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Reflection Symmetry Breaking in Achiral Rod-Shaped Smectic Liquid Crystals?

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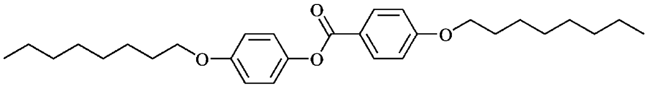
In a recent publication, Kishikawa et al. presented data[1] on the classic and much-studied achiral calamitic smectic mesogen, 4′-octyloxyphenyl-4-octyloxybenzoate (**1**, transition temperatures are °C, heating/cooling rate 1 °C/min),[2] which they interpret to indicate that the SmC phase of **1** is chiral and forms a conglomerate. Here we describe results of an investigation showing that the reported evidence for chirality of this SmC phase actually derives from surface interactions. In addition, new lines of optical and electrooptical investigation probing both the chirality and polarity (macroscopic polarization **P**[3]) of this phase are described. On the basis of this work, we conclude that the SmC phase of **1** is neither chiral nor polar.



1: On heating: X — 63.3 — SmC — 73.8 — N — 93.1 — I
On cooling: X — 51.2 — SmC — 72.4 — N — 90.5 — I

It is now well established that chiral liquid crystal phases can be produced by achiral bent-core or banana-shaped molecules.[4] The most well-studied of these are the SmCP phases, where four anisometric supermolecular structures (two conglomerates and two macroscopic racemates) share the same chiral layer structure. The chiral SmCP phases represent the first example of conglomerate formation in a fluid, and several mechanisms regarding the origins of the chirality of the phases have been suggested.[1,4b,5]

One of the most interesting proposals in this regard has become known as the conformational chirality hypothesis.[5] On the basis of the observation of an unexpected anisochrony of certain nominally homotopic carbon atoms as seen by ^{13}C CP-MAS spectroscopic analysis of mesogens in the SmCP phase,[5] this hypothesis holds that chiral phenylbenzoate conformations, with small barriers separating enantiomeric conformations in the gas phase or in solution, can be "frozen" in the LC phase, becoming essentially chiral configurations in the smectic. While the solid-state NMR result upon which this hypothesis is based has recently been refuted,[6] the conformational chirality hypothesis remains important and continues to motivate research.[5,7]

By this hypothesis, the SmCP layers are essentially composed of a racemate. Formation of the chiral layer structure then involves spontaneous deracemization of the atropisomeric chiral molecules. The latter phenomenon is, of course, very common in organic crystals[8] and has been reported in a racemic rod-shaped (calamitic) smectic liquid crystal composed of conventionally chiral molecules.[7a,9]

The conformational chirality hypothesis applied to smectics is of fundamental importance, really speaking to the most basic nature of a smectic LC—is a smectic more crystal-like or more fluid-like? It can be argued that "freezing of conformations" is a defining characteristic of crystals, while conformational mobility is defining of the fluid state.

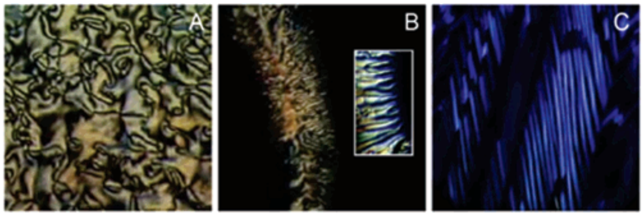


Figure 1. (A) Random schlieren texture observed for **1** in an LC cell prepared using native glass substrates. (B) Splay stripes at the LC/air interface of a droplet (solid black areas have no LC) of **1** placed on a glass substrate (inset at higher magnification). (C) Quasi bookshelf stripes formed after application of an electric field.

The study of ref 1 represents the first claim of formation of a chiral SmC phase from an achiral calamitic mesogen. This result reasonably flows directly from a combination of "frozen" conformational chirality and spontaneous deracemization in smectic layers, as has been suggested as the origin of the chirality of the SmCP phases (why would these phenomena be restricted to bent-core mesogens?), and provides a strong argument in favor of the conformational chirality hypothesis. The result, however, is surprising since careful prior studies of **1**, which should have revealed such chirality if it were present, failed to do so.[2d]

The key observations of ref 1 leading to assignment of a chiral structure to the SmC phase of **1** include the following: (1) homeotropically aligned cells of **1** exhibit optically active domains by polarized light microscopy; (2) circular dichroism (CD) in the wavelength range of 300−310 nm is observed for homeotropic cells of **1**; and (3) parallel-aligned cells show chiral SmC helical pitch lines. In addition, mixing experiments are described. Doping of **1** into an achiral SmC host causes the helical pitch to increase in parallel-aligned cells, while addition of a chiral dopant to **1** enhances the CD signal and increases the area of one handedness of the optically active domains observable in homeotropic cells.[1]

We have reproduced all of the key textural observations of ref 1. Homeotropic domains are found (see Supporting Information for details on cell fabrication) in which, consistent with ref 1, optically active domains of both handedness are easily observed. In addition, optically inactive homeotropic domains showing a random schlieren texture are also seen (Figure 1A). We find in these observations no evidence suggesting that the SmC phase of **1** is chiral. Rather, the observations can be understood on the basis of well-known textural and interfacial effects of achiral SmCs (see below).

Furthermore, the "helix pitch lines" reported in ref 1 are not similar to the texture normally seen in parallel-aligned chiral SmC cells. These patterns are, however, precisely identical to periodic splay stripes, which are seen at a SmC/air interface[10,11] or in certain

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10.1021/ja060478o CCC: $33.50

banana phases.[12] In the textures shown in ref 1, the stripes apparently appear only at LC/air interfaces, caused by the presence of air bubbles in the cells. Such stripes are very easily produced at the free surface of LC droplets of **1** placed on a single glass substrate (Figure 1B). Interestingly, the appearance of these splay stripes, which are especially prominent for **1**, does involve spontaneous reflection symmetry breaking—driven by the polar nature of the LC/air interface (see Supporting Information).[11]

The occurrence of optically active domains in homeotropic cells of the SmC phase of **1** is simply a result of pinning of the *c*-director at the two surfaces,[13] at some relative angle different from 0°, giving twisted configurations. The CD spectra reported in ref 1 provide no evidence for a chiral phase, also deriving from the surface-induced twist of the *c*-director. It has been shown that a surface-stabilized twisted nematic of achiral molecules shows CD spectra very similar to those given in ref 1.[14]

To summarize, the observation of an optically inactive random schlieren texture in homeotropic domains of **1** along with optically active domains by itself provides strong evidence that the optically active domains result from surface interactions. This, combined with the fact that the stripe texture reported in ref 1 is not due to the presence of a SmC helix, calls into question the interpretation suggesting a chiral SmC phase for **1**.

To probe the issue further, additional tests for chirality and polarity were applied to preparations of **1**. Polarity is of relevance since a SmC phase that is chiral must also be polar (ferroelectric), due to its monoclinic symmetry, following the argument of Meyer.[3] This coupling is particularly useful in probing either chirality or polarity in SmC phases, as it produces distinctive electrooptic behavior highly and uniquely sensitive to the presence of chirality.

First, to remove possible influences on the director structure of anisotropy in the surfaces contacting the LC, thick freely suspended films (>100 layers) were prepared and studied by depolarized reflected light microscopy (DRLM).[15] No evidence of chirality was observed in these films; random schlieren textures of the *c*-director (the projection of the molecular director onto the layers) were observed, exhibiting no optical activity. In addition, splay stripes were observed at the LC/air interface of the films.[11] As expected, the pitch of these stripes was a function of film thickness.[10] These being necessarily "homeotropic" samples, the observed periodic pattern cannot be SmC helix pitch lines.

The response of thin freely suspended films of **1** (two and three layer films were studied) to electric fields applied parallel to the layers was measured using high-resolution null-transmission ellipsometry (NTE).[16] This experiment provides an ultra-sensitive probe of polarity and *c*-director twist through the film. In fact, NTE exhibits no observable ferroelectric response, showing that either the phase is achiral or the polarization is so small that it cannot be observed.

Finally, samples of **1** were prepared using commercial 4 μm ITO/glass cells possessing parallel-rubbed low pre-tilt polyimide alignment layers.[17] Such cells are expected to provide parallel alignment, with the director in the nematic phase oriented along the rubbing direction. These cells, on cooling from the isotropic through the nematic into the SmC phase, behaved in a manner consistent with the formation of an achiral SmC phase with a chevron layer structure. No suggestion of helix pitch lines could be observed. In addition, application of small electric fields gave electrooptic switching behavior, which was dielectric in nature. Again, no evidence for ferroelectric polarization could be detected in this extremely sensitive probe for chirality.[18] Interestingly, at high fields (>12 V/μm), boat-wake defects appeared,[19] evolving to yet another periodic stripe texture, these being "quasi-bookshelf" stripes due to the formation of horizontal chevrons (Figure 1C).[20]

In conclusion, the optically active homeotropic domains described in ref 1 derive from interactions with the substrate surfaces. The stripe patterns described in ref 1 in putatively parallel-aligned cells are actually splay stripes deriving from the presence of an LC/air interface. In addition, no evidence for the presence of a ferroelectric polarization in the SmC phase of **1**, a necessary result of chiral symmetry of the phase, could be found, even though very sensitive tests for such polarization were applied. On the basis of the results presented here, no credible evidence for chirality of the SmC phase of **1** has been presented to date.

Acknowledgment. We thank the Liquid Crystal Materials Research Center (NSF MRSEC Award No. DMR-0213918) for financial support of this work.

Supporting Information Available: Synthesis and characterization of **1**, details of cell fabrication, photomicrographs of chiral domains in homeotropic cells, electrooptics and formation of boat-wake defects in aligned polyimide cells, photomicrographs of splay stripes in freely suspended films, data obtained in the NTE experiments, additional discussion, and complete ref 12. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA060478O