

Induced and spontaneous deracemization in bent-core liquid crystal phases and in other phases doped with bent-core molecules

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Recently discovered chiral properties of several bent-core smectic liquid crystal phases are summarized and discussed in detail under the assumption that typical bent-core molecules may exist in chiral conformational states and are achiral only on average. Results of atomistic computer simulations are presented which indicate the existence of strongly chiral conformational states for typical bent-core mesogens. A theory is developed which describes a possible shift of equilibrium between left- and right-handed conformations in a macroscopically chiral phase. The theory describes a chirality induction in the $B2$ bent-core phase and a reduction of the helical pitch in cholesteric and chiral SmC^* phases doped with bent-core molecules. Finally, the possibility of spontaneous deracemization in bent-core smectic phases is discussed in detail.

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I. INTRODUCTION

Chirality is a subject of great interest to liquid crystal (LC) scientists [1]. In addition to the conventional cholesteric phase, a variety of chiral phases such as the blue phases (BP's) [2,3] including the smectic BP's [4–6], chiral smectic phases such as SmC^* [7] and SmC_A^* [8], and the twist grain boundary (TGB) [9] phases have continuously been the subject of significant interest. The discovery and study of these phases has led to new breakthroughs in science and frequently to new applications in technological devices. Further interesting topics in chirality in LC's have been brought about by the discovery of bent-core liquid crystals composed of achiral bow-shaped molecules [10]. In these phases there exists a spontaneous polar order of short molecular axes determined mainly by the close packing of bent-core molecules in a smectic layer [10]. If the long molecular axes are tilted with respect to the smectic layer normal, the resulting structure may be macroscopically chiral if the spontaneous polarization is normal to the tilt plane, as in the $B2$ bent-core phase [11].

In addition to the polar order and the macroscopically chiral structure of the $B2$ phase, a variety of interesting chirality-related phenomena have been discovered and have become increasingly important. Some of these are quite unusual. For instance, there are experimental indications that achiral bent-core molecules may exist in chiral conforma-

tional states [12]. In these cases the molecules can be considered as achiral only on average. It has been proposed that the presence of a macroscopically chiral structure may induce a nonzero average enantiomeric excess (induced chirality) which can change the properties of the system. Moreover, under favorable conditions an enantiomeric excess may appear spontaneously, in a self-consistent way (spontaneous deracemization), and as a result chiral domains are likely to be formed. It has also been found experimentally that doping chiral host LC's, such as cholesteric, SmC^* , and SmC_A^* phases with bent-core molecules enhances the chirality of the systems, which is another example of induced chirality [13,14]. In this paper we summarize some of the recently discovered chiral properties of bent-core smectic phases and present results of atomistic computer simulations which indicate the existence of strongly chiral conformational states. We then develop a semiphenomenological theory to explain chiral induction effects and other unusual phenomena observed in bent-core LC's.

II. EXPERIMENTAL OBSERVATIONS

At least seven phases, $B1$ – $B7$, have been identified in bent-core LC's [15]. The phase most extensively studied is the $B2$ phase, where bent-core molecules tilt from the smectic layer normal. According to the interlayer correlation of clinicity and polarity, $B2$ phase structures are classified into four types: $SmC_{S,A}P_{A,F}^*$ [11], where the subscript S or A specifies synclinic or anticlinic and F or A specifies ferroelectric or antiferroelectric order. Chirality of bent-core LC's was pointed out to appear in the $B2$ phase, where the tilt of

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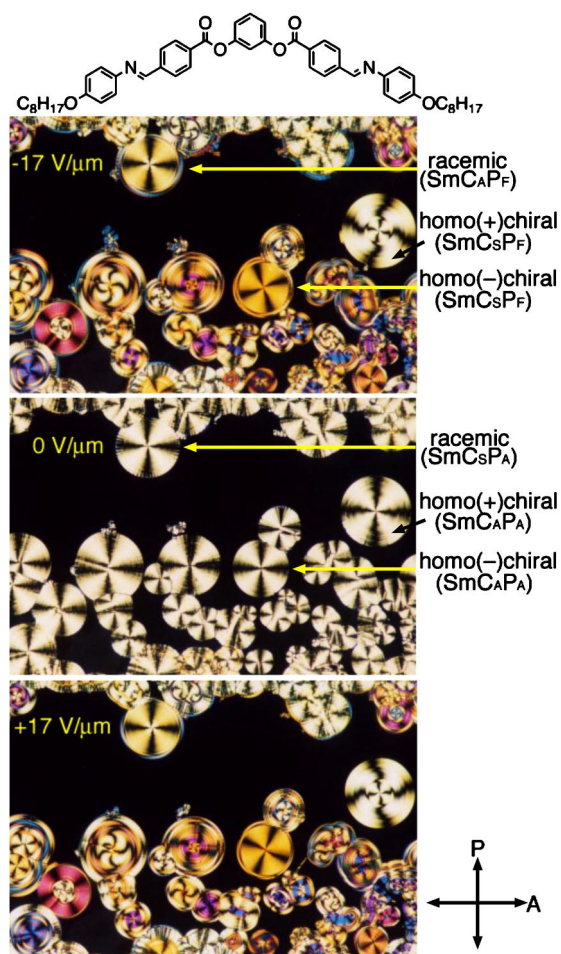


FIG. 1. (Color online) Microphotographs of P-8-O-PIMB (top) in the B_2 phase in the presence and absence of an electric field. Several domains with opposite chirality can be recognized as indicated.

the bent-core molecules breaks the symmetry of the system and induces layer chirality [11]. Here molecules are not necessarily chiral in their conformations. Thus $\text{SmC}_A P_A^*$ and $\text{SmC}_S P_F^*$ have structures with uniform chirality (homochiral layer structure), whereas $\text{SmC}_S P_A^*$ and $\text{SmC}_A P_F^*$ have structures with alternating layer chirality (racemic layer structure). In unperturbed cells, $\text{SmC}_S P_A^*$, with a racemic structure, usually emerges as the most stable state in the B_2 phase because of interlayer steric interactions [16]. The application of a rectangular field sometimes helps to nucleate the $\text{SmC}_A P_A^*$ structure [17,18]. One of the striking features of this state is the occurrence of two homochiral layers [17,18]. The coexistence of two homochiral layers (or domains) is a consequence of spontaneous chiral segregation. We can observe both homochiral domains, that exhibit electro-optic switching in opposite ways. Figure 1 shows microphotographs of the B_2 phase of one of the conventional bent-core LC's, 1,4-phenylene bis[4-(4-8-alkoxyphenyliminomethyl) benzoate](P-8-O-PIMB) (see top). In the absence of an electric field, the extinction direction is parallel to the layer normal. The rotation of the extinction brushes to the right and left is observed in two different circular domains, with positive and negative chiralities, respectively.

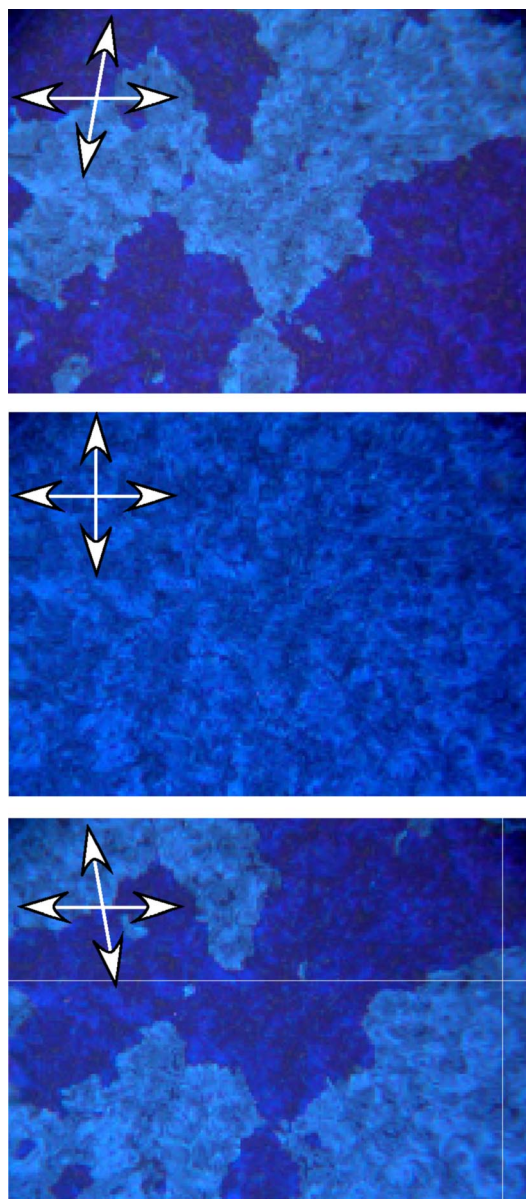


FIG. 2. (Color online) Microphotographs of P-8-O-PIMB in the B_4 phase. Two chiral domains can be recognized as bright and dark views by decrossing an analyzer clockwise and counterclockwise.

Apart from chirality due to the tilt of bent-shaped molecules, spontaneous chiral segregation occurs, even in the nontilted B_4 phase, as shown in Fig. 2. Different chirality can be recognized by decrossing an analyzer to a polarizer. Similar observations have been made in many phases in bent-core mesogens [19–22]. Under crossed polarizers, two chiral domains cannot be distinguished. By decrossing the polarizers, however, two chiral domains exhibit either a dark or bright view and the brightness of the views interchanges by decrossing the analyzer to the opposite direction. In the B_4 phase, chirality originates from chiral molecular conformations, since no layer chirality exists [23]. Actually, NMR measurements indicate asymmetrically twisted conformations of bent-core molecules in the B_4 phase [12,24]. Several experimental observations, such as NMR [12,24] and Fourier transform infrared (FTIR) [25], also suggest chiral conforma-

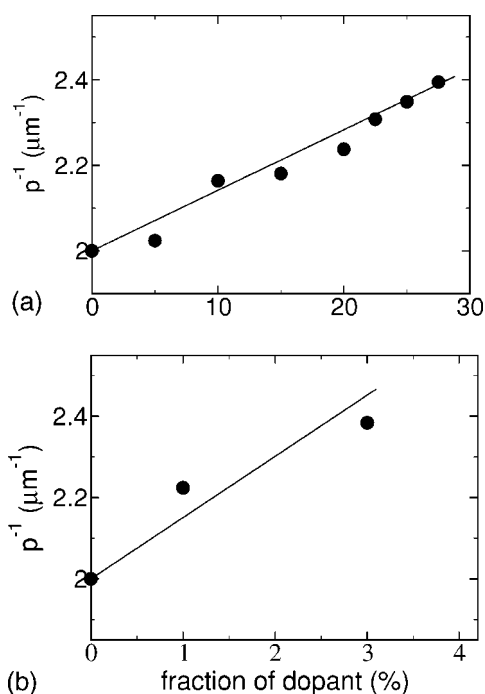


FIG. 3. Twisting power (inverse helical pitch) as a function of fraction of bent-core molecules. Chiral hosts are (a) a cholesteric liquid crystal and (b) a SmC^* liquid crystal.

tions are adopted, even in the $B2$ phase. The fact that chirality is preserved during the transition between the $B2$ and $B4$ phases [26] supports the existence of conformational chirality in the $B2$ phase. In addition to chiral properties observed in linear optics such as circular dichroism and optical rotatory power [26], chiral nonlinear optic effects have also been observed. Electrogyration (EG) effects [27], i.e., electric-field induced rotatory power, and second-harmonic generation circular difference (SHGCD) [28] have been observed in the $B4$ phase. Recently, the signs of chirality related nonlinear optic coefficients were confirmed to be opposite in two chiral domains [28]. Thus many experimental results unambiguously indicate deracemization both in tilted and nontilted bent-core LC phases. Another striking observation is the emergence of helical filaments in the $B7$ phase when it forms from the isotropic phase [29–33]. Filaments with left and right handedness exist, suggesting deracemization.

Another unexpected effect is an enhanced twisting power in chiral systems doped with achiral bent-core molecules. When a cholesteric LC is doped with bent-core molecules, the helical pitch becomes shorter [13]. Figure 3(a) reproduces reported data using 1,4-phenylene bis[4-(4-12-alkoxyphenyliminomethyl) benzoate] (P-12-O-PIMB) as a dopant, showing that the twisting power, i.e., inverse helical pitch, $1/p$, increases in proportion to the molar fraction, n , of achiral dopant [13]. This is quite unusual, since the addition of achiral molecules generally dilutes the chirality of a system, as in the case of rodlike molecules. The effect was qualitatively interpreted as follows. Bent-core molecules are achiral but can adopt chiral conformational structures. When bent-core molecules are dissolved in a chiral environment, chiral conformations of the bent-core molecules are predomi-

nantly selected and effectively behave as chiral dopants, resulting in the shortening of the pitch. The same behavior was observed in SmC^* and SmC_A^* phases [14]. The addition of bent-core molecules destabilizes SmC^* and stabilizes SmC_A^* due to the packing of bent-core molecules [34], and at the same time shortens the helical pitch in these phases [14]. The pitch change is also proportional to the fraction of achiral dopant, as shown in Fig. 3(b). A theoretical explanation was successfully made by considering the attractive van der Waals forces between mesogenic branches of bent-core molecules and rodlike molecules in nearest neighboring layers forming SmC^* or SmC_A^* phases. We should note a distinct difference in the power of chirality enhancement, $1/(pn)$, in cholesteric and tilted chiral smectic phases. Namely $1/(pn)$ is one order of magnitude larger in SmC^* phases than in cholesteric phases (see Fig. 3).

III. SIMULATIONS OF BENT-CORE MOLECULES

There has been considerable interest in techniques to calculate helical twisting powers (HTP's) for chiral molecules [35–47]. In a recent paper [35], an atomistic Monte Carlo simulation approach, coupled with calculations of the chirality order parameter [36–38], was used to study a range of flexible chiral molecules. The results of these studies demonstrated good agreement with experimentally observed HTP's and were able to explain a temperature dependent helical twist inversion in a cholesteric liquid crystalline material. The approach was also applied to three achiral bent-core molecules in the gas phase. In this section we analyze results from Monte Carlo simulations of the 2,7-naphthalene bis[(4-12-alkoxyphenyliminomethyl) benzoate] (N-12-O-PIMB) bent-core molecule and identify chiral conformations with extremely high helical twisting powers. When chiral molecules are added to an achiral nematic LC phase a chiral nematic phase results. The HTP of a chiral dopant is defined as $\beta_M = 1/(pnr)$ where p is the pitch of the chiral nematic, n is the weight concentration of chiral dopant, and r is the enantiomeric purity.

Here we employ the chirality order parameter approach of Nordio, Ferrarini, and co-workers to calculate HTP's of individual conformations. A detailed description of the approach is provided elsewhere [36–38], and for the purposes of this work it is sufficient to note that it has been shown to provide good predictions of the sign and magnitude of HTP's for relatively rigid chiral molecules (in comparison to experimental data), and has recently been extended to the study of flexible molecules by some of the authors [35]. In this approach the chirality order parameter χ has the same sign and is proportional to the HTP of a chiral molecule. For flexible molecules, many conformations will contribute to the average chirality order parameter. Consequently, a statistically significant and independent number of conformations, generated from an internal coordinate Monte Carlo simulation, are needed in order to predict an accurate HTP. Such an approach has been shown to provide excellent sampling of conformational space [48].

The bent-core molecule N-12-O-PIMB, that had previously been found to behave as a chiral dopant when added to

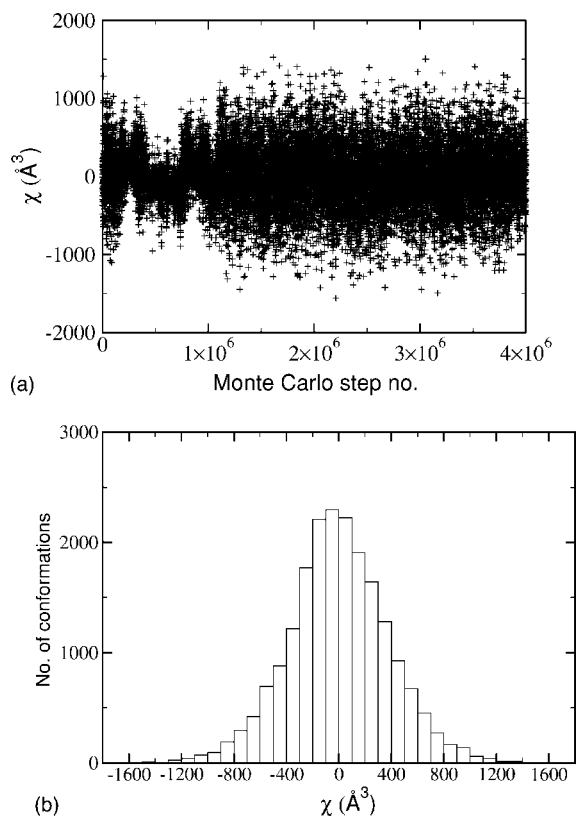


FIG. 4. (a) Chirality order parameter χ plotted against the Monte Carlo step number in our simulation. (b) Histogram showing the distribution of χ for N-12-O-PIMB.

a cholesteric phase [13], was simulated for 4 million Monte Carlo attempted moves, with calculations of the chirality order parameter χ , conducted at 200 step intervals, so that 20 000 conformations contributed to the overall average χ for the molecule. χ is plotted as a function of the Monte Carlo step number in Fig. 4(a). The approximately random and symmetrical distribution of chirality about 0 was expected, as was the overall average chirality order parameter $\langle\chi\rangle = -2.0 \pm 11.5 \text{ \AA}^3$ (achiral within statistical error). However, the extremely large magnitude of the twisting power associated with some of the conformations that the bent-core molecule adopted was very surprising. As a comparison to experimental helical twisting powers, a molecule with $\beta_M = 100 \mu\text{m}^{-1}$ is considered to have a high twisting power. In our previous study we found that β_M is approximately equal to $2 \times \chi \mu\text{m}^{-1} \text{ \AA}^{-3}$, so $\chi = 50 \text{ \AA}^3$ corresponds to $\beta_M \approx 100 \mu\text{m}^{-1}$. The vast majority of conformations sampled by the bent-core molecule had $|\chi| > 100 \text{ \AA}^3$, many had $|\chi| > 500 \text{ \AA}^3$, and a few percent had $|\chi| > 1000 \text{ \AA}^3$. A histogram showing the distribution of chirality order parameters for the conformations sampled by N-12-O-PIMB in our simulation is shown in Fig. 4(b). Figure 5 shows two different views of the N-12-O-PIMB molecule in highly chiral conformations with (a) $\chi = 1287 \text{ \AA}^3$, and (b) $\chi = -1187 \text{ \AA}^3$. In these conformations the exceptionally high χ values appear to arise from the molecule itself adopting a helical structure.

In recent works a number of authors have investigated the free energy difference between chiral dopants and their enan-

tiomers in a twisted nematic host solvent [40,41]. The free energy is lower when an enantiomer which wants to induce a helical twist in the same direction as the host is present. We therefore expect conformations of bent-core molecules with HTP's of the same handedness as the host to have a slightly lower free energy in a chiral LC phase. Consequently, we might expect preferential selection of chiral conformations to occur for the achiral bent-core molecules studied here.

We note that some changes in the conformational distribution would be expected in a liquid crystal, in cases where certain conformations are able to align better with the director of the host phase. An extension of the work to take this effect into account, would be to simulate the chiral dopant in the presence of a condensed phase, with the latter represented by hard or soft nonspherical potentials (for example, spherocylinders [49] or Gay-Berne [50] particles). However, this would be very computationally expensive at the current time, as extremely long simulations would be required in order to obtain accurate conformational averaging. Computational techniques to speed up the conformational averaging in these systems are currently being developed in our laboratory to attempt to quantify this effect.

IV. CHIRALITY INDUCTION IN THE *B2* BENT-CORE PHASE

As discussed in the previous two sections, there are many experimental and theoretical indications that bent-core molecules may exist in strongly chiral conformational states. Let us assume that each bent-core molecule exists, for simplicity, in one of two states which are characterized by opposite chirality, i.e., they are enantiomers. In the isotropic phase the probability to find a given molecule in one state is exactly the same as in the other state, and thus the whole system is achiral. However, in each layer of a *B2* phase, which possesses a chiral structure, the balance between the two enantiomeric conformations may be shifted, and as a result, on average, there may be a nonzero induced enantiomeric excess in every smectic layer. Let us denote the average molar fractions of bent-core molecules in the left- and right-handed conformational states by x_L and x_R , respectively. One notes that $x_L + x_R = 1$, and in an achiral phase one always has $x_L = x_R$.

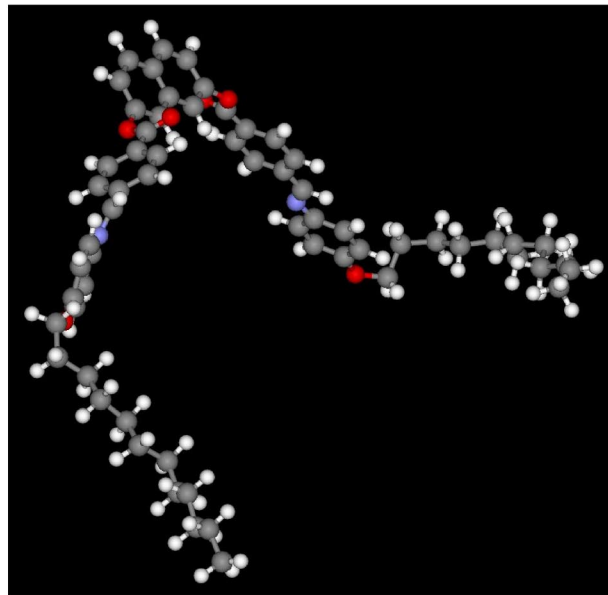
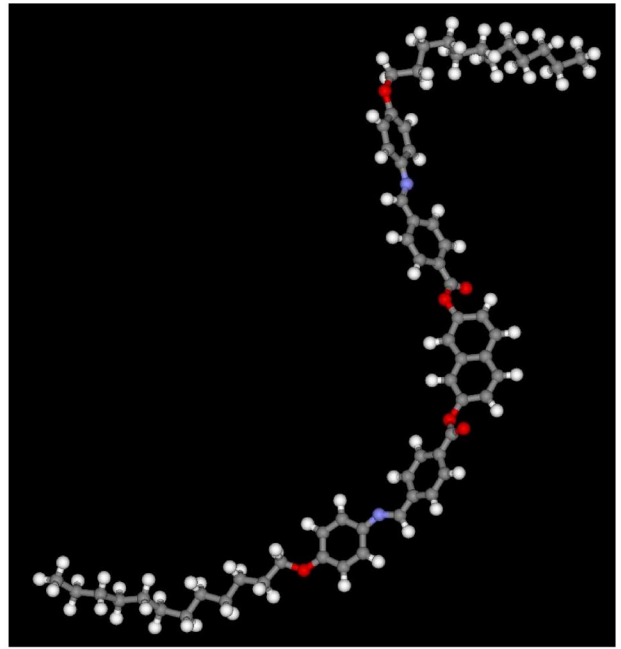
However, in the *B2* phase the balance between the two conformational states may be shifted locally because the structure of the phase is at least locally chiral (i.e., within one domain or within one smectic layer in the "racemic" state). Such partial induced deracemization, which corresponds to $x_L \neq x_R$, will be favorable if the free energy of such a chiral state is lower than that of the racemic mixture of the two conformations. The induced enantiomeric excess can be determined by minimization of the free energy of the *B2* phase, which depends on the molar fractions x_L and x_R :

$$\begin{aligned} \Delta F(x_L, x_R) = & kT\rho_0 x_L \ln x_L + kT\rho_0 x_R \ln x_R + \frac{1}{2} \rho_0^2 G_{LL} x_L^2 \\ & + \frac{1}{2} \rho_0^2 G_{RR} x_R^2 + \rho_0^2 G_{LR} x_L x_R + \mu_p (x_L - x_R) P_s \Theta, \end{aligned} \quad (1)$$

where ρ_0 is the average number density of bent-core mol-



(a)



(b)

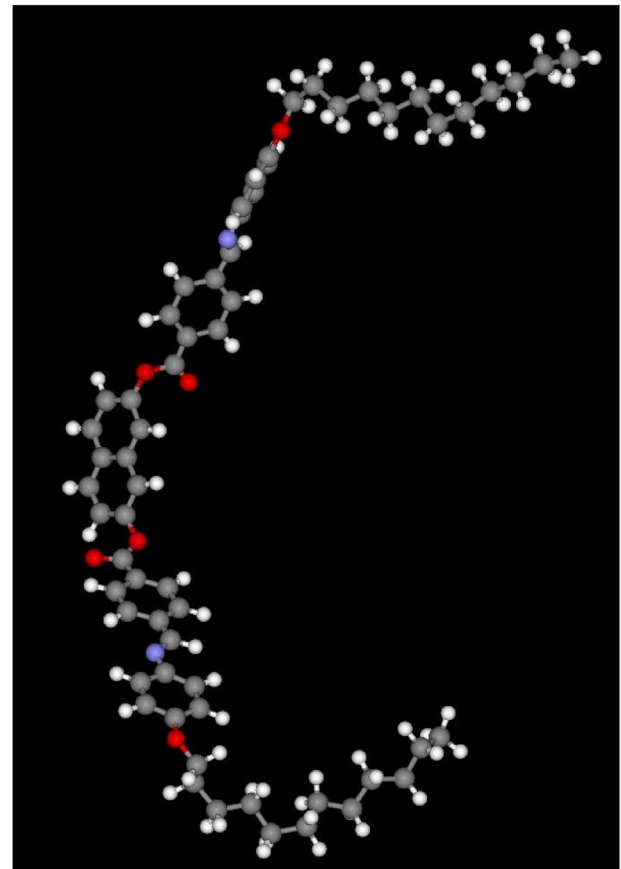


FIG. 5. (Color online) Snapshots from our simulation of N-12-O-PIMB showing two views of (a) a right-handed highly chiral conformation with $\chi=1287 \text{ \AA}^3$, and (b) a left-handed highly chiral conformation with $\chi=-1187 \text{ \AA}^3$.

eules, P_s is the spontaneous polarization of the $B2$ phase, and Θ is the tilt angle. The first two terms in Eq. (1) describe the mixing entropy of the molecules existing in one of the two conformational states. This entropy is maximal in the racemic mixture, and thus it does not favor deracemization. The third, fourth, and fifth terms in Eq. (1) represent an interaction between molecules in different conformational states. Here the coefficients G_{LL} and G_{RR} describe the effective interaction energy between two left-handed and two right-handed molecules, respectively. The enantiomers are absolutely equivalent and thus $G_{LL} = G_{RR} = G$. The coefficient G_{LR} characterizes an effective interaction energy between two molecules of opposite handedness, and thus in the general case the chiral discrimination parameter $\Delta G = G_{LR} - G \neq 0$. Finally, the last term in Eq. (1) describes a coupling between the local enantiomeric excess, $\Delta x = x_L - x_R$, the spontaneous polarization, and the tilt (see, for example, Refs. [51,52]). Here the coupling constant μ_p is a pseudoscalar coefficient which changes sign under space inversion, and which is determined by the chiral properties of the conformations. One notes that if $x_L \neq x_R$, there exists a local excess of chiral molecules. These molecules play the role of a chiral dopant and induce some additional polarization $P_i = 2\chi\mu_p\Delta x\Theta$ where χ is the transverse dielectric susceptibility. This polarization is expected to be much smaller than the spontaneous polarization of the $B2$ phase P_s , because it is proportional to the enantiomeric excess Δx , which is expected to be very small (as we will see below). One notes that the coefficient μ_p is related to the maximum possible polarization obtained in the hypothetical tilted phase composed of the conformers of the same handedness, $P_{max} \approx \chi\mu_p\Theta$. As discussed in Sec. II, typical conformations of bent-core molecules are strongly chiral, and thus the polarization P_{max} (and also μ_p which is proportional to P_{max}) is expected to be rather large. Importantly, in the presence of a nonzero enantiomeric excess there exists a linear coupling between the polarization and the tilt which is the same as in any conventional ferroelectric SmC^* . The corresponding coupling constant is approximately proportional to Δx at small Δx . The theory of ferroelectricity in enantiomeric mixtures of SmC^* phases is considered in detail in Ref. [51].

One may assume that the spontaneous polarization P_s and the tilt angle Θ in Eq. (1) do not depend on the enantiomeric excess Δx in the first approximation because they are mainly determined by nonchiral intermolecular interactions. Now, it can readily be seen from Eq. (1) that macroscopic chirality of the phase, i.e., the chiral structure of the layer which is characterized by the spontaneous polarization perpendicular to the tilt plane, induces some nonzero difference Δx between the molar fractions of bent-core molecules in the two conformational states. Minimizing the free energy in Eq. (1) with respect to Δx and assuming $\Delta x \ll 1$ one obtains

$$\Delta x \approx \frac{2\mu_p P_s \Theta}{kT\rho_0 - \Delta G\rho_0^2/2}, \quad (2)$$

where $\Delta G = G_{LR} - G$ is the chiral discrimination coefficient. The strength of the induced deracemization can be estimated from Eq. (2). For $\Theta = 30^\circ$, assuming $P_s \sim 400 \text{ nC/cm}^2$ and

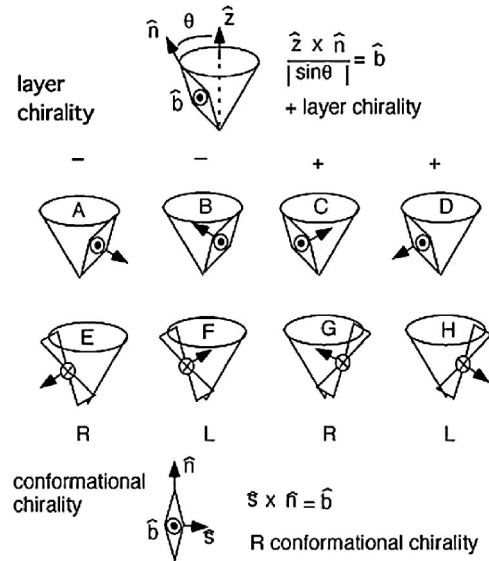


FIG. 6. Layer chirality (+ and -) and conformational chirality (R and L). There are four combinations, A(-,R), B(-,L), C(+,R), and D(+,L) and also the ones with opposite polarization direction (E to H).

taking μ_p to be of the same order as P_s , one estimates $\Delta x \sim 10^{-2}$. Thus one can expect deracemization on the order of only a few percent.

We can conclude that the induced enantiomeric excess is rather small. However, even a small deracemization may affect the behavior of the $B2$ phase in an external electric field. Indeed, let us first assume that there is no deracemization at all. In this case the free energy of the $B2$ phase is invariant under the sign reversal of the spontaneous polarization in each layer provided the orientation of the director in every layer remains the same. This means that the two states of the system, which differ only by the sign of the polarization in each layer, possess the same free energy. At the same time, if induced deracemization occurs, the two states of the system no longer possess the same free energy because there is a linear coupling term between the polarization, tilt angle, and enantiomeric excess in the free energy expression. Now, the two states which do possess the same energy are characterized by the opposite signs of both the polarization and the induced enantiomeric excess in each smectic layer. To make the discussion clearer, let us define the conformational chirality in addition to the layer chirality, as shown in Fig. 6. Consider for simplicity a single smectic layer in the $B2$ phase. If the polarization of such a layer is reversed by an external electric field without any rotation of the director in the layer (for instance A to G), the free energy of the final state is reduced if the enantiomeric excess changes sign. This is natural because polarization reversal without any change of the director orientation results in sign inversion of the macroscopic chirality of the layer (- to + in this example) determined by the relative orientation of the polarization, director, and layer normal. In this case the induced conformational chirality in the system of flexible bent-core molecules should also change sign (G to H in this example). By contrast, if the polarization reversal is accompanied by the

rotation of the director around the cone (for instance A to E), the macroscopic chirality of the layer remains the same as does the induced enantiomeric excess. It is known from experiment that the actual dynamical behavior of the $B2$ phase in an external electric field is rather complex and depends on the magnitude of the field. Thus in a general theoretical description of the switching dynamics one may also take into consideration the relaxation of the induced enantiomeric excess.

One notes that the induced enantiomeric excess Δx may be much larger if the chiral discrimination coefficient ΔG is close to $2kT\rho_0^{-1}$ in Eq. (2), i.e., if the denominator in Eq. (2) becomes small. However, this requires very high values of ΔG which must be of the order of kT (per molecule) which seems to be too high for most systems. In this semi-phenomenological description the chiral discrimination coefficient ΔG is considered as a parameter. In principle it can be estimated using atomistic simulations similar to those presented in Sec. III, or from a detailed molecular model. Existing theoretical models indicate that ΔG is strongly increased in the conditions of a confined geometry [51], i.e., if the interacting chiral molecules are confined to a smectic layer, as in a SmC^* or $B2$ phase.

V. INFLUENCE OF BENT-CORE MOLECULES ON THE CHOLESTERIC PITCH

Let us consider a cholesteric phase doped with bent-core molecules. In such a system bent-core molecules interact with chiral host molecules, and generally the interaction energy U_{LH} between a left-handed bent-core conformation and the chiral host molecule is different from the interaction energy U_{RH} between a right-handed conformation and the same host molecules. Thus in this case the solute-solvent interaction is also characterized by a chiral discrimination parameter $\Delta U_{HD} = U_{LH} - U_{RH} \neq 0$. The corresponding chiral interaction may also induce an enantiomeric excess in the system of bent-core molecules. As a result, the effective concentration of chiral molecules in the whole system will increase, and this will cause a reduction of the helical pitch in the cholesteric phase. On the other hand, one has to take into account the ordinary dilution effect (because not all bent-core molecules become chiral) which in itself leads to an increase of the pitch. Let us now consider these effects using the same simple theory as in the previous section.

The distortion free energy of the cholesteric phase is expressed as

$$F_d = \lambda(\mathbf{n} \text{curl} \mathbf{n}) + \frac{1}{2} K_{22}(\mathbf{n} \text{curl} \mathbf{n})^2, \quad (3)$$

where the coefficient λ is determined by molecular chirality. In the first approximation it is proportional to the number of chiral molecules. Minimization of the distortion energy yields the well known expression for the cholesteric pitch p :

$$\frac{2\pi}{p} = \frac{\lambda}{K_{22}}. \quad (4)$$

In a cholesteric phase doped with bent-core molecules the chiral constant λ can be expressed as

$$\lambda = \lambda_0 - x_b \lambda_d + (x_L - x_R) \lambda_b, \quad (5)$$

where λ_0 is the value of λ in the pure cholesteric phase and x_L and x_R are the average molar fractions of left- and right-handed bent-core conformers in the cholesteric solvent. One notes that $x_L + x_R = x_b$ where x_b is the total molar fraction of bent-core molecules. Thus the molar fraction of cholesteric host molecules is $x_{ch} = 1 - x_b$. The second term in Eq. (5) describes the dilution effect which leads to a decrease of the pseudoscalar coefficient λ with increasing total molar fraction of bent-core molecules. The third term in Eq. (5) leads to an increase in λ due to a nonzero average enantiomeric excess of bent-core conformations, $\Delta x = x_L - x_R$, induced by an interaction with chiral host molecules. This term is supposed to be predominant over the second one in the case of strongly chiral conformations of bent-core molecules. The induced enantiomeric excess can be determined by minimization of the free energy, similar to that considered in Sec. I:

$$\begin{aligned} \Delta F(x_L, x_R) = & kT\rho_0 x_L \ln x_L + kT\rho_0 x_R \ln x_R + \frac{1}{2} \rho_0^2 G_{LL} x_L^2 \\ & + \frac{1}{2} \rho_0^2 G_{RR} x_R^2 + \rho_0^2 G_{LR} x_L x_R + \rho_0^2 x_L x_{ch} U_{LH} \\ & + \rho_0^2 x_R x_{ch} U_{RH}, \end{aligned} \quad (6)$$

where the last two terms describe the interaction between chiral bent-core conformers with chiral host molecules.

We first assume that the total molar fraction of bent-core molecules, x_b , is small. Then, in the first approximation, one may neglect all terms in the free energy in Eq. (6) which are quadratic in x_L and x_R keeping only the linear terms. This means that at small concentrations of bent-core dopant molecules one may neglect a direct interaction between dopants if the average distance between them is sufficiently large. In this case the free energy can be rewritten in a simplified form:

$$\begin{aligned} \Delta F(x_L, x_R) = & kT\rho_0 x_L \ln x_L + kT\rho_0 x_R \ln x_R + \rho_0^2 x_L U_{LH} \\ & + \rho_0^2 x_R U_{RH}. \end{aligned} \quad (7)$$

Minimization of the free energy in Eq. (7) yields the following expression for the induced enantiomeric excess of bent-core conformations:

$$\Delta x = x_b \tanh\left(\frac{\rho_0 \Delta U}{2kT}\right). \quad (8)$$

For simplicity we use the shorthand notation $\Delta U = \Delta U_{HD}$ in Eq. (8) and thereafter.

Substitution of Eq. (8) into Eqs. (4) and (5) yields the final expression for the inverse pitch:

$$\frac{2\pi}{p} = \frac{\lambda_0 + x_b \left[\lambda_b \tanh\left(\frac{\rho_0 \Delta U}{2kT}\right) - \lambda_d \right]}{K_{22}}. \quad (9)$$

Equation (9) describes a decrease of pitch with increasing molar fraction of bent-core molecules, x_b , if $\lambda_b \tanh(\rho_0 \Delta U / 2kT) > \lambda_d$. In this case the inverse pitch grows linearly with an increasing concentration of bent-core mol-

ecules which corresponds to the experiment [see Fig. 3(a) and Ref. [13]]. One notes that the pitch decreases only if the constant λ_b , which is proportional to the helical twisting power of chiral bent-core conformers in the cholesteric host, is sufficiently large compared with the constant λ_d , which characterizes the strength of the dilution effect.

One notes that in this description we have neglected the dependence of the twist elastic constant K_{22} on the dopant concentration x_b . In general one may assume that the influence of a dopant (chiral or achiral) on the elastic constants of the nematic solvent is rather weak for small dopant concentrations. Recently, however, a significant decrease of the bend elastic constant K_{33} has been observed in a nematic material doped with bent-core molecules [53]. Presently, no information about the twist elastic constant of such a mixture is available. One notes that theoretical estimates presented in Ref. [53] indicate that the twist elastic constant may also be reduced in this case, but the corresponding change is expected to be very small, i.e., of the order of a few percent. Such a small reduction in the twist elastic constant will contribute to the decrease of the cholesteric pitch but, on its own, can hardly be responsible for the observed effect. On the other hand, it has been shown experimentally by Nakata *et al.* [54] that a relatively small concentration of bent-core molecules may even induce the blue phase. This effect has been interpreted in terms of chirality enhancement and possible changes of the elastic constants due to the presence of bent-core molecules. Thus the influence of bent-core dopants on the elastic constants of the nematic phase deserve further investigation. Theoretical estimates presented in Ref. [53] are based on a simple model of the interaction potentials between a bent-core dopant and rodlike host molecules, incorporated into the mean-field free energy, which is then expanded in powers of the gradients of the director. Such an approach may give a reasonable first estimate of the effect. At the same time, there exist at least two additional effects which may further contribute to the reduction of the bend and splay elastic constants in the presence of a bent-core dopant. First, it is well known that the elastic constants are renormalized by the flexoelectric effect. This renormalization leads to a decrease of the bend and splay constants proportional to the square of the corresponding flexoelectric coefficient. Normally this effect is considered to be rather small. However, typical bent-core molecules possess very large transverse steric dipoles, and therefore they should strongly contribute to the flexoelectric coefficient of the mixture. As a result, the corresponding reduction of the elastic constants may be abnormally large. It should be noted, however, that the flexoelectric effect does not influence the twist elastic constant because the flexopolarization contains only bend and splay terms. The second effect is also related to the specific bent shape of the dopant molecules. Such dopants may induce “bend correlations” into the solvent, determined by an interaction of two rodlike host molecules with the bent-core dopant. The latter effect can be taken into account only in the context of a molecular theory which goes beyond the mean-field approximation.

It should be noted that in principle one should also consider the energy of twist deformation, $\lambda(\mathbf{n} \text{ curl } \mathbf{n})$, in the total free energy of the doped cholesteric phase because this term

also depends on the enantiomeric excess Δx . This distortion energy, however, is much smaller than other terms contributing to the free energy in Eq. (6) which are not proportional to the gradients of the director. This means that chiral induction caused by the existence of the macroscopic helical structure should be very weak. In qualitative terms this means that bent-core molecules embedded in the cholesteric solvent practically do not “feel” the existence of the macroscopic helical structure because the period of this structure is much larger than their dimensions.

VI. INFLUENCE OF BENT-CORE MOLECULES ON THE PITCH OF THE FERROELECTRIC SMECTIC-C* PHASE

The reduction of the pitch in a SmC* phase doped with bent-core molecules can be explained qualitatively in the same way as in the cholesteric phase. The balance between left- and right-handed conformations of bent-core molecules may be shifted due to an interaction with the chiral host molecules of the SmC* phase, and the resulting enantiomeric excess of bent-core conformations will cause a decrease in the helical pitch. This effect must overcome the dilution effect to explain the experimental results. At the same time there are some differences caused by the different structure of the SmC* phase compared to that of the cholesteric phase.

The general expression for the pitch in the SmC* is more complex than the corresponding expression in the cholesteric phase [52]:

$$\frac{2\pi}{p} = \frac{\lambda + \chi_{\perp} \mu_p \mu_f}{K_{22} - \chi_{\perp} \mu_f^2}, \quad (10)$$

where λ is a pseudoscalar quantity which is determined by molecular chirality, and the coefficient μ_p determines the spontaneous polarization in the unwound phase, $P_s = \chi_{\perp} \mu_p \sin(2\Theta)$. χ_{\perp} is the transverse susceptibility of the SmC phase and μ_f is the flexoelectric coefficient. One notes that Eq. (10) is a general result of the phenomenological Landau-de Gennes theory, and it is determined only by the symmetry of the SmC* phase. It is reasonable to assume that the symmetry of the phase is not affected by the dopant. Then Eq. (10) should also be valid in the presence of bent-core molecules regardless of their actual location on the molecular level within the SmC* structure. A particular spatial distribution of bent-core molecules may only influence the coefficients in the general expression, Eq. (10).

In Eq. (10) the constants λ and μ_p are determined by molecular chirality, and therefore they should be affected by an induced enantiomeric excess of bent-core conformations. These coefficients can be written in the same general form as in Eq. (5),

$$\lambda = \lambda_0 - x_b \lambda_d + (x_L - x_R) \lambda_b \quad (11)$$

and

$$\mu_p = \mu_{p0} - x_b \mu_d + (x_L - x_R) \mu_{pb}, \quad (12)$$

where we have used the same notations as in the previous section. The coefficients λ_d and μ_d in Eqs. (11) and (12)

describe the dilution effect while the third term represents a contribution from the induced enantiomeric excess in the system of flexible bent-core molecules. The enantiomeric excess Δx can be determined by minimization of the free energy of the same type as in the previous section. The only important difference is determined by the fact that the SmC* phase possesses a local chiral structure determined by the mutual orientation of the director, layer normal, and the spontaneous polarization. As a result, the bent-core molecules are embedded in a chiral environment similar to the B2 phase, which may also induce some enantiomeric excess. Thus there are two different effects which induce a shift in the balance between left- and right-handed bent-core conformations: an interaction between bent-core molecules and chiral host molecules, and the coupling between the enantiomeric excess, tilt, spontaneous polarization similar to the one described in Sec. I. The latter effect is absent in the cholesteric phase.

The part of the free energy in the SmC* phase which depends on the enantiomeric excess Δx can be written in a form similar to Eq. (5), also taking into account a coupling between enantiomeric excess Δx , tilt angle Θ , and the polarization P_s discussed in Sec. I:

$$\Delta F(x_L, x_R) = kT\rho_0 x_L \ln x_L + kT\rho_0 x_R \ln x_R + \rho_0^2 x_L U_{LH} + \rho_0^2 x_R U_{RH} + \mu_p \Delta x P_s \Theta. \quad (13)$$

Minimization of the free energy in Eq. (13) yields the following equation for Δx which is similar to Eq. (9):

$$\Delta x = x_b \tanh\left(\frac{\rho_0 \Delta U + \mu_p P_s \Theta}{kT}\right). \quad (14)$$

Substituting Eq. (14) into Eqs. (11) and (12) and then into Eq. (10) one obtains the final expression for the helical pitch of the SmC* phase as a function of the molar fraction x_b of bent-core molecules:

$$\frac{2\pi}{P} = \frac{\tilde{\lambda}_0}{\tilde{K}_{22}} + \frac{x_b}{\tilde{K}_{22}} \left[\tanh\left(\frac{\rho_0 \Delta U + \mu_p P_s \Theta}{2kT}\right) \tilde{\lambda}_b - \tilde{\lambda}_d \right], \quad (15)$$

where

$$\tilde{\lambda}_0 = \lambda_0 + \chi_\perp \mu_{0p} \mu_f, \quad (16)$$

$$\tilde{\lambda}_b = \lambda_b + \chi_\perp \mu_{bp} \mu_f, \quad (17)$$

$$\tilde{\lambda}_d = \lambda_d + \chi_\perp \mu_{dp} \mu_f, \quad (18)$$

and

$$\tilde{K}_{22} = K_{22} - \chi_\perp \mu_f^2. \quad (19)$$

As in the cholesteric phase, the pitch of the SmC* phase decreases with an increase in concentration of bent-core molecules if

$$\tanh\left(\frac{\rho_0 \Delta U + \mu_p P_s \Theta}{2kT}\right) \tilde{\lambda}_b > \tilde{\lambda}_0. \quad (20)$$

Finally it should be noted that in the general Eq. (10) for the pitch of the SmC* phase, the flexoelectric coefficient μ_f

may also depend on the molar fraction of bent-core molecules. Bent-core molecules possess a strongly polar shape which may make a significant contribution to flexoelectricity. This contribution may also be strongly affected by the location of bent-core molecules between the layers. The corresponding mechanism of the pitch reduction in the SmC* phase related to an increase of the flexoelectric coefficient μ_f in Eq. (10) has recently been proposed by Goreka *et al.* [14].

As mentioned in Sec. I, the reduction of the pitch in the SmC* phase is much larger than that in the cholesteric phase. In the context of the present theoretical approach this difference may be attributed to two different factors. First, as discussed above, the nonzero enantiomeric excess in the SmC* phase may be induced by two different effects: an interaction between bent-core and chiral host molecules and the coupling between the enantiomeric excess, tilt, and the spontaneous polarization. The latter effect is absent in the cholesteric phase. As a result, there exists an additional term in the exponential function in Eqs. (14) and (15) which leads to an additional decrease of the pitch in the SmC* phase. Second, the chiral discrimination parameter ΔU is expected to be larger in the SmC* phase compared with the cholesteric one. As discussed in more detail in Ref. [51], this is related to a confined geometry of a smectic layer. Generally, the difference between the averaged interaction energies for the pairs of molecules of equal and opposite handedness is enhanced if the molecules are confined to a thin layer. In contrast, the energy discrimination is partially averaged out in the cholesteric phase due to the translational disorder. One notes that, according to Eq. (15), the pitch is very sensitive to both the value of the discrimination parameter ΔU and the spontaneous polarization P_s .

VII. DISCUSSION

It has been shown in this paper that there exists a large body of experimental and theoretical data which indicates that typical mesogenic bent-core molecules may exist in chiral conformational states. This means that bent-core molecules are achiral only on average, and thus the chirality of predominant conformational states may manifest itself strongly under appropriate conditions. In particular, the balance between left- and right-handed conformations may be shifted in any chiral liquid crystal phase. In the B2 bent-core smectic phase the existence of a macroscopically chiral structure determines the chiral induction effect which results in a nonzero average enantiomeric excess of the order of a few percent according to the estimates presented in Sec. IV. Thus the B2 phase also becomes chiral on the molecular level. This effect explains the unusual switching of polarization in weak electric fields which seems to preserve the chirality of each smectic layer. In conventional cholesteric and SmC* phases doped with bent-core molecules one finds a different chiral induction effect which is determined by direct interactions between chiral conformations of bent-core molecules and chiral molecules of the host phase. As a result, an average enantiomeric excess is again induced in the system of bent-core dopant molecules, and the effective concentration of chiral molecules in the whole system is increased.

This leads to a decrease of the helical pitch which has been observed experimentally in both phases. By contrast, doping the same host phase with achiral rigid molecules results in an increase of the pitch [13].

At the same time a number of recently discovered chiral properties of bent-core smectic phases cannot be explained by chiral induction. In particular, the existence of two chiral domains in the untilted B_4 smectic phase cannot be related to any macroscopic chiral structure. Indeed, x-ray data obtained, for example, in Ref. [23] strongly indicate that the molecules are not tilted in the B_4 phase and therefore the existence of the spontaneous polarization does not result in a chiral smectic layer. In the context of the present model this effect can only be explained assuming that spontaneous deracemization occurs in the B_4 phase. Spontaneous deracemization, i.e., a spontaneous transition from the racemic mixture of two (or more) chiral conformers into a chiral phase with a nonzero enantiomeric excess, was described theoretically by Zeldovitch more than 40 years ago but, to the best of our knowledge, it has never been observed in any bulk liquid. On the other hand, induced deracemization, for example by crystallization, is a common phenomenon. It is interesting to note that a spontaneous enantiomeric resolution has recently been observed by Takanishi *et al.* in the smectic phase of a racemate [55]. This may be an example of the spontaneous deracemization predicted by Zeldovich. Apparently the layered structure of smectic phases promotes the deracemization. As discussed above, the strongly confined geometry of the smectic layer may lead to an increase of the chiral discrimination parameter ΔU .

The spontaneous deracemization in the B_4 phase can be qualitatively described using the same free energy as considered in Sec. IV, but without the term that describes a coupling with the tilt:

$$\begin{aligned} \Delta F(x_L, x_R) = & kT\rho_0 x_L \ln x_L + kT\rho_0 x_R \ln x_R + \frac{1}{2}\rho_0^2 G_{LL} x_L^2 \\ & + \frac{1}{2}\rho_0^2 G_{RR} x_R^2 + \rho_0^2 G_{LR} x_L x_R, \end{aligned} \quad (21)$$

where the molar fractions of left- and right-handed conformers x_L and x_R depend on the enantiomeric excess Δx : $x_L = (1 + \Delta x)/2$, $x_R = (1 - \Delta x)/2$. Minimization of the free energy in Eq. (21) yields the following self-consistent equation for the enantiomeric excess:

$$\Delta x = \tanh\left(\frac{\rho_0 \Delta G \Delta x}{2kT}\right), \quad (22)$$

where ΔG is the chiral discrimination coefficient discussed in Sec. IV. Equation (22) always has a trivial solution, Δx

$= 0$, which corresponds to the racemic mixture of the two conformations. Expanding the free energy in Eq. (21) in powers of Δx one obtains

$$F \approx \frac{1}{2}\rho_0 kT \left(1 - \frac{\rho_0 \Delta G}{2kT}\right) (\Delta x)^2 + \dots \quad (23)$$

It follows from Eq. (23) that the trivial solution loses its stability if $\rho_0 \Delta G > 2kT$. In this temperature domain Eq. (22) has two additional symmetric solutions, $+\Delta x$ and $-\Delta x$, which correspond to a chiral phase with positive or negative spontaneous enantiomeric excess. At a temperature $T_c = \rho_0 \Delta G / 2$ the system undergoes a second order phase transition into a spontaneously chiral phase. One notes that this is a symmetry breaking phase transition, and therefore the two states with positive and negative spontaneous enantiomeric excess, Δx_0 , are fully equivalent. It should be noted that deracemization in the B_4 phase may, in principle, also be explained in a different way. The results of wide angle x-ray measurements [23] demonstrate the existence of two-dimensional order in the B_4 phase which indicates that the B_4 phase may be similar to a highly ordered smectic such as SmB . Thus the deracemization may in principle be induced by the onset of such a two-dimensional order. In this case it will not be spontaneous, and would be similar to the deracemization that sometimes occurs upon crystallization (although it is not expected to be so pronounced).

Finally, one notes that the chirality induction effects in bent-core smectic phases strongly depend upon two major parameters: the coefficient μ_p , which describes the coupling between polarization and tilt for chiral bent-core conformations, and the chiral discrimination parameter ΔU , which characterizes the difference in average interaction between chiral conformations of equal and opposite handedness. Both parameters can, in principle, be estimated from computer simulations and, to a certain extent, from molecular models. The corresponding studies are currently under way.

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- [1] *Chirality in Liquid Crystals*, edited by C. Bahr and H. Kitzrow (Springer, New York, 2001).
- [2] P. P. Crooker, *Liq. Cryst.* **5**, 751 (1989).
- [3] D. C. Wright and N. D. Mermin, *Rev. Mod. Phys.* **61**, 385 (1989).
- [4] M.-H. Li, V. Laux, H. T. Nguyen, G. Sigaud, P. Barois, and N. Isaert, *Liq. Cryst.* **23**, 389 (1997).
- [5] B. Pansu, M. H. Li, and N. T. Nguyen, *J. Phys. II* **7**, 751 (1997).
- [6] Y. Takanishi, T. Ogasawara, A. Yoshizawa, J. Umezawa, T. Kusumoto, T. Hiyama, K. Ishikawa, and H. Takezoe, *J. Mater. Chem.* **12**, 1325 (2002).
- [7] B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Phys. (France)* **36**, L69 (1975).
- [8] A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys., Part 2* **28**, L1265 (1989).
- [9] S. M. Stein, E. Chin, R. Pindak, and J. S. Patel, *Nature (London)* **337**, 449 (1989).
- [10] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, *J. Mater. Chem.* **6**, 1231 (1996).
- [11] D. R. Link, G. Natale, R. Shao, J. E. Maclennan, N. A. Clark, E. Korblova, and D. M. Walba, *Science* **278**, 1924 (1997).
- [12] T. Sekine, T. Niori, J. Watanabe, S. W. Choi, Y. Takanishi, H. Takezoe, and M. Sone, *Jpn. J. Appl. Phys., Part 1* **36**, 6455 (1997).
- [13] J. Thisayukta, H. Niwano, H. Takezoe, and J. Watanabe, *J. Am. Chem. Soc.* **124**, 3354 (2002).
- [14] E. Gorecka, M. Cepic, J. Mieczkowski, M. Nakata, H. Takezoe, and B. Zeks, *Phys. Rev. E* **67**, 061704 (2003).
- [15] G. Pelzl, S. Diele, and W. Weissflog, *Adv. Mater. (Weinheim, Ger.)* **11**, 707 (1999).
- [16] K. Kumazawa, M. Nakata, F. Araoka, Y. Takanishi, K. Ishikawa, J. Watanabe, and H. Takezoe, *J. Mater. Chem.* **14**, 157 (2004).
- [17] M. Zennoji, Y. Takanishi, K. Ishikawa, J. Thisayukta, J. Watanabe, and H. Takezoe, *Jpn. J. Appl. Phys., Part 1* **39**, 3536 (2000).
- [18] G. Heppke, A. Jakli, S. Rauch, and H. Sawade, *Phys. Rev. E* **60**, 5575 (1999).
- [19] J. Thisayukta, Y. Nakayama, S. Kawauchi, H. Takezoe, and J. Watanabe, *J. Am. Chem. Soc.* **122**, 7441 (2000).
- [20] N. V. S. Rao, M. Kr. Paul, I. Miyake, Y. Takanishi, I. Ken, and H. Takezoe, *J. Mater. Chem.* **13**, 2880 (2003).
- [21] G. Heppke, D. D. Parghi, and H. Sawade, *Liq. Cryst.* **27**, 313 (2000).
- [22] A. Eremin, S. Diele, G. Pelzl, and W. Weissflog, *Phys. Rev. E* **67**, 020702(R) (2003).
- [23] J. Thisayukta, H. Takezoe, and J. Watanabe, *Jpn. J. Appl. Phys., Part 1* **40**, 3277 (2001).
- [24] H. Kurosu, M. Kawasaki, M. Hirose, M. Yamada, S. Kang, M. Sone, H. Takezoe, and J. Watanabe, *J. Phys. Chem. A* **108**, 4674 (2004).
- [25] M. Zennoji, Y. Takanishi, K. Ishikawa, J. Thisayukta, J. Watanabe, and H. Takezoe, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **366**, 693 (2001).
- [26] H. Niwano, M. Nakata, J. Thisayukta, D. R. Link, H. Takezoe, and J. Watanabe, *J. Phys. Chem.* (to be published).
- [27] F. Araoka, Y. Takanishi, H. Takezoe, A. Kim, B. Park, and J. W. Wu, *J. Opt. Soc. Am. B* **20**, 314 (2003).
- [28] F. Araoka and H. Takezoe (unpublished).
- [29] J. P. Bedal, J. C. Rouillon, J. P. Marcerou, M. Laguerre, H. T. Nguyen, and M. F. Achard, *Liq. Cryst.* **27**, 1411 (2000).
- [30] A. Jakli, C. Lischka, W. Weissflog, G. Pelzl, and A. Saupe, *Liq. Cryst.* **27**, 1405 (2000).
- [31] A. Jakli, D. Kruerke, H. Sawade, and G. Heppke, *Phys. Rev. Lett.* **86**, 5715 (2001).
- [32] C.-K. Lee, A. Primak, A. Jakli, E.-J. Choi, W.-C. Zin, and L.-C. Chien, *Liq. Cryst.* **28**, 1293 (2001).
- [33] D. A. Coleman, J. Fernsler, N. Chattham, M. Nakata, Y. Takanishi, E. Korblova, D. R. Link, R.-F. Shao, W. G. Jang, J. E. Maclennan, O. Mondainn-Monval, C. Boyer, W. Weissflog, G. Pelzl, L.-C. Chien, J. Zasadzinski, J. Watanabe, D. M. Walba, H. Takezoe, and N. A. Clark, *Science* **301**, 1204 (2003).
- [34] E. Gorecka, M. Nakata, J. Mieczkowski, Y. Takanishi, K. Ishikawa, J. Watanabe, H. Takezoe, S. H. Eichhorn, and T. M. Swager, *Phys. Rev. Lett.* **85**, 2526 (2000).
- [35] D. J. Earl and M. R. Wilson, *J. Chem. Phys.* **119**, 10280 (2003).
- [36] L. Feltre, A. Ferrarini, F. Pacchiale, and P. L. Nordio, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **290**, 109 (1996).
- [37] A. Ferrarini, G. J. Moro, and P. L. Nordio, *Mol. Phys.* **87**, 485 (1996).
- [38] A. Ferrarini, G. J. Moro, and P. L. Nordio, *Phys. Rev. E* **53**, 681 (1996).
- [39] D. J. Earl and M. R. Wilson, *J. Chem. Phys.* **120**, 9679 (2004).
- [40] M. J. Cook and M. R. Wilson, *J. Chem. Phys.* **112**, 1560 (2000).
- [41] M. R. Wilson and D. J. Earl, *J. Mater. Chem.* **11**, 2672 (2001).
- [42] M. Solymosi, R. J. Low, M. Grayson, M. P. Neal, M. R. Wilson, and D. J. Earl, *Ferroelectrics* **277**, 483 (2002).
- [43] M. P. Neal, M. Solymosi, M. R. Wilson, and D. J. Earl, *J. Chem. Phys.* **119**, 3567 (2003).
- [44] G. Gottarelli, M. Hibert, B. Samori, G. Solladie, G. P. Spada, and R. Zimmermann, *J. Am. Chem. Soc.* **105**, 7318 (1983).
- [45] G. Gottarelli, G. Proni, G. P. Spada, D. Fabbri, S. Gladiali, and C. Rosini, *J. Org. Chem.* **61**, 2013 (1996).
- [46] S. Pieraccini, M. I. Donnoli, A. Ferrarini, G. Gottarelli, G. Licini, C. Rosini, S. Superchi, and G. P. Spada, *J. Org. Chem.* **68**, 519 (2003).
- [47] G. Heppke, D. Lotzch, and F. Oestreicher, *Z. Naturforsch. Teil A* **41a**, 1214 (1986).
- [48] M. R. Wilson, *Liq. Cryst.* **21**, 437 (1996).
- [49] D. J. Earl, J. Ilnytskyi, and M. R. Wilson, *Mol. Phys.* **99**, 1719 (2001).
- [50] J. G. Gay and B. J. Berne, *J. Chem. Phys.* **74**, 3316 (2003).
- [51] M. A. Osipov and D. Guillon, *Phys. Rev. E* **60**, 6855 (1999).
- [52] S. A. Pikin and M. A. Osipov, in *Ferroelectric Liquid Crystals, Principles, Properties and Applications*, Ferroelectricity and Related Phenomena No. 7 (Gordon and Breach, New York, 1992).
- [53] M. R. Dodge, C. Rosenblatt, R. G. Petschek, M. E. Neubert, and M. E. Walsh, *Phys. Rev. E* **62**, 5056 (2000).
- [54] M. Nakata, Y. Takanishi, J. Watanabe, and H. Takezoe, *Phys. Rev. E* **68**, 041710 (2003).
- [55] Y. Takanishi, H. Takezoe, Y. Suzuki, I. Kobayashi, T. Yajima, M. Terada, and K. Mikami, *Angew. Chem., Int. Ed. Engl.* **38**, 2354 (1999).