The first liquid crystalline dimers consisting of two banana-shaped mesogenic units: a new way for switching between ferroelectricity and antiferroelectricity with bent-core molecules

Gert Dantlgraber,[a] Siegmar Diele[b] 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 5527223; Tel: +49(0)345 5525664

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

Depending on the number of dimethylsiloxane units in the spacer connecting two banana-shaped molecules either ferroelectric or antiferroelectric switchable 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.* found that such materials organise into new liquid crystalline phases with polar order and chiral superstructures, despite of the fact that the molecules themselves are configurationally achiral.[1] Since then numerous bent-core liquid crystals have been synthesised and investigated and a variety of new liquid crystalline phases have been discovered for these compounds.[2] We have recently started a project with the intention to use micro-segregation[3] to modify the phase structure of bent-core molecules. Therefore we have synthesised molecules with oligosiloxane segments. These molecules turned out to have a ferroelectric switching behaviour in contrast to the antiferroelectric switching which is usually found for the smectic phases of related molecules with simple alkyl chains.[4] This leads to the idea that decoupling of the layers by the fluid microsegregated oligosiloxane units disfavours an antiferroelectric organisation of the bent core molecules ($SmCP_A$). Hence, it seems that the antiferroelectric order is not preliminary caused by compensation of the layer polarisation, rather than by the possibility of interlayer fluctuations of the molecules (as indicated by the dotted arrows in Fig. 1). If these fluctuations are suppressed or become otherwise less important,

then the molecules seem to favour an anticlinic, *i.e.* ferroelectric interlayer correlation ($SmCP_F$).

It is known from conventional calamitic LC molecules that the interlayer correlation can be engineered by covalently fixing two molecules at their terminal ends, leading to dimesogens.[5,6] In this case the shape of the connecting unit determines the arrangement of the molecules in adjacent layers. Linear spacers prefer a synclinic interlayer correlation, favouring conventional SmC phases whereas bent spacers usually lead to an anticlinic organisation (SmC_A). In the case of chiral molecules this gives rise to ferroelectric and antiferroelectric properties, respectively.[6]

Herein we report the first liquid crystalline dimers consisting of two bent-core mesogenic units (see Fig. 2). These were synthesised by hydrosilylation of terminally unsaturated bent-core mesogens with hexamethyltrisioxane or octamethyletrasiloxane using Karstedt's catalyst.[7]† The obtained compounds were investigated by polarised light optical microscopy, X-ray scattering and electrooptical investigations. Both compounds form liquid crystalline phases in rather broad temperature regions, which can easily be supercooled, and only partly crystallise even after prolonged storage.

The X-ray diffraction pattern of both liquid crystalline phases are very similar. In the wide angle region there is a diffuse scattering and in the small angle regions sharp layer reflections up to the third order can be found. This indicates well defined layer structures for the mesophases of both compounds, *i.e.* both have smectic phases without in-plane order. The length of the molecules is significantly larger than the layer distances (**1**; $L = 11.7$ nm, $d = 4.1$ nm; **2**: $L = 12.0$ nm, $d = 4.15$ nm). This indicates an interdigitated structure in which the layer period is determined by the length of the mesogenic groups and the thickness of the oligosiloxane sublayer. Additionally, the quite small layer distances indicate that in the mesophases of both compounds the mesogenic units should be tilted.

However, the textures of the mesophases observed for the two compounds under the polarising microscope are completely different. Compound **1** appears optically isotropic between crossed polarisers, but by rotating the polariser, regions of
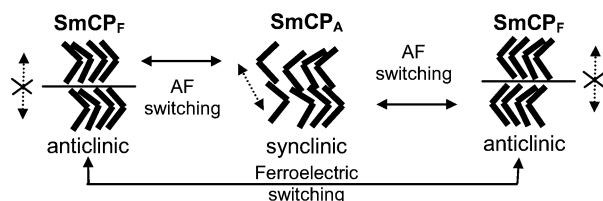

Fig. 1 Organisation of bent core molecules in the polar smectic phases, the molecules are additionally tilted with respect to the projection plane.
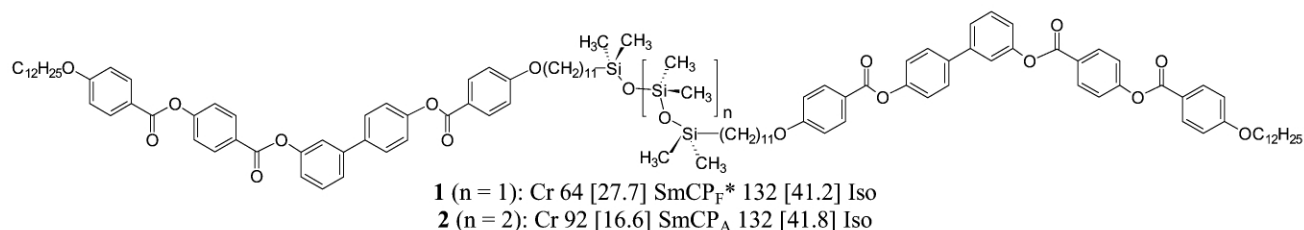

1 (n = 1): Cr 64 [27.7] $SmCP_F$* 132 [41.2] Iso
2 (n = 2): Cr 92 [16.6] $SmCP_A$ 132 [41.8] Iso

Fig. 2 Structures and transition temperatures (T/°C) of the investigated compounds; values in parentheses refer to the transition enthalpies (ΔH/kJ mol^{-1}; DSC; first heating scan; 10 K min^{-1}); abbreviations: Cr = crystalline solid, Iso = isotropic liquid state, $SmCP_F$*, $SmCP_A$ = polar ordered liquid crystalline phases with layer structure, without in-plane order and with a tilted arrangement of the molecules in the layers, which are ferroelectrical (F), respectively antiferroelectrical (A) switchable; * refers to the chiral superstructure in the ground state whereas the molecules themselves have an achiral configuration.

different brightness can be observed. Rotating the polariser in the other direction reverses the brightness of the domains (Fig. 3a,b). This is a clear indication of a chiral superstructure. The domains of different handedness occupy approximately the same area, but upon addition of a small amounts of a chiral dopant (*ca.* 5 mol%) one of the homogenous chiral domains becomes dominant (*ca.* 80% of the area). These textural features are completely identical with those of the siloxane substituted monomeric compounds.[4] Compound **2** exhibits a different texture. On fast cooling (3 K min^{-1}) the texture is similar to that of **1**, but no chiral domains can be detected. On very slow cooling (0.1 K min^{-1}), however, a schlieren texture and highly birefringent domains of a strongly disturbed focal conic texture can reproducibly be found (Fig. 3c). This texture is very typical for ferroelectric switchable SmCP$_A$ phases.
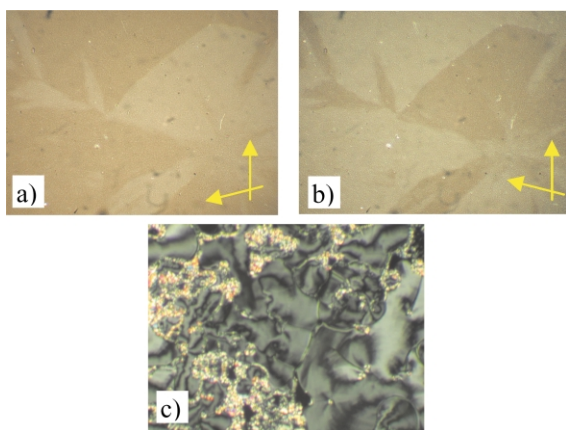

Fig. 3 Textures of the mesophases at $T = 125$ °C; (a,b) compound **1** as seen between slightly decrossed polarisers turned in different directions (images are strongly overexposed); (c) compound **2** between crossed polarisers after slow cooling from the isotropic liquid phase.

Also the switching behaviour which was measured using the triangular wave method is different for the two compounds. Compound **1** with an odd number of siloxane units shows only one peak in the switching current response, which is a strong indication of ferroelectric switching (Fig. 4a). The spontaneous polarisation is calculated as $P_S = 1600$ nC cm^{-2}. Also optical investigation of the switching process reveals a bistable switching. Compound **2** with an even number of siloxane units shows two repolarisation peaks (Fig. 4b) and the switching process is clearly tristable, indicating an antiferroelectric switching ($P_S = 900$ nC cm^{-2}).
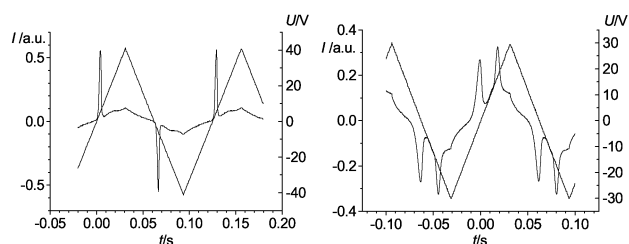

Fig. 4 Switching current response on applying a triangular wave voltage (ITO coated cells, EHC, Japan) at a frequency of 8 Hz: (a) compound **1** at 102 °C in a 5 µm cell (SmCP$_F$); (b) compound **2** at 124 °C in a 6 µm polyimide-coated cell (SmCP$_A$).

Hence there is a strong influence of the parity of the number of siloxane units on the mesophase type. The organisation is ferroelectric for compound **1** with an odd number of dimethylsiloxane units and antiferroelectric for compound **2** with an even number. This effect is due to the special helical conformation of the oligo(dimethylsiloxane) chains. For even numbers of dimethylsiloxane (SiO) units this gives rise to a nearly linear shape, whereas an odd number yields a bent shape.[6] Therefore even numbered SiO units stabilise a synclinic correlation between adjacent layers whereas odd numbered SiO spacers
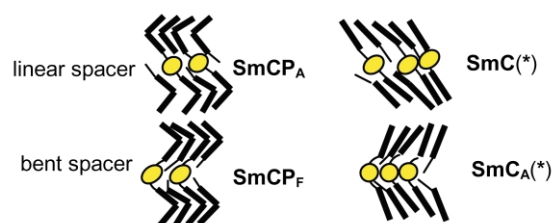

Fig. 5 The distinct influence of the spacer parity on the mesophase structure in dimesogens built up by bent core mesogens and linear rod-like mesogens.

stabilise the anticlinic interlayer correlation (see Fig. 5). Hence, the antiferroelectric structure is preferred by the even numbered spacer unit whereas the ferroelectric state is favoured by the odd numbered SiO unit. This effect of the parity is completely the reverse to that found for chiral dimesogens with linear rod-like mesogenic units, where ferroelectric properties were found for compounds with an even number of SiO units and antiferroelectric properties for those with an odd number.[6]

In summary, we have reported the first dimesogens in which two banana-shaped molecules are connected by a flexible spacer unit.[8] The oligosiloxane units which represent the central part of the spacers have two important effects on the organisation of bent core molecules. At first they segregate into separate sublayers which decouple the layers.[4] This leads to an inherent preference of an anticlinic correlation between adjacent layers, giving rise to ferroelectricity. Secondly, in the reported dimesogens the bent shaped mesogenic units are coupled to each other and therefore the geometry of the connecting unit—which changes with the parity of the SiO units—has an additional effect. Odd numbered SiO units which prefer a bent shape are compatible with the anticlinic correlation (ferroelectric order), whereas linear even numbered spacers disturb the anticlinic interlayer correlation and hence lead to antiferroelectricity.

Notes and references

† Expected C, H analyses and ^{1}H-NMR spectra were obtained, *e.g.* compound **2**: ^{1}H NMR (400 MHz; CDCl$_3$): 0.03 (s, 12H, Si-CH$_3$), 0.05 (s, 12H, Si-CH$_3$), 0.52 (t, *J* 7.6, 4H, Si-CH$_2$), 0.87 (t, *J* 6.6, 6H, CH$_3$), 1.26–1.30 (m, 60H, CH$_2$), 1.42–1.48 (m, 8H, CH$_2$), 1.82–1.79 (m, 8H, CH$_2$), 4.01–4.06 (m, 8H, OCH$_2$), 6.95 (d, *J* 8.8, 4H, Ar–H), 6.97 (d, *J* 8.9, 4H, Ar–H), 7.19–7.22 (m, 2H, Ar–H), 7.27 (d, *J* 8.8, 4H, Ar–H), 7.36 (d, *J* 8.8, 4H, Ar–H), 7.43 (m, 2H, Ar–H), 7.49 (d, *J* 5.0, 4H, Ar–H), 7.63 (d, *J* 8.8, 4H, Ar–H), 8.14 (d, *J* 9.0, 8H, Ar–H), 8.29 (d, *J* 9.0, 4H, Ar–H).

1 T. Niori, F. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, *J. Mater. Chem.*, 1996, **6**, 1231.
2 M. Nakata, D. R. Link, J. Thisayukta, Y. Takanishi, K. Ishikawa, J. Watanabe and H. Takezoe, *J. Mater Chem.*, 2001, **11**, 2694; D. M. Walba, E. Körblova, R. Shao, J. E. Maclennan, D. R. Link, M. A. Glaser and N. A. Clark, *Science*, 2000, **288**, 2181; H. Nadasi, W. Weissflog, A. Eremin, G. Pelzl, S. Diele, B. Das and S. Grande, *J. Mater. Chem.*, 2002, **12**, 1316; J. P. Bedel, J. C. Rouillon, J. P. Marcerou, M. Laguerre, H. T. Nguyen and M. F. Achard, *J. Mater. Chem.*, 2002, **12**, 2214; R. Amaranatha, R. A. Reddy and B. K. Sadashiva, *J. Mater. Chem.*, 2002, **12**, 2627.
3 C. Tschierske, *J. Mater. Chem.*, 2001, **11**, 2647.
4 G. Dantlgraber, A. Eremin, S. Diele, A. Hauser, H. Kresse, G. Pelzl and C. Tschierske, *Angew. Chem., Int. Ed.*, 2002, **41**, 2408.
5 C. T. Imrie, in, *Structure and Bonding, Vol 95, Liquid Crystals II*, ed. D. M. P. Mingos, Springer, Berlin, 1999, p. 149.
6 H. J. Coles, S. Meyer, P. Lehmann, R. Deschenaux and I. Jauslin, *J. Mater. Chem.*, 1999, **9**, 1085; D. Guillon, M. A. Osipov, S. Mery, M. Siffert, J.-F. Nicoud, C. Bourgogne and P. Sebastiao, *J. Mater. Chem.*, 2001, **11**, 2700.
7 G. H. Mehl and J. W. Goodby, *Chem. Ber.*, 1996, **129**, 521.
8 A W-shaped molecule composed of two bent core units connected by a rigid 1,3-disubstituted aromatic unit: P. A. Kumar, M. L. N. Madhu-Mohan and V. G. K. M. Pisipati, *Liq. Cryst.*, 2000, **27**, 1533.