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# Biaxial smectic A phase in homologous series of compounds composed of highly polar unsymmetrically substituted bent-core molecules

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Several compounds belonging to three new series of five-ring banana-shaped esters, which are unsymmetrically substituted with respect to the central phenyl ring, have been synthesised. One of the arms of these bent-core molecules has been terminally substituted with a highly polar cyano group while the other end contains an alkoxy chain. The mesophases exhibited by these compounds have been characterised using a combination of optical polarising microscopy, differential scanning calorimetry and X-ray diffraction studies. These studies indicate that most of the compounds show two smectic A mesophases which have a partial bilayer ordering. Conoscopic experiments clearly reveal that the lower temperature smectic A phase is biaxial in nature. A structural model has been proposed for the lower temperature biaxial smectic A phase. It is argued that quartets of molecules, which are conducive to the formation of the biaxial phase, can form in the layers. The in-layer birefringence of the biaxial smectic A phase has also been measured as a function of temperature for one of the compounds.

## Introduction

The credit for the preparation of the first compound with a bent molecular shape and exhibiting mesomorphic properties has been attributed[1,2] to Vorlander. However, it was Niori *et al.*[3] who showed that achiral compounds composed of banana-shaped or bow-shaped molecules exhibit a smectic phase with polarized layers. A little later Link *et al.*[4] demonstrated that the chirality arising in these smectic layers is due to the tilting of the molecules about the "arrow" directions of the bows, thus breaking the achiral symmetry of the layers. Since then, there has been intense research activity in this field.[5] In the last few years several hundred compounds composed of bent-core (BC) molecules have been synthesised[5–14] with a view to understanding the relationship between molecular structure and the mesophases exhibited by such compounds. At least five different B (banana) types of liquid crystals have been clearly identified in pure compounds and some new variants have been added recently.[10] In the electrically switchable $B_2$ phase, the bent-cores pack along a common axis to give rise to an electric polarisation of the layer. Also, the molecular plane tilts with respect to the layer-normal to produce a *chiral* layer, though the molecules themselves are usually achiral.[4] We reported earlier that binary mixtures of a compound exhibiting the $B_2$ phase with one composed of lath-like molecules exhibiting the bilayer smectic A phase showed a very interesting phase diagram.[15,16] At certain concentrations of the bent-core molecules a biaxial smectic $A_2$ ($SmA_{2b}$) phase was obtained in which the BC molecules had undergone an orientational transition as the temperature was lowered from the uniaxial smectic $A_2$ phase. The biaxial smectic A phase has also been observed in a binary mixture of a metallomesogen and 2,4,7-trinitrofluorenone.[17] There have been claims for the observation of the biaxial smectic A phase in a binary mixture of polymeric and monomeric materials[18] and in an oxadiazole compound.[19] However, in the latter two cases[18,19] unambiguous proof for the existence of the biaxial smectic A phase has not been provided.[17]

Recently, we have reported[20] the synthesis of a compound composed of highly polar unsymmetrically substituted BC molecules. The unsymmetrical molecule contains an *n*-alkoxy chain in one of the arms of the bent-core, while the other arm is terminally substituted with a highly polar cyano group. This compound exhibits a partial bilayer biaxial smectic A ($SmA_{db}$) phase in which the bent cores of two neighbouring molecules overlap in an antiparallel orientation as in the case of highly polar lath-like molecules.[21,22] In fact, this represents the first example of a single compound to undergo the biaxial smectic A to uniaxial smectic A transition. In this paper we report the synthesis and characterisation of compounds composed of highly polar unsymmetrically substituted BC molecules belonging to three different homologous series. These five-ring compounds are esters having the general molecular structure I.

Of the sixteen compounds reported here, fourteen exhibit the biaxial smectic A ($SmA_{db}$) phase. Based on the experimental observations, a structural model has been proposed for this $SmA_{db}$ phase.

## Experimental

### General

In general, the intermediate and final compounds were purified by column chromatography on silica gel (ACME, 60–120 mesh) using appropriate solvent systems. The purity of all the compounds was checked by thin layer chromatography (Merck Kieselgel $60F_{254}$ precoated plates) and by normal phase high performance liquid chromatography (μ porasil column, 3.9 mm × 300 mm, Waters Associates Inc.) using 1% ethyl acetate in dichloromethane as the eluent. The yields of the compounds were in the range of 60–80%.

The chemical structure of all the compounds was confirmed by using a combination of $^1H$ as well as $^{13}C$ nuclear magnetic resonance spectroscopy (Bruker AMX 400 spectrometer) with 1% tetramethylsilane in deuteriochloroform as an internal standard, infrared spectroscopy (Shimadzu FTIR-8400

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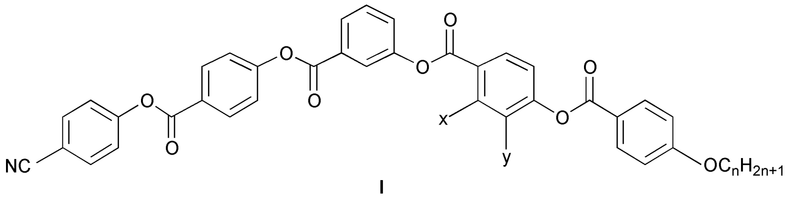

**I**

*n* =*12,13,............16,18*

| | | |
|---|---|---|
| x=H, | y=H | Series-**1g** |
| x=F, | y=H | Series-**1h** |
| x=H, | y=F | Series-**1i** |

spectrophotometer) and elemental analysis (Carlo-Erba 1106 analyser). The phase behaviour of all the compounds was examined by using a polarised light microscope (Leitz Laborlux 12 POL/Olympus BX50) equipped with a heating stage and a controller (Mettler FP52 and FP5 respectively) and also from thermograms recorded on a differential scanning calorimeter (Perkin-Elmer, Model Pyris 1D). The enthalpies for various transitions were also determined using the latter method. The calorimeter was calibrated using pure indium as a standard. X-Ray diffraction studies were carried out using Cu-K$_\alpha$ radiation from a rotating anode generator (Rigaku Ultrax 18) with a flat graphite crystal monochromator. The diffraction patterns were collected on an image plate (Marresearch). Unoriented samples were taken in Lindemann capillaries and the sample temperature in each case was controlled to within $\pm 0.1$ °C. Monodomain samples were also investigated, and will be described later. The conoscopic observations were made using a microscope (Leitz Ortholux-II POL BK) equipped with a heating stage and controller (Mettler FP82 and FP80HT respectively).

## Synthesis

The unsymmetrically substituted bent-core molecules **1g**, **1h** and **1i** were synthesised following the general synthetic pathway shown in Fig. 1. 3-Hydroxybenzoic acid and 4-cyanophenol were obtained commercially and used without further purification. 2-Fluoro-4-hydroxybenzoic acid and 3-fluoro-4-hydroxybenzoic acid were prepared following procedures described in the literature.[23] 4-Benzyloxybenzoic acid, 2-fluoro-4-benzyloxybenzoic acid and 3-fluoro-4-benzyloxybenzoic acid were prepared according to procedures used by us previously.[24] The detailed procedure used for the synthesis and characterisation of the compounds of series **1g** is given below.

**4′-Cyanophenyl 4-benzyloxybenzoate, 1a.** 4-Cyanophenol, **1** (5 g, 42 mmol) and 4-benzyloxybenzoic acid, **2** (9.58 g, 42 mmol) were dissolved in dry chloroform (100 ml). After the addition of *N*,*N*′-dicyclohexylcarbodiimide (DCC), (10 g, 48 mmol) and a catalytic amount of 4-(*N*,*N*-dimethylamino)-pyridine (DMAP), the mixture was stirred at room temperature for about 15 hours. The dicyclohexylurea which precipitated was filtered off and the filtrate diluted with chloroform. This solution was washed with 2% aqueous acetic acid solution (3 × 100 ml) and 5% ice cold sodium hydroxide solution (3 × 100 ml) and finally washed with water and dried over anhydrous sodium sulfate. The crude residue obtained was chromatographed on silica gel using chloroform as an eluent. Removal of solvent from the eluate afforded a white material which was crystallised from a mixture of chloroform and acetonitrile, yield 11.2 g (81%); mp 179.5–180 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): 8.14 (d, *J* 8.8 Hz, 2H, Ar-H), 7.72 (d, *J* 8.7 Hz, 2H, Ar-H), 7.4–7.33 (m, 7H, Ar-H), 7.07 (d, *J* 8.8 Hz, 2H, Ar-H), 5.17 (s, 2H, ArCH$_2$O-); IR (KBr) $\nu_{max}$: 3099, 3064, 2231, 1728, 1685, 1604, 1508, 1225, 1163, 1070 cm$^{-1}$; $C_{21}H_{15}NO_3$ requires C, 76.58; H, 4.59; N, 4.25%; found: C, 77.0; H, 4.53; N, 4.20%.

**4′-Cyanophenyl 4-hydroxybenzoate, 1b.** Compound **1a** (11.0 g) was dissolved in 1,4-dioxane (100 ml) and 5% Pd/C catalyst (2.2 g) was added. The mixture was stirred at 55 °C in an

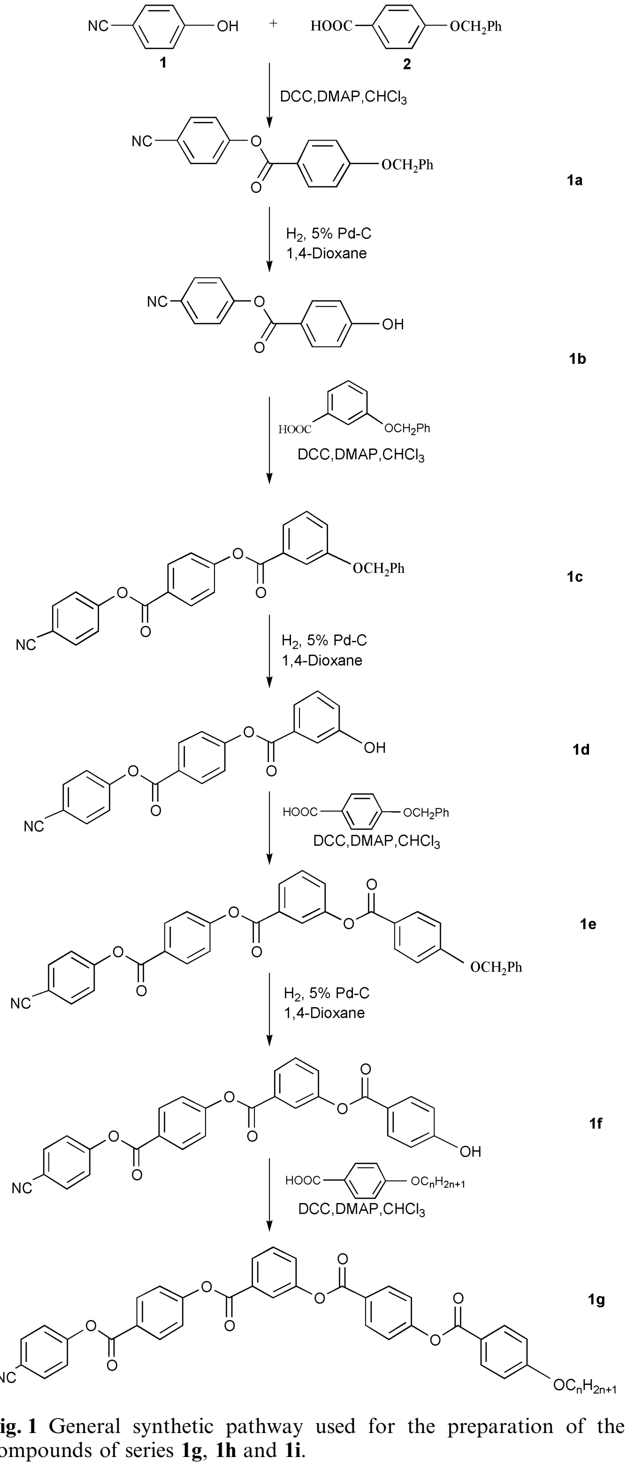

**Fig. 1** General synthetic pathway used for the preparation of the compounds of series **1g**, **1h** and **1i**.

atmosphere of hydrogen till the required quantity of hydrogen was absorbed. The mixture was filtered whilst hot and the solvent removed under reduced pressure. The residue was chromatographed on silica gel and eluted with a mixture of 5% acetone in chloroform. Removal of solvent from the eluate gave a product which was crystallised from a mixture of 1,4-dioxane and petroleum ether (bp 60–80 °C), yield 6 g (75%); mp 205–206 °C; $^1$H NMR (acetone-d$_6$, 400 MHz) $\delta$ (ppm): 8.1 (d, $J$ 7.6 Hz, 2H, Ar-H), 7.73 (d, $J$ 7.7 Hz, 2H, Ar-H), 7.35 (d, $J$ 7.6 Hz, 2H, Ar-H), 6.94 (d, $J$ 7.7 Hz, 2H, Ar-H), 5.73 (s, 1H, Ar-OH); IR (KBr) $\nu_{max}$: 3352, 3103, 3060, 2237, 1733, 1685, 1612, 1595, 1496, 1271, 1068 cm$^{-1}$; $C_{14}H_9NO_3$ requires C, 70.29; H, 3.79; N, 5.85%; found: C, 70.29; H, 3.7; N, 6.05%.

**4-Cyanophenyl 4′-(3″-benzyloxybenzoyloxy)benzoate, 1c.** Synthesised as described for the preparation of compound **1a**. Quantities: compound **1b** (5.5 g, 23 mmol), 3-benzyloxybenzoic acid (5.25 g, 23 mmol), DCC (5.6 g, 27 mmol), DMAP (cat. quantity), dry chloroform (75 ml); yield 7.3 g (72%); mp 146–147 °C; $^1$H NMR (CDCl$_3$, 400 MHz), $\delta$ (ppm): 8.28 (d, $J$ 8.5 Hz, 2H, Ar-H), 7.84–7.74 (m, 4H,Ar-H), 7.47–7.26 (m, 11H, Ar-H), 5.16 (s, 2H, ArCH$_2$O-); IR (KBr) $\nu_{max}$: 3100, 3066, 2227, 1726, 1602, 1581, 1508, 1485, 1417, 1270, 1016 cm$^{-1}$; $C_{28}H_{19}NO_3$ requires C, 74.82; H, 4.26; N, 3.11%; found: C, 74.53; H, 4.20; N, 3.12%.

**4-Cyanophenyl 4′-(3″-hydroxybenzoyloxy)benzoate, 1d.** Synthesised as described for the preparation of compound **1b**. Quantities: compound **1c** (7 g), 5% Pd/C (1.4 g), 1,4-dioxane (100 ml); yield 4.28 g (75%); mp 211–213 °C; $^1$H NMR (acetone-d$_6$) $\delta$ (ppm): 8.31 (d, $J$ 8.8 Hz, 2H, Ar-H), 7.94 (d, $J$ 8.8 Hz, 2H, Ar-H), 7.7–7.2 (m, 8H, Ar-H), 2.94 (s, 1H, Ar-OH); IR (KBr) $\nu_{max}$: 3298, 3105, 3068, 2245, 1730 1600, 1589, 1508, 1487, 1270, 1170, 1058 cm$^{-1}$; $C_{21}H_{13}NO_5$ requires C, 70.19; H, 3.64; N, 3.89%; found: C, 69.89; H, 3.53; N, 4.09%.

**4-Cyanophenyl 4′-[3″-(4‴-benzyloxybenzoyloxy)benzoyloxy]-benzoate, 1e.** Synthesised as described for the preparation of compound **1a**. Quantities: compound **1d** (6.5 g, 18 mmol), 4-benzyloxybenzoic acid (4.13 g, 18 mmol), DCC (4.5 g, 22 mmol), DMAP (cat. quantity), dry chloroform (75 ml); yield 7.2 g (70%); mp 167–168 °C; $^1$H NMR (CDCl$_3$) $\delta$ (ppm): 8.28 (d, $J$ 8.4 Hz, 2H, Ar-H), 8.18–8.06 (m, 4H, Ar-H), 7.75 (d, $J$8.3 Hz, 2H, Ar-H), 7.62–7.34 (m, 11H, Ar-H), 7.08 (d, $J$ 8.6 Hz, 2H, Ar-H), 5.17 (s, 2H, ArCH$_2$O-); IR (KBr) $\nu_{max}$: 3101, 3072, 2231, 1740, 1730, 1602, 1502, 1444, 1250, 1056 cm$^{-1}$; $C_{35}H_{23}NO_7$ requires C, 73.8; H, 4.07; N, 2.46%; found: C, 74.15; H, 3.97; N, 2.32%.

**4-Cyanophenyl 4′-[3″-(4‴-hydroxybenzoyloxy)benzoyloxy]-benzoate, 1f.** Synthesised as described for the preparation of compound **1b**. Quantities: compound **1e** (7 g), 5% Pd/C (1.4 g), 1,4-dioxane (75 ml); yield 4.2 g (71%); mp 206–207 °C; $^1$H NMR (acetone-d$_6$) $\delta$ (ppm): 8.32 (d, $J$ 8.6 Hz, 2H, Ar-H), 8.15–8.09 (m, 4H, Ar-H), 7.94 (d, $J$ 8.5Hz, 2H, Ar-H), 7.76–7.6 (m, 6H, Ar-H), 7.03 (d, $J$ 8.6 Hz, 2H, Ar-H), 2.82 (s, 1H, Ar-OH); IR (KBr) $\nu_{max}$: 3385, 3101, 3066, 2237, 1738, 1600, 1500, 1413, 1250, 1163, 1060 cm$^{-1}$; $C_{28}H_{17}NO_7$ requires C, 70.14; H, 3.57; N, 2.92%; found: C, 69.8; H, 3.59; N, 2.60%.

**4-Cyanophenyl 4′-{3″-[4‴-(4⁗-*n*-alkoxybenzoyloxy)benzoyloxy]benzoyloxy}benzoate, 1g.** Synthesised as described for the preparation of compound **1a**. Quantities: compound **1f** (0.2 g, 0.42 mmol), 4-*n*-tetradecyloxybenzoic acid (0.14 g, 0.42 mmol), DCC (0.1 g, 0.48 mmol), DMAP (cat. quantity), dry chloroform (10 ml); yield 0.2 g (60%); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): 8.31–8.27 (m, 4H, Ar-H), 8.16–8.08 (m, 4H, Ar-H), 7.77–7.74 (d, $J$ 8.5 Hz, 2H, Ar-H), 7.65–7.54 (m, 2H, Ar-H), 7.43–7.37 (m, 6H, Ar-H), 6.99 (d, $J$ 8.9 Hz, 2H, Ar-H), 4.05 (t, $J$ 6.6 Hz, 2H, Ar-OCH$_2$), 1.83 (quin, $J$ 7.9 Hz, 2H, Ar-OCH$_2$-C$\underline{H}_2$), 1.50–1.26 (m, 22H, 11 × CH$_2$), 0.89–0.86 (t, $J$ 7.0 Hz, 3H, 1 × CH$_3$); $^{13}$C NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): 164.2, 163.8, 163.5, 163.4, 155.7, 155.4, 154.2, 151.1, 133.7, 132.4, 132.0, 131.8, 130.5, 129.8, 127.7, 127.5, 126.3, 123.6, 122.8, 122.1, 120.9, 118.1, 114.4, 109.9, 68.4, 31.8, 29.6, 29.5, 29.3, 29.0, 25.9, 22.6, 14.0; IR (KBr) $\nu_{max}$: 2916, 2850, 2243, 1736, 1602, 1508, 1278, 1255, 1220, 1166, 1078 cm$^{-1}$; $C_{49}H_{49}NO_9$ requires C, 73.94; H, 6.21; N, 1.76%; found: C, 73.65; H, 6.27; N, 1.44%.

## Results and discussion

The phase transition temperatures and the associated enthalpies for the highly polar unsymmetrically substituted compounds belonging to the three different homologous series, *viz.*, **1g**, **1h** and **1i** are summarised in Tables 1–3 respectively. The compounds of series **1g** are not laterally substituted while in series **1h** and **1i**, a fluoro substituent is introduced in the *ortho* and *meta* positions respectively with respect to the carboxylate

**Table 1** Transition temperatures (°C) and enthalpies (kJ mol$^{-1}$) for compounds of series **1g**[a]

| Compound | $n$ | Cr | | SmA$_{db}$ | | SmA$_d$ | | I |
|---|---|---|---|---|---|---|---|---|
| **1g12** | 12 | . | 129.5<br>*41.11* | . | 130.5<br>*0.17* | . | 130.8<br>*3.48* | . |
| **1g13** | 13 | . | 129.0<br>*80.86*[b] | . | 135.0<br>*0.09* | . | 135.5<br>*4.24* | . |
| **1g14** | 14 | . | 129.5<br>*77.28*[b] | . | 138.0<br>*0.13* | . | 140.2<br>*4.81* | . |
| **1g15** | 15 | . | 129.5<br>*89.07*[b] | . | 140.2<br>*0.09* | . | 144.0<br>*5.27* | . |
| **1g16** | 16 | . | 130.0<br>*86.67*[b] | . | 141.9<br>*0.08* | . | 147.5<br>*5.79* | . |
| **1g18** | 18 | . | 129.5<br>*60.57*[b] | . | 143.2<br>*0.11* | . | 153.5<br>*6.17* | . |

[a] key for all three Tables 1–3. Cr: crystalline; SmA$_{db}$: partial bilayer biaxial smectic A phase; SmA$_d$: partial bilayer uniaxial smectic A phase; I: isotropic. [b] Has crystal-crystal transitions; the enthalpy denoted is the sum of all the transitions. Temperatures in parentheses indicate monotropic transitions.

**Table 2** Transition temperatures (°C) and enthalpies (kJ mol$^{-1}$) for compounds of series **1h**

| Compound | $n$ | Cr | | SmA$_{db}$ | | SmA$_d$ | | I |
|---|---|---|---|---|---|---|---|---|
| **1h12** | 12 | . | 130.0<br>*66.79* | — | | — | | . |
| **1h14** | 14 | . | 132.0<br>*68.32* | — | | (. | 130.5)<br>*4.19* | . |
| **1h16** | 16 | . | 131.5<br>*60.30* | (. | 130.0)<br>*0.12* | . | 137.5<br>*4.97* | . |
| **1h18** | 18 | . | 131.0<br>*60.26* | . | 132.5<br>*0.06* | . | 143.5<br>*5.95* | . |

**Table 3** Transition temperatures (°C) and enthalpies (kJ mol$^{-1}$) for compounds of series **1i**

| Compound | $n$ | Cr | | SmA$_{db}$ | | SmA$_d$ | | I |
|---|---|---|---|---|---|---|---|---|
| **1i12** | 12 | . | 119.5<br>*80.68* | (. | 119.2)<br>*0.019* | . | 120.0<br>*3.86* | . |
| **1i13** | 13 | . | 120.0<br>*82.75* | . | 123.4<br>*0.017* | . | 125.5<br>*4.22* | . |
| **1i14** | 14 | . | 120.5<br>*85.46* | . | 126.2<br>*0.044* | . | 130.0<br>*4.77* | . |
| **1i15** | 15 | . | 121.0<br>*72.64* | . | 128.0<br>*0.09* | . | 133.8<br>*4.95* | . |
| **1i16** | 16 | . | 121.0<br>*67.15* | . | 129.0<br>*0.08* | . | 137.0<br>*5.47* | . |
| **1i18** | 18 | . | 120.0<br>*44.8* | . | 130.0<br>*0.11* | . | 142.3<br>*5.85* | . |

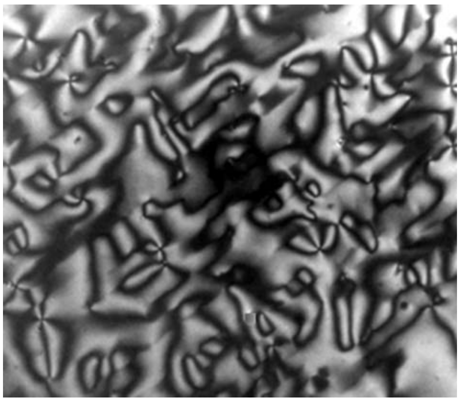

**Fig. 2** Photomicrograph of the optical texture of the $SmA_{db}$ phase of compound **1g14** at 135 °C (crossed polarisers), Magnification ×250.

group of the middle phenyl ring of the arm containing the *n*-alkoxy chain. Each compound is designated by a number which represents the series and the number of carbon atoms in the alkoxy chain (*e.g.* **1i12** means the compound containing the *n*-dodecyloxy chain in series **1i**). All the six compounds of series **1g** (Table 1) are dimesomorphic and enantiotropic. On cooling the isotropic liquid of a sample (compounds **1g12** to **1g18**) sandwiched between a glass slide and a coverslip and viewed under a polarising microscope a homeotropic texture is obtained. However, in some regions a focal-conic texture could also be seen. This mesophase has been identified as uniaxial smectic A phase. As the temperature is lowered further, a phase transition takes place in which the homeotropic regions exhibit a schlieren texture with both two-brush and four-brush defects. The presence of the two-brush defects in this lower temperature mesophase may be due to one of the three structural possibilities as discussed in our earlier communication.[20] As we have argued in that paper, the lower temperature phase corresponds to the biaxial smectic A ($SmA_b$) phase. As pointed out by Brand *et al.*[25] a distinguishing feature of the biaxial smectic A phase is the occurrence of ±½ strength defects, unlike in the smectic C phase with tilted molecules which allows only disclinations of strength ±1. A typical texture of the lower temperature mesophase is shown in Fig. 2. We can indeed see in Fig. 2 disclinations of strength ±½ as well as those with strength ±1. The latter could be expected to split to form the lower strength defects to reduce energy. However, this would require a large rearrangement of the director field. The two structures would be separated by a potential barrier which appears to lead to the metastability of the disclinations of strength ±1 in the systems studied by us. Strong fluctuations in intensity are seen in this phase as observed by us previously[20] and this phase has been identified as biaxial smectic A phase. Sometimes this mesophase exhibits a striped texture as shown in Fig. 3 and an investigation into the origin of this feature is underway, the results of which will be published elsewhere. A differential scanning calorimetric (DSC) thermogram obtained for compound **1g16** is shown in Fig. 4 and all the transitions can be seen clearly. While the clearing point enthalpy ranges from about 3.5 to 6 kJ mol$^{-1}$, that for the biaxial smectic A to uniaxial smectic A phase transition is quite low and is of the order of 0.1 kJ mol$^{-1}$. A plot of the transition temperatures against the number of carbon atoms in the alkoxy chain for this series is shown in Fig. 5. One can see smooth curve relationships for like transitions and both the mesophase–mesophase and mesophase–isotropic transition point curves rise gradually in ascending the series while the melting points remain more or less constant.

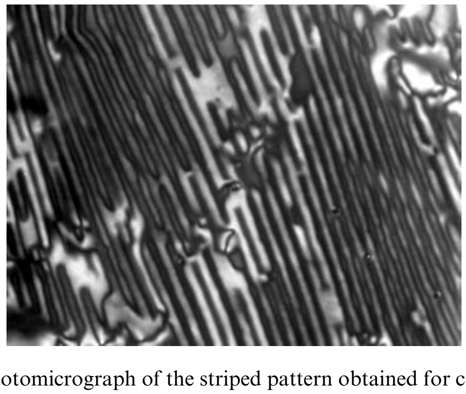

**Fig. 3** Photomicrograph of the striped pattern obtained for compound **1g14** at 132 °C (crossed polarisers), Magnification ×250.

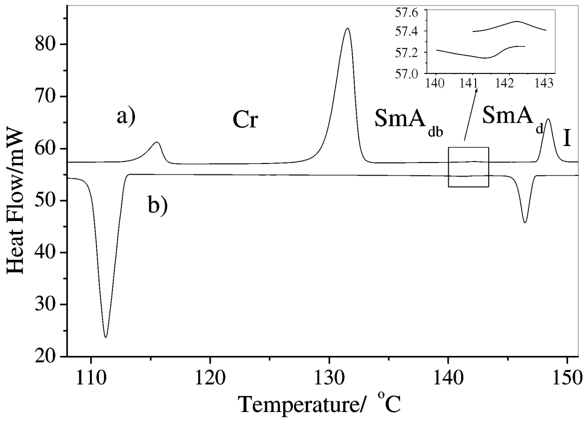

**Fig. 4** Differential scanning calorimetric scans at a rate of 5 °C min$^{-1}$ for compound **1g16**: a) heating cycle, b) cooling cycle. The insert shows the $SmA_{db} \rightarrow SmA_d$ phase transition in a magnified scale.

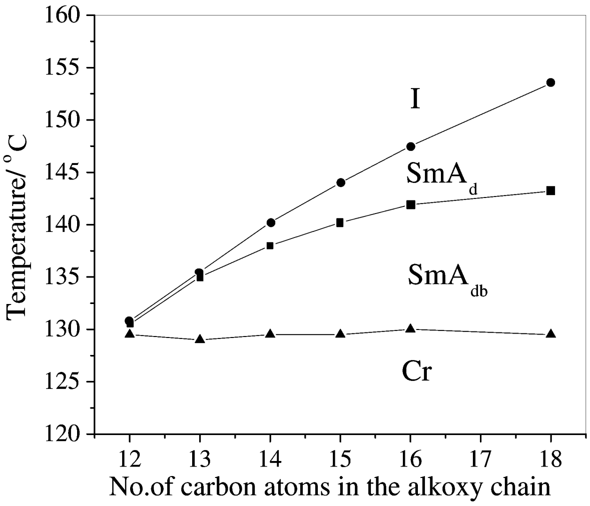

**Fig. 5** Plot of the transition temperatures *versus* the number of carbon atoms in the *n*-alkyloxy chain for homologues of series **1g**.

Only four compounds were synthesised in series **1h** as the compound **1h12** is non-mesomorphic and compound **1h14** does not exhibit the biaxial smectic A phase. Though compounds **1h16** and **1h18** do exhibit the biaxial smectic A phase, the former is monotropic. The characteristic textural features observed in series **1g** were observed for these two compounds as well. The six homologues of series **1i** shown in Table 3 do exhibit both the uniaxial as well as the biaxial smectic A phases. Again the textural characteristics and the DSC data are similar to those observed for homologues of series **1g**. A plot of the transition temperatures *versus* the number of carbon atoms in the alkoxy chain for the series **1i** is shown in Fig. 6. Again, a rising trend is obtained for like transitions and the melting points lie practically on a horizontal line on ascending the series. It is interesting to note that the near constancy of

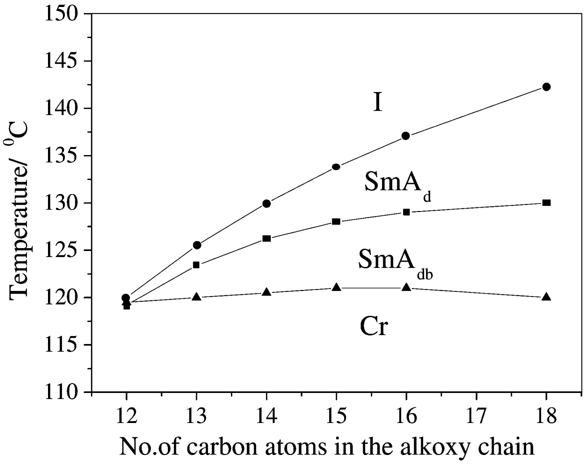

**Fig. 6** Plot of the transition temperatures *versus* the number of carbon atoms in the *n*-alkyloxy chain for homologues of series **1i**.

the melting points in each of the three series of compounds is rather unusual. A comparison of the transition temperatures of the three series of compounds **1g**, **1h** and **1i** reveal the following features. The introduction of an *ortho*-fluoro substituent (series **1h**) lowers the clearing temperatures by about 10 °C while the melting points are increased marginally. Also, the compound with *n*-dodecyloxy chain (**1h12**) is rendered non-mesogenic. However, in the case of *meta*-fluoro substituted compounds (series **1i**), both the melting and clearing points are reduced by about 10 °C. This suggests that the position of the fluoro substituent (dipolar interactions) has an effect on the stability of the mesophase in such bent-core compounds.

In order to confirm the optical biaxiality of the lower temperature smectic A phase, we have carried out conoscopic experiments. For this purpose, well aligned samples have to be used and we have achieved the same in the following way. A cell is constructed in which one of the glass plates has an ITO conducting coating with a gap of 1 mm that is etched out. The other plate is an ordinary glass slide and both are pretreated with octadecyltriethoxysilane (ODSE) which facilitates a homeotropic alignment of the smectic A liquid crystal. The thickness of the sample (usually ~30 μm) is controlled by using appropriate spacers and measured using an interference technique before filling the sample. For compound **1g15**, the conoscopic observations between crossed polarisers which are set at 45° to the direction of the electric field (178 V, 10 kHz) show the uniaxial interference pattern in the smectic A phase (140.5 °C) and as the temperature is lowered to 139.5 °C this splits to give the biaxial pattern. On further lowering the temperature (139.2 °C) the separation between the isogyres continuously increases. On reducing the temperature (139.0 °C) further the isogyres go out of the field of view. All the three conoscopic patterns are shown in Fig. 7.

The switching behaviour of the mesophase was examined as follows. A sample (compound **1i14**) was taken in a cell similar to the one used for conoscopic observations. The cell had a gap of 80 μm between the electrodes. As before, an electric field aligned the biaxial director. Careful observations under the action of a square wave voltage in the frequency range of 1 to 10 Hz did not reveal any switching in the sample upto an electric field of 3 V $\mu m^{-1}$. Further, observations using a half-wave compensator clearly showed that the field-induced alignment was such that the molecular plane was *orthogonal* to the electric field. The optical anisotropy in the layer plane did not vary with field upto 3 V $\mu m^{-1}$. We tried to get an aligned planar sample by using ITO plates coated with silicon monoxide at an oblique angle. As the sample was cooled at 0.5 °C $min^{-1}$ across the isotropic to uniaxial smectic A transition temperature, batonnets were seen to grow and merge to give a focal-conic (FC) texture. In some regions the FC domains were quite large, and remained so as the sample was cooled to the biaxial smectic phase. The application of a low frequency (1 to 5 Hz) square wave voltage across a sample, which was 5.8 μm thick did not show any switching behaviour in the biaxial phase. However, for voltages above ~15 V, there was electrohydrodynamic motion which did not change when the sample was heated to the uniaxial smectic A phase.

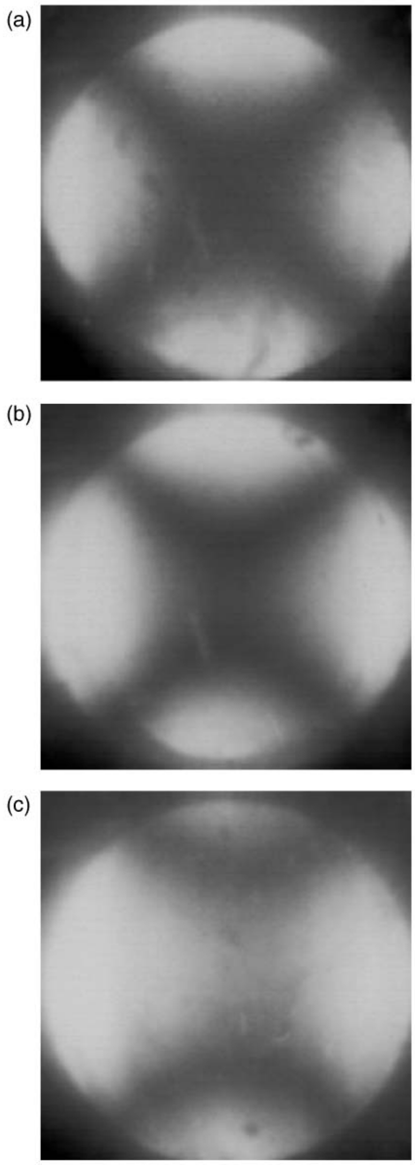

**Fig. 7** Photographs of the conoscopic patterns from a homeotropically aligned sample of compound **1g15**: a) the uniaxial smectic $A_d$ phase at $T = 140.5$ °C, b) biaxial smectic $A_d$ phase at $T = 139.5$ °C, c) biaxial smectic $A_d$ phase at $T = 139.2$ °C.

X-Ray diffraction studies were carried out on ten compounds. The detailed experimental procedure used has already been described in a recent communication.[20] For all the samples, in the small angle region, a sharp reflection corresponding to the smectic layer spacing could be seen. The second order reflection was found to be rather weak. The values obtained for both the first order as well as the second order reflections and the calculated molecular length $L$ in their most extended form with an all *trans* conformation of the alkoxy chain is given in Table 4. In addition, the X-ray diffraction pattern showed a diffuse scattering in the wide-angle region with a peak around 4.6 Å indicative of a liquid-like in-plane order. A significant point to note is that the $d$ values are almost

**Table 4** The layer spacings *d*, of the smectic phases of the ten compounds investigated and the molecular length *L*, in the most extended form with an all *trans* conformation of the alkoxy chain

| | *d*/Å | | |
|---|---|---|---|
| Compound | First order | Second order | *L*/Å |
| **1g13** | 50.8 | 25.4 | 47.9 |
| **1g14** | 52.3 | 26.1 | 49.2 |
| **1g16** | 54.0 | 27.0 | 51.9 |
| **1g18** | 55.7 | 27.9 | 54.5 |
| **1h16** | 53.0 | 26.5 | 51.9 |
| **1h18** | 54.8 | 27.4 | 54.5 |
| **1i13** | 52.4 | 26.2 | 47.9 |
| **1i14** | 53.9 | 27.0 | 49.2 |
| **1i16** | 55.5 | 27.7 | 51.9 |
| **1i18** | 56.6 | 28.3 | 54.5 |

temperature independent (within experimental error of ±0.2 Å) in the entire range of both smectic phases. It can be clearly seen that the layer spacing *d*, in most of the cases is significantly larger than the calculated molecular length. This evidently implies a partial bilayer structure of the smectic layers in both the higher and lower temperature smectic phases and hence we have designated them as $SmA_d$ and $SmA_{db}$ phases. However, it is seen that for very long alkyl chains such as *n*-octadecyloxy chain, the *d* values are closer to those of *L*. This perhaps implies that the long chains adopt *gauche* conformations for which there is sufficient space to fill. One can also see from this table that the *d* values increase as the terminal alkyl chain length is increased. We have also conducted X-ray diffraction experiments using samples mounted on a horizontal glass plate pretreated with ODSE. In the $SmA_{db}$ phase, we see equatorial spots corresponding to the layer order and the diffused scattering is now confined to arcs centered at an angle to the horizontal plane. The biaxial director is not aligned, but we may note the two spacings in the layer will not be very different for BC molecules unlike in the biaxial phase made of board-like molecules.[17] Hegmann *et al.*[17] have observed additional reflections in a monodomain sample for a mixture composed of a metallomesogen and trinitrofluorenone in the lower temperature biaxial smectic A phase.

From the molecular structure of these compounds (structure I), it is clear that all the four ester groups in the aromatic core have dipole moments whose long axis components are *parallel* to that of the cyano end group. In the case of compounds of series **1h** and **1i**, the C–F bond on one of the phenyl rings has a dipole moment which is almost exactly orthogonal to the long axis of the molecule. The dipolar interactions between two neighbouring molecules in all these cases favour an antiparallel configuration, and in view of the distribution of dipoles in the core, a complete overlap between the aromatic cores can be expected. The mutual configuration of a molecular pair can then be expected to be as shown in Fig. 8 which maximises dispersion interaction and allows for a better packing of the molecules. The length of the molecular core is ~32 Å along the 'bow string axis' between the nitrogen atom of the cyano group and the oxygen atom of the alkoxy chain. In the case of compound **1g14**, this would imply that each tetradecyl chain contributes about 11 Å to the layer thickness. The fully stretched all *trans* chain length is ~17 Å, but as the lowest temperature at which the $SmA_{db}$ phase occurs is above 118 °C or so, the chain can be expected to have considerable conformational flexibility. The effective length of the chain is then smaller than that of a fully stretched conformation, probably by 1 or 2 Å. Further, the chain is attached to the arm of a bent aromatic core which makes an angle of 30° with the bow-string axis. The chain-axis makes an angle of ~36° with the axis of the arm of the core to which it is attached, and the effective contribution of chain to the layer thickness depends on the angle between the chain axis and the plane of the aromatic core. In the usual BC molecules in which both ends have alkyl chains, packing efficiency would favour the chains to be in the plane defined by the central core. In the $SmA_d$ and $SmA_{db}$ structures, the number of chains in the aliphatic parts of the layer is only half the number of aromatic cores in the densely packed central part. This in turn gives rise to a relative orientational freedom for the chains to increase the entropy. The final effect is that the chain contributes about 11 Å to the effective thickness of the partial bilayer.

In order to understand the optical properties of the medium under an electric field, two possible structures can be considered. (i) Each layer has a polar order of the BC molecular *pairs*. As the arrow-axis aligns *orthogonal* to the electric field, the successive layers could have antiferroelectric order as shown schematically in Fig. 9. However, it can be noted that the in-plane polarization of the layers of **1g*n*** compounds would be quite large in view of the contribution from the strongly polar cyano end groups of *both* molecules in the pair. Hence we could expect that a relatively low electric field would have produced an induced ferroelectric order, and under the reversal of a field of ~3 V $\mu m^{-1}$, a switching in the induced ferroelectric state. As a switching is not seen, nor indeed even a change in the lateral optical anisotropy even at 3 V $\mu m^{-1}$ the model sketched in Fig. 9 can safely be ruled out. (ii) It is clear from Fig. 8 that the BC nature of the molecules leads to a fairly large lateral component of the cyano dipole moment unlike in the case of rod-like molecules. The dipolar interaction between the lateral components would favour the formation of a *pair* of molecular *pairs* with their arrow axes being antiparallel. Thus, we can expect that four molecules form a quartet (see Fig. 10) whose aromatic region is biaxial but apolar in both longitudinal and transverse directions. The orientational freedom of the chains can facilitate a relatively free rotation of the quartets about their long axes, giving rise to the uniaxial $SmA_d$ phase. As the temperature is lowered, the core region undergoes a rotational freezing giving rise to the biaxial $SmA_{db}$ phase, with an *apolar* in-layer director corresponding to the arrow axes.

We have made quantitative measurements of the in-layer birefringence ($\Delta\mu$) of the $SmA_{db}$ phase of compound **1i14** at $\lambda$ 5893 Å by using a quarter wave plate as a compensator. The oven temperature is maintained to an accuracy of about 5 mK. However, as a strong electric field (0.4 V $\mu m^{-1}$) is applied to get an aligned sample, the temperature of the latter

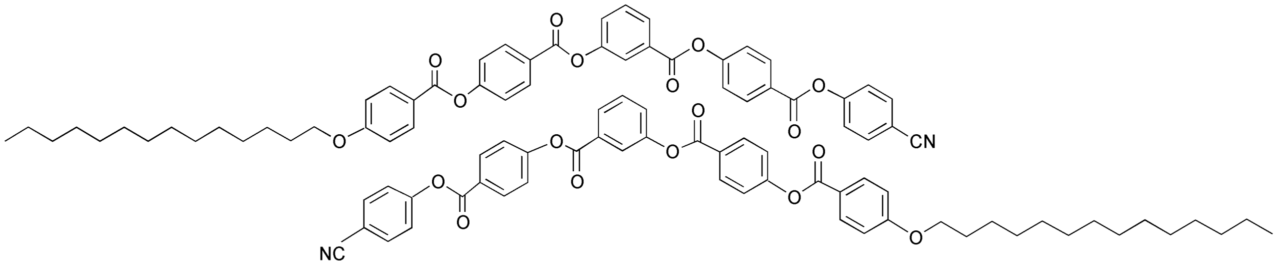

**Fig. 8** The antiparallel configuration of a pair of molecules showing the complete overlap of the aromatic cores.

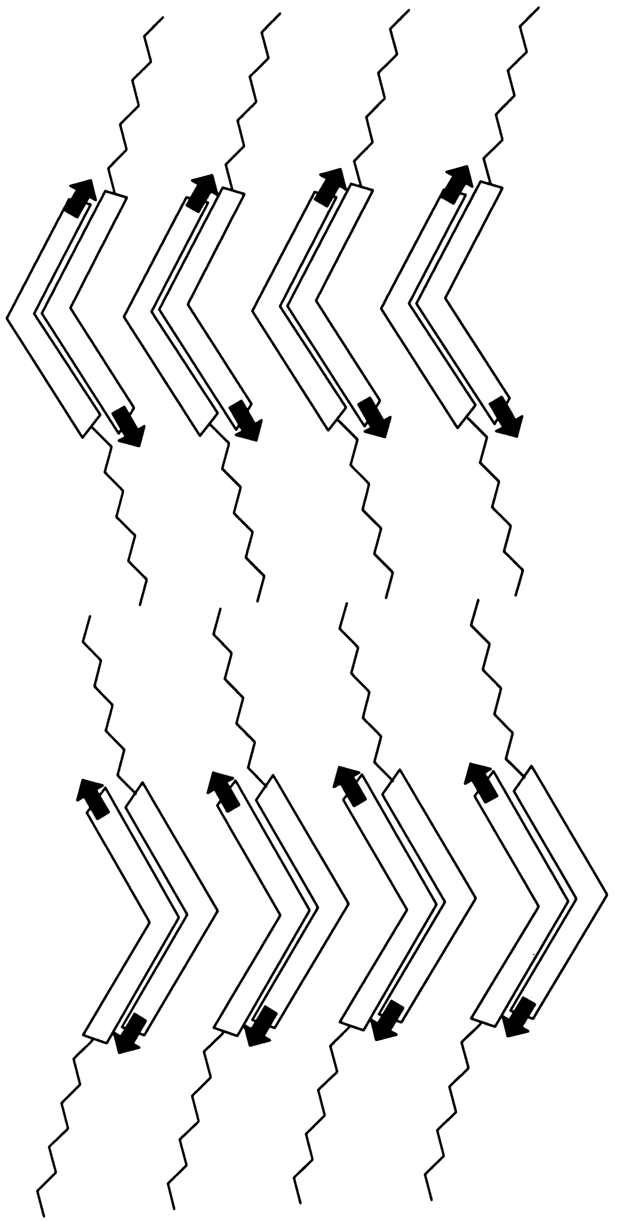

**Fig. 9** Schematic representation of a polar packing of molecular pairs within the layer with an antiferroelectric ordering between successive layers.

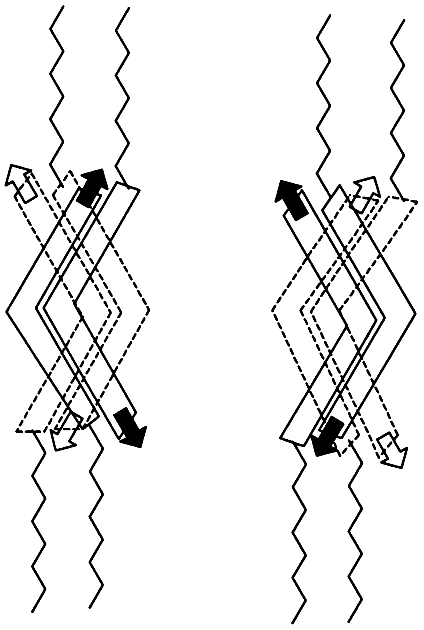

**Fig. 10** Schematic diagram of the proposed quartet structure of the highly polar BC molecules which is apolar in both longitudinal and transverse directions and gives rise to the partial bilayer smectic liquid crystal. The pair of molecules whose cores are shown in full lines are in the plane of the paper and those with the dotted lines are below that plane.

is found to be increased by about 1 °C, due to dissipation caused by ion flow. Hence the optical measurements were made on cooling the sample under a continuous application of the field and the temperatures indicated in Fig. 11 correspond to those of the oven. Though the DSC thermograms indicate a very weak first order transition between $\mathrm{SmA_d}$ and $\mathrm{SmA_{db}}$ phases (with $\Delta H \sim 400\ \mathrm{J\ mol^{-1}}$), the local heating problem mentioned above prevents us from measuring any small jump in $\Delta\mu$ at the transition point. $\Delta\mu$ increases continuously as the temperature is lowered in the $\mathrm{SmA_{db}}$ phase. The data can be fitted to an equation of the form $\Delta\mu = A(T_{\mathrm{ub}} - T)^{\beta}$ giving an index $\beta = 0.5$ (Fig. 11). The local heating problem perhaps has an influence on the measured value.

As a result of these investigations, we believe that the occurrence of both uniaxial and biaxial smectic A phases in compounds with highly polar groups such as a cyano group at one end of the bent-core is mainly due to 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. In these compounds, the BC molecules orientate with their arrow axes in the layer-plane.

## Conclusions

We have synthesised sixteen compounds belonging to three homologous series of unsymmetrically substituted compounds composed of bent-core molecules which contain a highly polar cyano group at one terminal position. Fourteen of these compounds exhibit the $\mathrm{SmA_{db}}$ phase. The mesophase–mesophase and mesophase–isotropic transition points follow smooth curves as functions of the alkoxy chain length. However, the melting points are about the same for all the homologues in each of the three series which is somewhat unusual. X-Ray diffraction studies show that both the smectic A phases are partially bilayer in nature. We have proposed a structural model for the lower temperature mesophase ($\mathrm{SmA_{db}}$) in which four molecules form a quartet whose aromatic region is biaxial but apolar in both longitudinal and transverse directions.

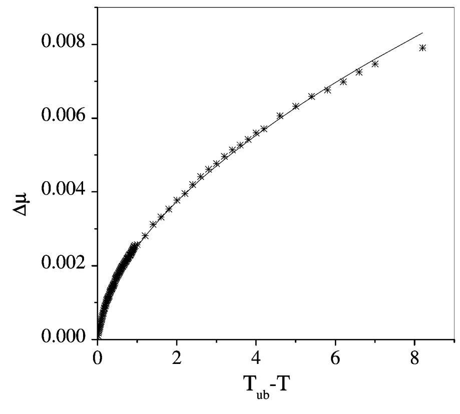

**Fig. 11** Temperature variation of the layer birefringence in the biaxial smectic A phase of compound **1i14**. Stars are experimental data and the continuous line is the theoretical fit referred to in the text.

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