Self-assembly of bent-core liquid crystals: formation of a modulated smectic phase with *p2gg* lattice to escape anticlinic tilt[†]

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A new silyl terminated bent-core mesogen was synthesized which shows a randomly tilted SmC_R phase and a columnar phase with p2gg lattice as new modes of self-assembly in this class of compounds.

Self-assembly enables chemists and physicists to construct complex functional systems at different length scales. Selfassembled soft matter is of special interest as it provides the possibility to modify its properties and functionality by external stimuli (electric, magnetic fields, light, *etc.*).¹ Liquid crystals (LCs) represent self-assembled soft matter structures with long range order, and these materials are of growing importance for electronic² and optoelectronic applications³ as well as being involved in biological structure formation.⁴ A relatively new blueprint for molecular tectons, useful for the design of LC soft matter, is provided by molecules incorporating a bent aromatic core, assigned as bent-core molecules (banana molecules). This specific shape provides a dense and directed packing of this kind of molecules which leads to macroscopic polar order and new LC phase structures.⁵

Herein we report the self-assembly of a new bent-shaped compound **1**, having a rigid aromatic core combining terephthalate based wings with a 2-methyl substituted bent resorcinol core⁶ and flexible end-chains composed of alkyl spacer units and trisiloxane groups.^{7,8}§ The combination of attractive forces (packing of terephthalate based cores) with nanoscale segregation (aromatics *vs.* alkyl *vs.* siloxane) and with steric distortion (2-methyl group, bulky siloxane units) leads to two new LC phases. One is a special type of random tilt phase (SmC_R) with some relation to the deVries type smectic phases,⁹ the other one is the first rectangular columnar phase with *p2gg* symmetry (Col_{rec}/*p2gg*) observed for bent-core mesogens.^{10,11}



1: Cr 120 Col_{rec}/p2gg 127 SmC_R 135 Iso (T/°C).

Differential scanning calorimetry (DSC) of 1[†] indicates three phase transitions, a melting point at 120 °C, a phase transition at 127 °C ($\Delta H = 15 \text{ kJ mol}^{-1}$) and the transition to the isotropic liquid state at 135 °C ($\Delta H = 3.7 \text{ kJ mol}^{-1}$). Upon cooling under a polarizing microscope between crossed polarizers, at 135 °C the formation of a weakly birefringent fan-shaped texture can be observed (Fig. 1b). Shearing the sample gives rise to an optically isotropic (dark) appearance, as is typical for uniaxial smectic phases (Fig. S1c, ESI[†]). On further cooling, at 127 °C, a striped pattern develops perpendicular to the fan texture as shown in Fig. 1d. In a homeotropically aligned sample a weak birefringence arises at this temperature (see Fig. S1d, ESI[†]). Electrooptical investigations indicate that both mesophases do not show any polar (ferroelectric or antiferroelectric) switching.

The X-ray diffraction pattern of a surface-aligned sample of the smectic phase (Fig. 1a) exhibits first and third order layer reflections on the meridian corresponding to a layer distance $d_1 = 5.35$ nm. This value is smaller than the molecular length $(L = 7.05 \text{ nm}, \text{see Fig. S2}, \text{ESI}^{\dagger})$ and this is the first hint of a tilted organization of the molecules. In the wide-angle region there are two diffuse maxima at $d_2 = 0.70$ nm¶ and at $d_3 = 0.50$ nm, assigned to the mean distances between the siloxane end groups and between the hydrocarbon segments (alkyl chains and aromatics), respectively. The diffuse character of both wide angle scatterings indicates a liquid-like disorder within the layers, as is typical for LC phases. Both form rings, but the scattering at $d_3 = 0.50$ nm has two maxima with equal intensity which make an angle with respect to the equator, confirming a tilted organization of the molecules within the layers. The maxima correspond to a tilt angle of about 34°. However, the proven tilted organization of the molecules is in conflict with the optical uniaxiality of this mesophase. Hence, the aromatic cores should be randomly tilted, similar to the models proposed for deVries type smectic phases⁹ (SmC_R phase). This means that either the individual molecules or-more likely-clusters of molecules have a randomized tilt direction.**

In the following discussion, we mainly focus on the low temperature phase developing upon cooling this SmC_R phase. At the transition to this mesophase the diffraction pattern is completely changed (see Fig. 1c and e). The rather high enthalpy of this transition indicates a significant increase of order. However, a transition to a crystalline phase can be excluded, because the wide angle scatterings remain diffuse. The diffuse ring positioned at $d_2 = 0.69$ nm, assigned to the packing of the disordered siloxane units, is not changed, but the positions of the maxima of the other diffuse scattering at $d_3 = 0.49$ nm (aromatics and aliphatics) were shifted (Fig. 1c).

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Fig. 1 Mesophases of compound 1: (a) X-ray diffraction pattern (surface-aligned sample, X-ray beam nearly parallel to the substrate) and (b) texture of the SmC_R phase at 130 °C; (c) X-ray diffraction pattern and (d) texture of the $Col_{rec}/p2gg$ phase at 115 °C; the optical textures actually shown were obtained under a triangular wave electric field (400 V_{pp} in a 5 μ m cell at 100 Hz), but they are very similar to the textures of the virgin samples shown in Fig. S1a and b, ESI[†]; (e) small angle X-ray diffraction pattern of the Col_{rec}/p2gg phase at 115 °C; (f) same diffraction pattern showing the lattices of three distinct, strongly scattering domains in the multi-domain sample with indexation; axes and indices labelled for the black lattice (see also Fig. S3, S4 and Tables S1, S2 (ESI⁺) for additional supporting X-ray data); all patterns are fibre-like disordered around an axis normal to the aligning interface and the scattering of the isotropic liquid was subtracted; (g) model of the organization of the bent-core molecules in the Col_{rec}/p2gg phase (the molecules are rotationally disordered around the long axis and therefore shown as black lines) and (h) in a columnar mesophase with antiferroelectric polar order (dots and crosses indicate opposite polar directions; there are actually 9 molecules in each ribbon, though a smaller number of molecules is shown).

In addition, though this wide angle scattering remains diffuse it is much less diffuse than that of the smectic phase, indicating a more ordered packing of the molecules (see Fig. S3 and Table S2, ESI†). In the small angle region there are several reflections which can be assigned to a rectangular p2gg lattice (a = 12.0 nm, b = 6.9 nm) disordered in a multi-domain sample with three distinct main orientations of the 2D lattice, as shown in Fig. 1f. According to this indexation (see also Fig. S4 and Table S1, ESI†) the lattice parameter *b* corresponds approximately to the molecular length (L = 7.05 nm) which is in line with an arrangement of the molecules on average parallel to the shorter direction *b* of this lattice (Fig. 1g). The maxima of the outer diffuse scattering, corresponding to the average lateral distances of the molecular cores, are in directions perpendicular to the *b*-axes of the three distinct orientations (see dotted lines in Fig. 1c, the colour is the same as that of the corresponding lattice in Fig. 1f, see also Fig. S4b, ESI†). This additionally supports the *p2gg* type of organization. A number of about 9 molecules in the cross section of each ribbon can be calculated from the lattice parameters and the molecular volume.

The three distinct lattice orientations with a $\sim 60^{\circ}$ angle between them (Fig. 1f) could result from different surface alignments of domains either parallel to the molecular long axes (blue lattice) or parallel to the ribbons (green and black lattice).^{††} In this case the tilt angle of the molecules in the ribbons should be about 30° which is in line with the proposed model (Fig. 1g) and it is also close to the tilt angle of 34° in the SmC_R phase. Remarkably, in different experiments the same diffraction pattern with the same relative intensities of the reflections, as shown in Fig. 1e and f, was always obtained. Based on this observation and the relatively diffuse character of the small angle scatterings, it is concluded that this diffraction pattern is intrinsic and the mesophase has only short range p2gg symmetry which is space averaged with preferred directions corresponding to those seen for surface alignment.¹²

Accordingly, this columnar phase can be regarded as a modulated smectic phase consisting of ribbons with alternating tilt of the molecules (tilt in the ribbons). Any organization with alternating tilt along the ribbon stacks $(Sm\tilde{C}_a)$ is forbidden due to the huge steric frustration occurring at the inter-ribbon interfaces (see Fig. 2). However, in the p2gg phase with the proposed herring-bone structure the tilt direction changes perpendicular to the stacking direction which leads to an overall parallel arrangement of the molecules and thus avoids unfavourable clashing of the ribbons. Hence, at the phase transition SmC_R-to-Col_{rec}/p2gg the randomly tilted domains of the SmC_R phase fuse and as a consequence of the denser packing the layers get broken into ribbons with opposite tilt direction which organize on a rectangular lattice. The special feature of this ribbon phase is that a p2gg lattice is formed instead of the c2mm type rectangular or the oblique lattices as usually observed for the nontilted (SmÃ) or synclinic tilted (SmCs, see Fig. 2) modulated smectic phase of bent-core mesogens.5,7,8

The rather high enthalpy of the transition from the smectic to the modulated smectic phase ($\Delta H = 15 \text{ kJ mol}^{-1}$) indicates



Fig. 2 Molecular organizations in the different types of ribbon phases; the $Sm\tilde{C}_a$ phase is not possible because of the disturbance of the molecular packing at the unfavourable inter-ribbon interfaces in this organization.

a significant increase of order at this transition which is in line with the observed less diffuse wide angle scattering. Hence, it is likely that the rotational disorder about the long molecular axis is reduced at the SmC_R-to-Col_{rec}/p2gg transition and polar order arises in the ribbons. A structure with synpolar order along the ribbon stacks and antipolar order in the other direction, leading to an overall antiferroelectric organization, corresponding to the layer group $p_{2_1}^{2_1} 2_1^{2_2}$ as shown in Fig. 1h,¹³ is most likely, because this structure can be stabilized by the parallel alignment of the rod-like aromatic wings at the interribbon interfaces (see Fig. S5a, ESI[†]).^{5a,8}^{‡‡} This stabilizes the antipolar organization with respect to the related synpolar (ferroelectric) structure (where the aromatic wings would not be parallel, see Fig. S5b, ESI[†]) and this could lead to a very high threshold voltage for polar switching which cannot be achieved under the available experimental conditions $(V_{pp,max} = 400 \text{ V at 5 } \mu\text{m cell gap})$. This is in line with observations in other B1 type Colrec phases of bent-core mesogens, which also do not show polar switching despite a polar order in the ribbons.^{5a,b}

In this way the missing case of a modulated smectic phase with rectangular lattice, anticlinic tilt and interdigitated layer defects was observed for the first time in a LC phase formed by bent-core molecules. The interesting point is that in this p2ggstructure the unfavourable clashing of the ribbons in an anticlinic organization of the molecules in adjacent ribbons is avoided by a staggered zigzag modulation of the layers. This shows once again that segregation and steric effects provided by oligo(siloxane) units, combined with the packing restrictions of bent rigid cores, is a powerful tool to program molecules for self-assembly into new soft matter structures.

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Notes and references

§ The related compound with reversed peripheral ester groups has the phase sequence Cr 103 °C Col_{obl} 111 °C Iso (Col_{obl} = ribbon phase with oblique lattice).^{8b} This indicates a strong effect of the direction of the ester group on mesophase stability and mesophase type, as no smectic phase is observed and the ribbons adopt a synclinic tilted arrangement in this isomeric compound. Similar effects on mesophase stability were seen for the change of the direction of the inner ester groups (resorcinol bisbenzoates *vs.* isophthalates).¹⁴

¶ The diffuse scattering at $d_2 = 0.7$ nm can be explained by a segregation of the siloxane units to form distinct sublayers (see Fig. S3, ESI†), the ring-like shape indicates the liquid-like disorder in these layers.⁸ The segregation is mainly due to the distinct shape of alkyl chains and oligosiloxanes, rather than due to a chemical incompatibility.

|| The two distinct wide angle scatterings at $d_3 = 0.5$ nm could not be due to the intrinsic tilt of the rod-like wings of the bent-core molecules. This was proven for aligned samples of SmAP phases of bent-core molecules where the layer reflection appears on the meridian and the diffuse wide angle scattering is centered on the equator.^{8a,15}

** This could be regarded as a non-polar variant of the ferroelectric SmC_RP_{FE} phase, recently reported for a carbosilane-based bent-core

dendrimer;^{16a} smectic phases of bent-core molecules with a random direction of polar order were also reported for non-silylated molecules.^{16b} †† All the domains are rotationally disordered around an axis normal to the aligning surface. Hence, all orientations parallel to the molecular long axes contribute to the diffuse scattering on the meridian of the pattern, but only two of those parallel to the ribbons with opposite tilt directions to that rotated by ~60° out of the meridian which explains the different intensities for both types of the outer diffuse scattering.

^{‡‡} Splay of polar direction might also be involved in the proposed structure composed of synpolar stacks of ribbons.^{11a,17}

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