Silylated bent-core molecules: the influence of the direction of the carboxyl connecting groups on the mesophase behaviour[†]

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Novel bent-core molecules based on phenyl benzoate rigid cores and heptamethyltrisiloxane units at one or at both ends of the aliphatic side chains were synthesized and investigated by polarized light microscopy, differential scanning calorimetry, X-ray diffraction and electrooptical methods and the effect of the direction of the carboxyl groups on the mesomorphic self assembly was investigated. A series of distinct liquid crystalline phases was found, among them ferroelectric and antiferroelectric switching and also non-switchable smectic, undulated smectic (USmC) and modulated smectic phases (columnar phases, Col_{ob}). All polar phases show field-induced inversion of chirality at least in a certain temperature range. Moreover, two non-polar and uniaxial smectic phases were observed, one with a hollow cone-like orientational director distribution (SmC_R) and the other one with a maximum of the director distribution at zero tilt (SmA). These two phases were discussed in relation to the distinct models of de Vries type smectic phases.

1. Introduction

Liquid crystals (LCs) are ordered fluids in which the segregation of incompatible units and parallel alignment of rigid units combine to give rise to positional and orientational long-range order.1 One of the most exciting areas in this field is provided by the so-called banana-shaped or bent-core liquid crystals, developed since 1996.^{2,3} The exciting feature of the molecules is that the bent shape of the aromatic core restricts the rotation around the long axis which leads to a preferred organization of these molecules with uniform bent direction. This gives rise to a macroscopic polar order within these LC phases providing ferroelectric (FE) and antiferroelectric (AF) switching LC materials being of interest for numerous potential applications in electrooptical switches, as optical phase modulators, nonlinear optical materials, etc.3d,4 In addition, in most mesophases of bent-core compounds the molecules are tilted with respect to the layer normal. The unique combination of tilted organization in layers and polar order reduces the symmetry of these structures. The resulting C_2 symmetry leads to an inherent superstructural chirality⁵ in which layer normal, tilt direction and polar direction describe either a right- or left-handed system and hence these structures are chiral.⁵ This superstructural chirality and the possibility of switching of chirality by external fields6 immediately arose broad and general scientific attention.3c-e

Oligo(siloxane) containing bent-core compounds appear to be one of the most successful classes of compounds showing macroscopic polar order and superstructural chirality.⁷⁻¹¹ This is mainly due to the nano-segregation of the oligo(siloxane) units into distinct sublayers located at the inter-layer interfaces. These sublayers influence the coupling between the layers which modifies the self-assembly of the bent-core molecules. In addition, the significant space required by these units leads to a frustration of flat layers and induces undulated and modulated morphologies. For this reason a large variety of bent-core molecules based on oligosiloxane and carbosilane segments have been synthesized in recent years,^{7–11} among them also dimesogens,^{8a,d,g} oligomesogens,^{8b,e} dendrimers^{8b,d,f} and side chain polymers.^{8c}

The majority of these oligosiloxane and carbosilane substituted bent core molecules incorporate a resorcinol or 3,4'-disubstituted biphenyl moiety as central bent unit, coupled with phenyl benzoate based rod-like wings derived from 4-hydroxy benzoic acid. In these molecules the COO linking groups have a uniform direction with all Ar–O bonds directed towards the bent unit in the middle of these molecules (see Chart 1, compounds of type 1). In previous work with non-silylated bent-core molecules it has been shown that reversing the direction of one, two, three or even all four of the COO groups has a strong impact on mesophase stability and mesophase types.¹²

In this contribution attention is focussed on the effects of changing the direction of the carboxyl groups in siloxane substituted bent core molecules (see Chart 1) which are compared with the effects of the same structural variation previously observed in non-silylated molecules.^{12a} Besides different types of ferroelectric or antiferroelectric switching smectic, undulated smectic (USmC) and modulated smectic (columnar, Col_{ob}) phases also two non-polar and uniaxial smectic phases were observed, one with a hollow cone-like

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Chart 1 Structures of compounds under investigation.

orientational director distribution (SmC_R) and a SmA phase with a maximum of the director orientation at zero tilt. These two phases are of interest with respect to the actual discussion around the distinct models of de Vries type smectic phases.

2. Synthesis and methods of investigation

The synthesis of the olefinic compounds **En-1–En-6** was carried out by esterification reactions as outlined in the ESI[†] (Schemes S1–S5). The silylated compounds **Si-1–Si-6** were obtained from these olefins and 1,1,1,3,3,5,5-heptamethyltrisiloxane by hydrosilylation reaction using Karstedts catalyst.¹³ All the silylated compounds were purified by column chromatography with a short pad of silica gel using chloroform and methanol mixture as eluent, followed by crystallization/precipitation using chloroform/acetonitrile solvent mixtures. The experimental procedures and analytical data are also reported in the ESI[†].

Phase transitions were determined by polarizing optical microscopy (Optiphot 2, Nikon) in conjunction with a heating stage (FP 82 HT, Mettler) and by differential scanning calorimetry (DSC-7, Perkin Elmer). The assignment of the mesophases was made on the basis of optical textures and by X-ray diffraction (XRD). Investigations of surface aligned samples were performed using a 2D detector (HI-Star, Siemens). Uniform orientation was achieved by slowly cooling a drop of the compound on a glass surface. The X-ray beam was applied parallel to the substrate (exposure time: between 30 min and 3 h). Electrooptical experiments have been carried out using a home built setup in commercially available ITO coated glass cells (E.H.C., Japan) with a measuring area of 1 cm². Dielectric investigations of compound Si-3 were performed in the range from 1 Hz to 10 MHz using a Solartron-Schlumberger Impendance Analyzer Si 1260 and a Chelesa Interface. A brass cell coated with gold (distance = 0.05 mm) was used as capacitor.

3. Results and discussion

3.1. Mesomorphic properties of bent-core compounds with olefinic end groups

3.1.1 Compounds with double bonds at each end (En-1-En-4). The transition temperatures and associated enthalpies of the diolefins En-1-En-4 are recorded in Table 1. All compounds consist of five phenyl rings interconnected by exclusively carboxyl groups. Compound En-1 with all COO groups directed towards the central 1,3-disubstituted phenyl ring, *i.e.* with the Ar-O bonds closer to the bent unit than the Ar-C bonds, shows a monotropic SmCPA^[*] phase which has already been investigated by Jakli et al.14 All other diolefins represent new compounds; compounds En-2 and En-4 show only monotropic LC phases which rapidly crystallize so that they were only detected by polarizing microscopy and a more precise phase assignment was not possible, whereas compound En-3 has an enantiotropic (thermodynamically stable) LC phase. In the series En-n the melting temperatures rise with increasing number of COO groups reversed compared to those in En-1, *i.e.* En-1 \approx En-2 < En-3 < En-4, and also the mesophase stability is increasing in this order.

The clearing temperature of the SmA phase of En-4 with all COO linking groups pointing away from the central 1,3-disubstituted benzene ring (isophthalate based bent core) is the highest and it is more than 80 K more stable than the SmCP_A phase of En-1, in which all COO groups point towards the central 1,3disubstituted benzene ring (resorcinol based bent core). This indicates that the orientation of the COO groups has a large effect on the mesophase stability. A similar effect has been reported for related bent-core molecules with simple alkyl chains, without olefinic end groups and was attributed to changes of the molecular flexibility, the torsional and bending angles, and the magnitude and distribution of the dipole/quadrupole moments.^{12b} As the rotational barrier of the Ar-COO bond is higher than the Ar-OOC bond, compounds with the COO groups directed towards the bent core-unit have a higher flexibility, providing lower transition temperatures.^{12b} Beside conformational effects also the effects of the COO direction upon the electrostatic surface potential have to be considered as electron deficient aromatics and also an alternation of electron rich and electron deficient aromatics favors intermolecular interactions, hence stabilizing smectic phases.¹⁵ This should also contribute to the mesophase stability of compounds En-3 and En-4 incorporating electron deficient terephthalate and isophthalate units, respectively.¹⁶ Together with the effects provided by the terminal chains (segregation, intercalation, space filling, flexibility, etc.) these factors influence the packing mode of the molecules in a complex and hardly predictable way.

Compound En-3 is the most interesting compound in this series. This molecule is symmetric with respect to the central 1,3-disubstituted benzene ring and the direction of the COO groups in the inner and outer positions of the rod-like wing groups is opposite (terephthalate based rod-like wings). This compound shows spherulitic textures (Fig. 1a), the same texture as observed for the related compounds with simple alkoxy chains, assigned to an undulated smectic phase (USmCP_{FE} phase).^{6c} However, only the layer reflections (01 and 02) at

Table 1 Phase transition temperatures ($T/^{\circ}$ C) and enthalpy values ($\Delta H/kJ \text{ mol}^{-1}$, in square brackets) obtained for the olefinic bent-core compounds **En-1** to **En-4**^{*a*}



No	\mathbf{X}^{1}	\mathbf{Y}^{1}	Y^2	X^2	Phase transitions
En-1	COO	COO	OOC	OOC	Cr 101 [52] (SmCP _A ^[*] 95 [18]) Iso ^{10,14}
En-2	COO	OOC	OOC	OOC	Cr 107 [66] (SmC 92 [14]) ^b Iso
En-3	OOC	COO	OOC	COO	Cr 147 [88] USmCP _{FE} 153 [22] Iso
En-4	OOC	OOC	COO	COO	Cr 182 [80] (SmA 177) ^b Iso

^{*a*} COO groups which are reversed compared to **En-1** are highlighted in bold; peak temperatures (temperatures at maximum heat flow) of the first DSC heating curves (10 K min⁻¹) are given; monotropic transitions (shown in parenthesis) were taken from the second heating run; abbreviations: Cr = crystalline solid; Iso = isotropic liquid; SmC = polar or non-polar tilted smectic phase with unknown structure (Schlieren texture with relatively low viscosity and spherulitic domains were observed by polarizing microscopy); SmA = nontilted smectic phase; SmCP_A^[*] = antiferroelectric switching tilted smectic phase with dark conglomerate texture in the ground state; USmCP_{FE} = ferroelectric switching undulated SmC phase. ^{*b*} Mesophase crystallizes immediately.



Fig. 1 Investigation of compound **En-3**: (a) optical photomicrograph (crossed polarizers) showing the growth of the mesophase from the isotropic liquid at 153 °C (dark areas are residues of the liquid phase in equilibrium); (b) FE switching current response obtained under a triangular wave field (320 V_{pp}, 20 Hz, 5 μ m, $P_s = 220$ nC cm⁻²); (c–e) bistable switching as seen under a DC electric field at 145 °C; (c) texture under an applied DC field of +50 V; (d) texture as observed after removing the field and (e) texture at 0 V after application of an field with opposite sign; arrows indicate the direction of polarizer and analyzer.

d = 4.5 nm could be measured with sufficient accuracy by XRD for the mesophase of compound **En-3** (see Fig. S1, Table S1†). The additional *hk* reflections expected for an undulated smectic phase are very weak or coincide with the strong 01 reflection, therefore exact 2D lattice parameters cannot be calculated. Assigning the indices 10 or 20 to the weak inner reflection at d = 9.0 nm an undulation period of about 9 or 18 nm would result,¹⁷ a reasonable value if compared with those for **En-5** and **En-6** (see next Section 3.1.2). The splitting of the diffuse wide angle scattering indicates a tilted organization of the molecules in the layers with a tilt angle in the range of 25° (see Fig. S1 and S2[†]). Though tilt is proven by XRD, the extinction crosses in the circular domains of the textures (Fig. 1a) are parallel to polarizer and analyzer. This can be explained by a polarization modulated and undulated B7-like structure of this mesophase as described by Clark *et al.*¹⁸

Triangular-wave electric field experiments evidence a single polarization peak for each half period indicating a ferroelectric switching for this mesophase (see Fig. 1b). The spontaneous polarization is 220 nC cm^{-2} , which is also comparable to the



Fig. 2 Mechanisms of polar switching in SmCP phases and their modulated and undulated variants. (a) Switching by collective rotation of the molecules on the tilt cone and (b) switching by collective rotation of the molecules around their long axes; mechanism (b) is accompanied by an inversion of the layer chirality.

values obtained for the related alkyloxy substituted analogues without double bonds.^{6c} Moreover, bistable switching is clearly confirmed by electro-optical investigations as follows. As seen in Fig. 1c-e, under an electric field the dark extinction crosses are inclined with the positions of polarizer and analyzer which indicates a field-induced homogeneously chiral SmC_sP_F structure (actually a (+)-SmC_s P_F and a (-)-SmC_s P_F domain can be seen in Fig. 1c-e). The extinction crosses are inclined by 30°, indicating an optical tilt of 30°.19 This mesophase evidences a temperature and frequency dependent change of the switching process. Under an applied voltage of 320 V_{pp} (peak-to-peak voltage of the applied triangular wave AC voltage) in a 5 µm cell at high temperature (T > 145 °C) or at low frequency (f < 10 Hz) no rotation of the extinction crosses is observed. This indicates that under these conditions a switching around the long axes takes place, which changes only the polar direction. Hence, the layer chirality and also the phase chirality are reversed in this switching process, *i.e.* the (+)-SmC_s P_F domains become (-)-SmC_s P_F and the (-)-SmC_sP_F domains become (+)-SmC_sP_F (see Fig. 2b).

However, at lower temperature (T < 145 °C) or at higher frequency (f > 10 Hz) switching around a tilt cone is observed. In this switching process polar direction and tilt direction are changed simultaneously (see Fig. 2a), *i.e.* this switching process is associated with a rotation of the extinction crosses and it retains the layer chirality. These extinction crosses do not change their position after switching off the electric field, and only rotate after reversal of the applied field, which confirms bistable, *i.e.* FE switching on a cone. This indicates that under an electric field the layer modulation is largely removed and an SmC phase is induced.²⁰

3.1.2 Compounds with only one double bond (En-5 and En-6). The mesophase of compound En-5 (Table 2) with only one terminal double bond is very similar to En-3, having the same direction of the COO linking groups. Not only the texture but also the XRD patterns and the electrooptical switching of both compounds are very similar (Fig. S10-S12[†]). As in the case of En-3 beside the layer reflections (layer spacing 4.9 nm) weak additional reflections were observed in the XRD pattern (see Fig. S1, Table S1^{\dagger}), the inner reflection (d = 8.9 nm) pointing to a similar period of about 9 or 18 nm as in the case of En-3, confirming an undulated or modulated SmC structure of this mesophase.¹⁷ This compound also shows FE switching ($P_s = 240$ nC cm⁻²) with a temperature and frequency dependent transition from rotation on a cone at low temperature (T < 142 °C) and high frequency (>10 Hz) to collective rotation around the long axis at high temperature and low frequency (Fig. S11 and S12⁺).

Compound **En-6** which differs in the direction of the two COO groups Y¹ and X² from **En-5** shows a distinct, more fan-like texture (Fig. S13†). Since we got a well aligned sample of this compound for XRD measurements (Fig. 3), the 2D lattice could be determined as an oblique one with lattice parameters a = 15.6 nm, b = 4.8 nm, and $\gamma = 103^{\circ}$ at 110 °C, indicating a similar layer spacing as observed for **En-3** and **En-5**, and an undulation period of 15.6 nm (see Table S2†). At 120 °C, a = 13.9 nm, b = 4.8 nm, and $\gamma = 102^{\circ}$ have been calculated that means the layer distance remains almost constant with rising temperature and the undulation period decreases. The wide angle XRD pattern proves the tilted organization of the molecules with respect to the normal to a by 26° (see Fig. 3 and S2†). Based on

Table 2 Phase transition temperatures ($T/^{\circ}C$), enthalpy values ($\Delta H/kJ \text{ mol}^{-1}$, in square brackets) and lattice parameters obtained for the bent-core compounds **En-5** and **En-6** with one terminal double bond^{*a*}

			C ₁₄ H ₂₉ O	X1	1 Y ² () () () () () () () () () ()	
No	\mathbf{X}^{1}	\mathbf{Y}^1	Y ²	X ²	Phase transitions	Lattice parameters/nm (T/°C)
En-5 En-6		COO 00C	OOC OOC	COO OOC	Cr 144 [82] USmCP _{FE} 156 [24] Iso Cr 103 [55] Col _{ob} P _{FE} 123 [19] Iso	d = 4.9 $a = 15.6, b = 4.8, \gamma = 103^{\circ} (110)$ $a = 13.9, b = 4.8, \gamma = 102^{\circ} (120)$

^{*a*} Peak temperatures in the first DSC heating curves (10 K min⁻¹), for a representative DSC curve see Fig. S9[†]; abbreviations: $Col_{ob}P_{FE}$ = ferroelectric switching Col_{ob} phase; for further explanations see Table 1.



Fig. 3 XRD patterns obtained in the USmCP_{FE} phase of compound En-6: (a) complete XRD pattern at 100 °C; the diffuse character of the wide angle scattering indicates the absence of positional long range order as typical for LC phases; the maxima of the wide angle scattering are located between equator and meridian, indicating a tilted arrangement of the molecules (XRD tilt = 26°); (b) small angle region at $110 ^{\circ}$ C, and (c) same pattern with indexation to an oblique lattice.

this XRD evidence this mesophase is assigned as $\text{Col}_{ob}\text{P}_{\text{FE}}$. The same temperature and frequency dependence of the FE switching process as reported for the USmCP_{FE} phases of **En-3** and **En-5** are observed with a transition between switching on a cone and switching around the long axis at T = 110 °C and 10 Hz (300 V_{pp} in a 5 µm cell), but the spontaneous polarization is larger ($P_{\rm s} = 800 \text{ nC} \text{ cm}^{-2}$, see Fig. S13–S15†)²¹ and all transition temperatures are shifted to lower values.

In all three compounds En-3, En-5 and En-6 the ground state texture is transformed under an electric field into a spherulitic texture (see Fig. 1c-e, S12 and S15[†]) which can be interpreted as a field induced transition from the undulated/modulated ground state structures into a field induced smectic phase with uniform polar order (SmCP_F), *i.e.* as a partial suppression or even a complete removal of layer undulations/modulations under the influence of the electric field (Fig. 4).18 As the degree of layer undulation/modulation influences the switching process, it strongly depends on the experimental conditions, such as the strength of applied voltage, cell thickness, applied frequency, temperature, etc. In general, switching by rotation on a cone is the faster process in flat layers as obtained at low temperature and high voltage, but it is inhibited by layer modulations. As the modulation/undulation wave length is temperature (and voltage) dependent and for the compounds under discussion decreases (*i.e.* layer modulation increases) with rising temperature, sharp layer modulation remaining at higher temperature (or at lower voltage) inhibits the switching by rotation on a cone. In this case switching around the long axis becomes the dominating switching process. On the other hand, the increase of the viscosity with decreasing temperature has a stronger retarding effect on the



Fig. 4 Schematic sketches comparing the molecular assembly in smectic C phases with those in modulated (Col_{ob}) and undulated (USmC) smectic C phases. Only non-symmetric undulation and non-polar variants of the phases are shown, in which the bent-core molecules are rotationally disordered around their long axes (therefore simplified to straight lines); restricted rotation leads to polar order and hence to ferroelectric or antiferroelectric variants; the transition between these three phase types is continuous and is often influenced by different effects; the most often observed effects of temperature (T) and electric fields (E) are shown with arrows.

rotation around the long axis, making this process at lower T slower than the switching on a cone. Therefore, the switching frequency must be decreased to give the system sufficient time for switching around the long axis, which explains the frequency dependence of the switching process. Though for all three compounds **En-3**, **En-5** and **En-6** an undulated/modulated layer structure was confirmed, only the USmCP_{FE} phases of compounds **En-3** and **En-5** seem to be similar to polarization undulated/modulated B7 phases whereas the Col_{ob}P_{FE} phase of **En-6** is a mesophase with oblique lattice and non-symmetric layer modulation, more similar to B1-type phases.

3.2. Mesomorphic properties of bent-core compounds with two oligosiloxane groups (Si-1 to Si-4)

Phase transition temperatures and associated enthalpies for the Si-containing compounds **Si-***n* consisting of five phenyl rings interconnected exclusively by COO groups and heptamethyl-trisiloxane units at both the terminals are collated in Table 3.

As observed in the series of compounds En-1–En-4, also in the series Si-1–Si-4 there is a strong impact of the direction of the COO groups upon the mesophase type, the melting temperatures and the mesophase stability. Also in this series compound Si-1 (ref. 10) with all COO groups directed towards the central 1,3-disubstituted benzene ring has a significantly lower mesophase stability than compound Si-4 with all COO groups pointing away from the centre (ΔT is about 70 K). Hence, the general trends concerning the mesophase stability are the same as seen for the olefin terminated molecules. However, the silyl groups reduce the melting points and in most cases stabilize the LC phases and increase the mesophase region

Table 3 Phase transition temperatures ($T/^{\circ}C$), enthalpy values ($\Delta H/kJ \text{ mol}^{-1}$, in square brackets) and lattice parameters obtained for the silicon containing bent-core compounds Si-1 to Si-4^{*a*}



No	\mathbf{X}^{1}	\mathbf{Y}^{1}	\mathbf{Y}^2	\mathbf{X}^2	Phase transitions	Lattice parameters/nm ($T/^{\circ}C$)
Si-1	COO	COO	OOC	OOC	Cr 83 [13] Col _{ob} P _A 116 [22] Iso ¹⁰	$a = 2.0, b = 4.3, \gamma = 97^{\circ}$ (105)
Si-2	COO	OOC	OOC	OOC	Cr 70 [6.4] Col _{ob} ' 90 [—] Col _{ob} P _A 107 [—] Col _{ob} 115 [17.5] Iso	d = 4.7 (100)
Si-3	OOC	COO	OOC	COO	Cr 69 [6.6] Col _{ob} 125 [3.8] SmC _R 140 [3.5] Iso	$d = 5.2 (132), a = 7.9, b = 5.5, \gamma = 112^{\circ} (86)$
Si-4	OOC	OOC	COO	COO	Cr 161 [59] SmC _a P _A 174 [7.1] SmA 185 [15.6] Iso	d = 5.3 (180), d = 5.3 (165)

^{*a*} COO groups which are reversed compared to Si-1 are highlighted in bold; peak temperatures in the first DSC heating curves (10 K min⁻¹), for DSC scans see Fig. S16–S18†; abbreviations: Col_{ob} , Col_{ob}' = oblique columnar phases showing no polar switching; $Col_{ob}P_A$ = antiferroelectric switching Col_{ob} phase; SmC_R = optical uniaxial smectic phase with randomly tilted organization of the molecules; SmA = nontilted smectic phase; SmC_aP_A = antiferroelectric switching SmC phase with anticlinic layer corrrelation; for further explanations, see Table 1.

compared to related non-silylated compounds. Therefore, in contrast to the diolefins **En**-*n*, all silylated molecules **Si**-*n* show enantiotropic LC phases and there is a larger diversity of different mesophases.

3.2.1 Compounds Si-1 and Si-2: modulated smectic phases. As reported earlier, compound Si-1 exhibits an AF switching oblique columnar phase (Col_{ob}P_A, a = 2.0 nm, b = 4.3 nm and $\gamma = 97^{\circ}$).¹⁰ As typical for the AF switching in Col_{ob}P_A phases also for this compound the switching takes place (at all temperatures) by rotation around the molecular long axis which reverses the chirality.

In compound Si-2 (with a 3-hydroxybenzoate bent unit) only one of the inner ester groups (Y¹) is reversed in comparison to compound Si-1. Upon cooling from the isotropic liquid state a rather low birefringent texture develops (see Fig. 5a). This mesophase cannot be aligned homeotropically; instead by shearing a more birefringent texture is induced, as often observed for columnar LC phases. However, X-ray investigations indicate only a layer reflection corresponding to d = 4.7 nm with the second order (Fig. 5b and c) for the whole temperature region. The *d*-spacing is significantly smaller than the molecular length L (estimated from CPK molecular models as L = 7.1 nm in a conformation shown in Fig. S21d[†]), indicating a strongly tilted arrangement of the molecules in the mesophase. In the wide angle region there are two diffuse scatterings, one with the maximum at d = 0.7 nm forms a closed ring and is assigned to the mean distance between the siloxane units; the second one at d = 0.47nm is assigned to the mean distances between the aliphatic and aromatic units. It has maxima at $\chi = 134^{\circ}$ and 226°, confirming a tilt of ca. 44° (see Fig. 5b and S3[†]). Though no clear indication of a layer modulation or undulation can be found in the XRD pattern, the texture is more typical for a mesophase with 2D lattice than for a lamellar LC phase (see mosaic-like features in the texture in Fig. 5a at the left). This assumption is also in line with the observed switching behaviour.

In electric field experiments two repolarisation current peaks per half period of an applied triangular wave voltage were found in the temperature range between T = 90 and 107 °C (Fig. 5d), indicating an AF switching (ColobPA) with a spontaneous polarization $P_s = 165$ nC cm⁻² at T = 100 °C. No switching current peak is observed below 90 °C and above T = 107 °C (however, these temperatures can be slightly shifted to higher or lower depending on the experimental conditions, such as applied voltage and frequency). The changes of the switching behaviour are not associated with any enthalpy change in the DSC curves (see Fig. S16[†]) and there is also no distinct change of the textures at these temperatures. The extinction crosses of circular domains, grown under a triangular wave electric field upon cooling from the isotropic state, are inclined with the directions of polarizer and analyzer and this indicates a synclinic tilted organization (Fig. 5e) with an optical tilt of about 30°. The position of the extinction crosses does not change at the transition to the polar switching phase at T = 107 °C, but below this temperature a reduction of the birefringence is observed (probably due to a change of the mode of anchoring of the ribbons with respect to the surface²²). The extinction crosses do not rotate upon polarization reversal and hence, switching takes place by a collective rotation around the long axis of the molecules. This mode of switching and the strong splitting of the polarization peaks associated with a significant threshold voltage are similar to observations made for the ColobPA phases of other double silylated bent-core compounds^{9b} as for example compound Si-1.¹⁰ Hence, it seems that compound Si-2 behaves similar to Si-1, forming a modulated and AF switching tilted smectic phase $(Col_{ob}P_A)$ in the temperature range between 90 and 107 °C. The loss of polar switching below 90 °C (Col_{ob}' phase) might be due to the enhanced viscosity which makes the rotation around the long axis too slow to follow the reversal of the field direction under the maximal available threshold voltage. A rotation on a cone, as observed for compounds En-3, En-5 and En-6, is disfavoured in this case due to the presence of sharp boundaries



Fig. 5 Investigation of compound **Si-2**: (a) texture as observed between crossed polarizers at T = 110 °C; X-ray diffraction pattern at 110 °C: (b) complete pattern showing the two diffuse wide angle scatterings and (c) small angle region; (d) repolarization current response curves under a triangular wave electric field (300 V_{pp} at 30 Hz, ITO coated 5 µm cell) in the Col_{ob}P_A phase at 100 °C, $P_S = 165$ nC cm⁻²; (e) synclinic domain as seen under the same conditions between crossed polarizers.

within the layer modulation even under a relatively high applied electric field.²³ At higher temperature (T > 107 °C, assigned as Col_{ob}) the polar order might be lost due to the thermal expansion of the bulky siloxane units, which reduces the packing density of the aromatic cores.²⁴

3.2.2 Compound Si-3: randomly tilted SmC_R phase. In compound Si-3 both outer COO groups (X¹ and X²) were

reversed compared to Si-1, whereas the direction of the inner COO groups (Y¹ and Y²) was retained (resorcinol bisbenzoates with terephthalate based rod-like wings). This compound shows two mesophases (Table 3, Fig. S17[†]), the high temperature phase exhibits a weakly birefringent fan-shaped texture (see Fig. 6a). On shearing it becomes completely dark (optically isotropic), very similar to SmA phases (Fig. 6c, left).²⁵ This indicates the optical uniaxiality of this LC phase. XRD confirms a layer structure, but the layer distance (d = 5.2 nm, Table S1[†]) is significantly smaller than the length L = 7.1 nm estimated for this kind of molecules (see Fig. S21d[†]). This is a first indication for a tilted organization of the molecules in this smectic phase which is confirmed by the XRD pattern of an aligned sample in which the diffuse wide-angle maxima make an angle of about 30° with respect to the equator (Fig. 6d and S4[†]).²⁶ The clearly proven tilted organization is in conflict with the optical uniaxiality of this smectic phase. This can be explained either by a tilted organization with a random distribution of the tilt direction in adjacent layers (non-correlated SmC phase) or by an orientationally disordered micro-domain structure, where the differently tilted domains have a size which is smaller than the wave length of light.

No electro-optical switching could be observed even at high electric fields and therefore we assign this phase as SmC_R , where R stands for the random distribution of the tilt director. The random tilt is also assumed to be responsible for the low bire-fringence of the fan-texture in this mesophase. The same phase type was also observed for a recently reported molecule related to **Si-3**, but with an additional methyl group in 2-position of the resorcinol unit.¹¹ For this methyl substituted compound a transition to a columnar phase with *p2gg* lattice was observed at reduced temperature.

Also for compound **Si-3**, on decreasing temperature, a phase transition to a columnar phase takes place (Fig. 6b and c), which is associated with the occurrence of a birefringent texture in the homeotropically aligned regions (Fig. 6c, inset). This mesophase is more viscous than the smectic phase and the reflections in the XRD pattern of an aligned sample can be indexed to an oblique lattice having lattice parameters a = 7.9 nm, b = 5.45 nm and $\gamma = 112^{\circ}$ at 86 °C (see Fig. 6e, g and h, Table S3†). Also in this mesophase no electro-optical switching could be observed even at high electric fields up to 400 V_{pp} in a 5 µm cell. Hence, the low temperature mesophase is designated as Col_{ob}. This Col_{ob} phase seems to be a non-polar variant of the Col_{ob}P_A phase of compound **Si-1**¹⁰ with the additional difference that the cross-section of the ribbons is about four times larger (Table S5†).

Based on these observations and the fact that the fluid smectic phase at higher temperature also does not show any polar switching, it is assumed that the absence of long-range polar order in this ribbon phase (Col_{ob}) is due to the nearly free rotation of the molecules around their long axes, which is retained in the ribbon phase. This macroscopically nonpolar structure is also in agreement with the comparatively small transition enthalpy values of $3.5 \text{ kJ} \text{ mol}^{-1}$ for the Iso–SmC_R transition and $3.8 \text{ kJ} \text{ mol}^{-1}$ for the SmC_R–Col_{ob} transition, whereas the enthalpy values for transitions to polar ordered phases are typically much higher, usually in the order of $15-25 \text{ kJ} \text{ mol}^{-1}$.

Dielectric measurements on a non-oriented sample of compound Si-3 were performed in a brass cell coated with gold, and a distance between the capacitor plates of 0.05 mm.²⁷ The



Fig. 6 Investigation of compound **Si-3**: optical images obtained under a polarizing microscope between crossed polarizers: (a) SmC_R phase at 135 °C, (b) phase transition to the Col_{ob} phase at 125 °C, (c) phase transition as observed in a homeotropically aligned sample at 125 °C, inset shows the texture of the Col_{ob} phase developed from the homeotropically aligned smectic phase; XRD patterns of a surface aligned sample: (d) complete pattern obtained in the SmC_R phase at T = 132 °C showing two maxima of the outer diffuse scattering, (e) in the Col_{ob} phase at 86 °C; small angle region (f) in the SmC_R phase, (g) in the Col_{ob} phase, and (h) same pattern with reciprocal lattices for two domains and reciprocal axes and indices for one domain.

calculated limits of the dielectric permittivity and the relaxation times are presented in Fig. 7a and b, respectively.27 In the SmC_R phase only one well visible relaxation in the MHz range was detected. No hints to a kHz process, typical for ferroelectric clusters, are seen. Due to the compensation of the longitudinal dipole components of compound Si-3 this relaxation must be related to the fast reorientation of the molecules about the long axis. The low frequency limit of the permittivity decreases strongly at the transition into the Colob phase. This effect is related to a spontaneous orientation of the long axes of the molecules in direction of the measuring field and reduces considerably the dielectric strength of the processes to the experimental limit. A second, also very weak absorption, is seen at high frequencies during crystallization where the homeotropic order is destroyed. This process may be related to the faster dynamics of the terminal groups in the molecules. It has to be

noted that relaxation process 1 did not show a strong decrease of relaxation frequency at the phase transition $\text{SmC}_{R}/\text{Col}_{ob}$. Therefore, there is no evidence for a ferroelectric order in the columnar phase, as well. Hence, the dielectric investigations are in line with a non-polar structure of the SmC_{R} as well as Col_{ob} phase (see Fig. 7).

3.2.3 Compound Si-4: SmC_aP_A–SmA transition. In compound Si-4, all the ester groups are reversed with respect to compound Si-1. This compound has the highest transition temperatures of all reported compounds Si-*n* (see Table 3, Fig. S18†). There are two mesophases, separated by a phase transition at T = 174 °C with a substantial transition enthalpy $(\Delta H = 7.1 \text{ kJ mol}^{-1})$. The high temperature phase shows a strongly birefringent fan-shaped texture as typical for non-polar smectic A phases (see Fig. 8a). Shearing indicates a relatively low viscosity,



Fig. 7 (a) Limits of the dielectric permittivity of **Si-3** *vs.* temperature; ε_0 and ε_1 representing the low and high frequency limits of the first relaxation mechanism, ε_1 and ε_2 that of the second mechanism; (b) relaxation frequency of the two mechanism *vs.* temperature.

as typical for usual SmA phases, and immediately leads to homeotropic alignment which appears completely dark (optically isotropic) between crossed polarizers, indicating an optically uniaxial mesophase. The texture becomes broken at the transition to the low temperature phase (Fig. 8b) and in the homeotropically aligned sample a mixture of regions with Schlieren texture and regions with non-specific birefringent texture, as often seen for SmCP_A phases, develops (Fig. 8c). The XRD patterns of the high temperature phase show a diffuse wide-angle scattering at d = 0.48nm with maxima perpendicular to the layer reflection in the small angle region (see Fig. 8e and S5, Table S1†), confirming a SmA structure with on average non-tilted molecular cores and a layer spacing of d = 5.3 nm. There are only very weak second order layer reflections indicating an almost sinusoidal electron density distribution along the layer normal.

The layer distance is the same in the low temperature phase, but it is derived from layer reflections of first to third order resulting from sharper defined layers, and the outer diffuse scattering at d = 0.47 nm shows a broader azimuthal distribution with maxima between equator and meridian from which an average tilt of the long molecular axes of about 23° can be calculated (Fig. 8d and S5†). These features clearly hint to an SmC structure at low temperature. In both phases there is a weak second outer diffuse scattering at about d = 0.7 nm showing uniform intensity distribution along a ring which can be attributed to the average distance between the siloxane units.

Under an applied triangular-wave field, no polarization current response could be detected at T > 174 °C (SmA phase). Upon decreasing temperature at the phase transition to the low temperature phase two polarization current peaks appeared, which clearly evidence AF switching with a polarization value of 530 nC cm⁻² (SmC_aP_A phase, Fig. 8f). In circular domains the extinction crosses are oriented along the directions of the crossed polarizers and no change in the position of the extinction crosses could be observed either on field-removal or reversing the field direction (Fig. 8g and h). Hence, there should be an anticlinic tilt (SmC_aP_A phase) and polarization reversal seems to take place by collective rotation around the long axes. This might be due to the bulkiness of the siloxane units providing additional space for rotation around the long axis.⁹ Related direct SmCP_A-to-SmA transitions (without intermediate SmC phase) are rare and have been previously observed only for few compounds.^{12c,28–30}

3.2.4 Relation of the SmC_R and SmA phases of Si-3 and Si-4 with de Vries type smectic phases. No layer shrinkage could be observed for the SmA–SmC_aP_A transition of compound Si-4 which is in line with the behaviour typically observed for SmA–SmCP_A transitions of (non-silylated) bent-core mesogens, where at the transition to the tilted phase no layer shrinkage and some times even an expansion of the *d*-value is observed.^{28,30} This can be explained as a consequence of the more dense packing of bent core molecules in smectic phases with polar order, where layer shrinkage by tilt is compensated by stretching the alkyl chains due to packing constraints resulting from a more dense core packing.

However, in the case of rod-like molecules non-layer shrinkage at the SmA-SmC transition is regarded as a first indication of a de Vries like behaviour.³¹⁻³³ According to the present understanding of de Vries type smectic phases there are two distinct models. One assumes a diffuse orientational director distribution having a maximum at zero tilt, and the other model suggests a hollow-cone type director distribution with maxima at a preferred tilt angle and a local minimum at zero tilt.³² It is proposed that de Vries type smectic phases combine unusual low orientational order and high smectic order, e.g. they are stabilized by micro-segregation rather than orientational ordering.³² Hence, de Vries behaviour is generally found in materials with a strong tendency for nano-segregation,³⁴ as compounds with fluorinated tails and siloxane units.35 Bent-core mesogens, especially those with silvlated segments clearly belong to this type of mesogens.⁷⁻⁹ Hence, it is interesting to compare the optically uniaxial mesophases of compounds Si-3 and Si-4 under this aspect.

There are significant differences between compounds Si-3 and Si-4 with respect to the detailed structures of their mesophases. In both cases the high temperature phase is an optically uniaxial smectic phase with nearly identical layer spacing (d = 5.2-5.3 nm) which is much smaller than the molecular length (L = 7.1 nm, see Fig. S21d[†]). However, the director distribution is distinct in these two smectic phases as evident from the XRD patterns of aligned samples (Fig. 6d, 8e, S4 and S5[†]). Compound Si-4 with an isophthalate core seems to favour anticlinic tilt at lower temperature and a randomization of the tilt with an orientational director distribution having a maximum at zero tilt is observed in the smectic phase at higher temperature (SmA). In the case of compound Si-3 with a resorcinol core and terephthalate based wings synclinic organization is preferred in the low temperature phase (Col_{ob}) and randomization of tilt with hollow-cone type orientational director distribution is observed for the smectic phases at higher temperature (SmC_R, see Fig. 9a). In this case the



Fig. 8 Investigation of compound **Si-4**: optical images obtained between crossed polarizers: (a) broken focal-conic texture of the SmA phase at 180 °C, (b) weakly birefringent texture of SmC_aP_A phase at 165 °C, (c) birefringent texture developing in the homeotropically aligned sample of the SmA phase at the transition to the SmC_aP_A phase at 174 °C; XRD patterns of a partially surface aligned sample on heating (see also θ -scans over the wide angle scattering, shown in Fig. S5†): (d) SmC_aP_A phase at 165 °C and (e) SmA phase at T = 180 °C; (f) antiferroelectric switching current response in the SmC_aP_A phase at 164 °C (130 V_{pp}, 6 Hz, 5 µm, P_S = 530 nC cm⁻²); optical images: (g) under a DC electric field, no change in the position of the extinction crosses is observed even after changing the sign of the applied field, (h) same extinction cross after field removal.

orientational order parameter has a preferred angle ($\beta = 30^{\circ}$) and a minimum at zero tilt. It appears that the SmC_R phase is formed by SmC clusters with only short range correlation of the tilt direction in adjacent clusters. Upon cooling, these clusters coalesce with formation of ribbons which organize to a 2D lattice, leading to the Col_{ob} phase. For Si-4 anticlinic tilt seems to be more preferred which inhibits formation of a ribbon structure and leads to a SmC_aP_A phase at lower temperature. In the high temperature smectic phase of Si-4 the preference for anticlinic tilt is retained and together with the generally reduced tendency for a uniform tilt, provided by this kind of aromatic core (also the non-silylated compound En-4 forms a SmA phase), an orientational director distribution with a maximum at zero tilt is obtained (see Fig. 9b). Hence, the uniaxial smectic phases SmA and SmC_R of these two compounds can be regarded as examples for the two distinct models of organization in optically uniaxial smectic phases which are under discussion for de Vries type smectic phases.^{31b,32} The fact that relatively sharp layers showing a second and third order layer reflection were observed for the SmC_R phase of Si-3, but only a sinusoidal electron density modulation is found for the SmA phase of Si-4 is in line with these two distinct models. In the SmA phase sinusoidal director distribution leads to a stronger distribution of the effective molecular length which requires a stronger interpenetration of molecules in adjacent layers and hence the interfaces are more diffuse in this phase.

To the best of our knowledge, there is presently no direct XRD proof for a hollow cone director distribution in a de Vries type



Fig. 9 Schematic sketches of the proposed molecular organizations and schematic plots of the director distributions in the smectic phases of compounds Si-3 and Si-4 as deduced from the distinct XRD patterns: (a) SmC_R phase of compound Si-3 with preferred synclinic tilt correlation (only two tilt directions are shown, but in reality all tilt directions are possible) and (b) SmA phase of compound Si-4; in both cases the bent core molecules are rotationally disordered around their long axes (hence shown as solid lines).

smectic phase of rod-like mesogens. However, for bent-core mesogens, beside the non-polar SmC_{R} type reported herein and also found for a related compound, similar to Si-4, but with additional methyl group in 2-position of the resorcinol core,¹¹ there is also an example of a bent-core mesogen with a ferroelectric switching smectic phase with randomization of tilt and polar order, assigned as SmCP_R.^{8b} Hence, it appears that for bent-core mesogens de Vries type smectic phase with hollow cone-like director distribution are more common, or it is easier to detect them experimentally because for these compounds the tilt angle is sufficiently large. It appears that formation of SmC_R phases requires a sufficiently dense packing, leading to a strong tendency for clustering as provided by bent core molecules. This has to be combined with a preference for relatively large tilt angles and synclinic tilt. In the case of bent-core mesogens there is a high intrinsic tendency for strongly tilted arrangements which is mainly due to the distinct space filling of the densely packed aromatic cores and fluid aliphatic chains.³⁶ This intrinsic tilt is strengthened or weakened by dipolar, quadrupolar and electrostatic (donoracceptor) interactions between the aromatic cores, and hence, is affected by the orientation of the linking groups. If the tendency for tilt is relatively weak, as in most rod-like mesogens and also in the case of the terephthalate Si-4 and, in addition, anticlinic tilt is preferred, then it is more likely that the maximum of the orientational director distribution is along the layer normal.

Based on the shape of the diffuse wide angle scattering (see Fig. S5†) and the relatively high birefringence of the smectic phase (Fig. 8a) it seems that the SmA phase of compound Si-4 is more similar to classical SmA phases and layer shrinkage at the SmA-to-SmC transition is compensated by the more dense packing achieved in the SmC_aP_A phase where rotation around the long axis is reduced. However, the SmC_R phase of compound Si-3 has some relation to de Vries type smectic phases with hollow cone-like director distribution.

3.3 Mesomorphic properties of bent-core compounds Si-5 and Si-6 with only one silyl group

Attaching a siloxane unit to only one alkyl chain of a bent-core mesogen is in the case of phenyl benzoate based resorcinols of type 1 (see Chart 1) often associated with replacement of antiferroelectric switching SmCP_A phases (B2 phases) by ferroelectric switching dark conglomerate phases (SmCP_{FE}^[*] phases).⁷ This was attributed to the softening and decoupling of the smectic layers by the micro-segregated sublayers formed by the silyl groups.⁷ Layer distortion due to the bulkiness of the silyl groups is in the case of monosilylated compounds minimized by antiparallel packing of the molecules in the layers.⁷ Also for compounds Si-5 and Si-6 the siloxane units modify the properties of the non-silylated precursors En-5 and En-6 (see Tables 2 and 4).

The textures of compounds Si-5 and Si-6 are very similar to each other and indicate mesophases with 2D-lattice (Fig. 10a and 11a), which is confirmed by the XRD patterns (Fig. S7[†] and 11c-e). For both compounds there are two diffuse wide angle scatterings. The one at d = 0.7 nm assigned to the mean distance between the siloxanes is very weak, as the number of siloxane units is reduced compared to compounds Si-1-Si-4.7 This wide angle scattering is circular without distinct maximum whereas the second one at d = 0.46 nm, assigned to the mean distance between alkyl chains and aromatics, is more intense and in the case of compound Si-6 has maxima at $\chi = 64, 123, 237, \text{ and } 302^{\circ}$ indicating a tilt of about 30° with respect to the normal to the modulated layers (Fig. 11c and S6[†]). For this compound the small angle region shows a strong layer reflection with three harmonics and additional hk and k0 reflections which can be indexed to an oblique lattice with parameters a = 17.9 nm,

Table 4 Phase transition temperatures ($T/^{\circ}C$), enthalpy values ($\Delta H/kJ \text{ mol}^{-1}$, in square brackets) and lattice parameters obtained for the silicon containing bent-core compounds Si-5 and Si-6^{*a*}

	/2 .
	×2
X	si si si
C ₁₄ H ₂₉ O ⁻	• O(CH ₂)11 0 0

Si-5 OOC COO OOC COO $Cr 127 [19] Col_{ob} 140 [] Col_{ob} P_{FE} 157 [23] Iso d_{10} = 15, d_{01} = 5.5 (130)Si-6 OOC OOC OOC Cr 112 [33] Col_{+-} 130 [] Col_{+} P_{FE} 136 [21] Iso d_{} = 17, 9, b_{} = 53, \alpha = 10$	No	\mathbf{X}^1	\mathbf{Y}^1	Y ²	X^2	Phase transitions	Lattice parameters/nm ($T/^{\circ}C$)
Si-6 OOC OOC OCC $r = 112 [33] Col + 130 [-1] Col + P_{} [36 [21]] Iso a = 17.9 \ b = 5.3 \ w = 10^{-1}$	Si-5	OOC	COO	OOC	COO	Cr 127 [19] Col _{ob} 140 [—] Col _{ob} P _{FE} 157 [23] Iso	$d_{10} = 15, d_{01} = 5.5 (130)$
u = 17.5, v = 5.5, v = 100	Si-6	00C	OOC	OOC	OOC	Cr 112 [33] Col _{ob} 130 [—] Col _{ob} P _{FE} 136 [21] Iso	$a = 17.9, b = 5.3, \gamma = 100^{\circ} (130)$



Fig. 10 Investigation of compound **Si-5**: (a) optical texture as obtained under a polarizing microscope between crossed polarizers at T = 157 °C during growing from the isotropic liquid (dark areas); (b) texture as obtained by cooling from the isotropic liquid under a triangular wave field (with or without applied field, T = 153 °C); (c) polarization current curve as obtained under an applied triangular wave voltage (400 V_{pp}, 10 Hz, 5 µm ITO cell, $P_{\rm S} = 220$ nC cm⁻²) at T = 153 °C.

b = 5.3 nm and $\gamma = 100^{\circ}$ (Fig. 11d and e, Table S4). For Si-5 we could not get as well aligned samples for the XRD measurements as in the case of compound Si-6. Only *h*0 and 0*k* reflections could be distinguished for a tentative indexing analogous to that for Si-6 (see Fig. S7 and Table S1[†]) and therefore the angle γ of the 2D lattice could not be determined. From the calculated *d* values for these reflections ($d_{10} = 15$ nm, $d_{01} = 5.5$ nm) a similar 2D lattice as in the case of Si-6 may be considered. Because of few other similarities between Si-5 and Si-6, as textures and switching behaviour (see below), it is quite sure that the mesophases of both compounds represent the same type of Col_{ob}P_{FE} phase.

Like compounds En-5 and En-6 also compounds Si-5 and Si-6 show ferroelectric switching (Fig. 10c and 11b). However, for Si-5 and Si-6 polar switching is restricted to certain temperature ranges, which depend on the strength of the applied electric field and the frequency. Under a voltage of 400 V_{pp} with a frequency of 10 Hz in a 5 µm cell for compound Si-5 ferroelectric switching takes place between 140 and 157 °C ($P_{\rm S} = 220 \text{ nC cm}^{-2}$) and under the same conditions for compound Si-6 switching is observed between 130 and 136 °C ($P_{\rm S} = 180$ nC cm⁻²). No switching could be observed below 140° C and 130 °C, respectively. For both compounds there is no change of the position of the extinction crosses during switching, indicating a polar switching around the long axis at all frequencies. The loss of polar switching below a certain temperature limit might in both cases be due to an increased threshold voltage for this switching process at reduced temperature, as viscosity increases; an alternative switching by rotation on a cone, as observed for the polar phases of the corresponding olefins En-5 and En-6 seems to be inhibited by the modulated (broken) layer structure of the mesophases of compounds Si-5 and Si-6 (Colob phases) which seems to be not removed under the applied voltage (see Fig. 10b, this kind of mosaic-like texture is typically observed for modulated smectic phases) and these modulations are unfavorable for rotation on a cone.

Though there is some similarity between the mesophases of the silvlated compounds Si-5 and Si-6 and the corresponding olefin En-5 and En-6, both showing large modulation wave lengths and ferroelectric switching, the mesophases of the non-silvlated compounds have less steric frustration and these mesophases are more similar to undulated/modulated smectic phases for which the contribution of polarization splay to layer modulation is important.18,37 In these mesophases layer undulation/modulation can be completely removed at sufficiently high threshold voltage and switching around the cone can take place in distinct temperature ranges and at sufficiently low frequencies after completely suppressing the layer modulation under the applied electric field. However, in the broken layers of the Col_{ob} phases of the silvlated compounds Si-5 and Si-6, where the steric layer distortion by the bulky silyl units provides a significant additional contribution to layer modulation which in this case cannot be completely removed under the applied electric field, a switching on a cone is not possible.

4. Summary and conclusions

The present investigation is focussed on the effects of the direction of COO linking groups on the mesomorphic behaviour of silyl substituted bent core mesogens and the comparison with related non-silylated compounds. It turned out that reversing the direction of one, two, or all four COO groups in silylated bentcore molecules leads to a change of mesophase stability and mesophase structure, similar to the previously reported nonsilylated bent-core compounds. The mesophases formed by molecules with oligosiloxane groups at only one end are in some respect similar to those of the related olefins, though modulated variants of smectic phases are more common in the series of silylated compounds due to the steric layer frustration provided by the bulky oligosiloxane groups. A stronger effect of the silyl groups on mesophase structure is observed for bent core



Fig. 11 Investigation of compound **Si-6**: (a) optical texture obtained under a polarizing microscope between crossed polarizers at T = 133 °C; (b) polarization current curve as obtained under an applied triangular wave voltage (400 V_{pp}, 10 Hz, 5 µm ITO cell; $P_S = 165$ nC cm⁻²) at T = 132 °C; XRD patterns of surface aligned samples at $T = 130^{\circ}$ in the Col_{ob}P_{FE} phase: (c) complete pattern, (d) small angle region, and (e) part of the small angle region with reciprocal axes, 2D lattice and indices for the observed reflections for one domain.

molecules silylated at both ends. This is most likely due to the stronger steric frustration resulting from the bulky siloxane units at both ends, which in this case cannot be compensated by antiparallel packing of the molecules.^{7,9} Nevertheless, it is remarkable that for some compounds in distinct temperature regions polar switching phases can be achieved despite this significant steric frustration. However, if polar switching is observed it is of the antiferroelectric type, whereas compounds with only one silyl end group show ferroelectric switching.

Among the mesophases formed by the double silvlated compounds the modulated tilted smectic phases (Col_{ob}) are dominating which can be non-polar or antiferroelectric. In the modulated smectic phases of silvlated compounds polar switching usually takes place by collective rotation around the long axis which reverses the chirality, whereas in the undulated USmCP_{FE} and modulated ColobPFE phases of the non-silylated compounds also rotation on a cone is possible if the rotation around the long axis becomes slow due to enhanced viscosity. An especially interesting phase is formed by the resorcinol bisbenzoates with terephthalate based rod-like wings (Si-3), which represents a randomly tilted SmC_R phase. It is considered as a kind of de Vries type smectic phase with hollow cone-like orientational director distribution and represents a new variant of mesophases formed by bent-core mesogens.³⁸ It seems to have a cluster structure composed of synclinic tilted molecules with randomized tilt direction.³⁹ Moreover, in all siloxane-containing compounds melting points are lower than for the corresponding compounds with hydrocarbon chains or olefinic double bonds. Therefore, the introduction of siloxane units widens the LC phase ranges and provides enantiotropic LC properties for

compounds which otherwise would be crystalline or only monotropic. Moreover, the mesophases formed by silylated bent-core compounds are less viscous; this solves one of the major problems in investigation and application of bent-core compounds.

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