

Structural study of a bent-core liquid crystal showing the B_1 - B_2 transition

Cesar Luis Folcia and J. Etxebarria

Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

J. Ortega

Departamento de Física Aplicada II, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

M. B. Ros

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain

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An experimental study of the B_1 - B_2 transition is carried out in a bent-core liquid crystal. The study is essentially based on x-ray measurements as a function of temperature. The B_1 - B_2 transition is extremely unusual and implies a deep structural change from a columnar phase to a lamellar phase. We have found that the B_1 phase in our compound is similar to the so-called B_1 reversed phase, with an additional splay of the polarization in the columns. On approaching the B_2 phase the width of the cross section of the columns increases. The transition is clearly first order, with a large hysteresis though the enthalpy content is very small. A possible mechanism for the transition is briefly sketched.

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I. INTRODUCTION

Liquid-crystalline phases formed by bent-core molecules have been the object of intensive research over the last years. At least eight different phases (designated as B_1 - B_8) have been officially identified, though this nomenclature is now being revised and most likely will be changed in the near future. The topic has been object of several review papers [1-5].

Among the eight referred mesophases the most extensively studied is the B_2 phase with all its variants [6] (ferroelectric and antiferroelectric, synclitic and anticlinic) followed by the columnar B_1 phase. In a great amount of material families, with the same core and different terminal chains, it has been found that on increasing the chain length the phase sequence B_6 - B_1 - B_2 takes place [7-9]. The B_2 and B_6 phases are single-layer and intercalated smectics, respectively, whereas the B_1 phase is a smectic-frustrated intermediate structure with a two-dimensional modulation. Accordingly, the above sequence has been roughly explained in terms of the different degree of overlap between cores and chains in the different structures (maximum in the B_6 phase and minimum in the B_2 phase). Usually the materials present only one of the three referred phases though sometimes the B_1 - B_6 dimorphism is also found [10]. However, the B_1 - B_2 dimorphism (both on heating and cooling) has been reported for very few compounds [11-14]. In some cases [13,14] it has been found that a strong electric field applied to the B_1 phase can also induce the transition to B_2 or to another unidentified mesophase [15].

The peculiarity of the B_1 - B_2 transition is not surprising because, in principle, it would suppose a drastic change in the structure of the material from columnar to lamellar. The mechanism of the transition is not evident at all, and thus it seems of interest to analyze this question in some detail. Part of the problem is the structure of the B_1 phase itself. Up to now several models for the molecular arrangement in the B_1

phase have been proposed in the literature [5,16-20]. Probably most of them are correct but, however, several structures with different symmetry groups are being designated under the common name of B_1 . It is then interesting to identify what B_1 phase can give rise to a B_2 phase and how the transition takes place.

In this work we present an experimental study of one the compounds of Ref. [13] around its B_1 - B_2 transition. The investigation is based on x-ray diffraction and textures observation. The chemical structure and phase sequence are shown in Fig. 1. We present an analysis of the B_1 structure as a function of temperature. Based on these results a structural model for the B_1 phase of the compound is proposed, and the character and mechanisms of the transition are discussed.

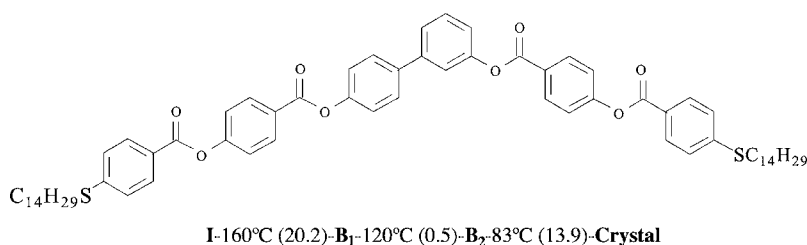
II. EXPERIMENTAL

X-ray measurements were carried out on nonoriented samples by means of a small-angle goniometer with a high-temperature attachment. The materials were introduced in the isotropic phase into Lindeman capillaries of diameter 0.5 mm. The x-ray intensity was detected with a linear position-sensitive detector (PSD) of 4° of angular range.

Monochromatic Cu K_α radiation was used. The electrooptic study was performed through texture observation in the polarizing microscope of samples prepared in commercially available cells (Linkam), of nominal thickness 5 μm . Electric fields of various amplitudes and frequencies were applied, and the birefringence was measured at different regions of the sample with a Berek compensator.

III. RESULTS

X-ray measurements were carried out on cooling from the isotropic phase down to the low-temperature SmC_AP_A phase. Figure 2 represents the small-angle x-ray diagram obtained



at 140 °C. Similar diagrams were obtained for different temperatures in the range 160–130 °C. In all the cases the peaks were indexed on the basis of a rectangular lattice, assigning the (hl) indices shown in Fig. 2. The fact that the lattice is rectangular irrespective of temperature means that its geometry is imposed by the symmetry of the structure, and cannot be a mere accidental situation that is usually temperature dependent. The structure is therefore orthorhombic, and previously reported models [5,15,21,22] displaying monoclinic symmetry, although with rectangular translation lattices, must be discarded for our compound.

The temperature dependence of the observed reflections in the hl reciprocal plane is schematized in Fig. 3. Our results indicate that the reciprocal lattice vector c^* is constant in the whole temperature range of the B_1 phase [the Bragg angle of the (02) reflection does not change]. The cell parameter $c=53.9$ Å. On the other hand, a^* decreases continuously on cooling. The cell parameter a increases from 77.3 Å at 160°C to 90.7 Å at 120°C. The phase transition into the SmC_AP_A phase, whose diffraction diagram is schematized by the solid dots in Fig. 3(c), occurs at about 120°C. The temperature dependence of a , c , and the smectic layer spacing of the SmC_AP_A phase, is represented in Fig. 4. A clear superposition of diffraction peaks from both phases is present at the transition temperature. In principle, even when this fact indicates a discontinuous transition, it could be also originated by a temperature gradient at the sample. The character of the B_1 - SmC_AP_A phase transition will be discussed in the next section.

From our x-ray diagrams the following aspects can be pointed out: the structure presents an orthorhombic symmetry and the (hl) reflection indices satisfy the systematic

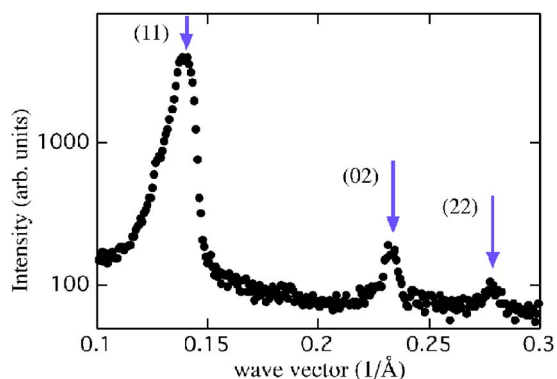


FIG. 2. (Color online) X-ray diffraction intensity as a function of the wave vector $q=4\pi/\lambda \sin \theta_B$, where λ is the wavelength and θ_B is the Bragg angle, for the B_1 phase of the studied material. Three peaks are observed for $\theta_B < 2^\circ$, which were indexed as shown in the figure.

FIG. 1. Chemical structure and phase sequence on cooling of the studied compound. I represents the isotropic phase. The transition enthalpies, in brackets, are expressed in kJ/mol.

extinction rule $h+l=2n$. For nonresonant x-ray measurements, as is our case, the diffraction diagram corresponds to a lattice of columns where the molecules are projected on the lattice plane. Thus, the above extinction rule indicates that the translation lattice is centered. Two different structural models have been proposed to account for these conditions (see Fig. 5). They are antiferroelectric columnar phases with rectangular translation lattices, and have been extensively considered in the literature [16–19,22–24]. In both cases the c parameter is just the molecular length. The first of these models was proposed by Watanabe *et al.* [16] and is normally known simply as B_1 (or conventional B_1) phase [Fig. 5(a)]. The molecules pack in such a way that their dipole moments are parallel to the lattice plane ac . The other model is the B_1 reversed ($B_{1\text{rev}}$) phase [Fig. 5(b)], and was proposed by Szydłowska *et al.* [19]. In this model the dipoles are perpendicular to the translation lattice.

We now analyze both models in more detail in order to decide if they are in agreement with our x-ray diagrams. Concerning the conventional B_1 structure, an important aspect to be pointed out is that the translation lattice of columns is not centered. This is a consequence of the geometry of the cross section of the columns, which are oriented differently at the origin and at the cell center [see Fig. 5(a)]. This situation does not occur in the case of the $B_{1\text{rev}}$ structure, where the lattice of columns is strictly centered, and therefore the structure factor results

$$F(hl) = f_c(hl)[1 + e^{\pi i(h+l)}], \quad (1)$$

where $f_c(hl)$ is the Fourier transform of the charge density of a given column. However, one problem arises: If the structure of Fig. 5(b) is considered, the charge density ρ inside each column should depend only on the z coordinate. This

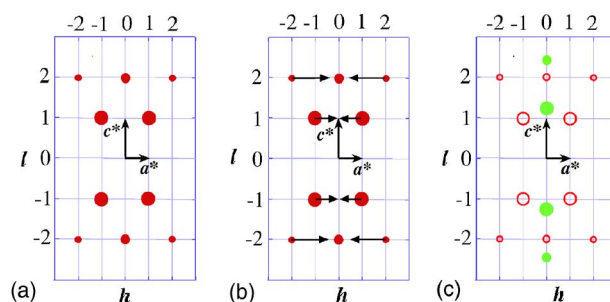


FIG. 3. (Color online) (a) Scheme of the hl reciprocal plane where the observed reflections in the B_1 phase are indicated by dots. (b) On decreasing temperature c^* is constant and a^* diminishes. This trend is represented by the arrows. The solid dots in (c) represent the diffraction diagram of the low-temperature SmC_AP_A phase. The missed reflections are indicated by open circles.

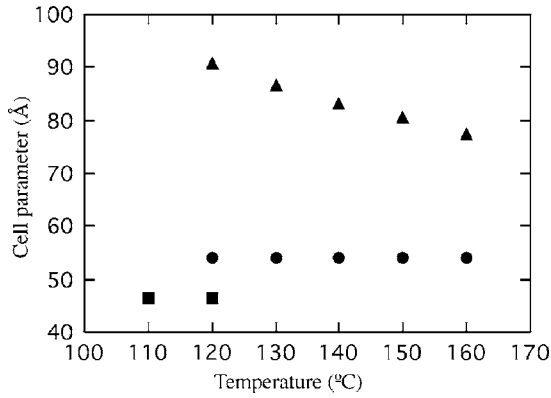


FIG. 4. Temperature dependence of the cell parameters a (triangles) and c (circles) of the B_1 phase, and the smectic layer spacing of the SmC_AP_A phase (squares). A clear coexistence of both phases was detected at the transition temperature.

fact is a consequence of the liquid disorder inside the columns. Thus, since the columns width is just $a/2$, $f_c(hl)$ for a column that extends from x_0 to $x_0 + 1/2$ (in units of a), and z_0 to $z_0 + 1$ (in units of c) is

$$f_c(hl) = \int_{z_0}^{z_0+1} \int_{x_0}^{x_0+1/2} \rho(z) e^{2\pi i(hx+lz)} dx dz$$

$$= \left[\frac{e^{2\pi i h x_0}}{2\pi i h} [e^{\pi i h} - 1] \right] \int_{z_0}^{z_0+1} \rho(z) e^{2\pi i l z} dz, \quad (2)$$

i.e., it is zero for $h=2,4,6,\dots$, and, therefore, the (22) reflection that we observe in our diffraction diagrams should not be present. This inconsistency would imply either a column width different from $a/2$ or an explicit dependence of ρ both on z and x coordinates. This can only occur if there are packing defects (empty regions or superposition of columns), or splay of the polarization at the columns.

In summary, the structural models represented in Fig. 5 do not account for the diffraction diagrams that were obtained in the material under study, and a different model is therefore required. A discussion of different possibilities is presented in the next section.

The x-ray data above were complemented with a study of the optical textures to try to deduce a structural model for the B_1 phase. Figure 6 shows some selected textures obtained under the polarizing microscope. On slow cooling from the isotropic phase, the B_1 phase presents circular domains of purple color ($\Delta n=0.11$) with the extinction brushes parallel

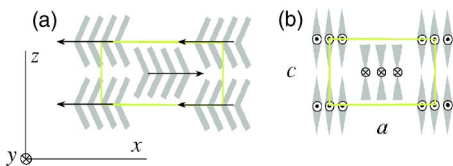


FIG. 5. (Color online) Structural models proposed for the conventional B_1 phase (a) and $B_{1\text{rev}}$ phase (b). The rectangle represents the crystallographic cell, and the arrows indicate the polarization of each column.

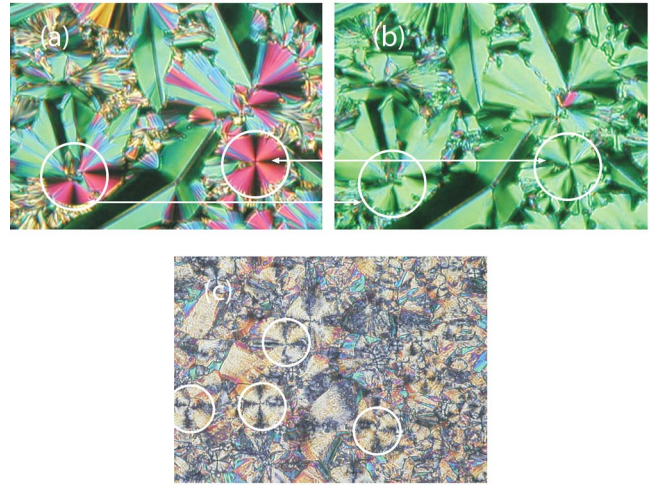


FIG. 6. (Color online) (a) Textures of the studied compound in the columnar phase on slow cooling under no field. The green banana-leaf domains present the maximum birefringence. (b) Under a square-wave electric field of $15 \text{ V } \mu\text{m}^{-1}$ the texture becomes green (with maximum birefringence) as a consequence of the dielectric anisotropy. The extinction brushes of the circular domains (see white circles) remain unaltered and along the polarizer directions. This fact indicates that the structure is nontilted (width of the photographs $200 \mu\text{m}$). (c) Texture of the SmC_AP_A phase obtained on cooling from the virgin columnar phase. The purple circular domains in the columnar phase transform into the yellowish circular domains (see white circles) below the transition. In the latter domains the smectic layers are in a bookshelf disposition with the molecular dipolar moments parallel to the substrates (width of the photograph $300 \mu\text{m}$).

to the polarizer and analyzer directions [Fig. 6(a)]. Some green banana-leaf domains are also visible, with higher birefringence ($\Delta n=0.16$). If a square-wave electric field of frequency 100 Hz and amplitude $15 \text{ V}/\mu\text{m}$ is applied, the purple domains change their color into green ($\Delta n=0.16$) but the extinction directions are maintained [Fig. 6(b)]. With still larger fields ($>25 \text{ V}/\mu\text{m}$) the transition to B_2 takes place, and circular domains of green color ($\Delta n=0.16$) with extinction directions at about 45° appear (not shown in the figure) [13]. These domains are not correlated with any other domain in the B_1 phase. At lower temperatures, this material presents a B_2 ground state that under field exhibits the same texture than the B_2 phase obtained from B_1 by application of a strong field. On terminating the field, the green circular domains in the B_2 phase transform into gray color ($\Delta n < 0.02$) with vertical and horizontal extinction directions (not shown in Fig. 6) [13]. This clearly means that the B_2 phase is SmC_AP_A without field and SmC_5P_F under field. Finally, if the B_1 phase is cooled down without any field the shape of the purple domains and the extinction directions are maintained in the smectic phase, but present now a yellowish white color [Fig. 6(c)], with a birefringence $\Delta n=0.06$.

IV. DISCUSSION

Now it is interesting to comment the experimental results described above in order to explain the structure of the co-

lumnar phase. According to the texture observations, some important conclusions can be drawn: The birefringence of the SmC_SP_F is the same as that of the banana-leaf domains [Fig. 6(a)], or the green circular domains under field in the columnar phase [Fig. 6(b)]. This fact implies that the structure of the green domains in the columnar phase is synclinal with the molecular dipole moments perpendicular to the substrate, as is the case in the SmC_SP_F structure. Therefore, as the extinction brushes of the green circular domains in Fig. 6(b) are parallel to the polarizers, the structure must be nontilted.

This conclusion is compatible with the orthorhombic symmetry deduced from the x-ray measurements. However, one point deserves some comment. The value of the c parameter obtained for this phase is not compatible with a nontilted structure in which the molecules are in the most extended configuration (the calculated molecular length is about 15% larger than c). This fact is in contrast with what is usual in banana-type mesophases, where the smectic and molecular lengths are usually compatible with the tilt. There are two possible explanations to this discrepancy: interdigitation or terminal chain disorder [25]. In both cases a reduction of the effective chain length takes place, which would allow the core-core interaction between adjacent ribbons to compete with the core-chain segregation tendency. This interaction competition is believed to be essential for the existence of columnar phases [7,26]. In fact, Shen *et al.* [7] studied the phase sequences of a family of compounds with the same core as the compound of the present work and found that in compounds with alkoxy terminal chains the columnar phases were present up to 11 carbon atoms. In addition, in that work, an increasing mismatch between the molecular length and c parameter was observed as the number of carbon atoms in the terminal chain increases. This fact would also imply interdigitation or chain disorder. In our compound the terminal chain is longer (14 carbon atoms), and therefore, this effect is expected to be much more pronounced.

The study of the temperature dependence of the columnar phase as the transition is approached can be also helpful for the understanding of the columnar phase structure. Two experimental aspects should be pointed out.

(1) According to DSC results the phase transition is weakly first order but definitely discontinuous. This conclusion is based on the existence of a small but non-null transition enthalpy (0.5 kJ/mol) and rather remarkable transition-temperature hysteresis ($\Delta T=10$ °C). Both values have been obtained from the extrapolation to zero deduced from different heating and cooling rates. However, the transition enthalpy is quite small for bent-core liquid-crystal standards. This fact indicates that the energy cost for the phase transition must be low and therefore the molecular rearrangement that takes place in the process must not be very drastic. This point is especially important in this case since the high-temperature mesophase is nontilted whereas the SmC_AP_A presents a tilt of 42°. The order of magnitude of the enthalpy cost for the tilting process can be estimated from the results obtained by Wirth *et al.* [27] in several banana compounds in a first-order transition $\text{Sm}_A\text{-Sm}_C$. In all cases the obtained enthalpies have the same order of magnitude than that of the transition in our compound. This fact implies that the process

of layer formation at the transition cannot take place with large energy requirements.

(2) The length of the lattice vector \mathbf{a} increases as the temperature approaches the transition. This effect could be considered as a trend of the phase towards the SmC_AP_A structure. This point can be easily understood if we consider the smectic phase as a limit case of the columnar one in which the lattice vector \mathbf{a} becomes infinite. This behavior has been also observed in other compounds presenting phase transitions from two-dimensional (2D) undulated structures to SmCP lamellar phases [20,28,29].

As stated above, the columnar phase is orthorhombic, nontilted and, for nonresonant x-rays, centered. Additionally, this phase has been reported to be antiferroelectric [13]. A ferroelectric ground state can be excluded because no second-harmonic generation can be observed in the material under no field. Figure 7(a) represents a proposed structure compatible with all those experimental features. In this model a splay of the polarization is incorporated which would allow for the existence of the x-ray reflection (22) (for simplicity in the figure a splay that implies a 180° rotation of the dipole moments between the edges of the column has been drawn but a weaker splay is more likely). The existence of splay of the polarization in columnar phases has also been proposed by Coleman *et al.* [20]. As can be seen, the dipole moment distribution in adjacent ribbons implies a frustrated lamellar phase. Under this model the ribbon cross sections will elongate as the temperature decreases, up to a maximum length at which the columnar phase becomes unstable. At this point, half of the ribbons undergo a displacement of $c/2$ along the z direction with respect to the others to form the SmC_AP_A phase. Although it is impossible to determine the polarization in adjacent ribbons by common x-ray experiments, the proposed structure implies a less dramatic molecular rearrangement at the transition than other possibilities.

Figure 7(b) represents a scheme of the proposed structure where the symmetry elements are indicated. The layer group referred to the setting (x,y,z) indicated in the figure is ρmca (layer group No. 45 [30]). The yellow rectangle is the same crystallographic cell as in Fig 7(a). The cell parameter along z is twice the cell parameter c obtained from the x-ray measurements. Since experimentally we cannot distinguish the polarization direction of the ribbons, the lattice of columns appears as rectangular centered with lattice parameters a and c .

A final remark can be made regarding the different types of domains that the texture of the columnar phase exhibits. Figure 8 shows the most often found types of domains. As can be seen, the green domains are leaf-shaped whereas the purple ones are always circular with the extinction brushes parallel to the polarizers. As reported in Ref. [13], considering the molecule as formed by two uniaxial wings that form a bending angle of about 120°, with ordinary and extraordinary indices, respectively, $n_o=1.5$, $n_e=1.7$, the birefringence of both types of domains can be quantitatively explained. In the banana-leaf domains the birefringence is consistent with an orientation of the dipolar moments perpendicular to the substrate whereas in the purple domains, the molecules are in planar disposition with the dipolar moments parallel to the

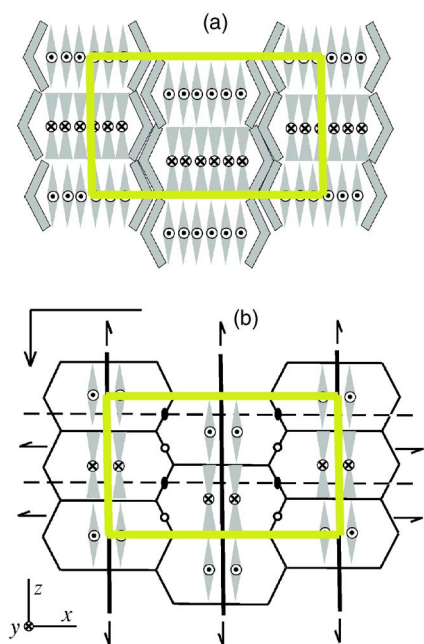


FIG. 7. (Color online) (a) Schematic structure for the columnar phase of the studied compound. The structure is a rectangular non-tilted phase with splay of the polarization inside the columns (for simplicity in the figure a splay that implies a 180° rotation of the dipole moments between the edges of the column has been drawn but this extreme is not a requirement and a weaker splay is expected). The dipolar moment disposition in adjacent layers can be understood as a frustration of a lamellar phase. (b) Schematic representation of the symmetry elements of the structure. The corresponding layer group is $pmca$.

glass surfaces. Under this scheme the correlation between molecular orientation and domain shape can be explained on the basis of the structural model proposed for this phase. The situation is sketched in Fig. 8. In the banana-leaf domains the column axes are perpendicular to the substrate. Therefore this orientation of the columns prevents the structure from forming circular domains. In contrast, in the purple domains the columnar axes are parallel to the substrate allowing the domains to grow in circular shape to minimize the energy of the domain walls. The molecular disposition in the circular domains is also in agreement with the texture that they present in the $SmC_A P_A$ phase. As shown in Fig. 6(c), on cooling from the columnar phase without field down to the $SmC_A P_A$ structure, the circular domains remain but they present now a yellowish color with smaller birefringence $\Delta n=0.06$. This value is consistent with a planar domain wherein the molecules are oriented with the dipole moments parallel to the substrate, as is the case in those domains in the parent phase. In fact, under the birefringence calculation scheme explained above and using the same parameters together with the corresponding tilt of the $SmC_A P_A$ phase (42°), a very good agreement is obtained also for the birefringence of the yellowish domains (calculated birefringence $\Delta n=0.06$).

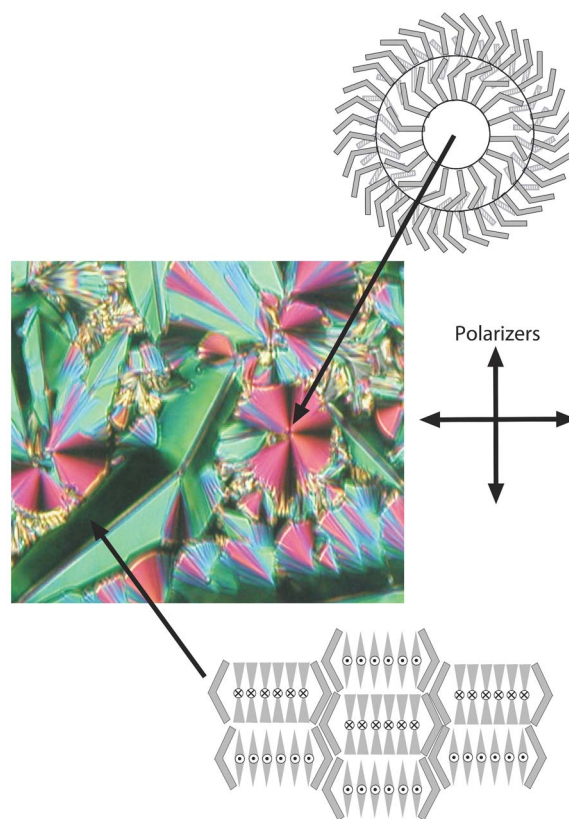


FIG. 8. (Color online) The most representative types of domains in the columnar phase. This texture is obtained on slow cooling from the isotropic phase under no field. The molecular disposition in the banana-leaf and circular domains appears schematized in the figure. The width of the photograph is $150 \mu m$.

In summary, we have studied a columnar to smectic transition by means of x-ray measurements as a function of the temperature. The columnar structure is similar to the B_{1rev} phase with the addition of some splay of the polarization. On decreasing the temperature the length of the columns cross section increases and, at the transition point, a displacement of the molecules along the layer normal in every second column takes place. The transition is clearly first order though the enthalpy content is surprisingly small. It would be interesting to carry out studies in other materials to confirm whether this transitional behavior is general in the columnar to $SmCP$ transition or not. Unfortunately, very few materials exhibiting this kind of phase transition have been reported and, apart from the present work, studies of the evolution of the structure with the temperature are scarce.

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