Chiral Isotropic Liquids from Achiral Molecules

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A variety of simple bent-core molecules exhibit smectic liquid crystal phases of planar fluid layers that are spontaneously both polar and chiral in the absence of crystalline order. We found that because of intralayer structural mismatch, such layers are also only marginally stable against spontaneous splay deformation, which is incompatible with long-range order. This results in macroscopically isotropic fluids that possess only short-range orientational and positional order, in which the only macroscopically broken symmetry is chirality—even though the phases are formed from achiral molecules. Their conglomerate domains exhibit optical rotatory powers comparable to the highest ever found for isotropic fluids of chiral molecules.

P Pasteur discovered molecular chirality in sodium ammonium tartrate by showing that molecular species of opposite handedness phase-separated into distinct crystals upon growth from solution (1). Such an appearance of macroscopic chiral domains is now a commonly observed feature of the crystallization of both chiral and achiral molecules, and serves as the basis for a broad range of chemical and medical technology (2). Spontaneous resolution of chiral molecules or conglomerate domain formation of achiral molecules requires intermolecular interactions that are specific and strong enough to collectively expel or rearrange molecules of the wrong handedness. This situation is most readily achieved in the phases with the lowest translational symmetry—the packed periodic environments of crystals—but was recently found in more symmetric phases, where stacked fluid layers of achiral bent-core molecules having a single broken translational symmetry in the form of the smectic layering were shown to exhibit macroscopic chiral conglomerate domains (3). Here we extend the exploration of macroscopic spontaneous chirality to fluids that are fully translationally symmetric and isotropic.

We show that even in a liquid with only short-range translational and orientational order, it is possible to preserve local structural specificity sufficient to enable the long-range propagation of chirality. The resulting phases are strongly optically active, exhibiting optical rotations of ∼1°μm for visible light; such values are exceeded only by macroscopically helixed liquid crystal phases (4).

Banana-shaped molecules with bent cores and one or two flexible tails exhibit a wide variety of novel structural phenomena involving the interplay of chiral, polar, and liquid crystalline (LC) order (5–7). The strong local preference for layering, coupled with the bent shape of the molecules, promotes molecular packing that is both polar [with the arrows of the molecular bows aligning in a direction \( \mathbf{p} \) in the layer plane (7)] and tilted (3) (with the molecular plane rotated about \( \mathbf{p} \)) to drive the formation of chiral layered phases such as the B2 and B7 phases (Fig. 1, A and B), (8, 9). One of the striking and mysterious properties of many of these bent-core systems is the presence of layered phases that we have termed “dark conglomerates” (DCs), which (as with the B2 phase) appear via first-order transitions from the high-temperature isotropic phase (10–18). The DCs, unlike the B2 smectics, have little or no birefringence and thus are nearly dark between crossed polarizers. However, they exhibit spontaneous macroscopic chirality more robustly than does the B2 phase, manifested by conglomerate domains up to hundreds of micrometers in size. We show that such DC phases are macroscopically isotropic fluids, with handedness as the only macroscopic ordering: a chiral coupling of local tilt, polarization, and layer deformation that limits the orientational and translational order.

We combined freeze-fracture transmission electron microscopy (TEM), x-ray diffraction

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Fig. 1. Simultaneous tilt and polar ordering is a common feature of phases formed from bent-core molecules. (A) The B2 phase is formed from the stacking of fluid layers of bent-core molecules, where the molecular long axis (\( \mathbf{n} \)) is tilted (by angle \( \theta \)) relative to the layer normal (\( \mathbf{z} \)). In addition, polar order of the molecules leads to a macroscopic polarization \( \mathbf{p} \) orthogonal to \( \mathbf{n} \) and \( \mathbf{z} \), and in the molecular plane—the plane that contains both of the half-molecular arms (\( \mathbf{a}_1 \) and \( \mathbf{a}_2 \)). The projections of the half-molecular arms onto the layer plane (\( \mathbf{a}_1' \) and \( \mathbf{a}_2' \)) are nearly perpendicular for most bent-core molecules. (B) The left- and right-handed layer structures. The B2 subphases consist of the four possible bilayer alternations of direction of \( \mathbf{p} \) and \( \mathbf{c} \). (C) The chemical structures, phase sequences, and layer spacing and correlation lengths (as measured by XRD and freeze-fracture TEM) of the three compounds studied here. The notation DC/B7 indicates that either the DC or B7 structure may be present, depending on sample thermal history or field application; similar notations have similar meanings.

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(XRD), and depolarized transmission light microscopy (DTLM) to establish the molecular organization of the DC phase in the materials W508, GDa226 (15), and racemic CITRO (19) (Fig. 1C), all of which transformed to chiral B2 phases under application of sufficiently large electric field (20), indicating that the inherent local layer structure is fluid, polar, and chiral (Fig. 1, A and B). The local chirality is maintained in this type of transition (21). We performed freeze-fracture TEM (20, 22), which enables visualization of the layer structure of smectic phases (9, 23) and, in the case of the DCs, shows the local layering as well as the layer curvature and distortion on larger length scales (Fig. 2, A, B, C, and F, Fig. 3A, and figs. S3 to S5). These images reveal the well-defined local smectic layering and its interfacial topography, showing a strong tendency for saddle splay layer deformation, as seen in GDa226 in Fig. 2, A and D, and Fig. 3A. The layer topography for CITRO appears more broken, although distinct saddle-shaped domains can still be seen and are decorated with undulations of the polarization splay stripes of the B7 phase (Fig. 2, C and F), which have a short wavelength in CITRO (9).

Occasionally, fracture occurs at the LC-glass interface, where the layers have a tendency to terminate normal to the surface. This partially constrains the DC texture, but enables excellent visualization of the disorder characterizing the DC in the surface plane [Fig. 2A (upper half), Fig. 2B, and figs. S3 to S5]. Individual smectic layers are visible and form a periodic structure with layer spacing of ~5 nm, consistent with the layer spacing measured by XRD (Fig. 1C). Unlike smectic lamellar phases, the layers of the DC are planar over only very short distances (<100 nm), as a result of the layer folding, bending, and twisting, although (as in bulk smectics) the layer spacing appears to be uniform throughout. The layer disorder of the phase was further confirmed by XRD, where diffuse Bragg lamellar reflections are indicative of only short-range layer ordering (Fig. 1C and figs. S1, S2, and S6). Additionally, despite their substantial curvature, the layers intersecting the fracture plane are continuous over long distances, with edge dislocations marking the end of a layer only occasionally visible (Fig. 2B and figs. S4 and S5). The DC layer structure is characterized by sets of nested curved layers with defects localized to lines where the radius of layer curvature approaches the layer spacing.

In the DC structure, the layer surfaces are largely continuous, enabling a local field (e.g., the handedness) to percolate through space and attain long-range order. In particular, the DC optical texture exhibits chiral conglomerate domains—macroscopic patches of highly uniform optical activity of opposite handedness, 10 to 100 μm in size (Fig. 2, I to K). The optical rotation is clearly visible because of the low birefringence, which is the result of the isotropy of the DC phase and its having an orientational correlation length that is small relative to the wavelength of visible light. Typically there are ~100 independently oriented domains per cubic wavelength of green light, so that although the local birefringence is large, it is reduced by orientational averaging. The optical activity of the DC phases of W508 and GDa226 was characterized by measuring the optical rotation as a function of wavelength (fig. S8), which

![Freeze-fracture TEM (A to F) and DTLM (I to K) images of the DC phase (A) to (D), (F), and (I) to (K) and B7 phase [(E) and (K)] of GDa226 [(A), (D), and (I)], W508 [(B), (E), and (J)], and CITRO [(C), (F), and (K)]. The freeze-fracture TEM images reveal that in the DC, although the local layering is well defined, the layer topography is highly curved, forming saddle-shaped domains. Occasional layer steps in the freeze-fracture TEM [red arrow, (A); magnified in (D)] identify the saddle-shaped domains as the surfaces of individual layers. When the fracture occurs at the nylon-coated glass surface [(B) and upper half of (A)], the layer orientation is preferentially perpendicular to the surface, and the ends of individual layers are apparent as faint lines whose measured spacing is consistent with that measured by XRD (see also figs. S3 to S5). As is particularly apparent in (B), the layers, although highly curved, are continuous over long distances (see also figs. S3 to S5). These two features, layer curvature and layer continuity, are characteristic of the lyotropic sponge phase [(H), from (36)], with the empty volume filled with smectic layers [(G)]. The layer topography of CITRO [(C) and (F)], in addition to showing a distinct saddle shape, is decorated with undulations of its B7 phase. W508 shows B7 undulations in the focal conic texture of (E), but not in the DC phase. The orientation of the layer undulations is governed by the layer curvature, with the polarization direction between the two principal curvature directions. In (I) to (K), the DC phase appears dark between crossed polarizers (center images), and domains of opposite-handed optical activity become apparent upon decrossing of the analyzer relative to the polarizer (top and bottom images). Coexisting B7 domains in CITRO are bright because of their birefringence (K). Image widths in (I) to (K) are 300 μm.
was found to be well described by models typically used to account for the dispersion of the optical anisotropy of LC materials (24). This finding is consistent with the view that there is no chiral organization on a length scale larger than the wavelength and that the optical rotation is a result of the chiral organization of the local molecular optical anisotropy (25, 26). A local structure of flat synclinic or anticlinic chiral layers does not appear to generate enough optical rotation to account for the DC data (27, 28), indicating that saddle splay layer curvature may have to be introduced into the optical modeling of the optical rotation.

The topology of individual layers in the DC phase resembles that of the layers of the lyotropic sponge phase (Fig. 2H and Fig. 3D) (29, 30), an isotropic phase of bilayer sheets of amphiphiles characterized by well-defined interfaces and layer deformation. These phases are produced in systems with sufficiently low membrane rigidity (31) or an inherent preference for membrane curvature (32). Such phases are not typically seen in lyotropics at high surfactant concentration or in thermotropic smectics because in these systems the layers are in more intimate contact and cannot act independently; rather, they are constrained to more definite layer spacing everywhere. Under this constraint, layer curvature is possible but is limited to the familiar focal conic-like structures observed as defects of lamellar smectics (29) (Fig. 3). Several reports of isotropic phases with observable layering correlations suggest that this type of behavior might be possible in thermotropic smectics (33, 34).

The freeze-fracture TEM images show that the DC layer system is locally lamellar but globally disordered. Disorder must arise either from thermally generated fluctuations (as in the case of the lyotropic sponge phase) or enthalpically, from an energetic preference for local saddle splay of the layers—the dominant motif of disorder in the freeze-fracture TEM images. The local lamellar structure does not exhibit any features consistent with enhanced fluctuations; the layers are smooth.

**Fig. 3.** (A) The layer structure of the DC phase is characterized by sets of nested curved layers with defects localized to lines where the radius of layer curvature approaches the layer spacing. (B) This overall organization is analogous to that of focal conic (FC) defects, particularly those of type I (characterized by negative Gaussian curvature) rather than of type II (characterized by mean curvature). We consider the toric focal conic defect in (B) to be a good model for the spatial organization of the DC phase. (C) Space can be filled with predominantly FC I and little contribution from FC II—for example, to form (D), the cubic bicontinuous (P-surface) plumber’s-nightmare structure (30).

**Fig. 4.** Frustration between molecular fragments in a tilted bent-core molecule can be relieved by saddle splay curvature of the layers. (A) The projections of the two half-molecular arms (green and blue cylinders) onto the layer plane ($a_x^1$ and $a_x^2$) are nearly orthogonal (the case shown here) for most tilted bent-core molecules. (B) Simulation of the SmC phase of rod-shaped molecules shows an elongation of the in-plane pair correlation function, $g(r)$, in the direction of the molecular tilt. The bent-core molecular arms, each tilted by $\gamma$ relative to the layer normal, will also have oblong preferred in-plane correlations (C to E), which costs energy to deform into a circularly symmetric organization required for the formation of flat layers with tilted molecules. This energy cost can be relieved by layer curvature. (F) For example, consider the case of two elastic sheets of different length; if the longer (green) is compressed and the shorter (blue) is dilated, they can be made to match. If they are then attached at the interface and left to relax, the structure will curve, partially relieving the compressional and dilational stresses imposed on the sheets. (G) Similarly, the orthogonal tilt directions of the two half-molecular arms produces in each direction a dilation in one half-layer and compression in the other half; saddle splay curvature can reduce this frustration. Upon passing from one sublayer to the other, opposite pairs of molecules in groups of four exchange their nearest-neighbor status, as shown in (E).
and of nearly constant thickness, with variations in spacing suppressed by the layer compressional elasticity. We therefore explored the possibility of an energetic preference for layer saddle splay, specifically related to the bent molecular shape and polar order.

The fluid bent-core smectics possess structural frustration not present in other layered LCs or crystals. The molecular length (larger than for typical calamitic LCs) and molecular bend reduce out-of-layer fluctuations, strongly stratifying the layers. For molecules with flexible tails at either end, the areal confinement of the tails results in an entropic pressure tendency to increase the in-plane area per tail, a response that can be achieved by the tilting of the molecular planes defined by the half-molecular arm directors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) (Fig. 1A) through an angle \( \theta \) with respect to the layer normal \( \mathbf{z} \). Because of the molecular bend (i.e., the finite angle \( \psi \) between \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \)), the tilting of the \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) molecular planes leads to different in-plane azimuthal orientations of the tilt planes of the individual molecular arms about \( \mathbf{z} \), given by the half-molecular arm tilt directors \( \mathbf{a}_1' \) and \( \mathbf{a}_2' \) (Fig. 1A and Fig. 4A). For the geometry typical of bent-core fluid smectics (\( \psi = 120^\circ \) and \( \theta = 30^\circ \)), \( \mathbf{a}_1' \) and \( \mathbf{a}_2' \) are nearly perpendicular.

This situation produces a strong tendency for negative Gaussian curvature of the layers via the coupling of the tilt of the molecular arms to molecular positional correlations in the two-dimensional (2D) molecular liquid that is the layer. Figure 4C shows a computer simulation of the molecular positional pair correlation function \( g(r) \) (the average distribution of molecules about a given molecule) of a fluid, tilted, smectic layer, in this case a smectic C (SmC) of rod-shaped molecules, which should serve as a good model of the half-layer of half-molecular arms of a bent-core system (35). We assume a half-molecular arm tilt from the layer normal, \( \mathbf{z} \), of \( \gamma = 30^\circ \). The molecular 2D fluid is characterized by a local stretched hexagonal lattice, evident from the ellipsoidal ring of six peaks about the origin, with a correlation hexagonal lattice, evident from the ellipsoidal ring of six peaks about the origin, with a correlation hexagonal lattice, evident from the ellipsoidal ring of six peaks about the origin, with a correlation.

The situation depicted in Fig. 4F and G—where the sublayers are subjected to compression in order to match their pair correlations, laminated together, and then left to relax to a curved state—can be quantitatively modeled using the rotational coupling \( \mathbf{P} \cdot \mathbf{L} \) between layers (20) by regarding the sublayers as elastic sheets of thickness \( d/2 \), in which there is in-plane dilation and shear under a condition of zero stress along the layer normal. For simplicity we assume that the half-layer sheets are of isotropic elastic material, characterized by compressional and shear moduli \( M \) and \( \mu \), respectively. The upper and lower sheets are subjected to a pure in-plane shear strain of opposite sign, \( \epsilon_{\nu\nu} \), given by the elastic shear coupling \( \nu \) leading to Eq. 1, meaning that of the B2 subphases, the four possible bilayer alternations of \( c \) and \( f \) (Figs. 1 and 4), only the homochiral SmC\( \text{P}_2 \) and SmC\( \text{P}_4 \) give a tendency for homogeneous saddle splay [i.e., have the same sign of saddle splay in adjacent layers (20)], with the racemic SmC\( \text{P}_2 \) and SmC\( \text{P}_4 \) cases producing alternating sign and thus remaining flat. Because \( L \) is symmetric under combined mirror reflection and 90° rotation about \( z \), racemic alternations with longer pitch (e.g., a four-layer 90° clock; Fig. S9) will also produce homogeneous saddle splay, which may explain the observation of achiral DCs (36). Second, the freeze-fracture TEM images reveal a layer organization that, although disordered on length scales longer than \( \sim 100 \) nm, exhibits distinctly focal chiral-like structures locally. In space-filling focal conic arrays, neighboring defects shift continuous layers, a feature also exhibited by the DC disordered focal conic arrays shown in Fig. 2 and figs. S3 to S5, and illustrated by the paths in figs. S4 and S5. Changes in chirality between adjacent layers in the planar layered B2 phases are much more prevalent than in layer chirality changes (5, 37); as a result, layer continuity becomes an effective means of propagating layer chirality changes in the DC phases and constitutes a basic reason why such isotropic chiral fluids can be formed from achiral molecules (20).

**References and Notes**

Helical Nanofilament Phases

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In the formation of chiral crystals, the tendency for twist in the orientation of neighboring molecules is incompatible with ordering into a lattice: Twist is expelled from planar layers at the expense of local strain. We report the ordered state of a neat material in which a local chiral twist order is induced by its achiral molecules, the layers in the planar smectic phase being broken into twisted and rigorously chiral—a broken symmetry. The precise structural definition achieved in filament self-assembly enables collective organization into arrays in which an additional broken symmetry—the appearance of macroscopic coherence of the filament twist—produces a liquid crystal phase of helically precessing layers.

The principal ordering motif of materials at low temperature is crystallization, the organization of atoms or molecules into layers. However, some species—for example, pear-shaped molecules with mutually adhesive stems—prefer to assemble into aggregates that do not pack very well into layers. With such frustration, crystallization can take place at the expense of local strain or may be suppressed entirely. In addition to these homogeneous possibilities, ordering into inhomogeneous states can occur in which the local preference is manifest only in some places, leading to order that is spatially modulated on the mesoscopic scale. Interesting and useful phenomena result, including vortex lattice (1) and magnetic stripe phases (2), lipid bilayer ripples (3), and polarization splay modulation (4).

A particularly noteworthy instance of competition between local preference and global ordering is that between chirality and layering, present in all chiral crystals and layered chiral liquid crystals. The chiral packing of molecules induces local molecular twist, but macroscopic ordering into layers expels twist, leaving the local organization strained. In fluid layered (smectic) liquid crystals of rod-shaped molecules, this competition produces inhomogeneous phases in which molecular and layer twist coexist, the latter enabled by periodic arrays of (twist) grain boundaries (5, 6) or melted sheets (7). Here, we studied a system of simple bent-core molecules in which a particularly strong coupling between chirality and layering originates in the requirement to accommodate the size of shape of the molecules and layers into a robust tendency for layering. The bent-core molecules are achiral, but spontaneous polar order and chirality appear as broken symmetries, coupling to drive local Gaussian curvature (saddle splay deformation) of the layers—a local solution that cannot fill space. This frustration leads to a spectacular hierarchical structure in which layering can appear only if twisted, doing so in the form of nanofilaments of twisted layers. The nanofilaments in turn collectively organize into a homochiral liquid crystalline array with coherent twist. Such macroscopic nanoporous assemblies of helically precessing layers are unanticipated solutions to the problem of obtaining coexisting layering and twist in a condensed phase, and may be useful in applications requiring chiral nanoporous media.

The helical nanofilament (HNF) phase, hertofore known as the B4 phase, was one of the first new phases to be observed once the directed exploration of thermotropic smectics of bent-core molecules commenced (8–10). However, its structure and origin have remained obscure and controversial despite extensive study (11–13). The observation of strong optical activity (14) (fig. S11), indicating twist of molecular orientation, as well as x-ray diffraction (XRD) evidence for smectic layering (9, 15) led to the proposal that the B4 phase was some kind of smectic phase with twisted layers (9). However, both the presence of in-plane two-dimensional (2D) positional ordering (15) and XRD evidence showing that the layer ordering in the B4 phase was only short-range (Fig. 1C) were inconsistent with the available models of twisted smectics of chiral molecules—long-range ordered smectic blocks separated by twist grain boundaries (TGBs) (16). Here, we present the structure and origin of a quite distinct way of accommodating twist and layering, which suggests the existence of alternative modes of accommodation of tendencies for local and long-range ordering in a variety of modulated materials systems.

We studied the B4 phase of bent-core compounds in the phenylene bis(alkoxyphenyliminomethyl) benzoate (PnP0IMB) series (9) with the use of atomic force microscopy (AFM), freeze-fracture transmission electron microscopy (FFTEM), x-ray and electron diffraction (XRD, ED), and depolarized transmission light microscopy (DTLM) (Fig. 1A) (16). The B4 phase appears upon cooling from the isotropic phase or from the B2 or B3 phases, smectics in which the achiral bent-core molecules have spontaneously developed polar order and tilt to form chiral planar layers with long-range lamellar order (17, 18). The transition to the B4 phase is marked by the in-plane hexatic