxy-2,3,6,7-tetrahexyloxy-9,10-anthraquinone (DHT6A)*

Yellow needles (m.p. 106.5–107.8°C) in 28% yield. IR: 2925, 2852, 1600, 1466, 1417, 1401, 1362, 1326, 1279, 1143, 1090 cm^{-1}; ^{1}H NMR: δ 12.78 (s, 2H), 7.41 (s, 2H), 4.16 (q, 8H, $J = 6.5$ Hz), 1.90–1.70 (m, 8H), 1.53–1.20 (m, 24H), 0.91 (m, 12H) ppm; ^{13}C NMR: δ 186.2, 158.0, 157.1, 141.1, 128.7, 111.7, 104.6, 73.7, 69.3, 31.64, 31.47, 30.2, 29.0, 25.62, 25.54, 22.6, 14.0 ppm; Mass (FAB): 642.3 $(M + 1)^+$.

2.4.6. *1,5-Dihydroxy-2,3,6,7-tetrapentyloxy-9,10-anthraquinone (DHT5A)*

Yellow needles (m.p. 113.1–114.7°C) in 23% yield. IR: 2930, 2856, 1600, 1466, 1417, 1362, 1324, 1281, 1140, 1090 cm^{-1}; ^{1}H NMR: δ 12.78 (s, 2H), 7.41 (s, 2H), 4.16 (q, 8H, $J = 6.5$ Hz), 1.90–1.70 (m, 8H), 1.53–1.20 (m, 16H), 0.94 (m, 12H) ppm; Mass (FAB): 586.2 $(M + 1)^+$.

2.4.7. *1,5-Dihydroxy-2,3,6,7-tetrabutyloxy-9,10-anthraquinone (DHT4A)*

Yellow needles in 20% yield. Elemental analysis: found C 68.10, H 7.69; $C_{30}H_{40}O_8$ requires C 68.16, H 7.63%; IR: 2954, 2868, 1601, 1464, 1417, 1361, 1326, 1278, 1145, 1089 cm^{-1}; ^{1}H NMR: δ 12.78 (s, 2H), 7.41 (s, 2H), 4.10 (q, 8H, $J = 6.5$ Hz), 1.90–1.70 (m, 8H), 1.53–1.20 (m, 8H), 0.94 (m, 12H) ppm; ^{13}C NMR: δ 185.9, 157.9, 156.9, 140.9, 128.5, 111.5, 104.4, 73.2, 68.9, 32.2, 31.0, 19.08, 18.98, 13.76, 13.69 ppm; Mass (EI): 528.3 (M^+). Found to be monotropic, Cr $\rightarrow$ I, 123°C (lit. [9 *b*], reported to be non-mesomorphic, m.p. 120°C).

2.4.8. *1,5-Dibenzyloxy-2,3,6,7-tetradecyloxy-9,10-anthraquinone (DBT10A)*

A stirred mixture of 1,5-dihydroxy-2,3,6,7-tetradecyloxy-9,10-anthraquinone (DHT10A, 217 mg, 0.25 mmol), anhydrous potassium carbonate (553 mg, 4 mmol), benzyl bromide (0.36 ml, 3 mmol) and tetrabutylammonium iodide (75 mg) in dry DMF (8 ml) was heated to 105°C and held at that temperature for 20 h under a nitrogen atmosphere. The reaction mixture was cooled, filtered and the filter-cake was washed with chloroform (200 ml). The combined filtrate and washings were washed with water (3×200 ml) followed by brine (200 ml), and then dried (Na_2SO_4). Solvents were removed to give a yellow oil, which was crystallized from cold chloroform–ethanol to give a yellow solid. The yellow solid was recrystallized once again from cold chloroform–ethanol to yield a yellow solid of pure DBT10A, 225 mg, 86% yield. IR: 2953, 2922, 2858, 1662, 1574, 1464, 1323, 1125 cm^{-1}; ^{1}H NMR: δ 7.71–7.64 (m, 6H), 7.45–7.37 (m, 6H), 5.12

(s, 4H), 4.19 (t, 4H, $J = 6.4$ Hz), 4.07 (t, 4H, $J = 6.4$ Hz), 2.0–1.67 (m, 8H), 1.6–1.15 (m, 56H), 0.88 (t, 12H, $J = 6.7$ Hz); Mass (FAB): 1046.4 $(M + 1)^+$.

The other DBT*n*A compounds were prepared by analogous processes.

2.4.9. *1,5-Dibenzyloxy-2,3,6,7-tetranonyloxy-9,10-anthraquinone (DBT9A)*

Yellow solid in 85% yield. IR: 2954, 2924, 2854, 1664, 1573, 1468, 1322, 1127 cm^{-1}; ^{1}H NMR: δ 7.71–7.64 (m, 6H), 7.42–7.34 (m, 6H), 5.12 (s, 4H), 4.19 (t, 4H, $J = 6.4$ Hz), 4.07 (t, 4H, $J = 6.4$ Hz), 2.0–1.67 (m, 8H), 1.6–1.15 (m, 48H), 0.88 (t, 12H, $J = 6.7$ Hz); Mass (FAB): 991.1 $(M + 1)^+$.

2.4.10. *1,5-Dibenzyloxy-2,3,6,7-tetraoctyloxy-9,10-anthraquinone (DBT8A)*

Yellow solid in 89% yield. IR: 2953, 2923, 2855, 1662, 1574, 1464, 1323, 1125 cm^{-1}; ^{1}H NMR: δ 7.71–7.64 (m, 6H), 7.45–7.37 (m, 6H), 5.12 (s, 4H), 4.19 (t, 4H, $J = 6.4$ Hz), 4.07 (t, 4H, $J = 6.4$ Hz), 2.0–1.67 (m, 8H), 1.6–1.15 (m, 40H), 0.88 (t, 12H, $J = 6.7$ Hz); Mass (FAB): 934.9 $(M + 1)^+$.

2.4.11. *1,5-Dibenzyloxy-2,3,6,7-tetraheptyloxy-9,10-anthraquinone (DBT7A)*

Yellow solid in 90% yield. IR: 2954, 2927, 2856, 1663, 1573, 1321, 1125 cm^{-1}; ^{1}H NMR: δ 7.75–7.64 (m, 6H), 7.51–7.32 (m, 6H), 5.12 (s, 4H), 4.19 (t, 4H, $J = 6.5$ Hz), 4.07 (t, 4H, $J = 6.5$ Hz), 1.98–1.70 (m, 8H), 1.65–1.15 (m, 32H), 0.90–0.84 (m, 12H) ppm; ^{13}C NMR: δ 181.1, 157.4, 153.0, 147.1, 137.3, 132.5, 128.6, 128.3, 127.9, 120.6, 107.3, 75.6, 74.2, 69.1, 31.7, 30.2, 29.06, 29.0, 28.93, 25.9, 22.5, 14.0 ppm; Mass (FAB): 878.4 $(M + 1)^+$.

2.4.12. *1,5-Dibenzyloxy-2,3,6,7-tetrahexyloxy-9,10-anthraquinone (DBT6A)*

Yellow solid in 83% yield. IR: 2930, 1664, 1573, 1322, 1126 cm^{-1}; ^{1}H NMR: δ 7.75–7.64 (m, 6H), 7.51–7.32 (m, 6H), 5.12 (s, 4H), 4.19 (t, 4H, $J = 6.5$ Hz), 4.07 (t, 4H, $J = 6.5$ Hz), 1.98–1.70 (m, 8H), 1.65–1.15 (m, 24H), 0.90–0.84 (m, 12H) ppm; ^{13}C NMR: δ 181.1, 157.4, 153.0, 147.1, 137.3, 132.5, 128.6, 128.3, 127.9, 120.6, 107.3, 75.6, 74.2, 69.1, 31.57, 31.42, 30.19, 30.0, 25.6, 22.5, 13.9 ppm; Mass (FAB): 822.4 $(M + 1)^+$.

2.4.13. *1,5-Dibenzyloxy-2,3,6,7-tetrapentyloxy-9,10-anthraquinone (DBT5A)*

Yellow solid in 87% yield. IR: 2955, 2872, 1663, 1573, 1322, 1125 cm^{-1}; ^{1}H NMR: δ 7.75–7.64 (m, 6H), 7.51–7.32 (m, 6H), 5.12 (s, 4H), 4.19 (t, 4H, $J = 6.5$ Hz), 4.08 (t, 4H, $J = 6.5$ Hz), 1.98–1.70 (m, 8H), 1.65–1.15 (m, 16H), 0.99–0.85 (m, 12H) ppm; Mass (FAB): 764.8 $(M)^+$.

2.4.14. *1,5-Dibenzyloxy-2,3,6,7-tetrabutyloxy-*
 9,10-anthraquinone (DBT4A)

Yellow solid in 84% yield (m.p. 185.4–186.7°C). IR: 3054, 2960, 2875, 1665, 1571, 1319, 1129 cm^{-1}; ^{1}H NMR: δ 7.75–7.64 (m, 6H), 7.51–7.32 (m, 6H), 5.12 (s, 4H), 4.19 (t, 4H, $J = 6.5$ Hz), 4.07 (t, 4H, $J = 6.5$ Hz), 1.98–1.23 (m, 16H), 1.01 (t, 6H, $J = 7.3$ Hz), 0.92 (t, 6H, $J = 7.3$ Hz) ppm; Mass (FAB): 710 (M + 1)$^{+}$.

3. Phase characterization results and discussion
3.1. *Polarized light microscopic studies*

Optical microscopic observations of the dihydroxy-tetraethers (DHTnA, $n = 4 \ldots 10$) showed that all except the lowest homologue are non-mesomorphic. 1,5-Dihydroxy-2,3,6,7-tetrabutyloxy-9,10-anthraquinone, DHT4A, exhibited a monotropic mesophase over a 23° temperature range, contradicting an earlier report [9b] that this compound is non-mesomorphic.

Among the synthesized dibenzyloxytetraalkyloxy-anthraquinone derivatives (DBTnA, $n = 4 \ldots 10$), the lowest homologue (DBT4A) is non-mesogenic (m.p. 185.4–186.7°C), the next higher homologue (DBT5A) exhibits a monotropic columnar mesophase, and all the others (DBTnA, $n = 6, 7 \ldots 10$) exhibit enantiotropic columnar mesophases. The microscope slide preparations of solution-crystallized samples of homologues DBT6A, DBT8A and DBT10A are found to deform easily under stress at room temperature, suggesting that they are in a mesomorphic state. On the other hand, similar preparations of DBT7A and DBT9A are found hardly to deform under stress, suggesting that they are in a crystalline phase at room temperature.

The textures obtained for the homologues (DBTnA, $n = 5 \ldots 10$), while cooling from the isotropic liquid are typical columnar textures with largely homeotropic regions and some π-disclination-like regions (figure 3).
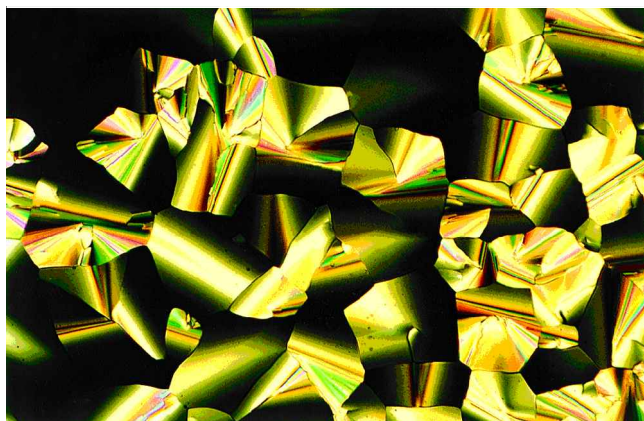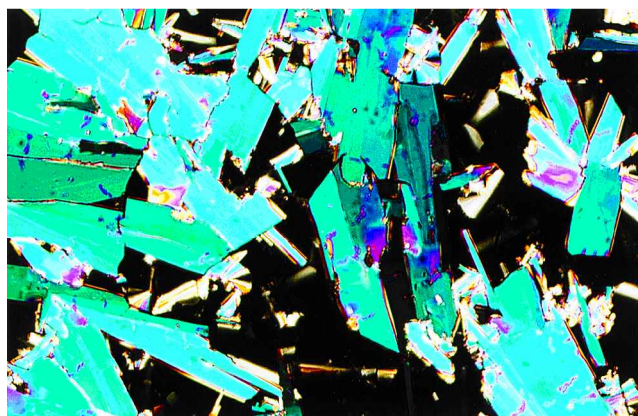

Figure 4. Mosaic domains observed under the polarized light microscope for a sample of DBT8A left at room temperature for several months after a few heating–cooling cycles.

The textures are very similar to those observed in anthraquinone hexaethers [11], alkoxytriphenylene and thioalkoxytriphenylenes, suggesting the presence of a hexagonal columnar phase (Col$_h$). Interestingly, while cooling from the columnar phase, the textures are almost preserved even across the other transitions, with only the formation of some cracks over the textures, and there is no sign of crystallization. A sample prepared by mixing (1:1 molar ratio) compound DBT8A and 1,5-didecyloxy-2,3,6,7-tetraoctyloxy-9,10-anthraquinone which is known to form the Col$_h$ phase [11], was analysed under the microscope. It was found that while heating, the mixture showed an isotropic transition at 111–116°C and, while cooling from the isotropic liquid it gave a columnar texture at 115–110°C which remained until room temperature was reached. These observations further suggest that the high temperature phase exhibited by these derivatives could be the Col$_h$ phase.

A microscope slide preparation of a solution-crystallized sample of DBT8A, left at room temperature for several months after a few heating–cooling cycles, showed the development of mosaic domains in many regions (figure 4)†, suggesting that the low-temperature phase could be a three-dimensionally ordered phase. Thus, the textural observations suggest that the high temperature mesophase could be hexagonal columnar (Col$_h$) and the low-temperature one three-dimensionally ordered (Col$_x$). X-ray diffraction studies would ascertain the precise nature of the phases.

Figure 3. Texture observed under the polarized light microscope for DBT8A at 121.6°C, obtained after cooling from the isotropic.

† This behaviour is similar to that observed in hexahexyl-thiotriphenylene although the mosaic domains will quickly start forming out of largely homeotropic texture when cooled from the Col$_h$ phase to the highly ordered helical phase (H).

3.2. *Differential scanning calorimetric studies*

DSC thermograms of 1,5-dihydroxy-2,3,6,7-tetra-butyloxy-9,10-anthraquinone (DHT4A) for different runs are given in figure 5. As seen in figure 5, the heating run which is started from the mesomorphic state exhibits an isotropic transition different from that observed in the first heating (of a solution-crystallised sample), confirming the presence of a monotropic columnar phase [9(b)] as indicated by the polarized light microscopic observations. To our knowledge, this is the first report of a columnar phase in an anthraquinone-based disc-like molecule having only four alkyl chains attached to the core.

The DSC data of dibenzyloxytetraalkyloxyanthra-quinones (DBT nA, $n = 5 \ldots 10$) are presented in the table. The first heating thermograms for all the homologues which exhibit enantiotropic mesomorphic behaviour, and the first cooling thermogram for the mesogen which
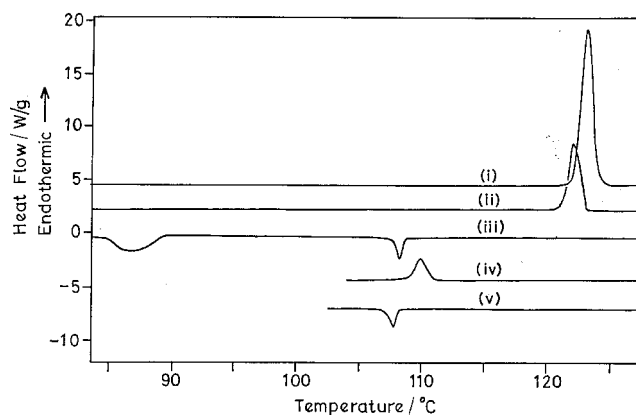

Figure 5.   DSC thermograms for (i) the first heating, (ii) second heating, (iii) first cooling, (iv) heating from the mesophase to isotropic, and (v) cooling from the isotropic to mesophase runs of DHT4A. The DSC runs, (iii), (v) were recorded at a rate of 5°C min^{-1}; (i), (ii) and (iv) were recorded at a rate of 10°C min^{-1}.

Table.   DSC data for the 1,5-benzyloxy-2,3,6,7-tetraalkyloxy-9,10-anthraquinones (DBT nA series). Temperatures are in °C, enthalpies (in brackets) are in kJ mol^{-1}.

Compound number	Run	$Cr \rightarrow Col_x$ (or) $Cr \rightarrow I$ on heating. $Col_h \rightarrow Cr$ (or) $Col_x \rightarrow Cr$ on cooling.	$Col_x \rightarrow Col_h$ on heating. $Col_h \rightarrow Col_x$ on cooling.	$Col_h \rightarrow I$ on heating. $I \rightarrow Col_h$ on cooling.
DBT5A		171.9[a] (36.2)		—
	1st heating	153.6[b] (− 17.3)		167.2[c] (− 16.0)
	1st cooling	171.9[a] (35.7)		—
	2nd heating			167.2 (− 15.7)
	2nd cooling			168.6[d] (15.0)
	Heating from mesophase			
DBT6A	1st heating	—	135.8 (14.4)	151.0 (14.8)
	1st cooling	—	121.3 (− 11.2)	149.8 (− 14.7)
	2nd heating	—	133.9 (13.1)	151.1 (14.7)
DBT7A	1st heating	77.0[e] (58.1)	128.9 (13.9)	143.5 (14.8)
	1st cooling	—	113.6 (− 9.4)	142.0 (− 14.6)
	2nd heating	—	127.7 (11.9)	143.5 (14.3)
DBT8A	1st heating	—	121.4 (9.4)	137.0 (14.6)
	1st cooling	—	104.7 (− 7.0)	135.5 (− 14.0)
	2nd heating	—	119.8 (9.4)	137.0 (14.4)
DBT9A	1st heating	84.2[f] (79.7)	104.8 (4.1)	132.1 (13.7)
	1st cooling	—	92.4 (− 3.5)	130.3 (− 13.8)
	2nd heating	—	105.6 (4.4)	132.1 (13.8)
DBT10A	1st heating	—	92.8 (3.3)	129.6 (15.0)
	1st cooling	—	74.8 (− 2.4)	127.3 (− 14.7)
	2nd heating	—	91.7 (3.0)	129.6 (15.0)

[a] $Cr \rightarrow I$ transition.
[b] $Col_h \rightarrow Cr$ transition.
[c] $I \rightarrow Col_h$ transition.
[d] Second isotropic transition ($Col_h \rightarrow I$).
[e] $Cr \rightarrow Col_x$ transition.
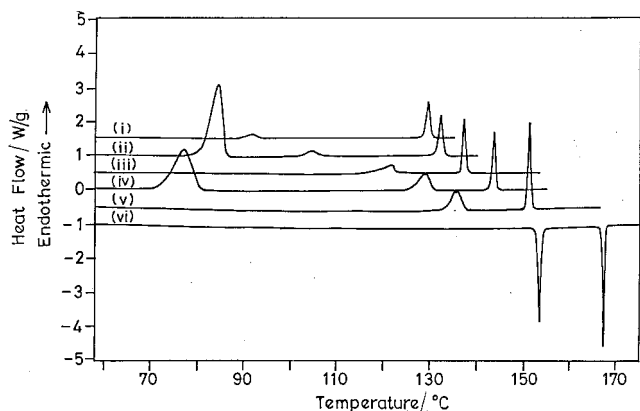[f] $Cr \rightarrow Col_x$ transition.

Figure 6. DSC thermograms for the first heating runs of compounds DBTnA, $n = 6, 7 \dots 10$, and first cooling run of compound DBT5A. The DSC runs were recorded at a heating/cooling rate of 5°C min^{-1}. (i)–(vi) correspond to the compounds DBT10A, DBT9A, DBT8A, DBT7A, DBT6A and DBT5A respectively.
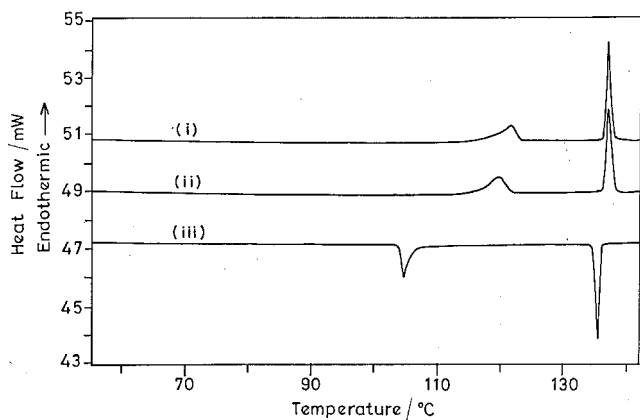

Figure 7. DSC thermograms for (i) the first heating, (ii) second heating, and (iii) first cooling runs of compound DBT8A. The DSC runs were recorded at a heating/cooling rate of 5°C min^{-1}.

exhibits a monotropic behaviour are shown in figure 6. DSC thermograms of homologues, DBT6A, DBT8A and DBT10A show two endothermic transitions, $Col_x \rightarrow Col_h$ and $Col_h \rightarrow I$ in the heating runs, which are reversible in nature as we can see the corresponding transitions, $I \rightarrow col_h$ and $Col_h \rightarrow Col_x$ in the cooling runs (see figure 7). There were no crystallization transitions observed until -50°C†. The low enthalpies of the first transitions of the homologues, DBT6A, DBT8A and DBT10A during the first heating support the polarized light microscopic observations that they exist in a highly ordered columnar phase (Col_x) rather than crystalline phase at room temperature. On the other hand, homologues DBT7A and DBT9A show three endothermic transitions (the

† This is the lowest temperature we could reach in the DSC runs.

first one being very strong) in the first heating runs, namely $Cr \rightarrow Col_x$, $Col_x \rightarrow Col_h$ and $Col_h \rightarrow I$. But, while cooling from the isotropic liquid, we find only two transitions, $I \rightarrow Col_h$ and $Col_h \rightarrow Col_x$ (figure 8) and, we do not see any crystallization transition until -50°C. Moreover, transitions corresponding to the crystal melting transitions ($Cr \rightarrow Col_x$) observed in the first heating runs did not appear in the second and subsequent heating runs. The high enthalpies of the first very strong transitions in the first heating runs of homologues DBT7A and DBT9A support the polarized light microscopic observations that they exist in a crystalline phase at room temperature.

Finally, a sample prepared by mixing (1:1 molar ratio) compound DBT8A and 1,5-didecyloxy-2,3,6,7-tetra-octyloxy-9,10-anthraquinone—the latter is known to form the Col_h phase [11]—was analysed by DSC (figure 9). A single endothermic transition ($M \rightarrow I$) was found at
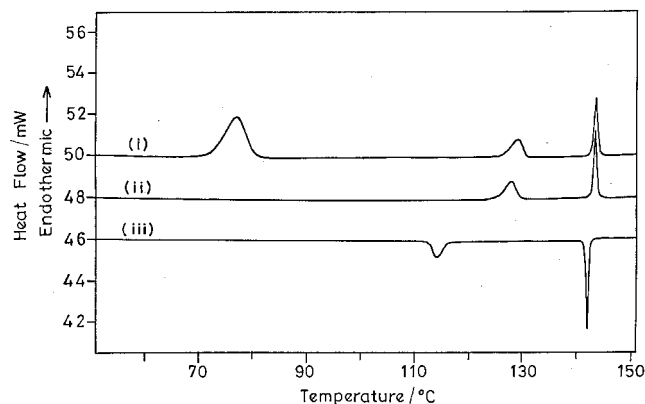

Figure 8. DSC thermograms for (i) the first heating, (ii) second heating, and (iii) first cooling runs of compound DBT7A. The DSC runs were recorded at a heating/cooling rate of 5°C min^{-1}.
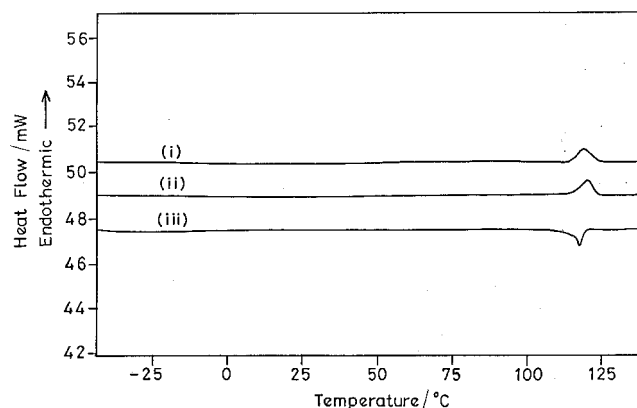

Figure 9. DSC thermograms for (i) the first heating, (ii) second heating, and (iii) first cooling runs of a 1:1 mixture of DBT8A and 1,5-didecyloxy-2,3,6,7-tetraoctyloxy-9,10-anthraquinone. The DSC runs were recorded at a heating/cooling rate of 10°C min^{-1}.

118°C (enthalpy, 13.6 kJ mol^{-1}) during the first heating, and the corresponding exothermic transition $(I \rightarrow M)$ was the only transition found (117.4°C, enthalpy, -12.7 kJ mol^{-1}) until -50°C during the first cooling run. The second heating thermogram was similar to the first heating and it showed an endothermic transition $(M \rightarrow I)$ at 119.9°C (enthalpy, 13.0 kJ mol^{-1}). The complete mixing of these two compounds in the mesophase is similar to that observed in the case of the 1:1 mixture of rufiganoll hexaoctanoate and triphenylene hexaoctanoate [8(*a*, *b*)]. Hence, the thermal behaviour of the mixture studied supports the proposal that the high temperature mesophase of these novel benzyl derivatives could be a Col_h phase.

In general, within this homologous series, the high temperature hexagonal columnar phase (Col_h) becomes stabilized as the alkoxy chain lengths are increased. The enthalpy of $Col_x \rightarrow Col_h$ decreases with increase in alkoxy chain length. The transition temperatures of $Col_h \rightarrow I$ of these homologues are significantly higher than those of the corresponding symmetrical hexaethers [9(*a*)]. They are significantly higher, even when one compares the transition temperature of the homologue with the longest chain in this series, DBT10A, with that of the short chain homologue of symmetrical hexaethers, e.g. 1,2,3,5,6,7-hexahexyloxy-9,10-anthraquinon e [9(*a*)]. Further, the enthalpies of $Col_h \rightarrow I$ of the benzyl substituted derivatives were also found to be significantly higher than those of corresponding symmetrical hexaethers [9(*a*)]. These characteristics suggest that the substitution of the benzyl groups for alkyl chains at the 1,5-positions of anthraquinone hexaethers increases the interaction between the molecular cores, although no group with a strong dipole moment is present in the substitution. This behaviour may be contrasted with that found in the phenyl substituted triphenylene system, through a carbonyloxy linkage, where the $Col_h \rightarrow I$ transition temperature is significantly lowered and the Col_h mesophase range widened [12] (crystallization is suppressed until room temperature and it is not known whether there is any three-dimensionally ordered mesophase below room temperature). However, the behaviour observed here is rather similar to that observed in triphenylene systems with one alkoxy chain substituted with more bulkier groups namely, triflate, pivaloate and adamantanoate, where the Col_h phase is destabilized and a three-dimensionally ordered mesophase induced. In this novel homologous series, the $Col_h \rightarrow I$ transition temperatures decrease when the length of the alkoxy chains increases, as observed in other discotic systems including the anthraquinone-based systems. The $Col_x \rightarrow Col_h$ transition temperatures and enthalpies decrease with increase in alkoxy chain length.

Detailed X-ray diffraction studies with aligned and monodomain samples would show whether the columns containing long range order are arranged in a 2D hexagonal or rectangular lattice; these are in progress. Further it would show whether there is helical symmetry within the columns. It would also be interesting to probe the dynamics of the molecular rotations across the $Col_h \rightarrow Col_x$ transition with quasi-elastic neutron scattering, to determine whether the benzyl group substituents have nearly independent rotation in the Col_h phase and how that induces the transition [13].

4. Conclusions

We have prepared a novel series of anthraquinone-based discotic liquid crystalline compounds with bulky benzyl substituents at the 1,5-positions through an ether linkage, without destroying the C_2-symmetry, providing the first example of such substitution in a discotic C_2-symmetric molecule. All the homologues (DBT*n*A, $n = 4 \ldots 10$), except the lowest (DBT4A) exhibit the hexagonal columnar phase (Col_h) at high temperature and a three-dimensionally ordered columnar phase (Col_x) at low temperature, the latter extending down to -50°C. However, the exact nature of the phases, especially the phase designated as Col_x can be ascertained only by detailed X-ray diffraction studies, which are currently in progress. The introduction of bulky benzyl substituents at the 1,5-positions of the anthraquinone core stabilizes the low temperature three-dimensionally ordered mesophase (Col_x) whereas it destabilizes the high temperature columnar phase (Col_h), when compared with the anthraquinone hexaalkoxylates. This behaviour is at variance with a triphenylene system substituted by a phenyl group in place of one alkoxy chain out of the six attached to the core but linked through a carbonyloxy group. We believe the present work will stimulate studies of the dynamics of molecular rotations across the phase transition, $Col_h \rightarrow Col_x$.

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