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Synthesis and properties of new materials with banana-shaped achiral cores and chiral end groups

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New chiral bent-core mesogens, derivatives of 1,3-phenylene bis[4-(alkanyloxyphenylimino-methyl)benzoate], were synthesized with variation of a substituent (X = F, Cl); their antiferroelectric properties are described. The mesomorphic and switching properties were characterized by differential scanning calorimetry, polarizing optical microscopy, triangular wave method, and X-ray diffractometry in the small and wide angle regions. The presence of chiral tails at the terminals of side wings in the bent-core molecules induced a decrease in transition temperature and formation of the switchable SmC* phase in the melt. In addition, the introduction of a lateral halogen substituent in the Schiff's base moiety prevented the regular stacking of the molecules, resulting in the formation of very complex optical textures. The smectic phase with F-substituted PBFDOB and Cl-substituted PBCDOB showed layer spacings of 39 and 38.5 Å, respectively, corresponding to the end-to-end distance of molecules with a bent conformation. Significantly, the smectic phases of PBFDOB and PBCDOB exhibited a period of 179.5 and 131 Å, respectively, compatible with a helical structure with periodicity about 4.6 and 3.4 times the layer spacings.

1. Introduction

Since Meyer *et al.* [1] discovered ferroelectricity in the chiral smectic C phase formed by a chiral compound, molecular chirality has been accepted as the essential requirement for the smectic phase to show ferroelectricity. In this case molecular chirality is used to reduce the overall symmetry of the smectic phase. If other structural factors decrease the symmetry of the liquid crystal phase in the same manner as molecular chirality [2], ferroelectricity or antiferroelectricity could appear even in liquid crystal systems derived from achiral molecules [3, 4]. The mesomorphic properties of achiral bent-core molecules have been studied extensively in recent years [5–9], but little study has been given to the properties of the smectic phases of chiral bent-core molecules. Watanabe *et al.* [10] reported the synthesis of a bent-core material with chiral tails in order to investigate the role of tails in the formation of the superstructure in bent-core liquid crystal materials.

For this study, new bent-core compounds having a F- or Cl-substituent in the 3-position, and a chiral tail in the 4-position of an aniline ring, were synthesized and characterized. We describe the syntheses of the bent-core compounds and the effect of electron-withdrawing and chiral groups on its mesomorphism, crystallinity, and antiferroelectricity. The addition of citronellol tails in the construction of a bent-shaped molecule having a F- or Cl-substituent in the 3-position of a *p*-alkoxyaniline Schiff's base moiety is expected to yield special molecular assemblies in the chiral smectic phases.

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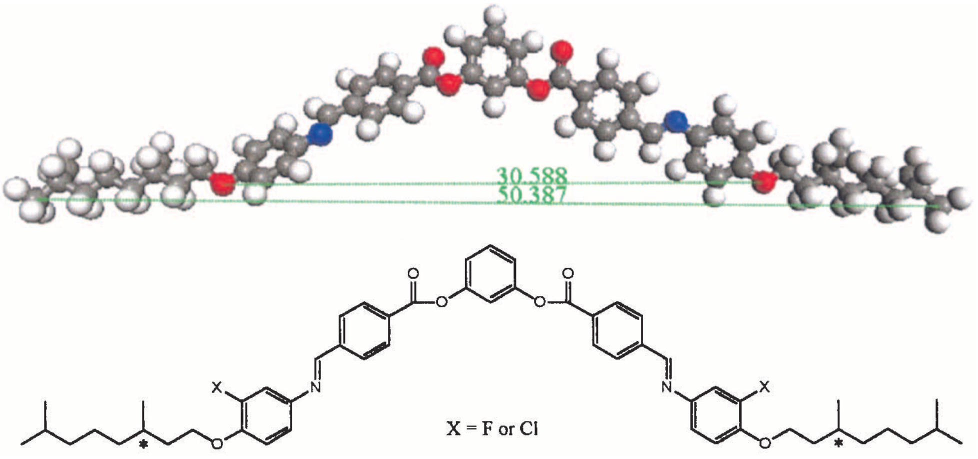


1,3-phenlene bis {4-[3-halo-4-(3(*S*),7-dimethyloctyloxy)phenyliminomethyl]benzoate}

2. Experimental

As shown in the scheme, the syntheses of the new bent-core molecules containing chiral tails, 1,3-phenylene bis{4-[3-fluoro---4-(3(*S*),7-dimethyloctyloxy)-phenyliminomethyl]benzoate} (PBFDOB) and 1, 3-phenylene bis{4-[3-chloro---4-(3(*S*),7-dimethyloctyloxy phenyliminomethyl]benzoate} (PBCDOB), were achieved by general synthetic methods [11–13]. The product was purified by chromatography on silica gel, and recrystallized several times from ethanol/dimethylformamide (50/1 v/v). Yield after purification was 20–30%. ^{1}H NMR ($CDCl_3$, 500 MHz) for compound with $X=F$; $\delta=0.6$(6H, d), 1.0–1.9 (32H, m), 4.0(4H, t), 6.9–7.5 (10H, m), 8.03(4H, d), 8.25(4H, d), 8.5(2H, s). Anal: calcd for $C_{54}H_{62}F_2N_2O_6$ C 74.46, H 6.94, N 3.22; found C 73.95, H 7.353, N 3.256.

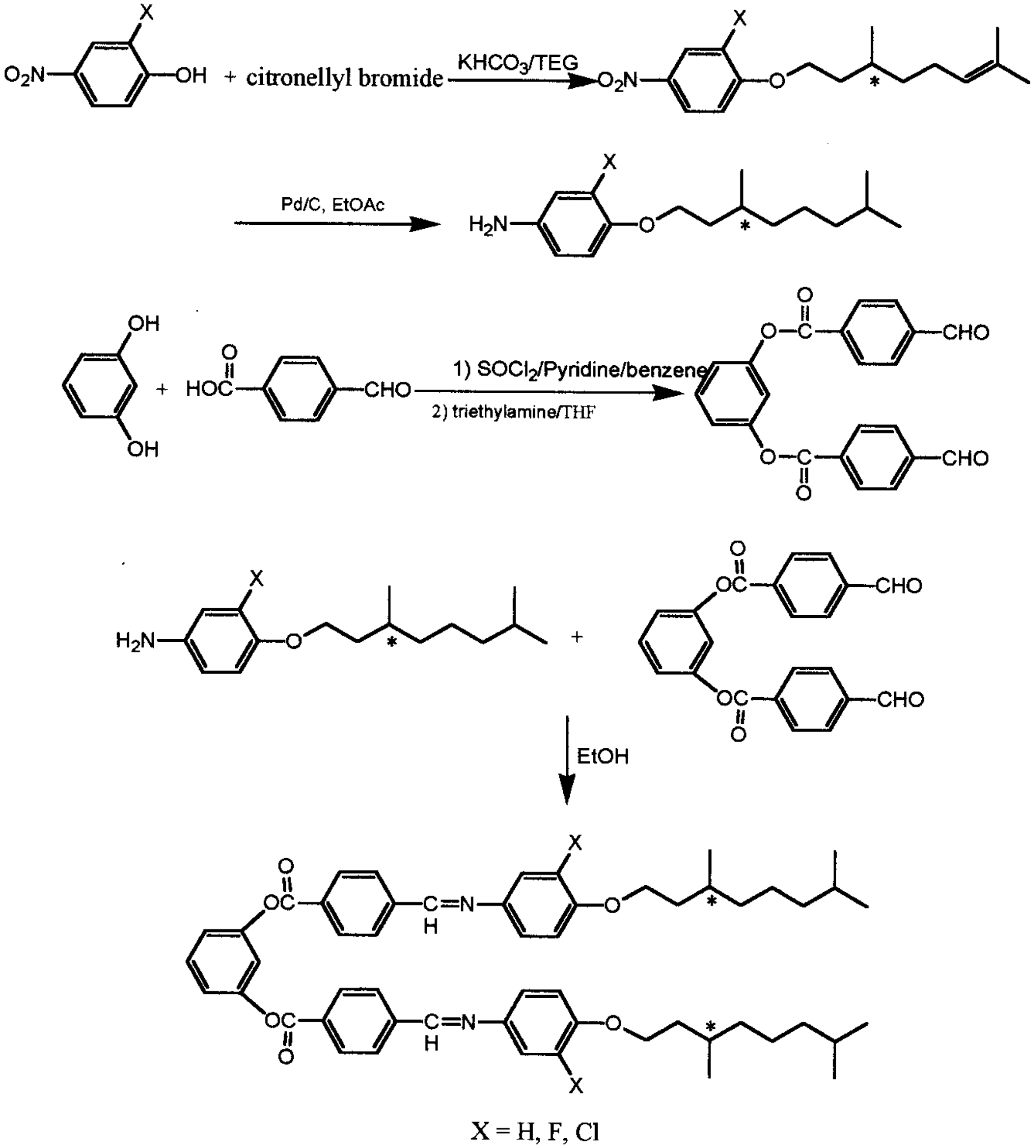
NMR spectra were obtained with a Brucker DRX NMR spectrometer. Elemental analysis was carried out using a Leco CHNS-932 (USA). The transition behaviours were characterized by differential scanning calorimetry (Perkin-Elmer DSC7) and by polarizing microscopy (POM) (Nikon Eclipse E400 POL). DSC measurements were performed under N_2 with a cooling rate of $10^{\circ}\mathrm{C\,min}^{-1}$. Texture observation was carried out using POM with a hot plate. Wide angle X-ray diffraction and small angle X-ray scattering measurements were carried out using a Siemens D5000 X-ray diffractometer. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the Pohang Accelerator Laboratory, Korea. In order to investigate structural change on heating, the sample was held in an aluminum sample holder, sealed with a window of 7 μm thick Kapton film on both sides. The sample was heated by two catridge heaters and the temperature of the sample was monitored by a thermocouple placed close to the sample. A background scattering correction was made by subtracting the scattering from the Kapton. The switching current was examined by the triangular wave method [14].

3. Results and discussion

3.1. *Thermal and electro-optical properties*

Figure 1 shows the DSC thermograms for the new bent-core molecules with chiral tails. In figure 1 (*a*) for PBFDOB, two endothermic peaks are observed on heating, indicating the existence of one mesophase such as a smectic C phase. On cooling, two exothermic peaks appear from the isotropic phase. The introduction of a lateral substitutent in the 1,3-phenylene moiety results in a decrease of the smectic thermal stability [15]. The presence of a lateral fluoro-substituent in the 3-position of the Schiff's base moiety prevents regular stacking of the molecules, so the melting and isotropic points are depressed. Besides its effect on steric hindrance, the lateral substituent could lead to increased spontaneous polarization. Akutakawa *et al.* [16] concluded that the smectic phase would be affected more than the nematic phase by a lateral chloro-substituent, although the relative effects depend upon the nature of the molecule into which it is introduced. In figure 1 (*b*) for PBCDOB a sharp peak and a broad peak are observed on cooling.

Figure 2 displays the optical textures of the compounds. As shown in figure 2 (*a*), PBFDOB showed a fern-like texture on cooling the isotropic liquid. In figure 2 (*b*), PBCDOB showed a broken fan-shaped texture on cooling the isotropic liquid. The bent-core molecules should be packed into a polar C_{2V} or C_2 symmetry in the smectic layers. Hence, the smectic



Scheme.

phase should be ferroelectric and antiferroelectric as reported by Watnabe *et al.* [17].

Figure 3 shows the textural changes of the switched states on applying different electric fields. When PBFDOB is filled in the cell, virgin domains, which are formed spontaneously on cooling the isotropic phases, are sensitive to the sign of the electric field. Applying an electric field of $20\,\mathrm{V\,\mu m^{-1}}$ to the electro-optical cell, birefrigence colour on the virgin domain with a black substrate is formed. But, with a $-20\,\mathrm{V\,\mu m^{-1}}$ field, the birefrigence colour of the domain disappears, and then a new birefringence colour forms in the area of the black substrate. According to Link *et al.* [5], there are regions within an electro-optical cell where the texture of the switched state differs with opposing sign of the applied electric field. The occurrence of such regions depends on the history of the sample but also on the material.

Figure 4 shows the dependence of spontaneous polarization of the samples on decreasing temperature. The data indicate that the switchable smectic phases exhibit

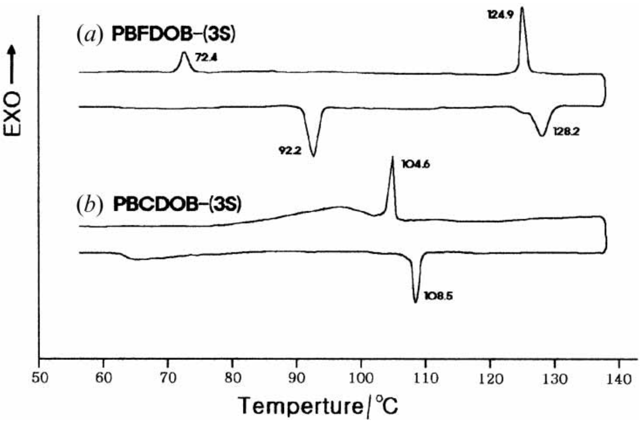


Figure 1. DSC thermograms of the bent-core compounds with chiral tails: (*a*) X=F (PBFDOB); (*b*) X=Cl (PBCDOB).

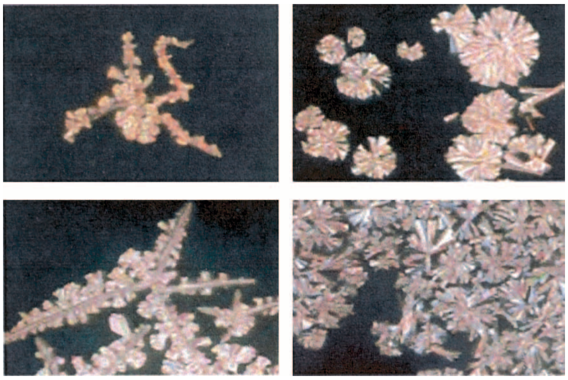
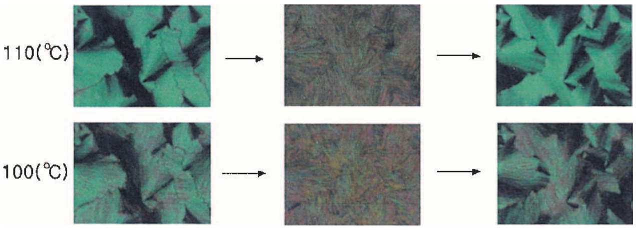

(*a*) (*b*)

Figure 2. Optical micrographs of the smectic phase taken on cooling from the isotropic liquid: (*a*) PBFDOB showed a fern-like texture; (*b*) PBCDOB showed a broken fan-shaped texture.



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

Figure 3. Textural change of the switched states of a PBFDOB cell under different electric fields. The domains formed after cooling from the clear isotropic phase: (*a*) $E=+20$, (*b*) $E=0$, (*c*) $E=-20\,\mathrm{V\,\mu m^{-1}}$.

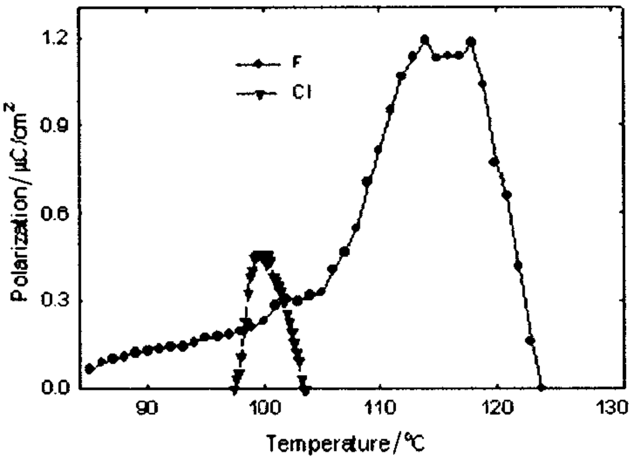


Figure 4. The temperature dependence of the spontaneous polarization of the bent-core compounds with chiral tails.

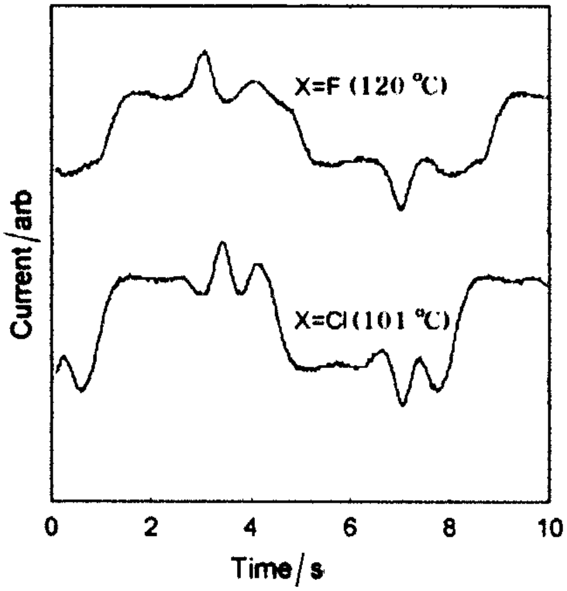


Figure 5. Switching current curves obtained by applying a triangular wave voltage: (*a*) X=F (120°C); (*b*) X=Cl (101°C).

a maximum polarization of about $1\,200\,\mathrm{nC\,cm^{-2}}$ for PBFDOB and $500\,\mathrm{nC\,cm^{-2}}$ for PBCDOB respectively. Figure 5 shows the polarization reversal current of the cells at temperatures corresponding to clear isotropic liquid and the smectic phase. The compounds exhibit two reversal current peaks for every half-period, with the peak observed at 120, and 101°C for X=F and Cl, respectively. Such low-reversal current peaks may be due to the association of large domains. This means that the smectic phases are antiferroelectric.

3.2. *X-ray study*

Figure 6 displays the wide angle and small angle X-ray diffraction (XRD) patterns of PBFDOB. In

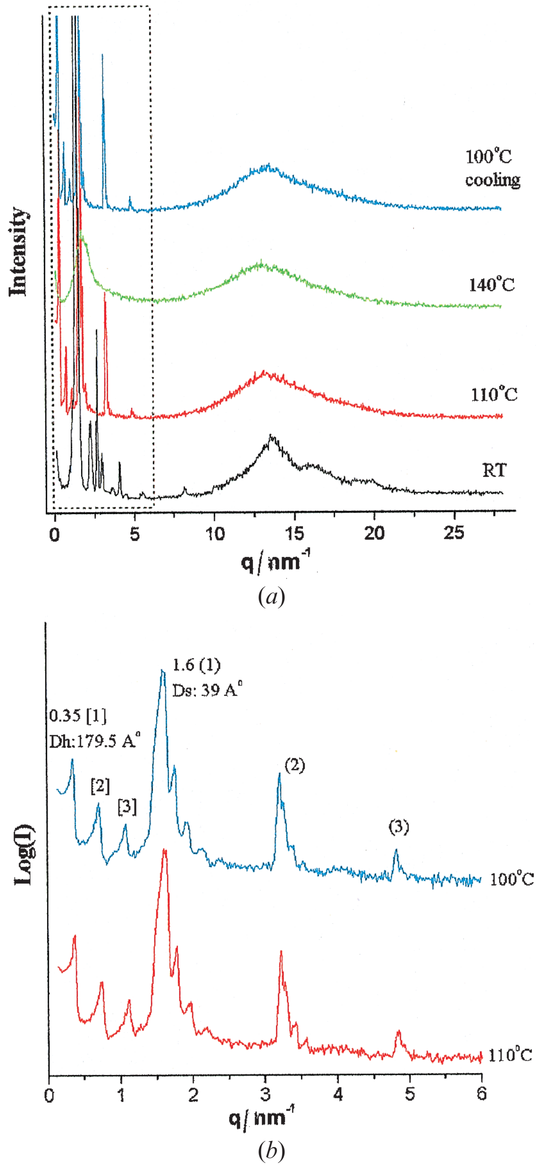


Figure 6. Temperature dependence of the X-ray scattering patterns of PBFDOB: (*a*) wide angle, (*b*) small angle.

figure 6 (*a*), the XRD pattern at room temperature indicates the crystal structure. On heating to 110°C (above the transition temperature of 72.4°C by DSC), an amorphous hollow appears in the wide angle XRD pattern, but in the small angle region a very sharp and strong diffraction pattern is observed (inside the dash-line box); this is indicative of smectic structure. Upon further heating above the isotropization temperature defined by DSC, no diffraction peaks are observed in the XRD pattern. In figure 6 (*b*), the scattering pattern obtained at 110°C on heating and at 100°C on cooling (below the transition temperature of 124.8°C by DSC) shows three sharp reflections at reciprocal space ratios of 1:2:3, indicative of a structure with layer spacing of 39 Å. In this smectic phase, three additional reflections at very low angle are developed at the relative positions 1, 2, and 3, where the *d*-spacing of the first peak at $q=0.35\,\mathrm{nm}^{-1}$ is 179.5 Å. The periodicity of 179.5 Å, about 4.6 times 39 Å, may correspond to a helical pitch distance of the smectic phase.

Figure 7 displays the XRD pattern of PBCDOB. As can be seen from the figure, the XRD pattern of this compound is very similar to that of PBFDOB. In figure 7, the XRD pattern of PBCDOB at room temperature displays several high order reflections with integral spacing ratios in the small angle region. All the peaks in the small angle diffraction pattern disappear at 120°C (above the transition temperature of 108.5°C by DSC). On cooling to 90°C (below the transition temperature of 104.5°C by DSC), two reflections with integral spacing ratios appear in the small angle region; this is indicative of smectic liquid crystal structure. The lattice spacing was calculated to be 38.5 Å. The smectic phase of PBCDOB exhibited a period of 131 Å, about 3.4 times 38.5 Å.

4. Conclusions

Two new liquid crystalline compounds comprising a bent-core mesogen with chiral tails, derivatives of 1,3-phenylene bis{4-[4-(3(*S*),7-dimethyloctyloxy)phenyliminomethyl]benzoate}, were synthesized with variation of a substituent (X=F, or Cl). The presence of chiral tails at the terminals of the side wings, in the bent-core molecules containing a Schiff's base moiety, induced a decrease in melting temperature and formation of the

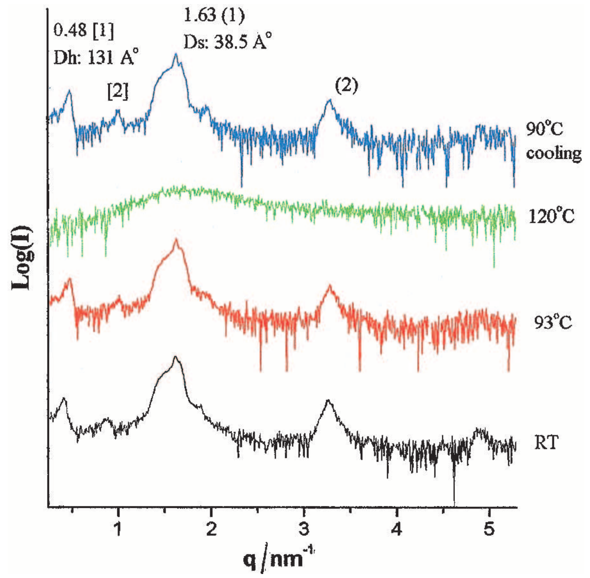


Figure 7. Temperature dependence of the small angle XRD pattern of PBCDOB.

switchable SmC* phase in the melt. From consideration of the switching current in relation to the spontaneous polarization, optical microscopic texture, and XRD pattern, the mesophases of the fluorinated (PBFDOB) and chlorinated (PBCDOB) compounds were antiferroelectric. Moreover, the introduction of lateral halogen substituents in the Schiff's base moiety prevents regular stacking of the molecules and results in the formation of very complex optical textures. The smectic phases of PBFDOB and PBCDOB showed layer spacings of 39 and 38.5 Å, respectively. Significantly, the smectic phases of PBFDOB and PBCDOB have a periodicity about 4.6 and 3.4 times the spacing of a smectic layer, respectively, corresponding to a supermolecular helical structure.

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References

[1] Meyer, R. B., Lievert, L., Strzelecki, L., and Keller, P., 1975, *J. Phys. (Paris) Lett.*, **36,** L69.

[2] Blinov, L. M., 1998, *Liq. Cryst.*, **24,** 143.

[3] Niori, T., Sekine, T., and Takezoe, H., 1996, *J. mater. Chem.*, **6,** 1231.

[4] Jakli, A., Saupe, A., Scherowsky, G., and Chen, X. H., 1997, *Liq. Cryst.*, **22,** 309.

[5] Link, D. R., Natale, G., Shao, R., Maclennan, J., Clark, J., Korblova, N. A., and Walba, D. M., 1997, *Science*, **278,** 1924.

[6] Sekine, T., Niori, T., Sone, M., Watanabe, J., Choi, S. W., Takanishi, Y., and Takezoe, H., 1997, *Jpn. J. appl. Phys.*, **36,** 6455.

[7] Chien, L. C., and Lee, C. K., 1999, *Liq. Cryst.*, **26,** 609.

[8] Niori, T., Sekine, T., Watanabe, J., and Takezoe, H., 1997, *Mol. Cryst. liq. Cryst.*, **301,** 337.

[9] Pelzl, G., Diele, S., and Weissflog, W., 1999, *Liq. Cryst.*, **26,** 135.

[10] Watanabe, J., Takezoe, H. D. R., Link, Nakata, M., Thisayukta, J., Niwano, H., Takanishi, Y., and Ishikawa, K., 2002, 19th in Proceedings of the International Liquid Crystal Conference, Edinburgh, UK, 30 June–5 July, 2002, P634.

[11] Hassen, A., and Alexanian, V., 1978, *Tetrahedron Lett.*, 4475.

[12] Gray, G. W., and Jones, B., 1954, *J. chem. Soc.*, 1467.

[13] Kuhn, W. E., 1943, *Org. Synth., Collect*, **2,** 447.

[14] Miyasato, S., Abe, H., and Kuze, E., 1983, *Jpn. appl. Phys.*, **22,** L661.

[15] Sethna, V. M., and Spielberg, N., 1980, *Mol. Cryst. liq. Cryst.*, **62,** 141.

[16] Akutagawa, T., Matsunaga, Y., and Yasuhara, K., 1994, *Liq. Cryst.*, **17,** 659.

[17] Watanabe, J., Niori, T., Choi, S. W., Taknishi, Y., and Takezoe, H., 1998, *Jpn. J. appl. Phys.*, **37,** L 401.