# Development of polar order in liquid crystalline phases of a banana compound with a unique sequence of three orthogonal phases†

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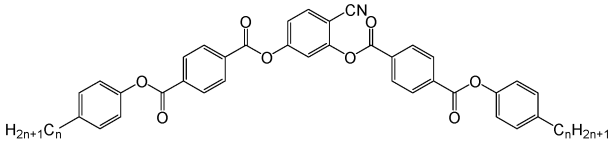
**Alkyl substituted 4-cyanoresorcinol 1,3-bisbenzoates with terephthalate based rod-like wings show a series of three orthogonal smectic phases SmA–SmAP$_R$–SmAP$_A$.**

Liquid crystalline (LC) materials with a bent molecular shape (banana-molecules)[1] represent a fascinating area in soft matter science, providing new supramolecular structures, phenomena and properties, unknown for other materials. Among them there is the formation of macroscopic chirality by spontaneous symmetry breaking in fluids composed of achiral molecules[2] and a series of new types of polar (ferroelectric, antiferroelectric) switching LC phases which are of interest for electro-optical[3] and non-linear optical devices.[4]

Most of the smectic LC phases of bent-core mesogens, reported so far, represent tilted smectic phases (SmC type) for which it is difficult to obtain well aligned samples over large areas. Therefore, smectic phases with an orthogonal organization of the molecules (SmA type) are more promising applicants for new technologies. However, orthogonal smectic phases are extremely rare for bent-core molecules and require special molecular design. An orthogonal polar smectic phase with alternating polar direction (SmAP$_A$) was predicted in 1992[5] and observed about ten years later.[6,7] Very recently another interesting bent-core phase with a random distribution of polar direction (SmAP$_R$) was found.[8]



Herein we report a first compound (**1b**) showing the phase sequence SmA–SmAP$_R$–SmAP$_A$,‡ which for the first time combines all three orthogonal banana phases and allows the investigation of the stepwise development of polar order. In addition, this is a new lead structure for design of the extremly rare SmAP$_R$ phase over broad temperature ranges. The synthesis is straight forward requiring only few synthetic steps starting from commercially available materials. This is important for large scale synthesis which was not possible with previously reported materials.[8]

For the synthesis 4-cyanoresorcinol was acylated with appropriate 4-[(4-*n*-alkylphenoxycarbonyl)benzoyloxy]benzoic acids,[9] which were obtained by esterification of 4-formyl benzoic acid with 4-alkylphenols followed by oxidation of CHO to COOH[10] (for details see ESI†). Investigation of the mesomorphic properties is based on polarizing microscopy, differential scanning calorimetry X-ray diffraction (XRD) of surface aligned samples as well as electrooptical experiments. The mesophases and transition temperatures of the two synthesized homologous compounds **1a** ($n$ = 6) and **1b** ($n$ = 12) are collated in Table 1. Compound **1a** with short chains has only two LC phases, a nonpolar SmA phase and an antiferroelectric switching SmAP$_A$ phase. The typical textures observed for these two mesophases are shown in Fig. 1. Upon cooling the samples from the isotropic state a highly birefringent fan-like texture is formed (Fig. 1a) which can be homeotropically aligned as typical for optically uniaxial SmA phases (see Fig. 1b). In the regions with fan texture the fans get broken at the phase transitions at 112 °C (Fig. 1c), and a birefringent schlieren texture appears in the homeotropically aligned areas, indicating a transition to a biaxial LC phase (Fig. 1d).

The optical textures observed for compound **1b** are identical with those of compound **1a**, characterized by an onset of biaxiality in the homeotropically aligned regions at $T$ = 111 °C (Fig. S5, ESI†). However, for this compound an additional relatively broad DSC peak is observed around $T$ = 158 °C in the DSC heating and cooling scans within the temperature range of the optically uniaxial SmA phase region (Fig. 2).

XRD patterns of the LC phases of compound **1b**, obtained from oriented samples, show Bragg reflections on the meridian and a diffuse outer scattering located on the equator (Fig. 3c–e).

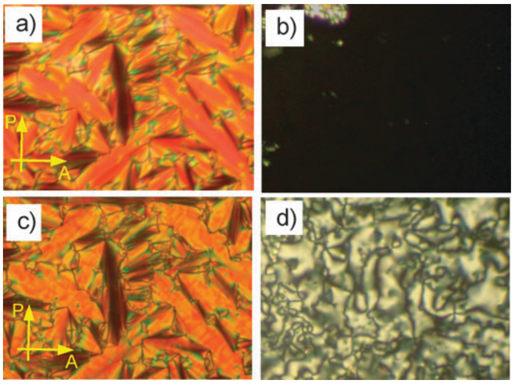


**Fig. 1** Changes of the textures of compound **1a** at the SmA-to-SmAP$_A$ phase transition (crossed polarizers); (a,b) SmA phase at $T$ = 130 °C; (c,d) SmAP$_A$ phase at $T$ = 100 °C; (a,c) fan-like texture; (b,d) homeotropically aligned sample.

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**Table 1** Phase transitions of compounds **1**[a]

| Comp. | *n* | *T*/°C [Δ*H*/kJ mol$^{-1}$] |
|---|---|---|
| **1a** | 6 | Cr • 128 [39.6] (SmAP$_A$ 112 [1.1]) • SmA • 150 [5.3] • Iso |
| **1b** | 12 | Cr • 112 [38.4] (SmAP$_A$ 111 [0.5]) • SmAP$_R$ • 158 [2.8] • SmA • 166 [4.6] • Iso |

[a] Cr = crystalline solid; SmA = uniaxial smectic phase without in-plane order; SmAP$_R$ = polar switching uniaxial SmA phase with randomized polar direction; SmAP$_A$ = antiferroelectric switching biaxial SmA phase; Iso = isotropic liquid.

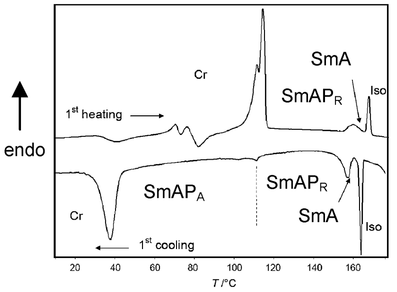

**Fig. 2** DSC heating and cooling curves (10 K min$^{-1}$) of compound **1b**.

The XRD pattern does not significantly change in the temperature range of the smectic phases, *i.e.* at all temperatures the maxima of the diffuse scattering are located on the equator and the layer reflection retains its position on the meridian. This indicates that also in the biaxial smectic phase the molecular long axis is on average perpendicular to the layer planes. This on average orthogonal alignment of the molecules and the occurrence of a birefringent schlieren texture at the phase transition at 111 °C, indicates that the low temperature phase of compounds **1a** (for XRD patterns see Fig. S1, ESI†) and **1b** is a biaxial SmA phase. With decreasing temperature the diffuse outer scattering maximum is slightly shifted from $d$ = 0.48 nm at 160 °C (SmA) to $d$ = 0.47 nm at 90 °C (SmAP$_A$, compound **1b**, see Fig. 3b), indicating an increasing packing density. This is in line with the development of the *d*-spacing depending on temperature (Fig. 3a) which significantly increases from $d$ = 4.6 nm at $T$ = 160 °C (SmA) to $d$ = 5.0 nm at $T$ = 90 °C (SmAP$_A$).

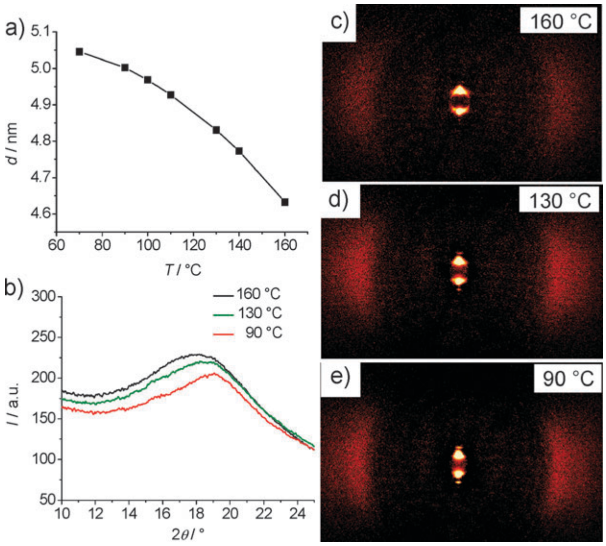

**Fig. 3** XRD data of compound **1b**: (a) dependence of layer distance *d* and (b) shape of the diffuse wide angle scattering on temperature; (c–e) diffraction pattern of a surface aligned sample (after subtraction of the scattering pattern in the Iso phase at $T$ = 178 °C); (c) SmA at $T$ = 160 °C; (d) SmAP$_R$ at $T$ = 130 °C; (e) SmAP$_A$ at $T$ = 90 °C (for original patterns, see Fig. S2, XRD patterns of compound **1a** are shown in Fig. S1, ESI†).

Electrooptical investigations were carried out in 6 μm ITO cells. For compound **1a**, in the optically uniaxial SmA phase, no current response could be observed, confirming a non-polar SmA phase. At the transition to the biaxial phase at 112 °C two well developed sharp peaks can be detected per half period of the applied triangular wave field (see Fig. S4, ESI†). This is a clear indication for a tristable switching process between an antiferroelectric ground state and two ferroelectric states, hence, this biaxial SmA phase is assigned as SmAP$_A$. The value of the spontaneous polarization was calculated to 770 nC cm$^{-2}$.

Surprisingly, for compound **1b** polar switching can already be observed in the temperature range of the uniaxial SmA phase. It starts shortly below the phase transition from the isotropic liquid to the SmA phase at approximately 155–160 °C, where within the SmA phase region a relatively broad peak can be seen in the DSC traces (see Fig. 2). This broad peak is not associated with any change of the texture or XRD pattern except an continuous increase of the packing density as discussed above. There is a relatively broad polarization peak in each half cycle which is typical for the switching process in SmAP$_R$ phases (Fig. 4a).[8] The broadness indicates the field-induced alignment of the dipoles from random orientation.[8] The polarization value increases with further decreasing

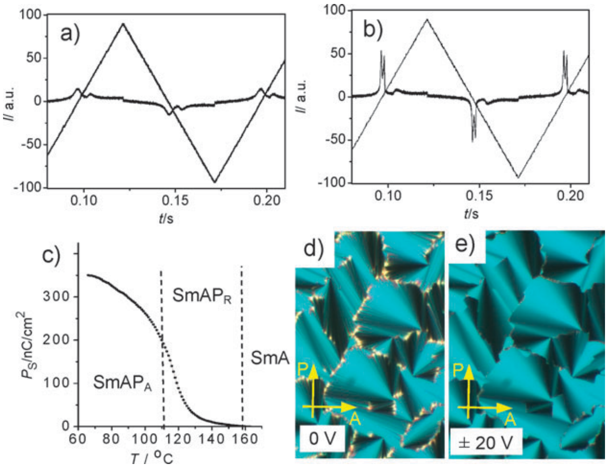

**Fig. 4** Electrooptical investigation of compound **1b**: (a,b) Switching current response in a 6 μm ITO cell (18 $V_{pp}$, 10 Hz, 5 kΩ) on applying a triangular wave field; (a) in the SmAP$_R$ phase at $T$ = 112 °C; (b) in the SmAP$_A$ phase at $T$ = 105 °C; (c) temperature dependence of the spontaneous polarization (9.5 μm, 20 V, 100 Hz); (d,e) textures of the SmAP$_R$ phase at 153 °C depending on applied voltage.

temperature to a value of about 150 nC cm$^{-2}$. Below the phase transition at 111 °C the polarization peak splits into two sharp peaks (Fig. 4b) and the polarization value increases to *ca.* 350 nC cm$^{-2}$, confirming a transition to a SmAP$_A$ phase. The $P_s(T)$ curve (Fig. 4c) shows soft-mode like behaviour on approaching the SmAP$_R$–SmAP$_A$ transition. In the SmAP$_A$ and SmAP$_R$ phases no textural changes take place during switching, *i.e.* the position of the dark extinction brushes, located parallel to the crossed polarizers, does not move (Fig. 4d and e), indicating a switching by collective rotation around the molecular long axis.

Whereas the uniaxial-to-biaxial phase transition enthalpy of **1b** is very small (0.5 kJ mol$^{-1}$), the SmA-to-SmAP$_R$ transition enthalpy value is much higher (2.8 kJ mol$^{-1}$) and it is relatively broad compared to the sharp Iso–SmA transition (4.6 kJ mol$^{-1}$). This indicates that the major structural change takes place at the SmA–SmAP$_R$ transition, whereas polar order develops nearly continuously. Furthermore, the current peaks are close to the 0 V line of the applied voltage (Fig. 4b), which is untypical for antiferroelectric switching. For this type of polarization current curves a superparaelectric type of switching was discussed previously.[11]

There are two distinct models for the SmA–SmAP$_R$–SmAP$_A$ transition. (i) In the first model uniform polarity develops at the transition SmA-to-SmAP$_R$ within the layers but without correlation of the polar direction in adjacent layers (Fig. 5b). These polar layers register in an antiparallel correlation at the transition to the SmAP$_A$ phase (Fig. 5a).[8a] (ii) In an alternative model[8b] the molecules, which are rotationally disordered around the long axis in the SmA phase, become organized in polar clusters with a preferred polar direction at the transition to SmAP$_R$ (Fig. 5c, note that there is randomization of polar direction in the layers, but correlation between the layers). In the SmAP$_R$ phase these clusters are rotational disordered around the director **n** and their size increases with decreasing temperature. These ferroelectric clusters can be aligned under a sufficiently strong electric field, leading to a field induced switching. At a certain size these clusters align spontaneously, giving rise to macroscopic phase biaxiality and polar order (SmAP$_R$–SmAP$_A$ transition). Further detailed investigations are in progress to clarify the modes of supramolecular organization in the SmAP$_R$ and SmAP$_A$ phases.

In summary, the unique phase sequence SmA–SmAP$_R$–SmAP$_A$ was observed for the first time and broad SmAP$_R$ regions were obtained in a new class of easily accessable bent-core mesogens.

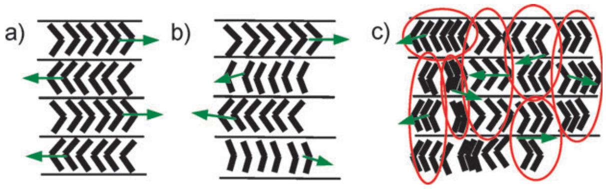

**Fig. 5** Models of molecular arrangements (green arrows = polar direction, skewed arrows point out of or into the projection plane): (a) SmAP$_A$; (b,c) SmAP$_R$; (b) randomization of polar direction between the layers, (c) randomization of polar direction within the layers (ferroelectric clusters).

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## Notes and references

‡ Compounds related to **1**, but with alkoxy chains instead of alkyl chains show SmA and SmAP$_A$ phases, but no SmAP$_R$ phase;[7a] reversal of the outer ester groups leads to N and (tilted) SmC phases with much lower transition temperatures.[12] The effect of the direction of the ester linking groups has several origins. An alternation of electron rich and electron deficit aromatics (electrostatic surface potential) favours intermolecular interactions, hence stabilizing smectic phases (in **1** alternation of electron deficit terephthalate and electron rich phenylether units).[13] Moreover, the different rotational barriers of the Ar–COO and Ar–OOC bonds gives rise to distinct molecular flexibilities. Also torsional angles, bending angles, dipole moments and quadrupole moments are affected by reversal of the COO groups and influence the mesophase stability.[14] The prediction of tilt is even more difficult and presently based on empiric observations.

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