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Electric-field-induced chiral separation in liquid crystals

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Recently it was shown that smectic liquid crystal phases formed by achiral banana-shaped molecules are chiral. Films of such phases generally contain both homochiral (consisting of layers of the same chirality) and racemic (the chirality alternates in subsequent layers) domains. So far it has not been clear how to control the overall chirality of the sample. By observing the effects of the application of suitable electric fields, it was noted that chirality of a film of banana shaped molecules was interchanged between homochiral and racemic. We present dielectric, electro-optic, and polarization current measurements on both the racemic and chiral states. The observations indicate that the synclinic states have minimum free energies. The observed dielectric modes can be explained by a simple model assuming that the antiferroelectric state is very weak. [S1063-651X(99)19410-8]

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I. INTRODUCTION

In 1975 Meyer *et al.* [1] showed by symmetry considerations that tilted smectic liquid crystalline phases composed of chiral molecules possess a spontaneous polarization. Since then great progress has been made in the development of ferroelectric liquid crystals allowing commercial applications. Until now the chirality of molecules has been a prerequisite for manufacturing Ferroelectric Liquid Crystal Displays.

Recently ferroelectric (and polar) liquid crystal phases composed of achiral molecules [2] were also reported. Examples contain columnar phases of bowl shaped molecules [3,4] and polymer-monomer mixtures, which tend to form bilayered antiferroelectric smectic-*C*-like structures [5]. In 1996 it was demonstrated that smectic phases of banana shaped molecules show ferroelectric switching [6]. Although similar molecules have been known since the work of Vorländer in 1923 [7], it was actually the observations of Niori *et al.* [6] that led to an intensive study of ferroelectricity and chirality in liquid crystalline phases of achiral molecules [8]. First it was suggested [9] that the ground state of the switchable (B_2) phase is antiferroelectric. The antiferroelectric nature of the switching behavior was proved by Macdonald *et al.* [10] and Link *et al.* [11]. There remained, however, some dispute about the actual structure of the B_2 phase. Niori *et al.* [6] have suggested that it has a layered structure with a C_{2v} symmetry, where the planes of the banana-shaped molecules are perpendicular with respect to the layer. According to the Boulder model [11] the molecules are tilted which, together with the polar molecular ordering, results in a chiral layer structure leading to the coexistence of racemic and and chiral domains.

Electro-optical observations indicated that during switching the chirality of the layers remains unchanged [11]. Although it was also shown that in some cases chiral domains disappear under long term application of moderate fields [12], the transformation could not be reversed and the purely chiral state could not be achieved. In this contribution we show that chirality can be reversibly controlled by application of suitable electric fields. We also discuss the consequences for the switching dynamics and dielectric responses.

II. EXPERIMENT

The studied compound 1,3-phenylen bis[4-(4-tetradecylphenyliminomethyl)benzoate] differs only in the achiral side chain from the material studied by Niori *et al.* [6]. It possesses the following phase transition temperatures (differential scanning calorimeter, Perkin Elmer DSC7, heating or cooling rate respectively: 3K/min):

$$\text{Crystal} \underset{66.1}{\overset{90.7}{\rightleftarrows}} \mathrm{B}_3 \ \text{phase} \underset{124.7}{\overset{130.2}{\rightleftarrows}} \mathrm{B}_2 \ \text{phase} \underset{151.8}{\overset{152.9}{\rightleftarrows}} \text{isotropic phase.}$$

The assignment of the phases is based on miscibility studies with the octyl homologue [6].

Electro-optic studies were carried out using commercially test available (EHC Co., Japan) cells (two parallel glass plates, inner surface coated with indium tin oxide layers and treated with parallel rubbed polyimide) with the cell spacing varying between 4 and 25 μm. The temperature was controlled by a Linkam heating stage (TMS90).

A. Investigations by polarizing microscope

We observed that on cooling from the isotropic phase the samples tend to have mainly racemic domains, whereas on heating from the B_3 phase more chiral domains appear. Results obtained in the B_2 phase at constant temperatures are summarized in Fig. 1. An overall chiral state [Fig. 1(a)] appeared after the application of a rectangular electric field (300 Vpp, 10 Hz). It remains stable even after the field is removed. At zero fields the texture is similar to the fan-shaped texture of a Sm-*A* phase. No domain walls parallel to the layers can be observed within a single fan. The chiral

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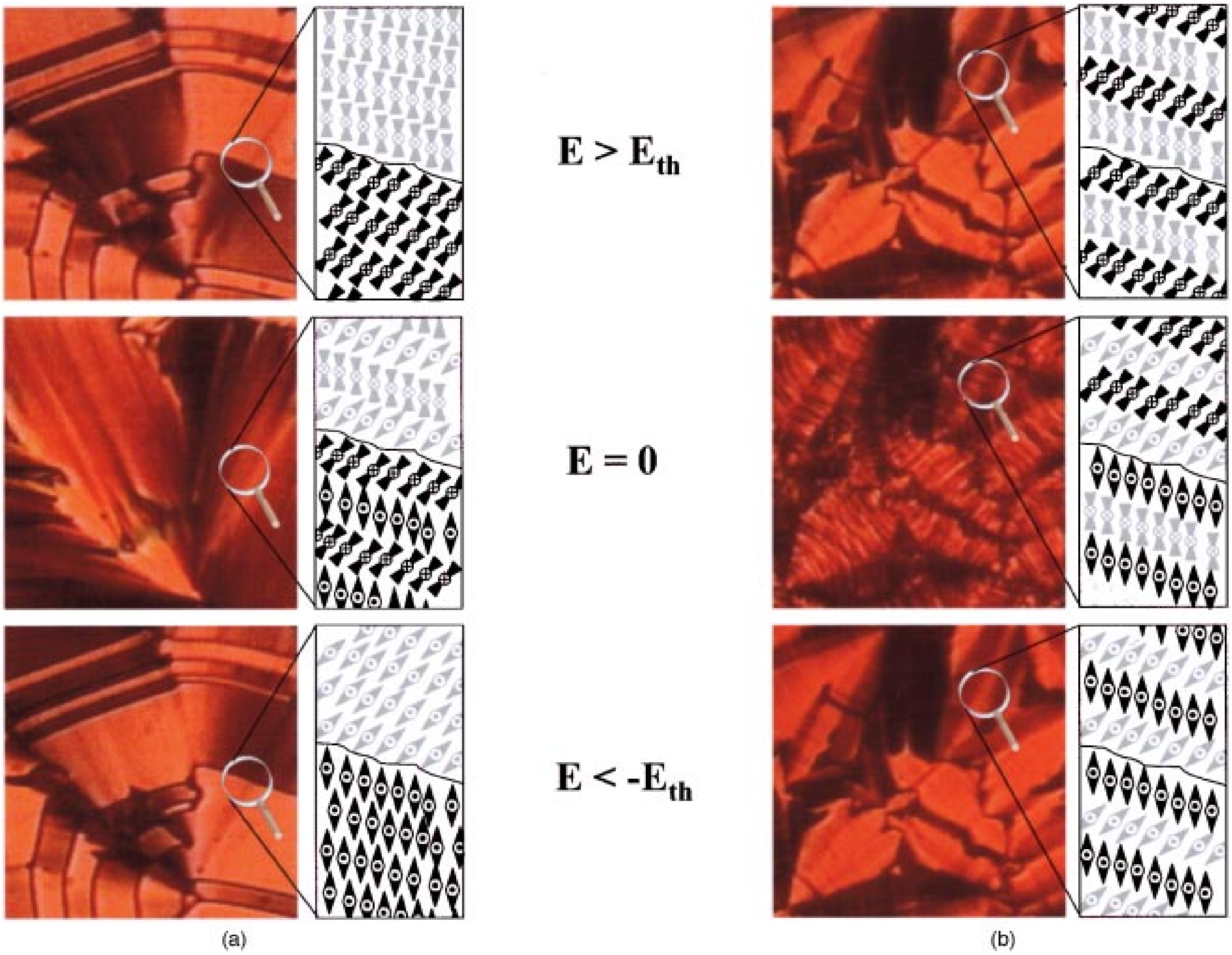

FIG. 1. (Color) A series of videoprints representing the switching of a planar-aligned sample in an external electric field ($|E| = 9$ V/μm, $f = 1$ Hz, cell gap 10 μm). (a) Homochiral texture formed by a rectangular voltage. Domain walls running parallel to the layers are separating domains of opposite handedness. At zero electric field stripes disappear. (b) A racemic sample has been prepared by applying a triangular voltage. At zero field the typical striped texture can be seen. States at both polarities of electric field do not differ in their optical properties.

character of the domains appears only when the field is applied. In the field induced ferroelectric state the fans consist of broad stripes with domain walls running parallel to the layers. Neighboring stripes have opposite chirality with optical axes rotating in opposite directions under sign reversal of the electric field. We estimate that the total areas of the domains of opposite chirality are approximately equal.

The overall chiral texture can be transferred into the racemic texture [Fig. 1(b)] by a triangular electric field of 300 Vpp, $f = 10$ Hz. The ground state at zero fields consists of thin stripes parallel to the layers. According to the model of Link *et al.* [11] this striped pattern can be explained by the formation of racemic domains of opposite tilt directions. Applying a rectangular field for a short time (the same conditions as given above) the stripes nearly vanish and, at both polarities of the electric field, the states possess the same optical properties, that is there is no difference in the orientation of the extinction directions. After applying the electric field for only a few minutes the sample returns into the homochiral state. The time needed for retransformation is roughly inversely proportional to the frequency, indicating that the number of electric field cycles has to reach a critical value ($\sim 10^4$ cycles).

B. Dielectric responses

It is known [13] that in the B_2 phase of banana-shaped compounds a high frequency dielectric mode appears. We have studied how the relaxation frequency and the dielectric strength of this mode depend on the overall chirality. Both chiral and racemic textures were prepared in the B_2 phase at 135 °C, as described above. The measurements of the dielectric spectra were carried out using an Hewlett Packard 4194 impedance analyzer starting from the B_2-B_3 phase transition up to the isotropic phase in temperature steps of 1 °C. In order to confirm domain stability we also checked the texture by polarizing microscopy. The weak electric fields we used did not cause texture transformation. This enabled the measurement of a complete dielectric spectrum without loosing domain chirality. In Fig. 2 the dielectric loss is given as a function of frequency and temperature for both types of textures.

In both spectra a nearly Debye-type relaxation mode can be seen at around ~1 MHz. The mode disappears at the transition to the isotropic phase. In the racemic state the switching is about twice as fast [Fig. 3(a)] as in the chiral. The dielectric strength $\Delta\varepsilon$, however, is about twice as high in

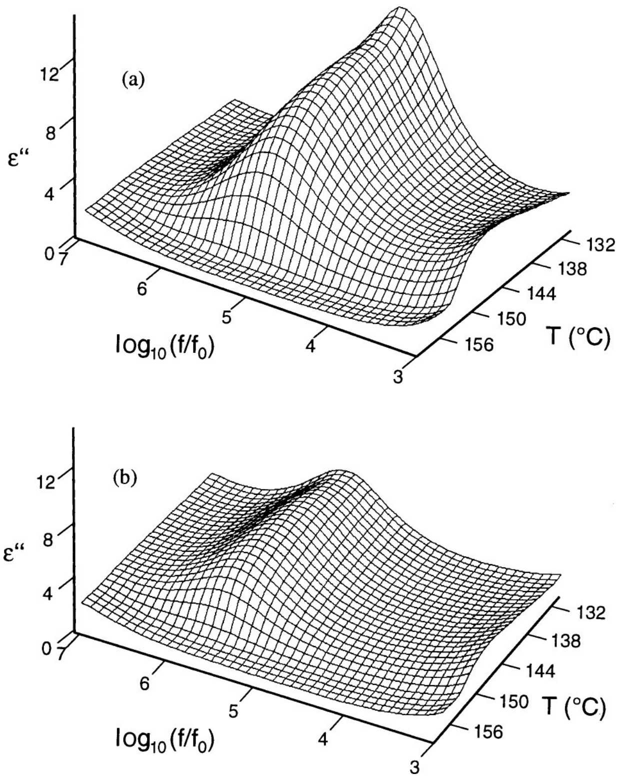

FIG. 2. Dielectric losses as the function of temperature and frequency ($f_0 = 1$ Hz) for a 10 μm cell. (a) Homochiral state, (b) racemic state. In the low frequency part the slight increase is due to freely moving ions. The increase at about 10 MHz is connected to the ITO layer.

the chiral sample [e.g., at $T = 144\,°\mathrm{C}\ \Delta\varepsilon(\mathrm{chi}) = 21$, and $\Delta\varepsilon(\mathrm{rac}) = 9.5$; see Fig. 3(b)].

The corresponding activation energies are $\Delta E_A = 55$ kJ/mol in the chiral case and $\Delta E_A = 45$ kJ/mol in the racemic state, respectively. Both values are in between those reported for the rotation around the long and short axis of rodlike molecules in the Sm-C_A* phase [14]. Taking into account the bent-shape of the molecules the observed mode may be assigned to the rotation around the long axis of the molecules.

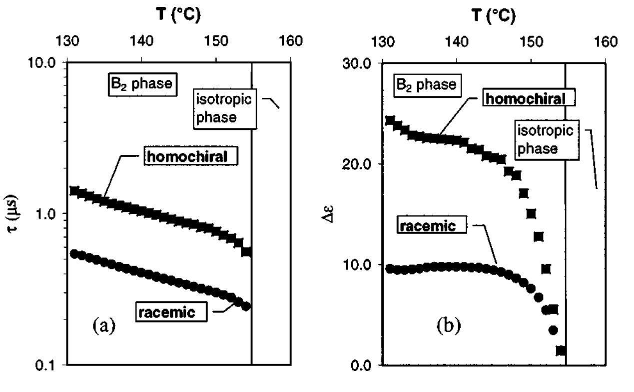

FIG. 3. (a) Temperature dependence of the relaxation time determined from the maximum of Fig. 2 as $\tau = 2\pi/f$. (b) Temperature dependence of $\Delta\varepsilon$.

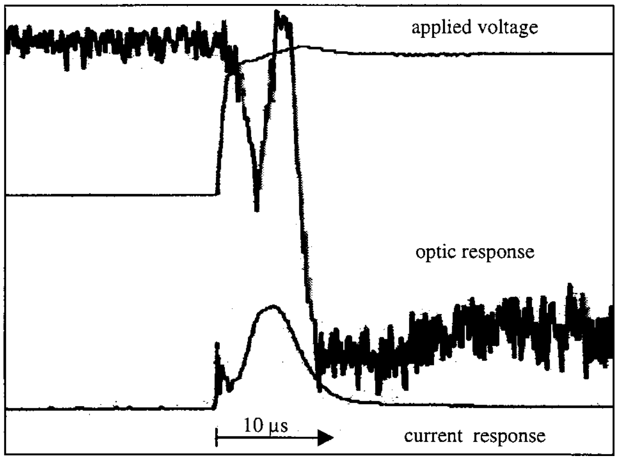

FIG. 4. Time dependencies of electro-optic and polarization current responses after fast field reversal.

C. Switching dynamics

Typical time dependencies of the optical and current signals are shown in Fig. 4. As can be seen the polarization current sets on when the optical response starts and have a maximum during the switching.

This indicates that the switching of the polarization takes place by rotation of the director around the smectic layer normal (if it happened just by the rotation around the long axis of the director, then no optical signal could be observed). It means that during switching the chirality is mainly conserved. Recent Fourier transform infrared spectroscopic measurements [15] also indicate a motion of the long molecular axis on the cone as in the Sm-C* phase [16]. Switching times have been estimated from both the electro-optical response and from the time elapsed between appearance of the maximum of the polarization reversal current and the field reversal. They are shown in Figs. 5(a) and 5(b) as a function of temperature and applied electric field, respectively.

The activation energies calculated from the temperature dependencies of the switching times, $\Delta E_A = 12.2$ kJ/mol in the chiral case and $\Delta E_A = 16.4$ kJ/mol in the racemic state are considerably smaller than those calculated from the dielectric measurements. This is not surprising, since during

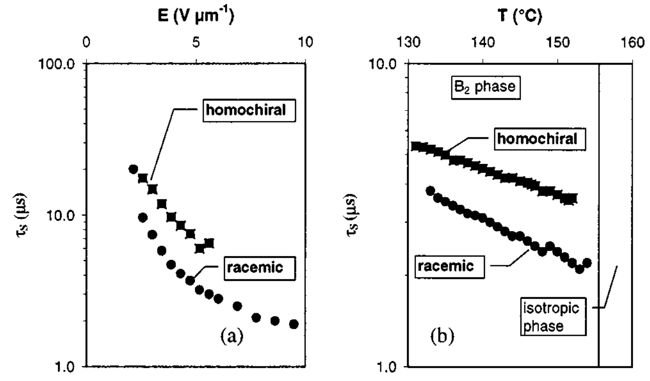

FIG. 5. Temperature (a) and electric field dependence (b) of the switching time, τ_s, of a 10 μm cell, as determined by the time needed to reach the maximum polarization current following field reversal.

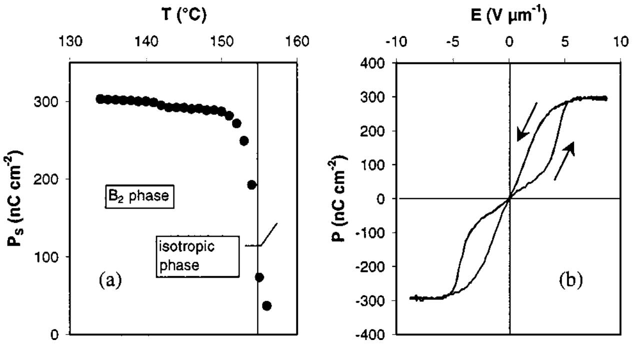

FIG. 6. Temperature dependence of the polarization as measured under triangular fields in the racemic state (a). Electric field dependence of the polarization measured at low frequency by the Diamant-bridge method (b). Arrows are showing increasing and decreasing electric field strength, respectively. At low electric field strengths a linear response of the polarization could be seen, indicating a deformation of the antiferroelectric order.

electro-optical switching a voltage is applied, and the material is in the ferroelectric state, while during dielectric measurements they are in the antiferroelectric ground state.

D. Polarization measurements

The temperature and electric field dependence of the spontaneous polarization was measured by the Diamant-Bridge method and by analyzing the polarization current associated to the switching under triangular and rectangular fields. The temperature dependence of the polarization as measured in the racemic state under triangular fields is shown in Fig. 6(a).

The maximum value of the polarization is around 300 nC/cm^2, which is typical for banana-shaped materials [9]. The polarization values measured under rectangular fields give similar results for both racemic and chiral textures. The electric field dependence of the polarization measured at low frequency by the Diamant-bridge method is shown in Fig. 6(b). It is remarkable that under increasing fields the polarization linearly increases even at low fields. This indicates that the antiferroelectric order (characterized by zero average polarization) becomes deformed even at low fields.

III. DISCUSSION

For a qualitative explanation of the field induced chiral separation we can assume that there is a difference in free energies of the synclinic and anticlinic states. The racemic state is synclinic at zero fields, whereas the chiral state is synclinic under strong fields when it is in the ferroelectric state. This would mean that the synclinic structure is favored, perhaps for steric reasons. This explains the racemic-chiral transformation under strong rectangular fields. When triangular fields are applied the system periodically goes through states where the racemic structure is favored. For the chiral-racemic texture transformation at zero field an energy barrier has to be overcome. This requires nucleation, and is very slow. The role of the periodic electric excitation is to facilitate this nucleation process.

The dielectric relaxation modes below 1 MHz resemble those observed in antiferroelectric Sm-C_A^* phases, assignable to the distortion of the antiferroelectric ordering [17]. The difference is that in this case $\Delta\varepsilon$ is more than an order of magnitude larger than in Sm-C_A^*, indicating that the antiferroelectric order is much softer and there is not strict threshold for the AF-FE transition. This can indeed be seen on the $P(E)$ curve [see Fig. 6(b)].

The director rotation is viscoelastic, since it leads to a distortion of the antiferroelectric order. This can be taken into account by a complex rotational viscosity $\gamma=\gamma+i\gamma''$ (γ' is the real viscosity, and $\gamma''=G/\omega$, where G is the elastic modulus associated to the distortion of the antiferroelectric order).

Assuming that the sample reacts to an applied field uniformly the torque balance equation reads

$$P_0E\sin(\psi)=-\gamma\dot{\psi}. \tag{1}$$

The electric field inside the sample is nearly constant and has the time dependence

$$E(t)=E_0\sin(\omega t). \tag{2}$$

In the limit of small fields the director rotates so that the azimuthal angles of the subsequent layers deviate from the positions ψ_0 and $\psi_0+180°$ by a small angle $\psi_1\ll 1$ ($\psi=\psi_0+\psi_1$, and $\psi=\psi_0+180°-\psi_1$). Thus it can be written

$$\psi_1(t)=P_0E_0\sin\psi_0\,\frac{\gamma''\sin(\omega t)-\gamma\cos(\omega t)}{\omega(\gamma'^2+\gamma''^2)}. \tag{3}$$

The rotation of the spontaneous polarization contributes to the dielectric constant of the material by $\Delta\varepsilon$, as

$$\Delta\varepsilon=\Delta P/E, \tag{4}$$

where

$$\begin{aligned}\Delta P=&(1/2)P_0\{[\cos(\psi_0)-\cos(\psi_0+\psi_1)]\\&+[\cos(\psi_0+180°)-\cos(\psi_0+180°-\psi_1)]\}\\&\cong P_0\psi_1\sin\psi_0=P_0^2E_0\,\frac{\sin^2\psi_0(\gamma''\sin(\omega t)+\gamma'\cos(\omega t))}{\omega(\gamma'^2+\gamma''^2)}.\end{aligned} \tag{5}$$

The component of ΔP in phase with the electric field yields a contribution to the real part of the dielectric constant ε', while the out-of-phase component contributes to the loss ε''. From Eq. (4) we get that

$$\varepsilon'=P_0^2\,\frac{\gamma''\sin^2\psi_0}{\omega(\gamma'^2+\gamma''^2)}\quad\text{and}\quad\varepsilon''=P_0^2\,\frac{\gamma'\sin^2\psi_0}{\omega(\gamma'^2+\gamma''^2)}. \tag{6}$$

The polarization has a maximum contribution to the dielectric constant when it is perpendicular to the field. At low frequencies where $G/\omega\gg\gamma'$, the director rotation contributes only to the real part, whereas it has a maximum contribution to ε'' when $\omega_1=G/\gamma'$. Figure 3 gives that at 135 °C $\omega_1(\text{rac})\sim2.5\times10^6$ 1/s and $\omega_1(\text{chi})\sim1.0\times10^6$ 1/s. From Fig. 4 we can assume that during switching between ferroelectric states the director rotates around a cone of angle ca. 16°. This means that the switching time τ_s can be expressed [16] as $\tau_s \approx 2(\gamma/PE)$. From the measured switching times [see Fig. 5(b)] we get $\gamma'(\text{rac}) = 4.5\times 10^{-2}$ Pa s and $\gamma'(\text{chi}) = 7.5\times 10^{-2}$ Pa s. With these the elastic moduli for the distortion of the antiferroelectric order are $G(\text{rac}) = 1.1\times 10^5$ N/m^2, and $G(\text{chi}) = 0.7\times 10^5$ N/m^2. $G(\text{rac})$ can be calculated also from the linear slope of $P(E)$ of Fig. 6(b) using Eq. (3) and utilizing that at low frequencies $\gamma' \ll \gamma''$. The estimated value is 0.8×10^5 N/m^2, which agrees well with the value calculated above. This supports our theoretical model.

The strength of the contribution to $\Delta\varepsilon$ can be approximated from Eq. (6) as

$$\Delta\varepsilon|_{\omega\to 0} = \frac{P_0^2 \sin^2 \psi_0}{G}. \tag{7}$$

With the value of the polarization measured in the racemic state ($P_0 = 3\times 10^{-3}$ C/m^2) and with $\psi_0 = 90°$, we get that $\Delta\varepsilon(\text{rac}) \sim 9\varepsilon_0$ and $\Delta\varepsilon(\text{chi}) \sim 15\varepsilon_0$. Comparing these values to those shown in Fig. 3(b) we see a good agreement for the racemic texture. In the chiral state the measured strength of the dielectric mode is about 50% larger than the calculated. This may indicate that the polarization is about 25% larger in the chiral, than in the racemic state. Within the error of the polarization measurement under rectangular fields we cannot exclude this possibility.

As a summary, we observed that the macroscopic chirality of a material with achiral molecules can be reversibly influenced by suitable electric field treatments. It is possible to obtain films containing either racemic or chiral domains. The observations indicate that the synclinic states (racemic in zero fields and chiral in high fields) have the minimum free energy. Our analysis leads us to conclude that the antiferroelectric ground state is weak, especially in the chiral domains. We determined the elastic constants associated to the deformation of the antiferroelectric order. The calculations are consistent with the measurements.

ACKNOWLEDGMENTS

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