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SIGN INVERSION OF INDUCED MOLECULAR TILT IN CHIRAL SMECTIC A LIQUID CRYSTALS

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Abstract We have observed a peculiar sign inversion of the field-induced molecular tilt with respect to the layer normal in the smectic A phase of some chiral compounds as temperature increases. At a characteristic temperature, the electroclinic response of the system to an external electric field completely disappears, and thus in turn, the induced molecular tilt vanishes. This unusual behavior can be understood in terms of a dynamically fluctuating mixture of at least two molecular conformers, separated by an energy barrier in their liquid crystalline state. It is suggested that these two conformers are associated with the rotation of normal hydrocarbons in the compounds.

INTRODUCTION

Since the discovery of ferroelectricity in tilted chiral smectic phases (LCs), particularly, in the smectic C* (Sm C*) phase,[1,2] ferroelectric liquid crystals (FLCs) have attracted great interest from fundamental and practical points of view.[3–5] Ferroelectricity in these materials arises from a reduced symmetry in the structure of the mesophase caused by the inclusion of a chiral center within the molecular structure of some of the constituent molecules of the phase.[2] Although symmetry arguments allow for the existence of ferroelectricity, the arguments give no prediction for the magnitude of the resulting polarization. Recent experimental results[6] show that the magnitude of the polarization is primarily determined by such molecular factors as the size of the dipole moment at the chiral center of the molecule, the range of intermolecular forces producing molecular tilt, and the details of the local molecular environment.

In most FLCs, the spontaneous polarization and the molecular tilt monotonically decreases and vanishes at the smectic A-smectic C* (Sm A-Sm C*) transition. However, depending on the subtle change in the chemical structure, for some materials, a sign inversion of those parameters at a characteristic temperature has been observed in the Sm C* state.[7–11] This peculiar behavior of the sign inversion can be explained in terms of a dynamic interplay between various molecular species.[8] More recently, it has been reported[12] that for a class of some chiral compounds the electric-field induced molecular tilt in the Sm A phase also vanishes at a certain temperature below the isotropic-smectic A (I-Sm A) transition, and reappears in the opposite sense with increasing temperature. This implies that the two unusual phenomena observed in two different systems should have *a common physical origin.* Thus, one of the interesting questions is whether a system of *dynamically competing molecular species* generally exhibits an anomaly in a macroscopic quantity. It is also important to examine the effect of molecular correlations between various species on the associated anomaly.

In this paper we describe the peculiar sign inversion of the electric field-induced molecular tilt in chiral Sm A LCs which possess a direct I-Sm A transition in a simplified model which contains the essential features of the experimental data. The model is based on a dynamically fluctuating mixture of at least two species interconvertible via an activation energy with changing temperature. Within this model, the two species are identified as most likely the rotational conformers in their liquid crystalline state. We also present accurate numerical results for the anomaly described above, serving as a guide for studying other complex systems.

EXPERIMENTAL

For this study, we used two chiral compounds, S-2-methylbuthyl 4'-n-hexyloxybiphenyl-4-carboxylates (C6) and S-2-methylbuthyl 4'-n-heptyloxybiphenyl-4-carboxylates (C7), the higher homologues of which exhibit a sign inversion in the spontaneous polarization in the Sm C* phase.[7,8]

The phase sequence of these materials is as follows: isotropic → Sm A → Sm C* → crystalline. The sample cell was made of conductive indium-tin-oxide coated glasses with buffed polymer layers (poly-1,4-butyleneterephthalate) on both surfaces, which promoted the homogeneous alignment.[13] The cell thickness was maintained by using 5 μm spacers. The cell was mounted in a microfurnace for temperature control, and temperature fluctuations were approximately 0.1° C. Measurements of the induced tilt angle were made with a square wave of variable amplitudes. The transmitted light intensity through the cell, placed between crossed polarizers, was monitored with a photodiode, a digitizing oscilloscope, and a lock-in amplifier.

RESULTS AND DISCUSSION

The temperature dependences of the tilt angle θ at various field strength E for the two compounds, C6 and C7, are shown in Figures 1 and 2, respectively. Similar results were also obtained in a thicker cell ($\approx$ 10 μm). Clearly, the fact that θ vanishes at a temperature T_o in the Sm A phase can not be understood by a simple power-law of $(T - T_c)^{-1}$ with T_c the critical temperature for the Sm A-Sm C* transition, predicted by a mean-field theory.[14]

In describing the anomaly in the induced molecular tilt, we consider the Landau-type free energy near the Sm A-Sm C* transition which includes a direct coupling[15] between the molecular tilt θ and an external electric field E. Ignoring the elastic and surface polarization terms,[16] we have the expression for the tilt angle θ as $(cE/a')(T - T_c)^{-1}$, where $c = t\chi$ with t the electroclinic (EC) coefficient and χ the generalized susceptibility. Here a' is a phenomenological coefficient of the lowest order in the Landau expansion. Since a' is independent of temperature, the anomalous behavior of θ results essentially from that of the effective EC coefficient c. In analogy to the spontaneous polarization in the Sm C* phase,[17] the anomaly in c can be understood by the presence of various dynamically fluctuating species, undergoing interconversions with each other at a rapid rate.

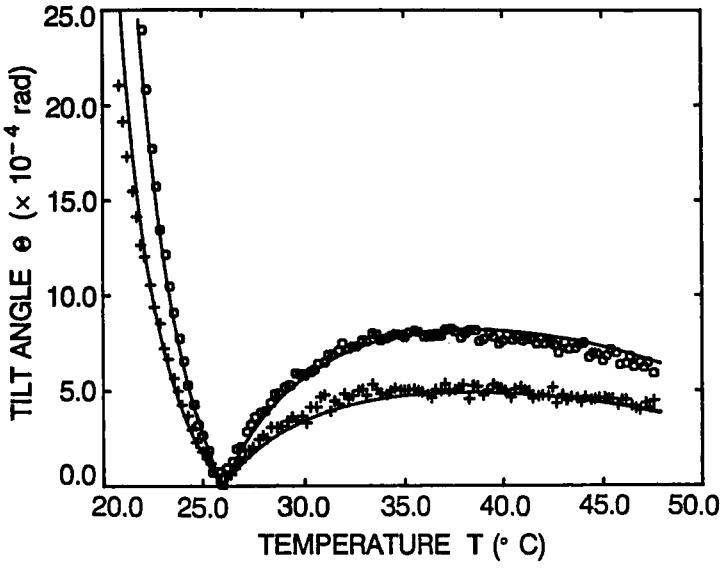

FIGURE 1: Induced tilt angle θ as a function of temperature T at various electric fields E for C6 compound. The cross and circular symbols represent E =4.8 V/μm and 8 V/μm. Each solid line is the least square fit of the data to Eq. (6).

These species are thought of as conformers of the constituent molecules which compete with each other in the magnitude of the polarization in the Sm C* phase. Thus, at a given temperature, the effective EC coefficient c of the system is determined by the relative number density n_i of the molecular species and the associated molecular EC coefficient c_i. We may then write c as

$$c = \sum_{i=1} c_i \, n_i \quad , \tag{1}$$

Denoting the energy barrier between two species i and j by U_{ij}, the relative population of the species is given by

$$n_i = \frac{\sum_j exp(-U_{ij}/k_B T)}{V \sum\sum_{i \neq j} exp(-U_{ij}/k_B T)} \quad , \tag{2}$$

where k_B is the Boltzmann constant and V is the volume of the system.

Furthermore, since the induced molecular tilt vanishes in the isotropic phase, we introduce an extra temperature dependence for c as $(T* - T)^{\beta}$ where $T*$ represents the virtual critical temperature for the continuous version of the I-Sm A transition, and β is the associated exponent.

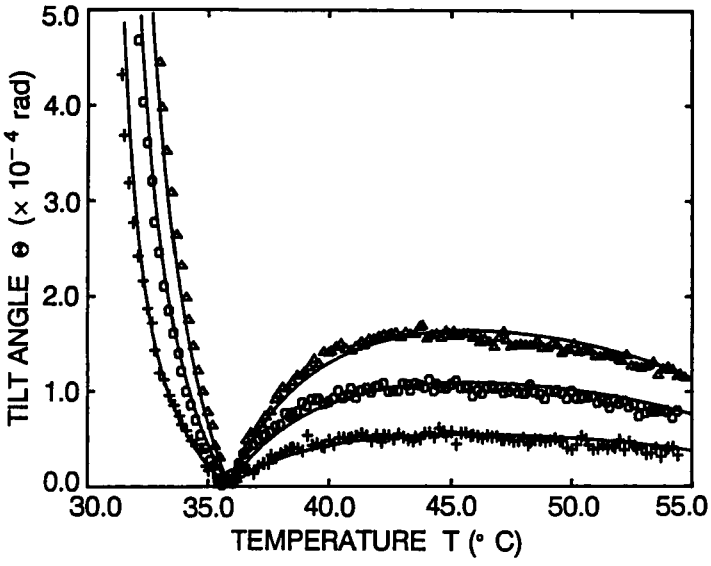

FIGURE 2: Induced tilt angle θ as a function of temperature T at various electric fields E for C7 compound. The cross, circular, and triangular symbols represent E = 2.4 V/μm, 4.8 V/μm, and 7.2 V/μm. Each solid line is the least square fit of the data to Eq. (6).

In fact, $T*$ represents the extrapolated temperature at which the EC response continuously disappears in the isotropic state. Both $T*$ and β may reflect the range as well as the strength of intermolecular interactions and the nature of the smectic order. The characteristic temperature dependence of c is readily written as

$$c = \left[\sum_i c_i n_i\right] (T* - T)^{\beta} \quad . \tag{3}$$

As will be shown later, the above expression for c contains the essential features of the experimental data.

Assuming that there exist only two different species in the system, one of which rotates clockwise and the other rotates counterclockwise with respect to an applied electric field, the resultant expression for c is given by

$$c = \left[\frac{c_a}{(1+e^{-U/k_BT})} + \frac{c_b}{(1+e^{U/k_BT})}\right](T*-T)^{\beta} \quad . \tag{4}$$

In order to fit the experimental data showing an anomaly in the induced molecular tilt, we first determine a characteristic temperature T_o at which the tilt angle θ vanishes in the Sm A phase. In other words, at $T = T_o$, $c = 0$, which leads to

$$c_b = -c_a \frac{1+e^{U/k_BT_o}}{1+e^{-U/k_BT_o}} \quad . \tag{5}$$

Using Eq. (4), together with Eq. (5), we have the following expression for the tilt angle which contains essentially three parameters, c_a/a', U, and $T*$ if T_c and T_o are known from the experiment.

$$\theta = (c_a/a')\, E \left[\frac{1}{(1+e^{-U/k_BT})} - \frac{(1+e^{U/k_BT_o})}{(1+e^{U/k_BT})(1+e^{-U/k_BT_o})}\right] \frac{(T*-T)^{\beta}}{T-T_c} \quad . \tag{6}$$

The value of β lies between zero and one because the tilt angle θ should vanish in the isotropic phase. Although its actual magnitude is not known, the mean-field value, 0.5, is simply taken to limit the number of fitting parameters as in the case for the spontaneous polarization in the Sm C* phase.[17] Each solid line in Figures 1 and 2 is the least squares fit of the data to the above equation, Eq. (6), as a function of temperature at various field strengths. The fit was found to be quite insensitive to variations of β between 0.4 and 0.6.

Note that the two curves for θ in Figure 1 (or the three curves in Figure 2) were fitted with exactly same values of the parameters as a function of the field strength E. It is clear that the model, based on the presence of at least two different species, remarkably well describes the essential features of the experimental results. Nevertheless, it should be noted that in our system as well as in other more complex systems, there might exist many conformers that all contribute to the anomaly in the induced molecular tilt in a complicated way. The values of c_a/a' (or c_b/a'), U, and $T*$ obtained from the least squares fits for the two compounds were collected

in Table I. In the fitting procedure, the exponent β was taken as 0.5, and the values of T_c and T_o, experimentally known, were not varied.

Table 1: Material parameters obtained from the fit of the data in Figures 1 and 2 to Eq. (6) for the two compounds. T_o's for C6 and C7 were experimentally determined as 26.0° C and 35.9° C, respectively. The fitted T_c's for C6 and C7 are given by 18.5° C and 30.4° C, respectively.

Compound	c_a/a' [$\times 10^{-9}$ mK/V]	c_b/a' [$\times 10^{-9}$ mK/V]	U [eV]	$T*$ [° C]
C6	1.48 ± 0.04	-4.45 ± 0.11	0.028 ± 0.002	55.6 ± 0.5
C7	1.36 ± 0.03	-14.6 ± 0.3	0.062 ± 0.002	59.6 ± 0.4

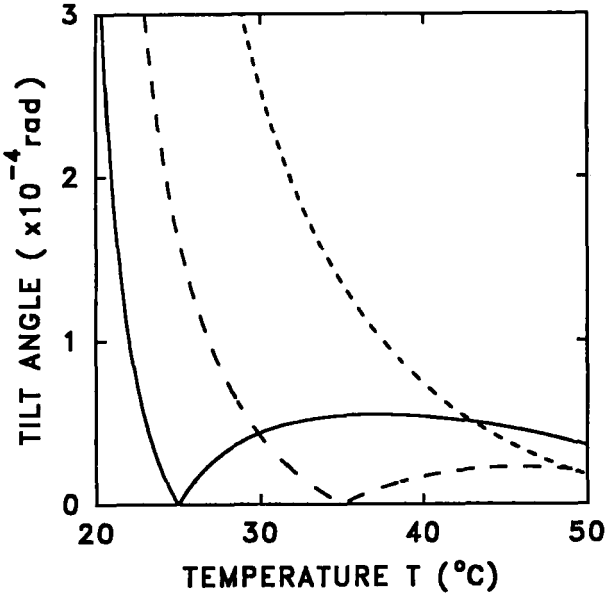

FIGURE 3: Induced tilt angle θ for C6 at various T_o's, calculated from Eq. (6). Other material parameters were taken from Table 1. The solid, long-dashed, and short-dashed lines represent T_o = 25° C, 35° C, and 65° C, respectively.

We now discuss the relationship between the anomaly in c and material parameters, particularly, T_o and $T*$. For materials showing that T_o is greater than $T*$, no anomaly in c would be expected. As an example, Figure 3 shows numerical results for the induced molecular tilt of C6 at various T_o's, calculated from Eq. (6). It is clear that no anomaly in c can be seen if $T_o > T*$, in which case the usual EC response will be observed. Recent experimental work[18] on DOBAMBC near the Sm A - Sm C* transition also suggests that the temperature dependence of c is rather related to molecular structure, which is consistent with an earlier argument for the electroclinic anomaly.[20]

We examine the magnitude of U extracted from the fit of the experimental data to Eq. (6) and attempt to identify the type of the two molecular species. As collected in Table I, the fitted values for the two compounds which differ only in the terminal group are close to those obtained for the rotational barrier in normal hydrocarbons.[20] Therefore, the two species are most likely the rotational conformers, produced by the rotation about the carbon-carbon bond adjacent to the chiral carbon atom. This is physically reasonable since the molecular model shows that such a rotation would result in an inversion of the effective dipole moment that contributes to the polarizability.[10] Furthermore, such rotation does not change the overall length of the molecule and thus it can pack well in the liquid-crystalline state without deforming the layers or forming dimers. In fact, x-ray diffraction, differential scanning calorimetry, and optical studies, all suggest that there is no considerable change in molecular ordering at the inversion point T_o.

Another point is that a factor of two difference in the magnitudes of U for the two compounds may be attributed to the change in intermolecular forces as well as that in the nature of the carbon-carbon bond about which the rotation of the chiral atom takes place. The variation in the intermolecular interactions strongly influences the nature of the internal rotation of the molecules, which is evident from the fact that the transition temperatures of the two compounds are quite different.

CONCLUSION

We have observed the anomaly in the EC effect in chiral smectic LCs, showing that there is a peculiar sign inversion of the field-induced molecular tilt at a particular temperature in the Sm A phase. This phenomenon seems to be related to a delicate interplay between the relative number densities of dynamic molecular species and the associated molecular EC coefficients of the individual species. This unusual behavior can be understood in terms of a dynamically fluctuating mixture of at least two molecular conformers, separated by an energy barrier in their liquid crystalline state. Its underlying physical mechanism might be very general and fairly common to other complex systems,[21,22] involving a hierarchically organized set of free energy barriers.

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REFERENCES

1. R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. (Paris) Lett. 36, L-69 (1975).
2. R. B. Meyer, Mol. Cryst. Liq. Cryst. 40, 30 (1977).
3. J. E. Maclennan and N. A. Clark, Phys. Rev. A 44, 2543 (1991).
4. M.-H. Lu, K. A. Crandall, and C. Rosenblatt, Phys. Rev. Lett. 68, 3575 (1992).
5. For a comprehensive discussion, see K. Skarp and M. A. Handschy, Mol. Cryst. Liq. Cryst. 165, 439 (1988).
6. H. Y. Liu, C. C. Huang, T. Min, M. D. Wand, D. M. Walba, N. A. Clark, Ch. Bahr, and G. Heppke, Phys. Rev. A 40, 6759 (1989).
7. J. W. Goodby, E. Chin, .T. M. Leslie, J. M. Geary, and J. S. Patel, J. Am. Chem. Soc. 108, 4729 (1986).
8. J. S. Patel and J. W. Goodby, Phil. Mag. Lett. 55, 293 (1987); J.W. Goodby, E. Chin, J. M. Geary, J. S. Patel, and P. L. Finn, J. Chem. Soc. Faraday Trans., 83, 3429 (1987).

9. R. Eidenschink, T. Geehaar, G. Anderson, A. Dahlgren, K. Flatischler, F. Gouda, S. T. Lagerwall, and K. Skarp, Ferroelectrics 84, 167 (1988).
10. K. Yoshino, M. Ozaki, K. Nakano, H. Taniguchi, N. Yamasaki, and K. Satoh, Liq. Cryst. 5, 1203 (1989).
11. L. Komitov, K. Flatischler, G. Andersson, S. T. Lagerwall, B. Stebler, B. Otterholm, T. Olsson, and Chr. Alstermark, Ferroelectrics 114, 151 (1991); F. Gouda, T. Carlsson, K. Flatichler, L. Komitov, S. T. Lagerwall, K. Skarp, and B. Stebler, Phys. Rev. A 45, R5362 (1992).
12. S.-D. Lee, J. S. Patel, and J. W. Goodby, Phys. Rev. Lett. 66, 449 (1991); Rev. Mod. Phys. B 5, 821 (1991).
13. J. S. Patel, G. W. Goodby, and T. M. Leslie, Ferroelectrics 59, 137 (1984).
14. R. Blinc, Ferroelectrics, **14**, 603 (1976); S. A. Pikin, Mol. Cryst. Liq. Cryst. 63, 181 (1981).
15. S. Garoff and R. B. Meyer, Phys. Rev. Lett. 38, 848 (1977); Phys. Rev. A 19, 338 (1979).
16. J. Xue and N. A. Clark, Phys. Rev. Lett. 64, 307 (1990).
17. A. M. Glass, J. W. Goodby, and D. H. Olson, Phys. Rev. A 38, 1673 (1988).
18. Z. Li and C. Rosenblatt, Phys. Rev. A 39, 1594 (1989).
19. L. A. Berensev, L. M. Blinov, M. A. Osipov, and S. A. Pikin, Mol. Cryst. Liq. Cryst. 158A, 3 (1988).
20. E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, Conformational Analysis (Interscience Publishers, New York, 1986).
21. G. Scherowsky, B. Brauer, K. Grünegerg, U. Müller, L. Komitov, S. T. Lagerwall, K. Skarp, and B. Stebler, Mol. Cryst. Liq. Cryst. 215, 257 (1992).
22. See, for example, K. L. Ngai, in Non-Debye Relaxation in Condensed Matter, edited by T. V. Ramakrishnan and M. Rajlakshmi (World Scientific, Singapore, 1987), p.23.