

Occurrence of Transition between Lamellar Antiferroelectric and Columnar Ferroelectric Phases in Achiral Seven-Ring Bent-Core Compounds Derived from 5-methoxyisophthalic Acid

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The synthesis and characterization of the mesophases formed by several homologues of a series of achiral seven-ring bent-core compounds that are derived from 5-methoxyisophthalic acid are described. The lower homologues show only one phase which is non-switchable. Interestingly however, many of the higher homologues exhibit two mesophases. The higher temperature phase is lamellar and shows antiferroelectric behaviour while the lower temperature phase is columnar and exhibits ferroelectric characteristics. The mesophases have been investigated using a combination of standard techniques such as differential scanning calorimetry, polarizing light optical microscopy, electro-optical methods and X-ray diffraction.

Keywords Bent-core; lamellar; columnar; ferroelectric; antiferroelectric

Introduction

It is just over a decade since the first observation [1] of an electro-optical switching was observed in the mesophase of an achiral bent-core (BC) compound. During this period, remarkable progress has been made, both in the number of different types of such compounds synthesized and in the investigations carried out to understand the structure of the mesophase/s exhibited by them [2–5]. Initially, five-ring BC systems were investigated and now a large number of compounds composed of six and seven rings are also known. Introduction of lateral substituents on the aromatic rings is one of the ways of modifying the mesomorphic properties and such studies have been carried out quite extensively [6–10]. Infact, it has been shown that polar substituents in either the bay or apex position can induce drastic changes in the type of phase observed [11, 12]. Although, these substituents can be introduced at almost any position along the bent-core, they are found generally in the arms of the system.

The number of BC compounds containing a substituent at the apex position are few in number. Unlike most calamitic systems, BC compounds are generally monomorphic. Recently, we investigated five-ring BC compounds derived from 5-methoxyisophthalic acid

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[13]. These showed quite interesting mesomorphic properties including transition between switchable phases. However, the thermal range of the mesophases was narrow and one of the mesophases was metastable. In an effort to stabilize the mesophases and also enhance the thermal range of these, a series of seven-ring BC compounds were synthesized and herein we report their properties.

Experimental

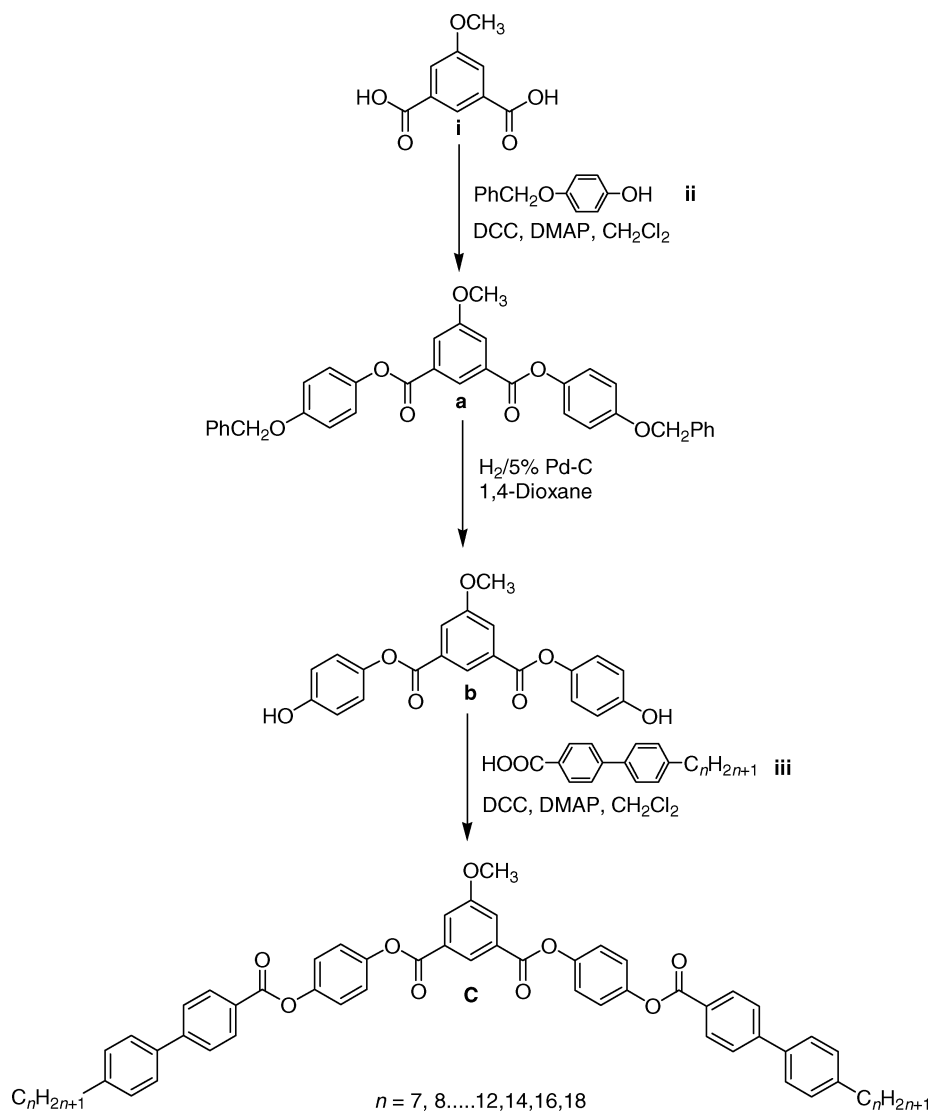
The chemical structure of all the compounds was confirmed by a combination of infrared spectroscopy (Shimadzu FTIR-8400 spectrophotometer), ^1H NMR (Bruker AMX 400 spectrometer), and elemental analysis (Carlo-Erba 1106 analyser). The thermal behaviour of the compounds was investigated using differential scanning calorimetry (DSC Perkin-Elmer, Model Pyris 1D). The reported transition temperatures and the associated enthalpy values were obtained from thermograms recorded on a DSC. The optical textures were observed using polarizing optical microscopy (POM) (Olympus BX50) using a heating stage and a central processor (Mettler FP82HT and Mettler FP90, respectively). X-ray diffraction (XRD) measurements on oriented as well as non-oriented samples were carried out using Cu-K α radiation from a rotating anode generator (Rigaku Ultrax18) with graphite crystal as monochromator. The diffraction patterns were recorded on an image plate (Marresearch). The electro-optical studies and the polarization measurements were carried out using a standard triangular-wave method (waveform generator WAVETEK model 39, amplifier TREK model 601B-3 and an oscilloscope, Agilent 54621A) using commercially available polyimide-coated ITO glass cells (EHC, Japan, cell thickness 8 μm).

Synthesis

The symmetrical seven-ring bent-core compounds of series C were prepared following the synthetic pathway shown in the scheme. 5-Methoxyisophthalic acid, **i**, was prepared according to the procedure already described [13]. 4-Benzyloxyphenol, **ii**, obtained commercially was used without further purification. 4-*n*-Alkylbiphenyl-4-carboxylic acids, **iii**, were prepared as described previously [14]. 5-Methoxyisophthalic acid, **i**, was condensed with 4-benzyloxyphenol, **ii** in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) and a catalytic amount of 4-(*N,N'*-dimethylamino)pyridine (DMAP) to obtain compound **a**. The resultant dibenzyloxy ester was subjected to hydrogenolysis in the presence of 5% Pd-C in 1,4-dioxane. The bisphenol, **b**, thus obtained was purified and esterified with an appropriate 4-*n*-alkylbiphenyl-4-carboxylic acid, **iii** to obtain the desired compound C. All the compounds were purified by column chromatography on silica gel (60–120 mesh) followed by repeated crystallization using suitable solvents.

5-Methoxy bis(4-benzyloxy)phenylisophthalate, **a**

A mixture of 5-Methoxyisophthalic acid, **i**, (2 g, 0.01 mol), 4-benzyloxyphenol, **ii**, (4 g, 0.02 mol) and a catalytic amount of 4-(*N,N'*-dimethylamino)pyridine (DMAP) in dry dichloromethane (30 ml) was stirred for 10 minutes. To this mixture *N,N'*-dicyclohexylcarbodiimide (DCC), (4.5 g, .022 mol) was added and stirring continued overnight at room temperature. The precipitated *N,N'*-dicyclohexylurea was filtered off and washed with an excess of chloroform. Evaporation of the solvent from the filtrate gave a white material, which was passed through a column of silica gel using chloroform as an



SCHEME 1. Synthetic route for the preparation of seven-ring BC compounds

eluant. The required material **a** thus obtained was further purified by repeated crystallization using ethanol. Yield 4.85 g (85%), m.p.135–136.5°C. IR (nujol) ν_{\max} : 2922, 2852, 1739, 1732, 1595, 1504, 1454 cm^{-1} . ^1H NMR (400MHz, CDCl_3) δ (ppm): 8.58 (t, 1H, Ar–H), 7.94 (d, 2H, Ar–H), 7.45–7.34 (m, 10H, Ar–H), 7.16–7.14 (d, 4H, Ar–H), 7.04–7.01(d, 4H, Ar–H), 5.08 (s, 4H, 2 \times -O-CH₂-Ar), 3.96 (s, 3H, Ar-O-CH₃). Elemental analysis: C₃₅H₂₈O₇ requires C 74.99, H 5.03; found C 74.81, H 4.66 %.

5-Methoxy bis(4-hydroxy)phenylisophthalate, **b**

Compound **a** (4 g, 7.14×10^{-3} mol) was dissolved in 1,4-dioxane (60 ml) and 5% Pd-C catalyst (0.8g) was added to it. The mixture was stirred at 60°C in an atmosphere of

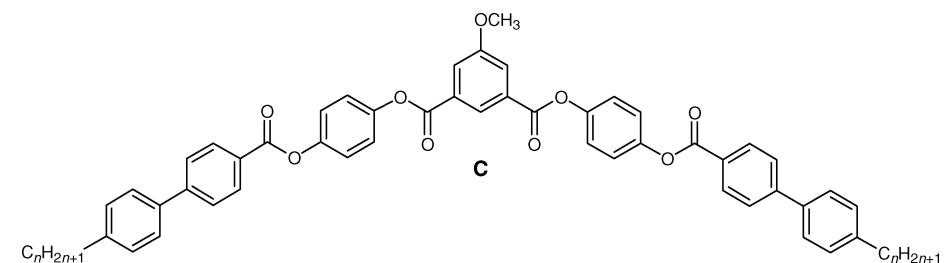
hydrogen until the required quantity of hydrogen was absorbed. The resulting mixture was filtered hot and the solvent removed under reduced pressure. The material obtained was crystallized using a mixture of 1,4-dioxane and petroleum ether (b.p.60–80°C). Yield 2.34g (87%), m.p.214–215.5 °C. IR (nujol) ν_{\max} : 3280, 2923, 2854, 1747, 1735, 1602, 1510, 1461 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 8.58 (t, 1H, Ar–H), 7.94 (d, 2H, Ar–H), 7.11–7.09 (d, 4H, Ar–H), 6.89–6.87(d, 4H, Ar–H), 4.86 (s, 2H), 3.95 (s, 3H, Ar–O–CH₃). Elemental analysis: C₂₁H₁₆O₇ requires C 66.32, H 4.23; found C 66.63, H 4.17 %.

5-Methoxy bis[4-(4-*n*-tetradecylbiphenyl-4'-carbonyloxy)phenylisophthalate], 7

This compound was prepared using the procedure as described for compound **a**. Quantities: compound **b** (0.15g, 3.94×10^{-4} mol), 4-*n*-tetradecylbiphenyl-4-carboxylic acid

Table 1

Transition temperatures (°C) and the associated enthalpies (kJ mol^{-1}) for compounds **C**.



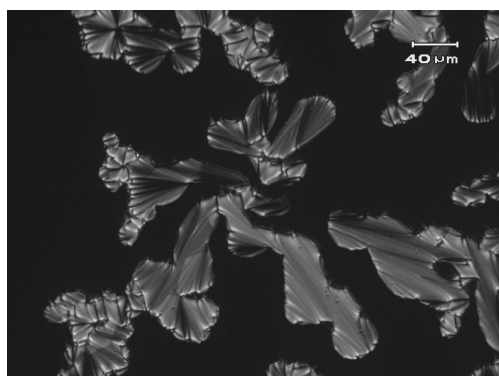
Compound	<i>n</i>	Cr	Col P _{FE}	SmC _s P _{AF}	Col _r	B ₆	I
1	7	174.0	–	–	–	205.0	·
		28.5				18.5	·
2	8	173.0	–	–	·	195.0	–
		28.0				22.0	·
3	9	166.0	–	–	·	188.0	–
		21.0				22.0	·
4	10	161.0	–	–	·	182.5	–
		23.5				23.5	·
5	11	156.0	–	·	179.5	–	·
		28.0			22.5		
6	12	135.0	·	149.5	·	179.0	–
		31.5		11.0		22.0	
7	14	130.0	·	148.5	·	179.0	–
		21.0		9.0		21.5	
8	16	130.5	·	147.0	·	179.0	–
		25.0		10.0		22.0	
9	18	130.0	·	143.0	·	176.0	–
		30.0		9.0		18.0	

Cr = crystalline phase; B₆ = intercalated smectic phase; Col_r = columnar phase with a rectangular lattice; SmC_sP_{AF} = polar smectic C phase with synclinal tilt in adjacent layers and antiferroelectric characteristics; ColP_{FE} = polar columnar phase with ferroelectric switching characteristics; I = isotropic phase.

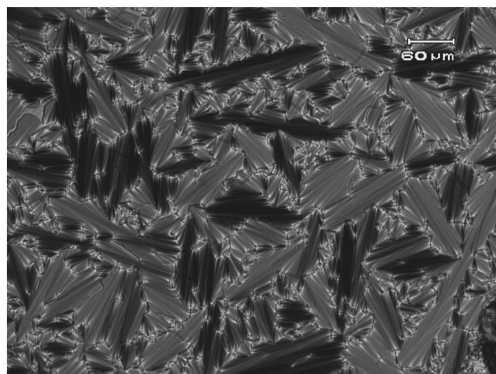
(0.311 g, 7.89×10^{-4} mol), DCC (0.171g, 8.28×10^{-4} mol), DMAP (cat.amount), dry dichloromethane (15 ml); solvent for crystallization: a mixture of chloroform and acetonitrile. Yield 0.335 g (75%), m. p. 130°C . IR (KBr) ν_{max} : 2918, 2848, 1739, 1732, 1604, 1504, 1471 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 8.64 (t, 1H, Ar-H), 8.27–8.25 (d, 4H, Ar-H), 7.99 (d, 2H, Ar-H), 7.75–7.73 (d, 4H, Ar-H), 7.60–7.58 (d, 4H, Ar-H), 7.33–7.29 (m, 12H, Ar-H), 3.98 (s, 3H, Ar-O-CH₃), 2.67 (t, 4H, 2 X Ar-CH₂-), 1.67–1.62 (quin, 4H, 2 X Ar-CH₂-CH₂-), 1.34–1.28 (m, 20 H, 2X-(CH₂)₅), 0.88 (t, 6H, 2 X-CH₃). Elemental analysis: C₇₅H₈₈O₉ requires C 79.47, H 7.81; found C 79.64, H 7.81%.

Results and discussion

The transition temperatures and the associated enthalpy values obtained for the nine bent-core compounds having general structure **C** are summarized in Table 1. Compound **1** shows only one mesophase with a thermal range of 31° . When a sample of this compound is cooled slowly from the isotropic phase, batonnets appear which coalesce to form a fan-shaped texture with fairly high birefringence. Photomicrographs of the texture obtained are shown in Fig. 1. Either on shearing or viewing the sample in cells treated for homeotropic alignment, dark or homeotropic texture could not be obtained. Similar behavior was observed in our

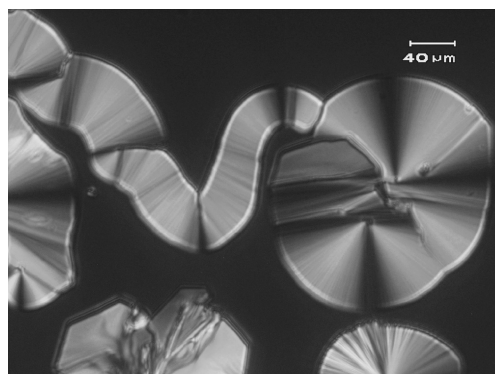


(a)

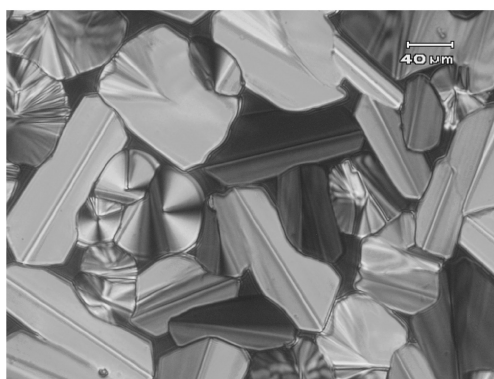


(b)

Figure 1. Photomicrographs obtained for B₆ mesophase of compound **1**. (a) Developing from isotropic phase, T = 202.8°C (b) Completely formed phase, T = 195.6°C . (See Color Plate I)



(a)

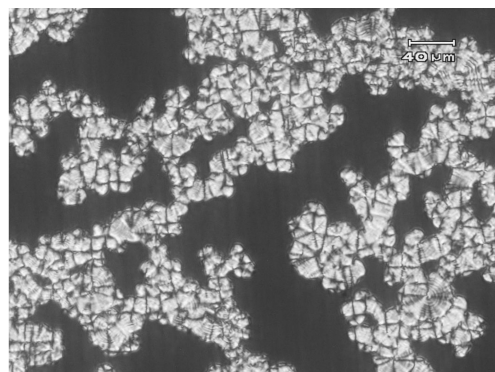


(b)

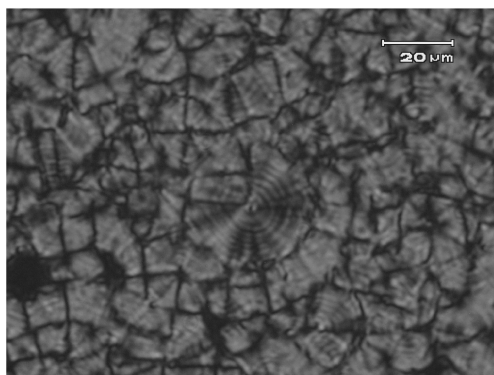
Figure 2. Photomicrographs of the texture obtained for the Col_r mesophase of compound **4**. (a) Developing from isotropic phase, $T = 180.2^\circ\text{C}$ (b) Completely formed mosaic texture, $T = 173.5^\circ\text{C}$. (See Color Plate II)

[8, 15] earlier investigations on the B_6 phase which was confirmed on the basis of XRD experiments. Hence, we have assigned the symbol B_6 to this phase. Compounds **2**, **3**, and **4** exhibit similar textures and that obtained for compound **4** is shown in Fig. 2. These textures are very typical for those observed for the B_1 or Col_r phase, and on the basis of XRD and electro-optical studies, the phase has been characterized as such. The thermal range of this mesophase is about 22° .

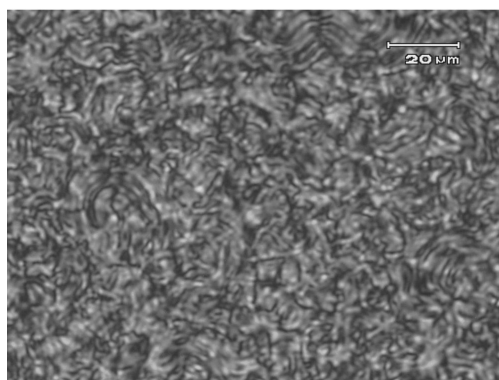
Compound **5** exhibits only one phase with a temperature range of 23.5° . XRD studies show that this is a lamellar phase and electric field experiments indicate an antiferroelectric behaviour with a synclinal tilt and hence this phase can be assigned the symbol SmC_sP_{AF} . Remarkably, compounds **6–9** are dimorphic with well defined transitions which are first order. The thermal range of each of the phases is sufficiently large. A majority of the BC compounds exhibit only one phase, particularly the electro-optically switchable phase. These seven-ring compounds derived from 5-methoxyisophthalic acid are somewhat different. The mesophase of compound **5** and the higher temperature phase of compounds **6–9** are similar. When a sample of compound **7** is cooled from the isotropic phase, a fan-shaped texture develops and photomicrographs obtained for this phase are depicted in Fig. 3(a) and (b). On further cooling a transition takes place at 148.5°C which can be clearly seen under a microscope and a typical photomicrograph is shown in Fig. 3(c). A DSC thermogram



(a)



(b)



(c)

Figure 3. Photomicrographs obtained for SmCP phase (a) $T = 177.4^{\circ}\text{C}$, (b) $T = 176.4^{\circ}\text{C}$ and (c) columnar phase, $T = 142.6^{\circ}\text{C}$ of compound 7. (See Color Plate III)

obtained for this compound is shown in Fig. 4 and one can clearly see the transition between these two phases. Although there are a few reports [16–20] on the occurrence of transition between SmCP and a columnar phase, the observation made in the present series of compounds is unusual. Infact, electric field induced transitions between SmCP and columnar phases have also been observed [18–20]. Another interesting aspect of BC compounds is

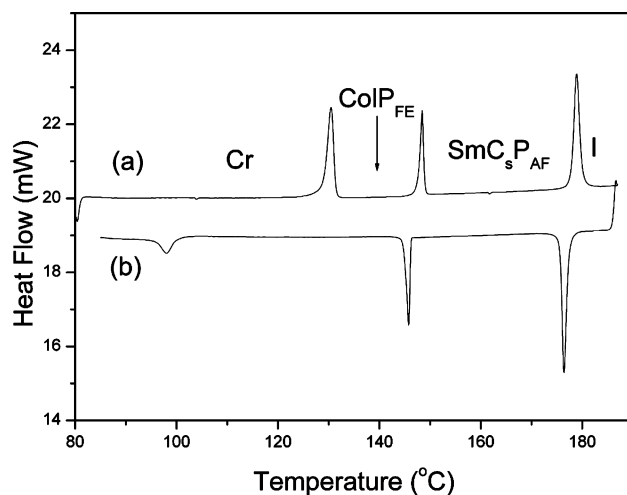


Figure 4. A DSC thermogram obtained for compound 7 showing the transition between lamellar antiferroelectric and columnar ferroelectric phases, (a) Heating cycle (b) Cooling cycle, rate, $5^{\circ}\text{C min}^{-1}$. (See Color Plate IV)

that they are quite sensitive to the orientation of the linking groups, for example as observed in the case of azomethine [21, 22] or ester group [23]. When the ester linkage between the biphenyl moiety and the phenyl group was reversed, it was found that both melting and clearing points increased and only a SmCP phase was observed [13]. In addition, a five-ring system similar to series C did not show any mesophase. A plot of transition temperature as a function of terminal chain length for the homologous series C is shown in Fig. 5. Clearly one can see smooth curve relationship for like transitions and a general reduction in the melting points on ascending the homologous series.

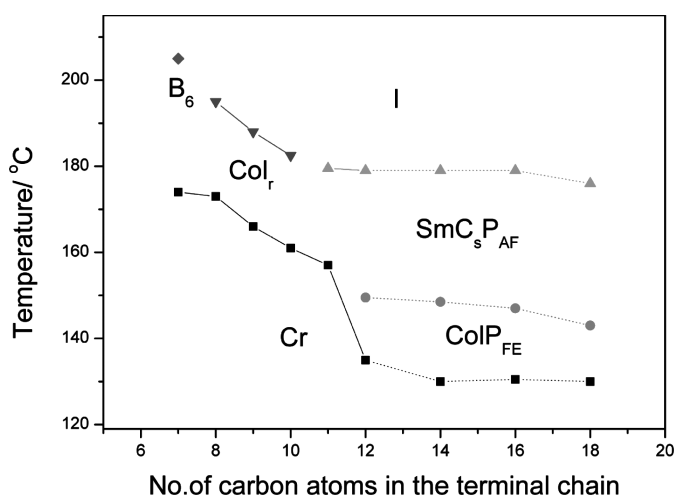


Figure 5. Plot of transition temperature Vs number of carbon atoms in the terminal chain for compounds of series C. (See Color Plate V)

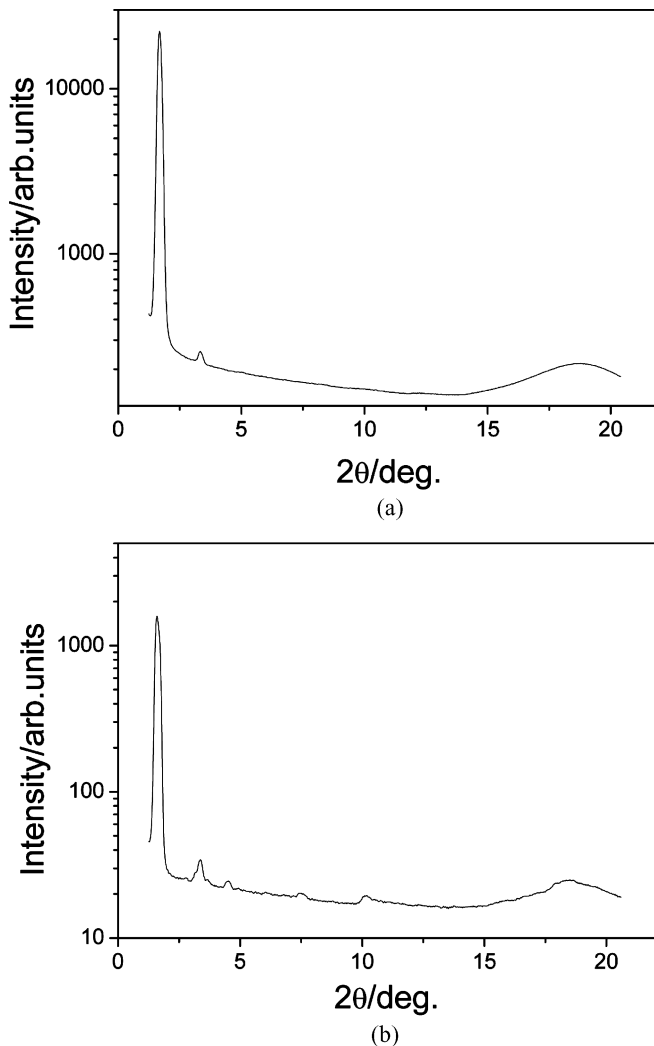


Figure 6. XRD intensity profile obtained for the mesophases of compound 7, (a) Higher temperature $\text{SmC}_s\text{P}_{AF}$ phase at $T = 165^\circ\text{C}$, (b) Lower temperature ColP_{FE} phase at $T = 145^\circ\text{C}$

X-ray Diffraction Studies

In order to understand the mesophase structure, XRD studies were carried out on a few samples. For example, a sample of compound 4 was filled into a Lindemann capillary (dia: 0.7 mm) in the isotropic phase and the ends were sealed. The sample was cooled to the mesophase and on irradiation, gave two reflections in the small angle region with $d_1 = 40.1 \text{ \AA}$ and $d_2 = 25.9 \text{ \AA}$. These could be indexed as the (11) and (20) reflections of a rectangular lattice with the lattice parameters $a = 51.8 \text{ \AA}$, $b = 63 \text{ \AA}$. In addition, a broad peak in the wide angle region at 4.7 \AA was seen which indicates the fluidity of the phase. On the basis of these, we have assigned the symbol Col_r to this phase.

A partially oriented pattern could be obtained for the higher temperature phase of compound 7 and the XRD intensity profile is shown in Fig. 6(a). This showed two reflections

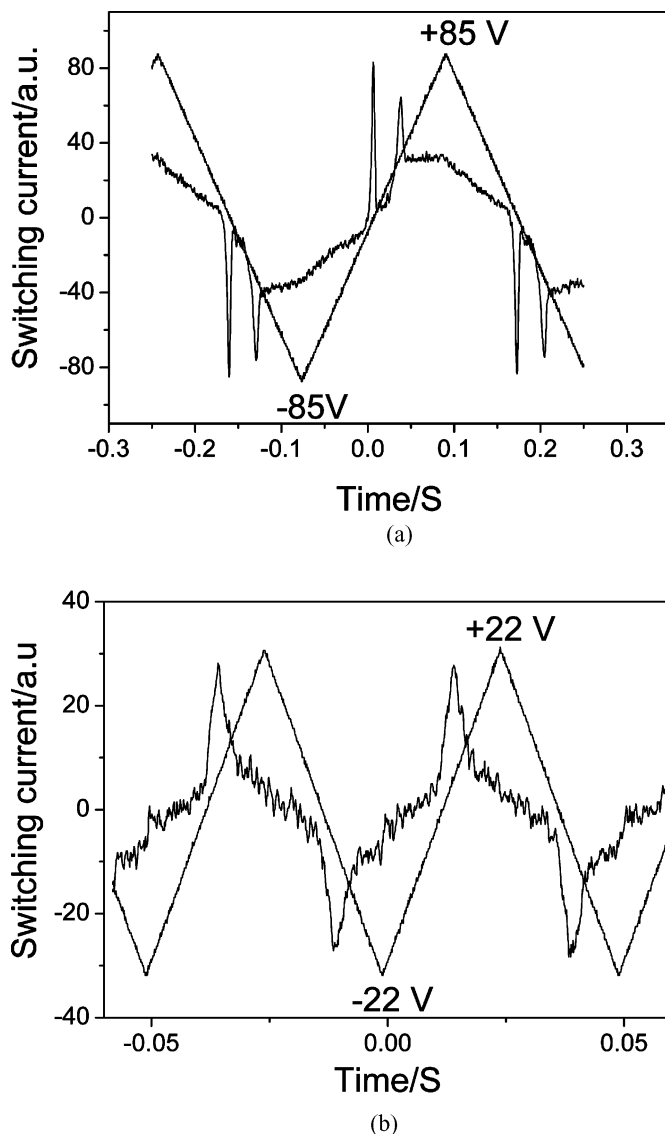


Figure 7. Switching current response traces obtained for the mesophase of compound **7** (a) on applying a triangular-wave electric field, $T=170^{\circ}\text{C}$; 4 Hz; $170V_{pp}$; $P_s=492\text{ nC cm}^{-2}$ (b) $T=139^{\circ}\text{C}$; 25 Hz; $44V_{pp}$; $P_s=48\text{ nC cm}^{-2}$

in the small angle region. These correspond to d -spacing of $d_1=53.0\text{ \AA}$ and $d_2=26.5\text{ \AA}$ which are in the ratio 1:1/2 indicating a lamellar ordering and a tilt angle of 43° was estimated. When the sample was cooled to the lower temperature phase, a few additional reflections corresponding to $d_1=55.4\text{ \AA}$, $d_2=27.2\text{ \AA}$, $d_3=19.6\text{ \AA}$, $d_4=11.89\text{ \AA}$ and $d_5=8.7\text{ \AA}$ were obtained and the X-ray intensity profile is shown in Fig. 6(b). However, in the absence of a completely oriented pattern, we have not been able to index these reflections to any particular lattice. Electro-optical studies and textural observations suggest a columnar structure for this mesophase. Further experiments are necessary to unambiguously arrive at the structure of this mesophase.

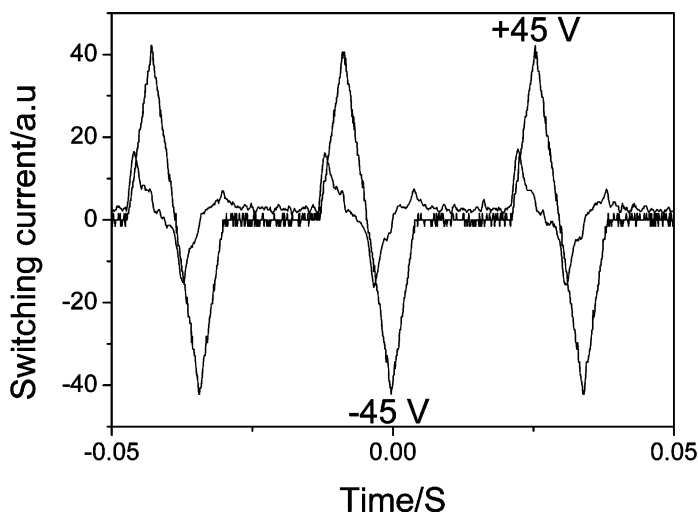


Figure 8. Switching current response trace obtained for the mesophase of compound **7** on applying a modified triangular-wave electric field at $T = 139^\circ\text{C}$; 25 Hz; 90V_{pp}

Electro-Optical Studies

Compounds **6**, **7**, **8** and **9** exhibit two phases. In order to confirm the polar nature of these phases, electro-optical studies were carried out using ITO-coated cells treated with polyimide for planar alignment of the mesophase. The switching current measurements were carried out using triangular-wave and modified triangular-wave methods. For example, a sample of compound **7** was filled into a cell (thickness; $8\mu\text{m}$) in the isotropic phase through capillary action. Then, the sample was cooled to the mesophase under an electric field and at a voltage of $8.7\text{V}\mu\text{m}^{-1}$, two current peaks per half cycle were observed. This indicates that the mesophase is antiferroelectric in nature. On further cooling under the same conditions, the amplitude of the two peaks decreased gradually and a single peak appeared accompanied by a corresponding textural change indicating the transition. On applying a field of 44V_{pp} and a frequency of 25 Hz, a single peak was clearly seen and this confirmed the polar nature of the phase that shows ferroelectric characteristics. The current response traces obtained for these mesophases are shown in Fig. 7(a) and (b) respectively.

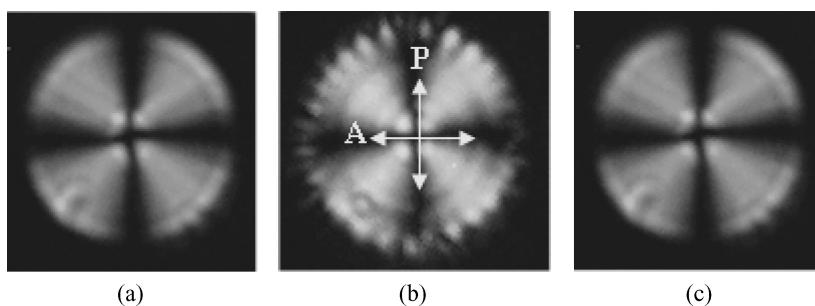


Figure 9. Circular domains obtained for the $\text{SmC}_s\text{P}_{AF}$ phase of compound **7** under a d.c. field. (a) $+7\text{V}\mu\text{m}^{-1}$ (b) 0V , (c) $-7\text{V}\mu\text{m}^{-1}$. (See Color Plate VI)

In addition, modified triangular-wave experiment supports the ferroelectric nature of the columnar phase of compound **7**. The current response trace obtained for the columnar phase is shown in Fig. 8. To study the clinicity of the molecules in the higher temperature SmCP phase, we carried out d.c. field experiments. A sample of compound **7** was cooled slowly from the isotropic phase under a d.c. field of $7 \text{ V } \mu\text{m}^{-1}$. The mesophase appeared in the form of smooth circular domains in which extinction brushes were oriented parallel to the position of the crossed polarizers. On reversing the sign of the applied field, there was no change in the orientation of the dark brushes. However, when the field was switched off, a change of colour accompanied by stripes on the smooth circular domains were observed. This indicates that the molecular organization in the ground state is synclitic and the phase exhibits antiferroelectric characteristics. Hence the mesophase is racemic and assigned the symbol $\text{SmC}_s\text{P}_{AF}$. The optical photomicrographs of the circular domains obtained under a d.c. field are shown in Fig. 9.

Conclusions

A new series of seven-ring achiral BC compounds derived from 5-methoxyisophthalic acid has been synthesized and the mesomorphic properties of these investigated. Four different types of mesophases were observed. While compound **1** shows an intercalated smectic (B_6) phase, compounds **2**, **3** and **4** exhibit a columnar (Col_r) phase with a rectangular lattice and both these phases do not switch electro-optically. Compound **5** shows a lamellar phase with antiferroelectric characteristics. Very interestingly, compounds **6**, **7**, **8** and **9** show two phases and both of them respond to an applied electric field. These mesophases have been characterized as ColP_{FE} and $\text{SmC}_s\text{P}_{AF}$ phases and transition between such phases are not common.

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