

## Interpretation of unusual textures in the $B_2$ phase of a liquid crystal composed of bent-core molecules

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A liquid crystal material of bent-core molecules is investigated by means of optical texture observations, x-ray measurements, and miscibility studies. While the x-ray and miscibility data point towards a  $B_2$  phase, the texture is however unusual, showing optical isotropy and segregation in two domains with opposite gyrations. It is shown that the texture can be interpreted successfully in terms of a smectic- $C_A P_A$  structure in small domains with random orientations. The optical activity data are also explained semiquantitatively.

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### I. INTRODUCTION

Liquid crystals composed of bent-core molecules are the subject of extensive investigation during the last years [1–3]. However, many basic features remain still obscure in these compounds. In particular, the phase assignment when based exclusively on the similarity of optical textures is quite problematic since, in general, the textures are not characteristic of one mesophase. For example, the  $B_7$  phase defects (telephone-wire-like structures, spirals, ribbons) have been observed in several other cases which definitely are not  $B_7$  [4–7]. One then must resort to more cumbersome techniques such as x-ray measurements or miscibility studies to properly assign the type of mesophase.

One peculiar texture that has recently appeared in this kind of materials with certain frequency is an optically isotropic texture [8–15], sometimes with gyrotropic domains of opposite handedness. The texture resembles (except for the blue color) that of the  $B_4$  phase and has been assigned to phase with unknown structures and with different names such as smectic-1,  $B_{X1}$  or smectic- $X$ . Here, we present a material with this kind of texture. We will show that in this case x-ray and miscibility data are consistent with a  $B_2$  phase with the smectic- $C_A P_A$  ( $Sm-C_A P_A$ ) structure. Assuming this structure, we will also give a semiquantitative interpretation of the observed texture.

### II. RESULTS

The compound here studied is part of a series of new bent-shaped materials designed for nonlinear optics. Its preliminary characterization (see Fig. 1) has been recently reported [16], where it was named as CH<sub>2</sub>C2. Its synthesis will be published elsewhere.

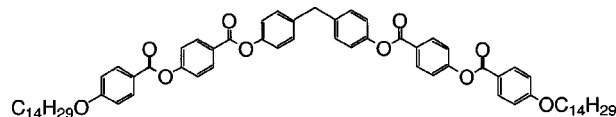
The differential scanning calorimetry data indicate two transitions. The observation of the optical textures was carried out in commercial cells (Linkam) of 5  $\mu\text{m}$  of thickness. On cooling from the isotropic phase and in the absence of any electric field, an optically isotropic texture different from the isotropic liquid appears at 162 °C. The texture is easily noticed if the analyzer is rotated a few degrees from the

crossed position. In these conditions, two domains without birefringence but with opposite optical rotations are clearly detected (Fig. 2). The color of the domains is interchanged if the direction of rotation of the analyzer is inverted. The material is quite transparent and within each gyrotropic domain the texture is very uniform. Although this texture is not conventional for the  $B_2$  phase, we consider that this is, in fact, the structure of the phase. This identification is based on the following facts.

(i) X-ray patterns present sharp inner reflections (up to third order) and an outer broad reflection, which are perfectly consistent with the  $B_2$  phase. The layer spacing deduced from these data is  $d=4.62$  nm, which means a tilt angle of 44.7° for a theoretical molecular length of 6.50 nm. Within each layer there is a liquid disorder with an average intralayer molecular distance of 0.47 nm.

(ii) Upon application of an electric field (of the order of several tens of V/ $\mu\text{m}$ ) a brilliant grainy texture appears which is typical of the  $B_2$  phase (Fig. 3). When the field is removed the initial dark texture is reestablished with a certain relaxation time (from 1 s to several hours depending on temperature and field strength).

(iii) Miscibility studies with the conventional bent-core mesogen 12-OPIMB (which presents a  $B_2$  phase between 170 °C and 97 °C) [17] indicate that both mesophases are well miscible for all the range of concentrations (Fig. 4). This means that the symmetry of the phases is the same for both materials. The analyzed texture was mainly observed



Crystal-110 °C- $B_2$ -162 °C-Iso

FIG. 1. Chemical structure and phase sequence of the studied material.

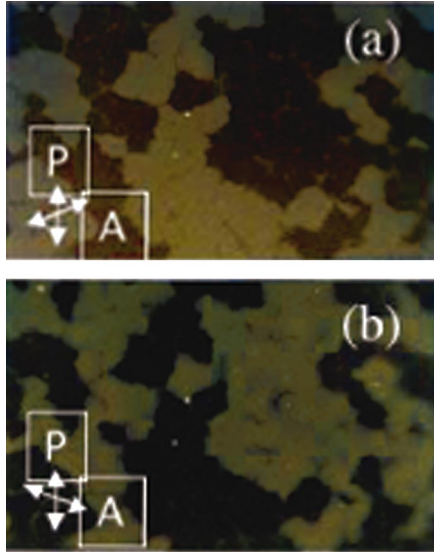


FIG. 2. (Color) Texture of the  $B_2$  phase with the polarizers slightly uncrossed. The phase is optically isotropic and presents domains with opposite optical activity. Figures (a) and (b) correspond to opposite rotations of the analyzer with respect to the crossed position. The texture is black for the crossed-polarizer's position and both chirality domains are no longer distinguishable. The width of the photographs corresponds to 500  $\mu\text{m}$ .

for those blends enriched in  $\text{CH}_2\text{C}_2$ .

(iv) Finally, on heating from the crystal phase, the texture is birefringent and looks more conventional for the  $B_2$  phase. The initial dark texture is only recovered if the material is heated above the clearing point.

### III. DISCUSSION

We now turn to interpret the optical textures. The first point is the appearance of optical isotropy in the  $B_2$  phase. One simple way to give account of this fact is to propose that the  $B_2$  phase is composed of very small domains almost isotropic and oriented at random [Fig. 5(a)]. The small birefringence of the domains can be explained assuming an anticlinic arrangement. The bent-shaped molecules are considered as formed by two optically uniaxial wings making an angle  $\beta$  and with refractive indices  $n_e$  and  $n_o$  [Fig. 5(b)]. The principal refractive indices can then be easily calculated by averaging the contribution of the molecular wings in the  $\text{Sm-C}_A P_A$  configuration. The result is

$$\begin{aligned} n_x^2 &= n_o^2 + (n_e^2 - n_o^2) \sin^2 \theta \sin^2 \frac{\beta}{2}, \\ n_y^2 &= \frac{1}{2} [n_e^2 + n_o^2 + (n_e^2 - n_o^2) \cos \beta], \\ n_z^2 &= n_o^2 + (n_e^2 - n_o^2) \cos^2 \theta \sin^2 \frac{\beta}{2}, \end{aligned} \quad (1)$$

where  $\theta$  is the molecular tilt angle [Fig. 5(c)]. For typical values  $n_e = 1.64$ ,  $n_o = 1.50$ ,  $\beta = 120^\circ$ , and  $\theta = 45^\circ$ , we obtain

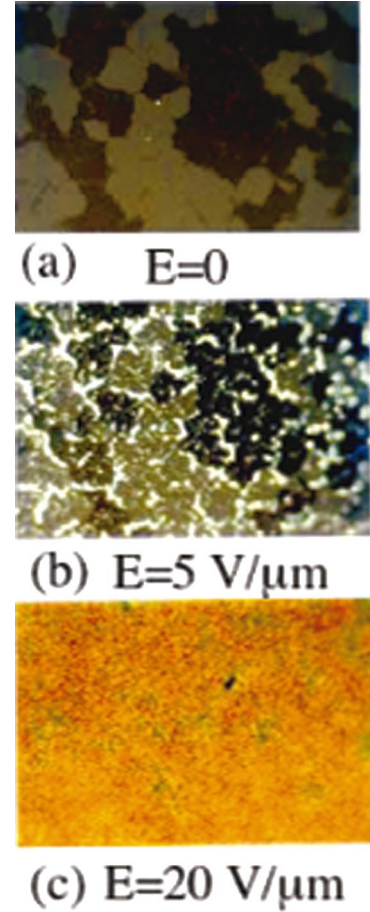


FIG. 3. (Color) Field-induced texture change in the  $B_2$  phase. (a) Without field the material is isotropic and exhibits optical activity. (b) Above a threshold field of 5  $\text{V}/\mu\text{m}$  a grainy brilliant texture appears. (c) At 20  $\text{V}/\mu\text{m}$ , the whole sample shows the grainy brilliant texture. The brightness of the small domains is due to the high birefringence of the synclinic molecular arrangement that they present under the electric field. The width of the photographs corresponds to 500  $\mu\text{m}$ .

$n_x = 1.554$ ,  $n_y = 1.536$ ,  $n_z = 1.554$ . As can be seen, the birefringence along any direction is about 0.01 or less. This fact added to the small size of the domains and their random orientation gives rise to a nearly perfect isotropy of the material.

On the other hand, the material shows optical rotation and, experimentally, we have measured a rotatory power  $\rho = 50^\circ/\text{mm}$  at  $\lambda = 633 \text{ nm}$ . As will be shown below, this result can be explained as due to the helicoidal structure shown in Fig. 6.

The helix is described by the optical dielectric ellipsoid associated with the wings of the bent-core molecules in the proposed configuration. This helix is always present in a  $\text{Sm-C}_A P_A$  structure irrespective of the existence of an incommensurate helix of larger pitch as in a normal  $\text{Sm-C}^*$  phase. Here, the pitch is always small and equal to twice the smectic layer spacing.

Having this helix in mind, the optical rotation can be explained by using the so-called homogeneous optical model for short-pitch materials [18,19]. The model is easily de-

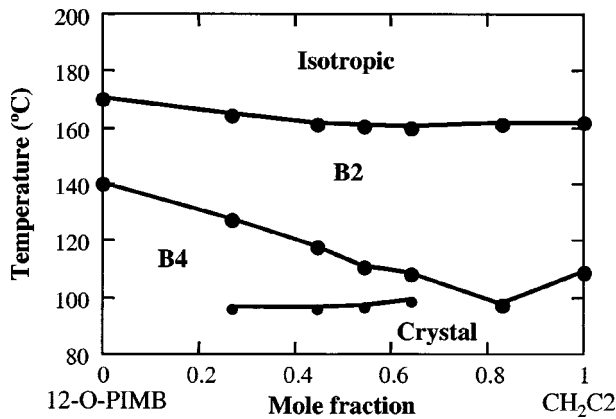


FIG. 4. Binary phase diagram between compound 12-*O*-PIMB and the compound studied in this work (data taken from the cooling processes). As can be appreciated the phase below the clearing point of the present compound is miscible with the  $B_2$  phase of 12-*O*-PIMB for any concentration.

scribed in the case of a regular helix of homogeneously tilted molecules. In this situation, it can be shown that an optical medium where the optical dielectric tensor varies in a short-pitch helicoidal fashion behaves as a uniaxial crystal with the optic axis along the helix axis and with non-null optical activity. This approach is valid whenever the pitch is much smaller than the optical wavelength.

The anisotropy in the refractive indices is not visible in our case because of the averaging mentioned above and will not be considered here. On the other hand, with reference to

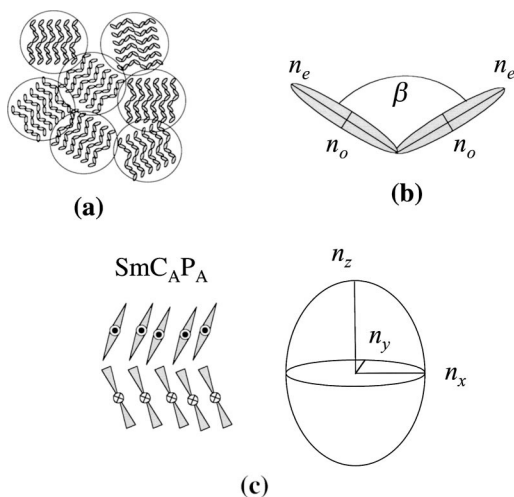


FIG. 5. Schematic representation of the optically isotropic  $B_2$  phase of the compound. (a) The material is formed of very small domains randomly oriented that present a Sm- $C_A P_A$  structure. For simplicity, a random planar distribution is represented in the figure, but it should be understood as a truly uniform distribution in the three space dimensions. (b) The birefringence of each domain can be estimated assuming that the molecules are composed of two uniaxial wings making an angle  $\beta$  and with refractive indices  $n_e$  and  $n_o$ . (c) The principal refractive indices of the index ellipsoid are obtained by averaging the contribution of the four uniaxial wings in the Sm- $C_A P_A$  structure.

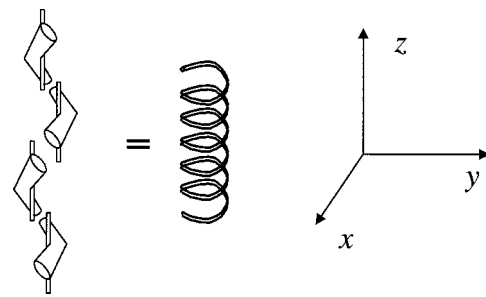


FIG. 6. Helicoidal arrangement described by the molecular wings of the bent-core molecules in the homochiral antiferroelectric configuration. These helices are the origin of the optical activity exhibited by this material.

the coordinate system of Fig. 6, the gyrotropic tensor is given by

$$g = \begin{pmatrix} g_{\perp} & 0 & 0 \\ 0 & g_{\perp} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (2)$$

where  $g_{\perp}$  is expressed as [18]

$$g_{\perp} = -\frac{p}{\lambda} \frac{(n_e^2 - n_o^2)^2}{8\bar{n}^2} \sin^2 2\alpha \quad (3)$$

in terms of the pitch  $p$ , the wavelength in vacuum  $\lambda$ , the angle  $\alpha$  between the helix axis and the wings of the molecule, and the average refractive index  $\bar{n}$ .

The form of the gyrotropic tensor [Eq. (2)] indicates there is no optical activity along the  $z$  axis (helix axis) and, in contrast, the gyrotropy is maximal along any direction per-

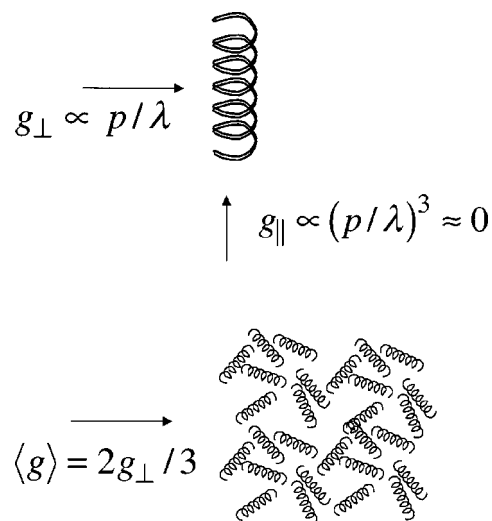


FIG. 7. Gyrotropic tensor for a short-pitch material according to the homogeneous optical model. The optical activity along any direction perpendicular to the helix axis scales as  $p/\lambda$ . The gyrotropy along the helix axis scales as  $(p/\lambda)^3$  and is not observable for  $p \ll \lambda$ . The random orientation of the helicoidal arrangements of the small domains in the  $B_2$  phase represented in the figure, gives rise to an averaged optical activity.

pendicular to  $z$ , with magnitude  $g_{\perp}$ . The lack of optical activity along  $z$  ( $g_{\parallel}=0$ ) is, in principle, surprising because, according to the de Vries formula, gyrations along this direction are very important in other materials. However, it can be checked that  $g_{\parallel}$  scales as  $(p/\lambda)^3$  and is negligible for all practical purposes for  $p < \lambda/5$ .

The effect of the random orientation of the domains in the optical activity is to average this quantity, but now this averaging does not have a cancellation effect as happens with the birefringence (Fig. 7). Using Eq. (2), it is easily shown that the optical rotation per unit length in our sample is simply given by

$$\rho = \frac{2}{3} \frac{\pi g_{\perp}}{\lambda}, \quad (4)$$

Taking  $\alpha=45^{\circ}$ ,  $n_e=1.64$ , and  $n_o=1.50$ , Eqs. (3) and (4) yield  $p \sim 16$  nm for the experimental value of  $\rho$ . This  $p$  value is comparable to  $2d \sim 9$  nm from the x-rays results. Therefore, as can be seen, the gyrations deduced from the model are correct at least at the level of orders of magnitude. This idea about the origin of the gyrotropy can thus be extended, in general, to all homochiral  $B_2$  structures. Further contribu-

tions to the gyration from macroscopic helices are probably negligible, since most materials are approximately uniaxial at the mesoscopic scale. Normally, the gyration effect cannot be observed on the microscope because it coexists with macroscopic birefringence. The studied compound is, in this sense, an exceptional case.

Finally, a few words about the effects of the electric field on the texture. If the electric-field magnitude is above a certain threshold there is a transformation from the Sm- $C_A P_A$  to the Sm- $C_S P_F$  structure, which is highly birefringent. This gives rise to a brilliant grainy texture with a small size of grain oriented at random (the texture as a whole does not show an extinction direction) and without observable optical activity. These characteristics are in fact experimentally verified.

#### ACKNOWLEDGMENTS

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