PHYSICAL REVIEW E **67**, 042702 (2003)

Induction of ferroelectricity in the B_2 phase of a liquid crystal composed of achiral bent-core molecules

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(Received 13 November 2002; published 29 April 2003)

We report the observation of a transition from the antiferroelectric B_2 phase to a ferroelectric phase in a liquid crystal composed of achiral bent-core (banana-shaped) molecules. The transition is induced by an electric field of magnitude larger than the switching threshold and is not reversible, i.e., the original B_2 phase does not reappear upon field removal. The transformation is accompanied by a dramatic texture change, resulting in an almost optically isotropic structure in the absence of field. The ferroelectric character assigned to the structure is based on the electro-optic behavior of the material and on previously reported dielectric measurements. A short-pitch smectic-C^*-type structure is proposed for the ferroelectric phase.

DOI: 10.1103/PhysRevE.67.042702 PACS number(s): 64.70.Md

Liquid crystals composed of bent-core (banana-shaped) molecules have become an important subfield in the investigation of mesogenic compounds [1–3]. These materials give rise to phases that have specific peculiarities, rather different from the liquid crystal compounds formed by normal rodlike molecules. In particular, chiral and polar phases can be achieved with achiral molecules of this kind, and some of these phases present ferro- or antiferroelectric switching. An interesting question in this respect is the fact that to date the overwhelming majority of banana-shaped mesogens display antiferrolectricity, while there are very few cases showing ferroelectric ordering [4–7]. Here we present an example of a ferroelectric material composed of achiral molecules. In contrast to the materials reported up to now, the compound has an interesting peculiarity. As we will see, the ferroelectricity is not a completely intrinsic property in the investigated material, but is achieved via electric field induction through a phenomenon called ‘‘learning of ferrolectricity’’ [8] recently discovered in some calamitic antiferroelectric compounds.

The chemical structure of the studied material appears in Fig. 1. It is an asymmetric bent-core molecule whose synthesis has already been published together with a preliminary characterization of the different phases of the material [9]. Our differential scanning calorimetry and x-ray data confirm essentially the phase sequence reported before. The identification of the mesophase as B_2 is based on texture observations on the polarizing microscope (Fig. 2) and x-ray diffraction patterns, which present sharp inner reflections (up to third order) and an outer broad reflection. The layer spacing obtained from these data is $d=4.25$ nm, which means a tilt angle close to $\theta=45°$ for a theoretical molecular length of 6.3 nm deduced for an all-*trans* molecular conformation.

Upon application of a strong electric field (>10 V/μm) and its subsequent removal, the B_2 texture undergoes a large modification: the material becomes dark gray between crossed polarizers, indicating a transition to an almost optically isotropic state. A similar transformation has been observed in another B_2 compound by Bedel *et al.* [10]. The textural change is even more dramatic if the material is subjected to the electric field during the cooling process from the isotropic phase. In this case, when the field is suppressed the texture is almost perfectly black between crossed polarizers. In addition, if the analyzer is rotated a few degrees from the crossed position, two domains without birefringence but with opposite optical rotation are clearly detected (Fig. 3). This texture resembles (except for the color) the typical one of the B_4 phase [11] or the smectic-1 (Sm1) phase described in Ref. [12]. The material is quite transparent and, within each gyrotropic domain, the texture is rather uniform. If the field is applied after having reached the B_2 phase the presence of the gyrotropic domains is hardly evidenced, which suggests that the macroscopic chiral segregation induced by the electric field is efficient only when the smectic layers are being formed, i.e., at the isotropic-polar phase transition. In any case, the dark texture is stable after the field treatment (at least for several days) and the original one (Fig. 2) can be recovered only by heating the material up to the isotropic phase and cooling down again.

Now we will try to interpret these observations. First of all, the existence of gyrotropy together with the almost isotropy of the material strongly points toward the presence of helicoidal arrangements in the structure. We show next that, given the usual tilts and molecular bend angles in these materials, the birefringence can average out almost to zero on the hypothesis of a short-pitch structural helix.

We consider the bent-core molecule as formed by two optically uniaxial parts making an angle β, the angle

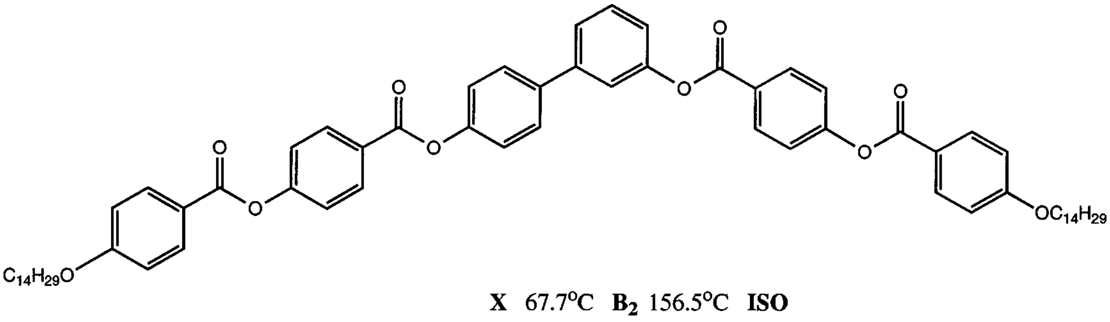

FIG. 1. Chemical structure and phase sequence of the studied material. *X* represents a solid phase.

between the two wings of the molecule. The optical dielectric tensor of one molecule can then be calculated by averaging the contribution of both uniaxial parts. In this way a biaxial tensor is obtained. In addition, the molecular plane is supposed to be defined by a tilt angle θ with respect to the smectic layer normal and an azimuthal angle ϕ. If the pitch is shorter than the optical wavelength, the macroscopic dielectric tensor can be obtained by averaging the microscopic tensor of one layer for all azimuthal angles. Under these conditions the resulting material is uniaxial with a birefringence perpendicular to the helix axis given by

$$\Delta n = \frac{n_e^2 - n_o^2}{4\overline{n}} \left(3\cos^2\theta \sin^2\frac{\beta}{2} - 1 \right),$$

where $\overline{n}$ is the mean refractive index of the material and n_e and n_o the extraordinary and ordinary indices of the uniaxial wings of the molecule. For $\beta = 120°$, $\theta = 45°$, $n_e = 1.63$, and $n_o = 1.50$, the material is almost isotropic, the birefringence being of the order of 10^{-3}. It is the low value of Δn in this structure that allows the optical activity to be observed (Fig. 3).

The electro-optical behavior of this texture is not typical of banana-shaped mesogens. Two regimes can be distinguished depending on the magnitude of the electric field. For fields about 1 V/μm, the birefringence increases and the two chirality domains are no longer visible. The texture becomes much clearer, with a gray color, and focal conic domains are evident. On the other hand, fingerprint patterns with closely spaced stripes and Maltese crosses can be observed in the different fan-shaped domains. Under a low-frequency triangular field these crosses rotate continuously, following the field. The rotation direction is opposite in domains of opposite chiralities. The rotation angle increases with the electric field intensity although it is clearly not a linear dependence. Figure 4 shows the two different orientations of a Maltese cross for both polarities of a field of 2 V/μm. This electro-optical behavior can be explained in terms of a deformed helix ferroelectric (DHF) regime [13], typical of short-pitch SmC*-phases. Normally in this regime the birefringence is not field dependent and the optic axis rotates linearly with the field. However, in the present compound the uniaxiality is hardly defined for null field. This fact results in a more complicated field dependence of the rotation angle and birefringence.

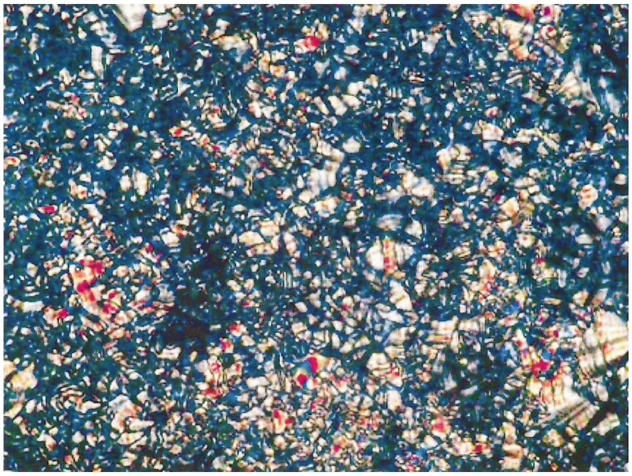

FIG. 2. (Color) Texture observed after cooling the material down to the B_2 phase in the absence of field. The width of the photograph corresponds to 125 μm.

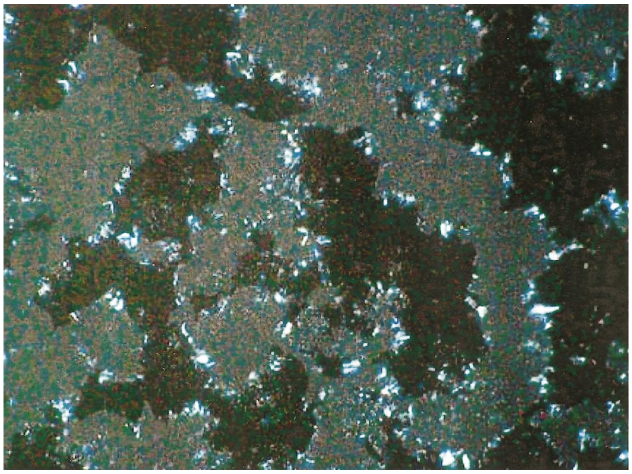

FIG. 3. (Color) Texture observed for null field after cooling the sample from the isotropic phase in a low-frequency square-wave field of ±15 V/μm. The polarizers are slightly uncrossed (~5°). The two kinds of domain interchange their colors for an opposite rotation of the polarizers from the crossed position. For crossed polarizers the texture is almost perfectly black. The width of the photograph corresponds to 125 μm.

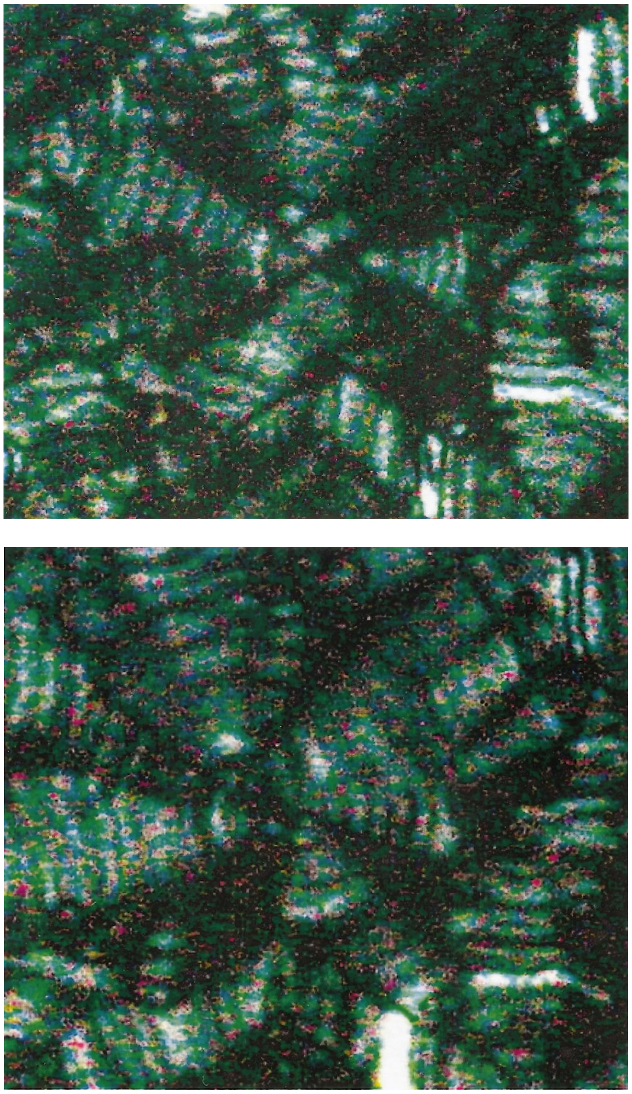

FIG. 4. (Color) Textures of the ferroelectric phase under a low-frequency field of magnitude ±2 V/μm for both polarities of the field. The rotation of the extinction brushes is visible. The width of the photograph corresponds approximately to 25 μm.

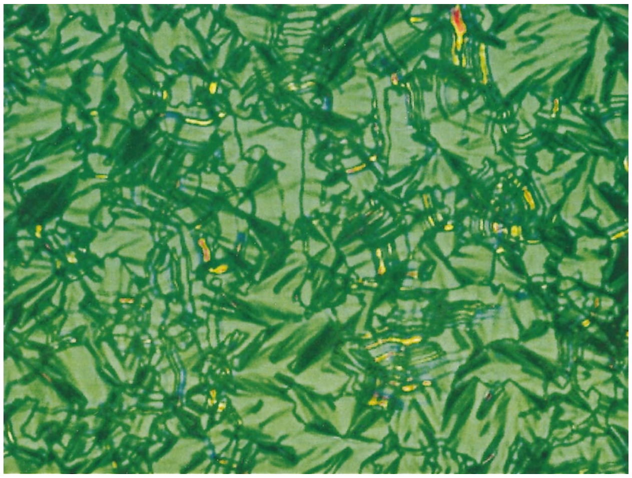

FIG. 5. (Color) Texture of the mesophase under an electric field of 10 V/μm. The width of the photograph corresponds to 125 μm.

For electric fields above 10 V/μm a colored fan-shaped texture similar to that of a Sm*A* phase is observed. Most of the fringes have disappeared, as can be seen in Fig. 5. When inverting the sign of the field the extinction brushes remain essentially unchanged, which is consistent with a tilt angle close to 45°.

The continuous rotation depicted in Fig. 4 strongly suggests the existence of a ferroelectric structure where the electric field couples linearly to the spontaneous polarization. In this way, the DHF regime is evidenced through the rotation of the helix axis. No rotation is possible in an antiferroelectric arrangement where the field couples quadratically to the dielectric anisotropy. In an antiferroelectric phase, the field-induced deformation does not rotate the helix axis since the molecules tend to align indistinctly in the $+\mathbf{E}$ and $-\mathbf{E}$ directions, in agreement with conoscopic observations [14]. In other words, the observed rotation is symmetry forbidden in a helical antiferroelectric structure. Ferroelectricity is also induced once the material is in the B_2 phase, as concluded from the texture change observed after the field treatment. However, no clear optical rotation can be observed in this case because both chiralities are mixed. In agreement with these conclusions, it has been recently reported that a huge increase of the dielectric constant takes place in the B_2 phase of this material when a strong bias field is applied and subsequently removed (the dielectric loss in the kilohertz range increases from 5 to about 50) [15]. It has also been observed that both components of the dielectric constant are quenched when a bias electric field is further applied to the resulting phase. This behavior resembles the expected one for a Goldstone mode, characteristic of a ferroelectric state.

The change of character from antiferro- to ferroelectric is a phenomenon that has been recently observed by Gorecka *et al.* [8] in binary mixtures of calamitic liquid crystals showing antiferroelectric and ferroelectric phases. According to these authors, the material is brought into a ferroelectric state after treating the sample with an electric field of strength above the switching threshold. Furthermore, as in our case, the transition is also accompanied by a clear increase of the low-frequency dielectric constant and is not reversible, i.e., the original antiferroelectric phase cannot be restored. The process is called ‘‘learning of ferroelectricity’’ [8].

In summary, a short-pitch helical ferroelectric structure was evidenced in a liquid crystal composed of achiral bent-core molecules. The ferroelectric state is achieved through an irreversible process driven by an electric field. On cooling from the isotropic phase under the influence of a strong bias field, the material can be considered to be intrinsically ferroelectric since the antiferroelectric phase is not displayed. Large chiral regions are segregated below the clearing point as evidenced when the field is removed and the texture of Fig. 3 is obtained. This field-induced chiral segregation has permitted us to identify the dark texture as ferroelectric through field-induced DHF rotations. On the other hand, there is no macroscopic chiral segregation when the compound is in the B_2 phase. As a final conclusion we can state that the present experimental results are compatible with a SmC^*-type structure for the ferroelectric phase of the material, which, in terms of the nomenclature proposed in [2], would be SmC_SP_F.

This work was supported by the CICYT of Spain (Project No. MAT2000-1293-C02) and the University of the Basque Country (Project No. 9/UPV 00060.310-13562/2001). We gratefully acknowledge Dr. J. Barberá for the x-ray measurements.

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