Flexoelectrically Driven Electroclinic Effect in the Twist-Bend Nematic Phase of Achiral Molecules with Bent Shapes

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We extend the twist-bend nematic (N_{TB}) model to describe the electro-optics of this novel phase. We predict an electroclinic effect (ECE) subject to a dc electric field **E** applied perpendicular to the helix axis or wave vector **q**, with rotation of the N_{TB} optic axis around **E**. This linear effect, with its flexoelectric origin, is a close analog to the electro-optic effects observed for chiral liquid crystals. However, in nematics composed of achiral molecules having a bent shape, it is the electro-optic signature of the N_{TB} phase. We test our model experimentally in the low-temperature nematic phase of the odd liquid crystal dimer, CB7CB, with its molecules having, on average, a bent shape. The ECE measurements confirm the previously proposed twist-bend nematic structure of this phase, with its broken chiral symmetry, extremely short (<10 nm) doubly degenerate pitch and ultrafast, submicrosecond response times.

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Chirality plays an important role in physics, chemistry, and biology, and especially for soft matter systems such as biological tissues, polymers, and liquid crystals (LC). This lack of mirror symmetry often leads to qualitative new effects, impossible in achiral systems. For example, chiral nematics (N^*) and chiral smectics (SmA^*, SmC^*) exhibit strong polar electro-optic effects [1–3], which are symmetry forbidden in their achiral analogs (N, SmA, and SmC). Normally, the chirality of LC phases results from their chiral building blocks, typically molecules. Calamitic molecules tend to orient along an average direction, the nematic director, **n**. For achiral molecules, the equilibrium state corresponds to uniform **n**, $\nabla \mathbf{n} = 0$. Chiral molecules distort the director field, inducing a twist distortion, $\mathbf{n} \cdot (\nabla \times \mathbf{n}) \neq 0$. The phase then has a chiral superstructure, with **n** arranged on a helix (N^*), or on a conical helix (SmC^*), enhancing some of the chirality-dependent properties, e.g., resulting in a huge optical activity in both N^* and SmC^*.

Macroscopic chirality can also be created with achiral molecules, by surface alignment [4], or due to symmetry breaking at an interface [5]. Bulk chiral-symmetry breaking is also possible with achiral molecules of low symmetry, as has been discovered by the Takezoe Group [6,7] for bent-core smectics. In these phases, the coupling between the orientational, translational, and polar order results in a spontaneous twist, with doubly degenerate handedness, and spectacular electric properties [8].

Twelve years ago, Dozov [9] proposed that chiral symmetry breaking might also take place in the nematic phase of achiral, bent-shaped molecules. Independently, Memmer [10] arrived at the same conclusion by Monte Carlo simulations of idealized bent-core molecules. Indeed, such molecules induce a bend distortion of the nematic director. Formally, this is equivalent to a decrease of the bend elastic constant, K_3. If K_3 becomes negative, as expected for highly bent molecules [11], the usual uniform nematic is destabilized with respect to periodically distorted states. In one of the predicted states [9], the twist-bend nematic phase N_{TB}, the directors form a conical helix with a doubly degenerate handedness. Indeed, the chiral symmetry is spontaneously broken in the N_{TB} phase, even though there is no positional order as in bent-core smectics.

Recently, several optical experiments on achiral bent-shaped mesogens [12–17] reported nematic phases with doubly degenerate chirality, predicted for N_{TB}. However, the unambiguous identification of this phase remains difficult, the observed textures being much more complex than those predicted.

Here we extend the original macroscopic model to describe the electro-optic behavior of the N_{TB} phase. In addition to the trivial helical reorientation, we predict an electroclinic effect (ECE): a dc field **E** applied perpendicular to the helix axis, induces a rotation of the N_{TB} optic axis **N** around **E**. This linear electro-optic effect of flexoelectric origin is a close analog to both the ECE in SmA^* [2] and the flexoelectric effect [3] in N^*. However, if observed in nematics composed of achiral molecules, the ECE is the signature of the N_{TB} phase. To test our model, we study the electric-field behavior of the low-temperature nematic phase of the odd LC dimer, CB7CB. We observe the predicted ECE, consistent with the N_{TB} nature of the phase, with an extremely short (<10 nm) and doubly degenerate pitch.

We consider the elastic energy density of a uniaxial nematic, composed of achiral bent-shaped molecules, whose shape leads to a negative value of the bend elastic constant. For simplicity, we assume a constant nematic order parameter and a 1D distortion of the director, $\mathbf{n} = \mathbf{n}(z)$. The expansion of f_{dist} in a series of spatial derivatives of the director gives [9]

$$f_{\rm dist} = \tfrac{1}{2}[K_1\mathbf{s}^2 + K_2 t^2 + K_3\mathbf{b}^2] + f_4, \quad (1)$$

where K_i are the Frank-Oseen elastic constants [4] for splay $\mathbf{s} = \mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n})$, twist $t = \mathbf{n}\cdot(\boldsymbol{\nabla}\times\mathbf{n})$ and bend $\mathbf{b} = \mathbf{n}\times(\boldsymbol{\nabla}\times\mathbf{n})$. The fourth-order elastic term f_4 [see Eq. (3) of Ref. [9]], contains scalar invariants of order $\boldsymbol{\nabla}^4$, ensuring the convergence of the series when $K_3 < 0$. As shown previously, if $K_3 < 0$ and $K_2 < K_1/2$, $f_{\rm dist}$ is minimized by a twist-bend distortion, $\mathbf{n}(z) = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, with constant θ and $\varphi = qz$, a periodic rotation of $\mathbf{n}$ on a cone (see Fig. 1). Up to the lowest-order terms in q^2 and $\sin^2\theta$ we obtain

$$f_{\rm dist} = \tfrac{1}{2}[K_2 q^2\sin^4\theta + K_3 q^2\sin^2\theta + Cq^4\sin^2\theta], \quad (2)$$

where C is a fourth-order elastic constant [9]. Minimization of Eq. (2) gives the ground state of the $N_{\rm TB}$ phase, with a spontaneous tilt θ_s of the director defined by $\sin^2\theta_s = -K_3/(3K_2)$ and spontaneous wave vector $q_s^2 = -K_3/(3C)$. Both $\sin\theta_s$ and q_s might be considered as order parameters describing the $N_{\rm TB}$-N phase transition. However, the sign of $\sin\theta_s$ has no physical meaning; by symmetry, its inversion is equivalent to a half-period translation along the $\mathbf{z}$ axis. In contrast, the sign of q_s defines the helix handedness: the states q_s and $-q_s$ are physically distinct, although they are degenerate.

Its periodic structure makes the $N_{\rm TB}$ phase similar to other periodic LC states. The analogy with N^* is quite obvious, both states being helically twisted. However, the $N_{\rm TB}$ helix is conical, with $\theta_s < \pi/2$, generating a spontaneous bend, $\mathbf{b_s} = q_s\sin\theta_s\cos\theta_s[\sin(q_s z), -\cos(q_s z), 0]$, which is absent for N^*. This also implies a spontaneous

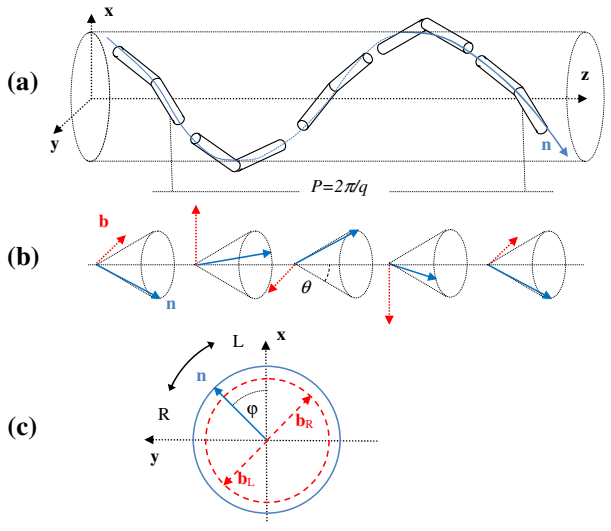

FIG. 1 (color online). Spontaneous distortion of the $N_{\rm TB}$ phase: (a) Spatial arrangement of the bent molecules which are locally intercalated. (b) Director $\mathbf{n}$ (blue) and spontaneous bend $\mathbf{b}$ (red) in the conical twist-bend helix. (c) Trajectories of the $\mathbf{n}$ and $\mathbf{b}$ projections on the $\mathbf{xy}$ plane. The arrows show the rotation direction for right-(R) and left-(L) handed helices. The sign of $\mathbf{b}$ is reversed with the handedness.

flexoelectric polarization for $N_{\rm TB}$, $\mathbf{P}_{\rm fl} = -e_3\mathbf{b_s}$, rotating on a helix, with $\mathbf{P}_{\rm fl}$ remaining everywhere perpendicular to both the director and the helix axis. This arrangement is similar to the ferroelectric and the flexoelectric polarizations of the SmC^* phase, where again the helix is conical.

A more subtle analogy exists between the $N_{\rm TB}$ and the SmA^* phases, both of them being chiral and periodic (density wave for SmA^* and $\mathbf{n}$ distortion wave for $N_{\rm TB}$). In SmA^*, the optic axis $\mathbf{N}$ of the phase is parallel to $\mathbf{n}$ and to the wave vector $\mathbf{q}$ of the smectic layers. However, $\mathbf{N}$ might deviate from $\mathbf{q}$ under an applied torque. In the $N_{\rm TB}$ phase the pitch is expected to be short [9], $P_s = 2\pi/q_s \ll 100$ nm, and the optic axis $\mathbf{N}$ is along the macroscopic average of the director $\mathbf{n}$, i.e., along the helix axis of the twist-bend cone. Although $\mathbf{N} \parallel \mathbf{q}$ in the ground state, subject to external torques $\mathbf{N}$ might tilt away from $\mathbf{q}$, for only a moderate energy cost.

The 1D periodicity of the $N_{\rm TB}$ phase implies $curl\ \mathbf{q} = \mathbf{0}$, as for the smectic and N^* phases. By analogy with these phases, focal conic textures should be found for the $N_{\rm TB}$ phase. Indeed, such textures have been reported [12,18] and are observed in the present work [19].

On application of $\mathbf{E}$, the energy density of the $N_{\rm TB}$ phase becomes

$$f_{\rm TB} = f_{\rm dist} - \tfrac{1}{2}\varepsilon_0\Delta\varepsilon(\mathbf{E}\cdot\mathbf{n})^2 - (e_1\mathbf{s} - e_3\mathbf{b})\cdot\mathbf{E}, \quad (3)$$

where the two electric terms are dielectric and flexoelectric, respectively. Here, $\Delta\varepsilon$ is the dielectric anisotropy (in the director frame) and e_1 and e_3 are the splay and bend flexoelectric coefficients (here we follow Meyer's notation [20], although subsequently notation $e_s = e_1$ and $e_b = -e_3$ has been used [3]).

Here we are interested in electric field effects related to the broken chiral symmetry of the $N_{\rm TB}$ phase and only the flexoelectric term is sensitive to the sign of q_s. To favor the flexoelectric coupling, we choose $\mathbf{E} \perp \mathbf{q}$ (see Fig. 2). However, at a strong enough field the dielectric term, quadratic in E, necessarily dominates the linear flexoelectric one. A large average dielectric torque is applied to the optic axis $\mathbf{N}$ and transmitted to $\mathbf{q}$ (since $\mathbf{N} \parallel \mathbf{q}$ minimizes the $N_{\rm TB}$ free energy). This torque aligns $\mathbf{q}$ (and the entire $N_{\rm TB}$ structure) along $\mathbf{E}$ (for $\Delta\varepsilon > 0$) or stabilizes the initial $\mathbf{q} \perp \mathbf{E}$ orientation (for $\Delta\varepsilon < 0$). This effect, common for all LC phases, might mask the subtler polar effects that we are interested in here. However, although a uniform rotation of $\mathbf{q}$ strictly costs no energy, it does require a large variation of the twist-bend phase φ everywhere, and so a huge energy dissipation. In practice, the $\mathbf{q}$ rotation is possible only by nucleation and propagation of defects, dislocations of the φ field. This slow process can be avoided if the field is applied in short pulses.

At fixed $\mathbf{q}$, the residual dielectric effect is a minor distortion of the director inside each period (see Fig. 2). The optic axis $\mathbf{N}$ is not rotated in this case and the only optical effect is a small variation of the birefringence

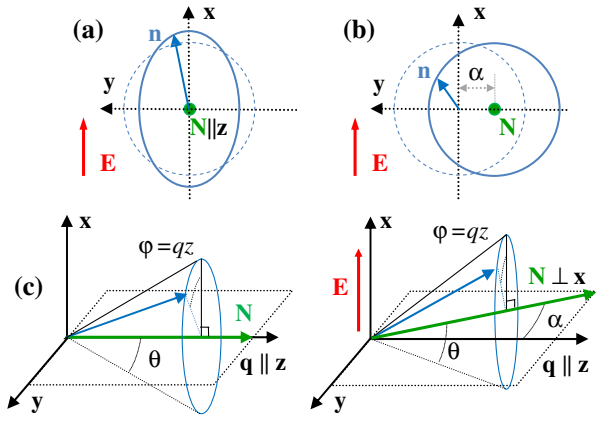

FIG. 2 (color online). N_{TB} phase subject to an electric field $\mathbf{E}$ at a fixed wave vector $\mathbf{q}$: (a) Dielectric distortion of the $\mathbf{n}$ trajectory ($\Delta\varepsilon > 0$ is assumed). (b) Electroclinic effect due to the flexoelectric coupling. The director $\mathbf{n}(z)$ and the optic axis $\mathbf{N}$ (in green) are uniformly rotated around $\mathbf{E}$ with respect to the $E = 0$ case (dashed line). (c) 3D geometry of the flexoelectric tilt of the twist-bend cone and the optic axis.

(averaged over one N_{TB} period). By analogy with N^*, up to the critical field for complete unwinding of the helix [4], namely, $E_c \approx q_s\sqrt{K_2/(\varepsilon_0\Delta\varepsilon)}$, the distortion is weak enough [21] to be neglected [22].

We now consider the flexoelectric contribution, supposing that a field $E \ll E_c$ is applied in short ($\ll 1$ ms) pulses, enabling us to neglect completely the dielectric effects. In the ground-state, with $\mathbf{N} \parallel \mathbf{q}$, the flexoelectric term in Eq. (3) integrates to zero over one N_{TB} period and can be omitted. In fact, the energy gain in the regions where $\mathbf{P}_{fl} \cdot \mathbf{E} > 0$ is exactly compensated by the energy loss in the other half-period, where $\mathbf{P}_{fl} \cdot \mathbf{E} < 0$. However, if $\mathbf{N}$ tilts away from $\mathbf{q}$ in the $\mathbf{yz}$ plane [see Fig. 2(b)], the compensation is no longer exact, showing that a flexoelectric torque is applied to $\mathbf{N}$. For the periodic N_{TB} structure, $\mathbf{n_0}(z) = \mathbf{n_0}(z + 2\pi/q_s)$, the most general flexoelectric distortion is a uniform rotation of $\mathbf{n}$ around $\mathbf{E}$ at an angle α [19], i.e., a tilt of the N_{TB} cone and the optic axis $\mathbf{N}$ in the $\mathbf{q_s} \times \mathbf{E}$ direction. Up to small terms $O(\alpha^3)$, the total energy, averaged over one N_{TB} period, becomes [19]

$$\langle f_{TB}\rangle = f_{TB}^0 + \frac{1}{2}K_N\tan^2\alpha - G_eE\tan\alpha, \qquad (4)$$

where $f_{TB}^0 = (1/2)\{K_2q_s^2\sin^4\theta_s + K_3q_s^2\sin^2\theta_s + Cq_s^4\sin^2\theta_s\}$ is the free energy density at $\alpha = 0$, $K_N = (1/2) \times (K_1 + K_2)q_s^2\sin^2\theta_s$ is the elastic constant for tilting $\mathbf{N}$ with respect to $\mathbf{q}$ (N.B. higher order terms in $\sin^2\theta_s \ll 1$ are neglected), and $G_e = (1/2)(e_1 - e_3)q_s\sin^2\theta_s$ is an electroclinic coefficient, describing the gain in flexoelectric energy resulting from a tilt of $\mathbf{N}$.

Minimizing the energy with respect to α gives

$$\tan\alpha(E) = \frac{G_e}{K_N}E = \frac{(e_1 - e_3)E}{q_s(K_1 + K_2)}. \qquad (5)$$

This result describes a linear electro-optic effect in the N_{TB} phase, with the field-induced rotation of the optic axis, $\mathbf{N}$, in a plane perpendicular to $\mathbf{E}$. These features suggest that it is a close analog to well-known effects in other chiral mesophases, namely, the electroclinic (ECE) effect in SmA^* [2] and the flexoelectric effect [3] in N^*. The analogy with the N^* effect [3] is even closer, both effects being of flexoelectric origin and occurring with a helix distortion. The only difference with the N^* case is the effective elastic constant $(K_1 + K_2)$ in Eq. (5), instead of $(K_1 + K_3)$; see Ref. [23]. However, in the N_{TB} phase the electroclinic effect should also be observed with achiral mesogens, with both signs of the tilt in different regions of the same sample, instead of just a single sign as for the SmA^* and N^* cases (defined by the molecular chirality). The double degeneracy of the ECE tilt then provides the electro-optic signature of the N_{TB} phase.

By analogy with N^*, we expect to find short ECE relaxation times in the N_{TB} phase. Suppose that the field is switched off at time $t = 0$, with $\alpha(t = 0)$ given by Eq. (5). The elastic torque applied to $\mathbf{N}$ is $\Gamma_N = -K_N\alpha(t)$ and the viscous torque, for uniform rotation of $\mathbf{n}$ back to equilibrium, is $\Gamma_v = -\gamma_1 d\alpha(t)/dt$, where γ_1 is the nematic rotational viscosity coefficient. The solution for small $\alpha(t)$ is $\alpha(t) = \alpha(0)\exp(-t/\tau_{off})$, where

$$\tau_{off} = \frac{\gamma_1}{K_N} = \frac{2\gamma_1}{(K_1 + K_2)q_s^2\sin^2\theta_s}. \qquad (6)$$

A similar result is obtained when the field is switched on, with $\tau_{on} = \tau_{off}$.

Most probably, the ECE has already been observed recently in the N_{TB} phase by Panov *et al.* [17,24]. They report, for a LC dimer, a fast, linear electro-optic effect with a doubly degenerate sign. However, the striped textures observed by Panov *et al.* [17] are complex, with at least distortions in two dimensions, difficult to interpret with our simple 1D model. To test our model more directly, we have studied the electro-optics of CB7CB with its average bent shape. This compound exhibits a phase transition from the standard nematic phase, N, to another, low-temperature nematic phase. A number of experimental techniques [12] provide strong evidence that this is the twist-bend nematic phase, N_{TB}.

A thin (1.6 μm) cell with planar alignment along the $\mathbf{z}$ axis (in-plane) was filled with CB7CB, placed on a heating stage and observed under a polarizing microscope. Using indium tin oxide (ITO) electrodes, short pulses of a dc electric field were applied along the $\mathbf{x}$ axis, parallel to the cell normal and the observation direction. The experimental setup and optical geometry were chosen to provide very sensitive, linear variation of the transmitted intensity with α [19].

In the N phase, above $T_{N_{TB}N}$ at 101.8 °C, we observe a good planar alignment with $\mathbf{n} \parallel \mathbf{z}$ and the usual nematic electro-optic effects, e.g., Fréedericksz transition [25] and Bobylev-Pikin [26,27] instabilities. At $T_{N_{TB}N}$ we observe

thin stripes of the N_{TB} phase, growing along the **y** axis. Each stripe is quite uniform, but under slightly uncrossed polarizers two kinds of stripe are identified, consistent with the double degeneracy expected in the N_{TB} phase. When two stripes are in contact, they reorganize until the cell is filled with large bands, single-domains with quasiuniform orientation, showing alternation of the contrast between uncrossed polarizers (see Fig. 3). All of the electro-optic measurements were made in a small area localized inside a single domain. Keeping the pulses short enough (≤ 100 μs) and at a low repetition rate (≤ 10 Hz) we inhibit the unwanted dielectric effects, e.g., defect-mediated reorientation of the helix.

In Fig. 3(c) we show the typical tilt response to a square voltage pulse $U(t)$. The sign of α changes with the sign of U and from one domain to the next; in addition, its amplitude is proportional to U. Both relaxation times, τ_{on} and τ_{off}, are very fast (~ 0.7 μs), close to our experimental time-resolution limit. In Fig. 3(d) we show the tilt of the optic axis induced by triangular pulses in two adjacent domains, confirming the linear $\alpha(E)$ response and the sign inversion of α between the different domains. The same behavior is observed down to 50 °C in the highly supercooled N_{TB} phase, with decreasing amplitude of $\alpha(T)$ at a fixed voltage [see Fig. 3(e)].

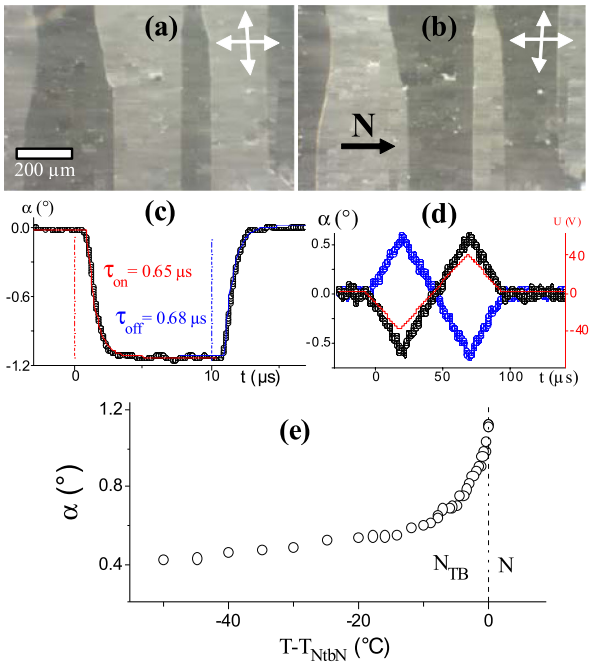

FIG. 3 (color online). Electroclinic effect in the low-temperature nematic phase of CB7CB: (a),(b) Single domains observed with slightly uncrossed polarizers (white arrows); (c) Tilt angle $\alpha(t)$ determined with short square pulses ($\tau = 10$ μs, $U = 40$ V), shown at the start and end of the pulse with dashed lines. The relaxation times were obtained from an exponential fit (red and blue lines) of the data. (d) Tilt angles $\alpha(t)$ measured in two single domains with opposite handedness (black and blue data points) with triangular voltage pulses (red line), and (e) temperature dependence of the ECE tilt angle ($U = 40$ V square pulses, $d = 1.6$ μm).

All of these features agree well with the predicted ECE behavior, that is a linear electro-optic response of a chiral phase, with doubly degenerate handedness. This result strongly and directly suggests that the low-temperature nematic phase of CB7CB is an N_{TB} phase, as proposed previously [12]. Moreover, from Eqs. (5) and (6) we can estimate q_s and $\sin\theta_s$, the order parameters for the N_{TB} phase. In this estimation we use the values $K_1 = 5$ pN and $\gamma_1 = 0.075$ Pa s measured [19] at $T_{N_{TB}N}$ in the N phase, and $K_2 \approx 2$ pN (estimated from the inequality $K_2 < K_1/2$ [9] for the existence of N_{TB}), supposing that they are continuous at the transition. In the absence of a reliable measurement for $(e_1 - e_3)$ in the N phase, we take $(e_1 - e_3) \approx 5$ pC/m [19], close to the values reported for the nematic monomers 8CB [28], 7CB [23], and 7OCB [29]. From $\alpha = 0.0194$ rad ($T = T_{N_{TB}N}$, $U = 25$ MV/m), we obtain $q_s = 0.9$ nm^{-1}, giving an extremely short pitch for the N_{TB} phase, of 7 nm. Far below $T_{N_{TB}N}$, the pitch decreases further by a factor of ~ 2. From the measured value of the relaxation time, τ_{off}, of about 0.7 μs at $T_{N_{TB}N}$, we obtain $\theta_s(T_{N_{TB}N}) \approx 11°$. Although these estimates of $q_s(T_{N_{TB}N})$ and $\theta_s(T_{N_{TB}N})$ will vary with the choice of the coefficient $(e_1 - e_3)$, they are clearly not vanishingly small, indicating that the N_{TB}-N phase transition in CB7CB is first order, as already reported [12], rather than of second order, as has been predicted [9]. Further improvement of the model, taking into account the temperature variation of the orientational order parameter and possibly the flexibility of the CB7CB dimer, is needed to resolve this discrepancy [19].

In conclusion, with a macroscopic model we have shown that an electroclinic effect of flexoelectric origin should exist in the N_{TB} phase composed of bent-shaped molecules. On application of an electric field **E**, perpendicular to the helix axis, the optic axis **N** of the phase rotates around **E** through an angle α proportional to E. This effect, with doubly degenerate sign, is related to chiral symmetry breaking of the phase, and provides an electro-optic signature for the N_{TB} phase. We have observed experimentally the ECE in the low-temperature nematic phase of CB7CB with its bent average shape, consistent with a twist-bend structure for this phase. From the measured small amplitude of α and its submicrosecond response times we estimate that the N_{TB} pitch is extremely short, <10 nm. We are aware that this fast response makes the N_{TB} phase promising for potential applications.

Note added.—We recently viewed a paper by Chen *et al.* [30] which, based on freeze-fracture transmission electron microscopy, confirms the structure of the twist-bend nematic phase for CB7CB [12] and found values of the pitch and the director cone angle consistent with the results reported here but determined with a totally different technique.

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