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Observation of filamentary growth patterns at the isotropic-SmCP$_A$ phase transition in new unsymmetrical compounds composed of bent-core molecules

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Observation of filamentary growth patterns at the isotropic–SmCP$_A$ phase transition in new unsymmetrical compounds composed of bent-core molecules

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The synthesis and mesomorphic properties of several compounds composed of bent-core molecules, unsymmetrically substituted about the central phenyl ring, are discussed. These compounds contain substituents such as fluoro, chloro and trifluoromethyl at the terminal position of one of the arms of the bent-core molecules. Many of the compounds containing a chloro terminal substituent show filamentary growth patterns at the transition from isotropic to polar antiferroelectric smectic C phase. The liquid crystalline phase exhibited by these compounds has been characterized using a combination of polarizing optical microscopy, differential scanning calorimetry, X-ray diffraction and electro-optical studies.

1. Introduction

The sub-field of liquid crystals comprising achiral bent-core compounds has grown steadily over the past few years. The mesophases exhibited by these banana liquid crystals [1], as they are commonly known, have been assigned the symbol B, which signifies the bent shape of the constituent molecules. Although seven B phases were identified initially, i.e. B_1, B_2, ……B_7, it is well known now that the B_3 and B_4 phases actually show characteristics of crystals. Subsequently another new mesophase was observed, assigned the symbol B_8 and added to the list [2]. However, over the last couple of years, a fairly large number of new mesophase types with totally different physical properties have been reported, but the symbols assigned to these are quite arbitrary [3–6]. The assignment of proper symbols to these mesophases has been an arduous task and there is now a need to resolve this situation.

Since the discovery of electro-optical switching in an achiral compound composed of banana-shaped molecules [7], several hundred compounds with bent molecular structures and exhibiting mesophases have been reported [6–13]; most of these are symmetrical about the central phenyl ring. However, unsymmetrical bent-core mesogens are also known, but are very few in number [1, 14–17]. Normally, banana-shaped mesogens contain two terminal chains; systems containing only one chain and some other substituent at the second terminal position have not been thoroughly explored. In this paper, we report the investigation of several unsymmetrical compounds containing only one terminal chain in relation to their mesomorphic behaviour. The compounds investigated are derived from 3-hydroxybenzoic acid. The terminally chloro-substituted compounds show unusual growth patterns at the isotropic to mesophase transition. The location of the terminal substituent has a bearing on the occurrence of the mesophase.

2. Synthesis

The compounds reported here have 3-hydroxybenzoic acid as the central unit. The general synthetic pathway used to synthesize the bent-core compounds is shown in the scheme. 4-Benzyloxybenzoic acid and 3-benzyloxybenzoic acid were prepared according to the procedure already described [18]. 4-Fluorophenol, 4-chlorophenol, 4-trifluoromethylphenol and 4-chlorobenzoic acid are commercial compounds and were used without further purification. The detailed procedure for the synthesis of the representative compound **11** and its physical data are given below.

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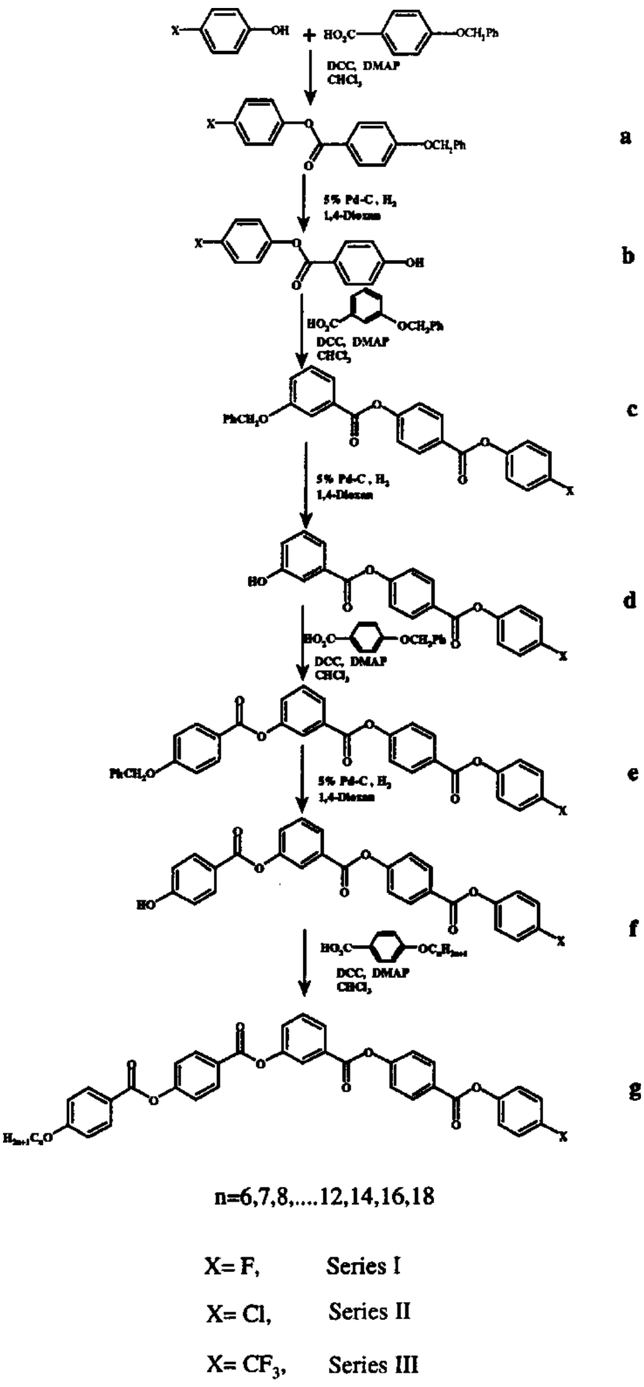


Scheme. Synthetic route used to prepare the unsymmetrical bent-core compounds.

2.1. *4-Chlorophenyl 4′-benzyloxybenzoate, X = Cl (**a**)*

A mixture of 4-chlorophenol (4.0 g, 31 mmol), 4-benzyloxybenzoic acid (7.0 g, 31 mmol), a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) and dry chloroform (50 ml) was stirred for 10 min. To this, *N*,*N*′-dicyclohexylcarbodiimide (DCC, 7.02 g, 34 mmol) was added and the mixture was stirred for 10 h at room temperature. The precipitated *N*,*N*′-dicyclohexylurea was filtered off. The filtrate was diluted with chloroform and washed successively with 5% acetic acid (25 ml × 2), 5% ice-cold sodium hydroxide solution (25 ml × 2) and water (50 ml × 3); it was then dried over anhydrous sodium sulphate. Removal of the solvent gave a residue that was chromatographed on silica gel using chloroform as eluent. Final removal of the solvent afforded a white material, which was recrystallized from a mixture of chloroform and acetonitrile; yield 8.2 g (78%), m.p. 171–171.5°C. IR (nujol) ν_{max}: 2924, 2855, 1726, 1602, 1280, 766 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29–8.27 (dd, ^3J 8.76 Hz, ^4J 2.1 Hz, 2H, Ar–H), 7.84–7.81 (m, 2H, Ar–H), 7.48–7.27 (m, 7H, Ar–H), 7.19–7.17 (dd, ^3J 8.76 Hz, ^4J 2.1 Hz, 2H, Ar–H), 5.2 (s, 2H, Ar–O–CH$_2$–). Elemental analysis: $C_{20}H_{15}O_3Cl$ requires C 70.91, H 4.46; found C 71.50, H 4.55%.

2.2. *4-Chlorophenyl 4′-hydroxybenzoate, X = Cl (**b**)*

Compound **a** (8.0 g, 23.6 mmol) was dissolved in 1,4-dioxan (100 ml) and 5% Pd-C catalyst (2 g) was added. The mixture was stirred at 50°C in an atmosphere of hydrogen, until the required quantity of hydrogen was absorbed. The mixture was then filtered, the solvent removed under reduced pressure, and the residue crystallized from a mixture of 1, 4-dioxan and petroleum-ether (b.p. 60–80°C); yield 4.5 g (76.5%), m.p. 196–197°C. IR (nujol) ν_{max}: 3352, 2924, 2854, 1703, 1608, 1273, 690 cm^{-1}. ^{1}H NMR (400 MHz, CD_3COCD_3) δ: 9.8 (s, 1H, Ar–OH, exchangeable with D_2O), 8.19–8.16 (d, ^3J 8.8 Hz, 2H, Ar–H), 7.62–7.60 (d, ^3J 8.8 Hz, 2H Ar–H), 7.42–7.40 (d, ^3J 8.8 Hz, 2H, Ar–H), 7.14–7.12 (d, ^3J 8.8 Hz, 2H, Ar–H). Elemental analysis: $C_{13}H_9O_3Cl$ requires C 62.79, H 3.65; found C 63.11, H 3.89%.

2.3. *4-Chlorophenyl 4-(3-benzyloxybenzoyloxy)benzoate, X = Cl, (**c**)*

This was synthesized following the procedure described for the preparation of compound **a**. Quantities: compound **b** (4.3 g, 17.3 mmol), 3-benzyloxybenzoic acid (3.95 g, 17.3 mmol), DCC (3.93 g, 19.1 mmol), DMAP (cat. amount) and dry chloroform (30 ml); yield 5.8 g (73%), m.p. 137.5–138°C. IR (nujol) ν_{max}: 2924, 2854, 1730, 1589, 1275, 758 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15–8.13 (dd, ^3J 8.96 Hz, ^4J 2.0 Hz, 2H, Ar–H), 7.46–7.36 (m, 11H, Ar–H), 7.16–7.14 (dd, ^3J 8.88 Hz, ^4J 2.2 Hz, 2H, Ar–H), 7.07–7.05 (dd, ^3J 8.92 Hz, ^4J 2.0 Hz, 2H, Ar–H), 5.20 (s, 2H, Ar–O–CH$_2$–). Elemental analysis: $C_{27}H_{19}O_5Cl$ requires C 70.67, H 4.17; found C 70.25, H 4.07%.

2.4. *4-Chlorophenyl 4-(3-hydroxybenzoyloxy)benzoate, X = Cl (**d**)*

This was prepared following the procedure described for the synthesis of compound **b**. Quantities: compound **c** (5.5 g, 12 mmol), 1,4-dioxan (50 ml) and 5% Pd-C (1.3 g); yield 3.5 g (79%), m.p. 163–164°C. IR (nujol) ν_{max}: 3349, 2924, 2855, 1720, 1605, 1456, 1196, 752 cm^{-1}. ^{1}H NMR (400 MHz, CD_3COCD_3) δ: 9.25 (s, 1H, Ar–OH, exchangeable with D_2O), 8.43–8.41 (dd, ^3J 8.88 Hz, ^4J 2.1 Hz, 2H, Ar–H), 7.84–7.77 (m, 2H, Ar–H), 7.7–7.63 (m, 4H, Ar–H), 7.59–7.57 (t, ^3J 8.0 Hz, 1H, Ar–H), 7.45–7.43 (dd, ^3J 8.88 Hz, ^4J 2.1 Hz, 2H, Ar–H), 7.36–7.33 (m, 1H, Ar–H,). Elemental analysis: $C_{20}H_{13}O_5Cl$ requires C 65.14, H 3.55; found C 64.98, H 3.55%.

2.5. *4-Chlorophenyl 4-[3-(4-benzyloxybenzoyloxy)benzoyloxy]benzoate, X = Cl (**e**)*

This was synthesized following the procedure described for the preparation of compound **a**. Quantities: compound **d** (3.5 g, 9.5 mmol), 4-benzyloxybenzoic acid (2.17 g, 9.5 mmol), DCC (2.16 g, 10.5 mmol), DMAP (cat. amount), dry chloroform (20 ml); yield 4.0 g (72%), m.p. 178.5–179.5°C. IR (nujol) ν_{max}: 2924, 2855, 1732, 1603, 1458, 1252, 762 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29–8.27 (d, ^3J 8.72 Hz, 2H, Ar–H), 8.19–8.17 (d, ^3J 8.88 Hz, 2H, Ar–H), 8.13–8.06 (m, 2H, Ar–H), 7.62–7.58 (t, ^3J 8.0 Hz, 1H, Ar–H), 7.54–7.52 (m, 1H, Ar–H), 7.46–7.35 (m, 9H, Ar–H), 7.19–7.16 (d, ^3J 8.8 Hz, 2H, Ar–H), 7.09–7.07 (d, ^3J 8.88 Hz, 2H, Ar–H), 5.18 (s, 2H, Ar–O–CH_2–). Elemental analysis: $C_{34}H_{23}O_7Cl$ requires C 70.57, H 4.0; found C 70.45, H 4.09%.

2.6. *4-Chlorophenyl 4-[3-(4-hydroxybenzoyloxy)benzoyloxy]benzoate, X = Cl (**f**)*

This was prepared following the procedure described for the synthesis of compound **b**. Quantities: compound **e** (3.5 g, 6.1 mmol), 1,4-dioxan (35 ml), 5% Pd-C (0.8 g); yield 2.2 g (75%), m.p. 174.5–175.5°C. IR (nujol) ν_{max}: 3456, 3369, 2924, 2855, 1740, 1715, 1609, 1269, 758 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 9.59 (s, 1H, Ar–OH, exchangeable with D_2O), 8.44–8.42 (dd, ^3J 8.72 Hz, ^4J 2 Hz, 2H, Ar–H), 8.29–8.21 (m, 4H, Ar–H), 7.88–7.84 (t, ^3J 8 Hz, 1H, Ar–H) 7.82–7.79 (m, 1H, Ar–H), 7.73–7.71 (dd, ^3J 8.76 Hz, ^4J 2.0 Hz, 2H, Ar–H), 7.66–7.64 (dd, ^3J 8.88 Hz, ^4J 2.1 Hz, 2H, Ar–H), 7.53–7.51 (dd, ^3J 8.88 Hz, ^4J 2.1 Hz, 2H, Ar–H), 7.17–7.15 (dd, ^3J 8.88 Hz, ^4J 2.0 Hz, 2H, Ar–H). Elemental analysis: $C_{27}H_{17}O_7Cl$ requires C 66.33, H 3.5; found C 66.77, H 3.67%.

2.7. *4-Chlorophenyl 4-{3-[4-(4-n-hexadecyloxybenzoyloxy)benzoyloxy] benzoyloxy}benzoate, **11***

This was synthesized following the procedure described for the preparation of compound **a**. Quantities: compound **f** (0.15 g, 0.3 mmol), 4-*n*-hexadecyloxybenzoic acid (0.11 g, 0.3 mmol), DCC (0.07 g, 0.33 mmol), DMAP (cat. amount), dry chloroform (10 ml); yield 0.16 g (63%), m.p. 127°C. IR (KBr) ν_{max}: 3076, 2934, 2916, 2849, 1736, 1732, 1728, 1609, 1279, 756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31–8.27 (m, 4H, Ar–H), 8.17–8.09 (m, 4H, Ar–H), 7.64–7.60 (t, ^3J 8 Hz, 1H, Ar–H), 7.57–7.55 (m, 1H, Ar–H), 7.42–7.39 (m, 6H, Ar–H) 7.19–7.17 (dd, ^3J 8.68 Hz, ^4J 2.1 Hz, 2H, Ar–H), 7.0–6.98 (dd, ^3J 8.8 Hz, ^4J 2.0 Hz, 2H, Ar–H), 4.07–4.04 (t, ^3J 6.52 Hz, 2H, Ar–O–CH_2–), 1.86–1.79 (quin, ^3J 6.68 Hz, 2H, Ar–O–CH_2–CH_2–), 1.48–1.22 (m, 26H, –$(CH_2–)_{13}$), 0.89–0.86 (t, ^3J 6.72 Hz, 3H, –CH_3). Elemental analysis: $C_{50}H_{53}O_9Cl$ requires C 72.07, H 6.40; found C 71.89, H 6.46%.

3. Characterization

In general, all the compounds were purified by column chromatography on silica gel (ACME, 60–120 mesh), and repeated crystallization using suitable solvents. The chemical structures of the compounds were confirmed by infrared spectroscopy (Shimadzu FTIR-8400 spectrophotometer), ^{1}H NMR (Bruker, 400 AMX spectrometer) and elmental analysis (Carlo-Erba 1106 analyser). The texture of the mesophases was observed under a polarizing microscope (Leitz Laborlux 12 POL/ Olympus BX 50) in conjunction with a heating stage and controller (Mettler FP 52 and FP 5, respectively). The mesophases were confirmed by X-ray diffraction (XRD) studies using a 4 kW rotating anode X-ray source (Rigaku Ultrax-18) and graphite monochromatic Cu-K_α radiation. The compounds were held in Lindemann capillaries (0.7 mm thickness). The diffraction patterns were collected on an image plate (Marresearch). The transition temperatures and associated enthalpies were recorded on a differential scanning calorimeter (Perkin-Elmer, Model Pyris 1D) which was calibrated using indium as standard.

4. Results and discussion

The unsymmetrically substituted bent-core compounds investigated here contain a fluoro, chloro, or trifluoromethyl group at one terminal position. Such compounds are rare and the analogous terminally cyano-substituted derivatives have been reported to exhibit uniaxial as well as biaxial smectic A phases [16, 17]. A cyano group has a large dipole moment and hence it was our desire to explore the mesomorphic properties of such bent-core compounds with terminal groups having a smaller dipole moment. The transition temperatures and the associated enthalpy values for the three compounds containing a terminal fluoro substitutent (series I) are summarized in table 1. Since compounds **1** and **2**, with, respectively, *n*-tetradecyloxy and *n*-hexadecyloxy terminal chains, were monotropic in nature, the lower homologues were not prepared. However, compound **3** showed a thermal range of 5°C for the mesophase. When a thin film of this compound was cooled from the isotropic phase and observed under a polarizing microscope, a focal-conic texture typical of a smectic phase was obtained. However, when the same sample was sandwiched between two glass slides which were treated for homeotropic alignment, a schlieren texture was observed, thus eliminating the possibility of the mesophase being a smectic A phase. Interestingly the schlieren texture showed defects of strength ±1/2, ±1, ±3/2, etc. This is a characteristic feature of an antiferroelectric ordering in a smectic phase [19]. A typical focal-conic texture obtained for compound **3** is shown in figure 1.

The transition temperatures and associated enthalpy values obtained for compounds of series II, which contain a chloro terminal substituent, are summarized in table 2. Compound **4** is non-mesomorphic, compounds **5** and **6** are monotropic and the remaining are enantiotropic. All these compounds show the same type of mesophase. As a result of chloro substitution, a marginal increase in the melting points and a large increase in the clearing points were obtained (compare compounds **1**, **2** and **3** with compounds **10**, **11**, and **12**). The melting enthalpy is relatively high, in the range of 60–90 kJ mol^{-1}, while the clearing enthalpies are similar to those obtained for smectic phases of bent-core compounds and in the range 12–15 kJ mol^{-1}. A DSC thermogram obtained for compound **11** is shown in figure 2. A plot of transition temperature as a function of alkyl chain length is shown in figure 3. It can be seen that the clearing temperature rises initially and then reaches a plateau value on increasing the chain length.

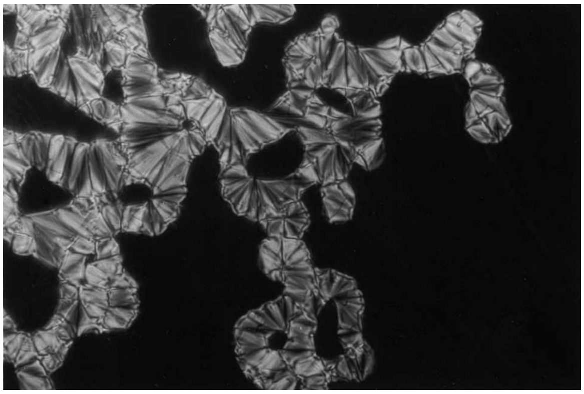
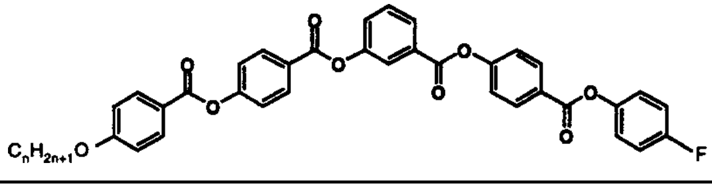


Figure 1. Optical photomicrograph of SmCP$_A$ phase growing from isotropic phase of compound **3**.

An interesting feature of the mesophases of these compounds is their growth from the isotropic phase. For example, when a thin film of compound **11** is cooled very slowly from the isotropic phase, filaments start to develop and grow in size. Sometimes the fully developed filaments curl up to form a texture resembling a bird's nest. The growth of these filaments at different intervals of time is shown as photomicrographs in figure 4; they are unstable and collapse to form a focal-conic texture. The stability of the filaments appears to increase on increasing the length of the *n*-alkoxy chain. Photomicrographs of the partial collapse of the filamentary pattern exhibited by compound **11** are shown in figures 5 (*a*) and 5 (*b*).

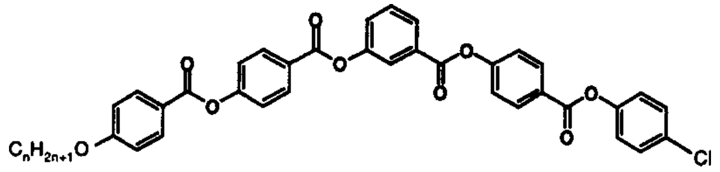
Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) in italics, for series I compounds. Cr = crystalline phase; SmCP$_A$ = polar antiferroelectric smectic C phase; I = isotropic phase; () indicates monotropic mesophase.



Compound	*n*	Cr		SmCP$_A$		I
1	14	●	125.5[a] *87.6*	(●	122.0) *12.6*	●
2	16	●	125.0[a] *99.6*	(●	124.5) *13.1*	●
3	18	●	122.0[a] *89.8*	●	127.0 *13.3*	●

[a] Compound has crystal–crystal transition; enthalpy given is the sum of all previous transitions.

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



Compound	*n*	Cr		SmCP$_A$		I
4	6	●	147.0[a] *59.9*	—		●
5	8	●	139.0[a] *62.1*	(●	132.0) *12.2*	●
6	9	●	137.0[a] *74.1*	(●	135.0) *12.9*	●
7	10	●	133.0[a] *58.0*	●	138.0 *13.5*	●
8	11	●	129.0[a] *67.4*	●	140.0 *14.3*	●
9	12	●	128.5[a] *65.8*	●	141.5 *14.6*	●
10	14	●	130.0[a] *70.3*	●	144.5 *15.0*	●
11	16	●	127.0[a] *82.2*	●	145.0 *15.4*	●
12	18	●	126.0[a] *88.4*	●	146.0 *15.3*	●

[a] Compound has crystal–crystal transition; enthalpy given is the sum of all previous transitions.

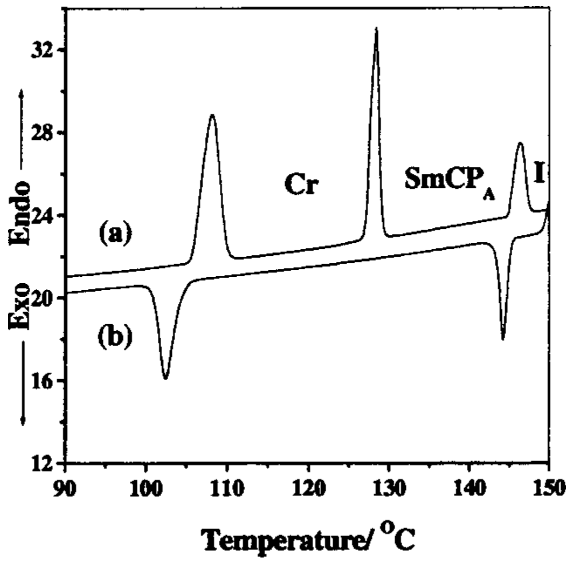


Figure 2. A DSC thermogram of compound **11**: (*a*) heating cycle, (*b*) cooling cycle; rate 5°C min^{-1}.

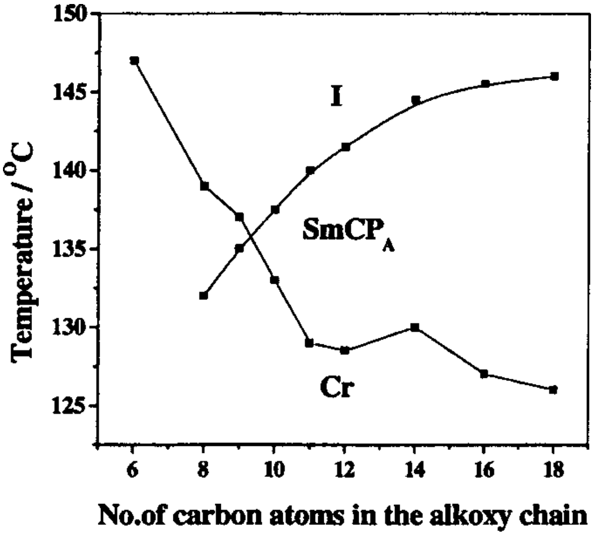


Figure 3. Plot of transition temperature as a function of the number of carbon atoms in the *n*-alkoxy chain for series II.

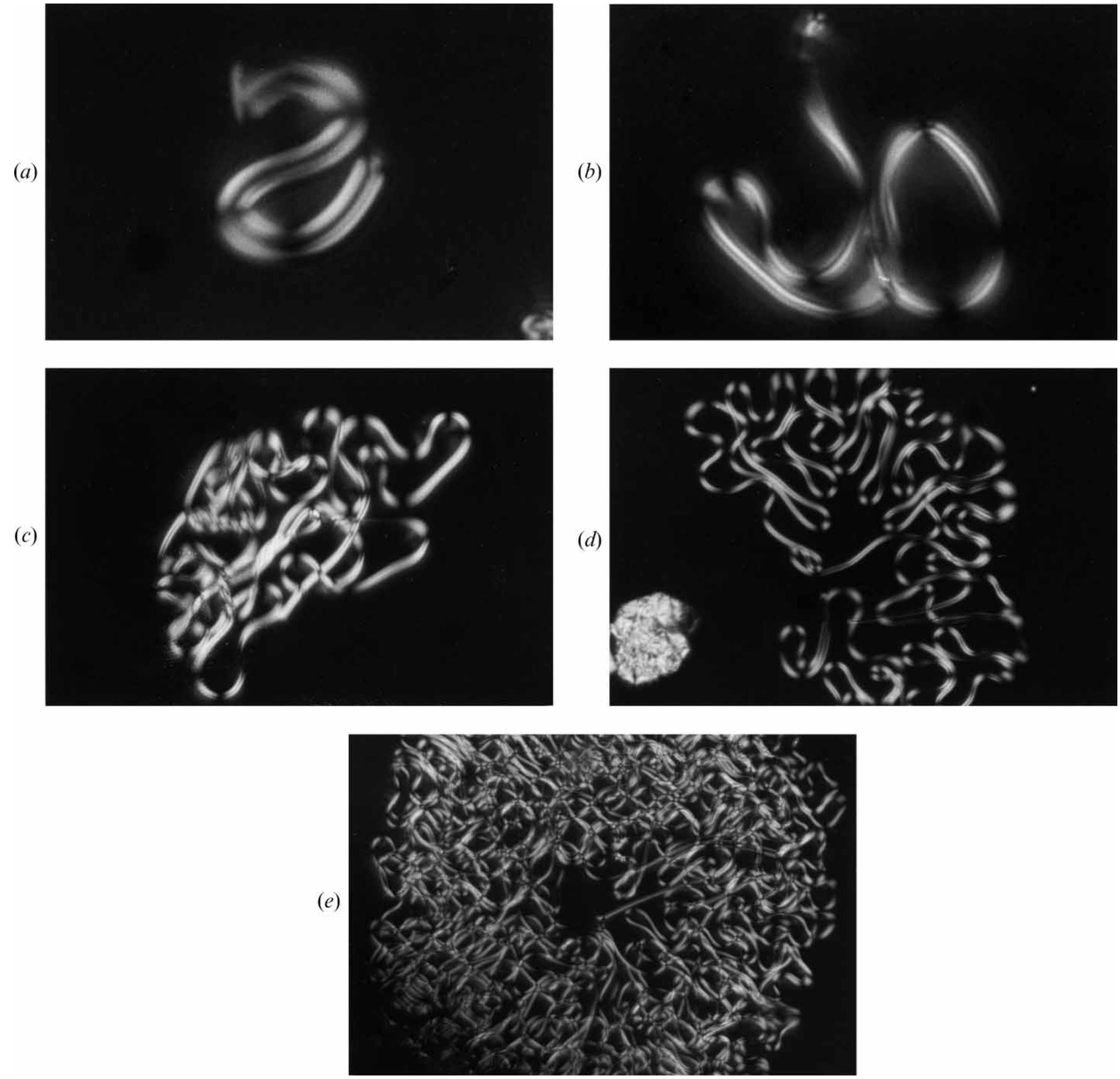


Figure 4. Stepwise growth of filamentary textures on cooling the isotropic phase of compound **11**.

Depending on the rate of cooling, fan-shaped textures with irregularly spaced concentric arcs, or schlieren textures with multiple defects, are sometimes also obtained. A typical fan-shaped texture obtained for compound **11** is shown in figure 6 (*a*) and the schlieren textures are shown in 6 (*b*) and 6 (*c*). As we shall see later, the mesophase exhibited by all these compounds has been characterized as a polar smectic C ($SmCP_A$) phase with antiferroelectric properties. Another interesting point to note is that the thermal range of this $SmCP_A$ phase increases on ascending the homologous series with compound **12** having a mesophase range of 20°C.

By introducing a fluorine substituent *ortho* to the terminal *n*-octadecyloxy chain of compound **12**, we obtained compound **13** which showed the $SmCP_A$ phase over a 23°C thermal range. However, when the terminal *n*-octadecyloxyphenyl group was replaced by the 4-*n*-decylbiphenyl moiety (compound **14**), the melting point increased by 26°C while the clearing temperature increased by 51°C, and the same mesophase was retained. The transition temperatures and the associated enthalpies for these two compounds are shown in table 3. The optical textures exhibited by these two compounds are similar to those of compounds **5** to **12**. When the terminal *n*-alkoxy chain and the chloro

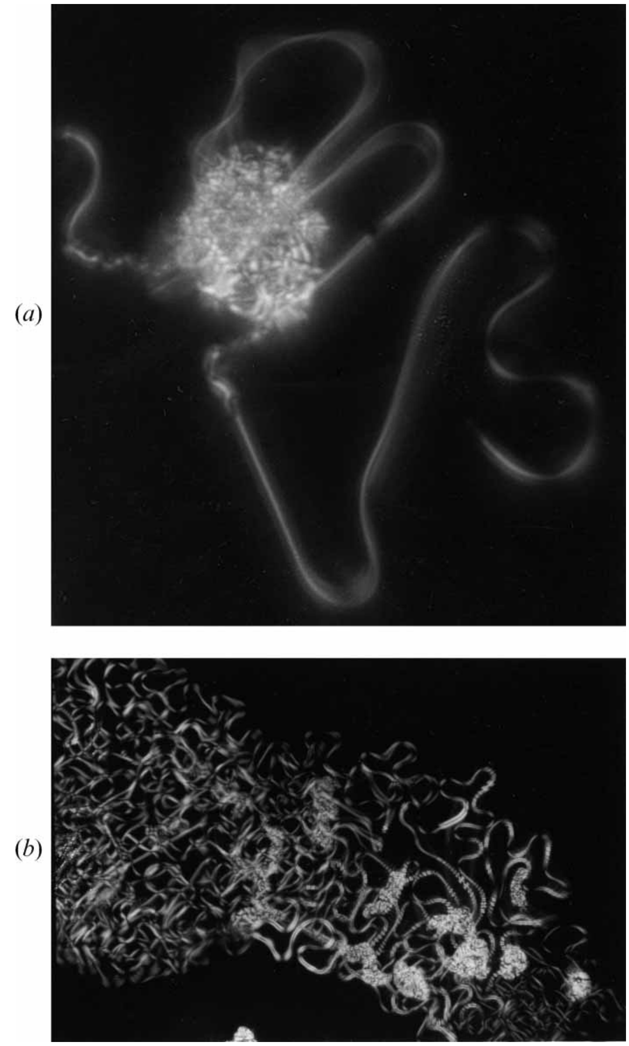


Figure 5 (*a*) and (*b*). Optical photomicrographs illustrating the collapse of the filaments exhibited by compound **11**.

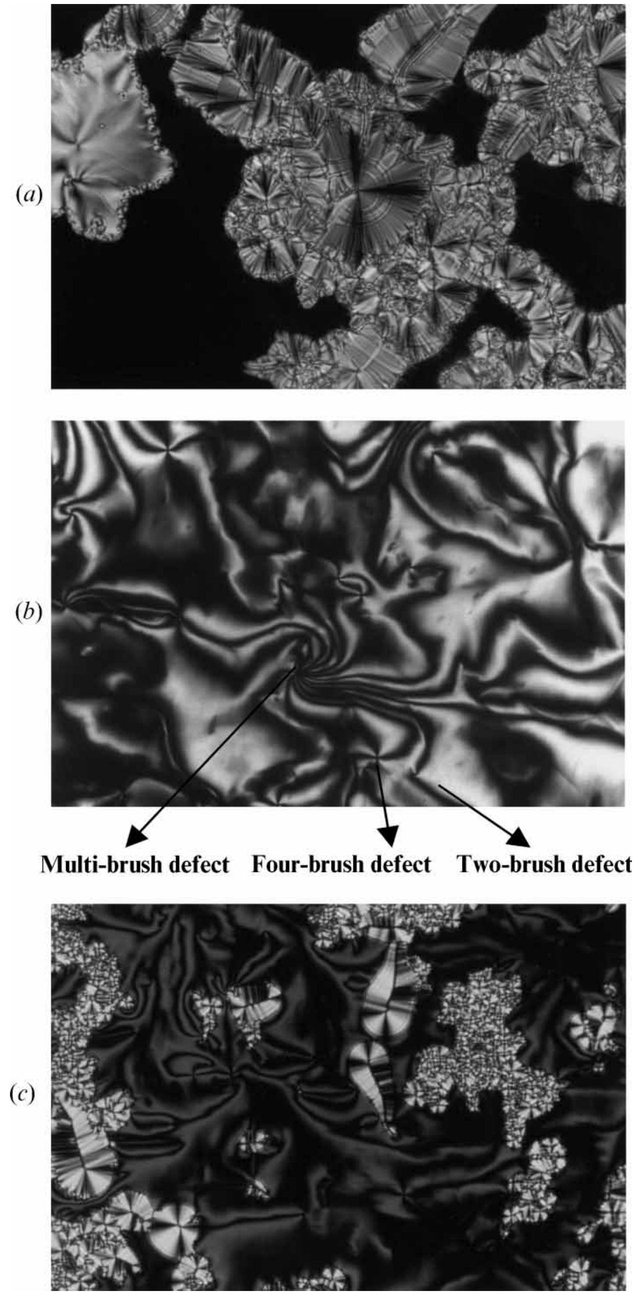
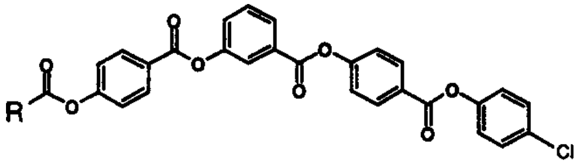


Figure 6. Optical photomicrographs of (*a*) fan-shaped texture, (*b*) and (*c*) schlieren textures of a homeotropically aligned sample of compound **11**.

substituents are interchanged, surprisingly the mesomorphic behaviour is completely lost; see, for example, the properties of compounds **15** and **16** given in table 4. Although the melting points increased considerably, the polarizability of the system was also affected, which is perhaps critical for the occurrence of the mesophase.

We have also synthesized four compounds having a terminal trifluoromethyl group. The dipole moment of this group is almost half that of the cyano group. The transition temperatures and associated enthalpy values for these four compounds, **17**–**20**, are summarized in table 5. Although the melting points are higher than those of the analogous chloro-substituted compounds, all are enantiotropic with a thermal range for the mesophase slightly smaller. We do see the filamentary texture for these compounds as well but these are extremely short lived. The mesophase of these compounds exhibits schlieren textures with both two- and four-brush strength defects, but predominantly a focal-conic texture with concentric arcs is obtained. Also no homeotropic region could be observed. A typical photomicrograph of a fan-shaped texture with unequally spaced concentric arcs obtained for compound **20** is shown in figure 7. We have characterized this mesophase to be an $\mathrm{SmCP_A}$ phase. In these unsymmetrically substituted compounds the terminal electronegative substituent will interact with

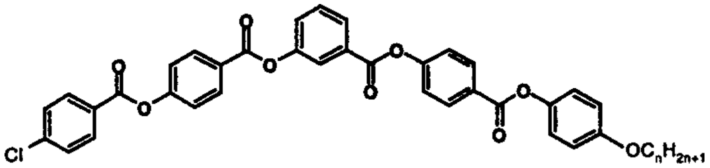
Table 3. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) in italics, for compounds **13** and **14**.



R	Compound	Cr		SmCP$_A$		I
3-Fluoro-4-*n*-octadecyloxyphenyl	**13**	●	125.0[a] *70.3*	●	148.0 *15.8*	●
4-*n*-Decylbiphenyl	**14**	●	152.0[a] *91.0*	●	197.0 *15.0*	●

[a] Compound has crystal–crystal transition; enthalpy given is the sum of all previous transitions.

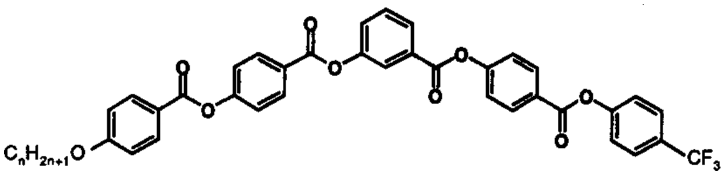
Table 4. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) in italics, for compounds **15** and **16**.



Compound	*n*	Cr		I
15	8	●	159.0[a] *70.0*	●
16	14	●	152.0[a] *91.0*	●

[a] Compound has crystal–crystal transition; enthalpy given is the sum of all previous transitions.

Table 5. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) in italics, for series III compounds.



Compound	*n*	Cr		SmCP$_A$		I
17	12	●	150.5 *34.4*	●	158.0 *16.4*	●
18	14	●	146.5 *35.3*	●	159.0 *17.1*	●
19	16	●	144.0 *33.7*	●	160.0 *17.4*	●
20	18	●	141.0 *32.2*	●	159.0 *17.5*	●

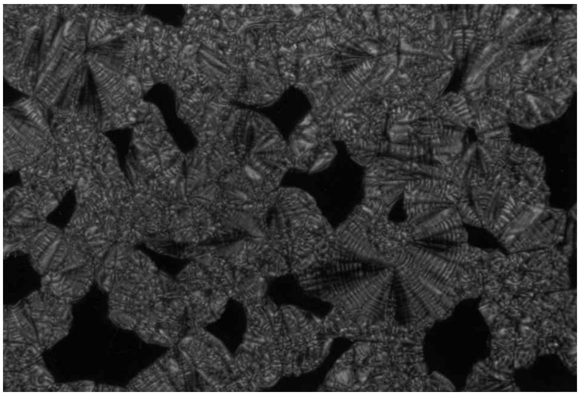


Figure 7. Photomicrograph of the $\mathrm{SmCP_A}$ phase growing from the isotropic liquid of compound **20**.

the methyl group of the *n*-alkoxy chain in adjacent layers, thus stabilizing a smectic phase having an antiferroelectric ordering of the molecules.

The occurrence of filamentary growth patterns at the isotropic to smectic A phase transition in calamitic liquid crystals is not new; it has been seen in a number of different mixtures as well as in pure mesogenic materials [20]. One pure compound which has been examined in detail by Palffy-Muhoray *et al.* [21] is 4′-decyloxyphenyl 4-(4-cyano-4-oxybiphenyl)butanoate which showed filaments when the isotropic phase was cooled slowly to the smectic A phase. The growth of such long cylindrical structures in smectic A liquid crystals has been attributed to negative interfacial tension anisotropy [20, 21]. Such filamentary growth patterns have also been observed in smectic C liquid crystals composed of binary mixtures [22]. To the best of our knowledge, such long cylindrical growth patterns have not been observed previously in bent-core mesogens. It would be interesting to study the kinetics of the growth of the filaments and other physical properties of such polar smectic C materials.

Table 6. Layer spacings (*d*) from XRD studies and the corresponding molecular length (*L*) of compounds assuming the *n*-alkoxy chain to be in an all-*trans*-conformation.

Compound	Layer spacings *d*/Å	Molecular length *L*/Å
3	45.1 (01), 14.9 (03)	53.5
7	38.7 (01), 19.3 (02)	43.8
9	41.8 (01), 20.9 (02)	46.4
10	44.4 (01), 22.2 (02)	48.3
11	45.2 (01), 22.6 (02) 15.1 (03), 11.3 (04)	51.7
18	45.7 (01), 22.7 (02)	49.0

5. X-ray diffraction investigations

In order to confirm the mesophase structure we have carried out XRD studies on non-oriented samples. A sample of an appropriate compound was heated to the isotropic phase and after drawing this liquid into a Lindemann capillary, the ends were sealed. The temperature of the sample heater was controlled to within ±0.1°C. The reflections in the small angle region clearly indicate the lamellar ordering of the mesophase. The first-order layer reflection is less than the estimated molecular length in each case, which was measured assuming that the methylene units of *n*-alkoxy chain were in the all-*trans*-conformation. The calculated tilt angle is of the order of 25°–30°. The higher-order reflections (up to four reflections) clearly indicate the formation of a well-defined layer structure for the mesophase. The wide angle diffuse peak at 4.6 Å observed in all the compounds is indicative of the absence of in-plane periodicity. The layer spacings and the calculated molecular length for the various compounds studied are given in table 6. The X-ray intensity profile for compound **11**, showing four orders of smectic reflections, is shown in figure 8. From the XRD studies we have concluded that the mesophase under investigation is a tilted smectic phase.

6. Electro-optical investigations

To examine the effect of an electric field on the mesophase, we used the standard triangular wave method. Representative compounds from all three series were investigated, and the general behaviour was the same. For example, compound **11** was placed in an ITO coated cell of uniform thickness of 9.6 μm, the inner surfaces of which were treated for homogeneous alignment. The sample was cooled slowly from

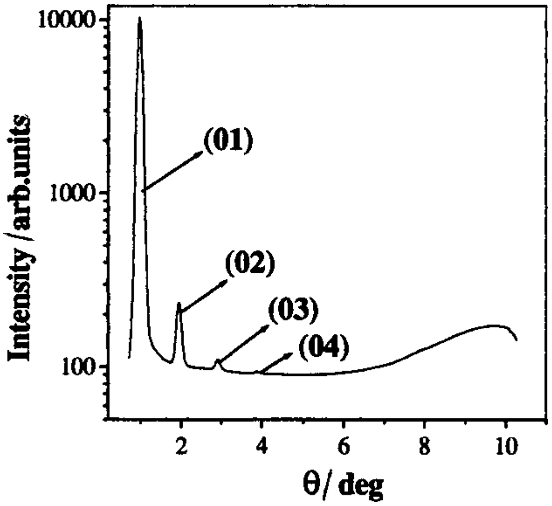


Figure 8. X-ray diffractogram of the $\mathrm{SmCP_A}$ phase of compound **11**.

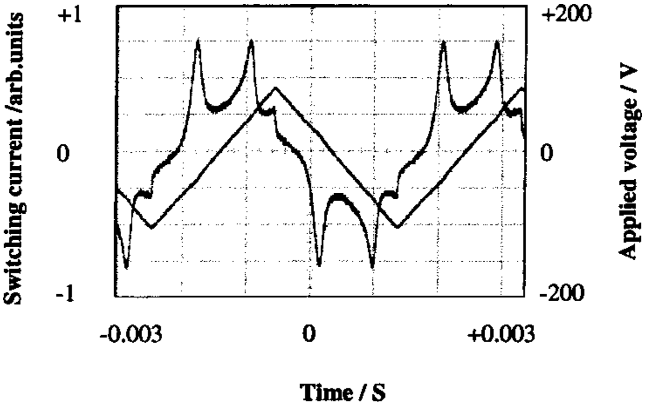


Figure 9. The switching current response trace obtained for compound **11** by applying a triangular wave electric field ($190\,V_{pp}$) at 250 Hz: cell thickness 9.6 μm, saturated polarization is about $125\,nC\,cm^{-2}$.

the isotropic phase under a triangular wave electric field. At a threshold of $110\,V_{pp}$ at a frequency of 200 Hz, two polarization current peaks per half cycle were observed, indicating an antiferroelectric ground state for the mesophase. The switching current response obtained for this compound is shown in figure 9. The saturated polarization value obtained by integrating the area under the two current peaks is about $125\,nC\,cm^{-2}$. Thus, from XRD data and electro-optical studies, we can conclude that the mesophase is a polar smectic C phase with antiferroelectric characteristics, i.e. an $SmCP_A$ phase.

7. Conclusions

Several bent-core compounds, belonging to three different series having unsymmetrical substitution about the central phenyl ring, are described. These contain either a fluoro, chloro, or trifluoromethyl group as a terminal substituent. The mesophase exhibited by these compounds has been characterized as a polar smectic C phase with antiferroelectric properties. The terminally chloro-substituted compounds show filamentary growth patterns at the isotropic to $SmCP_A$ phase transition which is rather unusual. The nature of the linking group or the location of the terminal group has an influence on the occurrence of the mesophase.

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