A Chameleon Chiral Polar Liquid Crystal: Rod-Shaped When Nematic, Bent-Shaped When Smectic

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The first antiferroelectric liquid crystal (AFLC) exhibiting a (chiral) nematic phase, a combination which has long been the goal of synthetic chemists working with polar liquid crystals but which at the same time represents a fundamental contradiction in terms of translational order, was recently reported by Nishiyama and co-workers. We have investigated this chiral twin dimer by optic, electrooptic, and dielectric methods and conclude that it is not an ordinary AFLC material, but one where the peculiar properties of bent-core smectics are combined with those of ordinary rod-shaped liquid crystals. The compound exhibits a new type of nematic–smectic phase transition, connected with a change of molecule conformation from rod- to bent-shaped. This also has an important impact on the chiral interactions in the system. Toward the high-temperature end of the smectic phase, the energy balance between bent conformation smectic and straight conformation nematic can be shifted by an electric field such that the transition to the nematic phase with stretched-out molecules can be field-induced.

Introduction

In a recent report by Nishiyama et al., the synthesis and initial characterization of a highly interesting chiral dimeric liquid crystal were described.[1] It was suggested that this compound, code-named BMHBOP-8, is the first antiferroelectric liquid crystal (AFLC) that exhibits a chiral nematic (also called cholesteric) phase, a quality which is of very large applicational interest. Soon after their discovery in the late 1980s, AFLCs were pointed out as one of the most promising active materials for future display devices,[2] meeting demands on high resolution and high speed not achievable with the nematic liquid crystals which today dominate the market. However, a major obstacle turned out to be the difficulty in obtaining a uniform alignment, believed to be due to the lack of AFLC materials with a chiral nematic phase, N*, between the isotropic and the smectic phases. The past 15 years have therefore seen a strong effort in trying to develop N*-AFLC materials but this has turned out to be an extremely difficult task. Indeed, the nematic phase, lacking translational order, is fundamentally very different from the antiferroelectric SmC$_a$* phase which must have an exceptionally high degree of translational order along the smectic layer normal (smectic order),[3–5] making it far from

obvious that the two phases can at all be combined in a single material.[6] The report of Nishiyama and co-workers therefore came as a surprise. Yet another compound has recently been reported to exhibit the N*-AFLC combination[7] but the evidence for the existence of an antiferroelectric phase is in that case inconclusive, and there are indications that the phase in question is actually a short-pitch SmC* phase. We are currently investigating also this compound. The only other cases where antiferroelectric smectic phases have been seen in materials exhibiting nematic order at higher temperatures are some nonchiral bent-core liquid crystals.[8,9] In these cases the antiferroelectric phase is however not the one normally desired for display application purposes, but one belonging to a special class of phases strictly related to the bent shape of the molecule. It turns out that this class plays an unexpected lead role in the present work.

The technologically most important AFLC phase is designated SmC$_a$*, where SmC indicates that it belongs to the class of tilted fluid smectics, i.e., with molecules organized in a layered structure with a nonzero average

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tilt θ with respect to the layer normal $\mathbf{k}$. As in N*, the star indicates that the phase is chiral. In this paper we furthermore restrict the use of the star to the case that the constituent molecules are chiral. Chirality in a tilted smectic structure allows for a spontaneous polarization[10] $\mathbf{P_s} \sim \mathbf{k} \times \mathbf{n}$, where $\mathbf{n}$ is the director (the average main molecular symmetry axis), and the family of chiral smectic C phases therefore exhibits varying types of polar order. The ordinary SmC* phase is *synclinic*; i.e., molecules in adjacent layers tilt in the same direction (neglecting the helical macrostructure which is also an effect of the chirality), and hence synpolar: adjacent layers are polarized in the same direction. Such materials can be made ferroelectric if the helix is quenched and surface constraints provide the necessary hysteresis in switching between bistable states.[11] The index "a" in SmC$_a$* indicates that the structure in this case is *anticlinic*, i.e., with molecular tilt in opposite directions in adjacent layers. This makes the SmC$_a$* phase antipolar, hence antiferroelectric. In the case of smectics made up of molecules with a bent core—one of the hottest topics in today's fundamental liquid crystal research[12–24]—the situation is more complex. In this case we can obtain ferro- and antiferroelectric phases even with achiral molecules because the additional vector introduced by the bending direction makes the layers chiral, even if the molecules themselves are not.[18,14] For these systems the notation SmC$_x$P$_Y$, where the index x is either "s" or "a", for synclinic and anticlinic, respectively, and Y is either "F" or "A", for ferroelectric and antiferroelectric, respectively, is often used.[17,18] Following this notation scheme, we add in the present work the possibility of SmC$_a$P$_A$* and SmC$_s$P$_F$* phases, both constructed of chiral bent-core molecules. We point out, however, that the index "F" in the latter case is slightly misleading since the SmC$_s$P$_F$* phase is not—in contrast to the SmC$_s$P$_F$ phase—intrinsically ferroelectric; it lacks bistability. This is because the molecular chirality gives the phase a helical modulation of $\mathbf{n}$, and consequently of P_s, along the smectic layer normal, canceling out the polarization on a macroscopic scale.

Figure 1. The BMHBOP-8 molecule (a) can change shape radically by changing the torsional angle around a bond at the center of the octylene spacer. As expected for an even-numbered spacer, the energy as a function of torsional angle (b) shows a global minimum for the stretched-out all trans conformation but, surprisingly, two bent conformations give local minima with very similar single-molecule energy. The energy balance between bent and straight conformation is thus very sensitive and can be expected to be strongly biased by packing effects. The phase change from nematic to smectic can therefore lead to a change in average molecule shape. With one chiral moiety on each side of the spacer, bending of the molecule radically changes the directions of chiral interactions in the case of a nematic-type molecule organization as illustrated in (c) and (d). The stereogenic centers are highlighted with transparent balls; the twisting direction is symbolized by yellow-ball-ended lines.

We have resynthesized the (*R*,*R*)-BMHBOP-8 compound, the structure of which is indicated in Figure 1a, and investigated it extensively by means of dielectric spectroscopy and polarizing microscopy while varying the influence from surfaces and electric fields, complementing with MOPAC/AM1 computer modeling. In this report we show that the compound is actually even more unusual than initially proposed by the Nishiyama team. Based on our observations, we propose the following phase sequence (temperatures in °C):

$$\text{crystal} \xrightarrow{\sim 142}$$
$$(\xleftarrow{\sim 130} \text{SmC}_a\text{P}_A{}^* \xleftrightarrow{\sim 140}) \text{SmC}_s\text{P}_F{}^* \xleftrightarrow{\sim 148} \text{N}^*$$
$$(\xleftarrow{\sim 160} \text{BP}_{\text{Sm}}{}^*) \xleftrightarrow{\sim 165} \text{isotropic}$$

The phases listed between parantheses are monotropic; i.e., they only appear as a result of supercooling. Since transitions involving supercooled phases depend strongly on the experimental conditions (cooling rate, sample thickness, etc.), it is impossible to define a strict transition temperature. The numbers listed in parantheses are typical values of the transition temperatures that we measured during different experiments. They should be understood only as guidelines. We tentatively classify the high-temperature monotropic phase, appearing between the isotropic liquid and N*, as a smectic blue phase (BP$_{\text{Sm}}$*) based on its characteristic

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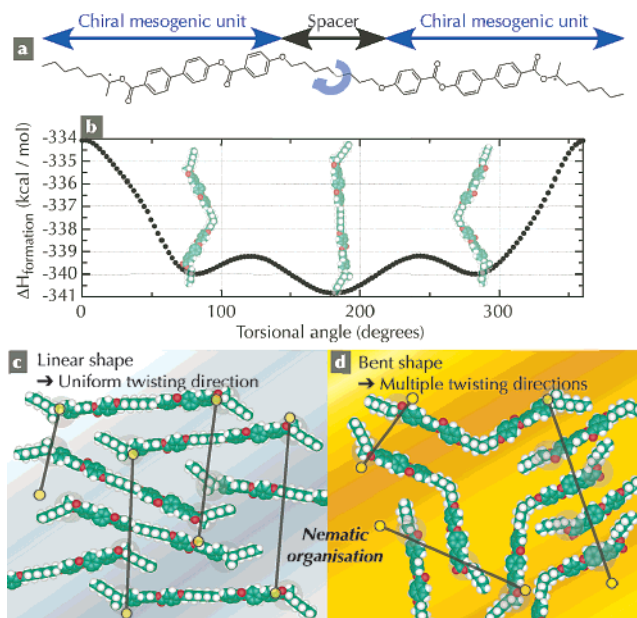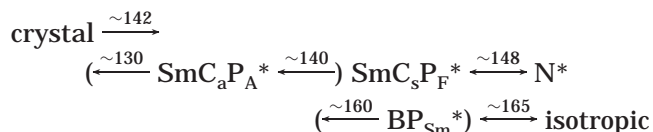
low-birefringence texture (see Supporting Information), reminding of the BP_{Sm}* textures published by Grelet et al.[25] The second monotropic phase, appearing between SmC_sP_F* and crystallization, we designate as SmC_aP_A*. It is this phase that the Nishiyama team designated as the ordinary AFLC phase SmC_a*. In the following we do not consider the high-temperature monotropic phase, and we concentrate mainly on the N* and SmC_sP_F* phases and the transition between them.

Although BMHBOP-8 is unlikely to find use in an AFLC display device, it is of high fundamental interest because it represents something completely new in liquid crystals, combining characteristics of ordinary rod-shaped mesogens with the peculiar properties of smectics made out of bent-core molecules. The flexibility of the central octylene spacer in combination with the two identical chiral moieties on both sides gives this compound a chameleon-like behavior: it changes conformation at the nematic−smectic transition, adopting a rod shape in the nematic phase but bending in the smectic phases.

Experimental Details

The synthesis followed the scheme described by Nishiyama et al.[1] The sample cells used for all investigations were equipped with antiparallel-buffed polyimide as the alignment layer and patterned transparent indium-tin-oxide (ITO) electrodes. Dielectric spectroscopy experiments were carried out using an HP4192A impedance analyzer. During the course of these experiments, the sample texture was automatically photographed, making the phase designation of each spectrum more reliable. Various hot stages (Instec, Linkam, Julabo) and polarizing microscopes (Olympus, Leitz) were used. During electrooptic measurements a photodiode (FLC Electronics) was attached to the microscope. The macroscopic polarization was obtained by measuring and integrating the current response to an applied triangular wave driving voltage.[26]

Results

Figure 2 shows the polarizing microscopy textures observed during the N*-SmC_sP_F* transition as it appeared on cooling in differently thick planar-aligning cells. The N* texture (top parts of a and g, bottom part of k) was very dark and devoid of both features and color in all samples. It did not change appearance by rotating the hot stage, as expected for a planar-aligned helical N* phase. The absence of color shows that the helix pitch is very short. The start of the transition to the first smectic phase was in all cells thicker than 1 μm, recognized by the emergence of weakly birefringent focal conic "islands" in the N* texture, cf. Figure 2a, d, and g. Very soon these islands were however replaced by a colorful mosaic texture. This texture, best studied in the 4 μm sample (e), is quite spectacular because all colors coexist side by side. Studies in reflection showed that the light is circularly polarized, a clear indication that the colors are produced by selective reflection/transmission due to a helical structure.[27] The multicolored
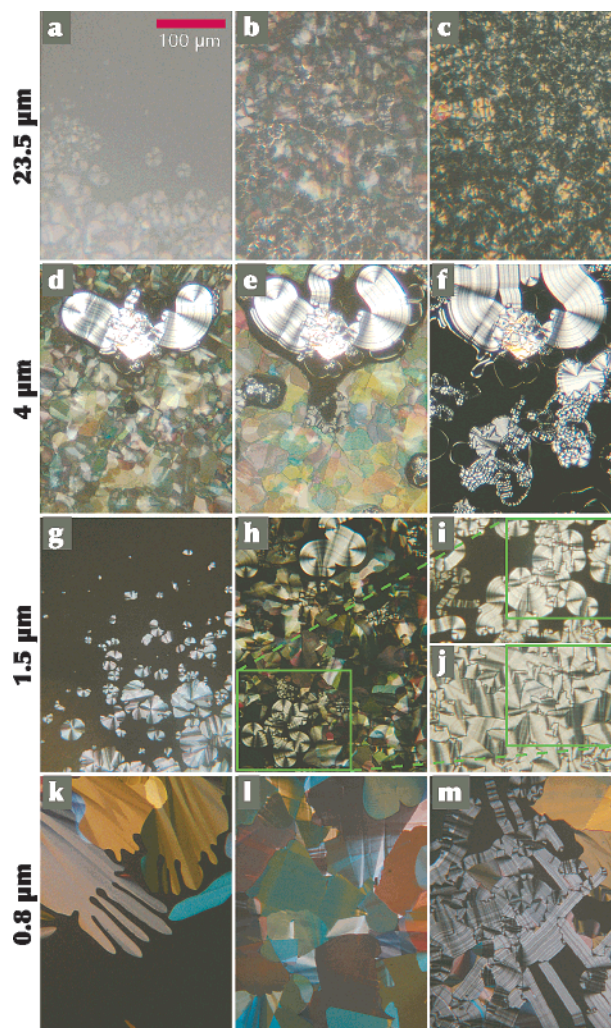
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Figure 2. Polarizing microscopy textures in the vicinity of the N*-SmC_sP_F* transition (T_0) in planar-aligning cells of varying thickness. Pictures a, b, d, e, g, h, and k are all taken at T_0, those in the first column at the beginning of the transition and those in the second 10−30 s later. The other pictures are taken at (c) $T_0 − T = 4$ K, (f) $T_0 − T = 1$ K, (i) $T_0 − T = 1$ K, (j) $T_0 − T = 3$ K, (l) $T_0 − T = 0.8$ K, and (m) $T_0 − T = 1$ K. The three 0.8 μm cell pictures are taken at slightly different positions in the sample.

texture is a reminder of the platelet texture of nematic blue phases[28] and we believe that the structure indeed has some similarity to blue phases, although it is a transitional, not a stable, state, separating N* from the smectic phase.

The type of texture that finally stabilized after the transition depended very much on the cell gap. In the 4 and 23.5 μm samples the alignment was not planar (i.e., director in the cell plane, smectic layers standing perpendicular to the cell substrate) but mixed, despite the fact that the smectic phase formed on cooling from a fully planar-aligned cholesteric phase in cells with planar-aligning surface treatment. Apart from many bright defects, the basic texture of the 23.5 μm sample was black regardless of sample rotation, suggesting that the smectic phase formed mainly in quasi-homeotropic alignment, i.e., with the layers more or less parallel to the substrates. The lack of color can be explained by a

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short-pitch helical director tilt direction modulation along the smectic layer normal. The reason for the unexpected change of alignment is probably to be found in the colored mosaic transitional texture: if the transition from N* to smectic goes via a blue phase-like structure, the system twists in all three dimensions during the transition[27,28] and the alignment is lost in the smectic phase.

In the 4, 1.5, and 0.8 μm samples the smectic phase developed a very characteristic—and beautiful—white-and-black myelinic texture in some areas, similar to one of the typical textures of the SmC_sP_F achiral bent-core mesogen smectic phase, the most famous version of which is called B7.[20,24,28−31] This is the first striking indication that the BMHBOP-8 molecules bend in the smectic phase. Although most achiral compounds developing the SmC_xP_Y-type phases have a rather stiff bent core, some examples exist where the bent shape comes about through an alkylene spacer,[12,32−35] showing that the bend does not need to be built rigidly into the molecule structure.

Yet another birefringent texture type, characterized by a dark-gray checkered pattern, developed in other areas of the 4 μm thick sample. Examples of both birefringent 4 μm sample texture types are shown in Figure 2f (the black areas are homeotropic). In the 1.5 μm sample the tendency to develop planar alignment in the smectic phase was even stronger and, indeed, in this cell the smectic texture that finally stabilized was an ordinary focal conic texture (Figure 2j). This final texture is very different from those spontaneously formed in the thicker cells. The stronger influence of the alignment layers in the thin cell dominates the formation of the smectic structure to such an extent that the sample gets fully planar-aligned.

In the 0.8 μm sample the transition looked slightly different. Instead of the weakly birefringent focal conics the first sign of the phase transition was the appearance of rather strongly colored circular domains. In some parts (e.g., Figure 2k) they had a distinct dendritic character with fingers stretching out into the N* regions, and on the whole the texture had many similarities with textures of columnar phases.[28,36,37] Such phases are generally produced by discotic mesogens but in recent years they have also been seen in systems built up of bent molecules.[22,36,37] With rodlike mesogens, on the other hand, they have to the best of our knowledge never been seen. Hence, this is another textural indication that the molecules bend in the smectic phase. On further cooling, the myelinic texture formed also in this very thin sample (cf. Figure 2m) but

it never grew to dominate the sample. The colorful columnar-like domains remained in parts of the sample down to crystallization, unless an electric field was applied. With electric field treatment a more or less ordinary smectic texture could be formed.

When the nematic phase becomes unstable on cooling, the bending and appearance of positional order occur simultaneously. As the phase transition is first-order, there is no reason to expect any pretransitional positional order and thus the appearance of an intermediate short-range positionally ordered intercalated columnar structure is quite reasonable. It may even be that the colored mosaic transitional texture seen in the thicker cells could be produced by a columnar structure, although this would not explain the loss of planar alignment. Probably, the columnar organization at the surfaces is here combined with nematic in the bulk during the phase transition. In these thicker samples the global-energy-minimum smectic phase quickly takes over, but in the 0.8 μm cell the surface anchoring may be too strong to allow the necessary reorganization of the molecules to get an extended smectic structure; hence, the columnar state gets a temperature range which is not present in bulk.

The 0.8 μm cell was the only sample that could be aligned uniformly enough to do electrooptic investigations. Some representative electrooptic and current response curves, obtained in the SmC_sP_F* phase with a triangular wave driving waveform of varying amplitude, are shown in Figure 3. The very short pitch of the SmC_sP_F* phase gives the response a complex dependence on the amplitude of the driving voltage. At small amplitude analogue deformed-helix-mode response is detected and at large amplitude ferroelectric switching directly between the two uniform nonhelical states are seen, both response types clear indications of the phase being synpolar. At intermediate amplitude, in the range where the helix is unwound and rewound during every switching cycle, the response is quite complex, having a component of ferroelectric switching as well as of the helix unwinding/rewinding process, effectively antiferroelectric.[11,38,39] This gives the current response three peaks per half cycle at this amplitude, a response which one may mistakenly interpret as a sign of the phase being ferrielectric. The strong influence of the cell surfaces in the 0.8 μm sample strongly favored supercooling of the SmC_sP_F* phase which made investigations of the SmC_aP_A* phase very difficult but had the advantage that the spontaneous polarization could be measured at temperatures far below the melting point of the material. The results for saturated switching are shown in Figure 4.

The 23.5 μm cell was investigated by means of dielectric spectroscopy, some representative results of which are shown in Figure 5. The spectrum at high temperatures was free from absorptions, as expected from a planar-aligned cholesteric phase, the only dielectrically active mode of which is the rotation around the long axis. The absorption frequency of this mode is outside the range of the equipment used. In contrast,

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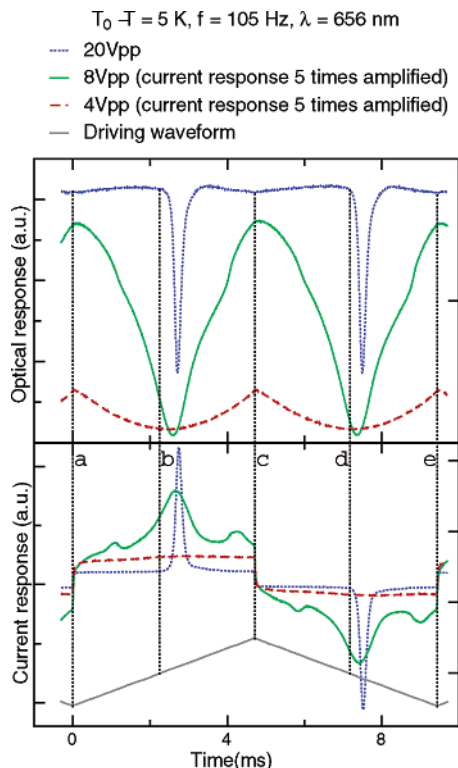
Figure 3. Optical (upper diagram) and current (lower diagram) response of the 0.8 μm sample to an applied triangular wave voltage (bottom gray curve) in the SmC$_s$P$_F$* phase, 5 K below the N*-SmC$_s$P$_F$* transition (T_0). With 20 V$_{pp}$ the sample is fully switched between the two nonhelical ferroelectric end states, giving a distinct single peak per half-cycle in the current response just after the sign changes of the driving voltage (b, d). The optical response decreases somewhat at the maxima and minima of the applied voltage (a, c, e), an effect of the saturated optical tilt being above 45°. 4 V$_{pp}$ produces helix deformation without unwinding and thus gives analogue electrooptic response without current peaks. The helix unwinding threshold is just reached with 8 V$_{pp}$, giving a complex response with a component of ferroelectric switching as well as of (antiferroelectric) helix unwinding/rewinding. Note that the 4 V$_{pp}$ and 8 V$_{pp}$ current response curves are scaled up five times in order to make the details resolvable.

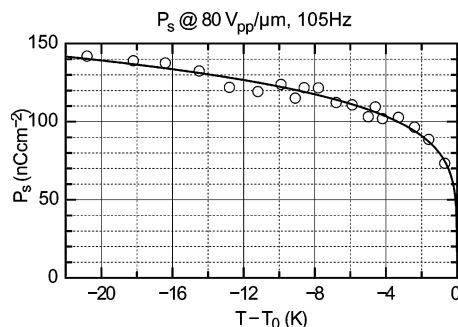**Figure 4.** Spontaneous polarization P_s as a function of temperature below the N*-SmC$_s$P$_F$* transition (T_0), measured in the 0.8 μm sample.

the SmC$_s$P$_F$* phase, after it had been fully planar-aligned through electric field treatment, had a distinct polar response showing that the phase is synpolar. The absorption is however very much weaker than that in a normal SmC* phase where the susceptibility of the helix distortion mode is often in the order of 100−300 in AFLC compounds. In BMHBOP-8 it is only ∼6. Since the susceptibility is a function of the helical pitch as
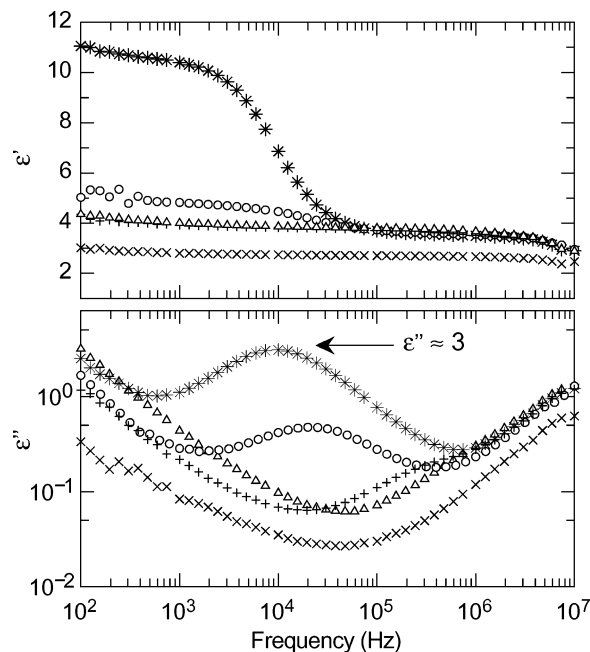

Figure 5. Real (top) and imaginary (bottom) components of the dielectric permittivity of BMHBOP-8 as a function of frequency, in N* (△), nonuniform (virgin) SmC$_s$P$_F$* (○), planar-aligned SmC$_s$P$_F$* (∗), SmC$_A$P$_A$* (+), and the crystalline phase (×). The SmC$_s$P$_F$* phase stands out as the only polar phase, but the response is much weaker than that in ordinary SmC*, even after a fully planar alignment was achieved through electric field treatment. The low- and high-frequency tails present in all spectra are due to the ionic conduction and the sample cell relaxation, respectively; hence, they do not reflect the characteristics of the particular phase studied.

well as of P_s,[40] we can understand this mainly as a result of the extremely short pitch of BMHBOP-8, although the magnitude of the polarization which effectively contributes to the dielectric response may also be quite low, as discussed below. In the nonuniform virgin state the response of the SmC$_s$P$_F$* phase (rings in Figure 5) was much weaker still, reflecting that a large part of the sample was in quasi-homeotropic alignment.

In their original report, Nishiyama et al. suggested that the phase below the nematic phase is one of the chiral smectic-C subphases, SmC$_\beta$* or SmC$_\gamma$* (in that paper referred to as a ferrielectric phase). The basis for this interpretation was the observation of a dynamic texture below the nematic−smectic transition and a small step in the optical tilt θ vs electric field curve. During our investigations of the smectic phase in question, we never observed the textures which are typical of the subphases. The different textures described above and pictured in Figure 2 are all very different from the characteristic subphase textures. However, we noticed that if the sample is cooled quickly from the cholesteric to the smectic phase, the transitional texture may to some extent resemble a subphase texture. It may be this texture that Nishiyama et al. referred to. The step in the tilt angle vs field curve is no convincing argument for the phase being ferrielectric because, as Nishiyama et al. correctly point out, the step occurs at a voltage and tilt angle combination which

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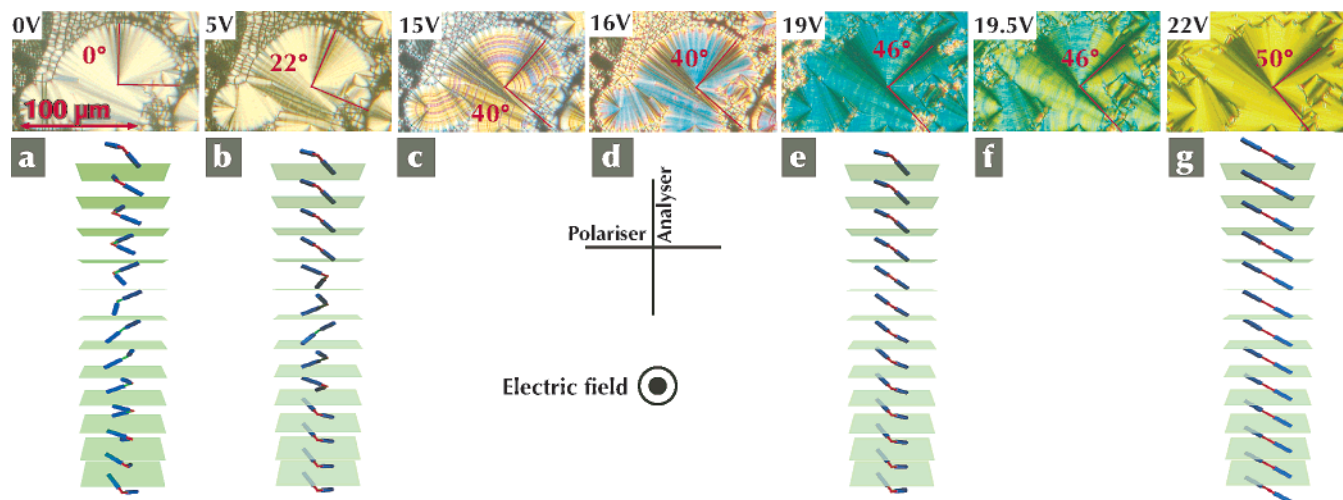
Figure 6. The four-stage switching process observed in the low-temperature region of the $SmC_sP_F^*$ phase, as illustrated with polarizing microscopy textures (4 μm sample) and pictures of the molecule shape and organization in the smectic layer structure at each stage: (a) virgin state; (b) analogue regime (deformed helix mode); (c−e) helix unwinding, revealing a 46° tilt in the final state; (f−g) conformation change. In the pictures the octylene spacer is colored red on the bend tip side and green on the bend opening side, and the mesogenic rods are blue.

does not correlate with the structures proposed for any of the subphases. We also observed the step in the switching behavior (Figure 6 f) and are able to give a more plausible explanation to it within the framework of the smectic phase being $SmC_sP_F^*$, as discussed below. Finally, the dielectric response (cf. Supporting Information in addition to Figure 5) is different from that expected from either subphase type: SmC_β^* is antiferroelectric and thus has no polar response, and SmC_γ^* has a polar mode which is generally quite strong and has a relatively low (below 1 kHz) absorption frequency.

Also the textural response to electric fields was carefully investigated with the different samples, as this was quite illuminating. After the 4 μm sample was cooled slowly from the isotropic to the $SmC_sP_F^*$ phase, the temperature was held constant and a dc field was applied to the sample. The texture was photographed at selected voltages, cf. Figure 6. At low voltages only the planar-aligned areas responded, giving a continuously increased birefringence and a likewise continuous rotation of the optic axis away from its 0 V orientation parallel to the layer normal **k**. The tilt away from **k** is reflected in the orientation of the extinction crosses (one cross has been emphasized and the measured tilt is indicated). At ∼15 V a discontinuous change could be seen as high-birefringence lines directed along the smectic layers. They started out purple on the now orange background, but with slightly increased voltage the color changed first to blue and then to green, after which the color as well as the optical tilt first seemed to have reached saturation ($\theta \sim 46°$). In this voltage range, also the initially homeotropic areas reacted to the field, rearranging irreversibly to planar alignment. Surprisingly, on increasing the voltage slightly further, a second discontinuous transition occurred (Figure 6f), producing a color change from green to yellow, as well as a further increase in tilt angle, which now saturated at the remarkably high value of $\theta_{sat} \sim 50°$.

The first discontinuous change in the switching process resembles anticlinic to synclinic switching in a SmC_a^* phase and one would therefore perhaps think that the green state (Figure 6e) corresponds to the fully

switched synclinic state of this antiferroelectric phase. But the low-voltage regime, in which the field continuously increases the optical tilt angle up to ∼30°, is not compatible with this model. A more likely explanation can be found in the very tightly wound helix. In the analogue regime the helix is only distorted, giving an electrooptic effect which can be identified as the deformed helix mode.[41,42] The regions of twist are compressed but not expelled,[43] giving the continuous electrooptic response seen at 4 V_{pp} amplitude in Figure 3. The helix unwinding starts first on passing a certain threshold voltage corresponding to the first discontinuous texture change. As the helix is expelled turn by turn, the effective optical tilt angle jumps discontinuously toward the director tilt angle at the same time as the birefringence Δn increases in discrete steps. In the experiment of Figure 3 the sample reached this stage at the extreme positions of the 8 V_{pp} amplitude driving voltage, leading to a much increased optical response compared to the analogue regime, reflecting the increase in effective θ and Δn.

The presence or absence of a helical structure in bent-core smectics is a debated issue, and one might argue that also the $SmC_sP_F^*$ phase in BMHBOP-8 may not be helical. However, it is problematic to explain the black homeotropic texture and the electrooptic response in the planar-aligned regions without a helix. When the 4 μm or 23.5 μm sample was cooled quickly past the $SmC_sP_F^*$−$SmC_sP_A^*$ transition, the black regions briefly developed a flash of dynamic schlieren texture, as is typical at a transition between syn- and anticlinic smectic phases (at which the helix always changes sense in the case of phases built up of chiral molecules) observed in homeotropic alignment. This shows that the black regions are indeed homeotropic and the absence of any schlieren texture in these regions at temperatures

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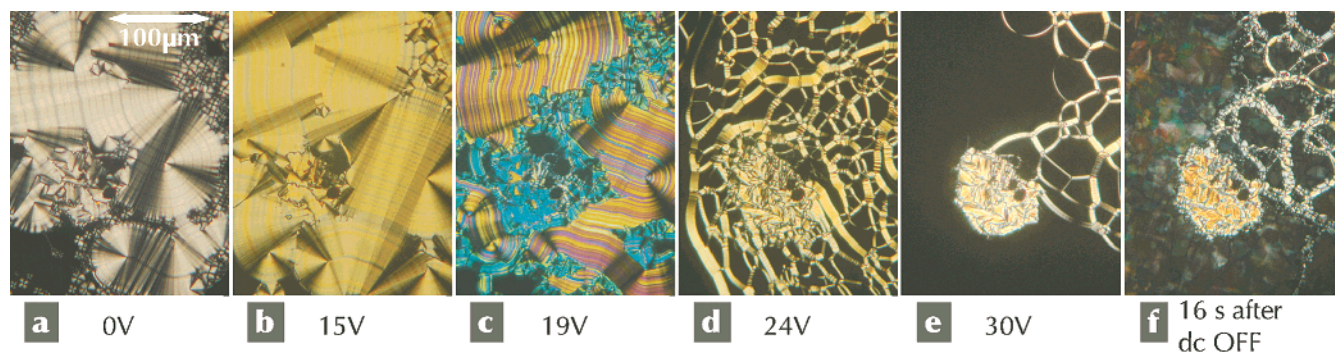(43) Jakli, A.; Markscheffel, S.; Saupe, A. *J. Appl. Phys.* **1996**, *79*, 1891.

Figure 7. Switching the 4 μm sample at a temperature just below the SmC$_s$P$_F$*-N* transition: (a) virgin state; (b) analogue regime (deformed helix mode); (c) helix unwinding (striped regions) together with field-induced transition to N* (green); (d–e) oily streak texture of the field-induced N* phase; (f) transition back to SmC$_s$P$_F$* after the field is switched off.

away from the synclinic–anticlinic transition can only be understood by assuming a very short-pitch helix. Furthermore, during experiments on the 0.8 μm sample helix unwinding lines were repeatedly observed. Comparing our observations with those reported on nonhelical SmC$_s$P$_F$/B7 systems built up of achiral molecules, we note that both systems exhibit analogue response at low voltages.[24] But at the threshold voltage the SmC$_s$P$_F$ system jumps into the bistable blue state, in contrast to SmC$_s$P$_F$* which shows no bistability. When the field is decreased below the unwinding threshold, the short-pitch helix of the BMHBOP-8 SmC$_s$P$_F$* phase rewinds.

Figure 7 shows the response to the same kind of switching experiment at somewhat higher temperature, 0.5 K below T_0, the SmC$_s$P$_F$*-N* transition temperature in absence of field. Up to 17 V the process was similar to the low-voltage analogue regime described above. But this time, at about the same voltage as where helix unwinding took place, a drastic textural change occurred (Figure 7c): the smectic texture dissolved and was replaced by a green schlieren texture, reminiscent of a planar texture of an achiral nematic. At 24 V there was no trace of smectic texture anymore, nor of the green schlieren texture. Instead, a very characteristic oily streak cholesteric texture covered the whole electrode area. Obviously, the cholesteric phase can in BMH-BOP-8 be field-induced from within the SmC$_s$P$_F$* phase. If the field was now switched off, the transition back into SmC$_s$P$_F$* could easily be recognized after some 15 s (Figure 7f), looking exactly as that on cooling past the N*-SmC$_s$P$_F$* transition: the low-birefringence focal conic smectic areas flashed by, followed by the colored mosaic texture, finally followed by a rather nonuniform smectic texture that remained. To rule out that the observed phase transition was due to electric current-induced heating, we repeated the experiment, this time on the 1.5 μm sample with an ac field, leaving the field on for 25 min. The temperature was again set to 0.5 K below T_0. On application of the field, the texture changed from the smectic focal conic texture to an almost completely black N* texture. During the time in which the field was left on, which was more than enough for the hot stage to compensate any current-induced heating effects, no changes whatsoever were observed in the texture. When we switched off the field after 25 min, the smectic focal conic texture reappeared after 6 s.
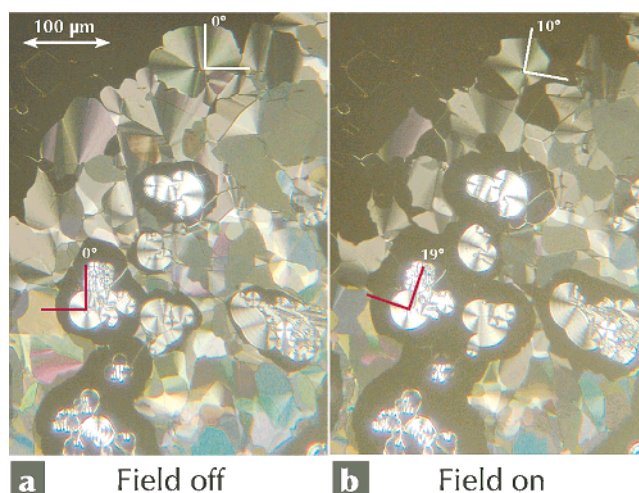

Figure 8. The N* to SmC$_s$P$_F$* transition being pushed back by applying an electric field. The focal conic and the B7-like regions show electrooptic response, whereas the colored ones do not. If the field is left on ~20 s, the focal conics and mosaic texture areas disappear completely. The sample is 1.5 μm thick.

The textural response to an electric field during the first-order N*-SmC$_s$P$_F$* transition, finally, was quite illuminating, as demonstrated with photos from the 1.5 μm sample in Figure 8. The low-birefringence focal conic texture, which is the forerunner of the transition, responded by rotating the optic axis (see white cross at the top), as expected for a planar-aligned chiral tilted smectic. The rotation was smaller than that in the B7-like textures (red cross below and left of center), probably a result of the latter domains being in book-shelf geometry (vertical layers), whereas the initial focal conics form with the layers tilted.[24] The colorful mosaic domains, in contrast, did not give any electrooptic response for the voltages applied, showing that the liquid crystal there is in the N* phase (or in an intermediate columnar state). The colored mosaic as well as the initial focal conic texture types rapidly disappeared if the field was left on, giving evidence that the transition from N* to SmC$_s$P$_F$* was pushed back by the application of the electric field.

Because the SmC$_a$P$_A$* phase is monotropic, it was difficult to investigate this phase. However, since the strong influence of the surfaces in the 0.8 μm cell delayed the crystallization, it was possible to work with this sample below the melting point in supercooled liquid crystal phases for several hours. On the other
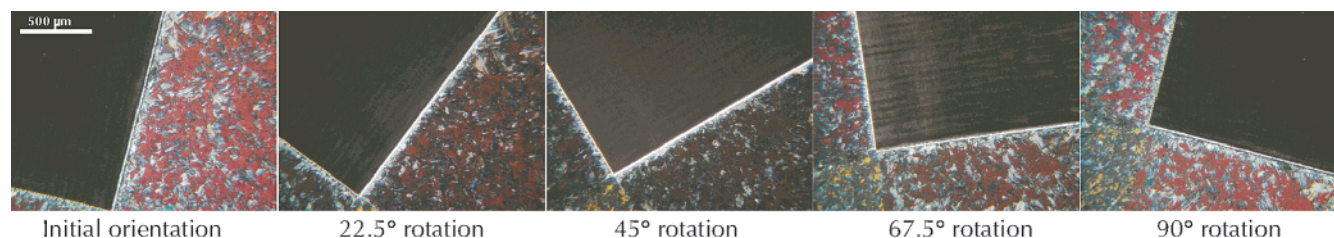
Figure 9. By means of electric field treatment at temperatures below the melting point, a metastable nonhelical supercooled anticlinic SmC_aP_A* phase could be obtained in the 0.8 μm sample. Since $\theta \sim 45°$, this state is orthoconic and therefore optically isotropic in the plane of the cell, as seen through the constantly black texture while rotating the cell between crossed polarizers. Only the electrode area is orthoconic since the surrounding liquid crystal has not been treated with electric field. This is in a mixed state, having components of the columnar-like texture (red) and the B7-like smectic texture (gray).

hand, a small cell gap also strongly promotes synpolar phases at the cost of antipolar organization[44,45] and therefore the sample was at these temperatures in most cases in states varying between 100% supercooled SmC_sP_F* and mixed synclinic–anticlinic state, generally helical even in this very thin sample. By application of an ac electric field and rapid cut-off, a metastable nonhelical antipolar state could however be stabilized for several minutes. As θ is about 45°, this anticlinic state, with the tilt plane parallel to the cell plane, is what is referred to as an orthoconic state, characterized by optical isotropy in the plane of the sample.[46–49] This effect is easily recognized by rotating the sample between crossed polarizers, as illustrated in Figure 9. Further investigations of the SmC_aP_A* phase, apart from the dielectric investigations already mentioned, were not possible due to crystallization in thick cells and supercooled SmC_sP_F* phase in thin cells.

Discussion

The key to understanding the amazing behavior of BMHBOP-8 is to recognize the conformational freedom of the quite flexible octylene spacer group and that the two molecule ends are, each on their own, typical AFLC mesogens with one stereogenic center of the same absolute configuration each. (Each part connected to the spacer is essentially a 10B1M7 mesogen,[50] an AFLC molecule with a $SmC_a*–SmC_\gamma*–SmC*$ phase sequence and P_s saturating at $\sim$100 nC/cm^2.) If we vary the torsional angle around the bond at the center of the spacer, the overall molecule shape changes between linear and bent-shaped. For the case of isolated molecules we calculated the potential during such an angular variation using MOPAC/AM1, the result of which is shown in Figure 1b. The global minimum corresponds to the linear, all trans conformation, but there are two local minima having energies only 0.8

kcal/mol higher than the linear conformation, both corresponding to a bent shape. Basic Boltzmann statistics considering only the rotational freedom around the central bond show that the probability of bent shape, taking the 2-fold degeneracy into account, at the temperature of the $N*$-SmC_sP_F* transition would actually be larger than that of the rodlike shape in the isolated-molecule case. The conclusion of this quite crude conformational energy analysis is that one cannot say from the molecular structure alone if the molecules will be bent- or rod-shaped because the energies of the different shapes are very close, with a difference much below the level of typical packing energies. Most important, the general rule of thumb that an even-numbered spacer produces a linear molecule[33,35] obviously breaks down when the spacer is as long as that in BMHBOP-8. We can here expect that the intermolecular interactions, which may be very different in different liquid crystal phases due to, e.g., different packing schemes, will have the decisive role in determining the molecule shape.

In the case of the highly dynamic nematic phase, the bent conformation is sterically problematic, counteracting efficient packing, and it is thus reasonable to assume that the all trans conformation corresponds to a deeper energy minimum in $N*$ than in the curve in Figure 1b. Although cases of bent molecules forming nematic phases are known, the overwhelming majority forms smectic phases directly out of the isotropic phase on cooling. The best way for strongly bent molecules to pack efficiently is obviously to organize in a layered structure; hence, the bent shape strongly promotes smectic ordering. Knowing how close the rod- and bent-shaped conformations of an isolated molecule are in energy, it is thus not surprising that the phase transition from nematic to smectic is connected with a conformational change from rod-shaped to bent. In addition, since the molecule we are studying is basically two AFLC molecules linked together via a flexible spacer, we know that the two subunits—if they were separated from one another—would prefer to form anticlinic structures in a smectic phase. In the bent shape they adopt such a structure on the molecular level. Because the smectic phase made out of bent molecules has a higher translational order—or less out-of-layer fluctuations—than what it would have had with linear molecules, we can now also understand why this compound exhibits the unique combination of a cholesteric phase and an antiferroelectric smectic phase: the high translational order required to form an antiferroelectric smectic phase comes about through the molecule bending at the nematic–smectic transition.

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The weak polar response as well as the various unusual textures of BMHBOP-8 can now be well understood. The bent molecule shape in the smectic phase can be expected to lead to a certain polarization cancellation already on a molecular scale, such that the effective polarization which contributes to the dielectric response is considerably lower than the values in Figure 4, obtained at saturated ferroelectric switching. In ordinary SmC* the appearance of P_s is attributed to a biased rotation around the molecule long axis, the polarization direction depending on the tilt direction.[51] In BMHBOP-8 the same mechanism may to some extent be active on the level of each chiral mesogenic unit. In a stretched-out conformation, both units would experience the same type of biasing, thus cooperate constructively to the spontaneous polarization. If the two units instead tilt in opposite directions, as is the case in the bent conformation, we can expect a cancellation at least of the polarization components due to biased intramolecular rotations. This should reduce the effective polarization somewhat, thereby weakening the dielectric response. The impact of intramolecular rotations on P_s has been clearly identified, e.g., by comparing SmC*-forming mesogens with identical lateral dipoles but varying distance between dipole and stereogenic center.[51]

The electrooptic response of the focal conics appearing at the N*-SmC$_s$P$_F$* transition front in the 4 and 1.5 μm samples shows that these areas have a smectic structure. These regions most likely nucleate at the surface, where the degree of order is higher than that in the bulk. Since the N*-smectic transition is coupled to a change from straight to bent conformation, there will during the transition be some volume in the bulk where the phase is cholesteric but the molecules start bending. This creates a very interesting situation in terms of chirality effects. With rod-shaped molecules the chiral interactions of the planar-aligned system promote twist along the substrate normal, leading to a uniform helical structure (Figure 1c). But when the molecules bend, the two well-separated chiral carbons of each molecule promote twisting along axes which are close to perpendicular to one another, and we can expect twisting in all possible directions, cf. Figure 1d (the three-dimensional situation is of course even more complex). It is this situation that produces the blue phase-like texture that we see at the N*-SmC$_s$P$_F$* transition in all cells thicker than 1 μm, and which leads to the loss of uniform alignment. The thicker the cell, the weaker the influence of the surfaces and the more nonuniform the final orientation of the smectic layers. The bent conformation may also explain why the mosaic structure produces visible selective reflection, whereas the helices of the stable phases are apparently much shorter than visible light wavelengths. The very short pitch in N* and SmC$_s$P$_F$* can be understood as a result of the two stereogenic centers of each molecule cooperating, increasing the twisting power. In contrast, the stereogenic centers act independently in the transitional state, trying to build up different helical structures. Though hypothetical, it could even be that the system in the transitional state may adopt a very peculiar type of

helical nematic phase, with the helix axis along the director, predicted by Memmer based on computer simulations of liquid crystalline organization of bent molecules.[52]

We are now in a position to address the question of the origin of the second field threshold seen in the experiment in Figure 6. The field-induced transition to the N* phase, taking place at the same threshold but at higher temperatures, is obviously a related issue. Because of the very small energy difference between rod- and bent-shaped conformations, we have to consider the possibility of a reaction to the electric field not only on a macroscopic scale but also on a molecular level. Without field the bent conformation is preferred both for packing and for polarization cancellation reasons (molecular anticlinic structure). But in the presence of a strong electric field the stretched-out all trans conformation may be preferable since it should lead to the maximum possible field-aligned polarization and thus correspond to a deeper energy minimum. This type of conformation switching due to the interaction between an electric field and the polarization of molecular subunits has been postulated for other polar dimeric liquid crystals, where the chiral mesogenic units are linked via a much longer spacer containing a siloxane unit at the center.[53,54] We note, however, that what in that case is interpreted as anticlinic to synclinic conformation switching gives an electrooptic response which is analogue, not like the typical steplike response of an AFLC switched to its synclinic state. Since no account is given of the helix pitch, one cannot rule out that the observed effect in those studies is actually the short-pitch helix unwinding process seen in Figure 6a–e.

Because the molecule in the all trans conformation is longer than that in the bent conformation (MOPAC/AM1 gives an all trans length of 60.4 Å and an end-to-end distance in the bent conformations of 56.4 and 57.4 Å), the stretched-out molecules would have to tilt slightly more in order to fit in the layer geometry. This could explain why the second threshold not only gives an increased birefringence, due to the increased effective molecular polarizability anisotropy, but also an increased tilt angle, reaching the rather uniquely high value of ∼50°. Looking at the texture at the second threshold, the lines along the layers are much more diffuse than those at the first threshold, which might be a sign that the layer structure is indeed a bit strained at this stage. The four main stages of the switching in the SmC$_s$P$_F$* phase are illustrated in the drawing in Figure 6.

Since at high temperatures the SmC$_s$P$_F$*-N* transition can be field-induced, the energy of the N* phase with straight molecules must there be decreased by the presence of an electric field, relative to all minima corresponding to smectic organization. A similar example of smectic to nematic transition related to an induced change of molecular shape was recently reported for the case of photoactive mesogens.[55] The role of the photoinduced trans−cis isomerization in that

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study is in BMHBOP-8 taken by the field-induced conformational change. The effect cannot simply be a result of $SmC_sP_F^*$ being superheated because then the system would not go back to smectic on field removal, nor would this explain why the N^*-$SmC_sP_F^*$ transition, once this has begun in the cooling experiment of Figure 8, is pushed back by the field. We also cooled the sample from N^* to $SmC_sP_F^*$ in the presence of a 20 Hz square wave electric field, strong enough to induce the transition to N^* in the high-temperature region of $SmC_sP_F^*$. There was then no trace of the colored mosaic texture; i.e., once the smectic phase formed under the influence of the field (at slightly lower temperature than in the field-free case), it did so with stretched-out molecules. Hence, the spiralling in all directions never took place. Instead, an ordinary smectic focal conic texture developed directly out of the black N^* texture. The reason the lowest free energy state is shifted from bent-core smectic to linear nematic by the electric field is far from obvious. Entropic contributions may play an important role. This is the matter of continued investigations.

Considering the change between rod and bent shape at the N^*-smectic transition of BMHBOP-8, it is finally interesting to look into the odd−even effect that Nishiyama et al. reported for the BMHBOP-n homologous series. It turns out that only the homologues with an even number of carbons in the linking chain develop the cholesteric phase. We can now immediately understand this by looking at the shapes of the odd-numbered homologues. In contrast to the BMHBOP-8 molecule, the all trans conformation is in these cases not linear, but bent-shaped. Moreover, the molecule remains bent-shaped throughout all variations of the torsional angle around the central spacer bond. This is why we never see the cholesteric phase in these homologues; the molecules are always bent, so the first liquid crystalline phase forming on cooling from the isotropic phase is smectic. It is equally interesting that the smectic layer spacings of the 7- and 8-homologues were found to be basically the same, just as were their θ vs electric field behavior. This clearly shows that the rule of thumb

saying that an even-numbered spacer gives a linear molecule whereas an odd-numbered one gives a bent molecule[33,35] does not hold in the BMHBOP-n series. If BMHBOP-8 had had linear molecules in the smectic phase, the layer spacing should have been distinctly larger than that of BMHBOP-7. Furthermore, the layer spacing reported by Nishiyama et al. for BMHBOP-8 was ~41 Å, fitting very well with the lengths of the bent conformations and a tilt angle of ~45°.

Conclusions

We have shown that the chiral twin molecule presented as the first AFLC with a cholesteric phase changes conformation at the transition between nematic and smectic. It is straightened out in N^* but adopts a bent conformation in the $SmC_sP_F^*$ phase. This is a helical synclinic and synpolar phase which however has a certain polarization cancellation on a molecular scale due to the bent conformation. The low-temperature smectic phase is most likely $SmC_aP_A^*$, a bent-core smectic phase which is antipolar also in terms of the mesoscopic molecular organization. Hence, the compound is indeed an AFLC with an N^* phase, but the antiferroelectric phase is not the ordinary SmC_a^* phase. The first liquid crystal with SmC_a^* and N^* in the phase sequence thus still remains to be synthesized, if indeed it can be done.

Supporting Information Available: Texture of monotropic high-temperature liquid crystal phase and complete 3D dielectric absorption spectrum (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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