Flexoelectric Electro-optics of a Cholesteric Liquid Crystal

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A linear electro-optic effect in a cholesteric liquid crystal is described and attributed to the flexoelectric effect. An electric field applied perpendicular to the helix axis rotates the director about an axis parallel to the field. This produces a periodic splay-bend pattern in the helix, which couples flexoelectrically to the field.

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The helical structure of a cholesteric liquid crystal can be modified or even completely unwound by an applied electric field. This is well understood in terms of the coupling of the electric field to the dielectric anisotropy of the liquid crystal, an effect which is quadratic in the amplitude of the electric field. In this Letter, a new effect is described which is linear in the electric field, and therefore arises from a different coupling mechanism. Following a description of the observations, an explanation is proposed in terms of the linear flexoelectric effect, which accounts for all the experimental observations, and predicts some other properties that can be tested.

The phenomenon is readily observed in a uniformly aligned parallel-plate cell in which the helical axis of the cholesteric lies parallel to the glass surfaces in a unique direction. The inner surfaces of the cell are coated with transparent electrically conductive layers so that an electric field can be applied perpendicular to the plates and to the helix axis. When such a cell is observed between crossed polarizers, extinction is observed whenever the helix axis is parallel or perpendicular to the polarizer, since macroscopically a small-pitch cholesteric acts like a uniaxial crystal with the helix as its optical axis. In this extinction configuration, when a small electric field is applied, the cell transmits light, indicating a rotation of the optical axis in the plane of the cell. By rotation of the cell through a small angle, extinction is once again achieved. It is found that the rotation direction changes with the polarity of the field and the rotation angle is linear in the field amplitude, at least for small fields.

This effect has been observed in several different cholesterics. Figure 1 displays results for *S*-4-*n*-nonyloxyphenyl-4′-(3″,7″-dimethyloctyloxybenzoyloxy) benzoate, in a cell approximately 2.75 μm thick and with indium-tin oxide electrodes coated with poly-1,4-butyleneterephthalate to produce parallel molecular alignment at the surface.[1] Initial alignment of the helix axis parallel to the glass was achieved by cooling of the sample from the isotropic state in the presence of an electric field. Because this material has a positive dielectric anisotropy, this orientation of the helix has the lowest dielectric energy. This geometry should produce a fingerprint texture. However, this texture was not visible at low fields, in the material being examined, because of the short pitch comparable to the wavelength of the light. It was nevertheless clearly evident in the presence of an electric field at values close to the unwinding voltage. Measurements of the effect were then made with a 40-Hz square wave of variable amplitude, monitoring the

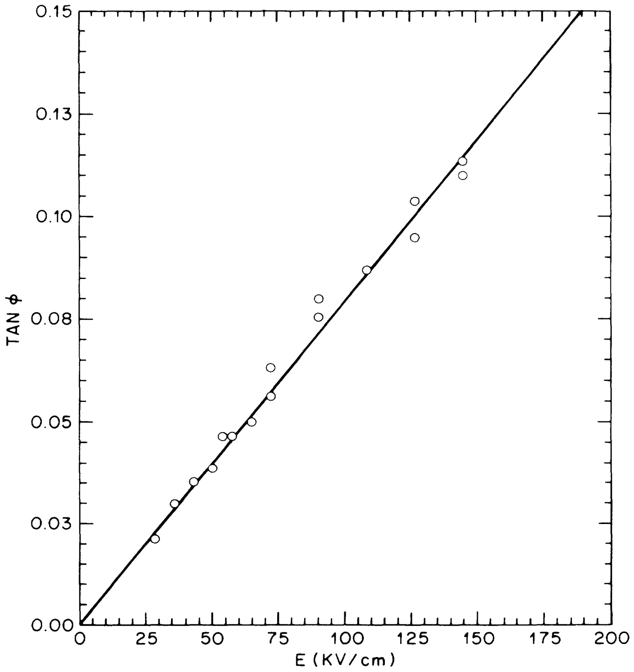

FIG. 1. Rotation of the optical axis (tanϕ) vs applied field (E).

transmitted light intensity with a photodiode and an oscilloscope. For each field amplitude the cell was rotated clockwise and counterclockwise to find the extinction angles for each polarity of field. The dependence of rotation angle on field is linear up to the field at which the dielectric coupling results in unwinding the helix. Although this effect is clearly observed in thicker samples (14 μm), the poor quality of alignment prevented quantitative measurements in these samples for this material.

It is proposed that these observations are explained by the flexoelectric effect, which is a linear coupling between an electric polarization and splay and bend deformations of the liquid crystal. Although the flexoelectric effect has been known and studied for a long time, it has played a secondary role in the phenomenology of liquid crystals because of its complex geometrical requirements. It is most easily observed when either the liquid crystal[2,3] or the electric field[4] is highly inhomogeneous in orientation. The present case is no exception in this regard, although it is simpler in practical respects than other flexoelectric phenomena.

One of the first flexoelectric phenomena proposed by Meyer[5] is one in which a uniform electric field induces the formation of a continuously rotating director structure consisting of alternating bands of splay and bend deformation, as seen in Figs. 2(d) and 2(e). The formation of such a structure from a uniformly aligned nematic has never been observed, for two reasons. First, the flexoelectric effect must compete with ordinary dielectric anisotropy, and the latter coupling usually dominates, maintaining uniform orientation. Second, the continuously rotating director pattern would have to be formed by the generation and movement of defects through the sample, which would occur most easily with high static fields. However, high static fields usually induce electrohydrodynamic instabilities that would obscure the flexoelectric structure.

Starting from the helical cholesteric structure rather than the nematic ground state circumvents these two problems. The director is already continuously rotating in the cholesteric, in a pure twist fashion. It remains only for the flexoelectric effect to modify this structure to introduce components of splay and bend curvature. This is achieved by rotation of the director about an axis parallel to the electric field, as shown in Fig. 2. In both sign and magnitude the splay and bend deformations vary linearly with the rotation angle, at least at small angles. Our understanding of this geometry came partly from the elegant work of Bouligand, among others, who studied cholesteric structures in biological materials such as insect and crab cuticle and dinoflagellate chromosomes.[6] Microtomed specimens in which the slice is taken at an oblique angle to the cholesteric helix exhibit the multiply arched pattern of Figs. 2(d) and 2(e).

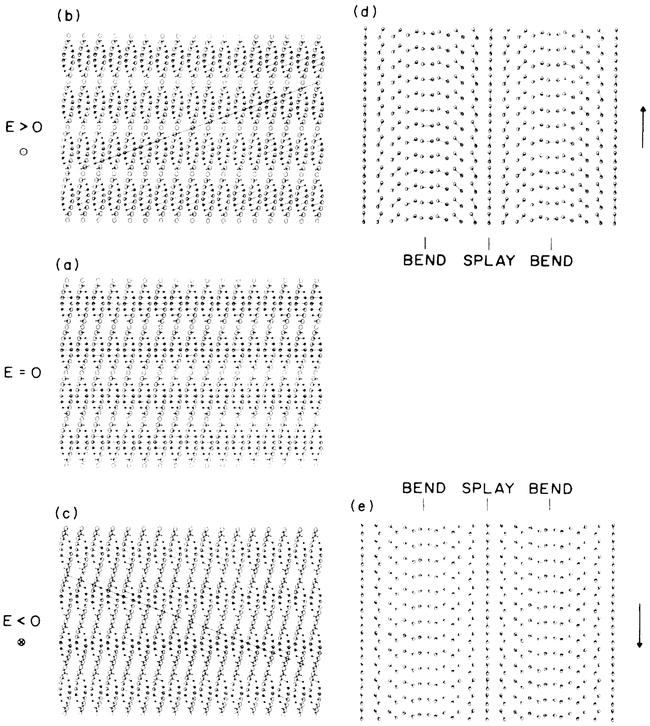

FIG. 2. The helical structure viewed normal to the helix axis, (a) in the absence of an electric field, and (b),(c) in the presence of an electric field perpendicular to the plane of the drawing, which shows the induced director rotation. (d),(e) Cross sections of the helix as indicated by the lines in (b) and (c), displaying the splay-bend pattern.

To make this model quantitative, consider a cholesteric helix in which the director $\hat{\mathbf{n}}$ is parallel to the x-y plane, with $n_x = \cos\theta$ and $n_y = \sin\theta$. In the presence of an electric field $\mathbf{E}$ along the x direction, it is proposed that the helix axis which was initially along the z direction rotates by an angle ϕ about the x axis (in the laboratory frame of reference, the helix axis is fixed for the sample geometry studied, and the x-y plane rotates by $-\phi$). Splay and bend deformations are described by vector fields $\mathbf{S}$ and $\mathbf{B}$, parallel to the x-y plane, given by $\mathbf{S} = \hat{\mathbf{n}}(\nabla \cdot \hat{\mathbf{n}})$ and $\mathbf{B} = \hat{\mathbf{n}} \times \nabla \times \hat{\mathbf{n}}$. Twist is described by $t = \hat{\mathbf{n}} \cdot \nabla \times \hat{\mathbf{n}}$. The free-energy density f for a cholesteric of equilibrium twist t_0 is

$$f = \tfrac{1}{2}\{K_1 S^2 + K_2(t_0 - t)^2 + K_3 B^2\} - e_s \mathbf{E}\cdot\mathbf{S} - e_b \mathbf{E}\cdot\mathbf{B} + (1/8\pi)\epsilon_a E^2 \sin^2\theta, \qquad (1)$$

in which the K_i are the splay, twist, and bend elastic constants, e_s and e_b are the splay and bend flexoelectric coefficients, and ϵ_a is the anisotropic part of the dielectric constant.

To see the consequences of the flexoelectric effect in the simplest form, it is assumed that $K_1 = K_3$, $\epsilon_a = 0$, and $e_s = e_b = \bar{e}$, the mean flexoelectric coefficient. If we denote partial derivatives by subscripts, the free-energy density reduces to

$$f=\tfrac{1}{2}K_1\theta_y^2-\bar{e}E\theta_y+\tfrac{1}{2}K_2(t_0-\theta_z)^2. \qquad (2)$$

This is clearly minimized by $\theta_z=t_0$ and $\theta_y=\bar{e}E/K_1$. If we denote the rotated helix axis by a wave vector $\mathbf{k}$, with $\theta=\theta_0+\mathbf{k}\cdot\mathbf{r}$, then $k\cos\phi=t_0$ and $k\sin\phi=\bar{e}E/K_1$. The rotation angle is given by $\tan\phi=\bar{e}E/t_0K_1$, which is linear in E for small rotations. With use of this expression, and the value of the slope in Fig. 1, it is found that $\bar{e}=3\times10^{-5}$ cgs units, for $K_1=K_3=1\times10^{-6}$ dyn and helix pitch $=0.5$ μm. This value is similar to those for other liquid crystals.[4,7] At first it may seem strange that the free energy is lowered by a uniform rotation of the molecules about the electric field direction, but it should be recalled that the flexoelectric coupling induces curvature, not alignment.

A drawback of this simplified theory is that it ignores the dielectric coupling, which distorts and eventually unwinds the helix. It is interesting to determine how the flexoelectric effect influences the helix unwinding field. Still, under the assumption of a uniformly rotated helix axis, the definition of a spatial coordinate h along the helix axis results in $\theta_z=\theta_h\cos\phi$ and $\theta_y=\theta_h\sin\phi$. Let us assume $K_1=K_3$ to simplify the mathematics without serious loss of generality; then the free energy can be written

$$f=A\theta_h^2+B\theta_h+C+\tfrac{1}{2}K_2t_0^2, \qquad (3)$$

$$A=\tfrac{1}{2}(K_1\sin^2\phi+K_2\cos^2\phi), \qquad (4)$$

$$B=(-e_s\cos^2\theta-e_b\sin^2\theta)E\sin\phi-K_2t_0\cos\phi, \qquad (5)$$

$$C=(1/8\pi)\epsilon_aE^2\sin^2\theta. \qquad (6)$$

This form of free-energy density can be dealt with by the same methods used to understand the unwinding of the helix by the simple dielectric coupling. The first integral of the Euler-Lagrange equation is given by $\theta_h=\pm[(C+Q)/A]^{1/2}$, in which Q is a constant of integration. θ can be written in terms of elliptic integrals. By our substituting this form of θ_h into the mean free energy and minimizing with respect to ϕ and Q, it is possible to derive expressions for the pitch of the helix and the rotation angle ϕ as a function of electric field. Surprisingly, the simple result for $\tan\phi$, derived above, remains valid even in this much more general case.

The critical field E_c for unwinding the helix is, however, modified by the flexoelectric coupling:

$$E_c=\tfrac{1}{2}\pi t_0[4\pi K_2/(\epsilon_a-\pi^3\bar{e}^2K_1^{-1})]^{1/2}. \qquad (7)$$

The effective dielectric anisotropy is thus reduced by the flexoelectric effect. Since the flexoelectric coupling tends to keep the director in a helical configuration, it opposes the dielectric coupling, and can substantially increase the critical field over what it would be if $\bar{e}$ were zero.

This prediction can be tested by the study of the frequency dependence of the flexoelectric effect and of the critical field. A remarkable feature of this form of the flexoelectric effect is that a small homogeneous rotation of all the molecules in the system produces a short wavelength periodic splay-bend structure with a small intrinsic relaxation time. In the materials that have been studied, the flexoelectric distortions follow the field up to frequencies of several kilohertz, above which rotational viscosity suppresses the response. At high frequencies therefore the critical field for unwinding the helix should decrease. In the materials that have been tested, the flexoelectric effect has been small enough and the frequency dependence of the dielectric anisotropy large enough to make this experiment ambiguous.

The practical applications of this new effect remain to be explored. To maximize the reponse, it is desirable to have a material which has large flexoelectric coefficients of the same sign, a requirement about which little is known at the level of designing new molecules. To achieve large rotation angles in this effect, it is necessary to avoid the unwinding of the helix by the dielectric coupling, which suggests that the dielectric anisotropy should be small. Eventually this effect may have application as a modulator of optical transmission or optical Bragg scattering.

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