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The carbosilane unit as a stable building block for liquid crystal design: a new class of ferroelectric switching banana-shaped mesogens

Christina Keith,[a] R. Amaranatha Reddy,[b] Harald Hahn,[c] Heinrich Lang[c] and Carsten Tschierske*[a]

[a] *Institute of Organic Chemistry, Martin-Luther-University Halle-Wittenberg, Kurt-Mothes Str. 2, D-06120 Halle, Germany. E-mail: Tschierske@chemie.uni-halle.de; Fax: +49(0)345 5527346; Tel: +49(0)345 5525664*

[b] *Institute of Physical Chemistry, Martin-Luther-University Halle-Wittenberg, Mühlpforte 1, D-06108 Halle, Germany*

[c] *Department of Chemistry, TU Chemnitz, Institute of Inorganic Chemistry, Str. der Nationen 62, D-09111 Chemnitz, Germany*

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New banana shaped liquid crystals with a carbosilane unit at one end were synthesised and depending on the number of Si-atoms either antiferroelectric (AF) or ferroelectric (FE) switching polar smectic C phases have been obtained.

Liquid crystalline molecules with a bent molecular shape, so-called banana-shaped LC, have attracted much attention since Niori *et al.*[1] found that such materials organise into new ordered fluid (liquid crystalline) phases with polar order and chiral superstructures, despite of the fact that the molecules themselves have an achiral configuration. Since then numerous bent-core liquid crystals have been synthesised and investigated and new liquid crystalline phases have been discovered for these compounds.[2] Such molecules might be of interest, for example, as switchable nonlinear optical materials in light modulating devices.[3]

Molecules with an oligo(siloxane) segment at one of the termini (*e.g.* compound **2**) have recently been synthesised in our laboratory.[4] These molecules turned out to have ferroelectric (FE) switching behaviour[5] in contrast to the antiferroelectric (AF) switching which is usually found for the smectic phases of related molecules with simple alkyl chains (*e.g.* compound **1**).[4] This lead to the idea that the micro-segregation of the oligo(siloxane) units from the aliphatic and rigid aromatic molecular parts gives rise to distinct oligo(siloxane) sublayers and these sublayers stabilise the FE organisation (SmCP$_F$) of the molecules.[4] It is thought that this stabilisation is due to the suppression of the interlayer fluctuations of the molecules by these distinct oligo(siloxane) sublayers, as shown in Fig. 1.

Herein we report the first low molecular weight liquid crystalline bent-core mesogens (**3** and **4**) having carbosilane units[6] instead of the oligosiloxane entities (compound **2**) and it will be shown that these chemically more stable molecules behave very similar to the oligosiloxane derivatives, *i.e.* they form FE switching banana phases instead of the AF usually observed.

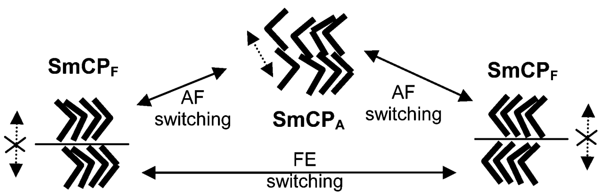
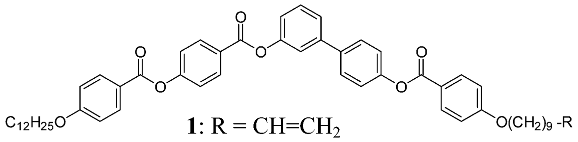


Fig. 1 Organisation of bent-core molecules in the polar smectic phases, the molecules are additionally tilted with respect to the projection plane. The SmCP$_A$ structure is stabilised energetically by the escape from a macroscopic polarisation and entropically by the out-of-plane interlayer fluctuations (indicated by the dotted arrows), which are more difficult in the corresponding SmCP$_F$ states. If the layers are separated by a micro-segregated sublayer, then the out-of-plane interlayer fluctuations are less important for the stabilisation of the SmCP$_A$ structure and in this case surface stabilisation within the measurement cells can lead to a stabilisation of the SmCP$_F$ state with respect to the SmCP$_A$ state, leading to bistable FE switching instead of the tristable AF switching.

Molecules **3** and **4** can be synthesised by hydrosilylation of the terminally unsaturated bent-core mesogen **1** with the appropriate H end-grafted carbosilanes using Karstedt's catalyst.[7],† The obtained compounds were investigated by polarised light optical microscopy, X-ray scattering and electro-optical investigations.



1: R = CH=CH$_2$
2: R = $CH_2CH_2(SiMe_2O)_2SiMe_3$
3: R = $CH_2CH_2SiMe_2C_2H_5$
4: R= $CH_2CH_2[SiMe_2(CH_2)_3]_nSiMe_3$

Compounds **3, 4a** and **4b** form liquid crystalline phases over rather broad temperature regions. The powder X-ray diffraction pattern‡ of the liquid crystalline phases of all three compounds are very similar. In the small angle region sharp layer reflections up to the fourth order can be found which indicates well defined layer structures for the mesophases. The length of the molecules is significantly larger than the layer thickness (*e.g.* **4a**; L = 7.1 nm, most extended conformation, d = 5.17 nm) which is in line with a monolayer structure, resulting from an antiparallel end-to-end packing of tilted molecules. A very broad diffuse scattering, found in the wide-angle region with a maximum at about 0.51 nm confirms the absence of in-plane order. Furthermore, this value is relatively large when compared with the mean distance between the aliphatic chains usually observed. This is attributed to the dimethylsilyl groups at the ends of the chains, but in contrast to the related compounds with oligo(siloxane) terminal groups (*e.g.* **2**) no distinct maximum for the mean distance of the Si-containing segments can be found.

The texture of compound **3**, having the rather small ethyldimethylsilyl end group is very similar to the conventional AF switching SmCP$_A$ phase of the parent compound **1** with a terminal C=C double bond (birefringent schlieren texture). The mesophases of **4a** and **4b** having longer carbosilane units appear optically isotropic between crossed polarisers, but by rotating the polariser, regions of different brightness can be observed. Rotating the polariser in the other direction reverses the brightness of the domains. This is a clear indication of a chiral superstructure and these textural features are completely identical with those reported for the related siloxane substituted compounds.[4]

The switching behaviour, which was investigated using the triangular wave method, is different for **3** and the compounds **4a** and **4b**. Compound **3** with a ethyldimethylsilyl end group shows two repolarisation peaks in the modified triangular wave where a plateau is introduced at zero voltage,[8] although only a single peak is observed in a simple triangular wave even at a very low frequency of only 1 Hz (Fig. 2a). Hence, the switching process is clearly tristable, indicating an AF ground state (P_S = 890 nC cm^{-2}). Compounds **4** with larger carbosilane units show only one peak in the switching current response. This single peak does not

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split if a modified triangular wave voltage is applied (Fig. 2b), which are strong indications of FE switching (P_S = 690 nC cm^{-2}).[9] Also optical investigation of the switching (DC field) reveals a bistable switching process for **4a** and **4b** (Fig. 3, the extinction brushes do not relax at zero voltage) and a tristable switching process for **3** (the extinction brushes do relax at zero voltage).

There is a strong similarity between the behaviour of the siloxane substituted compounds, as **2** and the related carbosilane derivatives **4a** and **4b**. FE switching is found in both series of compounds if the Si-containing segment is sufficiently large. This is a strong indication that the effect of the carbosilane units upon the liquid crystalline behaviour is almost the same as that of the oligo(siloxane) unit. Not only the type of mesophase, but also the transition temperatures are very similar for both series of compounds. A major advantage of the carbosilanes is their significantly higher hydrolytic stability compared to the siloxanes. For example, the carbosilane unit can be introduced at any step of the synthetic sequence, whereas the introduction of the oligo(siloxane) units has to be done in one of the final steps. This increased stability is also of importance for potential applications of such materials in devices and for the design of other LC materials. Possible reasons for the observed similarity in LC phase behaviour might be a certain segregation of the branched carbosilane segments from linear alkyl chains, a stronger incompatibility of these units with the rigid aromatic cores and the relatively large space occupied by these units, effects which are very similar to those of the oligo(siloxane) moeties.

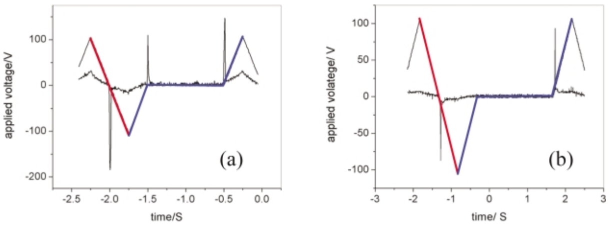

Fig. 2 Switching current response of (a) compound **3** (AF) at T = 107 °C in a 6 μm cell (±105 V, 1 Hz); (b) compound **4a** (FE) at T = 100 °C in a 10 μm cell (±105 V, 0.5 Hz) on applying an alternating simple (red line) and modified triangular wave voltage (along blue line) in ITO coated cells (EHC, Japan).

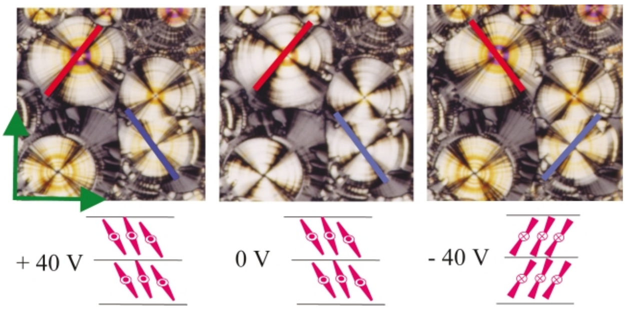

Fig. 3 Bistable (FE) switching of chiral domains (conglomerate of domains with opposite handedness§ as indicated by red and blue lines)¶ obtained for compound **4a** (between crossed polarisers, indicated by the green arrows, T = 100 °C, 10 μm).

Table 1 Phase transition temperatures (T/°C) and transition enthalpy values (ΔH/kJ mol^{-1}, values in italics in brackets) of compounds **1–4**[a]

Comp.	*n*	Phase transitions
1		Cr 108 (SmCP$_A$ 98) Iso
2		Cr 70 [*29.3*] SmCP$_F$ 115 [*24.3*] Iso
3		Cr$_1$ 79 [*13.6*] Cr$_2$ 100 [*23.1*] SmCP$_A$ 114 [*23.3*] Iso
4a	2	Cr 63 [*38.5*] SmCP$_F$ 110 [*27.8*] Iso
4a	3	Cr 66 [*13.2*] SmCP$_F$ 107 [*22.7*] Iso

[a] Determined by DSC (first heating scan, 10 K min^{-1}) and confirmed by polarising microscopy; abbreviations: Cr = crystalline solid state, SmCP$_A$ = AF switching polar tilted lamellar liquid crystalline mesophase, SmCP$_F$ = FE switching polar tilted lamellar liquid crystalline mesophase, Iso = isotropic liquid state.

In summary, banana-shaped molecules incorporating a carbosilane unit at one end have been synthesised and it was shown that these units give rise to a transition from antiferroelectric to ferroelectric switching behaviour in bent-core LC.

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Notes and references

† Expected C, H analyses and ^{1}H-NMR spectra were obtained, *e.g.* compound **4b**: ^{1}H NMR (400 MHz, CDCl$_3$): 8.28 (d, J 8.5, 2H, ArH), 8.14 (d, J 8.9, 4H, ArH), 7.63 (d, J 8.5, 2H, ArH), 7.49 (d, J 5.2, 2H, ArH), 7.44 (m, 1H, ArH), 7.36 (d, J 8.7, 2H, ArH), 7.27 (d, J 8.5, 2H, ArH), 7.21 (m, 1H, ArH), 6.97 (d, J 8.9, 2H, ArH), 6.96 (d, J 8.9, 2H, ArH), 4.03 (m, 4H, OCH$_2$), 1.81 (m, 4H, CH$_2$), 1.45 (m, 4H, CH$_2$), 1.29 (m, 36H, CH$_2$), 0.87 (t, J 6.8, 3H, CH$_3$), 0.53 (m, 12H, SiCH$_2$), 0.46 (m, 2H, SiCH$_2$), −0.05 [s, 9H, Si(CH$_3$)$_3$], −0.07 [s, 18H, Si(CH$_3$)$_2$]; ^{29}Si NMR (99.3 MHz, CDCl$_3$): 1.59, 0.98 (2Si), 0.57.

‡ Aligned samples could not be obtained with compounds **4**.

§ Chirality in these mesophases is due to the tilted organisation of the bent molecules in layers, whereas the molecules themselves have a achiral configuration. The tilt direction, the polar direction and the layer normal define a chiral coordinate system, which can be either right or left handed, depending on tilt-direction and polar direction of the molecules in the layers, see ref. 10 for details.

¶ It is interesting to note that chiral switching domains of opposite handedness could be clearly seen in both FE (SmC$_S$P$_F$; C$_S$ = synclinic correlation between adjacent layers, *i.e.* identical tilt direction in adjacent layers) and AF phases (SmC$_A$P$_A$; C$_A$ = anticlinic correlation between adjacent layers *i.e.* alternating tilt direction in adjacent layers), whereas racemic domains (SmC$_S$P$_A$) were only found for the AF switching phase of compound **3**.

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