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Synthesis and mesomorphic properties of banana-shaped achiral molecules with central and lateral halogen substituents

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Three banana-shaped achiral compounds, derivatives of 4-chloro-1,3-phenylene bis[4-(4-*n*-decanyloxyphenyliminomethyl)benzoate], were synthesized with variation of a substituent (X=H, F, or Cl); their antiferroelectric properties are described. The mesomorphic and switching properties were characterized by polarizing optical microscopy, differential scanning calorimetry, triangular wave method, and X-ray diffraction. The introduction of a lateral halogen substituent in the Schiff's base moiety prevents the regular stacking of the molecules, resulting in a decrease of melting temperature and leads to formation of the switchable SmC* phase in the melt. All of the compounds showed antiferroelectric switching, and their values of spontaneous polarization on reversal of an applied electric field were 260, 480, and 300 nC cm^{-2}, respectively, for X=H, F and Cl.

1. Introduction

Most chiral liquid crystal phases can be obtained by the introduction of a group containing a chiral carbon. However, a chiral mesophase in the absence of chiral structure can also occur, due to spontaneous polarization derived from symmetry breaking [1–4]. Ferroelectric liquid crystals (FLCs) resulting from spontaneous polarization are now regarded as one of the most promising classes of optoelectronic materials [5, 6]. A fascinating example of achiral symmetry breaking was found in the tilted smectic phases of certain banana-shaped molecules [7–9]. Because of the director tilt and simultaneous polar ordering, each smectic layer loses its inversion symmetry and becomes chiral, although the molecules contain no chiral carbons. Vorländer [10] was the first to synthesize mesogenic materials with a bent molecular shape; he noted that some compounds, such as bis[4-(4-methoxyphenylazoxy)phenyl] isophthalate and 1,2-phenylene bis[4-(4-ethoxyphenylazoxy)benzoate] are liquid crystalline [11, 12]. Later, Niori *et al.* [13] detected ferroelectricity in a smectic phase formed by banana-shaped achiral molecules. From X-ray measurements they concluded that the angled molecules are uniformly arranged in the bend direction. Such a structure possesses a C_{2V} symmetry, while the direction of spontaneous polarization should be in the direction of the two-fold symmetry axis. Link *et al.* [7] reported the spontaneous formation of chirality in a smectic phase of banana-shaped achiral molecules, a chiral layer structure with a handedness depending on the

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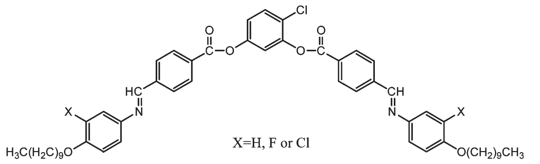
tilted molecular direction. Consistently, Weissflog *et al.* [14] reported that ferroelectricity could be induced in one of the mesophases in some achiral banana-shaped molecules by varying the substituents and the direction of connecting groups.

In this paper, we report the synthesis and mesomorphic properties of banana-shaped achiral compounds containing a Cl atom at the central core and a halogen substituent ($X=$H, F or Cl) in the 3-position of the *p*-alkoxyaniline Schiff's base moiety.

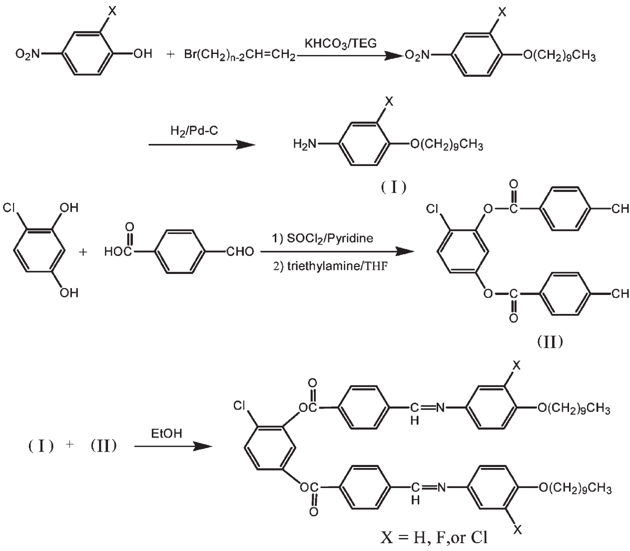


4-Chloro-1,3-phenylene bis[4-(4-*n*-decanyloxyphenyliminomethyl)-benzoate]

2. Experimental procedures

2.1. *Synthesis*

The synthetic route to the banana-shaped molecules used a modified literature procedure [15–17], and is shown in the scheme. Since the synthetic procedures for 4-chloro-1,3-phenylene bis[4-(4-*n*-decanyloxyphenyliminomethyl)benzoate] (C-PBDB), 4-chloro-1,3-phenylene bis[4-(3-fluoro-4-*n*-decanyloxyphenyliminomethyl)benzoate] (C-PBFDB), and 4-chloro-1,3-phenylene bis[4-(3-chloro-4-*n*-decanyloxyphenyliminomethyl)-benzoate] (C-PBCDB) were essentially the same, we show only the representative synthesis for C-PBDB. First, 4-nitro-1-decanyloxybenzene was prepared by the substitution reaction of 4-nitrophenol and 1-bromodecane, followed by hydrogenation with H_2 gas in the presence of palladium on activated carbon to give the substituted aniline (I). Then, 4-chloro-1,3-phenylene bis(4-formylbenzoate) (II) was prepared by esterification of 4-chlororesorcinol and 4-formyl benzoylchloride in tetrahydrofuran with triethylamine at 0°C. The final product was prepared by condensation reaction between the aniline (I) and the dialdehyde (II). It was purified by chromatography on silica gel and repeated recrystallization from a mixture of ethanol and dimethylformamide (20/1, v/v). Yield after purification was 20–30%. ^{1}H NMR ($CDCl_3$, 500 MHz) for PBDB; δ in ppm $=0.97$–1.82 (m, 38H, CH_2CH_3), 4.01 (t, 4H, OCH_2, $J=6.5$ Hz), 6.82–8.30 (m, 19H, Ar), 8.55 (s, 2H, CH$=$N). EIMS *m/z* 870 (M^+). HRMS (EI) calcd. for $C_{54}H_{63}ClN_2O_6$ (M^+) 870.4375; found 870.4361.



Scheme 1.

2.2. *Characterization*

NMR spectra were obtained on a Bruker DRX NMR spectrometer; mass spectra were recorded on a Jeol JMS-700 spectrometer. The phase transition temperatures were determined by differential scanning calorimetry (Perkin-Elmer DSC7) and polarizing optical microscopy (Nikon Eclipse E400 POL). DSC measurements were performed in a N_2 atmosphere, with heating and cooling rates of 10 and 0.5°C min^{-1}, respectively. Optical textures were observed using a polarizing microscope equipped with a digital camera and a temperature controller. The switching current was examined by the triangular wave method [18]. For the measurement of spontaneous polarization with varying temperature, the sample cell was mounted in a microfurnace where temperature fluctuations were approximately 0.1°C. For direct measurement of the polarization, we used the triangular wave method for ease of subtracting the background current. The polarization current, converted into a voltage signal through an amplifier, was measured with a digitizing oscilloscope and fed into a computer for data analysis.

SAXS measurements were performed in transmission mode with synchrotron radiation at the beamline 4Cl. Two-dimensional scattering patterns were collected on a CCD detector (Roper Scientific) with a wavelength of 1.608 Å. The observed intensity was corrected for background scatter and absorption by the sample. Since the samples exhibited typical isotropic scattering patterns in the absence of an external field, the intensity data were normalized to one-dimensional scattering patterns by integration through circular averaging to improve the data resolution, and therefore to reduce the measurement time.

WAXS measurements were conducted with an apparatus consisting of an 18 kW rotating anode X-ray generator (Rigaku Co.) operated at 50 kV × 20 mA, mirror optics with point focusing, and a one-dimensional position sensitive detector (M. Braun Co.). The CuK$_\alpha$ radiation ($\lambda = 1.542$ Å) from a $0.1 \times 1\,\mathrm{mm}^2$ microfocus cathode was used. A beam path was maintained under vacuum to reduce air scattering, and tungsten foil (50 µm) was used for primary beam protection. The data are presented as a function of $q = 4\pi \sin(2\theta)/\lambda$, where 2θ is the scattering angle and λ is the X-ray wavelength. In order to investigate structural changes on heating and cooling, the samples were held in an aluminum sample holder, sealed with a window of 7 µm thick Kapton film on both sides. The sample was heated with two cartridge heaters and its temperature monitored by a thermocouple placed close to the sample.

3. Results and discussion

3.1. *Synthesis and mesogenic properties*

The synthetic route to the banana-shaped compounds is quite straightforward and each reaction step is relatively well known. The obtained compounds were characterized by means of NMR and mass spectroscopy. NMR and mass spectral data were in accordance with expected formulae. The phase transition temperatures depended on lateral halogen substituents in the Schiff's base moiety are shown in the table.

The introduction of a lateral polar substituent in the 3-position of the Schiff's base moiety results in a decrease of the melting temperature over the non-polar substituted compound. This is because the presence of the lateral substituent prevents the regular stacking of molecules. The introduction of a polar group into the 3-position of the Schiff's base moiety could affect mesophase formation in two ways depending on polarity. First, it is expected that an electron-donating group could enhance electrostatic repulsion in the direction of the dipoles. Secondly, an electron-withdrawing group could decrease electrostatic repulsion in the direction of the dipoles. Thus, banana-shaped molecules with a polar substituent can form switchable smectic phases.

3.2. *Optical textures*

Using an optical microscope with crossed polarizers, on cooling the samples we could identify every phase transition shown in the table. When the isotropic liquid of compound C-PBDB (without substituent) is cooled slowly, optical textures of the smectic phase appear as a fern-like texture, as shown in figure 1 (*a*), and they tend to grow into mosaic textures with a fringe pattern as shown in figures 1 (*b*) and 1 (*c*). When the isotropic liquid of the compound C-PBFDB (with $X = \mathrm{F}$) is cooled slowly, optical textures of the smectic phase appear as grainy textures, as shown in figure 2 (*a*), and then tend to grow into mosaic textures consisting of a fringe pattern, as shown in figures 2 (*b*) and 2 (*c*). Optical textures of C-PBCDB (with $X = \mathrm{Cl}$) appear as a seed-like texture as shown in figure 3 (*a*), and then tend to grow into finger prints textures as shown in figures 3 (*b*) and 3 (*c*).

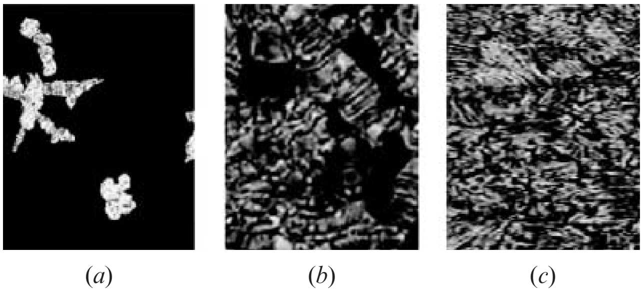

(*a*) (*b*) (*c*)

Figure 1. Optical micrographs of the SmC* phase for C-PBDB on cooling from the isotropic liquid: (*a*) the smectic phase initially appears as a fern-like texture; in (*b*) and (*c*) this grows to become a mosaic texture with a fringe pattern.

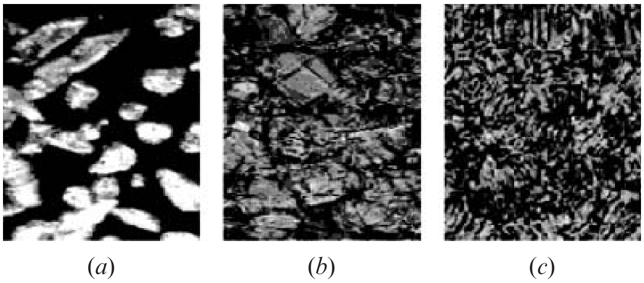
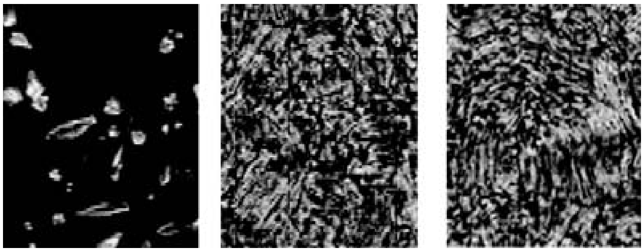

(*a*) (*b*) (*c*)

Figure 2. Optical micrographs of the SmC* phase for C-PBFDB on cooling from the isotropic liquid: (*a*) the smectic phase initially appears as a texture with granular pattern; in (*b*) and (*c*) the granules grow to become mosaic textures consisting of small domains.

Table. Phase transition temperatures and switching property.

X (Sample code)	Transition temperature/°C (enthalpy/J mol^{-1})	Switching property
H (C-PBDB)	Cr 83.7(14.2) SmC* 134.8(11.9) I	Switchable (antiferroelectric)
F (C-PBFDB)	Cr 44.5(12.3) SmC* 132.6(10.2) I	Switchable (antiferroelectric)
Cl (C-PBCDB)	Cr 38.3(2.1) SmC* 108.3(14.1) I	Switchable (antiferroelectric)



(*a*) (*b*) (*c*)

Figure 3. Optical micrographs of the SmC* phase for C-PBCDB on cooling from the isotropic liquid: (*a*) the smectic phase initially appeared as a seed-like texture; in (*b*) and (*c*) this grows to become a finger printer texture.

3.3. *Spontaneous polarization and switching current*

In order to measure spontaneous polarization of the smectic phases, a cell was fabricated of glass plates coated with conductive indium tin oxide and treated with rubbed polyimide for alignment. The cell gap was maintained by a patterned organic spacer of 1.5 μm thickness. The spontaneous polarization was measured by applying a triangular shape voltage, and switching was observed with polarizing microscope. Figure 4 shows the polarization reversal currents for the smectic phases of C-PBDB (X=H), C-PBFDB (X=F), and C-PBCDB (X=Cl). As shown in figure 4 (*a*), within the smectic phase-forming temperature region, C-PBDB exhibits two current reversal peaks for every half period at 130°C and a broader pattern at 134°C. As shown in figure 4 (*b*), C-PBFDB exhibits two peaks of current reversal for every half period at 130, 119 and 72°C. In figure 4 (*c*) for C-PBCDB, two peaks of current reversal are seen for every half period at 101 and 80°C. We can conclude that the smectic phases of compounds with lateral substitutents in the 3-position of the Schiff's base moiety are antiferroelectric, with the tip of the bent molecules orienting along the electric field and reversing their orientation with the polarity of the field.

Figure 5 shows the temperature dependence of spontaneous polarization for compounds C-PBDB, C-PBFDB, and C-PBCDB. The switchable smectic phase exhibits a maximum polarization of 260 nC cm^{-2} for C-PBDB, 480 nC cm^{-2} for C-PBFDB and 300 nC cm^{-2} for C-PBCDB. As shown in figure 5, on cooling the isotropic liquid, the spontaneous polarization is sharply increased, suggesting that the isotropic-to-smectic phase transition is first order. However, on further decreasing the temperature below 50°C, the polarization decreases and then vanishes. This is probably due to gradual crystallization of the central rod segments of the molecules.

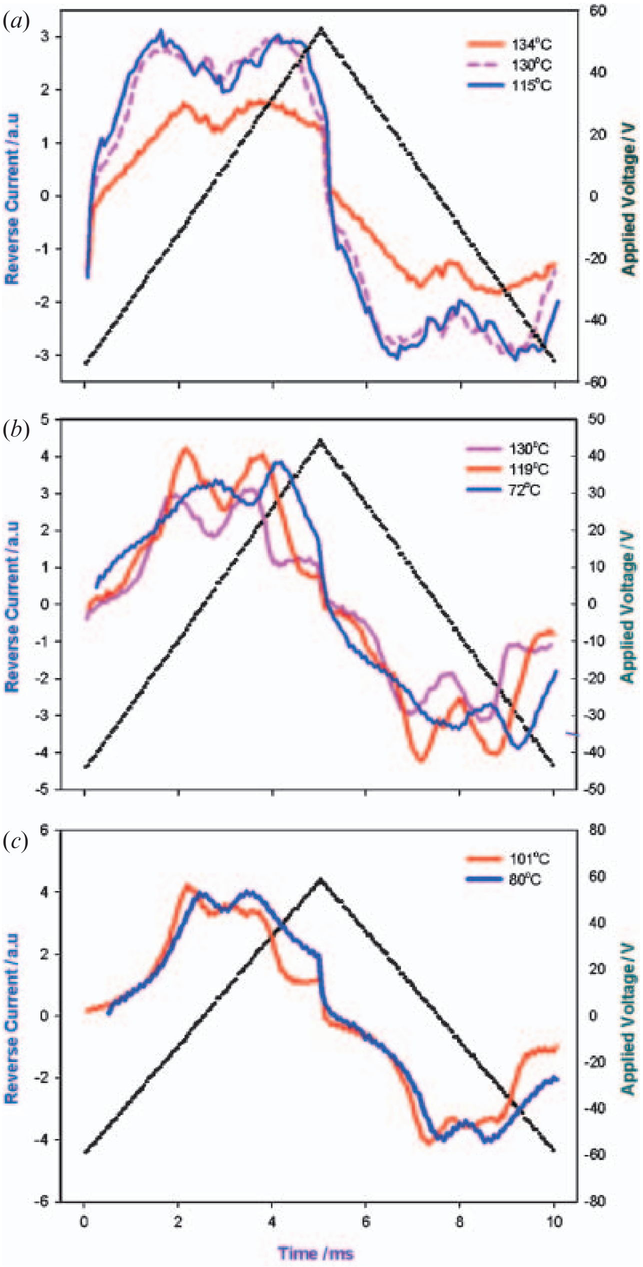


Figure 4. Switching current curves for smectic phases obtained by applying a triangular voltage: (*a*) C-PBDB (X=H); (*b*) C-PBFDB (X=F); (*c*) C-PBCDB (X=Cl).

3.4. *X-ray diffraction*

Figure 6 displays the X-ray diffraction (XRD) patterns obtained at given temperatures. In figure 6 (*a*), the XRD pattern of C-PBDB (X=H) at room temperature shows several diffraction peaks (denoted as K_1), indicating the presence of a crystalline structure. As the sample was heated to 133°C (above the transition temperature of 83.7°C by DSC), the

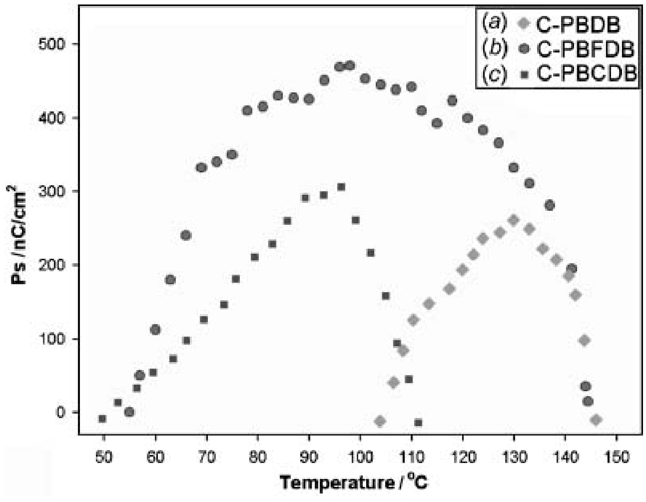


Figure 5. Temperature dependence of spontaneous polarization for C-PBDB (X=H), C-PBFDB (X=F) and C-PBCDB (X=Cl).

smectic characteristics (denoted as S) of a broad wide angle peak and a narrow small angle peak were obtained. Since no crystalline peaks are found at the wide angle region, this XRD pattern is indicative of a smectic phase having a layer spacing with a 1:2 ratio of peak scattering vectors. The lattice spacing of the smectic phase was calculated to be 40 Å from the relative sharp peak at $q=1.58\,\mathrm{nm}^{-1}$. In the isotropic phase, the small angle peak (denoted as I) disappeared, as shown in figure 6 (*a*).

In figure 6 (*b*), the XRD pattern of C-PBFDB (X=F) at room temperature displays several diffraction peaks (denoted as K), indicating a crystalline structure. On heating to 130°C (above the transition temperature of 44.5°C by DSC), a second weak peak in the small angle region was developed. Since no crystalline peaks are found at the wide angle region, this XRD pattern is indicative of a smectic phase having a layer spacing with a 1:2 ratio of peak scattering vectors. The lattice spacing of the smectic phase was calculated to be 42 Å from the relative sharp peak at $q=1.5\,\mathrm{nm}^{-1}$.

As shown in figure 6 (*c*), the XRD pattern of C-PBCDB (X=Cl) at room temperature shows few diffraction peaks, indicating the presence of a crystalline structure. As the sample was heated to 110°C (above the transition temperature of 38.3°C by DSC), smectic characteristics were obtained. But, in the isotropic phase, the small angle peak disappeared. The lattice spacing of smectic and crystal phases was calculated to be 41 Å from the relative sharp peak at $q=1.52\,\mathrm{nm}^{-1}$.

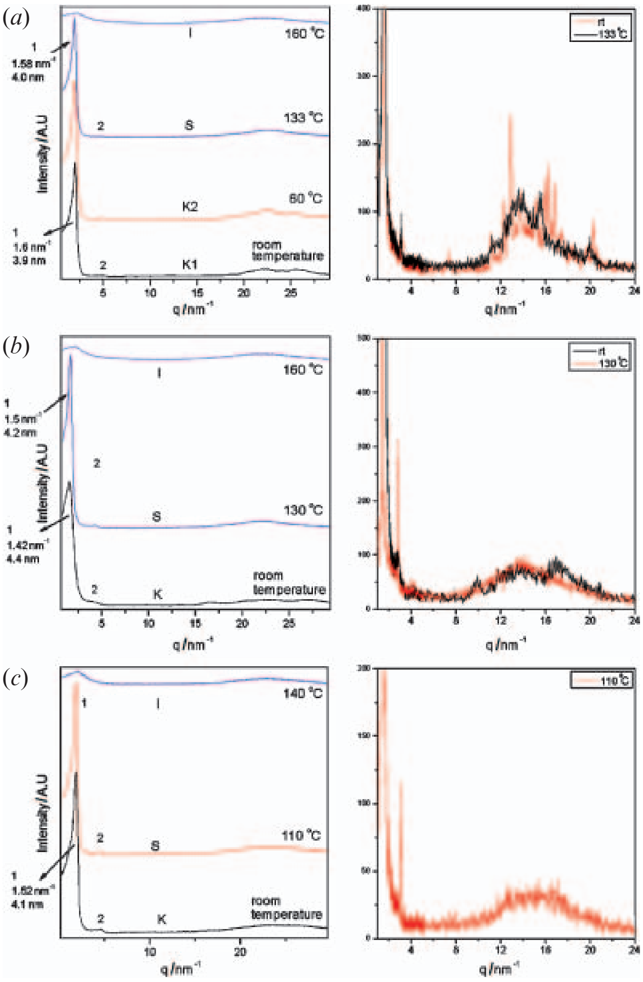


Figure 6. Wide and small angle X-ray diffraction patterns: (*a*) C-PBDB (X=H); (*b*) C-PBFDB (X=F); (*c*) C-PBCDB (X=Cl).

4. Conclusions

The introduction of a lateral halogen substituent in the 3-position of a Schiff's base moiety reduced the transition temperature and prevented the regular stacking of the molecules, resulting in reduced crystallinity of the switchable banana phase, and formation of very complex optical textures. The switching current corresponding to the spontaneous polarization, and the optical microscopic texture indicated that the aligned smectic mesophase was antiferroelectric.

By analysing the phase transition from solid crystalline phase to liquid crystalline phase, we also found that the smallest layer spacing of 40 Å in C-PBDB (X=H) among the synthesized compounds may originate from the overlapping of decanyloxy chains as well as from the increasing director tilt angle.

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