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Bistable Linear Electro-Optical Switching in the B-7' Phase of Novel Bent-Core

S. Umadevi
Antal Jakli, Kent State University - Kent Campus
B. K. Sadashiva

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Bistable linear electro-optical switching in the B$_7'$ phase of novel bent-core molecules†

S. Umadevi,* A. Jáklí and B. K. Sadashiva*†

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Three novel symmetrical bent-core compounds were synthesized where the terminal alkoxy linkages of the original bent-core mesogen forming a B$_2$ phase was converted to n-alkyl carboxylates. It is found that instead of the B$_2$ phase, all three compounds exhibit a transition between B$_7'$ and B$_9$ mesophases. The physical and electro-optical properties have been investigated by polarizing optical microscopy, differential scanning calorimetry, X-ray diffraction and electric field experiments. The higher temperature B$_7'$ phase has been shown to exhibit bistable but analogous linear electro-optical switching without any observable polarization peak. We analyze two theoretical models and find that a local triclinic symmetry may be responsible for the unusual electro-optical switching.

Introduction

The study of chiral liquid crystalline phases formed by compounds composed of achiral molecules is one of the important and exciting topics of current research activity. Since the discovery of electro-optical switching in the mesophase of an achiral compound whose constituent molecules have a bent-core structure, there have been numerous studies on the synthesis of such compounds as well as on the mesophases exhibited by them. Although the identification of mesophases by optical textures is somewhat easy in calamitic systems, it is not the case with bent-core mesogens. For example, the B$_2$ mesophase exhibited by many derivatives of 2-nitro- and 2-cyano-resorcinol show a variety of beautiful textures. One such texture is the characteristic growth of a spiral domain obtained on slow cooling of the isotropic liquid. The B$_7$ mesophase occurring in this type of compounds and investigated so far do not switch electro-optically at least up to about 40 V µm$^{-1}$, except two antiferroelectric B$_7$ sub-phases and probably they have a columnar structure. However, very interestingly there are a few other systems not containing these highly polar substituents, which also show spiral growth patterns, and have also been assigned the symbol B$_7$, but they respond to an externally applied electric field. They typically show ferroelectric structures, although a couple of examples for antiferroelectric structure was also found. Presently two different models about the structure of the switchable B$_7$ phase have been proposed. One model corresponds to a double tilted SmC$_G$ phase, i.e., an out-of-layer polarization component is assumed. The other model, on the basis of observed layer modulation assumes modulated in-layer polarization structures. It is very well possible, however that both in-layer and out-of-layer polarization components are present, at least at the defect areas.

Although a large number of different types of bent-core mesogens have been synthesized, and in many cases the mesophases are characterized as switching ferroelectrically or antiferroelectrically, there are only a few compounds in which a transition between two such phases have been seen.

Herein, we report the synthesis of three new five-ring bent-core compounds which exhibit some unusual electro-optical switching characteristics. These compounds have the general chemical structure which is symmetrical and contain two terminal n-alkyl carboxylate groups. Note that the well known prototype bent-core materials have the same core, but contain terminal n-alkyl or n-alkyloxy group. As we will see later that this “small” difference induces significant changes in the phase behavior.

Experimental

Chemical synthesis

The symmetrical five-ring bent-core compounds were prepared following a synthetic pathway shown in Scheme 1. 4-Nitrobenzoic acid and 4-formylbenzoic acid were obtained...
commercially and used without further purification. 4-Nitrobenzoic acid 1 was esterified with an appropriate aliphatic alcohol using N,N'-dicyclohexylcarbodiimide (DCC) and 4-(N,N-dimethylamino)pyridine (DMAP). Then, the nitro group of ester 2 was reduced using 5% Pd/C catalyst in an atmosphere of hydrogen to yield the amine ester 3. This was reacted with 4-formylbenzoic acid in refluxing toluene in the presence of a trace of acetic acid to furnish compound 4. In the final step two equivalents of compound 4 was treated with 1,3-dihydroxybenzene in the presence of DCC and DMAP which provided the required mesogenic materials 1.

All the compounds were purified by column chromatography followed by repeated crystallization using suitable analytical grade solvents. As an example, procedure for the synthesis of compound 1a is given below. Compounds 1b and 1c were synthesized following a similar procedure. The detailed procedure for preparing the intermediates of compound 1a and the physical data obtained for all these compounds as well as for compounds 1b and 1c is available as electronic supplementary information (ESI)†.

1,3-Phenylene-bis-[4-(4-n-dodecyl oxy carbonylphenylinomethyl)benzoate], 1a. A mixture of 1,3-dihydroxybenzene (0.05 g, 4.6 × 10⁻⁴ mol), 4-(4-n-dodecyl oxy carbonyl phenylinomethyl)benzoic acid 4 (0.4 g, 9.2 × 10⁻⁴ mol) and a catalytic amount of DMAP in dichloromethane (20 ml) was stirred for 15 min at room temperature. To this stirred mixture DCC (0.2 g, 10.0 × 10⁻⁴ mol) was added and stirring continued for a further 12 h. The precipitated N,N'-dicyclohexylurea was filtered off and washed with excess of chloroform. The solvent from the filtrate was evaporated and the residue obtained was passed through a column of basic alumina using chloroform as an eluant. The material obtained on removal of chloroform was further purified by repeated crystallization using a mixture of chloroform and acetonitrile. Yield 0.35 g (81%); mp 134.0 °C; IR (KBr) ν_max: 3084, 2954, 2918, 2848, 1745, 1737, 1712, 1596, 1278, 1168 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.54 (s, 2H, –CHL–N–), 8.32 (d, 4H, 3J 8.31 Hz, Ar–H), 8.10 (d, 4H, 3J 8.52 Hz, Ar–H), 8.07 (d, 4H, 3J 8.36 Hz, Ar–H), 7.53 (t, 1H, 3J 8.18 Hz, Ar–H), 7.26 (d, 4H, 3J 8.48 Hz, Ar–H), 7.24–7.21 (m, 3H, Ar–H), 4.33 (t, 4H, 3J 6.64 Hz, 2–Ar–COO–CH₂–), 1.82–1.75 (quin, 4H, 3J 7.0 Hz, 2–Ar–COO–CH₂–CH₂–), 1.55–1.27 (m, 36H, 2–(–CH₂–)₉), 0.88 (t, 6H, 3J 6.8 Hz, 2–(–CH₃)); C₆₀H₇₂N₂O₈ requires C 75.95, H 7.65, N 2.95; found C 76.4, H 7.76, N 2.64%.

Measurements

Structural characterization of the compounds was carried out using IR, NMR and elemental analysis. IR spectra were
recorded using Shimadzu FTIR-8400 spectrophotometer. $^1$H NMR spectra were recorded on a Bruker AMX 400 spectrometer with tetramethylsilane as an internal standard. The elemental analysis was carried out using Carlo-Erba 1106 analyser.

The mesophase behaviour was studied using polarizing optical microscopy, X-ray diffraction and electro-optical techniques. The textural observations were carried out using an Olympus BX50 (or Olympus BX60) polarizing optical microscope provided with a Mettler FP82HT heating stage and a Mettler FP90 central processor. The transition temperatures and the associated enthalpy values were obtained from thermograms recorded on a Perkin-Elmer (Model Pyris 1D) differential scanning calorimeter (DSC), which was calibrated using pure indium as a standard. X-Ray diffraction measurements were carried out on powder samples using Cu Kα ($\lambda = 1.54$ Å) radiation from a Rigaku Ultrax 18 rotating anode generator (4 kW) monochromated with a graphite crystal. The samples were held in sealed Lindemann capillary tubes (0.7 mm diameter) and the diffraction patterns of the mesophase were collected 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 or 6 μm) and on 5 μm thick homemade test cells with antiparallel rubbed polyimide coated substrates. 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 SmCP ranges in 1 °C steps by employing the standard triangular-wave method. For these measurements a Digital Oscilloscope (HP 54600B), a Digital Multimeter (HP34401A) and an Arbitrary Waveform Generator (HP 33120A) were used. The d.c. field experiments were carried out using a regulated dual dc power supply (APLAB, Model LD6401).

**Results**

The phase behaviour of the three compounds Ia–c investigated together with the transition enthalpy values determined are given in Table 1. Although only one mesophase was observed on heating the crystals, transition to a metastable state was clearly seen both under a polarizing microscope and on a DSC thermogram. A typical DSC thermogram obtained for compound Ib is shown in Fig. 1. The two mesophases were identified and characterized as follows. On slow cooling the isotropic phase of compound Ia, one could see helical structures (Fig. 2a) as well as other beautiful textures (Fig. 2b and c) that are normally seen for a B$^7$ phase.

On cooling the 8 μm thick samples under zero electric field we find a clear textural transition at 128 °C wherein the focal-conic domains (Fig. 3a) disappear and a finger-print texture appears (Fig. 3b). Similar behaviour was observed for compounds Ib and Ic. This transition does not show up in the textures of 5 μm thick films (Fig. 3c and d), and the accompanying enthalpy is very small showing a second order transition.

Dielectric spectra of a 5 μm cell show relaxations in the 130 kHz to 35 kHz range at decreasing temperatures (Fig. 4a). This indicates antiferroelectric type in-layer ordering. The increase in $\varepsilon''$ above 500 kHz is electrode effect ($1/(\varepsilon R_{ITO}C_{LC}) \sim 1$ MHz). The temperature dependence of the dielectric constants $\varepsilon'$ and $\varepsilon''$ at 2 kHz are shown in Fig. 4b. They show only one phase between the clearing point and crystallization that takes place at around 100 °C. On heating the melting takes place at around 131 °C.

![Fig. 1](https://example.com/fig1.png)  
**Fig. 1** DSC thermogram of a sample of compound Ib; (a) heating cycle, (b) cooling cycle; rate 5 °C min$^{-1}$; the transition between the two states is indicated by an arrow; inset shows the expanded region of this transition.

![Fig. 2](https://example.com/fig2.png)  
**Fig. 2** (a) A texture of the helical filamentary growth pattern obtained on cooling the isotropic liquid of compound Ia, 139.8 °C; (b) and (c) other beautiful textures obtained on slow cooling the isotropic liquid of compound Ia, 139 °C.
The temperature dependence of the transmittance of the 5 \( \mu \)m film shows smooth variation at zero field, but indicates clear transition at 128 \( ^\circ \)C, when the material is cooled under a rectangular electric field of 13 V \( \mu \)m\(^2\) (Fig. 5c). Also note in Fig. 5c that the isotropic-smectic transition is larger when the sample is cooled under an electric field. In Fig. 5d we have plotted the electric field dependence of the shift of phase transition temperature \( \Delta T \). It can be seen that \( \Delta T \) is proportional to the electric field, which indicates the presence of ferroelectric polarization that forms along the electric field. Knowing the transition enthalpy (see Table 1) one can estimate the polarization at the transition using the modified Kirkwood–Helfrich equation (neglecting the dielectric interaction), which gives that

\[
P_0 = \frac{\Delta T \Delta H \rho}{E T_0 M}
\]

where \( T_0 \) is the transition temperature at \( E = 0 \), \( \Delta H \) is the transition enthalpy, \( \rho \) is the mass density and \( M \) is the molecular weight. With \( \Delta H = 18.5 \text{ kJmol}^{-1} \), \( M = 0.948 \text{ kgmol}^{-1} \), \( T_0 = 401 \text{ K} \), \( \rho \sim 10^3 \text{ kgm}^{-3} \), and \( \Delta T = 0.5 \text{ K at 15 V \( \mu \)m}^{-1} \) (Fig. 5d) we get \( P_0 = 166 \text{ nC cm}^{-2} \). This value actually is quite usual for bent core materials of this type of molecular structures.

The textures observed on cooling under strong electric fields, also show the clear difference between the phase above and below 128 \( ^\circ \)C even for the 5 \( \mu \)m cell (Fig. 5). This unambiguously shows that we have two mesophases, which we tentatively label as B\(_{9}^7\) for the higher temperature phase and B\(_2\) for the lower temperature phase.

**X-Ray diffraction measurements**

The X-ray diffraction (XRD) pattern of an unoriented sample of each of the three compounds indicated a lamellar ordering of the molecules in the two mesophases. For example, the XRD pattern of a powder sample of compound I\(_{a}\) at 135 \( ^\circ \)C exhibited three reflections in the small angle region with periodicities of 45.5 Å, 22.7 Å and 15.2 Å indicating a well-defined smectic ordering. The first order layer spacing \( (d = 45.5 \text{ Å}) \) is less than the measured molecular length assuming an all-trans conformation of chains and a bend angle of 120\(^\circ\) (\( L = 66.5 \text{ Å for I}_{a} \)) indicating tilt of the molecules in the mesophase. The diffuse peak at 4.5 Å in the wide-angle region is indicative of liquid-like in-plane order. The layer spacing was found to be temperature independent suggesting that both mesophases are lamellar in nature. The X-ray diffractogram obtained for the mesophase of compound I\(_{a}\) at 135\(^\circ\)C is shown in Fig. 6.

**Electro-optical investigations**

The electro-optic switching properties of these two phases are also different and their analysis helps us to identify the structures of the phases. During switching in the B\(_{9}^7\) phase, above about 6 V \( \mu \)m\(^{-1}\) field needle like domains form, which rotate about their long axes (similar observations were made by Rauch et al.\(^\text{9}\) on another material), but they do not change the birefringence or optic axis up to a field strength of about...
Switching off the field at this stage, a relaxation to the original low birefringence state occurs. Above 12 V μm⁻¹ the birefringence of the needles increases (color changes to blue), and the domains start to glue together. Above 15 V μm⁻¹ field, the needles become glued together and a relatively smooth texture forms, where the optic axis rotates with the sign of the electric field, as can be seen in Fig. 7b and c. This state is bistable, i.e., the optic axis stays and the birefringence changes only slightly (blue changing to violet, shows a decrease of the birefringence) after field removal. These indicate polar nature of the switching, but interestingly as we will show below no polarization peak could be observed during this switching.

The switching in the B₁₂ phase is also quite complex (Fig. 8). When cooled from B₁ from fields above 12 V μm⁻¹ the switching between high birefringent states prevail, but it is not bistable, and a smooth yellow (low birefringence) texture forms after switching off the field. This behavior can be understood in terms of a chiral antiferroelectric texture, i.e., SmCaPA at zero field which becomes SmC₃F under a strong field. However, even if we keep applying the strong rectangular field the texture transforms eventually (in about 10 min) to the low birefringent texture that does not show rotation of the optic axis. The same scenario occurs when we cool the material at zero field from the B₁₂ phase. At zero field there are some stripes observable, as is usual for a synclinic structure, but now it does not result in high birefringence, which shows that the synclinic tilt plane is parallel to the smectic layers.

Additional information about the mesophase behaviour was obtained from the dc field experiment. On slow cooling the isotropic liquid of compound Ia in a 8 μm cell into the

![Image](attachment:image.png)

Fig. 7 Electro-optical observations in the B₁₂ phase. (a) E = 12 V μm⁻¹, f = 13 Hz, T = 136 °C; (b) and (c) E = +18 V μm⁻¹ and E = −18 V μm⁻¹, T = 132 °C; (d) E = 0 after turning off from E = −18 V μm⁻¹. (bar indicates 0.1 mm length).
mesophase \((T = 137 \,^\circ C)\) under an applied electric field of 130 V, a circular domain with extinction cross making an angle with respect to the polarisers was observed. On reversing the polarity of the applied field the extinction cross tilts in the opposite direction and remain unchanged on removal of the field, indicating a synclinic ferroelectric state for the higher temperature mesophase \((SmC_{\alpha}PF)\). The bistable states thus obtained were stable for several hours. However, on cooling under the same conditions to 128 \(^\circ C\), and terminating the field, the extinction cross oriented along the polariser and analyser directions. Hence, the switching process is clearly tristable and indicates an anticalinic antiferroelectric state for the lower temperature phase \((SmCaPA)\). The bistable switching circular domains obtained for compound Ia at 137 \(^\circ C\) and the tristable switching circular domains obtained at 125 \(^\circ C\) are shown in Fig. 9.

For further understanding of the phase structure we have measured the polarization current under a triangular-wave electric field. The typical results are shown in Fig. 10. In the B2 phase, till 40 V \(\mu m^{-1}\) no polarization current peak was observed (Fig. 10a). But interestingly a bistable linear electro-optical switching was observed. In the B2 phase an antiferroelectric type double peak appears (Fig. 10b, integrated current \(\sim 55 \, nC \, cm^{-2}\) at 126 \(^\circ C\)) at much lower threshold field (about 9 V \(\mu m^{-1}\)) than the threshold for the bistable linear electro-optical switching observed in the B2 phase. This polarization current curve does not change although a textural change was observed on prolonged application of field (Fig. 8c) indicating that the stable B2 phase is also antiferroelectric.

**Discussion**

The observations revealed complex electric field and temperature dependent transitions of these symmetric and relatively simple materials. The B2 phase has chiral SmC,PA structure, which shows chiral switching for a while when cooled from the B2 phase. As a function of time however, it relaxes to a synclinic (racemic) antiferroelectric structure. An even more extraordinary feature of our observations is that of linear electro-optical switching without observable polarization current peak (electroclinic-type switching) and the simultaneous bistability observed in the thermal range of the B2 phase.

First we try to explain this behavior by the modulated in-plane polarization model. According to this model the smectic layers consist of stripes with periodicity below optical wavelength where the direction of the polarization varies up to \(180^\circ\). This structure has no long-range azimuthal order or net polarization in the absence of electric field. However application of the electric field distorts the polarization structure of the defect array and leads to a large electroclinic effect. Since the net polarization is proportional to the applied electric field, under a triangular electric field this would give only a linear...
contribution to the electric current, which would be indistinguishable from the Ohmic current. We note that large electroclinic effect observed in chiral calamitic SmA* materials have already been explained by a modulated polarization structural model by Meyer and Pelcovits.\textsuperscript{18} The bistability that has been observed above a threshold can also be explained by assuming a field-induced unwinding of the modulated structure. Just as in the case of short pitch SmC* samples, the reformation of the modulated structure would require modulation, thus the texture would remain stable after turning off the field. This bistability, however would necessarily involve switching of the polarization in reversed electric field, which would show up as peak in the polarization current measurements. This peak was clearly not present in a wide voltage range where the bistability (optic axis remains stable after field removal) was observed. In addition, similar to that of Goldstone mode of helical SmC* materials one would expect a large ($\epsilon \sim 50$) dielectric constant

\[ \Delta \varepsilon_G = \frac{1}{8\pi\varepsilon_0 K} p p^2, \]

where $P \sim 0.002 \text{ C m}^{-2}$ is the spontaneous polarization, $K \sim 10^{-11}$ N is the relevant distortion elastic constant, $p \sim 0.1 \mu$m is the periodicity and $\theta \sim 0.5 \text{ rad}$ is the tilt angle) with low ($f_r \sim 10 \text{ kHz}$) relaxation frequency

\[ f_r \sim \frac{4\pi^2 K}{\gamma p^2}, \]

where $\gamma \sim 1 \text{ Pa s}$ is the rotational viscosity). Instead we find a small ($\Delta \varepsilon \sim 2$) contribution of the dielectric constant that relaxes only in the 100 kHz range. To get the observed $\Delta \varepsilon$ and $f_r$ values one need to assume about 4 times smaller modulation periodicity. This however would clearly show up in the small angle X-ray diffractogram in the form of multiple peaks separated by about 0.01\AA\textsuperscript{-1}wave numbers,\textsuperscript{13} which we could not find in the limitation of our X-ray setup.

It is also possible to consider another model, which assumes an out-of-layer polarization component (SmC\textsubscript{G} structure). To describe this model we start out from using the geometry shown in Fig. 11. The long axis (the line connecting the end points of the average molecules) makes an angle $\theta$ with the layer normal, which is set along the $z$-axis. The molecular plane is described by the azimuth angle $\phi$, $\phi = 0$ or $\pi$ corresponds to the SmCP (B\textsubscript{2}) phase, whereas $0 < \phi < \pi$ describes the SmC\textsubscript{G} phase, with chirality changing sign at $\phi = -\pi/2$ and $\pi/2$.

The low birefringence in the higher temperature phase at zero electric field indicates that the tilt is antiniclinic, i.e., the sign of $\theta$ alternates from one layer to the other. When $0 < \phi < \pi$, the out-of-plane polarization results in a torque on the electric field applied across the cell along the smectic layers. When the layers are fully formed, they can be considered rigid typically below 10 V mm\textsuperscript{-1} field, however the direction of the polarization can be rotated with respect to the layers by rotating $\phi$ closer to $\pi/2$. In order to keep the layer spacing, the component of the tilt along the film and normal to the electric field has to increase. This also results in an electro-clinic type switching. In this case, however when we turn off the field, $\phi$ can relax back to the original $\phi_0$ just by rotation around the long axis, so the tilt angle component along the film surface (i.e. the optical axis) may remain the same, and only the birefringence decreases slightly, just as found experimentally. Remarkably, this model can also account for the rotation of the smectic layers upon field reversal (Fig. 7a) and can be explained as follows. In different domains, where $P_{op}$ points in opposite directions, the switching would require opposite rotation of the layers, which results in the breaking of the layers to needles with long axis parallel to the layers, as observed experimentally (Fig. 7a).

Finally, we can also explain the transition from the needle-like inhomogeneous texture to the smooth continuous texture above a second threshold field $E_2 \sim 18$ V mm\textsuperscript{-1} and is very similar to that observed\textsuperscript{21} earlier for a fluorinated material. Just as in that case, here also we propose that this corresponds to a field induced SmC\textsubscript{G}–SmCP transition. At this transition the second tilt angle becomes $\phi = \pi/2$, i.e., the out-of-plane polarization component becomes zero, which means a transition to the B\textsubscript{2} phase with C\textsubscript{2} symmetry. In this thermal range the switching does not require any rotation of the layers, thus resulting in the observed smooth texture.

We note that the transition from an inhomogeneous structure to a smooth one can also be accounted by the modulated polarization model as the transition where the modulation disappears. The only difference is that the bistability and the absence of the polarization peak cannot be explained assuming only in-plane polarization components.

It is important to point out here the influence of an applied electric field to the mesophase structure of bent-core compounds. Infact, Bedel et al.\textsuperscript{19} have carried out a fairly detailed investigation of the influence of an applied electric field on the phase behaviour of a series of compounds. They show that (for a particular homologue) at zero voltage only one phase is seen while on increasing the field at elevated temperatures, two different phases are observed at two different threshold voltages and these phase transitions are reversible. Similarly, Ortega et al.\textsuperscript{20} found a field induced transition from a Col to a SmCP\textsubscript{A} phase which was found to be reversible. Recently we have reported\textsuperscript{21,22} field induced irreversible columnar to smectic phases as well as racemic to homochiral smectic phase transitions. Such effects were also observed\textsuperscript{10b,23} earlier and a summary of the effect of electric field on the mesophase structure can be found in an excellent review.\textsuperscript{17}

**Conclusions**

Three new novel symmetrical bent-core compounds containing terminal $n$-alkyl carboxylate groups have been prepared. These compounds show two mesophases with unusual optical
textures as well as electro-optical behaviour. On the basis of experimental investigations the higher temperature mesophase which has been designated as B22 phase shows bistable but analogous linear electro-optical switching without any observable polarization peak. We analyze two theoretical models and find that a local triclinic symmetry may be responsible for the observed unusual electro-optical switching.

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