

# 4-Cyanoresorcinol-Based Bent-Core Mesogens with Azobenzene Wings: Emergence of Sterically Stabilized Polar Order in Liquid Crystalline Phases

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A new series of azobenzene containing bent-core molecules incorporating 4-cyanoresorcinol as the central core unit exhibiting cybotactic nematic, rectangular, columnar, and different types of tilted smectic (SmC) phases are synthesized. The mesophase behavior and phase structures are characterized in bulk and freely suspended films using a variety of experimental techniques. Depending on the chain length and temperature a series of different mesophases is observed in these compounds, ranging from cybotactic nematic via paraelectric SmC phases, polarization randomized SmC<sub>s</sub>P<sub>R</sub> phases to ferroelectric and antiferroelectric SmC phases, associated with increasing size and correlation length of the polar domains. Spontaneous formation of chiral domains is observed in the paraelectric SmC and the SmC<sub>s</sub>P<sub>R</sub> phases and discussed in relation with superstructural chirality, bend elastic constants, and surface effects.

# 1. Introduction

Materials with spontaneous or induced polar order, which can be switched between polar and apolar states, are of potential interest for applications in sensors, memory and display devices. Most ferroelectrics and antiferroelectrics represent inorganic and organic solid state materials.<sup>[1]</sup> Liquid crystalline (LC) ferroelectrics are of special interest as they can be easily processed into devices and their configuration can be switched by external stimuli.<sup>[1]</sup> LC phases of chiral molecules in tilted smectic phases (SmC\* phases) provided the first examples of LC ferroelectric and antiferroelectric materials.<sup>[3]</sup> In the mid 90's a novel type of mesogenic material breathed new life into

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this field and brought new expectations: the so-called banana-shaped LCs or bentcore LCs. Since the pioneering results by Niori et al.,<sup>[4]</sup> extensive research has been carried out on these LCs, and the results have allowed to appreciate new kind of truly fascinating materials. The occurrence of novel and intriguing polar mesophases, the induction of supramolecular chirality using achiral molecules and the noticeable optical, ferroelectric and antiferroelelectric responses of these materials are, among others, aspects that are now well documented.<sup>[5]</sup>

Recently, the research became focused on materials at the borderline between rod-shaped and bent-core mesogens: such as hockey stick molecules, mesogenic

dimers combining rod-like and bent-core units, molecules with exceptionally short core units with only four or less aromatic rings and molecules with a reduced bend.<sup>[6]</sup> Varying the chemical structure of these compounds made it possible to design materials exhibiting a whole spectrum of phases from paraelectric to ferro- and antiferroelectric phases.<sup>[7,8]</sup> 4-Cyanoresorcinols represent a typical structure of this kind providing a reduced bend due to the effects of the CN group on the conformation of the adjacent ester group.<sup>[9-11]</sup> It was demonstrated in previous studies that this structural unit can be used to generate bent-core mesogens with broad regions of cybotactic nematic phases,<sup>[11]</sup> transitions between different types of orthogonal phases, non-polar SmA phases,<sup>[10]</sup> SmAP<sub>R</sub> phases with randomized polarization<sup>[1,2]</sup> and antiferroelectric SmAP<sub>A</sub> phases<sup>[10,13]</sup> have been observed. A new SmAP phase, in which the polarization rotates uniformly from layer to layer with a fixed angle between adjacent layers, was also suggested recently.<sup>[14]</sup>

In this work new bent-core mesogens combining the bent 4-cyanoresorcinol core with two rod-like azobenzene wings were synthesized and investigated. The azobenzene units could lead to materials with enhanced nonlinear optical (NLO) properties.<sup>[15]</sup> Another important attractive feature of these compounds is the transformation between its *trans* and *cis* configurations by light absorption (photoisomerism) which can be used to modify the mesophase structure.<sup>[16]</sup> Such materials could be used for holographic media, optical storage, reversible optical waveguides, and other applications.<sup>[17–20]</sup> Azobenzene cores have previously been used for photoisomerizable bentcore mesogens<sup>[21,22]</sup> and in attempts to produce biaxial nematic phases.<sup>[23,24]</sup> Combining photoswitchable azobenzenes with

## DOI: 10.1002/adfm.201302295



liquid crystalline ferroelectrics also provides access to potential new multifunctional materials where polar response can be modulated by light.<sup>[25–29]</sup> Recently we have reported a first example of a 4-cyanoresorcinol with two azobenzene wings (compound A14).<sup>[8]</sup> An interesting feature of this compound is the formation of synclinic tilted SmC phases with an enhanced polarizability, which show surface supported achiral symmetry breaking.



Herein, we report the synthesis and investigation of the complete series of these azobenzene bent-core mesogens An having even numbered alkyl chains with n ranging from 8 to 18. With these compounds additional investigations, especially Second Harmonic Generation (SHG) experiments and investigations of freely suspended thin films were performed and the whole sequence of different phases formed by these compounds was investigated and gained important new insights into the development of polar order in tilted smectic phases. It turned out to be more complex than in the orthogonal case due to the effects of tilt on packing density, layer modulation, elastic constants and superstructural chirality. The sequence observed on decreasing temperature is Iso –  $N_{CybC}$  – SmC –  $SmC_{s}P_{R}$  –  $SmC_sP_F - M_1 - SmC_sP_A$  associated with increasing correlation length of polar domains. Already the isotropic and the nematic phases show field-induced polar order indicated by SHG activity as also found for all other tilted smectic phases of these compounds. This behavior is attributed to polar domains occurring well before the conventional antiferroelectric switchable SmCP<sub>A</sub> phase is reached. In the paraelectric SmC phase the domains are small. The SmC<sub>s</sub>P<sub>R</sub> phase indicates a temperature range of the SmC phase where the size of the polar domains reaches an appreciable size and which can be regarded as the tilted analog to the previously reported SmAP<sub>R</sub> phase.<sup>[12,13]</sup> Further growth of the ferroelectric domains leads to a SmC<sub>s</sub>P<sub>F</sub> phase which becomes modulated in the temperature range of the phase assigned as M<sub>1</sub>, before the antiferroelectric switching SmC<sub>s</sub>P<sub>A</sub> phase with alternating polar direction in adjacent layers is formed. Spontaneous formation of chiral domains was observed for all compounds under certain conditions in the SmC and SmC<sub>s</sub>P<sub>R</sub> phases and it is assumed to be the result of the combined effects of superstructural chirality and surface anchoring.

### 2. Results

#### 2.1. Synthesis

The synthesis of the bent-core compounds **A8–A18** is shown in **Scheme 1**. As reported previously 2,4-dihydroxybenzonitrile (4) was prepared from commercially available 2,4-dihydroxybenzaldehyde by the formation of the oxime, followed by





**Scheme 1.** Synthetic route to the bent core molecules *An*; reagents and conditions: *i*) 1. NaNO<sub>2</sub>, HCl, H<sub>2</sub>O, 0–5 °C, 2. phenol, NaOH, 3. NaHCO<sub>3</sub>; *ii*) C<sub>n</sub>H<sub>2n+1</sub>Br, KI, K<sub>2</sub>CO<sub>3</sub>, 2-butanone, reflux 6 h; *iii*) 1. EtOH, KOH, reflux, 12 h, 2. HCl/H<sub>2</sub>O, 20 °C; *iv*) H<sub>2</sub>NOH·HCl, Ac<sub>2</sub>O, *v*) NaOH, H<sub>2</sub>O;<sup>[30]</sup> *vi*) *N*,*N*'-dicyclohexylcarbodiimide, 4-dimethylaminopyridine, 20 °C, 24 h.

dehydration.<sup>[30]</sup> All the homologues acids IIIn were synthesized according to the method described before in four steps.<sup>[22]</sup> First the azobenzene was prepared by diazotization of ethyl 4-aminobenzoate and coupling of the resulting diazonium salt with phenol yielding ethyl 4-(4-hydroxyphenylazo)benzoate (I). Compound I was alkylated with 1-bromoalkane in the presence of potassium carbonate to give ester compounds IIn. Then the ester compounds IIn were hydrolyzed under basic conditions to yield the benzoic acids IIIn. In the final step, the benzoic acids IIIn were esterified with 4-cyanoresorcinol (4) in the presence of N,N'-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) as catalyst using dry dichloromethane as solvent to achieve the target compounds A8-A18. The final bent-core compounds were first purified by column chromatography and then by crystallization using ethanol/chloroform mixture. Complete synthetic procedures and analytical data are reported in the electronic supporting information.

#### 2.2. Investigation Methods

The synthesized compounds **A8–A18** were investigated by polarised light optical microscopy (Optiphot 2, Nikon) in conjunction with a heating stage (FP82HT, Mettler) and by differential scanning calorimetry (DSC-7 Perkin Elmer). The assignment of the mesophases was made on the basis of combined results of optical textures and X-ray diffraction (XRD). The measurements were done at Cu-K<sub> $\alpha$ </sub> line ( $\lambda = 1.54$  Å) using standard Coolidge tube source with a Ni-filter. Investigations of oriented samples were performed using a 2D-detector (HI-Star, Siemens AG). Uniform orientation was achieved by alignment in a magnetic field (B  $\approx$  1 T) using thin capillaries. The orientation once achieved is maintained by slow cooling (0.1 K min<sup>-1</sup>) in the presence of the magnetic field. Electro-optical experiments

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have been carried out using a home built electro-optical setup in commercially available ITO coated glass cells (E.H.C., Japan, polyimide coated for planar alignment, antiparallel rubbing, thickness  $6 \,\mu\text{m}$  and measuring area  $1 \,\text{cm}^2$ ).

Measurements of optical second harmonic generation (SHG) have been performed using a Nd:YAG laser operating at  $\lambda = 1064$  nm (10 ns pulse width and 10 Hz repetition rate). The primary beam was incident at an angle of 30° to the cell normal. The SHG signal was detected in transmission by a photomultiplier tube (Hamamatsu). The acquired signal was calibrated using a 50  $\mu$ m reference quartz plate.

Freely-suspended films were drawn over a custom-made rectangular glass frame with a 10 mm × 3 mm slit and two brass electrodes. The frame has been mounted into a Linkam LTS 350 heating stage. The temperature controller provided an accuracy of 0.1 K. Optical observations have been made with a polarizing microscope AxioImager Pol (Carl Zeiss GmbH) equipped with a high-resolution cooled charge-coupled device (CCD) camera AxioCam HR (Carl Zeiss GmbH). We carried out the observations in reflected light between crossed polarizers as well as between slightly uncrossed polarizers.

# 2.3. Mesophases and Transition Temperatures Depending on Alkyl Chain Length and Temperature

**Figure 1** shows the mesophases and the transition temperatures for the synthesized homologous compounds with different terminal alkoxy chain lengths (for numerical data, see **Table 1**, DSC traces are shown in Figure S1). As can be seen from Figure 1, for the shortest homologue **A8** a nematic phase (N<sub>CybC</sub>) is observed in a relatively wide temperature range, which on cooling to 83 °C is replaced by a mesophase with spherulitic texture which was identified as a rectangular columnar phase by XRD (Col<sub>rec</sub>, see **Figure 2**c–e and Section 2.5) also known as B<sub>1rev</sub> phase. Increasing the alkoxy chain length to n = 10



**Figure 1.** Plot of the transition temperatures of compounds **A8–A18** as a function of the alkyl chain length. The connections between the data points serve as guides for the eyes and indicate the upper temperature limits for the distinct mesophases; stars (connected by a dashed line) indicate the melting temperatures observed on heating,  $\blacktriangleright$  (bottom solid line) the crystallization temperature on cooling.

(compound A10) induces additional tilted smectic phases (SmC and SmC<sub>s</sub>P<sub>R</sub> phases) between the N<sub>CybC</sub> and the Col<sub>rec</sub> phase and modifies the structure of the Col<sub>rec</sub>-phase. A typical feature of the SmC phases is SHG activity under an applied electric field and that under certain conditions a conglomerate of chiral domains is observed (see below).

For the next homologue A12, the Col<sub>rec</sub> phase completely disappears. The nematic range becomes smaller and the SmC phase is stabilized. Additional phase transitions with very small enthalpy values can be observed in the smectic phase region on cooling before crystallization takes place. For all compounds A12–A18 there is a sequence of five distinct smectic phases, assigned as SmC, SmC<sub>s</sub>P<sub>R</sub>, SmC<sub>s</sub>P<sub>F</sub>, M<sub>1</sub> and SmC<sub>s</sub>P<sub>A</sub>. For

$H_{2n+1}C_nO$ $N > N > N > N > N > OC_nH_{2n+1}$						
Compd.	п	Phase transitions				
A8	8	Cr 102 [60.7] (Col <sub>rec</sub> 83 [6.6]) N <sub>Cybc</sub> 143 [1.0] Iso				
A10	10	Cr 68 [22.7] Col <sub>rec2</sub> 69 [3.0] <sup>b)</sup> Col <sub>rec1</sub> 73 [0.5] SmC <sub>s</sub> P <sub>R</sub> 87 [-] SmC 105 [<0.01] N <sub>CybC</sub> 136 [1.1] Iso				
A12	12	Cr 71 [17.4] (SmC <sub>s</sub> P <sub>A</sub> 70 [0.3]) M <sub>1</sub> 75 [0.2] SmC <sub>s</sub> P <sub>F</sub> 83 [-] SmC <sub>s</sub> P <sub>R</sub> 96 [-] SmC 127 [0.15] N <sub>CybC</sub> 137 [2.0] Iso				
A14	14	Cr 72 [23.0] SmC <sub>s</sub> P <sub>A</sub> 76 [0.4] M <sub>1</sub> 78 [0.1] SmC <sub>s</sub> P <sub>F</sub> 90 [-] SmC <sub>s</sub> P <sub>R</sub> [-] 102 SmC 136 [0.5] N <sub>CvbC</sub> 139 [3.0] Iso				
A16 <sup>[8]</sup>	16	Cr 75 [41.8] (SmC <sub>s</sub> P <sub>A</sub> 76 [0.4]) M <sub>1</sub> 79 [0.15] SmC <sub>s</sub> P <sub>F</sub> [-] 95 SmC <sub>s</sub> P <sub>R</sub> [-] 109 SmC 139.5 N <sub>CybC</sub> 140 [5.8] <sup>c)</sup> Iso				
A18	18	Cr 80 [40.7] (SmC <sub>2</sub> P <sub>A</sub> 76 [0.4] M <sub>1</sub> 79 [0.1]) SmC <sub>2</sub> P <sub>F</sub> 98 [-] SmC <sub>2</sub> P <sub>8</sub> [-] 116 SmC 142 [6.3] Iso				

**Table 1.** Phase transition temperatures (T in  $^{\circ}$ C) and associated enthalpy values (in square brackets,  $\Delta H$  in kJ mol<sup>-1</sup>) of compounds **A8-A18**.<sup>a</sup>)

<sup>a)</sup>Transition temperatures and enthalpy values were taken from the second DSC heating scans (10 K min<sup>-1</sup>, see also Figure S1); transition without detectable DSC peak were determined by polarizing microscopy; values between brackets are monotropic phase transitions and in this case the enthalpy values are taken from the first DSC cooling scans; abbreviations: Cr = crystalline solid; Iso = isotropic liquid;  $N_{CybC} = nematic phase composed of SmC-type cybotactic clusters; SmC = synclinic tilted paralelectric SmC phase composed of small SmC<sub>s</sub>P<sub>F</sub> domains; SmC<sub>s</sub>P<sub>R</sub> = SmC phase with significantly increased domain size; SmC<sub>s</sub>P<sub>F</sub> = ferroelectric SmC phase; <math>M_1 = highly$  viscous LC phase; SmC<sub>s</sub>P<sub>A</sub> = synclinic tilted antiferroelectric SmC phase (B2 phase); Col<sub>rec</sub> and Col<sub>rec1</sub> = centered rectangular columnar phases with *c2mm* lattice (B1<sub>rev</sub> phase); Col<sub>rec2</sub> = non-centered rectangular columnar phase (undulated smectic phase); <sup>b</sup>this transition shows significant hysteresis, on cooling the transition takes place at 62 °C; <sup>c1</sup>transitions not resolved, enthalpy value is the total of the SmC – N<sub>CybC</sub> – Iso transitions.

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a) b) c) d) e)  $\int_{0}^{0}$ 

**Figure 2.** XRD investigation of an aligned sample of compound **A8**: a) wide angle and b) small angle scattering of the N<sub>CybC</sub> phase at T = 120 °C, c) wide angle and d) small angle scattering with reciprocal lattice and indexation as a centered Col<sub>rec</sub> phase at T = 80 °C; e) model of the Col<sub>rec</sub> (B1<sub>rev</sub>) phase.

longer chains, the nematic range becomes smaller and it completely disappears for A18 with the longest alkoxy chains. In the following, the distinct LC phases will be discussed in more detail.

#### 2.4. Nematic Phases

On cooling from the isotropic liquid state, all compounds with the exception of A18 form a nematic phase. The Iso-N transitions are associated with transition enthalpies between 1.0 (A8) and 3.0 kJ mol<sup>-1</sup> (A14), increasing with growing chain length. For the longer homologue A16, the Iso-N<sub>CvbC</sub> transition is close to the N<sub>CvbC</sub>-SmC transition and therefore, the contributions of the enthalpies of the Iso- $N_{CybC}$  and  $N_{CybC}$ -SmC transitions cannot be separated. In the temperature range of the nematic phases the XRD patterns of magnetically aligned samples ( $B \sim 1T$ ) show a diffuse scattering in the wide angle region centered at the equator (Figure 2a, see also Figure S3 and S4 for the other homologues) with a maximum at d = 0.46 nm (T = 140 °C). The diffuse scattering in the small angle region has a dumbbell-like shape, indicating the existence of cybotactic clusters of the SmC type; hence these nematic phases are assigned as N<sub>CybC</sub>.<sup>[10,31]</sup> The splitting of the small angle scattering maxima of compound A8 is  $\Delta \chi/2 = 28^{\circ}$  (T = 140 °C) and it only slightly decreases to  $\Delta \chi/2 = 25^{\circ}$  at  $T = 90 \ ^{\circ}C$  (see Figure S2). In case of compound A10, the maximum close to the clearing temperature is  $\Delta \chi/2 = 18^{\circ}$  and a strong temperature dependence is observed, reaching a minimum of  $\Delta \chi/2 = 4-5^{\circ}$ close to the transition to the SmC phase (Figure 3a). This obser-



**Figure 3.** Temperature dependence a) of the splitting  $(\Delta \chi/2)$  of the small angle scattering and b) of the *d*-value of the maxima of the small angle scattering in the N<sub>Cybc</sub>, the SmC and the SmC<sub>s</sub>P<sub>R</sub> phases of compound **A10**.

vation is in line with the increase of the *d*-value on decreasing temperature (Figure 3b).

For compounds A12 and A14 with longer chains and short nematic ranges  $\Delta \chi/2$  is only around 12° (see Figure S5 and Figure 4a). As the  $\Delta \chi/2$  splitting can in a first approximation be related to the tilt of the molecules in the SmC clusters, this indicates a tilted organization of the molecules in all N<sub>CybC</sub> phases with a tendency of decreasing tilt with increasing chain length. The transition enthalpies N<sub>CybC</sub> to SmC (<0.01–0.5 kJ mol<sup>-1</sup>) are much smaller than the Iso – N<sub>CybC</sub> transition enthalpy values (1.0–3.0 kJ mol<sup>-1</sup>), in line with the cybotactic cluster structure of the nematic phases.

#### 2.5. Col<sub>rec</sub> Phases of Compounds A8 and A10

Upon cooling the nematic phase of **A8** the XRD pattern changes significantly at T = 83 °C, at the transition to the low temperature phase with spherulitic texture (**Figure 5**b). This transition is associated with a significant enthalpy change (see

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100 µm



Figure 4. Temperature dependence a) of the tilt angle  $\beta$  (calculated from the splitting  $\Delta \chi/2$ ) and b) of the *d*-value of the XRD patterns in the LC phases of compound A14.

Figure 6a). At this transition the wide angle scattering remains

diffuse, indicating a fluid LC phase, and in the small angle

region several sharp Bragg peaks appear (Figure 2c,d). These

peaks can be indexed on a centered rectangular lattice with



Figure 5. Optical micrographs of textures observed between crossed

polarizers in a homeotropic cell for compound A8: a) nematic phase at

the parameters a = 3.7 nm and b = 4.6 nm (T = 70 °C, see completely. Table S1). The position of the wide-angle scattering maxima For compound A10 additional SmC phases appear between remain on the equator, indicating the alignment of the molthe  $N_{CybC}$  phase and the  $Col_{rec}$  phase. The parameters a =5.43 nm and b = 4.95 nm (at T = 70 °C; see Figure S3e and ecules with their long axes parallel to b. The parameter b is in good agreement with the molecular length ( $L_{mol} = 4.6$  nm for Table S1) indicate a Col<sub>rec</sub> phase composed of broader riba 120° bent molecule with stretched wing groups and the alkyl bons, formed by about 6 molecules in the cross section (Col<sub>rec1</sub> chains in all-trans conformation as determined using space phase; B1<sub>rev</sub> phase). On further cooling a transition to a second filling models). Both observations are in line with a nontilted mesophase with 2D lattice takes place, associated with a sigorganization of the molecules. The 2D lattice results from nificant enthalpy change. For this non-centered rectangular the formation of ribbons; the lateral diameter of these ribcolumnar phase with the parameters a = 10.10 nm and b =bons can be calculated from a/2 to be approximately 4–5 mol-4.93 nm (T = 60 °C, see Figure S3f and Table S1) an undulated ecules organized side-by side. These XRD data, together with smectic structure is assumed ( $Col_{rec2}$  phase, USm phase). In the typical texture indicate a rectangular columnar LC ribbon both low temperature phases the parameter b corresponds well phase (Col<sub>rec</sub>), typical for short chain bent core mesogens also with the molecular length ( $L_{mol} = 5.1 \text{ nm}$ ), which is in line with

the LC T = 130 °C and b) Col<sub>rec</sub> phase (B<sub>1rev</sub> phase) at T = 80 °C. For a colour version of the textures, see Figure S8 in the Supporting Information.

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Adv. Funct. Mater. 2014, 24, 1703-1717



**Figure 6.** a,b) DSC heating (top) and cooling (bottom) traces at a rate of 10 K min<sup>-1</sup>: a) compound **A8** and b) compound **A14**; c) shows the DSC cooling trace of compound **A14** for the temperature range of the SmC<sub>s</sub>P<sub>R</sub>-M<sub>1</sub>-SmC<sub>s</sub>P<sub>F</sub> transition between 80 °C and 65 °C.

a non-tilted organization of the molecules. These 2D-modulated low temperature LC phases of compounds A8 and A10 do not exhibit any response to an applied electric field.<sup>[32]</sup>



#### 2.6. Smectic Phases

#### 2.6.1. DSC and Optical Investigations

A different kind of behavior is observed for compounds A12–A18. All these compounds show essentially the same sequence of five distinct smectic phases occurring below the nematic phase (compounds A12–A16), only for A18 the nematic phase is missing (see Figure 1 and Table 1). The smectic phase sequence for all these compounds is SmC – SmC<sub>s</sub>P<sub>R</sub> – SmC<sub>s</sub>P<sub>F</sub> –  $M_1 - SmC_sP_A$ , the assignment of the distinct smectic phases is based on the experimental results described below.

All enthalpies of the phase transitions between the smectic phases are very small (only 0.1–0.4 kJ mol<sup>-1</sup>) and increase slightly with growing chain length (Table 1, Figure 6b and S1). No enthalpy values could be determined for the transition between the phases assigned as SmC,  $SmC_sP_R$  and  $SmC_sP_F$  in any case. The enthalpy of the phase transition  $SmC_sP_F - M_1$  is very small (0.1–0.2 kJ mol<sup>-1</sup>). The highest transition enthalpy in the smectic LC range is observed for the  $M_1 - SmC_sP_A$  transition which is for all compounds around 0.4 kJ mol<sup>-1</sup>. Hence, it appears that this is the major transition in the smectic region, associated with the most significant changes of the phase structure.

In planar cells the smectic phases develop with a typical fan texture. With decreasing temperature the smooth fans become sharper and the birefringence significantly increases, indicated by the change of the interference color from red to dark green, due to the increase of the order parameter of the aromatic cores with decreasing temperature (see Figure 7f,g, 6 µm cell, any bluish interference color appears green due to orange color of the compound). A tiny, but distinct jump in interference color is observed at a specific temperature in the SmC region of all compounds (see Figure S10). At this temperature also other effects were observed, like a step in the dielectric strength, as previously reported in ref. [8] for compound A16 (see Figure S15), and stripe pattern formation in free standing films of compound A14 (see below). Therefore, the region previously assigned as SmC<sub>s</sub>P<sub>R</sub><sup>[8]</sup> obviously includes two very similar phases, a high temperature paraelectric SmC phase and a low temperature phase assigned as SmC<sub>s</sub>P<sub>R</sub> (Figure 1, hexagonal dots connected by a dotted line). Additional phase transitions to the following phases are associated with only slight textural changes. The major changes are a further jump of the birefringence color from green to yellowish green at the SmC<sub>s</sub>P<sub>R</sub>-SmC<sub>s</sub>P<sub>F</sub> transition (Figure 7g,h) and an increased viscosity occurring at the transition to the phase assigned as M1 (Figure 7i) which becomes fluid again at the next transition to SmC<sub>s</sub>P<sub>A</sub> (Figure 7j).

Under homeotropic anchoring conditions some of the textural changes are better pronounced. Especially remarkable are the SmC and  $\text{SmC}_{s}P_{R}$  phase regions for which a low birefringent texture composed of distinct chiral domains is reproducibly observed for all compounds An by uncrossing the polarizers by a small angle (**Figure 8**a–c). This leads to the appearance of dark and bright domains; uncrossing the polarizer in the opposite direction reverses the brightness of the domains (Figure 8a,b). That the domains are due to chirality and not the result of a different tilt-alignment is shown by rotation of the



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**Figure 7.** Optical micrographs of the textures observed for the different LC phases of compound **A14** in a homeotropic cell (left column), in a planar cell (middle column, arrows indicate a region where textural changes can be identified) and in free standing films (right column) at the indicated temperatures for the indicated LC phase types. In a) the homeotropic alignment (dark areas) is developing from the initially formed homogeneous alignment (green areas).

sample between crossed polarizers, which gives no significant change of brightness, independent on the angle. (Figure 8d,e). This corroborates that the distinct regions indeed represent chiral domains with opposite handedness.<sup>[8]</sup> The chiral domains are clearly visible for the SmC and SmC<sub>s</sub>P<sub>R</sub> phases of all compounds without any change at the SmC - SmC<sub>s</sub>P<sub>R</sub> transition, but they disappear at the transition to the N<sub>CybC</sub> phases. The transition of the SmC<sub>s</sub>P<sub>R</sub> phase to the SmC<sub>s</sub>P<sub>F</sub> phase is associated with an anchoring transition to a birefringent defect texture (Figure 7b,c). At this transition birefringence strongly increases and it becomes difficult to detect the chiral domains anymore. However, it appears that chirality is conserved in the few remaining low birefringent regions and reheating into the SmC<sub>s</sub>P<sub>R</sub> phase completely restores the chiral domains. Possible reasons for achiral symmetry breaking in the SmC and SmC<sub>s</sub>P<sub>R</sub> phases are discussed in Section 3.3. The next phase transitions

to the phases assigned as  $M_1$  and  $SmC_sP_A$  are associated with minor textural changes (Figure 7c–e,h–j).

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#### 2.6.2. Behavior in Freely Suspended Films

The polar character of the smectic phases was studied in freely suspended films in compound A14. The films where prepared in the smectic phase near the transition into the nematic. The SmC phase exhibited a typical schlieren texture in thin (<200 nm) and in thick films (>5 µm). Observing the films under inclined incidence, we could confirm that the phase has a synclinic character. No polar response to an in-plane DC electric field was found. On the contrary, dielectric re-orientation was observed in an AC field. The slow (optical) axis is aligned perpendicular to the electric field. Distinct changes occur at the SmC - SmC<sub>s</sub>P<sub>R</sub> transition at about 102 °C, which is accompanied by the formation of a network of strings, similar to that described previously<sup>[34]</sup> (Figure 7k,l). The width of the stripes increases with decreasing temperature over an interval of 3-4 K (Figure 7m). This transition coincides with the inflection points in the SHG signal intensity vs. T (see Section 2.6.5) and polarization vs. T curves (see Section 2.6.4). There is also a distinct jump in dielectric strength  $\Delta \varepsilon$  at this transition, as reported previously for A16 (see Figure S15).<sup>[8]</sup> So the SmC -SmC<sub>s</sub>P<sub>R</sub> transition appears to be associated with a distinct increase of the size of the polar domains.

At about 90 °C, corresponding to the  $SmC_sP_R - SmC_sP_F$  transition, the stripe pattern has disappeared and a smooth schlieren texture is observed (Figure 7m). This phase shows a clear polar response to an electric field exhibiting  $2\pi$  director inversion walls typical for polar films (see Section 2.6.4).

These findings indicate that the phase has a residual polarization. That is why we designated it as  $SmC_sP_F$ . The polar director aligns along the electric field and the c-director (tilt) is perpendicular to it. We found this behavior in thick and in very thin films as well.

The transition into the  $M_1$  phase is marked by development of a mosaic-like schlieren texture (Figure 7n). No response to an electric field could by found in this phase.

During the next transition, the texture becomes more distorted in thick films. On the other hand, thin films exhibit a typical schlieren texture (Figure 7o). The texture response to an electric field was found only in thin films. The switching character showed an odd-even effect as typical for antiferroelectrics. There is a reorganization of the *c*-director only in films with odd number of layers; for films with an even number of layers either no response is observed or the *c*-director aligns parallel





**Figure 8.** Textures of the SmC phase of compound **A14** at T = 130 °C between glass slides (homeotropic alignment): c) between crossed polarizers and a,b) between slightly uncrossed polarizers, showing dark and bright domains, indicating the presence of areas with opposite chirality sense; d,e) show the texture between crossed polarizers, but after rotation of the sample by 20° either clockwise or anticlockwise; the birefringence does not change which confirms chirality as origin of the effects seen in a–c); there is no change of the textures at the transition to the SmC<sub>s</sub>P<sub>R</sub> phase. For a colour version, see Figure S9 in the Supporting Information.

to the applied field. This effect is a direct evidence for an antiferroelectric structure of the phase.<sup>[35]</sup> Therefore, we designated this phase as  $SmC_sP_{A}$ .

#### 2.6.3. XRD Studies

Samples of A14 aligned by magnetic field were studied by 2D XRD. At the transition from the  $N_{CybC}$  to the SmC phase the four diffuse spots in the small angle region transform into two peaks located beside the meridian, whereas the maxima



of the diffuse scattering in the wide angle region remains on the equator, indicating a synclinic arrangement of the molecules in the smectic phase (Figure 9c,d). No fundamental changes in the XRD patterns are visible at the following phase transitions until crystallization. A more detailed analysis of the XRD data indicates an increase of the tilt angle with decreasing temperature in all SmC and SmC<sub>s</sub>P<sub>R</sub> phases. In agreement with this, the *d*-values become smaller with decreasing temperature (Figure 4, S5 and S7). These trends continue in the SmC<sub>s</sub>P<sub>F</sub> phase. As shown in Figure 4a for compound A14, in the SmC<sub>s</sub>P<sub>A</sub> phases at lower temperature the tilt angles ( $\beta$  = 29–31°) are larger than in the  $SmC_sP_R$ and  $SmC_sP_F$  phases and the *d*-values are also increased (Figure 4b). This is due to a chain stretching induced by the denser packing of the molecules in the SmC<sub>s</sub>P<sub>A</sub> phases. An increase of the packing density in the SmC<sub>s</sub>P<sub>A</sub> phases is also found for compounds A12 (Figure S5) and compound A16 (Figure S7). The M<sub>1</sub>-phases represent a discontinuity in the development of the d-values and tilt-angles. There is a jump to smaller tilt angles at the  $SmC_sP_F - M_1$ transition and an increase of the *d*-values in the M<sub>1</sub>-phase. This confirms that a denser packing of the molecules starts in the M<sub>1</sub> phase region. Overall the transition SmC - SmC<sub>s</sub>P<sub>R</sub> - SmC<sub>s</sub>P<sub>F</sub> is nearly continuous, as also indicated by the absence of any transition enthalpy. Major changes with significant increase of the packing density, associated with distinct jumps in *d*-values and tilt angles, take place at the  $SmC_sP_F$  - $M_1$  and  $M_1 - SmC_sP_A$  transitions.

Denser packing in the  $M_1$  and  $SmC_sP_A$ phases is also evident from a slight shift of the position of the wide angle scattering maximum from 0.48 to 0.46 nm (Figure 10b and S7c). Also the layer reflection becomes more intense in the  $M_1$  and  $SmC_sP_A$  phases which is in line with the development of sharper interlayer interfaces resulting from a denser packing of the aromatic cores (Figure 10a and S7d).

#### 2.6.4. Electro-Optical Studies in ITO Cells and Free Standing Films

Electro-optical investigations were carried out in 6  $\mu$ m indium tin oxide (ITO) coated cells with polyimide alignment layer under an applied triangular wave voltage. Figure 11 shows the current response curves at different temperatures for A14 and Figure 12 shows the dependence of the polarization on temperature for the same compound. Switching curves obtained in 2  $\mu$ m cells are shown in Figure S12. Upon application of a triangular wave voltage of frequency



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**Figure 9.** XRD investigation of an aligned sample of compound **A14**: a,b)  $N_{CybC}$  phase at T = 138 °C; c,d) SmC phase at T = 132 °C; a,c) wide angle patterns after subtraction of the pattern of the isotropic phase (150 °C) and b,d) small angle scattering after subtraction of the pattern of the isotropic phase (150 °C).

10 Hz a relatively weak and rather broad single peak per half cycle of the applied voltage was observed in the current curves in the SmC phase range, which increases in intensity as temperature decreases (see Figure 11a,b). In the SmC<sub>s</sub>P<sub>R</sub> region the slope of the I vs. T curve increases and reaches a polarization value of  $P_{\rm S} \sim 130~{\rm nC~cm^{-2}}$  close to the transition to the SmC<sub>s</sub>P<sub>F</sub> phase occurring at T = 90 °C (see Figure 12). Below this temperature, the shape of the current response curves changes and two widely separated peaks appear and grow in intensity (Figure 11c,d,  $P_{\rm S} \sim 360$  nC cm<sup>-2</sup>). Both peaks appear to be positioned at the ends of the conductive part of the curve symmetrically with respect to the field inversion point (Figure 11c and S12c,d). This indicates that the switching occurs hysteresis free. With further decreasing temperature the distance between the peaks decreases and the polarization value rises to  $P_{\rm S} \sim 440 \text{ nC cm}^{-2}$  (Figure 11d) A switching with two polarization peaks and similar polarization values between 540 and 660 nC  $\rm cm^{-2}$  is also observed in the two LC phases at lower temperature (M1, SmCsPA, Figure 11e,f).

Under the field applied across a homogeneously aligned cell a birefringent fan-like texture, with dark extinctions inclined with the directions of polarizer and analyzer, is observed (Figure S11). This confirms a synclinic tilt in these smectic phases as also deduced from the XRD investigation of aligned samples (Figure 9c,d). Neither in the SmC or SmC<sub>s</sub>P<sub>R</sub> phases nor in the SmC<sub>s</sub>P<sub>F</sub> phase or in one of the low temperature phases the switching process is associated with a change of the orientation of the extinctions (see Figure S11), which indicates



**Figure 10.** a) Small angle and b) wide angle  $\theta$ -scans over the XRD patterns of compound **A14** at different temperatures. For a clearer identification of the distinct curves, see colour version in Figure S6 in the Supporting Information.

that in all phases switching takes place by a collective rotation around the molecular long axis.

Electro-optical investigation of free standing films shows only a dielectric response to a 100 Hz AC electric field in the SmC phase down to 102 °C. Below this temperature, in the  $SmC_sP_R$  and  $SmC_sP_F$  regions, a polar response on an external electric field is observed; the switching is ferroelectric and independent on the film thickness and the number of layers (Figure 13). In the whole temperature range of both phases the molecular long axis is perpendicular to the field direction, in line with the polar moment being along the bend direction and the switching taking place around the molecular long axis. Only regions with a fine stripe pattern, occurring in the SmC<sub>s</sub>P<sub>R</sub> phase below the transition at 102 °C do not respond to the electric field. It appears that the modulation resulting in stripe formation is responsible for the absence of a response in these regions of the thin films. As the stripes are dominating in the SmC<sub>s</sub>P<sub>R</sub> range and disappear in the SmC<sub>s</sub>P<sub>F</sub> phase, the switching becomes uniformly ferroelectric in the temperature



**Figure 11.** a–f) Switching current response curves for compound A14 in a 6  $\mu$ m ITO cell on applying a triangular wave field (10 Hz); the dotted line indicates the applied triangular wave voltage; a) SmC phase at T = 120 °C; b) SmC<sub>S</sub>P<sub>R</sub> phase at T = 100 °C; c) SmC<sub>S</sub>P<sub>R</sub> – SmC<sub>S</sub>P<sub>F</sub> transition at T = 90 °C; d) SmC<sub>S</sub>P<sub>F</sub> phase at T = 85 °C; e) M<sub>1</sub> phase at T = 74 °C and f) SmC<sub>s</sub>P<sub>A</sub> phase at T = 65 °C; different scales are used for the current response plots; for more switching current curves in the SmC region, see Figure S13 and for investigations in 2  $\mu$ m cells, see Figure S12.

range of the SmC<sub>s</sub>P<sub>F</sub> phase. This is in line with dielectric results obtained for the SmC/SmC<sub>s</sub>P<sub>R</sub> phase region of compound A16 (Figure S15), where a high dielectric strength is observed in the SmC<sub>s</sub>P<sub>R</sub> region close to the SmC<sub>s</sub>P<sub>F</sub> phase and it steeply decreases on approaching the M<sub>1</sub> phase.<sup>[8]</sup> This is indicative of a strong increase of the polar domain size in the temperature range of the SmC<sub>s</sub>P<sub>F</sub> phase.

The  $M_1$  phase does not show any response in freely suspended films, neither to DC nor to AC fields, most probably due to the high viscosity. In ITO cells, under higher field strength, antiferroelectric switching is observed in both phases  $M_1$  and  $SmC_sP_A$  (Figure 11e). In the  $SmC_sP_A$  phase antiferroelectric switching is observed as well in free standing films. In the films the response depends on the film thickness and occurs with an odd-even effect of the number of layers on the response. This phase at lowest temperature behaves like a typical B2 phase of bent-core molecules.

#### 2.6.5. SHG Investigations

Second harmonic generation (SHG) is a powerful tool to detect macroscopic polar order in the ground state and in



field induced states of LC phases.<sup>[36]</sup> A plot of SHG intensity versus temperature for compound A14 is shown in Figure 14a. Under constant applied electric field ( $E_{pp}$ = 20 V  $\mu$ m<sup>-1</sup>) a very weak SHG signal is already observed in the isotropic phase at T = 148 °C. It is retained in the nematic phase. In the temperature range of the SmC phase it slightly grows on cooling,<sup>[37]</sup> the slope increases in the SmC<sub>s</sub>P<sub>R</sub> region and then it continuously and rapidly increases in the SmC<sub>s</sub>P<sub>F</sub> phase range to reach the saturation in the M1 phase. The SHG response remains nearly constant in the temperature region of the M1 phase and also in the upper temperature range of the  $SmC_sP_A$  phase and then it drops (s. Figure S14b). There is a different field dependence of the SHG signal in the temperature range of the SmC and SmC<sub>s</sub>P<sub>F</sub> phases. In the SmC range the SHG signal continuously grows without reaching a saturation upon increasing the applied voltage (maximum: 25 V µm<sup>-1</sup>, Figure 14b), whereas in the  $SmC_sP_F$  phase, close to the transition to the M1 phase a distinct plateau is reached at a voltage of ~17 V $\mu$ m<sup>-1</sup> (Figure 14c) the former typical for paraelectric switching, the latter indicating polar switching above a certain threshold voltage.

In concord with the current reversal measurements, no residual SHG signal was found after switching off the applied field in ITO cells in the switchable phases. It appears that the SmC phase behaves as a paraelectric phase<sup>[7,34,37]</sup> with unusually high



Figure 12. Polarization as function of temperature as measured for compound A14 in a 6  $\mu$ m ITO cell on applying a triangular wave field (10 Hz) at 160 V<sub>pp</sub>.

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Figure 13. Reorientation of the polar director in a freely-suspended film in the SmC<sub>s</sub>P<sub>R</sub> phase of A14 at T = 97 °C: a) E = -12 V/mm, b) E = 0 V/mm, c) E = +12 V/mm; the field direction is indicated by arrows; the film is observed under inclined incidence.

Figure 14. a) SHG intensity of compound A14  $\nu s.$  temperature (6  $\mu m$ ITO cell, applied voltage: 20 V/ $\mu$ m) and dependence of the SHG-Intensity on the applied voltage b) in the SmC phase at T = 110 °C and c) in the  $SmC_sP_F$  phase at T = 78 °C.

susceptibility to an electric field, in the  $\mbox{SmC}_{\rm s} P_{\rm R}$  phase range the switching appears to be ferroelectric as in the SmC<sub>s</sub>P<sub>F</sub> phase. On the contrary, all switchable phases below SmC<sub>s</sub>P<sub>R</sub> behave as antiferroelectrics in ITO cells; even the phase designated as SmC<sub>s</sub>P<sub>F</sub> does not exhibit bistable switching. Possible reasons are outlined in the discussion.



# 3. Discussion

# 3.1. Phase Sequence Depending on Alkyl Chain Length and Temperature

As expected, nematic phases dominate for the short chain compounds and the nematic range decreases with chain elongation. All nematic phases represent N<sub>CvbC</sub> phases as typical for bent-core mesogens and the size of the cybotactic SmC clusters increases with alkyl chain length and with decreasing temperature.<sup>[10]</sup> The tilt in the SmC clusters decreases with rising chain length, but there is no uniform temperature dependence. For the compounds with short chains (n = 8, 10) the core-core interactions dominate, which lead to a transition from the N<sub>cybc</sub> phases to Col<sub>rec</sub> phases, occurring directly (A8) or via a SmC phase (A10). In the Col<sub>rec</sub> phases polar ribbons of nontilted molecules arranged on a centered rectangular lattice with antiparallel correlation between the ribbons (B<sub>1rev</sub> phases). In this Col<sub>rec</sub> phase of A8 there are relatively large interfaces between the aromatic ribbons and the columns incorporating the aliphatic chains and this is unfavorable for molecules with longer chains. At first the ribbon diameter is increased for compound A10 in the Col<sub>rec1</sub> phase and at lower temperature a transition to non-centered rectangular columnar phase (Col<sub>rec2</sub> phase), presumably representing an undulated smectic phase, takes place. For molecules with n > 10 columnar phases are removed and formation of smectic phases is favored. In the smectic phases there is a tendency to increased tilt with rising alkyl chain length, which is the result of the increased area required by longer conformationally disordered chains. With decreasing temperature the packing density of the aromatic cores increases. This gives rise to local polar domains in the SmC phase, the size and the correlation length of these domains increases with decreasing temperature leading to the  $SmC_sP_R$  phase. At the transition to the  $M_1$  phase the combination of a denser packing and enhanced polar order most probably leads to a layer modulation, which is assumed to be the reason for the relatively high viscosity of this phase. In the SmC<sub>s</sub>P<sub>A</sub> phase with highest packing density the molecules adopt antiferroelectric order (see Figure 15).

#### 3.2. Development of Polar Order

The phase sequence Iso –  $(N_{cybC}) - SmC - SmC_sP_R - SmC_sP_F - M_1 - SmC_sP_A - Cr is typically observed for compounds An with sufficient chain length (<math>n > 10$ ). Figure 15 shows the observed development of polar order in the series of smectic phases. SmC-type cybotactic clusters were already found in the nematic phase ( $N_{CybC}$ ) which persisted also in the isotropic phase. Field-induced SHG in the nematic and isotropic phases may be attributed to the polar order within the clusters.<sup>[38]</sup> The polar domains persist in the SmC phase too, which are probably responsible for the current response observed in the ITO cells and an enhanced field-induced SHG. On the other hand, the response of the phase to an electric field remains paraelectric in the SmC region. In the SmC\_sP\_R region these domains reach appreciable size and macroscopic ferroelectric domains can be





**Figure 15.** Development of polar order in the SmC phases of compounds **A***n* depending on temperature; PE, FE and AF denote paraelectric, ferroelectric and antiferroelectric switching, respectively.

observed in freely suspended films. In analogy to the SmAP<sub>R</sub> phase, we designate this phase as SmC<sub>s</sub>P<sub>R</sub>, as a SmC phase with uniform tilt, but with randomly distributed polar domains. In the SmC<sub>s</sub>P<sub>F</sub> phase the size of the polar domains diverges and a polar phase develops. Observation of the polar response and inversion walls in freely-suspended films unambiguously indicates that the phase has a residual polarization. Hence, we designate it as SmC<sub>s</sub>P<sub>F</sub>. Antiferroelectric-type switching found in ITO cells seems to contradict our finding. This contradiction can be explained by a strong surface anchoring on the glass, which prevents a bistable switching and leads to a hysteresisfree director reorientation. Another possibility is the formation of a modulated structure of the director as observed in freely suspended films, which suppress the uniform ferroelectric state in the absence of a field. As the polarization is still relatively small a relatively high threshold field is required for ferroelectric switching, despite the switching itself appears to be thresholdless.

Further increased polar coupling leads to the highly viscous phase  $M_1$ . The viscosity in this  $M_1$  phase might be due to the layer distorting effect provided by polar order and chirality to the layers, though a layer modulation is not evident from the XRD patterns. As polar order becomes stronger the packing density in the layers is further increased and the layers become sufficiently robust to withstand layer distortion, leading to the transition to the SmC<sub>s</sub>P<sub>A</sub> phase. The fact that there are two polarization peaks in the whole temperature region from SmC<sub>s</sub>P<sub>F</sub> via  $M_1$  to SmC<sub>s</sub>P<sub>A</sub> and that these peaks come closer by reducing the temperature without distinct jump at the phase transitions (Figure 11b–e) supports the suggested stabilization of the SmC<sub>s</sub>P<sub>A</sub> structure in the ITO cells.

As the largest enthalpy value is associated with the  $M_1$ -SmC<sub>s</sub>P<sub>A</sub> transition it is assumed that major changes take place at this transition and therefore all phases above this temperature are associated with a growing size of the polar SmC<sub>s</sub>P<sub>F</sub>

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Table 2. Comparison of 4-cyano substituted bent-shad mesogens with different linking groups  $X_1$  and  $X_2$ .

		H <sub>2n+1</sub> C <sub>n</sub> O A	$B$ $C$ $C$ $B$ $C$ $C$ $C$ $C$ $C$ $C$ $H_{2n+1}$	
Comp.	X <sub>1</sub>	X <sub>2</sub>	Phase transitions T/°C	Ref.
A12	-N=N-	-N=N-	Cr 71 (SmC <sub>s</sub> P <sub>A</sub> 70) M <sub>1</sub> 75 SmC <sub>s</sub> P <sub>F</sub> 83 SmC <sub>s</sub> P <sub>R</sub> 96 SmC 127 N <sub>CybC</sub> 137 Iso	
B12	-N=CH-	-CH=N-	Cr 65 SmCP <sub>A</sub> 122 SmC 141 SmA 188 Iso	[9]
C12	-00C-	-COO-	Cr 100 SmAP <sub>A</sub> 112 SmA 185 Iso	[10]
D12	-COO-	-00C-	Cr 103 (SmCP <sub>A</sub> " 68 SmCP <sub>A</sub> ' 75 SmCP <sub>A</sub> 94) SmC 109 N <sub>CvbC</sub> 129 Iso	[10]

domains and increasing polar correlation between them. Some of the continuous transitions, especially the  $\rm SmC-SmC_sP_R$  transitions, manifest only under certain conditions.

### 3.3. Achiral Symmetry Breaking

Another important observation is the chirality in the SmC/ SmC<sub>s</sub>P<sub>R</sub> phase region, which is observed by the formation of conglomerates of macroscopic chiral domains for all compounds in sufficiently thin cells. It appears at the  $N_{CybC}$ - SmC transition and is retained in the SmC<sub>s</sub>P<sub>R</sub> phase. The origin of this chirality should be the locally chiral SmC<sub>s</sub>P<sub>F</sub> structure in the polar domains. The coupling of this suprastructural chirality with the molecular chirality,<sup>[39]</sup> in this case with the conformational molecular chirality<sup>[40,41]</sup> favors molecular conformations with a helical shape and a distinct helix sense. As helical molecules cannot pack exactly parallel<sup>[42]</sup> the emergence of chirality leads to a reduction or even possibly to an inversion of the bend elastic constant  $k_{33}$ .<sup>[43]</sup> Formation of the chiral domains is supported by surface anchoring, as indicated by the thickness dependence of this phenomenon<sup>[8]</sup> and the absence of chiral domains in freely suspended films. However also the above mentioned specific molecular and superstructural factors provided by the compounds and their distinct modes of self-assembly are favorable for the occurrence of chiral segregation for the compounds under discussion. Hence, the combined effects of superstructural chirality and surface interaction should contribute to achiral symmetry breaking.

#### 3.4. Comparison with Related 4-Cyanoresorcinol-Based Bent-Core Mesogens

A comparison of compound A12 with the liquid crystalline properties of previously reported related compounds with the same chain length, where only the azo group is replaced by other linking groups, like -CH=N-, -COO- or -OOC-<sup>[9,10]</sup> (compounds B12-D12), is shown in Table 2.

Considering the mesophase stability (clearing temperatures) the azobenzene A12 is similar to compound D12 with phenylbenzoate wings. For both compounds, only tilted smectic phases were observed and a nematic phase  $(N_{CvbC})$  is formed at higher temperatures. The Schiff base mesogen B12 and the terephthalate C12 behave differently; they have about 50 K higher clearing temperatures; show no nematic phases and have a higher tendency to form non-tilted phases, the terepthalate forming exclusively SmA phases. The absence of N phases and the higher mesophase stability indicate a denser molecular packing, which is most likely due to the reduced electron density in rings B which provides stronger  $\pi$ -stacking interactions between these rings.<sup>[22]</sup> The presence of electron deficit rings seems also to favor the formation of nontilted phases. Compounds A12 and B12 with double bonds involved in the  $\pi$ -conjugation pathway between the benzene rings have about 30-40 K lower melting points compared to the ester compounds C12 and D12, being more flexible, but having a significant component of the C = O dipole aligned perpendicular to the molecular long axis. In all cases polar order develops in a stepwise manner via paraelectric SmA or SmC phases on decreasing temperature. The specific feature of the azobenzenes An is that this transition takes place via a new  $SmC_sP_R$  phase, a ferroelectric  ${\rm SmC}_{\rm s} P_{\rm F}$  phase  $^{[44,45]}$  and an additional highly viscous phase M1. Moreover, among the compounds mentioned in Table 2 only for A12 chiral domains were reported in the SmC range. Advantageous is also the low melting point of A12 which is comparable with the Schiff base compound B12. The azobenzenes An provide the additional option of modulation of the phase structure and mode of polar order by photoisomerization,<sup>[25–29]</sup> which is presently under investigation.

## 4. Summary and Conclusions

We have reported the synthesis and phase behavior of a series of photosensitive azo functionalized bent-core molecules consisting of 4-cyanoresorcinol as central core. This series allowed the investigation of the development of polar order in tilted smectic phases depending on chain length and temperature. It appears that with increasing polar domain size a ferroelectric phase is formed first which becomes modulated and then changes to the antiferroelectric phase. It turned out that this transition from nonpolar to polar phases is more com-



plex than that observed for the nontilted smectic phases, most probably due to the restrictions provided by tilt and chirality in the SmC<sub>s</sub>P<sub>F</sub> clusters. All observed LC phases, with exception of the SmC<sub>s</sub>P<sub>A</sub> phase at lowest temperature are composed of polar SmC<sub>s</sub>P<sub>F</sub> domains with distinct size. The SmC phase is a paraelectric SmC phase; especially in the SmC<sub>s</sub>P<sub>R</sub> region the domains reach an appreciable size and this region is considered as a close relative of the SmAP<sub>R</sub> phase. Overall, the phase structures are very sensitive to the conditions and the proposed models need further confirmation by additional investigations and comparison with phase sequences of other series of structural related compounds which are in progress. Besides these fundamental studies of the phase structures reported herein, the trans-cis photoisomerization of the azobenzene wings (see Figure S16) provides additional possibilities for the modification of the phase structure, polar order and chirality with these new bent-core mesogens, potentially leading to photoswitchable multifunctional ferro- and antiferroelectric LCs.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

# Acknowledgements

M. Alaasar is grateful to the Alexander von Humboldt Foundation for the research fellowship at the Martin-Luther University Halle-Wittenberg; A. Eremin acknowledges German Research Foundstion DFG (project ER 467/2) for the financial support.

> Received: July 8, 2013 Revised: August 15, 2013

Published online: November 27, 2013

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