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An Efficient Synthesis, and Characterisation of Anthraquinone-based Discotic Liquid Crystals and Their X-Ray Diffraction Studies

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An Efficient Synthesis, and Characterisation of Anthraquinone-based Discotic Liquid Crystals and Their X-Ray Diffraction Studies*

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We herein report an efficient synthesis of 1,2,3,5,6,7-hexaalkoxy-9,10-anthraquinones (also called rufigallol hexaethers) starting from gallic acid. These ethers are known to form columnar phases which are suitable for the study of charge transport, photoconductivity etc. Our X-ray diffraction studies show that the high-temperature mesophase is hexagonal columnar with correlation among the molecular cores along the column (Col_h, also called D_h), and that, identified for the first time in these systems, there are one or two additional mesophases at low temperature depending on the system, some of them three-dimensionally ordered. Our results show that the mesophase (high-temperature) range does not dramatically decrease as the length of the alkyl chains at the 1,5 positions become longer than the rest. Since these molecules have absorption in the visible region they may also be the potential candidates for studying photovoltaic effects that are of interest in developing energy conversion applications.

Keywords: Discotic liquid crystals; columnar phases; x-ray diffraction; anthraquinone; rufigallol

I. INTRODUCTION

Since the discovery of discotic liquid crystals [1], a very large number of molecules have been found to form columnar mesophases. Recently, there has been significant interest in designing and synthesizing discotic liquid crystals suitable for applications in molecular electronics, based on their quasi-one-dimensional electrical (p-type and n-type) conductivity, photoconductivity and so on. Hexa-substituted triphenylene derivatives with alkoxy chains [2] or thioalkyl

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chains [3] that form columnar phases ($D_h$or Col_h) in which good positional correlation exists among the molecular cores along the column have been shown to exhibit high conductivity along the columns, on doping with electron-acceptors such as Lewis acids, iodine, and trinitroflourenone, with the highest conductivity among them reaching 10^{-1} S/m. Tricycloquinazolines that form similar columnar phases have been shown to reach a conductivity of $\sim 10^{-5}$ S/m after doping with electron-donors such as potassium [4]. Recently, columnar phases (D_r or Col_r) formed by tetra-thia-fulvalene derivatives have also been reported to exhibit high conductivity along the columns on doping with the electron-acceptor [5], $SbCl_5$. In triphenylene alkoxy systems photoconductivity studies have also been carried out with white light illumination [6], though they do not have strong absorption in the visible region.

Carfagna *et al.* reported rufigallol hexaalkoxylates [7] forming a hexagonal columnar phase possessing a mean separation of 3.6Å between the molecular cores along the columns (obtained from the x-ray diffraction photographic studies). Very recently, Raja *et al.* [8] reported a three-step synthetic sequence which can also be used for the synthesis of these. The mean separation of the cores lies in the range of values observed for the homologous series of triphenylene ethers. This suggests that rufigallol hexaalkoxylates would also be good candidates for studying charge transport and photoconductivity properties. Since they have absorption in the visible region they may be potential candidates for studying photovoltaic effects that are also of interest in developing energy conversion applications.

Carfagna *et al.* synthesised the rufigallol hexaalkoxylates which have all the six alkyl chains of equal length. Raja *et al.* reported the synthesis of rufigallol hexaethers with alkyl chains of two different lengths; those in the two positions (1,5) β- to the anthraquinone carbonyl-carbons of one length and those in the other four positions (2,3,6, and 7) a different length. Raja *et al.* have elegantly used the difference in the reactivity of the two different kinds of phenoxyl groups to achieve this [8]. Their method can also be used to make the hexaethers with all six alkyl chains of equal length. We herein report an efficient synthetic method to prepare the hexaethers of anthraquinone forming columnar liquid crystals.

II. EXPERIMENTAL METHODS

A) Synthesis

Our synthetic sequence is depicted in scheme 1. Acid-mediated dimerisation of gallic acid using conc. H_2SO_4 at 100°C gave the crude rufigallol in 49% yield.

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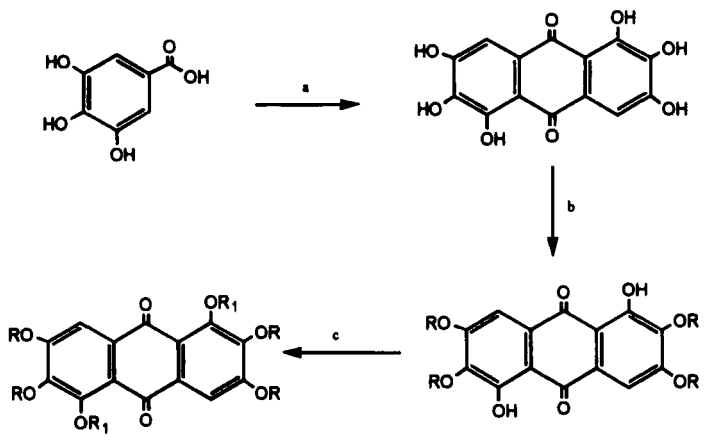
The crude rufigallol upon treatment with powdered NaOH (4 equiv.), bromooctane (4.4 equiv.) in DMSO at 70°C for 18h gave the C_2-symmetric tetraether **(DHT8A)** in 30% yield. The melting point of the recrystallised **(DHT8A)** was found to be 107.4–108.8°C (uncorrected, lit. 111°C) when we checked under the microscope at a heating rate of 2°C per minute. The IR spectrum of recrystallised tetraether **(DHT8A)** showed an absorbtion peak at 1599 cm^{-1}, characteristic of an intramolecularly hydrogen-bonded anthraquinone-carbonyl moiety and the mass spectrum (FAB) showed a molecular ion peak at 754.5 $(M+1)^+$. The PMR spectrum of the tetraether **(DHT8A)** showed a singlet resonance at δ 12.78 ppm integrating for two protons, characteristic of an intramolecularly hydrogen-bonded phenoxyl hydrogen and another singlet resonance at δ 7.41 ppm corresponding to the two aromatic protons in addition to the phenoxymethylene, methylene and methyl resonances and, we do not see any other resonances in the aromatic region (not even traces). The CMR spectrum of **(DHT8A)** showed (fig. 1a) an intramolecularly hydrogen-bonded quinone-carbonyl-carbon resonance at δ 186.8 ppm., six aromatic carbon resonances at δ 158.4, 157.6, 141.6, 129.2, 112.2, 105.2, ppm and, more importantly only two aryloxymethylene-carbon resonances at δ 73.2 and 68.9 ppm in addition to the methylene- and methyl-carbon resonances. If there were any detectable quantity of tri- or penta-octylated product present in the purified tetraether, one would see more than six aromatic-carbon resonances but we do not see any more aromatic-carbon resonances. In addition, if there were any detectable quantity of penta-octylated product present in the purified tetraether one would see a carbonyl resonance at *ca.* δ 182 ppm, (*cf.* fig 1b and 1c) but we do not see any such resonances in that region. These spectral features (IR, Mass, PMR and CMR) and the actual combustion analysis data obtained (*cf.* Synthetic procedures) for the tetraether confirm the structure as well as purity of the tetraether **(DHT8A)** unambiguously. We believe that the regio- or site-selectivity in the tetraoctylation reaction is due to the labile nature of the octyloxy substituents at the activated 1,5 positions of the rufigallol-core under (NaOH/DMSO/ Δ 70°C)-conditions rather than the pKa difference between the protons of two kinds (hydrogen-bonded and non-hydrogen-bonded phenolic hydrogens). In other words, we believe that during the reaction the octylation does occur at 1,5 positions also, but the octyl groups at these very reactive positions (1,5) easily get cleaved back to the sodium phenoxide under the tetraoctylation reaction conditions.

In our view, for the preparation of hexaethers one does not have to convert [8] the tetraether **(DHT8A)** to the corresponding 1,5-diacetylated-**(DHT8A)** unless the tetraether **(DHT8A)** has some serious solubility problems. Because, whether one starts with a phenol or acetate, the reactive intermediate is going to be the



a) Conc. H_2SO_4, 100°C, 2.5h, 49%; b) R-Br (4 eq.), NaOH (4 eq.), DMSO, 70°C, 18h, 30%;

c) R1-Br (12 eq.), K_2CO_3 (16 eq.), KI or n-Bu_4NI (cat.), DMF, 105°C, 20h, 77-86%.

SCHEME 1

same potassium phenoxide. As long as the potassium phenoxide is formed effectively (either by deacetylation or by deprotonation), the alkylation (S_N2 displacement) will go successfully. Thus, tetraether **(DHT8A)** when subjected to direct alkylation with bromoalkanes (16 equiv.), in the presence of K_2CO_3 (12 equiv.) and a catalytic amount of potassium iodide or tetrabutylammonium iodide in DMF at 105°C for 20h, afforded the C_2-symmetric hexaethers **(DmT8A)** in 77–86% yield. In our experience, duration of this reaction and, especially work-up of this reaction plays a crucial role in getting the pure hexaethers without any contamination with pentaalkylated products. The IR spectra of the hexaethers **(DmT8A)** showed an absorption peak at *ca.* 1664 cm^{-1} characteristic of a non-hydrogen-bonded anthraquinone-carbonyl moiety. The mass spectra of these hexaethers **(DmT8A)** supported the formation of hexaethers by showing the expected $(M+1)^+$ peaks. The PMR spectra of these ethers exhibited a singlet at δ 7.59 ppm integrating for two protons corresponding to the aromatic protons in addition to the phenoxymethylene, methylene and methyl resonances. It is important to note the difference in the chemical shifts between an aromatic proton present in an aromatic ring bearing a free phenolic group (*e.g.* tetraoctyl derivative, the aromatic protons resonate at *ca.* δ 7.41 ppm) and the aromatic proton present in a corresponding alkylated product (*e.g.* the hexaethers, where they

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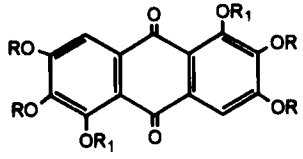
resonate at δ 7.59 ppm). PMR spectra of all the six hexaethers synthesised here were carefully analysed and found that there were no resonances appeared (not even traces) at δ 12.78 ppm or around that region and also no other resonances appeared above 7.26 ppm ($CHCl_3$) except the aromatic singlet resonance of the hexaethers at δ 7.59 ppm. Finally, all the hexaethers synthesised were characterised by CMR spectra in order to confirm the structure and purity of these homologues. The CMR spectra of these ethers (fig. 1b and 1c) showed six aromatic-carbon resonances at *ca.* δ 158, 155, 148, 133, 121, and 108 ppm, only one quinone-carbonyl-carbon resonance at *ca.* δ 182 ppm, and three aryloxymethylene-carbon resonances at *ca.* δ 75.4, 74.8, and 69.8 ppm in addition to the methylene- and methyl-carbon resonances. These spectral features (IR, Mass, PMR, and CMR) and the actual combustion analyses data obtained (*cf.* Synthetic procedures) for these hexaethers confirm the structure as well as purity of each and every hexaether synthesised here unambiguously.

B) Synthesised compounds



(D7T8A): R=C_8H_{17}; R_1=C_7H_{15}; **(H8A): R=C_8H_{17}; R_1=C_8H_{17}**

(D9T8A): R=C_8H_{17}; R_1=C_9H_{19}; **(D10T8A): R=C_8H_{17}; R_1=$C_{10}H_{21}$**

(D11T8A): R=C_8H_{17}; R_1=$C_{11}H_{23}$.

C) General experimental procedures

Bromoalkanes were received from Merck-Schuchardt. Sulfuric acid, dimethyl sulfoxide, sodium hydroxide, anhydrous potassium carbonate, potassium iodide and tetrabutylammonium iodide were obtained from E-Merck (India) ltd. Gallic acid was obtained locally and dimethyl formamide (HPLC grade) was received

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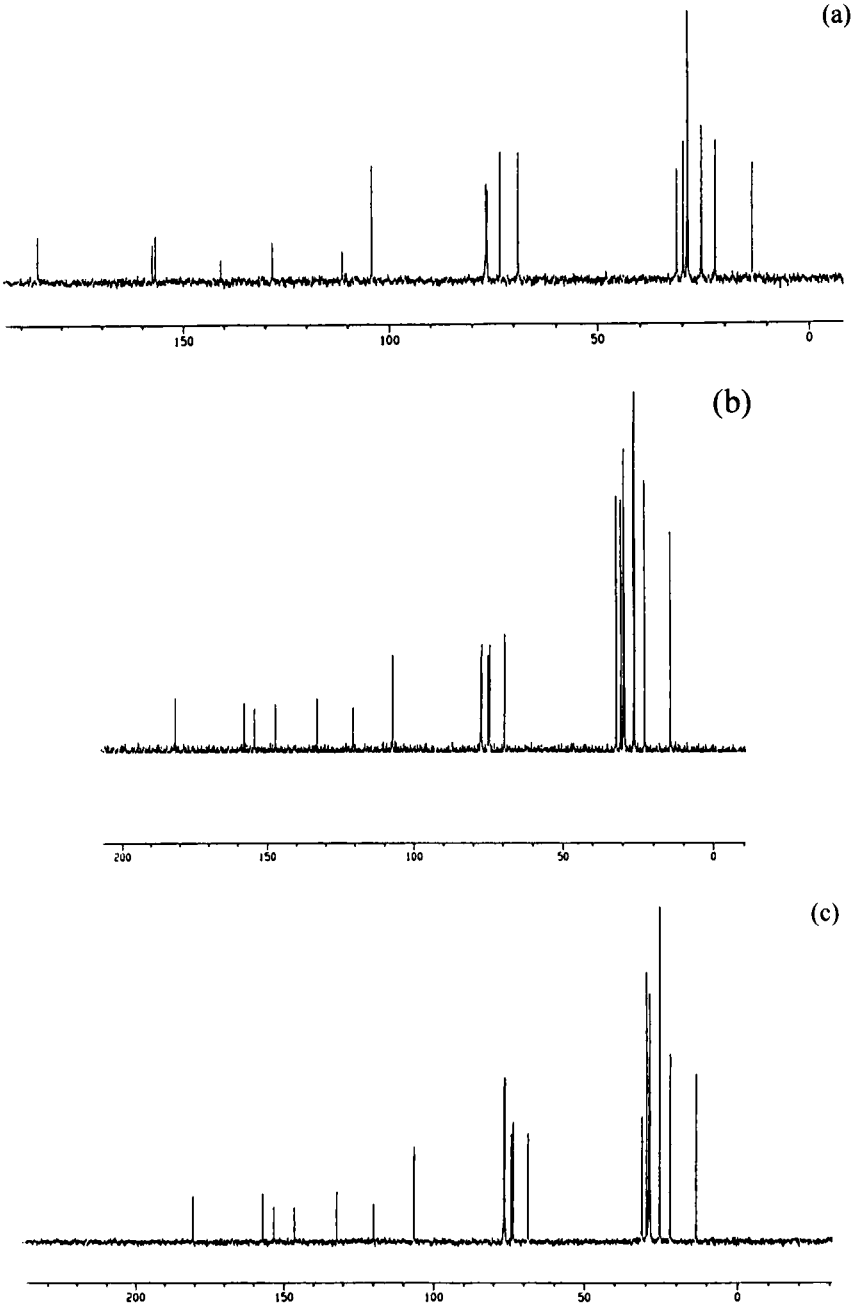

FIGURE 1 CMR (125 MHz, $CDCl_3$) spectra of (a) **DHT8A**, (b) **H8A**, and (c) **D10T8A**

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from Spectrochem. All the chemicals mentioned above were used as received. Unless otherwise noted, concentration of solutions was accomplished by rotary evaporation at water aspirator pressures. PMR spectra were recorded on a Bruker (Avance DPX 200) 200 MHz spectrometer using $CDCl_3$ as solvent, and FT-IR were recorded as thin film on a Perkin Elmer FT-IR (spectrum 1000) spectrometer. CMR spectra were recorded either on a Bruker (DRX 500) operating at 125 (^{13}C) MHz or a Bruker (AMX 400) operating at 100 (^{13}C) MHz spectrometer using $CDCl_3$ as solvent. Mass spectra were recorded on a JEOL JMS600 instrument. Combustion analyses were carried out by Atlantic Microlab, Inc., Norcross, Georgia, U.S.A. Samples for combustion analyses were dried at room temperature under high vacuum for 36 hours just before analysing them. All the new compounds have been characterised by PMR, CMR, IR and Mass spectral analyses. Optical observations of the phase transitions and melting transitions of non-mesogenic compounds were carried out with a Leitz (DMRXP) polarised-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 Differential Scanning Calorimeter (DSC 7) instrument, at a scanning rate of 10° per minute unless otherwise specified and the peak-position values are given as the transition-temperature.

D) Synthetic procedures

1,2,3,5,6,7-Hexahydroxy-9,10-anthraquinone (rufigallol)

A stirred mixture of gallic acid (20 g) and conc. H_2SO_4 (60 mL) was heated at 100°C for 2.5 h. The reaction mixture was cooled and poured into crushed ice to give a brown solid, which was filtered and the filter-cake was washed with cold water (four times), and dried under high vacuum for 36 h to yield crude rufigallol as a brown solid (8 g, 49%). The crude rufigallol was used in the subsequent steps without any further purification.

1,5-Dihydroxy-2,3,6,7-tetraoctyloxy-9,10-anthraquinone DHT8A

A stirred mixture of crude rufigallol (2.5 g, 8.2 mmol), powdered NaOH (1.36 g, 33.9 mmol, 4 equiv.), bromooctane (6.2 mL, 36.1 mmol, 4.4 equiv.) in DMSO (50 mL) was heated at 70°C under nitrogen atmosphere for 18 h. The reaction mixture was cooled on an ice-water bath and diluted with 15 mL of water and filtered. The filter-cake was washed with cold water and dried to give a brownish-yellow solid, which was crystallised from chloroform-methanol to give a yellow solid. The yellow solid was further recrystallised from chloroform-methanol to give the analytically pure material of title compound (**DHT8A**, 1.82 g,

30%) as yellow needles (mp. 107.4–108.8°C). **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}.; **PMR**: 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, 40 H), 0.89 (m, 12 H) ppm.; **CMR** (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, and 14.5 ppm.; **Mass** (FAB): 754.5 $(M+1)^+$.

1,5-Diheptyloxy-2,3,6,7-tetraoctyloxy-9,10-anthraquinone D7T8A

A stirred mixture of 1,5-dihydroxy-2,3,6,7-tetraoctyloxy-9,10-anthraquinone **DHT8A** (752 mg, 1 mmol), anhydrous potassium carbonate (1.66 g, 12 mmol), bromoheptane (2.5 mL, 16 mmol) and potassium iodide (100 mg) in dry DMF (8 mL) was heated at 105°C 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 transferred to a separatory funnel and washed with water (3 x 200 mL) followed by brine (200 mL) and dried (Na_2SO_4). Solvents were removed to give a yellow oil, which was crystallised from cold chloroform-ethanol to give a yellow solid. The yellow solid was recrystallised once again from cold chloroform-ethanol solvent system to yield a yellow solid of analytically pure material of (**D7T8A**, 729 mg, 77%). **Elemental Analysis**: Found: C 75.83, H 10.55; $C_{60}H_{100}O_8$ requires: C 75.90, H 10.67.; **IR**: 2959, 2925, 2854, 1664, 1574, 1468, 1323, 1132 cm^{-1}.; **PMR**: δ 7.59 (s, 2H), 4.18–4.03 (m, 12 H), 1.95–1.25 (m, 68 H), 0.91–0.84 (m, 18 H) ppm.; **CMR** (100 MHz, $CDCl_3$): δ 181.9, 158.1, 154.6, 147.7, 133.4, 121.1, 107.7, 75.4, 74.8, 69.8, 32.6, 32.5, 31.0, 30.2, 30.0, 29.9, 29.8, 26.7, 23.3, and 14.7 ppm.; **Mass** (FAB): 950.4 $(M+1)^+$.

1,2,3,5,6,7-Hexaoctyloxy-9,10-anthraquinone H8A

Prepared according to the procedure described for compound (**D7T8A**) in 79% yield but used tetrabutylammonium iodide as catalyst instead of potassium iodide, and obtained the compound (**H8A**) as a pasty yellow solid. **Elemental Analysis**: Found: C 76.00, H 10.60; $C_{62}H_{104}O_8$ requires: C 76.18, H 10.72.; **IR**: 2956, 2924, 2854, 1665, 1574, 1468, 1323, 1131 cm^{-1}.; **PMR**: δ 7.59 (s, 2H), 4.18–4.03 (m, 12 H), 2.0–1.24 (m, 72 H), 0.91–0.84 (m, 18 H) ppm.; **CMR** (125 MHz, $CDCl_3$): δ 181.7, 157.9, 154.3, 147.4, 133.1, 120.8, 107.4, 75.1, 74.5, 69.5, 32.3, 30.7, 29.9, 29.7, 29.5, 26.4, 23.1, and 14.5 ppm.; **Mass** (FAB): 978.4 $(M+1)^+$.

1,5-Dinonyloxy-2,3,6,7-tetraoctyloxy-9,10-anthraquinone D9T8A

Prepared using a procedure similar to the one described for compound (**D7T8A**) in 81% yield and obtained as a yellow solid. **Elemental Analysis**: Found: C

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76.21, H 10.69; $C_{64}H_{108}O_8$ requires: C 76.45, H 10.83.; **IR**: 2956, 2924, 2854, 1665, 1574, 1469, 1323, 1131 cm^{-1}.; **PMR**: δ 7.59 (s, 2H), 4.18–4.0 (m, 12 H), 1.98–1.20 (m, 76 H), 0.95–0.85 (m, 18 H) ppm.; **CMR** (100 MHz, $CDCl_3$): δ 181.9, 158.1, 154.6, 147.7, 133.3, 121.1, 107.7, 75.4, 74.8, 69.8, 32.6, 32.5, 31.0, 30.31, 30.26, 30.16, 30.0, 29.8, 26.7, 23.3 and 14.7.; **Mass** (FAB): 1007.2 $(M+1)^+$.

1,5-Didecyloxy-2,3,6,7-tetraoctyloxy-9,10-anthraquinone D10T8A

Prepared using a similar procedure as described for compound **(D7T8A)** in 79% yield but used tetrabutylammonium iodide as catalyst instead of potassium iodide, and obtained the compound **(D10T8A)** as a yellow solid. **Elemental Analysis**: Found: C 76.62, H 10.94; $C_{66}H_{112}O_8$ requires: C 76.69, H 10.92.; **IR**: 2956, 2924, 2854, 1665, 1574, 1469, 1323, 1131 cm^{-1}.; **PMR**: δ 7.59 (s, 2H), 4.18–4.0 (m, 12 H), 2.0–1.18 (m, 80 H), 0.95–0.82 (m, 18 H) ppm.; **CMR** (125 MHz, $CDCl_3$): δ 181.6, 157.9, 154.4, 147.4, 133.1, 120.9, 107.5, 75.2, 74.6, 69.6, 32.3, 32.2, 30.8, 30.13, 30.02, 29.92, 29.8, 29.7, 29.5, 26.5, 23.1, and 14.5 ppm.; **Mass** (FAB): 1035.2 $(M+1)^+$.

1,5-Diundecyloxy-2,3,6,7-tetraoctyloxy-9,10-anthraquinone D11T8A

A similar procedure as described for the preparation of compound **(D7T8A)** was used (86% yield) and compound **(D11T8A)** was obtained as a pasty yellow solid. **Elemental Analysis**: Found: C 76.66, H 10.88; $C_{68}H_{116}O_8$ requires: C 76.93, H 11.01.; **IR**: 2957, 2923, 2853, 1665, 1574, 1468, 1323, 1130 cm^{-1}.; **PMR**: δ 7.59 (s, 2H), 4.15–4.03 (m, 12 H), 1.98–1.15 (m, 84 H), 0.95–0.83 (m, 18 H) ppm.; **CMR** (100 MHz, $CDCl_3$): δ 181.9, 158.1, 154.6, 147.7, 133.4, 121.1, 107.7, 75.4, 74.8, 69.8, 32.6, 32.5, 31.0, 30.4, 30.3, 30.2, 30.0, 29.8, 26.7, 23.3, and 14.7 ppm.; **Mass** (FAB): 1062.8 $(M+1)^+$.

III. RESULTS AND DISCUSSION

A) Polarised-light microscopic and thermal studies

Polarised-light microscopic studies on hexaethers with mixed chains (C_nH_{2n+1}, n=7–11 at the 1,5 positions and n=8 at the other positions) show on cooling from the isotropic phase the appearance of a large number of highly homeotropic domains with some of them having either dark full or half (L-shaped) crosses over them or one set of dark and bright straight bands (fig. 2). The appearance of these straight bands has been suggested to result from a specific arrangement of the columns of molecules similar to the formation of π-disclinations [9] which is one of the characteristics of columnar mesophase texture. On subsequent cooling

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the texture remains the same till near room temperature and then shows development of channel-like structure along the domain boundaries (for most of the systems). This might suggest that there is another mesophase near room temperature. The DSC studies show a weak transition near room temperature further supporting this possibility. When the microscopic slide preparation is left at room temperature for a long time (over several months) **(D7T8A)** shows the appearance of mosaic domains suggesting that the low-temperature mesophase could be a three dimensionally ordered one as confirmed by x-ray diffraction studies discussed later.

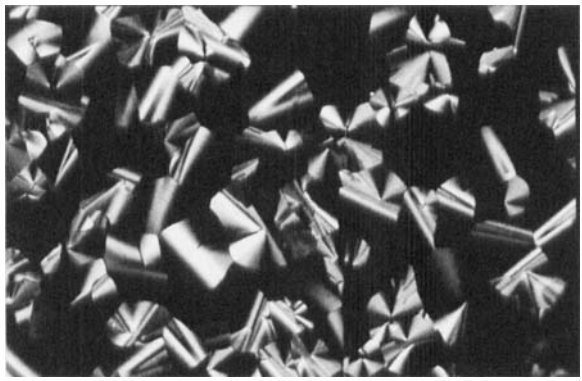

FIGURE 2 Texture observed under the polarised-light microscope for **D11T8A** at room temperature, obtained after cooling from the isotropic (See Color Plate I at the back of this issue)

Thermodynamic phase transitions in the various homologues have been identified with differential scanning calorimetric (DSC) experiments carried out in the heating as well as cooling modes in the temperature range of around −65°C to just above the isotropic transition (~105°C) run at a rate of 10°/min. The DSC data for different heating and cooling runs have been summarised in table-I. They show, in general, on heating from around −65°C a strong endothermic transition suggesting that it could be a crystal-mesophase transition (fig. 3a). This is followed by one weak endothermic transition except in the case of **(H8A)** where one more weak transition is observed indicating that these could be mesophase-mesophase transitions as confirmed by x-ray diffraction studies which is discussed later. Subsequent to this transition one observes the mesophase-isotropic transition consistent with the microscopic observations. In the cooling runs (fig. 3b) corresponding exothermic transitions are observed showing that all these transitions are reversible. However, in some systems monotropic transitions are also observed (below room temperature). The overall thermal behaviour suggests that there could be two mesophases in almost half of the cases and three in others as shown by x-ray diffraction studies we have carried out.

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TABLE I DSC data for the hexacthers of anthraquinone (DmTnA series)

Compound name	*Run*	*K→ M_1 on heating* *M_1→ K on cooling*	*M_1→ M_2 on heating* *M_2→ M_1 on cooling*	*$M_{1(2)}$→ Col_h on heating* *Col_h→ $M_{1(2)}$ on cooling*	*Col_h→ Isotr. on heating* *Isotr.→ Col_h on cooling*
D7T8A	1st heating	−8.6[a] (*13.1*[b])	–	44.8 (*2.8*)	93.4 (*11.8*)
	1st cooling	−22.8 (*-13.6*)	–	30.4 (*-1.9*)	91.1 (*-11.3*)
	2nd heating	−10.8 (*13.1*)	–	44.0 (*2.8*)	93.2 (*11.3*)
H8A	1st heating	6.7 (*21.2*)	22.2 (*0.9*)	35.2 (*1.2*)	96.9 (*13.2*)
	1st cooling	−3.3 (*-24.2*)	7.9 (*-1.8*)	21.1 (*-1.1*)	94.4 (*-11.6*)
	2nd heating	3.0[c] (*22.0*)	21.2 (*0.9*)	34.2 (*1.3*)	96.6 (*11.6*)
D9T8A	1st heating	53.9[d] (*113.8*)	–	–	96.6 (*11.4*)
	1st cooling	3.3 (*-31.9*)	–	22.3 (*-2.4*)	94.0 (*-11.1*)
	2nd heating	8.8 (*32.3*)	–	35.5 (*3.8*)	96.6 (*11.0*)
D10T8A	1st heating	48.5[e] (*106.3*)	–	–	95.3 (*11.7*)
	1st cooling	−3.7 (*-34.4*)	–	12.9 (*-2.3*)	93.1 (*-11.8*)
	2nd heating	1.9 (*32.3*)	–	29.7[f] (*2.7*)	95.0 (*11.9*)
D11T8A	1st heating	22.2[g] (*29.9*)	–	–	91.9 (*12.5*)
	1st cooling	−7.8 (*-20.8*)	–	−0.8 (-1.4)	89.7 (*-11.7*)
	2nd heating	19.0[h] (*27.1*)	–	–	91.7 (*11.7*)

a. Peak values of the transition temperatures are given in Celsius.
b. The enthalpies of the transitions are given in kJ/mole.
c. Two overlapping peaks.
d. K→ Col_h transition.
e. K→ Col_h transition.
f. Two overlapping peaks.
g. K→ Col_h transition.
h. K→ Col_h transition.

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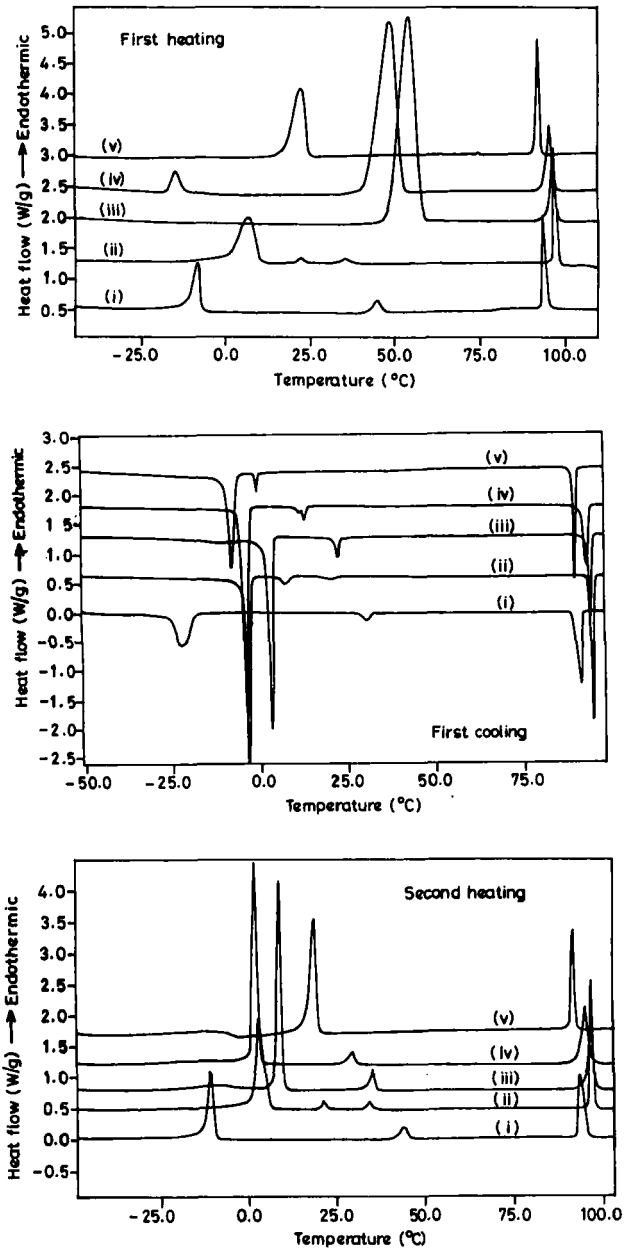

FIGURE 3 DSC thermograms for the (a) first heating, (b) first cooling and (c) second heating runs for all the homologues. The DSC runs were recorded at a heating/cooling rate of 10°C per minute. (i)-(v) corresponds to the compounds **D7T8A, H8A, D9T8A, D10T8A** and **D11T8A**, respectively

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The thermal behaviour of the compounds **(D7T8A)** and **(H8A)** is in agreement with that observed by Raja *et al.* [8]; the Col_h-isotropic transition temperatures agree within 2°C and we observe little higher enthalpies. It may be pointed out that the DSC peaks observed by us are sharper. On the other hand the DSC thermograms of the other hexaethers with mixed chain lengths, namely **(D9T8A)**, **(D10T8A)** and **(D11T8A)** were substantially different from the thermal data reported by Raja *et al.* [8]. The mesophase-isotropic transition temperatures observed here for **(D10T8A)** and **(D11T8A)** are higher by up to 35°C and the enthalpies are also higher by three and eight times, respectively. It should be noted that the Col_h-isotropic transition temperatures for **(D9T8A)**, **(D10T8A)** and **(D11T8A)** lie close to each other within 1.5°C resulting in almost the same mesophase range for **(D9T8A)** compared to **(H8A)** and little higher range for **(D10T8A)** calculated from the first cooling DSC runs. Hence, a decrease is not observed in the mesophase range and the enthalpies (for the mesophase-isotropic transition) as one moves away from **(H8A)** and consequently it is reflected in the corresponding entropies of the transformation as well. The entropies observed for **(D7T8A)**, **(D9T8A)**, **(D10T8A)** and **(D11T8A)** are nearly the same whereas for **(H8A)** it is slightly higher than the rest.

B) X-ray diffraction studies

We have carried out x-ray diffraction studies of all the members of the homologous series described above in the temperature ranges below the isotropic-mesophase transition and the subsequent thermal transition to ascertain the nature of the mesophases. The experiments were performed with a MAC-SCIENCE (Japan) x-ray imaging plate system that has mirror-mirror optics which filters and collimates the Cu-K radiation from a sealed-tube x-ray generator allowing only the $K_\alpha$line to emerge. The sample-detector distance was calibrated with standard polycrystalline Silicon powder. The sample was filled either in a Lindemann capillary or sandwich-type cell made from Kapton films and kept inside the temperature-controlled (±1°C) chamber during the experiments. The scattering from the beam-catch in the low-angle region, air-scattering and background diffuse scattering from Kapton film were all subtracted from the diffraction patterns and then analyzed. The mean separation between the molecular cores, and that between the alkyl chains were calculated after curve-fitting their diffraction peaks.

X-ray diffraction patterns showed the existence of one broad diffuse peak and one relatively narrow diffuse peak in the wide angle region for all the members of the series recorded below the isotropic-mesophase transition. The sample tem-

perature for the members **(H8A)**, **(D9T8A)** and **(D10T8A)** was held at 60°C whereas it was 61°C for **(D7T8A)**, controlled within ±1°C. The broad diffuse peak occurred at a diffraction angle corresponding to a d-spacing range of 4.40–4.52 Å which indicates that this peak arises due to the alkyl chains [10]. The broad nature of the peak shows that the alkyl chains are in a liquid-like state. The relatively narrow diffuse peak is located in the region corresponding to a d-spacing range of 3.47 to 3.55 Å. This value is close to that observed in the columnar phases formed by triphenylene systems [11] suggesting that it corresponds to the average separation between the rigid molecular cores. Further the diffuse nature of the peak shows that the correlation between them is only of short range. In the small-angle region there were three sharp peaks for all the members. The ratio of the reciprocal of the d-spacing of the first reflection (lowest diffraction angle) to that of the other reflections taken in the ascending order of the diffraction-angle is very close to 1, $\sqrt{3}$, $\sqrt{4}$, respectively. This ratio corresponds to that for the first three reflections, namely, (10), (11) and (20), that would be observed from a two-dimensional hexagonal lattice. As these reflections are sharp the lattice should have long-range order in the plane. The observed diffraction data is consistent with the well-accepted model in which the disk-like core of the molecules stack one on top of the other to form columns surrounded by the aliphatic "sea" constituted by the liquid-like alkyl chains and these columns are in turn arranged in a 2d hexagonal lattice. In other words the columns formed by the molecular cores are embedded in the aliphatic "sea". The fact that all the three observed sharp reflections can be indexed to a two-dimensional hexagonal lattice implies that there is no correlation between the molecular positions across different columns; only short-range order exists among the molecular cores in the same column along the axis of the column as exemplified by the relatively narrow diffuse peak observed in the wide-angle region. Hence this phase can be classified as Col_h (also called D_h).

X-ray diffraction experiment was performed at room temperature (~21°C) for **(D11T8A)** (fig. 4) and also for **(D10T8A)** since they do not show any thermal transition on cooling below the isotropic-mesophase transition until room temperature. The diffraction pattern had features similar to those observed for **(D7T8A)**, **(H8A)**, **(D9T8A)** and **(D10T8A)** at high temperature; the wide-angle region showed one broad diffuse peak and one relatively narrow diffuse peak. In the low-angle region there were three sharp peaks which could be indexed to a 2d hexagonal lattice. Thus, these two homologues form a Col_h (also called D_h) phase that extends down to room temperature.

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TABLE II X-ray diffraction data for the hexacthers of anthraquinone (DmTnA series) in the 2d hexagonal columnar mesophase (Col_h or D_h)

Compound name	*Temperature (°C)*	*Observed peaks*					*Average Lattice constant[a] (a) in Å*	*Average correlation length between the cores along the column (Å)*	*Intra columnar order*
		Inter columnar (in Å)			*Diffuse, wide-angle (in Å)*				
		(10)	*(11)*	*(20)*	*alkyl chain*	*core-core*			
D7T8A	61	18.4	11.0	9.7	4.52 ± 0.01	3.47 ± 0.01	21.9	22.2 (≈6[b])	liquide-like
H8A	60	19.3	11.3	9.6	4.40 ± 0.02	3.55 ± 0.01	22.4	16.4 (≈5)	liquid-like
D9T8A	60	19.4	11.3	9.8	4.49 ± 0.06	3.49 ± 0.04	22.5	16.7 (≈5)	liquide-like
D10T8A	RT[c]	19.7	11.7	10.2	4.36 ± 0.01	3.42 ± 0.01	23.2	27.0 (≈8)	liquid-like
	60	19.6	11.7	10.1	4.52 ± 0.01	3.54 ± 0.01	23.1	16.1 (≈5)	liquide-like
D11T8A	RT	20.1	11.7	10.3	4.33 ± 0.02	3.42 ± 0.01	23.4	31.3 (≈9)	liquid-like

a. average of that calculated from all the three observed reflections, namely, (10), (11) and (20).
b. nearest neighbour distance.
c. ~21°C.

The correlation length between the molecular cores along the column has been calculated from the half-widths of the fitted curves of the corresponding diffraction peak profiles. It is found to be nearly the same for different members of the series calculated at almost the same temperature (table-II). The diffraction data recorded at two different temperatures for **(D10T8A)** clearly show that the correlation length increases (5 nearest neighbour distance at 60°C to 8 at ~21°C i.e., room temperature) with decrease in temperature. It also shows that the mean separation between the molecular cores decreases with the decrease in temperature. The mean separation observed for the different members lies in the range of 3.47–3.55Å. The smallest value observed here is little smaller than that observed for hexa-alkoxy-triphenylene and hexa-alkyl-thiotriphenylene in which the electrical conductivity has been observed to increase by many orders on doping [2]. This suggests that this is also a suitable system to study quasi-one-dimensional charge transport on appropriate doping [12].

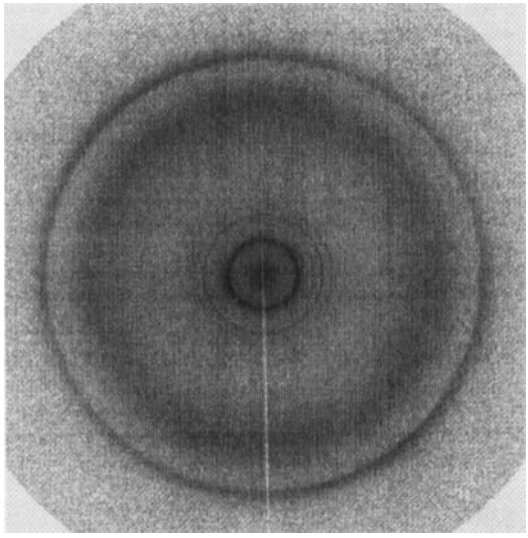

FIGURE 4 The diffraction pattern recorded for the homologue **D11T8A** at room temperature in the 2d hexagonal columnar phase

As discussed before, the homologues **(D7T8A), (H8A)**, and **(D9T8A)** show, on cooling, weak exothermic peaks near room temperature (~21°C). X-ray experiments were performed for these homologues at room temperature to ascertain the nature of the phases below these transitions. For **(D9T8A)**, the wide-angle region shows only diffuse peaks; one corresponding to the alkyl chains and the other to the correlation between molecular cores. In the low-angle

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region there are more sharp peaks than that would be expected from a 2d hexagonal lattice. This implies that the low-temperature phase is a columnar mesophase with the columns not arranged in a hexagonal lattice. In the case of **(D7T8A)** and **(H8A)** the wide-angle peak corresponding to that arising from the correlation between the molecular cores observed in the high-temperature Col_h-phase splits into sharper peaks. Here again the number of observed sharp peaks in the low-angle region are more than what would be expected from a 2d hexagonal lattice. The observed features in the diffraction pattern suggest that this phase is a three-dimensionally ordered one. Experiments with monodomain samples are being planned which would settle the question of the exact nature of the additional ordering in these phases and this would be reported elsewhere. It should be mentioned that although Raja *et al.* and Carfagna *et al.* have carried out x-ray diffraction experiments in the high-temperature mesophase, namely, Col_h, not much attention has been paid, to the low-temperature mesophase. The transition corresponding to this low-temperature mesophase to high-temperature one is observed in the DSC plots of Raja *et al.* for **(H8A)** and **(D7T8A)** in nearly the same temperature range and with nearly the same enthalpy as observed by us.

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IV. CONCLUSIONS

We have synthesised various homologues of 1,2,3,5,6,7-hexaalkoxy-9,10-anthraquinones (also called rufigallol hexaethers) starting from gallic acid by varying the length of the alkyl chain at the 1,5 positions. They form two or three columnar mesophases; the high-temperature one extending down to room temperature in some of them, the others occurring near and below room temperature. The high-temperature mesophase is hexagonal columnar with correlation among the molecular cores along the column extending up to about 9 nearest neighbours at room temperature. In the low-temperature mesophase the columns are not arranged in a hexagonal lattice. There is no additional ordering within the columns in one of the homologues **(D9T8A)**, whereas in some other homologues **(H8A and D7T8A)** there is three-dimensional ordering. The latter homologues may be better suited for charge transport studies as there is long-range order among the molecular cores along the column similar to the helical phase of hexa-hexyl-thiotriphenylene. Our studies show that in contrast to the observations of Raja *et al.* [8] the high-temperature mesophase range is not dramatically affected by the increase of the length of the alkyl chains attached to the 1,5 positions which are longer than those in the other positions.

Our preliminary studies of these systems show that the ac electrical conductivity along the column can be increased by nearly 7 orders of magnitude on dop-

ing, reaching a value of nearly 10^{-2}S/m. Work is in progress to study the effect of the bulky substituents in the 1,5 positions on the nature of the mesophase.

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[12] Our preliminary measurements on one of the homologues show that the ac conductivity along the columns can be increased by at least 7 orders on doping, reaching a value of nearly 10^{-2} S/m.

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