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## Liquid Crystals

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### Non-symmetrical discotic liquid crystalline dimers: molecular design, synthesis and mesomorphic properties<sup>‡</sup>

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## Non-symmetrical discotic liquid crystalline dimers: molecular design, synthesis and mesomorphic properties<sup>‡</sup>

S.K. Varshney<sup>a</sup>, H. Monobe<sup>b</sup>, Y. Shimizu<sup>b</sup>, H. Takezoe<sup>c</sup> and V. Prasad<sup>a\*</sup>

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The synthesis and mesomorphic properties of novel non-symmetrical discotic dimers have been investigated. Dimers have been prepared by the combination of electron-deficient (*n*-type) anthraquinone and electron-rich (*p*-type) triphenylene discotic monomers. The mesophases have been characterised using polarising optical microscopy, differential scanning calorimetry and X-ray diffraction. Most of the dimers have been shown to exhibit a rectangular columnar mesophase and one has a nematic columnar mesophase also. Charge transfer behaviour has been studied by UV–Vis spectroscopy.

**Keywords:** triphenylene; anthraquinone; dimers; nematic; columnar

### 1. Introduction

Due to their value in a broad range of electronic equipment, liquid crystalline materials have now achieved considerable importance. In particular, columnar liquid crystals formed by disc-shaped molecules [1, 2] have been investigated for over 30 years for their potential electron- and hole-conducting properties in electronic devices. These devices include organic light emitting diodes [3–5], organic photovoltaic cells [6–8] and field-effect transistors [9–11].

The design and synthesis of novel discotic liquid crystalline dimers is currently of interest for a variety of reasons. It is well known that connecting two discotic molecules by means of a spacer significantly stabilises the columnar mesophase and often leads to the formation of glassy columnar phases which have useful applications [12–13]. In addition, these discotic dimers can serve as good model compounds for the study of oligomers and polymers formed by the disc-shaped molecules. A number of dimers with the disc-like core have been reported in the literature [14–16], and much attention has been devoted to dimers based on triphenylene (TP) [17–19]. Several examples of dimers have recently been reported in which an electron acceptor such as 2,4,7-trinitrofluorene-9-one or anthraquinone (AQ) is covalently connected to an electron-rich donor [20–24].

Liquid crystalline charge transfer (CT) complexes have been known since 1968 [25]. CT complex formation can have a profound effect on the induction and stabilisation of the mesophases [26–28]. However, in all the compounds reported the electron-deficient moiety is limited to non-liquid crystalline materials. The first

example of asymmetric discotic dimers formed of electron acceptor (*n*-type) and electron donor (*p*-type) liquid crystalline monomers has been reported only fairly recently [29]. A discotic twin was formed in which an electron-rich TP moiety is connected to an electron-deficient AQ moiety by means of an alkoxy functional group.

In the present study we have studied the design, synthesis and physical properties of a range of new discotic dimers. These have been obtained by the combination of *n*- and *p*-type discotic monomers, comprising a combination of donor–donor (*p*–*p*), acceptor–acceptor (*n*–*n*) and acceptor–donor (*n*–*p*) types of mesogens. Unlike previous studies, the monomers are connected by an alkyl chain *via* an ester linkage on one side and an ether linkage on the other. In other words the monomer units are linked by two different terminal functional groups on the spacer chain.

### 2. Experimental

#### 2.1 Materials and equipment

AR quality chemicals and solvents were obtained locally and solvents were dried using standard procedures. The purity and chemical structures of all the compounds synthesised were confirmed by spectral data. <sup>1</sup>H NMR spectra were recorded using a Bruker 200 or 400 MHz spectrometer, using CDCl<sub>3</sub> as solvent and tetramethylsilane as internal standard; *J* values are given in hertz. <sup>13</sup>C NMR spectra were recorded using a Bruker 400 MHz spectrometer. Mass spectra were obtained on a JEOL JMS600H spectrometer in

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<sup>‡</sup>Part of this work has been presented as a poster in 2004 at the 20th International Liquid Crystal Conference, Ljubljana, Slovenia.

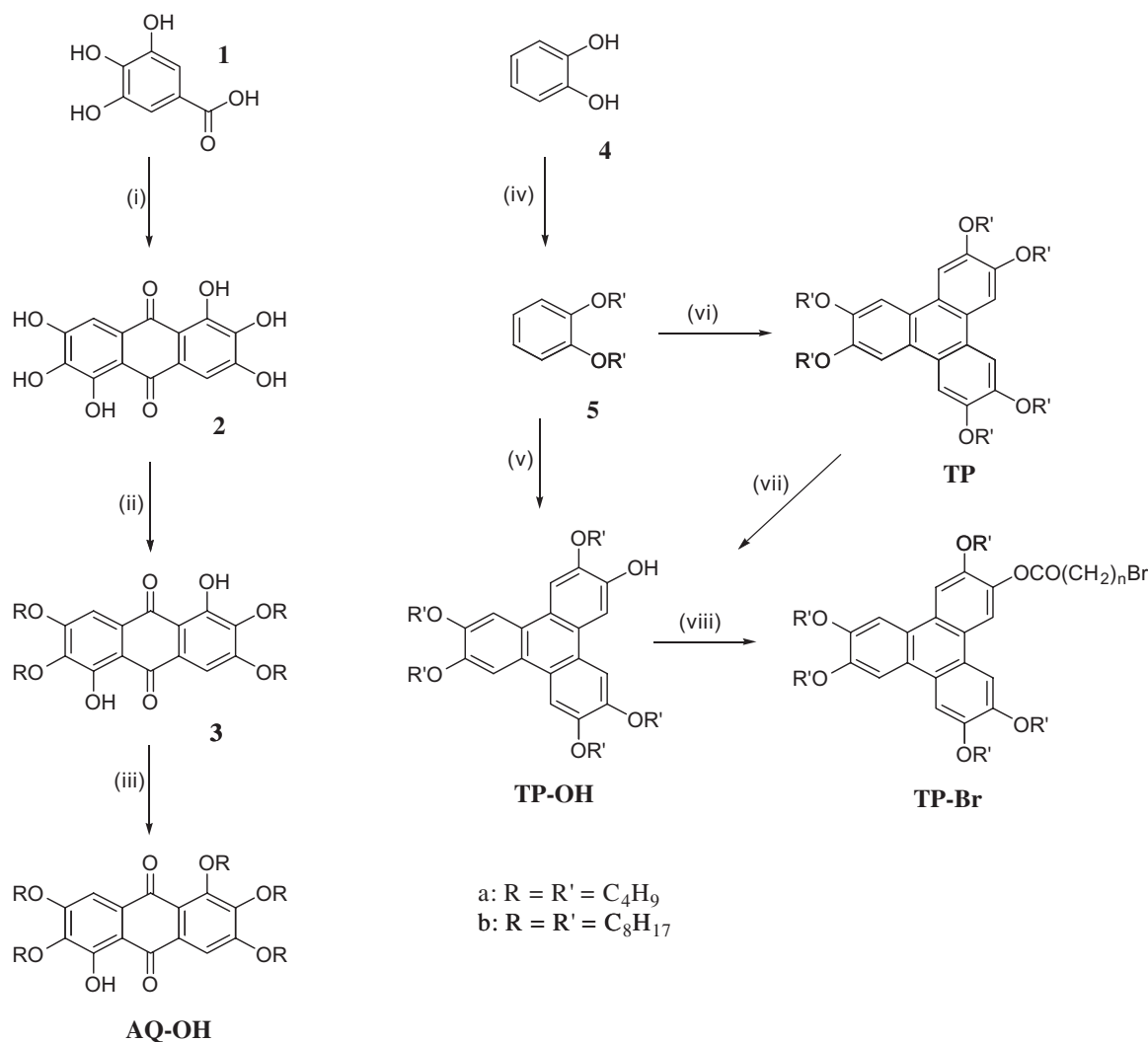
FAB<sup>+</sup> mode using a *m*-nitrobenzyl alcohol matrix. Micro-analyses were performed using a Eurovector Elemental Analyzer, Model Euro EA 3000.

## 2.2 Synthesis

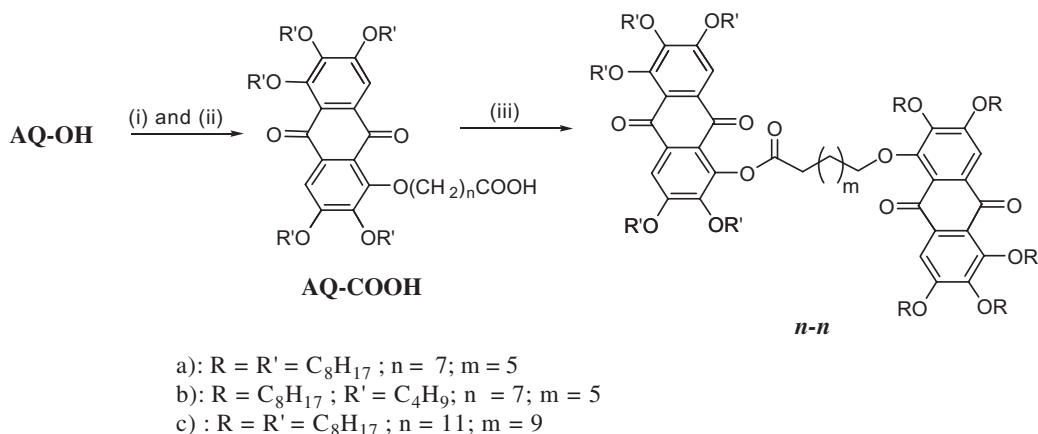
Discotic dimers were obtained by connecting two monomeric units by means of a flexible spacer. The key intermediate, monohydroxypentakis(alkoxy)triphenylene (TP-OH), was synthesised by oxidative trimerisation of 1,2-dialkoxybenzene or by the conventional ether cleavage method described elsewhere [30–32]. Monohydroxypentakis(alkoxy)anthraquinone (AQ-OH) was prepared by regiospecific alkylation [33] of hexahydroxyanthraquinone (**2**, in Scheme 1) with a *n*-bromoalkane to obtain tetrakis(alkoxy)anthraquinone (**3**). The latter was further alkylated

under mild reaction conditions, so that one of the hydrogen-bonded hydroxyl groups in the 1 and 5 positions of **2** remained unreacted. In this manner an approximate 3 : 2 mixture of hexakis(alkoxy)anthraquinone and AQ-OH was obtained and separated by column chromatography, yielding about 65% of pure AQ-OH (Scheme 1).

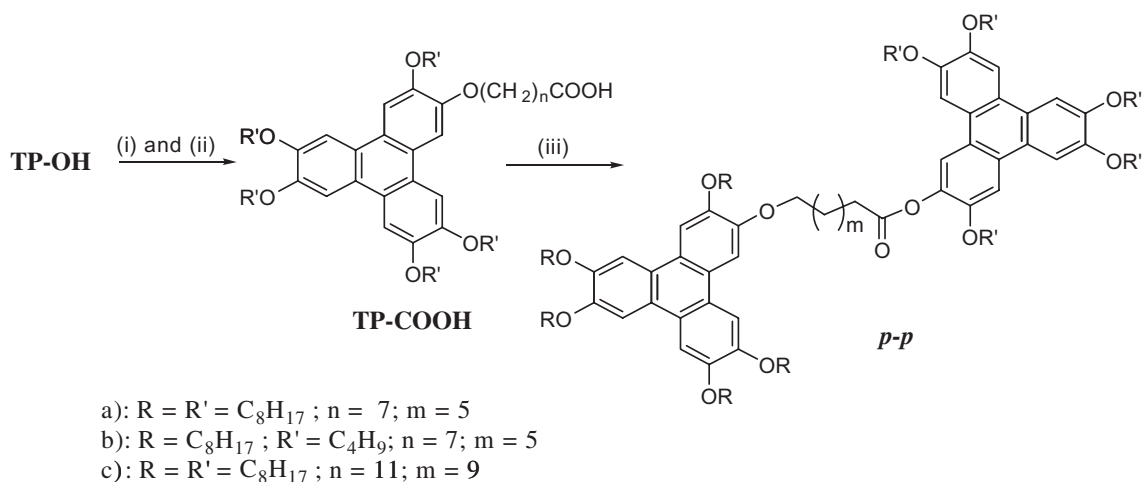
The synthesis of the final non-symmetrical dimers *n*-*n*, *p*-*p* and *n*-*p* types is shown in Schemes 2, 3 and 4, respectively. The length of the peripheral aliphatic chains on the discotic core and the spacer chain length are varied in a similar fashion for each of these series of dimers. Thus, AQ-OH was alkylated with ethylbromoalkanoate to obtain ethyl-alkanoyloxypentakis(alkoxy)anthraquinone, which was hydrolysed under basic conditions to the corresponding acids, AQ-COOH. The *n*-*n* dimers were synthesized by



Scheme 1. Synthesis of the key intermediate compounds. Reagents and reaction conditions: (i) H<sub>2</sub>SO<sub>4</sub>/100°C, 2h; (ii) NaOH/DMF/RBR/100°C, 15h; (iii) BrC<sub>n</sub>H<sub>2n</sub>COOEt/Cs<sub>2</sub>CO<sub>3</sub>/MEK/80°C, 15h, (iv) C<sub>n</sub>H<sub>2n+1</sub>Br/KOH/DMSO/50°C, 15h; (v) FeCl<sub>3</sub>/Con. H<sub>2</sub>SO<sub>4</sub>/0.5h, r.t.; (vi) VOCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>, r.t. 10 min; (vii) BBr<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>, 15h, r.t.; (viii) DCC/DMAP/Br(CH<sub>2</sub>)<sub>n</sub>COOH/CH<sub>2</sub>CH<sub>2</sub>/r.t. 15h.



Scheme 2. Synthesis of  $n-n$  dimers. Reagents and reaction conditions: (i)  $BrC_nH_{2n}COOEt/Cs_2CO_3/MEK/80^\circ C$ , 15h; (ii)  $KOH/EtOH/80^\circ C$ , 2h; (iii)  $AQ-OH/DCC/DMAP/CH_2Cl_2$ , r.t. 24h.



Scheme 3. Synthesis of  $p-p$  dimers. Reagents and reaction conditions: (i)  $BrC_nH_{2n}COOEt/Cs_2CO_3/MEK/80^\circ C$ , 15h; (ii)  $KOH/EtOH/80^\circ C$ , 2h; (iii)  $TP-OH/DCC/DMAP/CH_2Cl_2$ , r.t. 24h.

the dicyclohexylcarbodiimide (DCC) coupling of  $AQ-OH$  with  $AQ-COOH$ , which yielded 55% of the product ( $n-n$ ), as shown in Scheme 2.

Dimers of the  $p-p$  type were obtained in a similar fashion (Scheme 3).

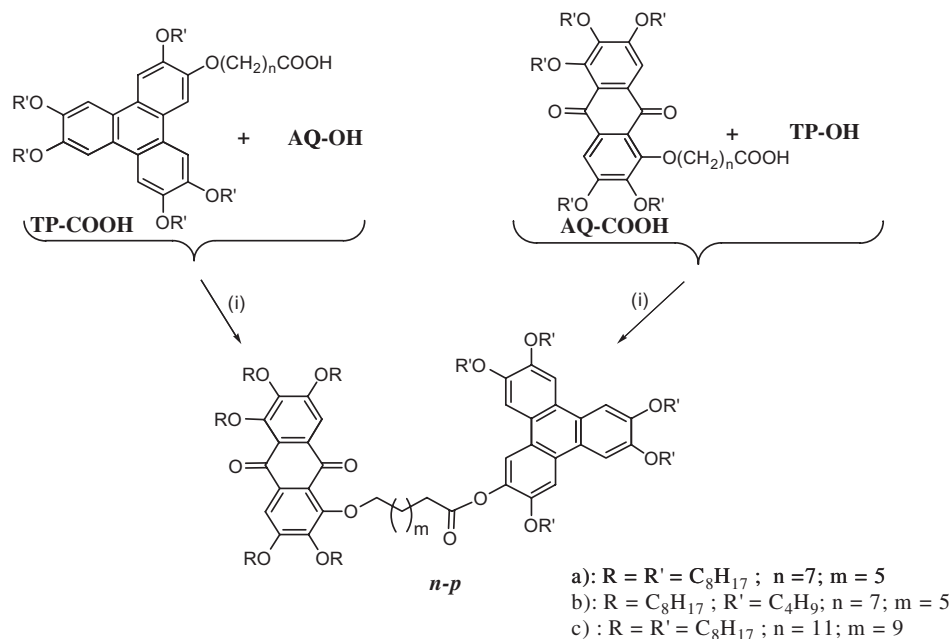
Dimers of the  $n-p$  type were obtained by one of two methods: (a) by the DCC coupling of compound  $TP-OH$  with  $\omega$ -bromoalkanoic acid to give the product  $TP-Br$ , followed by using  $TP-Br$  for alkylation of  $AQ-OH$  to give the required  $n-p$  dimer; (b) by DCC coupling of  $AQ-COOH$  with  $TP-OH$  to give the  $n-p$  dimer, as shown in Scheme 4. Method (b) gave slightly higher yield.

The spectral and the microanalysis data obtained for all these compounds are in agreement with their chemical structure. The experimental details and the data obtained for a representative dimer from each

$n-n$ ,  $p-p$  and  $n-p$  series, and key intermediates from each series, are given below.

### 2.2.1 General method of preparation of $AQ-COOH$ (a and b)

**Step 1:** A stirred anhydrous mixture of  $AQ-OH$  (1 mmol), ethyl- $\alpha$ - $\omega$ -bromoalkynoate (4 mmol) and anhydrous  $K_2CO_3$  (4 mmol) was heated at  $80^\circ C$  in dry dimethylformamide for 24 h. After cooling, the solution was decanted into water and the product extracted with methylene chloride. The extract was dried over sodium sulphate and the solvent removed under vacuum. The crude products (ethyl 8-(2,3,6,7-tetrakis(octyloxy)-9,10-dioxo-9,10-dihydroanthracen-1-yloxy)octanoate and ethyl 12-(2,3,6,7-tetrakis(octyloxy)-9,10-dioxo-9,10-dihydroanthracen-1-yloxy)dodecanoate) were separated by chromatography on a silica gel column.



Scheme 4. Synthesis of  $n-p$  dimers. Reagents and reaction conditions: (i) DCC/DMAP/ $CH_2Cl_2$ , r.t. 24h.

**Step 2:** A stirred mixture of ethyl- $n$ -(2,3,5,6,7-pentakis(alkoxy)-9,10-anthraquinone-1-yloxy)alkanoate and a 5% aqueous solution of sodium hydroxide (5 ml) and methanol (10 ml) were refluxed for 24 h. The cold mixture was carefully poured into 5M aqueous hydrochloric acid, extracted with chloroform, then washed with water and dried over anhydrous sodium sulphate. The solvent was removed under vacuum and the crude product purified by crystallisation using a mixture of methanol and diethyl ether, yielding the compounds AQ-COOH (a and b) as a yellow solid in 80% overall yield.

(a)  $\nu_{\max}$  (KBr)/ $cm^{-1}$ : 2927, 2855, 1711, 1665, 1573, 1468, 1323, 1131;  $^1H$  NMR:  $\delta$  7.59 (s, 2H), 4.15 (t,  $J = 6.4$ , 4H), 4.05 (t,  $J = 6.6$ , 8H), 2.32 (t,  $J = 7.5$ , 2H), 1.95–1.63 (m, 12H), 1.48–1.29 (m, 58H), 0.88 (m, 15H); MS: (FAB<sup>+</sup>)  $m/z$ ;  $C_{62}H_{102}O_{10}$ : 1006 (100%).  
 (b)  $\nu_{\max}$  (KBr)/ $cm^{-1}$ : 2924, 2854, 1714, 1664, 1573, 1466, 1323, 1263, 1132;  $^1H$  NMR:  $\delta$  7.63 (s, 2H), 4.19 (t,  $J = 6.4$ , 4H), 4.1 (t,  $J = 6.5$ , 8H), 2.39 (t,  $J = 7.4$ , 2H), 1.95–1.64 (m, 16H), 1.52–1.34 (m, 62H), 0.92 (t,  $J = 5.6$ , 15H); MS: (FAB<sup>+</sup>)  $m/z$ ;  $C_{66}H_{110}O_{10}$ : 1063 (25%), 1066 (16%), 1067 (18%).

### 2.2.2 General procedures for the preparation of TP-COOH (a and b)

TP-COOH (a and b) were prepared in an analogous manner.

(a)  $^1H$  NMR:  $\delta$  7.83 (s, 6H), 4.22 (t,  $J = 6.5$ , 12H), 2.37 (t,  $J = 7.4$ , 2H), 1.93–1.86 (m, 12H), 1.57–1.3 (m, 58H), 0.89 (m, 15H); MS: (FAB<sup>+</sup>)  $m/z$ ;  $C_{66}H_{106}O_8$ : 1027 (100%). (b):  $^1H$  NMR:  $\delta$  7.87

(s, 6H), 4.26 (t,  $J = 6.6$ , 12H), 2.38 (t,  $J = 7.3$ , 2H), 2.0–1.91 (m, 12H), 1.6–1.34 (m, 66H), 0.9 (m, 15H); MS: (FAB<sup>+</sup>)  $m/z$ ;  $C_{70}H_{114}O_8$ : 1084 (100%).

### 2.2.3 General procedure for the preparation of dimers of type $n-n$ , $p-p$ and $n-p$

To a mixture of AQ-COOH (1 mmol), AQ-OH (1 mmol) and DCC (1.5 mmol) in dry dichloromethane was added under an atmosphere of nitrogen a catalytic amount of *NN*-dimethylaminopyridine and stirred at room temperature for 24 h. The mixture was filtered and the solvent evaporated. The crude product was purified by chromatography on a silica gel column, eluting with methylene chloride : hexane (1 : 10). Recrystallisation from a mixture of methanol and diethyl ether gave the  $n-n$  dimers as yellow semi-solids in ~46% yield.

$n-n$ (a) Yield, 46%;  $\nu_{\max}$  (KBr)/ $cm^{-1}$ : 2925, 2854, 1774, 1666, 1574, 1468, 1378, 1323, 1265, 1135;  $^1H$  NMR:  $\delta$  7.69 (s, 1H), 7.59 (s, 2H), 7.53 (s, 1H), 4.17–4.06 (m, 22H), 2.75 (t,  $J = 7.6$ , 2H), 1.88–1.74 (m, 22H), 1.55–1.29 (m, 108H), 0.88 (m, 30H);  $^{13}C$  NMR:  $\delta$  181.2, 180.5, 171.7, 157.5, 154.2, 153.9, 147.4, 147.0, 145.5, 143.9, 132.7, 132.1, 120.5, 119.0, 108.7, 107.1, 76.7, 74.7, 74.4, 74.1, 74.0, 69.4, 69.2, 34.3, 31.8, 30.4, 29.5, 29.3, 29.2, 29.1, 26.0, 24.7, 22.6, 14.0; MS: (FAB<sup>+</sup>)  $m/z$ ;  $C_{116}H_{188}O_{17}$ : 1853 (42%), 1856 (21%); Anal. calcd.: C, 75.12; H, 10.22. Found: C, 75.52; H, 10.39.

$n-n$ (b)  $\nu_{\max}$  (KBr)/ $cm^{-1}$ : 2927, 2857, 1773, 1666, 1574, 1468, 1378, 1322, 1265, 1133;  $^1H$  NMR:  $\delta$  7.7(s,

1H), 7.59 (s, 2H), 7.54 (s, 1H), 4.22–4.02 (m, 22H), 2.75 (t,  $J = 7.3$ , 2H), 1.86–1.68 (m, 22H), 1.56–1.03 (m, 68H), 1.03–0.095 (m, 15H), 0.88 (t,  $J = 6.4$ , 15H);  $^{13}\text{C}$  NMR: same as for (a) except the aliphatic chains; MS: (FAB<sup>+</sup>)  $m/z$ ;  $\text{C}_{96}\text{H}_{148}\text{O}_{17}$ : 1574 (8%); Anal. calcd.: C, 73.25; H, 9.48. Found: C, 73.45; H, 9.5.

$n$ - $n$ (c)  $\nu_{\text{max}}$  (KBr)/  $\text{cm}^{-1}$ : 2925, 2854, 1766, 1666, 1573, 1468, 1378, 1323, 1131;  $^1\text{H}$  NMR:  $\delta$  7.69 (s, 1H), 7.59 (s, 2H), 7.53 (s, 1H), 4.18–4.03 (m, 22H), 2.78 (t,  $J = 7.3$ , 2H), 1.87–1.74 (m, 22H), 1.5–1.3 (m, 116H), 0.88 (t,  $J = 6.2$ , 30H);  $^{13}\text{C}$  NMR: same as for (a) except the aliphatic chains; Anal. calcd.: C, 75.43; H, 10.34. Found: C, 75.7; H, 10.58.

The procedure for the  $p$ - $p$ (a-c) dimer was analogous to that used for the  $n$ - $n$  dimer.  $p$ - $p$ (a)  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$ : 2925, 2854, 1754, 1641, 1618, 1517, 1437, 1390, 1263, 1169;  $^1\text{H}$  NMR:  $\delta$  8.05 (s, 1H), 7.82 (s, 10H), 7.76 (s, 1H), 4.19 (t,  $J = 4.8$ , 22H), 2.65 (t,  $J = 7.4$ , 2H), 1.9 (m, 22H), 1.55 (m, 108H), 0.89 (m, 30H);  $^{13}\text{C}$  NMR: same as for (c) except the aliphatic chains; MS: (FAB<sup>+</sup>)  $m/z$ ;  $\text{C}_{124}\text{H}_{196}\text{O}_{13}$ : 1892 (24%); Anal. calcd.: C, 78.6; H, 10.43. Found: C, 78.6; H, 10.24.

$p$ - $p$ (b)  $\nu_{\text{max}}$  (KBr)/  $\text{cm}^{-1}$ : 2927, 2855, 1754, 1619, 1518, 1437, 1391, 1263, 1169, 1054;  $^1\text{H}$  NMR:  $\delta$  8.05 (s, 1H), 7.83 (s, 10H), 7.76 (s, 1H), 4.26–4.2 (m, 22H), 2.65 (t,  $J = 7.6$ , 2H), 1.92–1.89 (m, 22H), 1.69–1.25 (m, 68H), 1.04 (t,  $J = 7.3$ , 15H), 0.89 (m, 15H);  $^{13}\text{C}$  NMR: same as for (c) except the aliphatic chains; MS: (FAB<sup>+</sup>)  $m/z$ ;  $\text{C}_{104}\text{H}_{156}\text{O}_{13}$ : 1613 (36%), 1614 (51%), 1615 (31%); Anal. calcd.: C, 77.38; H, 9.74. Found: C, 77.03; H, 9.42.

$p$ - $p$ (c) Yield, 45%;  $\nu_{\text{max}}$  (KBr)/  $\text{cm}^{-1}$ : 2924, 2854, 1754, 1618, 1517, 1437, 1391, 1264, 1168;  $^1\text{H}$  NMR:  $\delta$  8.05 (s, 1H), 7.83 (s, 10H), 7.78 (s, 1H), 4.42 (t,  $J = 5$ , 22H), 2.67 (t,  $J = 7$ , 2H), 1.94–1.9 (m, 22H), 1.57–1.32 (m, 116H), 0.9 (m, 30H);  $^{13}\text{C}$  NMR:  $\delta$  149.6, 149.1, 123.7, 107.7, 107.3, 106.2, 69.9, 69.7, 69.4, 69.0, 34.2, 31.8, 29.5, 29.3, 26.2, 25.1, 22.6, 14.0; Anal. calcd.: C, 78.8; H, 10.54. Found: C, 79.1; H, 10.8.

The procedure for the  $n$ - $p$ (a-c) dimer was analogous to that used for the  $n$ - $n$  dimer.  $n$ - $p$ (a) Yield, 40%;  $\nu_{\text{max}}$  (KBr)/  $\text{cm}^{-1}$ : 2926, 2855, 1727, 1665, 1572, 1513, 1467, 1434, 1378, 1321, 1264, 1132;  $^1\text{H}$  NMR:  $\delta$  8.06 (s, 1H), 7.85 (s, 2H), 7.81 (s, 2H), 7.78 (s, 1H), 7.6 (s, 2H), 4.25–4.13 (m, 10H), 4.17–4.13 (m, 2H), 4.1–4.04 (m, 10H), 2.68 (t,  $J = 7.6$ , 2H), 1.94–1.76 (m, 24H), 1.56–1.43 (m, 106H), 0.88 (m, 30H);  $^{13}\text{C}$  NMR:  $\delta$  181.2, 157.4, 153.9, 149.9, 149.6, 149.0, 147.0, 132.7, 124.7, 123.6, 120.5, 116.7, 108.4, 107.7, 107.3, 107.0, 106.2, 74.7, 74.6, 74.1, 70.1, 69.7, 69.4, 69.2, 68.9, 34.2, 31.8, 30.3, 29.4, 29.3, 29.1, 26.2, 26.0, 25.1, 22.6, 14.0; MS: (FAB<sup>+</sup>)  $m/z$ ;  $\text{C}_{120}\text{H}_{192}\text{O}_{15}$ : 1872 (39%), 1874 (37%); Anal. calcd.: C, 76.88; H, 10.32. Found: C, 76.95; H, 10.57.

$n$ - $p$ (b)  $\nu_{\text{max}}$  (KBr)/  $\text{cm}^{-1}$ : 2956, 2855, 1751, 1664, 1617, 1573, 1518, 1436, 1322, 1263, 1133;  $^1\text{H}$  NMR:  $\delta$  8.06 (s, 1H), 7.82 (s, 4H), 7.78 (s, 1H), 7.59 (s, 2H), 4.26–4.04 (m, 22H), 2.68 (t,  $J = 7.4$ , 2H), 1.96–1.74 (m, 24H), 1.65–1.29 (m, 66H), 1.04 (m, 15H), 0.88 (m, 15H);  $^{13}\text{C}$  NMR:  $\delta$  181.2, 157.4, 153.9, 149.9, 149.4, 149.0, 147.0, 132.7, 123.6, 123.2, 120.4, 116.7, 108.3, 107.6, 107.3, 107.1, 106.1, 74.7, 74.6, 74.1, 69.7, 69.6, 69.3, 69.2, 68.6, 34.2, 31.8, 31.5, 30.3, 29.7, 29.3, 29.1, 26.0, 25.9, 25.1, 22.6, 19.3, 14.0, 13.9; MS: (FAB<sup>+</sup>)  $m/z$ ;  $\text{C}_{100}\text{H}_{152}\text{O}_{15}$ : 1590 (41%), 1593 (66%); Anal. calcd.: C, 75.34; H, 9.61. Found: C, 75.57; H, 9.69.

$n$ - $p$ (c)  $\nu_{\text{max}}$  (KBr)/  $\text{cm}^{-1}$ : 2924, 2854, 1753, 1664, 1618, 1517, 1467, 1437, 1323, 1264, 1132;  $^1\text{H}$  NMR:  $\delta$  8.06 (s, 1H), 7.86 (s, 2H), 7.82 (s, 2H), 7.78 (s, 1H), 7.59 (s, 2H), 4.24–4.11 (m, 12H), 4.06 (t,  $J = 6.6$ , 10H), 2.67 (t,  $J = 7.5$ , 2H), 1.93–1.71 (m, 24H), 1.55–1.3 (m, 114H), 0.89–0.86 (m, 30H);  $^{13}\text{C}$  NMR:  $\delta$  181.2, 171.9, 157.4, 153.9, 149.9, 149.6, 149.4, 149.1, 147.0, 132.7, 127.9, 124.7, 123.6, 123.2, 120.5, 116.7, 108.4, 107.7, 107.3, 107.0, 106.2, 74.7, 74.1, 69.9, 69.7, 69.4, 69.1, 69.0, 34.2, 31.8, 30.3, 29.4, 29.3, 29.1, 26.2, 26.0, 25.1, 22.6, 14.0; Anal. calcd.: C, 77.13; H, 10.44. Found: C, 76.82; H, 10.52.

### 2.3 Mesophase characterisation

The textural observations were carried out using a Mettler FP82HT hot stage in conjunction with Leica DMLP microscope. The transition temperatures and the enthalpies associated with different transitions were determined using differential scanning calorimetry (DSC; Perkin-Elmer DSC7), with heating and cooling rates of  $5^\circ\text{C min}^{-1}$ . X-ray diffraction (XRD) patterns were obtained by a Rigaku RINT-2500 using Cu K $[\alpha]$  radiation ( $\lambda$ : 0.15405 nm) with a monochromator in  $\theta$ - $2\theta$  Bragg-Brentano geometry or a Rigaku Raxis-IV imaging plate system for 2D images. UV-Vis absorption spectra were obtained at room temperature using a UV-Vis spectrometer (Perkin-Elmer).

## 3. Results and discussion

### 3.1 Phase behaviour

In the present study three different series of compounds,  $n$ - $n$ ,  $p$ - $p$  and  $n$ - $p$  types, have been synthesised. All the compounds exhibited liquid crystalline properties. The thermal behaviour of these compounds was studied using polarising optical microscopy (POM) and DSC. The transition temperatures ( $^\circ\text{C}$ ) and the associated enthalpies ( $\text{kJ mol}^{-1}$ ) obtained from the DSC thermograms are shown in Table 1. All the compounds were thermally stable, as is confirmed by the

Table 1. Phase transition temperatures ( $^{\circ}\text{C}$ ) obtained from DSC thermograms and enthalpies ( $\text{kJ mol}^{-1}$ ) of transitions given in parentheses for  $n$ - $n$ ,  $p$ - $p$  and  $n$ - $p$  type dimers.

Compound		Thermal transitions ( $^{\circ}\text{C}$ ) and enthalpy changes ( $\text{kJ mol}^{-1}$ )	
		Heating scan	Cooling scan
$n$ - $n$	(a)	Cr $-15.6$ (14.3) Col <sub>x</sub> $78.2$ (65.2) I	I $67.2$ (63.7) Col <sub>x</sub> $-21.5$ g
	(b)	Col <sub>y</sub> $58.2$ (31.9) I	I $34.0$ (15.6) Col <sub>y</sub>
	(c)	Col <sub>y</sub> $61.9$ (11.1) I	I $57.1$ (11.3) Col <sub>y</sub> $30.2$ g
$p$ - $p$	(a)	Col <sub>r</sub> $93.4$ (4.7) I	I $88.2$ (7.0) Col <sub>r</sub>
	(b)	Cr $44.8$ (2.9) Col <sub>r</sub> $123.1$ (4.7) I	I $118.2$ (4.4) Col <sub>r</sub> $40.9$ (2.9) Cr
	(c)	Col <sub>r</sub> $104.5$ (12.8) I	I $101.1$ (11.7) Col <sub>r</sub>
$n$ - $p$	(a)	Cr $58.5$ (54.3) I	I $50.4$ (7.3) N <sub>C</sub> $36.1$ (2.8) Col <sub>r</sub>
	(b)	Col <sub>r</sub> $88.65$ (16.5) I	I $63.8$ (3.9) Col <sub>r</sub> $55.15$ (13.4) Cr
	(c)	Col <sub>r</sub> $103.8$ (11.9) I	I $101.5$ (11.4) Col <sub>r</sub>

Notes: Cr: crystal; Col<sub>r</sub>: rectangular columnar mesophase; N<sub>C</sub>: columnar nematic; I: isotropic liquid; Col<sub>x</sub>/Col<sub>y</sub>: columnar phase, yet to be identified; g: preserved columnar mesophase in glassy state.

reproducibility of the thermograms over a number of heating and cooling cycles.

In all the dimers the peripheral chain length ( $R$ ) was fixed so that one moiety of dimer was  $\text{C}_8\text{H}_{17}$ . The peripheral chain length ( $R'$ ) of the second moiety was chosen to be either  $\text{C}_4\text{H}_9$  or  $\text{C}_8\text{H}_{17}$ . The spacer length ( $m$ ) was either 5 or 9.

### 3.1.1 $n$ - $n$ type dimers

All the  $n$ - $n$  type dimers were found to be enantiotropic in nature and exhibited room temperature columnar (Col) phase. Compound  $n$ - $n$ (a), having peripheral chains of similar length to that of the spacer chain, showed two transitions, the first at  $-15.6^{\circ}\text{C}$  ( $14.3 \text{ kJ mol}^{-1}$ ), and another at  $78.2^{\circ}\text{C}$  with higher enthalpy ( $65.2 \text{ kJ mol}^{-1}$ ). On cooling, the isotropic phase became supercooled to a greater extent before formation of the mesophase, and exhibited the texture of a columnar mesophase (Col<sub>x</sub>) as shown in Figure 1(a). Compound  $n$ - $n$ (b) exhibited a Col<sub>y</sub> mesophase at room temperature, which cleared at  $58.2^{\circ}\text{C}$ . The same mesophase, obtained on cooling the isotropic liquid, did not crystallise above  $-50^{\circ}\text{C}$ . Due to increased flexibility of the spacer ( $m = 9$ ), derivative  $n$ - $n$ (c) exhibited the Col<sub>y</sub>

mesophase shown in Figure 1(b), which cleared at  $61.9^{\circ}\text{C}$ . The same mesophase, obtained on cooling the isotropic liquid, was transformed to a glassy state at  $30.2^{\circ}\text{C}$ . This glass-forming behaviour above room temperature has a direct parallel in the behaviour of pyrene-based dimers [34, 35] and azomethine dimers [24].

The POM textural studies revealed that the nature of the mesophases exhibited by the dimers  $n$ - $n$ (b) and  $n$ - $n$ (c) were of similar type, but were different from that formed by  $n$ - $n$ (a). XRD studies were carried out on  $n$ - $n$ (a), and the results are discussed later.

### 3.1.2 $p$ - $p$ type dimers

All the  $p$ - $p$  dimers were found to be enantiotropic in nature, exhibiting a Col<sub>r</sub> phase. The dimers  $p$ - $p$ (a) and  $p$ - $p$ (c) had liquid crystalline properties at room temperature, but  $p$ - $p$ (b) did not and adopted Col<sub>r</sub> phase only at  $44.8^{\circ}\text{C}$ . The compound  $p$ - $p$ (a) showed focal conic domains of the Col<sub>r</sub> mesophase which cleared at  $93.4^{\circ}\text{C}$  (Figure 2). Compounds  $p$ - $p$ (b) and (c) exhibited the Col<sub>r</sub> mesophase which cleared at  $123.1^{\circ}\text{C}$  and  $104.5^{\circ}\text{C}$  respectively (Table 1, above).

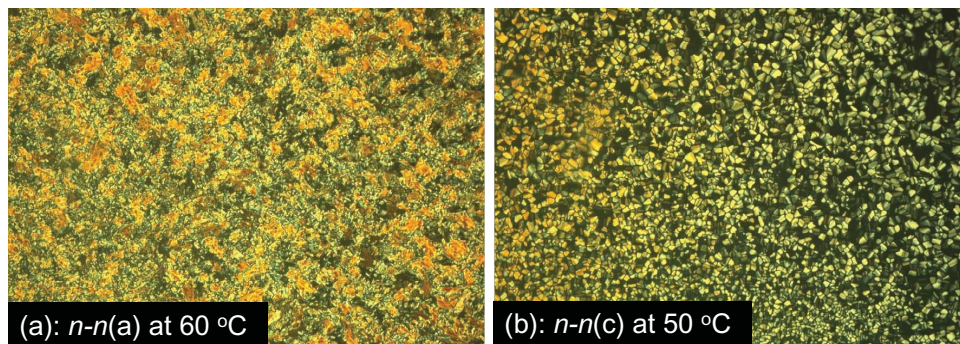


Figure 1. The optical texture on cooling the isotropic liquid of the  $n$ - $n$  dimer under the POM: (a) unidentified columnar phase at  $60^{\circ}\text{C}$ ; (b) rectangular columnar mesophase of  $n$ - $n$ (c) at  $50^{\circ}\text{C}$  (colour version online).

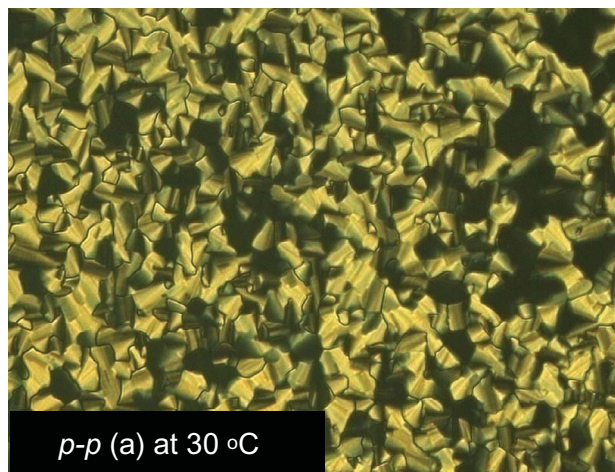


Figure 2. The optical texture on cooling the isotropic liquid of compound  $p-p(a)$  under the POM at 30°C (colour version online).

### 3.1.3 $n-p$ type dimers

All the compounds in this series showed a  $Col_r$  mesophase. The compound  $n-p(c)$  ( $R = R' = C_8H_{17}$ ) showed a monotropic nematic phase ( $N_c$ ) in addition to a monotropic  $Col_r$  phase. The schlieren texture of the nematic phase is shown in Figure 3(a). On further cooling to 36.1°C it changed to a  $Col_r$  phase and did not recover until it had reached room temperature.

The structure-property relationship of these dimers showed that spacer length played a significant role in their molecular self-assembly. The mesophase was found to be stabilised more in the case of shorter spacer chains. Increasing the spacer chain induced a crystalline nature to the mesophases, reducing the mesophase range of these compounds. For characterisation of mesophase nature, one compound from each of the series  $n-n$ ,  $p-p$  and  $n-p$  was selected for detailed investigation.

### 3.2 X-ray studies

XRD experiments were carried out on derivatives  $n-n(a)$ ,  $p-p(c)$  and  $n-p(a)$ , representing each type of

dimer. The resulting indexation, experimental and calculated reciprocal spacings are summarised in Table 2.

Rectangular columnar phases often displayed two intense peaks in the low angle region, which were indexed as (20) and (11) reflections of the 2D lattice. The discotic dimer  $p-p(c)$  gave a diffraction pattern at 90°C with two strong reflections at  $d$ -spacing 22.3 and 20.2 Å and a broad diffuse peak at 4.5 and 3.6 Å. This diffraction pattern corresponded to rectangular lattice constants,  $a = 44.6$  and  $b = 22.7$  Å. The drop of intensity in the small angle region in 1D intensity was a result of the limitations of the instrument – signal integration in the XRD image is carried out along a circle, but the image is square. Different  $Col_r$  phases were detected, but could not be identified due to insufficient information caused by lack of reflection. The dimer  $n-n(a)$  gave more reflections in both small and wide angle regions at 45°C (Figure 4).

Reflection peaks were observed at  $d$  21.1, 20.2, 11.7, 11.2, 10.4, 9.8, 7.3, 6.8, 5.8, 4.6, 3.5 and 3.4 Å and a broad diffuse peak around 4.5 Å. In conjunction with POM observations, there appeared to be a rigid columnar or soft crystalline phase ( $Col_x$ ). The pattern observed for the upper temperature region in the case of  $n-p(a)$  could be ascribed to a  $N_c$  phase. Broad diffuse peaks at  $d = 21.1$ , 4.5 and 3.6 Å were also observed (Figure 5(a)) which could be attributed to the average molecular length, alkyl-alkyl chain correlation and core-core distances, respectively. The lower temperature phase exhibited peaks at  $d = 26.4$ , 20.8, 17.6, 14.2, 12.9, 11.8, 10.2 and 8.7 Å, and broad diffuse peaks at 4.5 and 3.6 Å, at 20°C. The (01) and (30) reflections observed for  $Col_r$  are only possible for the  $P2mm$  plane group. On the other hand, assumption of  $Col_r$  with  $P2mm$  symmetry (unit cell dimensions:  $a = 51.5$ ,  $b = 23.5$  and  $c = 3.6$  Å) leads to a  $Z$  value (molecules per lattice) of 1.0 (assuming a density of 1.0 g cm<sup>-3</sup>) and is consistent with the required value of  $Z = 1$  for the symmetry of the phase. This diffraction pattern corresponds to rectangular lattice constants:  $a = 51.5$ ,  $b = 23.5$  Å with  $Col_r$ - $P2mm$  symmetry (Figure 5(b)).

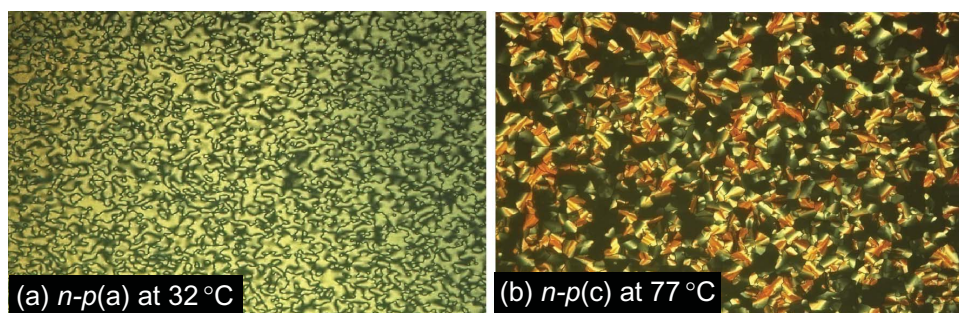


Figure 3. The optical texture on cooling the isotropic liquid of compound  $n-p$  under the POM: (a) Schlieren texture of nematic columnar mesophase of compound  $n-p(a)$  at 30°C; (b) rectangular columnar mesophase of  $n-p(c)$  at 77°C (colour version online).



Table 2. XRD data for compounds  $p$ - $p$ (c),  $n$ - $p$ (a) and  $n$ - $n$ (a) in their respective mesophases.

Phase and parameters	$d_{\text{exp}}/\text{\AA}^{(a)}$	$hk^{(b)}$	$d_{\text{cal}}/\text{\AA}^{(a)}$
$p$ - $p$ (c), Col <sub>r</sub> , 90°C $a = 44.6 \text{\AA}$ , $b = 22.7 \text{\AA}$	22.3	20	22.3
	20.2	11	20.2
	4.5	halo	
	3.6	core-core	
$n$ - $n$ (a), Col <sub>x</sub> , 45°C	21.1		
	20.2		
	11.7		
	11.2		
	10.4		
	9.8		
	7.3		
	6.8		
	5.8		
	4.6		
	3.5		
$n$ - $p$ (a), N <sub>c</sub> , 51°C	21.1	halo	
	4.5	halo	
	3.6	core-core	
$n$ - $p$ (a), Col <sub>r</sub> , $p2 \text{ mm}$ , 20°C $a = 35.2 \text{\AA}$ , $b = 25.8 \text{\AA}$	26.4	01	25.7
	20.8	11	21.4
	17.6	20	17.3
	14.2	21	13.9
	12.9	02	12.9
	11.8	30	11.7
	10.2	22	10.4
	8.5	03	8.6
	4.5	halo	
	3.6	core-core	

Notes: (a)  $d_{\text{exp}}$  and  $d_{\text{cal}}$  are the experimentally measured and theoretical calculated diffraction spacing, respectively. The distances are given in angstroms.

(b)  $hk$  are the Miller indices of the reflections of the 2D columnar phase.

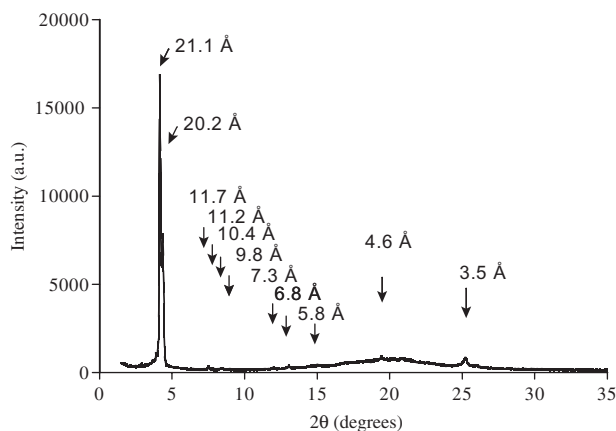


Figure 4. Powder X-ray diffraction pattern of the compound  $n$ - $n$ (a) at 45°C of unidentified columnar phase.

UV studies of these materials were performed in the solid state, as well as on solutions at a range of concentrations. Surprisingly, the additional absorption bands expected for CT complex formation

(~400 nm) in the solid state or in solution were not seen, in comparison with the UV spectra of the pure donor and acceptor monomers. This indicated the absence of CT complex formation in these dimers.

#### 4. Summary

Three varieties of non-symmetrical dimers bearing mesogenic anthraquinone–anthraquinone ( $n$ - $n$ ), triphenylene–triphenylene ( $p$ - $p$ ) and anthraquinone–triphenylene ( $n$ - $p$ ) moieties have been synthesised. The  $n$ - $n$  dimers exhibited unidentified Col<sub>x</sub> and Col<sub>y</sub> mesophases. The  $p$ - $p$  dimers exhibited a Col<sub>r</sub> mesophase, whereas the  $n$ - $p$  dimers showed Col<sub>r</sub> and N<sub>c</sub> mesophases. The mesophases in most of the derivatives were stable at room temperature and a glassy state was observed in only a few derivatives. It appears that the nature of the mesophases exhibited in these compounds depends mainly on the spacer chain length. A nematic phase was observed in one of the dimers of  $n$ - $p$  type.

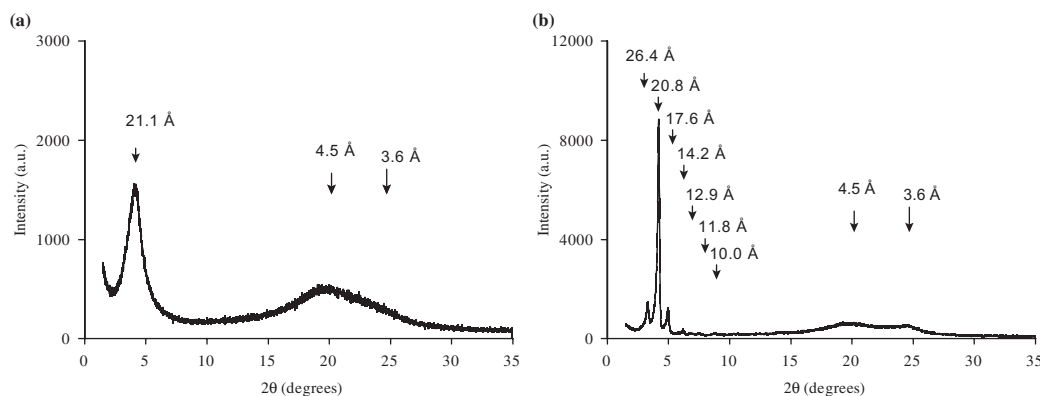


Figure 5. Powder X-ray diffraction pattern of the compound *n-p*(a): (a) nematic columnar phase at 51°C; (b) rectangular columnar mesophase at 20°C.

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