

Ferroelectric properties exhibited by mesophases of compounds composed of achiral banana-shaped molecules

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The synthesis and mesomorphic properties of a new series of five-ring esters composed of banana-shaped molecules are reported. The homologues containing *n*-dodecyloxy, *n*-tetradecyloxy and *n*-hexadecyloxy terminal chains exhibit a smectic phase while that with an *n*-octadecyloxy chain shows a two-dimensional structure. The structures of the mesophases have been determined by X-ray diffraction studies. Interestingly both these mesophases exhibit ferroelectric properties. The electro-optical switching characteristics have been investigated using both triangular-wave and d.c. electric fields. Ferroelectricity is clearly demonstrated in both the mesophases by bistable switching behaviour.

Introduction

Since the discovery of ferroelectricity in liquid crystals by Meyer *et al.*,¹ there has been remarkable progress in not only the synthesis of new compounds exhibiting ferroelectric properties but also in developing application devices using this property.^{2,3} The ferroelectric properties have been observed in pure compounds exhibiting a chiral smectic C (SmC*) phase or by doping a smectic C liquid crystal with a suitable chiral substance. In both of these cases chiral molecules are involved. However, molecular chirality is not a necessary condition for realising ferroelectric liquid crystals. Ferroelectricity may be observed in compounds with polar structures in which the direction of polarisation is reversed by the application of an electric field. Polar order may be realised in smectic phases of compounds composed of achiral bent-core or banana-shaped molecules because they cannot rotate easily about their long molecular axis.

In the last couple of years, there has been a number of reports on the electro-optical switching behaviour of banana-shaped compounds.^{4–11} One of the phases in which electro-optical behaviour has been studied extensively is the antiferroelectric B₂ phase.^{4,5} Ferroelectric behaviour in banana-shaped compounds was reported by Bedel *et al.*¹³ for the higher homologues of a series of five-ring Schiff's base esters containing a fluoro substituent *ortho* to the terminal *n*-alkoxy chains. These compounds show textures resembling banana-tree leaves, spiral germs, ribbons with equally spaced lines and myelinic textures which are normally associated with the B₇ mesophase.¹² Immediately thereafter Walba *et al.*¹⁴ reported a ferroelectric liquid crystal conglomerate composed of racemic molecules in which ferroelectric polarisation results from the spontaneous collapse of polar symmetry in a fluid smectic phase. Again, these five-ring Schiff's base esters showed textures characteristic of the B₇ mesophase such as helical ribbons or tubes which eventually coalesce to form focal-conic domains. Very recently Nadasi *et al.*¹⁵ reported a ferroelectric liquid crystalline phase in achiral five-ring Schiff's base esters with lateral fluoro substituents on the central phenyl ring as well as on the outer rings.

Herein we describe, what is believed to be the first example of two different banana-mesophases exhibited by two homologues of the same series which show ferroelectric properties.

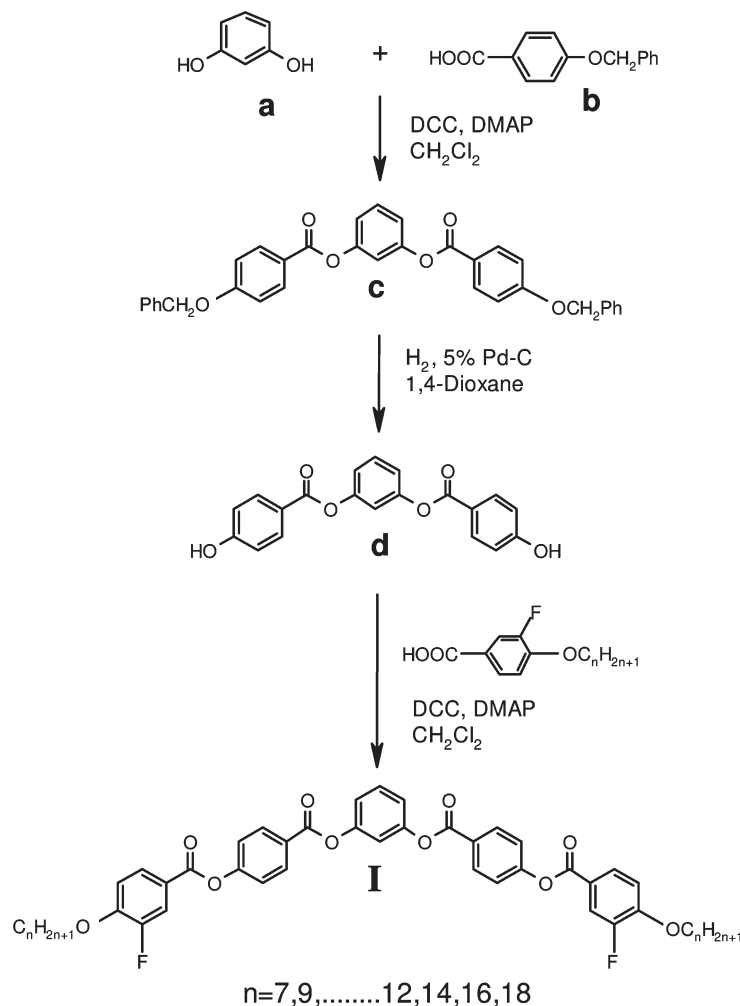
Experimental

All the compounds were purified by column chromatography (silica gel, 60–120 mesh) and were crystallised several times using suitable solvents. Merck Kieselgel 60F₂₅₄ precoated thin layer chromatographic plates were used to check the purity of both intermediates and the final esters. The normal phase high performance liquid chromatography on a μ -Porasil column (3.9 mm \times 300 mm, Waters Associates Inc.) was used to determine the purity of all the final esters using 1% ethyl acetate in dichloromethane as the eluent. ¹H NMR spectra were recorded using a Bruker AMX 400 spectrometer to confirm the chemical structure of intermediates as well as the final esters and ¹³C NMR spectra were also recorded for the final esters using 1% tetramethylsilane in deuteriochloroform or deuterioacetone as an internal standard. A Shimadzu FT IR-8400 spectrophotometer was used to record the infrared spectra and elemental analysis was carried out using a Carlo-Erba 1106 analyser.

The mesophase behaviour was examined under a Leitz Laborlux 12 POL/Olympus BX50 polarised light microscope. The phase transition temperatures and the associated enthalpies were determined from thermograms recorded on a Perkin-Elmer, Model Pyris 1D differential scanning calorimeter. The X-ray diffraction studies of the unoriented samples were carried out by using Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) from a rotating anode generator (Rigaku Ultrax 18) with a flat graphite crystal monochromator. The diffraction patterns were recorded on an image plate (Marresearch). The spontaneous polarisation was measured by a triangular-wave method. The triangular-wave and modified triangular-waves were generated using an Arbitrary Waveform Generator (WAVETEK, Model 395) and amplified using a TREK MODEL 601B-3 amplifier. The current response traces were recorded using a Tektronix Oscilloscope (Model TDS220). The d.c. field experiments were carried out using a Regulated Dual DC Power Supply (Model LD 6401).

Materials

The syntheses of the compounds under investigation were carried out following the pathway shown in Scheme 1. Following a procedure reported¹⁶ earlier, resorcinol, **a**, was reacted with 4-benzyloxybenzoic acid, **b**, to yield the diester, **c**. The



Scheme 1 Synthetic pathway used for the preparation of the banana-shaped compounds.

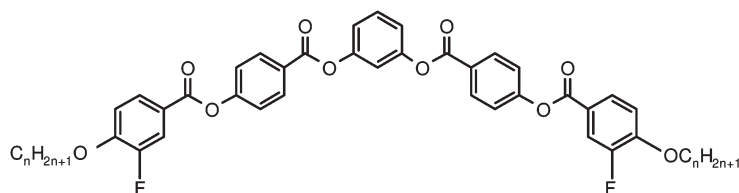
deprotection of the phenolic groups was carried out using 5% Pd–C catalyst in an atmosphere of hydrogen to give the diphenol, **d**. The final compounds **I** were obtained by reacting **d** with two equivalents of the appropriate 3-fluoro-4-*n*-alkoxybenzoic acid. The procedure is given in detail below.

1,3-Phenylene bis(4-benzyloxybenzoate), c. Resorcinol, **a** (1.1 g, 10 mmol), and 4-benzyloxybenzoic acid, **b** (4.56 g, 20 mmol), were dissolved in dry dichloromethane (50 ml). To this, *N,N'*-dicyclohexylcarbodiimide (DCC) (4.5 g, 22 mmol) and a catalytic amount of 4-(*N,N*-dimethylamino)pyridine (DMAP) was added and the mixture stirred at room temperature for about 15 hours. The precipitated dicyclohexylurea was filtered off and washed with an excess of chloroform (100 ml). The combined filtrate was washed with 2% aqueous acetic acid solution (3 × 50 ml), 5% ice cold sodium hydroxide solution (3 × 50 ml) and finally with water (3 × 75 ml) and dried over anhydrous sodium sulfate. The crude residue obtained after removal of the solvent was chromatographed on silica gel using chloroform as an eluent. Removal of solvent from the eluate afforded a white material which was crystallised from 1,4-dioxane. Yield 4.3 g (81%); mp 195–196 °C; ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.15 (d, ³*J* 8.9 Hz, 4H, Ar-H), 7.48–7.34 (m, 10H, Ar-H), 7.15–7.12 (m, 4H, Ar-H), 7.06 (d, ³*J* 8.9 Hz, 4H, Ar-H), 5.16 (s, 4H, ArCH₂O-); IR (KBr) ν_{\max} : 3068, 2924, 1736, 1603, 1508, 1250, 1171, 1132 cm⁻¹; C₃₄H₂₆O₆ requires C, 76.97; H, 4.94%; found: C, 76.85; H, 4.85%.

1,3-Phenylene bis(4-hydroxybenzoate), d. 1,3-Phenylene bis(4-benzyloxybenzoate), **c** (4 g), was dissolved in 1,4-dioxane

(50 ml) and 5% Pd–C catalyst (1.0 g) was added. The mixture was stirred at 50 °C in an atmosphere of hydrogen until the required quantity of hydrogen was absorbed. The resultant mixture was filtered hot and the solvent removed under reduced pressure. The residue was passed through a column of silica gel and eluted with a mixture of 4% acetone in chloroform. Removal of solvent from the eluate gave a white material, which was crystallised from ethyl acetate. Yield 2.35 g (89%); mp 237–238 °C; ¹H NMR (acetone-d₆, 400 MHz) δ (ppm): 9.7 (s, 2H, 2 × Ar–OH, exchangeable with D₂O), 8.06 (d, ³*J* 8.8 Hz, 4H, Ar-H), 7.54 (t, ³*J* 8.3 Hz, 1H, Ar-H), 7.22–7.2 (m, 3H, Ar-H), 7.0 (d, ³*J* 8.8 Hz, 4H, Ar-H); IR (KBr) ν_{\max} : 3367, 3060, 2972, 1705, 1607, 1591, 1512, 1244, 1167, 1134 cm⁻¹; C₂₀H₁₄O₆ requires C, 68.57; H, 4.03%; found: C, 69.01; H, 3.64%.

1,3-Phenylene bis[4-(3-fluoro-4-*n*-octadecyloxybenzoyloxy)benzoate], 8. Synthesised as described for the preparation of compound **c**. Quantities: compound **d** (0.2 g, 0.57 mmol), 3-fluoro-4-*n*-octadecyloxybenzoic acid (0.46 g, 1.14 mmol), DCC (0.28 g, 1.37 mmol), DMAP (cat. quantity), dry dichloromethane (10 ml); yield 0.45 g (69%); mp 118 °C; ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.29 (d, ³*J* 8.6 Hz, 4H, Ar-H), 7.97 (d, ³*J* 9.0 Hz, 2H, Ar-H), 7.92–7.89 (dd, ³*J* 11.4 Hz, ⁴*J* 2.0 Hz, 2H, Ar-H), 7.50 (t, ³*J* 8.0 Hz, 1H, Ar-H), 7.37 (d, ³*J* 8.6 Hz, 4H, Ar-H), 7.20–7.17 (m, 3H, Ar-H), 7.05 (t, ³*J* 8.3 Hz, 2H, Ar-H), 4.13 (t, ³*J* 6.6 Hz, 4H, 2 × Ar–OCH₂-), 1.89–1.84 (quint., ³*J* 7.6 Hz, 4H, 2 × Ar–OCH₂-CH₂-), 1.49–1.26 (m, 60H, 30 × -CH₂-), 0.88 (t, ³*J* 6.3 Hz, 6H, 2 × -CH₂-CH₃); ¹³C NMR (CDCl₃, 400 MHz) δ (ppm): 164.0, 163.5, 155.3, 153.3, 152.3,

Table 1 Transition temperatures ($^{\circ}\text{C}$) and enthalpies (kJ mol^{-1}) for the bent-core compounds **1** as determined by differential scanning calorimetry^a

Compound	n	Cr		B_{X1}		B_{X2}		I
1	7	●	130.0 73.3 ^a	—		—		●
2	9	●	130.0 47.6 ^b	—		—		●
3	10	●	129.0 85.7 ^b	—		—		●
4	11	●	129.0 111.0 ^b	—		—		●
5	12	●	128.0 110.0 ^b	●	127.5) 21.8	—		●
6	14	●	124.0 97.9 ^b	●	128.5 23.3	—		●
7	16	●	121.0 104.9 ^b	●	129.0 24.3	—		●
8	18	●	118.0 125.7 ^b	—		●	128.5 24.4	●

^aAbbreviations: Cr = crystalline solid, B_{X1} = banana ferroelectric lamellar phase, B_{X2} = banana ferroelectric two-dimensional phase, I = isotropic liquid. ^bHas crystal-crystal transition. Enthalpy denoted is the sum of all the transitions. Temperature in parentheses indicates a monotropic transition.

151.5, 150.8, 131.9, 129.9, 127.6, 126.9, 122.0, 121.3, 119.3, 118.0, 117.8, 115.8, 113.6, 69.6, 36.0, 31.9, 30.9, 29.7, 29.4, 29.0, 28.5, 25.9, 22.7, 14.1; IR (KBr) ν_{max} : 2914, 2849, 1742, 1734, 1726, 1618, 1608, 1472, 1283, 1238, 1138 cm^{-1} .

Results and discussion

Textural observations

The transition temperatures together with the associated enthalpies of the eight compounds, **1–8**, investigated are collected in Table 1. Compounds **1** to **4** do not exhibit any mesophase. Compound **5** is monotropic while compounds **6** and **7** are enantiotropic mesomorphic and these three compounds exhibit very similar textures. A sample of compound **7** was placed between an untreated glass slide and a coverslip and heated such that the mesophase appears. On observing the sample under a polarising microscope an unspecified grainy texture is seen. The viscosity of this mesophase is quite high and is difficult to shear. After shearing, the grainy texture is altered and the field of view becomes dark. A photomicrograph of the grainy texture exhibited by compound **7** on heating the crystalline phase is shown in Fig. 1. The clearing enthalpy of this mesophase is about 24 kJ mol^{-1} . On cooling the isotropic liquid of the same compound, the mesophase appears more

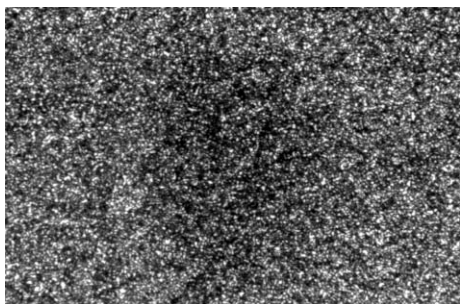


Fig. 1 Photomicrograph of the grainy texture of the lamellar phase of compound **7** at 125 $^{\circ}\text{C}$ (crossed polarisers), magnification $\times 250$.

or less dark under the field of view. From these observations it was difficult to identify this mesophase as any of the well known banana phases B_1 to B_7 .

Compound **8** exhibits an enantiotropic mesophase and has a thermal range of 10.5 $^{\circ}\text{C}$. On examination of a thin film of this material under a polarising microscope, two different types of textures could be seen. On slow cooling of the isotropic phase, reddish brown and grey coloured focal-conic domains appear and a photomicrograph of this mesophase is shown in Fig. 2. Sometimes spherulites could also be seen. In either case, shearing of the sample was quite easy indicating that the mesophase is less viscous and this results in an unspecified texture. The differential scanning calorimetric thermogram obtained for this compound is shown in Fig. 3. The clearing enthalpy is comparable to that obtained for compound **7**. The textural features of this mesophase also do not correspond to any of the other known banana phases.

X-Ray investigations

X-Ray diffraction studies were carried out on the mesophases of compounds **7** and **8**. The powder X-ray diffraction pattern obtained for compound **7** showed the following features. A diffuse wide angle peak at about 4.7 \AA indicating a liquid-like in-plane order. In the small angle region, three sharp reflections could be seen at $d_1 = 45.3 \text{ \AA}$, $d_2 = 22.7 \text{ \AA}$ and $d_3 = 15.1 \text{ \AA}$.

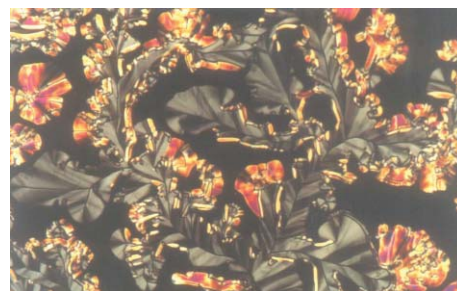


Fig. 2 Photomicrograph of the texture of the two-dimensional phase of compound **8** at 126.5 $^{\circ}\text{C}$ (crossed polarisers), magnification $\times 250$.

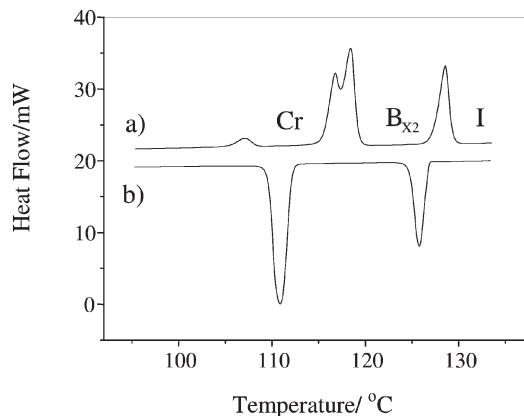


Fig. 3 Differential scanning calorimetric scans at a rate of $5\text{ }^{\circ}\text{C min}^{-1}$ for compound **8**; a) heating cycle b) cooling cycle.

These reflections are in the ratio $1 : \frac{1}{2} : \frac{1}{3}$ indicating a lamellar order in the mesophase and are independent of temperature. The layer spacing determined from these measurements are slightly lower than the calculated molecular length (assuming that all the methylene units in the alkoxy chain are in the fully extended all *trans* conformation) indicating that this is a tilted smectic phase with a tilt angle of 35° . Similar diffraction patterns were obtained for compounds **5** and **6** also suggesting that the mesophases of these three compounds are of the same type. A typical diffraction pattern obtained for compound **7** is shown in Fig. 4.

However, the diffraction pattern obtained for the mesophase of compound **8** is completely different from those seen for the above three compounds **5**, **6** and **7**. A diffuse wide-angle peak at 4.7 \AA , indicative of a liquid-like in-plane order, was seen as usual. In the small angle region, four sharp reflections could be seen at $d_1 = 46.7\text{ \AA}$, $d_2 = 26.6\text{ \AA}$, $d_3 = 17.8\text{ \AA}$ and $d_4 = 15.9\text{ \AA}$. This is probably indicative of a two-dimensional structure in the mesophase. The X-ray diffraction pattern obtained for compound **8** is shown in Fig. 5. Thus, it is clear that this mesophase is structurally different from those of compounds **5**, **6** and **7**.

Electro-optical investigations

The electro-optical behaviour of the mesophases exhibited by compounds **7** and **8** were examined in cells constructed with conducting plates and having a uniform thickness. The plates were pretreated with polyimide and unidirectionally rubbed to obtain homogeneous alignment. A sample of compound **7** was filled in the isotropic phase and cooled slowly to the mesophase. The mesophase appeared dark on observation under a

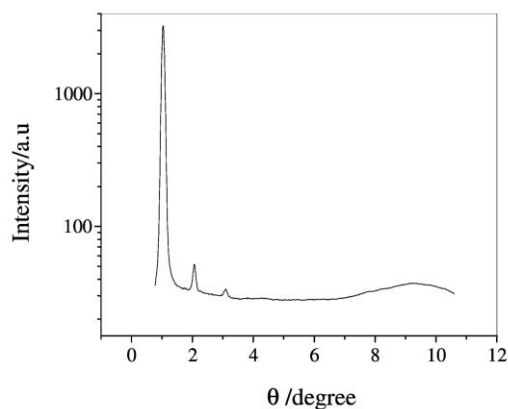


Fig. 4 X-Ray diffraction pattern obtained for the mesophase of compound **7** at $124\text{ }^{\circ}\text{C}$.

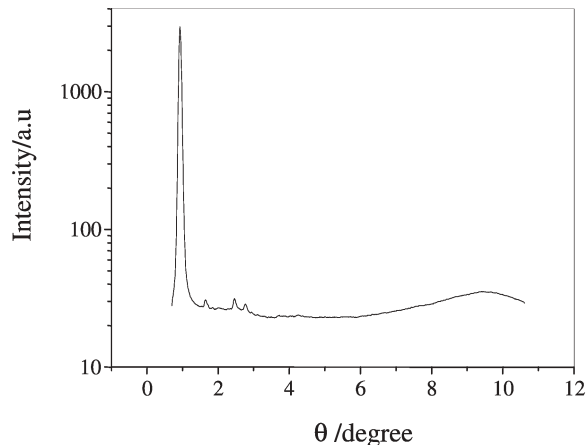


Fig. 5 X-Ray diffraction pattern obtained for the mesophase of compound **8** at $122\text{ }^{\circ}\text{C}$.

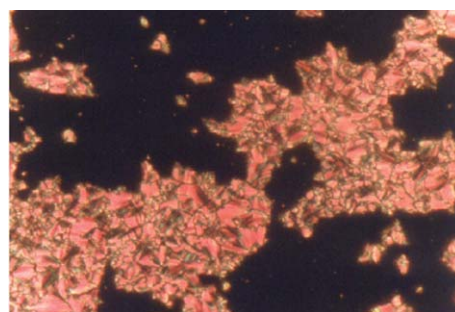


Fig. 6 Colourful broken focal-conic domains appearing from the dark field of view for compound **7**, at $\pm 10\text{ V }\mu\text{m}^{-1}$ (5 Hz), temperature $122\text{ }^{\circ}\text{C}$, magnification $\times 200$.

polarising microscope. On applying a triangular voltage, at a relatively high threshold ($\pm 10\text{ V }\mu\text{m}^{-1}$), colourful focal-conic domains appear from the dark field of view, as shown in Fig. 6. Simultaneously, a single current peak for each half cycle could be seen on the oscilloscope screen. By applying a sufficiently high triangular wave electric field ($\pm 12\text{ V }\mu\text{m}^{-1}$) and at a low frequency of 1 Hz at $122\text{ }^{\circ}\text{C}$, some of the aligned domains switch from one 'ferroelectric' state to the other. This bistable switching could be clearly seen under a polarising microscope. A typical switching current response obtained for the mesophase of compound **7** is shown in Fig. 7. The current was measured across a $10\text{ k}\Omega$ resistance. The saturated polarisation value, P_s , was calculated by integrating the area under the peak

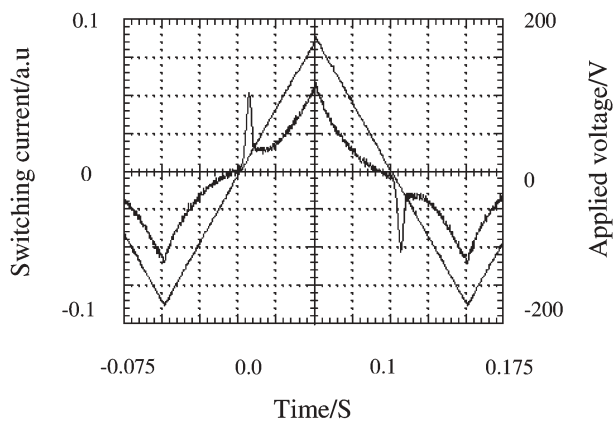


Fig. 7 Switching current response obtained in the mesophase of compound **7** by applying a triangular voltage ($\pm 175\text{ V}$, 5 Hz) at $122\text{ }^{\circ}\text{C}$, sample thickness $15\text{ }\mu\text{m}$. Spontaneous polarisation 290 nC cm^{-2} .

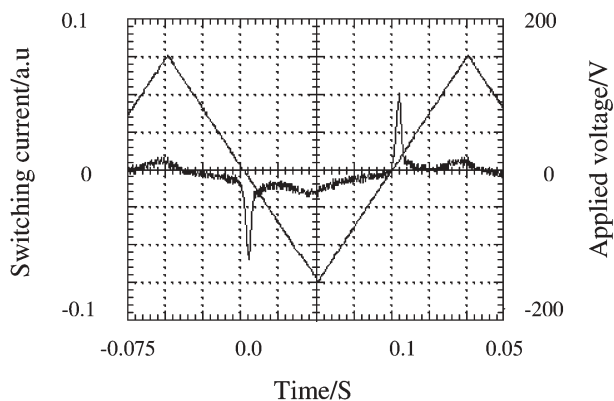


Fig. 8 Switching current response obtained in the mesophase of compound **8** by applying a triangular voltage (± 150 V, 5 Hz) at 121 °C, sample thickness 16 μm . Spontaneous polarisation 390 nC cm^{-2} .

of each half cycle and the average saturated spontaneous polarisation value was determined to be about 290 nC cm^{-2} . Similar changes in the texture at the threshold voltage as well as the switching behaviour (ferroelectric) could also be observed for the mesophase of compound **6**. The saturated spontaneous polarisation value determined for the mesophase of this compound is about 300 nC cm^{-2} . The textural features shown by the compounds **5**, **6** and **7** are not comparable to the mesophase of a compound which has been reported¹⁴ as a smectic ferroelectric phase. Also, since the compounds reported here are achiral, composed of banana-shaped molecules and switch (bistable), we have designated the mesophase as B_{X1} .

In the case of compound **8**, the isotropic phase was cooled slowly under a triangular-wave electric field to obtain uniformly aligned domains. Even at a relatively low threshold voltage (± 7 $\text{V } \mu\text{m}^{-1}$) at 1 Hz, some colourful circular domains could be seen under the microscope. At the same time, a single current peak for each half cycle was seen on the oscilloscope screen indicating the ferroelectric behaviour of the mesophase. A switching current response obtained in this mesophase is shown in Fig. 8. The saturated spontaneous polarisation value obtained at a sufficiently high triangular voltage (± 9.4 $\text{V } \mu\text{m}^{-1}$) is about 390 nC cm^{-2} . Though the X-ray data is indicative of a two-dimensional mesophase for this compound, it switches at relatively low threshold voltages. The spontaneous polarisation value obtained for the mesophase of this compound is higher than those obtained for compounds **6** and **7** which exhibit a lamellar ferroelectric phase. Also, the textural features of the mesophase of compound **8** are not comparable to the two-dimensional ferroelectric phase reported by Bedel *et al.*¹³ Hence we have designated this mesophase as B_{X2} .

In order to establish the ferroelectric behaviour of these two mesophases, we have carried out experiments using a modified triangular-wave electric field.¹⁷ A simple triangular voltage $-V$ to $+V$ is modified such that at $-V$ and $+V$ there is ample time for the switching to be complete and the polarised states are stable even when the field is switched off. The current response traces obtained for the mesophases of compounds **7** and **8** (B_{X1} and B_{X2}), are shown in Figs. 9 and 10 respectively. If the B_{X1} and B_{X2} mesophases are antiferroelectric, then the single current peak obtained would have split into two in the modified triangular wave as demonstrated by Bedel *et al.*¹⁷ in their experiments. This is further evidence in support of the ferroelectric switching behaviour of both these mesophases.

Finally, in order to establish the bistability of the two mesophases B_{X1} and B_{X2} , we have carried out some d.c. field experiments. A cell was constructed using ITO coated glass plates pre-treated with polyimide for homogeneous alignment of the sample. The cell thickness was adjusted to 7.9 μm using

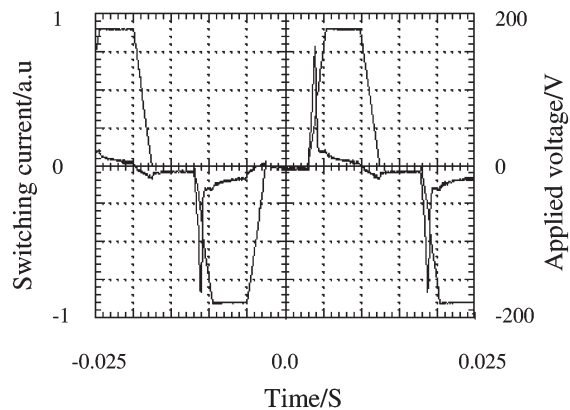


Fig. 9 Switching current response obtained in the mesophase of compound **7** by applying a modified triangular voltage (± 180 V, 33 Hz) at 122 °C, sample thickness 15 μm .

appropriate spacers. A sample of compound **7** was taken in such a cell and cooled slowly (0.1 °C min^{-1}) from the isotropic phase under a relatively high d.c. electric field (≈ 12 $\text{V } \mu\text{m}^{-1}$). Partially aligned circular domains could be observed under a microscope in which the dark brushes at an angle with respect to the orientation directions of the crossed polarisers. On reversing the polarity of the electric field, the dark brushes rotate in the opposite direction by the same amount. More importantly, on switching off the field the orientation of the brushes remain unchanged in the two different states. As a matter of fact, these bistable states remain unchanged for hours. This is ample proof for the ferroelectric ground state of the mesophase. Typical optical photomicrographs obtained for compound **7**, with and without an electric field, are shown in Fig. 11. The estimated director tilt of the molecules from the layer normal is about $\pm 26^\circ$. After obtaining the circular domains with high electric fields, the switching of the domains could be seen even at lower voltages (5 $\text{V } \mu\text{m}^{-1}$).

Similar experiments were carried out for the two-dimensional mesophase of compound **8**. In this case reddish brown circular domains were obtained (threshold ≈ 5 $\text{V } \mu\text{m}^{-1}$) and bistable switching was observed as in the case of compound **7**. On switching off the field, both the bistable states ($+V$ and $-V$) changed from reddish brown to bluish green in colour while retaining the orientation of the dark brushes. The bluish green colour is retained when the voltage is gradually reduced from the threshold voltage until it is switched off. The optical photomicrographs obtained in the different states for the B_{X2} mesophase are shown in Fig. 12.

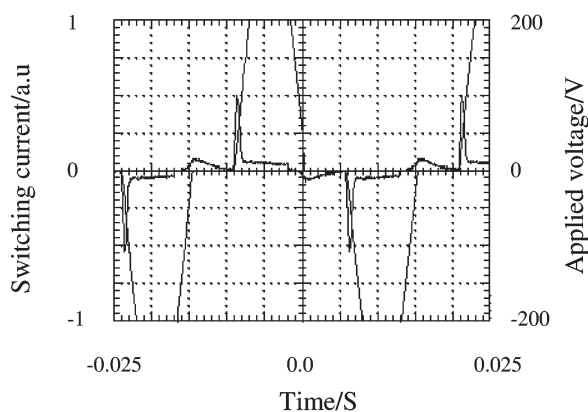


Fig. 10 Switching current response obtained in the mesophase of compound **8** by applying a modified triangular voltage (± 200 V, 33 Hz) at 120 °C, sample thickness 16 μm .

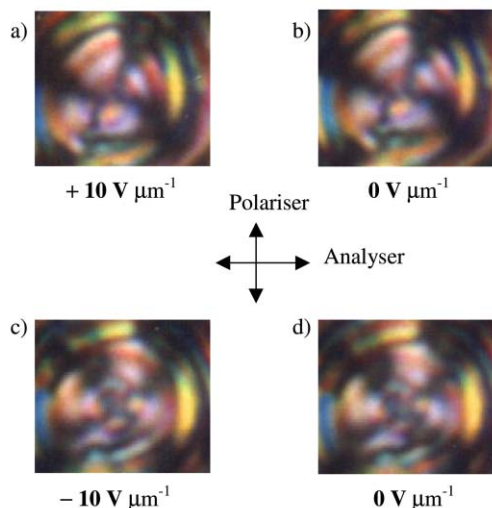


Fig. 11 Optical photomicrographs of circular domains obtained for compound **7** by applying a relatively high d.c. voltage ($12 \text{ V } \mu\text{m}^{-1}$) at 122°C . Cell thickness $7.9 \text{ } \mu\text{m}$. a) Domain obtained at $+10 \text{ V } \mu\text{m}^{-1}$ (dark brushes oriented in the anti-clock wise direction) and b) domain obtained after turning off the electric field; notice that there is no change in the orientation of the brushes. c) Domain obtained after the reversal of the polarity of the field ($-10 \text{ V } \mu\text{m}^{-1}$); notice the rotation of the brushes in the clock wise direction. d) Domain obtained after switching off the field where the orientation of the brushes is retained, demonstrating the bistable states.

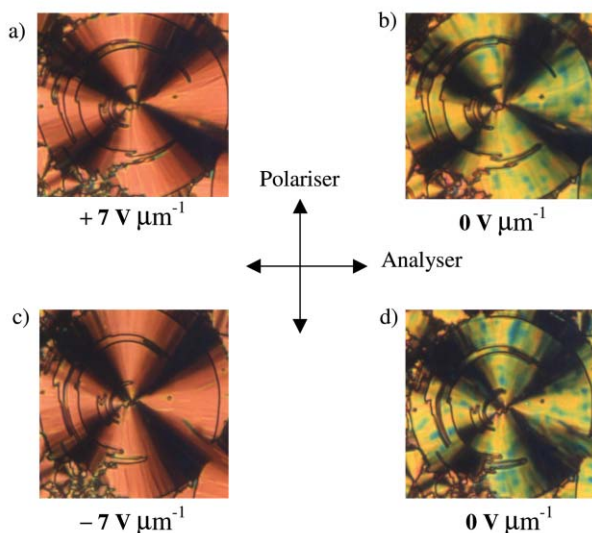


Fig. 12 Optical photomicrographs of circular domains obtained for compound **8** by applying a d.c. voltage ($7 \text{ V } \mu\text{m}^{-1}$) at 120°C . Cell thickness $8.5 \text{ } \mu\text{m}$. Changes similar to that observed for compound **7** are also seen for this compound. a) $+7 \text{ V}$, b) 0 V , c) -7 V and d) 0 V . Notice that the orientation of the brushes for both the cases a), b) and c), d) and also the colour changes in the presence and absence of the field clearly show the bistability.

Thus, the investigations carried out, *viz.*, the microscopic texture observations, X-ray diffraction patterns and particularly the electro-optical properties, have shown that two compounds (**7** and **8**) of the same homologous series exhibit two different types of mesophases both of which are ferroelectric.

Since there are not many banana-shaped compounds which exhibit ferroelectric properties, it is somewhat difficult at this stage to speculate the molecular structural requirements of a compound in order for it to exhibit such a phase. Of the four different systems exhibiting ferroelectric properties, including the one reported here, three of them contain a fluoro substituent on the outer phenyl rings and *ortho* to the *n*-alkoxy chain while in the fourth case there is no such lateral substituent on the phenyl rings. It would be interesting to make a systematic study of halo substitution on the outer phenyl rings on the occurrence of switchable mesophases, particularly the ferroelectric phase.

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