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Fluorine containing nonsymmetrical five-ring achiral banana-shaped compounds with columnar and synclinic antiferroelectric layered phases†

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The phase transitional behavior of two homologous series of five-ring banana-shaped compounds comprising fluorine substituents synthesized through covalent linking of two chemically dissimilar rod-like anisometric cores (arms) to central 1,3-phenylene is reported. The novelty of these molecules originates from the fact that the molecules are highly nonsymmetrical. One of the arms, which is either salicylaldimine or Schiff base core, possesses two vicinal fluorine atoms at the terminal ring having a n-decylxy tail; while the n-alkyl tail attached to the other arm was varied to realize a homologous series of compounds. The mesophases have been characterized by several complementary studies. The banana-shaped systems having short or medium alkyl chain lengths form apolar columnar (two-dimensional) structures, while on ascending the series, a polar smectic phase is stabilized. Detailed electro-optical investigations on one of the polar smectic phases revealed a synclinic antiferroelectric (racing) ground state structure, which switches, as expected, to an antclinic ferroelectric state by the application of an electrical field. At higher field strengths applied for an extended time interval, the anticolonferrelectric state switches to a synclinic ferroelectric (chiral) state. Upon field removal, these domains switch to an anticolonferrelectric (chiral) state, which eventually nucleates to the original antiferroelectric synclinic (racemic) state. Remarkably, the associated spontaneous polarization value exceeds 800 nC cm−2, which is among the highest reported hitherto.

Introduction

In the past ten years or so, there has been a revolution in the molecular design, synthesis, and characterization of liquid crystal (LC) materials having a bent or bow (twisted) anisometric shape possessing C2v symmetry.1 This is not only because of its unique feature of showing chiral induction in self-organizing systems in the form of layering (smectic)2,3,4 or two-dimensional (columnar)5,6,7 LC phases exhibiting spontaneous polarization (Ps), but also due to the formation of super helical (chiral) structures8,9,10 though the materials themselves are achiral. In general, the mesophases formed by these compounds are termed as “Banana” (Bn) phases, designated as B1–B6 (B stands for bent core, banana or bow),1 which have been identified based on their textural appearance, X-ray diffraction pattern, and switching behavior. The B1 and B4 phases are crystalline, while the others are mesomorphic.1 The most commonly encountered phases are B1, B2, and B7 which therefore have been investigated intensively. It must be mentioned here that other nomenclature types like SmCP (polar tilted smectic) for B2, Colc (rectangular columnar) for B4 and SmCintercal (intercalated smectic C) for B6 etc. have been used.1 Hitherto, several hundreds of both symmetrical and nonsymmetrical banana-shaped compounds have been synthesized to obtain such electrically switchable phases and to understand the relationship between chemical structure and mesomorphic behavior. Seemingly, different aspects, viz. the overall shape of the molecule, size, influence of lateral substituents and linkage groups as well as the length of the terminal chain have been taken into account for this purpose. Most importantly, several new molecular structural modifications have been undertaken in recent times mainly to address some trivial problems associated with them and also with the hope of obtaining new mesophase morphologies.1a,c For example, symmetrical bent-core molecules comprising an angular central core substituted with two identical linear rod-like mesogenic segments (arms) generally exhibit higher transition (melting and clearing) temperatures. To reduce the transition temperatures and to perhaps bridge the gap between bent-core and rodlike LCs (calamitics) nonsymmetrical bent-core molecules have been designed and synthesized. In these materials either the two halves (arms) of the molecule or the two linking functional groups attached to angular central core are different.5–13 Most innovatively, the symmetry of the bent-cores has also been reduced effectively by introducing various lateral substituents such as fluoro (F), chloro (Cl), bromo (Br), cyano (CN), nitro (NO2) and methyl (CH3) groups into either the central 1,3-phenylene ring at the 2-, 4- and 6-position(s) or the aromatic cores of the two arms attached to the central angular core.1,14,15

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Owing to the large electronegativity of the fluorine (F) atom, functional entities like F, CF₃, CF₂O, etc. are electron withdrawing and find many applications in materials.¹⁶ Fluoro substitution has in particular been used in LC materials, in which the electronic effects of a C–F bond in the form of inductive and resonance effects helps in modifying properties like melting point, transition temperatures, mesophase types and other physical properties of the parent system.¹⁷,¹⁸ Thus, as expected, among the various lateral substituents employed, the fluorine atom has profoundly influenced the properties of banana-shaped mesogens.¹⁵–¹⁹ It is now well established that the bent-core molecules with fluorine substitutions show interesting behavior to non-fluoro (bare) analogues and in particular their transitional behavior displays a remarkable dependence on the position and number of such substituents.¹⁹–²³ Fluorine substitution has been made at different locations within the rigid bent-core, viz. the central or inner or outer aromatic cores as well as at the terminal tails in the form of perfluorinated soft entities.⁸ However, their substitution at either the inner or the outer ring of the arms (inner or outer ring) of the bent-core seems to be more effective in changing the mesophase type, resulting in novel mesophases with interesting properties.¹¹ Such systems, therefore, pose demanding challenges to our understanding of their behavior at a molecular level requiring both synthetic investigations as well as molecular theories. Furthermore, the vast majority of the fluorine-based compounds have the fluorine substitution on both arms, leading to symmetrical systems. To the best of our knowledge, nonsymmetrical banana-shaped compounds with lateral fluorine atom substitutions in one of the arms are rather scarce.²¹–²３ Thus, in continuation of our investigations on the design and synthesis of banana-shaped molecules we intended to realize such novel molecular systems. Herein we report the synthesis and evaluation of the mesomorphic behavior of nonsymmetrical five-ring achiral banana-shaped LCs consisting of two chemically non-identical rodlike anisometric segments, viz. fluorine substituted Schiff base or its salicylaldehyde analogue, covalently linked at the 1,3-position of a central phenylene ring.

Experimental

Synthesis

Two series (I and II) of target compounds were prepared by acid catalyzed condensation of the key intermediates namely, 4-formyl-3-hydroxyphenyl 4-(n-decyloxy)-2,3-difluorobenzoate (1a) or 4-formylphenyl 4-(n-decyloxy)-2,3-difluorobenzoate (1b) with 4-[3-aminophenoxy]carbonyl]phenyl 4-(n-alkoxy) benzoate (2a–h) in ethanol as depicted in Scheme 1. The

Scheme 1 Reagents and conditions: (i) n-BuLi, THF, dry ice, −40 °C to rt, 2 h (95%); (ii) 2,4-dihydroxybenzaldehyde or 4-hydroxybenzaldehyde, DCC, DMAP, CH₂Cl₂, rt, 2 h (80%); (iii) EtOH, AcOH (catalytic amount), reflux, 2 h (85–91%).
intermediate 1a or 1b was obtained by esterification of 4-(n-decyl oxy)-2,3-difluoro benzoic acid (3) with 2,4-dihydroxybenzaldehyde or 4-hydroxybenzaldehyde in the presence of dicyclohexylcarbodiimide (DCC) and 4-(N,N-dimethylamino) pyridine (DMAP). The requisite difluorobenzoic acid 3 was prepared in one step.25 The reaction of 1-(n-decyl oxy)-2,3-difluorobenzene (4) with n-butyllithium in tetrahydrofuran at low temperatures yielded 0-lithiofluorobenzene, followed by treatment with frozen carbondioxide (dry ice) to obtain the alkoxybenzoic acid 3 in good yield. Amines 2a–b were prepared in four steps starting from 4-(n-alkoxy)benzoic acid as described in one of our earlier reports.26 The molecular structures of all the bent-core mesogens and intermediates were confirmed by standard spectroscopic methods as well as elemental analyses (see Experimental part given in the electronic supporting information (ESI) for the details).†

General information
In general all the intermediates prepared were purified by column chromatography using silica gel (100–200 mesh) as the stationary phase; in the case of solid intermediates further purification was achieved by the recrystallization technique. The target molecules were purified only by repeated recrystallizations using a mixture of appropriate solvents. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel 60, F254). IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FT-IR spectrometer. The spectral positions are given in wave numbers (cm−1).1H NMR spectra were recorded using either a Bruker AMX-400 (400 MHz) or Bruker Avance series DPX-200 (200 MHz) spectrometer. For 1H NMR spectra, the chemical shifts are reported in ppm relative to TMS as an internal standard and coupling constants are in Hz. Microanalyses were performed using a Eurovector model EA3000 CHNS elemental analyzer. Mass spectra were determined on a JOEL JMS-600H spectrometer in FAB+ mode using 3-nitrobenzyl alcohol as a liquid matrix. The mesophasic textures were observed under a polarizing optical microscope (POM) (Leitz DMRXP or Leica DMLP) equipped with a programmable hot stage (Melter FP90 or FP82HT). Phase transition enthalpy was measured under a differential scanning calorimeter (DSC) (Perkin Elmer DSC7). Optical observations were made using clean untreated glass slides. X-Ray diffraction (XRD) studies were carried out on powder samples in Lindemann capillaries with CuKα radiation using an Image Plate Detector (MAC Science, Japan) equipped with double mirror focusing optics.

Results and discussion
The liquid crystalline behaviour of the compounds was preliminarily investigated with the help of POM and DSC. Transition temperatures and associated enthalpies obtained from DSC thermograms for compounds of both series I and II are shown in Tables 1 and 2 respectively. Seemingly, the salicylaldimines (series I) and Schiff base (series II) analogues display virtually the same transitional behavior with the obvious exception that the transition (melting and clearing) temperatures are higher for the former case due to the presence of intramolecular H-bonding. In general, both homologous series of compounds display two types of mesophases. The shorter chain homologues of these two series of bent core molecules, viz. I-6, II-6 and II-7 show an identical thermal behavior with the exception of I-7, which exhibits a different mesophase. For example, on cooling the compound II-7 from the isotropic (I) phase, a mesophase appears with a striking dendritic growth pattern that eventually coalesces to a mosaic texture (Fig. 1a). This textural feature is well known to be observed for a two-dimensional rectangular columnar phase, namely the B1 phase.1 The structure of the B1 phase was further confirmed by XRD studies. The diffraction pattern of an unoriented sample of mesophase obtained at 110 °C for compound II-7 (Fig. 1b) shows a diffuse peak in the wide angle region with spacing (d) of 4.5 Å indicating the liquid-like in-plane order. In the small angle region two sharp reflections at d1 = 29.3 Å and d2 = 21.4 Å were seen, which could be indexed to (20) and (11) planes of a rectangular lattice. Thus, the textural observation coupled with X-ray data evidence the

Table 1  Phase transition temperatures (°C) and corresponding enthalpies [J g−1] for compounds of series I. Acronyms used (applicable to Table 2 also): Cr = Crystal; SmCPA (B2) = antiferroelectric polar smectic C phase; B1 = two-dimensional phase featuring a rectangular lattice (regarded as a rectangular columnar (Col.) phase); I = Isotropic phase. (• = Phase exists; — = phase does not exist)

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Cr Heating Cooling</th>
<th>SmCPA Heating Cooling</th>
<th>B1 Heating Cooling</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-6</td>
<td>CgH13</td>
<td>•</td>
<td>—</td>
<td>—</td>
<td>139.8 [67.8] 131.8 [23.3] —</td>
</tr>
<tr>
<td>I-7</td>
<td>CgH15</td>
<td>•</td>
<td>—</td>
<td>—</td>
<td>127.5 [9.2] 119.9 [9.9] —</td>
</tr>
<tr>
<td>I-8</td>
<td>CgH17</td>
<td>•</td>
<td>141.8 [18.8]</td>
<td>—</td>
<td>125.4 [8.1] 117.9 [9.7] —</td>
</tr>
<tr>
<td>I-9</td>
<td>CgH19</td>
<td>•</td>
<td>141.8 [22.1]</td>
<td>—</td>
<td>123.8 [7.0] 116.0 [11.3] —</td>
</tr>
<tr>
<td>I-10</td>
<td>CgH21</td>
<td>•</td>
<td>146.6 [24.6]</td>
<td>—</td>
<td>120.0 [12.4] 114.9 [12.9] —</td>
</tr>
<tr>
<td>I-12</td>
<td>CgH23</td>
<td>•</td>
<td>150.0 [23.6]</td>
<td>—</td>
<td>120.7 [10.3] 116.4 [10.5] —</td>
</tr>
<tr>
<td>I-20</td>
<td>CgH41</td>
<td>•</td>
<td>144.8 [17.3]</td>
<td>—</td>
<td>119.5 [14.1] 112.1 [21.6] —</td>
</tr>
</tbody>
</table>

*a Peak temperatures in the DSC thermograms obtained during the first heating and cooling cycles at a rate of 5 °C min−1 (also applicable to Table 2).
occurrence of the B1 phase. Furthermore, electrical switching experiments revealed that this phase is apolar in nature.

Optical transmission and electrical resistivity measurements as a function of temperature were made for the two representative cases I-10 and II-10 and the profiles obtained are shown in Fig. 2a and 2b respectively. The measurements were carried out at 100 kHz on samples filled in a 5 µm thick cell treated for planar boundary conditions. At the SmCP-I phase transition a noticeable variation can seen (cooling mode at a rate of 3 °C min⁻¹) for both the samples. The optical textures observed for all the higher homologues of salicylaldimines (I-7 to I-10 and I-12; except for I-20) as well as those of Schiff bases (II-8 to II-10, II-12 and II-20), were found to be similar, while they were noticeably different from the patterns seen for lower members. For example, for bent-core mesogen I-12 upon cooling from the isotropic liquid, a mesophase with small spherulitic domains appears. In some regions beaded filaments around the spherulites and fringe patterns emerge (Fig. 3a), which finally coalesces to a non-specific texture. These textural features are typical of a polar smectic C (SmCP) phase.1 In contrast, the mesogen I-20 shows a non-specific low birefringent texture when cooled at a rate of 3 °C min⁻¹. However, on slow cooling of the isotropic liquid (1 °C min⁻¹) tiny fractal domains appear that coalesce to a grainy texture with dark and (relatively) bright domains of opposite chirality. Upon slight rotation (5°) of one of the crossed polarizers the dark domains become bright, and vice versa. These textural patterns are reported to be seen for the antiferroelectric smectic C (SmCP A) phase.1,20

In order to ascertain the structure of the mesophase, XRD measurements were carried out for the samples I-12 and II-12. The diffractograms obtained for the mesophase of both the compounds, were found, as expected, to be identical and confirmed the layer structure. In the small angle region two sharp reflections obtained with d-values of 39.01 Å and 19.47 Å for I-12 and 37.85 Å and 18.87 Å for II-12 are in the ratio 1 : 2, confirming a lamellar ordering of the mesophase. In addition, the diffractograms of I-12 and II-12 show a diffuse peak in the wide angle region with d-values of 4.66 Å and 4.55 Å respectively.

Table 2  Phase transition temperatures (°C) and corresponding enthalpies [J g⁻¹] for compounds of series II

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Cr</th>
<th>Heating Cooling</th>
<th>SmCP_A Heating Cooling</th>
<th>B1 Heating Cooling</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-6</td>
<td>C₆H₁₃</td>
<td>•</td>
<td>100.9[17.5]</td>
<td>—</td>
<td>•</td>
<td>117.5[17.8]</td>
</tr>
<tr>
<td>II-7</td>
<td>C₇H₁₅</td>
<td>•</td>
<td>102.4[29.5]</td>
<td>70.9[18.7]</td>
<td>•</td>
<td>115.2[15.8]</td>
</tr>
<tr>
<td>II-8</td>
<td>C₆H₁₇</td>
<td>•</td>
<td>103.9[27.5]</td>
<td>65.9[23.8]</td>
<td>•</td>
<td>115.6[16.1]</td>
</tr>
<tr>
<td>II-9</td>
<td>C₈H₁₉</td>
<td>•</td>
<td>63.8[20.7]</td>
<td>98.9[28.1]</td>
<td>•</td>
<td>70.8[21.9]</td>
</tr>
<tr>
<td>II-10</td>
<td>C₁₀H₂₁</td>
<td>•</td>
<td>68.1[21.7]</td>
<td>103.6[29.5]</td>
<td>•</td>
<td>119.3[21.5]</td>
</tr>
<tr>
<td>II-12</td>
<td>C₁₂H₂₅</td>
<td>•</td>
<td>69.6[24.6]</td>
<td>106.7[31.4]</td>
<td>•</td>
<td>119.6[21.6]</td>
</tr>
<tr>
<td>II-20</td>
<td>C₂₀H₄₁</td>
<td>•</td>
<td>86.3[46.2]</td>
<td>68.0[21.9]</td>
<td>•</td>
<td>112.6[20.8]</td>
</tr>
</tbody>
</table>

Fig. 1  Photomicrograph of mosaic texture (a) and 1D-intensity vs. 2θ profile (b) obtained for the B1 phase of II-7 at 110 °C.

Fig. 2  The profiles of temperature dependence of the optical transmission (integrated area: ~1 mm²) and the electric conductivity measured at 100 kHz for samples I-10 (a) and II-10 (b) placed in a 5 µm thick cell treated for planar boundary conditions.
that can be attributed to the liquid-like in-plane order. As a representative case, the diffraction pattern obtained for mesogen I-12 at 121 °C is illustrated in Fig. 3b. The layer spacings \( d = 39.01 \, \text{Å} \) and \( 37.85 \, \text{Å} \) obtained for I-12 and II-12 respectively, are less than their individual estimated all-trans molecular length, \( l = 49.3 \, \text{Å} \) and \( 47.4 \, \text{Å} \), which indicate the tilted organization of the molecules. The tilt angle was measured as 37°, assuming a rigid rod configuration.

It is well known that due to the inherent tendency to escape from the macroscopic polar order, the majority of bent core molecules exhibit the SmCP phase possessing antiferroelectric ground state organization that can be ascertained with the help of electrical switching studies. In fact, according to the interlayer correlation and tilt direction, two ground states are possible for the SmCP \(_{A}\) phase. The first state is homochiral, in which the tilt direction (the clinicity) of the molecules in the successive layer is opposite (anticlinic; SmC\(_{sPA}\)). In the second state, the tilt direction is identical (synclinic; SmC\(_{sPF}\)) and layer chirality alters from layer to layer and hence is racemic. Similarly, two such distinct arrangements are possible for the rarely formed ferroelectric SmCP (SmC\(_{PF}\)) phase, among which the anticlinic (SmC\(_{sPF}\)) organization is racemic while the synclinic (SmC\(_{sPF}\)) is chiral. In order to know the characteristics of the SmCP phase shown by the compounds of the present investigation, they were subjected to detailed electrical switching studies. As a representative case, the mesogen I-10 was considered for detailed electrical and other studies as follows. For this purpose, samples in their isotropic phase were filled into the 5 \( \mu \)m cell (made by E.H.C. Company) by capillary action and cooled slowly. After transition to the phase under investigation, the field was applied and electro-optical switching features were observed under the microscope. The SmCP phase of compound I-10 could not be switched below a 6 \( \text{V} \, \mu \text{m}^{-1} \) rectangular wave field. However, after a sufficiently high rectangular field (18 \( \text{V} \, \mu \text{m}^{-1} \)) was applied, it showed an antiferroelectric type of polarization peak. The textural pattern changes; some low birefringent domains appear (Fig. 4a) featuring racemic type switching characteristics, i.e. the optic axis of the domains does not change (Fig. 4b) when the polarity of the electric field is altered. Upon removal of the field, birefringent stripes as well as relatively low birefringent fans appear as shown in Fig. 4c.

On further increasing the field strength (>20 \( \text{V} \, \mu \text{m}^{-1} \)) and keeping it on for 10–15 minutes, the textural pattern transforms into two types of domains differing in their birefringence (Fig. 4d). By slightly rotating one of the polarizers, the brighter domains become slightly darker and vice versa (Fig. 4e,f). This indicates rotation of polarized light in opposite directions in different domains and thus evidencing the occurrence of two chiral regions having opposite handedness.

Thus, it can be surmised here that the SmCP phase shown by compound I-10 has a synclinic antiferroelectric (SmC\(_{sPA}\)) ground state structure (Fig. 5a). When this racemic structure is switched it becomes SmC\(_{sPF}\) (Fig. 5b) as expected. Upon application of strong (>20 \( \text{V} \, \mu \text{m}^{-1} \)) rectangular electric fields for extended duration (10 minutes), the SmC\(_{sPF}\) domains transform to SmC\(_{PF}\) (chiral state) due to the preference for the synclinic state as observed and explained already for other bent core materials.27 Upon field removal, the SmC\(_{PF}\) domains switch to SmC\(_{sPA}\). However, in about 10 minutes, these domains relax back to SmC\(_{sPF}\). As mentioned already,
on application of a triangular wave electric field the current passing through sample I-10 showed two peaks per half period of the applied field as illustrated in Fig. 6. The temperature dependence of the magnitude of the spontaneous polarization (Ps) obtained by integrating the area under the peaks is shown in Fig. 7. As can be seen Ps has a weak temperature dependence far away from the isotropic phase (I), but near the SmCP-I transition it shows a steep drop and vanishes in the isotropic phase. The polarization reaches values as high as 900 nC cm$^{-2}$ which is larger than for the SmCP of banana-shaped compounds. It may be mentioned here that the Schiff base homologue II-10 also showed the SmCP A phase. The time dependence of the polarization current is shown in Fig. 10. Similar to I-10 it has a very high antiferroelectric polarization (860 nC cm$^{-2}$). The high polarization values obtained for both the compounds are undoubtedly due to the fluorine atoms incorporated in the molecules.

Conclusion

In summary, the synthesis and mesomorphic behavior of fourteen new banana-shaped compounds belonging to two homologous series, namely, salicylaldimines and Schiff bases (imines) having fluorine substitutions are reported. In terms of linking groups, the presence or otherwise of fluoro lateral substituents and end chains, the two rod-like molecular arms (wings) are highly nonsymmetrical. The salicylaldimines and their Schiff base analogues exhibit identical transitional behavior as envisaged with the understandable difference that the phase transition temperatures are higher for the salicylaldimines due to the presence of intramolecular H-bonding. In general, shorter chain homologues of both series stabilize an apolar columnar (B$_{1}$) phase, whereas the higher members...
electronegative fluorine atoms in the molecule.

form a feature that can be attributed to the presence of

triangular electric field (20 V \( \text{cm}^{-1} \)) of the compound

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**Fig. 9** Dielectric spectra at different temperatures in the SmCPA phase range (a), and relaxation frequency as the function of inverse temperature (b) of the compound I-10.

exhibit a synclinic antiferroelectric polar smectic C phase. The electro-optical studies showed that the polar smectic phase has an antiferroelectric synclinic (racemic) structure and switches to an ant клинический ферроэлектрический полимерный спектр CFI.

Furthermore, the high polarization values, viz. >800 nC cm\(^{-2}\), form a feature that can be attributed to the presence of electronegative fluorine atoms in the molecule.

**References**


