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Occurrence of a transition between two polar orthogonal smectic phases in a new homologous series of novel bent-core compounds

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Two new homologous series of isomeric achiral five-ring bent-core compounds containing 3,4-disubstituted biphenyl moiety have been synthesised and the mesophases that they exhibit characterised. Compounds of series **A** are obtained from 4-hydroxybiphenyl-3-carboxylic acid while those in series **B** are prepared by reversing the position of the hydroxyl and carboxylic groups. This change seems to have a profound effect on the mesophase properties. Interestingly, for compounds of series **A** containing the long terminal chain, a transition between two polar orthogonal smectic phases has been observed. The observed mesophases have been characterised using a combination of polarised light optical microscopy, differential scanning calorimetry, X-ray diffraction studies and electro-optical measurements. This is the first example of a transition between two partial bilayer polar orthogonal smectic phases. In addition, the effect of a fluoro substituent *ortho* to the strongly polar terminal cyano group on the mesophase has also been examined.

Key words: bent-core; biphenyl moiety; polar uniaxial smectic A; polar biaxial smectic A

1. Introduction

During the past few years, several thousand compounds composed of achiral bent-core (BC) molecules have been synthesised and the mesophases that they exhibit investigated. This is due to the discovery [1] of electro-optical switching in the mesophase of such a BC compound. In addition, the various results obtained with these compounds are quite fascinating, exciting and intriguing, with one of the most striking features being the observation of polar switching in such compounds even though the constituent molecules are achiral [2–5]. If the molecules of such a compound organise themselves orthogonally with respect to the layer planes then a polar smectic A phase can be realised. Although the theoretical prediction [6] of the existence of a biaxial smectic A phase was made more than 35 years ago, the first experimental evidence for the same was provided [7] much later in a binary mixture of a liquid crystalline polymer and a monomeric material. Subsequently, the first example of a single layer biaxial smectic A phase was reported [8] in a binary mixture of a metallomesogen and 2,4,7-trinitrofluorenone. We provided the first experimental evidence [9] for the existence of a biaxial smectic A phase in low molecular compounds, although in a mixture. This phase, designated as SmA_{2b}, is different from the polar biaxial smectic A phases in that the BC molecules orient with their arrow axes along the layer normal, where as in the SmA_dP_A phase the arrows lie in the layer plane. Also, unambiguous experimental proof for a biaxial smectic A phase in a pure compound exhibiting antiferroelectric switching behaviour has been provided [10].

We have been investigating the occurrence of biaxial smectic A phases in BC compounds for several years. For example, we have reported [11–14] the synthesis of several compounds composed of strongly polar unsymmetrically substituted BC molecules which exhibit the partial bilayer biaxial smectic A phase. All of these compounds derived from 3-hydroxybenzoic acid contain a highly polar terminal cyano group which overlaps in an antiparallel orientation. These studies have revealed transitions from a partial bilayer uniaxial smectic (SmA_d) phase to a partial bilayer polar biaxial smectic A (SmA_dP_A) phase with antiferroelectric properties and a nematic phase to a SmA_dP_A phase.

A few years ago, evidence was provided [15] for a smectic phase which has non-tilted, optically uniaxial and polarly ordered structure with a random direction of the layer polarisation occurring in asymmetric bent-shaped molecules. This was called the $SmAP_R$ phase and has been reported to be important for technological applications, particularly for fast switching display devices [16, 17]. Recently, some new asymmetric compounds exhibiting this phase have been reported [18]. The first symmetric compounds composed of BC molecules and exhibiting the $SmAP_R$ phase have been reported [19] very recently.

In this paper, we present results obtained from investigations carried out on two entirely new and novel series of five-ring unsymmetrical BC

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compounds derived from 3,4-disubstituted biphenyl moiety. The most interesting finding has been the occurrence of a transition between two partial bilayer polar orthogonal smectic phases.

2. Experimental section

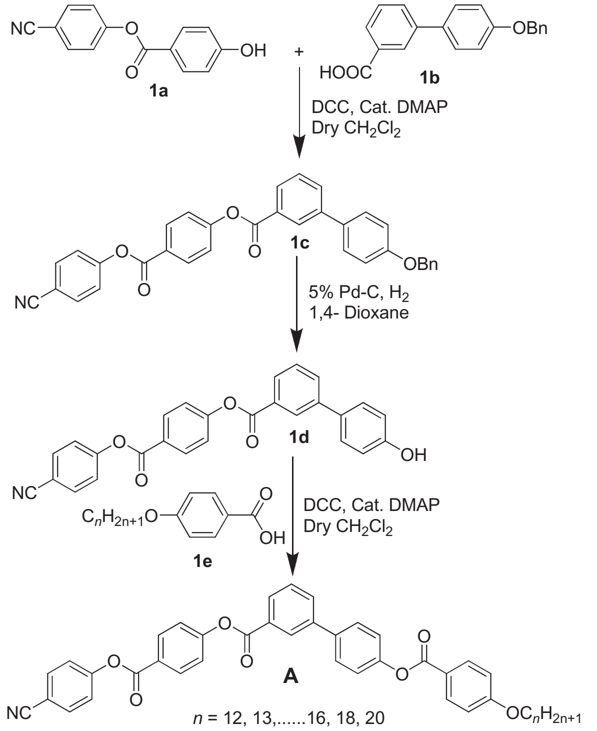
2.1 Equipment and experiments

All synthesised intermediates as well as target compounds were purified by column chromatography on silica gel (60–120 mesh, ACME) and crystallisation using analytical grade solvents. The chemical structure of the compounds was determined by standard techniques such as infrared spectroscopy (Shimadzu FTIR-8400 spectrophotometer), ^{1}H NMR spectroscopy (Bruker AMX 400 spectrometer) and elemental analysis (Carlo-Erba 1106 analyser). The thermal behaviour (transition temperature and associated enthalpy) of compounds was examined by differential scanning calorimetry (DSC Perkin-Elmer, Model Pyris 1D). The optical textures of mesophases were observed using polarising optical microscopy (POM) (Olympus BX50 microscope) equipped with a heating stage (Mettler FP82HT) and a central processor (Mettler FP90).

X-ray diffraction (XRD) measurements of oriented (on a glass plate) as well as non-oriented (Lindemann capillary, with diameter 0.7 mm) samples were performed using Cu-K$_\alpha$ radiation from a rotating anode generator (Rigaku Ultrax-18) having a graphite crystal as monochromator. The diffraction pattern of each sample was recorded on a 2D image plate (Marresearch). The electro-optical switching studies of the samples were carried out in homemade cells and commercial cells (EHC, Japan, cell thickness 8 μm) by using the standard triangular-wave method (waveform generator WAVETEK model 39, amplifier TREK model 601B-3 and an oscilloscope, Agilent 54621A). The conoscopic experiments were performed in homemade cells using a microscope (Leitz Ortholux-II POL BK) equipped with a heating stage and a controller (Mettler FP82 and FP80HT, respectively).

2.2 Synthesis

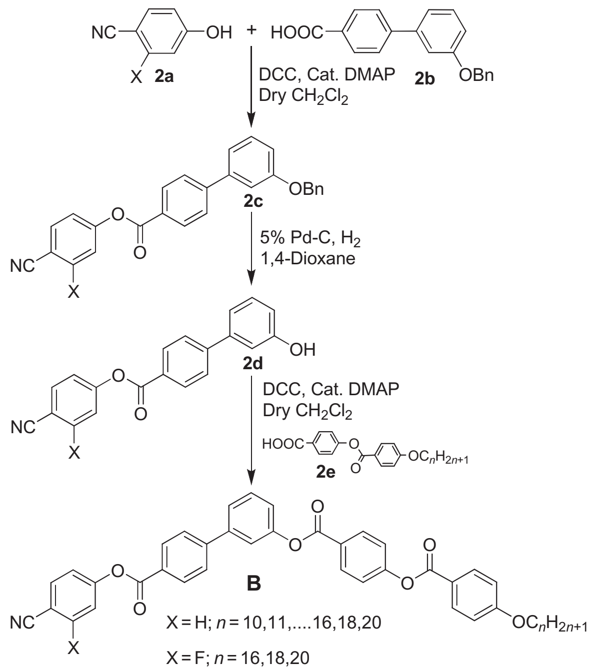
Two new homologous series of novel five-ring unsymmetrical BC compounds containing a 3,4-disubstituted biphenyl unit have been synthesised. Compounds of series **A** were synthesised by following the process shown in Scheme 1, and compounds of series **B** were prepared following the pathway shown in Scheme 2. 4-Benzyloxybiphenyl-3-carboxylic acid and 3-benzyloxybiphenyl-4-carboxylic acid were prepared from the corresponding hydroxy esters which were obtained commercially. The other materials, 4-cyanophenol and 2-fluoro-4-cyanophenol, were also obtained from commercial sources. 4-Cyanophenyl-4-hydroxybenzoate, **1a**, was prepared as described in an earlier paper [12]. 4-Benzyloxybiphenyl-3-carboxylic acid, **1b**, was prepared by benzylation of methyl 3-(4-hydroxyphenyl)-benzoate using benzyl chloride and anhydrous potassium carbonate in anhydrous butan-2-one followed by hydrolysis of the ester using aqueous KOH and ethanol.



Scheme 1. Synthetic route followed for preparing a new series of BC compounds.

*2.2.1. 4-Cyanophenyl[4-benzyloxybiphenyl]-3-carbonyloxybenzoate, **1c***

A mixture of 4-benzyloxybiphenyl-3-carboxylic acid, **1b** (2 g, 6.57 mmol), and 4-cyanophenyl-4-hydroxybenzoate, **1a** (1.57 g, 6.57 mmol), was stirred in anhydrous dichloromethane in the presence of a catalytic amount of 4-(*N, N*-dimethylamino)pyridine (DMAP). To this reaction mixture was added *N, N*′-dicyclohexylcarbodiimide (DCC, 1.49g, 7.23 mmol) and the resultant solution was stirred overnight at room temperature. The dicyclohexylurea formed was filtered off and washed with chloroform several times. Removal of the solvent from the filtrate gave a white material.



Scheme 2. Synthetic path for preparation of compounds of series **B**.

This material was purified by column chromatography on silica gel using a mixture of 1% ethylacetate in chloroform as an eluent. Evaporation of the solvent from the eluate gave compound **1c**, which was further crystallised from a mixture of chloroform and hexane. Yield: 2.59 g (75%); melting point (m.p.) 202–204°C; IR (nujol) ν_{max}: 2923, 2852, 2243, 1737, 1683, 1604, 1585, 1542, 1506, 1456 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ_{H}: 8.39 (t, 1H, J = 1.68 Hz, Ar-H), 8.28 (d, 2H, J = 8.72 Hz, Ar-H), 8.14 (d, 1H, J = 7.88 Hz, Ar-H), 7.85 (d, 1H, J = 8.38 Hz, Ar-H), 7.75 (d, 2H, J = 8.68 Hz, Ar-H), 7.59 (d, 3H, J = 8.84 Hz, Ar-H), 7.46 (d, 2H, J = 8.52 Hz, Ar-H), 7.44-7.33 (m, 7H, Ar-H), 7.09 (d, 2H, J = 8.76, Ar-H), 5.13 (s, 2H, Ar-O-*CH$_2$*-); elemental analysis: $C_{34}H_{23}NO_5$ requires C 77.7, H 4.4, N 2.66; found C 77.33, H 4.02, N 2.44%.

*2.2.2. 4-Cyanophenyl[4-hydroxybiphenyl]-3-carbonyloxybenzoate, **1d***

Compound **1c** (2.5 g, 4.76 mmol) was dissolved in 1,4-dioxane and 5% Pd-C (0.5 g) was added to it. The reaction mixture was stirred at 55°C in an atmosphere of hydrogen until the required quantity of hydrogen was absorbed. The reaction mixture was filtered whilst hot and removal of the solvent under reduced pressure gave a white material which was purified by column chromatography on silica gel using 5% acetone in chloroform as an eluent. Removal of the solvent from the eluate followed by crystallisation of the residue in a mixture of 1,4-dioxane and hexane provided pure compound **1d**. Yield: 1.4 g (70%); m.p. 209–211°C; IR (nujol) ν_{max}: 3377, 2923, 2852, 2243, 1728, 1683, 1598, 1577, 1558, 1456 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d$_6$) δ_{H}: 8.76 (s, 1H, Ar-OH), 8.38 (t, 1H, J = 1.68 Hz, Ar-H), 8.31 (d, 2H, J = 8.72 Hz, Ar-H), 8.11 (d, 1H, J = 8.12 Hz, Ar-H), 7.96 (d, 1H, J = 8.56 Hz, Ar-H), 7.93 (d, 2H, J = 8.72 Hz, Ar-H), 7.66 (t, 1H, J = 7.76, Ar-H), 7.61 (d, 2H, J = 2.72, Ar-H), 7.60 (t, 2H, J = 1.92 Hz, Ar-H), 7.58 (d, 2H, J = 5.24 Hz, Ar-H), 6.97 (d, 2H, J = 8.76 Hz, Ar-H); elemental analysis: $C_{27}H_{17}NO_5$ requires C 74.48, H 3.93, N 3.21; found C 74.15, H 3.62, N 3.54%.

*2.2.3. 4-Cyanophenyl-4-[4-*n*-octadecyloxybenzoyloxybiphenyl]-3-carbonyloxy benzoate, **A6***

Esterification of phenol **1d** (0.2 g, 4.59 mmol) with *n*-octadecyloxy benzoic acid (0.179 g, 4.59 mmol) using DCC (0.104 g, 5.05 mmol) and DMAP in anhydrous dichloromethane (20 ml) following a procedure similar to that used for preparing compound **1c** gave compound **A6**. Yield: 0.278 g (75%); m.p. 134.5°C; IR (KBr) ν_{max}: 3101, 3070, 2918, 2848, 2243, 1735, 1733, 1604, 1577, 1508, 1473 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ_{H}: 8.44 (t, 1H, J = 1.66 Hz, Ar-H), 8.30 (d, 2H, J = 8.72 Hz, Ar-H), 8.20(d, 1H, J = 7.8 Hz, Ar-H), 8.16 (d, 2H, J = 8.88 Hz, Ar-H), 7.90 (d, 1H, J = 8.03 Hz, Ar-H), 7.75 (d, 2H, J = 6.75 Hz, Ar-H), 7.71 (d, 2H, J = 8.6 Hz, Ar-H), 7.63 (t, 1H, J = 7.73 Hz, Ar-H), 7.44 (d, 2H, J = 8.74 Hz, Ar-H), 7.39 (d, 2H, J = 8.71, Ar-H), 7.33 (d, 2H, J = 8.59 Hz, Ar-H), 6.98 (d, 2H, J = 8.9 Hz, Ar-H), 4.05 (t, 2H, J = 6.5 Hz, Ar-O-*CH$_2$*-),1.86–1.79 (quin, 2H, J = 6.63 Hz, Ar-O-CH$_2$-*CH$_2$*-), 1.50–1.26 (m, 30H, -(CH$_2$)$_{15}$-), 0.87 (t, 3H, J = 6.58 Hz, -CH$_3$); elemental analysis: $C_{52}H_{57}NO_7$ requires C 77.3, H 7.1, N 1.73; found C 77.03, H 7.2, N 1.97%.

3. Results and discussion

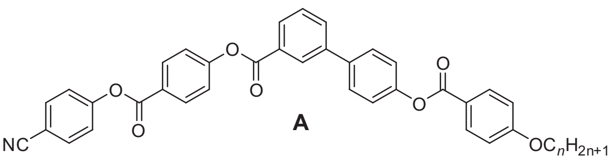
3.1 Mesomorphic properties

Two series of novel unsymmetrical BC compounds derived from 3,4-disubstituted biphenyl moiety have been synthesised and the mesomorphic properties exhibited are investigated. All the compounds contain a strongly polar cyano group at one terminal position while the other end is substituted by an *n*-alkoxy chain. In one of the series, the effect of a fluoro substituent *ortho* to the terminal cyano group is also examined. Interestingly, as we shall see later, all the compounds investigated exhibit an orthogonal biaxial smectic phase. The transition temperatures and the associated enthalpy values obtained for these novel five-ring BC compounds belonging to series **A** and **B** are summarised in Tables 1 and 2, respectively.

As can be seen in Table 1, compounds **A1–A5** show only one mesophase while compounds **A6** and **A7** exhibit an additional mesophase at higher temperature. The mesophase exhibited by compounds **A1**–**A5** and the lower temperature phase of compounds **A6** and **A7** displays a schlieren texture with two- and four-brush defects while the higher temperature phase of the latter two compounds can easily be aligned homeotropically to produce a dark texture. Hence the two mesophases can be assumed to be biaxial and uniaxial, respectively, as the temperature is increased. A plot of the transition temperature as a function of the number of carbon atoms in the terminal chain is shown in Figure 1. One can clearly see a smooth ascending curve for the mesophase to isotropic/mesophase transition points.

When a sample of compound **A7** was cooled slowly from the isotropic phase in a cell treated for homogeneous alignment, a focal-conic texture that is typically seen for a smectic A phase was observed and, on lowering the temperature further, transition bars were seen to grow across the focal-conics as shown in Figure 2(a) and (b), respectively. When a sample of this compound was cooled slowly from the isotropic phase in a cell treated for homeotropic alignment, a

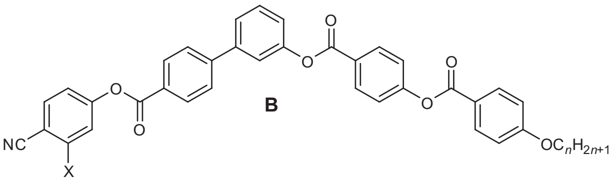
Table 1. Transition temperatures (°C) and the associated enthalpy values *(kJ mol^{-1})* for compounds of series A^a.



Compound	n	Cr		SmA_dP_A		SmA_dP_R		I
A1	12	•	147.0	(•	131.0)	-		•
			163.0		*9.5*			
A2	13	•	134.5	•	136.0	-		•
			112.0		*10.0*			
A3	14	•	135.5	•	140.0	-		•
			122.5		*10.5*			
A4	15	•	134.5	•	143.0	-		•
			117.0		10.5			
A5	16	•	135.0	•	146.0	-		•
			114.5		*11.0*			
A6	18	•	134.5	•	148.0	•	150.0	•
			101.0		*0.06*		*10.0*	
A7	20	•	134.5	•	149.0	•	153.0	•
			113.5		*0.09*		*9.5*	

Notes: ^{a}Abbreviations: Cr: crystalline phase; SmA_dP_A: partial bilayer biaxial antiferroelectric smectic A phase; SmA_dP_R: partial bilayer polar uniaxial smectic A phase; I: isotropic phase; ( ): phase is monotropic.

Table 2. Transition temperatures (°C) and the associated enthalpy values *(kJ mol^{-1})* for compounds of series **B**$^{\mathbf{a}}$.



Compound	n	X	Cr		SmA_{db}		SmA_d		I
B1	10	H	•	115.5	(•	95.5)	-		•
				145.5		*6.5*			
B2	11	H	•	104.0	(•	101.5)	-		•
				116.0		*7.5*			
B3	12	H	•	118.0	(•	107.5)	-		•
				*217.5**		9.5			
B4	13	H	•	122.0	(•	113.0)	-		•
				151.5		*9.5*			
B5	14	H	•	115.5	•	117.5	-		•
				*108.0**		*9.5*			
B6	15	H	•	116.5	•	121.5	-		•
				*109.0**		*10.0*			
B7	16	H	•	115.0	•	125.0	-		•
				*101.0**		*10.5*			
B8	18	H	•	116.0	•	130.5	-		•
				*113.5**		*10.5*			
B9	20	H	•	116.0	•	133.0	-		•
				99.0		*10.0*	-		
B10	16	F	•	114.5	•	112.5	-		•
				120.5		*7.5*			
B11	18	F	•	117.0	•	118.5	•	120.0	•
				123.5		*0.06*		*6.5*	
B12	20	F	•	118.5	•	120.0	•	125.0	•
				124.0		*0.2*		*5.5*	

Notes: ^{a}See Table 1: *Has crystal–crystal transitions; enthalpy denoted is the sum of all such transitions. SmA_{db}: partial bilayer biaxial smectic A phase; SmA_d: partial bilayer uniaxial smectic A phase.

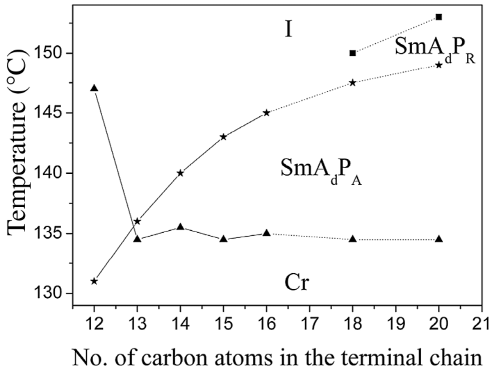


Figure 1. Plot of transition temperature versus number of carbon atoms in the terminal *n*-alkoxy chain for the homologues of series **A**.

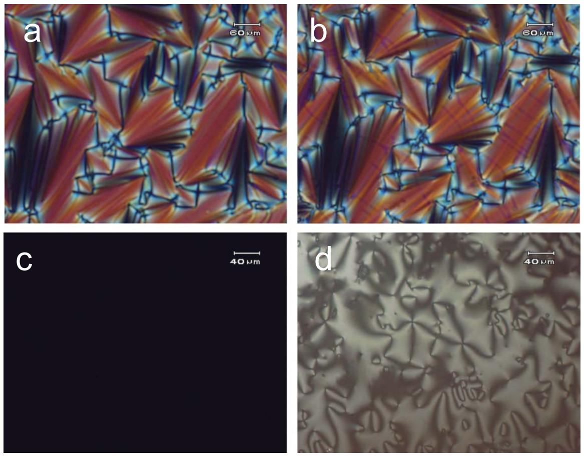


Figure 2. (a) and (b) Optical textures of the mesophases exhibited by compound **A7** in a cell treated for planar alignment at $T = 150°C$ and $T = 145°C$ respectively; (c) and (d) Textures of the same mesophases in a cell treated for homeotropic alignment (same temperatures) (colour version online).

dark texture (Figure 2(c)) could be seen indicating uniaxiality of the phase. On cooling further to the lower temperature phase, a schlieren texture with two- and four-brush defects as shown in Figure 2(d) was obtained. This is a clear signature for the biaxial smectic A phase as reported earlier [12, 13]. A DSC thermogram obtained for compound **A7** is given in Figure 3 which clearly shows the phase transitions.

Compounds belonging to series **B** were obtained from 3-benzyloxybiphenyl-4-carboxylic acid. As can be seen in Table 2, all the parent compounds exhibit only one mesophase. While compounds **B1–B4** are metastable, compounds **B5–B9** are enantiotropic with compound **B9** having the widest thermal range of 17°C. A plot of transition temperature as a function of the number of carbon atoms in the terminal chain is given in Figure 4(a). Clearly, a smooth ascending curve for the mesophase/isotropic transition points is seen as before. In order to examine the effect of a fluorine substituent *ortho* to the terminal cyano group, three such compounds **B10–B12** were prepared. Interestingly, the melting points were not affected much, but the clearing points decreased. Surprisingly, an additional phase was induced which has been identified as a partial bilayer uniaxial smectic A phase. A plot of transition temperature versus the number of carbon atoms in the terminal chain for these three compounds is given in Figure 4(b) and the trends are similar to the parent compounds.

When compound **B8** was sandwiched between two untreated glass plates and cooled slowly from the isotropic state, a schlieren texture with predominantly two- and four-brush defects along with focal-conics as

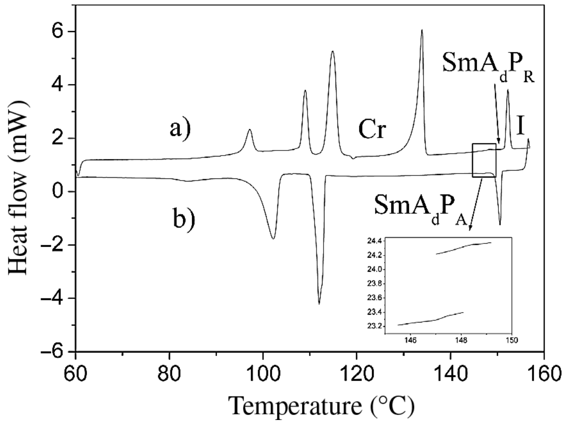


Figure 3. A DSC thermogram of compound **A7** showing phase transitions: (a) heating cycle; (b) cooling cycle; rate 5°C min^{-1}. The expanded region of transition from a polar uniaxial SmA to a polar biaxial SmA phase is shown in the inset.

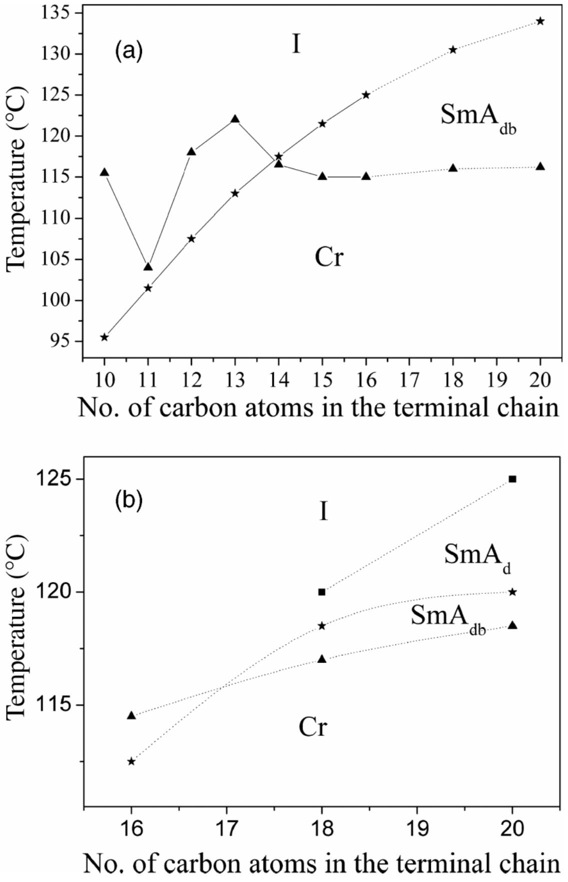


Figure 4. (a) Plot of transition temperature as a function of the number of carbon atoms in the terminal *n*-alkoxy chain for the homologues of parent compounds **(B1–B9)** of series **B**. (b) A similar plot for fluorine substituted compounds **(B10–B12)** of series **B**.

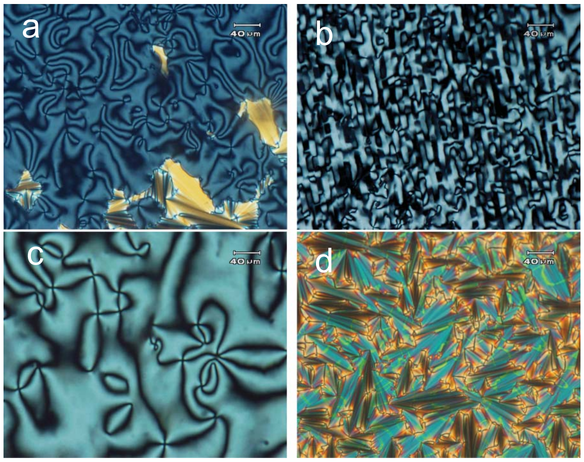


Figure 5. Photomicrographs of the optical textures exhibited by compound **B8** between two ordinary glass plates: (a) schlieren texture with focal conics at $T = 125.6°\mathrm{C}$; (b) striped pattern of $\mathrm{SmA_{db}}$ phase at $T = 125°\mathrm{C}$; (c) schlieren texture with two- and four-brush defects at $T = 125°\mathrm{C}$ in a cell treated for homeotropic alignment; (d) fan-shaped texture with arcs across the fans at $T = 122.8°\mathrm{C}$ of the same sample in a cell treated for homogeneous alignment.

well was obtained as shown in Figure 5(a). After shearing the cover glass the sample was heated to the isotropic phase and cooled again to the mesophase. A striped pattern as shown in Figure 5(b) was obtained. This behaviour is typically seen for an orthogonal biaxial smectic phase. A confirmation of this was obtained when a sample of this compound was observed in cells treated for homeotropic and homogeneous alignments. A schlieren texture with two- and four-brush defects for the homeotropic alignment and a focal-conic texture with arcs across the fans for the homogeneous alignment were obtained as shown in Figure 5(c) and (d), respectively. Similar optical textures were seen for the fluorine substituted compounds as well; for example, for **B11** a similar optical texture was seen after slow cooling of the isotropic phase in a cell treated for homeotropic alignment. These textures are depicted in Figure 6(a)–(c). As described later this mesophase has been designated as the smectic $\mathrm{A_{db}}$ phase.

3.2. *X-ray diffraction measurements*

In order to examine the mesophase structure, XRD measurements were carried out on the mesophases of compounds belonging to both series. The XRD patterns of the powder samples were obtained using Lindemann capillaries with diameter 0.7 mm. Samples were filled in the isotropic phase and the ends of the capillaries were sealed carefully. On irradiation, compound **A6** gave two reflections at 140°C in the small angle region with d-spacing $d_1 = 54.5$ Å and $d_2 = 27.27$ Å which are in the ratio 1:1/2 confirming a layer structure. In addition, a diffuse wide-angle peak with a maximum at 4.7 Å was obtained indicating a liquid-like in-plane order. The measured molecular length in the most extended form with an all *trans* conformation of the alkyl chain $L = 46.4$ Å is less than the d-spacing obtained. The values obtained for compounds **A3**–**A7** are given in Table 3. It can be seen that the layer spacing d is significantly larger than the

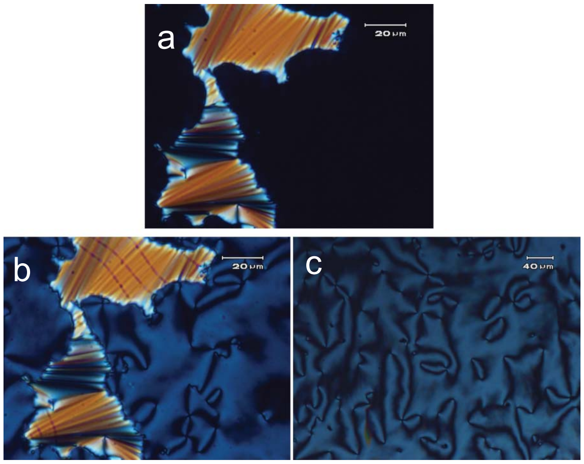


Figure 6. Photomicrographs of the textures exhibited by compound **B11**: (a) $\mathrm{SmA_d}$ phase at $T = 119°\mathrm{C}$; (b) same region as in (a) at $T = 117°\mathrm{C}$ showing the appearance of the biaxial smectic ($\mathrm{SmA_{db}}$) phase, note the dark lines appearing across the fans. (c) different region of the same cell showing two- and four-brush defects in the schlieren texture.

Table 3. Layer spacing date obtained from XRD for compounds of series **A** and series **B**.

		d-spacing / Å			
Compound	T / °C	d_1	d_2	d_3	Measured molecular length /Å
A3	135	50.39	25.2		
A4	136	51.0	25.5		
A5	140	52.74	26.39		
A6	140	54.5	27.27		46.4
A7	151	55.82			
	140	55.82			
B3	103	46.65	23.35	15.3	
B4	107	47.34	23.69	16.39	
B5	110	49.52	24.78	17.07	
B6	115	49.5	24.7	16.5	
B8	120	52.8	26.4	17.6	44.8
B9	124	54.2	27.1	18.0	
B11	119	53.09	26.5	17.66	
	110	53.09	26.5	17.66	
B12	123	53.36			
	115	53.36			

calculated molecular length L but less than $2L$, indicating a partial bilayer structure. It is well known [11–14] that in compounds containing a strongly polar terminal cyano group, the molecules organise themselves in an antiparallel fashion. Such an arrangement of molecules in the mesophase should exist in these compounds as well.

The orthogonal arrangement of molecules in the mesophase was confirmed by carrying out XRD of the oriented samples using the open drop method. Since the thermal range of the higher temperature uniaxial phase is small, the experiment was carried out in the lower temperature phase of compound **A6**. The XRD pattern thus obtained for this material is given in Figure 7. It can be seen that the layer reflections up to the fourth order are positioned on the meridian while the diffuse wide-angle reflection is along the equator, clearly confirming the orthogonal arrangement of molecules. In addition, it was also found that the layer spacing did not change when a sample of **A7** was cooled from the higher temperature uniaxial phase to the lower temperature biaxial phase as shown in Figure 8.

Similar XRD measurements were carried out on the mesophase of compounds of series **B**. Three reflections in the small angle region were seen and the d values obtained are given in Table 3. Also, when a fluoro substituent was introduced *ortho* to the terminal cyano substituent, a uniaxial smectic phase was induced (compounds **B11** and **B12**). The XRD measurements clearly indicate a partial bilayer arrangement of molecules in both the mesophases.

3.3. Conoscopy

Further confirmation for the uniaxiality and biaxiality of the smectic A phases was obtained by conoscopy. For this, fairly well aligned samples were obtained in a cell constructed using an indium tin oxide (ITO) coated conducting glass plate and an ordinary non-conducting glass plate, the inner surfaces of which were treated for homeotropic alignment. The ITO coated plate had an etched gap of ~1 mm across which an electric field could be applied. The sample of **A7** was filled into such a cell (thickness 25 μm) and conoscopic observations made between crossed polarisers set at 45° to the direction in which the electric field could be applied. When the sample of **A7** was cooled slowly from the isotropic phase, at 150°C a uniaxial interference pattern was obtained (Figure 9(a)). From the uniaxial phase the sample was cooled further under the electric field (square-wave field, 100 V and frequency 400 Hz). At a temperature of 147°C a biaxial pattern in which the isogyres split was obtained and the gap between the isogyres increased as the temperature was lowered even further indicating that the lower temperature phase is indeed biaxial. Photomicrographs of the conoscopic patterns obtained for **A7** in the uniaxial

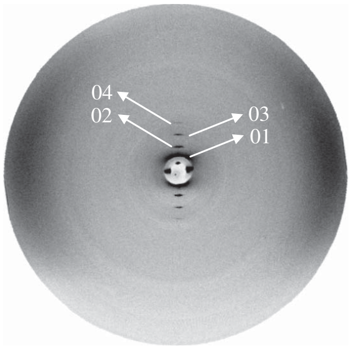


Figure 7. Oriented XRD pattern obtained for compound **A6** in the SmA$_d$P$_A$ phase at $T = 140$°C.

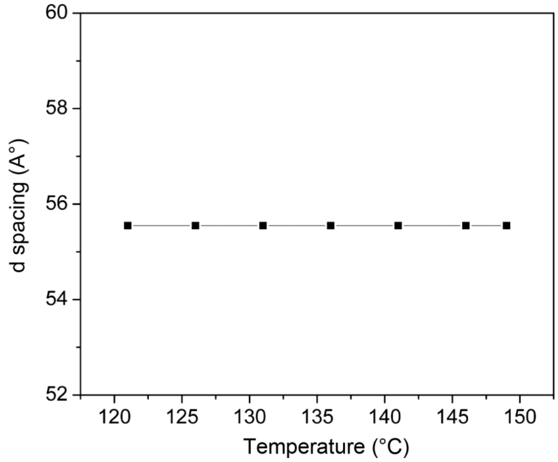


Figure 8. Plot of d-spacing as a function of temperature for compound **A7**.

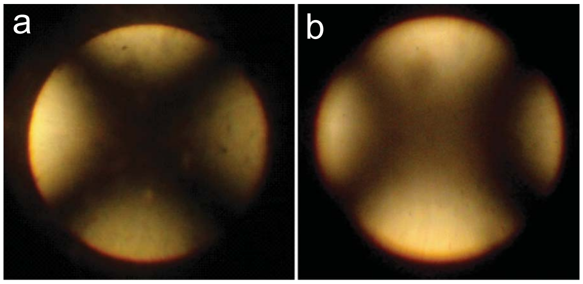


Figure 9. Conoscopic patterns obtained for a homeotropically aligned sample of compound **A7**: (a) the polar uniaxial smectic A$_d$ phase at 150.0°C; (b) the polar biaxial smectic A$_d$ phase at 147.2°C (colour version online).

and biaxial phases are shown in Figure 9(a) and (b), respectively.

3.4. *Electro-optical studies*

In order to examine whether the mesophases exhibited by these compounds respond to an applied electric field, electro-optic studies using the standard triangular-wave field have been carried out. As an example, the switching behaviour of compound **A7** is described here. A commercial cell (EHC, Japan) having a thickness of 8 μm and treated for homogeneous alignment was chosen. This compound was cooled slowly from the isotropic phase into the smectic phase and the triangular-wave electric field was applied; above a threshold field (80 V), optical switching could clearly be seen in the higher temperature uniaxial phase. Thus, by applying an appropriate voltage and frequency (178 V and 200 Hz), a single broad current peak was obtained for each half cycle. The current response as well as the textural change observed under these conditions in the field-on and field-off states at 149°C are shown in Figure 10. On cooling further into the lower temperature phase under the same conditions, the current response splits to give two peaks per half period of the applied field. This indicates the antiferroelectric behaviour of the lower temperature phase. The current response trace and the corresponding optical changes seen are shown in Figure 11. Very interestingly, the mesophases of compounds belonging to series **B** did not respond to an applied electric field (as high as 400 V) although some textural change could be seen above 100 V.

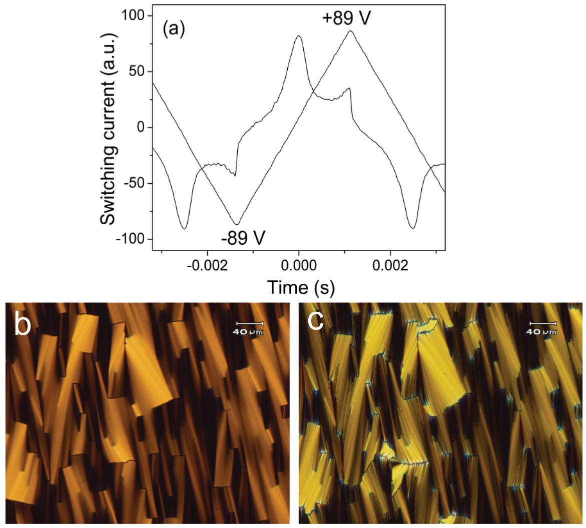


Figure 10. (a) Switching current response obtained for compound **A7** in the SmA$_d$P$_R$ phase at $T = 150°C$ by applying a triangular-wave field; (b) and (c) photomicrographs at 178 V, 200 Hz and 0 V respectively, with polarisation value $P \approx 36$ nC cm^{-2}; cell thickness, 8 μm.

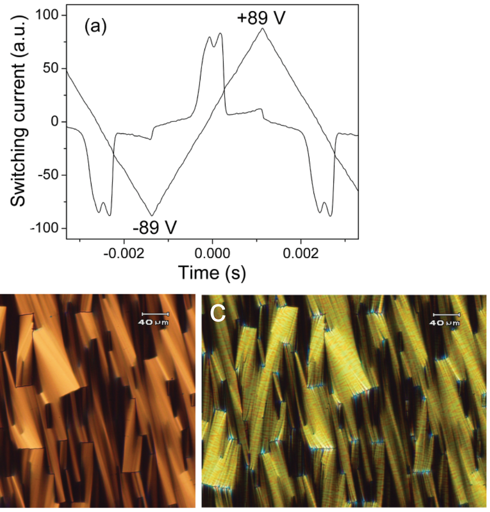


Figure 11. (a) Switching current response obtained for compound **A7** in the SmA$_d$P$_A$ phase at $T = 140°C$ by applying a triangular-wave field; (b) and (c) photomicrographs (same region as in Figure 10(b) and (c)) at 178 V, 200 Hz and 0 V respectively, with polarisation value $P \approx 81$ nC cm^{-2}; cell thickness, 8 μm.

From the above experimental results, characterisation and mesophase assignments can be described as follows. For the compounds of series **A**, the lower homologues exhibit a partial bilayer polar orthogonal smectic phase with antiferroelectric characteristics. The partial bilayer structure has been determined from XRD data. Hence we have assigned the symbol SmA$_d$P$_A$ for this phase and this is well supported by optical textures and conoscopy. The higher temperature mesophase of compounds **A6** and **A7** give a dark texture in a cell treated for homeotropic alignment, has a partial bilayer structure as determined by XRD and is polar as determined from electro-optical studies (a single broad current response peak). It is interesting to point out that Pociecha *et al.* [15] have described a structure formed by asymmetric bent-shaped molecules, which is layered, is optically uniaxial and has a non-tilted arrangement of molecules having a polar order with a random direction of the layer polarisation. They have ascribed this structure to the sign degeneracy of the difference in the polarisation directions in the neighbouring layers and assigned the symbol SmAP$_R$ to this mesophase. Very recently, Gomola *et al.* [18, 19] have described new, both asymmetrical as well as symmetrical BC mesogens which exhibit the polarisation-randomised non-tilted smectic A (SmAP$_R$) phase. The observation of a single broad polarisation switching current peak for each half cycle of the applied field has been attributed to a field-induced alignment of dipoles from random orientation through the Langevin process.

We observe similar switching current responses in the higher temperature phases of compounds **A6** and **A7** which have a partial bilayer non-tilted structure. In analogy with what has been observed recently [15, 18, 19] in other systems, we have assigned the symbol $\mathrm{SmA_dP_R}$ to this phase. In other words, the single broad current response peak suggests a polarisation-randomised interlayer structure. Of course, other detailed experimental studies are required to unequivocally establish the real structure of this phase.

In the case of compounds of series **B**, the parent compounds exhibit a non-tilted, non-polar partial bilayer biaxial smectic phase and hence we have assigned the symbol $\mathrm{SmA_{db}}$. For the two fluoro substituted compounds **B11** and **B12**, the higher temperature mesophase is a non-tilted, non-polar uniaxial partial bilayer smectic phase and has been designated the symbol $\mathrm{SmA_d}$.

Although these two series of compounds are isomeric, their electro-optical behaviour is very different and interesting.

4. Conclusions

Two new series of novel five-ring BC compounds have been synthesised. The compounds of series **A** are derived from 4-hydroxybiphenyl-3-carboxylic acid while those of series **B** are obtained from 3-hydroxybiphenyl-4-carboxylic acid. These represent the first examples of BC compounds derived from such moieties. While the biaxial smectic A phase has been observed in both series of compounds, their physical properties are quite contrasting. In series **A** both the uniaxial and biaxial phases are polar in nature and in series **B** both these phases are apolar. The introduction of a fluorine substituent *ortho* to the highly polar terminal cyano group has the effect of inducing a non-polar uniaxial partial bilayer smectic A phase. The most interesting result has been the occurrence of a transition between two polar partial bilayer orthogonal smectic phases, one of which is biaxial and the other uniaxial. The dark texture of the polar uniaxial partial bilayer smectic phase shown by compounds **A6** and **A7** is interesting. To understand the exact structure of this phase, further experiments are in progress and the results will be reported elsewhere.

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