Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006

To cite this article: A. Fukuda, S. S. Seomun, T. Takahashi, Y. Takanishi & K. Ishikawa (1997): Tilting Correlation in Adjacent Layers and Possible Thresholdless Antiferroelectricity IN SC*-Like Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 303:1, 379-390

To link to this article: http://dx.doi.org/10.1080/10587259708039449

Mol. Cryst. Liq. Cryst., 1997, Vol. 303, pp. 379–390
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Printed in India

TILTING CORRELATION IN ADJACENT LAYERS AND POSSIBLE THRESHOLDLESS ANTIFERROELECTRICITY IN SC*-LIKE LIQUID CRYSTALS

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Abstract We have first reviewed (1) the extremely bent molecular shape, (2) in-layer spontaneous polarizations near smectic layer boundaries parallel to the tilt plane in SC_A*, (3) a difference in the molecular states of rotation about their long axes between SC_A* and SC*, and (4) the ANNNI model with J_3 by Yamashita (C1P.12 (P-124) at this Conf.). Then we have observed the pretransitional effect in the tristable switching in three compounds and analyzed it through a thought experiment based on the above review; tilting directions in adjacent layers are concluded to be correlated with the biased directions of molecular rotation about the long axes. Finally we have presented evolution of switching characteristics from tristable to V-shaped in the first component compound of the mixture reported to show the thresholdless antiferroelectricity (Inui *et al.*, J. Mater. Chem., 6, 671 (1996)), and discussed it in terms of the above thought experiment.

MOLECULAR ARRANGEMENTS IN SC* AND SC_A*

In both of the phases, SC* and SC_A*, the tilting is restricted parallel to a single plane not only in a layer but also in the neighboring layers as illustrated in Figure 1,[1] if we disregard the slight spontaneous twist and/or bend of C-directors.[2] The excluded volume effect in a smectic layer structure preserving the density wave character must be

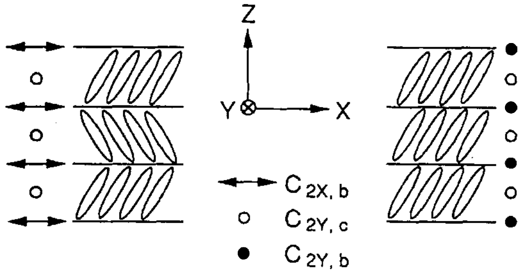


FIGURE 1. Molecular arrangements in SC* and SC_A*, symmetry axes, and the liquid crystal coordinate system (*X*, *Y*, *Z*).

the main factor in the intermolecular interactions that causes this restriction in SC*. The tilting of the molecular long axes with respect to the smectic layer normal is caused by other intermolecular interactions, which must be effective in the SC*-like liquid crystals general; one of the most probable, intuitive causes for the tilting is the dispersion force between the transverse permanent dipoles on the end chains and the polarizable centers of neighboring molecules in a smectic layer.[3] If that is the case, what molecular interactions are responsible for stabilizing SC_A* as against SC*? Although Nishiyama and Goodby[4] suggested a possible important role of the steric interaction even in SC_A*, it is rather difficult to explain naturally why the tilting occurs parallel to a single plane. The electric Coulomb interaction between transverse permanent dipoles of chiral end chains in adjacent layers, on the other hand, inevitably results in the tilting restriction in SC_A*.[1,5,6]

EXTREMELY BENT CHIRAL ALKYL CHAINS AND THEIR PRECESSION AROUND LONG CORE AXES IN SA

We will first explain that almost all antiferroelectric liquid crystal (AFLC) molecules are of extremely bent shape. Because of the potential application to display devices, a large number of, probably almost 1,000, AFLC and related compounds have been synthesized. Most AFLC compounds so far synthesized have similar structures to those of MHPOBC and TFMHPOBC, two prototype AFLCs. The structure can be considered to consist of three substructures, achiral chain, central core, and chiral chain with connector, as illustrated in Figure 2. X-ray crystallographic studies by Hori and Endo[7] revealed the

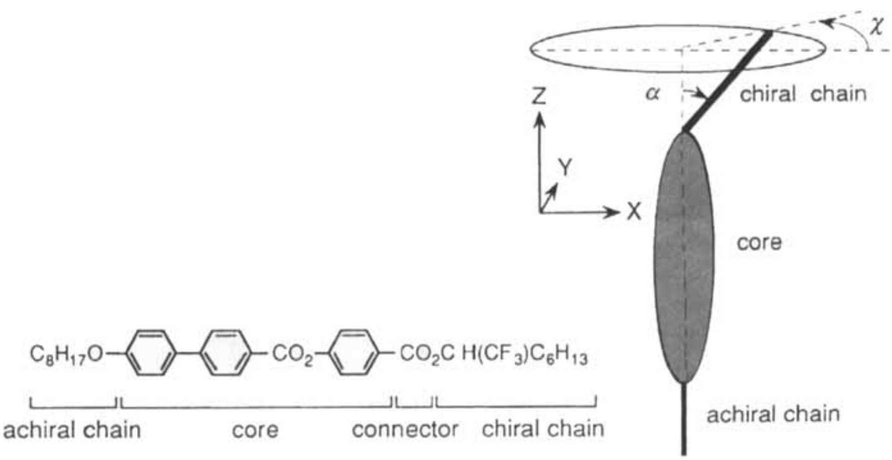


FIGURE 2. Three substructures as illustrated in TFMHPOBC, chiral chain with connector, central core, and achiral chain, and a model of the extremely bent chiral chain precessing around the long core axis.

unexpected bent molecular shape of MHPOBC in its crystal phase just below SC_A*. Quite recently, Jin *et al.*[8] unambiguously showed that the chiral chain is projecting obliquely with an angle >54.7° (the magic angle) from the core long axis and is precessing around it even in liquid crystalline phases, as illustrated in Figure 2. This bent molecular shape has also been confirmed by NMR and other investigations.[9,10]

IN-LAYER SPONTANEOUS POLARIZATIONS NEAR BOUNDARIES AND INTERMOLECULAR INTERACTION STABILIZING SC_A*

The extremely bent molecular structure may allow permanent dipoles locating near the chiral carbons to adequately interact in adjacent layers through the Coulomb force. Before considering this interaction in detail, let us first clarify the symmetry axes existing in SC* and SC_A*. As shown in Figure 1, there are two kinds of twofold axes. In SC_A*, one at the layer boundary is parallel to the X axis in the tilt plane ($C_{2X,b}$), and the other is located in the center of the layer perpendicularly ($C_{2Y,c}$). In SC*, on the other hand, both of the twofold axes in the center ($C_{2Y,c}$) and the boundary ($C_{2Y,b}$) are perpendicular to the tilt plane. When the anticlinic SC_A* model was proposed, the $C_{2Y,c}$ axis was the only one taken into consideration explicitly; the in-layer spontaneous polarization along $C_{2Y,c}$, P_Y, alternates its sign from layer to layer, thereby canceling each other to stabilize antiferroelectricity.[1]

Since SC_A is observed even in the racemate, however, Takanishi *et al.*[5] applied this simple P_Y model to the understanding of antiferroelectricity not in SC_A* but in the chiral smectic-C_α (SC_α*) phase. They proposed instead the pairing model for SC_A* where transverse dipole moments in adjacent smectic layers form pairs; some molecular interactions considered necessary to cause the local spontaneous optical resolution that promotes the association of each like enantiomer R or S. On the other hand, Cladis and Brand[11] insisted on the importance of the $C_{2X,b}$ axis in the tilt plane and Miyachi *et al.*[6] proposed the P_X model for the understanding of antiferroelectricity in SC_A* (SC_A). Note that the P_X model is independent of chirality. The aforementioned bent molecular shape[8] and the following carbonyl biased (or hindered) rotational motion[6,12,13] appear to support the P_X model.

Figure 3 show the IR absorbance vs polarizer rotation angle in a homogeneously aligned cell for the stretching vibrations of C=O near the chiral carbon (1720 cm^{-1}), C=O in the core (1739 cm^{-1}), and the phenyl ring (1604 cm^{-1}).[12] The IR radiation is incident along the Y axis in Figure 1. The simulated results plotted as a function of $\omega' = \omega - \theta$ were obtained using a distribution function in the molecular frame,

$$f(\psi) = (1/2\pi)\,\{1 + a\,\cos(\psi - \psi_0)\}.$$

Here a is the degree of biasing and ψ_0 the biased direction. Core C=O must have $\psi_0 = 0$ in this distribution function because of mirror symmetry with respect to the tilt plane. By comparing the experimental results with the simulated ones, we can conclude $a \sim 0.3$ and $\psi_0 \sim -75°$ for chiral C=O.

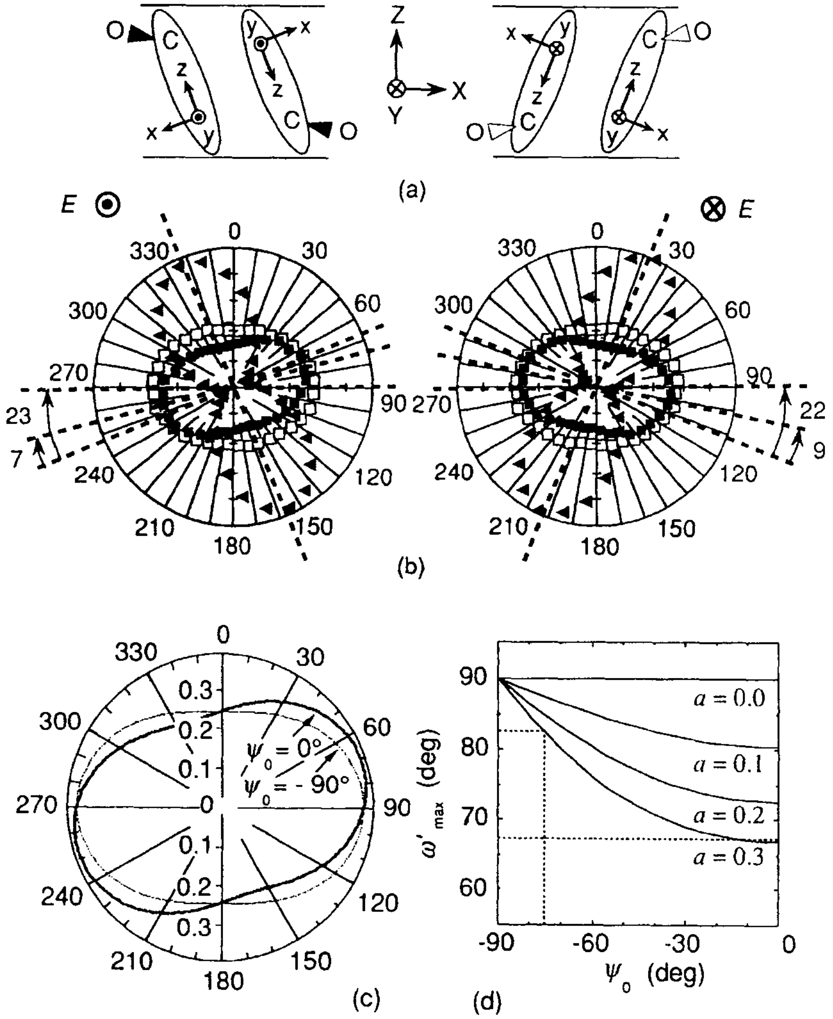


FIGURE 3. The IR absorbance vs polarizer rotation angle for C=O and phenyl ring stretching peaks in SC* of a homogeneous cell. (a) The molecular coordinate system (x, y, z) satisfying the symmetry requirement of the phase, (b) experimentally obtained results for C=O near the chiral carbon (■), C=O in the core (□), and phenyl rings (▼), (c) calculated results for C=O, and (d) the relationship between ω'_{max} and ψ_0, where ψ_0 is the biased or hindered direction and ω'_{max} is the polarizer rotation angle where the absorbance becomes maximum.

Figure 4 summarizes the corresponding results obtained for a homeotropically aligned cell.[6,12] The IR radiation is incident along the Z axis in Figure 1; the polarizer is rotated clockwise when viewed from the negative side of the Z axis and $\omega=0$ is the X axis. The degree of polarization experimentally determined, ~ −0.025 in SC* and ~ 0.015 in SC$_A$*, indicates that $\psi_0^F \sim 85°$ and $\psi_0^{AF} \sim -45° \sim +45°$. The point is that ψ_0^F and ψ_0^{AF} are different; combining this fact with the symmetry consideration above, we insist on the appropriateness of the P_χ model. The biased rotation of permanent dipoles about the molecular long axes tends to produce in-layer spontaneous polarizations parallel to the

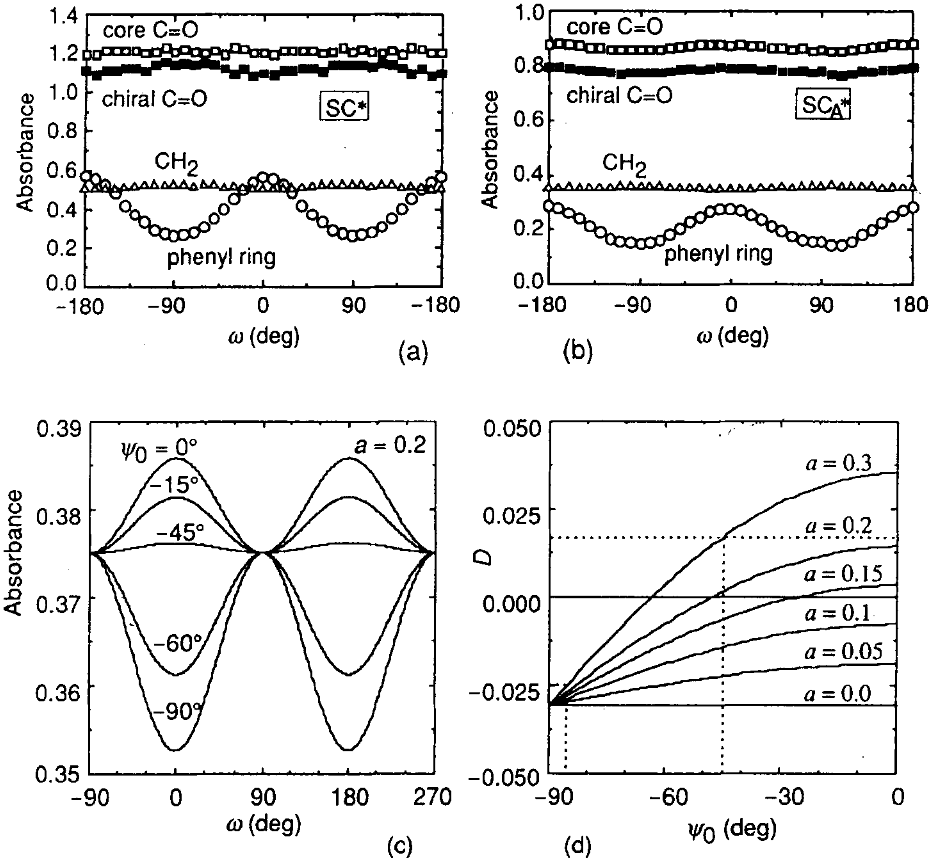


FIGURE 4. The IR absorbance vs polarizer rotation angle for C=O and phenyl ring stretching peaks in SC* and SC$_A$* of a homeotropic cell. (a) Experimentally obtained results for C=O near the chiral carbon, C=O in the core, and phenyl rings, (b) calculated results for C=O, and the relationship between D and ψ_0, where D is the degree of polarization defined by

$$D = (A_{0°} - A_{90°})/(A_{0°} + A_{90°}).$$

tilt plane, P_χ s, at the smectic layer boundaries; the existence of P_χ s themselves together with their interaction between the boundaries through the fluctuation force results in the stabilization of the antiferroelectricity. In fact, when permanent dipoles of equal magnitude are distributed on a hexagonal lattice in a plane, they may align in the same direction and sense to minimize the Coulomb interaction energy. Actually, however, the permanent dipoles are rotating about the molecular long axes and are distributed randomly near smectic layer boundaries. Theoretical justification of the P_χ model is a future problem to be studied.

ANNNI MODEL WITH THIRD NEAREST NEIGHBOR INTERACTION AND MOLECULAR STATES OF ROTATION

The preceding discussion may allow us to consider that a free energy difference between ferroelectric SC* and antiferroelectric $\mathrm{SC_A}$* is small, and that the difference principally results from that in the molecular states of rotation about their long axes, in particular, in the biased directions of the carbonyl groups, the chiral alkyl chains, etc. Competition between the ferroelectricity and the antiferroelectricity sometimes produces a series of ferrielectric and antiferroelectric subphases.[1,14-18] The most general subphase sequence currently known is

$$\begin{array}{ccccc} \mathrm{SI^*-SI_A^*-}\boxed{\mathrm{SC_A^*}} & \mathrm{-FI_L-SC_\gamma^*} & \mathrm{-FI_H-AF-FI/AF-} & \boxed{\mathrm{SC^*}} & \mathrm{-SC_\alpha^*-SA} \\ q=\frac{1}{2} & \frac{1}{3} & \frac{1}{4} & 0 & \end{array}$$

The phase transition from SA occurs directly to $\mathrm{SC_A}$* or SC*, when the antiferro- or ferro-electricity is stable enough. Otherwise, some subphases may emerge. Since $\mathrm{SC_\alpha}$* sometimes appears on the high temperature side of SC*, it is slightly different from the other subphases. Various theoretical explanations for the subphases proposed so far are based either on the Ising model[19-30] or on the *X*-*Y* model[31-34] Several experimental facts appear to support the Ising model.[1,16] Two statistical mechanics models have been developed; Bak and Bruinsma's one-dimensional Ising model with weak long-range forces[19,20] and the so-called ANNNI (Axial Next-Nearest Neighbor Ising) model.[21]

The Bak-Bruinsma Ising model can explain the observed sequence of the subphases to some extent, but several difficulties have been pointed out.[1] Yamashita and Miyazima[22] and Yamashita[23,24] applied the ANNNI model to this problem, introducing the third nearest neighbor interaction for the possible wide stability of $\mathrm{SC_\gamma}$*. Although they did not show any realistic physical grounds for these rather long range interactions at the beginning, Yamashita[25-27] quite recently insisted an important role played by the senses of molecular long axes,[28-30] decimated in the partition function the pseudo-spins describing the senses of molecular long axes, and eventually obtained the effective long range interactions, J_2 and J_3. Four ground states, q=0, 1/4, 1/3, and 1/2, emerge, which correspond to SC*, AF, SC$_\gamma$*, and SC$_A$*, respectively. The experimental fact which stimulated Yamashita to take into consideration the tilting senses of molecular long axes with head-and-tail asymmetry was the difference between the biased directions, $\psi_0{}^{AF}$ and $\psi_0{}^{F}$, although he did not discuss the directions of dipole moments directly. He also emphasized the correlation between the tilting senses and the rotational states. Moreover, it is worthwhile noting that the average of $\sigma_i = \langle s_i \rangle$ is given by

$$\langle\sigma\rangle = \Sigma_i\ \sigma_i / p \ \propto (T - T_c)^{p/2},$$

where p is the period in the sense that $\sigma_{i+p} = \sigma_i$ and pq the integer. Phenomenologically, thresholdless antiferroellectricity (TLAF) is expected to be observed in the disordered phase of the ANNNI+J_3 model.[35,36]

TRISTABLE SWITCHING AND PRETRANSITIONAL EFFECT

So long as we consider the static structures of various subphases between SC$_A$* and SC* in the absence of an electric field, the Ising model appears to be well substantiated. During the pretransitional effect of the tristable switching, however, tilting directions of the molecular long axes in adjacent layers must not be parallel to a single plane.[1] The pretransitonal effect induces an apparent tilt angle in SC$_A$* and appears as a slight increase in the transmittance below the threshold field as given in Figure 5. It shows that pretransitional effect may be very small in some materials but very large in some others. Let us consider more in detail what is happening in the tilting directions and the rotational states of molecules.

Figure 6 illustrates a thought experiment. An electric field is applied parallel to the page as indicated. Suppose a low enough field can unwind the helicoidal structure of SC$_A$* so that the tilting plane becomes parallel to the field. Conventionally, the liquid crystal coordinate system is chosen in such a way that the Z axis is parallel to the smectic layer normal and the X axis is in the tilt plane as already shown in Figure 1. In-layer spontaneous polarizations emerge at boundaries parallel to the X axis as indicated. This means that, in the molecular frame, the biased direction is $\psi_0{}^{AF}$. A field higher than the threshold induces SC*. The conventional liquid crystal frame rotates by 90 degrees; the tilting plane becomes perpendicular to the field and in-layer spontaneous polarizations located at boundaries are parallel to the Y axis as indicated. Note that the Y axis is now parallel to the page. In the molecular frame, the biased direction is $\psi_0{}^{F}$.

Even in the pretransitional process, the field and hence in-layer spontaneous polarizations at boundaries are always parallel to the page. Consequently, the tilting

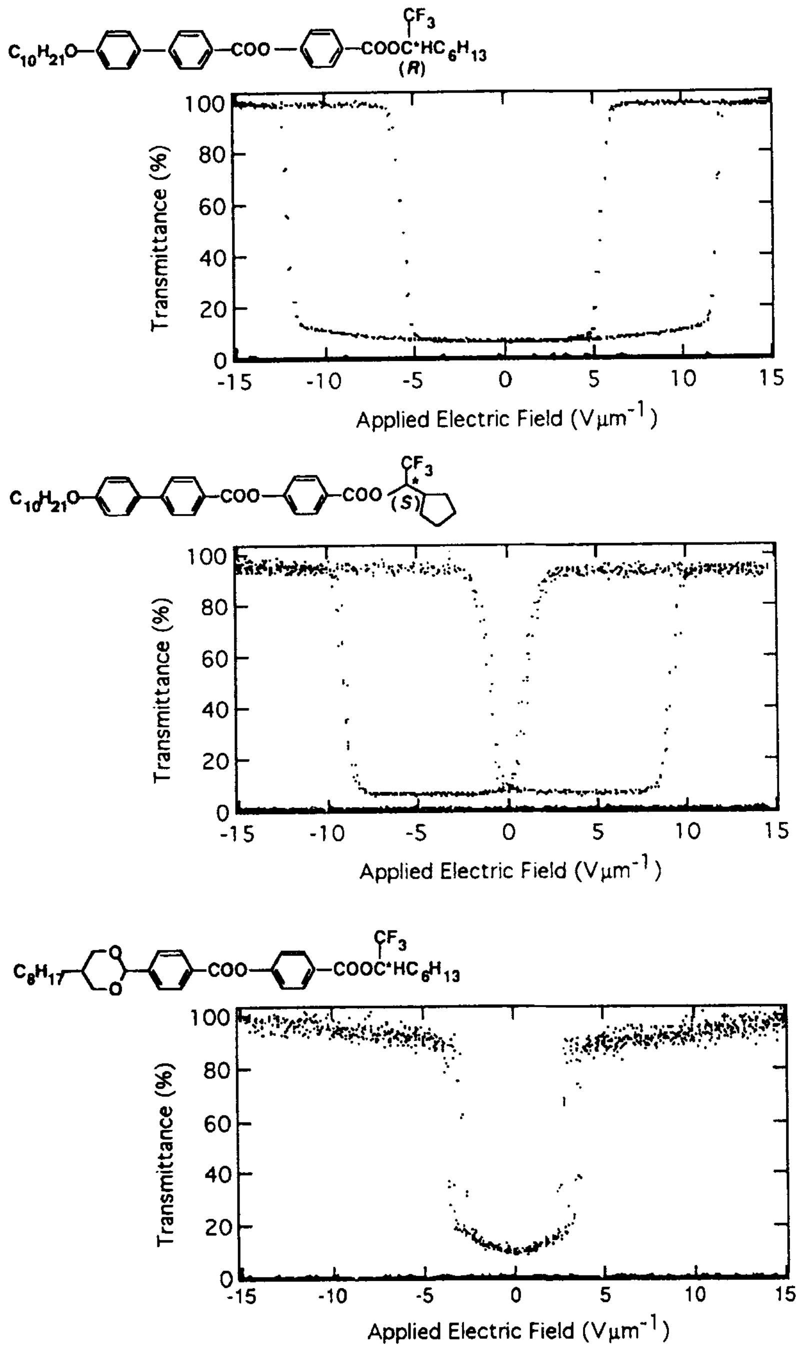


FIGURE 5. Three examples of tristable switching observed in a homogeneous cell placed between crossed polarizers, whose axes are parallel and perpendicular to the smectic layer normal.

directions are neither parallel nor perpendicular to the page. The directions are conveniently specified by the projections of the molecular long axes onto a boundary as shown in the upper and lower parts of Figure 6; thin solid and dotted lines in circles indicate the projections of the upper and lower layers of a boundary, respectively. In a boundary with $+P_X$, the in-layer spontaneous polarization changes into $+P_Y$ without becoming zero (without changing its polarity). In another boundary with $-P_X$, it may become zero because its polarity is just opposite. This means that, in the molecular frame, the biased direction $\psi_0{}^{AF}$ rotates toward $\psi_0{}^{F}$ clockwise in the $+P_X$ boundary and counterclockwise in the $-P_X$ boundary, respectively, when viewed from the positive side of the z axis. In this way, it is quite natural to speculate that tilting directions in adjacent layers are correlated with the biased directions of molecular rotation about the long axis.

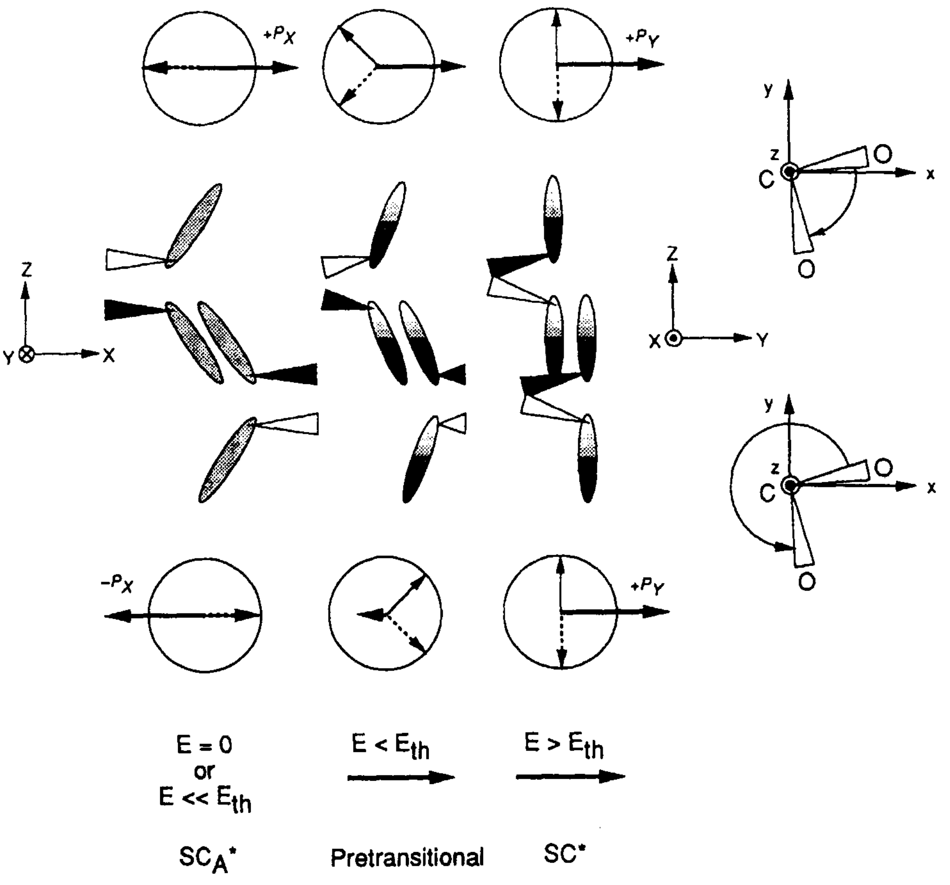


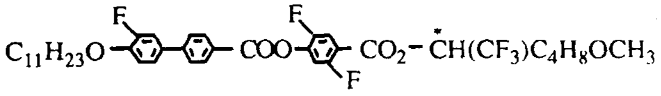
FIGURE 6. A thought experiment clarifying what is happening in the tilt directions and the rotational states of molecules about their long axes.

V-SHAPED SWITCHING AND THRESHOLDLESS ANTIFERROELECTRICITY

The tristable switching clearly indicates that the transition between $\mathrm{SC_A}^*$ and SC^* is of first order, because there exists a barrier between the molecular rotational states specified by ψ_0^{AF} and ψ_0^{F}. The barrier may be large in some materials but small in some others, as illustrated in Figure 5. Let us consider what happens if the barrier diminishes or is buried in the thermal fluctuations. As speculated in previous papers,[35,36] the states characterized by any ψ_0 between ψ_0^{AF} and ψ_0^{F} are equally thermally excited at zero electric field; this arbitrariness of ψ_0 makes the tilting directions non-correlated between adjacent layers. The director tilting is uniform and has constant polar and azimuthal angles in a smectic layer, but its azimuthal angle varies randomly from layer to layer. In-layer spontaneous polarizations exist at smectic-layer boundaries, with random orientations and variable magnitudes from boundary to boundary; hence there is no net spontaneous polarization. TLAF is also expected to appear from a molecular point of view.[35,36]

In previous papers,[35,36] the three-component mixture of compounds was reported to show the thresholdless V-shaped switching in a homogeneously aligned cell. Because of its extremely limited sample amount available at that time, no detailed fundamental properties of each component compound were investigated in the previous papers. Consequently, we obtained the first component compound,

(I)



and elucidated its fundamental properties. The phase sequence determined by observing conoscopic figures in free standing films is antiferro (29 °C) ferri (36 °C) SA (46°C) iso. We could not identify whether the antiferroelectric phase below 29 °C is $\mathrm{SC_A}^*$ or AF (q=1/4), but it is an ordinary (not a thresholdless) antiferroelectric phase anyway. These antiferro- and ferri-electric phases show characteristic reflection bands due to the helicoidal structure in the near IR region. However, a homogeneous cell shows evolution of switching characteristics from tristable to V-shaped.

Figure 7 illustrates the transmittance vs electric field obtained in a 3 μm homogeneous cell by applying a field of triangular wave form. The response critically depends on temperature and frequency. The almost typical tristable switching is observed at 20 °C and 50 mHz. With increasing temperature and/or frequency, the V-shaped character manifests itself. At 29 °C and, in particular, at 0.1 Hz, the typical V-shaped switching is observed. Even at this temperature, however, threshold was observed at 1 mHz. Generally, both of the tristable and V-shaped characters appear to coexist. When the field is turned off, the transmittance stays zero. If we rotate the polarizer axis by $\pm\omega$ ($\omega \leq \theta$) from the smectic layer normal, keeping the analyzer crossed, the transmittance becomes zero at $\pm E(\omega) \neq 0$. Here ω is smaller than the tilt angle θ and $E(\omega)$ is lower than the critical field E_C which completes the switching to ferroelectric SC*. This means that the V-shaped switching occurs uniformly and that the apparent tilt angle continuously rotates from zero to θ. Consequently, molecules are considered to rotate either coherently throughout smectic layers or randomly from layer to layer. Since no domains characteristic to ferroelectric SC* were observed after turning off the applied electric field, we can conclude that TLAF characterized by randomization and the Langevin type aligning process[35,36] is realized when the homogeneous cell at appropriate temperatures is stimulated properly with an applied electric field. It is worthwhile noting that a prototype AM(TFT)-TLAF-LCD has already been reported.[37]

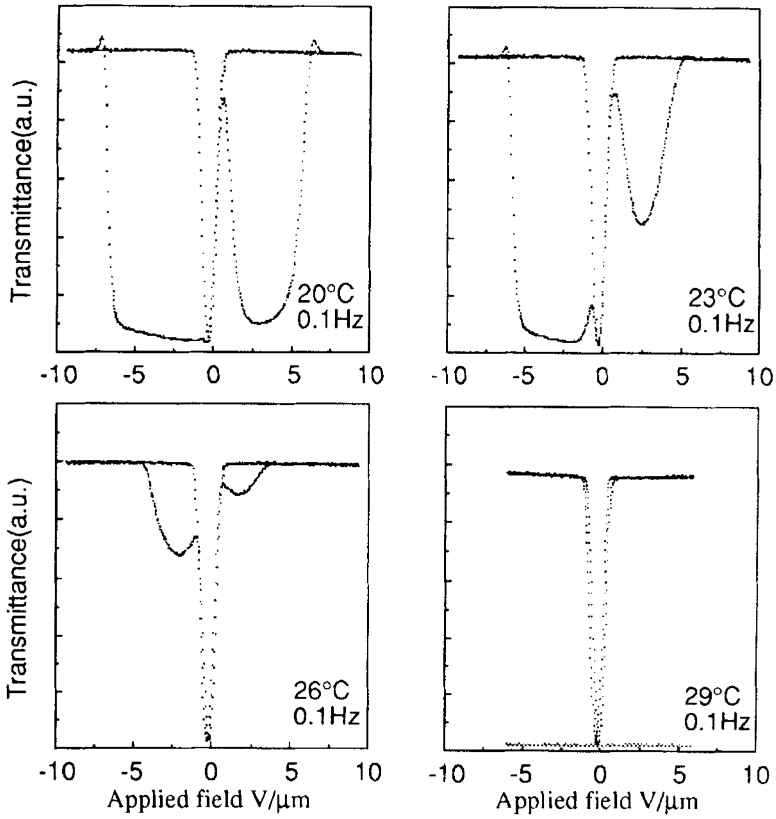


FIGURE 7. Transmittance vs electric filed curve obtained in a 3 μm homogeneous cell by applying a field of triangular wave form.

This work was supported by a Grant-in-Aid for Scientific Research (Specially Promoted Research No. 06102005) from Monbusho.

REFERENCES

1. A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa and H. Takezoe, J. Mater. Chem., 4, 997 (1994).
2. M. Glogarova, Invited Lecture at this Conf., C2.I02 (125).
3. B. W. van der Meer and G. Vertogen, J. Phys. (France), 40, C3-222 (1979).
4. I. Nishiyama and J. W. Goodby, J. Mater. Chem., 2, 1015 (1992).
5. Y. Takanishi, K. Hiraoka, V. K. Agrawal, H. Takezoe, A. Fukuda and M. Matsushita, Jpn. J. Appl. Phys., 30, 2023 (1991).
6. K. Miyachi, J. Matsushima, Y. Takanishi, K. Ishikawa, H. Takezoe and A. Fukuda, Phys. Rev. E, 52, R2153 (1995).
7. K. Hori and K. Endo, Bull. Chem. Soc. Jpn., 66, 46 (1993).
8. B. Jin, Z. Ling, Y. Takanishi, K. Ishikawa, H. Takezoe, A. Fukuda, M. Kakimoto and T. Kitazume, Phys. Rev. E, 53, R4295 (1996).
9. T. Nakai, S. Miyajima, S. Yoshida, Y. Takanishi and A. Fukuda, (umpublished).
10. Y. Ouchi, Y. Yoshioka, H. Ishii, K. Seki, M. Kitamura, R. Noyori, Y. Takanishi and I. Nishiyama, J. Mater. Chem., 5, 2297 (1995).
11. P. E. Cladis and H. R. Brand, Liq. Cryst., 14, 1327 (1993).
12. K. H. Kim, K. Ishikawa, H. Takezoe, and A. Fukuda, Phys. Rev. E, 51, 2166 (1995).
13. W. G. Jang, C. S. Park, J. E. Maclennan, K. H. Kim, and N. A. Clark, Ferroelectrics, 180, 213 (1996).
14. T. Isozaki, T. Fujikawa, H. Takezoe, A. Fukuda, T. Hagiwara, Y. Suzuki and I. Kawamura, Jpn. J. Appl. Phys., 31, L1435 (1992).
15. J. Hatano, Y. Hanakai, H. Furue, H. Uehara, S. Saito and K. Murashiro, Jpn. J. Appl. Phys., 33, 5498 (1994).
16. K. Itoh, M. Kabe, Y. Takanishi, H. Takezoe and A. Fukuda, (umpublished)
17. J. W. O'Sullivan, Yu. P. Panarin and J. K. Vij, Poster Presentation at this Conf., C1P.15 (P-125).
18. P. Cluzeau, H. T. Nguyen, C. Destrade, N. Isaert, P. Barois and A. Babeau, Mol. Cryst. Liq. Cryst., 260, 69 (1995).
19. P. Bak and R. Bruinsma, Phys. Rev. Lett., 49, 249 (1982).
20. R. Bruinsma and P. Bak, Phys. Rev. B, 27, 5824 (1983).
21. P. Bak and J. von Boem, Phys. Rev. B, 21, 5297 (1980).
22. M. Yamashita and S. Miyazima, Ferroelectrics, 148, 1 (1993).
23. M. Yamashita, Mol. Cryst. Liq. Cryst., 263, 93 (1995).
24. M. Yamashita, Ferroelectrics, 181, 201 (1996).
25. M. Yamashita, J. Phys. Soc. Jpn., 65, to appear in No. 7 (1996).
26. M. Yamashita, J. Phys. Soc. Jpn., 65, to appear in No. 9 (1996).
27. M. Yamashita, Poster Presentation at this Conf., C1P.12 (P-124).
28. T. Koda and H. Kimura, Ferroelectrics, 148, 31 (1993).
29. T. Koda and H. Kimura, J. Phys. Soc. Jpn., 64, 3787 (1995).
30. T. Koda and H. Kimura, J. Phys. Soc. Jpn., 65, in press (1996).
31. H. Sun, H. Orihara and Y. Ishibashi, J. Phys. Soc. Jpn., 62, 2706 (1993).
32. M. Cepic and B. Zeks, Mol. Cryst. Liq. Cryst., 263, 61 (1995).
33. S. A. Pikin, S. Hiller and W. Haase, Mol. Cryst. Liq. Cryst., 262, 425 (1995).
34. V. L. Lorman, Mol. Cryst. Liq. Cryst., 262, 437 (1995).
35. S. Inui, N. Iimura, T. Suzuki, H. Iwane, K. Miyachi, Y. Takanishi and A. Fukuda, J. Mater. Chem., 6, 671 (1996).
36. A. Fukuda, Proc. 15th Int. Display Research Conf. (Asia Display '95), S6-1, p.61
37. T. Saishu, K. Takatoh, R. Iida, H. Nagata and Y. Mori, SID '96 Digest, 28.4.