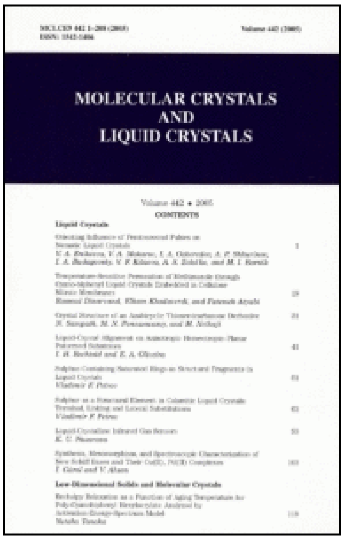

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Structure and Pyroelectric Behaviour of a Twin-Tapered Bent Core Mesogen

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Mesomorphism, structure and thermo-electric properties were investigated for a new achiral banana-shaped compound which, unlike the analogues considered earlier, contains cyclic fragments in its lateral substituents. It is shown that this compound displays linear pyroelectric behaviour and possesses an enantiotropic high-temperature chiral phase.

Keywords Banana-shaped compound; chirality; mesomorphism; pyroelectric effect

Introduction

In 1996 Niori *et al.* first demonstrated that achiral banana-shaped (bent core) molecules may form polar smectic (Sm) layers with ferroelectric or antiferroelectric behaviour [1]. Chirality in such systems is a consequence of packing-induced spontaneous symmetry breaking, taking shape as chiral smectic (Sm) or columnar structures [2]. These Sm phases are different from the classic chiral smectics, which consist of chiral molecules. The phases displayed by the bent core mesogens are referred to as B phases. The molecules may or may not be tilted. Most intriguingly, their compact packing can lead to the occurrence of polarity of layers or columns [3]. Detection in some "B" phases (B2, B3 and B5) of supramolecular chirality (i.e., spontaneous symmetry breaking) has spurred intense interest in synthesis and physical research on mesomorphic banana-shaped compounds. The spontaneous polarization exhibited by some of these compounds is clearly of interest in terms of their application potential.

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In this work mesomorphic properties of a novel twin-tapered bent core compound were studied by X-ray diffraction, thermal polarizing optical microscopy, and pyroelectric and calorimetric analysis.

Results and Discussion

We synthesized a liquid crystalline (LC) compound with novel architecture: a twin-tapered rigid bent core molecule bis-[3,4,5-tri[4-(4-*n*-nonyloxybenzoyloxy)] benzoylamino]-1,3-phenylene (**I**) (Fig. 1). Unlike the bent core banana-shaped mesogens investigated previously, in compound **I** not only the terminal groups but also the lateral substitutes contain a benzene ring. The synthesis and identification of this compound were described earlier [4].

Mesomorphic properties were determined using a Leitz Laborlux 12 Pol optical polarizing microscope equipped with a Mettler FP 82 hot stage. The temperatures and enthalpies of the phase transitions were measured by a Netzsch DSC 200 PC Phox differential scanning calorimeter. X-ray diffraction studies were performed on bamline I22 of the Diamond Light Source, Harwell, UK. Rapid II area detector and a curved HOTWAXS detector were used to record simultaneously the small- and wide-angle diffraction. The sample capillary was held in a modified Linkam hot stage. The laser pulse pyroelectric set-up was used for measurement of pyroelectric response [5].

1. Mesomorphic Properties of the Compound I

The mesomorphic properties of compound **I** were studied by polarized optical microscopy. The occurrence of rotating disk-shaped domains surrounded by the viscous isotropic phase has been observed on heating near the clearing point (Fig. 2a). This important fact suggests the presence of chirality in the structure of the observed LC-phase and the ferroelectric/antiferroelectric nature of the smectic layers at the mesophase – isotropic phase transition. As can be seen in Figure 2b, broken fan texture, characteristic of a smectic, can be seen on cooling the sample from isotropic melt. As the temperature is lowered further, and into the crystal phase, a regular stacking of alternating bright and dark lines develops (“fingerprint” texture, Fig. 2c). This texture is retained down to room temperature (Fig. 2d). The absence of equivalent striations in Figure 2b may be tentatively attributed to surface stabilization of unwound helices in the confined sample. For comparison, Figure 3 shows the texture of the Sm phase appearing from the isotropic in a sample without a cover slip. The micrograph (Fig. 3) demonstrates convincingly that the mesophase is chiral

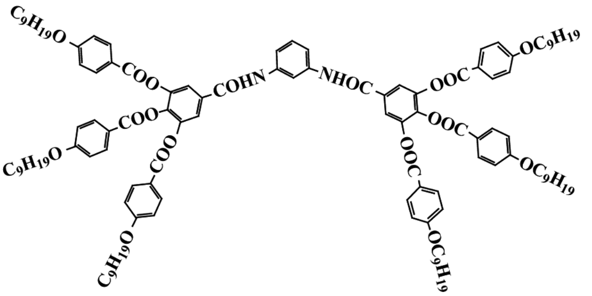

Figure 1. Molecular structure of compound **I**.

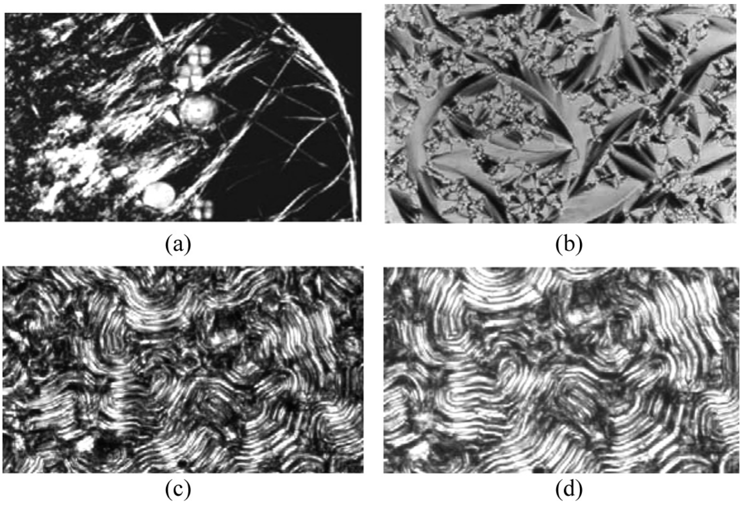

Figure 2. Optical textures of compound I: (a) the appearance of rotational domains at the moment of mesophase transition into isotropic phase on heating, T = 281.6°C; (b) SmCP(B2) phase (fan-shaped texture) observed on cooling from the isotropic phase, T = 280.8°C; (c) formation of periodic streaks, reminiscent of the "fingerprint" texture recorded on further cooling to T = 280.4°C, i.e., at the transition from the mesophase to the crystalline phase; (d) optical micrograph of the crystalline phase of compound I after cooling, T = 25.0°C. Figures 2a, 2b and 2c – polarizers are crossed, × 250. Figure 2d – parallel polarizers, × 250.

and shows a number of spiral domains both clockwise and anticlockwise. Such a texture closely resembles that of the so-called SmCP or B2 phase [3, 6–9]. We believe that the double bright lines prevalent in Figure 3 present half a turn of a helix with an axis across the lines.

2. DSC and X-Ray Diffraction of Compound I

The high-temperature mesophase of compound **I** have been studied by DSC and powder X-ray diffraction using synchrotron radiation.

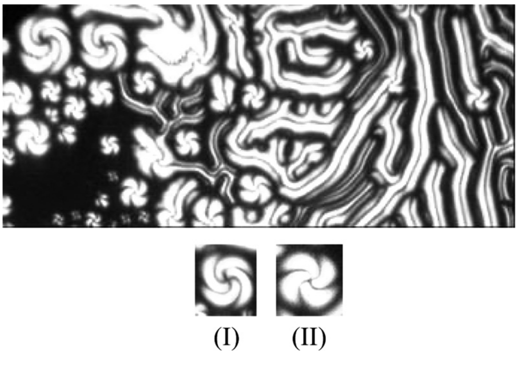

Figure 3. Optical micrograph of SmCP(B2) phase growing from the isotropic phase in a sample with an open surface at the temperature of T = 286.1°C, right- and left-handed spiral domains (I and II, respectively) can be seen. Polarizers are crossed, × 250.

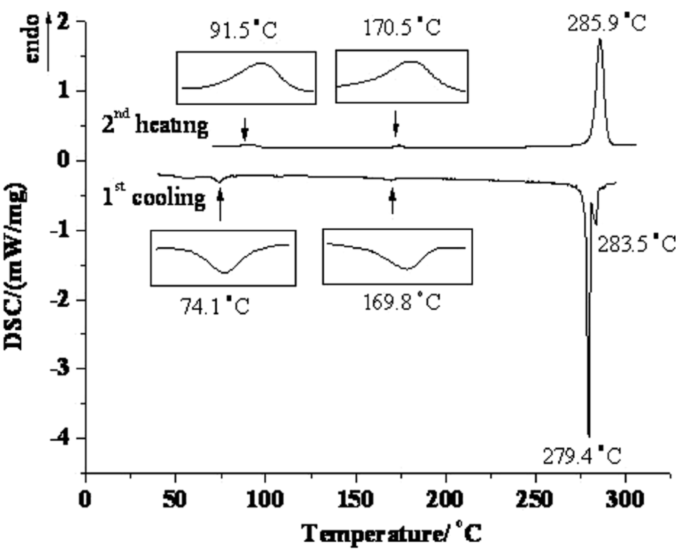

Figure 4. DSC thermograms of compound **I** recorded on cooling and second heating at scan rate of 5.0°C min^{-1}.

The small exotherm at 283.5°C in the DSC cooling curve (Fig. 4) is attributed to the isotropic – mesophase transition. The reverse mesophase – isotropic transition was not detected by DSC on heating, where it appears to coincide with the crystal – mesophase or crystal – isotropic transition. The large endotherm at 279.4°C on cooling is ascribed to the transition from the mesophase to the crystal. The above DSC peak assignment has been confirmed by X-ray data.

Simultaneous small and wide-angle synchrotron powder X-ray diffraction experiments were carried out on samples in vacuum-sealed capillaries and the results are shown in Figure 5. On cooling the LC phase appears only in a 4.0°C temperature interval, i.e., between 291.0 and 287.0°C (Fig. 5c,d), with a layer spacing of 30.3 Å. The liquid crystal nature of this phase is confirmed by the absence of wide-angle Bragg reflections (Fig. 5d). The smectic phase transforms to a crystalline phase at 281°C, consistent with the large DSC exotherm at 279.4°C. This highest temperature crystal form is designated Cr α. Reflections corresponding to two further crystalline polymorphs, Cr β and Cr γ, were observed on continued cooling (see Fig. 5e,f) at temperatures closely corresponding to the two small exotherms in the DSC cooling scan (Fig. 4). The phase sequence on cooling can thus be summarized as follows:

$$\text{Iso} \bullet (284 \pm 1°\text{C})\ \text{SmCP(B2)} \bullet (280 \pm 1°\text{C})\ \text{Cr}\ \alpha \bullet (172 \pm 3°\text{C})\ \text{Cr}\ \beta \bullet (73 \pm 2°\text{C})\ \text{Cr}\ \gamma.$$

The shift of the small-angle reflections indicates a considerable lattice contraction taking place on cooling through the entire temperature range of crystalline phases. Decrease in long spacings is likely due to increasing chain tilt. The continuous reduction in layer thickness is interrupted by two stepwise contractions associated with the $\alpha - \beta$ and $\beta - \gamma$ polymorphic transitions, as seen in Figure 5e,f.

The existence of two adjacent SAXS peaks seen in Figure 5e suggests that the layers in all three crystal phases are modulated, probably divided in blocks. The unit

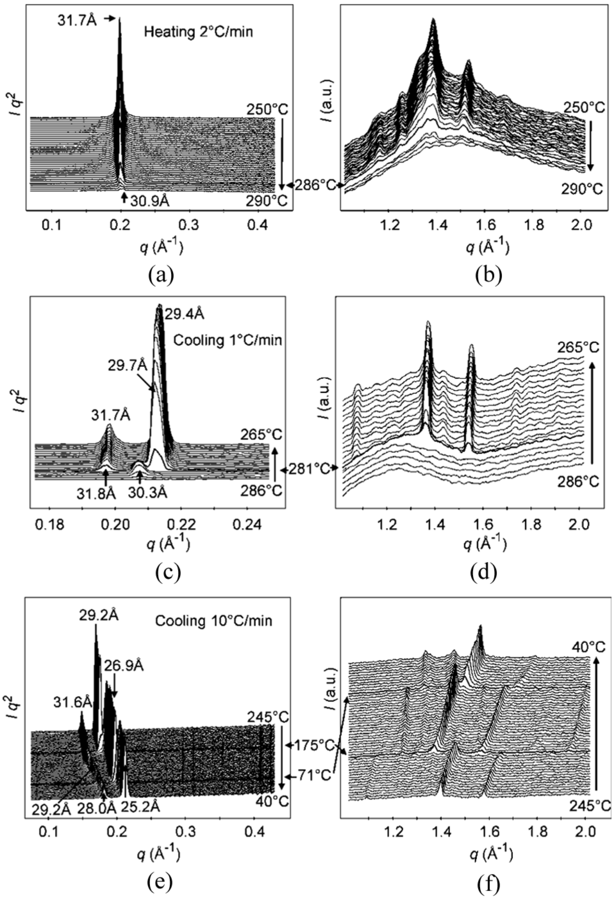

Figure 5. Powder X-ray diffraction intensities *vs.* wavevector for compound **I** as a function of temperature (°C). a, c, e: small-angle scattering region, b, d, f: wide-angle region. a,b: first heating 250°C–290°C at 2°C/min; c, d: cooling 294°C–273°C at 1°C/min; e, f: continued cooling 245°C–40°C at 10°C /min. Bragg *d*-spacings are indicated. The layer spacing of the smectic LC phase is 30.3 ÷ 30.9 Å (Figs. a and c). Other phases are crystalline.

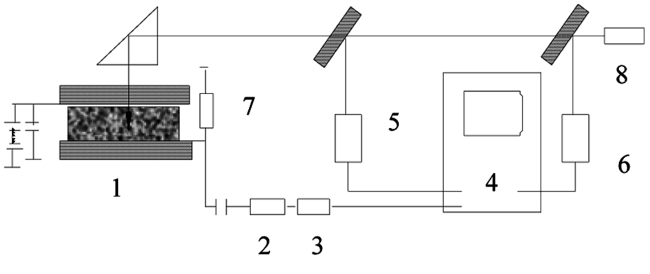

Figure 6. Block diagram of the set-up for pulse pyroelectric measurements. 1 – liquid crystal cell; 2 – amplifier; 3 – delay line; 4 – oscilloscope; 5 – photomultiplier for pulse control; 6 – photomultiplier for triggering; 7 – load resistor of (100 κOhm), 8 – YAG laser.

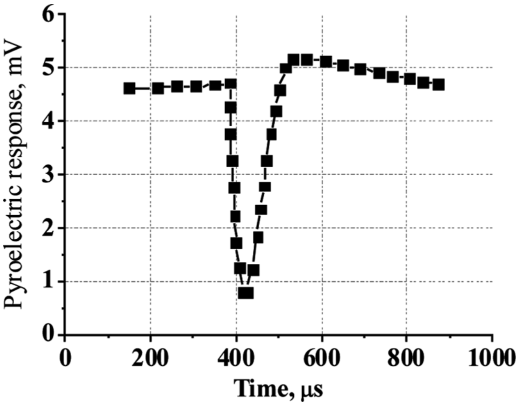

Figure 7. Oscillogram of the pyroelectric response of compound **I** at room temperature.

cells are large. The preservation of "fingerprint" texture down to room temperature (Fig. 2c and 2d) implies that the helicity of the smectic phase is preserved in the three crystal phases. However it is not known if the helicity is an equilibrium feature or a frozen-in state; the textures may be paramorphotic, i.e., nonequilibrium.

3. *Pyroelectric Measurements*

The investigation of pyroelectric effect was carried out by the pulse pyroelectric method [5]. This method is based on the measurement of the electric voltage pulse arising in an external circuit induced by heating the sample with a pulse of laser radiation. The pyroelectric set-up used in the measurements is shown schematically in Figure 6.

The solution of compound **I** in chloroform (0.01 weight %) was cast onto a not rubbed glass plate covered with an ITO electrode deposited by centrifugation (thickness $1 \div 2\,\mu\text{m}$) or Langmuir-Blodgett method (thickness 15 and 40 monolayers). After preliminary drying a second aluminum electrode is spread onto the surface of the film of compound **I** by thermal vacuum dispersion.

The pyroelectric measurements were carried out at room temperature. Figure 7 presents the recorded pulse of pyroelectric voltage. The pyroelectric coefficient was defined as $\gamma = 0.4\ \text{nC} \cdot \text{cm}^{-2}\,\text{K}^{-1}$. This value is typical of the known linear crystalline pyroelectrics. In a subsequent experiment the films were polarized using the corona poling technique [10]. As no visible improvement in pyroelectric response was observed, this material is to be considered as linear pyroelectric at room temperature.

Conclusion

The new twin-tapered compound with a bent rigid core was synthesized. It was established that it exhibits a high temperature chiral smectic phase, presumably, SmCP (B2). There is evidence that the chiral structure is preserved in the three crystalline polymorphs down to room temperature. It is demonstrated that compound **I** has the ability to form polar polydomain films at room temperature and thus it is pyroelectric.

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