

Linear Electroclinic Effect in a Chiral Nematic Liquid Crystal

Zili Li, Rolfe G. Petschek, and Charles Rosenblatt

Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106

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A tilt θ of the optic axis linear in transverse electric field was observed in a surface-stabilized chiral nematic liquid crystal. The electroclinic constant $d\theta/dE$ was found to exhibit significant pretransitional behavior on approaching the nematic-smectic-*A* transition temperature from above. A simple theoretical discussion involving coupled order parameters is presented.

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In 1977 Garoff and Meyer demonstrated the existence of an electroclinic effect above the smectic-*A*-smectic-*C** transition in liquid crystals containing chiral molecules.^{1,2} An electric field E is applied in the plane of the smectic layers, coupling to the molecular dipole moment. If the molecules lack inversion symmetry, a nonzero molecular tilt angle θ obtains, such that $\theta \propto E$. Although this effect was first studied in the weakly polarizable material *e*-(*n*-decyloxy-benzylidene)-*p*'-amino-(2-methylbutyl)cinnamate (DOBAMBC), recent work has centered on more highly polar materials, resulting in enhanced electroclinic constants.^{3,4} In addition, the electroclinic effect was recently observed in other smectic phases, including the smectic-*B* and smectic-*E* phases.⁵ In all these cases, smectic symmetry is present, and a tilt proportional to the electric field can be observed. In general, however, the electroclinic effect requires only that there be an electric field perpendicular to a unique special axis in the material, and thus other phases, particularly the nematic, might also be expected to exhibit such an effect. In this paper we report on experimental observations of an electroclinic effect in a surface-stabilized chiral nematic, and discuss its origins and consequences theoretically.

We studied the material SCE12, which was kindly supplied to us by BDH Ltd. through EM Industries. The material was used as is. SCE12 is a compensated mixture with a pitch of many tens of microns over a temperature range several degrees above the nematic-smectic-*A* (NA) transition temperature. The material was inserted between two indium-tin-oxide-coated glass microscope slides which were treated with the polymer nylon 6/6 and rubbed to give homogeneous orientation. Sample spacing was nominally 25 μm , as determined by the thickness of a pair of Mylar spacers. The sample was housed in a brass oven, where the temperature was controlled by a YSI model 72 controller to $\pm 0.015^\circ\text{C}$. At the temperatures under investigation (within 10°C of the NA transition), the pitch is sufficiently large that the sample unwinds and is totally oriented by the action of the polymer surface treatment. Finally, in order to investigate possible magnetic effects, the oven was mounted in the bore of an 8.2-T superconducting magnet with

transverse optical ports; the magnetic field \mathbf{H} was set parallel to the nematic director along the z axis.

The beam from a He-Ne laser attenuated to approximately 0.1 mW was incident perpendicular to the sample along the x axis and polarized at an angle $\pi/8$ from the z axis in the y - z plane. (Note that the applied E field was also in the x direction and, given that the dielectric anisotropy $\Delta\epsilon < 0$, no Freedericksz transition was present.) After passing through a crossed polarizer, the beam intensity was measured by means of a photodiode. The electroclinic effect, which is a tilt θ of the optic axis in the y - z plane linear in applied field E_x , corresponds to the introduction of an off-diagonal component ϵ_{yz} in the dielectric tensor. When such a tilt occurs, there is a concomitant change in the intensity δI at the detector^{2,3,6} such that

$$\theta \equiv \epsilon_{yz}/(\epsilon_{zz} - \epsilon_{yy}) = \delta I/4I_0, \quad (1)$$

where I_0 is the beam intensity in the absence of E . An ac electric field E_x at frequency $\nu = 2$ kHz was applied to the sample, and the induced intensity change δI vs E_x was measured at the modulation frequency with a lock-in amplifier. I_0 was measured simultaneously with a dc voltmeter, and the absolute electroclinic constant $d\theta/dE$ was obtained with Eq. (1). (It was found that the electroclinic constant is independent of frequency between 250 Hz and 10 kHz; at lower frequencies we observed a Carr-Helfrich instability.⁷) Note that if a tilt were to occur in the x - z plane, δI to lowest order would scale as θ^2 , and no signal would be observed at the modulation frequency.

Figure 1 shows the magnitude of θ versus the magnitude of the applied ac electric field at $T = 81.81^\circ\text{C}$ in the absence of a magnetic field. As is readily apparent, θ is linear in E , analogous to the usual electroclinic effect found in a number of smectic phases. Data were taken over a temperature range from 68.37°C (near the smectic-*A*-smectic-*C** phase transition), through the NA transition temperature at approximately 81.45°C , and in the nematic phase up to 89.06°C . Within the smectic-*A* phase, the usual pretransitional divergence (not shown) was observed near the *A*-*C** transition.^{1,2,4} Within the nematic phase, however, it was found that

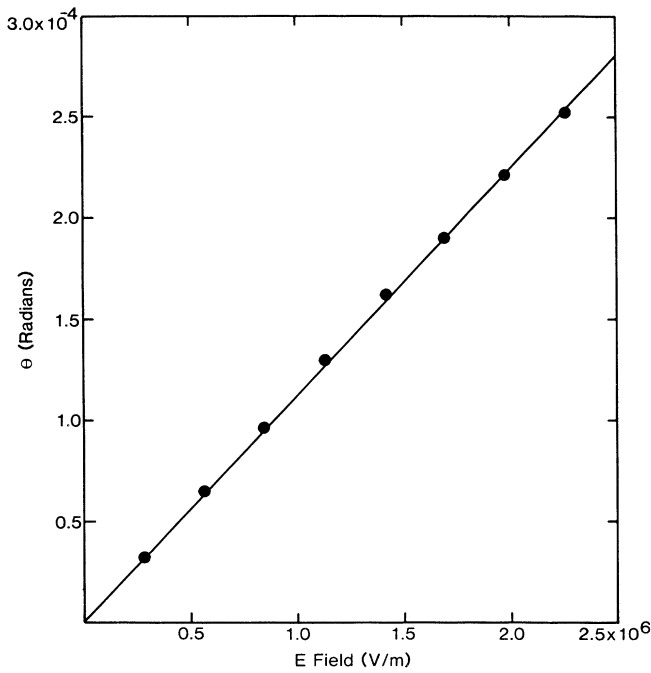


FIG. 1. θ vs E at $T=81.81^\circ\text{C}$ and at frequency $\nu=2$ kHz.

$d\theta/dE$ is quite small far above T_{NA} (being 2 to 3 orders of magnitude smaller than values of the electroclinic constant within 1°C of the $A-C^*$ transition), but that $d\theta/dE$ grows substantially on approaching T_{NA} from above. This behavior is shown in Fig. 2, where several data points within the smectic- A phase are exhibited to emphasize the change of slope with temperature at T_{NA} . From the results in Fig. 2 we deduce that in this material smectic layering, in this case in the form of smectic fluctuations, is important to the magnitude of the electroclinic effect; we will discuss this below.

In order to ascertain whether a magnetic field oriented parallel to the z axis has any substantive effect, we measured the electroclinic constant $d\theta/dE$ vs H up to nearly 8 T at $T=83.42^\circ\text{C}$; the results are shown in Fig. 3. Although a very slight increase was observed at higher fields, we feel this effect is due to the magnetic field improving the surface-induced alignment, rather than to any underlying physics. This conclusion is confirmed by the fact that $d\theta/dE$ approaches a constant value at high fields, whereas the change in $d\theta/dE$ occurs at fields below 1 T. In this range of fields the magnetic penetration depth ξ , the distance over which any surface misalignment is rotated parallel to H , crosses over from being larger than to being smaller than the sample spacing. Here $\xi = (K_{22}/\Delta\chi H^2)^{1/2}$, where K_{22} is a twist elastic constant and $\Delta\chi$ is the magnetic susceptibility anisotropy. Thus, a magnetic field does not seem to play an important role in the electroclinic effect.

We note that if the order parameter were spatially varying there would be a linear coupling between the

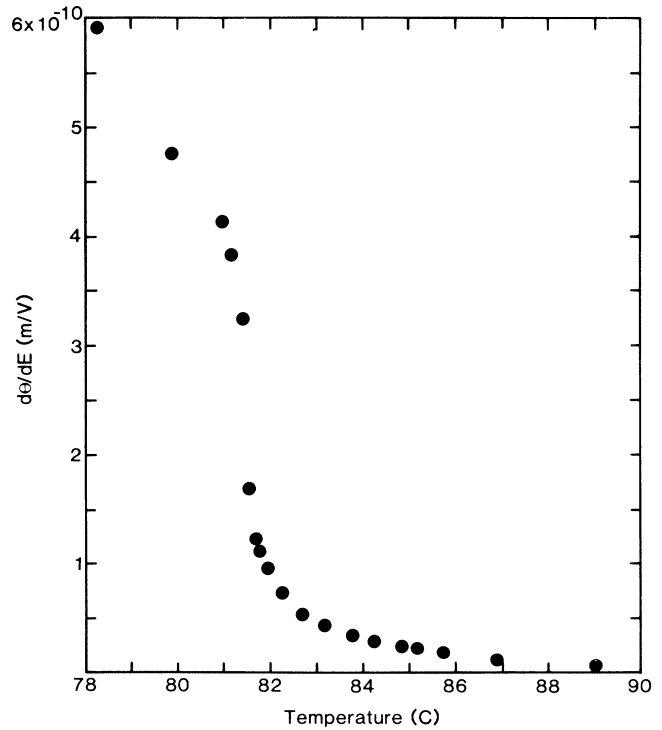


FIG. 2. $d\theta/dE$ vs temperature. Note the change in slope at the NA phase transition temperature. Error bars are approximately $\frac{1}{5}$ the diameter of the points.

director and the electric field—the so-called flexoelectric effect.⁸ However, we have checked the possible flexoelectric terms and find that they are small in our geometry. Moreover, as discussed above, our large field would be expected to significantly alter the director if it were spatially varying. Because the total optical phase shift of the sample is of order 60π , a flexoelectric effect would imply a rapidly varying optical signal as a function of applied magnetic field, which was not observed.

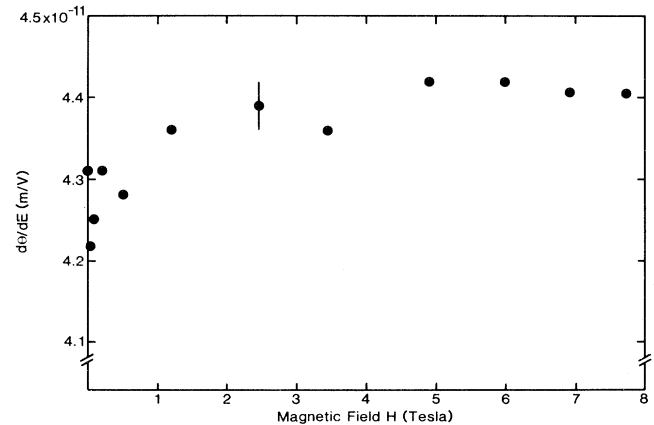


FIG. 3. $d\theta/dE$ vs magnetic field H_z at $T=83.42^\circ\text{C}$.

Similarly, if the observed phenomenon were actually a surface effect rather than a bulk electroclinic effect, the optical signal would also be expected to vary rapidly with sample thickness, which was not observed either. Finally, in order to verify that the observed effect indeed requires chiral symmetry, we measured the electroclinic constant in the nonchiral material methoxybenzylidene butylaniline (MBBA) in the nematic phase near room temperature. As is the case with SCE12, this material is characterized by $\Delta\epsilon < 0$. Within the resolution of our apparatus ($d\theta/dE \sim 1.5 \times 10^{-13}$ m/V), no electroclinic effect was observed.

In the remainder of the paper we offer a simple, heuristic discussion of the nematic electroclinic effect. This effect in the nematic phase, as in smectics, can be viewed as a matter of symmetry. An electric field (which is a true vector) is applied perpendicular to a special axis which is unique in the sample. If the system is chiral the field will couple linearly to any pseudovector with the same direction and, in particular, to a molecular rotation around the axis of the field. The origin of such a tilt is intuitively easy to understand in the smectic phases: The layer normal provides a well-defined axis conceptually distinct from the optic axis. On the other hand, since the nematic phase is usually described by one direction only, i.e., the direction along which the long molecular axis points, it is somewhat more difficult to intuit the nematic electroclinic effect. Nevertheless, the effects are very similar. To understand the electroclinic effect in the nematic phase at the level of a macroscopic or Landau theory, note that it is necessary to use a number of directions to fully describe the orientation of the molecule. Consider the two order parameters $Q \equiv \langle q \rangle$ and $T \equiv \langle t \rangle$, where

$$q_{ij} = \mathbf{n}_{1i} \mathbf{n}_{1j} - \frac{1}{3} \delta_{ij},$$

$$t_{ij} = \mathbf{n}_{1i} \mathbf{n}_{2j} + \mathbf{n}_{2i} \mathbf{n}_{1j} - \frac{2}{3} \delta_{ij} \mathbf{n}_1 \cdot \mathbf{n}_2,$$

and \mathbf{n}_{aj} is the j th component of the a th unit vector specifying the direction of the molecule(s) or some portion thereof (see Fig. 4). Note that $\langle \dots \rangle$ indicates macroscopic, thermodynamic averages and that Q is the usual nematic-order parameter. In an ordinary uniaxial nematic or smectic phase these order parameters, indeed all traceless symmetric tensors, are diagonal in the same frame (codiagonal) with the direction of the diagonal element having the largest absolute value defining the special direction, i.e., the nematic "director." In the presence of an electric field, however, these tensors need not and generally will not be codiagonal. It is this difference between the directions described by two different tensors which makes the electroclinic effect in a chiral nematic possible. Mathematically, consider the additional terms in a Landau free energy

$$\delta F = a \epsilon_{ijk} E_i Q_{jk} T_{ij} - b Q_{ij} T_{ij} + \frac{1}{2} c T_{ij} T_{ij}, \quad (2)$$

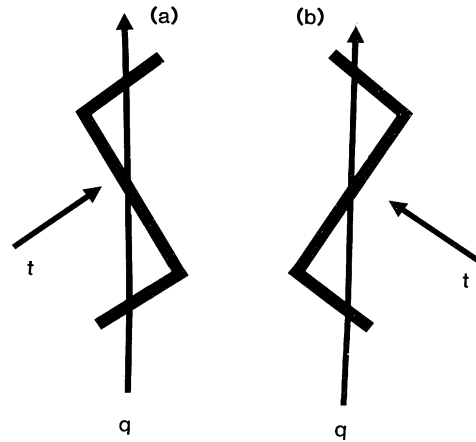


FIG. 4. Schematic representation of molecules. Arrows indicate the principle directions of the tensors q and t . For $E=0$, both configurations are equally likely and Q and T are codiagonal. For $E \neq 0$, either (a) or (b) is preferred, such that Q remains unchanged but T is no longer codiagonal with Q .

where we have used the convention that all repeated Roman indices are summed over and that ϵ is the totally antisymmetric Levi-Civita tensor. The term proportional to a is the chiral term which describes the tendency of the directors defined by Q and T to differ in the presence of an electric field; the term proportional to b describes the tendency of the tensors Q and T to define the same director, and the coefficient c is the inverse susceptibility for the order parameter T . In the presence of an electric field only, no chiral term is possible involving just one order parameter (Q). This is because the direction of the polarization is given by the cross product of two molecular directions, e.g., \mathbf{n}_1 and \mathbf{n}_2 , whereas a single-order parameter essentially describes a single molecular direction. Minimizing the free energy with respect to T , we find

$$T_{ij} = c^{-1} [b Q_{ij} - \frac{1}{2} (E_l \epsilon_{ljk} Q_{ik} + E_l \epsilon_{lik} Q_{jk})]. \quad (3)$$

The fact that T and Q are codiagonal in the absence of a field is expressed by the term proportional to b , and the tilt of T relative to Q in the presence of an electric field is given by the term proportional to a , resulting in off-diagonal elements in T . To lowest order the dielectric tensor is given by

$$\epsilon_{ij} = \epsilon_0 \delta_{ij} + \epsilon_Q Q_{ij} + \epsilon_T T_{ij}, \quad (4)$$

where ϵ_0 , ϵ_Q , and ϵ_T are constants. Thus from Eq. (1) we find

$$\begin{aligned} \frac{d\theta}{dE} &\propto \epsilon_T \frac{\partial T_{yz}}{\partial E_x} [\epsilon_Q Q_{zz} + \epsilon_T T_{zz} - \epsilon_Q Q_{yy} - \epsilon_T T_{yy}]^{-1} \\ &\propto \frac{a \epsilon_T}{c \epsilon_Q + b \epsilon_T}. \end{aligned} \quad (5)$$

It is now interesting to ask how this calculation would change at the second-order NA transition. Far above the smectic-*C* phase, the calculations in the nematic and smectic-*A* phases are virtually identical, e.g., there are two different tensors which couple to each other through a term of the form above. The parameters *a*, *b*, and *c* are determined by the local interactions of neighboring molecules. Thus they can change with a change in the *local* environment, for example, with the local value of the square of the smectic order parameter $\langle |\psi|^2 \rangle$. Near the NA critical point, $\langle |\psi|^2 \rangle$ exhibits the same critical behavior as does the energy, i.e., it has a cusp and its derivative (proportional to the specific heat) grows significantly. The specific heat has been measured at other NA transitions⁹⁻¹² and has a behavior consistent with our data.

It is perhaps surprising that the pretransitional effect is so large. This implies that layering, while not required for the existence of the electroclinic effect, substantially enhances it. It is reasonable to assume that the parameters in the free energy *a*, *b*, and *c*, and not their inverses, are smooth functions of $\langle |\psi|^2 \rangle$. As the pretransitional effect is very large, if the increase in $d\theta/dE$ were due to a decrease in the denominator, one would reasonably expect that the denominator would become zero close to the region in which the electroclinic constant is rapidly increasing. This behavior would imply a divergent $d\theta/dE$ and possibly a transition to some other phase, such as the smectic *C*. However, this transition occurs only at temperatures well below the NA transition. It therefore seems most reasonable that the observed pretransitional effect is due to a rapid increase in *a*, the coupling coefficient between the molecular tilt and the electric field, as the tendency to form layers increases.

In summary, we have observed an electroclinic effect in a surface-stabilized chiral nematic liquid crystal. This effect increases very rapidly near the NA transition, indicating that smectic order in this material has a strong effect on the coupling between tilt and the electric field.

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¹S. Garoff and R. B. Meyer, Phys. Rev. Lett. **38**, 848 (1977).

²S. Garoff and R. B. Meyer, Phys. Rev. A **19**, 338 (1979).

³Ch. Bahr and G. Heppke, Liq. Cryst. **2**, 825 (1987).

⁴R. Qiu, J. T. Ho, and S. K. Hark, Phys. Rev. A **38**, 1653 (1988).

⁵Ch. Bahr and G. Heppke, Phys. Rev. A **37**, 3179 (1988).

⁶G. Andersson, I. Dahl, P. Keller, W. Kuczynski, S. T. Lagerwall, K. Sharp, and B. Stebler, Appl. Phys. Lett. **51**, 640 (1987).

⁷See P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1975).

⁸R. B. Meyer, Phys. Rev. Lett. **22**, 918 (1969).

⁹C. W. Garland, M. Meichle, B. M. Ocko, A. R. Kortan, C. R. Safinya, L. J. Yu, J. D. Litster, and R. J. Birgeneau, Phys. Rev. A **27**, 3234 (1983).

¹⁰G. B. Kasting, K. J. Lushington, and C. W. Garland, Phys. Rev. B **22**, 321 (1980).

¹¹J. Thoen, H. Marynissen, and W. Van Dael, Phys. Rev. A **26**, 2886 (1982).

¹²C. A. Schantz and D. L. Johnson, Phys. Rev. A **17**, 1504 (1978).