# Ferroelectric and Antiferroelectric Smectic and Columnar Liquid Crystalline Phases Formed by Silylated and Non-Silylated Molecules with Fluorinated Bent Cores

Christina Keith,[†] Gert Dantlgraber,[†] R. Amaranatha Reddy,[†,§] Ute Baumeister,[‡] and Carsten Tschierske*,[†]

*Institute of Organic Chemistry, Martin-Luther University Halle-Wittenberg, Kurt-Mothes Strasse 2, D-06120 Halle, Germany and Institute of Physical Chemistry, Martin-Luther University Halle-Wittenberg, Mühlpforte 1, D-06108 Halle, Germany*

Novel liquid crystalline materials with fluorinated biphenyl-based bent aromatic cores have been synthesized. The influence of fluorine substitution at the aromatic core and the effects of combining oligosiloxane units and fluorine substitution were studied. The mesophases were investigated by polarizing microscopy, calorimetry, X-ray diffraction, and electrooptical investigations. Different types of polar smectic and columnar phases were observed. Depending on the position of the F substituents antiferroelectric and surface-stabilized ferroelectric switching subtypes of optically isotropic smectic phases composed of domains with opposite chirality sense (dark conglomerate phases) were obtained. All columnar phases represent ribbon phases with an oblique lattice. One type of columnar phase shows ferroelectric switching ($Col_{ob}P_{FE}$), and the other shows antiferroelectric switching ($Col_{ob}P_A$) which changes to a "nonclassical" antiferroelectric switching at reduced temperature. During the switching process the molecules reorganize by rotation on a cone in the $Col_{ob}P_{FE}$ phase and by rotation around the molecular long axis in the antiferroelectric columnar phase. The switching around the long axis is of special interest as it changes the suprastructural chirality of the LC system. Development of phase structures and switching behavior is discussed with respect to the influences of internal and external interfaces.

## 1. Introduction

Design of materials with polar order is of importance for piezoelectric, pyroelectric, and nonlinear optical applications.[1] Polar ordered liquid crystalline (LC) soft matter, in which the configuration of polar order can be switched by means of electric fields, can be used in fast switching electrooptical microdisplays and light modulators.[2] At first, chiral rod-like molecules, organized in a tilted configuration in layers (SmC* and SmCA* phases), were used as ferroelectric (FE) and antiferroelectric (AF) switchable LC materials.[3] In the past decade achiral molecules incorporating a bent aromatic core were found to give AF materials with exceptional high values of the spontaneous polarization, much larger than achieved with rod-like chiral molecules.[4] Since then, these bent-core molecules represent a new and highly innovative area in liquid crystal research, providing new insights into

soft matter self-organization with spontaneous formation of polar ordered superstructures as well as achiral symmetry breaking.[5] These special properties are due to the packing of bent-core molecules in layers. The bent shape gives rise to a restricted rotation around the long axis, leading to a spontaneous polar order with polarization (P) parallel to the layer planes. Escape from this polar order gives rise to numerous new types of organization in these LC phases. Besides layer structures (polar smectic phases = SmP) there are numerous organizations resulting from the frustration of these layers either by steric effects or in order to escape from a macroscopically polar phase structure.[5] There are different possible combinations of polar order, synpolar, assigned as ferroelectric ($P_F$) and antipolar, assigned as antiferroelectric ($P_A$). In the polar smectic phases the molecules are tilted in most cases, and the tilt direction can be either identical (synclinic, $SmC_s$) or opposite (anticlinic, $SmC_a$) in adjacent layers. This gives rise to in total four possible smectic phase structures, namely, $SmC_sP_F$, $SmC_aP_F$, $SmC_sP_A$, and $SmC_aP_A$. Figure 1 shows simple models of the distinct arrangements in the tilted smectic phases of these bent-core molecules.[6]

In most cases the bent direction in adjacent layers is antiparallel, so that the layer polarization alternates from layer

* To whom correspondence should be addressed. Fax: ++49 (0) 345 55 27 346. E-mail: Carsten.Tschierske@chemie.uni-halle.de.
　† Institute of Organic Chemistry.
　‡ Institute of Physical Chemistry.
　§ Present address: Department of Chemistry & Biochemistry, University of Colorado at Boulder, Boulder, CO 80309-0215.

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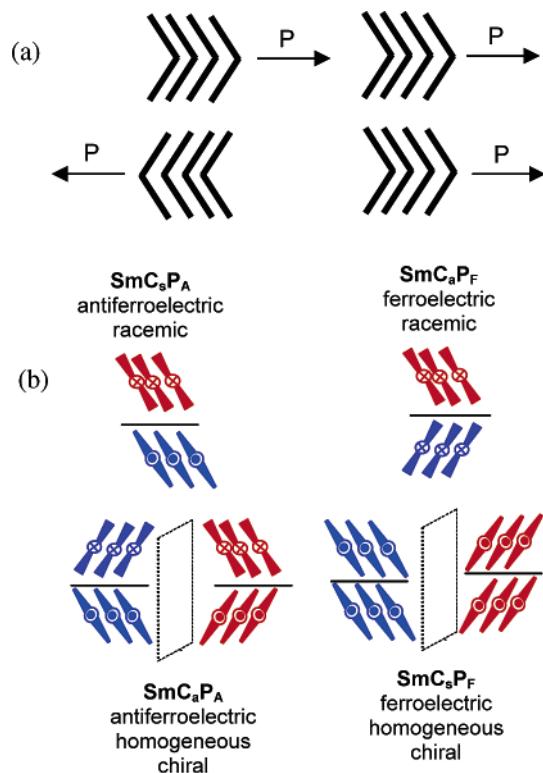
**Figure 1.** Bent-core molecules: (a) side views and (b) front and back views of the four possible arrangements in tilted polar smectic phases. The subscripts s and a indicate the correlation of the tilt direction in adjacent layers (s = synclinic, a = anticlinic). A and F indicate AF (polar direction alternates from layer to layer) and FE structures (polar direction is identical), respectively. The color indicates the chirality of the layers. The SmC$_a$P$_A$ and SmC$_s$P$_F$ structures are homogeneously chiral (identical chirality sense in adjacent layers); the SmC$_s$P$_A$ and SmC$_a$P$_F$ structures are macroscopically racemic (alternating chirality sense in adjacent layers).

to layer, which leads to macroscopically apolar AF structures (SmC$_s$P$_A$ and SmC$_a$P$_A$ phases) as ground-state structures.[6] These nonpolar states can be switched into the polar states under a sufficiently strong external electric field, which stabilizes the polar SmC$_s$P$_F$ and SmC$_a$P$_F$ structures, respectively. This switching process can be observed under an applied triangular wave voltage; then switching takes place between three stable states (tristable switching), from one polar SmCP$_F$ state via the ground state (SmCP$_A$) to the polar SmCP$_F$ state with opposite polar direction after field reversal. This AF switching process is characterized by two polarization current reversal peaks in each half period of the applied triangular wave voltage. FE switching mesophases (SmCP$_F$/ SmCP$_{FE}$)[7] have also been reported for selected bent-core materials.[8] Here, the switching takes place directly between the two energetically equivalent polar structures, and this bistable switching process is characterized by only one polarization current reversal peak in each half period of the applied triangular wave voltage.

Due to the tilted organization of the molecules in polar layers the layers have $C_2$ symmetry, which lacks mirror symmetry, and hence, these layers are inherently chiral. The directions of layer normal, polar direction, and tilt direction determine either a right-handed or a left-handed system.[6] If adjacent layers have the same chirality sense the structure of the polar smectic phase is homogeneously chiral (SmC$_a$P$_A$ and SmC$_s$P$_F$); if the layers have opposite chirality sense, the structure is macroscopically racemic (SmC$_s$P$_A$ and SmC$_a$P$_F$).[6]

An additional remarkable feature of some mesophases formed by bent-core molecules is a macroscopic chirality, which can be seen by slightly uncrossing the polarizers. Under these conditions a domain structure composed of dark and bright regions can be observed. Reversing the direction of polarizer and analyzer reverses the brightness of these domains. This is an indication of a mesophase structure composed of a conglomerate of macroscopic domains of opposite handedness (these so-called dark conglomerate phases are assigned with "[*]").[9,10] It was proposed that this optical activity is due to the inherent chirality of the polar SmCP layers,[11] but it can only be observed if the phase structure is homogeneously chiral, i.e., for a SmC$_a$P$_A$ or SmC$_s$P$_F$ structure, and if, in addition, the birefringence of the mesophase itself is sufficiently low. The low birefringence is thought to result from a sponge-like deformation of the layers.[11,12]

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(7) The subscript "F" is used for FE switching phases with a proven FE ground-state structure in the bulk (before application of an external field, see ref 8l); for mesophases where a FE switching is found experimentally, but where the virgin ground-state structure is unknown or nonpolar the subscript FE is used, as suggested in ref 5d.

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**Chart 1. Selected Examples of Bent-Core Molecules Forming FE Switching Smectic Phases[a]**



1: Cr 70 SmCP$_{FE}$[*] 115 Iso[13a,12]

2: Cr 128 (SmCP$_{FE}$[*] 127.5) Iso[8h,e]
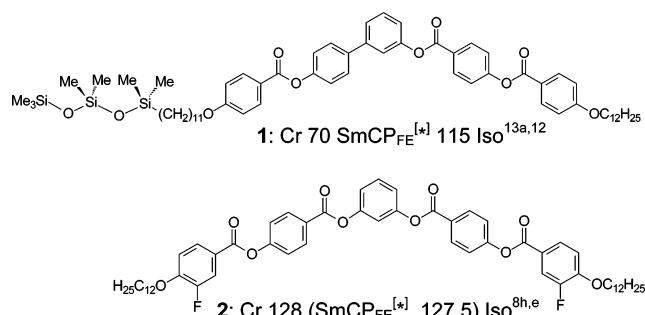
[a] Abbreviations: Cr = crystalline solid, SmCP$_{FE}$[*] = ferroelectric switching smectic phase with dark conglomerate texture, Iso = isotropic liquid).

One group of compounds, which has a pronounced tendency to form FE switching smectic phases with dark conglomerate textures, incorporates oligo(siloxane)[13] or carbosilane units at one end of the bent-core unit,[14] as, for example, compound **1** (see Chart 1).[12,13a] Also, compounds with siloxane units at both ends,[15] dimers,[16,17] oligomers, dendrimers,[18] and side chain polymers[19] derived from oligosiloxane and carbosilane units have been reported. Another structurally different class of FE switching materials with dark conglomerate textures is provided by non-silylated molecules containing fluorine substituents at the periphery of the bent aromatic core, in the ortho positions to the adjacent alkoxy chains (e.g., compound **2**, Chart 1).[8c−e,h,k,9e,20,21]

Herein we report a study concerning the combination of these two different structural features (F substitution and microsegregating oligosiloxane units) both facilitating ferroelectricity and supramolecular chirality. First, the influence of fluorination upon the properties of the biphenyl derived

**Chart 2. Parent Biphenyl-Based Bent-Core Mesogen 3H and Compounds 4−7 Reported Herein[a]**



3H: Cr 106 SmCP$_A$ 159 Iso[22]

4: A-E = H, F

5: A-E = H, F

6: A-D = H, F

7: A-D = H, F
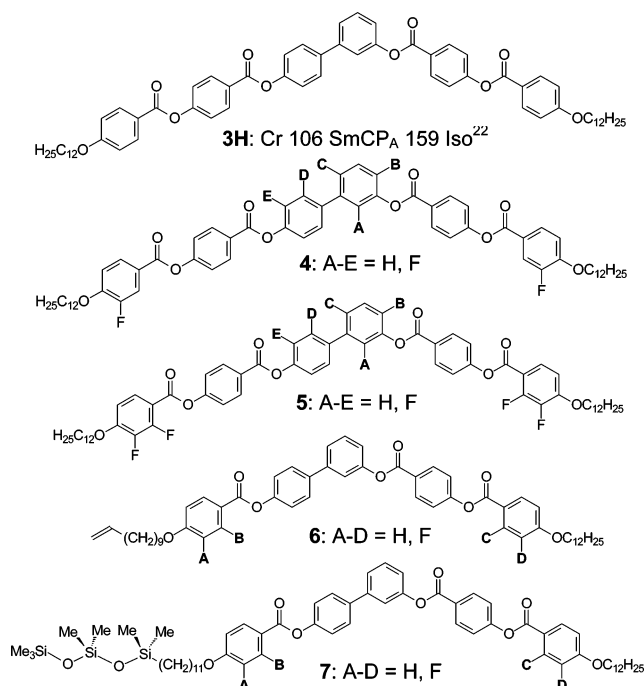
[a] SmCP$_A$ = antiferroelectric switching smectic phase = B$_2$ phase.

mesogen **3H**[22,23] is investigated (compounds **4−6**), and then the influence of fluorination on the properties of polyphilic bent-core molecules **7** with a 5,5,5,3,3,1,1-heptamethyltrisiloxane-1-yl-terminated alkyl chain will be reported (see Chart 2). These two structural features enable a tuning of the polar properties from conventional AF switching via "nonclassical" AF switching to FE switching materials. In addition, distinct substitution patterns provide access to AF and FE switching polar columnar phases.

## 2. Results and Discussion

**2.1. Synthesis.** Synthesis of compounds **4** and **5** with identical side wings at the biphenyl core was carried out by esterification of F-substituted 3,4′-dihydroxybiphenyls[23] with appropriately F-substituted 4-(4-alkoxybenzoyloxy)benzoic acids.[8c−e,h,20,24] Syntheses of the 3,4′-dihydroxybiphenyls[23] and benzoic acids[8d,e,24] were reported earlier. Synthesis of compounds **6** and **7** was done as shown in Scheme 1 starting from 4′-benzyloxybiphenyl-3-ol[22b] and nonsubstituted or F-substituted 4-(4-dodecyloxybenzoyloxy)benzoic acids,[22b] deprotection, and esterification with nonsubstituted or F-substituted 4-(10-undecen-1-yloxy)benzoic acids[25] to yield the olefins **6**. Hydrosilylation with 1,1,1,3,3,5,5-heptamethyltrisiloxane yielded the siloxane-substituted compounds **7**.[12,13] Purification was done by centrifugal thin-layer chro-

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**Scheme 1. Synthesis of the Olefins 6 and Oligosiloxane Derivatives 7 (A−D = H, F)**[a]
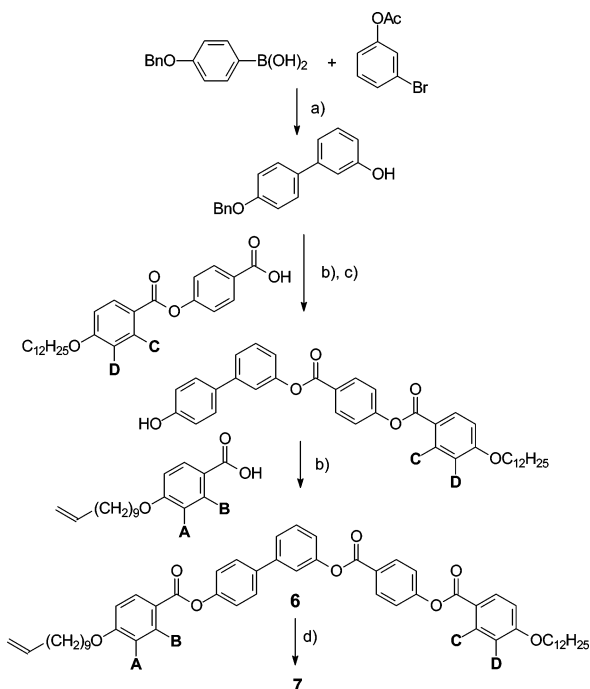


[a] Reagents and conditions:  (a) cat. [Pd(PPh₃)₄], NaHCO₃, H₂O, glyme, reflux, 8 h. (b) DCC, DMAP, CH₂Cl₂, 20 °C, 24 h. (c) H₂, Pd/C, AcOEt, 20 °C, 24 h. (d) Me₃Si(OSiMe₂)₂H, Karstedt's catalyst, toluene, 20 °C, 24 h.

matography followed by crystallization. The obtained compounds were checked by NMR, elemental analysis, and thin-layer chromatography. Representative experimental procedures and analytical data of the target compounds are collated in the Supporting Information. Investigation of the liquid crystalline properties was carried out by polarizing microscopy, differential scanning calorimetry, X-ray diffraction on powder-like and surface-aligned samples, as well as electrooptical investigation.

**2.2. Influence of the Position of F Substituents at the Central Biphenyl Unit on the Liquid Crystalline Properties of Peripheral F-Substituted Bent-Core Mesogens.** *2.2.1. Polar Smectic Phases of the Non-Silylated Compounds 4.* The non-fluorinated compound **3H** (see Chart 2) is a

prototype compound forming an AF switching polar smectic phase (SmCP_A also abbreviated as B₂ phase) over a wide temperature range.[22] Typically this type of mesophase is highly birefringent and optical biaxial (see Figure S1). Introduction of F atoms into the bent aromatic core at both ortho positions adjacent to the alkoxy chains of compound **3H** has a stabilizing effect on this SmCP_A phase (compound **4H,** see Table 1), but no change of the mesophase structure and switching behavior is observed. Hence, in contrast to the related fluorine-substituted resorcinol bisbenzoate **2**[8e,h] (see Chart 1) which shows a FE switching smectic phase (SmCP_FE[*]), the related biphenyl derivative **4H** is an AF switching material showing the typical birefringent texture of the classical SmCP_A (B₂-type) phases. This indicates that elongation of the bent aromatic core by replacing the resorcinol core by a larger 3,4′-biphenyldiol core with reduced symmetry is less favorable for the occurrence of ferroelectricity.

In contrast to the effect of peripheral F substitution, which stabilizes the mesophases, a mesophase destabilizing effect is seen for F substitution at the biphenyl core. If in compound **4H** one more F substituent is introduced at the biphenyl core into position B or E, which are adjacent to the ester linking groups (compounds **4b** and **4e**), birefringent SmCP_A phases can be observed also, though there is a reduction of the mesophase stability compared to **4H**. For all compounds **4** with the exception of **4a** (which has a columnar phase) two peaks were observed in the polarization current curves, as shown in Figure 4 for compound **4e** as an example. This indicates an AF switching behavior of these mesophases with values of the spontaneous polarization between 600 and 900 nC cm⁻².

Compounds **4a**, **4c**, and **4d**, i.e., the molecules having the F substituent adjacent to the connection between the two benzene rings of the biphenyl unit, show distinct optical textures. Compound **4a** forms a columnar phase, which will be discussed in the next section. For compound **4c** cooling from the isotropic liquid state leads to a mesophase which appears completely dark between crossed polarizers. This mesophase shows a high viscosity, similar to cubic phases, though only a well-defined layer structure with $d$ = 4.6 nm

**Table 1. Mesophases, Transition Temperatures, and Corresponding Enthalpy Values for the F-Substituted Compounds 4**[a]



| compd | A | B | C | D | E | | | $T$/°C [$\Delta H$/kJ mol⁻¹] | | | lattice parameters/nm |
|-------|---|---|---|---|---|---|---|---|---|---|------|
| **4H** | H | H | H | H | H | Cr | 101 [29.3] | SmCP_A | 170 [22.0] | iso | $d$ = 4.42 (140 °C) |
| **4a** | F | H | H | H | H | Cr | 120[32.3] | Col_ob P_FE | 165 [23.1] | iso | $a$ = 8.10, $b$ = 4.90, $\gamma$ = 99.2° (160 °C) |
| **4b** | H | F | H | H | H | Cr | 114 [25.1] | SmCP_A | 152 [16.5] | iso | |
| **4c** | H | H | F | H | H | Cr | 92 [22.3] | SmCP_A[*] | 162 [24.3] | iso | $d$ = 4.42 (140 °C); $d$ = 4.59 (100 °C) |
| **4d** | H | H | H | F | H | Cr | 113 [33.6] | SmCP_A[*/○]b | 157 [23.9] | iso | |
| **4e** | H | H | H | H | F | Cr | 109 [33.5] | SmCP_A | 158 [22.1] | iso | |

[a] Abbreviations:  SmCP_A[*] = AF switching tilted polar smectic phase showing an optically isotropic texture composed of domains of opposite chirality sense; Col_ob P_FE = oblique columnar phase which shows FE switching under an applied electric field. [b] [*/○] indicates that regions with dark conglomerate texture can be found beside birefringent textures. The other abbreviations are explained in the captions to Charts 1 and 2. DSC: scanning rate 10 K min⁻¹; peak temperatures from the first heating scans were used.
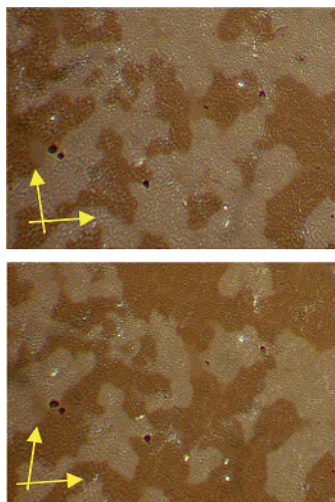
**Figure 2.** Texture of the SmCP$_A$[*] phase (dark conglomerate phase) of compound **4c** at 160 °C between slightly uncrossed polarizers. The brightness of the domains is exchanged by uncrossing the polarizers in either one or the other direction, indicating regions of opposite chirality sense.



**Figure 3.** CPK models of compounds **4H** (top, $L = 6.4$ nm) and **7ad** (bottom, $L = 6.3$ nm) showing the conformation used for determination of the molecular length.

at $T = 100$ °C can be detected by X-ray diffraction, confirming a smectic phase. The layer spacing $d$ is much smaller than the molecular length ($L = 6.4$ nm, in a conformation as shown for the related compound **4H** with the same length in Figure 3), evidencing a monolayer structure of this smectic phase with a rather large tilt angle of the molecules ($\theta = 44°$, as calculated according to cos $\theta = d/L$). The layer distance is nearly the same as that observed for the birefringent SmCP$_A$ phases (e.g., compound **4H**: $d = 4.4$ nm at $T = 140$ °C). A diffuse scattering in the wide-angle region at ca. 0.47 nm indicates a smectic phase without in-plane order in all cases. Regions of opposite chirality sense can be distinguished by polarizing microscopy after rotating the polarizer into slightly uncrossed positions (see Figure 2). Upon applying a sufficiently strong electric field the texture becomes strongly birefringent, suggesting a change of the mesophase structure under the influence of the applied field. This birefringent texture is also obtained upon cooling from the isotropic liquid under an electric field. Upon cooling under a dc field a more specific texture with circular domains and extinction crosses can be seen. Two polarization current peaks within a half period of an applied triangular wave voltage clearly demonstrate an AF switching behavior of this mesophase. Optical investigations (dc−field experiments) confirm a tristable switching process, as shown in Figure 5. Under an applied electric field the extinction crosses in the circular domains are inclined with the directions of polarizer and analyzer, evidencing a synclinic organization (Figure 5a, SmC$_s$P$_F$). Upon switching off the applied field the extinction
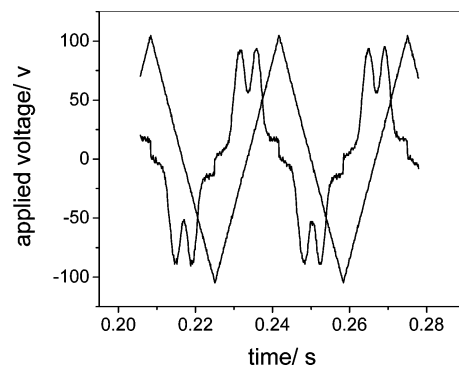


**Figure 4.** Current response curve of the AF switching compound **4e** at 120 °C (210 V$_{pp}$, 30 Hz, 5 $\mu$m noncoated ITO cell, $P_s = 800$ nC cm$^{-2}$).
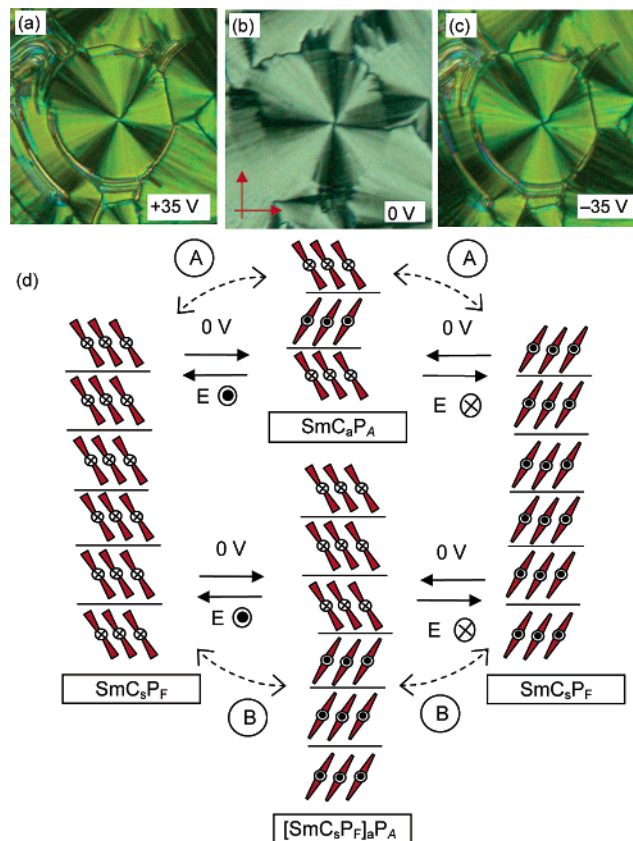


**Figure 5.** Switching process as observed in the mesophase of compound **4c** at 120 °C (6 $\mu$m polyimide-coated ITO cell). Under the applied field (a, c) the extinction crosses are inclined with the direction of the polarizers (indicated by arrows), which indicates a SmC$_s$P$_F$ organization of the molecules. On switching off the field (b) the extinction crosses relax to a position parallel to the polarizers, as typical for an anticlinic organization, which indicates a tristable (AF) switching process. (d) Two different modes of switching between the polar SmC$_s$P$_F$ states. In the classical AF switching process (A) the relaxation of the FE states at 0 V gives rise to a SmC$_a$P$_A$ structure where the polar direction reverses from layer to layer. The relaxation can also take place by reorganization of stacks of layers, as shown at the bottom (B) and discussed in section 3, leading to an anticlinic and antipolar organization of SmC$_s$P$_F$ layer stacks and giving rise to a [SmC$_s$P$_F$]$_a$P$_A$ ground-state structure (nonclassical AF switching). If in this structure the size of the uniform SmC$_s$P$_F$ layer stacks is smaller than the wavelength of light, only an average optical axis is seen and the extinction crosses are parallel to the polarizers.

crosses rotate into positions parallel to polarizer and analyzer (Figure 5b). This indicates relaxation into an anticlinic structure at 0 V. Rotation is continued in the same direction after application of an electric field with opposite direction, leading to a SmC$_s$P$_F$ structure with opposite polar direction
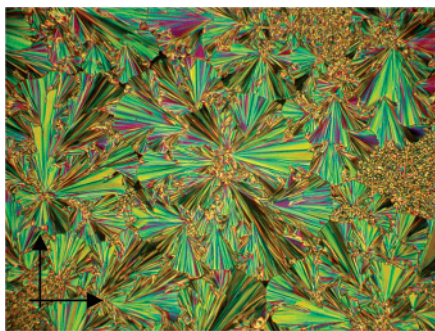
**Figure 6.** Texture of compound **4a** as seen after cooling from the isotropic liquid at 156 °C between crossed polarizers (position of the polarizers is indicated by arrows).

(Figure 5c). On the basis of these investigations the ground-state structure of compound **4c** should be AF with an anticlinic organization of the molecules.[26] Compound **4d** behaves as a borderline case between the birefringent $SmCP_A$ phases of compounds **4H**, **4b**, and **4e** and the dark conglomerate $SmCP_A^{[*]}$ phase of compound **4c**. The texture is birefringent but very nonspecific (grainy), and occasionally isotropic regions composed of domains with opposite chirality sense can also be seen.

*2.2.2. Ferroelectric Switching Columnar Mesophase of Compound 4a.* Compound **4a** is the only compound in this series which does not show a simple layer structure but a mesophase with 2D lattice instead[27] and a texture as shown in Figure 6. The powder-like X-ray diffraction pattern of the mesophase of this compound shows three incommensurate reflections in the small-angle region, which confirm a mesophase with a 2D lattice. The diffuse scattering around $d = 0.47$ nm indicates a fluid liquid crystalline phase. The small-angle reflections point to an oblique 2D lattice with $a = 8.1$ nm, $b = 4.9$ nm, and $\gamma = 99°$. A unique indexing of the reflections was not possible in this case because only powder patterns were obtained, but for the similar compound **5a** (section 2.2.3) a partial alignment of the sample was achieved. Here, an assignment of the lattice parameters was possible with much higher reliability. Because the mesophases of series **5** are very similar to those of series **4** (phase types, textures, lattice parameters) we assume that the organization in the $Col_{ob}$ phases of **4a** and **5a** is essentially the same. In addition, the parameter $b$ is in both cases close to the layer distance in the smectic phases
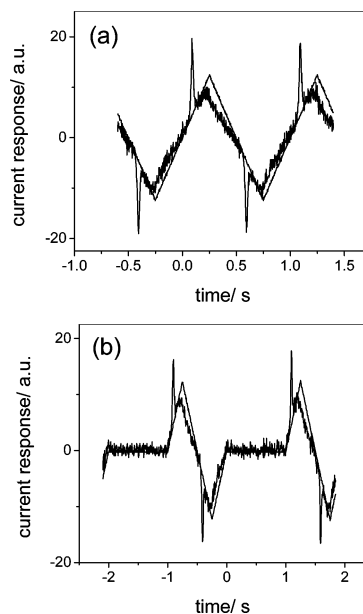


**Figure 7.** Switching current curves observed for the mesophase of compound **4a** at 125 °C in a polyimide-coated ITO cell (6 $\mu$m, 1 Hz, 250 $V_{pp}$) (a) under a triangular wave field and (b) under a modified triangular wave field with a pause at 0 V; the presence of only one peak indicates a FE switching process.

of the other compounds **4** and **5**, and this is in line with a modulated smectic phase where the molecules adopt a tilted organization. The periodicity $a$ is quite large, and about 13 molecules are organized in average in the cross-section of these ribbons.[28]

The most remarkable feature of the columnar phase of **4a** is that, in contrast to the smectic phases of the other compounds **4**, it shows only one very sharp peak in the half period of an applied triangular wave field, even under a modified triangular wave voltage,[29] which is a strong indication of a FE switching behavior (Figure 7). The spontaneous polarization is about 550 nC cm$^{-2}$, which is a quite large value for a columnar phase.[8d,h,15a,30,31] It was possible to grow circular domains under a relatively high electric field (300 $V_{pp}$ in a 6 $\mu$m polyimide-coated ITO cell at 100 Hz), and the extinction crosses in these domains are inclined with the positions of polarizer and analyzer (see Figure 8a). This indicates a $SmC_sP_F$ organization with a

(26) As shown in Figure 4 and discussed in section 3, in principle, there are two possibilities for an anticlinic organization; the tilt direction changes either between each layer ($SmC_aP_A$) or between stacks of $SmC_sP_F$ layers ($[SmC_sP_F]_aP_A$).

(27) Examples of columnar phases formed by bent-core molecules: (a) Watanabe, J.; Niori, T.; Sekine, T.; Takezoe, H. *Jpn. J. Appl. Phys.* **1998**, *37*, L139−L142. (b) Mieczkowski, J.; Gomola, K.; Koseska, J.; Pociecha, D.; Szydlowska, J.; Gorecka, E. *J. Mater. Chem.* **2003**, *13*, 2132−2137. (c) Reddy, R. A.; Sadashiva, B. K.; Raghunathan, V. A. *Chem. Mater.* **2004**, *16*, 4050−4062. (d) Pelz, K.; Weissflog, W.; Baumeister, U.; Diele, S. *Liq. Cryst.* **2003**, *30*, 1151−1158. (e) Kardas, D.; Prehm, M.; Baumeister, U.; Pociecha, D.; Reddy, R. A.; Mehl, G. H.; Tschierske, C. *J. Mater. Chem.* **2005**, *15*, 1722−1733. (f) See ref 21b. (h) Nguyen, H. T.; Bedel, J. P.; Rouillon, J. C.; Marcerou, J. P.; Achard, M. F. *Pramana, J. Phys.* **2003**, *61, 395−*404. Gorecka, E.; Vaupotic, N.; Pociecha, D.; Cepic, M.; Mieczkowski, J. *ChemPhysChem* **2005**, *6*, 1087−1093. (g) Takanishi, Y.; Takezoe, H.; Watanabe, J.; Takahashi, Y.; Lida, A. *J. Mater. Chem.* **2006**, *16*, 816−818.

(28) Calculated from the volume of the unit cell ($V_{cell}$, obtained from the lattice parameters and assuming a height of $h = 0.52$ nm) and the molecular volume ($V_{mol}$, calculated using the crystal volume increments of Immirzi and Perini: Immirzi, A.; Perini, B. *Acta Crystallogr., Sect. A* **1977**, *33*, 216−218) according to $n = V_{cell}/V_{mol}$ corrected for the less dense packing in the liquid crystal assuming the packing coefficient to be intermediate between the average packing coefficient in the crystalline ($k = 0.7$) and liquid state ($k = 0.55$) (Kitaigorodski, A. I. "Molekülkristalle", Akademieverlag Berlin, 1979, see Table S2).

(29) Achard, M. F.; Bedel, J. Ph.; Marcerou, J. P.; Nguyen, H. T.; Rouillon, J. C. *Eur. Phys. J. E* **2003**, *10*, 129−134.

(30) Reddy R. A.; Sadashiva, B. K. *J. Mater. Chem.* **2004***, 14*, 1936−1947.

(31) Examples of polar switching columnar phases of non-silylated compounds: (a) Reddy, R. A.; Sadashiva, B. K.; Baumeister, U. *J. Mater. Chem.* **2005**, *15*, 3303−3316. (b) Umadevi, S.; Sadashiva, B. K.; Shreenivasa Murthy, H. N.; Raghunathan, V. A. *Soft Matter* **2006**, *2*, 210−214. (c) Gorecka, E.; Pociecha, D.; Mieczkowski, J.; Matraszek, J.; Guillon, D.; Donnio, B. *J. Am. Chem. Soc.* **2004**, *126*, 15946−15947. (d) Weissflog, W.; Naumann, G.; Kosata, B.; Schröder, M. W.; Eremin, A.; Diele, S.; Vakhovskaya, Z.; Kresse, H.; Friedemann, R.; Ananda Ramakrishnan, S.; Pelzl, G. *J. Mater. Chem.* **2005**, *15*, 4328−4337.
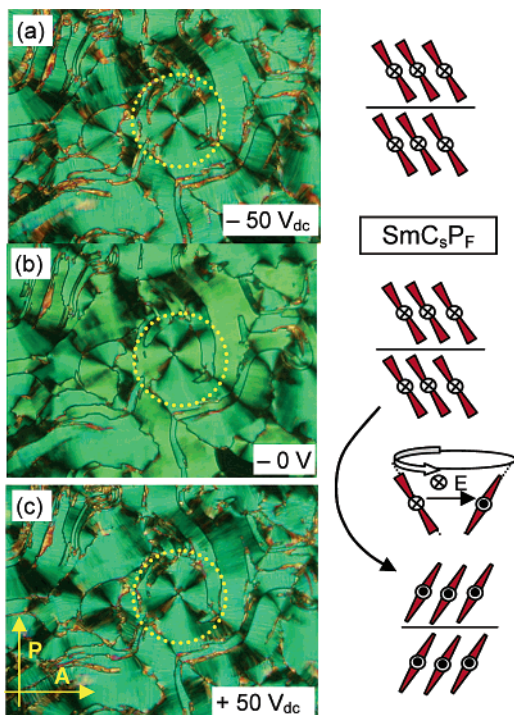
**Figure 8.** Switching process as observed in the mesophase of compound **4a** at 125 °C (6 μm polyimide-coated ITO cell): (a) under the applied electric field the extinction crosses are inclined with the direction of the polarizer and analyzer, which indicates a synclinic FE organization of the molecules ($SmC_sP_F$); (b) on switching off the field the position of the extinction crosses does not change (i.e., the structure remains $SmC_sP_F$); (c) rotation of the extinction crosses and reorganization to the $SmC_sP_F$ structure with opposite tilt direction and reversed polar direction takes place by rotation on a cone after applying the opposite field, and this indicates a bistable (FE) switching process.

synclinic tilt of the molecules and an optical tilt angle of about 40°. On switching off the applied electric field the extinction crosses do not rotate, and even after several hours no change of the position of the extinction crosses, only a small change of the birefringence, could be detected (Figure 8b). This means that the polar state is stable or extremely long living metastable under the experimental conditions. Only after applying a voltage with opposite sign the extinction crosses rotate by ca. 80° either clockwise or counterclockwise (Figure 8c). Hence, optical investigation clearly indicates a bistable switching by a collective rotation around a cone, which is an additional confirmation of the FE switching process.

It is quite difficult to deduce an appropriate model for the organization of the molecules in this $Col_{ob}P_{FE}$ phase. In the texture shown in Figure 6 the dark brushes are inclined with the positions of the polarizers, indicating a synclinic tilted organization also in the ground-state structure of this mesophase. As discussed earlier, the parameter *a* should correspond to the width of the ribbons, whereas *b* is associated with the thickness of the ribbons. The lattice parameter *b* is significantly smaller than the molecular length (*L* = 6.4 nm), and therefore, the molecules should be inclined with respect to direction *b*. The relatively large lattice parameters of the $Col_{ob}P_{FE}$ phase of **4a** makes it also likely that splay of polarization is involved in the stabilization of the 2D lattice.[32] A splay-modulated arrangement of ribbons, as shown in Figure 9a, with an overall synclinic correlation
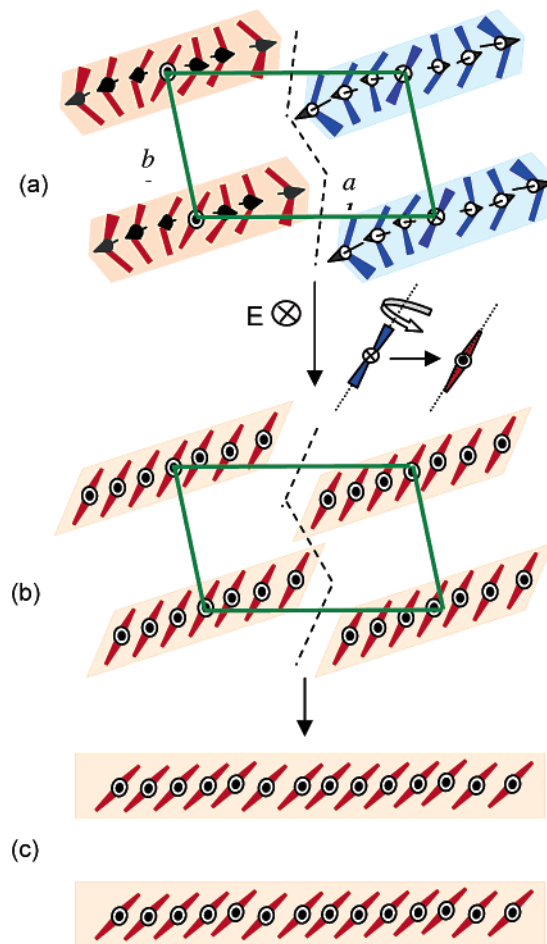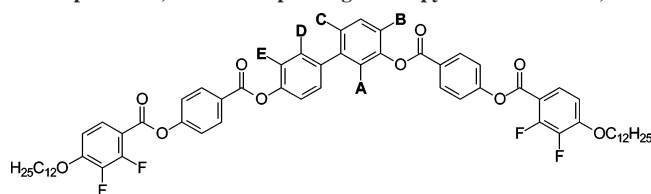


**Figure 9.** (a) Proposed model of ground-state organization in the $Col_{ob}P_{FE}$ phase of compounds **4a** and **5a** with polarization splay between adjacent ribbons; (b) field-induced synpolar ribbon structure which is unstable due to the unfavorable interfaces between the ribbons (broken line); (c) field-induced $SmC_sP_F$ phase. In a and b only 7 instead of the actual 13 (**4a**) and 11 (**5a**) molecules in the cross section of the ribbons are shown. The space between the ribbons and layers is filled by the alkyl chains.

between adjacent ribbons ($SmC_sP_F$ along direction *b*) and an AF organization along direction *a* seems to be the most reasonable structure for the $Col_{ob}P_{FE}$ phase of **4a**.[33] Remarkably, the only difference of the molecular structure of **4a** with respect to the other isomers in the series of compounds **4** is the special position of the electron-accepting F substituent in the bay region of the bent aromatic core at the central 1,3-substituted benzene ring. This molecular structure is very similar to other molecules forming mesophases involving splay of polarization. Bent-core molecules having other electron-withdrawing substituents, such as $NO_2$ or $CN$,[21c,34a−e] in the bay position (mainly resorcinol derivatives) or an F atom at the apex of this central ring[34f] are known to form $B_7$-type mesophases which are polarization-modulated smectic phases with a 2D lattice.[32] This structural similarity

(32) Coleman, D. A.; Fernsler, J.; Chattham, N.; Nakata, M.; Takanishi, Y.; Korblova, E.; Link, D. R.; Shao, R.-F.; Jang, W. G.; Maclennan, J. E.; Mondainn-Monval, O.; Boyer, C.; Weissflog, W.; Pelzl, G.; Chien, L.-C.; Zasadzinski, J.; Watanabe, J.; Walba, D. M.; Takezoe H.; Clark, N. A. *Science* **2003**, *301*, 1204−1211.
(33) In the $Col_{ob}P_{FE}$ phases of **4a** and **5a** the splay seems to be relatively weak, as it can be removed under an electric field, leading to a FE switching smectic phase. Also, formation of an oblique lattice instead of a rectangular one is in line with a relatively weak splay of polarization.

**Table 2. Mesophases, Transition Temperatures, and Corresponding Enthalpy Values for the 2,3-Difluorosubstituted Compounds 5**



| compd | A | B | C | D | E | | T/°C [ΔH/kJ mol⁻¹] | | | lattice parameters/nm |
|-------|---|---|---|---|---|----|---------------------------|----|-----|------------------------|
| **5H** | H | H | H | H | H | Cr | 120 [28.3] | SmCP$_A$[*/º] | 177 [25.9] iso | |
| **5a** | F | H | H | H | H | Cr | 141 [27.8] | Col$_{ob}$P$_{FE}$ | 171 [25.7] iso | $a = 7.20$, $b = 4.83$, $\gamma = 98.5°$ (165 °C) |
| **5b** | H | F | H | H | H | Cr | 80 [18.8] | SmCP$_A$ | 156 [18.0] iso | $d = 4.35$ (140 °C) |
| **5c** | H | H | F | H | H | Cr | 123 [27.5] | SmCP$_A$[*] | 171 [26.4] iso | $d = 4.37$ (150 °C) |
| **5d** | H | H | H | F | H | Cr | 119 [35.0] | SmCP$_A$[*/º] | 165 [25.2] iso | $d = 4.25$ (140 °C) |
| **5e** | H | H | H | H | F | Cr | 119 [35.4] | SmCP$_A$ | 166 [24.7] iso | |

suggests that also for the Col$_{ob}$P$_{FE}$ phase of compound **4a** there could be a mesophase structure incorporating polarization splay. However, this phase is different from typical B$_7$ phases[34a] and other polarization-modulated smectic phases[32] as no helical filaments or spiral textures can be observed.

In the proposed ground-state structure, shown in Figure 9a, the molecules are organized in ribbons with a reversal of the polar direction along direction *a*. In ribbon phases the field-induced reorganization of the molecules usually takes place by collective rotation around the long axis because the inter-ribbon interfaces hinder rotation on a cone. This reorganization would lead to a synpolar (FE) ribbon structure where the synclinic tilt of the molecules is retained. However, in such a modulated smectic phase with a synpolar organization of the molecules in adjacent ribbons (along direction *a*) there would be unfavorable steric interactions at the interfaces between the ribbons (see Figure 9b). Therefore, these interfaces are unstable and a nonmodulated smectic phase without these interfaces is formed instead (see Figure 9c). This field-induced transition to a synclinic and synpolar smectic phase (SmC$_s$P$_F$) was observed previously also for other polarization-modulated smectic phases.[35] The rather high threshold voltage (33 V$_{pp}$/$\mu$m) required for FE switching and the unusually high polarization values are in line with a change of the mesophase structure under the influence of the applied electric field to a field-induced polar smectic phase.[32,36] Also, the fact that the field-induced texture is different from the texture observed before applying the electric field (compare Figures 6 and 8) indicates a modifica-

**Table 3. Mesophases and Transition Temperatures for Compounds 3 without Peripheral F Substituents[23]**
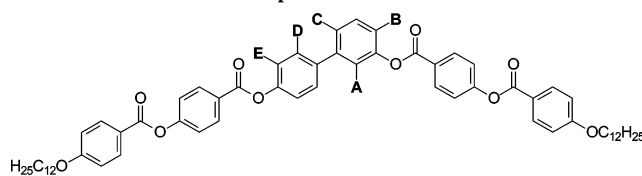


| compd | A | B | C | D | E | | T/°C | | |
|-------|---|---|---|---|---|----|------|---------|-----|
| **3H** | H | H | H | H | H | Cr | 106 | SmCP$_A$ | 159 iso |
| **3a** | F | H | H | H | H | Cr | 120 | SmCP$_A$ | 148 iso |
| **3b** | H | F | H | H | H | Cr | 110 | SmCP$_A$ | 136 iso |
| **3c** | H | H | F | H | H | Cr | 115 | SmCP$_A$ | 153 iso |
| **3d** | H | H | H | F | H | Cr | 103 | SmCP$_A$ | 146 iso |
| **3e** | H | H | H | H | F | Cr | 88 | SmCP$_A$ | 137 iso |

tion of the phase structure. In the field-induced smectic phase bistable (FE) switching is observed, which takes place by rotation on a cone as typical for nondistorted smectic phases and indicated by the rotation of the extinction crosses after field reversal.[15,37,38,39]

*2.2.3. Smectic and Columnar Mesophases of Compounds 5.* In Table 2 the transition temperatures of compounds **5H** and **5a**−**e** are collated, which differ from compounds **4** by additional F substituents at each of the outer aromatic rings (2,3-difluoro-substituted aromatics). Comparison with the data given for the related compounds **4** in Table 1 indicates that introduction of the additional peripheral F atoms has a stabilizing effect on the mesophase in all cases. In comparison with the non-fluorinated compounds **3** (see Table 3),[23] the mesophase stabilizing and mesophase modifying effect of the lateral F atoms becomes even more evident.[40] If the

(34) (a) Pelzl, G.; Diele, S.; Jakli, A.; Lischka, C.; Wirth, I.; Weissflog, W. *Liq. Cryst.* **1999**, *26*, 135−139. (b) Reddy, R. A.; Sadashiva, B. K. *Liq. Cryst.* **2003**, *30*, 273−283. (b) Shreenivasa Murthy H. N.; Sadashiva, B. K. *J. Mater. Chem.* **2003**, *13*, 2863−2869. (c) Shreenivasa Murthy, H. N.; Sadashiva, B. K. *Liq. Cryst.* **2003**, *30*, 1051−1055. (d) Shreenivasa Murthy, H. N.; Sadashiva, B. K. *J. Mater. Chem.* **2003**, *13*, 2863−2869. (e) Dunemann, U.; Schröder, M. W.; Reddy, R. A.; Pelzl, G.; Diele, S.; Weissflog, W. *J. Mater. Chem.* **2005**, *15*, 4051−4061. (f) Pelzl, G.; Schröder, M. W; Dunemann, U.; Diele, S.; Weissflog, W.; Jones, C.; Coleman, D.; Clark, N.A.; Stannarius, R.; Li, J.; Dasc, B.; Grande, S. *J. Mater. Chem.* **2004**, *14*, 2492−2498.

(35) Such a change of the mesophase structure was also observed for B$_7$-type phases: Nakata, M.; Link, D. R.; Takanishi, Y.; Takahasi, Y.; Thisayukta, J.; Niwano.H. Coleman, D.A.; Watanabe, J.; Iida, A.; Clark, N. A.; Takezoe, H. *Phys. Rev. E* **2005**, *71*, 011705.

(36) Examples of field-induced Col to Sm transitions: (a) Ortega, J.; de la Fuente, M. R.; Etxebarria, J.; Folcia, C. L.; Diez, S.; Gallastegui, J. A.; Gimeno, N.; Ros, M. B. *Phys. Rev. E* **2004**, *69*, 011703. (b) Etxebarria, J.; Folcia, C. L.; Ortega, J.; Ros, M. B. *Phys. Rev. E* **2003**, *67*, 042702.

(37) FE switching on a cone is in principle possible in flat layers as well as in modulated and undulated layers. In contrast, in AF switching modulated (columnar) phases the switching on a cone is hindered for steric reasons (an unfavorable packing would arise at the inter-ribbon interfaces), and therefore, switching around the molecular long axis is observed instead of the switching on a cone.

(38) FE switching by rotation on a cone was also observed for a FE switching columnar phase of bent-core dimesogens: Umadevi, S.; Jakli, A.; Sadashiva, B. K. *Soft Matter* **2006**, *2*, 215−222.

(39) Examples for switching of suprastructural chirality by collective rotation around the long axis: (a) Schröder, M. W.; Diele, S.; Pelzl, G.; Weissflog, W. *ChemPhysChem* **2004**, *5*, 99−103. (b) Szydlowska, J.; Mieczkowski, J.; Matraszek, J.; Bruce, D. W.; Gorecka, E.; Pociecha, D.; Guillon, D. *Phys. Rev. E* **2003**, *67*, 031702. (c) Reddy, R. A.; Schröder, M. W.; Bodyagin, M.; Kresse, H.; Diele, S.; Pelzl, G.; Weissflog, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 774−778. (d) Weissflog, W.; Dunemann, U.; Schröder, M. W.; Diele, S.; Pelzl, G.; Kresse, H.; Grande, S. *J. Mater. Chem.* **2005**, *15*, 939−946. (e) Nakata, M.; Shao, R. F.; Maclennan, J.; Weissflog, W.; Clark, N. A. *Phys. Rev. Lett.* **2006**, *96*, 067802.
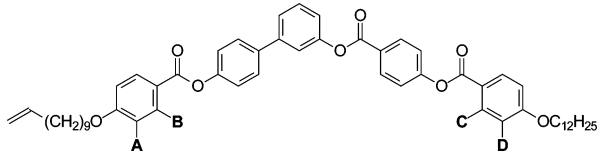
mesophase types are compared, it appears that the 2,3-difluorosubstituted compounds have the same mesophases as the related 3-fluorosubstituted compounds **4**, namely, a columnar mesophase is found for **5a** and a SmCP$_A$[*] phase is found for **5c**, whereas **5b** and **5e** show conventional birefringent SmCP$_A$ phases with layer distances very similar to those measured for compounds **4** (see Table 2). Only the behavior of **5H** is distinct from **4H**. For this compound a coexistence of a birefringent and a dark texture was observed. However, for the dark texture no chiral domains can be detected. This means that either these domains are too small to be identified or the phase structure itself is racemic.[18b,41] In contrast, for the SmCP$_A$[*] phase of **5c** and the SmCP$_A$[*/○] phase of **5d** these domains are clearly visible. This indicates that the additional F atoms at the periphery slightly strengthen the effect of the already present F atoms.

In both series of compounds, F substitution in the bay position of the bent aromatic core (compounds **4a** and **5a**) has the largest impact on the mesophase structure, leading to FE switching columnar phases (Col$_{ob}$P$_{FE}$). However, also the peripheral F substitution is required for formation of this columnar phase as compound **3a** without these peripheral F atoms (see Table 3) forms an AF switching and birefringent smectic phase (SmCP$_A$). The textures of the Col$_{ob}$P$_{FE}$ mesophases of compounds **4a** and **5a** are very similar (see Figure S2a). The powder X-ray diffraction pattern can be indexed to an oblique lattice with $a = 7.2$ nm, $b = 4.8$ nm, and $\gamma = 98.5°$, and this phase assignment is in line with the diffraction pattern seen in a partially aligned sample of this compound (see Figure S4). The same model as proposed for **4a** (see Figure 9) can also be applied for **5a** (about 11 molecules are organized in the cross section of the ribbons[28]). Also, the switching behavior is FE and takes place by rotation on a cone, as reported for **4a** (see Figure S2b,c); only the value of the spontaneous polarization is nearly twice as large ($P_s = 990$ nC cm$^{-2}$). This might be due to the enhanced molecular dipole moment which is provided by the additional F atoms.

**2.3. Influence of Silyl Groups on the Liquid Crystalline Properties of Peripheral F-Substituted Bent-Core Mesogens.** *2.3.1. Antiferroelectric Smectic Phases of the Olefins 6.* The influence of silylation on the phase behavior of peripherally F-substituted bent-core mesogens was studied by comparing the olefin-terminated biphenyl derivatives **6** with their hydrosilylated counterparts **7**. These compounds have one benzoate unit less than compounds **4** and **5**, and there is no F substitution at the central biphenyl unit. In this study the number of F atoms at the periphery was changed from one via two to four, and different substitution patterns were compared. This includes also compounds with a "nonsymmetric" F-substitution pattern, i.e., with F atoms at only one side,[20] either adjacent to the functionalized chain

(40) This mesophase stabilizing effect was also observed for compounds of structure **2** (Chart 1),[8d,20,21,30] whereas in calamitic mesogens lateral F substituents usually reduce the transition temperatures: Takeshi, I. In *Organofluorine Chemistry: Principles and Commercial Applications*; Banks, R.E., et al., Eds.; Plenum Press: New York, 1994; pp 263−286.

(41) Liao, G.; Stojadinovic, S.; Pelzl, G.; Weissflog, W.; Sprunt, S.; Jákli, A. *Phys. Rev. E*, **2005**, *72*, 021710.

**Table 4. Mesophases, Transition Temperatures, and Corresponding Enthalpy Values for the Olefins 6**



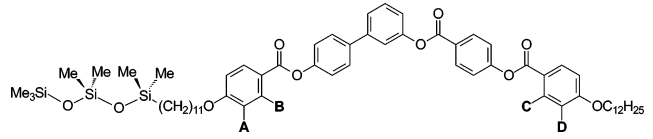| compd | A | B | C | D | T/°C [ΔH/kJ mol⁻¹] | | | d/nm |
|---|---|---|---|---|---|---|---|---|
| **6H**$^a$ | H | H | H | H | Cr 108 | SmCP$_A$ 98 | iso | |
| **6a** | F | H | H | H | Cr 82 [26.6] | SmCP$_A$ 105 [15.7] | iso | 3.83 (88 °C) |
| **6d** | H | H | H | F | Cr 92 [28.4] | SmCP$_A$ 105 [14.7] | iso | |
| **6ad** | F | H | H | F | Cr 95 [35.6] | SmCP$_A$ 116 [20.1] | iso | 4.15 (90 °C) |
| **6ab** | F | F | H | H | Cr 93 [26.4] | SmCP$_A$ 112 [21.2] | iso | 3.75 (100 °C) |
| **6cd** | H | H | F | F | Cr 87 [17.2] | SmCP$_A$ 111 [19.1] | iso | |
| **6abcd** | F | F | F | F | Cr 127 [51.3] | | iso | |

$^a$ See refs 12 and 13a.

(positions A and B, compounds **6a** and **6ab**) or adjacent to the nonfunctionalized dodecyloxy chain (positions C and D, compounds **6d**, **6cd**). Table 4 summarizes the transition temperatures of the olefins **6**. As observed in the series of compounds **3**−**5** increasing fluorination raises the mesophase stability. Only in the case of the tetrafluorinated compound **6abcd** no LC phase can be detected due to the high melting point of this compound. All LC compounds show birefringent textures as typical for SmCP$_A$ phases (see Figure 15a). X-ray investigations indicate simple layer structures without in-plane order for all compounds with layer distances corresponding to a monolayer organization of tilted molecules (see Table 4). Exclusively AF switching, characterized by two well-separated peaks under a triangular wave voltage and a tristable switching in electrooptical experiments (see Figure S3a), is found for the mesophases of all compounds independent of the number of the F atoms. The values of the spontaneous polarization are in the range between 800 and 1000 nC cm$^{-2}$ (see Table S3).

*2.3.2. Influence of Silylation on the Liquid Crystalline Properties of Peripheral F-Substituted Bent-Core Mesogens.* Hydrosilylation of the olefinic double bond leads to a mesophase stabilization and a change of the properties in all cases (compounds **7**, Table 5). The SmCP$_A$ phases of the non-silylated compounds **6** are replaced by optically isotropic smectic phases, showing domains of opposite chirality sense for all compounds **7** with the exception of **7ad**, which shows a columnar mesophase (see section 2.3.4). For compounds **7a** and especially **7b** the dark conglomerate texture coexists with a birefringent texture, whereas for compounds **7ab, 7cd,** and **7abcd** with at least one 2,3-difluoro-substituted benzene ring well developed dark conglomerate textures without birefringent regions were observed. The layer distance of compound **7cd**, as a representative example, is $d = 4.7$ nm at 110 °C, which indicates a smectic single-layer structure with a strongly tilted organization of the molecules in the layers (calculated tilt angle $\theta = 43°$), very similar to the smectic phases observed for the non-fluorinated silyl-substituted compound **1**.[12,13a] Due to the additional hepta-methyltrisiloxane unit the molecular length is increased ($L = 6.3$ nm) with respect to the olefins **6**, and therefore, the measured layer distances are larger than those observed for the olefins (see Figure 3). Similar to the non-fluorinated molecule **1** there are two distinct diffuse maxima in the wide-

**Table 5. Mesophases, Transition Temperatures, and Corresponding Enthalpy Values for the Phase Transitions of the Oligo(siloxane)-Substituted Compounds 1 and 7[a]**

| compd | A | B | C | D | T/°C [ΔH/kJ mol⁻¹] | | | | lattice parameters/nm |
|-------|---|---|---|---|---|---|---|---|---|
| **1** | H | H | H | H | Cr | 70 [29.3] | SmCP$_{FE}$[*] | 115 [24.3] iso | |
| **7a** | F | H | H | H | Cr | 69 [23.7] | SmCP$_{FE}$[*/o] | 121 [22.7] iso | |
| **7d** | H | H | H | F | Cr | 75 [17.0] | SmCP$_{A}$[*/o] | 121 [23.8] iso | |
| **7ad** | F | H | H | F | Cr | 85 [10.1] | Col$_{ob}$P$_A$ | 121 [19.5] iso | $a = 5.12$, $b = 5.35$, $\gamma = 108.5°$ (100 °C) |
| **7ab** | F | F | H | H | Cr | 50, 76 [12.1, 17.0] | SmCP$_{FE}$[*] | 114 [21.5] iso | $d = 4.57$ (105 °C) |
| **7cd** | H | H | F | F | Cr | 41 [9.4] | SmCP$_{FE}$[*] | 125 [22.9] iso | $d = 4.71$ (110 °C) |
| **7abcd** | F | F | F | F | Cr | 92 [17.1] | SmCP$_{A}$[*] | 125 [17.6] iso | $d = 4.77$ (110 °C) |

[a] Abbreviations: SmCP$_{FE}$[*] = polar smectic C phase showing surface-stabilized FE switching; SmCP$_{A}$[*] = "nonclassical" AF switching polar smectic C phase, characterized by a tristable switching, but only one repolarization current peak observed in a half-period of a triangular wave voltage; Col$_{ob}$P$_A$ = AF switching oblique columnar mesophase.
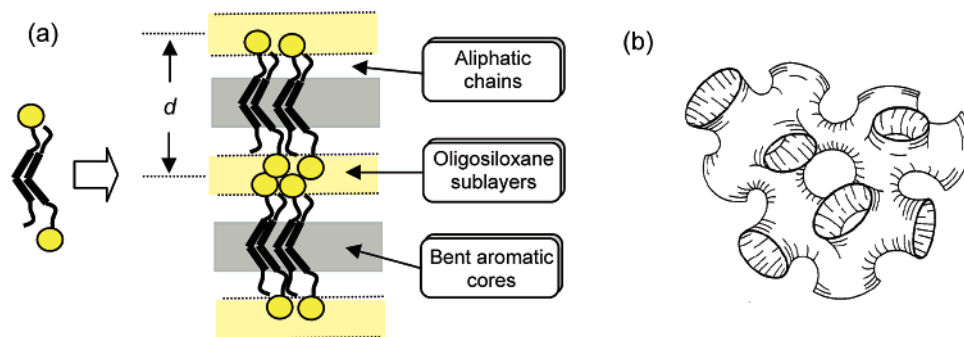


**Figure 10.** Models of the organization of the siloxane-substituted bent-core molecules **7** (a) in the triply segregated smectic phases. (b) Model of a sponge phase composed of deformed stacks of layers (only one interface is shown).[12,13a]

angle region of the X-ray diffraction pattern of compound **7cd** (and the other compounds **7**). One at ca. 0.46 nm is associated with the mean distances between the alkyl chain and the aromatic cores; the second one corresponding to about 0.62 nm is assigned to the microsegregated sublayers of the heptamethytrisiloxane units.

The model of the organization of the molecules in this smectic phase is shown in Figure 10. There is a segregation of the silyl units, aromatic bent cores, and aliphatic chains (spacers plus end chains) into distinct sublayers. In this triply segregated structure the layer distance is smaller than the molecular length, and this indicates a monolayer structure with a tilted organization of the molecules. Usually such molecules with two different ends form bilayer structures where the molecules form end-to-end pairs and the layer distance is larger than the molecular length. The monolayer structure is in the case of compound **7** due to the antiparallel packing of the molecules in a side-by-side mode as shown in Figure 10a, which is caused by the different cross sections of the alkyl chains and the silyl groups.[12] This kind of antiparallel packing of the molecules reduces the steric stress, and therefore, the expected bilayer structure is not found. The dark conglomerate textures are thought to result from a sponge-like deformation of these layer structures, and it was proposed that the layer distortion is due to an escape from a mesoscale polar order in polar smectic phases composed of SmC$_s$P$_F$ layer stacks.[15b,16b]

*2.3.3. Electrooptical Investigations of the Smectic Phases of Compounds 7.* In switching experiments a single peak is found under a triangular wave voltage for the smectic phases

of all compounds **7**, except **7ad**, which shows an AF columnar phase. The single peak does not split under a modified triangular wave voltage, which suggests a FE switching process (see Figure S3b–d).

Under an applied electric field the dark conglomerate texture of the ground state becomes birefringent, and in this field-induced birefringent texture circular domains with extinction crosses can be observed. If these domains were grown under a dc field the extinction crosses are inclined with the directions of polarizer and analyzer, and this indicates a synclinic organization of the molecules in the field-induced state under the applied electric field (see Figure 11a). For the nonfluorinated compound **1** and the fluorinated molecules **7a**, **7ab**, and **7cd** these extinction crosses do not change their position if the field is switched off, but they rotate after field reversal, which confirms the bistability of the switching process (see Figure 11b,c). Hence, the field-induced structure should be SmC$_s$P$_F$ (see Figure 11a) and the switching takes place between the two different surface-stabilized SmC$_s$P$_F$ states by rotation on a cone, which leads to a single repolarization current peak. Therefore, the smectic phases of these compounds are assigned as SmCP$_{FE}$[*].[7]

For the smectic phases of compounds **7d** and **7abcd** the switching process observed within the synclinic domains (as grown under a dc field) is distinct from the other compounds **7**. Switching off the field immediately leads to a change of the extinction crosses into positions parallel to polarizer and analyzer, and also the birefringence is strongly reduced at 0 V (see Figure 12a–c). It seems that in this case the surface alignment forces are not strong enough to retain a uniform
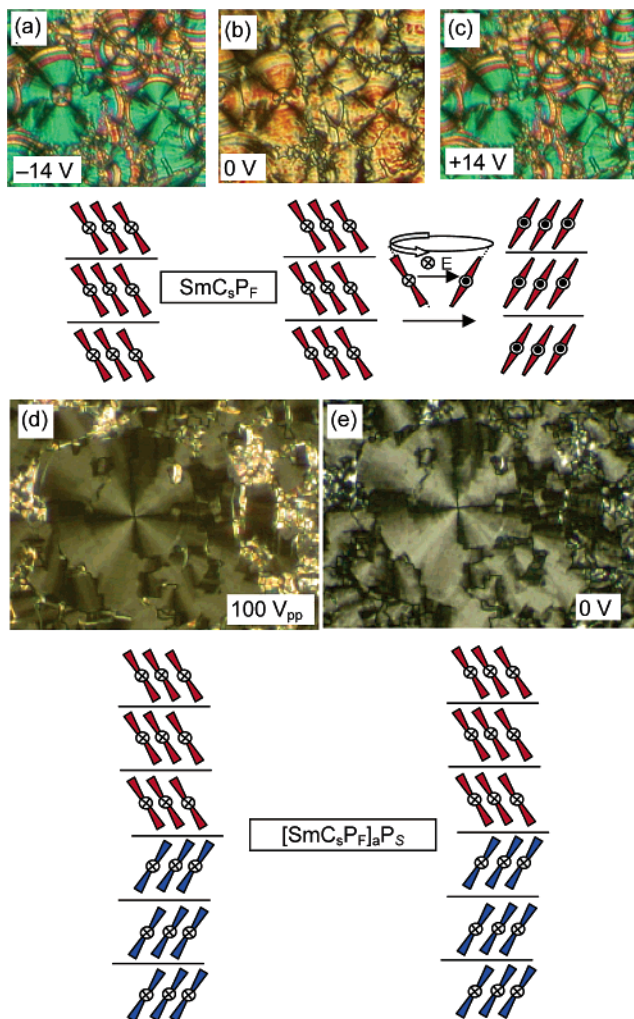
**Figure 11.** Optical investigation of the switching behavior of compound **7cd** at $T = 100$ °C in a 6 $\mu$m noncoated ITO cell: (a) circular domains obtained by cooling from the isotropic state under a dc electric field; (b) after switching off the field; (c) under an electric field with opposite direction; rotation of the extinction crosses takes place from b to c; (d) circular domains obtained by cooling from the isotropic state under a triangular wave ac field (200 Hz, 100 $V_{pp}$, $T = 100$ °C); (e) texture as seen after switching off the applied ac field. Models illustrating the proposed organization of the molecules are shown below the textures.

$SmC_sP_F$ organization also after switching off the electric field. A relaxation of the uniform $SmC_sP_F$ structure to an anticlinic and antipolar $[SmC_sP_F]_aP_A$ structure, consisting of $SmC_sP_F$ layer stacks with opposite tilt direction and opposite polar direction, is assumed to take place. As the relaxation to the $[SmC_sP_F]_aP_A$ structure changes the organization of the molecules only at the interfaces between the $SmC_sP_F$ layer stacks, the voltage required for the switching of the $SmC_sP_F$ layer stacks into the uniform $SmC_sP_F$ structure is relatively small and the two polarization current peaks, expected for an AF switching process, merge to only one. This switching process is assigned as "nonclassical" AF, and the mesophase is designated as $SmCP_{A'}$[*]. The size of the uniform $SmC_sP_F$ layer stacks is smaller than the wavelength of light, and therefore, only an average optical axis perpendicular to the layer planes is seen at 0 V, which leads to a low birefringent texture with extinction crosses parallel to the polarizers.[42]

A partial relaxation of the surface-stabilized $SmC_sP_F$ structure to a $[SmC_sP_F]_aP_A$ structure is also assumed to be responsible for the reduction of the birefringence seen in the



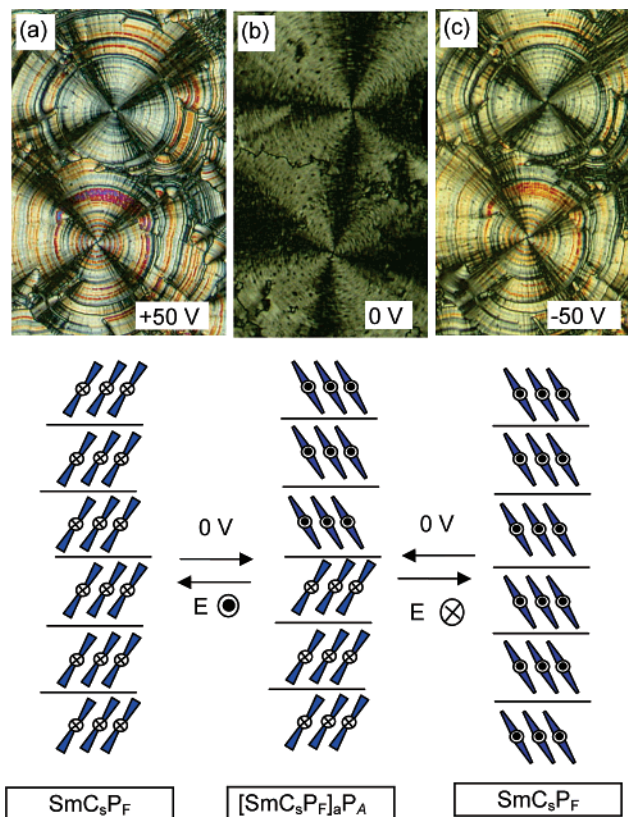**Figure 12.** Optical investigation of the switching behavior of compound **7d** at $T = 112$ °C in a 6 $\mu$m polyimide-coated ITO cell: (a) circular domains obtained by cooling from the isotropic state under a dc electric field of 50 V; (b) after switching off the field; (c) under an electric field with opposite direction. The models show the reorganization of the molecules during the switching process.

synclinic domains of the surface-stabilized FE switching mesophases of compounds **7a**, **7ab**, and **7cd** after switching off the voltage (see Figure 11b). It is likely that at a certain distance from the surfaces the stabilizing effect of these surfaces is too weak to retain a uniform $SmC_sP_F$ structure at 0 V. In these regions of the sample a relaxation into the $[SmC_sP_F]_aP_A$ structure takes place which adopts a sponge-like disordered organization, appearing optically isotropic. Hence, the switching is surface-stabilized FE at the surfaces and nonclassical AF in the center of the sample. In these mesophases (also assigned as $SmCP_{FE}$[*]) due to the surface-stabilized $SmC_sP_F$ structure at the substrate surfaces the position of the extinction crosses does not change at 0 V (they remain inclined with the polarizers, see Figure 11b), but the birefringence is reduced due to formation of an optically isotropic mesophase in the center. Only a single peak is observed in all cases, probably because the repolarization current peak of the "nonclassical" AF switching merges with the peak of the FE switching.

If domains were grown under a triangular ac field, for all smectic phases of compounds **7** low birefringent textures were obtained where the positions of the extinction crosses coincide with the directions of polarizer and analyzer. In these domains no change of the position of the extinction crosses and also no change of the birefringence can be seen

(42) The $[SmC_sP_F]_aP_A$ structure obtained at 0 V should be the same as that proposed for the dark conglomerate textures in the ground state of these mesophases with the difference that it is not optically isotropic.
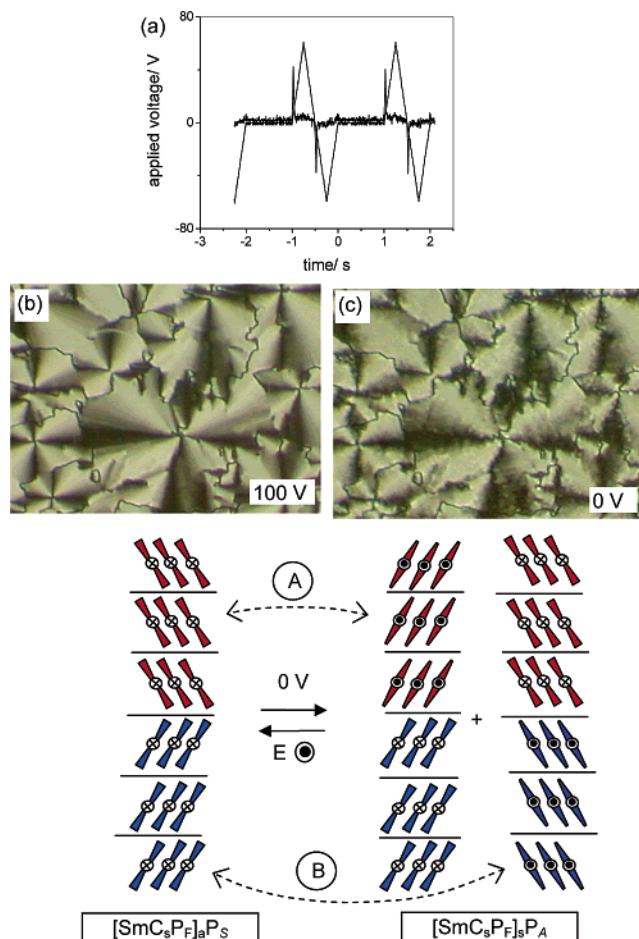
**Figure 13.** Investigation of compound **7d**: (a) switching current curve observed at 90 °C in a polyimide-coated ITO cell (6 μm, 1 Hz, 120 $V_{pp}$) under a modified triangular wave field with a pause at 0 V (the same curves were obtained in noncoated ITO cells); (b) circular domains obtained by cooling from the isotropic state under a triangular ac field (6 μm noncoated ITO cell, 200 Hz, 100 $V_{pp}$); (c) texture as seen after switching off the applied field. The models show the reorganization of the molecules during the switching process which can take place along A or B, leading to microdomains with opposite tilt direction. These microdomains are mixed and give rise to an average optical axis perpendicular to the layer planes.

in the switching process (see Figures 11d,e and 13b,c). A polar structure consisting of $SmC_sP_F$ layer stacks with opposite tilt direction (and hence opposite chirality), assigned as $[SmC_sP_F]_aP_S$, is proposed for this texture grown under a dynamic ac field (see models in Figures 11d and 13b).[43] At 0 V this structure can be retained due to surface stabilization ($SmCP_{FE}^{[*]}$ phases of compounds **7a**, **7ab**, and **7cd**, see Figure 11e). Alternatively, relaxation to an AF structure composed of $[SmC_sP_F]_sP_A$ domains with alternating tilt direction (nonclassical AF switching compounds **7d** and **7abcd**, see Figure 13c) can take place.[44] Because the position of the extinction crosses is not changed in both modes of switching, the switching processes cannot be distinguished under an ac field.

(43) (a) Folcia, C. L.; Ortega, J.; Etxebarria, J. *Liq. Cryst.* **2003**, *30*, 1189−1191. (b) Pyc, P.; Mieczkowski, J.; Pociecha, D.; Gorecka, E.; Donnio, B.; Guillon, D. *J. Mater. Chem.* **2004**, *14*, 2374−2379.

(44) The smooth texture under the applied field (Figure 13b) is replaced by a stripe texture at 0 V (Figure 13c). Such stripe pattern could have different reasons. One possibility is that the size of the $[SmC_sP_F]_sP_A$ domains under the field is larger than the size of the $SmC_sP_F$ layer stacks in the $[SmC_sP_F]_sP_A$ structure at 0 V.

An additional special feature of compounds **7d** and **7abcd** is that the birefringence of the field-on states (in domains grown under a dc field) decreases with each switching cycle, as seen in Figure 12, where the bluish-red area in Figure 12a becomes orange after the first reversal of the applied field (Figure 12c). On continuing switching the number and size of the synclinic domains is reduced, and after about 5−10 cycles the extinction crosses adopt positions parallel to the polarizers, as obtained under an ac field. This confirms that the dynamic ac field favors equilibration of the uniform and homogeneous chiral $SmC_sP_F$ structure into the racemic $[SmC_sP_F]_aP_S$ structure where (+)- and (−)-$SmC_sP_F$ layers are mixed and separated by racemic $SmC_aP_S$ defects (see Figure 13b).

The phase structures obtained under different conditions are summarized in Figure 14. Accordingly, the fundamental phase structure of all smectic phases of compounds **7** is $SmC_sP_F$. However, this structure is not uniform, and usually stacks of layers with $SmC_sP_F$ correlation are separated by defect layers. The number of adjacent layers with synclinic and FE correlation within uniform layer stacks depends on the material and experimental conditions. Surface alignment can lead to a uniform $SmC_sP_F$ structure if the mesophase is obtained under a dc field (Figure 14d), whereas growing under a dynamic ac field leads to a racemic $[SmC_sP_F]_aP_S$ structure (Figure 14a). Growing the mesophase in the absence of an external field gives rise to an overall nonpolar $[SmC_sP_F]_aP_A$ structure which is homogeneously chiral (Figure 14c). In this phase escape from the mesoscopic polar structure leads to a sponge-like layer deformation if no field or surface effects inhibit this layer distortion. In this case a conglomerate of macroscopically chiral domains (dark conglomerate texture) is formed. The preference for uniform $SmC_sP_F$ organization is stronger for compounds **7a**, **7ab**, and **7cd** than for compounds **7d** and **7abcd**. Hence, formation of a uniform $SmC_sP_F$ structure by surface alignment and surface-stabilized FE switching is achieved for the first group of compounds ($SmCP_{FE}^{[*]}$ phases), whereas "nonclassical" (single peak) AF switching is observed for **7d** and **7abcd** ($SmCP_A^{[*]}$ phases). Overall, there seems to be a continuous transition from surface-stabilized FE switching to AF switching.

*2.3.4. Columnar and Induced Smectic Phases of Compound **7ad**.* The mesophase of compound **7ad** is completely different from all other compounds **7**. It appears with a birefringent optical texture and leaf-like patterns together with low birefringent circular domains, as shown in Figure 15b,c. These features are indicative of the columnar structure of the mesophase, which is confirmed by X-ray scattering experiments. The X-ray diffraction pattern obtained shows many sharp reflections in the small-angle region which can be indexed to an oblique lattice with lattice parameters $a = 5.12$ nm, $b = 5.35$ nm, and an oblique angle of $\gamma = 108.5°$ (Figures 16b and S5). In the wide-angle region two diffuse maxima can be seen at $d_2 = 0.49$ nm and $d_3 = 0.74$ nm, which are indicative of the segregation of the siloxane units ($d_3 = 0.74$ nm) into distinct regions.[12] The XRD pattern of the aligned sample shows a preferred orientation direction of the wide-angle scattering at $d = 0.49$ nm, indicating a
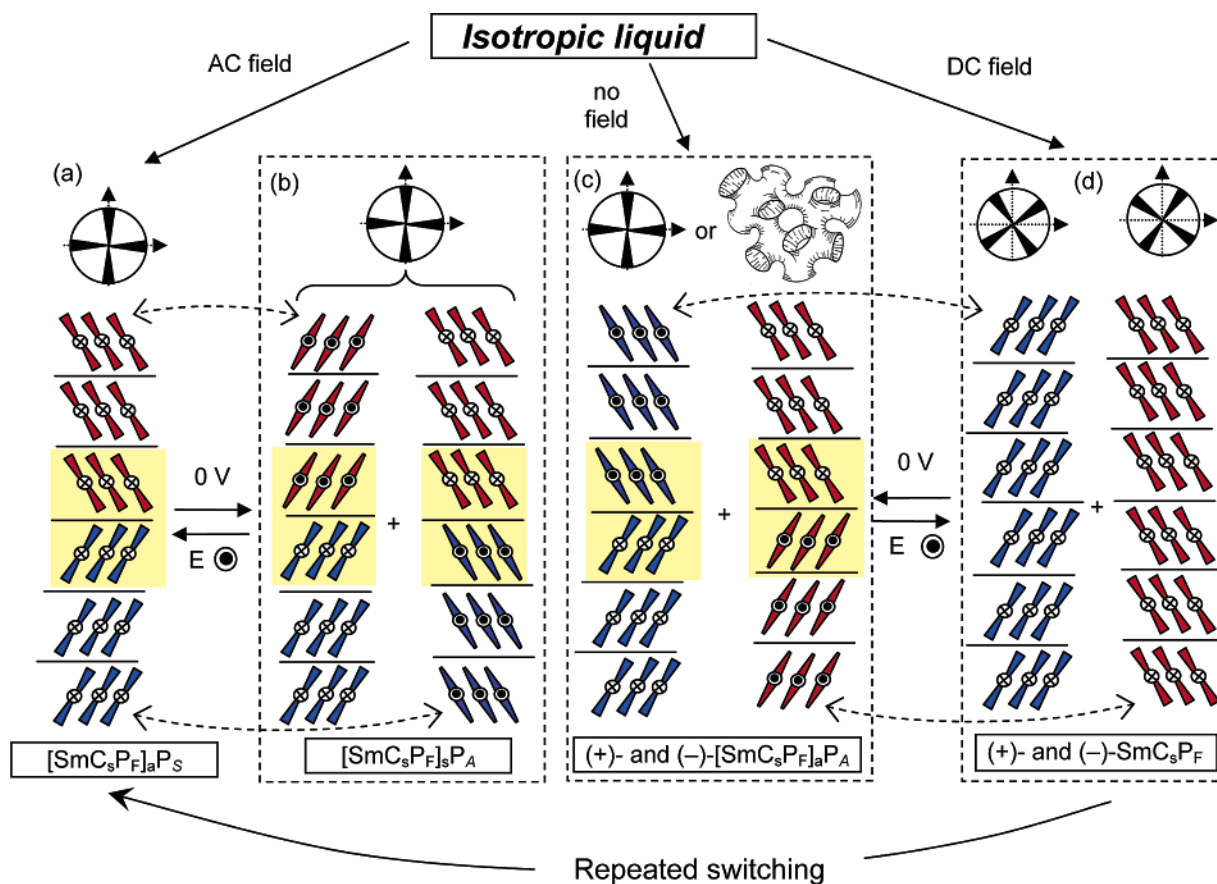
**Figure 14.** Models showing the proposed structures of the smectic mesophases of compounds **7** as formed under different conditions upon cooling from the isotropic liquid state or as a result of a switching process: (a) polar structure, as obtained under an ac field, where the $SmC_sP_F$ domains are separated by anticlinic and synpolar $SmC_aP_S$ interfaces, providing an overall polar and racemic structure, assigned as $[SmC_sP_F]_aP_S$; (b) racemic and nonpolar $[SmC_sP_F]_sP_A$ phase as obtained from structure a after switching off the field; the two oppositely tilted structures are formed simultaneously with an equal probability, so that in the resulting texture the extinction crosses are parallel to polarizer and analyzer; (c) $[SmC_sP_F]_aP_A$ structure as suggested for the dark conglomerate phases; this structure could also be obtained by relaxation of the polar and synclinic structure if layer deformation is inhibited (e.g., by surface stabilization); the texture shows extinction crosses parallel to the polarizers; (d) field-induced $SmC_sP_F$ structure as obtained under a dc field.

synclinic tilt of the molecules (Figures 16a and S5, tilt angle ca. 30°, calculated using $\cos\theta = d/L$, $\theta = 36°$). Hence, the columnar phase of **7ad** should have a ribbon structure with about eight molecules in the diameter of the ribbons.[28] This indicates a stronger frustration of the layer structure compared to the $Col_{ob}P_{FE}$ phases of compounds **4a** and **5a** (with 11−13 molecules in the cross section) due to the additional space required by the silyl group. Within the ribbons the molecules are tilted toward the long diagonal of the oblique cell as deduced from the direction of the maxima of the diffuse wide-angle scattering at $d = 0.49$ nm (mean distance between the bent cores) with respect to the position and distribution of the small-angle reflections of the oblique lattice, as seen in the 2D X-ray diffraction pattern of an aligned sample (see Figure S5).

On the basis of these X-ray data a ribbon structure with an overlapping of the rod-like wings of the bent cores in adjacent ribbons (see Figure 18d−g) can be assumed. This enables a continuous sublayer of the aromatic cores and also allows the maintenance of a continuous sublayer of the oligosiloxane groups. The arrangements shown in Figure 18e,f, where the polar direction changes between the ribbons within the modulated layers, appear to be most likely. In these arrangements a parallel packing of the rod-like wings of the aromatic cores at the interfaces between the ribbons

(along direction *a*) is possible. In contrast, any structure with uniform polar direction within the modulated layers (along direction *a*) as in the FE structures shown in Figure 18d,g, should be destabilized because the aromatic cores are not parallel at these inter-ribbon interfaces. For the polar direction of adjacent ribbons along the ribbon stacks (along direction *b*) there are also two possibilities, as shown in Figure 18e and 18f. Neither nonresonant X-ray scattering nor electro-optical investigation can distinguish these two possibilities. A synpolar correlation between adjacent ribbons, as shown in Figure 18e ($SmC_sP_F$-like structure) would be similar to the organization in the smectic phases of the other compounds **7** and therefore is assumed to be more likely. However, in these relatively small ribbons with only eight molecules in the cross section this synpolar organization along direction *b* cannot be efficiently stabilized by a splay of polarization. Hence, an AF structure along *b*, as shown in Figure 18f, cannot be completely ruled out.

As it can be seen in Figure 17a, in switching experiments two well-resolved repolarization current peaks in each half period of the applied triangular voltage can be observed above a threshold voltage of 100 $V_{pp}$, which clearly confirms the AF ground-state structure of the $Col_{ob}P_A$ phase. The polarization value obtained is about 650 nC cm$^{-2}$. Hence, a clear (classical) AF switching is observed[12] where the
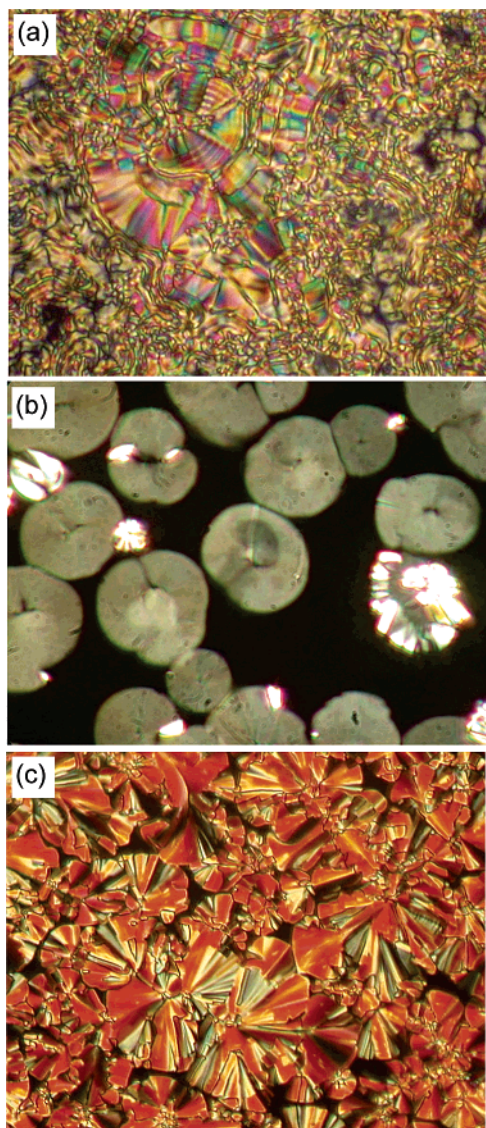
**Figure 15.** Textures as seen between crossed polarizers under a polarizing microscope: (a) SmCP$_A$ phase of compound **6ab** at $T = 100$ °C; (b, c) Col$_{ob}$P$_A$ phase of compound **7ad** (b) at 121 °C (dark areas are residues of the isotropic liquid phase) and (c) at 110 °C (different sample of the same compound).
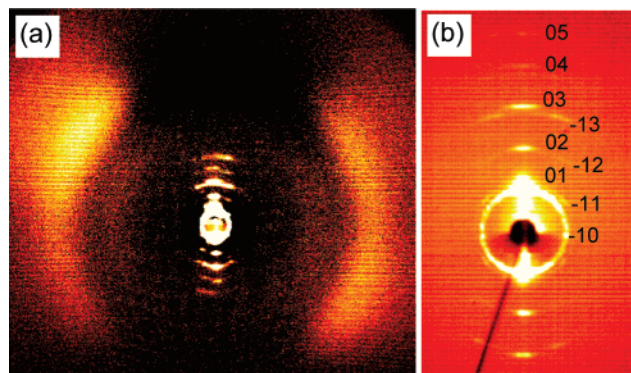


**Figure 16.** X-ray diffraction pattern of an aligned sample of compound **7ad** at 100 °C: (a) wide and small-angle region (intensity corrected by subtracting the scattering of the isotropic sample to enhance the effect of the anisotropy of the outer diffuse scattering in the liquid-crystalline phase) and (b) small-angle region.

switching from the AF ground state to the FE state requires significant energy, and in addition, the threshold voltage for this switching process is much higher than that observed in

**Table 6. Comparison of the Parameters for the Columnar Phases**

| compd | phase type | lattice parameters/nm | $n_{cell}{}^a$ |
|-------|-----------|----------------------|------------|
| **4a** | Col$_{ob}$P$_{FE}$ | $a = 8.10, b = 4.90, \gamma = 99.2°$ | 13 |
| **5a** | Col$_{ob}$P$_{FE}$ | $a = 7.20, b = 4.83, \gamma = 98.5°$ | 11 |
| **7ad** | Col$_{ob}$P$_A$ | $a = 5.12, b = 5.35, \gamma = 108.5°$ | 8 |

$^a$ $n_{cell} =$ number of molecules per unit cell, corresponding to the number of molecules in the cross section of the ribbons.
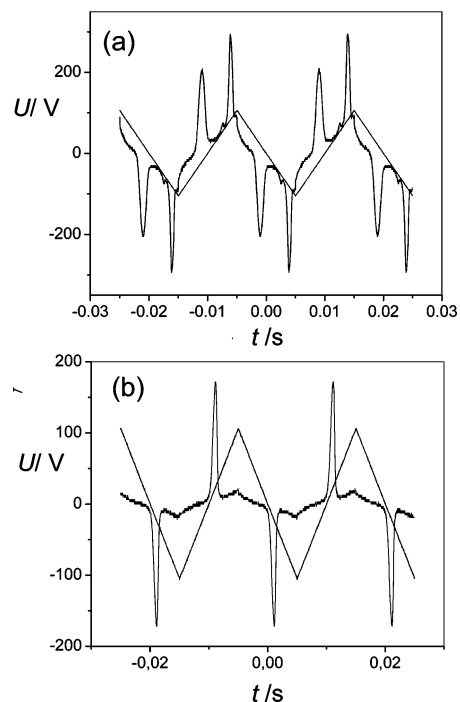


**Figure 17.** Switching current response curves obtained for compound **7ad**: (a) "classical" AF switching at 110 °C in the Col$_{ob}$P$_A$ phase (210 V$_{pp}$, 50 Hz, 5 $\mu$m, $P_s \approx 650$ nC cm$^{-2}$); (b) "nonclassical" AF switching at 80 °C in the field-induced smectic phase (same conditions as a, $P_s = 760$ nC cm$^{-2}$).

the smectic phases of related compounds. This is in line with a field-induced switching between an AF structure shown in Figure 18e and the FE structures shown in Figure 18d and 18g. Due to the unfavorable steric interactions occurring at the inter-ribbon interfaces between synpolar ribbons in the field-induced FE states (see Figure 18d,g) the FE organization should be only obtained under a relatively high applied electric field and should be significantly less stable than the corresponding AF structure.

With decreasing temperature, however, at 85 °C the two polarization peaks transform into a single peak (Figure 17b), which is accompanied by a change in the birefringence of the mesophase. This transition depends on the experimental conditions, such as frequency and applied voltage. An increase in the voltage or frequency stabilizes the single-peak switching. For example, at a frequency of 1 Hz the transition between two-peak and single-peak switching takes place at 84 °C, and at a frequency of 100 Hz it is shifted to 96 °C. This phase transition cannot be observed in the bulk sample, either by DSC or polarizing microscopy. The X-ray diffraction pattern also does not change at this temperature. These observations, together with the strong dependence of this transition on the conditions, indicate that it is a field-induced phase transition.[36]

In electrooptical investigations under a dc electric field circular domains were obtained (threshold 50 V, 5 $\mu$m
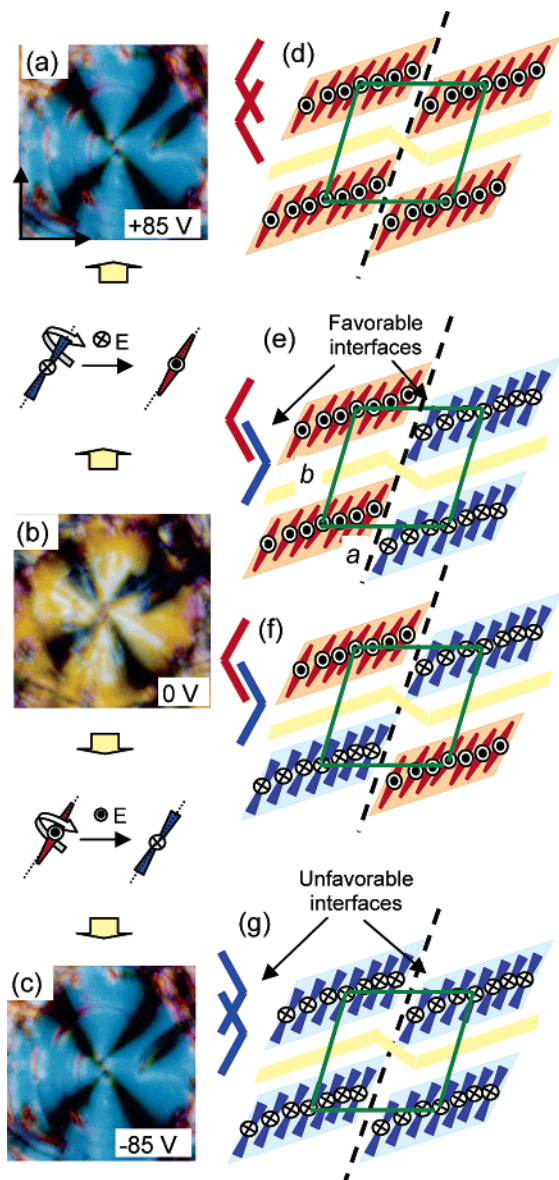
**Figure 18.** Electrooptical investigation of the Col$_{ob}$ phase of compound **7ad** under a dc electric field at 95 °C in a 5 $\mu$m noncoated ITO cell: (a–c) circular domains (arrows indicate the positions of analyzer and polarizer); (d–g) models of the organization of the molecules; in the FE states (d and g) there is an unfavorable nonparallel organization of the aromatic cores at the inter-ribbon interfaces (dotted lines), whereas in the AF organizations (e and f) the rod-like wings of the aromatic cores adopt a favorable parallel alignment at the inter-ribbon interfaces; there are two models for the AF organization; (e) the organization of the molecules between the modulated layers (along direction *b*) is syncline FE, as found in the smectic phases of the other compounds **7**; (f) the organization is synclinic AF. No rotation of the extinction crosses can be seen by switching off the applied electric field or reversing the applied voltage, indicating a switching around the long axis (see left); hence, the AF structures (e and f) are racemic, whereas the field-induced FE structures (d and g) are homogeneously chiral.

noncoated ITO cell) in which the extinction crosses are inclined between the crossed polarizers, which confirms the synclinic organization (Figure 18a). At high temperature, on terminating the applied field, the extinction crosses do not change their position, as shown in Figure 18b. Also, upon reversal of the field no change can be seen (Figure 18c). As an AF switching process is clearly seen in the current response (Figure 17a), it must be concluded that AF switching takes place by a collective rotation around the molecular long axis. Such a rotation around the long axis is
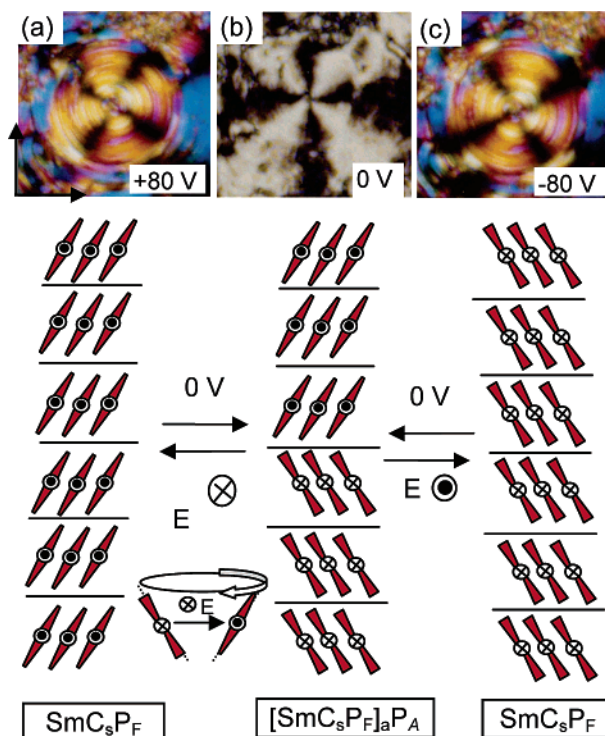


**Figure 19.** Electrooptical investigation of the field-induced smectic phase of compound **7ad** under a dc electric field at 85 °C in a 5 $\mu$m noncoated ITO cell; the circular domains are shown at the top (arrows indicate the positions of analyzer and polarizer); the models on the bottom show the mode of reorganization of the molecules; rotation takes place around the long axis, which retains the layer chirality.

the only possible mechanism of AF switching in columnar ribbon phases with relatively small ribbons because the inter-ribbon interfaces inhibit reorientation of the molecules by rotation on a cone.

At lower temperature, where only a single peak is observed in the switching current curves (Figure 17b), a completely different switching behavior is seen (see Figure 19a–c). Under the applied field the extinction crosses are inclined with the positions of polarizer and analyzer as also seen in the high-temperature phase. However, switching off the field leads to a change of the position of the extinction crosses into positions parallel to polarizer and analyzer and also the birefringence is strongly reduced at 0 V (Figure 19b). This appearance is very similar to the switching process observed for the smectic phases of compounds **7d** and **7abcd** (see Figure 12a–c) and can be explained in the same way. Hence, it is likely that the field induces a transition from an AF ribbon phase (Col$_{ob}$P$_A$) at higher temperature to a flat smectic phase at lower temperature. It is most likely that this induced smectic phase is a nonclassical AF switching smectic phase ([SmC$_s$P$_F$]$_a$P$_A$ phase) as indicated by rotation of the extinction crosses at 0 V into a position inclined with the polarizers (see Figure 19). Hence, the field-induced mesophase is a SmC$_s$P$_F$ phase which relaxes to a [SmC$_s$P$_F$]$_a$P$_A$ structure at 0 V.

It can be assumed that at reduced temperature the steric frustration (caused by the bulky silyl groups) is reduced and a nonmodulated smectic phase is obtained under an applied electric field with sufficient strength. Because the unfavorable inter-ribbon interfaces are removed, a uniformly polar SmC$_s$P$_F$ layer structure is more easily formed. In this smectic

phase switching takes place by rotation on a cone and, in addition, anticlinic defect layers become possible between the synclinic layer stacks. This allows relaxation to a $[SmC_sP_F]_aP_A$ layer structure at 0 V, identified by an optical texture with extinction crosses parallel to the polarizers (see Figure 19b). Hence, the additional inter-ribbon interfaces within the columnar banana phases have three important functions: they (i) stabilize a uniform synclinic organization of the molecules, (ii) inhibit the rotation on a cone, and (iii) modify the observed switching process from surface-stabilized FE/"nonclassical" AF to "classical" AF.

### 3. Summary and Conclusions

The influence of fluorine substitution at the bent aromatic core was investigated with respect to its effects upon the structures and switching behavior of the mesophases formed by silylated and non-silylated bent-core molecules. Non-silylated compounds form birefringent AF switching smectic phases ($SmCP_A$) in most cases, but also AF switching dark conglomerate-type smectic phases ($SmCP_A^{[*]}$) and a FE switching columnar phase ($Col_{ob}P_{FE}$) were observed for special substitution patterns. For the silylated compounds smectic phases with dark conglomerate textures showing "nonclassical" AF switching ($SmCP_A^{[*]}$) or surface-stabilized FE switching ($SmCP_{FE}^{[*]}$) are dominating. Both types of switching are characterized by the appearance of only one polarization current peak in the half period of a triangular wave voltage. Also, in the series of silylated compounds a columnar phase ($Col_{ob}P_A$) was observed for one substitution pattern, but this columnar phase shows clear AF switching. It is interesting to note that the mode of polar switching of the smectic phases of each series of compounds is reversed in the columnar phases.

In the smectic phases there are three main contributions determining the correlation between neighboring layers. (i) The AF structure is generally stabilized with respect to the FE structure by escape from a macroscopic polar order ("polar term"). (ii) The fluctuations of the molecules between adjacent layers are easier in any synclinic organization, i.e., in a synclinic SmC organization and also in an AF organization (where the rod-like wings of the aromatic cores are organized in a synclinic fashion, see Figure 1a). These fluctuations provide a mainly entropic contribution to the stabilization of the synclinic and AF states ("entropic term"). (iii) Finally, anticlinic interfaces provide a closer contact between the ends of the alkyl chains, which tend to stabilize the anticlinic tilted SmC phases and the FE organization energetically (improved van der Waals contacts, "enthalpic term").[81] Hence, the structure and dynamics of the molecular parts located at the interlayer interfaces have a strong impact on the type of organization of the molecules in the smectic phases. Also, the differences in the self-organization and switching behavior of silylated and non-silylated molecules should be mainly determined by the distinct character of the interlayer interfaces in these two classes of compounds.

Linear alkyl chains can easily intercalate in any synclinic and AF organizations. For these compounds the entropic term, stabilizing the AF structure, is dominating, and therefore, $SmCP_A$ phases are typically found (e.g., com-

pounds **3** and **6**). However, also a stable ferroelectric $SmC_aP_F$ ground-state structure was recently proven for some alkyl-substituted bent-core molecules with branched end chains and a defined parity of the chains.[81] Though the $SmC_aP_F$ structure is disfavored by the polar term, the exclusively anticlinic interfaces involved in this structure can in this case provide a sufficient energetic stabilization of the ferroelectric structure. Therefore, a stable FE ground state becomes possible. Hence, for bent-core molecules with simple alkyl chains there is a broad range of different mesophases ranging from AF switching phases ($SmC_sP_A$ and $SmC_aP_A$) to FE switching phases. The $SmC_aP_F$ phase is a FE switching phase with a stable FE ground-state structure, because the anticlinic tilt correlation in the $SmC_aP_F$ phase disfavors any relaxation into a nonpolar modulated smectic phase. However, in the $SmC_sP_F$ structure these anticlinic interfaces are missing, and therefore, this polar structure is metastable and relaxes to overall nonpolar and polarization-modulated structures. Such a polarization-modulated $SmC_sP_F$ ribbon structure is proposed for the columnar phases ($Col_{ob}P_{FE}$) of the non-silylated compounds **4a** and **5a** with F substitution in the bay position of the bent aromatic core. If the layer modulation is removed under a sufficiently strong electric field, there is a bistable switching between the two FE states and no relaxation can be seen at 0 V. It seems that in this case the interactions with the substrate surfaces are mainly required to suppress layer modulation.

For the silylated compounds the situation is different. Here, the microsegregated oligosiloxane sublayers inhibit the interlayer fluctuations, and hence, there is no significant stabilization of synclinic and AF interfaces by the entropic term. Therefore, the AF state is less strongly preferred. Also, the enthalpic contribution which stabilizes anticlinic interfaces is comparatively weak due to the high flexibility of the silyl units and their disordered organization within the segregated sublayers (a diffuse circular ring without intensity maxima is always seen in the X-ray diffraction pattern). Hence, a stable FE mesophase structure, requiring close and directed van der Waals contacts, is unlikely to occur in the smectic phases of silylated molecules.[45] Overall, the energetic differences between the distinct types of organization are smaller for these mesogens than for the alkyl derivatives, and therefore, phase structures composed of layer stacks, separated by defect layers, i.e., mixed organizations, as shown in Figure 14, are typically found. In addition, surface interactions become more important for stabilization of the macroscopically polar FE states. Hence, for the silylated compounds FE switching is frequently found, but it is always a surface-stabilized switching because the polar term (stabilizing AF order) must be compensated by polar surface interactions. If the surface stabilization is weak or the contribution of the entropic term is increased, then "nonclassical" AF switching phases with only one repolarization current peak and AF switching phases with two close peaks can be observed.

It seems that for silylated compounds the $SmC_sP_F$ layer stacks are predominating and the mesoscale polar order

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(45) The absence of an odd−even effect (see ref 12) is an additional indication of the week coupling between the layers.

within these stacks is the driving force for layer distortion which gives rise to the dark conglomerate textures for most of the silylated compounds. These optically isotropic meso-phases are formed if the thickness of these layer stacks exceeds a certain size, if the polarization within the layer stacks is sufficiently high, and if the anticlinic interfaces between the layer stacks (which inhibit a regular modulation of the layers with formation of a 2D-lattice) cannot be suppressed. The $[SmC_sP_F]_aP_A$ structure where the chiral $SmC_sP_F$ stacks are separated by chiral $SmC_aP_A$ interfaces is homogeneously chiral, and therefore, according to the layer optical chirality concept,[11] the chiral and optically active domains in the dark conglomerate phases correspond to regions composed either of (+)- or (−)-$SmC_sP_F$ layer stacks.

However, dark conglomerate textures can also be observed for non-silylated compounds.[9] Also, in this class of mesogens the formation of this texture is associated with FE or AF switching, characterized by only one or two relatively close repolarization current peaks[5b] (see, for example, Figure 4). This indicates that for these compounds the energetic difference between the AF and FE states is relatively small (due to entropic and enthalpic contributions). Under these conditions mesophase structures composed of $SmC_sP_F$ layer stacks separated by anticlinic interfaces should also become possible. The anticlinic interfaces inhibit a regular layer modulation of the $SmC_sP_F$ stacks which would lead to columnar phases with splay of polarization. Instead, as described for the dark conglomerate phases of the silylated molecules, a disordered sponge-like deformation of the layers allows escape from the mesoscale polar order within the $SmC_sP_F$ stacks. Hence, it is proposed that the structure of these dark conglomerate phases should be related to those formed by silylated compounds and that also for these compounds a continuous change from AF to FE switching is possible by increasing the size of the $SmC_sP_F$ layer stacks. For compounds **4a** and **5a** stabilization of the $SmC_sP_F$ structure seems to be sufficiently strong that all anticlinic interfaces are removed, and therefore, a mesophase with a 2D lattice involving splay of polarization is formed.

Fluorine substitution has many different effects (steric, electronic, conformational) which can be competing, and hence, the structure−property relations of these compounds are very complex. One effect is the electron-acceptor ability which reduces the electron density of the aromatic rings. This is known to increase the $\pi$-stacking interactions[46] and can contribute to the mesophase stabilization by introduction of F atoms into the periphery. In addition, these attractive interactions can fix the molecules more strongly in the layers. This sharpens the interfaces, and hence, the structural changes in the core region seem to have a remote effect upon the chain packing at the interlayer interfaces, influencing the enthalpic and entropic terms, which in turn determines the correlation between adjacent layers. F substituents at the central biphenyl unit seem to have a mainly distorting steric effect (larger size of F compared to H), which influences the core packing and average molecular conformations. However, fluorine substitution in the bay position is excep-

tional. It seems that the special substitution pattern in compounds **4a** and **5a** is responsible for stabilization of the $SmC_sP_F$ organization and $SmC_aP_A$ interfaces are removed. Here, the escape from macroscopic polar order and splay of polarization in the $SmC_sP_F$ structure should be the major driving forces for layer modulation, leading to the $Col_{ob}P_{FE}$ phase. Under a sufficiently strong electric field the layer modulations can be removed and FE switching is observed for the field-induced $SmC_sP_F$ phase.

For the silylated compounds **7** steric effects provided by the bulkiness of the silyl groups are of major importance for the appearance of layer modulation. It seems that the substitution pattern in compound **7ad** provides an especially dense packing of the aromatic cores. Therefore, the silyl groups provide a stronger steric layer frustration which leads to formation of ribbons. The resulting interfaces destabilize a synpolar ordering of the ribbons within the modulated layers, and hence, the FE states are destabilized. Therefore, the surface-stabilized FE and "nonclassical" AF switching, seen in the smectic phases of the other compounds **7**, is replaced by a clear AF switching in the columnar phase of **7ad**. The influence of this steric effect is reduced by reduction of the temperature. Therefore, at reduced temper-ature the inter-ribbon interfaces can be removed by the applied electric field and an uninterrupted smectic phase showing "nonclassical" (single peak) AF switching is induced.

It is also remarkable that the switching mechanism is different in the two types of columnar phases. For the $Col_{ob}P_A$ phase of **7ad** (at high temperature) the inter-ribbon interfaces restrict rotation on a cone and a collective rotation around the long axis is the only possible mechanism. This switching process is of special interest as it changes the suprastructural chirality of the LC system, and this could lead to applications of such materials in chirooptical switches and devices. In the whole temperature range of the $Col_{ob}P_{FE}$ phases of **4a** and **5a** and for the $Col_{ob}P_A$ phase of **7ad** at lower temperature a smectic phase is induced by the applied field, and in these noninterrupted layers the switching takes place on a cone as usually observed in smectic phases of bent-core molecules, and in this switching process the layer chirality is retained.

In summary, the investigations have contributed to a better understanding of the self-organization in the LC phases formed by bent-core materials, especially concerning the effects of fluorination of the core and silylation of the chain ends, which provide clues for the design of new polar ordered soft materials.

**Supporting Information Available:** Table with crystallographic data, additional figures (optical textures, polarization current response curves, and 2D X-ray diffraction patterns), experimental procedures, and analytical data (NMR, elemental analysis) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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