A Ferroelectric Liquid Crystal Conglomerate Composed of Racemic Molecules

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We describe the design and synthesis of a ferroelectric liquid crystal composed of racemic molecules. The ferroelectric polarization results from spontaneous polar symmetry breaking in a fluid smectic. The ferroelectric phase is also chiral, resulting in the formation of a mixture of macroscopic domains of either handedness at the isotropic-to-liquid crystal phase transition. This smectic liquid crystal is thus a fluid conglomerate. Detailed investigation of the electrooptic and polarization current behavior within individual domains in liquid crystal cells shows the thermodynamically stable structure to be a uniformly tilted smectic bow-phase (banana phase), with all layer pairs homochiral and ferroelectric (SmC_SP_F).

Ferroelectric liquid crystals (FLCs) have been a wellspring of fruitful scientific investigation and innovation since Meyer first postulated, then proved, the polar ordering in chiral smectics (*1*), and Clark and Lagerwall produced and visualized switchable ferroelectric (FE) domains (*2*). After Meyer, the design paradigm for smectic FLCs has required enantiomerically enriched molecules to break reflection symmetry and force polar order. Here we report the directed design of a liquid crystal composed of racemic molecules, in which ferroelectricity is obtained by spontaneous polar symmetry breaking. In the fluid layers of this smectic LC, in addition to polar ordering, the bent-core (bow-shaped or banana-shaped) molecules adopt a uniform tilt about the polar axis. This structure eliminates reflection symmetry and renders the phase chiral. The resulting chiral optical response to applied electric fields enables unambiguous identification of ferroelectricity through the visualization of FE domains and their field-induced switching.

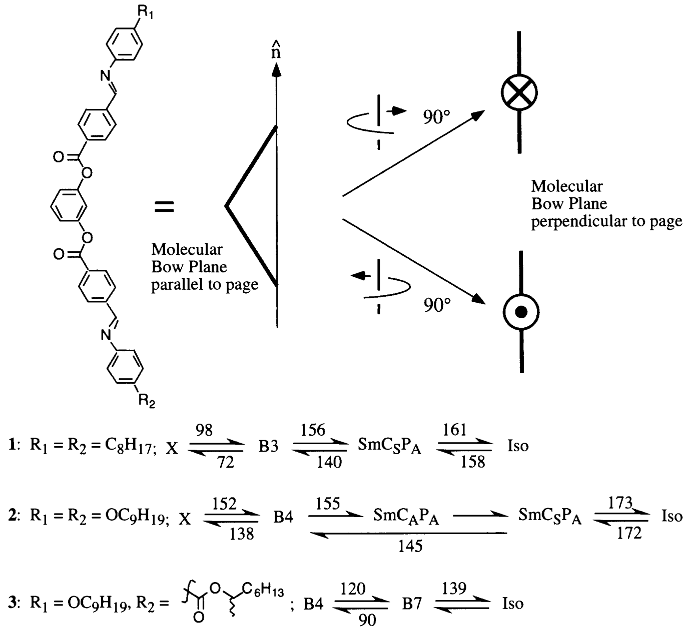
Our design approach builds upon several key earlier discoveries in the FLC field. First, Fukuda *et al.* demonstrated antiferroelectric (AFE) switching in a chiral tilted smectic wherein the polarization alternates in direction from layer to layer (*3*). More recently, AFE switching in a bilayer smectic phase composed of an achiral polymer-monomer blend of conventional calamitic (rod-shaped) mesogens was reported (*4*). This result was followed by the discovery of AFE switching in smectics composed of achiral bent-core mesogens (bow-phases or banana phases) (*5*, *6*). Elucidation of the supermolecular structure of the prototype AFE bow-phases showed them to be tilted polar smectics (SmCP phases), one being macroscopically chiral in bulk, to provide a liquid conglomerate (*7*). While these exciting discoveries have stimulated a very large number of synthetic and physical studies, to date all known switching smectic phases composed of achiral or racemic molecules have been AFE.

The structures, phases, and transition temperatures of the prototype AFE bent-core mesogens **1** and **2** are given in Fig. 1. We consider the molecular director **n** in this system to be along the "bow string" of the molecular bows. The molecular bow-plane contains the director and the symmetry axis of the *C*2 symmetrical structures **1** and **2**. Also shown in Fig. 1 are symbolic representations of the structure in orthogonal orientations. The indicated lower temperature B3 and B4 phases exhibited by diesters **1** and **2**, respectively, are actually crystal modifications. The fluid smectic phases of these materials are still often referred to as the "B2 phase."

The structures of these AFE phases (Fig. 2) were established by depolarized reflected light microscopy (DRLM) of freely suspended smectic films, in combination with measurements of the electrooptic (EO) and current response of transparent capacitor LC cells in the B2 temperature range. Upon melting of the chiral B4 "blue crystal" phase, the diester **2** forms a liquid conglomerate of chiral SmC_AP_A domains. In the SmC_AP_A supermolecular structure, spontaneous breaking of nonpolar symmetry within the layers combines with a tilt of the director from the layer normal to produce chiral layers. Furthermore, the AFE ordering of adjacent layer pairs and anticlinic layer interfaces produce macroscopically chiral domains where all layers possess the same handedness (*7*).

The SmC_AP_A phase of diester **2** is metastable, and most of the sample eventually anneals into the thermodynamically stable phase denoted SmC_SP_A. In this AFE structure, all adjacent layer pairs are heterochiral, leading to a macroscopic LC racemate. Even when cooling from the isotropic phase, however, some coexistence of the AFE racemate and the conglomerate is seen. This sort of phase coexistence seems to be common in the SmCP phases.

The chirality of the layers is preserved upon switching of these AFE phases into their corresponding FE states by application of an electric field **E**. The SmC_SP_A AFE racemate produces the racemic FE SmC_AP_F state for **E** above the



$$\mathbf{1}:\ R_1 = R_2 = C_8H_{17};\ \mathrm{X}\ \underset{72}{\overset{98}{\rightleftharpoons}}\ \mathrm{B3}\ \underset{140}{\overset{156}{\rightleftharpoons}}\ \mathrm{SmC_SP_A}\ \underset{158}{\overset{161}{\rightleftharpoons}}\ \mathrm{Iso}$$

$$\mathbf{2}:\ R_1 = R_2 = OC_9H_{19};\ \begin{tikzcd} \mathrm{X} \arrow[r, shift left, "152"] & \mathrm{B4} \arrow[l, shift left, "138"] \arrow[r, "155"] & \mathrm{SmC_AP_A} \arrow[r] & \mathrm{SmC_SP_A} \arrow[ll, bend left, "145"] \arrow[r, shift left, "173"] & \mathrm{Iso} \arrow[l, shift left, "172"] \end{tikzcd}$$

$$\mathbf{3}:\ R_1 = OC_9H_{19},\ R_2 = \ ;\ \mathrm{B4}\ \underset{90}{\overset{120}{\rightleftharpoons}}\ \mathrm{B7}\ \underset{}{\overset{139}{\rightleftharpoons}}\ \mathrm{Iso}$$

Fig. 1. The structures, phases, and transition temperatures of two previously described bow-phase mesogens **1** and **2**, and the new compound **3**, are given (all temperatures are in degrees centigrade). In addition, symbolic representations of the bow-shaped structures used throughout this report, with the molecular bow plane parallel and perpendicular to the plane of the page, are illustrated.

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switching threshold (about 5 V/μm), whereas the AFE SmC_AP_A conglomerate switches to the FE SmC_SP_F state.

Because of potential applications of FE bow-phase LCs (*8*), and also as an interesting exercise in supermolecular stereocontrol, we sought an approach for the creation of a bow-shaped mesogenic structure affording one of the FE SmCP diastereomers as a stable phase.

Conventional wisdom in the field holds that the polar order within each layer is driven by minimization of steric packing forces within the layer (*5*, *9*). Furthermore, it is intuitively attractive to suggest that the AFE nature of the stable phases derives from minimization of Coulombic free energy, with antiparallel orientation of the macroscopic polarization within adjacent layers preferred in the absence of applied fields. If the orientation of the polar axis within adjacent layers is not coupled by a nonelectrostatic effect, and AFE ordering is favored electrostatically (*10*), how then can a FE structure be created?

An approach for obtaining one of the FE ground states is suggested by examination of Fig. 2 as follows. Consider the bow-shaped molecules as liquid crystal dimers wherein a meta-disubstituted benzene ring links two rod-shaped mesogens, each with a distinct molecular director. In this model, when projected on the polar plane all of the SmCP phases possess a rigidly enforced anticlinic virtual layer interface cutting the molecules in half. For the two AFE structures (SmC_SP_A and SmC_AP_A), the actual layer interfaces are synclinic when projected on the polar plane, whereas for the two FE structures (SmC_SP_F and SmC_AP_F) these are anticlinic in projection on the polar plane. We suggest that the layer-to-layer AFE ordering in the known SmCP phases is driven at least in part by a collective preference for synclinic layer interfaces in the polar plane, providing coupling of the orientation between the layers that is not electrostatic. It seems reasonable that the layer interfaces should prefer this synclinic geometry, because for conventional calamitic tilted smectic mesogens with simple unbranched alkyl or alkoxy tails, the synclinic structure is always preferred.

If anticlinic methyl-terminated layer interfaces in the polar plane could be made the thermodynamic minimum, then an FE SmCP phase should result (*11*). While at this stage in the development of supermolecular stereocontrol in LCs it is not possible to design such a structure by means of a priori arguments, there is a reliable empirical approach to obtaining anticlinic layer interfaces in calamitic LCs. Specifically, the 1-methylheptyloxycarbonyl tail present in the prototype AFE chiral smectic LC **MHPOBC** (*3*) often produces anticlinic methyl-terminated layer interfaces in the tilt plane when incorporated into calamitic LC structures. The anticlinic structure occurs whether the tail is unichiral or racemic, although the racemate is neither FE nor AFE.

Given the geometry of the SmCP phases, it is expected that the 1-methylheptyloxycarbonyl tail, originally in the tilt plane of **MHPOBC**, will produce anticlinic layer interfaces projected on the polar plane of the SmCP structure. Although the geometry at the layer interfaces is not precisely the same for the FE SmCP polar plane and **MHPOBC** tilt plane, use of interlayer clinicity as a stereochemical control element in supermolecular synthesis seemed promising. On the basis of this rationale, the mesogen structure **3**, possessing one nonyloxy tail and one racemic 1-methylheptyloxycarbonyl tail, was prepared (Fig. 1) (*12*, *13*).

The phase sequence for triester **3** as determined by polarized light microscopy in transparent capacitor cells is shown in Fig. 1. The high-temperature LC phase shows the characteristic texture of the B7 bow-phase, as recently described (*14*). But, the EO response of triester **3** is distinctive. Although the details of the structure of the B7 phases are under intense debate, the EO data combined with polarization current measurements show that the bow-phase of compound **3** is an FE phase, in contrast to other AFE B7 materials (*15*). Additionally, we find that the B7 phase of triester **3** is indeed a SmC_SP_F conglomerate—one of the two FE SmCP targets of our design effort. Experimental evidence for these structural features follows.

DRLM of freely suspended thin films could not be performed on these polar smectics, which form fibers instead (*16*). The key evidence for the FE nature of this phase is based on the EO and current response behavior in 4-μm transparent capacitor LC cells (*17*). The isotropic-to-smectic transition is very interesting and complex, and many unusual textures are seen, as with other B7 materials (*14*). Application of an electric field above a well-defined threshold value (E_{th}), however, could produce a focal conic texture reminiscent of a SmC* in a cell with no azimuthal anchoring (Fig. 3). The smectic layers appear to be normal to the surfaces in the form of nested cylinders, the typical focal conic arrangement.

The orientation of extinction brushes between crossed polarizer and analyzer in such cylindrical focal conic domains (Fig. 3) indicates that with field applied, the optic axis is off the layer normal by a tilt angle of about ±30°. Removal of the field from either state left the brush orientation unchanged—the key signature of bookshelf SmC*-like surface-stabilized FLC (SSFLC) optical bistability (*2*). This EO behavior is emphatically chiral. and the sample is a conglomerate (a mixture of domains exhibiting enantiomorphous behavior). The current response of the sample as a function of applied field is clearly FE, with a large polarization (about 315 nC/cm^2) measured by integration of the polarization reversal current peaks. This FE response was observed for frequencies of applied fields from 10 Hz to 10 kHz. The EO switching corresponds temporally with the po-

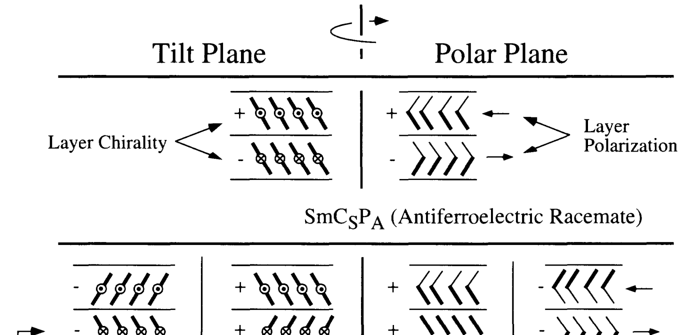

Fig. 2. Orthogonal views of the six SmCP supermolecular isomers, consisting of two conglomerates and two racemates. In the structures on the left, the tilt plane (defined as the plane normal to the twofold symmetry axis within each layer) is the plane of the page. The subscripts modifying the SmC (tilted smectic) notation (S and A) refer to synclinic or anticlinic tilt, respectively, of the director in adjacent layers. Representations on the right are rotated by 90°, with the polar plane (which by definition contains the twofold symmetry axis and the layer normal) in the plane of the page. The subscripts modifying the P (polar) notation (A and F) refer to AFE or FE relations, respectively, between adjacent layers. The sign to the left of each layer indicates the chirality descriptor for that layer (*7*).

larization reversal current peaks. The bistable domains persist for days in the absence of electric fields. Observation of a FE response even at low frequencies provides strong evidence for a FE ground state.

The birefringence of these samples is large ($\Delta n \sim 0.14$), yielding a first-order blue birefringence color. The EO behavior and birefringence are similar to that observed for the conglomerate of a $\mathrm{SmC_AP_A}$ phase when switched into the FE $\mathrm{SmC_SP_F}$ state (*7*). However, for known $\mathrm{SmC_AP_A}$ materials, upon removal of the field the sample reverts to the AFE ground state. Triester **3** has not been observed to show AFE behavior under any conditions.

The isotropic-to-B7 phase transition of **3** exhibits the appearance of helical ribbons or tubes of different widths growing from the isotropic melt. Helical pitch is seemingly constant within a ribbon, but varies from ribbon to ribbon (*14*) (Fig. 4A). About half the ribbons are right-handed and half are left-handed. In addition, large areas of the cell often exhibit focal conic domains with a gold birefringence color ($\Delta n \sim 0.07$) (Fig. 4, B and C). Eventually the ribbons can be seen to coalesce into focal conics as well, although often these domains are not "clean," as if showing a residue of the helical structure.

In the gold focal conic domains the optic axis is along the layer normal, as shown by extinction brushes parallel and perpendicular to the polarizer (Fig. 4, B and C). Application of small electric fields (below the threshold for switching into the bistable blue FE texture) produces an analog tilt of the optic axis (i.e., the opic axis rotation is approximately proportional to the applied field). This is a chiral response, and heterochiral domains are observed. At fields just below the alignment transition threshold, a maximum tilt of about ±10° can be seen, although not all domains exhibit the same susceptibility.

Application of a field larger than E_{th} (~12 V/μm) switches the gold texture to the bistable blue FE texture described in detail above, with a large increase in birefringence. Well-defined domain walls mediating this change can be easily seen when the field is close to the threshold (Fig. 4, C and D).

Analog switching in FLCs is well known, but to our knowledge has not been reported for the B7 phase. In the case of triester **3**, a model accounting for these observations is as follows. In the B7 temperature range, after the initial application of a field above E_{th}, the EO properties and current response of the sample are consistent with a $\mathrm{SmC_SP_F}$ structure and rule out any of the other diastereomeric structures shown in Fig. 2. We propose that in the gold focal conic domains obtained with triester **3** on cooling from the isotropic melt, the plane of the molecular bows is parallel to the bounding plates as indicated in Fig. 5A. The bow plane for synclinic SmCP structures such as this one is supermolecular, the molecular bow planes of all layers being parallel. This basically "parallel" or "homogeneous" alignment seems an especially reasonable alignment mode, being after all the type of alignment observed for other known anticlinic smectic structures such as racemic **MHPOBC**. Recently the same alignment has been observed for the synclinic AFE $\mathrm{SmC_SP_A}$ phase of a conventional achiral bow-phase mesogen (*18*). Weak analog EO switching was also observed in that case.

As shown in Fig. 5A, this surface-stabilized structure requires that the layers be tilted off the surface normal by an angle δ = θ, where θ is the SmCP tilt angle. In this orientation of the FE supermolecular structure, the polarization is uniform and parallel to the plates. This alignment is well known for chiral SmC* materials and shows an analog EO response ["Sony-Mode" V-shaped switching (*19*)]. The effective birefringence of this structure is quite low for light propagating normal to the plates, because there is a substantial contribution of the conjugated aromatic system to the polarizability both along

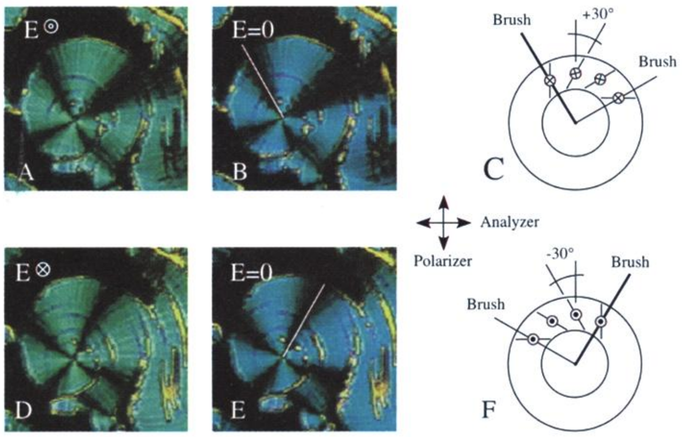

Fig. 3. (**A**) Polarized light microphotograph showing a 4-μm-thick slab of triester **3** in the B7 phase. The sample has been filled into a transparent capacitor LC cell and has been driven over the threshold for formation of the "bistable blue" texture by application of an electric field of greater than 12 V/μm. This image, showing a typical cylindrical focal conic domain, was obtained in the presence of a field +**E** (5 V/μm) normal to the substrates, oriented out of the page. The polarizer and analyzer are perpendicular, with the polarizer vertical. (**C**) Extinction brushes show regions where the optic axis is parallel or perpendicular to the polarizer. In this case it can be seen that the director is oriented parallel to the substrates and is rotated from the layer normal by +30°. Removal of the applied field leaves the brush orientation unchanged (**B**), indicating SSFLC bistable alignment, although a color change indicates a lower birefringence. Application of a field −**E**, oriented into the page, causes a marked reorientation of the brushes, to provide the texture shown in image (**D**). Removal of the field then provides the second bistable state (**E**). (**F**) The brush orientation indicates that the director is now rotated by −30° from the layer normal. Oscilloscope traces showing the FE polarization reversal current peaks obtained with LC cells of triester **3** can be found on *Science* Online (*21*).

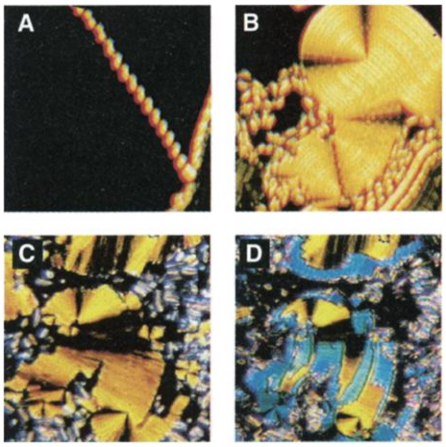

Fig. 4. (**A** and **B**) Low-birefringence gold texture growing from the isotropic melt of triester **3**, observed by polarized light microscopy in 4-μm transparent capacitor cells. The texture is characteristic of the B7 phase, showing helical ribbons or tubes (A) and focal conic domains (B). The polarizer is vertical in the photomicrographs; the optic axis in the focal conic domains is along the layer normal. (**C**) Gold focal conic texture before application of a field. (**D**) Bistable blue domains growing from the gold upon application then removal of a field just above E_{th}.

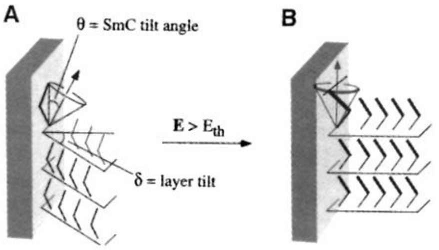

Fig. 5. The director, bow plane, and layer structure of samples of triester **3** in transparent capacitor cells. The initially formed low-birefringence gold texture has the bow plane parallel to the substrates and the layers tilted (**A**). In this case the polarization cannot orient parallel to a field **E** applied along the substrate normal, although subthreshold fields can rotate the director clockwise or counterclockwise on the tilt cone, with the rotation angle being a function of the applied field. When **E** is large enough, the layers straighten to provide the bistable bookshelf alignment (**B**), with a concomitant increase in birefringence.

the twofold symmetry axis and perpendicular to it. Thus, both refractive indices are large, and Δn is small.

With an applied field $\mathbf{E} > E_{\mathrm{th}}$, the sample switches to the bistable blue surface-stabilized structure with markedly increased birefringence. This texture appears to have the layers normal to the surfaces ($\delta = 0$, parallel to the applied field) (Fig. 5B). The system is driven to this bookshelf layer geometry by the tendency of the polarization to orient parallel to the applied field. Because the polarization is in the layer plane, this preferred orientation of the polarization parallel to the field cannot be achieved with tilted layers. The "straightening" of tilted layers in this case is similar to the formation of quasi-bookshelf alignment with chevron SmC* materials upon application of large electric fields and is not surprising (*20*). The bistable nature of the bookshelf-aligned system is in accord with the "monostable" behavior of the known AFE SmCP phases and is evidence that director alignment parallel to the surfaces is preferred. The birefringence increase is due to the highly biaxial nature of the molecules and the phase. In the bookshelf geometry (Fig. 5B), the conjugated aromatic units contribute to the polarizability only for light polarized along the director.

All of the EO and current response characteristics of known B7 materials are consistent with a simplified model in which the B2 and B7 phases are actually diastereomeric SmCP structures, as shown in Fig. 2. The classic bow-phase mesogens in the B2 phase form an AFE $\mathrm{SmC_SP_A}$ racemate, and other known B7 materials are AFE $\mathrm{SmC_AP_A}$ conglomerates. By using interlayer clinicity as a stereochemical control element, we have created a bow-phase mesogen exhibiting a conglomerate $\mathrm{SmC_SP_F}$ structure with desirable FE order. However, the natural rule requiring at least one twofold symmetry axis normal to the director in smectic liquid crystals remains apparently intact.

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10. There is, a priori, no electrostatic free energy difference between the macroscopic FE and AFE structures, assuming that the layers are infinite homogeneous dipolar sheets. At the molecular level, one or the other structure could be favored electrostatically, depending on the details of molecule-pair correlations across layers. In the SmCP system, the magnitude of this effect, or indeed which structure should be favored electrostatically, is not known.
11. A SmCP phase with anticlinic methyl-terminated layer interfaces may be considered a smectic bilayer with all anticlinic layer interfaces (one of these layer interfaces cuts the molecules in half and is rigidly anticlinic because of the covalent structure). The polar symmetry of a bilayer smectic with all anticlinic layer interfaces is discussed in P. E. Cladis and H. R. Brand, *Liq. Cryst.* **14**, 1327 (1993).
12. All new compounds in the synthesis gave satisfactory ^{1}H and ^{13}C nuclear magnetic resonance spectra, mass spectra, and combustion analyses.
13. Molecules of triester **3** do not possess twofold symmetry. Such molecules (or indeed twofold symmetrical molecules) may spontaneously organize such that the twofold symmetry of the phase is broken, leading to smectics with C_1 symmetry. For example, the bow-phase system could spontaneously organize to produce tilt in the projection of the director on the polar plane, leading to bow-phases with C_1 symmetry [H. R. Brand, P. E. Cladis, H. Pleiner, *Eur. Phys. J. B* **6**, 347 (1998)]. There is no compelling evidence to date, however, that such symmetry breaking occurs in the bow-phases. Thus, in the smectic phases of triester **3**, molecules are oriented randomly about the axis normal to the director, and the twofold symmetrical symbolic structures shown in Fig. 1 capture the symmetry of the phase rather than of the molecules. The presence of twofold symmetry normal to the director (about **P**), such that properties of the phase are invariant with sign of the director, is the only "symmetry rule" remaining intact in the smectic LC field.
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16. All attempts to prepare freely suspended films of triester **3** failed. Instead, stable freely suspended liquid crystal fibers of $\sim$10-μm diameter are produced. X-ray diffraction from these fibers shows them to consist of smectic layers in the form of concentric cylinders. Although this observation provides additional confirmation of the fluid smectic nature of the B7 phase, such fibers have not, to date, proven useful for determining the FE or AFE nature of the phase. On the basis of a very small number of examples, it appears that the tendency to form fibers instead of films is general for B7 materials. Details of the x-ray scattering observed for triester **3**, and apparently for all B7 materials, are quite unusual and complex. In bulk unaligned samples, there appear to be multiple coexisting phases with slightly different layer spacings that are all close to the extended length of the mesogen. This could result from metastable structures forming from the isotropic melt along with the thermodynamic phase. Additional scattering peaks suggest some kind of periodic order in the plane of the layers, on a very large length scale. A full understanding of the B7 structure requires an explanation of this unusual x-ray scattering behavior. The observed layer spacings, however, prove that no unusual interdigitation occurs in the B7 phase of compound **3**.
17. The LC cells used in the present work are of the same type as those used for characterization of the classic bow-phase materials (*7*). These cells, which are commercially available from Displaytech (www.displaytech.com), have glass substrates with a 3.5- to 4.5-μm cell gap, coated with low-pretilt polyimide alignment layers. The rubbing directions on the two substrates are parallel.
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An Orientational Transition of Bent-Core Molecules in an Anisotropic Matrix

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We report the discovery of an orientational transition of bent-core molecules in a background anisotropic medium, in this case a smectic liquid crystal made of rod-like molecules. The resulting director is apolar in nature, and the medium can be described as an orthogonal biaxial smectic. The detailed phase diagram of mixtures of the two types of compounds revealed the induction of two liquid crystalline phases that are specific to compounds with bent-core molecules. The chemical nature of the bounding surface had a marked influence on the observed textures.

Thermotropic liquid crystals are states of soft condensed matter that exhibit a large variety of orderings of molecules with shape anisotropy (*1, 2*). Nematics (N) exhibit a long-range orientational order of rod-like or disc-like molecules about a common axis called the director, which has apolar symmetry. They are used in practically all commercial flat panel display devices. If the molecules are rod-like, the translational symmetry can be broken along one direction, giving rise to different types of smectic liquid crystals (*1,*

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