Ferroelectric and antiferroelectric switching behaviour in new unsymmetrical bent-core compounds derived from 3-hydroxybenzoic acid†

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Herein we report the synthesis and characterization of several achiral bent-core unsymmetrical compounds exhibiting mesomorphic properties. The lower homologues in two series of compounds show a columnar phase with a rectangular lattice whereas the middle homologues exhibit a novel columnar phase with an oblique lattice. Interestingly, three of the higher homologues of the laterally unsubstituted compounds exhibit a smectic phase with ferroelectric switching characteristics and the analogous fluoro-substituted compounds show a smectic phase that is composed of antiferroelectric conglomerates.

Introduction

The occurrence of "ferro-/antiferro"-electricity in liquid crystals was first observed in chiral calamitic systems.[1,2] However, the discovery of electro-optical switching[3] in a mesophase exhibited by compounds composed of achiral bent-core (BC) molecules has aroused considerable interest. Chirality in such BC compounds arises due to a unique combination of polar order (due to a specific arrangement of molecules along the bent direction) and the tilt of the molecules in successive layers.[4] There are two possibilities for the molecules to arrange themselves in such chiral layers. The molecular arrangement in these chiral layers is such that the polarization (due to the directed organization) can be parallel or antiparallel in adjacent layers giving rise to ferro- and antiferro-electric properties respectively. In addition, these molecules can tilt in *syn* or *anti* fashion in successive layers which results in two types of arrangements in both ferro- (homochiral SmC_SP_F or racemic SmC_AP_F) and antiferro- (racemic SmC_SP_A or homochiral SmC_AP_A) electric phases. In the majority of the bent-core compounds investigated so far, the antiferroelectric properties are more prevalent. This is not very surprising and has been attributed to the interlayer fluctuations in successive layers of the antiferroelectric arrangement of the molecules and is stabilized by entropical gain. Also, in order to escape from a macroscopic polar order such an arrangement of molecules is preferred.

The first observation of ferroelectric switching in mesophases of BC compounds was made only a few years ago.[5,6] The compounds made by the Bordeaux group[5] contained fluorine substituent at the *ortho* position with respect to the two terminal *n*-alkoxy chains. Subsequently, ferroelectric switching behaviour was observed in different systems.[7–9] These systems also contain a fluorine substituent *ortho* to the terminal *n*-alkoxy chains. The Boulder group designed a new system[6] based on the information that ferroelectric structures require an anticlinic interlayer correlation of the molecules and indeed observed ferroelectric switching characteristics in their system. Ferroelectric properties have also been reported in other chiral bent-core compounds[10] as well as in some mixtures.[11] Another significant approach[12,13] to decouple the layer interfaces was made by the Halle group using incompatible siloxane units in the terminal position of the BC molecules which provided ferroelectric phases. Very recently, homochiral ferroelectric smectic as well as columnar phases in BC compounds derived from a 2,7-dihydroxynaphthalene central unit was observed.[14] We have reported earlier the influence of a lateral fluorine substituent on the mesomorphic properties of symmetrical[15] as well as unsymmetrical compounds[16] having resorcinol as the central unit. We have shown that the position and the number of fluorine substituents play a very important role in inducing ferro-/antiferro-electric properties in five-ring bent-core compounds.[16] Recently ferroelectric switching properties were also observed in unsubstituted compounds derived from resorcinol.[17]

The majority of bent-core compounds which have been reported so far are derived from resorcinol, which is also the central unit.[3,4,7,8,15,16] We reported[18] earlier a novel biaxial smectic A phase for the first time using 3-hydroxybenzoic acid as the central unit. We also reported[19] unusual filamentary growth patterns at the isotropic to $SmCP_A$ phase transition using this central core. These compounds represent[18–21] the first of several homologous series of compounds containing substituents such as cyano, nitro, fluoro, chloro or trifluoromethyl groups as one of the terminal groups while the other terminal group is an *n*-alkoxy chain.

In this paper, the synthesis and mesomorphic properties of three new homologous series of compounds derived from 3-hydroxybenzoic acid are reported. These are unsymmetrical compounds having two terminal chains but differing in the orientation of the ester-linking group (series I). The other two series of compounds are also unsymmetrical and contain a lateral fluorine substitutent (series II) and a biphenyl moiety at one of the terminal positions (series III). The salient features of the mesomorphic properties observed in these compounds are:

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† Electronic supplementary information (ESI) available: Detailed synthetic procedures, spectral and analytical data of the intermediates and the target compounds. See http://www.rsc.org/suppdata/jm/b4/b419404g/

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i) observation of a novel columnar phase with an oblique lattice for the middle homologues in two series (I and II) of compounds.

ii) observation of ferroelectric switching behaviour in higher homologues of unsubstituted compounds even though they do not contain any lateral substituent mentioned earlier (series I).

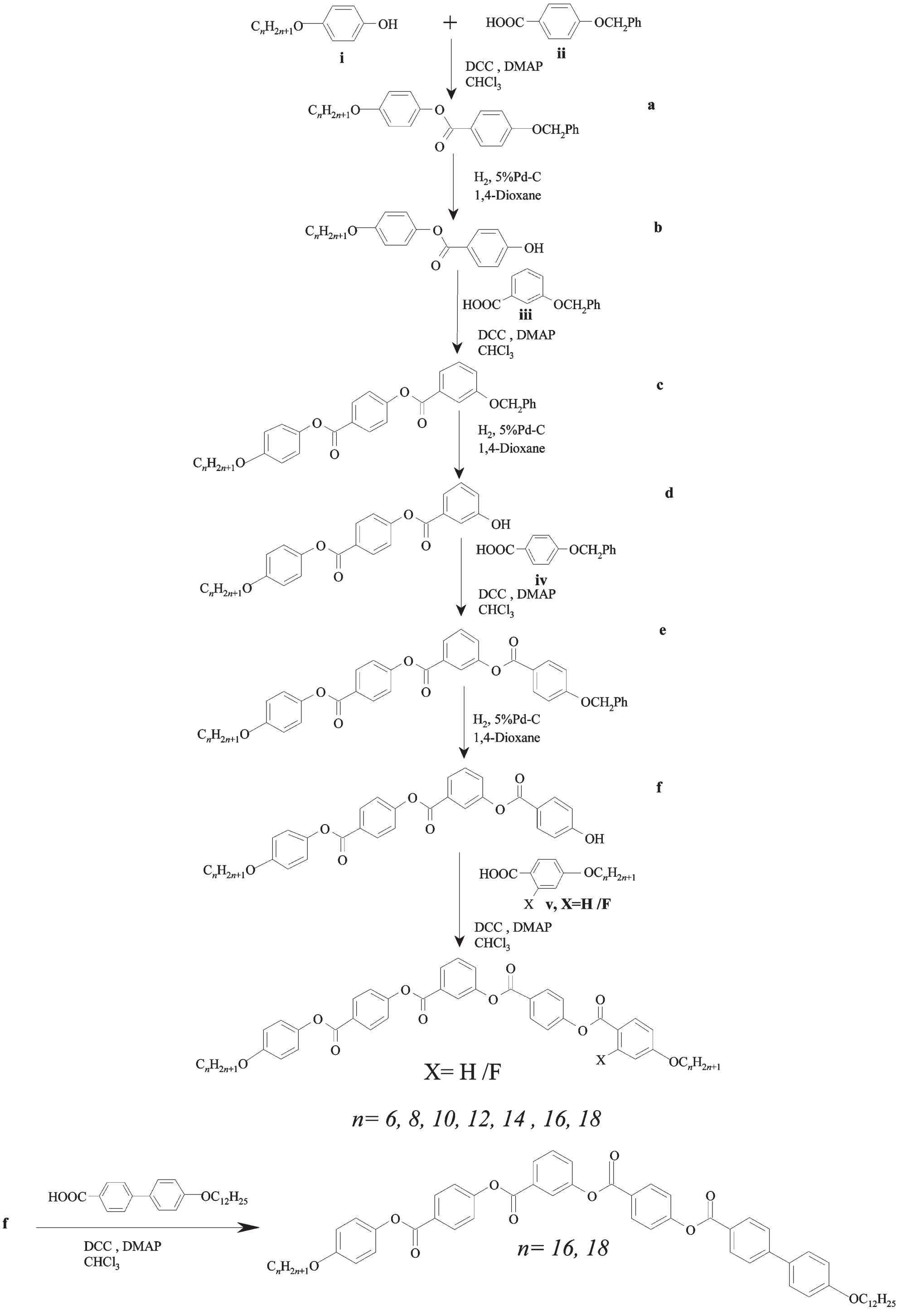
iii) analogous fluoro-substituted compounds (series II) showed antiferroelectric conglomerates.

iv) related compounds with a biphenyl moiety in one of the arms showed only calamitic phases.

Experimental

Materials

The synthesis of these achiral unsymmetrical compounds was carried out following a route depicted in Scheme 1. The synthesis of compounds **a–f** (in Scheme 1) has already been



Scheme 1

reported in an earlier paper.[21] The detailed synthetic procedures, spectral and analytical data of the intermediates and the target compounds are available as ESI.†

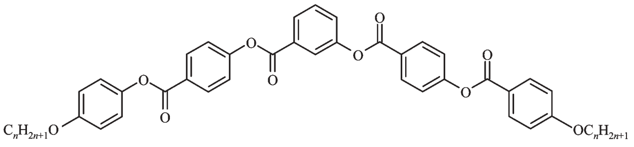
Results and discussion

Textural observations

The transition temperatures and the associated enthalpy values as determined from thermograms obtained on a differential scanning calorimeter (DSC, Perkin-Elmer, Model Pyris 1D) for the compounds of series I to III are summarized in Tables 1, 2 and 3 respectively.

Three types of mesophases were observed in the seven compounds of series I. The optical textures were observed using a polarizing microscope (Leitz Laborlux 12 POL/Olympus BX50) provided with a heating stage (Mettler FP 82 HT) and a temperature controller (Mettler FP 5). Compound **1** showed a mosaic texture that is typical for a classical Col$_r$ (B$_1$) phase. The optical texture obtained for the mesophase of compound **1** on cooling from the isotropic phase is shown in Fig. 1. On increasing the alkyl chain length, compounds **2–4** were obtained and some unusual textural patterns were observed for these. The textures obtained on cooling the isotropic phase of compounds **2** and **3** are shown in Fig. 2(a) and (b) respectively. Although these highly birefringent textures are different from those seen normally for a Col$_r$ phase, these are typical features of a columnar phase. However, very interestingly, the compounds with longer terminal alkyl chain length (n = 14, 16, 18) showed optical textures different from those seen for the lower homologues, but were all similar. A photomicrograph of a texture obtained for compound **5** is shown in Fig. 3.

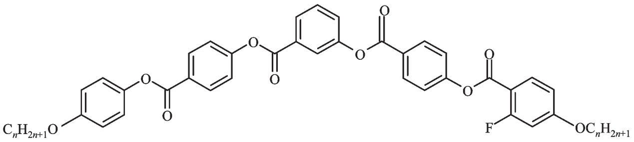
Table 1 Transition temperatures (°C) and the associated enthalpies (kJ mol^{-1}) for the compounds of series I[a]



Compound	n	Cr	SmC$_S$P$_F$	B$_X$ (Col$_{ob}$)	Col$_r$	I
1	6	· 142.0 *88.7*	—	—	(· 134.0) *15.5*	·
2	8	· 124.0* *39.2*	—	· 136.0 *18.0*	—	·
3	10	· 102.0 *42.2*	—	· 137.0 *19.7*	—	·
4	12	· 107.0 *49.7*	—	· 138.0 *20.8*	—	·
5	14	· 111.0* *96.6*	· 138.5 *20.6*	—	—	·
6	16	· 114.0* *104.2*	· 138.0 *20.7*	—	—	·
7	18	· 115.5* *111.6*	· 137.5 *20.7*	—	—	·

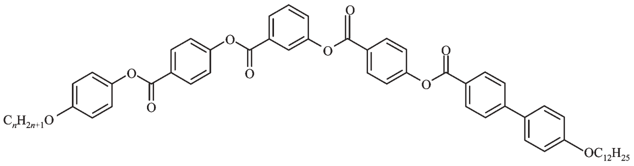
[a] Key: Cr: crystalline phase; SmC$_S$P$_F$: synclinic ferroelectric phase with smectic ordering of the molecules; SmC$_A$P$_A$: anticlinic antiferroelectric phase with smectic ordering of the molecules; B$_X$(Col$_{ob}$): columnar phase with an oblique lattice; Col$_r$: columnar phase with a rectangular lattice; SmX: smectic phase with unknown structure; I: isotropic phase; *: compound has crystal–crystal transition, enthalpy denoted is the sum of all such transitions.

Table 2 Transition temperatures (°C) and the associated enthalpies (kJ mol^{-1}) for the compounds of series II



Compound	n	Cr	SmC$_A$P$_A$	B$_X$ (Col$_{ob}$)	Col$_r$	I
8	6	· 131.0 *47.8*	—	—	(· 114.0) *12.0*	·
9	8	· 123.0 *54.6*	—	(· 118.5) *16.0*	—	·
10	10	· 116.0 *23.6*	—	· 120.0 *17.3*	—	·
11	12	· 112.5* *61.6*	—	· 123.5 *18.5*	—	·
12	14	· 112.0 *80.8*	· 126.0 *19.7*	—	—	·
13	16	· 109.0 73.4	· 127.0 *19.5*	—	—	·
14	18	· 108.0 *78.7*	· 128.0 *20.0*	—	—	·

Table 3 Transition temperatures (°C) and the associated enthalpies (kJ mol^{-1}) for the compounds of series II



Compound	n	Cr	SmX	SmC	SmA	I
15	16	· 141.0* *88.7*	· 183.0 *3.9*	· 197.0[a]	· 200.5 *10.4*	·
16	18	· 140.0* *98.2*	· 180.0 *3.1*	· 199.0[a]	· 200.0 *10.3*	·

[a] Enthalpy could not be determined.

The thermal behaviour of the compounds of series II as determined on DSC and a polarizing microscope is summarized in Table 2. In this series of compounds also three types of mesophases were observed. Compound **8** showed

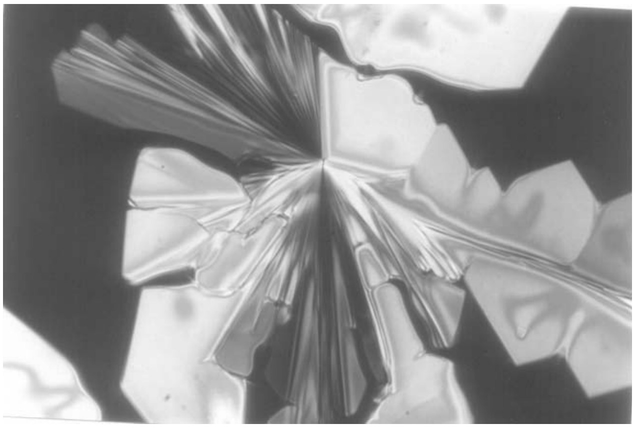


Fig. 1 An optical photomicrograph of the texture developing on cooling the isotropic phase of compound **1**.

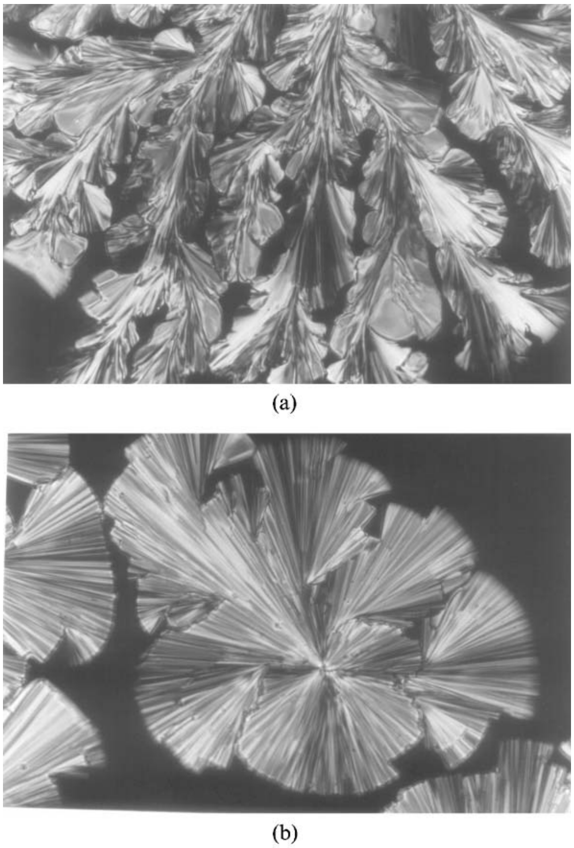


Fig. 2 (a) and (b) Optical photomicrographs of the textures developing on cooling the isotropic phase of compounds **2** and **3** respectively.

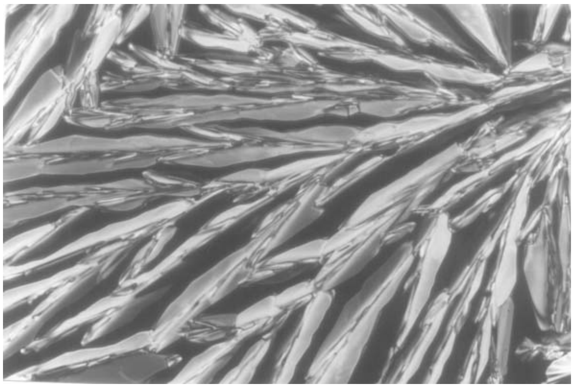


Fig. 3 An optical photomicrograph of the texture developing on cooling the isotropic phase of compound **5**.

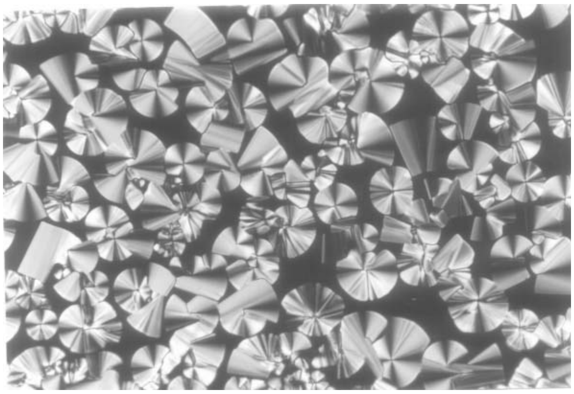


Fig. 4 An optical photomicrograph obtained for the mesophase of compound **10**.

typical features of a Col$_r$ phase, whereas compounds **9–11** showed textures which are slightly different from these. A photomicrograph obtained for the mesophase of compound **10** is shown in Fig. 4. These textural features also indicate that the mesophase could be a columnar phase. However, the textural features obtained for compounds **12–14** are completely different from those exhibited by the lower homologues. For example, the optical features of compound **12** showed banana leaf-like texture and a photomicrograph of this texture is shown in Fig. 5(a). In contrast, compounds **13** and **14** showed a fringe pattern, which is normally observed for an antiferroelectric SmCP phase. A photomicrograph of the texture obtained for the mesophase of compound **13** as observed under a polarizing microscope is shown in Fig. 5(b).

In order to examine the effect of increasing the core-length on only one side of these systems, we synthesized two compounds having a biphenyl moiety in one of the arms. The mesomorphic behaviour of these two compounds is quite interesting and is similar. The clearing temperature of these

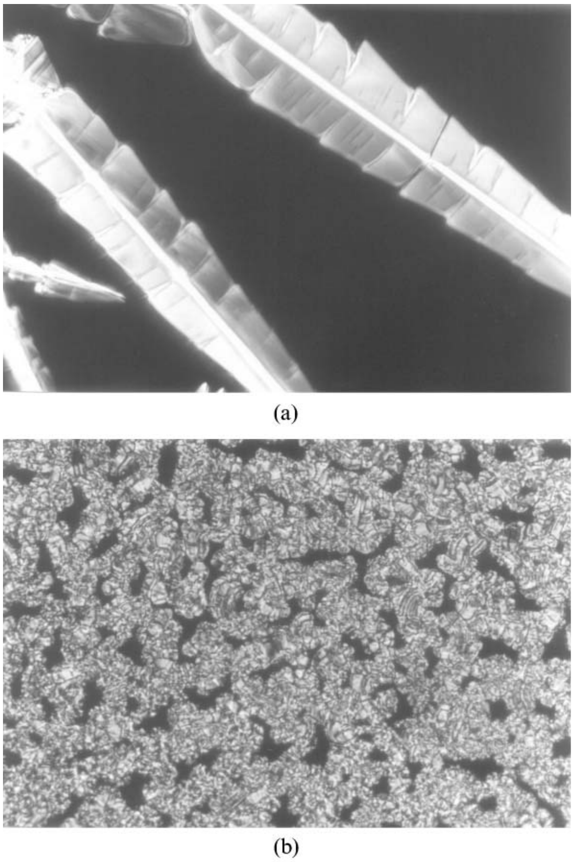


Fig. 5 (a) An optical photomicrograph showing banana leaf-like texture obtained for the mesophase of compound **12**. (b) An optical photomicrograph showing a fringe pattern obtained for the mesophase of compound **13**.

compounds increased considerably, as also the thermal range of the mesophases. On cooling from the isotropic phase of these compounds both homeotropic as well as smooth focal-conic textures could be observed which are the classical textures observed for a smectic A phase. On lowering the temperature, the homeotropic regions transformed to a schlieren texture whereas the focal-conic texture became broken focal-conic. These textural observations are typical for a SmA–SmC transition. On lowering the temperature further the patterns transform to an undefined texture. This transition is first order and the enthalpy value for the transition is about 3–4 kJ mol^{-1}. The textural changes were also observed in cells treated for both planar as well as homeotropic arrangement and the photomicrographs obtained for compound **16** are shown in Fig. 6(a–f). The lowest temperature phase is smectic and non-switchable (see later for details). Thus these compounds show polymorphic calamitic phases whereas the corresponding five-ring compounds with longer alkyl chain show switchable B phases. From these examples we can say that increasing the core length on only one of the arms (by a biphenyl moiety) effectively changes the bending angle between the arms of the bent-core compounds and the types of mesophases.

X-Ray diffraction studies

In order to examine the mesophase structure of all the compounds X-ray diffraction (XRD) studies (Cu-K$_\alpha$ radiation from Rigaku Ultrax 18) were carried out. Unless otherwise mentioned, XRD measurements were carried out on non-oriented samples. The mesophase of compound **1** gave three reflections in the small angle region, which could be indexed to the (11), (02) and (13) planes of a rectangular lattice. Hence this phase has been characterized as a Col$_r$ phase and the X-ray diffractogram is shown in Fig. 7(a). XRD studies on powder samples of compounds **2–4** showed many reflections in the small angle region, which rule out the possibility of a simple layered structure. The patterns are also different from what is normally seen for a Col$_r$ (B$_1$) phase. The X-ray diffractogram obtained for compound **2** is shown in Fig. 7(b). In order to gain more insight into this mesophase structure, an

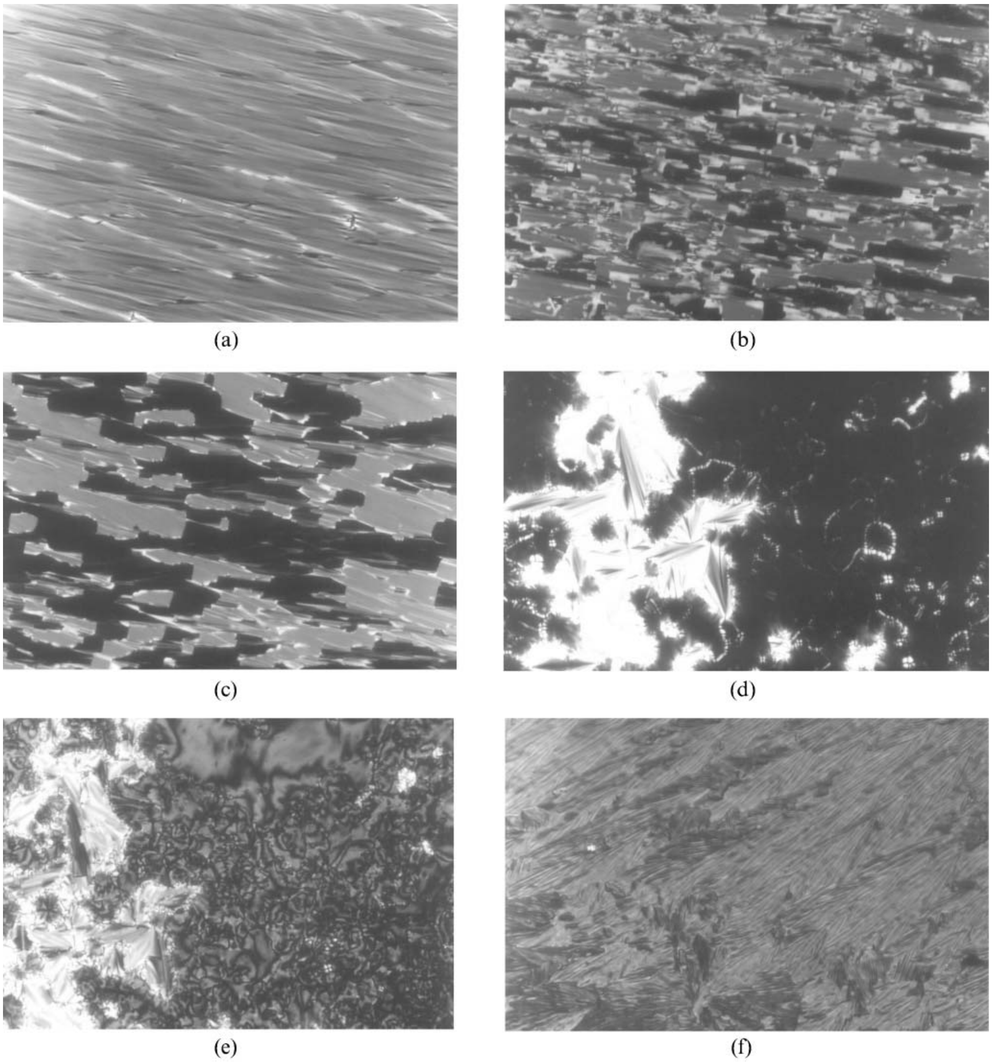


Fig. 6 (a–c) Optical photomicrographs obtained for SmA, SmC and SmX phases in cells treated for planar alignment; (d–f) the corresponding textures obtained in cells treated for homeotropic alignment; compound **16**.

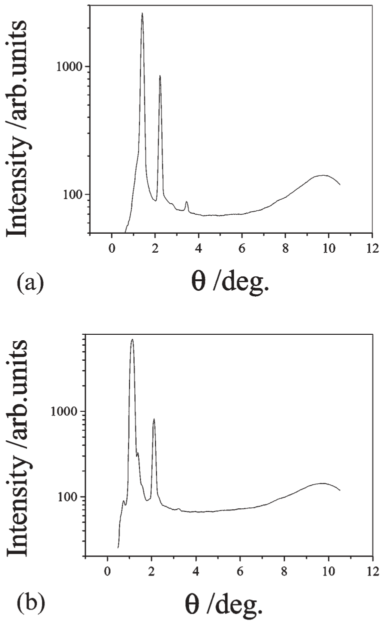


Fig. 7 X-Ray angular intensity profiles obtained for (a): $\mathrm{Col_r}$ phase of compound **1**; (b): $\mathrm{B_X}$ ($\mathrm{Col_{ob}}$) phase of compound **2**.

oriented XRD study of the sample is essential. We have obtained only a partially oriented pattern for compound **4** and the diffraction pattern is shown in Fig. 8.

The pattern on the meridian has a lamellar periodicity and these reflections can be indexed to (10), (20) and (30) planes. Interestingly, reflections on the equator are also observed. These reflections could be indexed to the 01 and 0$\bar{1}$ planes. Apart from these reflections, two other faint reflections were obtained which could be indexed to the 11 and 1$\bar{1}$ planes of an oblique lattice with the lattice parameters a = 43.2 Å and b = 66.2 Å. The calculated oblique angle is 84°. This partially oriented pattern indicates a columnar structure with an oblique lattice for the mesophase. However, this mesophase does not switch electro-optically and is a novel mesophase occurring between the rectangular columnar ($\mathrm{Col_r}$) phase and the switchable lamellar (SmCP) phase. Hence this new phase has been assigned the symbol $\mathrm{B_X}$ ($\mathrm{Col_{ob}}$).

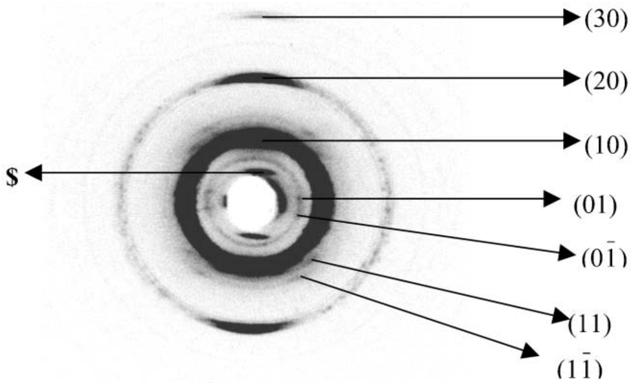


Fig. 8 X-Ray diffraction pattern obtained for a sample of compound **4**; $\mathrm{B_X}$ ($\mathrm{Col_{ob}}$) phase. $: escaping beam from the experimental setup.

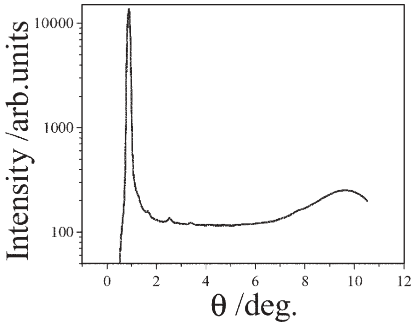


Fig. 9 X-Ray diffractogram obtained for the smectic phase of compound **6**.

Unoriented XRD patterns obtained for the mesophases of compounds **5–7** showed lamellar periodicity of the molecules. The d-spacing corresponding to the first reflection is less than the full molecular length (assuming a fully extended all-*trans* conformation of the terminal n-alkoxy chains) indicating a tilt of the molecules in the smectic layers. The X-ray diffractogram obtained for compound **6** is shown in Fig. 9.

XRD studies have been carried out on the mesophases of compounds of series II. From the experiments it was observed that the XRD patterns are similar to those observed for the compounds of series I. The three reflections obtained in the small angle region for the mesophase of compound **8** can be indexed to (11) (02) and (13) planes of a rectangular lattice. The reflections obtained for the mesophase of compounds **9–11** are comparable to those of compounds **2–4** and hence designated by the same symbol. The higher homologues (compounds **12–14**) showed lamellar periodicity. Interestingly the layer spacings obtained for the smectic phases of compounds (**12–14**) are less (by 2.5–3 Å) than the layer spacings obtained for the corresponding compounds (**5–7**) of series I. This may be due to different interlayer interactions between the mesophases of two series of compounds. The d-spacings obtained for the compounds under investigation are summarized in Table 4. XRD studies have also been carried out on the mesophases of compound **16**. One reflection in the small angle region at d = 53.6 Å was obtained at 192 °C and on lowering the temperature to 160 °C a second order smectic reflection was obtained without any change in the d-spacing. The d-spacing corresponding to the first reflection is less than the full molecular length, which confirms a tilt of molecules in the smectic strata (calc. tilt angle 47°). The additional reflection seen in the low temperature phase indicates that on transition from the SmC to the SmX phase, the molecules are arranged in well-defined smectic layers. In both SmC and SmX phases a diffuse wide-angle reflection was observed at 4.7 Å. In the SmX phase no additional reflection was observed in the wide-angle region, which rules out the possibility of a higher order smectic phase. An oriented pattern is necessary to arrive at the precise structure of the SmX phase, but owing to the high clearing temperatures of the compounds it has not been possible to get an oriented pattern. Since we are not sure of the exact structure of this mesophase, the symbol SmX has been assigned.

Table 4 Small angle Bragg reflections (Å) and their Miller indices (in parentheses) for the unsymmetrical compounds derived from 3-hydroxybenzoic acid

		Lattice parameters			
Compound	*d*-Spacings (Å) and Miller indices	*a*	*b*	Phase type	Oblique angle
1	31.2 (11), 19.8 (02), 12.6 (13) Calc: 12.8 (13)	50.7	39.6	$\mathrm{Col_r}$	—
2	62.0 (01), 39.5 (10), 30.9 $(1\bar{1})$, 27.3 (12), 19.7 (20), 13.5 (30) Calc: 27.0 (12)	40.2	63.0	$\mathrm{B_X}$ ($\mathrm{Col_{ob}}$)	79.6
4	65.8 (01), 43.0 (10), 37.5 (11), 34.1 $(1\bar{1})$, 21.8 (20), 14.5 (30) Calc: 37.8 (11), 34.4 $(1\bar{1})$	43.2	66.2	$\mathrm{B_X}$ ($\mathrm{Col_{ob}}$)	84.0
5	49.1(01), 24.6(02)	—	—	$\mathrm{SmC_SP_F}$	—
6	50.8 (01), 25.8 (02), 17.1(03), 13.0 (04)	—	—	$\mathrm{SmC_SP_F}$	—
7	53.4 (01), 26.6 (02), 17.9 (03), 13.4 (04)	—	—	$\mathrm{SmC_SP_F}$	—
8	28.9 (11), 19.8 (02), 12.3(13) Calc: 12.6 (13)	42.3	39.6	$\mathrm{Col_r}$	—
9	66.0 (01), 41.3 (10), 33.7 $(1\bar{1})$, 26.5 (12), 20.7 (20), 16.0 (30) Calc: 26.9 (12)	41.5	66.2	$\mathrm{B_X}$ ($\mathrm{Col_{ob}}$)	85.0
11	62.0 (01), 42.3 (10), 33.0 $(1\bar{1})$, 27.2 (12), 21.2 (20), 14.3 (30) Calc: 27.0 (12)	42.8	65.3	$\mathrm{B_X}$ ($\mathrm{Col_{ob}}$)	81.0
12	46.2 (01), 23.1 (02), 15.4 (03)	—	—	$\mathrm{SmC_AP_A}$	—
14	50.3 (01), 16.8 (03)	—	—	$\mathrm{SmC_AP_A}$	—
16	53.6 (01)	—	—	SmC	—
	53.6 (01), 26.7 (02)	—	—	SmX	—

Electro-optical investigations

In order to see the effect of electric field on the mesophases of these compounds, we have carried out detailed electro-optical investigations. For these experiments ITO coated home made cells treated with polyimide were used. The sample thickness was adjusted with suitable Mylar spacers. There was no response to an applied electric field on the mesophases of compounds **1–4**. In contrast however, interesting electro-optical effects were observed for the mesophases of compounds **5–7**. In general, the switching behaviour of the mesophases of all the three compounds is similar. Detailed electro-optical investigations carried out on the mesophase of compound **5** are described here. A sample of compound **5** was taken in a cell of thickness 10.3 μm and it was cooled slowly from the isotropic phase under a triangular-wave electric field. After a threshold voltage (39 $\mathrm{V_{pp}}$ $\mu\mathrm{m}^{-1}$) a single polarization current peak for each half period was observed even at low frequencies. This is an indication of a ferroelectric switching behaviour of the mesophase. The switching current response trace obtained for compound **5** is given in Fig. 10(a).

It has been reported[22] that a modified triangular-wave method could be used to check that the field induced polarized state remains stable even under zero field for a prolonged time until the sign of the field is reversed. Therefore, we employed this technique to study the ferroelectric switching in our compounds. Single polarization current peak observed in this experiment further supported that the mesophase exhibits ferroelectric switching characteristics. The switching current response trace obtained for the mesophase of compound **5** by employing the modified triangular-wave method is given in Fig. 10(b).

The bistability of this ferroelectric phase was further examined by dc field experiments. On applying a dc electric field (12.3 V $\mu\mathrm{m}^{-1}$) and cooling the isotropic phase of compound **5**, birefringent circular domains were observed. The feature of these domains is that the extinction brushes make an angle with respect to the direction of the polarizer and analyzer. On reversing the polarity of the applied dc field, the extinction brushes rotate in a counter-clockwise direction. On terminating the dc field the positions of the brushes remain in both the orientations. The bistable states remain

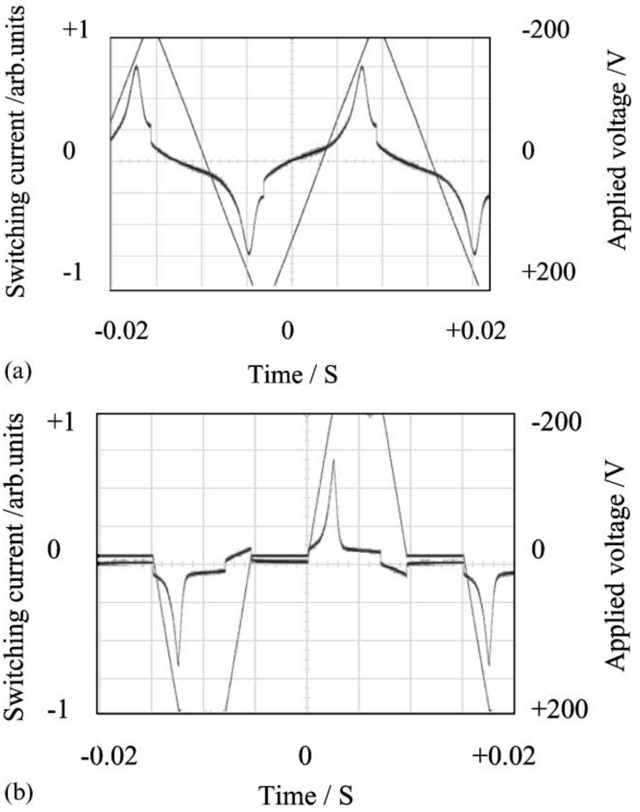


Fig. 10 Switching current response trace obtained for the mesophase of compound **5** by applying (a) a triangular-wave voltage (480 $\mathrm{V_{pp}}$, 40 Hz,); (b) a modified triangular-wave voltage (420 $\mathrm{V_{pp}}$, 33 Hz,); cell thickness 10.3 μm; saturated polarization value ≈225 nC cm^{-2}.

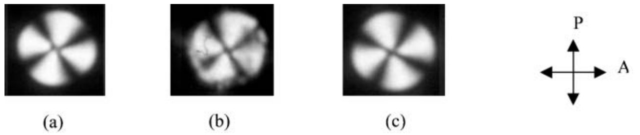


Fig. 11 Optical photomicrographs obtained under an applied dc electric field on the mesophase of compound **5**; (a) 12.3 V μm^{-1}; (b) 0 V; (c) −12.3 V μm^{-1}.

unchanged for several hours. This clearly confirms a ferroelectric switching (homochiral SmC_SP_F) for the mesophase of compound. The optical photomicrographs obtained with and without field are shown in Fig. 11(a)–(c). Thus from these different techniques we have established the ferroelectric properties for the higher homologues of series I.

Electro-optical studies were carried out on the mesophases of compounds of series II. The mesophases of compounds **8–11** did not show any response to an applied electric field at least up to 30 V μm^{-1}. However, those of compounds **12–14** responded to an applied electric field and the effect is more or less similar in all these three homologues.

For example, a sample of compound **13** was taken in a cell of uniform thickness of 6 μm, and subjected to a triangular-wave electric field. On applying a voltage of 130 V_{pp} at 40 Hz, two polarization current peaks per half cycle were obtained indicating the mesophase to be antiferroelectric. The calculated polarization is ≈105 nC cm^{-2}. The switching current response trace obtained for the mesophase of compound **13** is shown in Fig. 12.

To identify the tilt sense in the antiferroelectric phase of compound **13**, dc field experiments were carried out. The sample was cooled from the isotropic phase under a dc voltage of 5.5 V μm^{-1} and colourful circular domains which make an angle with respect to the polarizer/analyzer direction were obtained. Interestingly, the brushes in one domain (Domain 1) rotate in a clockwise direction whereas those in the other domain (Domain 2) rotate in a counter-clockwise direction. On reversing the polarity of the applied field these domains rotate in opposite directions. Thus, domains 1 and 2 are conglomerates having different tilt and polar directions. However, on terminating the applied field the extinction crosses orient along the direction of analyzer. This tristable switching confirms the antiferroelectric switching behaviour for this mesophase. The striking feature is the observation of antiferroelectric conglomerates in this compound. Optical photomicrographs showing the tristable antiferroelectric switching behaviour as well as the conglomerates are shown in Fig. 13(a–c).

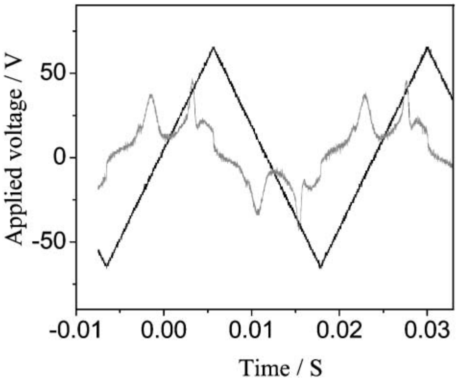


Fig. 12 Switching current response trace obtained for the mesophase of compound **13** by applying a triangular-wave voltage (130 V_{pp}, 40 Hz,); cell thickness 6 μm; saturated polarization value ≈105 nC cm^{-2}.

We have performed electric field experiments on the mesophases of compound **16**. It is interesting to note that all the three mesophases (SmA, SmC and SmX) did not show any response to an applied electric field at least up to 20 V μm^{-1}, indicating that the mesophases are achiral.

Comparison of the mesomorphic properties of compounds containing resorcinol and 3-hydroxybenzoic acid as central units

The mesomorphic properties of the compounds of series I can be compared with those of the isomeric compounds derived from resorcinol as the central unit.[15] The general structure of such compounds is shown in structure A. These compounds showed the well established[23] phase sequence $Sm_{intercal}$–Col_r–$SmCP_A$ as a function of increase in the terminal alkyl chain length. The compounds of series I showed Col_r–B_X (Col_{ob})–SmC_SP_F as a function of increasing alkyl chain length. The structure of this series of compounds differs from those derived from resorcinol with respect to the orientation of the ester linking group. As a result of this, the mesophase sequence completely changes and a novel mesophase has been obtained. This suggests that the charge distribution around the molecular structure is an important factor and is useful in designing new molecular architectures for bent-core compounds.

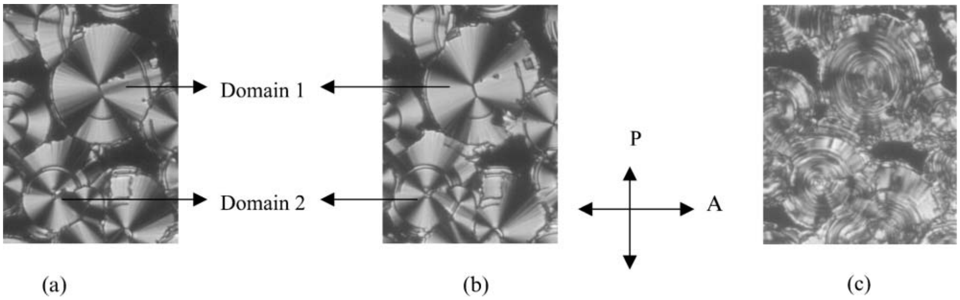
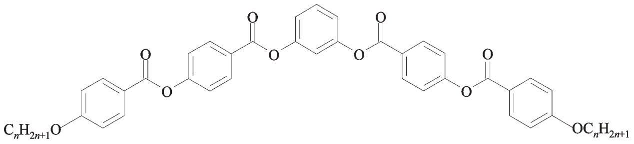
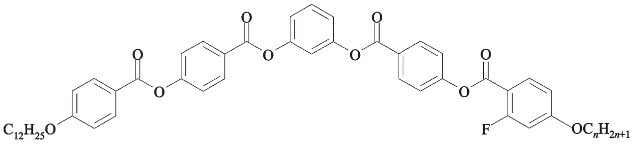


Fig. 13 The effect of dc field on the mesophase of compound **13**: (a) +5.5 V μm^{-1}; (b) −5.5 V μm^{-1}; (c) 0 V.



Structure A [15]

Similarly the mesophases exhibited by compounds of series II can be compared with those of the unsymmetrical compounds derived from resorcinol[16] (structure B). The compounds obtained from resorcinol show $\mathrm{Col_r}$ and $\mathrm{SmCP_A}$ phases, whereas compounds of series II show a $\mathrm{Col_r}$–$\mathrm{B_X}$ ($\mathrm{Col_{ob}}$)–$\mathrm{SmC_AP_A}$ phase sequence as a function of the increase in the number of carbon atoms in the alkyl chain. A comparison of these suggests that the compounds derived from resorcinol have lower transition temperatures than those derived from 3-hydroxybenzoic acid. The middle homologues of both the series I and II show a novel columnar oblique phase. The higher homologues exhibit a switchable homochiral mesophase ($\mathrm{SmC_SP_F}$ in series I and $\mathrm{SmC_AP_A}$ in series II). Thus, subtle changes in the chemical structure in these bent-core compounds result in varying mesomorphic behaviour. It is appropriate to mention here that it would be interesting to calculate the charge distribution around the molecule, the conformation of the molecule as a whole and the bending angle between the two arms in these closely related chemical structures, which may throw light on understanding the structure–property relationships in such bent-core compounds.



Structure B [16]

Conclusions

In summary, the synthesis of several unsymmetrical achiral BC compounds derived from 3-hydroxybenzoic acid has been carried out. The mesophases exhibited by these have been investigated by a number of different techniques. The lower homologues (**1** and **8**) exhibit the classical columnar phase with a rectangular lattice. The compounds with longer terminal chain lengths, *viz.* $n = 8$, 10 or 12 carbon atoms, in both the series show a novel columnar phase with an oblique lattice. Very interestingly, the mesophase of compounds **5**, **6** and **7** is smectic with ferroelectric properties whereas the analogous unsymmetrical compounds (**12–14**) with a fluorine substituent showed smectic antiferroelectric conglomerates. To the best of our knowledge this is first report of a columnar phase with an oblique lattice occurring between a $\mathrm{Col_r}$ and a polar smectic phase with ferro-/antiferro-electric properties. The compounds containing a biphenyl moiety showed only calamitic phases and no B phase could be observed. It has been shown that laterally unsubstituted compounds also exhibit ferroelectric properties though such compounds are very rare.

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