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H. N. Shreenivasa Murthy^a; B. K. Sadashiva Corresponding author^a

^a Raman Research Institute, C.V. Raman Avenue, Sadashivanagar, Bangalore-560 080, India

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A polar biaxial smectic A phase in new unsymmetrical compounds composed of bent-core molecules

H. N. SHREENIVASA MURTHY and B. K. SADASHIVA*

Raman Research Institute, C.V. Raman Avenue, Sadashivanagar,
Bangalore-560 080, India

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The synthesis and liquid crystalline properties of several new compounds unsymmetrically substituted about two different central phenyl rings are reported. All the compounds contain a strongly polar terminal cyano/nitro substituent. Some of the nitro-substituted compounds derived from 3-hydroxybenzoic acid show a transition from the partial bilayer uniaxial smectic A (SmA_d) phase to a polar partial bilayer biaxial smectic A (SmA_dP_A) phase. The analogous cyano-substituted derivatives exhibit only a SmA_d phase. However, compounds containing a 4-cyanobiphenyl moiety in the terminal position and derived from 1,3-dihydroxybenzene show the $\text{SmA}_d - \text{SmA}_d\text{P}_A$ transition. The mesophases were characterized using polarizing optical microscopy, differential scanning calorimetry, X-ray diffraction studies, conoscopic examination and miscibility studies.

1. Introduction

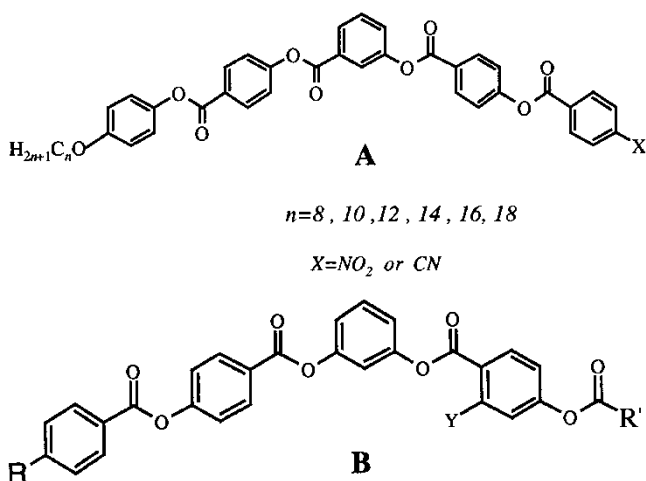
Mesophases exhibited by compounds composed of bent-core molecules have been the subject of extensive investigations in recent years. The impetus for this was the observation of electro-optical switching in a bent-core compound [1] and the subsequent discovery of macroscopic chirality in such materials [2]. Since then a large number of bent-core or banana-shaped mesogens have been synthesized to examine the novel mesophase structures [2–5]. Most of the compounds reported in the literature are symmetrical about the central phenyl ring and are derived from 1,3-dihydroxybenzene or 2,7-dihydroxynaphthalene [5–9]. Usually these are five- or six-ring compounds and are substituted with two terminal alkyl/alkoxy chains. Although about eight B-phases have been identified, the columnar B_1 and the antiferroelectric B_2 phases are commonly observed. When the central phenyl ring is substituted suitably, a nematic, a smectic A (SmA) and/or a smectic C (SmC) phase along with B-phases have been reported [10, 11]. However, the relationship between the molecular structure and the associated mesomorphic properties is still not clearly understood.

A biaxial and orthogonal smectic phase was predicted theoretically by de Gennes [12]; this has also been named a smectic C_M phase where M refers to

McMillan [13, 14]. The first experimental observation of a biaxial smectic A phase was made in a mixture of liquid crystalline side chain polymer and a monomeric compound [15]. The biaxial smectic A phase has also been observed in a binary mixture of a metallomesogen and 2,4,7-trinitrofluorenone [16]. Adequate proof for the existence of a biaxial smectic A phase in a binary mixture of low molecular mass compounds has been provided by Pratibha *et al.* [17]. This binary mixture consists of a compound exhibiting the B_2 phase and another compound composed of rod-like molecules exhibiting a bilayer SmA phase. There is also a claim for the observation of a biaxial SmA phase in an oxadiazole derivative [18], where the constituent molecules are boomerang in shape. Recently we have reported [19, 20] the synthesis and characterization of the mesophases exhibited by several unsymmetrical compounds composed of strongly polar molecules. Many of these exhibit the biaxial SmA phase. Very recently [21] we have shown that the biaxial smectic A phase reported earlier [19, 20] is actually a polar partially bilayer biaxial smectic A (SmA_dP_A) phase. It would not be out of place to mention here that Prehm *et al.* [22] have observed a biaxial SmA phase in some rod-like bolaamphiphiles containing a long semifluorinated chain. Also sufficient experimental proof for a biaxial SmA phase showing antiferroelectric characteristics has been provided by Eremin *et al.* [23] and Schroder *et al.* [24].

*Author for correspondence; e-mail: sadashiv@rri.res.in

The design and synthesis of unsymmetrical compounds exhibiting mesophases have not been explored thoroughly, particularly in compounds containing only one terminal chain and a small substituent at the other end [19–21, 25]. In this paper, we report the synthesis and characterization of several unsymmetrical compounds, which are derived from 3-hydroxybenzoic acid as well as 1,3-dihydroxybenzene. These compounds have only one terminal chain while the other end is substituted with either a cyano or a nitro group. The general molecular structures **A** and **B** of the investigated compounds are:



2. Experimental

2.1. General

In general all the compounds were purified by column chromatography on silica gel (60–120 mesh), and crystallization from analytical grade solvents. The purity of the sample was checked by thin-layer chromatography (Merck Kieselgel 60F₂₅₄). The chemical structures of the compounds were determined by IR (Shimadzu FTIR-8400 spectrophotometer), ¹H NMR (Bruker AMX 400 spectrometer), and elemental analysis (Carlo-Erba 1106 analyser). The optical textures and thermal behaviour were examined under a polarizing microscope (Leitz Laborlux 12 POL/Olympus BX50) equipped with a heating stage and a controller (Mettler FP52 and FP5). The transition temperatures and associated enthalpies were determined on a differential scanning calorimeter (Perkin-Elmer, Model Pyris 1D) which was calibrated using indium as a standard. X-ray diffraction measurements were carried out on non-oriented samples using Cu K_α radiation from a rotating anode generator (Rigaku Ultrax

18) with a graphite crystal monochromator. Samples were taken in Lindemann capillaries (0.7 mm), and the temperature of the heater was controlled to $\pm 0.1^\circ\text{C}$. The diffraction patterns were collected on a two-dimensional image plate detector (Marresearch). The polarization measurements were carried out by the standard triangular-wave method. The conoscopic observations were made using a microscope (Leitz Ortholux-II POL BK) equipped with a heating stage and a controller (Mettler FP82 and FP80HT).

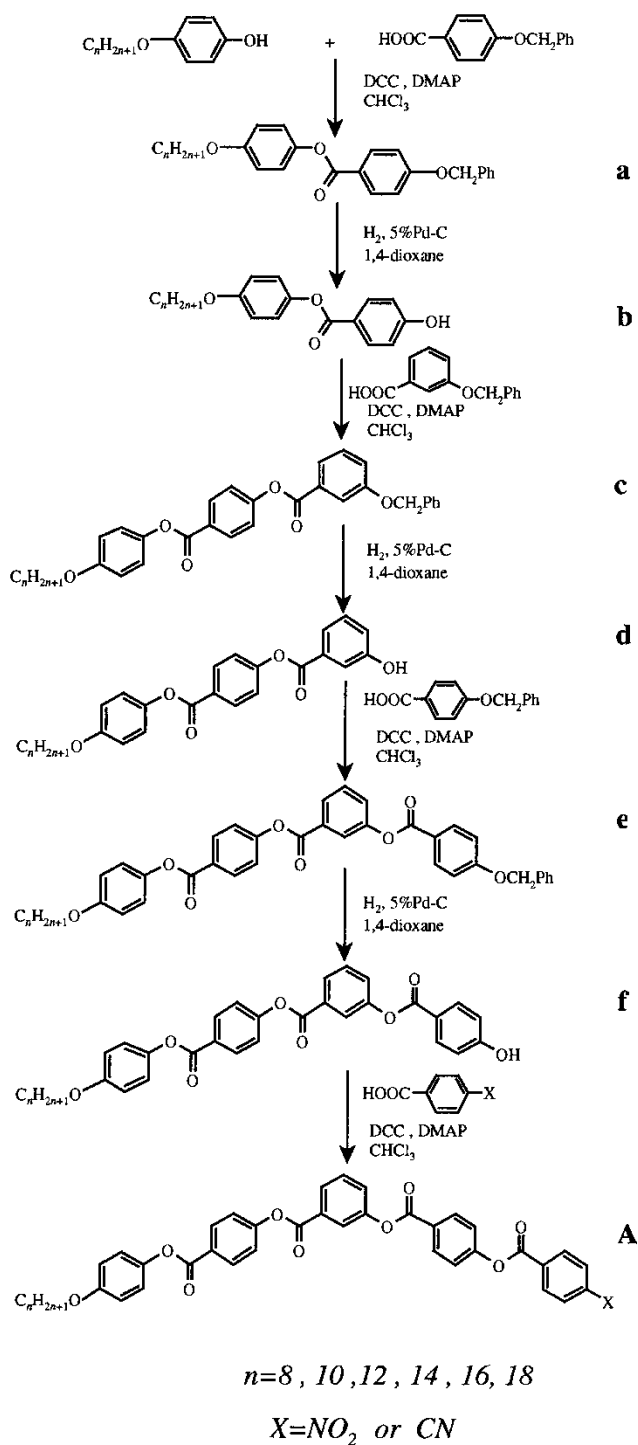
2.2. Synthesis

Compounds **1–14**, which are derived from 3-hydroxybenzoic acid, were prepared following the pathway shown in the scheme. However, the unsymmetrical compounds **15–19** were obtained from resorcinol, using a procedure which will be described elsewhere [26].

A typical procedure that was followed to synthesize the bent-core compounds, and the physical constants for a representative compound (**11**), are given below. 4-*n*-Alkoxyphenols were prepared by mono-alkylation of quinol with appropriate *n*-alkyl bromides in the presence of anhydrous potassium carbonate. 4-Benzyloxybenzoic acid, 3-benzyloxybenzoic acid, 2-fluoro-4-benzyloxybenzoic acid and 3-fluoro-4-benzyloxybenzoic acid were synthesized according to procedures described in the literature [27]. 4-Cyano- and 4-nitro-benzoic acids were commercial compounds and used without further purification.

2.2.1. 4-*n*-Hexadecyloxyphenyl 4-benzyloxybenzoate (**a**)

A mixture of 4-*n*-hexadecyloxyphenol (2.8 g, 8.4 mmol), 4-benzyloxybenzoic acid (1.91 g, 8.4 mmol), a catalytic amount of 4-(*N,N*-dimethylamino)pyridine (DMAP) and dry chloroform (20 ml) were stirred for 10 min. To this, *N,N'*-dicyclohexylcarbodiimide (DCC, 1.90 g, 9.2 mmol) was added and the mixture stirred overnight at room temperature. The precipitated *N,N'*-dicyclohexylurea was filtered off; the filtrate was diluted with chloroform (50 ml) and washed successively with 5% acetic acid (25 ml \times 2), 5% ice-cold sodium hydroxide solution (25 ml \times 2) and water (25 ml \times 3), then dried over anhydrous sodium sulphate. Removal of solvent gave a product which was chromatographed on silica gel using chloroform as eluant. Removal of solvent from the eluate afforded a white product which was recrystallized from a mixture of chloroform and acetonitrile. Yield: 3.6 g (79%); m.p. 119.5°C; IR ν_{max} (nujol): 2949, 2916, 1740, 1611, 1514, 1252 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.15–8.13 (d, ³*J*=8.64 Hz, Ar–H, 2H), 7.46–7.35 (m, Ar–H, 5H), 7.11–7.09 (d, ³*J*=8.8 Hz, Ar–H, 2H), 7.06–7.04 (d,



Scheme. Synthetic pathway for preparation of the bent-core compounds.

$^3J=8.68$ Hz, Ar-H, 2H), 6.93–6.91 (d, $^3J=8.8$ Hz, Ar-H, 2H), 5.16 (s, $-O-CH_2-Ar$, 2H), 3.97–3.94 (t, $^3J=6.48$ Hz, Ar-O- CH_2- , 2H), 1.82–1.75 (quin, $^3J=7.0$ Hz, Ar-O- CH_2-CH_2- , 2H), 1.57–1.26 (m,

($-CH_2-$)₁₃, 26H), 0.9–0.87 (t, $^3J=6.58$ Hz, $-CH_3$, 3H). Elemental analysis: C₃₆H₄₈O₄ requires C 79.37, H 8.88, found C 79.73, H 9.24%.

2.2.2. 4-*n*-Hexadecyloxyphenyl 4-hydroxybenzoate (**b**)

Compound **a**, (3.5 g, 6.4 mmol) was dissolved in 1,4-dioxane (50 ml), and 5% Pd-C catalyst (0.9 g) was added; the mixture was stirred at 50°C in hydrogen atmosphere until the required quantity of hydrogen was absorbed. The solution was filtered and removal of solvent gave a white product which was recrystallized, from 1,4-dioxane and petroleum-ether (b.p. 80–100°C). Yield: 2.4 g (82%); m.p. 134–135°C, IR ν_{max} (nujol): 3381, 2920, 2850, 1728, 1611, 1514 cm^{-1} ; 1H NMR (500 MHz, CD₃COCD₃) δ (ppm): 9.63 (s, exchangeable with D₂O, Ar-OH, 1H), 8.03–8.01 (d, $^3J=8.56$ Hz, Ar-H, 2H), 7.14–7.12 (d, $^3J=9.12$ Hz, Ar-H, 2H), 7.0–6.95 (m, Ar-H, 4H), 4.01–3.99 (t, $^3J=6.5$ Hz, Ar-O- CH_2- , 2H), 1.8–1.75 (quin, $^3J=7.0$ Hz, Ar-O- CH_2-CH_2- , 2H), 1.51–1.28 (m, ($-CH_2-$)₁₃, 26H), 0.88–0.86 (t, $^3J=6.6$ Hz, $-CH_3$, 3H). Elemental analysis: C₂₉H₄₂O₄ requires C 76.61, H 9.31, found C 77.20, H 9.75%.

2.2.3. 4-*n*-Hexadecyloxyphenyl 4-(3-benzyloxybenzoyloxy)-benzoate (**c**)

This was synthesized following the procedure described for the preparation of compound **a**. Quantities compound **b** (2.19 g, 4.8 mmol), 3-benzyloxybenzoic acid (1.09 g, 4.8 mmol), a catalytic amount of DMAP, DCC (1.09 g, 5.3 mmol), dry CHCl₃ (20 ml). Yield: 2.5 g (78%), m.p. 97–98°C; IR ν_{max} (nujol): 2918, 2849, 1747, 1583, 1512 cm^{-1} , 1H NMR (400 MHz, CDCl₃) δ (ppm): 8.29–8.27 (d, $^3J=8.56$ Hz, Ar-H, 2H), 7.85–7.83 (m, Ar-H, 2H), 7.48–7.26 (m Ar-H, 9H), 7.14–7.11 (d, $^3J=8.84$ Hz, Ar-H, 2H), 6.95–6.93 (d, $^3J=8.84$ Hz, Ar-H, 2H), 5.16 (s, O- CH_2-Ar , 2H), 3.98–3.95 (t, $^3J=6.48$ Hz, Ar-O- CH_2- , 2H), 1.83–1.76 (quin, $^3J=7.0$ Hz, Ar-O- CH_2-CH_2- , 2H), 1.57–1.27 (m, ($-CH_2-$)₁₃, 26H), 0.90–0.87 (t, $^3J=6.4$ Hz, $-CH_3$, 3H). Elemental analysis: C₄₃H₅₂O₆ requires C 77.68, H 8.07%; found C 77.90, H 8.07%.

2.2.4. 4-*n*-Hexadecyloxyphenyl-4-(3-hydroxybenzoyloxy)benzoate, (**d**)

This was synthesized following the procedure described for the preparation of compound **b**. Quantities: **c** (2.4 g, 3.6 mmol), 1,4-dioxane (30 ml), 5% Pd-C (0.6 g). Yield: 1.55 g (75%); m.p. 161–161.5°C, IR ν_{max} (nujol): 3439, 2918, 2851, 1722, 1604, 1506 cm^{-1} , 1H NMR (500 MHz, CD₃COCD₃) δ (ppm) 8.86 (s, exchangeable with D₂O, Ar-OH, 1H), 8.29–8.27 (d,

$^3J=8.75$ Hz, Ar-H, 2H), 7.71–7.63 (m, Ar-H, 2H), 7.53–7.51 (d, $^3J=8.7$ Hz, Ar-H, 2H), 7.46–7.43 (t, $^3J=8.0$ Hz, Ar-H, 1H), 7.23–7.21 (m, Ar-H, 3H), 7.02–7.00 (d, $^3J=9$ Hz, Ar-H, 2H), 4.04–4.02 (t, $^3J=6.5$ Hz, Ar-O-CH₂-, 2H), 1.82–1.77 (quin, $^3J=7.0$ Hz, Ar-O-CH₂-CH₂-, 2H), 1.53–1.29 (m, (-CH₂)₁₃, 26H), 0.89–0.86 (t, $^3J=6.7$ Hz, -CH₃, 3H). Elemental analysis: C₃₆H₄₆O₆ requires C 75.23, H 8.07, found C 75.25, H 8.22%.

2.2.5. 4-*n*-Hexadecyloxyphenyl 4-[3-(4-benzyloxybenzyloxy)benzyloxy]benzoate (*e*)

This was synthesized following the procedure described for the preparation of compound **a**. Quantities: **d** (1.4 g, 2.43 mmol), 4-benzyloxybenzoic acid (0.56 g, 2.43 mmol), DCC (0.55 g, 2.67 mmol), a catalytic amount of DMAP and dry CHCl₃ (15 ml). Yield: 1.5 g (78%), m.p. 119–119.7°C, IR ν_{\max} (nujol): 2920, 2850, 1734, 1605, 1512 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.29–8.27 (d, $^3J=8.48$ Hz, Ar-H, 2H), 8.19–8.17 (d, $^3J=8.48$ Hz, Ar-H, 2H), 8.14–8.12 (d, $^3J=7.64$ Hz, Ar-H, 1H), 8.06 (s, Ar-H, 1H), 7.62–7.58 (t, $^3J=7.96$ Hz, Ar-H, 1H), 7.54–7.52 (d, $^3J=8.04$ Hz, Ar-H, 1H), 7.46–7.36 (m, Ar-H, 7H), 7.13–7.11 (d, $^3J=8.8$ Hz, Ar-H, 2H), 7.09–7.07 (d, $^3J=8.68$ Hz, Ar-H, 2H), 6.94–6.92 (d, $^3J=8.76$ Hz, Ar-H, 2H), 5.18 (s, O-CH₂-Ar, 2H), 3.98–3.95 (t, $^3J=6.5$ Hz, Ar-O-CH₂-, 2H), 1.83–1.76 (quin, $^3J=7.0$ Hz, Ar-O-CH₂-CH₂-, 2H), 1.57–1.27 (m, (-CH₂)₁₃, 26H), 0.9–0.87 (t, $^3J=6.5$ Hz, -CH₃, 3H). Elemental analysis: C₅₀H₅₆O₈ requires C 76.50, H 7.19, found C 76.72, H 7.50%.

2.2.6. 4-*n*-Hexadecyloxyphenyl 4-[3-(4-hydroxybenzyloxy)benzyloxy]benzoate (*f*)

This was synthesized following the procedure for the preparation of compound **b**. Quantities: **e** (1.4 g, 1.78 mmol), 1,4-dioxane (20 ml), 5% Pd-C (0.4 g). Yield: 0.9 g (73%); m.p. 173–174.0°C, IR ν_{\max} (nujol): 3285, 2920, 2850, 1732, 1608, 1510 cm⁻¹; ¹H NMR (400 MHz, CD₃COCD₃) δ (ppm): 9.8 (s, exchangeable with D₂O, Ar-OH, 1H), 8.30–8.28 (d, $^3J=8.56$ Hz, Ar-H, 2H), 8.15–8.13 (m, Ar-H, 4H), 7.75–7.71 (t, $^3J=7.8$ Hz, Ar-H, 1H), 7.68–7.66 (d, $^3J=6.8$ Hz, Ar-H, 1H), 7.59–7.56 (d, $^3J=8.56$ Hz, Ar-H, 2H), 7.23–7.21 (d, $^3J=8.84$ Hz, Ar-H, 2H), 7.04–7.02 (m, Ar-H, 4H), 4.04–4.01 (t, $^3J=6.44$ Hz, Ar-O-CH₂-, 2H), 1.81–1.76 (quin, $^3J=7$ Hz, Ar-O-CH₂-CH₂-, 2H), 1.51–1.26 (m, (-CH₂)₁₃, 26H), 0.88–0.86 (t, $^3J=6.76$ Hz, -CH₃, 3H). Elemental analysis: C₄₃H₅₀O₈ requires C 74.33, H 7.25, found C 74.74, H 7.41%.

2.2.7. 4-*n*-Hexadecyloxyphenyl 4-{3-[4-(4-nitrobenzyloxy)benzyloxy]benzyloxy}benzoate **II**

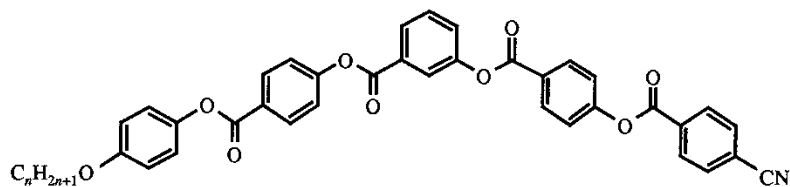
This was synthesized following a procedure described for the preparation of compound **a**. Quantities: **f** (0.2 g, 0.29 mmol), 4-nitrobenzoic acid (0.048 g, 0.29 mmol), DCC (0.065 g, 0.32 mmol), a catalytic amount of DMAP, dry CHCl₃ (10 ml). Yield: 0.15 g (62%) m.p. 145.0°C, IR ν_{\max} (KBr): 3112, 3082, 2918, 2851, 1736, 1734, 1608, 1510, 1458, 1273 cm⁻¹; ¹H NMR, (400 MHz, CDCl₃) δ (ppm); 8.43–8.37 (m, Ar-H, 4H), 8.36–8.34 (d, $^3J=8.64$ Hz, Ar-H, 2H), 8.30–8.28 (d, $^3J=8.64$ Hz, Ar-H, 2H), 8.17–8.15 (d, $J=7.68$ Hz, Ar-H, 1H), 8.1 (s, Ar-H, 1H), 7.65–7.63 (t, $^3J=7.96$ Hz, Ar-H, 1H), 7.57–7.55 (d, $^3J=7.12$ Hz, Ar-H, 1H), 7.45–7.43 (d, $^3J=8.68$ Hz, Ar-H, 2H), 7.39–7.37 (d, $^3J=8.64$ Hz, Ar-H, 2H), 7.13–7.11 (d, $^3J=8.96$ Hz, Ar-H, 2H), 6.94–6.92 (d, $^3J=8.96$ Hz, Ar-H, 2H), 3.98–3.95 (t, $^3J=6.48$ Hz, Ar-O-CH₂-, 2H), 1.82–1.75 (quin, $^3J=7$ Hz, Ar-O-CH₂-CH₂-, 2H), 1.57–1.26 (m, (-CH₂)₁₃, 26H), 0.90–0.86 (t, $^3J=6.48$ Hz, -CH₃, 3H). Elemental analysis: C₅₀H₅₃NO₁₁ requires C 71.16, H 6.33, N 1.66, found C 71.47, H 6.28, N 1.39%.

3. Results and discussion

3.1. Optical and thermal behaviour

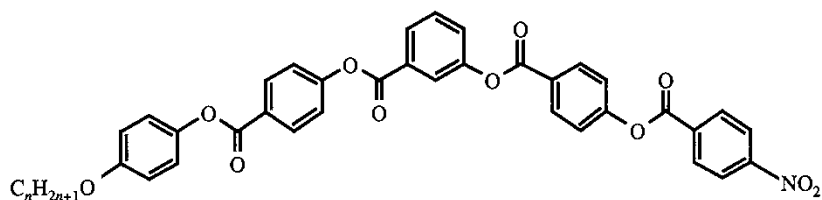
The transition temperatures and associated enthalpies for the two series I and II of unsymmetrically substituted bent-core compounds derived from 3-hydroxybenzoic acid, and containing a cyano and a nitro terminal group, are summarized in tables 1 and 2, respectively. Compounds **1–3** are non-mesomorphic, compounds **4** and **5** are monotropic mesomorphic and compound **6** is enantiotropic. All these compounds exhibit the same type of mesophase. When a sample of any of these is cooled slowly from the isotropic phase, both homeotropic regions as well as focal-conic domains could be seen, which are typical features of a uniaxial smectic A phase. As we shall see later, this mesophase has been characterized as a partial bilayer uniaxial smectic A (SmA_d) phase. We earlier reported [20] another homologous series compounds **1g**, many of which showed two types of mesophase, which were characterized as uniaxial smectic A phase with a partial bilayer structure (SmA_d), and a partial bilayer biaxial smectic A (SmA_{db}) phase. This SmA_{db} phase has now been established as a polar phase with antiferroelectric characteristics [21, 28] and has been designated as SmA_dP_A. These two series of compounds are isomeric, having the positions of the terminal cyano and the *n*-alkoxy chains interchanged. A comparison of these two isomeric series of compounds clearly indicates that reversing the polarity of the ester linkage group has the profound effect of increasing the melting points

Table 1. Transition temperatures ($^{\circ}\text{C}$) and associated enthalpy changes (kJ mol^{-1}) (in italics) for compounds of series I. Cr=crystalline phase, SmA_d =partial bilayer smectic A phase, SmA_dP_A =partial bilayer biaxial antiferroelectric smectic A phase, I=isotropic phase, ()=phase is monotropic.



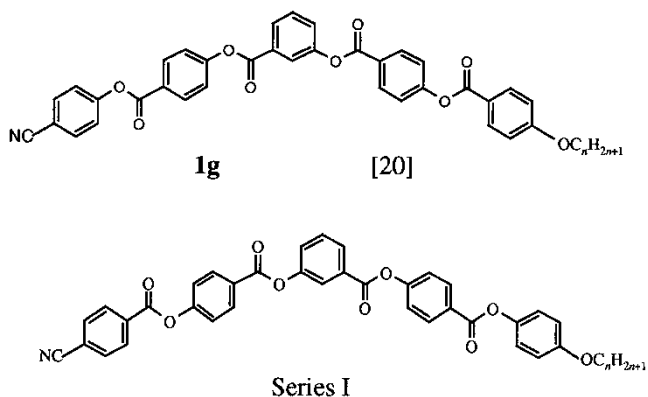
Compound	n	Cr		SmA_d	I
1	8	•	172.0 <i>66.2</i>	—	•
2	10	•	158.0 <i>89.0</i>	—	•
3	12	•	156.5 <i>97.2</i>	—	•
4	14	•	158.0 <i>94.3</i>	(• 154.5) <i>5.10</i>	•
5	16	•	161.5 <i>78.0</i>	(• 161.0) <i>5.56</i>	•
6	18	•	161.0 <i>74.2</i>	• 165.0 <i>5.96</i>	•

Table 2. Transition temperatures ($^{\circ}\text{C}$) and associated enthalpy changes (kJ mol^{-1}) (in italics) for compounds of series II.



Compound	n	Cr		SmA_dP_A	SmA_d	I
7	8	•	145.0 <i>43.0</i>	—	—	•
8	10	•	143.5 <i>43.9</i>	—	—	•
9	12	•	145.0 <i>47.0</i>	—	(• 144.0) <i>3.49</i>	•
10	14	•	146.5 <i>52.9</i>	(• 145.8) <i>0.12</i>	• 153.0 <i>4.66</i>	•
11	16	•	145.0 <i>60.0</i>	• 149.0 <i>0.13</i>	• 160.5 <i>5.15</i>	•
12	18	•	144.0 <i>65.7</i>	• 151.0 <i>0.10</i>	• 166.0 <i>5.74</i>	•

substantially and destabilizing the occurrence of the biaxial smectic A phase.



In the case of compounds of series II, where the terminal cyano group has been replaced by a nitro group, there is considerable reduction in the melting points. As can be seen in table 2, compounds **7** and **8** are non-mesomorphic while compound **9** has a metastable mesophase. Compounds **10**, **11** and **12** exhibit two mesophases, which were detected both under a polarizing microscope and in DSC thermograms. A DSC thermogram obtained for compound **12** is shown in figure 1. Although the clearing enthalpy is quite high, that of the mesophase–mesophase transition is rather small, about 0.1 kJ mol^{-1} .

When a thin film of a sample of compound **12** was sandwiched between two ordinary glass plates and cooled from the isotropic phase and observed under a

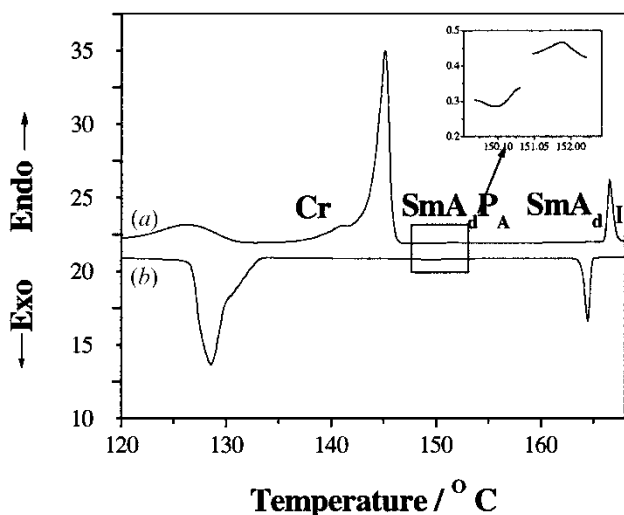


Figure 1. A DSC thermogram obtained for compound **12** showing phase transitions: (a) heating cycle, (b) cooling cycle, rate 5°C min^{-1} . Inset shows expanded region of transition from a uniaxial SmA to a polar biaxial SmA phase.

polarizing microscope, both homeotropic as well as focal-conic regions could be seen. This mesophase has been identified as a uniaxial SmA phase with a partial bilayer structure (see XRD studies). On cooling the sample further to a temperature of 150°C , no significant change in the texture was seen. However, when the sample was taken in a cell treated for homogeneous alignment and viewed as above, small change in the focal-conic texture could be seen at the phase transition (150.5°C). The optical photomicrographs of these two mesophases obtained in a cell treated for homogeneous alignment are shown in figures 2(a) and 2(b), respectively. Interestingly, when this compound **12** was taken in a cell treated for homeotropic alignment and cooled from the isotropic phase, the dark regions of the uniaxial SmA phase transformed to a schlieren texture at the transition to the biaxial form. The schlieren texture showed two- and four-brush strength defects. A photomicrograph of the schlieren texture is shown in figure 3. These optical textures can be attributed to (i) an anticlinic SmC phase or (ii) an antiferroelectric

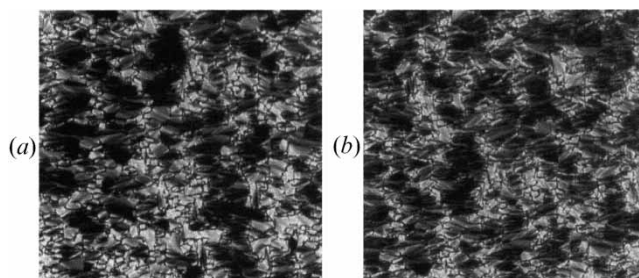


Figure 2. Optical photomicrographs of (a) uniaxial SmA phase and (b) biaxial SmA phase obtained for compound **12** in a homogeneously aligned cell.

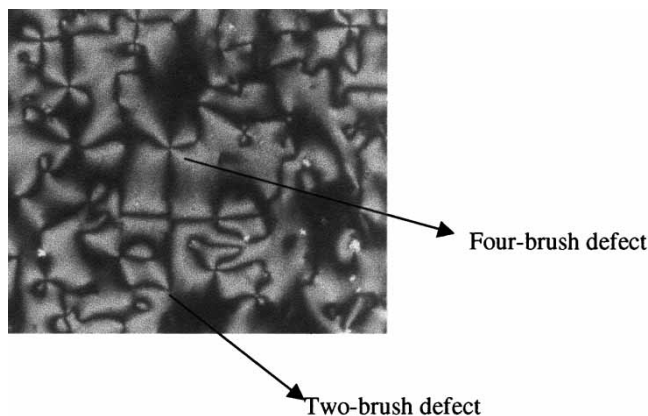


Figure 3. Optical photomicrograph of a schlieren texture (showing two- and four-brush strength defects) of the biaxial SmA phase of compound **12** in a homeotropically aligned cell.

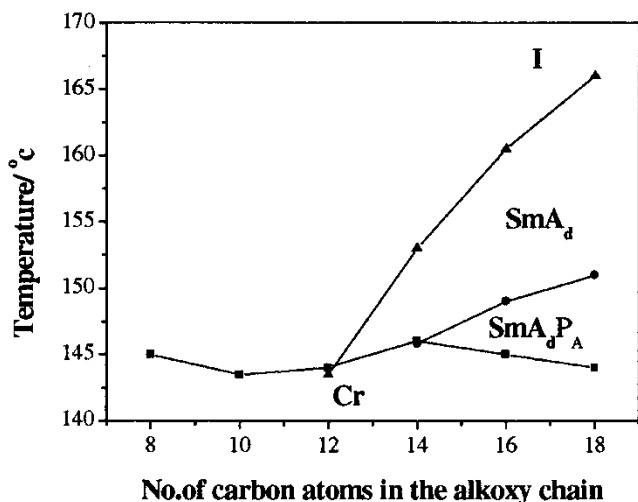


Figure 4. Plot of transition temperature as a function of n -alkoxy chain length for compounds of series II.

smectic phase. Based on XRD studies and electro-optical investigations (described later) we can say the mesophase is a partial bilayer antiferroelectric smectic A (SmA_dP_A) phase.

A plot of transition temperature as a function of n -alkoxy chain length for compounds of series II is shown in figure 4. The clearing transition points rise sharply as compared with the SmA_d to SmA_dP_A phase transition curve.

The introduction of a lateral fluorine substituent on one of the arms containing a strongly polar terminal nitro group has a detrimental effect on the mesophases. For example, the transition temperatures of compounds **11** (table 2), **13** and **14** (table 3) can be compared. The parent compound **11** shows enantiotropic SmA_dP_A and SmA_d phases, while in compound **13**, which has a fluorine substituent *ortho* to the carbonyl group, both

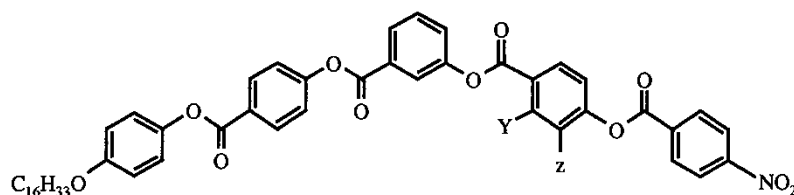
the mesophases are eliminated. However, in compound **14**, although the SmA_dP_A phase is eliminated, the SmA_d phase is retained as a monotropic phase. Curiously, in spite of a lateral substituent being introduced, the melting points have been enhanced. This is in contrast to our earlier studies where the introduction of a lateral substituent affected the melting points marginally but the mesophases were generally retained [20].

All the compounds exhibiting the polar biaxial SmA phase studied by us so far [19–21] have been derived from 3-hydroxybenzoic acid. In order to explore other possibilities, we have investigated a few compounds derived from resorcinol but substituted unsymmetrically. The transition temperatures and associated enthalpy values for these are given in table 4. Compound **15** is isomeric with compound **3** and is non-mesomorphic. Compound **9** shows a monotropic uniaxial SmA phase, while the corresponding resorcinol derivative (**16**) is non-mesomorphic. When a 4-cyanobiphenyl group replaces the terminal 4-cyanophenyl moiety of compound **15**, the resulting compound **17** not only becomes enantiotropic in nature but also exhibits both the SmA_d and SmA_dP_A phases. When a fluorine substituent is introduced *ortho* to the carbonyl group (**18**), the melting point rises, the clearing temperature falls and the SmA_dP_A phase becomes monotropic. Similarly, when the terminal n -dodecyloxy chain is replaced by an n -dodecyl chain, the melting and clearing temperatures are marginally affected while the SmA_dP_A phase becomes highly metastable.

3.2. X-ray diffraction studies

X-ray diffraction measurements were performed on the mesophases exhibited by many of the compounds investigated; the experimental procedure used has

Table 3. Transition temperatures (°C) and the associated enthalpy changes (kJ mol⁻¹) (in italics) for compounds with lateral substituents.



Compound	Cr		SmA _d		I
13 Y=F, Z=H	•	165.0 62.6	—		•
14 Y=H, Z=F	•	152.0 65.2	(•	149.5) 5.27	•

Table 4. Transition temperatures ($^{\circ}\text{C}$) and the associated enthalpy changes (kJ mol^{-1}) (in italics) for unsymmetrical compounds.

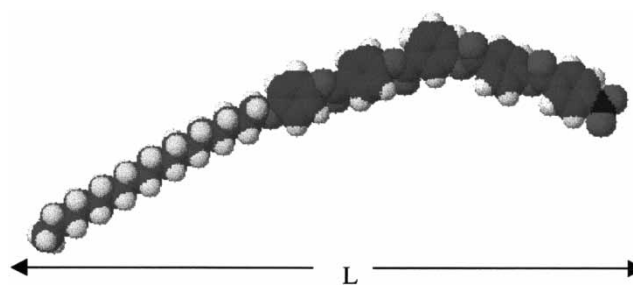
B

Compound	Cr		SmA _d P _A		SmA _d		I
15 $R = \text{OC}_{12}\text{H}_{25}$, $Y = \text{H}$ $R' = 4\text{-cyanophenyl}$	•	144.0 <i>40.7</i>	—		—		•
16 $R = \text{OC}_{12}\text{H}_{25}$, $Y = \text{H}$ $R' = 4\text{-nitrophenyl}$	•	150.0 <i>61.7</i>	—		—		•
17 $R = \text{OC}_{12}\text{H}_{25}$, $Y = \text{H}$ $R' = 4\text{-cyanobiphenyl}$	•	167.0 <i>71.1</i>	•	171.5 <i>0.06</i>	•	199.5 <i>3.32</i>	•
18 $R = \text{OC}_{12}\text{H}_{25}$, $Y = \text{F}$ $R' = 4\text{-cyanobiphenyl}$	•	172.0 <i>65.6</i>	(•)	160.5 <i>0.04</i>	•	191.5 <i>3.35</i>	•
19 $R = \text{C}_{12}\text{H}_{25}$, $Y = \text{F}$ $R' = 4\text{-cyanobiphenyl}$	•	175.0 <i>60.2</i>	(•)	148.5 <i>0.07</i>	•	190.0 <i>3.11</i>	•

already been described [19]. Unoriented samples in Lindemann capillaries were used for investigations. For all the compounds investigated, two reflections could be seen in the small angle region; these are in the ratio 1:1/2 suggesting a smectic ordering of the mesophases. The second-order reflection is weak suggesting a disordered smectic arrangement of the molecules. In addition, the diffuse scattering in the wide angle region with a maxima around 4.7 \AA confirms the fluid-like in-plane order for the mesophases. The layer spacing (d) values obtained for the various compounds and the measured molecular length (L) in their most extended form with an all-*trans*-conformation of the terminal n -alkoxy chain is given in table 5. As can be seen in this table, the d -value obtained for the first-order reflection is more than the calculated value of L . Hence the possibility that the lower temperature biaxial phase is a SmC phase can be ruled out. The molecules of these compounds, containing a strongly polar terminal substituent, organize themselves in an antiparallel configuration to compensate for dipolar interactions. This aspect has been discussed in detail in our earlier studies of other strongly polar compounds [19, 20]. Thus, it is sufficient to mention here that the antiparallel configuration results in a value for d which is greater than L but less than $2L$. Hence these phases have a partial bilayer structure. It was also found that the layer spacing is independent of temperature in the two smectic phases as observed previously [19, 20].

The X-ray angular intensity profile obtained for compound **12** in the SmA_dP_A phase is shown in figure 6. It is interesting to note that the compounds containing a terminal cyano substituent exhibit only one mesophase, and the first-order layer spacing of

Table 5. The d -values obtained from XRD studies of some of the investigated compounds and their molecular length measured by assuming a conformation as shown below wherein the methylene units of the n -alkoxy chain are in a fully extended all-*trans*-conformation.



Compound	d -values/ \AA		Molecular length $L/\text{\AA}$
	d_1	d_2	
6	68.7	34.5	52.4
10	55.6	27.8	47.5
11	57.6	28.8	50.1
12	59.2	29.6	52.3
16	53.2	26.8	48.4

these compounds is greater than that obtained for the terminal nitro-substituted compounds which exhibit two mesophases. A possible explanation for the observed values is as follows. In the case of compound **6**, the length of the individual molecule L is 52.4 Å, while the experimentally obtained value for d is 68.7 Å. If we assume a conformation as shown in figure 5(a) for an antiparallel configuration, then the measured length, $l=81$ Å. Since the chains are fairly long, it is possible to have *gauche* conformations and hence a reduced experimental value. This arrangement of the dimeric molecules also accounts for the occurrence of only the SmA_d phase.

However, in the case of the analogous nitro-substituted compounds, the obtained d -value is 59.2 Å and the calculated molecular length L is 52.3 Å. The dimeric molecules will then have a configuration as shown in figure 5(b). In this dimeric system, the measured molecular length l is 69.8 Å, which accounts not only for the experimentally obtained layer spacing but also the lower temperature antiferroelectric biaxial smectic A_d phase. Similar conformations of the *n*-alkoxy chains were considered by Eremin *et al.* [23] and Schröder *et al.* [24] for their studied systems.

3.3. Conoscopic examination

Conoscopy is a useful technique for ascertaining whether a mesophase is uniaxial or biaxial in nature.

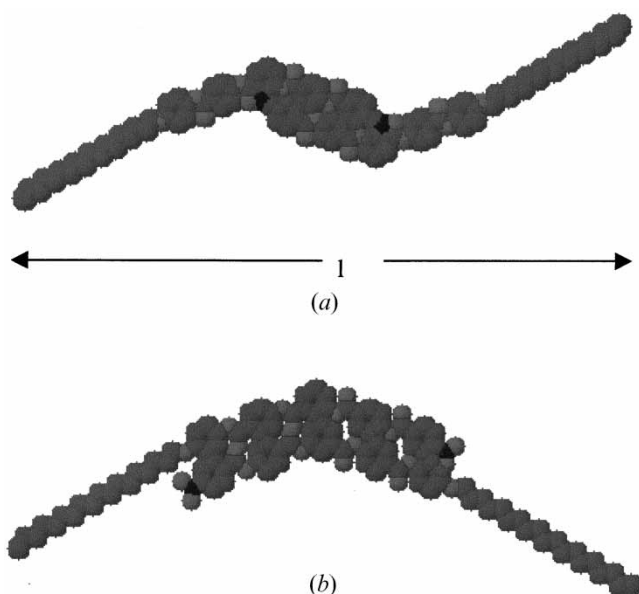


Figure 5. Space filling model showing the antiparallel arrangement of molecules for (a) compound **6** (measured length $l=81$ Å, experimental $d=68.7$ Å); (b) compound **12** (measured length $l=69.8$ Å, experimental $d=59.2$ Å).

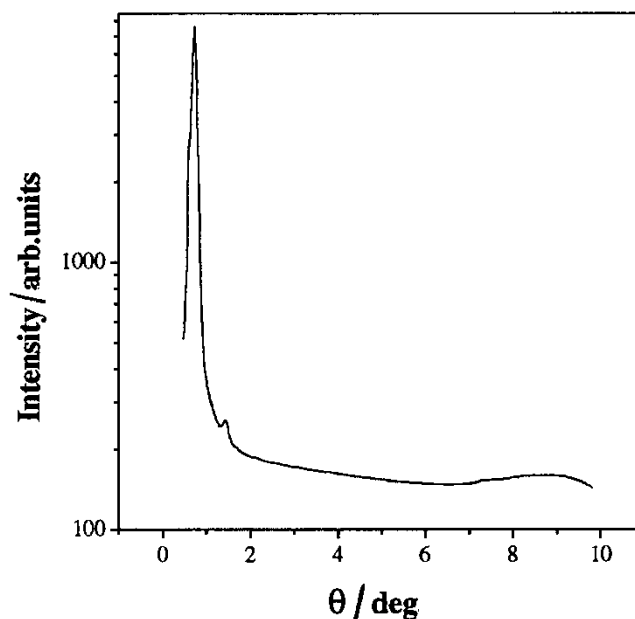


Figure 6. X-ray intensity profile showing smectic characteristics for compound **12**.

We have carried out conoscopic experiments on the mesophases exhibited by the compounds investigated here. For this experiment, fairly well aligned samples must be used and this was achieved as follows. A cell was constructed in which one of the glass plates was coated with ITO for electrical conduction with a gap of 1 mm that was etched out. The other plate was an ordinary glass plate, and inner surfaces of both the plates were treated with octadecyltriethoxysilane, which facilitates a homeotropic alignment of the SmA liquid crystal. The thickness of the cell was 35 μm, which was controlled by using appropriate spacers. A sample of compound **12** was filled in this cell and conoscopic observations were made between crossed polarizers set at 45° to the direction of the electric field (190 V, 10 kHz). A typical uniaxial pattern was observed in the high temperature SmA phase. On lowering the temperature to 150.5°C, the isogyres begin to split to give a biaxial pattern. On reducing the temperature further the isogyres left the field of view. Figure 7 comprises optical photomicrographs showing the patterns obtained in the uniaxial smectic A (a) and biaxial smectic A (b, c) phases for compound **12**.

3.4. Electro-optical investigations

In order to examine the electro-optical switching behaviour of the mesophases in these unsymmetrically substituted compounds, we have carried out triangular-wave electric field experiments. A sample of compound

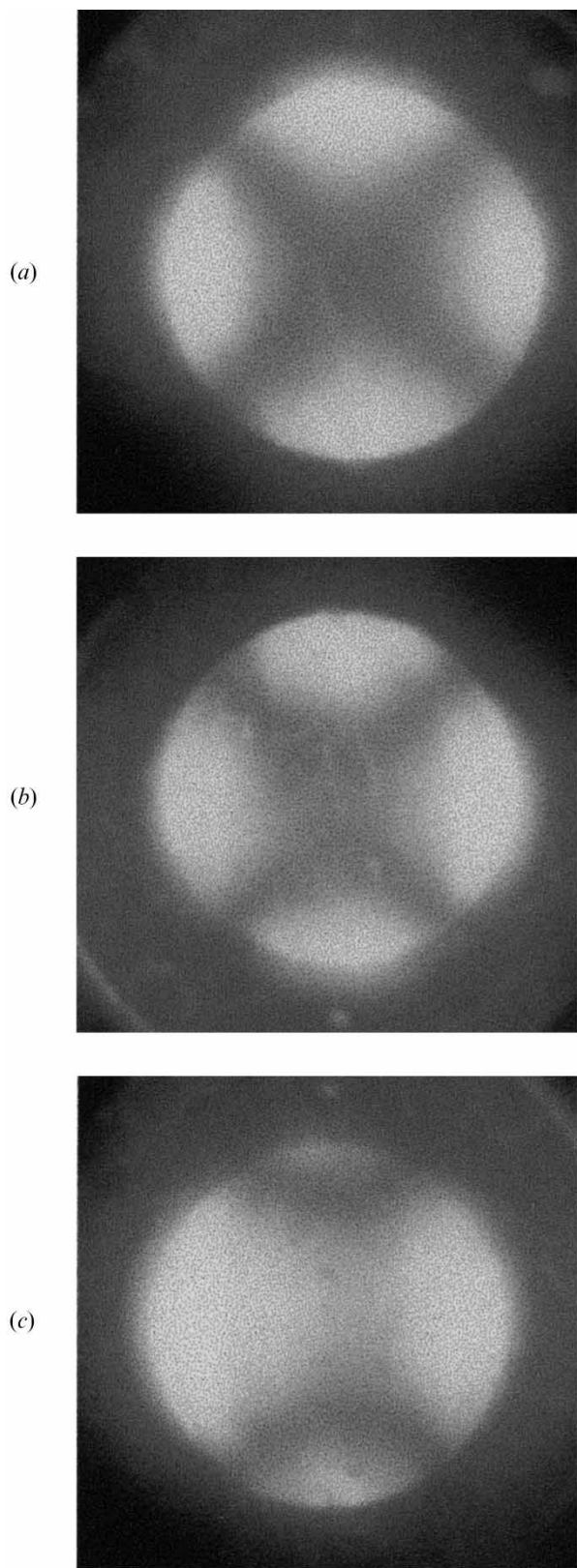


Figure 7. Conoscopic patterns in (a) uniaxial and (b, c) biaxial smectic A phases obtained for compound **12**.

12 in the isotropic phase was filled into a cell of thickness $14\ \mu\text{m}$, which was constructed for aligning the sample homogeneously. When this sample was cooled slowly under a triangular-wave electric field no polarization current peaks were observed, even at high voltages, in the uniaxial SmA phase over the entire mesophase range. However, on cooling the sample further to a temperature of 150°C , two polarization current peaks for each half cycle could be obtained at a threshold of $150\ \text{V}_{\text{pp}}$. This indicates that the lower temperature mesophase has an antiferroelectric ground state structure. The electro-optical current response trace obtained in the SmA_d phase is shown in figure 8(a) and the corresponding optical texture is shown in figure 8(b). The electro-optical current response trace obtained in the SmA_dP_A phase is shown in figure 9(a) and the corresponding optical texture is shown in figure 9(b). The current was measured across $10\ \text{k}\Omega$ resistance and the value obtained by integrating the area under the curve is about $190\ \text{nC cm}^{-2}$. No optical switching could be observed because of the absence of layer chirality. However, a small change in the form of the smooth focal-conic texture could be observed.

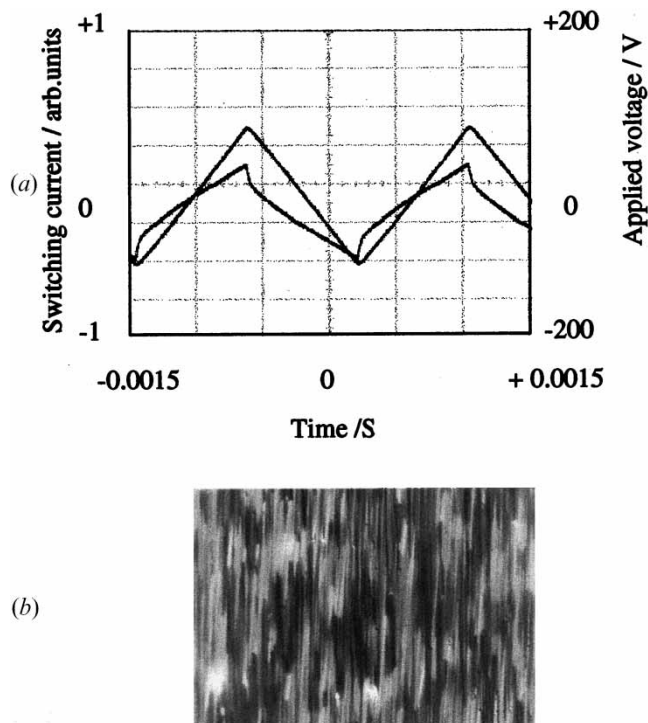


Figure 8. (a) Switching current response trace obtained for compound **12** by applying a triangular-wave electric field ($192\ \text{V}_{\text{pp}}$, frequency $600\ \text{Hz}$) in the uniaxial SmA phase, cell thickness $14\ \mu\text{m}$. (b) The optical texture obtained under the same conditions.

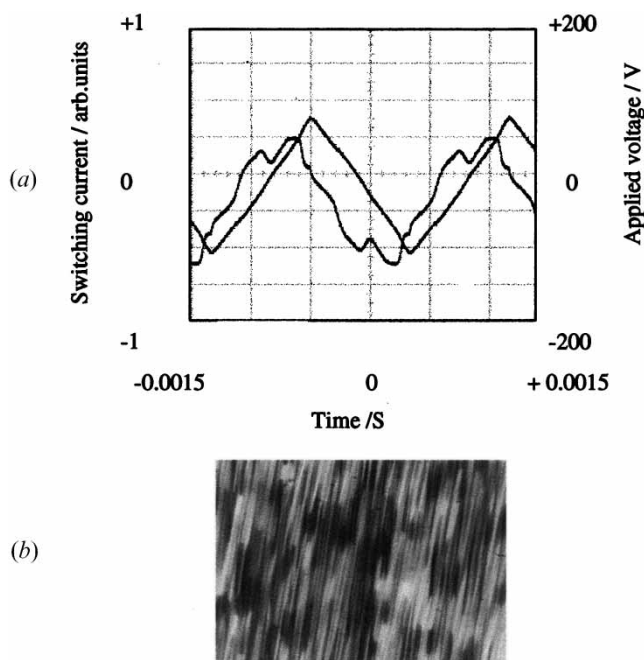


Figure 9. (a) Switching current response trace obtained for compound **12** by applying a triangular-wave electric field ($192 V_{pp}$, frequency 600 Hz) in the biaxial SmA phase; cell thickness $14 \mu\text{m}$, saturated polarization is about 190 nC cm^{-2} . (b) The optical texture obtained under the same conditions.

3.5. Miscibility studies

With a view to confirming the identity of the two mesophases observed in these compounds, we have carried out miscibility studies between compound **11** and the well studied compound 4-cyanophenyl 4-{3-[4-(4-*n*-tetradecyloxybenzoyloxy)-3-fluorobenzoyloxy]-benzoyloxy}benzoate, **1i14** [19, 20]. This reference compound has the following sequence of transitions Cr 120.5 SmA_dP_A 126.2 SmA_d 130.0 I ($^{\circ}\text{C}$). Although this reference compound was reported to be apolar, we have now established that it is polar and shows antiferroelectric characteristics. The binary phase diagram obtained for these two compounds is shown in figure 10. One can clearly see that the two phases of compound **11** are completely miscible with the mesophases of the standard material over the entire composition range, indicating that the two mesophases are the same. In other words, the mesophases exhibited by compound **11** as the temperature is lowered from the isotropic phase are SmA_d and SmA_dP_A phases.

4. Conclusions

The mesomorphic behaviour of several unsymmetrical bent-core compounds containing a strongly polar terminal cyano/nitro group has been investigated. These compounds are derived from either 3-hydroxybenzoic

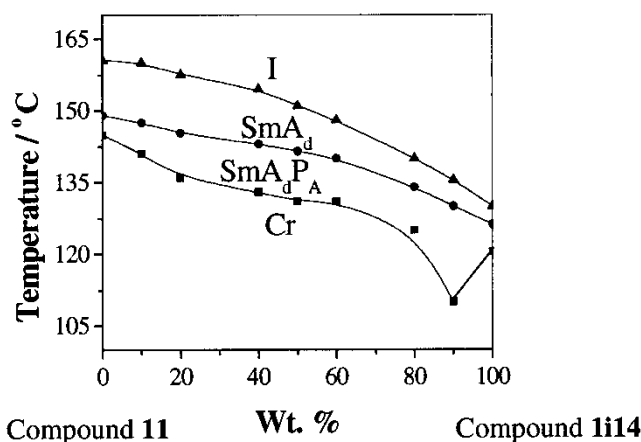


Figure 10. Binary phase diagram obtained for a mixture of compound **11** and a reference compound **1i14** [19, 20].

acid or resorcinol. The mesophases exhibited by these compounds have been characterized as the partial bilayer uniaxial smectic A phase or the polar partial bilayer biaxial smectic A phase with antiferroelectric characteristics. The latter mesophase has orthogonal arrangement and belongs to symmetry group C_{2v} . The orientation of the ester linkage group and the number of aromatic rings in the side wings seem to play an important role in inducing, particularly, the polar partial bilayer biaxial smectic A phase. In addition, a lateral fluorine substituent on the side arm containing the strongly polar terminal group has a strong influence on the occurrence of this SmA_dP_A phase in these materials.

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