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Reentrant $SmCP_A$ phases: unusual polymorphism variant $SmA–SmC_SP_A–Col_{ob}–SmC_SP_A$ observed in new bent-core mesogens†

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A new homologous series of achiral five-ring bent-core mesogens is presented. The mesophase behaviour has been studied by polarizing microscopy, differential scanning calorimetry, X-ray diffraction and electro-optical measurements. The homologues with shorter terminal chains (C_8, C_{12}) form an $SmCP_A$ phase, homologues with longer chains (C_{14}, C_{16}, C_{18}) show liquid-crystalline tetramorphism with a sequence $SmA–SmC_SP_A–Col_{ob}–SmC_SP_A$. The $SmCP_A$ phases are structurally identical and differ only in the mechanism of polar switching. The switching of the high-temperature SmC_SP_A phase takes place through the collective rotation of the molecules around their long axes whereas in the reentrant SmC_SP_A phase the switching is based on the director rotation around the tilt cone. By the application of an electric field the Col_{ob} phase can be irreversibly transformed to an $SmCP_A$ phase. In a limited temperature range the SmA phase shows a reversible field-induced transition into the SmC_SP_F phase. The electro-optical response of the mesophases is discussed on the basis of the structural features of these phases.

1. Introduction

Bent-core mesogens have been the subject of extensive investigations in the last years because they can form new mesophases with unusual properties which are different from those of calamitic mesogens. Due to their intrinsic shape the molecules can be packed in a polar fashion, which leads to a long-range correlation of the lateral dipoles. The polar packing of the bent molecules leads to ferroelectric or antiferroelectric properties.[1,2] The most frequently studied phase derived from bent molecules is the SmCP phase where P stands for "polar". As first shown by Link *et al.*[2] the structure of the SmCP phase depends on the stacking of the bent molecules in adjacent smectic layers. The molecules can have a synclinic or an anticlinic interlayer correlation and are denoted by the subscripts S and A after the C. With respect to the direction of the polar vector in adjacent layers the synclinic and anticlinic packing can form ferro- or antiferroelectric structures which are denoted by the suffixes F or A after the P. In this way we can distinguish four possible structures which are presented in Fig. 1: SmC_SP_A, SmC_AP_A, SmC_SP_F and SmC_AP_F. In order to avoid bulk polarization, antiferroelectric ground states exist in most cases and can be switched to the corresponding ferroelectric states.[2] Another aspect of fundamental interest is the combination of director tilt and polar order in the smectic layers of these bent-core compounds. This combination leads to chirality of the smectic layers although the constituent molecules are achiral.[2] The chirality alternates from layer to layer in the so-called racemic states (SmC_SP_A, SmC_AP_F), whereas the layer chirality is uniform within the macroscopic domains in the homochiral states (SmC_AP_A, SmC_SP_F). It should be noted that another way of avoiding bulk polarization in layered structures of bent-core molecules is to break the layers into a 2D modulated structure as described in columnar B_1 phases[3–8] or by splay polarization in the smectic layers.[9]

In this paper we report new results, emphasizing the complexity of the mesophase behaviour in a homologous series of bent-core mesogens. We found that on decreasing the temperature the member with dodecyloxy terminal chains shows a reversible field-induced transition from the homochiral SmC_AP_A to the racemic SmC_SP_A phase. The homologues with longer terminal chains exhibit a new polymorphism with an unusual sequence of phases—$SmA–SmC_SP_A–Col_{ob}–SmC_SP_A$—and an interesting electro-optical behaviour. The

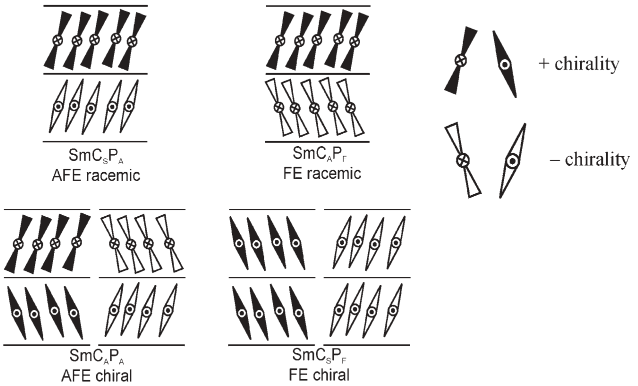

Fig. 1 Possible orientations of the direction of the tilt and the polar axes of bent-core molecules in adjacent layers leading to chiral or racemic ferroelectric and antiferroelectric SmCP phases. Full and open molecule symbols designate layers of opposite chirality; the signs ⊗ ⊙ indicate opposite bend direction (opposite polar axes).

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† Electronic supplementary information (ESI) available: Experimental procedure for compound **18** and analytical data of all final products: **8**, **12**, **14**, **16**, **18** and **16-Br**. See DOI: 10.1039/b516189d

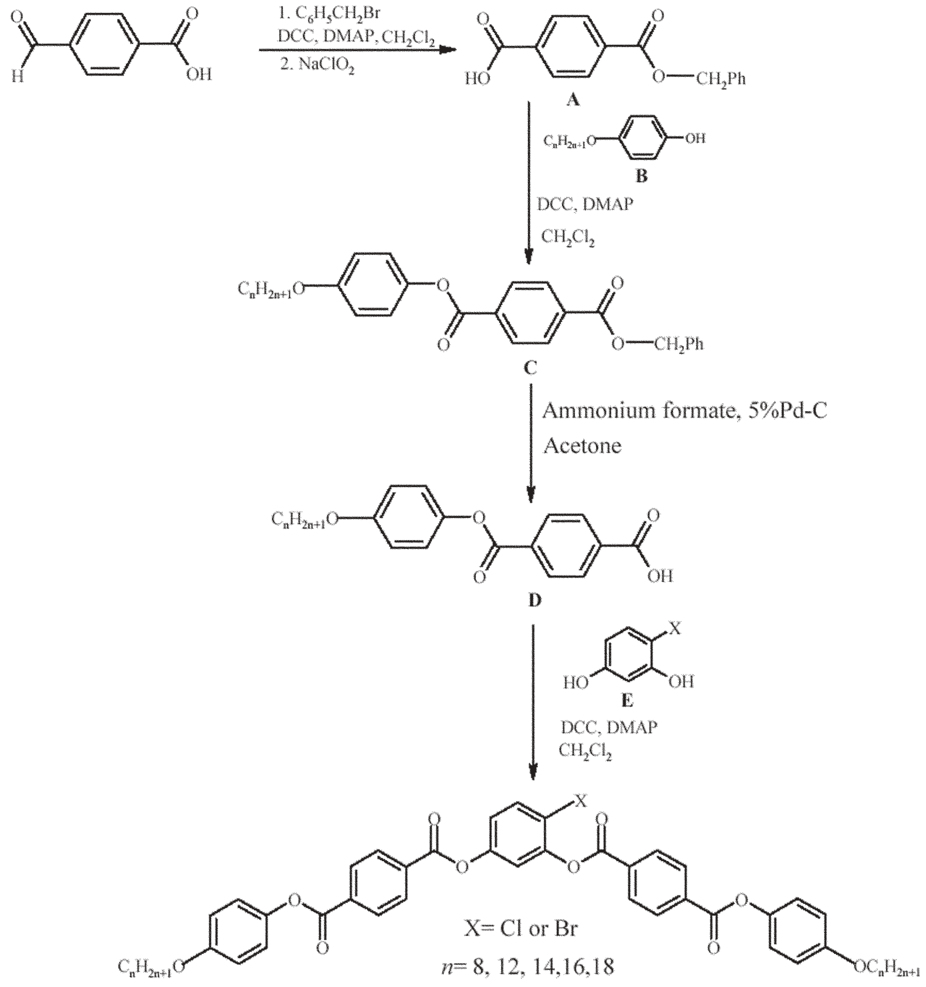
experimental results are discussed on the basis of intermolecular interactions.

2. Experimental

The thermal behaviour (transition temperatures and transition enthalpies) was determined using a differential scanning calorimeter (Perkin-Elmer Pyris 1). The optical textures and the field-induced texture changes were examined using a polarizing microscope (Leitz Laborlux) equipped with a Linkam hotstage (THM 600/S). X-Ray diffraction measurements of non-oriented samples were performed with a Guinier film camera (Huber, Germany) or a small angle camera with a linear position sensitive detector (M. Braun GmbH, Germany) (samples in glass capillaries with a diameter of 1 mm on a temperature controlled heating stage). X-Ray studies on oriented samples were carried out with a 2D detector (HI-Star, Siemens AG). Oriented samples were obtained by a long annealing of a drop of the liquid crystal on a glass plate after very slow cooling of the isotropic liquid. In this case the smectic layers could be oriented parallel to the substrates and the incident X-ray beam was parallel to the smectic layers. Electro-optical measurements were carried out in commercial ITO cells (E. H. C. Corp.; spacing: 5 μm or 6 μm). The switching polarization was measured by means of the triangular wave voltage method.[10]

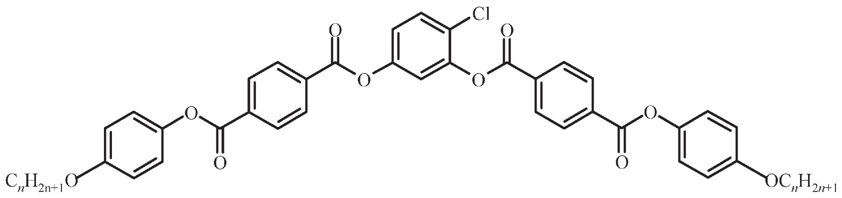
3. Materials

The homologous five-ring bent-core mesogens contain 4-chloro- or 4-bromoresorcinol as the central core and ester moieties as connecting groups between the aromatic rings (see Table 1). The synthetic approach to prepare the desired bent-core compounds is shown in Scheme 1. 4-Chloro- and 4-bromoresorcinol are commercial products. Monobenzyl terephthalate **A** was synthesized by esterification of 4-carboxybenzaldehyde followed by oxidation using sodium chlorite. 4-*n*-Alkoxyphenols **B** were prepared by the alkylation of 4-benzyloxyphenol with the corresponding alkyl bromides and deprotection by means of hydrogen in the presence of 5% Pd–C. Monobenzyl terephthalate **A** was esterificated with the corresponding 4-*n*-alkoxyphenols **B** in the presence of DCC to give the intermediates **C**, and their deprotection by means of ammonium formate and 5% Pd–C resulted in acids **D**. The final compounds **8**, **12**, **14**, **16**, **18** and **16-Br** were prepared by the condensation of the substituted resorcinols **E**



Scheme 1 Synthetic route.

Table 1 Transition temperatures (°C) and associated enthalpy values (italic) (kJ mol^{-1}) for compounds **8**, **12**, **14**, **16** and **18**



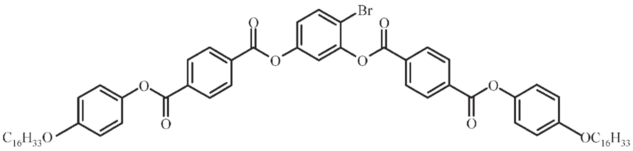
Compound	*n*	Cr		SmC_SP_A		Col_{ob}		SmC_SP_A		SmC_AP_A		SmA		I
8	8	•	113.0 *20.7*	•	145.0 *16.0*	—		—		—		—		•
12	12	•	110.0 *50.0*	• —	140.0[a]	—		—		•	147.0 *18.2*	—		•
14	14	•	105.0 *60.3*	• —	134.0[a]	•	138.0 *0.8*	•	139.5 *2.2*	—		•	144.0 *8.8*	•
16	16	•	108.0 *74.9*	• —	130.0[a]	•	135.0 *1.5*	•	138.5 *2.7*	—		•	145.5 *8.6*	•
18	18	•	107.0 *71.9*	• —	123.0[a]	•	128.0 *1.4*	•	134.0 *3.1*	—		•	142.5 *8.7*	•

[a] The enthalpy for this transition could not be determined.

with compounds **D**. The experimental procedure to prepare compound **18** is given together with the analytical data of all final products in the ESI.†

The transition temperatures and the associated enthalpies for the five compounds derived from 4-chlororesorcinol are given in Table 1.

In addition, we have also prepared one compound with a bromine substituent in the 4-position of the central core and hexadecyloxy terminal chains (compound **16-Br**). The mesophase sequence is the same when compared with the analogous 4-chloro substituted compound (**16**) but with a reduction of all transition temperatures by about 10–15 K which is obviously due to the increase in the size of the lateral substituent from chlorine to bromine.



16-Br Cr 98.0 SmC_SP_A 117.0 Col_{ob}119.5 SmC_SP_A 124.0 SmA 136.0 I
75.9 - *1.4* *1.5* *7.7*

4. Results

Compounds 8 and 12

On cooling the isotropic phase of compound **8** a fan-shaped texture with irregular stripes was observed—a photomicrograph is given in Fig. 2. The same textural features have also been observed in compound **12**.

X-Ray investigations on powder-like samples of both homologues gave two reflections, with *d* values in the ratio of 1 : 1/2 in the small angle region and a diffuse scattering in the wide-angle region. This indicates that the mesophase possesses a simple layer structure without in-plane order. The layer spacings (*d*) are 42.5 Å at 130 °C for compound **8** and 48.0 Å at 140 °C for compound **12**, respectively. They are clearly smaller than the molecular length *L* assuming a bending angle of 120° (*L* is 47 Å for compound **8** and 54 Å for compound **12**). This indicates the tilted arrangement of the bent-core molecules in the smectic layers. Using the relation $d/L = \cos\alpha$ the tilt angle α could be estimated and was found to be 25° for compound **8** and 28° for compound **12**.

In order to prove the polar character of the tilted smectic phase, detailed electro-optical investigations have been performed. The smectic phase of compound **8** shows two polarization current peaks per half period of a triangular voltage indicating an antiferroelectric ground state. No change in the extinction direction was observed when the polarity of the applied field was interchanged. This indicates that the ground state of the $SmCP_A$ phase is synclinic (racemic), *i.e.* on applying an electric field the transition from SmC_SP_A to SmC_AP_F could be achieved. The switching polarization current measured by integrating the area under the current curve is 430 nC cm^{-2}. The smectic phase of compound **12** could also be identified as an $SmCP_A$ phase and the polarization was found to be 355 nC cm^{-2}. The polarization value did not change markedly as the temperature was lowered. In contrast

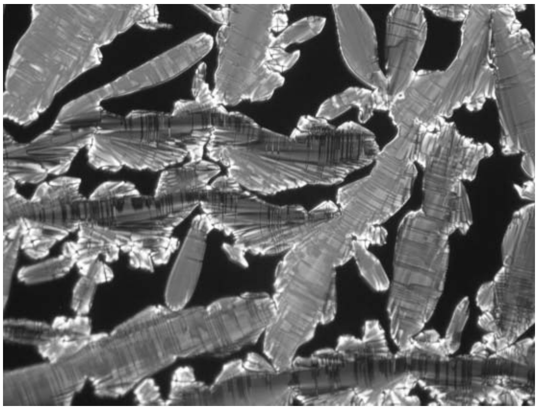


Fig. 2 Texture of the SmCP phase of compound **8** obtained on cooling from the isotropic phase.

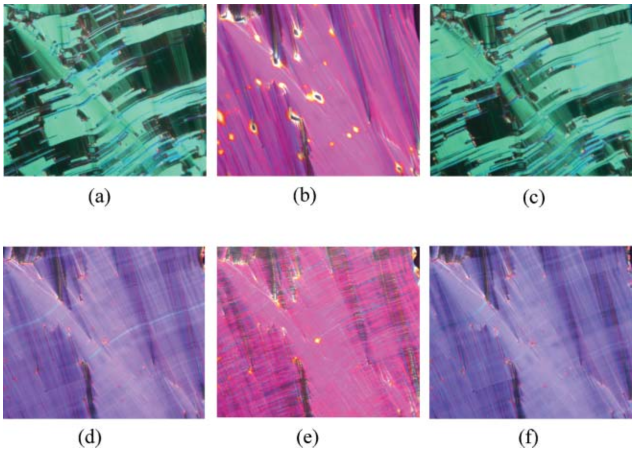


Fig. 3 Photomicrographs of the textures obtained for the SmC_AP_A phase of compound **12**, (a) +4 V μm^{-1}; (b) 0 V; (c) −4 V μm^{-1}; temperature: 144 °C; photomicrographs of textures obtained for the SmC_SP_A phase, (d) +4 V μm^{-1}; (e) 0 V; (f) −4 V μm^{-1}; temperature: 136 °C; cell thickness: 6 μm.

to compound **8**, the optical appearance of the polar switching of compound **12** clearly depends on the temperature. On cooling the isotropic liquid of compound **12** in an EHC cell of 6 μm thickness under a DC field of 4 V μm^{-1}, two types of domains (green and dark) were observed (Fig. 3a,c). On reversing the polarity of the applied field the colour of the textures is interchanged. On terminating the field the molecules relax to a ground state, which shows a different texture with a pink colour (Fig. 3b). The two inter-convertible green and dark regions represent the opposite ferroelectric states (SmC_SP_F) and are distinguished by the opposite tilt sense. On terminating the field the molecules relax to the antiferroelectric ground state (SmC_AP_A). This switching mechanism confirms the anticlinic interlayer correlation in the ground state of the mesophase. On lowering the temperature with the same applied field below 140 °C, the entire texture adopts a blue colour and changing the polarity of the applied field has no effect on the textural pattern (Fig. 3d,f). If the field is removed, the colour of the texture changes to pink and stripes appear perpendicular to the fans (Fig. 3e). The stripes represent synclinic regions with anticlinic ferroelectric boundaries.[11] This indicates that below 140 °C the ground state has a synclinic structure (racemic state; SmC_SP_A), which switches to the anticlinic ferroelectric phase (SmC_AP_F), similar to compound **8**. Thus we have established that at 140 °C there is a field-induced transition from a chiral antiferroelectric (SmC_AP_A) phase to a racemic antiferroelectric (SmC_SP_A) phase. It should be noted that the smooth fan-shaped structure of the chiral SmC_AP_A phase obtained on cooling the isotropic liquid in the absence of an electric field does not change below 140 °C. This means that the ground state structure remains as SmC_AP_A on lowering the temperature. On the other hand, the fan-shaped texture with irregular stripes of the racemic SmC_SP_A phase obtained below 140 °C after removal of the applied field, does not change on heating up to the clearing temperature. That means that in this case the SmC_SP_A ground state is stable in the whole temperature range of the $SmCP_A$ phase.

Compounds 14, 16, 18 and 16-Br

The long-chain members of the 4-chloro- or 4-bromo-substituted compounds (**14**, **16**, **18** and **16-Br**) exhibit tetramorphism in the liquid-crystalline state. First the phase transitions have been studied by observing the optical textures, and are described for compound **18** as a representative example. On cooling the sample from the isotropic phase, a homeotropic texture as well as a smooth focal-conic texture was observed. This is a typical feature of an SmA phase. On lowering the temperature (below 134 °C) the homeotropic regions transform to a weakly birefringent fluctuating schlieren texture, which is characteristic for a biaxial phase. At the next phase transition observed on cooling the sample below 128 °C, the fluctuations disappear and in the paramorphotic texture fine fan-like domains are visible. By further cooling the sample there is a minor change of the texture at 123 °C where the schlieren texture again becomes fluctuating. The texture changes between the polymorphic mesophases are more pronounced when we start from a fan-shaped texture of an SmA phase in a cell with planar alignment conditions (Fig. 4a). On cooling the fan-shaped texture a broken fan-shaped texture appears (Fig. 4b). This transition is coupled with an enthalpy change of 2.7 kJ mol^{-1}. At 128 °C a clear change of the texture occurs which can be recognized by a clear change of the birefringence (Fig. 4c). The corresponding transition enthalpy is rather low (1.5 kJ mol^{-1}). On a further decrease of the temperature to 123 °C a nearly identical paramorphotic texture was obtained. No enthalpy change was observed for this phase transition in the DSC thermogram indicating a second order phase transition.

X-Ray studies on the mesophases of compounds **14**, **16**, **18** and **16-Br** confirm the polymorphism in the liquid-crystalline state. As a representative example we present the results obtained for compound **18**. A well-aligned sample of the high-temperature phase shows one strong small angle reflection on the meridian of the pattern (Fig. 5a) from which a layer

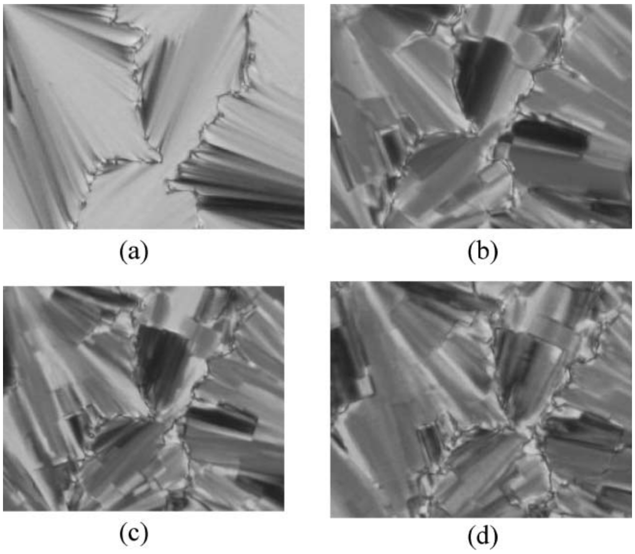


Fig. 4 Optical textures of compound **18** in the (a) SmA phase; (b) SmC_SP_A phase; (c) Col_{ob} phase; and (d) reentrant SmC_SP_A phase.

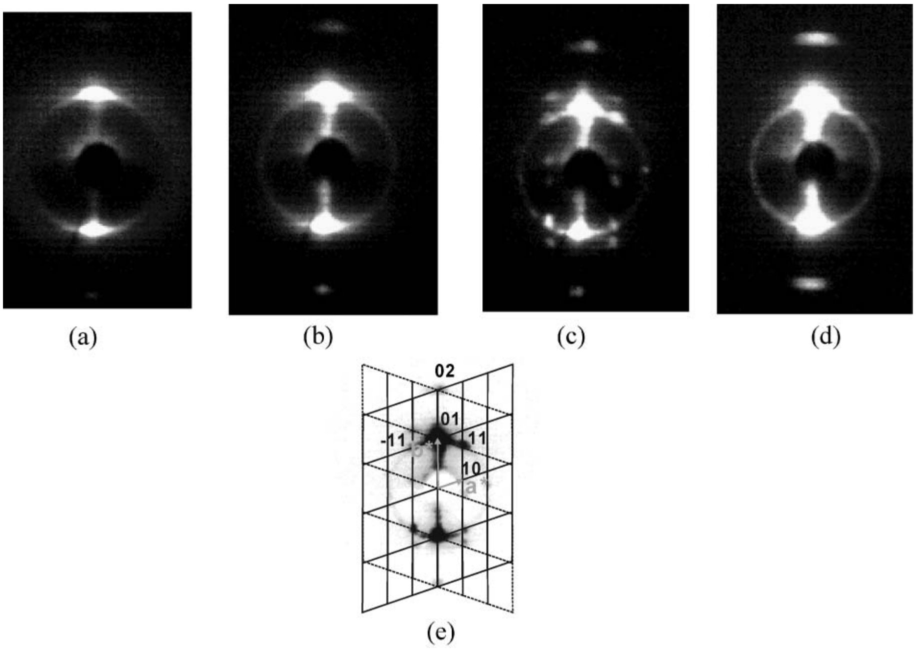


Fig. 5 The small-angle X-ray diffraction pattern of compound **18** in the (a) SmA phase; (b) SmC_SP_A phase; (c) Col_{ob} phase; and (d) reentrant SmC_SP_A phase; (e) indexing of the Col_{ob} phase.

spacing of 54 Å could be determined. On lowering the temperature to 132 °C, two reflections were obtained with *d* values in the ratio of 1 : 1/2 (Fig. 5b). The layer spacing was found to be 55 Å. The presence of second order reflections indicates that the smectic layer structure is more pronounced which means that the distribution of the electron density along the layer normal cannot be approximated by only one sinus wave. It can be understood that because of the polar packing of the bent-core molecules the smectic layer structure has become more pronounced.

On further lowering of the temperature to 126 °C, we can see additional reflections out of the meridian (Fig. 5c) which can be indexed to an oblique lattice with the lattice parameters a = 106 Å, b' = 58 Å, γ = 106° (Fig. 5e). In the following this parameter is doubled ($2b' = b$) because of the assumed model (see Discussion). Below 123 °C the X-ray pattern is quite similar to that of Fig. 5b which points to a transition of the Col_{ob} phase to the $SmCP_A$ phase (Fig. 5d). On heating the $SmCP_A$ phase (above 123 °C) the X-ray pattern of the Col_{ob} phase reappears; *i.e.* without field this transition is reversible. As seen from Table 1 this transition cannot be detected by calorimetric measurements. The corresponding wide-angle images in different mesophases are given in Fig. 6. In all the phases a diffuse scattering maximum is observed indicating the liquid-like arrangement of the molecules within the layers. For the highest temperature phase the diffuse scattering maxima are located at the equator (Fig. 6a). This corresponds to an orthogonal arrangement of the molecules within the layers and confirms the assignment as an SmA phase. In the smectic phase below the SmA phase the diffuse wide angle maxima are out of the equator which is a clear indication for a tilt of the molecules in the layers (Fig. 6b). On a further lowering of the temperature to 126 °C and 121 °C (the phase range of the oblique columnar and the lower temperature $SmCP_A$ phase), it can be seen from Fig. 6b–d that the maximum located in the upper left quarter of the pattern is much stronger than the corresponding one in the upper right one. Such an asymmetry can only be caused by a combination of a synclinic tilt of the molecules within the Col_{ob} and the $SmCP_A$ phases and a non-equal distribution of domains around the axis of the fibre-like disordered sample. The calculated tilt angle is about 25°. The lattice parameter b is comparable with twice the molecular length considering the tilt of the molecules. An

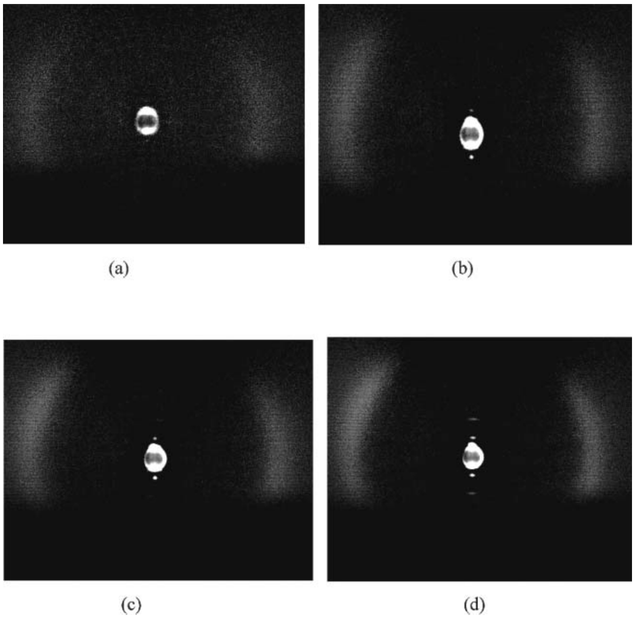


Fig. 6 The wide-angle X-ray diffraction pattern of compound **18** in the (a) SmA phase; (b) SmC_SP_A phase; (c) Col_{ob} phase; and (d) reentrant SmC_SP_A phase.

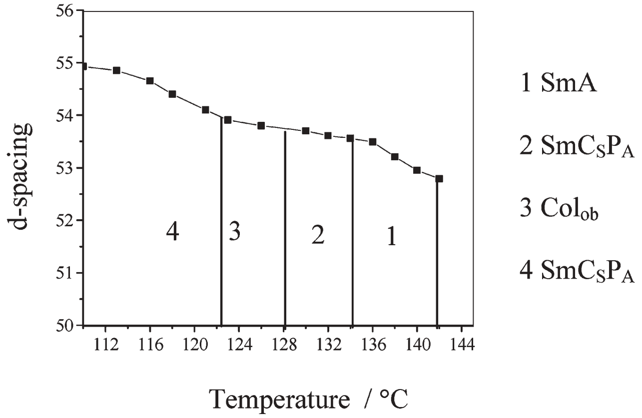


Fig. 7 Plot of the layer spacing *d* as a function of the temperature obtained for compound **16**.

estimation of the number of molecules per unit cell yields about 32 molecules.

Interestingly, the layer spacings gradually increase in the sequence SmA–SmC$_S$P$_A$–Col$_{ob}$–SmC$_S$P$_A$ (Fig. 7) although a transition from a non-tilted to a tilted phase takes place. This unusual result has been observed in earlier studies of laterally substituted bent-shaped molecules, too.[12] There, on the basis of detailed studies of the temperature dependence of the bending angle as well as the order parameter the unusual increase of the *d*-values was explained by a different degree of intercalation of the molecules of adjacent layers in the different phases. The increase in the layer spacings on lowering the temperature in the present set of compounds can be explained in a similar way.

We have also performed small-angle X-ray studies for compounds **14**, **16**, and **16-Br** and we obtained results similar to those for compound **18**. The *d*-values and the lattice parameters of the columnar phase of all compounds are summarized in Table 2.

Detailed electro-optical investigations described here for compound **18** should give additional information about the structural features of the polymorphic mesophases. The SmA phase does not show a polar electro-optical response. For the tilted smectic phase below the SmA phase two polarization current peaks per half period were observed on applying a triangular-wave voltage which indicates that the ground state structure is antiferroelectric (Fig. 8a). The measured polarization value is 250 nC cm^{-2}. The Col$_{ob}$ phase shows a similar current response (Fig. 8b); importantly the position of the current peaks is different from that of the higher temperature SmCP$_A$ phase. From the current response a switching polarization of 320 nC cm^{-2} could be determined. The low-temperature SmCP phase is also an antiferroelectric smectic phase with a slightly higher polarization (340 nC cm^{-2}).

To get more information about the organization of the molecules in the field-on and field-off states we have carried out DC field experiments. On cooling the sample of compound **18** from the isotropic phase, a focal-conic texture was observed which is typical for an SmA phase. It can be seen from Fig. 9a that the extinction directions of half circular domains are parallel to the crossed polarizers. This indicates that the director (optical axis) is perpendicular to the smectic layers. On lowering the temperature to 133 °C, the extinction directions enclose an angle of ~22° with respect to the directions of the crossed polarizers (see Fig. 9b). This tilt of the extinction directions indicates that the smectic phase has a tilted organization which rules out that the mesophase is a polar smectic A (SmAP) phase. If the antiferroelectric ground state is switched to the ferroelectric state or *vice versa*, the extinction directions do not change and also the birefringence remains unchanged (Fig. 9c). Furthermore, this effect is independent of the polarity of the applied field. This finding suggests that the antiferroelectric ground state as well as the switched ferroelectric states have a synclinic tilt and the switching corresponds to the transition from an SmC$_S$P$_A$ state to an

Table 2 The *d*-spacings, the lattice parameters and the polarization values for compounds **8**, **12**, **14**, **16**, **18** and **16-Br**. In column 2 (*d*-spacing) the evaluation of the X-ray pattern is given. In column 3 the lattice parameters are listed in agreement with the assumed model. Here the values of the *b* parameters are doubled in comparison to those resulting from the X-ray data (see Discussion)

		Lattice parameter				
No.	*d*-Spacing (order/*hk*)/Å	*a*/Å	*b*/Å	*γ*/°	Phase type	Polarization value/nC cm^{-2}
8	42.5 (1), 21.2 (2)	—	—	—	SmC$_S$P$_A$	460
12	48.0 (1), 24.0 (2)	—	—	—	SmC$_A$P$_A$	335
14	49.7 (1)	—	—	—	SmA	—
	50.1 (1), 25.0 (2)	—	—	—	SmC$_S$P$_A$	310
	121.8 (10), 54.5 (−11), 51.0 (01), 42.0 (11), 25.4 (02)	130	109	111	Col$_{ob}$/SmC$_A$P$_A$^{a}	350
	51.5 (1), 25.7 (2)	—	—	—	SmC$_S$P$_A$	400
16	52.8 (1)	—	—	—	SmA	—
	53.5 (1), 26.8 (2)	—	—	—	SmC$_S$P$_A$	330
	114.1 (10), 58.3 (20), 54.0 (01), 54.0 (−11), 44.2 (11)	119	113	106.5	Col$_{ob}$/SmC$_A$P$_A$^{a}	480
	55.0 (1), 27.5 (2)	—	—	—	SmC$_S$P$_A$	410
18	54.0 (1)	—	—	—	SmA	—
	55.0 (1), 27.4 (2)	—	—	—	SmC$_S$P$_A$	250
	102.2 (10), 55.8 (−11), 55.3 (01), 27.9 (02), 44.1 (11)	106	116	106	Col$_{ob}$/SmC$_A$P$_A$^{a}	320
	57.1 (1), 28.5 (2), 19.0 (3)	—	—	—	SmC$_S$P$_A$	340
16-Br	52.0 (1)	—	—	—	SmA	—
	52.5 (1), 26.3 (2)	—	—	—	SmC$_S$P$_A$	190
	120.8 (10), 53.4 (−11), 53.5 (01), 26.8 (02), 45.3 (11)	123.5	110	102.5	Col$_{ob}$/SmC$_A$P$_A$^{a}	250
	54.7 (1), 27.4 (2)	—	—	—	SmC$_S$P$_A$	275

[a] The SmC$_A$P$_A$ phase was obtained from the Col$_{ob}$ phase by application of an electric field.

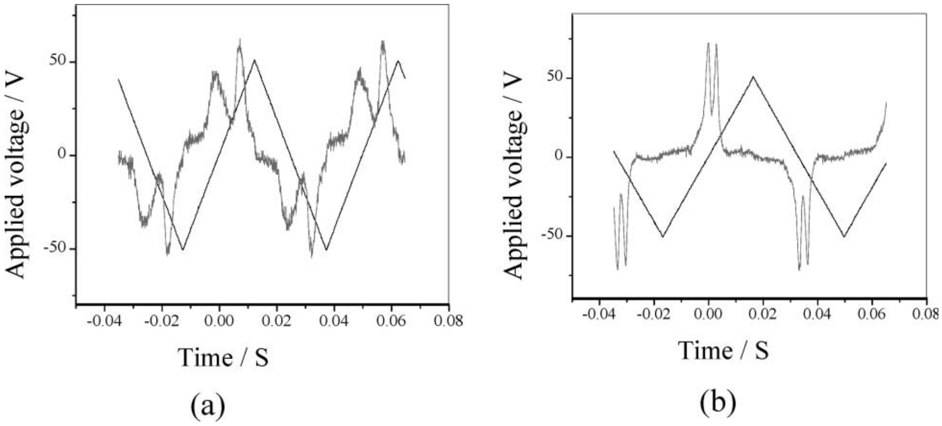


Fig. 8 Switching current response traces obtained for compound **18** on applying a triangular-wave electric field; (a) $\mathrm{SmC_SP_A}$ phase, polarization 250 nC cm^{-2} (132 °C); (b) $\mathrm{SmC_AP_A}$ phase, obtained from the Col$_{ob}$ phase by application of an electric field, polarization 320 nC cm^{-2} (126 °C).

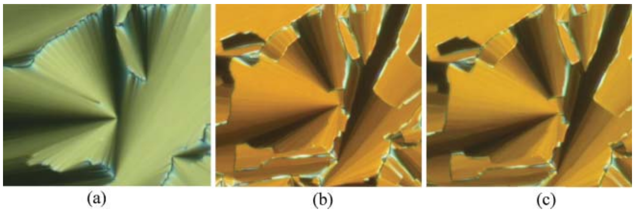


Fig. 9 (a) Texture obtained in the smectic A phase under DC field; (b) and (c): texture obtained in the $\mathrm{SmC_SP_A}$ phase with (±4 V μm^{-1}) and without an electric field, respectively; cell thickness: 5 μm; temperature: 131 °C (compound **18**).

$\mathrm{SmC_SP_F}$ state. The switching mechanism is based on the collective rotation of the molecules around their long axes. Such a polar switching is unusual for SmCP phases and was observed in only a few bent-core compounds.[13–16] It should be emphasized that such a field-induced transition is accompanied by an inversion of the layer chirality in each second layer.

If the synclinic $\mathrm{SmC_SP_F}$ (Fig. 9b) phase is cooled down to the Col$_{ob}$ phase in the presence of the electric field, the extinction directions remain unchanged but the change in the colour of the domains is clearly visible (Fig. 10a). If the polarity of the field is reversed, the extinction directions rotate in a counterclockwise direction (Fig. 10c). However on terminating the field the extinction directions rotate in the direction of the crossed polarizers (Fig. 10b), which indicates that the ground state has an anticlinic structure ($\mathrm{SmC_AP_A}$). It is important to note that the relaxed state is completely different from that obtained for the $\mathrm{SmC_SP_A}$ phase without a field. Since the anticlinic arrangement of the molecules in the layer fragments of the Col$_{ob}$ phase is unfavourable, we assume that under the electric field the modulated structure of the columnar phase transforms irreversibly to the smooth layer structure of the $\mathrm{SmC_SP_F}$ state, which relaxes to the $\mathrm{SmC_AP_A}$ on the removal of the field. This means that the transition from $\mathrm{SmC_AP_A}$ to $\mathrm{SmC_SP_F}$ and *vice versa* takes place in a usual way, by the collective rotation of the molecules around the tilt cone. During this phase transition the layer chirality does not change.

As seen from Fig. 11a,c the extinction directions rotate in the direction of the crossed polarizers on cooling to the low-temperature phase in the presence of an electric field and simultaneously the colour of the texture changes from red to yellow-green (Fig. 10a–c, Fig. 11a–c). Since the texture of the switched ferroelectric state is the same for a field of opposite polarity, this state corresponds to the anticlinic $\mathrm{SmC_AP_F}$ phase. On terminating the field the extinction directions remain parallel to the crossed polarizers but irregular stripes appear (Fig. 11b). The tilt within the striped domain is synclinic and the tilt sense is different in neighbouring stripes.[2,11] From the optical features under the field, we can confirm the ground state as $\mathrm{SmC_SP_A}$, which is switched to the $\mathrm{SmC_AP_F}$ phase.[2,11,17] On heating the sample under the same

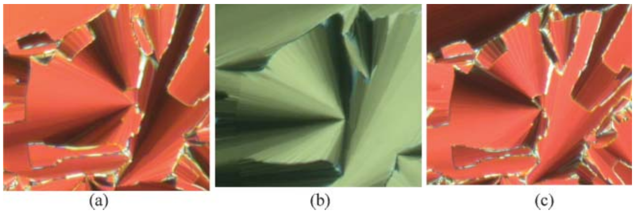


Fig. 10 (a) Texture of the field-induced ferroelectric structure ($\mathrm{SmC_SP_F}$: +4 V μm^{-1}); (b) texture of the antiferroelectric ground state at zero field ($\mathrm{SmC_AP_A}$); (c) texture of the field-induced ferroelectric structure ($\mathrm{SmC_SP_F}$: −4 V μm−1); cell thickness: 5 μm; temperature: 126 °C (compound **18**).

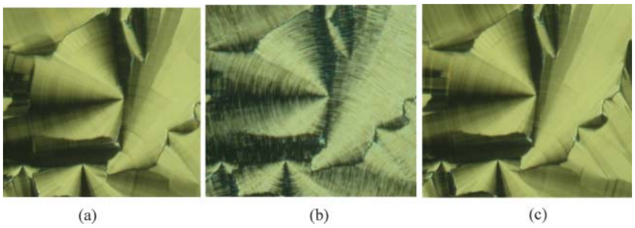


Fig. 11 (a) Texture of the field-induced ferroelectric structure ($\mathrm{SmC_AP_F}$: +4 V μm^{-1}); (b) texture of the ground state antiferroelectric structure at zero field ($\mathrm{SmC_SP_A}$); (c) texture of the field-induced ferroelectric structure ($\mathrm{SmC_AP_F}$: −4 V μm^{-1}); cell thickness: 5 μm; temperature: 118 °C (compound **18**).

experimental conditions the lower temperature SmC_SP_A phase is directly transformed to the higher temperature SmC_SP_A phase without passing through the Col_{ob} phase. From these results it is clear that the transition of the field-induced SmC_AP_A phase into the reentrant SmC_SP_A phase is irreversible. Furthermore, the Col_{ob} phase does not exist above a critical electric field.

We found that on application of a sufficiently high electric field above the transition temperature for SmC_SP_A to SmA (*i.e.* in the existence region of the SmA phase) the SmA fan-shaped texture can be transformed to another texture, which is identical to that of the field-induced SmC_SP_F phase. If the field is switched off the fan-shaped texture of the SmA phase reappears. Furthermore, the switching current response obtained in the field-induced $SmCP_A$ phase is identical to that of the lower temperature $SmCP_A$ phase. That means, by the application of a sufficiently high electric field the transition temperature for $SmCP_A$ to SmA can be enhanced. The critical field which is necessary for this field-induced transition from SmA to SmC_SP_F increases with the temperature. Applying a field of 35 V μm^{-1} the enhancement of the transition temperature was found to be 2 K. This effect is in a sense similar to the field-induced enhancement of the transition temperature for $SmCP_A$ to isotropic which was reported for a few bent-core mesogens.[18,19]

5. Discussion

It was shown that all members of the series form an antiferroelectric $SmCP_A$ phase. With the exception of compound **8**, the $SmCP_A$ phase can occur in different structural variants. In the case of compound **12** we found a field-induced transition from the anticlinic (chiral) SmC_AP_A phase to the synclinic (racemic) SmC_SP_A phase below a definite temperature. This field-induced transition is reversible. But in the absence of an electric field either the chiral SmC_AP_A (formed on cooling of the isotropic liquid) or the racemic SmC_SP_A (formed by relaxation of the field-induced SmC_AP_F state) is stable in the whole temperature range of the $SmCP_A$ phase. We have no explanation of why the anticlinic SmC_AP_A phase is the high-temperature phase with respect to the synclinic SmC_SP_A phase. Actually the synclinic structure should be more stable and should occur at a higher temperature because a synclinic stacking of the layers favours out-of layer fluctuations and therefore enhances the entropy. Heppke *et al.*[20] reported that the transition from the racemic SmC_SP_A phase into the chiral SmC_AP_A phase can be achieved by the application of a high rectangular or DC field whereas the reverse transition is possible by a high triangular field.

The longer-chain homologues **14**, **16**, **18** and the bromine-substituted compound **16-Br** show a rich polymorphism. On the basis of experimental observations of texture, X-ray diffraction and electro-optical measurements, four mesophases in the sequence SmA–SmC_SP_A–Col_{ob}–SmC_SP_A could be identified. Phase sequences with conventional smectic phases as well as "banana phases" are not unknown but are hitherto observed in only a few homologous series (see for example references 12,21,22). As shown by NMR measurements such polymorphism variants are mainly due to the decrease of the bending angle of the molecules with decreasing temperature. According to this it can be assumed that at higher temperatures the molecules adopt a more rod-like shape conformation, which enables an easier rotation of the molecules around their long axes, which is characteristic for SmA (or SmC) phases. It is important to note that in the present case only the compounds with longer terminal chains ($n \geqslant 14$) showed the SmA phase. This points to a situation, wherein the terminal alkyl chains too have a strong influence on the rotational freedom of the molecules about their long axes. Obviously, the higher conformational disorder of the long aliphatic chains in the highest temperature range enables a rotation of the molecules (or the aromatic middle parts) and as a result the SmA phase is obtained.

On lowering the temperature this rotation is hindered and the molecules are packed in a specific way that results in the polar order of the SmC_SP_A phase. Since the texture of the field-on and field-off states remained the same in the SmC_SP_A phase, the switching mechanism is based on a collective rotation of the molecules around their long axes (see Fig. 12).

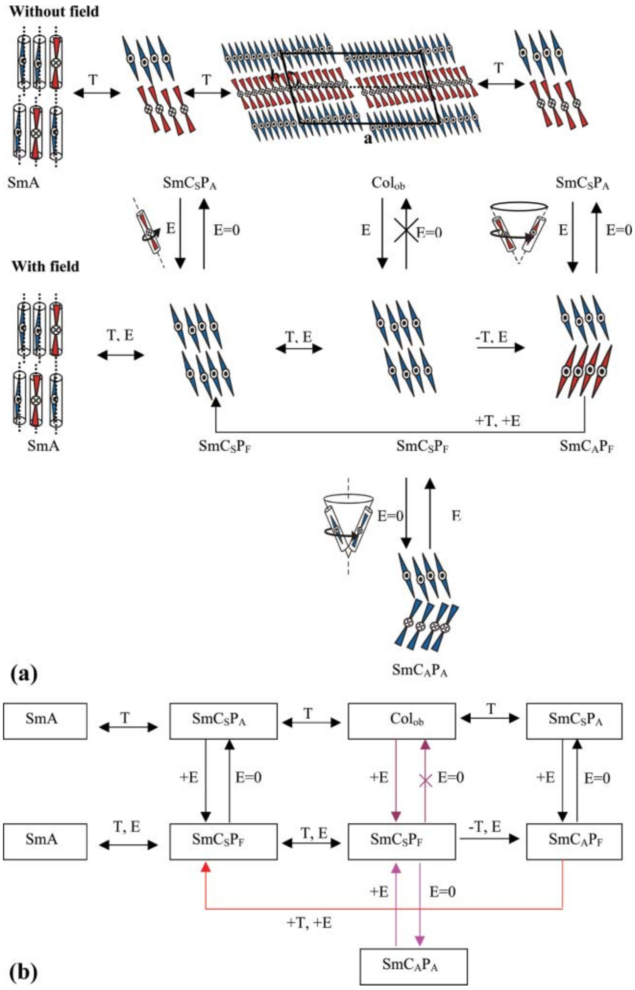


Fig. 12 (a) Possible molecular arrangements of the mesophases in the ground state and under the applied electric field (compounds **14**, **16**, **18** and **16-Br**); (b) block diagram explaining the transitions of the mesophases with temperature and electric field.

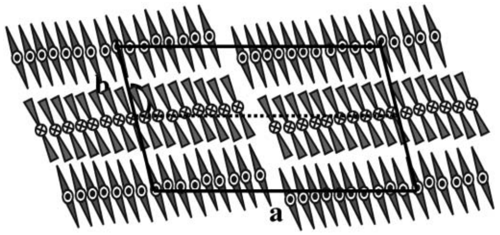


Fig. 13 Structure model for the $\mathrm{Col_{ob}}$ phase (considering the number of molecules in the unit cell).

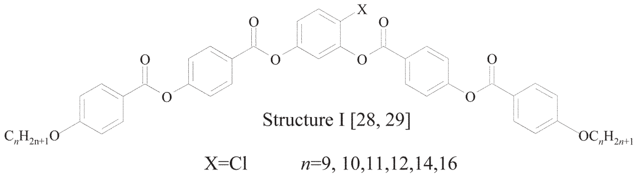
On further lowering of the temperature we have observed an interesting structural change in the arrangements of the molecules. The molecules, which are arranged in smectic layers, are fragmented into the broken-layer structure of a columnar phase with an oblique lattice. It is known from the electro-optical measurements that the $\mathrm{Col_{ob}}$ phase has an antiferroelectric packing of bent-core molecules. It is plausible because an intercalation of molecules of the adjacent layers favours a synclinic tilt (Fig. 13). From the X-ray studies a period in one direction is derived which corresponds to the length of the molecules if the tilt is considered. But the knowledge of the antiferroelectric packing demands a doubling of the translational period. Under an electric field this $\mathrm{Col_{ob}}$ phase can be transformed to a simple layered structure ($\mathrm{SmC_SP_F}$ state). On terminating the field this $\mathrm{SmC_SP_F}$ state does not relax to the $\mathrm{SmC_SP_A}$ state (as found for the high-temperature $\mathrm{SmC_SP_A}$ phase) but instead to the homochiral $\mathrm{SmC_AP_A}$ state by rotation of the molecules around the tilt cone (see the schematic representation in Fig. 12). On cooling of the field-induced homochiral $\mathrm{SmC_SP_F}$ phase below 123 °C, a transition to the racemic $\mathrm{SmC_AP_F}$ phase takes place (like in compound **12**), which relaxes to the $\mathrm{SmC_SP_A}$ ground state on termination of the field. In both of the mesophases the relaxation takes place by a collective rotation of the molecules around the tilt cone (Fig. 12a). Interestingly the racemic $\mathrm{SmC_AP_F}$ or $\mathrm{SmC_SP_A}$ state remains stable on heating up to 134 °C where the homochiral $\mathrm{SmC_SP_F}$ phase reappears (see block diagram in Fig. 12b).

An irreversible field-induced transition of a Col phase to an $\mathrm{SmCP_F}$ phase was observed by Reddy *et al.*[8,23] It is also reported in the literature that the field-induced transition from a columnar to a smectic phase can be reversible, *i.e.* on removal of the applied field the Col phase reappears. Such behaviour was found for $\mathrm{Col_r}$,[24] $\mathrm{Col_{ob}}$,[25] bilayer $\mathrm{Col_{ob}}$[26] and undulated $\mathrm{SmC_SP_F}$ phases.[27]

The significant point to be noticed is the occurrence of two $\mathrm{SmC_SP_A}$ phases, one above and the other one below the existence range of the $\mathrm{Col_{ob}}$ phase. These phases are structurally identical and exhibit a synclinic stacking of the smectic layers. Because of their structural identity the low-temperature $\mathrm{SmC_SP_A}$ phase can be regarded as a reentrant phase, which reappears on cooling the $\mathrm{Col_{ob}}$ phase. Both $\mathrm{SmC_SP_A}$ phases differ only in the mechanism of polar switching. In the reentrant $\mathrm{SmC_SP_A}$ phase the switching takes place in the usual way through a rotation of the director around the tilt cone ($\mathrm{SmC_SP_A} \rightarrow \mathrm{SmC_AP_F}$). However, in the high-temperature $\mathrm{SmC_SP_A}$ phase the switching is based on a collective rotation of the molecules around their long axes ($\mathrm{SmC_SP_A} \rightarrow \mathrm{SmC_SP_F}$). In the latter case the polar switching is accompanied by the inversion of the chirality in each second layer. Interestingly, there are a few examples reported in the literature where in the existence range of the $\mathrm{SmCP_A}$ phase the mechanism of the polar switching depends on the temperature. At a higher temperature the switching takes place by rotation of the molecules around their long axes and at a lower temperature by rotation around the tilt cone.[13–16] This dependency is identical in the high- and low-temperature $\mathrm{SmC_SP_A}$ phases of the present set of compounds.

Another finding of fundamental interest is the field-induced transition of the non-polar SmA phase to the polar $\mathrm{SmCP_A}$ phase above the transition temperature of $\mathrm{SmCP_A} \rightarrow \mathrm{SmA}$. This field-induced enhancement of this transition can be up to 2 K depending on the strength of the applied electric field. This effect is reminiscent of the field-induced enhancement of the $\mathrm{SmCP_A} \rightarrow$ isotropic temperature by application of the electric field.[18,19] This effect may be connected with the existence of polar clusters in a short-range order region already in the non-polar phases (SmA, isotropic).

Comparison with isomeric compounds ***I***



One of the basic problems, which are of interest to synthetic chemists as well as to theoreticians, is the pronounced influence of the direction of the linking groups (in our case of ester groups) on the mesophase behaviour in bent-core mesogens. Therefore we compare the homologues under discussion with analogous isomeric compounds **I**, which differ only by the direction of the outer ester groups.[28,29] The clearing temperatures of compounds **I** are about 50 K lower than those of compounds **8**, **12**, **14**, **16** and **18**. On the other hand, the mesophase behaviour is also completely different. The short-chain members of the series **I** ($\mathrm{C_9}$–$\mathrm{C_{12}}$) exhibit a nematic phase and a highly viscous and optically isotropic ferroelectric mesophase which spontaneously forms domains of opposite handedness.[28,29] The hexadecyloxy homologue shows—instead of the isotropic mesophase—a polar tilted smectic phase with unusual switching behaviour.[30]

We can notice that there are similar differences between analogous isomeric compounds without lateral substituents in the 4-position of the central core. In this case also the clearing temperatures differ by about 40 K and the mesophase behaviour is clearly different.[15,25] It could be shown that the direction of the ester linking groups has a significant influence on the dipole moment, on the conformation (in particular on the bending angle) and on the conformational flexibility. For example, isomers where the direction of the ester groups in each leg is opposite (like in the compounds under discussion) have a lower conformational degree of freedom, which is responsible for higher clearing temperatures and a distinct mesophase behaviour.[25,31]

6. Summary

We have presented a new homologous series of five-ring bent-core mesogens having chlorine substituents in the 4-position of the central phenyl ring. The homologues with shorter terminal chains formed an SmCP$_A$ phase, the homologues with longer terminal chains (**14**, **16** and **18**) showed a new polymorphism variant SmA–SmC$_S$P$_A$–Col$_{ob}$–SmC$_S$P$_A$ for the first time. The Col$_{ob}$ phase can be irreversibly transformed to the SmC$_S$P$_F$ phase by the application of a sufficiently high electric field. Both SmC$_S$P$_A$ phases are structurally identical and differ only by the mechanism of polar switching. The switching of the high-temperature SmC$_S$P$_A$ phase is based on a collective rotation of the molecules around their long axes whereas the switching of the reentrant SmC$_S$P$_A$ phase takes place through the collective rotation of the molecules around the tilt cone. It is remarkable that the SmA phase shows a reversible field-induced transition to the SmC$_S$P$_A$ phase. Comparing the mesophase behavior of isomeric compounds leads to the conclusion that the influence of the dipole moment and the conformational flexibility is more profound in bent-core compounds than in calamitic liquid crystals.

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