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Supermolecular stereochemistry in ferroelectric liquid crystals

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ABSTRACT: Until recently, it was an empirical fact that chiral liquid crystal phases were produced only from enantiomerically enriched liquid crystal materials. Ferroelectric smectic liquid crystals have always been composed of enantiomerically enriched molecules as well. Here we describe the first example of the formation of chiral supermolecular liquid crystalline structures from achiral bent-core molecules (bow phases or banana phases). In one case, a metastable antiferroelectric bow-phase structure is macroscopically chiral, with bulk samples composed of chiral macroscopic domains of either handedness. This system represents the first known liquid conglomerate. In addition, based upon a directed design approach exploiting control of interlayer clinicity, a ferroelectric liquid crystal conglomerate has been created from a racemic mixture. In this case bulk ferroelectricity is obtained by spontaneous polar symmetry breaking. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: ferroelectric liquid crystals; supermolecular stereochemistry

INTRODUCTION

Ferroelectric liquid crystals (FLCs) combine the powerful macroscopic property of net polar symmetry and a resulting spontaneous (indefinitely stable) macroscopic electric polarization, with the processibility of a fluid. This combination is unique, and has led to a huge research and engineering effort to create useful photonic devices and systems exploiting FLCs. At this point these are not commercial. However, it appears likely that high-volume products based upon FLCs, ranging from rear-projection HDTV sets based upon FLC-on-silicon microdisplays[1] to flexible displays for smart credit cards[2] and photonic switches for the Internet,[3] will become important in the first decade of the new century. At the same time, the fundamental science of chiral smectic liquid crystals (the most heavily studied variety of FLCs) continues to evolve at a pace surprising even to long-term members of the FLC research community.

One of the most exciting of these new FLC research areas involves the LC phases formed by bent-core smectic mesogens, often referred to as banana phases or bow phases. This area has proven a stereochemical delight, providing very interesting and unusual examples of spontaneous chiral symmetry breaking and spontaneous polar symmetry breaking in smectic LCs. These phenomena, of interest from both fundamental and applied viewpoints, are briefly described below.

BACKGROUND

The basic geometry of the well-known chiral smectic C* phase (SmC* = a tilted, layered LC phase composed of enantiomerically enriched molecules) is given in Fig. 1. The polar symmetry and macroscopic polarization of the SmC* phase was first proposed, then demonstrated by Meyer *et al.* based upon simple symmetry considerations.[4] The key spontaneous symmetry-breaking events which occur with formation of the SmC* phase are (1) breaking of isotropic symmetry with spontaneous formation of long-range orientational order characteristic of calamitic (composed of rod-shaped molecules) LC phases (the average long axis, or molecular director, of the molecules in the phase are, on average, parallel); (2) formation of long-range positional order in one dimension, producing the well-known layered structure characterizing smectic LCs; and (3) a uniform tilt of the molecular director within each layer, and from layer to layer, producing the synclinic layer interfaces of the SmC phase. These spontaneous symmetry breaking events by

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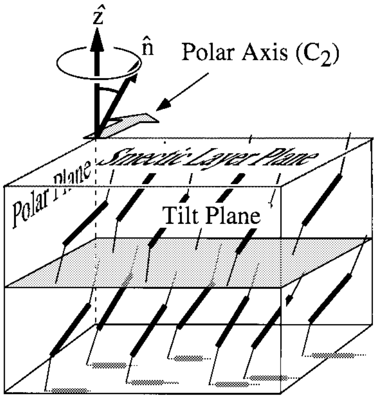

Figure 1. Basic structural features of the chiral smectic C* phase

themselves produce a phase with the non-polar C_i symmetry. Meyer's *et al.* key insight was to realize that if the molecules were made enantiomerically enriched (*not* a spontaneous symmetry breaking!), then the symmetry of this SmC* phase becomes C_2, a subgroup of $C_{\infty v}$ and therefore polar.

Still to this day, all known switchable polar smectics (both ferro- and antiferroelectric) possess one twofold symmetry axis (the polar axis) in the ferroelectric state. In order to avoid the problem of unambiguously establishing the 'director' to define the geometry of the system, we define the SmC tilt plane to be normal to this polar axis, as shown. Furthermore, we define the polar plane to contain the polar axis and the layer normal.

Achiral polar smectics

Until 1996, all known ferro-/antiferroelectric smectics were composed of enantiomerically enriched molecules after the Meyer paradigm. The polar nature of an anticlinic bilayer smectic composed of achiral molecules (C_{2v} symmetry), however, was pointed out in the literature at least as early as 1993 by Cladis and Brand.[5] In bilayer smectics, well known prior to the 1990s, adjacent layer interfaces are, by definition, different. Owing to this spontaneous symmetry breaking, each layer in a bilayer smectic is necessarily polar, with polar ordering along the layer normal. All known bilayer smectics were untilted, however, leading to a macroscopic non-polar structure where polar order within each layer is opposed in the next. Anticlinic layer interfaces are tilted smectic layer interfaces wherein the molecules tilt in opposite directions in adjacent layers.

Calamitic 'monolayer' smectics possessing all anticlinic layer interfaces, in both chiral and achiral systems, were well known as well. In 1996, Soto Bustamante *et al.*,[6] working in the Darmstadt group of Haase, discovered a tilted smectic bilayer in acrylate side-chain polymer–monomer mixtures. Their system was proven to be a smectic bilayer by x-ray scattering, which showed a smectic layer spacing much larger than the largest possible molecular length (this is the only unequivocal signature of a smectic bilayer to our knowledge). The pyroelectric behavior and dielectric response of the material showed it to be antiferroelectric, with switching to degenerate ferroelectric states upon application of electric fields of opposite sign.[6]

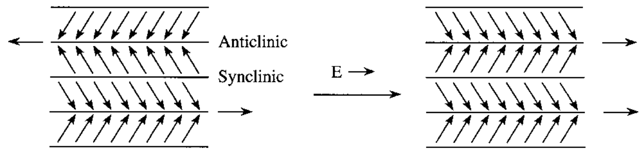

Figure 2. Structure of the achiral antiferroelectric SB/B phase and the achiral ferroelectric state produced upon application of an electric field

Soto Bustamante *et al.*[6] proposed a structure for this phase (hereafter referred to as the SB/B phase) where layer interfaces alternate between anticlinic and synclinic, as indicated in Fig. 2. The forces leading to the synclinic layer interfaces are apparently weak enough that switching to the all-anticlinic ferroelectric occurs, as indicated. Furthermore, there should be hysteresis in the switching, meaning that both the antiferroelectric phase and ferroelectric state both exist as minima on the hypersurface at some values of applied field (including possibly at zero applied field).

Since we define the tilt plane as being normal to the polar axis in the ferroelectric state of a smectic antiferroelectric, the average long axis of the molecules (director) in the SB/B bilayer phase is not tilted in projection on the tilt plane! We denote the polar ferroelectric state as an SmAP$_F$ structure (Sm indicating a layered structure, SmA indicating no tilt of the director

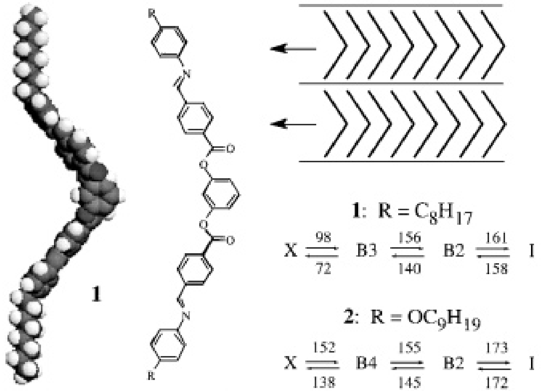

Figure 3. Structure, phase sequence and transition temperatures (°C) of two prototype bow-shaped mesogens. The structures of mesogens **1** and **2** were first reported in Refs [8] and [9], respectively. The C_{2v} structure proposed for the high-temperature LC phase of **1** in Ref. 8 is shown at top right

in the tilt plane, SmAP indicating a polar structure for layer pairs, and subscript F indicating ferroelectric order of the polarization of adjacent layer pairs). Similarly, the antiferroelectric ground state is denoted $\mathrm{SmAP_A}$ (subscript A for antiferroelectric). In the SB/B case, both the $\mathrm{SmAP_A}$ and $\mathrm{SmAP_F}$ structures are achiral, the ferroelectric state possessing C_{2v} symmetry. The $\mathrm{SmAP_A}$ structure of the SB/B ground state has been verified in thin freely suspended films.[7]

Application of an electric field to a pair of molecular isomers, one of which has a net dipole moment and the other of which does not, has a very small effect upon the relative free energies of the two isomers unless the field is extremely large. However, the collective free energy of LC phases is affected by applied fields in an exquisitely powerful way—this is the basis of most LC applications, and one of the most beautiful aspects of LC structure. In an antiferroelectric, application of a field causes the free energy of the ferroelectric state to become lower than that of the antiferroelectric structure at some accessible field strength owing to the free energy term associated with the coupling of ferroelectric polarization with applied field (see Fig. 5). This is the nature of a true antiferroelectric.

BANANA MANIA

At the 16th International Liquid Crystal Conference in June 1996, Takezoe and co-workers started a flurry of activity in the FLC community with the report of an achiral ferroelectric 'banana phase' observed for banana-shaped mesogens of type **1** (Fig. 3).[8,9] A ferroelectric structure was proposed for the high-temperature smectic phase in these compounds (labeled B2 in the phase sequences shown), as indicated. This proposed structure is $\mathrm{SmAP_F}$. Furthermore, textures observed by polarized light microscopy in this phase prompted Takezoe and co-workers to suggest the spontaneous formation of a helix normal to the polar axis, unwound by application of an electric field. It was suggested that this spontaneous chiral symmetry breaking might involve chiral conformations of the mesogens.

Since Takezoe and co-workers original report, the groups of Weissflog[10] and Heppke[11] have corroborated the key observations, and Weissflog's group has synthesized new variations on the structural theme showing similar phases.[10] Studies of the current response of parallel-aligned samples in response to applied fields by Weissflog led that group to propose an antiferroelectric ground state for the high temperature phase of the octyloxy homologue of **2**, and our work, as discussed below, shows this to be correct for both diesters **1** and **2**.

Takezoe, Weissflog and Heppke all suggest that packing of the banana-shaped molecules within the layers is the key to the observed polar order,[11] somewhat analogous to Osipov and Pikin's model for the polarization in the SmC* phase involving packing of steric dipoles in banana-shaped molecules.[12] Furthermore, it is at first attractive to consider the antiferroelectric nature of the bow phases to be a manifestation of an electrostatic free energy term favoring a non-polar ground state. The existence of the SB/B phase, however, suggests an alternative way of thinking about the molecular origins of both the polar order within each layer and the antiferroelectric ordering of adjacent layers in the bow phase system.

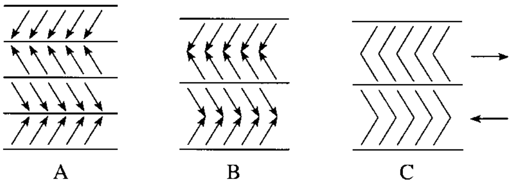

Figure 4. Illustration of the proposal that the in-layer polar order in the bow phase is driven by the layer interfaces (see discussion in the text)

Thus, consider the $\mathrm{SmAP_A}$ phase shown in Fig. 4(A). This graphic captures the essential structural features of the SB/B phase. Each layer is polar, but the 'steric dipole' argument does not seem to hold in these calamitic layers. The steric packing argument here simply favors the long-range orientational order within each layer (molecular directors parallel). The origins of the critical relative clinicity of adjacent layers in the bilayer smectic does not seem well suited to a conventional 'steric packing' argument. If the molecules in alternate adjacent layers were covalently linked to form dimers (e.g. at the arrowheads), the resulting structure [Fig. 4(B)] possesses antiferroelectric order if the dimers maintain a bent

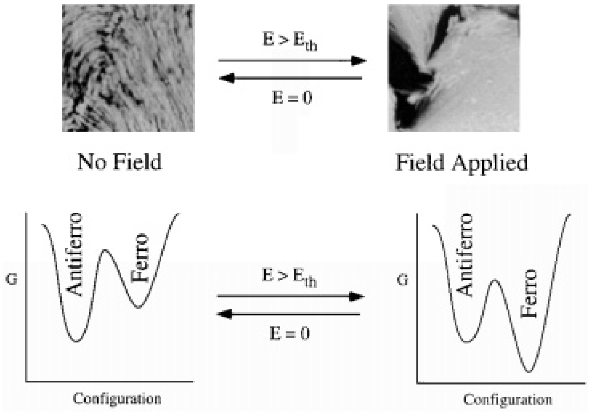

Figure 5. Antiferroelectric electrooptics observed for diester **2** in 4 μm transparent capacitor cells. The alignment has the tilt plane parallel to the substrates, with the polar axis within each layer perpendicular to the substrates. Here we have shown the ferroelectric state as a minimum on the configurational hypersurface at zero field. This is not necessarily the case, although at some value of the applied field both the ferroelectric and antiferroelectric structures must be minima on the surface

shape (a bow phase), although the ‘steric packing’ situation has not changed.

This dimer structure is the same as the antiferroelectric bow-phase structure illustrated in Fig. 4(C). In this model, molecules of type **1** and **2** are considered dimers, with a benzene ring linking two mesogens. The rigid nature of the *meta*-disubstituted linking group of the dimer enforces one ‘anticlinic layer interface.’ *A priori*, the other layer interface could be anticlinic (Fig. 3), or synclinic as shown in Fig. 4(C)—indeed, the latter would be expected based upon the typical behavior of alkyl-or alkoxybenzylideneanilines in tilted smectics. This model requires no special steric dipolar packing within the layers to maintain the in-layer polar order of the antiferroelectric phase. Rather, the structure is driven primarily by the layer interfaces. That is, bent mesogens (possessing effectively two ‘molecular directors’ linked by a rigid spacer enforcing a 120° angle between them) in a smectic with all synclinic layer interfaces of necessity possesses in-layer polar order and antiferroelectric order between layers, as shown in Fig. 4(C)

The first liquid conglomerate

As suggested above, our own experiments with diesters **1** and **2** in thin freely suspended films prove that in such films the high temperature ‘B2’ phase is antiferroelectric, in agreement with the current/voltage-based assignment of Weissflog and co-workers. The powerful technique of depolarized reflected light microscopy, with the polarizer and analyzer slightly uncrossed, revealed an additional structural feature not previously suggested.[13] Specifically, the data showed that in the freely suspended films, the average long axis of the bow-shaped dimers is tilted in the plane normal to the polar axis in each layer (the tilt plane), indicating a structure wherein the layers are chiral. This chirality results from a combination of uniform tilt within the layer and spontaneous polar order normal to the plane of this tilt. We use the descriptor SmCP to denote these phases (SmC = tilt, P = polar, no asterisk = molecules are achiral or racemic in the isotropic phase).

Additional studies of the electrooptic behavior of diester **2** in transparent capacitor cells (4 μm commercial Displaytech cells, parallel-rubbed, low pre-tilt polyimide on ITO/glass substrates) revealed the existence of four diastereomeric LC structures for **2**, a beautifully rich supermolecular stereochemistry for this material. Upon cooling from the isotropic melt, diester **2** forms an unusual smectic LC texture exhibiting two different types of domains in the polarized light microscope between crossed polarizer and analyzer. The majority domains (typically more than 90% of the sample) show a striped texture at zero field, as shown on the left in Fig. 5.

Application of an electric field above a threshold of about 5 V μm^{-1} causes a dramatic switching of the sample to a clean smectic A-like focal conic (here ‘SmA-like’ refers to a texture where the optic axis in the domains is oriented along the layer normal). Upon removal of the field the striped texture rapidly re-forms. The alignment is such that the layers are more or less normal to the substrates, with the director parallel to the substrates, and the polar axis in each layer normal to the substrates. There is apparently no azimuthal anchoring of the director relative to the rubbing direction. As indicated in Fig. 5, this behavior is consistent with an antiferroelectric phase which switches to a diastereomeric ferroelectric state upon application of a field. The antiferroelectric structure exhibits the striped texture in the cells, while the ferroelectric structure exhibits the smooth SmA-like texture.

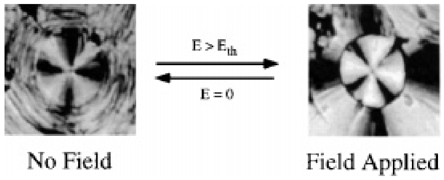

Figure 6. Minority domains formed by diester **2**. Domains often appear as a cylindrical focal conics (the layers are more or less perpendicular to the substrates, and are arranged as nested cylinders), as can be seen in these photomicrographs. The layer structure in the stripe texture of the majority domains and the SmA-like structure of the minority domains (zero field) is contiguous. The SmA-like nature of the ferroelectric state of majority domains (right, periphery), and the antiferroelectric phase of the minority domains (left, center), is easily seen in these photomicrographs (the polarizer is oriented vertically)

Interestingly, another pair of supermolecular structures is observed in the B2 temperature range for diester **2** in 4 μm cells. Upon cooling, these ‘minority domains’ appear as clean SmA-like focal conics surrounded by the striped texture at zero field, as shown on the left in Fig. 6. Most of the area of this picture consists of a single cylindrical focal conic layer structure. The minority domain in the center of the image clearly shows the optic axis is oriented parallel to the layer normal (the polarizer is vertical in these photomicrographs). Application of a field switches this structure to an SmC*-like texture where the optic axis rotates by $\pm\theta$ from the layer normal depending on the sign of the applied field. This behavior is strikingly chiral, in the sense that a clockwise or counterclockwise rotation of the optic axis occurs in response to application of an ‘up’ or ‘down’ field normal to plane of rotation. Half of such domains in the sample are ‘right handed,’ responding with clockwise rotation to a ‘down’ field, while half of the minority domains are ‘left handed,’ rotating counterclockwise in response to the same sign of applied field. To our knowledge, this chiral electrooptic behavior represents the first observation of a liquid conglomerate, analogous to Pasteur’s observation of the chiral nature of the famous racemic sodium ammonium tartrate crystals.

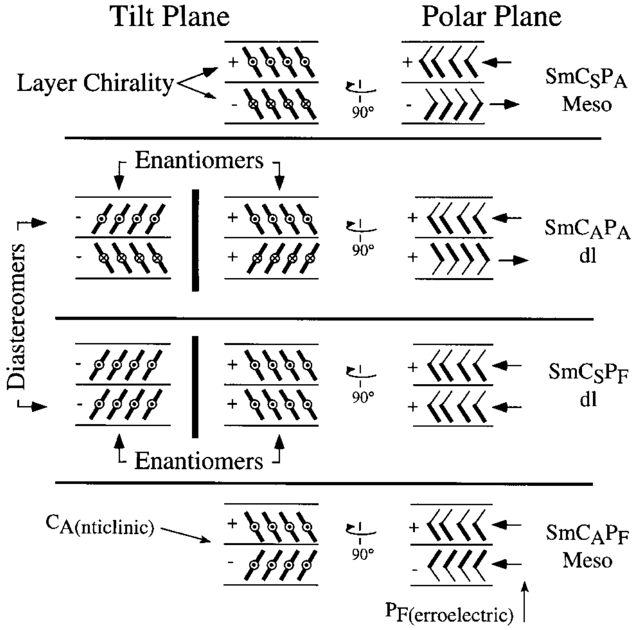

Figure 7. Structure of the SmCP diastereomers. The subscripts on C and P refer, respectively, to clinicity (Syn and Anti) and relative polar order (Ferro and Antiferro), of adjacent layers. The chirality descriptors + and − are defined as follows. If the 'arrows' fitted to the molecular bows are oriented parallel to the cross product of the layer normal and the director ($z \times n$), the chirality is said to be positive (+). If the arrows are opposed to $z \times n$, the chirality is negative (−). In all of these symbolic structures, the layer normal is in the plane of the page. When the molecules are viewed with the polar plane parallel to the page, the molecular directors are tilted out of the page, as suggested by using light and dark lines to build the structure

Cooling the sample of diester **2** produces a first-order transition into a new texture, labeled B4 in Fig. 3. Many experiments on this phase confirm that it is in fact a chiral crystalline phase with some sort of helical periodicity normal to the substrates, giving rise to Bragg reflection of left- or right-handed circularly polarized light from macroscopically chiral domains. The selectively reflected light is blue, leading to the name 'blue crystal' for the phase producing this texture. Many bent-core materials with alkoxy (but not alkyl) tails show the blue crystal phase.[11,14]

Melting of this crystal phase produces exclusively the macroscopically chiral 'minority' domains. The texture, essentially devoid of striped domains, may persist for many minutes, even under electric field driving. This is a remarkable example of the kinetic stability of a metastable liquid crystal structure. In addition, this observation suggests that somehow the structure of the blue crystal favors a transition into the metastable antiferroelectric phase of the minority domains rather than the striped antiferroelectric phase. This is analogous to kinetic control in an isomerization reaction—very common in chemical reactions but unusual in LC phase transitions.

The observation of the four distinct structures shown in Figs 5 and 6 proves the existence of at least two different (diastereomeric) minima on the hypersurface of diester **2**. The existence of a pair of macroscopically enantiomeric minima are also proven by the chiral response of the minority domains. The origins of the striped texture are complex, as described in detail in our previous publication on this subject.[13] Based upon the electrooptic behavior described above, coupled with careful measurements of the birefringence of the different domain types and detailed freely suspended film experiments, these results show that three antiferroelectric isomeric smectic structures are present as minima on the hypersurface for diester **2** at zero field. There may also be minima for the ferroelectric states at zero field, but not necessarily. A description of the interesting structures of these isomers, and the beautiful analogy between molecular and supermolecular stereochemistry in this system, follows.

The SmCP diastereomers

The structures of the four supermolecular diastereomeric structures observed for diester **2** are illustrated in Figure 7. Orthogonal views of each LC structure are given; a projection of the structure in the tilt plane on the left, and the structure projected on the polar plane on the right. The 'arrow heads' and 'arrow tails' indicated by ⊙ and ⊗, represent the orientation of imaginary arrows fitted to the molecular bows for the projections in the tilt plane. We consider the molecular director to be along the 'bow string' of the molecular bows. The director is parallel to the tilt plane, and tilted out of the polar plane. The key structural feature in this system is the geometric chirality of each layer, which derives from a combination of the tilt and spontaneous polar ordering within the layer.

The four diastereomers may be considered to result from the combination of three independent supermolecular stereogenic elements: (1) the chirality of each layer (+ or −); (2) the relative interlayer clinicity in the tilt plane for adjacent layers (synclinc or anticlinic); and (3) The relative orientation of the polar axes in adjacent layers (ferroelectric or antiferroelectric). Each 'element' has two possible configurations, leading to four diastereomeric structures. This is similar to, but not identical with, the presence of three tetrahedral stereogenic centers in a molecular structure.

The majority domains of **2** at zero field (the thermodynamically stable phase) possess a structure where the tilt is synclinic in adjacent layer pairs, while the polarization of adjacent layer pairs is antiferroelectric ($\mathrm{SmC_SP_A}$). Adjacent layers in this structure are necessarily heterochiral, affording a macroscopic supermolecular structure with net achiral symmetry. By supermolecular analogy with molecular stereochemical language, this diastereomer, which exists as one achiral structure composed of chiral parts, is termed '*meso*.' In solid-state organic stereochemistry, such a structure would be termed a macroscopic racemate. Application of an electric field to this antiferroelectric diastereomer produces the corresponding ferroelectric state with layer chirality unchanged. Thus, the *meso* antiferroelectric isomer SmC_SP_A switches to the *meso* ferroelectric isomer SmC_AP_F. The anticlinic SmC_AP_F appears optically like an Sm_A phase (optical axis along the layer normal) with smaller birefringence than the synclinic SmC_S structures when the layers are normal to the substrates and the input plane polarized light is propagating normal to the substrates.

The minority domains exhibited by diester **2** are macroscopically chiral, with an SmC_AP_A structure. There are two SmC_AP_A enantiomers, suggesting the descriptor '*dl*' for this diastereomer by analogy to conventional *dl* pairs of enantiomers in a racemate. In this case, however, the enantiomeric entities are macroscopic domains—the sample is a conglomerate. The antiferroelectric ground state has the optical axis along the layer normal (SmA-like), with both enantiomers exhibiting identical textures in the polarized light microscope. A single chiral domain of SmC_AP_A is similar to the ground state of the classic chiral antiferroelectric SmC_A* phase of MHPOBC,[15] but composed of molecules achiral in the isotropic melt. Again, electric field-induced switching maintains the layer chirality, affording the *dl* ferroelectric structure SmC_SP_F. The latter structure is analogous to a SmC* FLC.

A FERROELECTRIC BANANA

Since the initial discovery of polar electrooptics in the bow phases, many hundreds of bent-core mesogens have been synthesized and studied.[16] A variety of textures have been observed by polarized light microscopy, denoted B1 –B7. The B2 and B7 textures are electro-optically active, and the most heavily studied. As described above, the two phases making up samples with the classic B2 texture are antiferroelectric. Indeed, until recently all known electrooptically active bow phases were antiferroelectric. Owing to potential applications of ferroelectric bow phases (the largest second-order non-linear optical susceptibility observed to date for a liquid crystal was in a prototype bow-phase[17]), and as an interesting problem in supermolecular stereocontrol, we embarked on a project aimed at the design and synthesis of a thermodynamically stable (at zero field) ferroelectric bow phase.[18]

The structure of the new material, triester **3**, is given in Fig. 8. The design rationale behind this simple analog of the classic bow-phase mesogen **2** derives from consideration of the SmCP structures shown in Fig. 7, and reproduced in Fig. 8. Consider the synclinic antiferroelectric and ferroelectric structures SmC_SP_A and SmC_SP_F, respectively. Both are synclinic in the tilt plane. For these SmC_S structures, as shown in Fig. 8, the plane containing the director and the polar axis in each layer (the molecular bow plane) is macroscopic, since the bow plane in all the layers is parallel. Figure 8 also presents a projection of the structures in this macroscopic bow plane. In this orientation, it can be easily seen that the antiferroelectric structure is also 'synclinic' in the bow plane using the 'dimer mesogen' model for the bow phase mesogens described above (where each half of the molecule is considered an independent molecular director). The ferroelectric structure is 'anticlinic' in the bow plane.

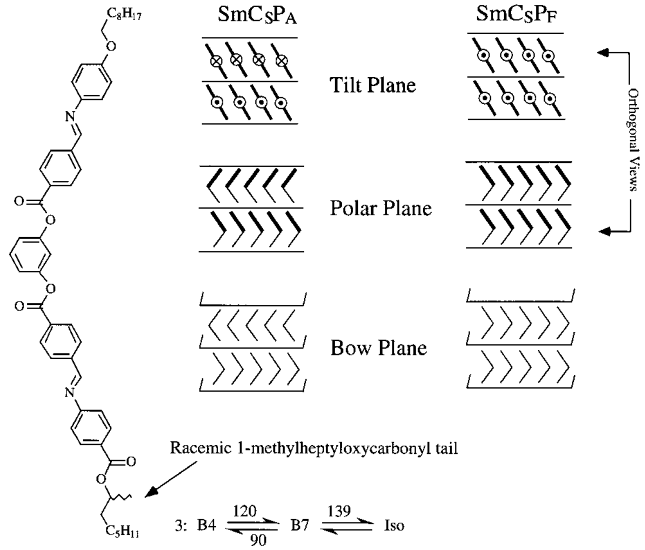

Figure 8. The structure and 'texture' sequence of triester **3**. In the representation of the structures of the SmC_SP isomers in the bow plane, the layer normal is *not* in the plane of the page (i.e. the layers are not perpendicular to the page)

It is well known that synclinic layer interfaces are preferred, perhaps owing to increased entropy from out of layer fluctuations. However, a powerful stereochemical control element favoring anticlinic layer interfaces in conventional calamitic LCs is also well known. Specifically, the 1-methylheptyloxycarbonyl (MHOC) tail found in MHPOBC,[15] either unichiral or racemic, promotes the formation of anticlinic layer interfaces in the tilt plane of the chiral antiferroelectrics. This plane becomes the polar plane in the SmCP structure, leading to the design of a bow-phase mesogen possessing one racemic MHOC tail as a candidate for the desired ferroelectric material.

Synthesis of the target triester **3** provided a mesogen exhibiting the beautiful and unmistakable B7 texture.[19] In 4 μm LC cells, this texture is characterized by the appearance of gold twisted ribbons or tubes at the isotropic to B7 phase transition. These twisted structures, clearly chiral, occur in either handedness. In addition, gold focal conic domains occur in the sample, and eventually the twisted tubes anneal into the focal conics.

The x-ray behavior, electrooptics and behavior in freely suspended samples are novel and complex for this material. The data taken as a whole, however, show that triester **3** possesses a ferroelectric ground state with the target SmC_SP_F structure.[18] Of course with racemic molecules a conglomerate is produced.

Our work suggests that both the B2 and B7 textures occur for SmCP phases, the textural differences involving the LC alignment. Antiferroelectric examples of both B2 (described in detail above) and B7[20] materials have been reported. Triester **3**, however, is to our knowledge the only ferroelectric bow-phase mesogen prepared to date. In this case the net polar order derives from a thermodynamic preference for anticlinic layer interfaces in the bow plane (or some other collective preference for the parallel orientation of the polar axes in all layers). This represents a spontaneous breaking of non-polar symmetry in a thermodynamically stable fluid smectic.

CONCLUSION

The first example of spontaneous chiral symmetry breaking in a liquid crystal, producing a liquid conglomerate, is described for diester **2**. In the new LC structures, composed of molecules which are achiral in the isotropic liquid, layers are polar, this polar order being key to the observed chirality. It is suggested that the clinicity at layer interfaces is an important driving force for the formation of this polar structure. Proof of the existence of six distinct supermolecular wells on the configurational hypersurface at zero field has been obtained. All six structures are easily seen in 4 μm transparent capacitor LC cells by polarized light microscopy. The apparent ground state of the system has a '*meso*' structure, here meaning macroscopically achiral but composed of chiral elements. This antiferroelectric phase switches to a *meso* ferroelectric state. A second pair of metastable structures are also easily seen. At zero field, an antiferroelectric *dl* pair of macroscopically chiral domains is observed. These domains are indistinguishable by polarized light microscopy. Electric field-induced switching, however, reveals heterochiral SmC*-like domains which respond in a dramatically chiral way to the applied field, producing beautiful visual evidence of the existence of the liquid conglomerate.

The first example of spontaneous polar symmetry breaking in a smectic LC, producing a ferroelectric bow phase composed of racemic molecules, is described for triester **3**. In this case, net macroscopic polar symmetry was created by design, by producing thermodynamically stable anticlinic layer interfaces in the bow plane of the SmCP system, providing a stable SmC_SP_F ferroelectric conglomerate.

Acknowledgements

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REFERENCES

1. Drabik TJ. In *Materials Research Society Symposium Proceedings. Thin Films for Integrated Optics Applications*, No. 392, Wessels BW, Marder SR, Walba DM (eds). Materials Research Society: San Francisco, 1995; 111–122.
2. Frey V, Randler M, Lueder E, Muecke M, Brill J, Frohna M. In *Abstracts of the 7th International Conference on Ferroelectric Liquid Crystals Darmstadt*, 1999; 88 (presentation I-14).
3. Walba DM. *Science* 1995; **270**: 250–251.
4. Meyer RB, Liebert L, Strzelecki L, Keller P. *J. Phys., Lett. (Orsay, Fr.)* 1975; **36**: L-69–L71.
5. Cladis PE, Brand HR. *Liq. Cryst.* 1993; **14**: 1327–1349.
6. Soto Bustamante EA, Yablonskii SV, Ostrovskii BI, Beresnev LA, Blinov LM, Haase W. *Liq. Cryst.* 1996; **21**: 829–839.
7. Link DR, Clark NA, Ostrovskii BI, Soto Bustamante EA. *Phys. Rev. E* 2000; **61**: R37–R40.
8. Niori T, Sekine T, Watanabe J, Furukawa T, Takezoe H. *J. Mater. Chem.* 1996; **6**: 1231–1233.
9. Akutagawa T, Matsunaga Y, Yashuhara K. *Liq. Cryst.* 1994; **17**: 659–666.
10. Weissflog W, Lischka C, Benne L, Scharf T, Pelzl G, Diele S, Kruth H. *Proc. SPIE* 1998; **3319**: 14–19.
11. Heppke G, Moro D. *Science* 1998; **279**: 1872–1873.
12. Osipov MA, Pikin SA. *Mol. Cryst. Liq. Cryst.* 1983; **103**: 57–75.
13. Link DR, Natale G, Shao R, Maclennan JE, Clark NA, Körblova E, Walba DM. *Science* 1997; **278**: 1924–1927.
14. Macdonald R, Kentischer F, Warnick P, Heppke G. *Phys. Rev. Lett.* 1998; **81**: 4408–4411.
15. Chandani ADL, Gorecka E, Ouchi Y, Takezoe H, Fukuda A. *Jpn. J. Appl. Phys.* 1989; **28**: L1265–L1268.
16. Pelzl G, Diele S, Weissflog W. *Adv. Mater.* 1999; **11**: 707–724.
17. Macdonald R, Kentischer F, Warnick P, Heppke G. *Phys. Rev. Lett.* 1998; **81**: 4408–4411.
18. Walba DM, Körblova E, Shao R, Maclennan JE, Link DR, Glaser MA, Clark NA. *Science* 2000; **288**: 2181–2184.
19. Pelzl G, Diele S, Jákli A, Lischka C, Wirth I, Weissflog W. *Liq. Cryst.* 1999; **26**: 135–139.
20. Heppke G, Parghi DD, Sawade H. In *Conference Summaries; 7th International Conference on Ferroelectric Liquid Crystals; Darmstadt University of Technology*, Germany. Darmstadt University of Technology: Darmstadt, 1999; 202–203 (Poster PC205).