

Banana-shaped mesogens: observation of a direct transition from the antiferroelectric B₂ to nematic phase†

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The synthesis and characterisation of the first banana-shaped mesogens which exhibit a direct transition from the antiferroelectric B₂ phase to the nematic phase are reported.

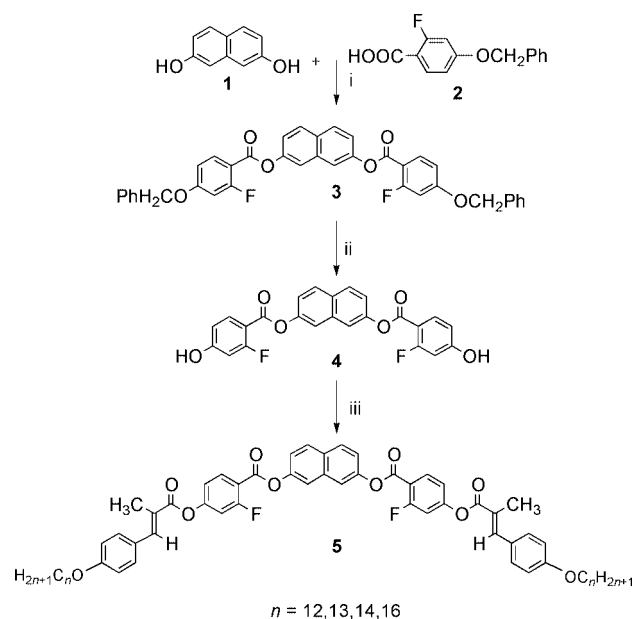
During the last couple of years there has been an upsurge in the synthesis and phase transition studies of compounds composed of banana-shaped or bent-core molecules because of the unusual and very interesting mesophases they exhibit. The detection of ferroelectricity in the mesophase of such an achiral compound by Niori *et al.*,¹ which was later determined to be antiferroelectric in the ground state^{2–4} by current response measurements, have stimulated further research in this field. Several hundred compounds with a bent molecular shape have been synthesised so far and at least seven different banana (B) phases characterised.^{5,6} It has been observed that in many homologous series of compounds only one banana phase exists in one homologue. However, smectic A, smectic C or nematic phases have been obtained either individually or in combination particularly for homologues with short terminal chains. Although the nematic phase has been observed in many series of bent-core molecules,^{7–11} there is no example of a compound exhibiting a direct transition from the B₂ phase to nematic. Very recently there was a report of a case in which the B₂ phase and a nematic phase are observed in the same substance and the two are separated by smectic A and smectic C phases.¹² It would be very interesting and useful from an experimental point of view if one could get a direct transition from the antiferroelectric B₂ phase to the nematic phase. We have achieved this objective and report our results in this communication.

The synthesis and characterisation of four compounds composed of banana-shaped molecules, three of which represent the first examples which show a direct transition from the antiferroelectric B₂ to nematic (N) phase transition, is described here. The general method of preparation of the compounds is shown in Scheme 1. As reported¹⁰ by us earlier, 2,7-dihydroxynaphthalene **1** was reacted with 2-fluoro-4-benzyloxybenzoic acid **2** to give the diester **3**. The protective benzyloxy groups were removed using 5% Pd–C as catalyst in a hydrogen atmosphere to yield the diphenol **4**. In the final step (iii) compound **4** was reacted with two equivalents of an appropriate (*E*)-4-*n*-alkoxy- α -methylcinnamic acid to furnish compound **5**.† All the compounds were purified by column chromatography (silica gel, 60–120 mesh) and were crystallised several times using suitable solvents.

The liquid-crystalline properties of the compounds were investigated by using optical polarising microscopy and differential scanning calorimetry (DSC). The transition temperatures together with the associated enthalpies are summarised in Table 1. On examination of the samples under a polarising microscope the following are observed. Compound **5**, *n* = 12, melts into a nematic phase and on cooling the isotropic (I) liquid shows typical schlieren texture. On further cooling, small broken-fan like texture emanates from the nematic phase and the field of view is completely filled with this

texture. Fig. 1 shows a typical texture wherein the broken-fans are appearing from the nematic phase and this phase transition is enantiotropic. Compounds **5**, *n* = 13 and *n* = 14, are enantiotropic in both nematic and the lower temperature phase while compound **5**, *n* = 16, is also enantiotropic but without the nematic phase. The N→I transition enthalpy is about 0.4 kJ mol^{–1}. A DSC thermogram obtained for compound **5**, *n* = 13, is shown in Fig. 2 and all the transitions can be seen clearly.

In order to confirm the nature of the lower temperature phase of these compounds, X-ray investigations were carried out. The X-ray diffraction experiments were conducted using Cu-K α radiation from a rotating anode generator with a flat graphite crystal monochromator. The diffraction patterns were collected on an image plate (Marresearch). The unoriented sample was contained in a Lindemann capillary and the temperature was controlled to within ± 0.1 °C. The diffraction pattern of an unoriented sample of the mesophase of compound **5**, *n* = 14,



Scheme 1 Reagents and conditions: i DCC, cat. DMAP, dry CHCl₃, room temp., 12 h, 78%; ii cat. 5% Pd–C, H₂, 1,4-dioxane, 55 °C, 90%; iii (*E*)-4-*n*-alkoxy- α -methylcinnamic acid, DCC, cat. DMAP, dry CHCl₃, room temp., 15 h, 65–70%.

Table 1 Transition temperatures and the associated enthalpies (in italics) as determined by DSC

Compound	<i>n</i>	Phase transition temp/°C; enthalpy/kJ mol ^{–1}		
5	12	Cr 119.5	[B ₂ 116.0]	N 127.0 I
		75.56	13.23	0.49
5	13	Cr 117.5	B ₂ 120.0	N 125.0 I
		59.28	13.92	0.43
5	14	Cr 107.0	B ₂ 123.0	N 124.0 I
		58.6	14.15	0.34
5	16	Cr 108.0	B ₂ 128.0 I	
		52.36	16.84	

† Electronic supplementary information (ESI) available: Fig. 1 in colour. See <http://www.rsc.org/suppdata/cc/b1/b106458b/>

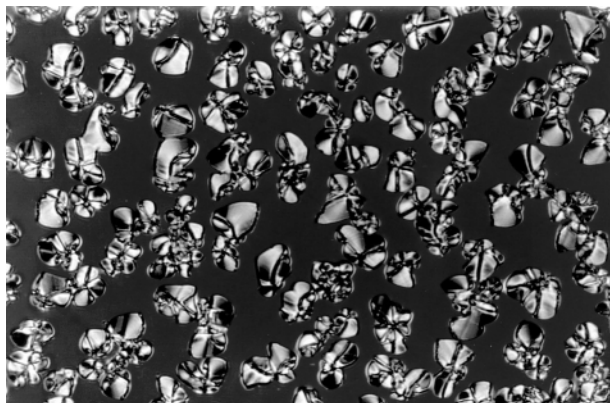


Fig. 1 Photo-micrograph of the B₂ phase appearing on cooling from a homogeneously aligned nematic phase, compound **5**, $n = 13$ (magnification $\times 300$).

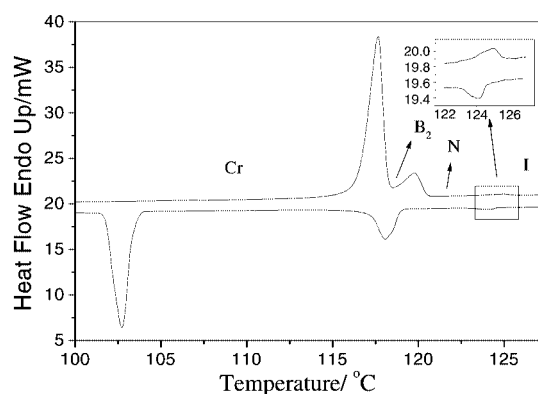


Fig. 2 Differential scanning calorimetric scan of compound **5**, $n = 13$ showing clearly the transition from the B₂ to the nematic phase. The insert shows the amplified N \rightarrow I transition.

shows a diffuse peak in the wide angle region with $d = 4.6$ Å, indicating liquid-like in-plane order. In addition, three orders of lamellar reflections (in the ratio 1 : 2 : 3) in the small angle region could be clearly seen. From this as well as the textural characteristics we have identified this mesophase to be a B₂ phase.

Finally, the characteristic feature of the B₂ phase, namely the switching current response, was carried out on the mesophase of compound **5**, $n = 14$. An electro-optical switching cell was constructed using two ITO coated glass plates pre-treated with polyimide which enables the sample to align homogeneously. The cell thickness was adjusted to be 6 μm by using appropriate spacers. The sample was filled in the isotropic phase and cooled slowly. A very good alignment of the nematic phase was obtained. On further slow cooling under a low frequency AC triangular voltage, well formed domains of the B₂ phase over the entire field of view were seen. From the visual observations under the polarising microscope, we see colourful circular domains which switch above a threshold voltage. Simultaneously two very sharp current peaks could be seen on the oscilloscope screen for the half period of the triangular voltage (250 V_{pp}). A typical switching current response for this compound is shown in Fig. 3. The current was measured across a 10 k Ω resistance. The apparent 'saturated polarisation' P_s was obtained by measuring the area under the peaks and is about 560 nC cm⁻². These observations clearly indicate the antiferroelectric nature of this phase.

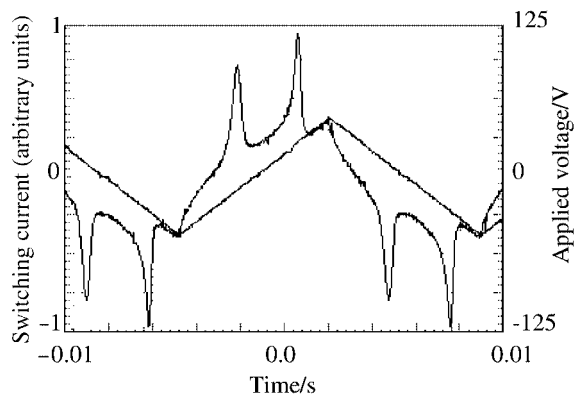


Fig. 3 Switching current response obtained in the B₂ phase of compound **5**, $n = 14$ at 120 °C by applying a triangular voltage (cell thickness: 6 μm , 250 V_{pp}, 29 Hz). (V_{pp} = volt peak-to-peak.)

The presence of this uniaxial nematic phase, as evidenced by numerous $s = \pm 1$ disclinations and fewer $s = \pm \frac{1}{2}$ defects above the B₂ phase helps to align the latter and may contribute to making the measurement of other physical properties of this interesting antiferroelectric phase rather easy.

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Notes and references

‡ The chemical structure of the compounds listed in Table 1 was determined from their spectral data. Typical data obtained for compound **5**, $n = 13$ is given below. γ_{max} (KBr) cm⁻¹ 2910, 2850, 1740, 1720, 1605, 1508, 1415, 1250, 1190; δ_{H} (400 MHz, CDCl₃) 8.22 (t, J 8.72 Hz, 2H, Ar-H), 7.94 (d, J 8.92 Hz, 2H, Ar-H), 7.9 (s, 2H, Ar-CH=C), 7.72 (d, J 2.0 Hz, 2H, Ar-H), 7.47 (d, J 8.76 Hz, 4H, Ar-H), 7.39 (dd, J 2.08 Hz, 2H, Ar-H), 7.13–7.17 (m, 4H, Ar-H), 6.96 (d, J 8.68 Hz, 4H, Ar-H), 4.01 (t, J 6.56 Hz, 4H, 2 \times Ar-OCH₂), 2.27 (d, J 0.88 Hz, 6H, 2 \times Ar-C=C(CH₃)), 1.81 (quin., J 6.68 Hz, 4H, 2 \times Ar-OCH₂-CH₂), 1.26–1.48 (m, 12H, 6 \times CH₂), 0.88 (t, J 6.64 Hz, 6H, 2 \times CH₃); δ_{C} (400 MHz, CDCl₃) 166.3, 162.1, 161.5, 159.9, 156.4, 149.0, 141.7, 134.3, 133.3, 131.8, 129.7, 129.3, 127.6, 124.2, 121.1, 118.6, 117.8, 115.1, 114.6, 111.4, 111.2, 68.2, 31.9, 29.6, 29.5, 29.3, 29.1, 25.9, 22.6, 14.2, 14.0.

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