First symmetrical banana compounds exhibiting $SmAP_R$ mesophase and unique transition between two orthogonal polar phases[†]

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Novel banana-shaped liquid crystals with stilbene bridges were synthesized. All presented materials exhibit the polarization-randomized non-tilted smectic phase $(SmAP_R)$ in a broad temperature range and the antiferroelectric non-tilted smectic phase $(SmAP_A)$ at room temperature.

Liquid crystalline materials possessing a bent molecular shape, so called banana-shaped LC, are fascinating in view of their academic research^{1,2} and their potential applications.³ Mainly because of the shape, smectic and columnar phases formed by these molecules exhibit polar order which lead to antiferroelectric and ferroelectric switching.⁴ The B₂ phase is the most common and the most widely studied phase in bent-core (BC) liquid crystals (BC-LCs). This tilted lamellar polar phase can appear in four different supramolecular packing arrangements, two of them form chiral conglomerates (SmC_aP_A, SmC_aP_F).⁵ Although much effort has been directed toward the synthesis of novel banana compounds, orthogonal polar smectic-A analogue phases have not been so often reported in the literature.

The first example of non-tilted polar biaxial smectic A phase (SmAP_A) was reported by Eremin⁶ for bent-core compounds possessing imine linkers in the arms and a cyano (CN) group in the central core. Another example of the biaxial polar SmA phase was reported by several groups; i.e., asymmetric BC-LCs with stilbene bridges in the arms,⁷ asymmetric BC-LCs, in which one of the terminal chains are replaced by a highly polar cyano group,8 and BC-LCs with cyclic ureas as a central unit.⁹ Usually, polar order within the layer leads to phase biaxiality. However, Pociecha et al.¹⁰ reported an example of a polar uniaxial SmA-like phase-SmAP_R, i.e., polarizationrandomized nontilted smectic phase. The important technological application of the SmAP_R phase for a fast switching display device has been described previously and was confirmed to be a promising candidate for a new-generation liquid crystal display.^{11,12} For such practical application, extensive syntheses of new materials which exhibit SmAP_R with wider and lower temperature ranges is an urgent issue.

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Recently we synthesized and reported some new asymmetric compounds, which show uniaxial, orthogonal phase with ferroelectric-like properties, SmAP_R.¹³ Herein, we report the first symmetric BC molecules showing the SmAP_R mesophase. In this work, we chose 1,3-dihydroxyacetophenone as a central unit. Stilbene arms were used, similarly as in previous compounds,¹³ bearing NO₂ or Cl substituents. The presented materials are interesting because: (1) they possess wide temperature ranges of the expected mesophase, (2) a lower temperature phase was found to be also non-tilted polar phase. To the best of our knowledge, this is the first example of compounds showing a direct transition between two orthogonal phases; i.e., polar uniaxial smectic A phase to polar biaxial smectic A phase. Only a few papers have described the transitions between non-polar and polar smectic A phases (SmA-SmAP_A).⁶⁻⁸

The synthetic pathway leading to symmetrical bananacompounds AP-*n*-NN-n¹⁴ with nitro groups and AP-*n*-ClCl-n with chlorine substituents is presented in Scheme 1, where AP



Scheme 1 Synthetic route for the preparation symmetric and asymmetric bent-core molecules. *Reagents and conditions*: (i) TEA, THF, DMAP, room temp. 4–5 h, (ii) 4-{(E)-2-[3-chloro-4-(tetra-decyloxy)phenyl]ethenyl}benzoic acid chloride, TEA, THF, DMAP, reflux 8 h; X = NO₂, Cl; n = 14, 16, 18, 20.

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stands for central unit - acetophenone. Appropriate benzoic acid chlorides 2, which were obtained previously,¹³ were subjected to esterification reaction with 1,3-dihydroxyacetophenone (1) in dry THF in the presence of triethylamine and DMAP as a catalyst. The usage of large excess of acid chlorides allowed synthesis of symmetrical banana compounds as the main products ($\sim 40\%$ average yield) possible, while monosubstituted central units were obtained as minor products. Monosubstituted central unit 3 was used in the synthesis of one asymmetrical analogue AP-14-NCI-14, possessing both nitro group and chlorine atom in the arms. After refluxing of compound 3 in THF for 8 h, in a presence of triethylamine, AP-14-NCl-14 was obtained with 30% yield. All final compounds were purified by column chromatography using toluene or toluene-ethyl acetate as eluents and single or double recrystallizations from ethyl acetate.

The mesomorphic behaviour of compounds AP-n-NN-n and AP-14-NCI-14 was investigated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC-7 Perkin Elmer), X-ray diffraction, and electrooptical measurements. The mesophases and transition temperatures of the synthesized compounds are summarized in Table 1. All the compounds exhibited LC phases, and the mesophase stability increased with elongation of terminal chains. We should note that the transition enthalpy at the SmAP_R-SmAP_A transition was quite small and was even hard to be detected, particularly in AP-20-NN-20 (see ESI[†]). The introduction of an asymmetric substituent leads to broader mesophase ranges at lower temperatures, as noticed by comparing AP-14-NN-14 with the asymmetric analogue AP-14-NCI-14. Fig. 1 and 2 reveal optical photomicrographs of homeotropic and homogeneous cells in SmAP_R and SmAP_A phases. In homeotropically aligned samples of AP-18-NN-18, the high-temperature phase exhibited a uniform dark texture with some minor defects, indicating optical uniaxiality of the phase (Fig. 1(a)). Then the transition to the low-temperature phase was recognized as the appearance of grain-like textures, as shown in Fig. 1(b).

The occurrence of grain texture in the homeotropicallyaligned sample indicates a transition to a biaxial smectic phase at 87 °C. When the compound was introduced in homogeneous cells, the sample gave the fan-shaped texture



Fig. 1 Photomicrographs in the SmAP_R phase of compound AP-18-NN-18 at 100 °C: homeotropic texture of the SmAP_R phase (a) and homeotropic texture of the SmAP_A phase (b). The sample thickness was $5.2 \ \mu m$.

characteristic of the SmA phase (Fig. 2(a)). During cooling the texture was retained with only birefringence change (Fig. 2(c). The application of an electric field also gave slight birefringence increase both in the SmAP_R and SmAP_A phases (Fig. 2(b) and (d)). A switching current measurement was also made. Under the application of a triangular wave voltage to AP-18-NN-18 in the SmAP_R phase (97 °C), one broad polarization switching current peak for each half cycle was obtained as shown in Fig. 3(a). The broad and single switching current peak indicates field-induced alignment of dipoles from random



Fig. 2 Photomicrographs in the SmAP_R phase of compound **AP-18-NN-18** at 100 °C: homogeneous cell at (a) E = 0 V and (b) E = 140 V_{pp}. Photomicrographs in the SmAP_A phase at 84 °C: homogeneous cell at (c) E = 0 V and (d) E = 140 V_{pp}. The sample thickness was 5.2 µm.

Code	Х	n	Cry	SmAP _A		SmAP _R		Iso	$\Delta T (\text{SmAP}_{\text{R}})$
AP-14-NN-14	NO ₂	14		•	105.23	•	118.70	•	13.44
AP-16-NN-16	NO_2	16		•	94.10 [0.20]	•	[3.70] 130.10 [4.73]	•	36.00
AP-18-NN-18	NO_2	18		•	[0.20] 88.97 [0.18]	•	136.03 [3.67]	•	44.30
AP-20-NN-20	NO_2	20		•	84 ^a	•	134.70	•	50.70
AP-14-NCl-14	NO_2/Cl	14		•	97 ^a	•	113.77	•	16.77
AP-14-CICI-14	Cl	14	•	79.10 [1.33]			[3.70]	•	—

Table 1 Phase transition temperatures (°C) and corresponding enthalpies (J g⁻¹) for compounds of **AP-n-NN-n**; **AP-14-NCl-14** and **AP-14-ClCl-14**. Numbers at the both sides of the sample names stand for the numbers of carbons in both end chains. AP stands for the central unit—acetophenone; N and Cl stand for substituents NO₂ and Cl at the left and right wings, respectively

^a Determined by texture observation, since corresponding DSC peaks are so small (see ESI[†]).



Fig. 3 Switching current response obtained under a triangular wave voltage (a) in the SmAP_R phase 97 °C (140 V_{pp}, 6 Hz) and (b) in the SmAP_A phase at 87 °C (140 V_{pp}, 0.2 Hz). Sample thickness was 5.2 μ m.



Fig. 4 X-Ray patterns of compound **AP-18-NN-18**: (a) SmAP_R at 140 °C, (b) SmAP_A phase at 30 °C. Slight up/down asymmetry in the pattern is due to shadowing by sample heating stage. (c) Temperature dependence of the layer spacing d.

orientation through the Langevin process,^{11,12} and is characteristic of the switching process in SmAP_R.¹⁰ The spontaneous polarization P_s obtained by current peak was ~170 nC cm⁻² at 92 °C. The low-temperature phase of **AP-18-NN-18** showed antiferroelectric switching behaviour ($P_s \sim 300$ nC cm⁻² at T = 87 °C). In addition, no rotation of the extinction crosses could be seen during the switching. Hence we can conclude that the low-temperature phase is the non-tilted SmAP_A phase. No changes in the texture were observed on cooling down to room temperatures, suggesting that the phase remained or froze at room temperature.

In order to convince the layer structure of the phases, X-ray analysis using the X-ray beam almost parallel to the substrate surface was also made using homeotropically aligned samples of **AP-18-NN-18**. As shown in Fig. 4(a), diffraction peaks were observed along the meridian line in SmAP_R, and were assigned to the reflection due to smectic layers parallel to the substrate surface. Diffuse scattering corresponding to the distance 4.5 Å appeared along the equatorial line, signifying the liquid-like non-tilted arrangement of molecules within each layer. The low-temperature SmAP_A phase exhibited qualitatively the same pattern except for the appearance of higher harmonics of the signal coming from layer periodicity indicating an increase of the smectic order parameter (Fig. 4(b)). The X-ray pattern did not change after cooling to room temperature. The layer spacing continuously increases with decreasing temperature in both phases (Fig. 4(c)), being almost equal to the estimated molecular length (61 Å in optimized conformation) in the SmAP_A phase. It is quite reasonable to conclude that both phases are non-tilted phases.

In summary, we reported herein the synthesis of the first symmetric bent-core liquid crystalline materials exhibiting the $SmAP_R$ phase with a broader temperature range comparing to previously reported unsymmetrical compounds. Additionally, we observed for the first time a new transition from a uniaxial non-tilted polar phase (SmAP_R) to a biaxial non-tilted polar phase (SmAP_A).

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- 13 K. Gomola, L. Guo, S. Dhara, Y. Shimbo, E. Gorecka, D. Pociecha, J. Mieczkowski and H. Takezoe, J. Mater. Chem., 2009, 19, 4240.
- 14 Typical procedure for the synthesis of AP-14-NN-14: To a solution of 2,6-dihydroxyacetophenone 1 (200 mg, 1.31 mmol), triethylamine (1 ml, 7.13 mmol) and DMAP (20 mg, 0.16 mmol) in tetrahydrofuran (100 ml), 4-{(E)-2-[4-nitro-3-(tetradecyloxy)phenyl]ethenyl]benzoic acid chloride 2 (1.44 g, 2.89 mmol) was added. The reaction mixture was kept under reflux for 8 h. The final product AP-14-NN-14 was purified by column chromatography and double recrystallization from ethyl acetate. Compound **ÅP-14-NN-14:** NMR: $\delta_{\rm H}$ (300 MHz, CDCl₃) 8.16 (d, J = 8.4 Hz, 4H, Ar), 8.03 (d, J = 2.1 Hz, 2H, Ar), 7.64 (dd, $J_1 = 2.1$ Hz, $J_2 = 8.7$ Hz, 2H, Ar), 7.55–7.52 (m, 5H, Ar), 7.25–7.07 (m, 8H, CH = CH, Ar), 4.14 (t, J = 6.6 Hz, 4H, OCH_2CH_3), 2.49 (s, 3H, COCH₃), 1.85-1.79 (m, 4H, OCH₂CH₂), 1.55-1.21 (m, 44H, CH₂), 0.88 (t, J = 6.9 Hz, 6H, CH₂CH₃); $\delta_{\rm C}$ (75 MHz, CDCl₃) 198.41, 164.20, 152.29, 148.01, 142.31, 140.03, 132.11, 130.87, 129.13, 129.08, 128.39, 127.80, 127.58, 126.62, 123.48, 120.62, 114.66, 69.88, 31.91, 31.40, 29.64, 29.57, 29.50, 29.35, 29.27, 28.89, 25.80, 22.69, 14.12; IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$, 2921, 2851, 1738, 1603, 1529, 1457, 1352, 1261, 1223, 1177, 1077; Elemental analysis: calc. (%) for C₆₆H₈₂N₂O₁₁ (1079.36): C, 73.44, H 7.66, N, 2.60, found: C, 73.13, H, 7.63, N, 2.60.