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# Electro-disclinic effect in tilted smectic phases of banana-shaped liquid crystal materials

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We give the first evidence that the director tilt angle can be reduced by electric fields in the tilted smectic phase of banana-shaped molecules. In these phases the value of polarization is determined by the molecular packing and no electro-clinic effect is expected. Our studies show that high electric fields eventually induce a meta-stable phase with zero director tilt. The tilted phase slowly recovers at low fields. We propose that the field-induced quenching of the layer fluctuations is responsible for the observed effects.

## 1. Introduction

Chiral smectic  $C^*$  materials [1] are improper ferroelectrics, i.e. the permanent polarization is governed by the director tilt angle, which is the order parameter. Because of this, an external electric field can induce a director tilt which results in a polarization proportional to the field above the  $SmC^*-SmA^*$  transition (electro-clinic effect) [2]. The electro-clinic effect also exists in the  $SmC^*$  phase: an electric field enhances the director tilting, thus increasing the permanent polarization.

The situation is different for the smectic phases of achiral bent-core molecules [3] where the value of polarization is determined by the molecular dipole moments along the two-fold symmetry axis, and by the packing order. Accordingly they are proper ferroelectrics and no electro-clinic effect is expected. Although studies under electric fields have revealed a rich variety of structures and structural transformations [4–6] no evidence for electric field-induced tilt angle change has so far been observed. Here we give the first evidence that the director tilt angle can be reduced by electric fields.

In figure 1 we represent the layer and director structures of the studied B2 banana phase. This is a two-dimensional fluid phase in which the molecules adopt a uniform tilt about the layer polarization, which is determined by the two-fold symmetry axis. Due to the tilt and the polar packing the layers have no reflection symmetry, i.e. they are chiral [4]. Depending on the

relative orientations of the two-fold symmetry axis and the tilt direction, the layers can be right (R), or left (L) handed (see figure 1). The B2 phase is called *racemic* if the chirality in the adjacent layers alternates, figure 1(b); it is called *chiral* if the adjacent layers have the same handedness, figure 1(c) [4]. Most of the known B2 phases have an antiferroelectric (AFE) ground state. Generally the AFE arrangement is soft [6] and can be easily switched to ferroelectric (FE) by applying an external electric field. It is assumed [4] that the chirality of the layers are conserved during the AFE  $\rightarrow$  FE transition. This assumption is generally true for short term application of the fields, although in some cases a gradual transformation of the layer chirality was observed [5, 6]. Very recently an example of a ferroelectric ground state was also found [7].

The AFE racemic B2 phase is synclinic ( $SmC_sP_A$  structure), i.e. the molecules in the adjacent layers tilt in the same direction. The textures of this phase usually consist of fan-shaped domains with fine stripes, the stripes being a few microns in width. Each stripe has synclinic director tilt structure (tilt angle  $\theta$ ), but in the subsequent stripes the tilt direction is opposite. In the FE state an anticlinic structure ( $SmC_aP_F$ ) forms, in which the optic axis is parallel to the layer normal, independent of the sign of the external a.c. field, therefore no electro-optical switching can be observed for square wave fields [4].

In the case of the B2 phase with chiral domains the AFE state is anticlinic and the optic axis is parallel to the layer normal regardless of the handedness of

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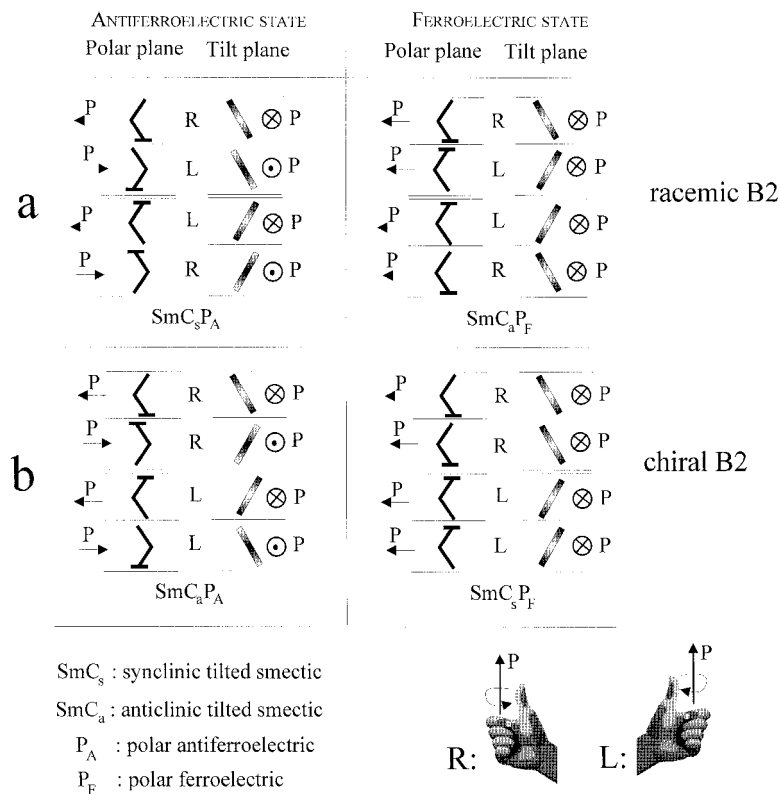


Figure 1. Orthogonal views of the B2 phase of achiral banana-shaped molecules in antiferroelectric (AFE) and ferroelectric (FE) states (left and right columns). The ‘Polar plane’ contains the layer normal and the layer polarization ( $\mathbf{P}$ ), whereas the ‘Tilt plane’ is perpendicular to  $\mathbf{P}$ . The molecular plane is tilted with respect to the layer normal (ends of the molecules with bars are pointing out from the polar plane). The shading of molecules in the tilt plane illustrates the bent shape of the molecules (brighter parts are closer to the reader). During the field-induced AFE  $\rightarrow$  FE transition the layer chirality is assumed to be conserved [4]. R(L) is the chirality descriptor corresponding to Right(Left)-handed layer conformations (a) Racemic B2 phase. The chirality alternates in the adjacent layers. In AFE domains with different tilt directions coexist; this shows as striped fan-shaped domains when observed under a polarizing microscope. (b) Chiral B2 phase. The adjacent layers have the same handedness, but domains of different chirality coexist.

the domains. In the FE state they become synclinic ( $\text{SmC}_s\text{P}_F$ ) and the optic axis makes an angle  $\theta$  with the layer normal. The tilt direction depends on the sign of the electric field, so an electro-optical switching can be observed when a square wave electric field is applied.

## 2. Experimental results

The material studied was 1,3-phenylene bis[3-fluoro-4-*n*-octyloxyphenyliminomethyl)benzoate] (PFBFB) [8], which has a B2 phase between 110 and 161°C. The material was filled in 5  $\mu\text{m}$  ‘EHC’ cells with planar and homeotropic coatings. On cooling from the isotropic to the B2 phase the racemic textures formed, i.e. fan-shaped domains with fine stripes, were seen at zero fields under the polarizing microscope. In figure 2(a) we show the polarization reversal current and the optical response curves obtained by applying square wave fields. The optical signal was measured by a photodiode placed on

the eyepiece of a polarizing microscope. It was observed that, irrespective of the relative orientation of the smectic layer normal and the crossed polarizers, the optical signal was insensitive to the sign of the applied electric field. The peak of the optical signal is very near to the polarization current peak indicating that it is caused by a birefringence change during switching. The temperature dependence of the magnitude of the polarization and the switching time (determined from the peak position of the polarization current) is plotted in figure 2(b). The values are typical for banana-shaped materials [9].

The polarization reversal current measurements revealed that two distinct states S and I could exist depending on the electric field treatment. S stands for ‘stable state’ and was observed at low fields. I stands for ‘induced state’ and was induced by fields greater than  $\mathbf{E}_{\text{th}}$  ( $\mathbf{E}_{\text{th}} = 8 \text{ V } \mu\text{m}^{-1}$  at 150°C and  $\mathbf{E}_{\text{th}} = 8.5 \text{ V } \mu\text{m}^{-1}$  at 145°C). Although I is stable at zero fields, it gradually transfers

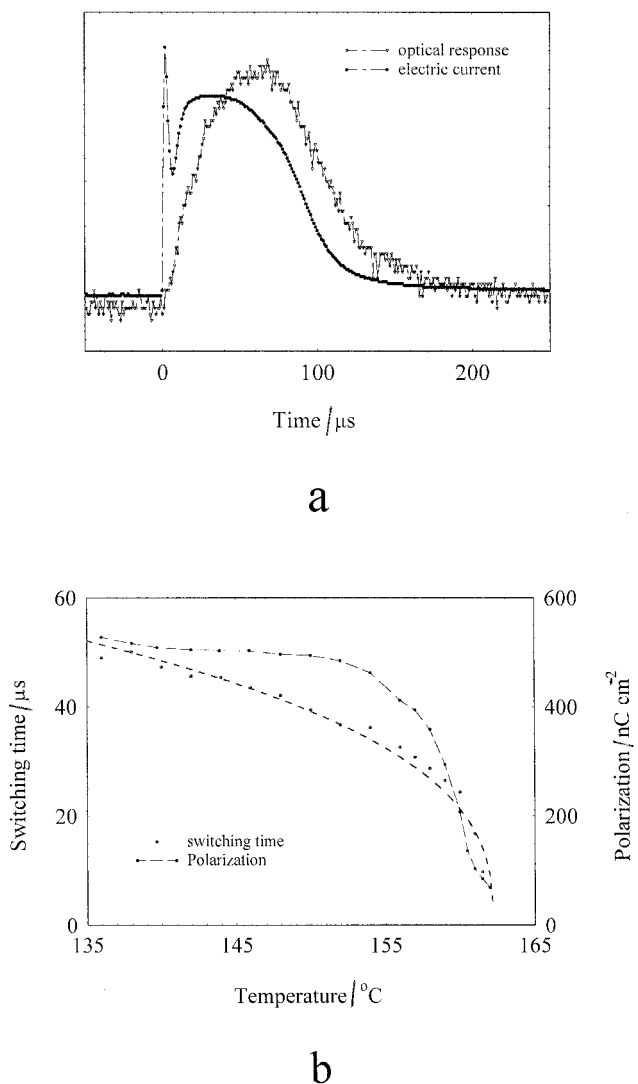


Figure 2. Polarizations and switching times of  $5\ \mu\text{m}$  'EHC' cells of PFBFB with rubbed polyimide substrates. (a) Optical and polarization reversal current responses under field reversals at  $145^{\circ}\text{C}$ . The optical signal was recorded by a photodiode placed in the eyepiece of the polarizing microscope. In the monitored area the smectic layer normal made  $20^{\circ}$  with the polarizer. The optical signal is noisy, because the sensitivity of the microscope was enhanced to emphasize the transient peak occurring due to the birefringence change during switching. (b) Temperature dependence of the spontaneous polarization and of the switching time (as determined by the peak position of the polarization current) under  $6\ \text{V}\ \mu\text{m}^{-1}$  square fields.

back to S in a field range of  $\mathbf{E}_o < \mathbf{E} < \mathbf{E}_{th}$  ( $\mathbf{E}_o$  is the threshold for switching). To monitor this behaviour we made the following measurement. After  $\mathbf{E} > \mathbf{E}_{th}$  square wave field was applied for a minute we decreased the field below  $\mathbf{E}_{th}$ , changed the waveform to triangular, and measured the polarization reversal current curves.

The polarization current curves changed in time as shown in figure 3. Soon after the field treatment the polarization current shows two peaks indicating an AFE  $\rightarrow$  FE switching at  $\mathbf{E}_{FI}$  (F stands for 'forward') and a FE  $\rightarrow$  AFE switching at  $\mathbf{E}_{BI}$  (B stands for 'backward'). In a few minutes, however, the magnitudes of the peaks at  $\mathbf{E}_{FI}$  and  $\mathbf{E}_{BI}$  decrease and additional peaks appear at  $\mathbf{E}_{FS}$  and  $\mathbf{E}_{BS}$ . Eventually the peaks at  $\mathbf{E}_{FI}$  and  $\mathbf{E}_{BI}$  disappear and only two peaks remain at  $\mathbf{E}_{FS}$  and  $\mathbf{E}_{BS}$ . Further, these peaks remain stable as long as no  $\mathbf{E} > \mathbf{E}_{th}$  is applied. However, the same relaxation process repeats when the high field is applied again. The measured polarization is about 10% larger in state I than in state S.

The time dependence of the relaxation processes for different alignment coatings is shown in figure 4. The relaxation process is faster for 'planar' than for 'homeotropic' alignment coatings. In the case of rod-shaped molecules 'planar' surfaces align the molecules parallel to the substrate, whereas 'homeotropic' surfaces align them perpendicular to the substrates. However it is difficult to know how they align bent-core molecules.

Simultaneous microscopic studies showed that in the state I the birefringence is larger than in S. Textures of S are reddish in the FE state corresponding to a birefringence of  $\Delta n \sim 0.10$ , figure 5(a). On removing the field from S, fine stripes are seen between crossed

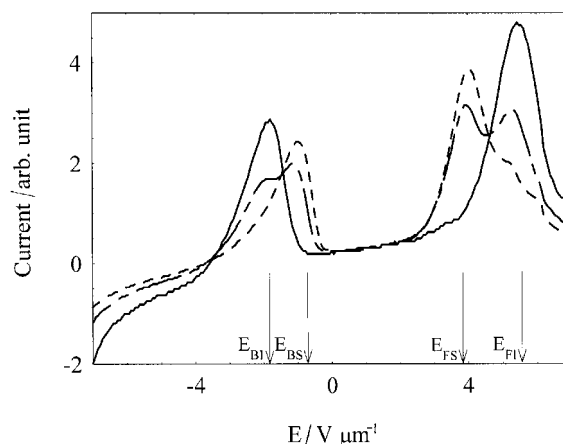


Figure 3. Electric field dependence of the polarization current under  $6.4\ \text{V}\ \mu\text{m}^{-1}$  ( $f = 24\ \text{Hz}$ ) triangular fields after application of  $8.9\ \text{V}\ \mu\text{m}^{-1}$  rectangular fields for 1 min. Induced state (I) (solid line) soon after the high field treatment (peaks at  $\mathbf{E}_{FI}$  and  $\mathbf{E}_{BI}$ ). Mixed state (M) (partly broken line) after 2 min of relaxation; the curve contains four peaks corresponding to  $\mathbf{E}_{FI}$ ,  $\mathbf{E}_{FS}$ ,  $\mathbf{E}_{BI}$  and  $\mathbf{E}_{BS}$ . Stable state (S) (broken line) after more than 10 min of relaxation with two peaks at  $\mathbf{E}_{FS}$  and  $\mathbf{E}_{BS}$ . ( $\mathbf{E}_{FI} = 5.5\ \text{V}\ \mu\text{m}^{-1}$ ,  $\mathbf{E}_{FS} = 4.1\ \text{V}\ \mu\text{m}^{-1}$ ,  $\mathbf{E}_{BI} = -1.65\ \text{V}\ \mu\text{m}^{-1}$  and  $\mathbf{E}_{BS} = -0.75\ \text{V}\ \mu\text{m}^{-1}$ ).

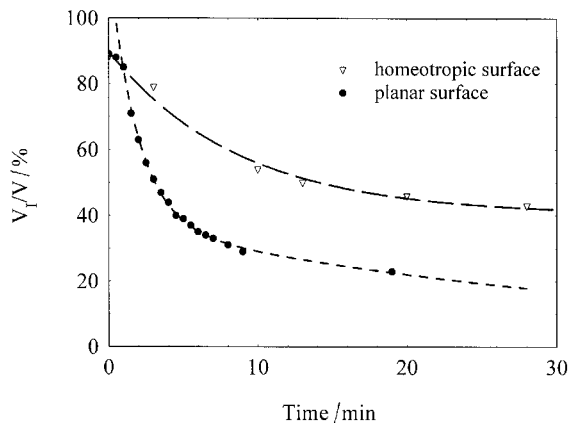


Figure 4. Relaxation of the induced state for PBFOB filled in  $5\ \mu\text{m}$  ‘EHC’ cells with homeotropic and planar alignment coatings. The vertical axis is the relative volume of material in I ( $V_I/V$ ). To determine it we measured  $\mathbf{P}_I/\mathbf{P}$  ( $\mathbf{P}_I$  is determined as the sum of the areas below the polarization current peaks at  $\mathbf{E}_{FI}$  and  $\mathbf{E}_{BI}$ ;  $\mathbf{P}$  is the total polarization) and assume that  $V_I/V = \mathbf{P}_I/\mathbf{P}$ .

polarizers, figure 5(b). Textures of state I are uniformly bluish both in the FE and AFE states, figure 5(c), corresponding to a birefringence of  $\Delta n \sim 0.15$ . It is important that no stripe formation is observed in state I at zero fields, see figure 5(d).

### 3. Discussion

Textures of states I and S are unchanged at field reversal, therefore their structures are certainly not the chiral shown in figure 1(b). The stripe formation of the stable state at zero fields indicates that it is in a racemic B2 state, figure 1(a). In addition, the layers are normal to the plates (bookshelf structure) since both tilt directors are equally possible. The suppression of stripes observed in I may be the result of a layer tilt [10] or it may indicate zero director tilt angle. In a cell where the layers are tilted by an angle  $\alpha$  with respect to the film normal, the polarization  $\mathbf{P}_I$  should be smaller than that in the bookshelf texture ( $\mathbf{P}_o$ ) as  $\mathbf{P}_I = \mathbf{P}_o \cos \alpha$ . In the present case the measured polarization is larger in I than in S with bookshelf texture. Accordingly I also should have a bookshelf structure. In addition, textural observations of I revealed that the extinction directions are parallel to the layer normal both in FE and AFE states, see figure 5(d). For  $\theta > 0$  this would be possible only if the FE state were also anticlinic. But in the FE states  $\Delta n(S) \sim 2/3 \Delta n(I)$ , indicating different tilt angles  $\theta_I$  and  $\theta_S$  in I and S, respectively. For anticlinic phases of rod-

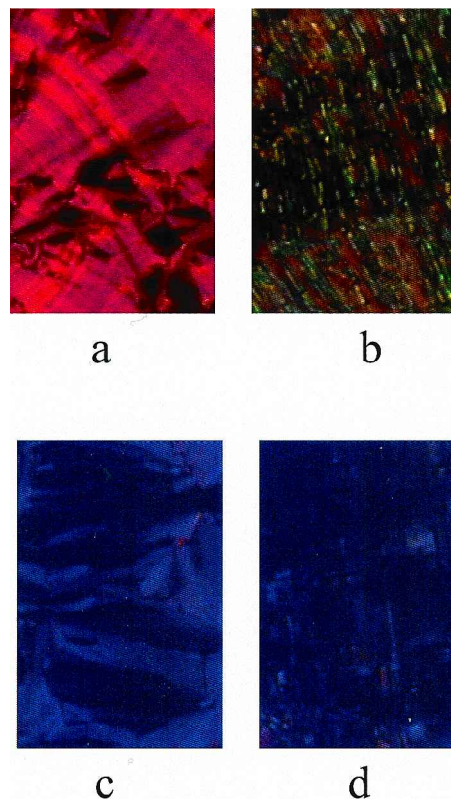
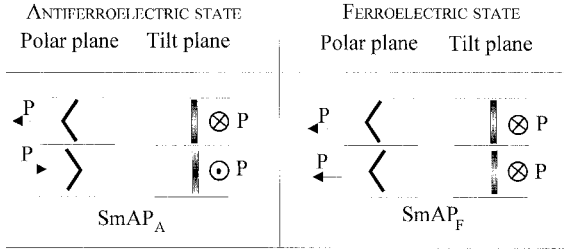


Figure 5. Typical textures between crossed polarizers of the stable (S) and induced (I) states. (a) S in FE structure (at  $6.4\ \text{V}\ \mu\text{m}^{-1}$  square wave fields); (b) S in AFE structure (at zero field); (c) texture of I (induced by  $8.4\ \text{V}\ \mu\text{m}^{-1}$  square wave fields) in the FE state; (d) texture of I in the AFE state ( $E = 0$ ). The pictures represent  $100 \times 150\ \mu\text{m}^2$  areas.

shaped molecules the ratio of the birefringences can be related to the tilt angles by  $\Delta n(S)/\Delta n(I) = \cos 2\theta_S/\cos 2\theta_I$ . Assuming that this approximation holds for bent-shaped molecules, the birefringence values are consistent with tilt angles  $\theta_S \sim 25^\circ$  and  $\theta_I = 0^\circ$ . We deduce therefore that the director tilt angle  $\theta_I$  is zero, i.e. I is a polar biaxial SmA phase with a  $C_{2v}$  symmetry (see figure 6). The antiferroelectric and ferroelectric structures of I can be designated as  $\text{SmAP}_A$  and  $\text{SmAP}_F$ , respectively. The optical axis is uniformly parallel to the layer normal both in the AFE and FE arrangements. The slightly larger polarization in the induced state indicates higher packing order in I than in S.

We propose that the electric field-induced quenching of the layer fluctuations is responsible for this transformation. The mean square fluctuation of the smectic layer spacing can be written as [11]

$$\langle u^2 \rangle_E = \frac{k_B T}{4\pi \sqrt{KB}} \ln \left( \frac{\xi}{l} \right) \quad (1)$$



SmA: non-tilted smectic

Figure 6. Orthogonal views of the proposed structure of the induced state (I) in antiferroelectric (AFE) and ferroelectric (FE) states (left and right columns). The ‘Polar plane’ contains the layer normal and the layer polarization ( $\mathbf{P}$ ). The ‘tilt plane’ is perpendicular to  $\mathbf{P}$  and refers to the plane in which the molecular plane of the stable state (S) was tilted.

where  $\xi = \sqrt{K/PE}$  is the electric correlation length ( $P = 5 \times 10^{-3} \text{ C m}^{-2}$  and  $E_{\text{th}} \sim 0.8 \times 10^7 \text{ V m}^{-1}$ ),  $l \sim 4 \text{ nm}$  is the smectic layer spacing,  $K \sim 10^{-11} \text{ N}$  is the effective elastic constant for director curvature,  $B \sim 10^6 \text{ N m}^{-2}$  is the layer compression modulus and  $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$  is the Boltzmann constant. At zero field the fluctuation is determined by the sample size corresponding to the sample thickness ( $L \sim 5 \times 10^{-6} \text{ m}$ ), i.e. equation (1) is replaced by

$$\langle u^2 \rangle_0 = \frac{k_B T}{4\pi \sqrt{KB}} \ln \left( \frac{L}{l} \right). \quad (2)$$

Inserting the material parameters and the threshold value in equations (1) and (2) we get

$$\sqrt{\langle u^2 \rangle_0} \cong 1 \text{ nm} \quad \text{and} \quad \sqrt{\langle u^2 \rangle_{E_{\text{th}}}} \cong 0.45 \text{ nm} \quad (3)$$

thus more than half of the fluctuations are quenched out by the electric field. Assuming no molecular overlapping of the adjacent layers, the equilibrium layer spacing is determined by the end-to-end distance of the molecules  $m \sim 4 \text{ nm}$ , the director tilt angle  $\theta$ , and by the mean fluctuation as

$$l = m \cos \theta + \sqrt{\langle u^2 \rangle}. \quad (4)$$

The quenching of the layer fluctuations imposes a thinner equilibrium layer spacing, which requires the formation of new layers. As new layers cannot form readily, a dilation stress acts on the layers. It is known that strong mechanical stress can induce a transition from SmC to SmA [12]. We assume that the same also occurs in case of the  $S \rightarrow I$  transition. Assuming constant layer spacing, the tilt angle  $\theta_E$  under electric fields can be calculated from equation (4) as:

$$\cos \theta_E = \cos \theta_s + \frac{\sqrt{\langle u^2 \rangle_0} - \sqrt{\langle u^2 \rangle_E}}{m}. \quad (5)$$

A tilted-to-orthogonal smectic transition occurs when  $\cos \theta_E = 1$ . This gives  $\theta_s \sim 25^\circ$  for the tilt angle of the stable state. This well agrees with the tilt angle determined from the birefringence values. The metastable nature of the induced state can be explained by the gradual layer formation due to the continuous strain acting on the layers. The relaxation process requires formation of new layers, which involves gliding of the molecules at the film surface. It depends on the surface conditions explaining the different relaxation dynamics at different surfaces (see figure 4).

#### 4. Summary

Our studies provide evidence of an electric field-induced metastable state (I). We observed that in I the birefringence, the magnitude of the polarization and the threshold for switching are larger than in S. In addition, the formation of stripes is suppressed after turning off the field from I. These observations indicate that strong electric fields lead to a decrease of the director tilt (electro-disclinic effect). This electro-disclinic effect is completely different in nature from the well-known electro-clinic effect of SmC\* liquid crystals [2], although it should be present even in chiral SmC\* phases resulting in a saturation of the electro-clinic effect at high fields. It also has an effect on the switching mechanism of the banana-shaped materials. According to our model even below the threshold for the S–I transition there should be a decrease of the tilt angle, so the director moves on a narrower cone than of the equilibrium tilt angle. The suppression of the fluctuation can be monitored by X-ray measurement of the gradual decrease of the layer spacing; we intend to carry out such studies. Dielectric measurements may also give extra information about the nature of the observed field-induced state.

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