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Synthesis and mesomorphic properties of unsymmetrical bent-core compounds containing 1,3-phenylene or 2,7-naphthylene as the central unit

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The synthesis and mesomorphic properties of four new homologous series of unsymmetrical bent-core compounds with 1,3-phenylene or 2,7-naphthylene as the central unit are reported. These compounds contain an α-methylcinnamoyloxy bridging group in one of the arms. Three types of mesophases, namely, N, B_1 and B_2 are observed in these compounds. The rarely observed transitions N to B_1 and N to B_2 have been observed in some of the compounds derived from 2,7-dihydroxynaphthalene. In one of the compounds derived from resorcinol, textural features of both B_1 and B_2 phases appear simultaneously on cooling the isotropic phase. The mesophases were characterized using conventional techniques.

1. Introduction

The study of the mesomorphic properties of achiral bent-core (banana-shaped) compounds forms the basis of a new sub-field of thermotropic liquid crystals. Since the discovery [1] of electro-optical switching, followed by the beautiful demonstration of the chirality of the mesophases [2] of bent-core compounds, there has been considerable progress in the study of such materials. In recent years, several hundred compounds having a bent molecular shape and exhibiting mesophases have been reported [3–8]. Most of these are derived from resorcinol, and are symmetrical about this central unit. Many bridging groups such as azomethine, azo and ester groups have been used in the design and synthesis of such compounds with *n*-alkoxy terminal chains. The commonly observed banana (B) phases are B_6, B_1 and B_2 which occur in this sequence on ascending a homologous series of compounds [4–6, 9]. The mesophase structures of all these phases are well established [3]. There are of course, a large number of B mesophase structures described in the literature for which a suitable assignment of symbols has yet to be given.

The occurrence of calamitic phases in conjunction with the B phases has been observed in a number of systems [7, 8, 10–12]. This seems to depend on the bend angle between the two arms of the bent-core molecules. The occurrence of a transition from a nematic phase to a chiral mesophase is itself an interesting phenomenon. There are only a few cases where a transition from a nematic phase to an antiferroelectric mesophase has been reported [7, 10, 11]. Therefore, it would be of considerable interest to explore the molecular structural requirements to obtain such a transition. The nematic to B phase transitions have been obtained in systems containing a 2,7-naphthylene central unit [10]. Reports on the mesomorphic properties of compounds derived from 2,7-dihydroxynaphthalene are few in number [12–15]. Although compounds containing two unsymmetrical arms about a central phenyl ring are known [3, 11, 16], those derived from resorcinol (except for [16]) or from 2,7-dihydroxynaphthalene are unknown.

Here, we report four homologous series of unsymmetrical compounds derived from both resorcinol and 2,7-dihydroxynaphthalene, transitions from N to B phases were observed only in the latter. The melting points of unsymmetrical compounds derived from resorcinol in one of the homologous series are relatively low. To the best of our knowledge, this is the series with the lowest melting points and exhibiting a B_2 phase.

The general molecular structure of the compounds under investigation is:

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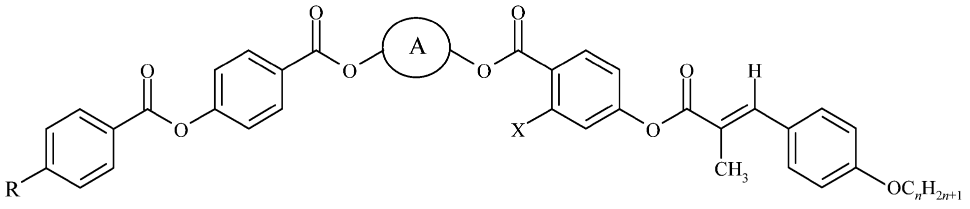
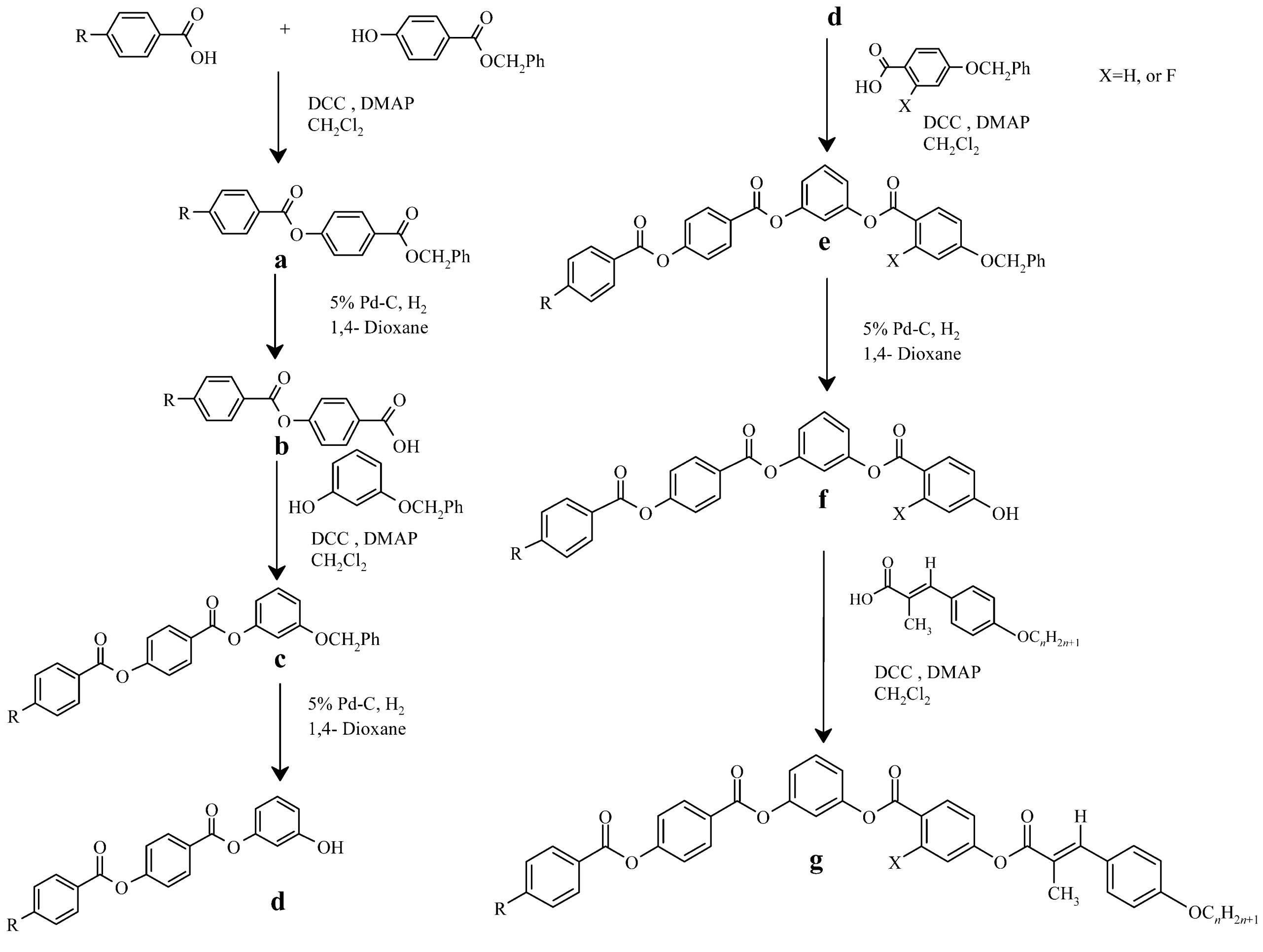


R= n-$C_{12}H_{25}O$,	A= 1, 3-Phenylene,	X=H,	Series I
R= n-$C_{12}H_{25}O$,	A= 1, 3-Phenylene,	X=F,	Series II
R= n-$C_{12}H_{25}$,	A= 1, 3-Phenylene,	X=F,	Series III
R= n-$C_{12}H_{25}O$,	A= 2, 7-Naphthylene,	X=F,	Series IV

Structure.



R= n-$C_{12}H_{25}O$ / n-$C_{12}H_{25}$

Scheme. Synthetic pathway for the preparation of the unsymmetrical bent-core mesogens.

2. Synthesis

The synthetic route used to prepare the unsymmetrical compounds is shown in the scheme. Resorcinol, 2,7-dihydroxynaphthalene and benzyl-4-hydroxybenzoate were commercial compounds and used as received. 4-Benzyloxybenzoic acid, 2-fluoro-4-benzyloxybenzoic acid [17] and *E*-4-*n*-alkoxy-α-methylcinnamic acid [18] were prepared according to procedures described in the literature. The esterification reaction was carried out using the carbodiimide method, and deprotection of the benzyl group was achieved by hydrogenolysis using 5% Pd-C as a catalyst. The detailed synthetic procedure for one of the target compounds and the physical data of the intermediate derivatives are given here.

2.1. *Benzyl 4- (4-n- dodecyloxybenzoyloxy)benzoate,* **a** *(R=n-$C_{12}H_{25}O$)*

A mixture of 4-*n*-dodecyloxybenzoic acid (9.0 g, 29.4 mmol), benzyl-4-hydroxybenzoate (6.7 g, 29.4 mmol), a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine (DMAP), and dry dichloromethane (100 ml) was stirred for 10 min. To this *N*,*N′*-dicyclohexylcarbodiimide (DCC), (6.66 g, 32.3 mmol) was added and the mixture stirred overnight at room temperature. The precipitated *N*,*N′*-dicyclohexylurea was filtered off and washed with dichloromethane. The filtrate was washed successively with 5% aqueous acetic acid (25 ml × 2), 5% ice-cold sodium hydroxide solution, (25 ml × 2) and water (25 ml × 3); it was dried over anhydrous sodium sulphate. The solvent was removed to yield a product, which was then purified by chromatography on silica gel using chloroform as eluant. Removal of solvent from the eluate gave a white material, which was crystallized from a mixture of chloroform and acetonitrile. Yield 13.1 g (86%), m. p. 62–63°C. IR (nujol) ν_{max}: 2918, 2851, 1732, 1714, 1608, 1470, 1292 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.16–8.12 (m, 4H, Ar–H), 7.46–7.35 (m, 5H, Ar–H), 7.30–7.28 (d, 2H, ^3J8.72 Hz, Ar–H), 6.98–6.96 (d, 2H, ^3J8.92 Hz, Ar–H), 5.38 (s, 2H, O–CH$_2$–Ar), 4.06–4.02 (t, 2H, ^3J6.52Hz, Ar–O–CH$_2$), 1.85–1.78 (quin, 2H, ^3J7.0 Hz, Ar–O–CH$_2$–CH$_2$), 1.50–1.27 (m, 18H, 9 × –CH$_2$–), 0.90–0.86 (t, 3H, ^3J6.6 Hz, –CH$_3$,). Elemental analysis: $C_{33}H_{40}O_5$ requires C 76.71, H 7.80; found C 76.65, H 7.94%.

2.2. *4-(4-n-Dodecyloxybenzoyloxy)benzoic acid,* **b**

Compound **a** (13.1 g, 25.1 mmol), was dissolved in 1, 4-dioxane (100 ml). To this solution 5% Pd-C catalyst (2.7 g) was added and the mixture stirred at 40°C under hydrogen until the required quantity was absorbed. The reaction mixture was filtered and the solvent removed from the filtrate under reduced pressure. The product thus obtained was crystallized from a mixture of 1,4-dioxane and petroleum ether (b.p.60–80°C). Yield 9.9 g (92%), Cr 120 SmC 209 N 220.5°C I. IR (nujol) ν_{max}: 3070, 2972, 2851, 2548, 1732, 1688, 1603, 1261, 1161 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.21–8.18 (d, 2H, ^3J8.68 Hz, Ar–H), 8.15–8.13 (d, 2H, ^3J8.88 Hz, Ar–H), 7.35–7.32 (d, 2H, ^3J8.68 Hz, Ar–H), 6.99–6.97 (d, 2H, ^3J8.88 Hz, Ar–H), 4.06–4.03 (t, 2H, ^3J6.52 Hz, Ar–O–CH$_2$–), 1.86–1.79 (quin, 2H, ^3J7.0 Hz, Ar–O–CH$_2$–CH$_2$–), 1.51–1.26 (m, 18H, 9 × –CH$_2$–), 0.90–0.86 (t, 3H, ^3J6.48 Hz, –CH$_3$). Elemental analysis: $C_{26}H_{34}O_5$ requires C 73.21, H 8.03; found C 73.61, H 8.3%.

2.3. *3-Benzyloxyphenyl 4-(4-n-dodecyloxybenzoyloxy)benzoate,* **c**

This compound was prepared using the same procedure as described for compound **a**. Quantities: compound **b** (9.8 g, 23 mmol), 3-benzyloxyphenol (4.6 g, 23 mmol), catalytic amount of DMAP, DCC (5.2 g, 25.3 mmol), dry dichloromethane (50 ml). Yield 12.0 g (86%), m.p. 97–98°C. IR (nujol) ν_{max}: 2924, 2856, 1736, 1605, 1256, 1061 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ: 8.28–8.26 (d, 2H, ^3J8.65 Hz, Ar–H), 8.16–8.14 (d, 2H, ^3J8.8 Hz, Ar–H), 7.45–7.32 (m, 8H, Ar–H,), 7.00–6.98 (d, 2H, ^3J8.8 Hz, Ar–H), 6.92–6.84 (m, 3H, Ar–H), 5.08 (s, 2H, O–CH$_2$–Ar), 4.07–4.04 (t, 2H, ^3J6.55 Hz, Ar–O–CH$_2$–), 1.86–1.80 (quin, 2H, ^3J7.1 Hz, Ar–O–CH$_2$–CH$_2$–), 1.51–1.28 (m, 18H, 9 × –CH$_2$–), 0.90–0.87 (t, 3H, ^3J6.7Hz, –CH$_3$). Elemental analysis: $C_{39}H_{44}O_6$ requires C 76.95, H 7.29; found C 76.50, H 7.43%.

2.4. *3-Hydroxyphenyl 4-(4-n-dodecyloxybenzoyloxy)benzoate,* **d**

This compound was prepared using the same procedure as described for compound **b**. Quantities: compound **c** (11.8 g, 19.4 mmol), 1, 4-dioxane (75 ml), 5% Pd-C (1.8 g). Yield 9.2 g (90%), m.p.124.5–125.5°C. IR (nujol) ν_{max}: 3377, 3315, 2922, 2853, 1734, 1713, 1605, 1252, 1067 cm^{-1}. ^{1}H NMR (500 MHz, CD$_3$COCD$_3$) δ: 8.66 (s, 1H, Ar–OH, exchangeable with D$_2$O), 8.27–8.25 (d, 2H, ^3J8.7 Hz, Ar–H), 8.16–8.14 (d, 2H, ^3J8.9 Hz, Ar–H), 7.51–7.49 (d, 2H, ^3J8.7 Hz, Ar–H), 7.29–7.26 (t, 1H, ^3J7.45 Hz, Ar–H), 7.14–7.12 (d, 2H, ^3J8.9 Hz, Ar–H), 6.81–6.77 (m, 3H, Ar–H), 4.17–4.14 (t, 2H, ^3J6.5 Hz, Ar–O–CH$_2$–), 1.86–1.81 (quin, ^3J7.1 Hz, 2H, Ar–O–CH$_2$–CH$_2$–), 1.54–1.30(m, 18H, 9 × –CH$_2$–), 0.90–0.87 (t, 3H, ^3J6.7 Hz, –CH$_3$). Elemental analysis: $C_{32}H_{38}O_6$ requires C 74.11, H 7.39; found C 74.52, H 7.35%.

2.5. *1-(4-Benzyloxybenzoyloxy)-3-[4-(4-n-dodecyloxybenzoyloxy)benzoyloxy]benzene,* ***e***

This compound was prepared using the same procedure as described for compound **a**. Quantities: compound **d** (5.5 g, 10.6 mmol), 4-benzyloxybenzoic acid (2.42 g, 10.6 mmol), catalytic amount of DMAP, DCC (2.40 g, 11.7 mmol), dry dichloromethane (50 ml). Yield 6.0g (78%), m. p.119–120°C. IR (nujol) ν_{max}: 2922, 2856, 1736, 1728, 1605, 1256, 1163, 1063 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.28–8.26 (d, 2H, ^{3}J8.7 Hz, Ar–H), 8.16–8.14 (d, 4H, ^{3}J8.0 Hz, Ar–H), 7.49–7.36 (m, 8H, Ar–H), 7.17–7.15 (m, 3H, Ar–H), 7.07–7.05 (d, 2H, ^{3}J8.9 Hz, Ar–H), 7.00–6.98 (d, 2H, ^{3}J8.9 Hz, Ar–H), 5.16 (s, 2H, O–CH_2–Ar), 4.07–4.04 (t, 2H, ^{3}J6.5 Hz, Ar–O–CH_2–), 1.86–1.80 (quin, 2H, ^{3}J7.1 Hz, Ar–O–CH_2–CH_2–), 1.50–1.27 (m, 18H, 9 × –CH_2–), 0.90–0.87 (t, 3H, ^{3}J6.65 Hz, –CH_3). Elemental analysis: $C_{46}H_{48}O_8$ requires C 75.80, H 6.64; found C 75.37, H 6.5%.

2.6. *1-(4-Hydroxybenzoyloxy)-3-[4-(4-n-dodecyloxybenzoyloxy)benzoyloxy]benzene,* ***f***

This was synthesized following a procedure described for the preparation of compound **b**. Quantities: compound **e** (5.8 g, 7.97 mmol), 1,4-dioxane (60 ml), 5% Pd-C (1.1 g). Yield 4.2 g (82.5%), m. p. 182–183°C. IR (nujol) ν_{max}: 3375, 3065, 2922, 2856, 1742, 1728, 1705, 1595, 1276, 1057 cm^{-1}. ^{1}H NMR (500 MHz, CD_3COCD_3) δ: 9.5(s, 1H, Ar–OH, exchangeable with D_2O), 8.31–8.29 (d, 2H, ^{3}J8.65 Hz, Ar–H), 8.16–8.14 (d, 2H, ^{3}J8.8 Hz, Ar–H), 8.08–8.06 (d, 2H, ^{3}J8.7 Hz, Ar–H), 7.58–7.55 (t, 1H, ^{3}J8.15 Hz, Ar–H), 7.53–7.51 (d, 2H, ^{3}J8.65 Hz, Ar–H), 7.31–7.24 (m, 3H, Ar–H), 7.14–7.12 (d, 2H, ^{3}J8.8 Hz, Ar–H), 7.02–7.00 (d, 2H, ^{3}J8.7 Hz, Ar–H), 4.17–4.14 (t, ^{3}J6.5 Hz, Ar–O–CH_2–, 2H), 1.85–1.81 (quin, 2H, ^{3}J7.0 Hz, Ar–O–CH_2–CH_2–), 1.53–1.30 (m, 18H, 9 × –CH_2–,), 0.89–0.87 (t, 3H, ^{3}J6.5 Hz, –CH_3). Elemental analysis: $C_{39}H_{42}O_8$ requires C 73.33, H 6.63; found C 73.36, H 6.64%.

2.7. *1-[4-(E-4-n-tetradecyloxy-α-methylcinnamoyloxy)benzoyloxy]-3-[4-(4-n-dodecyloxybenzoyloxy)benzoyloxy]benzene,* ***8***

This was prepared following a procedure described for the preparation of compound **b**. Quantities: compound **f** (0.15 g, 0.24 mmol), *E*-4-*n*-tetradecyloxy-α-methylcinnamic acid (0.090 g, 0.24 mmol), catalytic amount of DMAP, DCC (0.054 g, 0.26 mmol), dry dichloromethane (10 ml). Yield 0.150 g (64%), m. p. 85.5°C. IR (KBr) ν_{max}: 3089, 2920, 2851, 1732, 1730, 1605, 1256, 1138, 1070 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29–8.26 (m, 4H, Ar–H), 8.16–8.14 (d, 2H, ^{3}J8.76 Hz, Ar–H), 7.91 (s, 1H, =C(H)), 7.52–7.46 (m, 3H, Ar–H), 7.39–7.36 (d, 2H, ^{3}J8.64 Hz, Ar–H), 7.34–7.32 (d, 2H, ^{3}J8.64 Hz, Ar–H), 7.20–7.17 (m, 3H, Ar–H), 7.0–6.98 (d, 2H, ^{3}J8.88 Hz, Ar–H), 6.97–6.95 (d, 2H, ^{3}J8.76 Hz, Ar–H), 4.07–4.04 (t, 2H, ^{3}J6.52 Hz, Ar–O–CH_2–), 4.03–3.99 (t, 2H, ^{3}J6.56 Hz, Ar–O–CH_2–), 2.276–2.274 (d, 3H, ^{3}J1.0 Hz, =C(CH_3)–), 1.86–1.77 (m, 4H, 2 × Ar–O–CH_2–CH_2–), 1.47–1.27 (m, 40H, 20 × –CH_2–), 0.90–0.87 (m, 6H, 2 × –CH_3). Elemental analysis: $C_{63}H_{78}O_{10}$ requires C 76.03, H 7.90; found C 76.45, H 8.04%.

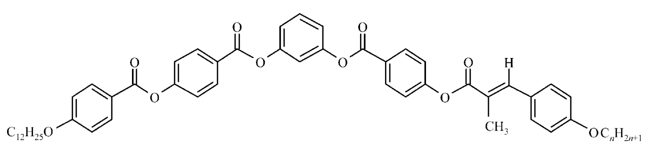
3. Results and discussion

The mesomorphic behaviour of all the compounds was investigated using a polarizing microscope (Leitz Laborlux 12 POL/Olympus BX50) equipped with a heating stage (Mettler FP 82 HT) and a controller (Mettler FP5). The transition temperatures and associated enthalpy values were determined from thermograms obtained on a differential scanning calorimeter (Model Pyris 1D); the heating and cooling rates were 5°C min^{-1}. The four homologous series (I, II, III and IV) of unsymmetrical compounds were prepared to examine the effect of (i) the lateral fluorine substituent, (ii) the type of terminal chain and (iii) the nature of the central unit.

The transition temperatures and associated enthalpy values for the parent compounds (series I) are summarized in table 1. Only two types of mesophase were observed in this series. Compounds **1** and **2** exhibit the same type of mesophase although the latter is monotropic. When a thin film of a sample of compound **1** was cooled from the isotropic phase, a mosaic texture appeared and filled the field of view. This is a characteristic feature of the two-dimensional B_1 phase and the structure of the phase was confirmed using XRD studies (see later). On increasing the terminal chain length to compound **3**, a lamellar B_2 phase was seen. This is not surprising since for this homologue, the core–chain interaction increases, resulting in the collapse of the two-dimensional mesophase, and any further increase in the chain length stabilizes the smectic mesophase. This general behaviour has been observed in a number of different homologous series of compounds [4–6, 9]. In fact compounds **3**–**10** show the same types of texture under the polarizing microscope. Either a schlieren texture or a fingerprint texture was observed, which is typical for the lamellar B_2 phase. The clearing enthalpy value for this mesophase is in the range 17.5–21.3 kJ mol^{-1}. It is also interesting to note that the melting points are not very high and the clearing temperatures are close to about 100°C, unlike many other five-ring systems [3, 7–9]. A plot of transition temperature as a function of the length of the terminal *n*-alkoxy chain is shown in figure 1.

A lateral fluorine substituent appears to have a

Table 1. Transition temperatures (°C) and the associated enthalpies (kJ mol^{-1}) (in italics) for compounds of series I. Cr = crystalline phase, B_2 = smectic antiferroelectric banana mesophase, B_1 = two-dimensional rectangular banana mesophase, N = nematic mesophase, I = isotropic, ( ) = mesophase is monotropic.



Compound	*n*	Cr		B_2		B_1		I
1	6	●	83.0 *29.5*	—		●	91.0 *14.2*	●
2	7	●	94.0 *59.9*	—		(●	90.5) *15.1*	●
3	8	●	86.5 *44.2*	●	92.0 *17.5*	—		●
4	9	●	91.0 *61.5*	●	94.5 *18.7*	—		●
5	10	●	79.0 *54.7*	●	97.5 *19.2*	—		●
6	11	●	89.0 *69.9*	●	98.5 *20.1*	—		●
7	12	●	89.0 *70.0*	●	99.0 *20.0*	—		●
8	14	●	85.5 *71.8*	●	100.5 *21.1*	—		●
9	16	●	89.0 *43.8*	●	101.0 *19.7*	—		●
10	18	●	83.5 *83.4*	●	101.0 *21.3*	—		●

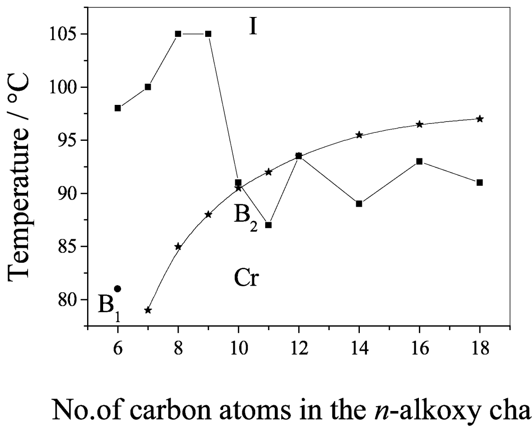
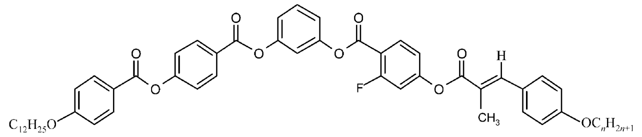


Figure 1. Plot of transition temperature as a function of terminal chain length for compounds of series I.

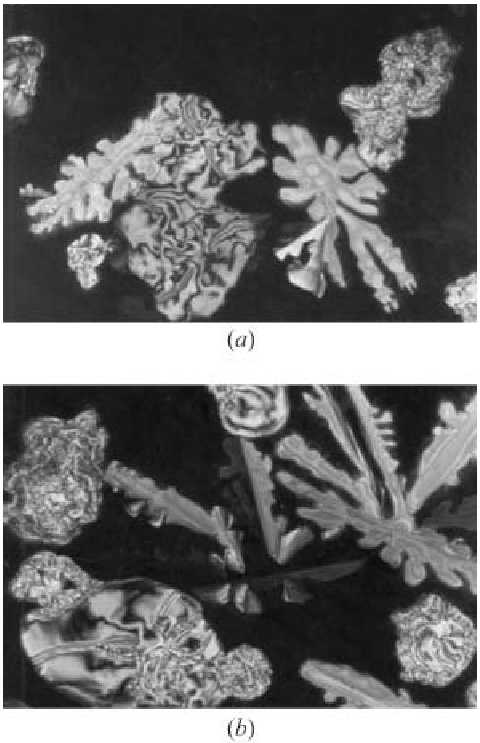
strong influence on the mesomorphic properties of banana-shaped mesogens [6, 19, 20]. We have reported [6] a large number of such compounds and the location of this substituent is the determining factor in modifying the properties. In the present study, we have introduced a fluorine into one of the arms of the bent-core compounds of series I. The transition temperatures and associated enthalpy values of these compounds (series II) are summarized in table 2. It can be seen that the melting points have increased while the clearing points are reduced by 4° to 12°C as a result of fluorine substitution. Hence, some of the homologues exhibit metastable mesophases and in others the thermal range of the mesophase has been reduced. Compound **11** shows a monotropic B_1 phase while compound **12** exhibits interesting optical features: on slow cooling of a thin film of this compound, both mosaic (B_1 phase) as well as a schlieren texture (B_2 phase) appear simultaneously. On heating, this textural feature transformed to the isotropic phase with no change. The remaining compounds **13**–**20** showed textures characteristic of the B_2 phase. Optical photomicrographs showing the simultaneous appearance of the two types of textures are shown in figures 2 (*a*) and (*b*). However, this transition $B_1 \rightarrow B_2$, could not also be

Table 2. Transition temperatures (°C) and the associated enthalpies (kJ mol^{-1}) (in italics) for compounds of series II.



Compound	*n*	Cr		B_2		B_1		I
11	6	●	98.0 *56.8*	—		(●	81.0) *14.7*	●
12	7	●	100.0 *66.7*	(●	79.0)[a] *14.7*	●		●
13	8	●	105.0 *59.6*	(●	85.0) *17.9*	—		●
14	9	●	105.0 *65.9*	(●	88.0) *18.6*	—		●
15	10	●	91.0 *72.5*	(●	90.5) *19.5*	—		●
16	11	●	89.5 *31.5*	●	92.0 *19.6*	—		●
17	12	●	93.5 *89.0*	(●	93.5) *20.0*	—		●
18	14	●	89.0 *70.1*	●	95.0 *21.2*	—		●
19	16	●	93.0 *81.1*	●	96.5 *21.7*	—		●
20	18	●	91.0 *82.8*	●	97.0 *22.0*	—		●

[a] This compound exhibits textures of B_1 and B_2 phases simultaneously upon cooling the isotropic phase.



(*a*)

(*b*)

Figure 2. (*a*) and (*b*). Optical photomicrographs showing the simultaneous appearance of mosaic and schlieren textures obtained on cooling the isotropic phase of compound **12**.

detected on a DSC thermogram. A plot of transition temperature as a function of the number of carbon atoms in the *n*-alkoxy chain is shown in figure 3. The clearing temperature curve for the B_2 phase shows the usual trend.

It is well known that terminal *n*-alkyl chain-containing compounds generally have lower transition temperatures than their corresponding *n*-alkoxy analogues. With a view to reducing the transition temperatures further, the *n*-alkoxy chain present in compounds of series II was replaced by an *n*-alkyl chain resulting in homologous series III. The transition temperatures and the associated enthalpy values obtained for this series of compounds are presented in table 3. It is evident from this table, and as expected, that the transition temperatures for series III are lower and the mesophases are retained. Compound **21** shows a monotropic B_1 phase while compounds **22**–**30** exhibit the B_2 phase. These homologues represent the series of bent-core compounds exhibiting the B_2 phase with the lowest melting points found so far. For example, compound **25** melts at 56°C, exhibiting a B_2 phase which becomes isotropic at 86°C. The mesophase could be easily cooled to room temperature. In addition, the thermal range of the B_2 phase has been increased as a result of the introduction of the *n*-alkyl group. A plot of transition temperature as a function of the *n*-alkoxy chain length is shown in figure 4. Again, a smooth rising curve, which is typical for the clearing temperatures of the B_2 phase, can be seen for this series of compounds.

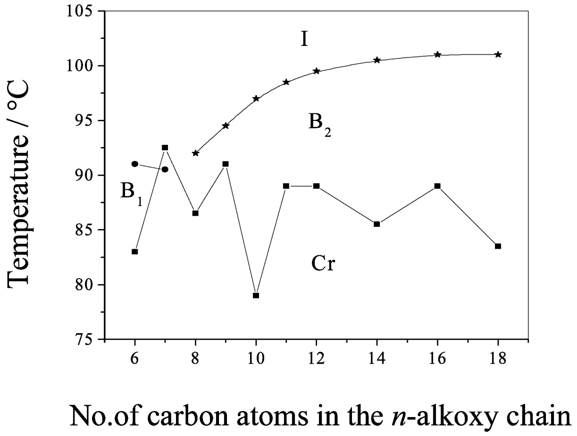
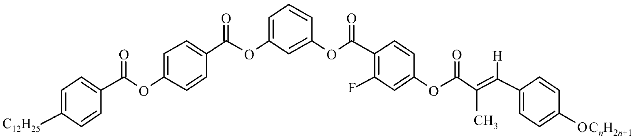


Figure 3. Plot of transition temperature as a function of terminal chain length for compounds of series II.

Table 3. Transition temperatures (°C) and the associated enthalpies (kJ mol^{-1}) (in italics) for compounds of series III.



Compound	*n*	Cr		B_2		B_1		I
21	6	•	82.0 *68.3*	—		(•	72.5) *14.3*	•
22	7	•	78.0 *62.6*	(•	76.0) *16.6*	—		•
23	8	•	80.5 *69.2*	(•	80.0) *17.6*	—		•
24	9	•	73.0 *46.4*	•	83.0 *18.5*	—		•
25	10	•	56.0 *33.8*	•	86.0 *19.3*	—		•
26	11	•	56.0 *30.7*	•	87.5 *20.4*	—		•
27	12	•	57.5 *36.2*	•	89.0 *20.4*	—		•
28	14	•	64.0 *32.1*	•	90.5 *20.6*	—		•
29	16	•	76.0 *34.0*	•	91.5 *20.8*	—		•
30	18	•	73.0 *57.9*	•	92.0 *21.8*	—		•

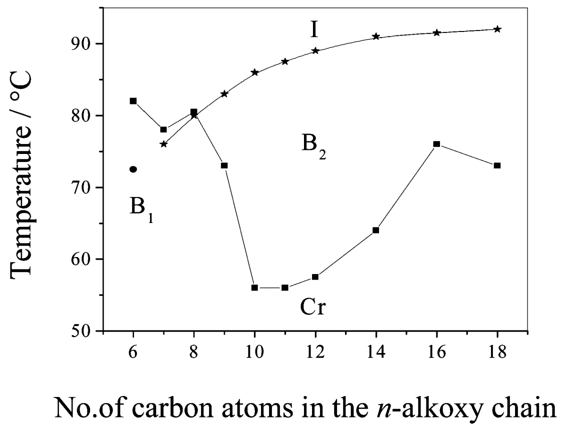
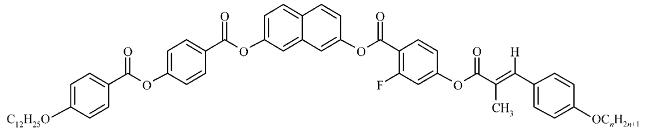


Figure 4. Plot of transition temperature as a function of terminal chain length for compounds of series III.

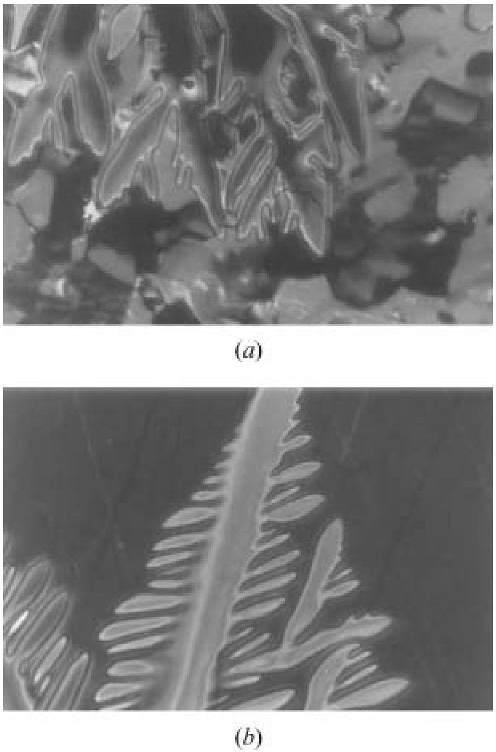
Table 4. Transition temperatures (°C) and the associated enthalpies (kJ mol^{-1}) (in italics) for compounds of series IV.



Compound	*n*	Cr	B_2	B_1	N	I
31	2	● 138.5 *59.6*	—	(● 128.0) *8.7*	● 168.0 *0.4*	●
32	4	● 103.0 *32.1*	—	● 140.0 *12.1*	● 155.0 *0.4*	●
33	5	● 104.0 *33.3*	—	● 139.0 *12.5*	● 149.0 *0.4*	●
34	6	● 98.0 *40.7*	—	● 138.5 *12.6*	● 148.0 *0.5*	●
35	7	● 94.5 *52.5*	—	● 136.0 *12.6*	● 144.0 *0.4*	●
36	8	● 101.0 *57.1*	—	● 135.0 *12.3*	● 143.5 *0.4*	●
37	9	● 99.0 *55.5*	● 136.0 *15.6*	—	● 141.5 *0.4*	●
38	10	● 99.0 *56.7*	● 139.0 *15.9*	—	● 140.0 *0.3*	●
39	11	● 105.0 *65.5*	● 141.0 *17.4*	—	—	●
40	12	● 109.0 *72.1*	● 142.5 *17.7*	—	—	●
41	14	● 104.0 *67.5*	● 143.5 *17.8*	—	—	●

Several hundred bent-core compounds exhibiting B-phases have been reported to date. The majority of them are derived from a 1,3-phenylene central unit. Although a few other central units have been used, derivatives based on 2,7-naphthylene are very limited [12–15]. From our earlier studies [14], we have found this group to be very useful in generating banana-phases. Curiously, we have been able to obtain banana-phases in combination with a nematic phase. For example, a direct transition from a lamellar B_2 phase to a nematic phase [7, 10–12], a two-dimensional columnar B_1 phase to a nematic phase [11, 12, 14], and an intercalated B_6 to a nematic phase [12] have been found. All these transitions were observed in symmetrical compounds. To date, there are very few reports of such transitions and we decided to explore the possibility of observing these in some unsymmetrical compounds derived from 2,7-dihydroxynaphthalene. The resulting compounds belong to homologous series IV whose transition temperatures and associated enthalpy values are summarized in table 4. Three types of mesophases namely, N, B_1 and B_2 were observed in the eleven compounds, eight of which are dimesomorphic while three are monomesomorphic. The mesomorphic behaviour along the series is somewhat unusual. Normally, the highest temperature mesophase disappears first on ascending the homologous series in calamitic liquid crystals. However, in this series, the nematic phase is retained although the lower temperature B_1 phase is extinguished in compounds **37** and **38**. This may be explained as follows. In the bent-core compounds the nematic phase is formed due to the increase in the bend angle between the two arms. When the terminal chain is sufficiently long the nematic phase is transformed to a lamellar B_2 phase instead of a two-dimensional B_1 phase, to avoid core-chain interactions. When a thin film of a sample of compound **33** sandwiched between two untreated glass plates was cooled from the isotropic phase, nematic droplets appeared and coalesced to give rise to a schlieren texture. On further cooling to 138.5°C, a mosaic texture developed on the existing nematic phase. An optical photomicrograph showing this transition is given in figure 5(*a*). When a sample of this compound was sandwiched between two glass plates treated for homogeneous alignment and cooled from the isotropic phase the nematic phase aligned very well. When the temperature reached 138.5°C, the B_1 phase developed as a dendritic pattern, see figure 5(*b*). Compounds **31**–**36** exhibited similar mesomorphic behaviour.

On increasing the terminal *n*-alkoxy chain length further, compound **37** is obtained. When a thin film sample of this compound sandwiched between untreated glass plates was cooled from the isotropic phase, the nematic phase appeared as a marbled texture; on lowering the temperature to 135.5°C, a fingerprint texture, which is typical for a B_2 phase, began to develop, see figure 6(*a*). When this transition


(*a*)

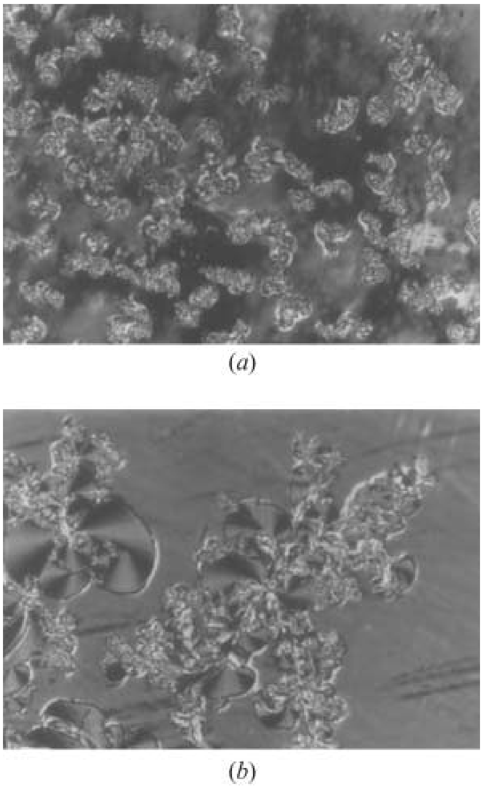
(*b*)

Figure 5. (*a*) Optical photomicrograph of compound **33** showing the transition from a nematic phase to a B_1 phase on an untreated glass plate; (*b*) the same phase transition in a homogeneously aligned cell.

was viewed for a sample sandwiched between two glass plates treated for planar alignment, the nematic phase aligned very well, and as the temperature was reduced focal-conic as well as fingerprint textures that are seen as a B_2 phase appeared, see figure 6 (*b*). On increasing the chain length further (compounds **39**–**41**), only antiferroelectric B_2 phase was seen. A plot of transition temperature as a function of the number of carbon atoms in the *n*-alkoxy chain for series IV is shown in figure 7. One can also see the odd–even effect in the nematic to isotropic transition curve, while the clearing temperature curve for the B_2 phase follows the usual trend.

4. XRD investigations

We have carried out XRD studies on various compounds representing all the four series of compounds. Samples were taken in Lindemann capillaries (0.7 mm diameter) and placed in a suitable heater whose temperature was controlled to ±0.1°C. The wavelength of the Cu Kα radiation was 1.54 Å; it was generated from a 4 kW rotating anode X-ray source (Rigaku Ultrax-18) and monochromated using a graphite crystal. The images were collected on a 2D detector (Marresearch).


(*a*)

(*b*)

Figure 6. (*a*) An optical photomicrograph of compound **37** showing a transition from a nematic phase to a B_2 phase on an untreated glass plate; (*b*) the same phase transition in a homogeneously aligned cell.

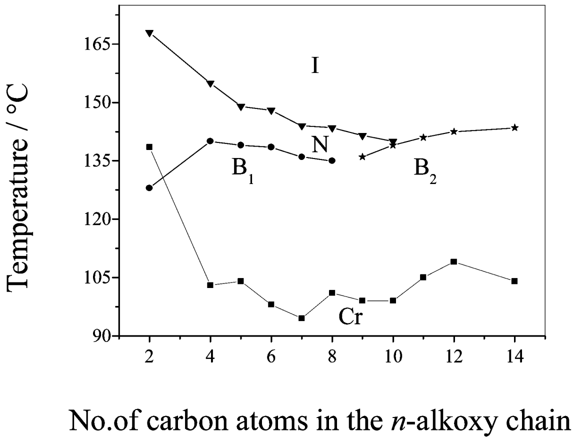


Figure 7. Plot of transition temperature as a function of terminal chain length for compounds of series IV.

The X-ray diffractogram of the mesophase of compound **1** showed two reflections in the small angle region at $d_1 = 27.6$ Å and $d_2 = 22.8$ Å, and a wide angle diffuse peak at 4.5 Å, the latter indicating the fluidity of the phase. The small angle reflections can be indexed to the (1 1), (0 2) planes of a rectangular lattice with lattice parameters $a = 34.7$ Å and $b = 45.6$ Å. The X-ray diffractogram of the mesophase of compound **3** showed two relections in the ratio 1:1/2 indicating a lamellar periodicity for the phase. The *d*-spacings obtained from XRD for representative compounds under investigation are summarized in table 5.

We obtained the XRD pattern of B_1 phase monodomain exhibited by compound **33**. On slow cooling of the isotropic liquid of this compound to a nematic phase, the XRD showed a diffuse reflection, which is typical for this phase. On lowering the temperature, the B_1 phase seemed to align well. The XRD pattern of this oriented sample displayed Bragg spots in the small as well as in the wide angle regions. The reflections in the small angle region could be indexed to the (1 1), (0 2) and (0 4) planes of a two-dimensional rectangular lattice. The dimension $b = 46.8$ Å of the crystallographic unit cell is related to the molecular length, which was estimated using a molecular model ($L = 55.3$ Å). The other lattice parameter was $a = 33.9$ Å. An XRD pattern of an oriented B_1 mesophase obtained on cooling the nematic phase of compound **33** is shown in figure 8. We could not obtain a monodomain for the B_2 phase obtained on cooling the nematic phase.

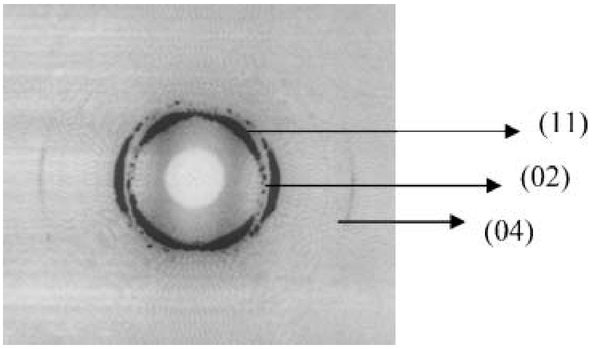


Figure 8. XRD pattern of an oriented B_1 mesophase obtained on cooling the nematic phase of compound **33**; temperature 133.0°C.

5. Electro-optical studies

Electric field experiments on the B_2 phase exhibited by representative compounds belonging to all the four homologous series were carried out using the standard triangular-wave method. The general behaviour was similar in all cases. For this experiment, a cell was constructed using ITO coated glass plates treated with polyimide and rubbed unidirectionally. The thickness of the cell was adjusted with appropriate Mylar spacers. A sample of compound **37** was filled into the cell in the isotropic state and cooled slowly under an electric field. This resulted in a reasonably good alignment of the nematic phase. On further cooling the mesophase to 134°C under a triangular-wave electric field, at a threshold of 285 V_{pp}, two-polarization current peaks were obtained, becoming saturated at a voltage of 313 V_{pp} and a frequency of 50 Hz. The saturated polarization value obtained by integrating the two current peaks was about 400 nC cm^{-2}. A typical current response obtained for compound **37** is shown in figure 9, which clearly indicates the antiferroelectric nature of the phase.

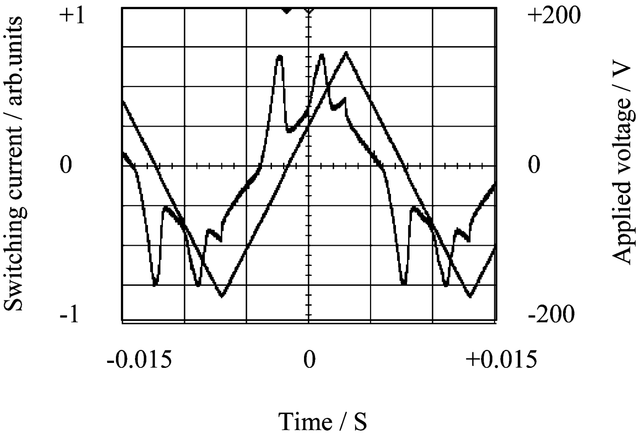


Figure 9. Switching current response obtained for compound **37** under a triangular-wave electric field (313 V_{pp}) at 50 Hz: cell thickness 10.3 μm; saturated polarization is about 400 nC cm^{-2}.

Table 5. Layer spacings from XRD studies of compounds under investigation are given below.

Compound	*d*-spacings/Å			Lattice parameters/Å		Measured molecular length *L*/Å	Phase type
	d_1	d_2	d_3	*a*	*b*		
1	27.6(11)	22.8(02)	—	34.7	45.6	55.0	B_1
3	34.9 (01)	17.5 (02)	—	—	—	56.6	B_2
9	39.2 (01)	19.6(02)	—	—	—	66.2	B_2
20	39.5 (01)	—	13.3(03)	—	—	68.2	B_2
25	35.2 (01)	17.6(02)	—	—	—	57.1	B_2
30	38.2 (01)	—	12.7 (03)	—	—	66.1	B_2
33	27.3 (11)	23.4(02)	11.8 (04)	33.9	46.8	55.9	B_1
37	35.3 (01)	—	17.7 (03)	—	—	58.1	B_2

6. Conclusions

Forty-one compounds unsymmetrically substituted about two central units and belonging to four different homologous series have been examined. The 2,7-naphthylene central unit seems to be better in generating mesophases which are not only enantiotropic but also exist over a wider thermal range. The 1,3-phenylene system with terminal *n*-alkyl chains yields compounds with low melting points and exhibiting the B_2 phase. The rarely observed transitions from a nematic to an antiferroelectric B_2 phase and from a nematic to a two-dimensional rectangular columnar B_1 phase have been obtained in the 2,7-naphthylene system.

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