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Biaxial smectic A liquid crystal in a pure compound†

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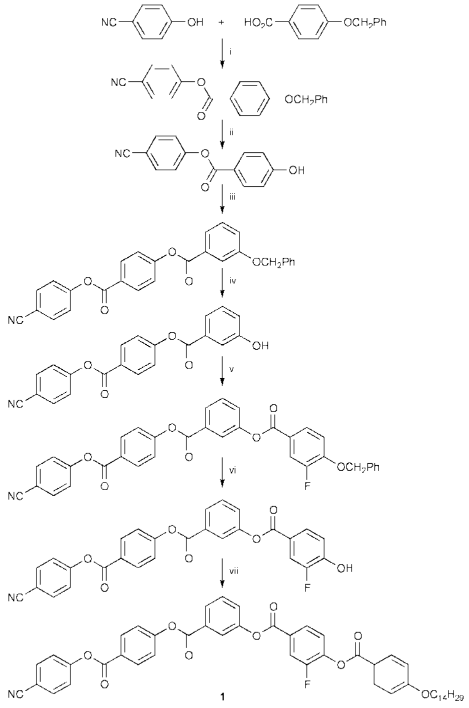
The synthesis and characterisation is reported of a low molecular weight organic compound to exhibit the biaxial smectic A (SmA_b) phase, which shows a transition from the partial bilayer uniaxial SmA_d phase to the SmA_{db} phase as the temperature is lowered.

The discovery of liquid crystalline phases in compounds with bent-core (BC) or banana-shaped molecules[1] has led to a very intense research activity in the field.[2] In the past couple of years several new compounds having this molecular architecture have been reported[3–8] in an effort to find the relationship between the molecular structure and the mesomorphic properties associated with it. At least five different B-(banana) types of liquid crystal have been clearly identified in pure compounds, though recently some new variants have been found.[8] The most fluid of the B-type of liquid crystals, which is also electrically switchable is the B_2 phase in which the bent-cores pack along a common axis to give rise to an electric polarisation of the layer. The molecular plane tilts with respect to the layer-normal to produce a *chiral* layer, though the molecules themselves are usually achiral.[9] In an earlier study, we found that binary mixtures of a compound exhibiting the B_2 phase with one made of rod-like molecules exhibiting the bilayer smectic A_2 phase showed a very interesting phase diagram.[10,11] If the concentration of the rods is between 4 and 13 mol% the mixtures exhibit a biaxial smectic A_2 (SmA_{2b}) phase in which the BC molecules undergo an orientational transition as the temperature is lowered from the uniaxial SmA_2 phase. The other known systems exhibiting the SmA_b phase were found (i) in a binary mixture of polymeric and monomeric species,[12] (ii) in an oxadiazole derivative[13] at high temperatures (above 235 °C), and (iii) in a binary mixture involving a metallomesogen.[14]

It is of obvious interest to find the biaxial SmA_b phase in a low molecular weight pure compound at a relatively low temperature. Compounds whose molecules have a strong biaxiality of shape are necessary for this purpose and the best systems appear to be those made of BC molecules. Indeed, several compounds with BC molecules are known to exhibit the smectic A (SmA) phase but NMR studies have shown that in such molecules the angle between the two arms of the bent-core is about 160°, which means that the deviation from a rod-like structure (in which this angle would be 180°) is quite small.[2] On the other hand, if the molecules have highly bent cores the compounds are known to exhibit only the B-type of liquid crystal.

Here, we report the synthesis of a compound made of BC molecules with a new architecture. The unsymmetrical molecule has an alkoxy chain attached to only one of the arms of the bent-core, while the other arm ends with the highly polar cyano group. The synthetic pathway used to obtain this compound is shown in Scheme 1.‡ Our studies show that the compound exhibits a partial bilayer smectic A_d phase in which the bent-cores of two neighbouring molecules overlap in an antiparallel orientation, as in the case of highly polar rod-like molecules.[15,16] Indeed, this is the first example of a single-component, low molecular weight compound to exhibit the biaxial smectic A to uniaxial smectic A transition.

The liquid crystalline properties were investigated by differential scanning calorimetry (DSC, Pyris 1D, 5 °C min^{-1}) and polarised optical microscopy (Leitz Laborlux 12 POL). Observation using a polarising microscope of a sample taken from between the untreated slide and coverslip shows the following sequence of textures as the temperature is lowered. The dark field of view, corresponding to the isotropic phase, goes over at a transition point to an SmA texture in which most of the sample has a homeotropic alignment, but some parts clearly show focal-conic domains. As the temperature is lowered further, there is another phase transition in which the homeotropic regions exhibit a schlieren texture (Fig. 1), with both two-brush and four-brush defects. Strong fluctuations in intensity are seen as in the SmA_{2b} phase.[10] The presence of two-brush defects indicates that the low temperature phase has one of the following structures: (i) a biaxial smectic A phase in which the two orthogonal directors in the plane of smectic layers are also *apolar* in nature; (ii) a packing of the BC molecules of compound **1** such that each layer is polarised, but with a mutually antiferroelectric arrangement in neighbouring layers (the two-brush defects in such a case are dispirations, which are combinations of half strength disclinations which are defect patterns in the in-plane director, and screw dislocations;[17] this structure can also be described as a biaxial SmA); and (iii) another possibility would be for the molecules to tilt with an anticlinic arrangement in successive layers, in which



Scheme 1 *Reagents and conditions*: i, DCC, cat. DMAP, dry $CHCl_3$, rt, 15 h, 81%; ii, cat. 5%Pd–C, H_2, 1,4-dioxane, 55 °C, 75%; iii, 3-benzyloxybenzoic acid, DCC, cat. DMAP, dry $CHCl_3$, rt, 15 h, 72%; iv, cat. 5% Pd–C, H_2, 1,4-dioxane, 55 °C, 73%; v, 3-fluoro-4-benzyloxybenzoic acid, DCC, cat. DMAP, dry $CHCl_3$, rt, 20 h, 68%; vi, cat. 5% Pd-C, H_2, 1,4-dioxane, 55 °C, 80%; vii, 4-*n*-tetradecyloxybenzoic acid, DCC, cat. DMAP, dry $CHCl_3$ rt, 20 h, 61%.

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† Electronic supplementary information (ESI) available: spectroscopic data for **1**. See http://www.rsc.org/suppdata/cc/b1/b106084h/

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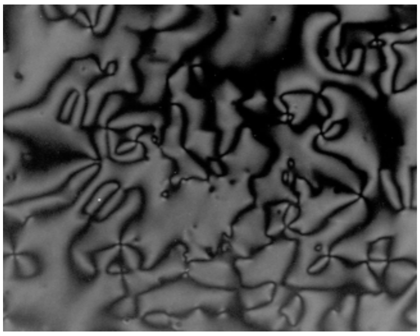

Fig. 1 Photograph of the schlieren texture of a homeotropic sample of the biaxial smectic liquid crystal of compound **1**. Note several half strength disclinations with two dark brushes which indicate an apolar in-layer director field (crossed polars, ×250).

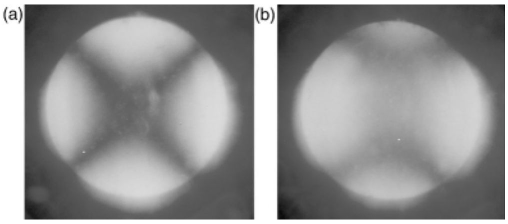

Fig. 2 Photographs of the conoscopic patterns from a homeotropically aligned sample of (a) the uniaxial smectic A_d phase at 128 °C, and (b) the biaxial smectic A_{db} phase at 124 °C.

case again dispirations can produce two-brush defects. We rule out the last possibility in view of the X-ray results to be described later.

DSC of compound **1** shows the following sequence of transitions. The numbers above the arrows are transition temperatures in °C and the numbers in parentheses are

$$\mathrm{Iso} \xleftrightarrow[(4.77)]{130} \mathrm{SmA} \xleftrightarrow[(0.04)]{126.2} \mathrm{SmA_b} \xleftrightarrow[(85.46)]{120.5} \mathrm{Cr} \qquad (1)$$

enthalpies in kJ mol^{-1}. In order to confirm the biaxiality of the low temperature phase, samples contained in a cell and well aligned using a lateral electric field are employed. The thickness of the sample is 37.3 μm which is controlled using appropriate spacers and measured using an interference technique before filling the sample. As the temperature of the cell is lowered below the SmA to SmA_b transition point (T_{bu}) again the schlieren texture is seen. The application of an electric voltage of *ca.* 200 V at 10 kHz between the two ITO regions aligns the sample uniformly in the gap. Conoscopic observations between crossed polarisers, which are set at 45° to the direction of the electric field, clearly show that the uniaxial cross in the SmA phase splits to give a biaxial pattern below the relevant transition temperature (Fig. 2). As the temperature is lowered, the separation between the hyperbolic isogyres [the two dark arcs seen in Fig. 2(b)] continuously increases.

X-Ray scattering studies have been carried out by taking the sample in a Lindemann capillary tube which is slowly cooled to the desired temperature under a magnetic field of strength *ca.* 2 kG applied perpendicular to the axis of the tube. The alignment is only partial as the isotropic to SmA transition has a strong first-order character. X-Rays of λ = 1.54 Å from a rotating anode generator are used to study the scattered pattern collected using a 2D image plate. In the small angle region, a sharp reflection corresponding to the smectic layer spacing can be clearly seen (Fig. 3). As usual, the second-order reflection is very weak. The wide angle scattering corresponds to a liquid-like pattern. The measured layer spacing is equal to *ca.* 54 Å which does not vary with temperature as the sample is cooled from the SmA to the lowest temperature to which the SmA_b phase can be supercooled. This, in conjunction with the observation of two-brush defects described earlier, clearly indicates that the lower temperature phase with layer birefringence is not a tilted SmC phase. The layer spacing d = 54 Å is significantly larger than the calculated molecular length $l \approx$ 49 Å in its most extended form with an all-*trans* configuration of the alkoxy chain. This clearly implies a partial bilayer structure of the smectic layers in both SmA and SmA_b phases, which we have to designate as SmA_d and SmA_{db} respectively.

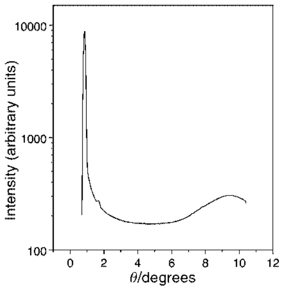

Fig. 3 Intensity profile of the X-ray diffraction pattern in the SmA_{db} phase of compound **1** at 123 °C as a function of the Bragg angle, θ. The sharp reflection corresponds to a layer spacing of 54 Å. A very weak second order reflection can also be seen. The diffuse maximum corresponds to 4.6 Å, which is a typical intermolecular separation in the liquid layers.

Thus, we believe that the occurrence of both the uniaxial and biaxial smectic A phases in compound **1** is mainly a consequence of the partial bilayer structure in which there is a dense region of biaxial aromatic cores and relatively sparsely populated aliphatic regions, which allow for considerable orientational freedom of the chains. The arrangement of the BC molecules in the SmA_{db} phase in the pure compound **1** is hence quite different from that proposed for the SmA_{2b} phase occurring in binary mixtures of rod-like and bent-core molecules. In the latter the BC molecules orient with their arrow axes along the layer-normal, whereas in the SmA_{db} phase the arrows lie in the layer-plane.

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Notes and references

‡ Compound **1** was synthesised according to a procedure which will be described in a publication under preparation. The intermediate compounds have spectral data consistent with their molecular structure.

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