

# Some aspects about the structure of the optically isotropic phase in a bent-core liquid crystal: Chiral, polar, or steric origin

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We have studied a bent-core liquid crystal where two different optically isotropic phases can be induced by a strong electric field. Depending on the field treatment the phases can present optical rotation or be optically inactive. The switching dynamics of the phases is studied by means of electrooptic and optical second-harmonic generation measurements. It is found that the ground state of the phases is locally antiferroelectric. The structure of the phases is consistent with a disordered version of the kind of structures recently proposed for the smectic blue phase: layered systems with high Gaussian curvature. The origin of the smectic layer distortion is discussed. It is concluded that the direct reason for the curvature of planes is of steric nature.

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## I. INTRODUCTION

One of the most remarkable phenomena in the physics of achiral bent-core liquid crystals is the so-called spontaneous desymmetrization, i.e., the spontaneous segregation of macroscopic chiral domains in the mesophase. This process takes place in several kinds of phases such as *B2* or *B4* [1–25]. An especially important case happens when the mesophase is optically isotropic. In this situation the desymmetrization is easily observable because the sample presents two types of domains with opposite optical rotation and circular dichroism. This is the case of the *B4* phase, where this phenomenon was first observed [1–3]. Afterwards a similar circumstance was reported in some isotropic smectic mesophases without in-plane positional order [4–25]. From the viewpoint of x-ray diffraction these dark phases present Bragg peaks at small angles with a certain width nonlimited by the apparatus resolution, and are characterized by a diffuse reflection at wide angles. In contrast, the *B4* phase presents sharp peaks both at wide and small angles, and really does not seem to be a genuine liquid crystal but a kind of soft crystalline material [26].

The structure of the dark fluid phases (from now on dark phases) is not fully clarified yet. The first structural models considered these phases as normal smectic-*CP* (*SmCP*) structures with very small domains oriented at random. However, currently it is believed that the disordered disposition of the domains is not extrinsic but inherent to the nature of the phases themselves. Recently it has been proposed [27] that they are the thermotropic counterparts of the lyotropic sponge phase *L3* [28]. It seems that they could be a disordered version of the kind of structures proposed for the smectic blue phase by DiDonna and Kamien [29]. According to these models, in these phases the smectic planes are strongly folded and the resulting structure is stabilized by a high negative value of the saddle-splay elastic constant  $K_{24}$ . The isotropy is explained as due to the small size of the flat smectic regions (smaller than the optical wavelength).

The origin of this strong distortion is not evident. Three different hypothesis have been proposed: (a) steric reasons (different cross-section areas required by different molecular segments) leading to an intralayer frustration, (b) escape from a macroscopic spontaneous polarization in *SmCP<sub>F</sub>* phases, and (c) molecular conformational chirality [23]. In this work we will discuss these proposals by analyzing the behavior of a material where the dark phase comes from a conventional *SmCP* phase perturbed by a strong electric field. The study is based on electrooptic and second-harmonic generation (SHG) measurements.

## II. EXPERIMENTAL RESULTS AND DISCUSSION

The chemical structure of the material and its phase sequence in the absence of field is shown in Fig. 1. The synthesis and a preliminary characterization of the compound was published in Ref. [30]. Previous dielectric and optical studies were reported in Refs. [31,14], respectively. Figure 2 shows the optical textures at  $T=146$  °C after cooling the material from the isotropic phase under a strong square-wave field ( $12 \text{ V } \mu\text{m}^{-1}$ , 10 Hz) and its subsequent removal. The dark phase with the chiral domains is clearly visible by slightly uncrossing the polarizers [Figs. 2(a) and 2(b)]. On

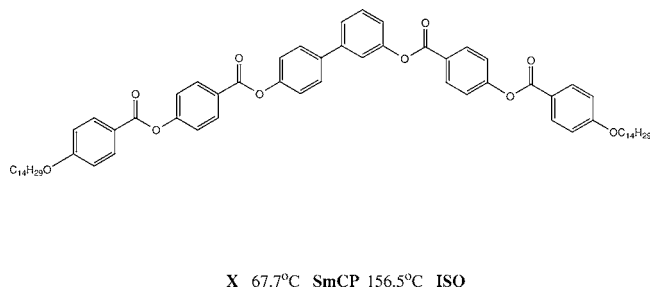


FIG. 1. Chemical structure and phase sequence of the studied material. X represents a solid crystal phase.

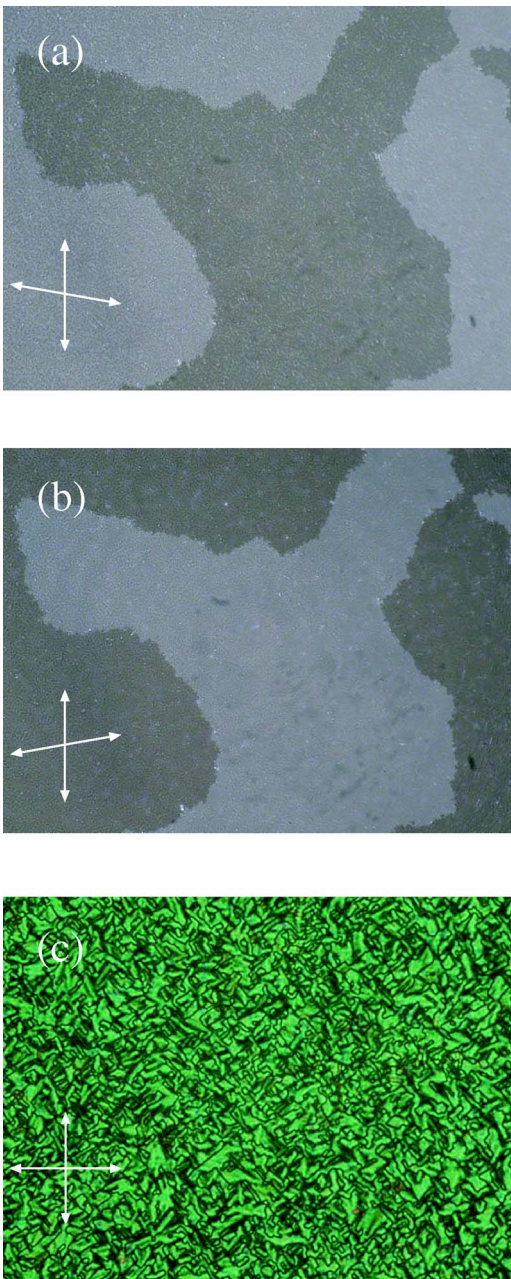


FIG. 2. (Color online) Homochiral phase. Textures observed at  $10^\circ\text{C}$  below the transition temperature after cooling from the isotropic phase under a square-wave electric field ( $12\text{ V }\mu\text{m}^{-1}$ ,  $10\text{ Hz}$ ). After field removal, domains of opposite chirality can be clearly seen uncrossing the analyzer slightly, as shown in pictures (a) and (b) ( $600\text{ }\mu\text{m}$  wide). Picture (c) ( $240\text{ }\mu\text{m}$  wide) shows the texture with the field on  $12\text{ V }\mu\text{m}^{-1}$ . Arrows indicate polarizer directions.

further application of fields the texture [Fig. 2(c)] becomes highly birefringent ( $\Delta n=0.14$ ). This indicates a  $\text{SmC}_S P_F$  structure. A different behavior results if the field is applied after cooling the material into the normal  $\text{SmCP}$  phase. In this case, again, a dark texture is obtained after field removal [Fig. 3(a)] but now there are no chiral domains. Furthermore, the texture aspect after a subsequent field application [Fig. 3(b)] is clearly different to that of the preceding case. The most abundant color of the photograph corresponds to a

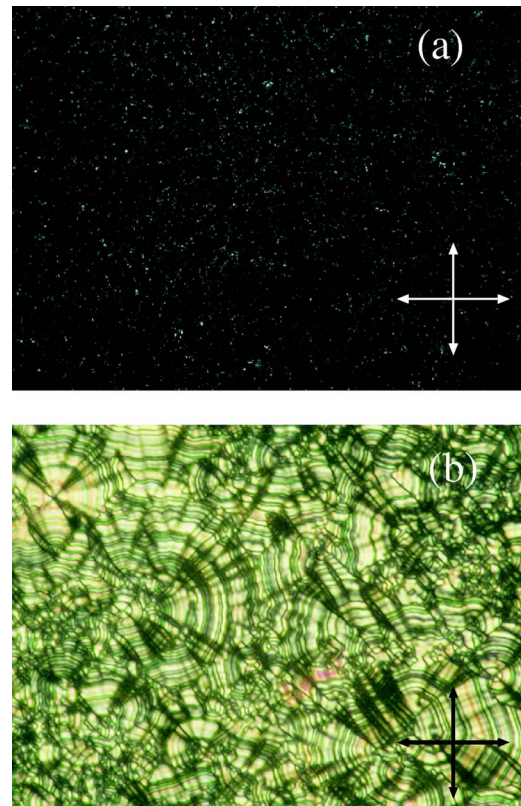


FIG. 3. (Color online) Racemic phase. Textures observed at  $10^\circ\text{C}$  below the transition temperature after cooling from the isotropic phase and then applying a square-wave electric field ( $15\text{ V }\mu\text{m}^{-1}$ ,  $10\text{ Hz}$ ): (a) ( $1200\text{ }\mu\text{m}$  wide) after field removal; (b) ( $150\text{ }\mu\text{m}$  wide) under a field of  $8\text{ V }\mu\text{m}^{-1}$ . Arrows indicate polarizer directions.

small birefringence (about  $\Delta n=0.06$ ). Sometimes a variety of colors can be found, indicating an inhomogeneous birefringence. The interpretation of this texture is not straightforward. As can be seen, the texture exhibits circular domains with extinction brushes rotated  $45^\circ$  with respect to the polarizers direction. This fact rules out the possibility of a simple racemic anticlinic structure ( $\text{SmC}_A P_F$ ). However, the birefringence is smaller than that corresponding to a synclinc state. A possible explanation of this fact could be made in terms of an unbalanced arrangement of chiral domains ( $\text{SmC}_S P_F$ ) of both hands along the sample thickness. In fact, in a first approximation, the birefringence should be smaller since the indicatrix of the adjacent domains of opposite chirality approximately alternate their fast and slow axes due to the proximity of the tilt to  $45^\circ$  [14]. Under this model the sample could be considered, from an optical point of view, as a synclinc structure of smaller birefringence and, therefore, the brushes of the circular domains should appear rotated  $45^\circ$ . The birefringence value must be roughly the enantiomeric excess proportion multiplied by the birefringence of the homochiral structure ( $\Delta n=0.14$ ). The domains with birefringence  $\Delta n=0.06$  should be composed of a proportion of different chiralities 70:30%. The rest of the birefringence colors are explained in a similar way with different proportions. Evidently, in the whole sample both chiralities are bal-

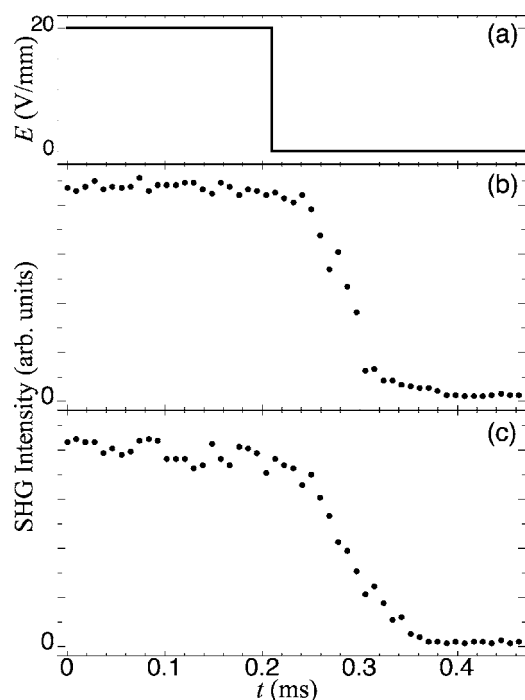


FIG. 4. SHG measurements as a function of time performed under the electric field depicted in (a) at  $10^\circ\text{C}$  below the clearing point. The 90%–10% fall times were obtained for the homochiral ( $130\ \mu\text{s}$ ) and the racemic ( $170\ \mu\text{s}$ ) phases from (b) and (c), respectively. The graphs are adapted to the optimal cell thickness for maximum transmission under field.

anced. A comment must be made regarding the dark state corresponding to this texture. If the proportion of different chiral domains remained after field removal, the optical activity should be about 40% of that of the chiral dark state of Figs. 2(a) and 2(b) and, therefore, gyrotropic domains should be easily observed taking into account our experimental resolution. However, this is not the case since the dark state [Fig. 3(a)] is optically inactive. This fact would imply a reversible field-induced chiral segregation in this material.

The existence of a racemic variant of the optically isotropic state means that the electric field is not able to segregate irreversibly the different chiralities from the (presumably racemic) SmCP initial structure. This behavior contrasts with what we have obtained on cooling the isotropic liquid under field. However, in both cases a dark phase has been induced by the field treatment. An important conclusion can be deduced from these observations: at least in our compound, chirality (supramolecular or conformational) does not play any relevant role in the generation of the dark phases. This is in agreement with the theoretical model of Ref. [29] where chirality is not necessary to induce the curvature of the flat smectic layers. It is not easy to explain why the chiral domains are separated if the field is applied in the isotropic phase. Probably in the isotropic phase there already exist some clusters of molecules with definite supramolecular chirality (cybotactic groups) segregated by the action of the field. However, the chirality segregation is less efficient and reversible if the field is applied to an already condensed racemic mesophase. A possible mechanism driving the chirality segregation was proposed by Pyc *et al.* [32], and is based on the change of chirality of layer regions by molecular ro-

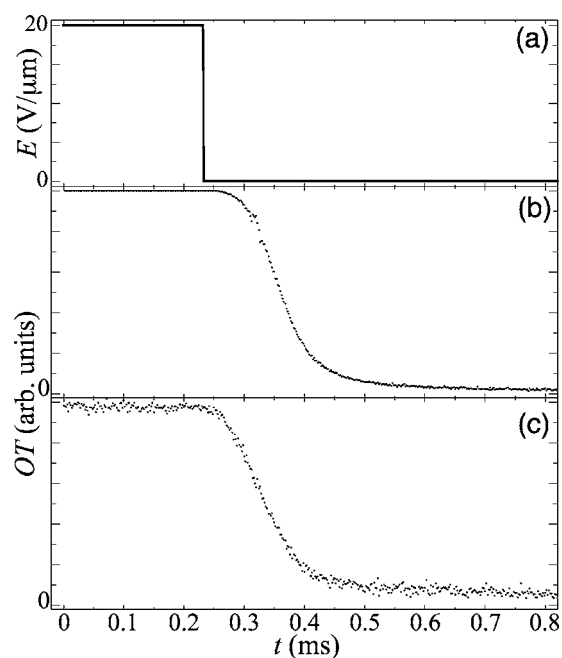


FIG. 5. Optical transmission measurements as a function of time performed under the electric field depicted in (a) at  $10^\circ\text{C}$  below the clearing point. The 90%–10% fall times were obtained for the homochiral ( $130\ \mu\text{s}$ ) and the racemic ( $170\ \mu\text{s}$ ) phases from (b) and (c), respectively. The graphs are adapted to the optimal cell thickness for maximum transmission under field.

tations about their long axes. It seems that in our material this mechanism is completely effective only when the layers are being formed from the isotropic phase. We have found that although the presence of an electric field is necessary to induce the dark phases, once they are formed, remain stable without any sign of relaxation into the normal SmCP phase, at least for time periods about 60 h.

An important point to be clarified in this material is what the structure of the dark phase at a microscopic scale is. According to x-ray measurements the molecules form a tilted lamellar structure [30]. However, determining the type of polar arrangement of the phase (ferroelectric or antiferroelectric) is not trivial due to the distortion of the structure that the material presents at a mesoscopic scale. In this respect, several experimental results pointing to a ferroelectric ground state have been reported up to now but none of them can be considered as conclusive.

A short-pitch ferroelectric helical structure was proposed by Etxebarria *et al.* [14] on the basis of the observation of a deformed helix regime under a triangular-wave electric field. In that work, it was assumed a macroscopic domain size in which the optical isotropy was achieved by averaging the dielectric tensor for all the azimuth angles of the molecular director due to the short pitch proposed for the helix [14]. However, in this compound a racemic variant of the dark phase appears, wherein helical arrangements cannot be justified. Therefore, the isotropic texture shown in Fig. 3(a) cannot be explained assuming a macroscopic domain size.

According to Diez *et al.* [31] the polarization-current response, under a triangular-wave electric field, presents two main peaks per half period, as is the case in an antiferroelec-

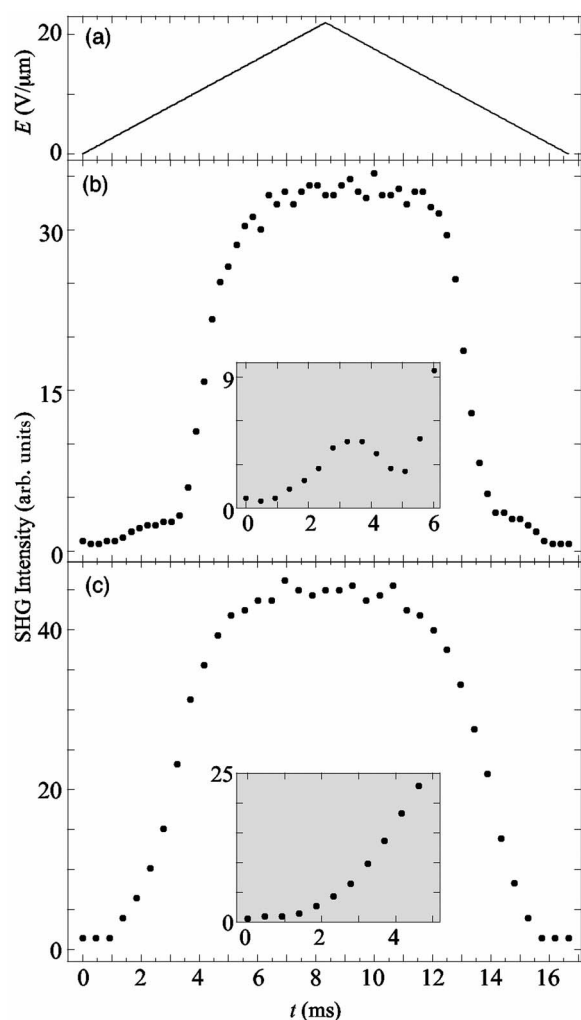


FIG. 6. SHG signal as a function of time performed under the 30 Hz triangular wave field shown in (a) at  $10^\circ\text{C}$  below the isotropic transition, for both (b) homochiral and (c) racemic phases. In the inset (wave amplitude  $12\text{ V }\mu\text{m}^{-1}$ ) the bottom of the main peak is detailed to highlight the anomalous behavior in the homochiral phase (see text). The scale used for SHG intensity is the same in all the graphics.

tric arrangement. The measured value of the polarization is  $900\text{ nC cm}^{-2}$ . However, as also reported in that work, this behavior is in contrast with the high values of the dielectric strength of the dominant mode ( $\Delta\epsilon \approx 70$ ), which suggests a ferroelectric structure. A short-pitch ferroelectric helical structure was also proposed by the authors to make both results compatible. Recently, however, Pociecha *et al.* [33] have shown that an intense dielectric mode (antiphase phason mode) exists in antiferroelectric smectic phases with weak antiferroelectric interaction (such as bent-core liquid crystals) and significant quadrupolar interlayer coupling. In addition, the predicted profile for the dielectric strength of this mode versus bias field is similar to that reported for this compound in Ref. [31].

The assumption that the dark phase is a disordered spongelike phase in which the coherence length of the smectic arrangement is mesoscopic, seems to be compatible with all the experimental observations. However, the dipole ordering

between adjacent layers in the ground state of the structure is not clarified yet. With that purpose, we carried out a comparison study between the switching dynamics of the SHG signal and the light transmission between crossed polarizers. The idea for this study is as follows. It is well known that for typical materials possessing dark phases the characteristic relaxation time to the dark state after the removal of an electric field is much longer than the times involved in the ferroelectric switching [9–11,13,17,18,25]. Therefore, if the phase presented antiferroelectric order, a difference between both characteristic times should arise that, in principle, could be detected. SHG and light transmittance measurements were carried out, after a sudden electric field removal, in order to measure both characteristic times. Measurements were carried out both in the homochiral and racemic variants of the dark phase.

Commercially available (Linkam)  $5\text{ }\mu\text{m}$  thick cells were used to prepare the samples for both experimental techniques. The experimental set-up for SHG measurements has been described elsewhere [34]. The fundamental light was a Nd-YAG laser (wavelength  $1064\text{ }\mu\text{m}$ ) with a pulse width of 6 ns and a frequency of 5 Hz. A periodic stepwise electric field [see Fig. 4(a)], synchronized to the laser trigger, was applied perpendicular to the sample substrates with  $20\text{ V }\mu\text{m}^{-1}$  step amplitude. The relative phase between the trigger of the laser and the electric field at the sample could be shifted in steps of  $0.01^\circ$ . This permits us to determine the dynamic response of the SHG signal. The sample was positioned at an oblique incidence making an angle of  $35^\circ$  with respect to the laser beam. Figures 4(b) and 4(c) show the SHG intensity versus time both for the homochiral and racemic phases, respectively at  $146^\circ\text{C}$ , for the falling part of the step electric field. By monitoring the 90%–10% fall times  $60\text{ }\mu\text{s}$  and  $100\text{ }\mu\text{s}$  were obtained for the homochiral and racemic phases, respectively.

The light transmittance experiments were carried out using a polarization microscope. The light intensity was detected using a photodiode connected to an oscilloscope. Figures 5(b) and 5(c) represent the transmitted intensity versus time under crossed polarizers for the homochiral and racemic phases, respectively, at the same conditions of temperature as in the SHG experiment and under a  $20\text{ V }\mu\text{m}^{-1}$  electric field. Using the same strategy to obtain the fall times, the obtained values were  $130\text{ }\mu\text{s}$  and  $170\text{ }\mu\text{s}$  for the homochiral and racemic phases, respectively. The fall times for both the SHG and transmittance experiment were checked to be independent of the intensity of the applied electric field in all the cases.

According to the results, it can be stated that the material is antiferroelectric in both variants of the dark phase since the fall times characteristic of the SHG measurements are shorter than those of the light transmittance. This fact implies a faster process for the switching from the ferroelectric to the antiferroelectric states than the time required for the structure to relax to the dark state.

It should be pointed out that in this compound the relaxation to the dark state, which implies a layer distortion at a mesoscopic scale, is extremely short in comparison to the standards in bent-core compounds [9–11,13,17,18,25]. Another important conclusion that can be drawn, at least for this

compound, is that the layer distortion characteristic of the dark state is not driven by the escape of the polar order, since the ground state is antiferroelectric. As a consequence it seems reasonable to assume that this distortion is due to steric reasons. However, the threshold electric field that must be applied in the isotropic phase (homochiral case) or the virgin SmCP phase (racemic case) to provoke the dark state can be understood as a promoter that enhances the steric interaction probably due to higher order induced inside the layer.

As a complementary measurement we show in Fig. 6 the SHG intensity for both phases when the material is subjected to a bipolar triangular wave of 30 Hz. The rest of the conditions are the same as in the above SHG measurements. These curves are a measure of the polarization response of the material, since, roughly, the SHG signal should be proportional to the polarization squared. Therefore they can be considered as an alternative to the most common polarization current method [35] for studying the switching dynamics.

Surprisingly, whereas the observations are as expected for the racemic sample, the dynamics in the appearance and disappearance of the SHG signal in the homochiral structure occurs through an unexpected two-step process. The existence of two mechanisms is especially evident [see the inset in Fig. 6(b)] if the applied voltage is not high enough to reach the SHG saturation. [Under the action of the step-wave field the second small hump can also be seen in Fig. 4(b)]. This behavior is perfectly reproducible at different temperatures and illuminating different sample areas. In contrast, the switching of the racemic samples always takes place in a single process. Thus it seems that chirality is in some way involved in the explanation of the difference. One can specu-

late that there should be some structural differences in both dark phases. Evidently, though the proposed models for these phases do not rely on chirality [29], its existence can alter to some extent the resulting structures. To what extent these modifications are important remains an open problem.

### III. CONCLUSIONS

In summary, we have studied a bent-core compound where two types of optically isotropic phases (homochiral and racemic) can be induced by an electric field. The SHG and electrooptic measurements indicate that the local ordering of dipoles in adjacent smectic layers is antiferroelectric in the ground state of both structures. As a conclusion we deduce that the main reasons for the folding of the smectic layers are steric effects. Chirality effects are ruled out, and the field induced polar order can perhaps reinforce the layer distortion since it promotes the separation of incompatible molecular fragments in different sublayers. However, the saddle-splay distortion must be of steric origin. Probably it is due to the mismatch of areas required by the different molecular fragments if they are to be accommodated in flat layers [23,27].

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