PAPER

Development of polar order in a bent-core liquid crystal with a new sequence of two orthogonal smectic and an adjacent nematic phase†

Govindaswamy Shanker,[a] Marko Prehm,[a] Mamatha Nagaraj,[b] Jagdish K. Vij[b] and Carsten Tschierske[*a]

A 4-cyanoresorcinol based bent-core liquid crystal shows a new phase sequence of two orthogonal smectic phases with short range (SmAP$_R$) and long range (SmAP$_A$) polar order beside a SmA-type cybotactic nematic phase (N$_{CybA}$), leading to the phase sequence SmAP$_A$–SmAP$_R$–N$_{CybA}$; this is of importance in LCD technology and provides a significant step forward towards polar and biaxial nematic phases.

1. Introduction

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]

Contemporary interest in the field of bent-core mesogens is focussed on the challenging task to produce a thermotropic biaxial nematic phase (N$_b$). This would not only be of fundamental importance for general soft-matter physics, but this phase is also considered as a possible candidate for next generation LC displays with enhanced switching performance compared to presently existing uniaxial nematogens.[5] Numerous attempts have already been made to realize N$_b$ phases with different molecular structures, but were unsuccessful in confirming spontaneous biaxiality unambiguously,[6] probably with the exception of LC polymers and laterally connected oligomeric mesogens at temperatures close to the glass transition.[7,8] However, these materials suffer from high viscosity and therefore short switching times cannot be expected. Recently it was proposed that local biaxiality can arise in the so-called cybotactic nematic phases (N$_{cyb}$) composed of small clusters with smectic structure.[6e,9] Such cybotactic nematic phases are typically formed by bent-core mesogens.[10]

However, in most cases the molecules are tilted in these clusters (N$_{cybC}$ phases) and this type of N$_b$ phases would lead to the monoclinic type of biaxial nematic phases (N$_{bm}$),[6e,9] where biaxiality is affected by the tilt and this is difficult to use for electro-optical applications. In contrast, the orthorhombic type of N$_b$ phases (N$_{bo}$) requires that the molecules be organized perpendicularly in the smectic clusters.[6e,9] N$_{cybA}$ phases occurring adjacent to biaxial or polar SmA phases (SmA$_b$ and SmAP) would be of special interest if at least a local biaxiality or polar order could be retained at the transition to the nematic phase. An orthogonal polar smectic phase with alternating polar direction (SmAP$_A$) was predicted in 1992[11] and observed about ten years later.[12,13] More recently polar smectic phases with a random distribution of the polar direction (SmAP$_R$ and SmAP$_{AR}$)[14] and also a ferroelectric switching SmA phase (SmAP$_F$)[15] were found.

Herein we report a first compound showing the phase sequence SmAP$_A$–SmAP$_R$–N$_{cybA}$ with a direct transition between a locally polar SmAP$_R$ phase and a cybotactic nematic phase (N$_{cybA}$). The importance of this observation is twofold. At first, the additional nematic phase allows an easy alignment of the SmAP$_R$ and SmAP$_A$ phases[16] as required for preparation of defect-free displays. Secondly, it provides a significant step forward to achieve the goal of biaxial nematic phases of the orthorhombic type[6e] and possibly also related polar nematic phases.[17]

2. Results and discussion

2.1 Synthesis

Compound **1** was obtained by esterification of the 4-[4-(undec-10-enyloxy)phenoxycarbonyl]benzoic acid **2** (ref. 14c) with the 4-cyanoresorcinol monoester **3** (ref. 10a) using DCC as condensation agent (Scheme 1). The synthetic procedure and analytical data are reported in the ESI†.

[a]Institute of Chemistry, Organic Chemistry, Martin-Luther-University Halle-Wittenberg, Kurt Mothes Str. 2, D-06120 Halle/Saale, Germany. E-mail: carsten.tschierske@chemie.uni-halle.de; Fax: +49(0)345 5527346; Tel: +49(0)345 5525664
[b]Department of Electronic and Electrical Engineering, Trinity College, University of Dublin, Dublin, 2, Ireland. E-mail: jvij@tcd.ie

† Electronic supplementary information (ESI) available: Synthetic procedure, analytical data, and additional XRD data. See DOI: 10.1039/c1jm14653j

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J. Mater. Chem., 2011, **21**, 18711–18714 | 18711
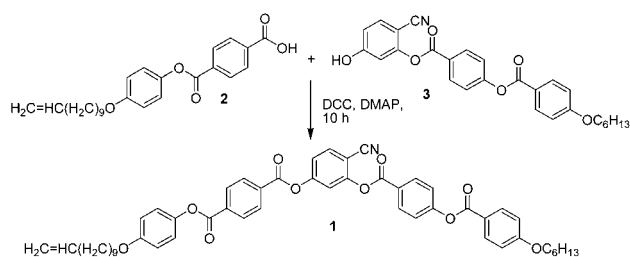
Scheme 1 Synthesis of compound **1**.

2.2 Optical investigations

On cooling from the isotropic liquid state, compound **1** shows three distinct phase transitions with relatively small transition enthalpy values (Scheme 2).

Fig. 1 shows the polarizing optical micrographs observed in a homeotropic cell and the 2D XRD patterns of a magnetically aligned sample for the different LC phases.

Upon cooling the samples in a homeotropic cell a schlieren texture is observed at $T = 146\ °C$ under the polarizing microscope (Fig. 1b), indicating a nematic phase (N).‡ This texture immediately adopts a homeotropic alignment which is completely dark, so that the next phase transition at $T = 136\ °C$ is difficult to identify optically.‡ However in a planar cell, this transition is clearly visible by a distinct increase of the birefringence (occurrence of blue stripes, see Fig. 2b). The dark texture of the homeotropically aligned sample under crossed polarizers indicates the uniaxiality of both, the nematic and the adjacent smectic phase, *i.e.* this smectic phase is an average non-tilted smectic phase (SmA, see Fig. 1d).

Upon further cooling at $T = 86\ °C$ a birefringent schlieren texture appears, indicating the transition to a biaxial smectic phase (Fig. 1f). This phase can be cooled down below room temperature without crystallization or any additional phase transition. At room temperature compound **1** remains in the LC state for prolonged periods (several hours) before crystallization takes place. The melting point of the crystallized sample is at $T = 98\ °C$ (Scheme 2).

In a planar cell the birefringence continuously increases in the temperature region of the optically uniaxial smectic phase (colour change from blue to green), indicating a continuous increase of the order parameter (Fig. 2c and d). In this alignment the transition between the uniaxial and the biaxial smectic phase appears to be continuous without any significant change of the texture (Fig. 2d and e). The birefringence does not further change below the transition between the two smectic phases (Fig. 2e and f).

2.3 XRD studies

XRD studies were performed with a sample aligned in a magnetic field of medium strength ($B \approx 1$ T). At $T = 140\ °C$ the diffraction pattern shows a diffuse scattering in the wide angle region with a maximum at $d = 0.47$ nm corresponding to the mean lateral distance between the molecules. The wide angle scattering is

‡ These temperatures correspond to the equilibrium temperatures as observed under the polarizing microscope at a fixed temperature, whereas the temperatures given in Scheme 2 were obtained by DSC during heating/cooling at a constant rate.
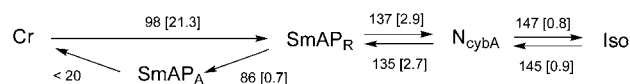
Scheme 2 Transition temperatures ($T/°C$) and associated enthalpy values (ΔH, kJ mol^{-1}, in parentheses) of the bent-core mesogen **1** (obtained by DSC with heating and cooling rates of 10 K min^{-1}, peak temperatures are shown); abbreviations: Cr = crystalline solid; Iso = isotropic liquid; SmAP$_A$ = antiferroelectric SmA phase; SmAP$_R$ = random polar SmA phase; N$_{cybA}$ = nematic phase composed of SmA type cybotactic clusters.

centred on the equator which indicates that the alignment of the molecules is along the long molecular axis (Fig. 1a). A diffuse scattering in the small angle region has its maximum at $d = 4.43$ nm, comparable with the molecular length $L_{mol} = 4.48$ nm (in a V-shaped molecular conformation with an angle of 140° and stretched alkyl chains in all-*trans* conformation). The intensity of the diffuse small angle scattering is much larger than that of the diffuse wide angle scattering indicating the presence of a cybotactic nematic phase composed of small smectic
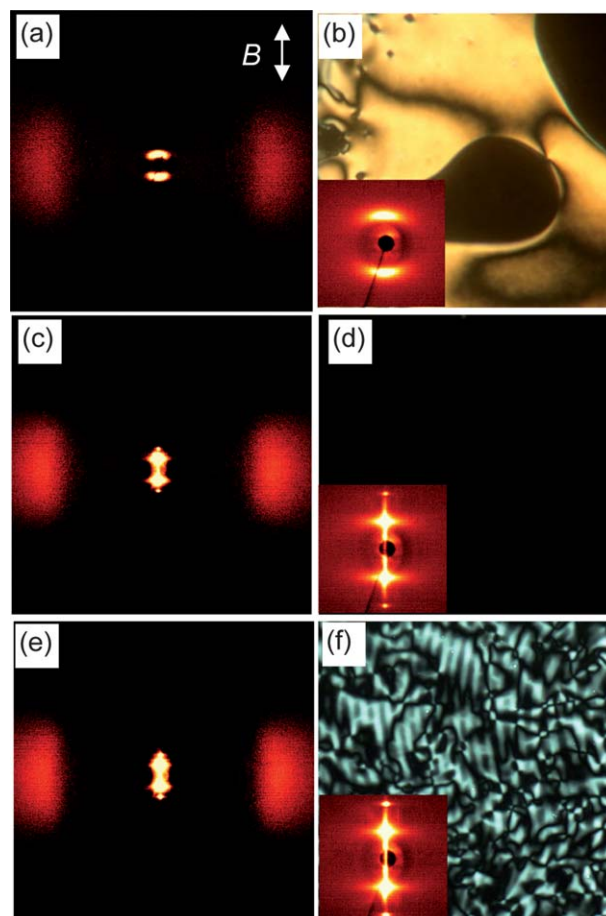

Fig. 1 Textures (right, crossed polarizers) and at the left 2D XRD patterns (complete patterns after subtraction of the scattering in the isotropic phase and as insets the small angle diffraction patterns) of the magnetically aligned compound (for the original diffraction patterns see Fig. S1†) (a) in the N$_{cybA}$ phase at $T = 140\ °C$, (b) in the N$_{cybA}$ phase at $T = 145\ °C$, (c and d) in the SmAP$_R$ phase at $T = 110\ °C$ and (e and f) in the SmAP$_A$ phase at $T = 70\ °C$; in the textures the dark areas are homeotropically aligned regions.
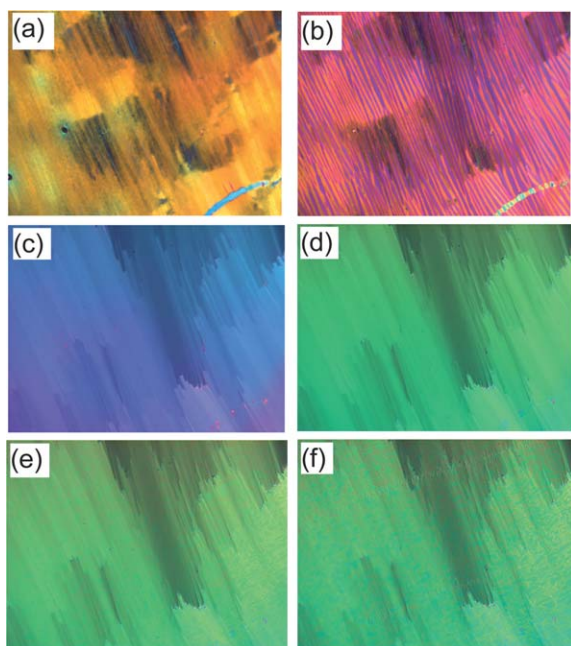
Fig. 2 Textures of compound **1** at different temperatures in an 8.9 μm planar cell as observed between crossed polarizers (a) nematic phase at 140 °C; (b) nematic to SmAP$_R$ transition at 136 °C (c) SmAP$_R$ phase at 130 °C and (d) at 100 °C; (e) SmAP$_A$ phase at 85 °C and (f) at 81 °C.

clusters.[10,18] The cluster size was estimated according to $L_{\parallel,\perp} \approx 3$ $(2/\Delta q)$[19] from the full width at half maximum (Δq)[19] as $L_{\parallel} \approx 26$ nm and $L_{\perp} \approx 8$ nm *i.e.* the clusters are comparatively large, incorporating about 5–6 layers and about 16 molecules in the diameter. The maxima of the small angle scattering are located at the meridian of the diffraction pattern (see Fig. 1a, c and e), which indicates that in the smectic clusters the molecules are non-tilted and this confirms a cybotactic nematic phase composed of SmA-like clusters (N$_{cybA}$).

On reducing the temperature, the position, shape and intensity of the wide angle scattering do not change, confirming that a LC phase is retained and also that the alignment of the molecules is retained (Fig. 1a–c and S1†). Only the diffuse scattering in the small angle region transforms into sharp Bragg peaks with maxima at the meridian, consistent with a transition to a SmA phase (Fig. 1c). This diffraction pattern is retained down to $T = 70$ °C (Fig. 1e), only the maxima of the diffuse scattering in the wide angle region change the d value slightly from $d = 0.47$ nm at 140 °C (N$_{cybA}$) to $d = 0.45$ nm at 70 °C (SmAP$_A$), indicating an increasing packing density (see Fig. S3†). This is in line with the development of the d-spacing which slightly increases from $d = 4.4$ nm at $T = 140$ °C (N$_{cybA}$) to $d = 4.6$ nm at $T = 70$ °C (SmAP$_A$). The orthogonal alignment of the molecules proven by the relative position of the XRD small angle and wide angle scatterings (see also Fig. S2†), as well as by the increase of d with decreasing T and the occurrence of a birefringent schlieren texture of both 1/2 and 1 desclination strength indicate a biaxial SmA phase at $T < 86$ °C.

2.4 Electrooptical studies

Electro-optical investigation was carried out in a 5 μm polyimide coated ITO cell. No current response could be measured in the
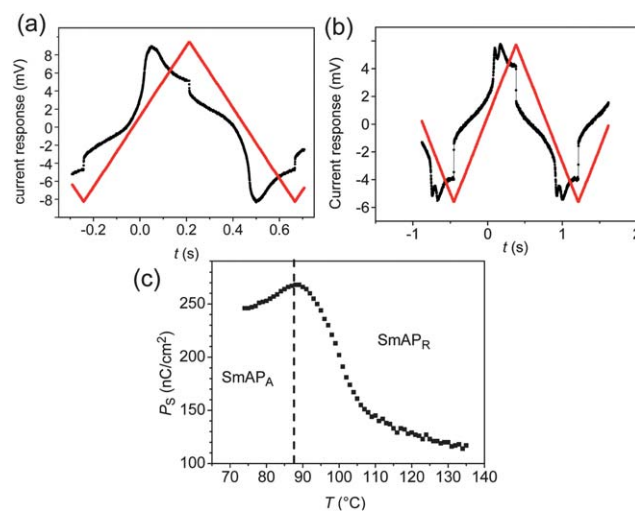

Fig. 3 Electro-optical investigations: (a and b) switching current response curves in 5 μm cells on applying a triangular wave field, (a) in the SmAP$_R$ phase at $T = 125$ °C (10 V μm^{-1}, 1.1 Hz, 5 kΩ) and (b) in the SmAP$_A$ phase at $T = 84$ °C (8 V μm^{-1}, 0.6 Hz, 5 kΩ) and (c) dependence of the spontaneous polarization on temperature (5 μm, 10 V μm^{-1}, 1.1 Hz).

temperature range of the N$_{cybA}$ phase, but after the transition to the uniaxial SmA phase at $T = 135$ °C, immediately a relatively broad polarization peak in each half cycle of the applied triangular wave voltage is observed which is typical for the switching process in SmAP$_R$ phases[14] (Fig. 3a). On cooling the spontaneous polarization (P_s) rises (see Fig. 3c) and at 84 °C two well developed sharp peaks appear (Fig. 3b), indicating the transition from a Langevin-type switching as typical for SmAP$_R$ phases to a tristable switching process between an antiferroelectric ground state and two ferroelectric states as characteristic for SmAP$_A$ phases. Hence, this biaxial SmA phase is a SmAP$_A$ phase and the maximum P_s value in this phase was calculated to ~260 nC cm^{-2}. Overall, the temperature dependence of the measured polarization $P_s(T)$ in the SmAP$_R$ and SmAP$_A$ phases (Fig. 3c) shows soft-mode like behaviour on approaching the SmAP$_R$–SmP$_A$ transition and then it reaches to a saturation value. The decrease in the polarization at lower temperature is due to the stronger antiferro packing which would require a higher saturation voltage.[16b]

3. Conclusions

In conclusion, the phase sequence N$_{CybA}$–SmAP$_R$–SmAP$_A$ with broad enantiotropic SmAP$_R$ and monotropic SmAP$_A$ phase ranges was observed for the first time. The SmAP$_A$ phase can be overcooled below room temperature and does not crystallize for a prolonged time. SmAP$_A$ phases are of special interest as recently a new and extremely fast switching process (<0.5 ms) was discovered for these phases.[16] Such fast rates would be required for improving LC displays with sequential colour switching and for 3D TV applications.[20] Compound **1** can be used as a component for room temperature SmAP$_A$ mixtures. More importantly, for display production a nematic phase is usually required, in which the LC is first aligned and then cooled to the smectic phase to achieve a defect-free structure of the SmAP$_A$ phase. For this reason the observation of polar smectic

and nematic phases in the phase sequence of a single compound with relatively low transition temperatures is an important step towards application of this new switching mode.[16]

A second important point concerns the nematic phase itself as the rare N_{cybA} phases are promising candidates for the realization of the illusive biaxial nematic phase of the orthorhombic type. As local polar order, and hence local biaxiality, are proven for the $SmAP_R$ phase and it is known for such phases that macroscopic biaxiality and polar order can be induced under an external electric field the question arises if this could probably also be achieved for N_{cybA} phases adjacent to $SmAP_R$ or $SmAP_A$ phases.§ At present we have no proof of such a behaviour, but optimization of the properties by further molecular design could pave the way to new low molecular weight materials with biaxial nematic phases (and possibly also the related polar nematic phases[17]¶) as field induced or even stable structures.

Acknowledgements

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§ There are only few examples of $SmAP_A$–N transitions and these transitions were observed only at very high temperatures.[21]

¶ Evidence for polar switching was recently reported for a skewed cybotactic nematic phase composed of tilted SmC clusters (N_{cybC}).[22]