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Evidence for Triclinic Symmetry in Smectic Liquid Crystals of Bent-Shape Molecules

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The first experimental evidence for triclinic symmetry of bulk smectic liquid-crystal samples of achiral banana-shaped molecules is presented. This phase corresponds to the so-called Sm-C_G phase consisting of biaxial molecules and characterized by two tilt directions with respect to the layer normal: tilt of the molecular plane (clinic) and tilt of the molecular kink direction (leaning). Each smectic layer has a polarization component normal to the smectic layers (C_1 symmetry). The observations suggest that the phase tentatively labeled as B_7 is identical with the Sm-C_G phase.

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The possibility of smectic phases with triclinic symmetry was predicted more than 25 years ago by de Gennes [1]. The phase was named Sm-C_G (where G stands for "generalized") and was noted that it differs from its mirror image. This prediction had no experimental significance until the discovery of the ferroelectric smectic phases of bent-core ("banana-shaped") molecules [2], which have the following four stable polar in-layer configurations [3,4] (see Fig. 1): (a) A transversely polarized achiral Sm-A–type structure with $C_2\nu$ symmetry [Fig. 1(a)]. This corresponds to the structure proposed by Niori *et al.* [2]. (b) A tilted Sm-C^*–type phase with monoclinic chiral symmetry C_2 [see Fig. 1(b)]. This is consistent with the structure of the so-called B_2 phase proposed by Link *et al.* [5]. The smectic layers have in-layer polarizations, and may form both antiferroelectric [6] and ferroelectric ground states [7,8]. (c) An achiral layer structure with a monoclinic symmetry C_s [Fig. 1(c)]. (d) A triclinic configuration with chiral C_1 symmetry corresponding to the Sm-C_G phase proposed by de Gennes [1] [Fig. 1(d)].

In Sm-C_G the director tilt has two components with respect to the layer normal: "*clinic*" [5] and "*leaning*" corresponding to tilting of the molecular planes and of the layer polarization, respectively. In addition to the "*synclinic*" and "*anticlinic*" configurations of the B_2 phase [5], "*synleaning*" and "*antileaning*" structures should be distinguished, too. The layer polarizations have both in-layer and out-of-layer components allowing eight different two-layer structures [3] (see Fig. 2). A and A' are antiferroelectric, i.e., the polarization is zero. In B and B' the out-of-layer polarizations compensate each other and only in-layer components remain. These structures could be indistinguishable from the ferroelectric B_2 phase (Sm-C_sP_F) observed by Walba *et al.* [7]. In C and C' the resulting in-layer polarization is zero, but the out-of-layer polarization is nonvanishing. Cases D and D' have both in-layer and out-of-layer polarizations.

Regarding experimental realizations, recently Clark *et al.* found evidences of the C_1 symmetry in free-standing films, although in bulk they do not show C_1 symmetry [9]. In bulk first the B_2 phase of asymmetric banana-shaped molecules were examined, but textural observations could not provide conclusive results [10]. On the other hand, microscopic observations on the B_7 phase revealed the coexistence of 4 states with different birefringences and electrical responses [11] suggesting that they represent Sm-C_G structures corresponding to Figs. 2(A), 2(A'), 2(C), and 2(C').

In this Letter we report studies on binary mixtures of banana-shaped compounds with B_2 and B_7 phases and show evidences for the Sm-C_G phase in bulk. We also suggest that the B_7 and Sm-C_G are identical.

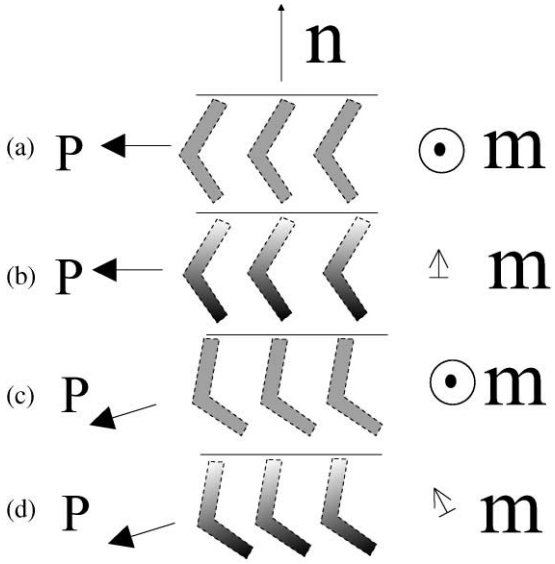

FIG. 1. Possibilities for the packing of the bent-shaped molecules into layers. Shading illustrates tilt out of the plane of the drawing: brighter areas are closer to the observer. The structures can be characterized by three vectors: the smectic layer normal **n**, the molecular plane normal **m**, and the direction of the molecular kink, which (due to the most efficient packing of the molecules) determines the layer polarization **P**. (a) **n** is normal both to **m** and **P**. This structure has $C_{2\nu}$ symmetry. (b) **n** is normal to **P**, but is not perpendicular to **m**. (c) **n** is perpendicular to **m**, but not to **P**. The smectic layers have C_s symmetry and the polarization has a component parallel to **n**. (d) **n** is neither perpendicular to **P** nor to **m**, and a double tilted smectic phase with C_1 symmetry results. This is the Sm-C_G phase.

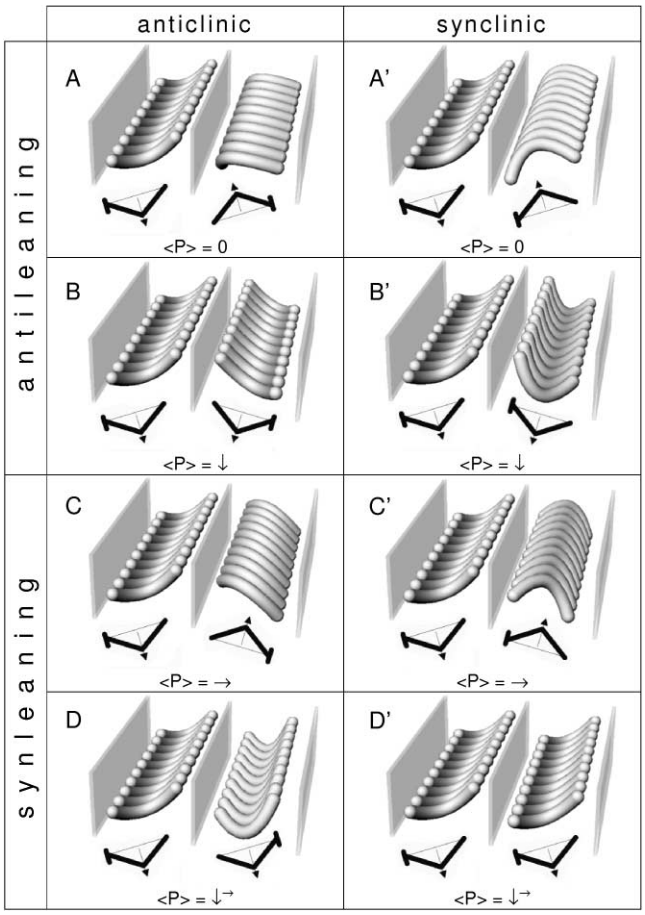

FIG. 2. Possible Sm-C_G structures allowing different configurations in two layers. The structures $A-D$ indicate anticlinic arrangements, whereas $A'-D'$ are synclinic. $\langle P\rangle$ is the resulting polarization vector. The end of the molecules with nails sticks out from the plane of the drawing.

Contact preparations were made between $12Bq$ [6] and $3FB10(O)$ [12] having B_2 and B_7 phases, respectively. The molecular structures and the phase sequences of the single compounds are shown in Fig. 3(a). The single compounds were inserted from the opposite sides of a 10 μm thick cell resulting in a composition gradient. The concentration dependence of the transition temperatures were studied in cooling. The clearing temperature shows a nearly linear dependence on the concentration, whereas the transition to the low temperature phases lowered to 30 °C in the region of the eutectic mixture. In the side of the pure B_2 material, the formation of small fan-shaped domains indicates the isotropic-smectic phase transition. The pure $3FB10q$ shows "telephone-wire-like" [12] formation on cooling from the isotropic liquid, which is the hallmark of the B_7 phase [13]. Within the concentration gradient the textures represent interesting transitions between fans and helical filaments.

At about 1:1 mixing ratio low birefringent ribbonlike domains form and grow. At constant temperature the ribbons can be stabilized, but under low frequency electric fields ($<$10 Hz) they show a striking effect. Depending on the polarity of the field they shrink or grow. At a given polarity shrinking and growing domains can coexist. Examples of this phenomenon are shown in Fig. 4. At low frequencies ($\leq$1 Hz) of fields $E \approx 4$ V/μm the ribbons grow roughly as much as under cooling by $\Delta T \approx 0.1$ °C at zero fields. Ribbons and coiling structures can coexist, but their behaviors are completely different. The ribbons shrink or grow periodically depending on the sign of the electric field, but the coiling domains either shrink, or are not effected by the electric fields. Examples for the monotonously shrinking coils together with the periodic behavior of the ribbons are shown in the bottom row of Fig. 4. At slightly lower temperatures some ribbons become highly birefringent corresponding to planar alignment (the director field is mainly parallel to the film surface). Neither the low birefringent homeotropic, nor the high birefringent planar structures showed electro-optical responses during the shrinking-growing process.

These observations clearly illustrate that the ribbons are polar (those that grow or shrink have opposite polarity) and the polarization could not be switched by the applied electric fields. Although the low birefringence indicates that the field-induced ribbons have a layer structure perpendicular to the electric fields, microscopic observations alone cannot exclude a small layer tilt. Layers tilted with respect to the boundary plates have a polarization component parallel to the electric field even for only in-layer polarization. Since the optical axes of the observed ribbons are parallel to the layers, this case would correspond to an Sm-C_aP_F structure, which has been observed only in chiral [8], but not in nonchiral banana-shaped molecules. In this case the polarization could be easily switched by electric fields in submilliseconds, just as in the case of Sm-C^* materials with tilted layers [14]. This switching would be much faster than the growth process, i.e., independent of the polarity, the electric field would always favor the growth. The lack of the electro-optical responses both in the homeotropic and planar textures also rules out the Sm-C_aP_F structures. It remains that the material should have an out-of-layer polarization component corresponding to the Sm-C_G structures shown in Figs. 2(C) and 2(C').

Further cooling the material with a 0.03 K/min rate below the two-phase range the ribbons coalesce to a regular stripe pattern with a periodicity of 5.5 μm [see the pictures in the middle of Fig. 3(b)]. The stripes are observable even without polarizers showing that they are defect walls. Between the defect walls the optical axis is parallel to the stripes indicating anticlinic structures [Figs. 2(C) and 2(D)]. The defect walls resemble the charged domain walls observed in Sm-C^* samples with large spontaneous polarizations [15]. We propose that the walls observed in the present case are also charged due to the opposite out-of layer polarizations of the neighbor uniform areas. Subsequent walls have opposite charges as depicted in Fig. 5. The distance between the walls should be determined by the balance of the electrostatic and elastic forces.

The observations that ribbons and coils can coexist indicate that the B_7 and the Sm-C_G phases are identical, as has

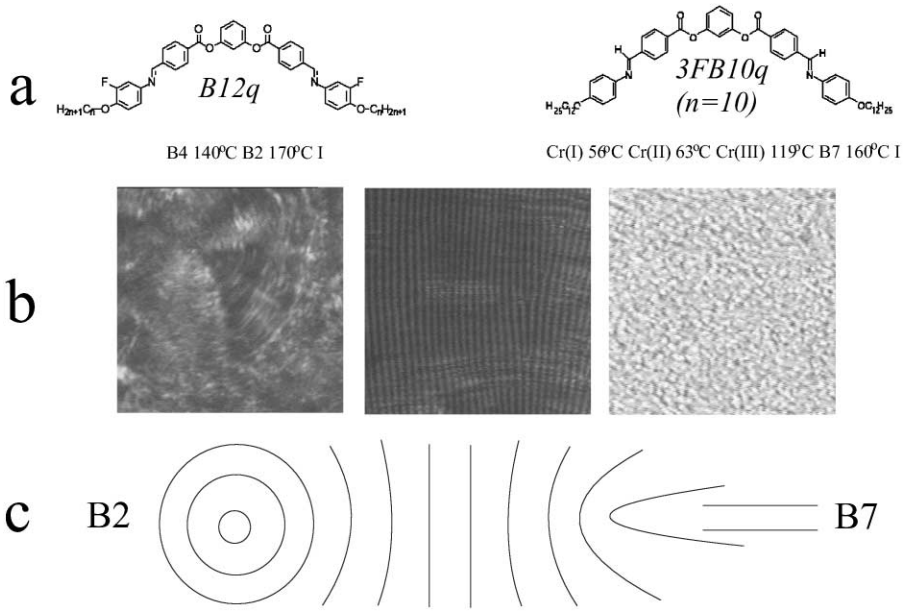

FIG. 3. Molecular structures (a), the equilibrium textures (b), and the corresponding layer configurations (c) in a 10 μm contact preparation cell between $B12q$ and $3FB10q$ at $T = 158\,^{\circ}\mathrm{C}$. The equilibrium textures appeared after slow cooling ($0.03\,^{\circ}\mathrm{C}/\mathrm{min}$).

already been suggested by Pleiner *et al.* [16]. This would explain the coexistence of four different domains of the B_7 phase [11].

An important feature of smectic layers with Sm-C_G structures is that they turn away from the direction of applied electric field by the leaning angle α. Under field reversal either the layer tilt, or the layer chirality should change. This results in an increase of the threshold field with increasing α. For α decreasing on cooling, lower thresholds would be observed at lower temperatures. Such an anomalous effect was indeed found recently in the pure $3FB10(O)$ [12]. We note that a decreasing leaning

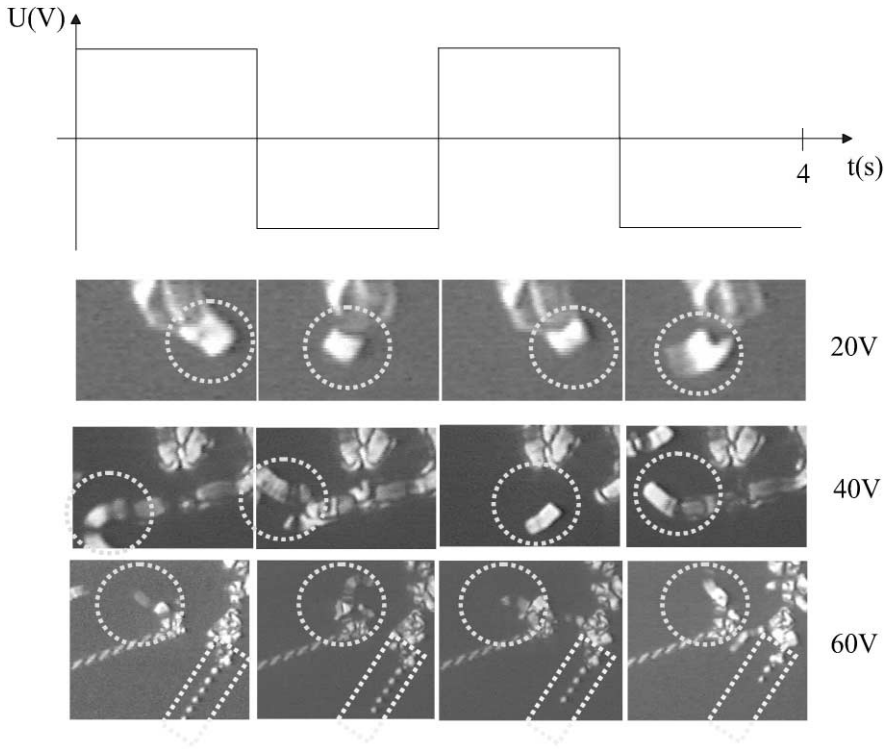

FIG. 4. Ribbons under alternating fields. The ribbons in the different rows have about the same width (10 μm), which is comparable with the sample thickness. The bottom row shows coexisting ribbons and coils. The ribbons grow or shrink periodically, whereas the coils shrink independent of the polarity of the field. To emphasize the important areas we drew dashed circles around the shrinking or growing ribbons and dashed rectangles around the monotonously shrinking coils.

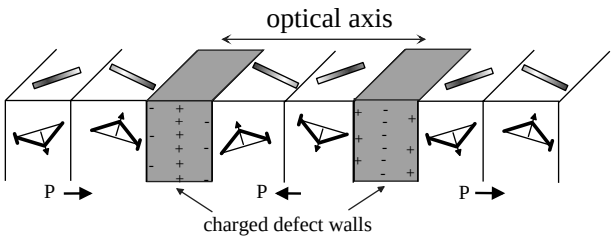

FIG. 5. Proposed structure of the periodic pattern observed at very slow cooling of the mixture of substances forming B_2 and B_7 phases, respectively. The two-layer structure corresponds to Fig. 2(C).

angle implies the possibility of a material with Iso-B_7-B_2 (Iso-Sm-CP-Sm-C_G) phase sequence.

The observed textures and their behavior under electric fields can also be understood assuming that B_7 is identical to Sm-C_G. The patterns at the phase transition are determined by the requirement that div$P = 0$. In the B_2 phase, where the polarization has only in-plane component, concentric cylinders (fan-shaped domains) can satisfy this requirement, whereas in the B_7 phase the compensation of divergence of the out-of-layer polarization requires an additional coiling of the filaments or ribbons. In the case of the helical filaments [11] even the dielectric anisotropy is averaged out explaining why they do not show any response to electric fields. In coils of ribbons the in-plane dielectric anisotropy is not averaged out, accounting for monotonous shrinkage under alternating fields. In uniform ribbons the net out-of-layer polarization P_{out} is not zero, and the free energy depends on the polarity of the electric field. When $\mathbf{P}_{\text{out}}$ is parallel to the electric field $\mathbf{E}$ the free energy decreases by $\mathbf{P}_{\text{out}} \cdot \mathbf{E}$ and transition to the Sm-C_G phase can be induced if $\mathbf{P}_{\text{out}} \cdot \mathbf{E} \geq \mathbf{\Delta H}$, where ΔH is the transition enthalpy. When $\mathbf{E}$ is opposite to $\mathbf{P}_{\text{out}}$ the free energy increases inducing a transition to the isotropic phase. Taking into account the ferroelectric interaction the decrease of the phase transition temperature, ΔT can be calculated from the modified Kirkwood-Helfrich equation [17] as

$$\frac{\Delta T}{T_0}\,\frac{\Delta H}{M\rho} = \frac{1}{2}\,\Delta\varepsilon\varepsilon_0 E^2 - PE\cos\varphi\,. \qquad (1)$$

T_0 is the transition temperature at zero fields, M is the molar mass, ρ is the density, $\Delta\varepsilon$ is the dielectric anisotropy, and φ is the angle between the polarization and the electric field. The observation that the rate of the shrinkage and growth are approximately equal indicates that the dielectric anisotropy is negligible compared to the contribution of the polarization. In this approximation (with $T_0 = 400$ K, $M \approx 10^3$ kg^{-1}, $\rho = 10^3$ kg m^{-3}, $\Delta H \approx 2 \times 10^4$ J/mol, $E = 4 \times 10^6$ V/m) $\Delta T/P_{\text{out}} \approx 64$. Taking into account that $E \approx 4$ V/μm corresponds to $\Delta T \approx 0.1$ °C, we get that $P_{\text{out}} \approx 150$ nC/cm^2. This value is about half of the pure $3FB10(O)$ [12] and is one third of the pure $B12q$, indicating that the leaning angle is about 20°.

Applying uniform electric fields on the cell there is a sharp boundary between the switchable and nonswitchable areas. At increasing fields this boundary could be slightly shifted toward the B_7 side indicating that there the leaning angle is small and the out-of-layer polarization could be switched, too. This shows that the transition between the B_2 phase (C_2 symmetry) and the B_7 phase (C_1 symmetry) is of second (or of weakly first) order.

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