Odd-Even Effects in Bent-Core Compounds Containing Terminal N-Alkyl Carboxylate Groups

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Odd–even effects in bent-core compounds containing terminal \( n \)-alkyl carboxylate groups†

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Received 7th April 2006, Accepted 3rd August 2006

A homologous series of eleven five-ring symmetrical bent-core compounds containing terminal \( n \)-alkyl carboxylate groups were synthesized, characterized and their dielectric and electro-optical properties have been investigated. The lower homologues (\( n = 6–11 \)) of the series show \( B_2 \) structures with an interesting odd–even effect concerning their local director tilt and polar arrangements. This odd–even effect probably is due to steric (entropic) reasons, which are not suppressed by the relatively low polar interaction. Three of the middle homologues display a \( B_{T'} \) phase, which is bistable and shows linear electro-optical switching with a transition to the chiral antiferroelectric smectic phase at a lower temperature. The higher homologues (\( n = 16, 18 \)) exhibit only a \( B_{T'} \) phase.

Introduction

Banana-shaped mesogens, formed by compounds whose constituent molecules have a bent-core (BC) structure, have been the subject of intense investigations during the past decade. The macroscopic polar order and chirality of the mesophases generated from such systems have provided a good platform to probe further the possible usefulness of such materials in applications. Soon after the discovery\(^1\) of ferroelectricity in a mesophase of such a BC compound a clear understanding of the mechanism of both ferroelectric as well as antiferroelectric switching was given by Link \textit{et al.}\(^2\) Subsequently a variety of compounds with a bent molecular structure were synthesized by various groups and this has yielded a number of new phases and phase sequences. Many aspects concerning these BC compounds including the mesophases exhibited by them, the phase structures and the physical properties can be found in three excellent review articles.\(^3–5\)

Although a few thousand of such BC compounds have been synthesized and their mesomorphic properties investigated, a proper understanding of the structure–property relationships is still elusive. Amongst all the mesophases exhibited by BC compounds, the SmCP (\( B_2 \)) phases (two homochiral-\( SmC_{P_Y} \), \( SmC_{P_X} \) and two racemic- \( SmC_{P_Y} \), \( SmC_{P_X} \) structures) are not only frequently encountered but are also investigated most extensively. The \( B_2 \) phase and its variants show the most beautiful optical textures. The \( B_{T'} \) phase was first observed\(^6\) in a Schiff’s base BC compound derived from 2-nitroresorcinol. This fascinating phase was subsequently observed in a number of compounds obtained from 2-cyanoresorcinol.\(^7\) The \( B_{T'} \) phase occurring in this type of compounds and investigated so far do not switch electro-optically at least up to about 40 V \( \mu \text{m}^{-1} \) except for two antiferroelectric \( B_{T'} \) sub-phases.\(^7d\) However, very recently we have found\(^8\) a switchable \( B_{T'} \) phase even in this type of compounds containing strongly polar substituents.

Remarkably, there are a number of compounds, which do not contain strongly polar substituents but the mesophases exhibit the beautiful optical textures shown by the \( B_{T'} \) phase. These mesophases designated as \( B_2 \) respond to an applied electric field and both ferroelectric\(^9–11\) and antiferroelectric\(^12,13\) structures have been found. At the present time two different structural models for the switchable \( B_{T'} \) phase have been proposed. One model\(^14\) corresponds to a \( SmC_G \) structure with a triclinic symmetry where an out-of-layer polarization component is assumed. In the other model,\(^15\) a splay of polarization results in a modulated-undulated layer structure. It should be pointed out that in such a structure both in-layer and out-of-layer polarization components are possibly present at least at the defect areas.\(^16\)

In an earlier publication,\(^17\) we had discussed the mesomorphic properties of three homologues of a novel series of symmetrical BC compounds containing terminal \( n \)-alkyl carboxylate groups. It was shown that the higher temperature phase, designated as \( B_{T'} \) phase exhibits bistable but analogous linear electro-optical switching without any observable polarization peak. The lower temperature metastable phase could be identified as a homochiral antiferroelectric smectic phase.

We have now prepared the remaining compounds of this homologous series, which is represented by the general structure 1 and describe here their mesomorphic properties.

Experimental

The five-ring bent-core compounds were obtained by esterification of two equivalents of an appropriate 4-(\( 4 \)-\( n \)-alkoxy carbonylphenyliminomethyl)benzoic acid with 1,3-dihydroxybenzene using \( N, N' \)-dicyclohexylcarbodiimide.
(DCC) as coupling reagent and 4-(N, N-dimethylamino)pyridine (DMAP) as a catalyst. The detailed procedure for the synthesis of these compounds is reported elsewhere. All the synthesized compounds were purified through repeated crystallization using analytical grade solvents. The spectral and analytical data obtained for compounds 2–6, 10 and 11 is provided as Electronic supplementary information (ESI).†

The chemical structure of the synthesized compounds was confirmed through a combination of IR spectroscopy (Shimadzu FTIR-8400 spectrophotometer), NMR spectroscopy (Bruker AMX 400 spectrometer) and elemental analysis (Carlo-Erba 1106 analyser). IR spectra were recorded as nujol mull for intermediate compounds and as KBr discs for the target compounds. *H NMR spectra were recorded using deuteriochloroform (CDCl 3) or deuterated dimethylsulfoxide (DMSO-d 6) as solvents. Tetramethylsilane (TMS) was used as an internal reference.

Textural observations were carried out under a polarizing light microscope (Olympus BX50) equipped with a heating stage (Mettler FP82HT) and a central processor (Mettler FP90). The transition temperatures were determined from polarizing light microscopic observations as well as from the thermograms obtained on a differential scanning calorimeter (DSC, Perkin-Elmer calorimeter, Model Pyris 1D). Enthalpy values associated with the transitions were also determined from these thermograms. The instrument was calibrated using indium as a standard (154.6 °C, 28.56 J g⁻¹) and operated at a scanning rate of 5 °C min⁻¹ both on heating and cooling cycles.

X-Ray diffraction measurements were carried out using Cu-Kα radiation (λ = 1.54 Å) generated from a 4 kW rotating anode generator (Rigaku Ultrax 18) equipped with a graphite crystal monochromator. A sample was filled in a Lindemann capillary (diameter: 0.7 mm; wall thickness: 0.01 mm), sealed and placed in a heater the temperature of which was controlled to within ±0.1 °C. The sample was cooled from the isotropic phase and the diffraction pattern of the mesophase was recorded on a two-dimensional (Marresearch) image plate.

Electro-optical behavior and polarization measurements were carried out using commercially available cells (EHC, Japan; Cell gap 8 µm) and on 8 µm thick homemade test cells without insulating alignment layers. The liquid crystal cells were placed in a computer controlled hot stage (STC200F from Instec) and the phase sequences were investigated by polarizing microscopy (BX60 from Olympus). Polarization current measurements and electro-optical studies were carried out in the entire thermal range of the mesophase in 1 °C steps by employing the standard triangular-wave method. For these measurements a Digital Oscilloscope (HP 54600B), a Digital Multimeter (HP 34401A) and an Arbitrary Waveform Generator (HP 33120A) were used. Dielectric measurements were carried out by a Qaudtech 1920 precision LCR meter in the frequency range between 20 Hz and 1 MHz. DC field experiments were carried out using a regulated dual dc power supply (Aplab, LD 6401).

Results and discussion

Mesomorphic properties

All the compounds investigated are liquid crystalline except compound 1. The transition temperatures and the associated enthalpy values for these compounds are summarized in Table 1.

Compounds 2–6 exhibit the same type of mesophase, which are all enantiotropic. When a sample of compound 2, sandwiched between a glass slide and a cover slip was cooled from its isotropic state and observed under a polarizing microscope, a fan-shaped texture was seen (Fig. 1a). When the inner surfaces of the substrates were treated for homeotropic alignment, a schlieren texture was obtained (Fig. 1b) indicating a tilt of the optic axis with respect to the layer normal. This was confirmed by X-ray studies, which are described later.

Table 1. Transition temperatures (°C) and associated enthalpy values (in italics, kJ mol⁻¹) obtained for the compounds of series I

<table>
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<tr>
<th>Compound</th>
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<th>B2'</th>
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<td>142.0 84.5</td>
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<td>128.5 0.07</td>
<td>140.5 19.0</td>
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<td>131.0 80.0</td>
<td>—</td>
<td>—</td>
<td>136.0 17.0</td>
</tr>
</tbody>
</table>

* Abbreviations: Cr = crystalline phase; B2° = polar homochiral smectic phase with tilted molecules; B2' = switchable B2 phase showing bistability; B2 = polar smectic phase with tilted molecules in the layers; I = isotropic phase; Sample has crystal–crystal transition; enthalpy denoted is the sum of all such transitions; ( ) = monotropic transition.
Compounds 3 and 4 also exhibit similar textural behaviour. In contrast however, when samples of compounds 5 and 6 are cooled slowly from the isotropic state, lath-like textures develop with stripes running across them (Fig. 1c and d) and these are independent of temperature. This suggests the existence of a multidomain structure with synclinic tilt of the molecules in each domain and alternating molecular tilt directions from one domain to the next as reported earlier. Stripes are indicative of domain boundaries where the tilt direction changes. In fact similar textural patterns have been seen for the B2 phase exhibited by compounds derived from 1-substituted naphthalene 2, 7-diol as well as 4-bromo- or 4-chloro- resorcinol. On the basis of these observations the mesophase exhibited by compounds 2–6 has been identified as B2 (SmCP) phase. Their antiferroelectric or ferroelectric, and anticlinic or synclinic structures will be discussed later, on the basis of other observations.

Interestingly as reported by us earlier, compounds 7–9 display two mesophases, one enantiotropic and the other monotropic. The higher temperature phase exhibits textures consisting of helices, myelin-like patterns etc. when the respective isotropic liquids are cooled very slowly. This mesophase has been characterized as a B2′ phase while the lower temperature monotropic phase has been identified as a polar homochiral lamellar phase and designated as B2′ (similar to SmCpPA) phase. The physical properties of these phases have been discussed in detail earlier.

The mesophase exhibited by compounds 10 and 11 is the same and the textures shown by these are completely different from those of the lower homologues. For example, on slow cooling the isotropic phase of compound 10, an unusual texture develops (Fig. 1e) and in some other regions of the same sample circular domains (Fig. 1f) could also be seen. Although these textures are reminiscent of those seen for some columnar phases, XRD data indicates a lamellar phase. As we shall see later, this mesophase has also been characterized as a B2′ phase.

A plot of transition temperatures versus the number of carbon atoms in the terminal chain for this homologous series is shown in Fig. 2.

**X-ray diffraction (XRD) studies**

In order to obtain more information on the phase structures, X-ray measurements were carried out on mesophases obtained on cooling the respective isotropic liquids. The diffraction patterns of all the samples showed a diffuse peak in the wide-angle region (around 4.2Å) confirming the fluidity of the

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**Fig. 1** Photomicrographs showing typical textural patterns. Compound 2: (a) in an ordinary glass plate, \( T = 141 \) °C; (b) in a substrate treated for homeotropic alignment, \( T = 135 \) °C. Compound 5 in an ordinary glass slide; (c) \( T = 142 \) °C; (d) \( T = 135 \) °C. Compound 10 sandwiched between an ordinary glass slide and a cover slip; (e) and (f) different regions of the same sample obtained on slow cooling the isotropic liquid, \( T = 137.8 \) °C.

**Fig. 2** A plot of transition temperatures as a function of number of carbon atoms in the terminal chain for compounds of series I.

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*Soft Matter, 2006, 2, 875–885* | 877

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chains. In the small angle region of the patterns, several Bragg reflections were obtained which are periodic. This clearly indicates a layer ordering in the mesophase. For example, mesophase of compound 2 showed three Bragg reflections in the small angle region corresponding to distances of 37.6 Å, 19.0 Å and 12.7 Å, which are in the ratio 1 : 1/2 : 1/3. An X-ray angular intensity profile obtained for the same sample is shown in Fig. 3. The first order layer spacing is smaller than the measured molecular length considering an extended all-trans conformation of the chains and a bend angle of 120°, indicating a tilted director structure. For sample 2 a tilt angle of about 45° was estimated using the relation \( \cos \theta = d / l \) (\( d \) = measured layer spacing; \( l \) = calculated molecular length). A molecular model of compound 2 used to calculate the molecular length.

A plot of \( d \)-spacing (Å) as a function of number of carbon atoms in the terminal \( n \)-alkyl chain is shown in Fig. 5. It is evident from the plot that, the layer spacing (\( d \)) increases linearly with the number of carbon atoms in the terminal chain. The increment in \( d \) per methylene group decreases in the higher homologues probably due to the fact that the longer chains may assume gauche conformation as observed in a number of long terminal chain containing calamitic mesogens.

**Table 2** The layer spacing (Å) and the corresponding Miller indices (shown in parentheses) obtained for the compounds of series I.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( n )</th>
<th>( d )-spacing/Å</th>
<th>Temperature / °C</th>
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<td>40.7(01), 20.6(02)</td>
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<td>42.9(01), 21.5(02)</td>
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<td>125</td>
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<td>7*</td>
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<td>45.5(01), 22.7(02), 15.2(03)</td>
<td>135</td>
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<tr>
<td>8*</td>
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<td>46.6(01), 23.5(02)</td>
<td>130</td>
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<td>10</td>
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<td>50.9(01), 25.5(02), 17.1(03)</td>
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</tr>
<tr>
<td>11</td>
<td>18</td>
<td>53.2(01)</td>
<td>125</td>
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</table>

* The layer spacing observed remain the same in the lower temperature phase, too.

**Dielectric measurements**

Compound 2 shows a large dielectric constant (~100) at low frequencies (see Fig. 6a, b) indicating a ferroelectric behaviour. The dielectric relaxation process is far from a single Debye relaxation as the Cole–Cole plot in the inset Fig. 6b shows the existence of a broad range of relaxation processes with relaxation frequencies ranging between less than 100 Hz and several kHz. It should be mentioned here that the relaxation frequencies \( f_r \), which are determined by the frequency where \( \varepsilon'' \) have a maximum are also indicative of the phase. In ferroelectrics \( f_r < 10 \) kHz, in antiferroelectrics \( f_r > 100 \) kHz, whereas in dielectrics \( f_r > 1 \) MHz.

Dielectric measurements of compound 3 indicate an antiferroelectric (AF) local arrangement, as the static susceptibility increase is small in the mesophase \( (\Delta \chi \sim 1) \) as compared to the isotropic steady susceptibility (Fig. 6c, d). Compound 6 has a relatively small dielectric susceptibility, \( \Delta \chi \sim 5 \) (i.e., less than that for 2, but larger than for 3. On the other hand, the threshold field for switching \( E_{th} \) for compound 6 is less than that for 3 and larger than for 2) in the mesophase range. The relaxation frequency range is relatively wide varying between 1 and 50 kHz (Fig. 6e, f).

**Electro-optical investigations**

**Ac field experiments.** Electro-optical behaviour of the mesophases of compounds 2–11 was investigated in ITO coated cells of thickness 8 µm without any alignment layers. Compound 2 shows a single polarization peak under a triangular-wave electric field even at very low frequencies (~0.1 Hz) indicating a ferroelectric (FE) switching behaviour. However, the peak position is not characteristic of the one obtained in classical FE switching in which case the peak appears after the applied voltage crosses zero.\(^{20}\) As can be seen in Fig. 7a, in the present case, the peak is centred at about the zero-crossing of the applied voltage. This gives an indication that the two polarization peaks of an AF state would have merged following a slow relaxation process from field induced FE to AF ground state. In order to confirm this, we have
employed a modified triangular-wave method in which a time gap has been introduced at zero voltage. The single peak separates into two, confirming AF behaviour (see Fig. 7b). The integrated area under the curve gives a polarization value of 160 nC cm$^{-2}$. It is very interesting to point out here that the polarization peak appears basically without any threshold (below 0.25 V \(\mu\)m$^{-1}$). The switching time as determined by the positions of the polarization current maxima following fast field reversal shows approximately 1/$E$ dependence (Fig. 7c).

To gain a better understanding of the nature of polarization we have carried out polarization current measurements under rectangular fields with dc offsets. In case of FE switching one does not expect any polarization current when the offset is over 50% of the peak-to-peak value, i.e. there is no sign inversion, whereas for AF or paraelectric situations one sees current even in this case. As can be seen from Fig. 7d, for material 2 polarization peaks were detected even when the offset is more than 50%. Another important feature of this

Fig. 6  Left column (a, c, e): Temperature dependences of the low-frequency (2 kHz) dielectric constants. Right column (b, d, f): Dielectric spectra at various temperatures. Top row—compound 2; Middle row—compound 3; Bottom row—compound 6.
graph is that both the integral area and peak position are decreasing with increasing offset.

Similar electro-optical behaviour was observed for compound 4, too.

Compounds 3 and 5 show two distinct peaks under triangular electric field above a threshold of 5 V µm⁻¹ (Fig. 8a) thus indicating an AF switching. The integrated area shows a relatively low polarization value of 85 nC cm⁻².

The “non-perfect” peaks are probably due to an unusual kick-back effect seen in the polarization current following fast field-reversal (Fig. 8b). This kick-back effect appears as a peak in the opposite direction after the main peak levels off. It indicates either overshooting of the director rotation or, based on the small plateau after the decay of the main peak, it is a kind of backflow effect induced by the reverse polarization current.

For compound 6, the time dependence of the polarization current under triangular electric field indicates ferroelectricity, since only one peak was observed even at a low frequency of about 1 Hz. This polarization peak appearing near zero electric field looks like polarization peaks obtained for helical SmC* materials. The current response traces obtained under a triangular-wave field with a frequency of 23 Hz and 4 Hz are shown in Fig. 9a and b respectively. However, the experiments employing modified triangular-wave showed two peaks per half period of the applied voltage indicating AF behaviour.

We have also investigated the polarization reversal currents at different offset values. Similar to the behaviour of compound 2, the polarization peak does not disappear at 50% of offset level. However in this case the switching time increases and broadens at offset level equal or larger than 50%, and the peak disappears above 60% offset level (Fig. 9c). This indicates AF behaviour with threshold for relaxation from the field induced FE state back to the antiferroelectric state at about 1.2 V µm⁻¹. The FE to AF switching time, as determined from the switching time at 50% offset, ranges between 50 to 180 µs which agrees well with the dielectrically observed range of relaxation frequencies. It is interesting to point out here that a single polarization peak was observed under triangular field down to less than a second, whereas there is relaxation to the AF state after fast field removal with relaxation time less than 200 µs.

Such a ferroelectric-like behaviour of the B₂ phase shown by compounds 2, 4 and 6 has also been observed in some asymmetric bent-core compounds reported recently.²¹

The electro-optical investigations for the B₇' and B₉' mesophases of compounds 7–9 have already been discussed.¹⁷ In contrast, compounds 10 and 11 exhibit only one phase which shows optical switching on application of an electric field without any corresponding polarization peak similar to the B₇' phase of compounds 7–9.¹⁷

Fig. 7 Electric current responses in the mesophase of compound 2; (a) triangular-wave, 150 V pp, 20 Hz, 130 °C; (b) modified triangular-wave, 150 V pp, 20 Hz, 130 °C; (c) Electric field dependence of the switching time at 130 °C determined from the peak positions of the time dependence of the polarization current following fast field reversal; (d) Time dependences of the polarization current following step-wise field reversal with different offset fields in % of the peak-to-peak value of the reversed field.

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DC field experiments. We have also carried out dc field experiments in order to gain a better understanding of the switching behaviour of the mesophase. Polyimide coated ITO glass cells of thickness 8 μm were used for the experiments. On slow cooling of the isotropic liquid of compound 2 under a field of 5.5 V μm\(^{-1}\), circular domains were obtained in which extinction brushes were oriented along the crossed polarizers which suggests an anticlinic organization of the molecules in the mesophase. The orientation of the brushes remains same either on reversing the field or on removing the field. However, a slight decrease in the birefringence was observed on switching off the field. The small difference in the birefringence between the field off and field on states can be explained by assuming that tilt direction of the anticlinic layers is different in the field off and on states. The texture obtained on turning off the field was stable for several hours. The photomicrographs obtained under these conditions are shown in Fig. 10a.

These observations indicate either a bistable switching process of FE structure, or the relaxation of the field-induced FE states to the ground state AF structure via the rotation of

Fig. 8 Time dependence of polarization current for compound 3; (a) under triangular voltage waveforms at 138 °C; (b) following fast field reversal at 136 °C. Note the negative hump after the positive one for high fields.

Fig. 9 Polarization measurements on compound 6 at 136 °C. (a) 23 Hz; (b) 4 Hz (The polarization is 60 nC cm\(^{-2}\)); (c) polarization current under rectangular fields with offset. The peak-to-peak value of the rectangular field is 14.5 V μm\(^{-1}\) for all cases; (d) electric field dependence of the switching time as determined from the peak position of the polarization current.
Fig. 10 (a) Photomicrographs obtained for the mesophase of compound 2 under dc electric field at 140.5 °C; (b) photomicrographs obtained for compound 4 under dc electric field at 142 °C; (c) possible molecular organization for the mesophase of compound 2 and 4 under +E, 0E and −E.

the molecules along their long molecular axis. Such a relaxation process preserves the orientation of the molecules (clinicity) but results in inversion of layer chirality. Although the ac field experiments (modified-triangular and rectangular fields) indicate an AF ground state, the high dielectric constant observed is not compatible with such an AF structure. To explain these observations we assume an anticlinic FE organization locally and an AF organization macroscopically. In other words, polarization does not get cancelled out in the clinicity after a few layers and this is repeated in the bulk. The stripes are indicative of the region where there is an alternation of clinicity. Under the field clinicity becomes uniform and hence stripes disappear. However, Folcia et al. have suggested a reinterpretation of this model for the racemic states (SmCPA) of the B2 phase in bulk samples. This is because the field induced SmCPA to SmCpF transition contradicts the Curie law, as the symmetry of the SmCpF phase (C2v) is not the intersection between the point group of SmCPA (C2h) and the point group of the electric field (C1v). Therefore, it was suggested that the Curie law could be satisfied if an additional periodicity in the SmCPA structure exists along the layer normal. The equally spaced anticlinic-ferroelectric interlayer boundaries (SmCpF) correlate near the boundaries of the FE domains, but on the average it is anticlinic organization, hence the orientation of the brushes are along the crossed polarizers at zero field.

Similar optical behaviour was also observed for compound 4 under dc electric field and the photomicrographs obtained under field are shown in Fig. 10b.

Compound 3 also grows in the form of circular domains on slow cooling from the isotropic state under the field. Two kinds of domains were observed (C and R in Fig. 11a). In domain C, the extinction brush is tilted in a clock-wise direction with respect to the crossed polarizers, whereas in domain R the extinction cross is oriented along the polarizers. On reversing the polarity of the applied field, the extinction cross in domain C tilts in a counter clock-wise direction but the domain R is unaffected. On switching off the field, the dark brushes in domain C orient along the polarizers and in domain R birefringent stripes running across the layer normal are observed.

These observations suggest that domain C is chiral with a SmCpF structure under the field, which relaxes to chiral SmCPA structure on removal of the field. Domain R represents a racemic structure. According to the model suggested by Link et al. the racemic structure has a synclinic AF organization (SmCPA) at zero voltage with an alternation in the clinicity after a few layers and this is repeated in the bulk. The stripes are indicative of the region where there is an alternation of clinicity. Under the field clinicity becomes uniform and hence stripes disappear. However, Folcia et al. have suggested a reinterpretation of this model for the racemic states (SmCPA) of the B2 phase in bulk samples. This is because the field induced SmCPA to SmCpF transition contradicts the Curie law, as the symmetry of the SmCpF phase (C2v) is not the intersection between the point group of SmCPA (C2h) and the point group of the electric field (C1v). Therefore, it was suggested that the Curie law could be satisfied if an additional periodicity in the SmCPA structure exists along the layer normal. The equally spaced anticlinic-ferroelectric interlayer boundaries (SmCpF) correlate at the domain boundaries: light blue region in the model shown in Fig. 11e) meet this requirement. This organization of the molecules changes the symmetry from C2h to C2v. These anticlinic-ferroelectric interlayer boundaries are observed as stripes at zero voltage. However, on application of the field, the clinicity becomes uniform and hence the stripes disappear.

Compound 5 also exhibits racemic (R) and chiral (C) domains under the field (Fig. 11b). A possible molecular organization in the domains C and R are shown in Fig. 11 d and e, respectively.

When the isotropic liquid of compound 6 was cooled slowly under the field a fan-shaped texture with extinction direction oriented along the crossed polarizers was observed. On turning off the field, stripes developed on the texture but the orientation direction of the extinction cross remained the same. This suggests a racemic antiferroelectric ground state structure similar to domain R described for compound 3. However, a
single polarization peak was observed for the mesophase under a triangular-wave electric field even at very low frequencies and at very low threshold voltages. On the basis of this observation we can also consider an anticlinic ferroelectric local structure for the mesophase, where the polarization averages out in a scale larger than layer spacing. Therefore the stripes we observe at zero field could be due to this random orientation of polarization. Hence, it is difficult to predict the exact ground state structure of the mesophase of compound 6.

The photomicrographs obtained for the mesophase of compounds 6 under the field are shown in Fig. 11c.

The phase behaviour of compounds 7–9 under dc electric field has been described earlier. On slow cooling a sample of compound 10 from the isotropic state under a dc electric field of 12 V μm⁻¹ the mesophase develops in the form of dark and bright domains which reverse on reversing the polarity of the applied field. However, removal of the field does not affect the texture, except for a small change in the birefringence. The optical textures obtained for the B₁ᵣ phase of compound 10 under the field and at zero field are shown in Fig. 12. This bistable switching indicates FE behaviour for the mesophase. But interestingly, no polarization peak was observed during the switching process on application of a triangular-wave electric field. Similar observations were made for compound 11, too. This switching process is very similar to the linear bistable switching observed for the B₁ᵣ phase of homologues 7–9, hence, we assume that they have the same structure, as well.

**Conclusions**

A homologous series of novel five ring bent-core compounds containing n-alkyl carboxylate groups in the terminal positions have been investigated. The lower homologues (compounds 2–6) exhibit macroscopically antiferroelectric B₂ phase. The middle homologues (compounds 7–9) exhibit two mesophases: the lower temperature one is identified as a B₂ᵣ (similar to SmCaPₐ phase), whereas the higher temperature phase is characterized as a B₁ᵣ phase, which is bistable and shows analogous linear electro-optical switching. The homologues 10 and 11 exhibit only a single B₁ᵣ phase.

It is interesting to point out here that, although the mesophase observed in the lower homologues (compounds 2–6) is macroscopically non-polar, an odd-even type alteration of the nanoscopic director organization can be observed as a function of the number of carbon atoms (n) in the terminal chains. The mesophases of compounds 2, 4 and 6 (for n = 7, 9 and 11, respectively) appear to have locally anticlinic FE structure and the polar order averages out in a range much larger than the layer spacing d. However, the mesophase of...
compounds and this behaviour has been attributed to the difference in the interlayer steric interactions.

The observed odd–even effects in the present series of compounds probably have entropic reasons. The end chain units prefer to be parallel because the out of layer fluctuations are allowed in this case. For odd carbon atoms the end segments of the neighbouring molecules are parallel to each other when the tilt of the molecular planes are antiparallel, whereas for n even the end segments are parallel for synclinic situation. Although the observations show that polar order averages out on long range even for the odd homologues, the correlation length \( \xi_P \) of the ferroelectric order shows an odd–even effect, too: \( \xi_P \gg d \) for odd \( n \) and \( \xi_P \sim d \) for even \( n \).

This is corroborated with the observed \( \Delta T \) and \( E_{th} \) values. We emphasize that these odd–even effects became possible, because the materials have relatively low polarization, which means that the polar interaction does not suppress the steric effects.

Acknowledgements

The authors wish to thank Ms. K. N. Vasudha for technical support and the NMR Research Center, Indian Institute of Science, Bangalore for recording the NMR spectra. A. Jakli acknowledges financial support from National Science Foundation DMS-0456221.

References


Fig. 12 Textures of the B\(_2\) phase of compound 10 obtained under dc electric field at 128 °C.
16 C. Bailey and A. Jakli, to be published.