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# Antiferroelectric liquid crystal from a banana-shaped achiral molecule

CHONG-KWANG LEE†‡, JAE-HOON KIM§, E-JOON CHOI¶,
WANG-CHEOL ZIN‖ and LIANG-CHY CHIEN*†

†Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA
‡Dept. of Chemistry, Gyeongsang National University, Chinju 660-701, Korea
§Dept. of Physics, Hallym University, Chunchon 200-702, Korea
¶Dept. of Polymer Science and Engineering,
Kumoh National University of Technology, Kumi 730-701, Korea
‖ Dept. of Materials Science and Engineering,
Pohang University of Science and Technology, Pohang 790-784, Korea

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A new banana-shaped achiral compound, 1,3-phenylene bis[4-(3-fluoro-4-*n*-octyloxyphenyliminomethyl)benzoate] (PBFOB) was synthesized and its antiferroelectric liquid crystallinity determined. The PBFOB was characterized by differential scanning calorimetry, X-ray diffractometry in the small and wide angle regions, and polarizing optical microscopy; its polarization and antiferroelectric properties were also investigated. The presence of a lateral fluoro-substituent in the banana-shaped achiral molecules containing a Schiff's base mesogen induced a decrease in melting temperature and formation of the switchable smectic $B_2$ phase in the melt. The spontaneous polarization for PBFOB was about 250 nC cm$^{-2}$ and the polarization of this phase switched on the reversal of an applied electric field.



## 1. Introduction

Since Meyer *et al.* [1] discovered ferroelectricity in the 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, ferroelectricity or antiferroelectricity could appear even in liquid crystal systems derived from achiral molecules. Recently ferroelectric liquid crystal phases from achiral molecules [2] were reported in which smectic phases of compounds with banana-shaped molecules show ferroelectric switching [3, 4]. The bent-shaped molecules are tightly packed and are all aligned in the bent direction forming polar order. If the bent-shaped molecules are tilted with respect to the layer normal or to the columnar axis, the materials have only $C_2$ symmetry. In recent years, the study of liquid crystals comprising non-chiral banana-shaped molecules has grown rapidly [5–9]. It has been established that the ground state of the switchable smectic $B_2$ ($SmB_2$) phase is antiferroelectric [10–12]. Niori *et al.* [3] first suggested that the $SmB_2$ phase was ferroelectric and has a $C_{2v}$ symmetry, where the planes of the banana-shaped molecules are normal to the layers. However, Link *et al.* [12] showed that the planes are at an angle to the normal layer and that the phase is antiferroelectric. From the structural point of view, the interest is mainly centred on the synthesis of various bent-shaped molecules having smectic phases, preferably with low transition temperatures [13]. The introduction of additional polar groups in the construction of bent-shaped molecules is expected to facilitate their ferroelectric properties [14].

For this study, a new banana-shaped molecule having a F-substituent in the 3-position of a *p*-alkoxyaniline Schiff's base moiety was synthesized and characterized. In this study we describe the synthesis of this banana-shaped liquid crystalline compound and the effect of

*Author for correspondence; e-mail: lcchien@lci.kent.edu

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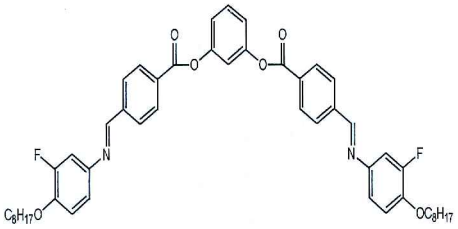
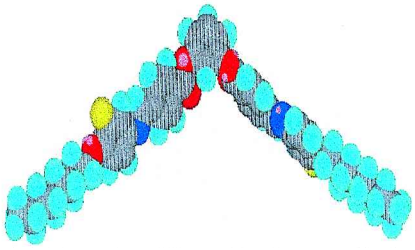
an electron withdrawing group on its mesomorphism, crystallinity, and ferroelectricity.



1,3-phenylene bis[4-(3-fluoro-4-n-octyloxyphenyliminomethyl)benzoate] (PBFOB)



## 2. Experimental procedures

The synthesis of 1,3-phenylene bis[4-(3-fluoro-4-*n*-octyloxyphenyliminomethyl)benzoate] (PBFOB) is shown in the scheme. 2-Fluoro-4-nitro-1-octylbenzene was first prepared by the substitution reaction of 2-fluoro-4-nitrophenol with 1-bromooctane. Then 3-fluoro-4-octyloxyaniline (**I**) was obtained by hydrogenation of the 2-fluoro-4-nitro-1-octyloxybenzene with $H_2$ gas in the presence of palladium on activated carbon. Next, 1,3-phenylene bis(4-formyl benzoate) (**II**) was prepared by the reaction of resorcinol and 4-formylbenzoyl chloride in tetrahydrofuran with triethylamine at 0°C. Finally, PBFOB was obtained by the condensation reaction between the aniline (**I**) and the dialdehyde (**II**). The final product was purified by chromatography on silica gel, and several recrystallizations from a mixture of ethanol and dimethylformamide (50 : 1 v/v). Yield after purification was 20 ~ 30%. $^1$H NMR ($CDCl_3$, 200 MHz): $\delta = 0.6$ (6H, t), 1.0–1.9 (24H, m), 4.0–4.1 (4H, t), 6.9–7.5 (10H, m), 8.01–8.05 (4H, d), 8.2–8.3 (4H, d), 8.5 (2H, s).

IR and NMR spectra were obtained with Hitachi 270-50 IR and Brucker DRX NMR spectrometers, respectively. The transition behaviour was characterized by differential scanning calorimetry (Perkin-Elmer DSC7) and by polarizing optical microscopy (POM) (Nikon Eclipse E400 POL). DSC measurements were performed in a $N_2$ atmosphere with heating and cooling rate of 10°C min$^{-1}$. Optical texture observation was carried out using a polarizing microscope with a hot plate. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the Pohang Accelerator Laboratory, Korea. In order to investigate structure changes on heating, the sample was held in an aluminum sample holder sealed with windows of 7 μm thick Kapton film on both sides. The sample was heated with two cartridge heaters and the temperature of the sample monitored by a thermocouple placed close to the sample. A background scattering correction was made by subtracting the scattering arising from the Kapton. The switching current was observed by the triangular wave method [15]. The sample cell was mounted in a microfurnace for measuring the spontaneous polarization with varying temperature. The temperature fluctuations inherent to the furnace were approximately 0.1 K. For direct measurement of the polarization, the triangular wave method was used 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.

## 3. Results and discussion

### 3.1. *Synthesis and mesogenic properties*

The synthetic route for the compound PBFOB is quite straightforward and each reaction step is of a relatively well known type. The PBFOB obtained was characterized by IR and NMR spectroscopy; the spectral data were in accordance with the expected formula. Figure 1 shows DSC thermograms for PBFOB. On heating, four endothermic peaks appeared in its thermogram: a peak at 64°C for the solid to solid transition, a peak at 118°C for melting, the peak at 147°C for the smectic X (SmX) to smectic $B_2$ ($SmB_2$) phase transition, and a peak at 154°C for clearing. On cooling, two exothermic peaks were observed, corresponding to the clear isotropic liquid to $SmB_2$ transition at 153°C and crystallization at 110°C. The introduction of a lateral F-substituent in the 1,3-phenylene moiety results in a decrease of the melting temperature over the non-fluorinated compound. This is because the presence of the lateral substituent in the 3-position of the Schiff's base moiety prevents the regular stacking of molecules.

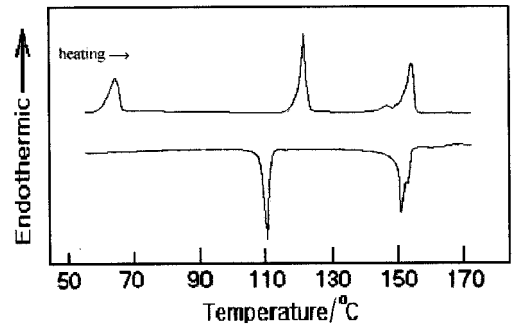
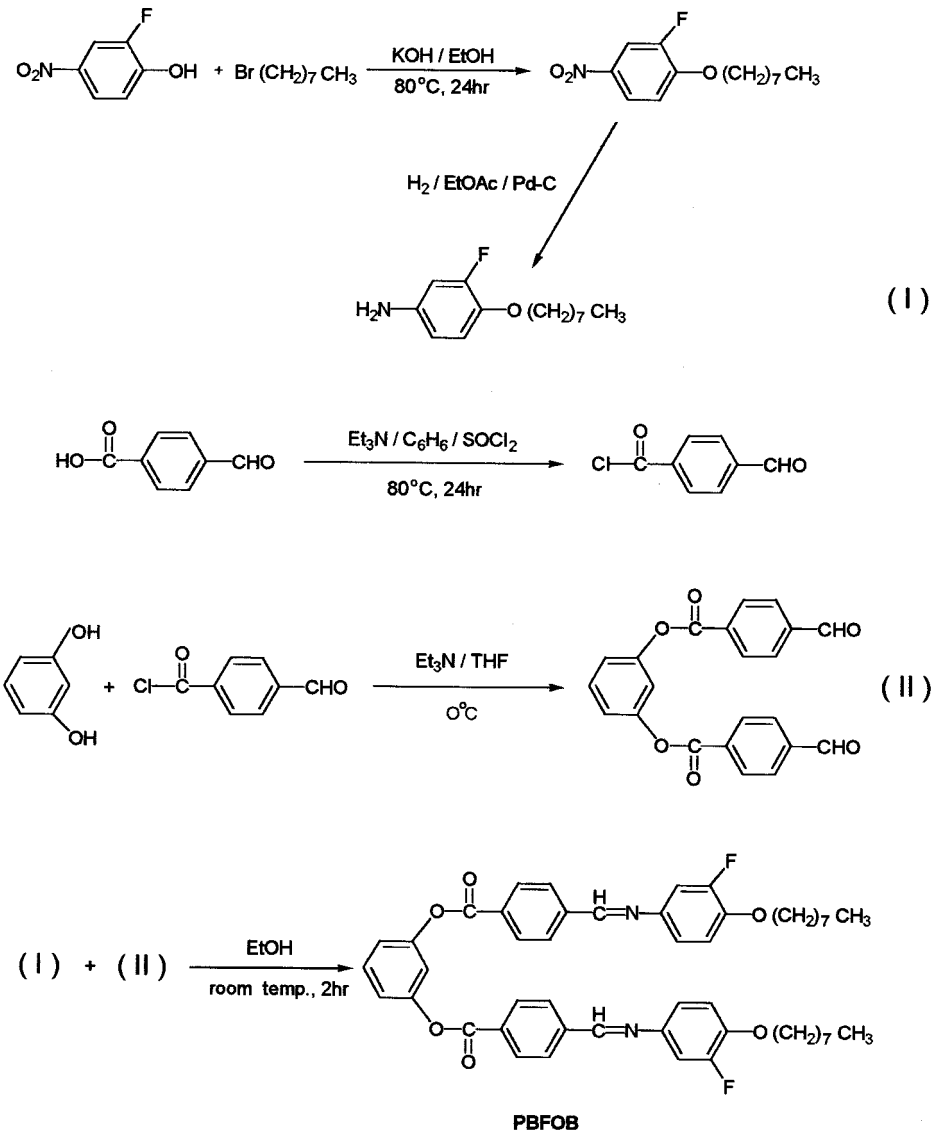



Figure 1. DSC thermogram heating and cooling scans of PBFOB.




Scheme.

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. Firstly, it is expected than 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, the banana-shaped molecule with a F-substituent might be expected to form a smectic phase.

### 3.2. *Microscopy texture*

Using an optical microscope, on heating the sample we could identify three phase transitions—for melting, SmX to $SmB_2$, and $SmB_2$ to clear isotropic liquid; on cooling we could observe only two transitions—for clearing and crystallization. This indicates that one of smectic phases could only appear as inversely monotropic. As shown in figure 2, when the clear isotropic liquid of PBFOB is cooled slowly, the optical texture of the smectic $B_2$ phase appears as textures with granular patterns at the iso–$SmB_2$ phase transition temperature (*a*); this tends to grow into mosaic textures consisting of small domains at room temperature (*b*).

### 3.3. *X-ray study*

Figures 3 and 4 display the XRD patterns obtained at given temperatures. In figure 3 (*a*) the XRD pattern of PBFOB at room temperature displays several high order reflections with integral spacing ratios in its small angle region; in figure 4 (*a*), many sharp reflections are

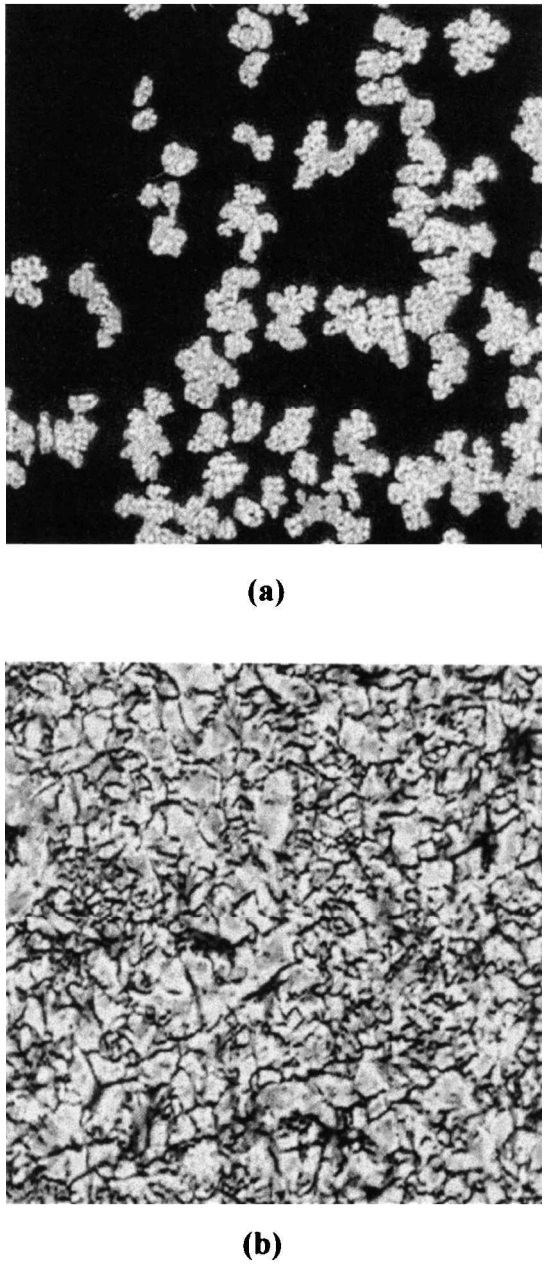



Figure 2. Optical micrographs of the $B_2$ phase of pure PBFOB on cooling from the clear isotropic liquid. (*a*) The $B_2$ phase initially appeared as a texture with granular pattern (×200). (*b*) The granules grow to become mosaic textures consisting of small domains (room temperature, ×40).

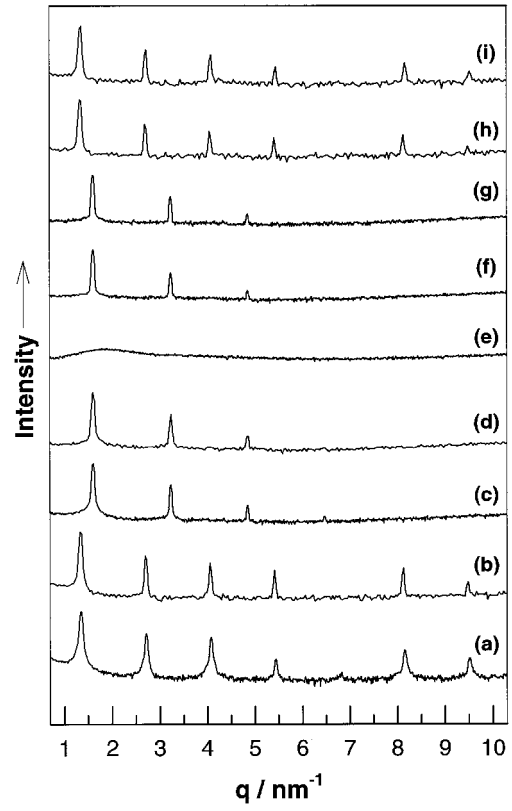



Figure 3. X-ray diffraction patterns in the small angle region: upon heating as prepared sample, measured at (*a*) room temperature, (*b*) 100°C, (*c*) 130°C, (*d*) 150°C, (*e*) 170°C; upon cooling the clear isotropic liquid of same sample, measured at (*f*) 150°C (*g*) 130°C, (*h*) 100°C, (*i*) room temperature.

observed in the wide angle region. This is indicative of a lamellar crystal structure with layer spacing of 46.5 Å. On heating to 100°C (above the transition temperature of 64°C by DSC) figure 3 (*b*), shows the interlayer distance slightly increased to 47 Å, and in figure 4 (*b*), the wide angle X-ray pattern still indicates the crystal structure. Upon further heating to 130°C (above the transition temperature of 118°C by DSC), the interlayer distance decreases to 39.3 Å as shown in figure 3 (*c*), and the wide angle X-ray pattern exhibits only a broad peak as shown in figure 4 (*c*); this is indicative of smectic liquid crystal structure. Although the DSC thermogram of PBFOB showed a significant enthalpy change at 147°C (transition temperature of SmX to $SmB_2$), the small angle region showed only minor changes between the SmX and $SmB_2$ phases in their diffraction patterns—compare figures 3 (*c*) and 3 (*d*). All the fine peaks in the small angle diffraction pattern disappeared at 170°C (above the transition temperature of 154°C by DSC) as shown in figure 3 (*e*).

To follow, upon cooling the isotropic melt to 150°C (below the transition temperature of 153°C by DSC) three sharp reflections with the integral spacing ratio appeared in the small angle region as shown in figure 3 (*f*) without any of the sharp wide angle peaks, shown in figure 4 (*d*); this is indicative of smectic liquid crystal structure. On further cooling, figure 3 (*g*), the smectic phase maintains the same diffraction pattern until 130°C (above the transition temperature of 110°C by DSC).

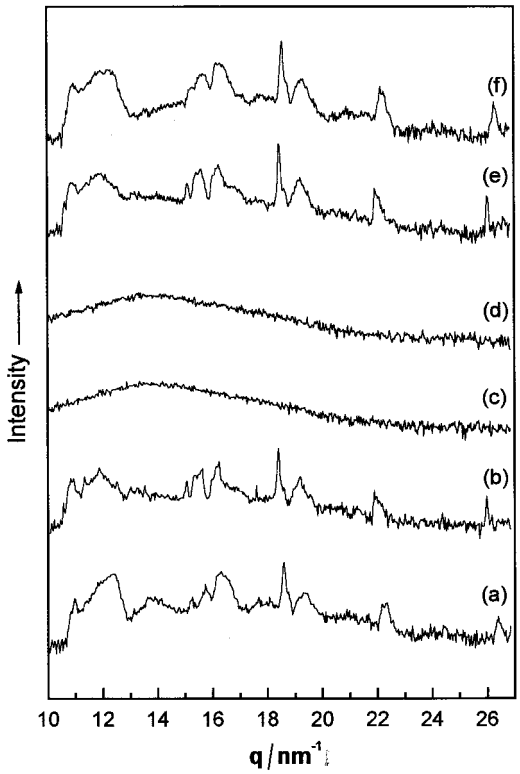



Figure 4. XRD patterns in the wide angle region: upon heating as-prepared sample, measured at (*a*) room temperature, (*b*) 100°C, (*c*) 130°C (*d*) 150°C; upon cooling the clear isotropic liquid of same sample, measured at (*e*) 100°C, (*f*) room temperature.



Below 110°C, the small angle region, as well as the wide angle region, gave many sharp reflections (see figures 3(*h*) and 4(*e*)). This is indicative of a lamellar crystal structure.

Our suggestions to explain the changes in interlayer distance are as follows. The most stable conformation of the central rod part of PBFOB is a bent structure, with an end-to-end distance of about 40 Å. At room temperature the central rod and stretched side coil parts are both crystallized. At 64°C the central rod part is crystal and the alkyl part melted so that the interlayer spacing is slightly increased. Upon further heating to 118°C, the rod part melts, the inter-rod distance and the interfacial area between rod and coil parts are increased, and the end-to-end distance of the coil is decreased to maintain a uniform density; in consequence the layer thickness is decreased.

### 3.4. *Spontaneous polarization and switching current*

In order to characterize the smectic phase, we measured the spontaneous polarization of the sample. For this measurement, a cell was made from conductive indium tin oxide coated glass plates treated with rubbed polyimide for alignment. The cell gap was maintained by 10 μm thick glass spacers. Figure 5 shows the polarization reversal current of the cell at temperatures corresponding to clear isotropic liquid and the $SmB_2$ phase. While there are no peaks at high temperature (155°C), two sharp reversal current peaks for every half period are clearly observed at low temperature (135°C). Thus, we can conclude that the $SmB_2$ phase of PBFOB is antiferroelectric, with the tip of the bent molecule orienting to the electric field and reversing its orientation on reversal of the polarity of the field. It is worth noting that the lack of optical contrast between the two polarization states indicates that the fluorinated banana-shaped liquid crystal is racemic. But under a high field it shows a smectic A like structure.

Figure 6 shows the spontaneous polarization of the sample with decreasing temperature. The data indicate

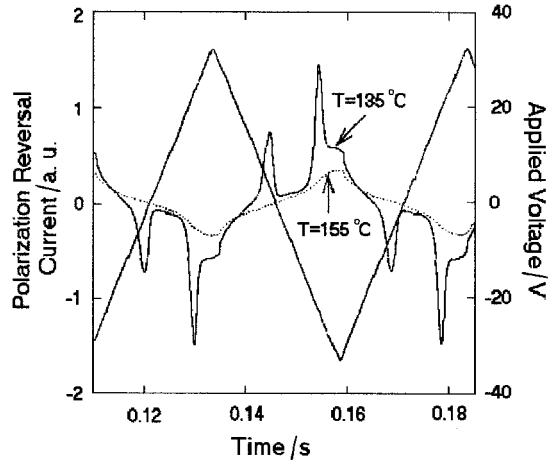



Figure 5. Switching current curve obtained by applying a triangular voltage wave at 150°C.

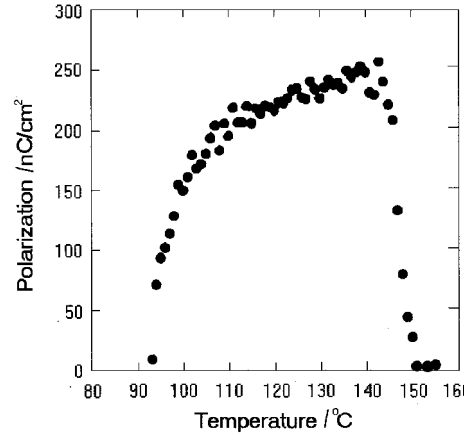



Figure 6. Temperature dependence of spontaneous polarization of PBFOB.

that this switchable smectic phase exhibits a maximum polarization of about 250 nC cm$^{-2}$. The spontaneous polarization is sharply increased with decreasing temperature below 150°C and becomes saturated at 140°C. This sharp increase of polarization suggests that the clear isotropic liquid to $SmB_2$ phase transition is first order. On further decreasing the temperature below 110°C, however, the polarization decreased and vanished at 93°C. This is probably due to the gradual crystallization of the central rod parts of the molecules.

## 4. Conclusions

The introduction of a lateral fluoro-substituent to banana-shaped compounds containing a Schiff's base mesogen reduced the melting and clearing temperatures without disturbing the formation of the smectic phase. The reported banana-shaped compound with a fluorine substituent in the 3-position of a Schiff's base moiety formed the switchable smectic $B_2$ phase even though the constituent molecules are achiral. From consideration of the switching current corresponding to the spontaneous polarization, and the optical microscopic texture, the aligned smectic phase was assigned as antiferroelectric.

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## References

[1] Meyer, R. B., Strzelcki, L., and Keller, P., 1975, *J. Phys. (Fr.)*, **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] Jàkli, A., Saupe, A., Scherowsky, G., and Chen, X. H., 1997, *Liq. Cryst*., **22,** 309.
[5] Niori, T., Sekine, T., Watanabe, J., and Takezoe, H., 1997, *Mol. Cryst. Liq. Cryst*., **301,** 337.
[6] Sekine, T., Takanishi, Y., and Takezoe, H., 1997, *J. Mater. Chem*., **7,** 1307.
[7] Cai, R., and Samulski, E., 1991, *Liq. Cryst*., **9,** 617.
[8] Matsunaga, Y., and Miyamoto, S., 1993, *Mol. Cryst. Liq. Cryst*., **237,** 311.
[9] Chien, L. C., and Lee, C. K., 1999, *Liq. Cryst*., **26,** 609.
[10] Lischka, C., and Weissflog, W., 1997, in Proceedings of the European Conference on Liquid Crystals, Zakopane, Poland, March 3–8, 1997, p. 126.
[11] Kentischer, F., Macdonald, R., Warnick, P., Heppke, G., and Rauch, S., 1997, *Proc. SPIE*, **3143,** 128.
[12] Link, D. R., Natale, G., Shao, R., Maclennan, J., Clark, N. A., Korblova, E., and Walba, D. M., 1997, *Science*, **278,** 1924.
[13] Pelzl, G., Diele, S., and Weissflog, W., 1999, *Liq. Cryst*., **26,** 135.
[14] Lee, C. K., Kwon, S. S., Chien, L. C., and Choi, E. J., 2000, *Bull. Korean Chem. Soc*., **21,** 1155.
[15] Miyasato, K., Abe, H., Takezoe, A., and Kuze, E., 1983, *Jpn. J. Appl. Phys*., **22,** L661.