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Stereochemical rules govern the soft self-assembly of achiral compounds: Understanding the heliconical liquid crystalline phases of bent-core mesogens

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Abstract

Spontaneous mirror symmetry breaking in achiral fluids is of actual interest for technological applications as well as for the understanding of the spontaneous formation of chirality and complexity in soft matter self-assembly. Here we report a series of achiral bent-shaped 4cvanoresorcinol bisterephthalates terminated by alkyl chains having a length *n* ranging from 2 to 22. Some of these achiral compounds with a specific chain length (n = 12-16)spontaneously form a short-pitch heliconical lamellar liquid crystalline phase with incommensurate 3-layer pitch and the helix axis parallel to the layer normal. The formation of this helical superstructure is observed at the paraelectric-(anti)ferroelectric transition, but only if it coincides with the transition from random to uniform tilt and with the transition from anticlinic to synclinic tilt correlation of the molecules in adjacent layers. For compounds with a bit longer chains (n = 18-22) the heliconical phase is only field-induced, but once formed it is stable in a distinct temperature range, even after switching off the field. The presence of the helix changes the phase properties and the switching mechanism in the LC phases from the naturally preferred rotation around the molecular long axis, which reverses the chirality, to a precession on a cone, which retains the chirality once established. These observations are explained by diastereomeric relations between two different and coexisting modes of superstructural chirality. One is the layer chirality, resulting from the combination of tilt and polar order, and the other one is provided by the helical twist evolving between the layers. At lower temperature, as the tilt is reduced, the helical structure is lost and replaced by a nontilted, nonchiral and ferreoelectric switching lamellar phase.

1. Introduction

In biological systems chirality of proteins, carbohydrates and DNA has developed into stable systems from initially achiral sources.¹ Formation of helical superstructures²⁻⁶ chirality amplification^{7,8} and spontaneous mirror symmetry breaking, are nowadays well documented for solid state and crystalline assembles.² In contrast, for the fluid state spontaneous mirror symmetry breaking was assumed to be impossible due to the significant contribution of the mixing entropy; nevertheless, it was experimentally observed recently.⁹ As biological chirality has presumably developed in the fluid state an understanding of the symmetry breaking in fluids is of significant importance.



Figure 1. Chirality and mirror symmetry breaking in LC soft matter formed by permanently and transiently chiral rod-like or bent molecules; a) longitudinal coupling of the helical twist leads to: c) heliconical smectic phases (SmC_{α}, SmC_{TB}, etc.) or d) the twist-bend nematic phases (N_{TB}), whereas b) transversal helix coupling leads to e) chiral nematic phases (N*), f) helical nanofilament phases (HNF) or g) the sponge-like dark conglomerate phases.

Liquid crystals (LCs) represent fluid systems with long range orientational or positional order, thus representing simple model systems for studying the fundamental concepts of symmetry breaking at the cross-over from long-range order in crystalline solids to short-range order in the isotropic liquids.¹⁰⁻¹² Moreover, LCs are of significant technological importance for displays and numerous non-display applications.¹¹ Especially, helical

superstructures formed by LCs arose interest as switchable optical and photonic materials for tunable lasers, circular polarized emitters and numerous other technological applications.¹³ It is known that chirality in LC systems can result from a permanent molecular chirality, providing a helical twist of molecular conformation with a twist sense determined by the sense of permanent chirality, and thus leading to helical LC phases with fixed helix sense (Fig. 1). In the nematic phases, involving only orientational order, permanent chirality of the involved molecules provides a helical twist between the molecular long axes (transversal twist correlation, Fig. 1b) leading to the chiral nematic phases (N*, see Fig. 1e).¹⁴ However, if there is additional positional order by formation of layers in the smectic phases, then these layers compete with this mode of twist, which distorts the layers and leads to a series of chirality frustrated LC phases (Fig. 1f,g).¹⁴⁻¹⁶ If the helical twist develops longitudinally, i.e. between the short molecular axes (Fig. 1a), then undistorted layers can be retained and heliconical lamellar phases, having the helix parallel to the layer normal, arise (Fig. 1c). These heliconical smectic phases are known for chiral rod-like molecules for which long pitch heliconical phases were typically observed in the synclinic SmC_s* and the anticlinic SmC_a* phases. However, the formation of short pitch heliconical LC phases (SmC_{α}^{*} , SmC_{FI}^{*}) requires a "strong" permanent chirality and a high enantiomeric purity of the involved molecules.14,17,18

The more surprising is the recent observation that similar short pitch heliconical phases can even be observed for achiral molecules.9,12,19,20 The use of achiral compounds reduces the costs, because it is independent on the chiral pool, and more importantly, both senses of handedness are easily accessible in a process of mirror symmetry breaking and chirality amplification.^{2,3,7,9,12} Moreover, this transient chirality of achiral molecules has the potential to be switched by external stimuli either on-off 21,22 or between the enantiomeric states.^{23,24} The mirror symmetry breaking in bent molecular systems is of significant interest²⁵⁻³⁰ because there are different sources of superstructural chirality.^{12,39,30} One is provided by the tilted organization of the molecules with uniform polar direction, providing a chiral C_{2v} symmetry of the layers (layer chirality, Fig. 2a).²⁶ The combination of tilt direction and polar direction determines the chirality sense which is inverted either by reversing tilt direction or polar direction and retained by the simultaneous inversion of both. As shown in Figure 2b,c, the chiral layers can pack in stacks with uniform or opposite tilt direction (s =synclinic or a = anticlinic) and polar direction (F = ferroelectric = synpolar or A = antiferroelectric = antipolar) thus leading to four stereoisomeric superstructures (see Fig. 2b,c). The SmC_sP_F and SmC_aP_A phases are homogeneously chiral because they are formed by layers

with uniform chirality sense (shown in blue or red). The other two, SmC_sP_A and SmC_aP_F, are formed by alternating layers with opposite chirality (blue and red) and therefore are achiral (racemic).²⁶ Another source of chirality is provided by the significant transient chirality of energy minimum helical molecular conformations of these bent-core molecules.^{12,31,32} This transient molecular helicity provides a twist and the synchronization of the twist sense could lead to mirror symmetry breaking.¹² In the cases of bent-core self assembly, known so far, the twist occurs transversal between the molecular long axes (Fig. 1b) and the helix axis develops along the layers, leading to layer distortion. Stiff layers break into helical nano-ribbons (helical nano-filament phases, HNF, B4 phases, Fig. 1f) ³³⁻³⁸ and soft layers form more disordered sponge-like structures, the so-called dark conglomerate phases (DC-phases, Fig. 1g).^{12,25,30, 39-44}



Figure 2. Layer chirality and the structures of the polar SmC phases of bent-core mesogens. a) The orthogonal combination of tilt and polar order leads to reduced C_{2v} symmetry and superstructural chirality of the layers (reproduced with permission from ref.²⁵, copyright 2006, RSC); blue/red color indicates the chirality sense. b, c) shows the four diastereomorphic structures of tilted polar smectic phases of bent-core mesogens: b) side views, showing synpolar ("ferroelectric": P_F) and antipolar (P_A) order in adjacent layers and c) front views showing the tilt correlation (C_a and C_s refer to the anticlinic and synclinic tilt, respectively) of the bent-core molecules in adjacent layers; here the polar direction is indicated by dots (pointing out from back to front) and crosses (pointing to the back); reproduced with permission from ref.⁵¹, copyright 2019, RSC.

Herein we focus on helicity occurring along the layer normal (longitudinal twist between the short, secondary, molecular axes, Fig. 1a) and its effects on the LC self-assembly of bent molecules. The investigated compounds 1/n (Scheme 1) are based on the 140° bent 4cvanoresorcinol core ($\alpha = 140^{\circ}$) with a reduced molecular bent compared to the 120° angle of ordinary bent-core molecules.⁴⁵⁻⁵¹ In these molecules the 4-cyanoresorcinol core is connected with two electron deficit terephthalate wings, 52-54 providing a dense packing. 45, 55, 56 A summary of previous work on selected individual members of the 4-cyanoresorcinol based LCs and the development of the distinct models of their phase structures is given in reference⁵⁷ as well as in Section S4 and Table S2 in the SI. Compounds 1/n with n = 14 and 16 are of special interest because for 1/16 the existence of a heliconical smectic LC phase was observed by optical investigations^{19,58-61} and AFM¹⁹ and was corroborated for 1/14 by soft resonant X-ray scattering (RSoXR).²⁰ Herein we report the complete homologous series of compounds 1/n from n = 2 to 22 to provide a fundamental understanding of spontaneous mirror symmetry breaking by helix formation and its effect on the phase sequence and the phase structure in the context of general stereochemical rules and based on diasteromeric relations between layer chirality 26 and helix chirality. It is shown that helix formation takes place at the paraelectric-(anti)ferroelectric transition if there is uniform layer chirality and a weak layer coupling at the SmA-SmC transition coinciding with the transition from anticlinic to synclinic tilt. This work also answers the question, why in some cases the heliconical phase represents a ground state structure, whereas in others it is only field induced. The relations with other heliconical structures, as for example found in the twist-bent nematic (N_{TB}, see Fig. 1d),⁶²⁻⁶⁶ related smectic phases (SmC_{TB}) of bent mesogenic dimers⁶⁷ and especially the heliconical smectic phases of permanently chiral rod-like mesogens (SmC_{α}^{*} , SmC_{FI}^{*}) phases),¹⁷ will be discussed briefly. Interestingly, with lowering temperature the helix and the chirality are removed⁵⁷ and it is shown that under these conditions a non-tilted and ferroelectric switching SmA'P_F phase represents an alternative non-chiral way for the transition from anticlinic to synclinic tilt.

2. Experimental

Synthesis. - The synthesis of the compounds was conducted as shown in Scheme 1 by acylation of 4-cyanoresorcinol with the properly substituted benzoic acid chlorides in CH_2Cl_2 in the presence of pyridine.¹⁹ The synthetic procedures and analytical data of the new compounds are collated in the supporting information, together with the structural analysis

data. The synthesis and analytical data of compounds 1/6, 1/12, 1/16 and 1/18 have been reported in previous work.^{19,56}



Scheme 1. Synthesis of compounds 1/*n*; *Reagents and conditions*: i: 1. 4-substituted benzoic acid, SOCl₂, 80 °C, 2 hrs, 2. phenol, DCM, pyridine, 50 °C, 2 hrs; ii: NaClO₃, KH₂PO₄, resorcinol, *t*-BuOH, 20 °C, 1 h.

Methods. – The investigation of the synthesized compounds was performed by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), X-ray diffraction (XRD) and by switching experiments, electro-optical and dielectric investigations as described in the Methods section in the SI.

3. Results and Discussions

The LC phases, transition temperatures and transition enthalpy values of all compounds, as recorded on heating, are collated in Table 1, whereas Figure 3 shows graphically the phase sequences on cooling (see Table S1 for the corresponding numerical values).

3.1. Nematic and uniaxial smectic phases of the short chain compounds 1/2 - 1/6

Only a nematic phase (N) was observed for the shortest compound 1/2. From the XRD patterns of magnetically aligned samples it can be deduced that this nematic phase is of the cybotactic type, characterized by a relatively high intensity of the small angle scattering. This scattering is perpendicular to the maxima of the diffuse wide angle scattering, indicating an on average non-tilted organization of the molecules in the cybotactic clusters (N_{CybA}, see Fig.

4a,b for the diffraction patterns of 1/4). This type of non-tilted cybotactic nematic phases is rare for bent-core mesogens⁶⁸ which usually form the skewed cybotactic nematic phases (N_{CybC}) .^{55,68} This N_{CybA} phase is observed for 1/4 as a high temperature phase only in a small temperature range above a uniaxial smectic phase (SmA) and it is removed for 1/6 and all following homologues. Upon cooling, at 126 °C, the diffuse small angle XRD of 1/4 condenses into a layer reflection (d = 3.4 nm; $L_{mol} = 3.9$ nm, $d/L_{mol} = 0.87$) with its second order on the meridian (Fig. 4d,e) and perpendicular to the maximum of the diffuse wide angle scattering on the equator, thus indicating the transition to an orthogonal smectic phase (SmA). In optical investigations the typical fan texture with extinction brushes parallel to the polarizers in planar alignment and the isotropic appearance in homeotropic alignment confirm the SmA phase.





1/ <i>n</i>	$T/$ °C [$\Delta H/$ kJ·mol ⁻¹]
1/2	Cr 117 [32.2] (N _{cybA} 117 [0.3]) Iso
1/4	Cr 153 [53.0] (SmC _a P _A 90 [1.5] SmA 126 [1.7] N _{CybA} 129 [0.8]) Iso
1/6 ⁵⁶	Cr 128 [39.6] (SmC _a P _A 113 [1.1] SmAP _{AR} ~118 [-]) SmA 150 [5.3] Iso
1/8	Cr 125 [43.9] (SmC _a P _A 116 [0.6] SmAP _{AR} ~118 [-]) SmA 161 [6.8] Iso
1/10	Cr 112 [38.2] SmC _a P _A 114 [0.5]) SmAP _R / SmA 165 [7.8] Iso
1/12 ⁵⁶	Cr 114 [42.6] (SmC _a P _A 101 [-] Sm(CP) ^{hel} 112 SmC _a P _A 113 [0.8]) SmAP _R /SmA ^[b] 167 [8.0] Iso
1/14	Cr 113 [48.3] (SmC _a P _A ^[c] 83 [-] SmC _a P _A ^(hel) 99 [-] Sm(CP)^{hel} 112 [1.0]) SmAP _R /SmA 165 [8.0] Iso
1/16 ¹⁹	Cr 110 [47.9] (SmA'P _F ^[d] 83 [-] SmC _a P _A 92 [-] Sm(CP) ^{hel} 110 [0.8]) SmC _x P _R 127 [-] SmAP _R /SmA 162 [7.7] Iso
1/18 ¹⁹	Cr 114 [60.8] (SmA'P _F ^[d] 85 [-] SmC _s P _A 110 [1.1]) SmC _s P _R ^[*] 135 [-] SmAP _R /SmA 161 [7.4] Iso After field treatment: ^[e] Cr 71 SmA'P _F 85 Sm(CP)^{hel} 110 SmC _s P _R ^[*] 135 SmAP _R /SmA 160 Iso
1/20	Cr 106 [79.5] (SmA' $P_F^{[d]}$ 87 [-]) SmC _s P_A 108 [1.2] SmC _s P_{AR} 113 [-] SmC _s 130 [-] SmA 156 [6.5] Iso After field treatment: ^[e] Cr' 82 SmA' P_F 86 SmC _s P_A 95 Sm(CP) ^{hel} 106 SmC _s P_{AR} 111 SmC _s 129 SmA 155 Iso
1/22	Cr 108 [91.7] (SmC _s P _A 105 [1.3] SmC _s P _{AR} 108 [-]) SmC _s 130 [-] SmA 153 [5.8] Iso After field treatment: ^[e] Cr' 87 SmC _s P _A 100 Sm(CP) ^{hel} 102 SmC _s P _{AR} 106 SmC _s 128 SmA 152 Iso
	^[a] Phase transitions on heating, for data on cooling, see Fig. 3 and Table S1. The references refer to the first reported synthesis of the compounds, for a complete list of references, see Table S2. All transition temperatures with enthalpies represent peak maxima in the DSC traces, recorded on heating with a rate of 10 K min ⁻¹ ; transitions without enthalpies were determined under similar conditions by optical or electro-optical methods in thin cells. Values in parenthesis refer to monotropic transitions, observed in second heating scans if crystallization could be suppressed. There could be a slight deviation of the DSC values given in Tables 1 and S1 from those observed by other investigations, usually performed in thin films (1-2 K, larger deviations can be found for the crystallization temperatures). Abbreviations: Cr, Cr' = crystalline solids (Cr' indicates an optically uniaxial crystalline phase, appearing with the same fan-like optical texture as SmA and Sm(CP) ^{hel} phases, see Fig. S51); Iso = isotropic liquid, N _{cvbA} = cybotactic nematic phase; SmA = de Vries type uniaxial lamellar phase; SmAP _R = high permittivity

paraelectric range of the SmA phase showing a single broad polarization peak per half period of an applied triangular E-field; $SmAP_{AR} = high permittivity paraelectric SmA range showing two broad polarization peaks; <math>SmA'P_F = non-tilted$ and ferroelectric switching lamellar phase; SmC_aP_A , anticlinic tilted and antiferroelectric switching lamellar phase; SmC_aP_A phase with short range helical structure; SmC_sP_A , synclinic tilted and antiferroelectric switching lamellar phase; $Sm(CP)^{hel} = heliconical lamellar phase; <math>SmC_s = synclinic tilted$ paraelectric lamellar phase; $SmC_sP_R^{[*]} = high$ permittivity paraelectric SmC_s phase showing a single broad polarization peak and domains with opposite optical rotation in homeotropic alignment (^[*]); $SmC_xP_R = high$ permittivity paraelectric SmC phase showing a single broad polarization peak; depending on the conditions the extinctions in the planar texture are either parallel or inclined to the direction of the polarizers. ^[b] There is no transition enthalpy for the $SmA-SmAP_R$ transition as mistakenly stated in ref⁵⁶, the corrected DSC is shown in Fig. 6b. ^[c] This phase was designated as SmC_aP_F in ref.²⁰, the reasons for using SmC_aP_A are given in Section 3.6. ^[e] Phase transitions were determined by optical observations (crystallization temperatures were observed on cooling).



Figure 3. Bar diagram of compounds 1/n showing the development of the LC phases on cooling and depending on chain length; for 1/18-1/22 the phase structures depend on pre-treatment; ^a shows the phase transitions before applying an external electric field and ^b after application of a few cycles of an AC field (see Table 1 for abbreviations and Table S1 for numerical values).



Figure 4. 2D-XRD patterns of a magnetically aligned sample and textures of compound 1/4, a-c) in the nematic phase at T = 133 °C (the double headed arrow indicates the direction of the magnetic field) and d-f) in the SmA phase at T = 125 °C; a,d) wide angle scans b,e) SAXS patterns and c,f) textures as observed between crossed polarizers; the arrows in c) indicate the directions of polarizer and analyzer.

3.2 Transition from randomized to anticlinic tilt in the smectic phases of compounds 1/4-1/10

On further cooling, at T = 90 °C, an additional phase transition is observed in the smectic range of compound 1/4, associated with a small peak in the thermograms ($\Delta H = 1.5$ kJ mol⁻¹, Table 1). Optical investigation of homeotropically aligned samples (layer planes organized parallel to the substrate surfaces) between crossed polarizers show that at this phase transition the isotropic appearance of the homeotropic SmA phase is replaced by a gray schlieren texture as typical for the transition to a biaxial smectic phase (Fig. 5a \rightarrow d). The developing periodic stripe pattern (yellow arrows in Fig. 5d) is typical for biaxial SmA_b phases as well as for anticlinic tilted SmC_a phases.⁶⁹⁻⁷¹ The presence of 4-brush disclinations (red arrow) between the stripes is in favour for an anticlinic SmC_a structure of this biaxial smectic phase; in a non-tilted biaxial SmA_b phase only two-brush disclinations would be expected.⁶⁹ In planar alignment, where the layers are organized perpendicular to the substrate surfaces, the dark extinctions retain their position parallel to the directions of polarizer and analyzer, confirming the absence of a uniform (synclinic) tilt in the low temperature smectic phase (Figs. S1, S2 and S7). Associated with this phase transition a speckled texture develops (Fig. $5b\rightarrow e$) which is unique for the anticlinic SmC_a phases (SmC_aP_A) of the compounds under investigation. It is assumed to be due to two different modes of planar alignments of the bent molecules, either with the bow plane parallel (low Δn , green) or perpendicular to the substrate surfaces (high Δn , yellow), see Fig. 5f, views B and A, respectively.²⁰



Figure 5. Optical investigation of compound 1/4 a, b) in the SmA phase at T = 118 °C and d,e) in the SmC_aP_A phase at T = 80 °C. a, d) show the homeotropic textures between plane microscopic glass plates and b, e) the planar textures (PI coated ITO cell 6 µm, *R* is the rubbing direction of the substrates); b) show the smooth texture in the SmA phase and e) the "speckled" texture in the SmC_aP_A phase; the inset in e) shows the polar directions in the distinct domains. c, f) show the models of the molecular organization in the two phases (the bent molecules are simplified and shown as rods; dots and crosses indicate the polar direction, corresponding to the bow direction, pointing out of and into the plane of projection, respectively; molecules in gray are tilted out of the plane and their polar direction is arbitrary); c, f) show the directions of view in homeotropic (perpendicular to the layer planes) and planar alignment (parallel to the layers); f) in the speckled texture the view in planar samples is along B in the green speckles and along direction A in the yellow continuum (for related textures of compounds 1/6 and 1/8, see Figs S1, S2, S7 and S11).

This transition with small enthalpy is observed for all investigated compounds and it is the only transition in the whole LC range which is associated with an enthalpy change, and for all compounds 1/6-1/20 it takes place around 112 ± 4 °C, as shown in Fig. 6 for the DSC traces of compounds 1/6, 1/12 and 1/18 as representative examples (see also Tables 1, S1 and Fig. 3). For compounds 1/4 to 1/14 this transition coincides with the onset of phase biaxiality, whereas for all following compounds with longer chains phase biaxiality already develops before this transition. In the powder XRD patterns there is an almost continuous increase of the layer spacing with decreasing temperature, but neither the expected decrease of *d*, nor any step in the *d*-values or change of the inclination of the d=f(T) curve takes place at this

transition (Fig. 7a). The absence of a *d*-value discontinuity at the transition from the SmA phase to the biaxial phase suggests that tilt is already present in the SmA phase, but it is randomized as typical for de Vries phases.^{72,73} The continuous increase of *d* with lowering temperature is attributed to a growing packing density of the molecules, leading to a stretching of the alkyl chains, compensating and exceeding the shrinkage of *d* due to the tilt.



Figure 6. Representative DSC traces (10 K min⁻¹) of compounds a) 1/6, b) 1/12 and c) 1/18 recorded on first heating (dashed magenta line) following cooling (blue) and on second heating after cooling to 100 °C (red). The insets show enlargements of the paraelectric-(anti)ferroelectric transition peak in second heating and on cooling (for other DSCs, see SI).



Figure 7: a) Dependence of the layer distance *d* from chain length and temperature; the gray bar indicates the temperature range of the paraelectric-(anti)ferroelectric transition; b) *d*-values measured at 100 °C and molecular length (L_{mol} , determined with CPK space filling molecular models in the most stretched conformation with 140° bending angle and *all-trans* conformation of the alkyl chains) of compounds 1/n; the values of 1/14 were taken from ref.²⁰; for individual plots of *d*-values, see Figs. S3, S8, S12, S16, S27, S33, S44 and S53.

The ratio d/L_{mol} is in the range between 0.85-0.89 for all compounds 1/4-1/16 (Fig. 7b), which in principle would allow tilted as well as non-tilted arrangements (see Section S4 in the SI). XRD of aligned samples also provides no clear indication of tilt (see Figs. S4, S15 and S28). Only in few cases of compounds 1/12-1/16, electro-optical investigations uncover the actually tilted organization with an optical tilt (tilt of the aromatic cores) of 15-20°.^{20,57,59} For compounds 1/18-1/22 with longer chains the d/L_{mol} ratio becomes smaller (0.80, Fig. 7b), in line with an enhanced tendency to form synclinic tilted SmC_s phases (Table 1), though the tilt angle itself appears to be not increased. In the polar smectic phases of compounds 1/4-1/10 with short chains the switching takes place exclusively by rotation around the long axis and in this case a SmC_aP_A phase cannot be distinguished from a non-tilted SmAP_A phase by optical and electro-optical investigations. However, the linear increase of *d* from 1/6 to 1/14 (Fig. 7b) suggests that the tilt should be almost identical in these smectic phases. Moreover, in the

speckled texture below the phase transition around $112 \pm 4^{\circ}C$ there are areas with increased birefringence (yellow) due to the developing polar order (see below) as well as areas with slightly reduced birefringence (green) compared to the SmA texture (Fig. 5b \rightarrow e), the latter might indicate the emerging tilt and thus supports the SmC_aP_A structure.



3.3 Development of polar order and the paraelectric-(anti)ferroelectric transition

Figure 8. Polarization current response curves depending on alkyl chain length. a) 1/4, b) 1/6, c) 1/8 and d) 1/10 as measured in a 6 μ m PI coated ITO cell at the indicated temperatures in the SmC_aP_A range about 10 K below the paraelectric-(anti)ferroelectric transition temperature under an applied peak-to-peak voltage of 160 V_{pp}; for data at other temperatures, see Figs. 9, S5, S9 and S14.

Electro-optial investigations. - For the short chain compound 1/4 there is no response on an electric field in the SmA phase region, meaning that this SmA phase is considered as apolar. Also in the biaxial smectic phase occurring below the transition peak at 90 °C no polarization peaks can be observed under a triangular wave AC field (Fig. 8a), even at an applied peak-to peak voltage of 200 V_{pp} . However, the shape of the polarization current curve shows that at higher voltage an antiferroelectric switching could be expected. For compound 1/6 two widely separated very broad peaks appear at 118 °C in the SmA range close to the DSC transition peak which become sharp at the phase transition at T = 113 °C (see Figs. 8b and S5). This means that in this SmA phase polar cluster (ferroelectric grains) with antipolar correlation grow under the applied field, leading to a high permittivity paraelectric SmAP_{AR} range⁷⁴ upon approaching the uniaxial-biaxial transition (Fig. 9a).^{48,49,53} Below the phase transition two sharp polarization peaks indicate antiferroelectric switching which reaches polarization values of about 500-700 nC cm⁻². Considering the anticlinic tilted organization of the molecules this phase is designated as SmC_aP_A. The two polarization current peaks come closer by alkyl chain elongation (Fig. 8c,d), indicating an increasing correlation length of polar order with growing chain length.



Figure 9. Distinct modes of development of the polarization current curves: a-c) via SmAP_{AR} for compound **1/8** and d-i) via SmAP_R for compound **1/10** (6 μ m PI coated ITO cell, 160 Vpp, 10 Hz) measured with decreasing temperature, the encircled peak is due to conductivity; see Fig. S9 and S14 for additional temperatures.



Figure 10. a) Switching in the helix-free SmC_aP_A phase by rotation around the long axis reverses the polar direction (dot vs. cross) and chirality in every second layer (indicated by red/blue color), the tilt direction does not change and therefore the position of the extinctions in the textures is retained (1/10 at 100 °C); b) In the $Sm(CP)^{hel}$ phase switching takes place by precession on a cone which reverses the polar direction and the tilt direction simultaneously, while the sign of layer chirality is retained; this switching is associated with a rotation of the optical axis (optical switching), often associated with tilt domain formation (1/14 at 110 °C).

In the SmA phases of compounds 1/10-1/14 only one broad single polarization peak develops upon approaching the paraelectric-(anti)ferroelectric phase transition on cooling (see

Fig. 9d). This single peak indicates a Langevin switching of ferroelectric grains with $\text{SmC}_{s}P_{F}$ structure developing a synpolar correlation under an applied E-field (SmAP_R range⁷⁵). As shown in Figure 9d \rightarrow e \rightarrow f for compound 1/10, it splits into two broad peaks just at the uniaxial-biaxial transition, and on further cooling the peaks become sharper in the macroscopic polar SmC_aP_A phase. Hence, with alkyl chain elongation the high permittivity paraelectric phase changes from SmAP_{AR} to SmAP_R (Fig. 3, Table1). For all compounds 1/4-1/10 the switching in the SmC_aP_A phase takes place by rotation around the long axis (SmC_aP_A \leftrightarrow SmC_aP_F) under all conditions, i.e. the switching can only be detected by a change of the birefringence, whereas the orientation of the dark extinctions, and thus the orientation of the molecules does not change (Figs. 10a, S13).⁷⁶



Figure 11. The plot of dielectric relaxation strength, $\delta \varepsilon_2$, and relaxation frequency, $f_{R,2}$, of compound 1/12, for the mid frequency process, P2, as a function of temperature.

Dielectric investigation. - Dielectric spectroscopy of 1/12, as example, was performed in the frequency range between 1 Hz and 10 MHz and three relaxation processes, P1, P2 and P3 were observed in the measured frequency range (for details, see Fig. S20 and related discussions in the SI). The medium frequency relaxation process P2, exists in the measured frequency range in all LC phases and was assigned to the polar switching mechanism. Figure 11 shows the temperature dependence of dielectric strength and relaxation frequency for P2. As the sample was cooled down from the isotropic phase, initially, $\delta\epsilon_2$ does not change significantly whereas $f_{R,2}$ continuously decreases. When the sample approaches 120 °C, a massive increase in $\delta\epsilon_2$, changing from ~5 to 45 and a significant decrease in $f_{R,2}$ (from 3*10⁶ to 2*10⁴ Hz) were observed. The increase of $\delta\epsilon_2$ confirms ferroelectric grains with growing polarization. Below T = 112 °C, in the polar phase range, $\delta\epsilon_2$ decreases, still remaining high in

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magnitude, with a smooth step like change in both $\delta \varepsilon_2$ and $f_{R,2}$ at the Sm(CP)^{hel} to SmC_aP_A phase transition (see next section). Further, $\delta \varepsilon_2$ continuously decreases until crystallization at 60 °C. This decrease is due to the significant growth of the ferroelectric grains, fusing to almost infinite layers in the polar smectic phases. Thus the phase transition around 112-113 °C can be attributed to the paraelectric-(anti)ferroelectric transition with Curie Weiss type divergence (see Fig. 11).⁷⁷

3.4 Helix formation in the smectic phases of the medium chain length compounds 1/12-1/16 - the heliconical smectic phase Sm(CP)^{hel}

For compounds 1/12-1/16 additional uniaxial and polar smectic phases were observed below the paraelectric-(anti)ferroelectric transition. Similar to the shorter homologues, on cooling in homeotropic samples of 1/12 a birefringent schlieren texture is formed at the onset of the transition from SmAP_R to SmC_aP_A at 113 °C (similar to Fig. 5d). However, the birefringence significantly decreases immediately after the phase transition and the homeotropically aligned phase becomes almost isotropic at the end-set of the phase transition at T = 111 °C (Fig. $12d \rightarrow e \rightarrow f$). The birefringence increases again on further cooling below ~101 °C (Fig. 12g), but without any indication of an additional phase transition in the DSC traces (Fig. 6b). For compounds 1/14 and 1/16 the homeotropic samples become even completely dark at the endset of this DSC peak, indicating the transition to a uniaxial LC phase (Figs. S23 and S29). For these compounds the small birefringent range around the phase transition can only be observed upon fast cooling (>10 K min⁻¹) whereas upon slower cooling or upon heating no intermediate birefringent state is observed. On further cooling the birefringence of the homeotropic sample emerges again at 91 °C and 90 °C, respectively (see Table S1 and Figs. 3, S23 and S29). This change is also not associated with a DSC peak. In planar samples the smooth SmA-like fan texture with extinctions parallel to the polarizers is observed at all temperatures; there is only a faint, almost invisible, stripe formation on the fans at the paraelectric-(anti)ferroelectric phase transition (Fig. 12a \rightarrow b) and a clearly visible strip pattern across the fans develops at the transition to the biaxial phase (Fig. $12b\rightarrow c$), which then changes to the speckled texture as typical for the SmC_aP_A phase.



Figure 12. Textural changes observed at the SmA \rightarrow Sm(CP)^{*hel*} \rightarrow SmC_aP_A transitions of 1/12 a-c) in a planar cell (6 µm PI coated ITO cell) and d-g) in homeotropic alignment (ordinary, non-treated microscopy glass plates) at the indicated temperatures (for textures of 1/14 and 1/16, see Figs. S23-S25 and S29 and S30).

Uniaxiality of a tilted smectic phase requires that either the tilt is randomized as in the de Vries SmA phases,^{72,73,78} or that a short pitch helical superstructure with a helix axis perpendicular to the layer planes is formed.^{78,14} A helical structure was first proposed for the polar and uniaxial smectic phase of compound 1/14.⁵⁸ It was observed that an in-plane electric field, applied to a homeotropic aligned sample at first induces a birefringence, but at a certain voltage a uniaxial state is formed. ^{58, 79,80} This was interpreted as deformation of a helical phase, designated as $SmAP_{\alpha}$.⁵⁸ The uniaxial state was assumed to result from helix deformation into a four layer structure with 90° twist between the secondary optical axes in adjacent layers.⁵⁸ Later, as the tilted organization was recognized, it was renamed to $SmCP_{\alpha}^{52}$ $Sm(CP)_{\alpha}^{20}$ and $SmC_{s}P_{F}^{hel 19}$ and is herein designated as $Sm(CP)^{hel}$ (for more details, see Section S4 in the SI). Helix formation was further confirmed for compound 1/16 by the observation of the so-called deformed helical ferroelectric (DHF) effect in planar cells, indicating a helix deformation under an electric field¹⁹ similar to that previously known for helical SmC* and SmC_{α}* phases of permanently chiral molecules.⁸¹ In addition, the helical superstructure with a pitch of only 14 nm was visualized by AFM of freeze fractured samples¹⁹ and finally unambiguous proven by soft resonant X-ray scattering at the carbon Kedge (RSoXS, see Fig 13a), confirming a pitch of 15 nm for compound 1/14.²⁰ The pitch of almost three times the layer distance is not exactly commensurate with a three-layer helix (see Figs. 3,13b,c and Table 1). Only one resonant scattering without umklapp peak confirms the formation of a SmC_{α}^* -like heliconical phase with incommensurate 2.8-layer periodicity $(Sm(CP)_{\alpha})$. Herein we prefer to use $Sm(CP)^{hel}$ as a general phase assignment of heliconical smectic phases, also including possible commensurate phase types.



Figure. 13. The Sm(CP)^{hel} phase. (a) Development of the XRD data (SAXS and RSoXS) in the LC phases of 1/14 depending on temperature; (b) shows a computer generated model of the helical structure with twist of 110° and 140° bent-core angle and (c) shows a simplified models; the helical pitch *P* in terms of a number of smectic layers is incommensurate and smaller than 3 times the thickness of a layer; a, b) were reprinted with permission from refs. 20 and 61, respectively, copyright (2019) by the American Physical Society (http://dx.doi.org/10.1103/PhysRevLett.122.107801;http://dx.doi.org/10.1103/PhysRevMateri als.3.045603).

In addition, the RSoXS investigation indicated the persistence of a local helical structure with a pitch between 13 and 15 nm (between two and three layers) in the birefringent SmC_aP_A range of 1/14 below the $Sm(CP)^{hel}$ phase down to 83 °C (Fig. 13a, encircled diffuse scattering).²⁰ The decreasing intensity of the diffuse scattering is associated with an increasing intensity and sharpening of the resonant scattering corresponding to the

double layer periodicity (d_{02}). This short range heliconical structure is assumed to contribute to the special properties of this SmC_aP_A^(hel) phase occurring in the vicinity of the heliconical smectic phase.



3.5 Effects of the heliconical structure on the switching mechanism

Figure 14. Electrooptical investigation of the switching process of compound 1/12 in planar alignment (6 μ m PI coated ITO cell) under an applied DC field in the Sm(CP)^{*hel*} range at *T* = 105 °C with modles of the distinct field-induced states; see Fig. S19 for the effect of changing the field direction.

Two distinct textures were induced in the temperature range of the $Sm(CP)^{hel}$ phase by application of an electric field. For compounds 1/12-1/14 a unique periodic "tiger stripe" texture develops in a limited temperature range of the $Sm(CP)^{hel}$ phase under an applied electric field with a certain strength (Fig. 14b).²⁰ Further increasing the applied voltage leads to the typical tilt domain texture indicating field induced SmC_sP_F states with opposite tilt direction (Fig. 14c). The transition from tiger stripes to tilt domains is shifted to higher temperature from 1/12 to 1/14; for 1/14 tiger stripes can only be found at the transition from $SmAP_R$ to $Sm(CP)^{hel}$ and for 1/16 no tiger stripes and exclusively the tilt domains can be observed. In the same sequence the threshold fields for tiger stripe formation and tilt domain formation decreases, meaning that the synclinic tilted states become stabilized with growing chain length, being in line with the observation of a SmC_aP_A - SmC_sP_A transition by further alkyl chain elongation from 1/16 to 1/18 (see Fig. 3). Thus, the field-induced tilt domain texture with synclinic tilt correlation becomes dominating with decreasing temperature and growing alkyl chain length. The dark and bright tiger stripes exchange upon inverting the field direction (Fig. S19), thus the stripes appear to represent regular arrays of SmC_sP_F layer stacks with opposite tilt direction and chirality. The periodicity obviously results from a residual long pitch heliconical organization in the micrometer range, after field induced deformation and partial unwinding of the short pitch heliconical $Sm(CP)^{hel}$ structure (Fig. 14e). Complete unwinding of the helix at higher voltage leads to the tilt domains, indicating a switching to a field stabilized non-helical SmC_sP_F state (Fig. 14f).



Figure 15. Diastereomeric relations between layer chirality and helix chirality (blue/red) in the $SmC_aP_A^{(hel)}$ phase with short-range helix; the blue-blue interactions are arbitrarily assumed to be low energy whereas blue-red combinations are considered to have higher energy (the used textures are only for illustration). a) Switching by rotation around the long axis reverses the layer chirality in half of the layers, which becomes chirality inverted and thus incompatible with the helical chirality; this leads to a higher energy for this diastereomeric pair between residual helix and developing layer chirality. b) Switching by precession on a cone retains the layer chirality and the low energy diastereomeric pair is retained during switching.

For compound 1/14 the switching into field induced tilt domains is retained in the adjacent $SmC_aP_A^{(hel)}$ phase with short range heliconical organization, occurring below the $Sm(CP)^{hel}$ phase.²⁰ As the naturally preferred switching for the weakly bent 4-cyanoresorcinols 1/*n* in the helix-free SmC_aP_A phases is around the long axis, which does not lead to tilt domains and retains the orientation of the extinctions parallel to the polarizers. This means that the residual helix obviously hinders the rotation around the long axis, because this process would invert the layer chirality of every second layer, thus leading to the racemic SmC_aP_F structure where half of the layers assumes the thermodynamically less stable (higher energy) state of the diastereomeric pair of layer chirality and helix sense (red layer + blue helix, Fig. 15a). Therefore, the presence of a helix changes the switching mechanism from SmC_aP_F by rotation around the long axis (chirality flipping) to $SmC_aP_A \leftrightarrow SmC_sP_F$ by a

precession on a cone, which retains the layer chirality of all layers, but flips the optical axis (optical switching, Fig. 15b). Hence, in this class of compounds the switching on a cone is an indication of a long- or short-range helical organization. Upon further cooling of compound 1/14 the short range helix is completely removed at 83 °C, as indicated by the disappearance of the diffuse resonant scattering (Fig. 13a).²⁰ The optical axis remains parallel to the layer normal, together with the d_{02} resonant scattering indicating an anticlinic tilted smectic phase. The loss of the helix leads to a change of the mode of switching from precession on a cone to rotation around the long axis (Fig. S25). For the shorter homologue 1/12 the mode of switching changes already at the Sm(CP)^{hel} to SmC_aP_A transition (Fig. 16a-c), meaning that for this compound no Sm(CP)^{hel} phase is formed and the helix is completely removed already at the Sm(CP)^{hel} to SmC_aP_A transition.



Figure 16. Electrooptical investigation of the switching process of compound 1/12 under an applied DC field in the SmC_aP_A phase at a-c) at 90 °C and d-f) at 70 °C; the switching is fully reversible at both temperatures; in d) the speckled texture is composed of coexisting areas of the SmC_aP_A phase with the bow planes parallel and perpendicular to the surface, whereas in e) all bow planes in the SmC_aP_F state are parallel and in f) perpendicular to the surfaces; for more details of this switching process, see explanations associated with Fig. S20.

3.6 The non-helical low temperature phases of compounds 1/14-1/20

The helix-free low temperature SmC_aP_A phase range. - In the SmC_aP_A phases of 1/8-1/14 the two polarization current peaks become increasingly non-symmetric on cooling (Figs. 9, S9, S14 and S17) and can even fuse to a non-symmetric broad single peak (Figs. 9g \rightarrow h \rightarrow i and S17). We attribute the broadening to a growing packing density with lowering temperature (see Fig. 17), which slows down the switching. The unsymmetrical shape could indicate the

coexistence of two different switching mechanisms. As shown in Figure 16d-f for 1/12, below a temperature around 80 °C the switching changes. Though the position of the extinctions does not change, an additional low birefringent state (blue, Fig. 16e) is formed under low applied field before the transition to the high birefringent SmC_aP_F state at higher voltage (orange, Fig. 16f). This low birefringent intermediate state is explained with an orientation of the bow-planes predominately parallel to the surfaces,⁸² which realigns into an orientation perpendicular to the surfaces at further increased voltage (Fig. 16e \rightarrow f).



Figure 17. a) FWHM and b) position of the scattering maximum of the WAXS of compounds 1/n depending on chain length and temperature, both indicating a growing packing density with decreasing temperature; the gray line indicates the paraelectric-(anti)ferroelectric transition range.

Obviously, with growing chain length $(1/8 \rightarrow 1/16)$ and decreasing temperature there is a stabilization of the anchoring of the molecules with the bow-planes parallel to the surface which might be due to a decreasing tilt and increasing stabilization of the SmC_aP_F state (see below) at lower temperature. A surface stabilized (SS) SmC_aP_F state was observed for the SmC_aP_A phase of $1/16^{57}$ and ferroelectric switching was also proposed for the helix-free

 SmC_aP_A phase of 1/14 (designated as SmC_aP_F in ref.²⁰). However, because the texture returns back to the speckled ground state texture after removal of the field we still consider the switching as antiferroelectric, and therefore we retain the phase assignment as SmC_aP_A . This is in line with a relatively high threshold voltage observed for this switching.⁵⁷

Upon further chain elongation, starting with compound 1/18, the synclinic tilt becomes dominating and the SmC_aP_A phase is replaced by a synclinic SmC_sP_A phase. Also for this compound an asymmetric double peak develops on cooling (Fig. S36), which turns into a symmetric single polarization current peak at 85 °C on further cooling (see Fig. 21p below).

The ferroelectric non-tilted low temperature SmA'P_F phase of compounds 1/16-1/20. – The development of a single peak switching for compounds 1/16-1/18 is obviously associated with a transition from the anticlinic tilted SmC_aP_A phase to a non-tilted smectic phase (SmA'P_F) taking place on cooling.⁵⁷ This transition is only recognizable by a slight increase of the birefringence in the ground- and field-induced states, whereas the extinctions retain

their position parallel to the layer normal (Figs. 19k-m and p-r, S32, S39, S40, S42, S46, and S50) and no peak can be observed in the DSC for this transition (Figs. 6c, S26, S43). This unusual inverted temperature dependence of the SmC-SmA transition was discovered and described for 1/16 in more detail in ref.⁵⁷ and is shown to be associated with a decreasing tilt angle with lowering temperature. The increased slope of the d = f(T) curves of the long chain compounds 1/16-1/22 compared to the compounds 1/6-1/12 with shorter chains (see Figure 7a) might be related to this decreasing tilt, adding to the effect of packing density (Fig. 17) to the development of the layer periodicity d. The decreasing tilt might also be the reason why the driving force for longitudinal helical twist decreases with lowering temperature. Below a certain critical tilt angle the secondary director might become too short for the helical correlation between the layers (see Fig. 18a) and in a first step the helix is lost. Upon further cooling even the tilt correlation between the layers is lost and the SmC_aP_A phase transforms into the SmA'P_F phase. The decreasing tilt is associated with a decrease of the full width at half maximum (FWHM) of the WAXS in the XRD pattern (Fig. 17a), indicating that the correlation length of in-plane order grows. Below a FWHM of 2.9° the transition to the SmA' phase takes place (Fig. 17a). That the increase of the packing density can indeed lead to a transition from tilted to non-tilted lamellar phases is known for SmC*-HexB* transitions.⁸³ As the change of the line shape of the WAXS is continuous and a Lorentzian line-shape is retained⁸⁴ we still consider the SmA'P_F phase as a smectic phase with enhanced in-plane order instead of a hexatic phase with long range bond orientational order (HexB).⁸⁵



Figure 18. Schematic sketches a) of the effect of tilt on the strength of interlayer tilt- and twist-correlation and b) the effect of inter-layer fluctuations on the mode of polar order; the double headed arrows in a) indicate the secondary director and in b) the direction of the fluctuations.

Associated with the transition to $SmA'P_F$ the shape of the polarization current peak changes from a non-symmetric double peak to a relatively sharp and fully symmetric single peak, which is especially well developed for 1/16 and 1/18 (Figs. 190 \rightarrow t, 21 l \rightarrow p, S31 and S36). This symmetric single peak, occurring shortly after zero-voltage crossing, is a first indication of a ferroelectric switching (SmA'P_F phase). In line with a transition to ferroelectric switching the threshold voltage of the switching significantly decreases at the SmC_aP_A-SmA'P_F transition (Fig. 21).⁵⁷ The reason for the growing contribution of (surface stabilized) ferroelectric switching with lowering temperature might be the reduced importance of interlayer fluctuations, entropically stabilizing the antiferroelectric state at higher temperature (Fig. 18b).⁴¹ The reduced contribution of this entropic effect at lower temperature allows easier formation of polar (ferroelectric) order, which is stabilized by polar surface anchoring. This reduced interlayer fluctuation, and hence layer coupling, could also contribute to the loss of long range tilt and tilt correlation (within and between the layers) at the SmC_aP_A -SmA'P_F transition. Though there is a clear single peak switching, the birefringence decreases after switching off the applied field, indicating an orientation of the bow-planes predominately parallel to the surfaces after release of the applied field (Fig. 19p-r), as previously observed for the SmAP_F phases of silylated bent-core molecules.⁸² In contrast to the switching in the SmC_aP_A phase (Fig. 16d-f) the 0V state has the lowest birefringence (Fig. 19q-r), meaning that the state with the bow planes parallel to the surfaces presumably does not relax to an antiferroelectric state.



Figure 19. Electro-optical investigation of the LC phases of compound 1/16, a-e) SmC_xP_R range at 115 °C (rand = randomized), f-j) $Sm(CP)^{hel}$ range at 105 °C, k-o) SmC_aP_A range at 85 °C and p-t) $SmA'P_F$ phase at 80 °C; see also Figs. S31 and S32.

For the longer homologue 1/20 there is a direct transition from the *synclinic* tilted SmC_sP_A phase (see below) to SmA'P_F. This means that the transition SmC-SmA is independent on the actual tilt correlation between the layers in the smectic phase as long as it is weak. On further cooling the SmA'P_F phase crystallizes with formation of a crystalline phase (Cr'). This Cr' phase cannot be distinguished from the SmA'P_F phase (and the high temperature SmA phase) by optical investigations (see Fig. S51), though the transition enthalpy values and the hysteresis of the phase transitions (as well as the sharp peaks in the WAXS patterns) clearly confirm a crystalline phase. For compound 1/22 the SmA'P_F phase is completely replaced by Cr' (Table 1 and Fig. 3).

Overall it appears that the removal of the tilt and the stabilization of the ferroelectric state in the SmA'P_F phase are associated with the anticlinic-synclinic transition taking place by chain elongation, especially in the chain length range from n = 14 to 18, i.e. it has

essentially the same origin as the helix formation occurring at higher temperature. This also provides a new alternative approach to materials with non-tilted ferroelectric (SmAP_F) phases without requiring chain silvlation.⁸²

3.7 Compound 1/16 – emergence of tilt correlation in the paraelectric SmC_xP_R phase

On cooling compound 1/16, long range tilt develops already in the paraelectric smectic phase range as indicated by the transition to a weakly birefringent texture in homeotropic alignment at T = 125 °C (Fig. 19d), i.e. 15 K above the paraelectric-(anti)ferroelectric transition. This means that starting with 1/16 tilt correlation sets in already before development of long range polar order. In the planar texture between 125 °C and the paraelectric-(anti)ferroelectric transition at 108/110 °C (cooling/heating) the orientation of the extinctions is parallel to the polarizers (Fig. 19b). Application of an electric field to the planar sample leads to a tiltdomain texture, indicating the switching into a polar state with synclinic tilt (SmC_sP_F) which relaxes back to the original smooth fan texture of the polarization randomized phase upon removing the applied field (Fig. 19a-c). This indicates a switching by precession on a cone and thus is likely to indicate that a short- or long-range heliconical structure could already develop in the high permittivity paraelectric range. In the polarization current curves there is only one broad maximum, indicating a ferroelectric-like paraelectric switching between 125 °C and the transition to the antiferroelectric phase around 110 °C (Fig. 19e),^{46,47} being typical for polarization randomized (P_R type) smectic phases. This phase, tentative designated as SmC_xP_R, requires further clarification by RSoXS investigations. It transforms to the uniaxial Sm(CP)^{hel} phase at around 110 °C, as indicated by the disappearance of birefringence in the homeotropic samples (Fig. $19d \rightarrow i$), by the retention of a smooth fan texture with extinctions parallel to the polarizers (Fig. 19b \rightarrow g) and by the emergence of two additional close polarization current peaks under a triangular wave voltage (Fig. 19j). The resulting three peak switching (two sharp and one broad) is considered as a ferrielectric switching as typical for heliconical smectic phases with three-layer periodicity.^{17,18,20} For this compound the long range helical Sm(CP)^{hel} structure is stable down to 92 °C. At this temperature the transition to the SmC_aP_A phase takes place and the two close polarization peaks merge to one, leading to the unsymmetrical double peak feature of the helix-free low-temperature SmC_aP_A phase (Fig. 19o→t).

3.8 The long chain compounds 1/18-1/22: Developing synclinic tilt and the field induced heliconical phase

For the next homologue 1/18 phase biaxiality sets in already at 134 °C, in the paraelectric range (Fig. 20a \rightarrow b). In this case the dark extinction brushes incline with the directions of the polarizers in the planar samples (Figs. 20e \rightarrow f, 21f). This confirms a uniform (synclinic) tilt emerging at 134 °C which is on further cooling retained across the paraelectric-(anti)ferroelectric transition at 107/110 °C (cooling/heating) down to the transition at 85 °C without formation of a heliconical phase. In the paraelectric SmC_sP_R phase the inclined extinction crosses do not rotate by inverting the field direction (Figs. 21e-g and S42), indicating a switching by rotation around the long axis and confirming the absence of a helix in the planar samples.⁸⁶

Homeotropic textures:



Figure 20. Textures of the LC phases of 1/18 at the indicated temperatures in the ground state: a-d) in homeotropic alignment and e-h) in planar alignment.

However, the paraelectric and biaxial smectic phase between ~110 and 135 °C shows the formation of a conglomerate of chiral domains in homeotropic alignment (Fig. S34) which, together with the single broad polarization peak under a triangular wave field (Fig. 21h), confirms a high permittivity paraelectric $SmC_sP_R^{[*]}$ phase. The optical rotation in this $SmC_sP_R^{[*]}$ phase is assumed to be caused by surface assisted alignment of the ferroelectric SmC_sP_F grains with a certain size to enable the formation of macroscopic SmC_sP_F domains, then assuming a long-pitch heliconical organization between the cell surfaces.^{46,47,48,49} Thus, the $SmC_sP_R^{[*]}$ phase is considered as a long pitch analogue of the short pitch $Sm(CP)^{hel}$ phase with some similarity to the partly unwounded helical state, being responsible for the tiger stripe texture. This is a first indication that heliconical phases can also appear if the phase structure is SmC_sP_F . It also indicates that helix formation can be supported or suppressed by surface anchoring.



Figure 21. Electro-optical investigation of the smectic phases of compound 1/18 at the indicated temperatures (6 μ m non-coated ITO cell, 160 Vpp); a-d) SmA phase, e-h) SmC_sP_R^[*] phase, i-l) SmC_aP_F^{hel} phase and m-p) SmA'P_F phase, with corresponding polarization current curves (right columns), see Figs. S36-S42 for more details.

At the small DSC peak around 110 °C the two broad polarization peaks emerge and develop into a pair of close peaks while the synclinic tilt is retained (Figs. 20g and 21l), indicating that the polar phase is no more an anticlinic SmC_aP_A phase as that of the shorter homologues, but has changed into a synclinic tilted SmC_sP_A phase for 1/18 and the following homologues. ⁵⁹ In this SmC_sP_A phase application of an AC-field, followed by switching off the field leads to a decrease of birefringence (blue to red, see Fig. 21i-k) and the orientation of the extinction crosses at 0V becomes parallel to the polarizers, indicating a field-induced transition to a state with the main optical axis parallel to the layer normal (Fig. 21j) as known for the $Sm(CP)^{hel}$ phases. That a heliconical $Sm(CP)^{hel}$ phase is indeed induced by the electric field is confirmed by the helix deformation (DHF effect, V-shaped switching) and a helix unwinding to a field-induced polar SmC_sP_F state upon application of a DC field to a planar sample (Fig. 21i-k), being identical to that observed for the $Sm(CP)^{hel}$ phase of 1/16.^{19,60,61} Field-induced and field modified helical structures are known for LC systems formed by

permanently chiral molecules,¹³ but to the best of our knowledge there is only one recent report about field induced helix formation in a (nematic) LC phase of achiral molecules.⁸⁷ The SmC_sP_A phase capable of assuming a field induced helix is found for all compounds 1/18-1/22 with long chains, though the temperature range of the field-induced helical state decreases with chain elongation. The heliconical Sm(CP)^{hel} phase is induced in the whole SmC_sP_A range of all three compounds, but only for 1/18 it is retained in the whole SmC_sP_A range also after removing the field. For 1/20 and 1/22 it is only stable in the upper temperature range of the SmC_sP_A transition temperature, which is easily determined by the change of the extinction direction under the polarizing microscope, rises with growing chain length, meaning that with growing synclinic tilt correlation the field-induced Sm(CP)^{hel} range tightens (see Fig. 3).

3.9 The long chain compounds 1/18-1/22 - paraelectric SmC_sP_{AR} phase and inversion of birefringence

For compounds 1/20 and 1/22 the paraelectric SmC_s phase above the SmC_sP_A phase does not show chiral domains under any conditions. However, two widely separated broad current peaks emerge about 5 K above the transition to the polar smectic phase (Figs. S48 and S55), indicating a short SmC_sP_{AR} range. The antipolar coupling between the ferroelectric grains leads to a racemic structure and thus might inhibit the development of a surface stabilized helix in the whole paraelectric SmC_s range.

As another typical feature of the synclinic tilted phases of compounds 1/18-1/22 there is an inversion of birefringence in the vicinity of the paraelectric-(anti)ferroelectric transition (see Fig. S35 and S47). This is assumed to be due to the changing orientation of the secondary optical axis, which depends on polarization and tilt which are perpendicular and compete with each other in the polar SmC phases of bent-core molecules.⁵² This inversion takes place around or a few degrees below the paraelectric-(anti)ferroelectric transition, at 110 °C for 1/18, at 98 °C for 1/20 and at 88 °C for 1/22. The shift to lower temperatures becomes larger with growing alkyl chain length, i.e. with growing synclinic tilt correlation. Thus, the direction of the main optical axis is likely to be mainly determined by the tilt at higher temperature and at lower temperature by the direction of polar order, becoming stronger with growing packing density.



3.10 Understanding of heliconical phase formation based on stereochemical rules



As shown in the previous Sections, helix formation in the ground state takes place in the SmC_aP_A phase, having uniform layer chirality, but as soon as the tilt changes from anticlinic to long range synclinic (from n = 16 to 18) the $Sm(CP)^{hel}$ phase is completely removed and replaced by a non-helical SmC_sP_A phase. This phase is racemic with alternating layer chirality between the layers and this is incompatible with helix formation, because the diastereomeric pair SmC_sP_A + helix would have a higher energy than SmC_aP_A + helix (see Figs. 15, 22; any red-blue combination is considered to have higher energy).

However, as soon as the chiral SmC_sP_F structure is induced under an applied E-field (SmC_sP_A to SmC_sP_F transition by rotation around the long axis) a helix can develop in the field-induced chiral SmC_sP_F structure (Fig. 22a) by a helical distribution of the polar layers during removal of the field (escape from macroscopic polarization). This field induced heliconical phase has the same structure composed of SmC_sP_F layers twisted around a helix axis parallel to the layer normal as the spontaneously formed Sm(CP)^{hel} phase and can be considered as the common degenerated helix structure derived from either of the two polar smectic phases with uniform chirality, the antiferroelectric SmC_aP_A or the ferroelectric SmC_sP_F phase; it makes no difference from which of the two phases it is formed. Based on stereochemical principles, there is an inherent driving force for helix formation associated with the homochirality of the SmC_aP_A and SmC_sP_F phases. Usually it develops as a transversal twist leading to frustrated smectic phases (HNF, DC^{12,30,39}). The alternative longitudinal twist along the layer normal, reported here, can obviously only develop if the interlayer coupling is sufficiently weak, i.e. at high temperature and close to the transition between anticlinic and synclinic tilt. The heliconical structure once formed (in the ground state or as a field-induced state) disfavors the chirality inverting switching around the long axis, which would lead to a racemic state, whereas the precession on a cone retains the layer chirality (Fig. 22b). Therefore, in the presence of a helix the switching process changes from chirality flipping by rotation around the long axis to the chirality preserving rotation on a cone. Thus, the complex phase behavior of the homologous series of compounds 1/n can be understood by the fundamental principles of stereochemistry.

3.11 Relations with other heliconical phases

The heliconical $\text{Sm}(\text{CP})^{hel}$ phase has some similarity with the long pitch heliconical SmC_{s}^{*} and SmC_{a}^{*} phases formed by permanently chiral rod-like molecules and especially with the short pitch SmC_{α}^{*} phase formed by molecules with high enantiomeric purity, known as a

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incommensurate heliconical phase with 5-50 layer pitch.¹⁷ In common with the Sm(CP)^{hel} phase its formation is associated with a small tilt in the SmC* phases ($\beta \sim 8^\circ$) and it occurs at the transition from SmA* to synclinic SmC_s* which on further cooling form anticlinic SmC_a* phases.¹⁷ Hence, both series of compounds have only weak coupling of the tilt between the layers, combined with a molecular chirality, being either permanent or transient. In the case of the SmC* phases of rod-like mesogens a permanent molecular chirality biases a specific sense of the helical molecular conformation⁸⁸ whereas for the achiral bent-core mesogens the pronounced helicity of the conformers of bent-core mesogens³¹ is responsible for the helix formation. The helix is energetically favored as it leads to a denser packing of the molecules than in the disordered structure in the absence of the helix. The developing helix sense is arbitrary (stochastic) in the case of achiral molecules.¹² The synchronized helical conformers prefer a correlation of the tilt between the layers being unequal to 0° (synclinic) or 180° (anticlinic) thus leading to an intermediate angle, providing the helical twist between the layers. A weak synclinic or anticlinic layer coupling, together with the inherent layer chirality of SmC_aP_A and SmC_sP_F phases, support the development of the helical twist either in the ground state (SmC_aP_A) or in the field-induced (SmC_sP_F) state. The helix pitch is about only 3 layers as this allows a twist of $\sim 120^{\circ}$ between adjacent layers. This angle is presumably close to that provided between the alkyl chains in the relevant helical conformations,³¹ thus allowing easy fluctuations of the molecules between adjacent layers and leading to an entropic advantage (this could additionally contribute to the formation of heliconical nematic phases if the layers are weak). Commensurate heliconical phases with 3- or 4-layer pitch are known to occur for rod-like molecules with high enantiomeric purity at the transition between SmC_s* and SmCa* phases (SmCFI1*, SmCFI2* phases).^{14,17,18} It is possible that besides the incommensurate SmC_{α}^* -like helix also structures with SmC_{FI} -like commensurate 3 and 4layer or other periodicities could be found for the transiently chiral bent-core molecules. Recently, heliconical smectic phases (designated as SmC_{TB}) have also been reported

Recently, heliconical smectic phases (designated as SmC_{TB}) have also been reported for bent mesogenic dimers; in this case predominately commensurate 4-layer structures have been reported for these non-polar smectic phases.⁶⁷ That the pitch in the $Sm(CP)^{hel}$ phases of the bent-core compounds 1/n (< 3 layers) is shorter than in the SmC_{TB} phases of bent dimesogens (4 layers) might be the result of the increased helicity of the molecular conformations of the bent-core mesogens, and especially due to the possibility to escape from the significant macroscopic polarization occurring in the layers of their polar smectic phases.^{89,90} For the bent-core molecules the combination of polar order and helicity provides the unique possibility of affecting the helical structure by application of external electric fields, leading to numerous potential applications.^{13,79,80} The V-shaped switching due to helix deformation (DHF effect)^{19,60} and an extremely fast optical switching between biaxial and optical uniaxial states in homeotropic device configurations⁷⁹ represent first examples for such applications.

4. Conclusions

A full series of 4-cyanoresorcinol bisterephthalates 1/n with chain lengths ranging from 2 to 22 was synthesized and investigated with respect to LC self-assembly and spontaneous development of heliconical superstructures. This allowed an understanding of the development of the complex phase sequence observed in this unique series of compounds, which was not possible in previous work considering only some individual compounds. All compounds with $n \ge 4$ form a uniaxial de-Vries-like SmA phase at high temperatures. With decreasing temperature ferroelectric grains grow, leading to paraelectric and superparaelectric smectic phases, being non-tilted (SmAP_R, SmAP_{AR}) for relatively short chains ($n \le 14$) and tilted (SmC_xP_R, SmC_sP_R, SmC_sP_{AR}) for compounds with longer chains (n > 14). All compounds with $n \ge 6$ show a transition from these paraelectric and high permittivity paraelectric to polar smectic phases, in all cases indicated by a small DSC peak around 109±4 °C. The polar smectic phases below this transition are either anticlinic tilted (SmC_aP_A) for compounds with n up to 16 and synclinic tilted (SmC_sP_A) for those with longer chains ($n \ge 1$ 18). The tilt is relatively small (15-20°) and only slightly changing with growing alkyl chain length. At the transition from the anticlinic SmC_aP_A to the synclinic SmC_sP_A phase new phases with unique properties emerge. At low temperature a non-tilted and ferroelectric switching phase (SmA'P_F) is observed for compounds with n = 16-20, leading to the unusual inverted phase sequence SmC-SmA on cooling. At high temperature a short pitch heliconical smectic phase is formed instead, which reaches a maximum stability for n = 14-16. It represents a new mode of spontaneous mirror symmetry breaking in LC phases of bent-core mesogens. In contrast to all previously reported cases with transversal twist (HNF³³ and DC phases^{41,42}) for compounds 1/n the twist develops longitudinal, see Fig. 1b,g), leading to a helix parallel to the layer normal (Fig. 1a,e). There are three prerequisites for this kind of helix formation, (i) a polar phase with inherent layer chirality $(SmC_aP_A \text{ or } SmC_sP_F)$, (ii) a weak layer coupling in the vicinity of the transition from randomized to long range tilt correlation (de Vries SmA to SmC transition) and polar order (paraelectric to antiferroelectric transition) and (iii) a small tilt and weak tilt-correlation at the synclinic-anticlinic cross-over. Once the Sm(CP)^{hel} phase, representing the common degenerated helical state of the SmC_aP_A

as well as the (field induced) SmC_sP_F phase, is formed the mode of switching changes from the originally preferred chirality inverting rotation around the long axis to a chirality retaining precession on a cone, even if the heliconical structure is only short range. This is a consequence of fundamental stereochemical principles based on the diastereomeric relations between the two spontaneously and simultaneously developing modes of superstructural chirality, the layer chirality and the helix formation. Thus, this work shows that fundamental stereochemical rules can determine the phase structures and properties of LC systems formed by achiral compounds. This contributes to the understanding of mirror symmetry breaking in other soft matter systems, as for example the bicontinuous cubic and related phases,^{12,91,92} the dark conglomerate phases,^{41,42} the heliconical nematic and smectic phases,⁶⁷ and the spontaneously chiral isotropic liquids.⁹ This contribution provides a snapshot of the present state of research on heliconical smectic phases of achiral bent-core mesogens. Further investigations might lead to a similar diversity of different heliconical phases as known for the permanently chiral rod-like molecules.^{14,17,18} Besides the fundamental scientific question of emergence of chirality in ordered fluids, these heliconical phases are of significant technological interest for fast optical switches, as tunable circular polarizing emitters, and for use as photonic materials.^{13,93}

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