Chapter 4

Synthesis and mesomorphic properties of

(i)   5-Methoxy bis(4-(4′-*n*-alkylbiphenylcarbonyloxy)-phenylisophthalates), (compounds 4.A.1 to 4.A.10)

4.1: Introduction

Almost 15 years are over since the first observation [1] of an electro-optical switching in the mesophase of an achiral bent-core (BC) compound by Niori *et al.* 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 core or wings of the BC compound is one of the ways of modifying the mesomorphic properties and such studies have been carried out quite extensively [6-11]. Infact, it has been shown that polar substituents in either the bay or apex position can induce drastic changes in the type of mesophase observed [12, 13]. 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. In 1998, Weissflog *et al.* [14] investigated a number of five-ring BC compounds, especially, the influence of the substituents situated at different positions of the core. Particularly, substituents such as methyl, methoxy and cyano at 5-position prevents the formation of mesophase in a five-ring system. However, synthesis of the first five-ring BC compounds containing substitution at apex position have been again reported by Weissflog *et al.* [9] with liquid crystalline properties. These compounds are derived from 5-fluororesorcinol. Mesophase characterization and detailed physical studies of these compounds have been reported by Nadasi *et al.* [15] later in 2002. Interestingly, BC compounds derived from 5-fluororesorcinol containing lateral fluorine substitutent on the outer phenyl rings *ortho* to the terminal chains exhibited variants of B_5 phase in addition to B_2 phase whereas the parent compound exhibited only B_2 phase. All these compounds are connected through azomethine linking group which show rich mesomorphism but the disadvantage of this group is that it is sensitive to air and moisture that leads to decomposition. Subsequently, Mieczkowski *et al.* [16] reported BC compounds derived from resorcinol which contain methyl substituent at 5-position on the central unit and also studied the effect of lateral substituents without imino linking group. Most of the

investigated five-ring BC compounds containing a substituent at 5-position are derivatives of resorcinol.

In 2005, we investigated five-ring BC compounds derived from 5-methoxyisophthalic acid [17] having stable ester linkage. These showed quite interesting mesomorphic properties including transition between electro-optically switchable phases. However, the thermal range of the mesophases was narrow and one of the mesophase was metastable. In an effort to stabilize the mesophase/s and also enhance the thermal range of these, a seven-ring BC compound was also synthesized. The mesophase exhibited by these five-ring as well as seven-ring BC compounds is the electro-optically switchable B_2 phase.

It is appropriate to mention here that several five-ring bent-core compounds derived from isophthalic acid and exhibiting interesting mesophases have been reported by Nguyen *et al.* [18]. They are derivatives of 2-methyl-, 4-bromo-, 4-fluoro- and 4-methylisophthalic acids. The effect of lateral substituent and orientation of ester linkage have also been investigated in detail to understand structure-property relationships.

However, the synthesis of the first seven-ring BC compounds comprising *m*-terphenyl central unit was reported by Shen *et al.* [19] in 1999. These compounds exhibit a columnar phase with a rectangular lattice and intercalated fluid smectic phases and surprisingly none of these compounds exhibited a switchable mesophase. Noticeably, there was no report on seven-ring BC compounds containing a substituent at 5-position until 2004. The first seven-ring bent-core compounds derived from 5-cyanoresorcinol and their mesomorphic properties were reported by Reddy *et al.* [13]. Subsequently, Umadevi *et al.* [20] reported seven-ring BC compounds derived from 5-chlororesorcinol. Interestingly, B_{2x} phase observed in the higher homologues of these two series of compounds exhibits helical and filamentary textures typical of B_7 phase when observed under a polarizing microscope. It has been suggested that, this B_{2x} phase be classified as a variant of B_7 phase and assigned the symbol B_7' [3]. Incidentally, there are only a few reports on seven-ring BC compounds containing a substituent at 5-position of the central unit.

In this chapter, the synthesis and mesomorphic properties exhibited by ten compounds of a series of seven-ring BC compounds derived from 5-methoxyisophthalic acid are described. Mainly, the effect of the orientation of a ester linkage on the mesomorphic properties is

examined. The symmetrical compounds investigated here have the general structure **4** shown below.
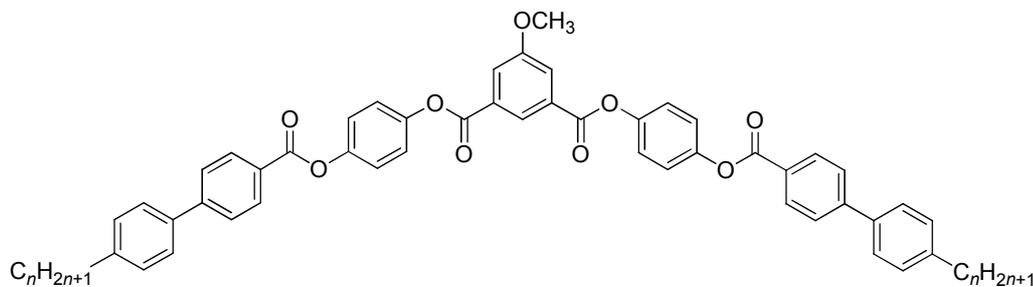
Structure 4

$n = 6, 7, 8, 9, 10, 11, 12, 14, 16, 18$ Series   **4.A**

4.2: Synthesis

The symmetrical seven-ring bent-core compounds belonging to series **4.A** were prepared following the synthetic pathway shown in scheme **4.1**. 5-Methoxyisophthalic acid, **4.a** was prepared according to the procedure already described [17]. 4-Benzyloxyphenol, **4.b** was obtained commercially from Fluka and used without further purification. 4-*n*-Alkylbiphenyl-4-carboxylic acids, **4.e** were prepared as described previously [21]. 5-Methoxyisophthalic acid, **4.a**, was condensed with 4-benzyloxyphenol, **4.b** in the presence of *N,N´*-dicyclohexylcarbodiimide (DCC) and a catalytic amount of 4-(*N,N*-dimethylamino)pyridine (DMAP) to obtain compound **4.c**. The resultant dibenzyloxy ester was subjected to hydrogenolysis in the presence of 5% Pd-C in 1,4-dioxane. The bisphenol, **4.d**, thus obtained was purified and esterified with an appropriate 4-*n*-alkylbiphenyl-4-carboxylic acid, **4.e** to obtain the desired compound belonging to series **4.A.**
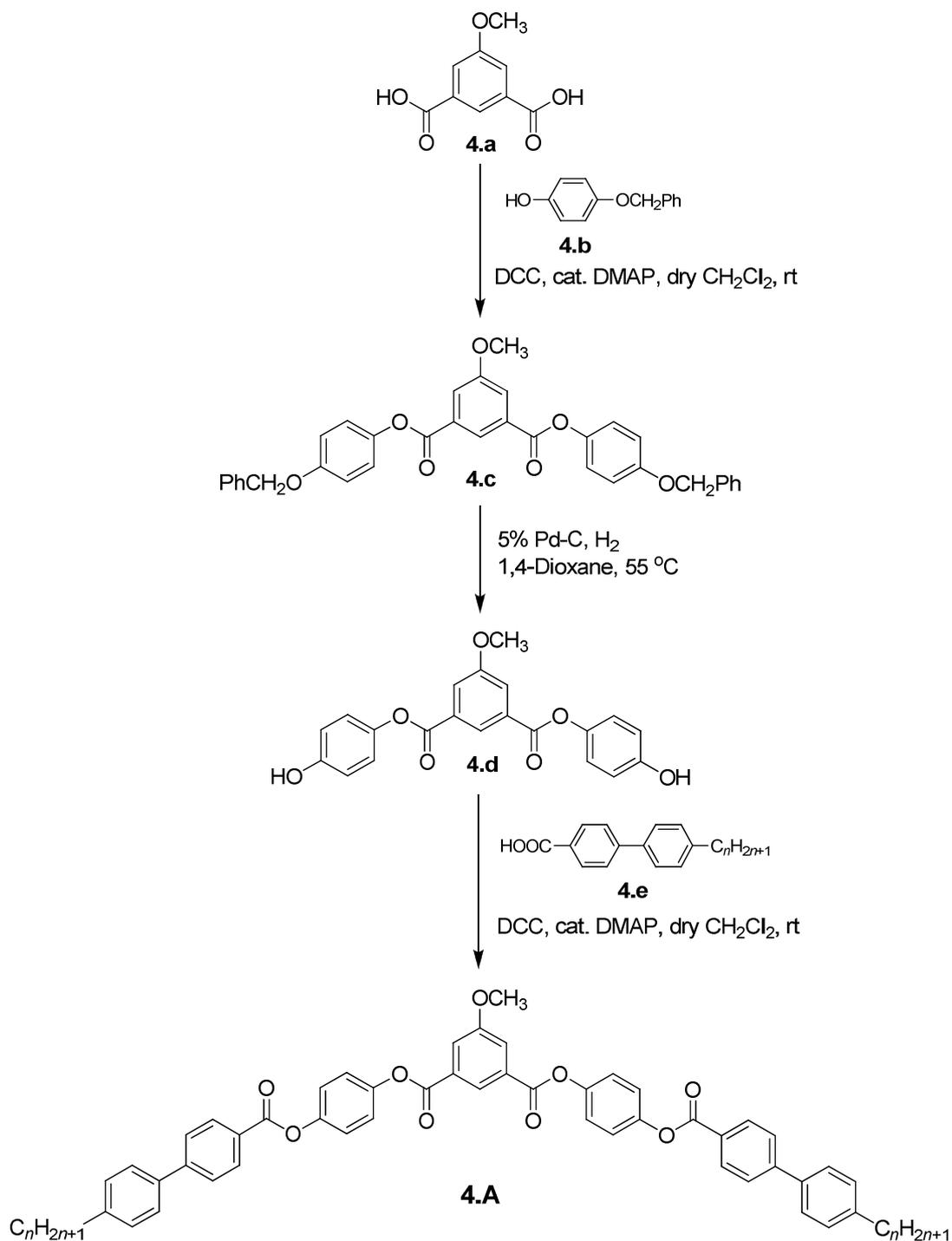
Scheme 4.1: Synthetic pathway followed for preparation of BC compounds 4.A.

4.3: Results and discussion

4.3.1: Mesomorphic properties

The transition temperatures and the associated enthalpy values obtained for the ten seven-ring bent-core compounds having general structure **4** are summarized in table **4.1.** As can be seen in table, all compounds are enantiotropic mesomorphic in nature. Compounds **4.A.1** and **4.A.2** show only one mesophase and compound **4.A.1** has a wide thermal range of 40 °C. When a sample of compound **4.A.1** sandwiched between two glass plates, is cooled slowly from the isotropic phase, batonnets appear which coalesce to form a fan-shaped texture with fairly high birefringence. A photomicrograph of the texture as obtained is shown in figure **4.1.a.** Either on shearing or viewing the sample in cells treated for homeotropic alignment, dark or homeotropic texture could not be obtained. Thus, the possibility of this being a smectic A phase is ruled out and its characteristic behaviour indicates that the mesophase is indeed B_6. Similar behaviour was observed in our [8, 22] earlier investigations on the B_6 phase. The optical textures obtained for the same phase on cooling the sample of compound **4.A.2** are also shown in figures **4.1.b** and **4.1.c.** XRD measurements also indicate that the mesophase is an intercalated smectic phase. Hence, we have assigned the symbol B_6 for this phase.

The middle homologues **4.A.3**, **4.A.4** and **4.A.5** are also monomesomorphic. The DSC thermogram obtained for compound **4.A.5** is depicted in figure **4.4.a.** When a thin film of compound **4.A.5** in its isotropic state is cooled slowly and viewed under a polarizing microscope, mosaic textures are obtained and the same are shown in figure **4.2.** This type of mosaic 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 (described later), the phase has been characterized as such. The thermal range of this mesophase is about 22 °C.

Compound **4.A.6** exhibits only one phase with a temperature range of 23.5 °C. XRD studies show that this is a lamellar phase and electric field experiments indicate an antiferroelectric behaviour with a synclinic tilt and hence this phase can be assigned the symbol SmC_sP_A. Remarkably, higher homologues **4.A.7** to **4.A.10** are dimesomorphic with well defined transitions which are first order. The thermal range of both the phases is sufficiently large. A majority of the BC compounds exhibit only one mesophase, particularly the electro-optically

**Table 4.1: Transition temperatures (°C) and the associated enthalpies (kJ mol^{-1}) for compounds 4.A[a].**

4.A
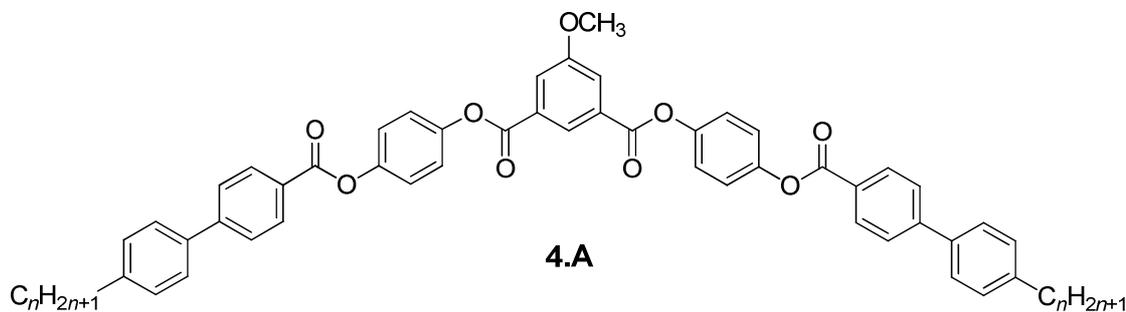
Compound	n	Cr		$Col_{ob}P_F$		SmC_sP_A		Col_r		B_6		I
4.A.1	6	•	172.5 *28.3*	-		-		-		•	212.0 *18.7*	•
4.A.2	7	•	174.0 *28.5*	-		-		-		•	205.0 *18.5*	•
4.A.3	8	•	173.0 *28.0*	-		-		•	195.0 *22.0*	-		•
4.A.4	9	•	166.0 *21.0*	-		-		•	188.0 *22.0*	-		•
4.A.5	10	•	161.0 *23.5*	-		-		•	182.5 *23.5*	-		•
4.A.6	11	•	156.0 *28.0*	-		•	179.5 *22.5*	-		-		•
4.A.7	12	•	135.0 *31.5*	•	149.0 *11.0*	•	179.0 *22.0*	-		-		•
4.A.8	14	•	130.0 *21.0*	•	148.5 *9.0*	•	179.0 *21.0*	-		-		•
4.A.9	16	•	130.5 *25.0*	•	147.0 *10.0*	•	179.0 *22.0*	-		-		•
4.A.10	18	•	130.0 *30.0*	•	143.0 *9.0*	•	179.0 *18.0*	-		-		•

[a]Abbreviations: Cr: crystalline phase; B_6: intercalated smectic phase; Col_r: columnar phase with a rectangular lattice; SmC_sP_A: polar smectic C phase with synclinic tilt in adjacent layers and antiferroelectric characteristics; $Col_{ob}P_F$: polar columnar oblique phase with ferroelectric switching characteristics; I: isotropic phase; •: phase exists; - : phase does not exist.
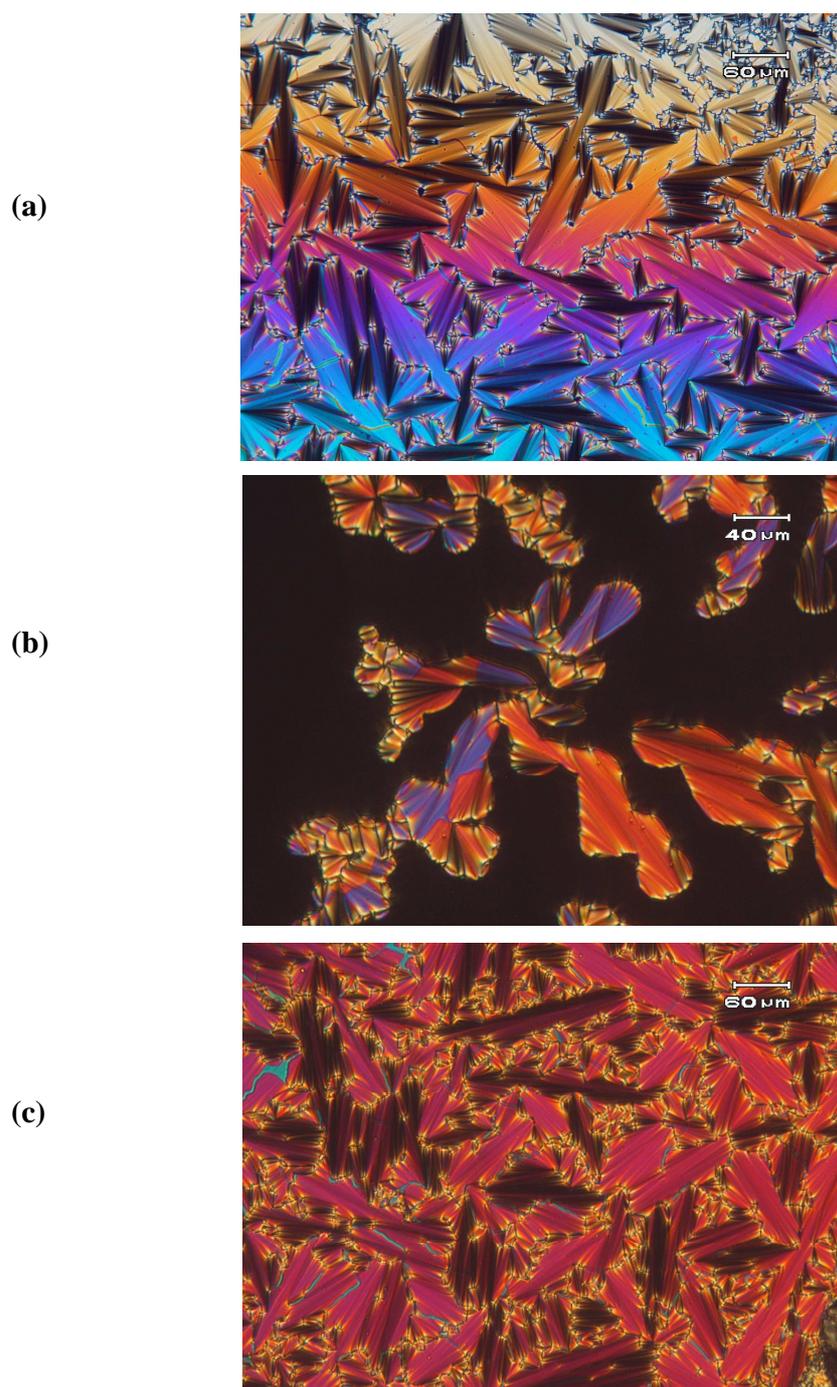
Figure 4.1: Photomicrographs obtained for B$_6$ mesophase: (a) Highly birefringent fan-shaped texture for compound 4.A.1, T = 210 °C (b) Developing from isotropic phase for compound 4.A.2, T = 202.8 °C and (c) Completely formed phase, T = 195.6 °C.

(a)

(b)
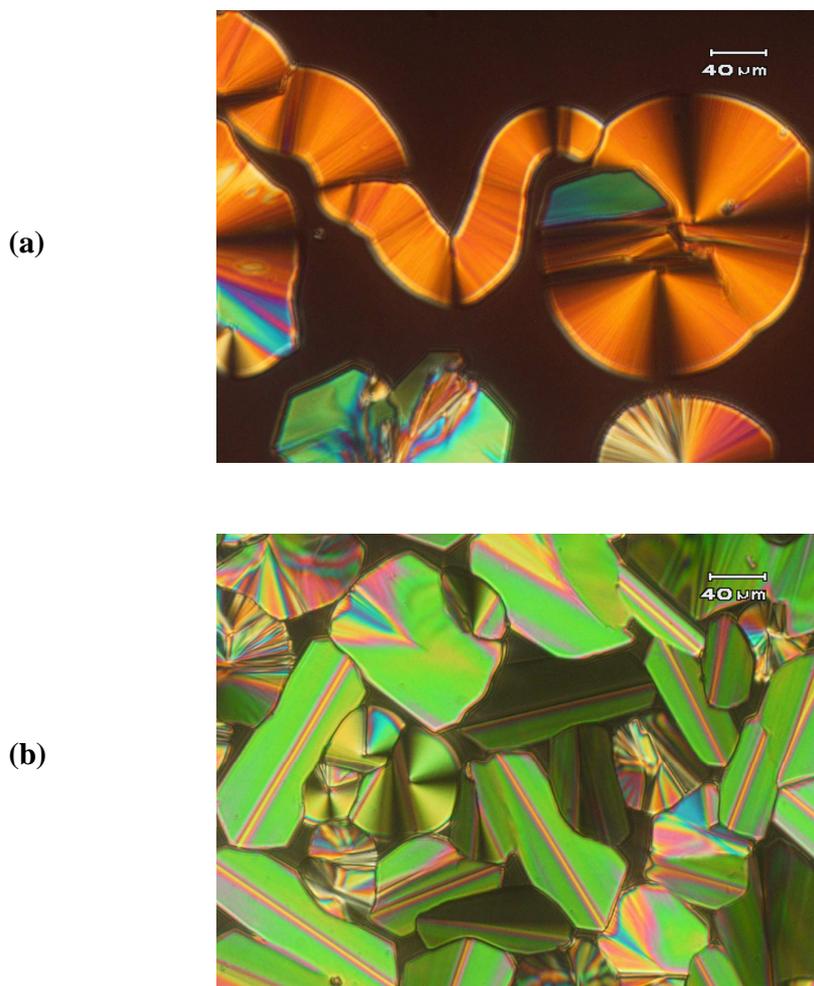
Figure 4.2: Photomicrographs of the texture obtained for the Col$_r$ mesophase of compound 4.A.5. (a) Developing from isotropic phase, T = 180.2 °C (b) completely formed mosaic texture, T = 173.5 °C.

switchable phase. Very interestingly these seven-ring compounds derived from 5-methoxyisophthalic acid are somewhat different. The mesophase of compound **4.A.6** and the higher temperature phase of compounds **4.A.7** to **4.A.10** are similar. When a sample of compound **4.A.8** is cooled from the isotropic phase in a cell treated for homogeneous alignment, a fan-shaped texture develops and the photomicrographs obtained for this phase are depicted in
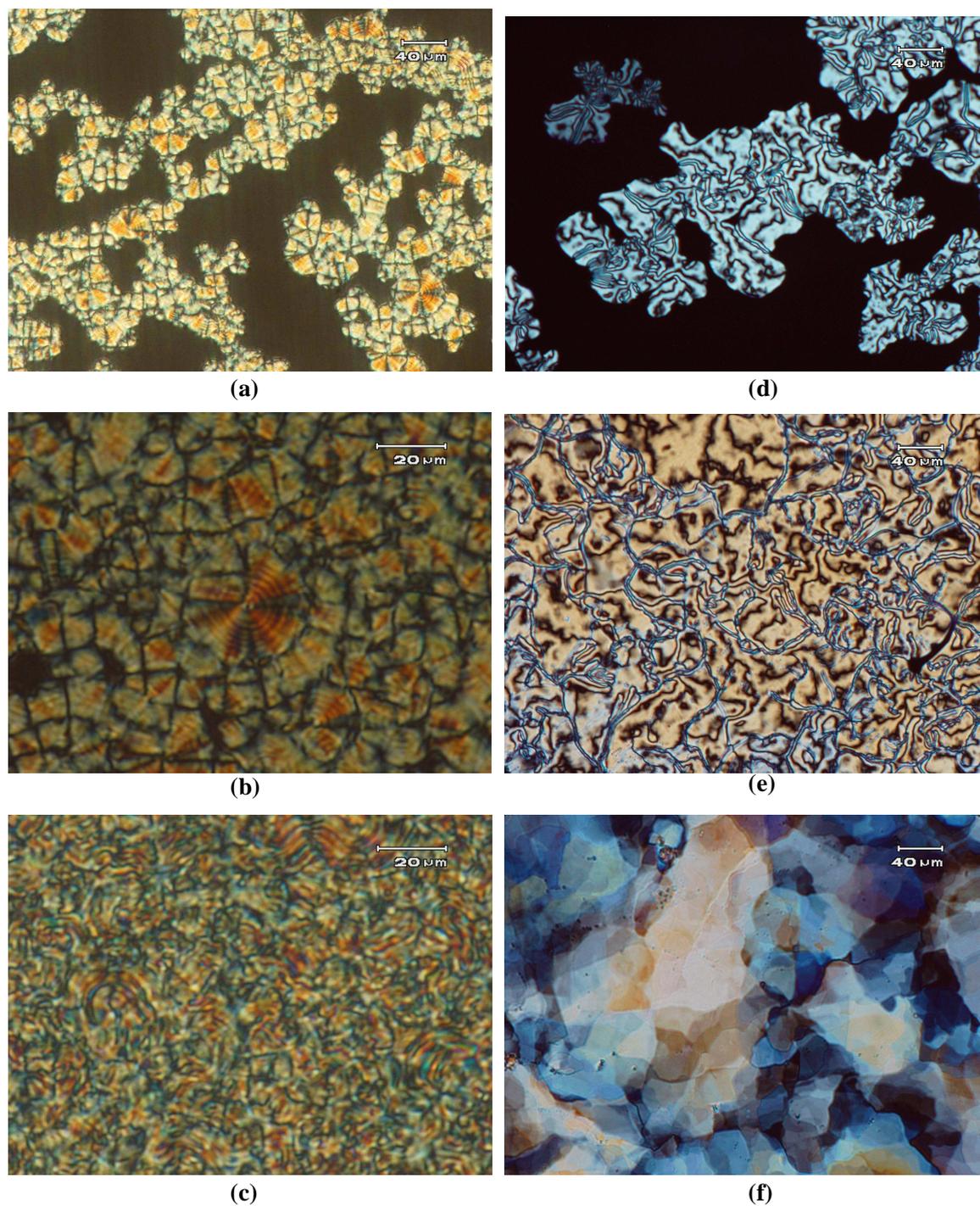
Figure 4.3: Optical textures obtained for SmC_sP_A phase of compound 4.A.8 in a cell treated for homogeneous alignment (a) T = 177.4 °C, (b) T = 176.4 °C and (c) $Col_{ob}P_F$ phase, T = 142.6 °C. Schlieren textures observed for SmC_sP_A phase in a cell treated for homeotropic alignment (d) T = 178.9 °C, (e) T = 178 °C, and (f) 2D-columnar phase, T = 140 °C.
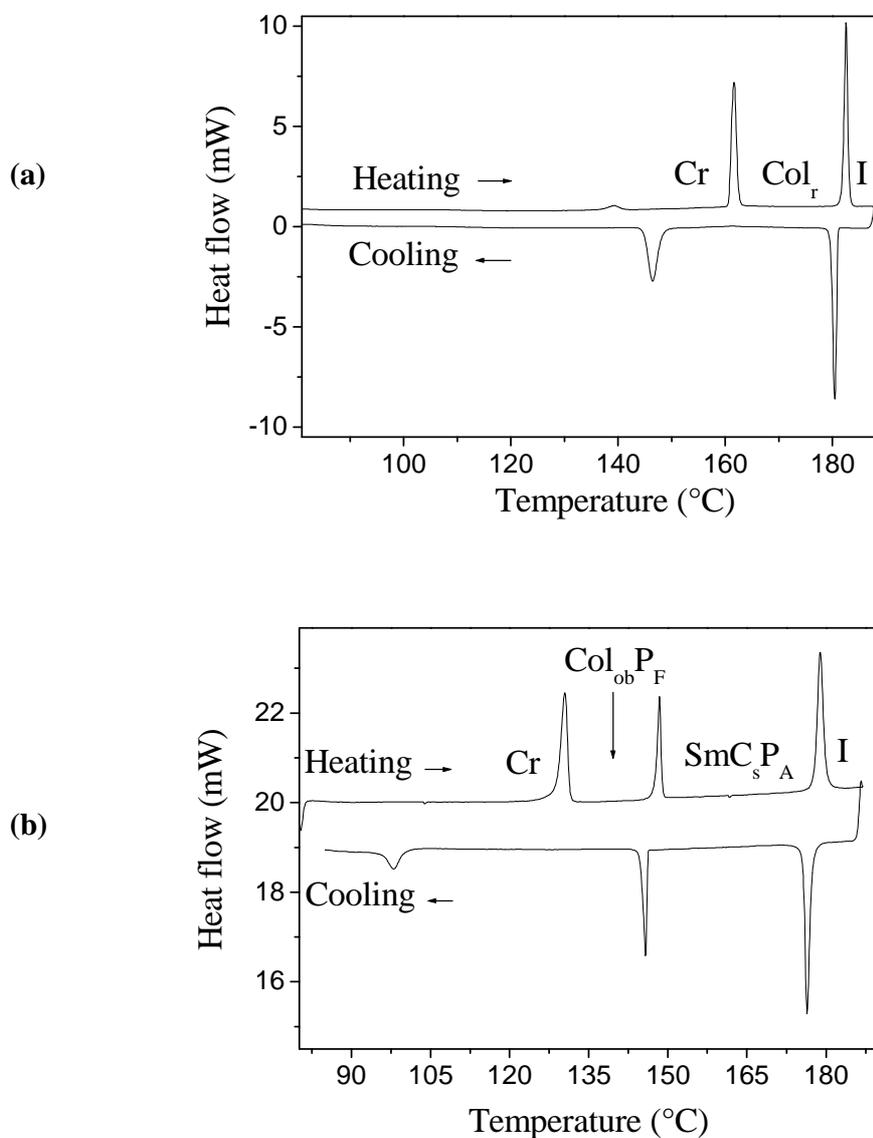
Figure 4.4: **DSC thermograms obtained for (a) compound 4.A.5 showing Col$_r$ mesophase.**
(b) Compound 4.A.8 showing the transition between lamellar antiferroelectric
and columnar ferroelectric phases, rate, 5 °C min^{-1}.
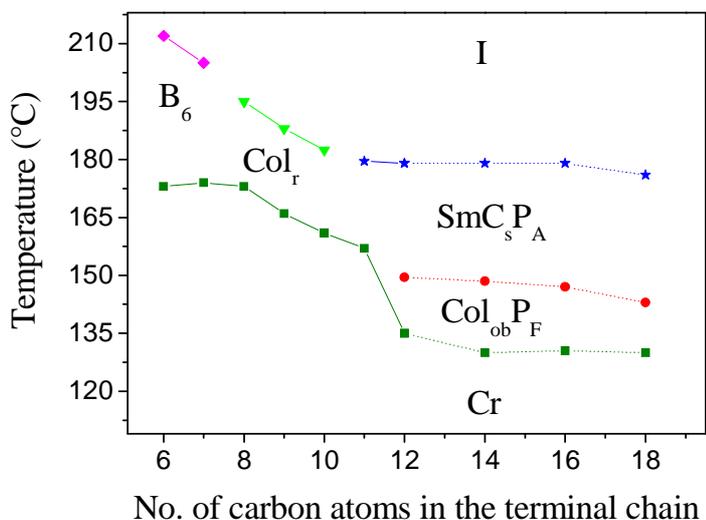
Figure 4.5: Plot of transition temperature *vs* number of carbon atoms in the terminal chain for compounds of series 4.A.

figures **4.3.a** and **4.3.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 figure **4.3.c.**

When the same sample is filled in a cell treated for homeotropic alignment and viewed under a polarizing optical microscope, a schlieren texture develops indicating that the mesophase is a tilted smectic phase and the same is shown in figure **4.3.d.** On further cooling, a transition takes place from a completely formed higher temperature smectic phase to a columnar phase with drastic textural change and typical textures observed are shown in figures **4.3.e** and **4.3.f** respectively. A DSC thermogram obtained for this compound is shown in figure **4.4.b** and one can clearly see the transition between these two phases. Based on XRD studies and electro-optics (described later), the higher temperature phase is designated as SmC_sP_A phase whereas the lower temperature phase is $Col_{ob}P_F$ phase. A plot of transition temperature as a function of terminal chain length for the homologous series **4.A** is shown in figure **4.5.** Clearly one can see smooth curve relationship for like transitions and a general reduction in the melting points on ascending the homologous series.

4.3.2: 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.A.2** 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 one reflection in the small angle region with d-spacing of $d_1 = 24.0$ Å. In addition to that a diffuse reflection at wide angle region was obtained indicating fluidity of the alkyl chain. The d-spacing obtained in the experiment was less than half the measured molecular length (L = 52.4 Å) which indicates that the mesophase is intercalated. Taking into account the optical textures and the XRD data, we have characterized this mesophase to be a B_6 phase.

Similarly, on irradiation of the mesophase of compound **4.A.5**, gave two reflections in the small angle region with $d_1 = 40.1$ Å and $d_2 = 25.9$ Å. These could be indexed as the (11) and (20) reflections of a rectangular lattice with the lattice parameters a = 51.8 Å, b = 63 Å. In addition, a broad peak in the wide angle region at 4.7 Å was seen which indicates the fluidity of
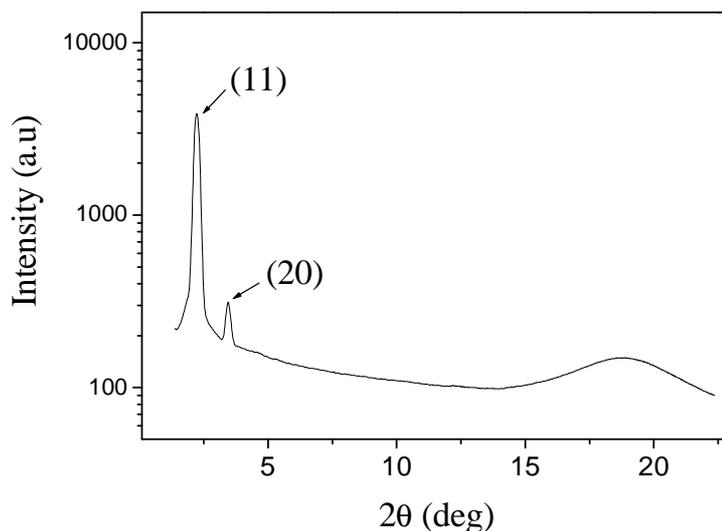
Figure 4.6: XRD intensity profile obtained for the Col$_r$ mesophase of compound 4.A.5, at T = 175 °C.
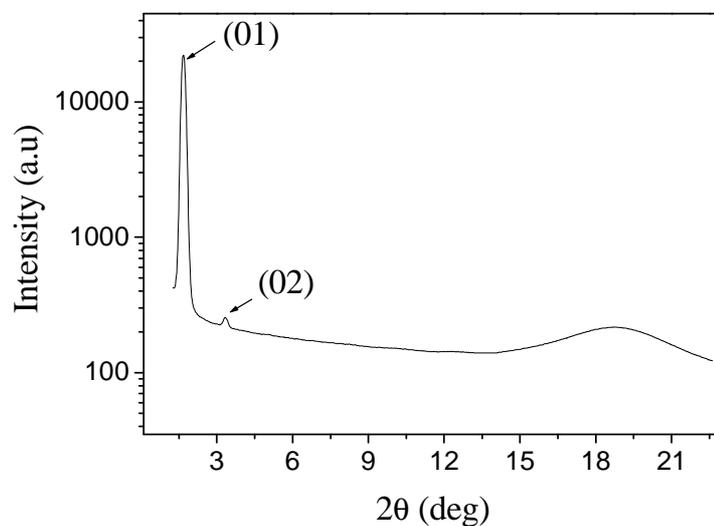
(a)
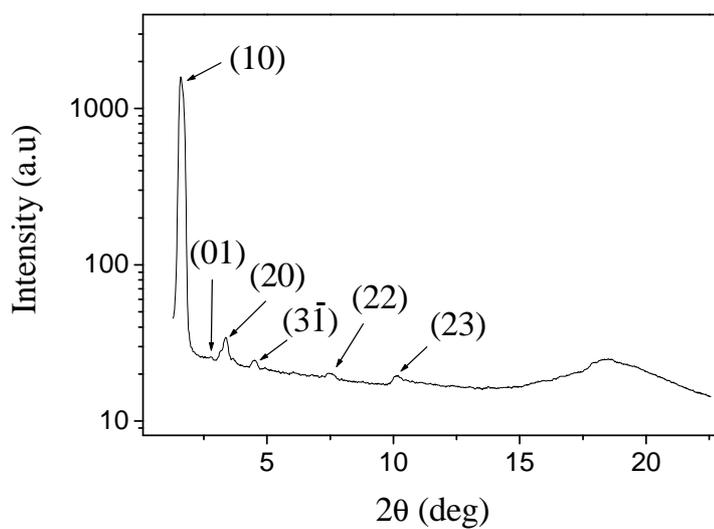
(b)

Figure 4.7: XRD intensity profile obtained for the mesophases of compound 4.A.8,

         (a) Higher temperature SmC_sP_A phase at T = 165 °C and

         (b) Lower temperature $Col_{ob}P_F$ phase at T = 145 °C.

Table 4.2: The d-spacings obtained for compounds of series 4.A by XRD measurements

| Compound	d-spacings/Å(Miller indices)	Lattice parameters/Å		Phase type	T/°C
		a	b		
4.A.2	24(01)	-	-	B_6	180
4.A.3	32.6(11), 24.78(20), 15.4(31)	49.4	43.4	Col_r	185
4.A.4	33.9(11), 24.78(20), 15.5(31)	49.5	46.5	Col_r	175
4.A.5	40.10(11), 25.9(20)	51.8	63.0	Col_r	175
4.A.7	50.42(01), 25.3(02)	-	-	SmC_sP_A	165
	52.83(10), 31.2(01), 26.7(20), 23.8(11), 13.5(31), 10.79(1 $\bar{3}$), 8.8(23), β=108.24	55.6	32.9	$Col_{ob}P_F$	145
4.A.8	53.0(01), 26.5(20)	-	-	SmC_sP_A	165
	55.4(10), 31.74(01), 27.2(20), 19.6(3 $\bar{1}$), 11.89(22), 8.7(23), β=112.76	60.0	34.3	$Col_{ob}P_F$	145

the phase. On the basis of XRD measurements, we have assigned the symbol Col_r to this phase. The XRD intensity profile obtained for this compound is shown in figure **4.6.** Similar XRD studies were carried out for other compounds **4.A.3** and **4.A.4** as well and the d-spacings obtained are summarized in table **4.2.**

XRD powder pattern measurements for the higher temperature mesophase of compound **4.A.8** were carried out and the intensity profile obtained is shown in figure **4.7.a.** This showed two reflections in the small angle region. These correspond to d-spacing of $d_1 = 53.0$ Å and $d_2 = 26.5$ Å which are in the ratio 1 : ½ 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 $d_1 = 55.4$ Å, $d_2 = 31.74$ Å, $d_3 = 27.2$ Å, $d_4 = 19.6$ Å, $d_5 = 11.89$ Å and

$d_6 = 8.7$ Å were obtained and the XRD intensity profile obtained for this columnar phase is shown in figure **4.7.b.** An additional diffuse reflection at wide-angle region in both the mesophases confirmed the fluidity of the mesophases. The reflections in the small angle region could not be indexed to an orthogonal rectangular lattice. However, a partially oriented pattern could be obtained in the lower temperature phase which indicated the presence of an oblique lattice. The observed and calculated Miller indices for these compounds are given in table **4.2.** The lattice parameter values a and b obtained as well as the oblique angle β determined are also summarized in table **4.2.** The XRD measurements were carried out for compound **4.A.7** as well. Similarly, the higher temperature mesophase shows a layer ordering and the lower temperature phase can be indexed to an oblique lattice. The XRD data obtained for the mesophases of compound **4.A.7** at higher temperature as well as lower temperature are given in table **4.2.**

4.3.3: Electro-optical studies

Compounds **4.A.7, 4.A.8, 4.A.9** and **4.A.10** exhibit two mesophases. 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 mesophases. The switching current measurements were carried out using the triangular-wave and the modified triangular-wave methods. For example, a sample of compound **4.A.8** was filled into a cell (thickness; 8 µm) in the isotropic phase through capillary action. Then, the sample was cooled to the mesophase under an ac electric field and at a voltage of 8.7 V µm^{-1} and frequency of 4 Hz, two current peaks per half cycle were observed. The current response trace obtained is given in figure **4.8.a.** This indicates that the mesophase is antiferroelectric in nature. The optical textures observed with and without the field are given in figures **4.8.b** and **4.8.c** respectively. 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 a transition. On applying a field of 44 V$_{pp}$ 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 trace and the corresponding optical textures obtained for this mesophase are shown in figures **4.9.a, 4.9.b** and **4.9.c** respectively.
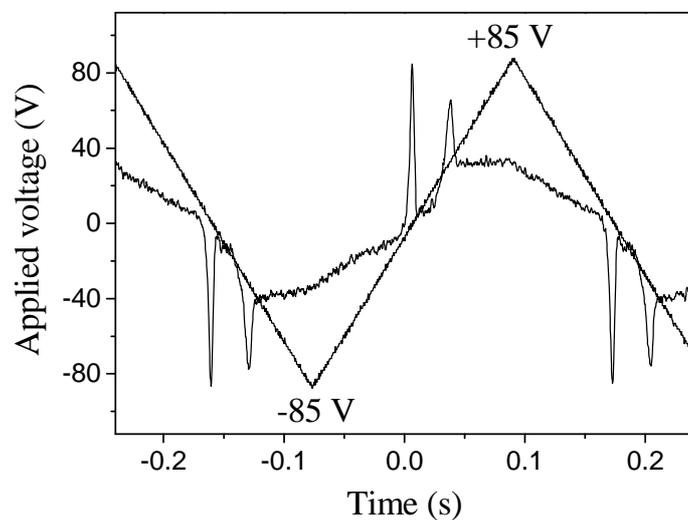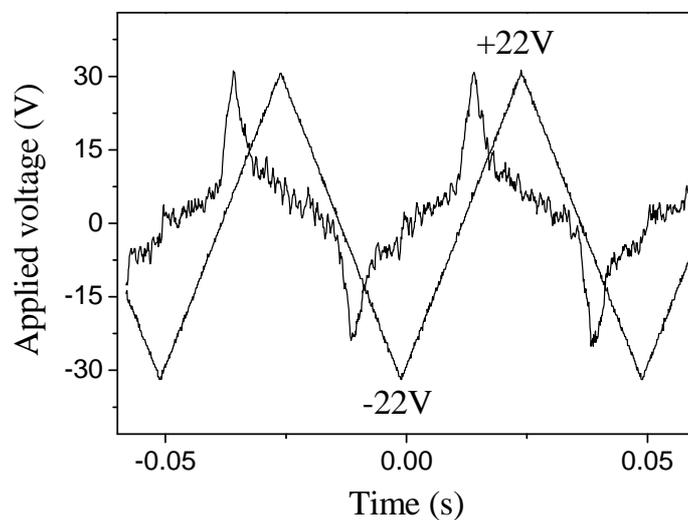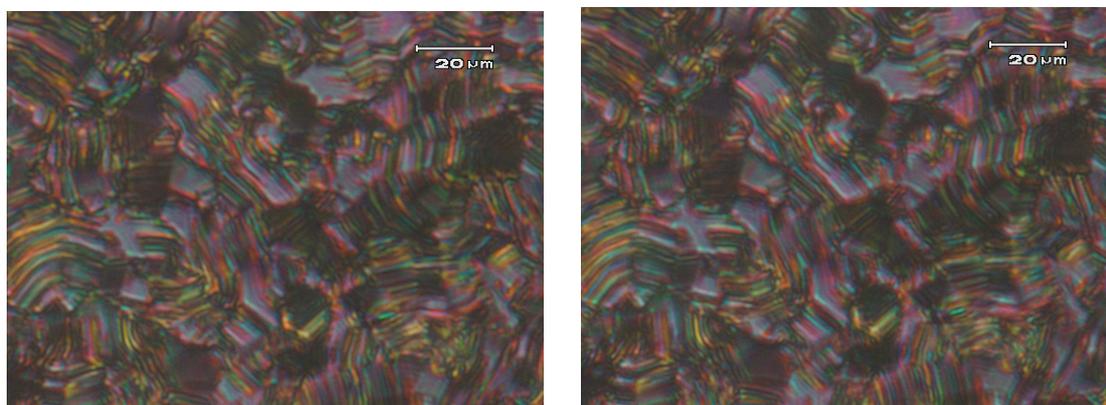
(a)
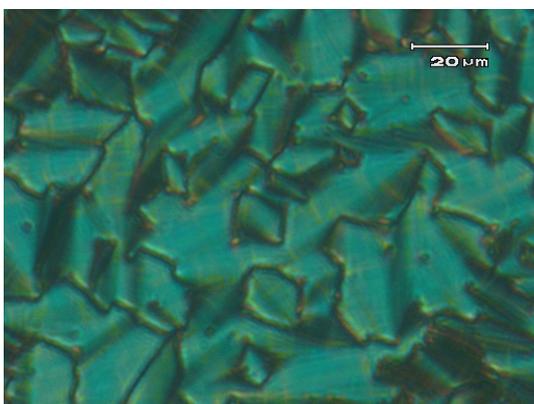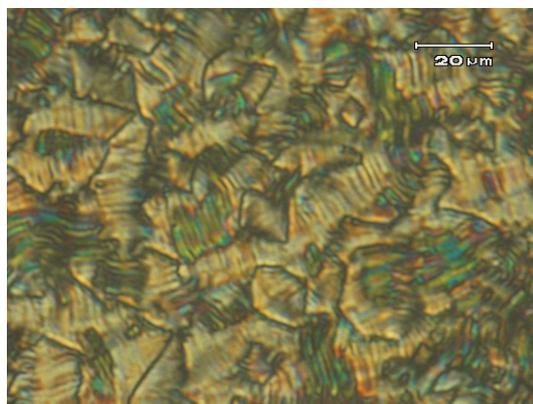
(b)   **(c)**

Figure 4.8: (a) Switching current response trace obtained in the higher temperature
SmC$_s$P$_A$ phase of compound 4.A.8 on applying a triangular-wave electric field,
at T = 170 °C; 4 Hz; 170 V$_{pp}$; P$_S \approx$ 492 nC cm^{-2}. Photomicrographs obtained in
**the SmC$_s$P$_A$ phase (b) with the electric field (c) without the electric field.**

(a)

(b)   **(c)**

Figure 4.9: Switching current response trace obtained in the lower temperature $Col_{ob}P_F$
          phase of compound 4.A.8 on applying a triangular-wave electric field,
          (a) T = 139 °C; 25 Hz; 44 V_{pp}; $P_S \approx 48$ nC cm^{-2}.   Optical textures obtained for
          the $Col_{ob}P_F$ phase (b) with the electric field (c) without the electric field.
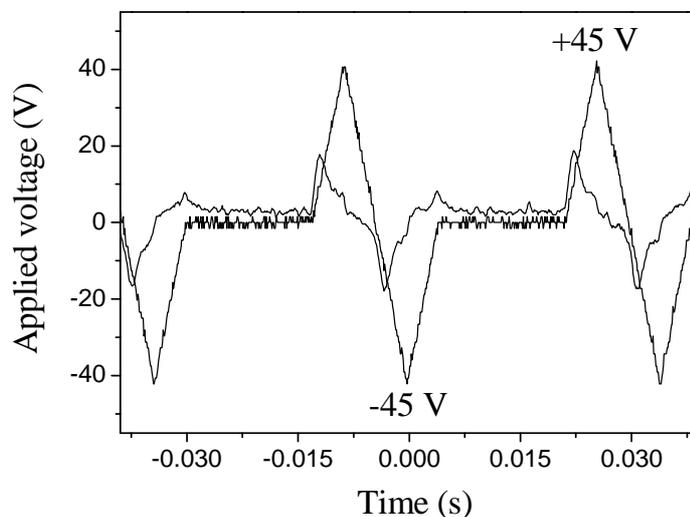
Figure 4.10: Switching current response trace obtained for the mesophase of compound 4.A.8 on applying a modified triangular-wave electric field in the $Col_{ob}P_F$ phase at T = 139 °C; 25 Hz; 90 V_{pp}.

In addition, modified triangular-wave experiment was carried out using the same cell to confirm the ferroelectric nature of the columnar phase. A sample of compound **4.A.8** was cooled to columnar phase, at T = 139 °C. On applying a voltage of 90 V_{pp} and a frequency of 25 Hz shows only one peak per half cycle of the applied field which confirms ferroelectric ground state of the mesophase. The current response trace obtained for the columnar phase is shown in figure **4.10.**

To study the clinicity of the molecules in the higher temperature SmCP phase, we carried out dc field experiments. A sample of compound **4.A.8** was cooled slowly from the isotropic phase under a dc field of 7 V μm^{-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. The optical photomicrographs of the

(a)   (b)   (c)

(d)
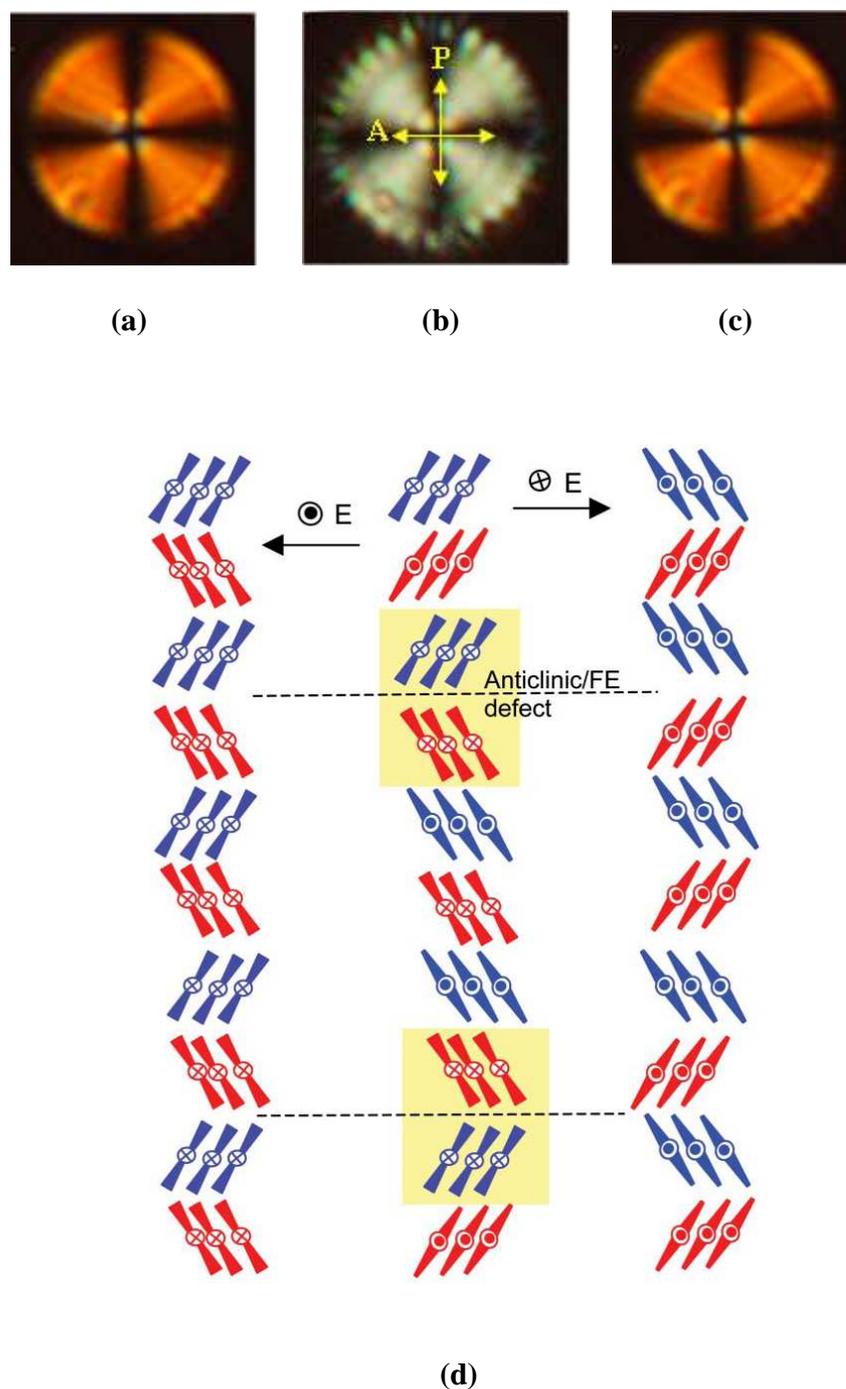
Figure 4.11: Circular domains obtained for the SmC$_s$P$_A$ phase of compound 4.A.8 under a dc field. (a) +7 Vµm^{-1} (b) 0 V and (c) -7 Vµm^{-1}. (d) Models showing the reorganization of the molecules during switching process around a cone (after Amaranatha Reddy and Tschierske [3]).

144

circular domains obtained under a dc field are shown in figure **4.11.** The synclinic structure with an antiferroelectric current response indicates racemic state of the mesophase. A very similar behaviour for the B_2 phase had already been reported by Zennyoji *et al.* [23]. However, Folcia *et al.* [24] pointed out that racemic state of the field induced SmC_sP_A to SmC_aP_A transition contradicts the Curie law as the symmetry of the SmC_aP_F phase (C_{2V}) is not the intersection between the point group of SmC_sP_A (C_{2h}) and the point group of the electric field ($C_{\infty V}$). Therefore, it was suggested that the Curie law could be satisfied if an additional periodicity in the SmC_sP_A structure exists along the layer normal. The equally spaced anticlinic-ferroelectric interlayer boundaries (SmC_aP_F correlation at the domain boundaries: yellow region in the model shown in figure **4.11.d**) meet this requirement. This organization of the molecules changes the symmetry from C_{2h} to C_{2V} and the same is shown as schematic representation in figure **4.11.d.** These anticlinic-ferroelectric interlayer boundaries are observed as stripes at zero voltage which is shown in figure **4.11.b.** However, on application of the field, the clinicity becomes uniform and hence the stripes disappear as shown in figure **4.11.a** and **4.11.c.** Hence the mesophase is racemic and assigned the symbol SmC_sP_A.

Although there are a few reports [25-29] on the occurrence of transition between SmCP and a columnar phase, the observation made in the present series of compounds is rather unusual. However, electric field induced transitions between SmCP and columnar phases have been observed [27-29]. Another interesting aspect of BC compounds is that they are quite sensitive to the orientation of the linking groups, for example as observed in the case of azomethine [30, 31] or ester groups [32].

B
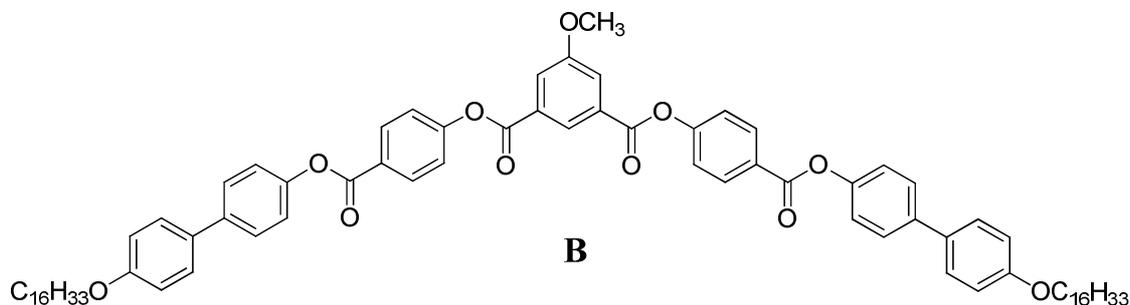
Cr 162.0 SmC_sP_A 214.0 I [17]

A comparison of the mesomorphic properties of series **4.A** with compound **B** clearly revealed that on reversing the polarity of the ester linkage induces the switchable columnar mesophase in addition to SmC_sP_A phase in case of series **4.A**. When the ester linkage between the biphenyl moiety and the phenyl group was reversed (compound **B**), it was found that both melting and clearing points increased and only a SmC_sP_A phase was observed [17]. In addition, interestingly a five-ring system similar to series **4.A** did not show any mesophase.

4.4: 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 lower homologues **4.A.1** and **4.A.2** show an intercalated smectic (B_6) phase, middle homologues **4.A.3, 4.A.4** and **4.A.5** exhibit a columnar phase with a rectangular lattice (Col_r) and both these phases do not switch electro-optically. Compound **4.A.6** shows a lamellar phase with antiferroelectric characteristics. Very interestingly, the higher homologues **4.A.7, 4.A.8, 4.A.9** and **4.A.10** show two mesophases and both of them respond to an applied electric field. These mesophases have been characterized as $Col_{ob}P_F$ and SmC_sP_A phases and the transition between such phases are very rare.

Experimental

5-Methoxyisophthalic acid, 4.a

This was synthesized following a procedure described in the literature [17].

5-Methoxy bis(4-benzyloxy)phenylisophthalate, 4.c

A mixture of 5-methoxyisophthalic acid, **4.a** (2 g, 10.2 mmol), 4-benzyloxyphenol, **4.b** (4 g, 20 mmol) and a catalytic amount of 4-(N,N-dimethylamino)pyridine (DMAP) in dry dichloromethane (30 mL) was stirred for 10 min. To this mixture N,N'-dicyclohexylcarbo-diimide (DCC, 4.5 g, 22 mmol) was added and stirring continued overnight at room temperature. The precipitated 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 eluant. The required material **4.c** thus obtained was further purified by repeated crystallization using ethanol. Yield: 4.85 g (85%); mp 135-136.5 °C; IR (nujol) ν_{max}: 2922, 2852, 1739, 1732, 1595, 1504, 1454, 1377 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.58 (t, J = 1.28 Hz, 1H, Ar-H), 7.94 (d, J = 1.32 Hz, 2H, Ar-H), 7.45-7.34 (m, 10H, Ar-H), 7.15 (d, J = 9.02 Hz, 4H, Ar-H), 7.02 (d, J = 9.04 Hz, 4H, Ar-H), 5.08 (s, 4H, 2 × Ar-O-CH$_2$-), 3.96 (s, 3H, Ar-O-CH$_3$); Elemental analysis: C$_{35}$H$_{28}$O$_7$ requires C 74.99, H 5.03; found C 74.81, H 4.66%.

5-Methoxy bis(4-hydroxy)phenylisophthalate, 4.d

Compound **4.c** (4 g) was dissolved in 1,4-dioxane (60 mL) and 5% Pd-C catalyst (0.8 g) was added to it. The mixture was stirred at 55 °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 (bp 60-80 °C). Yield: 2.34 g (87%); mp 214-215.5 ^{o}C; IR (nujol) ν_{max}: 3280, 2923, 2854, 1747, 1735, 1602, 1510, 1461, 1377 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.58 (t, J = 1.24 Hz, 1H, Ar-H), 7.94 (d, J = 1.3 Hz, 2H, Ar-H), 7.11 (d, J = 8.84 Hz, 4H, Ar-H), 6.88 (d, J = 8.86 Hz, 4H, Ar-H), 4.86 (s, 2H, Ar-OH), 3.95 (s, 3H, Ar-O-CH$_3$); Elemental analysis: C$_{21}$H$_{16}$O$_7$ requires C 66.32, H 4.23; found C 66.63, H 4.17%.

4-*n*-Alkylbiphenyl-4-carboxylic acids, 4.e

These were synthesized following a procedure described in the literature [21].

5-Methoxy bis(4-(4′-*n*-hexylbiphenylcarbonyloxy)phenylisophthalate), 4.A.1

This compound and other homologues of this series were prepared following the procedure described for the preparation of compound **4.c** using compound **4.d** and 4-*n*-hexylbiphenyl-4-carboxylic acid. Yield: (73%); mp 172.5 °C; IR (KBr) ν_{max}: 2956, 2926, 2848, 1739, 1732, 1604, 1504, 1473, 1338 cm^{-1}; ^{1}H NMR (400MHz, CDCl$_3$) δ: 8.64 (t, J = 1.22 Hz, 1H, Ar-H), 8.26 (d, J = 8.36 Hz, 4H, Ar-H), 7.99 (d, J = 1.24 Hz, 2H, Ar-H), 7.73 (d, J = 8.4 Hz, 4H, Ar-H), 7.58 (d, J = 8.1 Hz, 4H, Ar-H), 7.33-7.29 (m, 12H, Ar-H), 3.98 (s, 3H, Ar-O-CH$_3$), 2.66 (t, J = 7.2 Hz, 4H, 2 × Ar-CH$_2$-), 1.67-1.62 (quin, J = 6.72 Hz, 4H, 2 × Ar-CH$_2$-C$\underline{H}_2$), 1.35-1.29 (m, 12H, 2 × -(CH$_2$)$_3$-), 0.89 (t, J = 6.56 Hz, 6H, 2 × -CH$_3$); Elemental analysis: C$_{59}$H$_{56}$O$_9$ requires C 77.95, H 6.21; found C 77.98, H 6.38%.

5-Methoxy bis(4-(4′-*n*-heptylbiphenylcarbonyloxy)phenylisophthalate), 4.A.2

Yield: (75%); mp 174 °C; IR (KBr) ν_{max}: 2954, 2926, 2848, 1739, 1732, 1604, 1504, 1473, 1340 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.64 (t, J = 1.25 Hz, 1H, Ar-H), 8.26 (d, J = 8.37 Hz, 4H, Ar-H), 7.99 (d, J = 1.27 Hz, 2H, Ar-H), 7.73 (d, J = 8.39 Hz, 4H, Ar-H), 7.58 (d, J = 8.1 Hz, 4H, Ar-H), 7.33-7.29 (m, 12H, Ar-H), 3.98 (s, 3H, Ar-O-CH$_3$), 2.66 (t, J = 7.52 Hz, 4H, 2 × Ar-CH$_2$-), 1.67-1.62 (quin, J = 6.7 Hz, 4H, 2 × Ar-CH$_2$-C$\underline{H}_2$), 1.35-1.29 (m, 16H, 2 × -(CH$_2$)$_4$-), 0.89 (t, J = 6.56 Hz, 6H, 2×-CH$_3$); Elemental analysis: C$_{61}$H$_{60}$O$_9$ requires C 78.18, H 6.45; found C 77.96, H 6.81%.

5-Methoxy bis(4-(4′-*n*-octylbiphenylcarbonyloxy)phenylisophthalate), 4.A.3

Yield: (75%); mp 173 °C; IR (KBr) ν_{max}: 2952, 2923, 2852, 1743, 1732, 1606, 1506, 1458, 1340 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.63 (t, J = 1.2 Hz, 1H, Ar-H), 8.26 (d, J = 8.31 Hz, 4H, Ar-H), 7.99 (d, J = 1.23 Hz, 2H, Ar-H), 7.74 (d, J = 8.24 Hz, 4H, Ar-H), 7.59 (d, J = 8.1 Hz, 4H, Ar-H), 7.33-7.27 (m, 12H, Ar-H), 3.98 (s, 3H, Ar-O-CH$_3$), 2.67 (t, J = 7.33 Hz, 4H, 2 × Ar-CH$_2$-), 1.67-1.62 (quin, J = 6.9 Hz, 4H, 2 × Ar-CH$_2$-C$\underline{H}_2$-), 1.34-1.28 (m, 20H, 2 × -(CH$_2$)$_5$-), 0.88 (t, J = 6.72 Hz, 6H, 2 × -CH$_3$); Elemental analysis: C$_{63}$H$_{64}$O$_9$ requires C 78.4, H 6.67; found C 78.48, H 6.73%.

5-Methoxy bis(4-(4′-*n*-nonylbiphenylcarbonyloxy)phenylisophthalate), 4.A.4

Yield: (75%); mp 166 °C; IR (KBr) ν_{max}: 2954, 2920, 2850, 1741, 1737, 1608, 1506, 1456, 1340 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.64 (t, J = 1.23 Hz, 1H, Ar-H), 8.26 (d, J = 8.4 Hz, 4H, Ar-H), 7.99 (d, J = 1.29 Hz, 2H, Ar-H), 7.73 (d, J = 8.92 Hz, 4H, Ar-H), 7.58 (d, J = 8.12 Hz, 4H, Ar-H), 7.33-7.26 (m, 12H, Ar-H), 3.98 (s, 3H, Ar-O-CH$_3$), 2.67 (t, J = 7.51 Hz, 4H, 2 × Ar-CH$_2$-), 1.67-1.62 (quin, J = 6.4 Hz, 4H, 2 × Ar-CH$_2$-C$\underline{H}_2$-), 1.34-1.27 (m, 24H, 2 × -(CH$_2$)$_6$-), 0.88 (t, J = 6.51 Hz, 6H, 2 × -CH$_3$); Elemental analysis: C$_{65}$H$_{68}$O$_9$ requires C 78.60, H 6.9; found C 78.46, H 6.75%.

5-Methoxy bis(4-(4′-*n*-decylbiphenylcarbonyloxy)phenylisophthalate), 4.A.5

Yield: (70%); mp 161 °C; IR (KBr) ν_{max}: 2956, 2923, 2852, 1733, 1718, 1606, 1508, 1458, 1340, 1271 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.64 (t, J = 1.19 Hz, 1H, Ar-H), 8.27 (d, J = 8.64 Hz, 4H, Ar-H), 7.99 (d, J = 1.27 Hz, 2H, Ar-H), 7.74 (d, J = 8.96 Hz, 4H, Ar-H), 7.58 (d, J = 8.42 Hz, 4H, Ar-H), 7.33-7.29 (m, 12H, Ar-H), 3.98 (s, 3H, Ar-O-CH$_3$), 2.67 (t, J = 7.58 Hz, 4H, 2 × Ar-CH$_2$-), 1.67-1.64 (quin, J = 6.6 Hz, 4H, 2 × Ar-CH$_2$-C$\underline{H}_2$-), 1.34-1.27 (m, 28H, 2 × -(CH$_2$)$_7$-), 0.88 (t, J = 1.2 Hz, 6H, 2 × -CH$_3$); Elemental analysis: C$_{67}$H$_{72}$O$_9$ requires C 78.79, H 7.11; found C 78.70, H 6.91%.

5-Methoxy bis(4-(4′-*n*-undecylbiphenylcarbonyloxy)phenylisophthalate), 4.A.6

Yield: (72%); mp 156 °C; IR (KBr) ν_{max}: 2954, 2920, 2850, 1739, 1735, 1728, 1604, 1504, 1465, 1340, 1272 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.64 (t, J = 1.15 Hz, 1H, Ar-H), 8.26 (d, J = 8.39 Hz, 4H, Ar-H), 7.97 (d, J = 1.26 Hz, 2H, Ar-H), 7.74 (d, J = 8.7 Hz, 4H, Ar-H), 7.59 (d, J = 8.24 Hz, 4H, Ar-H), 7.33-7.27 (m, 12H, Ar-H), 3.98 (s, 3H, Ar-O-CH$_3$), 2.67 (t, J = 7.71 Hz, 4H, 2 × Ar-CH$_2$-), 1.67-1.59 (quin, J = 7.44 Hz, 4H, 2 × Ar-CH$_2$-C$\underline{H}_2$-), 1.34-1.26 (m, 32H, 2 × -(CH$_2$)$_8$-), 0.88 (t, J = 6.5 Hz, 6H, 2 × CH$_3$); Elemental analysis: C$_{69}$H$_{76}$O$_9$ requires C 78.98, H 7.29; found C 78.98, H 7.59%.

5-Methoxy bis(4-(4′-*n*-dodecylbiphenylcarbonyloxy)phenylisophthalate), 4.A.7

Yield: (75%); mp 135 °C; IR (KBr) ν_{max}: 2956, 2918, 2850, 1739, 1730, 1604, 1504, 1469, 1340 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.64 (t, J = 1.18 Hz, 1H, Ar-H), 8.26 (d, J = 8.34 Hz, 4H, Ar-H), 7.99 (d, J = 1.21 Hz, 2H, Ar-H), 7.74 (d, J = 8.35 Hz, 4H, Ar-H), 7.59

(d, J = 8.14 Hz, 4H, Ar-H), 7.33-7.29 (m, 12H, Ar-H), 3.98 (s, 3H, Ar-O-CH$_3$), 2.67 (t, J = 7.59 Hz, 4H, 2 × Ar-CH$_2$-), 1.67-1.62 (quin, J = 7.23 Hz, 4H, 2 × Ar-CH$_2$-C$\underline{H}_2$-), 1.34-1.26 (m, 36H, 2 × -(CH$_2$)$_9$-), 0.88 (t, J = 6.33 Hz, 6H, 2 × -CH$_3$); Elemental analysis: C$_{71}$H$_{80}$O$_9$ requires C 79.15, H 7.47; found C 79.17, H 7.44%.

5-Methoxy bis(4-(4′-*n*-tetradecylbiphenylcarbonyloxy)phenylisophthalate), 4.A.8

Yield: (75%); mp 130 °C; IR (KBr) ν_{max}: 2956, 2918, 2848, 1739, 1732, 1604, 1504, 1471, 1340, 1276 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.64 (t, J = 1.2 Hz, 1H, Ar-H), 8.26 (d, J = 8.16 Hz, 4H, Ar-H), 7.99 (d, J = 1.18 Hz, 2H, Ar-H), 7.74 (d, J = 8.48 Hz, 4H, Ar-H), 7.59 (d, J = 8.2 Hz, 4H, Ar-H), 7.33-7.29 (m, 12H, Ar-H), 3.98 (s, 3H, Ar-O-CH$_3$), 2.66 (t, J = 7.35 Hz, 4H, 2 × Ar-CH$_2$-), 1.67-1.62 (quin, J = 6.82 Hz, 4H, 2 × Ar-CH$_2$-C$\underline{H}_2$-), 1.34-1.28 (m, 44H, 2 × -(CH$_2$)$_{11}$-), 0.88 (t, J = 6.46 Hz, 6H, 2 × -CH$_3$); Elemental analysis: C$_{75}$H$_{88}$O$_9$ requires C 79.47, H 7.81; found C 79.64, H 7.81%.

5-Methoxy bis(4-(4′-*n*-hexadecylbiphenylcarbonyloxy)phenylisophthalate), 4.A.9

Yield: (70%); mp 130.5 °C; IR (KBr) ν_{max}: 2954, 2918, 2848, 1739, 1730, 1604, 1504, 1471, 1340, 1276, 1242 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.64 (t, J = 1.17 Hz, 1H, Ar-H), 8.26 (d, J = 8.3 Hz, 4H, Ar-H), 7.99 (d, J = 1.2 Hz, 2H, Ar-H), 7.74 (d, J = 8.41 Hz, 4H, Ar-H), 7.59 (d, J = 8.1 Hz, 4H, Ar-H), 7.33-7.29 (m, 12H, Ar-H), 3.98 (s, 3H, Ar-O-CH$_3$), 2.67 (t, J = 7.62 Hz, 4H, 2 × Ar-CH$_2$-), 1.67-1.62 (quin, J = 6.48 Hz, 4H, 2 × Ar-CH$_2$-C$\underline{H}_2$-), 1.34-1.25 (m, 52H, 2 × -(CH$_2$)$_{13}$-), 0.88 (t, J = 6.52 Hz, 6H, 2 × -CH$_3$); Elemental analysis: C$_{79}$H$_{96}$O$_9$ requires C 79.76, H 8.12; found C 79.55, H 8.16%.

5-Methoxy bis(4-(4′-*n*-octadecylbiphenylcarbonyloxy)phenylisophthalate), 4.A.10

Yield: (70%); mp 130 °C; IR (KBr) ν_{max}: 2954, 2918, 2848, 1741, 1732, 1604, 1504, 1471, 1338 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.64 (t, J = 1.2 Hz, 4H, Ar-H), 8.26 (d, J = 8.36 Hz, 4H, Ar-H), 7.99 (d, J = 1.26 Hz, 2H, Ar-H), 7.74 (d, J = 6.6 Hz, 4H, Ar-H), 7.59 (d, J = 6.64 Hz, 4H, Ar-H), 7.33-7.29 (m, 12H, Ar-H), 3.98 (s, 3H, Ar-O-CH$_3$), 2.67 (t, J = 7.62 Hz, 4H, 2 × Ar-CH$_2$-), 1.67-1.62 (quin, J = 6.48 Hz, 4H, 2 × Ar-CH$_2$-C$\underline{H}_2$-), 1.34-1.25 (m, 60H, 2 × -(CH$_2$)$_{15}$-), 0.88 (t, J = 6.54 Hz, 6H, 2 × -CH$_3$); Elemental analysis: C$_{83}$H$_{104}$O$_9$ requires C 79.83, H 8.48; found C 79.97, H 8.6%.

References

[1]   Niori, T.; Sekine, T.; Watanabe, J.; Furukawa, T.; Takezoe, H. *J. Mater. Chem.* **1996,** *6,* 1231-1233.

[2]   Pelzl, G.; Diele, S.; Weissflog, W. *Adv. Mater.* **1999,** *11,* 707-724.

[3]   Reddy, R. A.; Tschierske, C. *J. Mater. Chem.* **2006,** *16,* 907-961.

[4]   Takezoe, H.; Takanishi, Y. *Jpn, J. Appl. Phys. Part 1* **2006,** *45,* 597-625.

[5]   Ros, M. B.; Serrano, J. L.; Rosario de La Fuente, M.; Folcia, C. L. *J. Mater. Chem.* **2005,** *15,* 5093-5098.

[6]   Sadashiva, B. K.; Murthy, H. N. S.; Dhara, S. *Liq. Cryst.* **2001,** *28,* 483-487.

[7]   Murthy, H. N. S.; Sadashiva, B. K. *Liq. Cryst.* **2002,** *29,* 1223-1234.

[8]   Reddy, R. A.; Sadashiva, B. K. *Liq. Cryst.* **2003,** *30,* 1031-1050.

[9]   Weissflog, W.; Nadasi, H.; Dunemann, U.; Pelzl, G.; Diele, S.; Eremin, A.; Kresse, H. *J. Mater. Chem.* **2001,** *11,* 2748-2758.

[10]   Reddy, R. A.; Sadashiva, B. K.; Raghunathan, V. A. *Chem. Mater.* **2004,** *16,* 4050-4062.

[11]   Dunemann, U.; Schroder, M. W.; Reddy, R. A.; Pelzl, G.; Diele, S.; Weissflog, W. *J. Mater. Chem.* **2005,** *15,* 4051-4061.

[12]   Pelzl, G.; Jakli, A.; Lischka, C. H.; Wirth, I.; Weissflog, W. *Liq. Cryst.* **1999,** *26*, 135-139.

[13]   Reddy, R. A.; Sadashiva, B. K. *Liq. Cryst.* **2004,** *31,* 1069-1081.

[14]   Weissflog, W.; Lischka, Ch.; Benne, I.; Scharf, T.; Pelzl, G.; Diele, S.; Kruth, H. *Proc. SPIE: Int. Soc. Opt. Eng.* **1998,** *3319,* 14-19.

[15]   Nadasi, H.; Weissflog, W.; Eremin, A.; Pelzl, G.; Diele, S.; Das, B.; Grande, S. *J. Mater. Chem.* **2002,** *12,* 1316-1324.

[16]   Mieczkowski, J.; Szydlowska, J.; Matraszek, J.; Pociecha, D.; Gorecka, E.; Donnio, B.; Guillon, D. *J. Mater. Chem.* **2002,** *12,* 3392-3399.

[17]   (a) Umadevi, S.; Radhika, S.; Sadashiva, B. K. *Liq. Cryst.* **2006**, *33,*139-147.

        (b) Umadevi, S. Liquid crystals of some compounds composed of bent-core molecules: synthesis and characterization. Ph.D. Thesis, Jawaharlal Nehru Univeristy, New Delhi, **2006.**

[18]   Nguyen, H. T.; Bedel, J. P.; Rouillon, J. C.; Marcerou, J. P.; Achard, M. F. *Pramana* **2003,** *61,* 395-404.

[19]   Shen, D.; Diele, S.; Pelzl, G; Wirth, I.; Tschierske, C. *J. Mater. Chem.* **1999,** *9,* 661-672.

[20]   Umadevi, S.; Sadashiva, B. K. *Liq. Cryst.* **2005**, *32,* 287-297.

[21]   Coates, D.; Gray, G. W. *Mol. Cryst. Liq. Cryst.* **1976,** *37,* 249-262 and references there in.

[22]   Sadashiva, B. K.; Raghunathan, V. A.; Pratibha, R. *Ferroelectrics* **2000,** *243,* 249-260.

[23]   Zennyoji, M.; Takanishi, Y.; Ishikawa, K.; Thisayukta, J.; Watanabe, J.; Takezoe, H. *J. Mater. Chem.* **1999,** *9,* 2775-2778.

[24]   Folcia, C. L.; Ortega, J.; Etxebarria, J. *Liq. Cryst.* **2003,** *30,* 1189-1191.

[25]   Dantlgraber, G.; Shen, D.; Diele, S.; Tschierske, C. *Chem. Mater.* **2002,** *14,* 1149-1158.

[26]   Murthy, H. N. S.; Sadashiva, B. K. *Liq. Cryst.* **2004,** *31,* 1347-1356.

[27]   Ortega, J.; de la Fuente, M. R.; Etxebarria, J.; Folcia, C. L.; Diez, S.; Gallastegui, J. A.; Gimeno, N.; Ros, M. B.; Perez-Jubindo, M. A. *Phy. Rev. E* **2004,** *69,* 011703.

[28]   Reddy, R. A.; Raghunathan, V. A.; Sadashiva, B. K. *Chem. Mater.* **2005,** *17,* 274-283.

[29]   Murthy, H. N. S.; Bodyagin, M.; Diele, S.; Baumeister, U.; Pelzl, G.; Weissflog, W. *J. Mater. Chem.* **2006,** *16,* 1634-1643.

[30]   Umadevi, S.; Sadashiva, B. K. *Liq. Cryst.* **2005,** *32,* 1233-1241.

[31]   Umadevi, S.; Jakli, A.; Sadashiva, B. K. *Soft Matter* **2006,** *2,* 875-885.

[32]   Weissflog, W.; Naumann, G.; Kosata, B.; Schroder, M. W.; Eremin, A.; Diele, S.; Vokhovskaya, Z.; Kresse, H.; Friedemann, R.; Krishnan, S. A. R.; Pelzl, G. *J. Mater. Chem.* **2005,** *15,* 4328-4337.