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Preliminary communication

Helical superstructures in the mesophase of compounds derived from 2-cyanoresorcinol

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The mesophase exhibited by four members of a new homologous series of compounds composed of banana-shaped molecules derived from 2-cyanoresorcinol is reported. The characteristic optical textures showing helical filamentary growth patterns, coupled with the results from X-ray diffraction studies of these seven-ring compounds containing a biphenyl moiety indicate that the mesophase is indeed B_7.

The occurrence of helical superstructures in calamitic liquid crystalline phases such as chiral nematic, chiral smectic C etc., are well understood. Since the discovery of the first switchable smectic phase in compounds composed of achiral banana-shaped molecules [1], fascinating helical superstructures have been seen in many such compounds [2]. Among the seven B type phases that are described in the literature, the B_4 and B_7 phases are known to exhibit helical superstructures. While the B_4 phase is truly a crystalline phase [2], the B_7 phase is liquid crystalline. This mesophase was first reported in some 2-nitroresorcinol derivatives [3, 4]. The beautiful optical textures they exhibit are not seen in any of the other well characterized B phases. The structural features of the B_7 phase are not clear as yet, although some studies have been initiated in this direction [5]. The filamentary growth patterns are seen in a number of other systems not derived from 2-nitroresorcinol [6–12] and the symbol B_7 has been assigned to the mesophase. In some cases, electro-optic switching is seen and the mesophases are characterized as ferroelectric [8, 9], while in another case antiferroelectric switching has been reported [10]. In addition, the X-ray diffraction pattern (XRD) of the mesophases reported by Heppke *et al.* [6] and Walba *et al.* [8] show a simple layer structure. These results have led to further confusion over the proper identification of the B_7 phase. Thus the number of compounds exhibiting the true B_7 phase appears to be very limited [2, 13].

In this communication, we report the synthesis and characterization of four derivatives belonging to a new series of compounds composed of achiral banana-shaped molecules. These are derived from 2-cyanoresorcinol and contain a biphenyl moiety; their molecular structure is shown at the top of the table.

The synthesis of 2-cyano-1,3-phenylene bis[4-(4-*n*-alkylbiphenyl-4′-carbonyloxy) 3-fluorobenzoates] was carried out as follows. 3-Fluoro-4-benzyloxybenzoic acid was esterified with 2-cyanoresorcinol using *N*,*N*′-dicyclohexylcarbodiimide (DCC) in the presence of a small quantity of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) in anhydrous dichloromethane at room temperature. The product, 2-cyano-1,3-phenylene bis(3-fluoro-4-benzyloxybenzoate) was purified and subjected to hydrogenolysis with 5% Pd-C in 1,4-dioxane. The phenol obtained, viz. 2-cyano-1,3-phenylene bis(3-fluoro-4-hydroxybenzoate) was again esterified with the appropriate 4-*n*-alkylbiphenyl-4′-carboxylic acid using DCC and DMAP. The desired products were purified by column chromatography on silica gel using chloroform as eluent and finally by repeated crystallization using suitable solvents.

The purity of all four compounds was checked by thin layer chromatography and by normal phase high performance liquid chromatography. The chemical structure of each of the compounds was confirmed by ^{1}H as well as ^{13}C nuclear magnetic resonance spectroscopy and infrared spectroscopy. The phase behaviour of the compounds was examined by thermal polarizing optical microscopy (POM), and also using thermograms recorded by differential scanning calorimetry. The transition temperatures and the associated enthalpies for the new materials are summarized in the table. XRD studies were carried out using CuK_α radiation from a rotating anode generator with a graphite crystal monochromator. The

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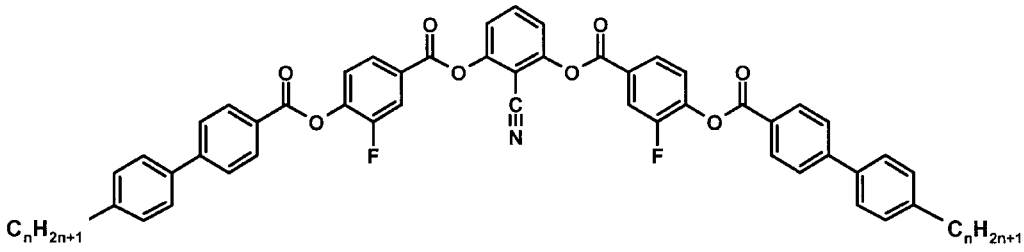
Table. Phase transition temperatures (°C) and the associated enthalpy values (kJ mol^{-1}, in italics) for the four compounds.



Compound	*n*	Cr		B_7		I
1	12	•	131.0	•	152.5	•
			44.6		*26.6*	
2	14	•	122.5	•	154.0	•
			35.9		*27.4*	
3	16	•	117.0	•	155.0	•
			47.5		*29.1*	
4	18	•	112.0	•	154.5	•
			38.4		*29.9*	

unoriented sample was contained in a Lindemann capillary and the sample temperature controlled to within ± 0.1°C. The diffraction patterns were collected on an image plate.

It is seen in the table that all four compounds **1**, **2**, **3** and **4** exhibit only one enantiotropic mesophase. The thermal range of the mesophase increases on ascending the series. This is because the clearing temperatures vary little, but the melting points decrease on going from compound **1** to **4**. The thermal range of the mesophase of compound **4** is twice that obtained for compound **1**. The clearing enthalpies for the four derivatives are quite high and comparable to those reported [2] for the B_7–isotropic phase transition. The DSC thermogram obtained for compound **2** is shown in figure 1. In all four compounds the mesophase supercools well below the melting points.

One of the remarkable features of these compounds is the fascinating microscopic textures they exhibit. When a thin film of the isotropic liquid of compound **2** is cooled slowly and viewed by POM, a number of different variants of the texture can be obtained. Typically long single-spiral domains resembling telephone wires, and double-spiral domains comparable to a chain, could be seen to grow. A typical texture obtained for compound **2** is illustrated in figure 2. As reported earlier by Pelzl *et al.* [4], we also have observed an equal number of right-handed and left-handed helices in a given cell for these cyano-substituted compounds. Another variant of the two-dimensional texture obtained for compound **2**, that is characteristic for this mesophase, is shown in

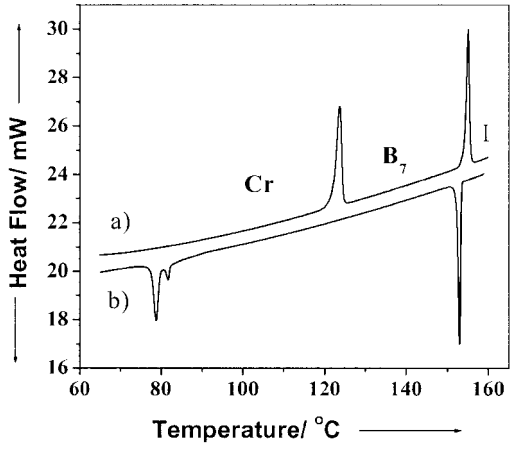


Figure 1. Differential scanning calorimetric scan of compound **2** at a rate of 5°C min^{-1}: (*a*) heating cycle, (*b*) cooling cycle.

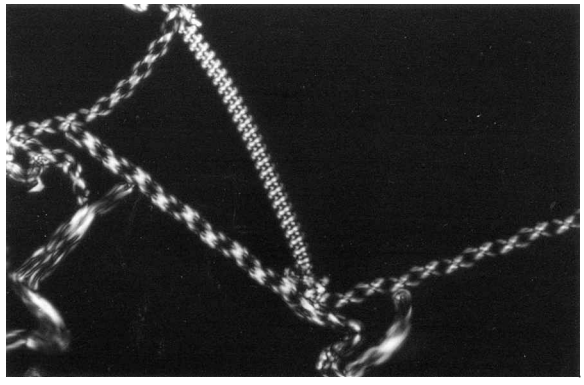


Figure 2. Optical photomicrograph of the mesophase of compound **2** exhibiting a twisted and double-twisted helical structure on slow cooling of the isotropic liquid.

figure 3. Based on microscopic textural observations we have identified this mesophase as B_7.

In order to confirm the identity of this mesophase, XRD measurements have been carried out. The diffraction pattern for an unoriented sample of compound **2** obtained at 135°C is shown in figure 4. In the wide angle region, a diffuse peak with $d \sim 4.7$ Å is observed and is indicative of a liquid-like ordering of the molecules. In the small angle region, several peaks are seen with $d_1 = 65.2$ Å, $d_2 = 40.6$ Å, $d_3 = 20.3$ Å, $d_4 = 13.5$ Å, $d_5 = 10.8$ Å and $d_6 = 7.7$ Å. It can be seen that the d_2, d_3 and d_4 reflections correspond to a lamellar ordering. The additional reflections indicate a two-dimensional ordering for the mesophase. A similar XRD pattern has been obtained for the B_7 phase of some of the 2-nitro-substituted compounds [13]. In view of this, we have identified the mesophase of compounds 1–4 as B_7. However, it should be pointed out that the exact structural features of the B_7 mesophase are yet to be understood completely.

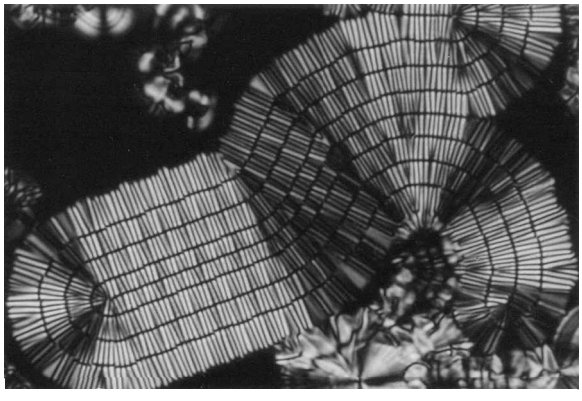


Figure 3. Optical photomicrograph of the mesophase of compound **2** exhibiting a two-dimensional structural pattern.

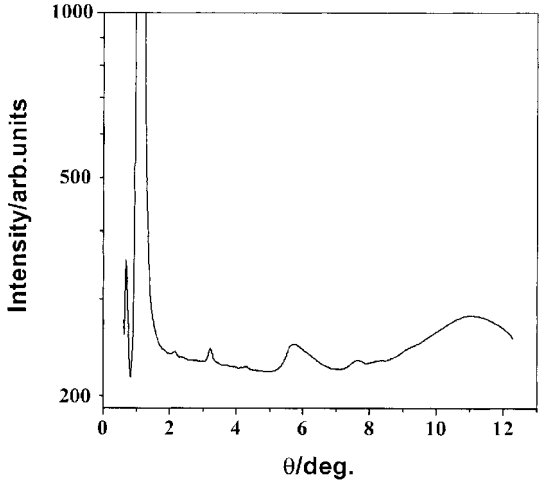


Figure 4. X-ray diffraction pattern obtained for the B_7 phase of compound **2** at 135°C.

We have carried out some experiments to examine if this mesophase switches electro-optically. Compound **2** was placed in a cell which was prepared for homogeneous alignment with a thickness of 8.1 μm. On applying a triangular wave electric field up to about 490 V_{PP} ($\pm$ 30.2 V μm^{-1}) at 130°C and a frequency of 30 Hz, no switching could be observed.

Finally, the fascinating textural features such as single- and double-spirals, myelinic growth patterns, etc. observed in these compounds point to a helical superstructure for this mesophase which appears to be complicated. We believe that the compounds described herein exhibit all the features shown by the standard compounds [2] for which the symbol B_7 was designated at the International Workshop on Banana-Shaped Liquid Crystals: Chirality by Achiral molecules, in Berlin in December 1997. It is also appropriate to note that in both the standard and the present systems, a strong dipole moment caused by the nitro and cyano groups of these achiral banana-shaped molecules may be responsible for obtaining the B_7 mesophase. Work is in progress to synthesize other derivatives and examine their physical properties; the results will be published later.

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