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Field-induced switching between states of opposite chirality in a liquid-crystalline phase

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A tilted smectic phase of a new achiral banana-shaped mesogen is presented. It possesses liquidlike order within the layers and appears with a fan-shaped texture. At sufficiently high electric fields, this texture can be transformed into a texture that displays a complete extinction between crossed polarizers and it forms randomly distributed chiral domains. Above a threshold these domains can be reversibly switched into a state of opposite handedness.

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Exhibiting unusual physical properties, the liquid-crystalline phases formed by bent-shaped mesogens [1,2] have recently attracted particular interest. A strong sterical moment of such molecules results in polar structures of the ''banana'' phases giving rise to ferroelectric and antiferroelectric properties. Particularly, the tilted versions of the smectic phases exhibit a spontaneous breaking of achiral symmetry even when the molecules themselves are achiral [3].

In this paper we present a new bent-shaped compound (Fig. 1) that besides a nematic (*N*) phase also exhibits a smectic phase (Sm-*X*) with a very peculiar electro-optical response. The phase transition temperatures are given in the scheme below where the numbers in the square brackets designate the corresponding transition enthalpies in kJ/mol (found by differential scanning calorimetry technique with a rate of 5 °C/min):

$$\text{Crystalline}\ \underset{[34.8]}{99\,^{\circ}\text{C}}\left(\text{Sm-}X\ \underset{[3.5]}{88\,^{\circ}\text{C}}\ N\ \underset{[1.2]}{92\,^{\circ}\text{C}}\right)\ \text{Isotropic.}$$

As seen from the transition scheme both of the mesophases are monotropic. Preliminary x-ray diffraction measurements made on nonoriented samples show a strong Bragg reflection in the small-angle region. The layer spacing $d=39.5$ Å has been determined which is considerably smaller than the length of the bent molecule (60Å assuming a bending angle of 120 deg). A broad diffuse scattering maximum in the wide-angle region ($2\theta\sim20$ deg) points to a liquidlike order within the smectic layers. We have not succeeded to obtain well oriented monodomains, however, the preliminary measurements on partially oriented samples still show the splitting of the outer-diffuse scattering confirming a tilt of the molecules with respect to the layer normal. Therefore, it is plausible to assume that the structure of the Sm-*X* phase is similar to that of the Sm-*C* or Sm-*P* phase.

Electro-optical measurements were made in 6 μm and 10 μm commercial ITO cells (EHC Corp., Japan). We used cells with untreated substrates as well as with a polyimide aligning layers. The substrates were rubbed in a certain direction so that the nematic liquid adopted a planar alignment, where the director is uniformly parallel to the rubbing direction. On cooling the nematic phase, the smectic phase appears as a fan-shaped texture (Fig. 2), in which the molecules are more or less parallel to the substrates. The electro-optical response is very weak. Only at relatively high electric fields ($\geqslant$15 V/μm), a minor change of the interference color has been observed. It is interesting to notice that in this fan-shaped texture (and also in the nematic phase), domains of opposite handedness spontaneously appear which are indicated by dark and light regions visible after decrossing the polarizers. If the strength of the applied field is further increased, the fan-shaped texture continuously transformes into a texture that shows a complete extinction between the crossed polarizers (dark state). This extinction does not change when the sample is rotated. The field-induced transition into the dark state is completely different from the usual switching of the Sm-*CP* phase. This process is rather reminiscent of the field-induced texture change from a planar into a homeotropic texture in Sm-*A* phases with a high positive dielectric anisotropy [4,5].

It is interesting to mention that the threshold field for the texture transformation decreases with decreasing temperature (from about 25 V/μm at 84 °C to 15 V/μm at 75 °C). At temperatures above $\sim$83 °C the dark texture relaxes into a birefringent ''grainy'' texture when the field is switched off. Below 83 °C the extinction of the texture remains unchanged if the field is removed. Two kinds of domains (dark and light) of opposite handedness become visible if one polarizer is rotated clockwise by a small angle (+10 deg) with respect to the crossed position. Rotating the polarizer anticlockwise by the same angle, we have observed exactly a reverse effect: the dark domains become light and vice versa (Fig. 3). Application of a sufficiently high electric field (>10–15 V/μm) to this texture resulted in switching of the dark domains into the light ones and the light domains turned into the dark ones. This effect is inverted by a field of opposite polarity (Fig. 3). It means, that the chiral domains can be reversibly switched into a state of opposite handedness and this switching is bistable. The switching between the states of opposite chirality could be observed up to about 70 °C, till the sample starts to crystallize.

The electrical response has been studied using both pulse

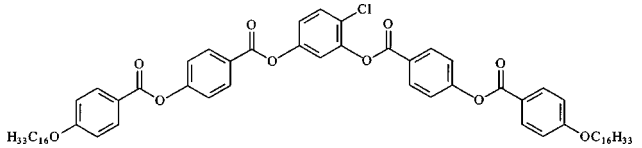

FIG. 1. Structural formula of the mesogen.

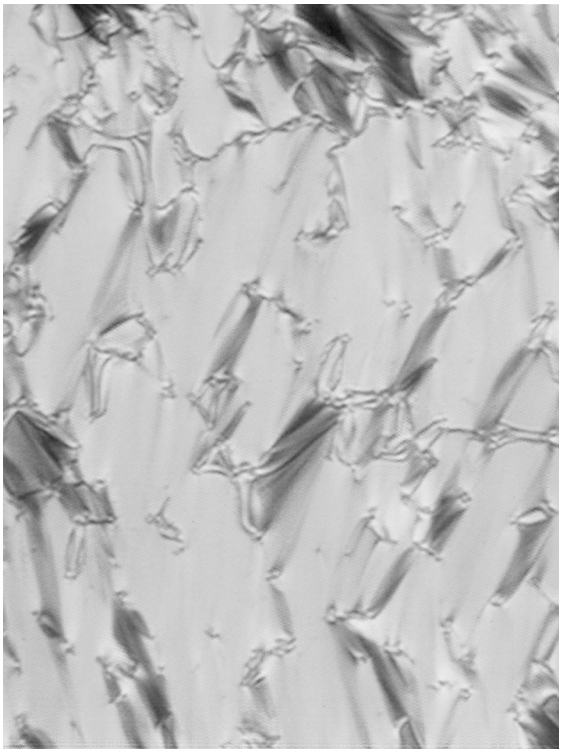

FIG. 2. Fan-shaped texture of the Sm-*X* phase formed on cooling the planar oriented nematic phase.

and triangular-wave methods. The temperature dependence of the current response to the pulse wave ($E_{pp}=20$ V/μm and the frequency of 5 Hz) is shown in Fig. 4. In the Sm-*X* phase the response curve contains two peaks, a broad and a narrow one indicated by the arrows. The narrow peak disappears upon the transition into the nematic phase. The broad peak remains in the nematic and the isotropic phases disappearing somewhere below 70 °C when the crystallization occurs. The field dependence of the narrow peak is different from the broad one. The narrow peak appears only when the field is higher than a certain threshold. The current response has been observed in both dark and fan-shaped textures. In the latter case the fan-shaped texture transforms into the dark one, exhibits the switching of the chiral domains and, depending on the temperature (as it is mentioned before), remains dark or relaxes back into the fan-shaped texture. In all these cases the current response peak appear on *switching of the chiral domains*. The measurements of the switching polarization P_{sw} made by triangular-wave technique on extra purified samples give ~ 300 nC cm^{-2} independently whether the initial texture is dark or fan shaped. Only one current response peak per half period of the external voltage has been observed, which is in agreement with the bistable optical switching of the chiral domains indicating a kind of ferroelectric structure.

How are the smectic layers aligned in the dark texture? In the nonbirefringent state the optical axis should be perpendicular to the substrate plane. One possibility is a reorientation of the smectic layers parallel to the substrates where the tilted molecules should adopt a helical superstructure like in the Sm-*C** phase. An indication for such a structure is the

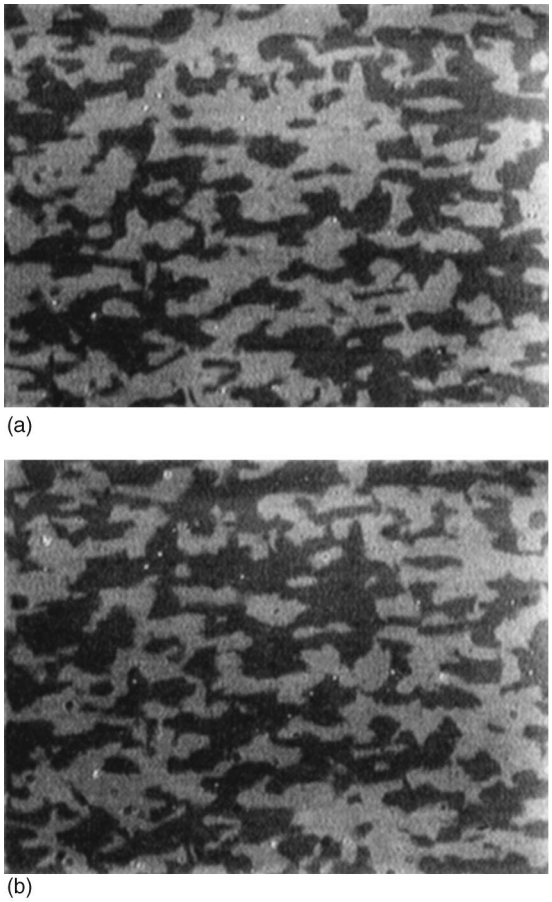

FIG. 3. Chiral domains of opposite handedness in the Sm-*X* phase visualized by the rotation of one polarizer by 8 deg from the crossed polarizer position (a) clockwise; (b) anticlockwise. The same texture change is observed when the angle between the crossed polarizers is fixed and the field (10 V/μm) of (a) positive or (b) negative polarity is applied.

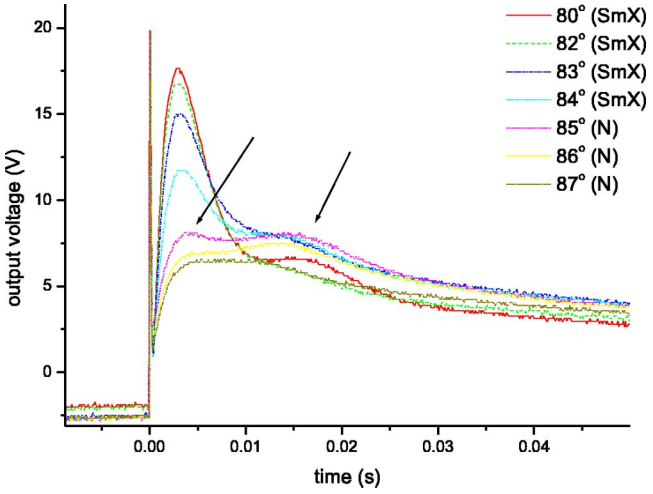

FIG. 4. Current response to a pulse wave field $E_{pp}=20$V/μm (frequency: 5 Hz) in dependence on the temperature.

apparent occurrence of the chiral domains in the fan-shaped texture that remain unchanged after the reorientation onto the black texture. Since the dielectric anisotropy is negative ($\Delta\varepsilon \sim -4$) a field-induced reorientation of the original planar texture into a quasihomeotropic state can be possible if the smectic layers have a considerable polarization component parallel to the layer normal. In this case, the Sm-*X* phase could be a candidate for a general Sm-C_G phase proposed by de Gennes [6]. The macroscopic properties of this phase were discussed by Brand *et al.* [7] and the first experimental evidences were reported by Jákli *et al.* [8] and Chattham *et al.* [9].

Another possibility is the occurrence of a planar orthoconic arrangement, where the tilt angle is 45 deg [10]. In this case the field-induced transformation from a bright birefringent texture into the nonbirefringent dark state could be realized by a transition from a Sm-C_SP_A into a Sm-C_AP_F state. But both Sm-C_SP_A and Sm-C_AP_F are "racemic" (macroscopically achiral), whereas the spontaneously formed chiral domains have been observed in the birefringent fan-shaped texture and in the nonbirefringent state. On the other hand, we have a clear indication for a ferroelectric ground state, for which a transition from the birefringent into the nonbirefringent texture should not be possible. These findings contradict to the orthoconic model.

In conclusion, we would like to mention that it is the first evidence for the reversible switching between the states of opposite chirality. Up to now we do not have a plausible explanation for such an unusual effect. Detailed investigations on the physical properties of the Sm-*X* phase and on the mechanism of this phenomenon are going to be done in future.

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