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Electroclinic effect in nematic liquid crystals: The role of molecular and environmental chirality

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The electroclinic (EC) effect is the tilt of the optical axis of a liquid crystal in the plane perpendicular to an applied electric field. Chirality plays a key role for its emergence. Based on the molecular and phase symmetry we derive a molecular expression for the EC coefficient, the material property that quantifies the linear coupling between tilt and electric field, in nematic liquid crystals. Modeling the relevant molecular properties (shape, electric dipole moment, and polarizability) with atomic resolution, we calculate the EC coefficient for prototype molecular structures. We demonstrate that molecular chirality, needed for the occurrence of the EC effect in nematics with a uniform director, is not a necessary requirement in the presence of a twisted director. Our results show that in the latter case conformational deracemization, invoked to explain recent experiments, is not the only mechanism.

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The electroclinic (EC) effect is an electro-optical coupling observed in liquid crystals, which consists in the rotation of the optical axis about an electric field, perpendicular to the optical axis itself. The tilt is linear in the electric field and the proportionality coefficient, the EC coefficient, is a property of the material. This effect was first reported in 1977 for the orthogonal smectic A phase of chiral mesogens [1]. Subsequently, it was also observed in chiral nematic liquid crystals [2] with unwound helix, so demonstrating that smectic layering is not essential for its appearance [3]. The origin of the EC effect in chiral nematics remained controversial and different molecular and environmental contributions have been proposed over the years; it was discussed whether it is a bulk or a surface effect, if it implies a change in the molecular orientation, and an important role of smectic fluctuations was proposed [3–6]. The EC effect is related to the lack of mirror symmetry with respect to the plane that contains the electric field and the director [4], so chirality plays a key role for its appearance. Indeed, the EC effect brings to the light the hidden chirality of nematic or smectic A samples, otherwise macroscopically indistinguishable from their achiral analogous; this feature has been exploited for chirality sensing [7]. More recently, the EC effect was observed in achiral nematic liquid crystals, in cells with a twisted director configuration [8,9]. This was interpreted as an expression of "top-down" chiral induction: The chiral environment would yield an imbalance in the relative population of chiral molecular conformations that are the mirror image of each other (enatiomorphic conformations), so leading to conformational deracemization in the sample.

The EC effect in nematics is fast (on the submicrosecond time scale), which could be beneficial for electro-optical applications, but has the drawback of being very small: Tilt angles smaller than 0.1° were reported upon application of electric fields of the order 10^6 V/m. The tilt depends upon the molecular structure, but this issue is fully unexplored. Only one study of the role of the molecular shape on the EC effect has been reported for smectic A liquid crystals [10]. Here we propose a molecular model for the EC effect in the nematic phase. Based on the molecular and phase symmetry, we obtain expressions of the EC coefficient as a function of the relevant molecular properties (shape, electric dipole moment, and polarizability). So, we can discuss the molecular determinants of the phenomenon and distinguish the role played by the molecular and environmental chirality. Two cases will be distinguished, denoted as (I) and (II).

(I) A nematic sample with uniform director has a C_∞ symmetry axis parallel to the director (Z axis); the system has $D_{\infty h}$ or D_∞ point symmetry, for achiral and chiral liquid crystals, respectively. Application of an electric field $\mathbf{E}$ perpendicular to the director breaks the uniaxial symmetry and only one C_2 axis remains ($X \parallel \mathbf{E}$). For achiral liquid crystals the plane containing the director and the electric field (XZ) and the plane perpendicular to the director (XY) are mirror planes; the system has orthorhombic symmetry (C_{2v} point symmetry) and any second rank tensor is diagonal in the (X,Y,Z) frame. For chiral liquid crystals no mirror symmetry plane survives; the system has monoclinic symmetry (C_2 point symmetry) and second rank tensorial properties share only one principal direction, the X axis.

(II) In the twisted director configuration the system has local D_2 point symmetry, irrespective of the liquid crystal chirality, with one C_2 symmetry axis along the twist axis (X), one parallel to the local director (Z), and the third perpendicular to both (Y). When an electric field parallel to the twist axis is switched on, only the former twofold axis (X) remains; the local point symmetry then lowers to C_2 and the same considerations reported above for case (I) with chiral liquid crystals can be made.

The (X,Y,Z) frame, whose orientation is fixed in case (I) and rotates with the director in case (II), will be henceforth denoted as local (LOC). From the above symmetry considerations it follows that for $E = 0$ the optical dielectric tensor is diagonal in the LOC frame, with $\varepsilon_{\infty,XX} = \varepsilon_{\infty,YY} \neq \varepsilon_{\infty,ZZ}$ in case (I) and $\varepsilon_{\infty,XX} \neq \varepsilon_{\infty,YY} \neq \varepsilon_{\infty,ZZ}$ in case (II). In the presence of the electric field, off diagonal (YZ) elements of the optical dielectric tensor may appear, $\varepsilon_{\infty,YZ} \neq 0$: This implies a tilt of the optical axis around the X axis, by the angle ϕ defined as

$$\frac{tg2\phi}{2} \approx \phi = \frac{\varepsilon_{\infty,YZ}}{\varepsilon_{\infty,YY} - \varepsilon_{\infty,ZZ}}, \qquad (1)$$

where the approximation holds for small tilt angle. The EC coefficient is defined as $ec = d\phi/dE$.

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Neglecting local field effects, the optical dielectric tensor is related to the molecular polarizability as

$$\varepsilon_{\infty,IJ} = \delta_{IJ} + \frac{N}{\varepsilon_0 \mathcal{V}} \langle \alpha_{IJ} \rangle, \quad I,J = (X,Y,Z), \tag{2}$$

where N is the number of molecules, $\mathcal{V}$ is the volume of the sample, and ε_0 is the dielectric permittivity of vacuum. The term within angular brackets is the average polarizability:

$$\langle \alpha_{IJ} \rangle = \int d\Omega \int_{X_-^M}^{X_+^M} dX^M \, p(\Omega|X^M) \alpha'_{IJ}(\Omega, X^M), \tag{3}$$

where $\alpha'_{IJ}(\Omega,X^M) = (\partial\alpha_{IJ}/\partial X^M)_{X=0}$ represents the linear density of polarizability along the X direction (or the polarizability of a molecular slice) at $X = 0$, for a molecule that has its center at the coordinate X^M. Coordinates are defined with respect to the LOC frame, where the $X = 0$ plane is the plane containing the local director. The integrals in Eq. (3) are over the molecular orientations, which in the LOC frame are defined by the Euler angles $\Omega = (\alpha,\beta,\gamma)$, and over molecular positions (between X_-^M and X_+^M) such that the plane $X = 0$ cuts the molecule. The function $p(\Omega|X^M)$ is the orientational distribution function of the molecule, which in the twisted configuration has a parametric dependence upon the X^M coordinate and is normalized as $\int d\Omega \, p(\Omega|X^M) = 1$. For uniform director $p(\Omega|X^M) = p(\Omega)$ and Eq. (3) can be written as

$$\langle \alpha_{IJ} \rangle = \int d\Omega \, p(\Omega) \alpha_{IJ}(\Omega) \tag{4}$$

with the molecular polarizability

$$\alpha_{IJ}(\Omega) = \int_{X_-^M}^{X_+^M} dX^M \, \alpha'_{IJ}(\Omega, X^M). \tag{5}$$

The integral over the positional coordinate in Eq. (3) can be viewed as an effective molecular polarizability that can account for the director twist. Thus, achiral molecules can acquire a chiral effective polarizability in a twisted environment.

The orientational distribution function $p(\Omega|X^M)$ can be expressed as

$$p(\Omega|X^M) = \frac{\exp\{-[U_0(\Omega|X^M) + U_E(\Omega)]/k_B T\}}{\int d\Omega \, \exp\{-[U_0(\Omega|X^M) + U_E(\Omega)]/k_B T\}}, \tag{6}$$

where the two contributions U_0 and U_E describe the potential of mean torque experienced by a molecule in the nematic environment and the interaction potential of the molecule with the electric field, respectively. The form of the molecular field potential U_0 will be specified below; for the next derivation we only need to specify that it is apolar, i.e., invariant under the $X \to -X$ transformation.

For weak electric field we can write $U_E \approx -\mu_X(\Omega)E$, where μ_X is the component of the (permanent) electric dipole of the molecule along the field, and we can approximate

$$\begin{aligned} &\exp\{-[U_0(\Omega|X^M) + U_E(\Omega)]/k_B T\} \\ &\quad \approx \left\{1 + \frac{\mu_X(\Omega)E}{k_B T}\right\} \exp[-U_0(\Omega|X^M)/k_B T]. \end{aligned} \tag{7}$$

Introducing this expression into Eq. (3) we obtain

$$\langle \alpha_{IJ} \rangle \approx \langle \alpha_{IJ} \rangle_0 + \frac{E}{k_B T} \langle \mu_X \alpha_{IJ} \rangle_0, \tag{8}$$

where the 0 index specifies that the integral is calculated over the orientational distribution function in the absence of the electric field, $p_0(\Omega|X^M)$, given by Eq. (6) with $U_E = 0$. In view of the symmetry of the system the only nonvanishing elements are

$$\begin{aligned} \text{(I)} \quad &\langle \alpha_{XX} \rangle_0 = \langle \alpha_{YY} \rangle_0 \neq \langle \alpha_{ZZ} \rangle_0, \\ &\langle \mu_X \alpha_{YZ} \rangle_0 = \langle \mu_X \alpha_{ZY} \rangle_0 \qquad (\neq 0 \text{ for chiral}), \end{aligned} \tag{9}$$

$$\begin{aligned} \text{(II)} \quad &\langle \alpha_{XX} \rangle_0 \neq \langle \alpha_{YY} \rangle_0 \neq \langle \alpha_{ZZ} \rangle_0, \\ &\langle \mu_X \alpha_{YZ} \rangle_0 = \langle \mu_X \alpha_{ZY} \rangle_0. \end{aligned} \tag{10}$$

Thus, the following molecular expressions are obtained for the nonvanishing elements of the optical dielectric tensor:

$$\varepsilon_{\infty,JJ} = 1 + \frac{N}{\varepsilon_0 \mathcal{V}} \langle \alpha_{JJ} \rangle_0, \tag{11}$$

$$\varepsilon_{\infty,YZ} = \varepsilon_{\infty,ZY} = \frac{NE}{\varepsilon_0 \mathcal{V} k_B T} \langle \mu_X \alpha_{YZ} \rangle_0 \tag{12}$$

and the EC coefficient is given by

$$ec = \frac{1}{k_B T} \frac{\langle \mu_X \alpha_{YZ} \rangle_0}{\langle \alpha_{YY} \rangle_0 - \langle \alpha_{ZZ} \rangle_0}. \tag{13}$$

Equation (13) can be used to calculate the EC coefficient on the basis of the molecular structure. To this purpose, models able to describe the polarizability and the orientational distribution with submolecular resolution are needed.

Polarizability. We have used the Thole model of mutually interacting atomic polarizabilities [11]. The induced dipole moment at the p atom position, in a molecule of N_a atoms, is expressed as $\boldsymbol{\mu}^{p,\mathrm{ind}} = \boldsymbol{\alpha}^p(\mathbf{E} - \sum_{q=1,q\neq p}^{N_a} \mathbf{t}^{pq} \boldsymbol{\mu}^{q,\mathrm{ind}})$, where $\boldsymbol{\alpha}^p$ is the bare (isotropic) polarizability of the atom and the term within parentheses is the total electric field at its position. Besides the applied field $\mathbf{E}$, this includes contributions deriving from the other induced dipoles in the molecule, which are accounted for through the dipole-dipole interaction tensors between pairs of atoms, $\mathbf{t}^{pq}$. We can write $\boldsymbol{\mu}^{p,\mathrm{ind}} = \mathbf{A}^p \mathbf{E}$, where $\mathbf{A}^p$ represents the polarizability of the p atom in the molecule, which differs from that of the bare atom for including the effect of all the induced dipoles: $\mathbf{A}^p = \sum_{q=1}^{N_a} (\mathbf{T}^{-1})^{pq}$. The $\mathbf{T}$ matrix $(3N_a \times 3N_a)$ is made of 3×3 blocks defined as $\mathbf{T}^{pq} = (\boldsymbol{\alpha}^p)^{-1}$ $(p = q)$, $\mathbf{T}^{pq} = \mathbf{t}^{pq}$ $(p \neq q)$. If the atom polarizability is assumed to be homogeneously distributed within the van der Waals radius r_{vdW}^p, its contribution to the polarizability of the molecular slice at $X = 0$ is given by $[3\mathbf{A}^p/4(r_{\mathrm{vdW}}^p)^3][(r_{\mathrm{vdW}}^p)^2 - (X^p)^2]\Theta(r_{\mathrm{vdW}}^p - |X^p|)$, where X^p is the atom coordinate and Θ is the Heaviside function [$\Theta(u) = 1$ for $u > 0$, otherwise $\Theta(u) = 0$]. So Eq. (3) becomes

$$\begin{aligned} \langle \alpha_{IJ} \rangle = \frac{3}{4} \sum_{p=1}^{N_a} \frac{\mathbf{A}^p}{\left(r_{\mathrm{vdW}}^p\right)^3} \int d\Omega \int_{X_-^M}^{X_+^M} dX^M \, p(\Omega|X^M) \\ \times \left[\left(r_{\mathrm{vdW}}^p\right)^2 - (X^p)^2\right] \Theta\left(r_{\mathrm{vdW}}^p - |X^p|\right). \end{aligned} \tag{14}$$

Orientational distribution function. We have used the surface interaction model [12], where the anisotropy of the molecular field potential is parametrized according to the anisotropy of the molecular surface. The potential of mean torque experienced by the molecule in the Ω orientation with its center at the X^M coordinate, in the LOC frame, is expressed as

TABLE I. Results for the A structure with uniform director. Point symmetry of the molecular polarizability (α) and of the molecular surface (S); average values in Eq. (9); EC coefficient. In all cases the whole molecular symmetry is C_1.

	Symm.		$\frac{\langle\alpha_{XX}\rangle_0}{4\pi\varepsilon_0}$	$\frac{\langle\alpha_{YY}\rangle_0}{4\pi\varepsilon_0}$	$\frac{\langle\alpha_{ZZ}\rangle_0}{4\pi\varepsilon_0}$	$\frac{\langle\mu_X\alpha_{YZ}\rangle_0}{4\pi\varepsilon_0}$	
	α	S		(10^{-3} nm^3)		($10^{-4}e$ nm^4)	ec (10^{-10} m/V)
A1	C_1	C_{2v}	23.67	23.67	30.78	−0.15	0.80
A2	C_{2v}	C_1	17.26	17.26	24.21	0.36	−1.97
A3	C_1	C_1	22.97	22.97	32.18	0.29	−1.20

$U_0(\Omega|X^M) = \xi k_B T \int_S dS\, P_2(\hat{\mathbf{n}}\cdot\hat{\mathbf{s}})$, where the integral is over the molecular surface (S). Here P_2 is the second Legendre polynomial, $\hat{\mathbf{s}}$ is a unit vector normal to the surface element dS and $\hat{\mathbf{n}}$ is a unit vector parallel to the director at the same position, and the parameter ξ represents the orienting strength in the nematic phase, which is a function of temperature. The dependence upon the molecular coordinate derives from the position dependence of the director, which in the LOC frame is expressed as $\hat{\mathbf{n}} = (0, -\sin 2\pi X/P, \cos 2\pi X/P)$, where P is the pitch of the twist distortion. The case of uniform director is recovered for $P \to \infty$, so that $\hat{\mathbf{n}} = (0,0,1)$.

Tables I and II report the results of calculations for the model structures shown in Fig. 1: In A two rings are coplanar and the third ring is perpendicular to them, whereas B is fully planar. All bond lengths are equal to 0.14 nm, the electric dipole moment is equal to 5.8 D, and different choices were considered for the van der Waals radii and bare polarizabilities of atoms. The values $r_{\mathrm{vdW}} = 0.2$ nm and $\alpha/4\pi\varepsilon_0 = 1.5 \times 10^{-3}$ nm^3 were generally assumed, but case by case also different choices were taken for starred atoms: $\alpha/4\pi\varepsilon_0 = 3 \times 10^{-3}$ nm^3 (A1, B1); $r_{\mathrm{vdW}} = 0.3$ nm (A2, B2); $\alpha/4\pi\varepsilon_0 = 3 \times 10^{-3}$ nm^3 and $r_{\mathrm{vdW}} = 0.3$ nm (A3, B3). The orienting strength $\xi = 3.5$ nm^{-2} and the temperature $T = 300$ K were assumed in all calculations.

The data reported in Table I were obtained for uniform director (I). In the former case, (A1), only the molecular polarizability is chiral and tilt of the optical axis occurs because the more polarizable parts of the molecule preferentially lie on one side of the XZ plane, due to the bias imposed on molecular rotations by the dipole-electric field coupling. Therefore the EC effect does not involve a net change of the average orientation of the long molecular axis. On the other hand, case (A2) provides an example of EC effect caused by the change of molecular orientation. In this case the molecular surface is chiral, which within the molecular field model used here implies that the orientational distribution function of the molecule is chiral. This means that the main ordering axis in the molecule does not coincide with the long molecular axis. Thus, the latter is preferentially tilted with respect to the local director (Z axis of the local frame); for $E = 0$ left-handed and right-handed tilts are equivalent, but the coupling with the electric field introduces a bias. The twofold origin of the EC effect in chiral nematics was envisaged in the earlier literature [6], in contrast to the mechanism accepted for chiral smectic A samples, which implies the physical tilt of molecules. In the last case in Table I, (A3), both the molecular shape and polarizability are chiral and the net EC effect is nearly the sum of the two individual contributions. For the mirror images of (A1)–(A3) the opposite of the EC coefficients reported in Table I are predicted, i.e., tilts of the optical axis in the opposite sense. Although the model molecules assumed here do not correspond to any real chemical structure, all the molecular properties (polarizability, electric dipole moment, size, and shape) take realistic values and the predicted EC coefficients are comparable to experimental data reported in the literature [3–5].

Table II reports the results obtained in the presence of a twisted director with pitch $P = 10$ nm. Symmetry considerations indicate that in this configuration the EC effect can be observed also for achiral molecules belonging to C_{2v} and C_h point groups [13]. This is illustrated by cases (B1)–(B3) which again show that the polarizability and the orientational distribution give independent contributions to the EC effect. Table II also shows the results obtained for a chiral molecule, (A3), and its mirror image, (A3*): Different EC coefficients are predicted for the two enantiomorphic structures, which do not sum up to zero. This implies that a racemic mixture, i.e., a mixture containing an equal amount of chiral species and their mirror images, can exhibit the EC effect. The results reported in Table II, showing that the EC

TABLE II. Results for A and B structures in the twisted nematic configuration with pitch $P = 10$ nm. Point symmetry of the molecular polarizability (α) and of the molecular surface (S); average values in Eq. (10); EC coefficient. The whole molecular symmetry is C_{2v} for B and C_1 for A cases.

	Symm.		$\frac{\langle\alpha_{XX}\rangle_0}{4\pi\varepsilon_0}$	$\frac{\langle\alpha_{YY}\rangle_0}{4\pi\varepsilon_0}$	$\frac{\langle\alpha_{ZZ}\rangle_0}{4\pi\varepsilon_0}$	$\frac{\langle\mu_X\alpha_{YZ}\rangle_0}{4\pi\varepsilon_0}$	
	α	S		(10^{-3} nm^3)		($10^{-4}e$ nm^4)	ec (10^{-10} m/V)
B1	C_{2v}	D_{2h}	23.30	23.59	31.74	0.10	−0.47
B2	D_{2h}	C_{2v}	17.04	17.24	24.65	−0.21	1.08
B3	C_{2v}	C_{2v}	22.62	22.90	33.10	−0.16	0.60
A3	C_1	C_1	23.02	23.07	32.04	0.16	−0.68
A3*	C_1	C_1	22.98	23.11	32.03	−0.40	1.70

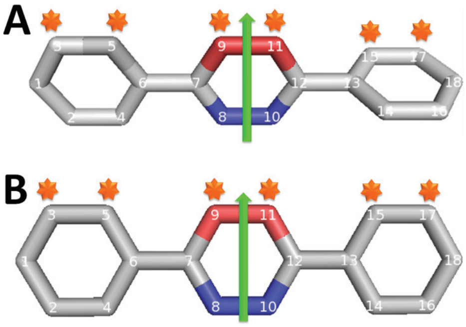

FIG. 1. (Color online) Molecular models used for calculations. Arrows indicate the electric dipole moment.

effect in a twisted director configuration does not require molecular chirality, are especially interesting in relation to recent findings in nematic twist cells filled with an achiral nematic liquid crystal [8]. The EC coefficients calculated for the twisted director configuration depend on the helical pitch: They increase as the pitch decreases, being approximately inversely proportional to it. This can be demonstrated using the approximation $\hat{\mathbf{n}} \approx (0, -2\pi X/P, 1)$, valid for pitch P much longer than the molecular size [14]. EC effects comparable in magnitude to those observed experimentally [8] are predicted for pitch values smaller than some hundreds of nanometers; such values are orders of magnitude lower than the typical pitch of the helical distortions imposed on cells. However, there are strong indications that the EC effect measured in nematic twist cells is determined by highly distorted regions near the cell surfaces, with a very tight effective helical pitch [9].

In conclusion, we have analyzed the microscopic basis of the EC effect in nematic liquid crystals and we have clarified the role played by chirality. We have derived molecular expressions for the EC coefficient and a computational methodology that allows its calculations on the basis of the molecular structure. In relation to the interpretation of the experiments proposed in Ref. [8], we have demonstrated that conformational deracemization is not the only explanation, because (i) even achiral molecules can produce an EC effect in nematic twist cells and (ii) the individual EC contributions of two enantiomorphic conformations are not the opposite of each other. The latter implies that even a racemic mixture of conformations can give rise to an EC effect. Here the general features of the EC effect have been investigated using simplified molecular models, but the proposed methodology is suitable to be used for realistic molecular representations. This can be helpful for a more detailed analysis of experiments and to explore whether the EC tilt can be increased by proper molecular design.

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

[2] Liquid crystals are denoted as chiral or achiral, according to whether they are made of chiral or achiral molecules. An achiral molecule can have chiral conformations, but these occur as enantiomorphic pairs, which are the mirror image of each other and are present in equal amounts (i.e., a racemic mixture of conformations).

[3] Z. Li, R. G. Petschek, and C. Rosenblatt, Phys. Rev. Lett. **62**, 796 (1989).

[4] L. Komitov, S. T. Lagerwall, B. Stebler, G. Andersson, and K. Flatischler, Ferroelectrics **114**, 167 (1991).

[5] J. Etxebarria and J. Zubia, Phys. Rev. A **44**, 6626 (1991).

[6] Z. Li, G. A. DiLisi, R. G. Petschek, and C. Rosenblatt, Phys. Rev. A **41**, 1997 (1990).

[7] N. Kapernaum, D. M. Walba, E. Korblova, C. Zhu, C. Jones, Y. Shen, N. A. Clark, and F. Giesselmann, ChemPhysChem **10**, 890 (2009).

[8] R. Basu, J. S. Pendery, R. G. Petschek, R. P. Lemieux, and C. Rosenblatt, Phys. Rev. Lett. **107**, 237804 (2011).

[9] T.-C. Lin, I. R. Nemitz, J. S. Pendery, C. P. J. Schubert, R. P. Lemieux, and C. Rosenblatt, Appl. Phys. Lett. **102**, 134101 (2013).

[10] J. Xu, R. L. B. Selinger, J. V. Selinger, B. R. Ratna, and R. Shashidhar, Phys. Rev. E **60**, 5584 (1999).

[11] B. T. Thole, Chem. Phys. **59**, 341 (1981).

[12] A. Ferrarini, G. J. Moro, P. L. Nordio, and G. R. Luckhurst, Mol. Phys. **77**, 1 (1992).

[13] D. Merlet, J. W. Emsley, P. Lesot, and J. Courtieu, J. Chem. Phys. **111**, 6890 (1999).

[14] A. Ferrarini, G. J. Moro, and P. L. Nordio, Mol. Phys. **87**, 485 (1996).