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Preliminary communication

Bent-core mesogens with biphenyl moieties: observation of a B_7 to B_4 phase transition

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Four new bent-core mesogens containing biphenyl moieties are reported. All these, except the first homologue, exhibit B_7 and B_4 banana phases, both of which are known to have a helical structure. The B_7 to B_4 phase transition is very rare, this being perhaps only the second report of the observation of such a phase sequence. The first homologue exhibits only one mesophase X_1 with textural features reminiscent of the B_1 phase. All the compounds synthesized are characterized by spectral data. The mesophases exhibited by these compounds are characterized by polarizing optical microscopy, differential scanning calorimetry and X-ray studies.

The discovery of achiral bent molecules exhibiting electro-optically switchable mesophases [1] has stimulated much synthetic work and many physical studies in this new field. Various structural variants of the parent compounds, 1,3-phenylene-bis(4-phenyliminomethyl) 4-*n*-alkoxybenzoates, have been reported [2–8]. As the structures of the different phases exhibited by these bent or banana-shaped compounds are not completely understood, a tentative classification scheme has been proposed in which the phases are labelled with the code letters B_1, B_2 ... B_7 according to the sequence of their discovery [3]. Of these, the B_3 and B_4 phases are solid-like. Among the physical properties of these 'banana phases', the electro-optical behaviour is of particular interest as this gives some hints about their structure. Up to the present, electro-optical switching has been observed only in the B_2, B_5 and B_7 mesophases.

Among the seven banana phases only B_4 and B_7 are found to have a helical structure. The existence of helical ordering in phases formed by banana-shaped molecules is believed to be a consequence of their chiral layer structure [2, 4]. The B_4 phase which has also been referred to as the SmBlue phase, exhibits a characteristic blue colour and is supposed to be a TGB-like phase

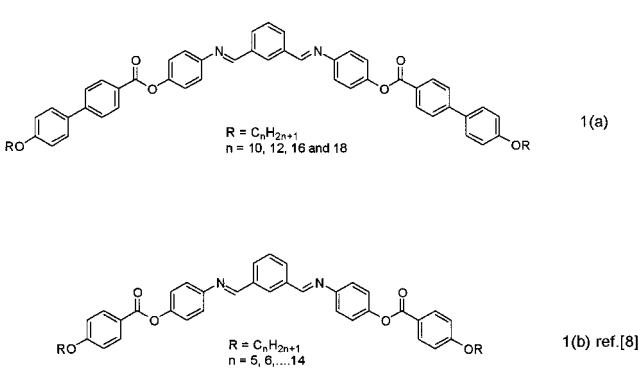

Figure 1. (*a*) Molecular structure of the bent-core compounds synthesized; (*b*) a similar compound reported in the literature.

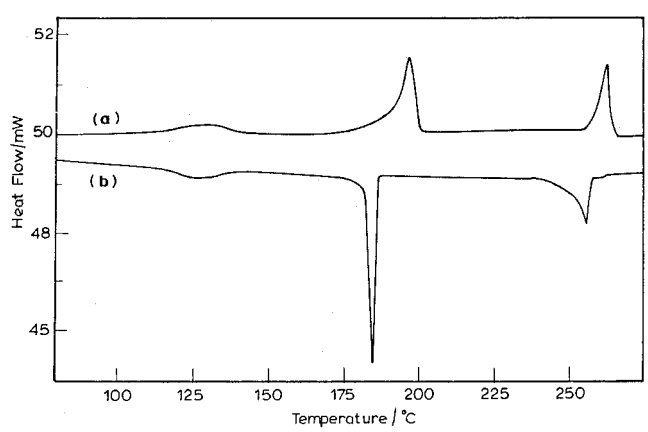

Figure 2. DSC thermograms for the compound with $n = 12$. Scans (*a*) and (*b*) represent the traces obtained in the heating and cooling cycles, respectively and show three peaks corresponding to the Cr–B_4, B_4–B_7 and B_7–I transitions.

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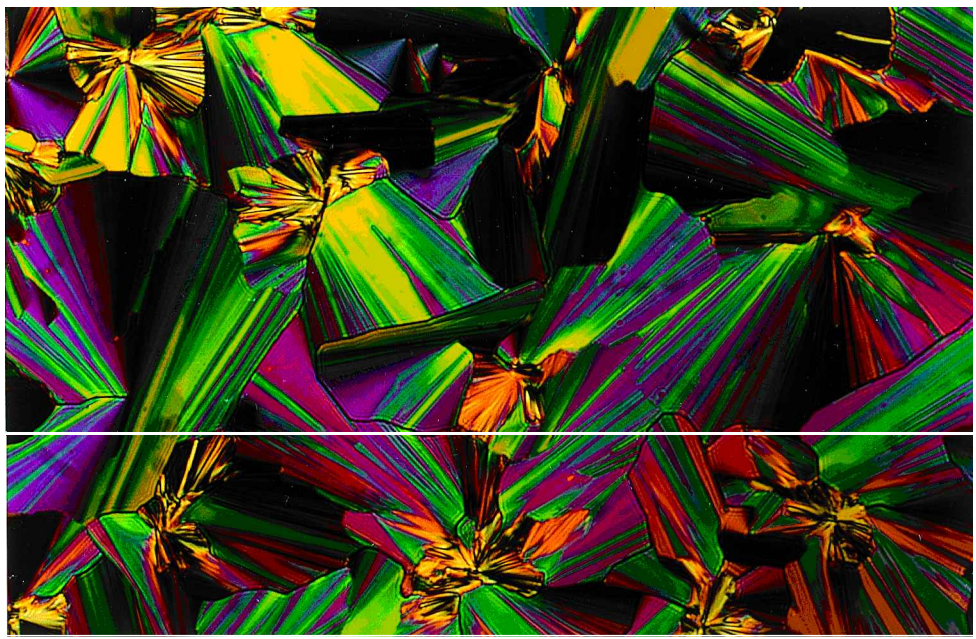
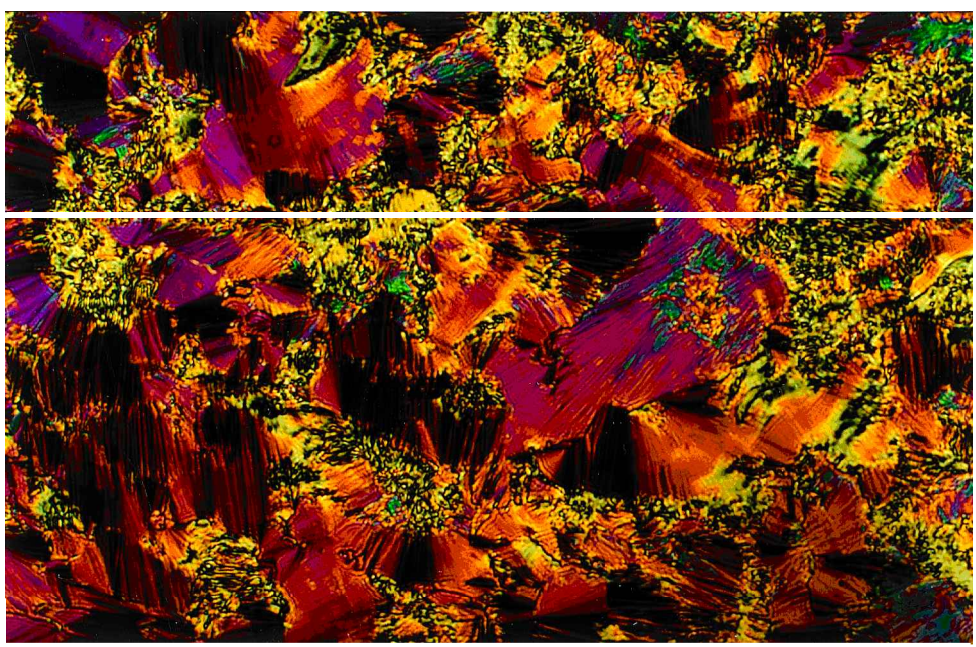
with a blue colour and three-dimensional order [2]. The 'spiral-domain' or 'helical-ribbon' like texture is a characteristic feature of the B_7 mesophase [4–6].

To elucidate the relationships between the chemical constitution and the phases exhibited by such banana-shaped compounds, we have synthesized and studied several compounds. Some of the results of these investigations have already been reported by us previously [9–13]. From the view point of chemical structure, bent-core mesogens consisting of a biphenyl moiety have been less studied in the literature. Therefore, as a continuation of our work on bent-core mesogens, we have synthesized some new compounds containing biphenyl moieties, see figure 1 (*a*). All four homologues synthesized are found



(*a*)

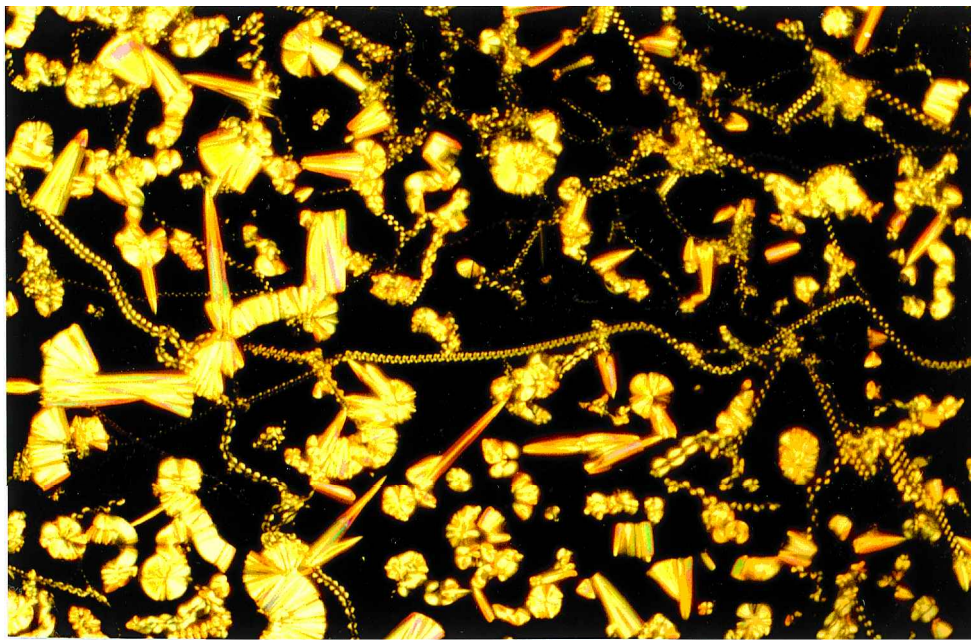


(*b*)

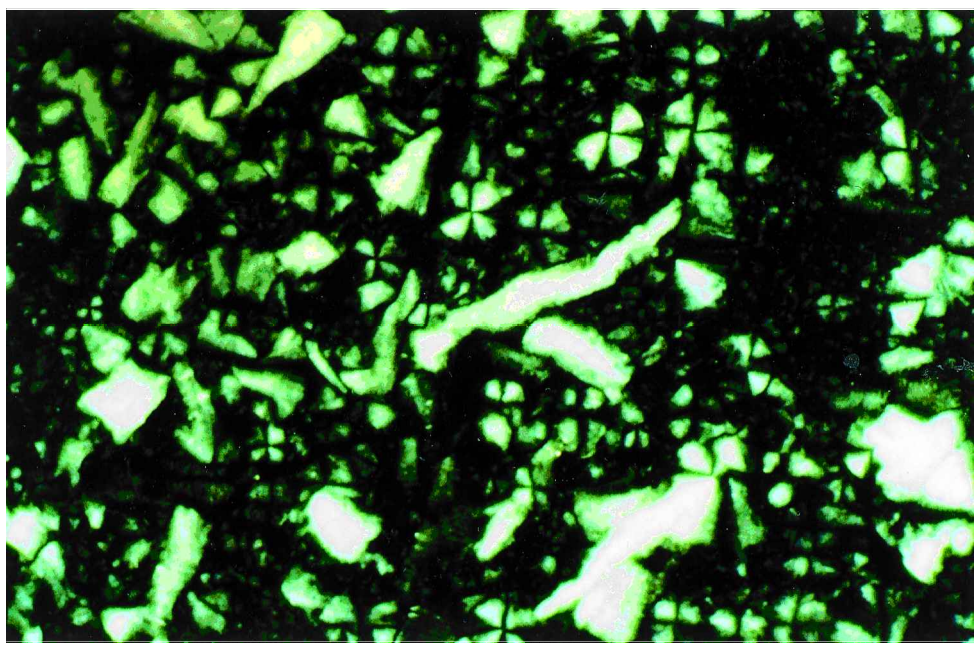
Figure 3. Optical microscopic texture showing (*a*) the mosaic pattern for the X_1 phase of the compound with $n = 10$ (at 250°C textural features are reminiscent of the B_1 phase); (*b*) the pattern obtained on shearing the texture shown in (*a*).

to be liquid crystalline; except for the first homologue, they all exhibit B_7 and B_4 phases. In the literature we find only one other example [14] of a B_7 to B_4 phase transition. We have also made a comparison of the mesomorphic properties of the compounds shown in figure 1 (*a*) with the similar known compounds shown in figure 1 (*b*) [8].

The synthesis of the bent-core compounds of figure 1 (*a*), was achieved by known synthetic routes [8]. The spectral data of all the intermediates and the final compounds were satisfactory. The transition temperatures were determined using a Mettler FP 82 HT hot stage and central processor in conjunction with a Leitz DMRXP polarizing microscope. The enthalpies of transitions were



(*a*)



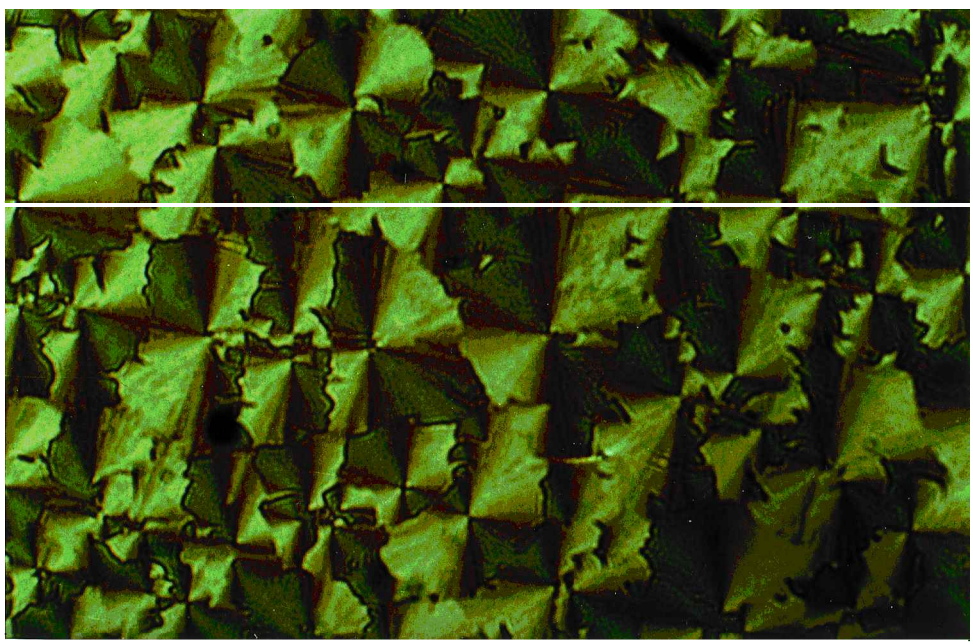
(*b*)

Figure 4. Photographs showing (*a*) the spiral domains along with some unspecified texture of the B_7 mesophase (at 236°C); (*b*) the texture seen in the SmBlue or B_4 phase (at 170°C) exhibited by the compound with $n = 16$.

determined from the thermograms recorded by differential scanning calorimetry (DSC 7 Perkin-Elmer). The heating and cooling rate was 10°C min^{-1}. X-ray measurements were carried out using a MAC Science image plate set-up (MAC Science DIP1030).

The transition temperatures and the enthalpies of transition for the compounds of figure 1 (*a*), are given in the table. All four homologues form enantiotropic liquid crystalline phases. The first homologue with $n = 10$ shows only one mesophase X_1 (textural features reminiscent of B_1 phase), whereas the compounds with $n = 12$, 16 and 18 exhibit two phases, viz. B_4 and B_7. All the phases exhibited by these compounds exist over large temperature ranges. The DSC thermogram for the compound

(*a*)



(*b*)

Figure 5. Photographs showing (*a*) the circular domains of the B_7 mesophase of the compound with $n = 12$ (at 225°C); (*b*) the texture of the B_4 mesophase obtained (at 180°C) on cooling the texture shown in (*a*).

Table. Transition temperatures (°C) and enthalpies of transitions (kJ mol^{-1}) in italics, for the compounds of figure 1 (*a*).

n	Cr		B_4		B_7		X_1		I
10	•	198.5	—		—		•	268.0	•
		31.6						*33.5*	
12	•	130.0	•	196.5	•	262.5	—		•
		15.1		*41.8*		*27.2*			
16	•	142.5	•	192.5	•	251.5	—		•
		14.9		*46.3*		*30.2*			
18	•	152.0	•	190.0	•	245.5	—		•
		13.9		*44.8*		*31.8*			

with $n = 12$ is shown in figure 2. We see three peaks in the heating cycle (*a*). The first broad peak at 130°C corresponds to the melting of the solid to the B_4 phase. The second peak (at 196.5°C) and the third (at 262.5°C) correspond to the B_4–B_7 and B_7–I transitions, respectively. In the cooling cyle (*b*), we also see three peaks, corresponding to the I–B_7, B_7–B_4 and B_4–Cr transitions.

Now, let us discuss the microscopic observations made on these compounds. On cooling from the isotropic liquid the compound with $n = 10$ exhibits a mesophase X_1 with a mosaic pattern, the texture of which is reminiscent of the B_1 phase, see figure 3 (*a*). The compounds with $n = 12$, 16 and 18, exhibit two different phases. On cooling from the isotropic liquid, the compound with $n = 16$ forms spiral domains along with some unspecified texture, a characteristic feature of the B_7 mesophase [4–6], see figure 4 (*a*). On further cooling, there is a transition to a phase with intense blue domains, the texture of which is shown in figure 4 (*b*) and resembles those reported for the SmBlue or B_4 phase [2]. This phase is supposed to have a twist grain boundary structure, but possess a solid-like three-dimensional order. Depending on the sample thickness, we were able to see other textural variants of the B_7 [4] and B_4 phases for the compounds with $n = 12$, 16 and 18, see figure 5. The magnitude of the enthalpy change across the B_7–I transition for the different homologues is also comparable with reported values [4].

The X-ray powder diffraction pattern, along with a one-dimensional cut for the compound with $n = 12$ (obtained at 220°C), is shown in figure 6. The diffuse reflection seen at wide angle ($2\theta \sim 20°$), corresponds to liquid-like ordering within the layer. In the low angle region three sharp reflections are seen. As we were unable to obtain a monodomain sample, these reflections have not been indexed. The presence of three sharp reflections at low angles rules out a simple layered structure for this mesophase and may indicate a two-dimensional structure. From the combination of these X-ray results and the optical microscopic textural observations of circular domains and/or spiral domains (depending on the sample thickness), we believe that the high temperature mesophase is a B_7 phase [4]. Figure 7 shows the X-ray diffraction pattern obtained at 180°C for the low temperature phase of the same sample. The presence of multiple peaks, points to a more ordered structure and in conjunction with its optical texture, which is blue in colour, we call this phase B_4 [3].

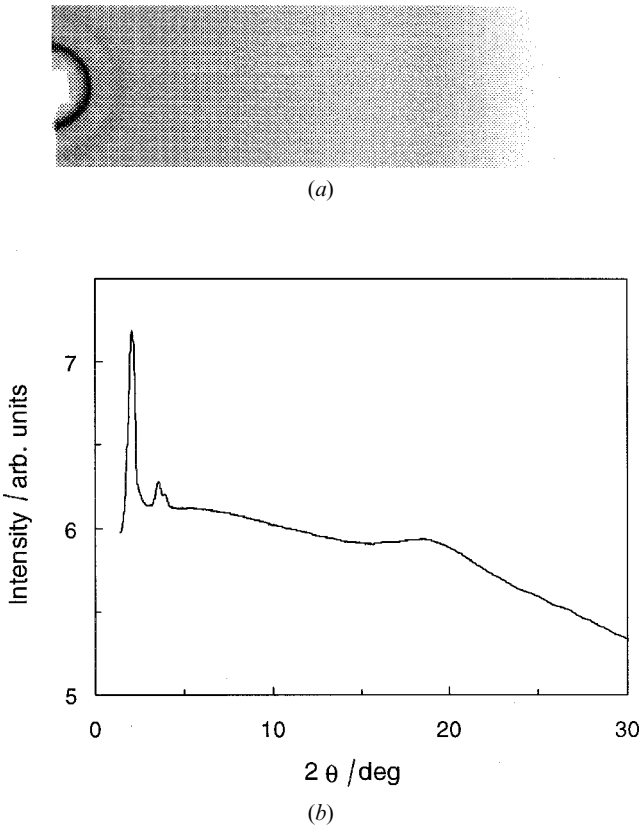
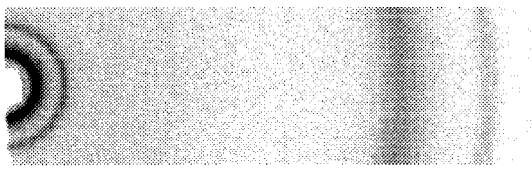
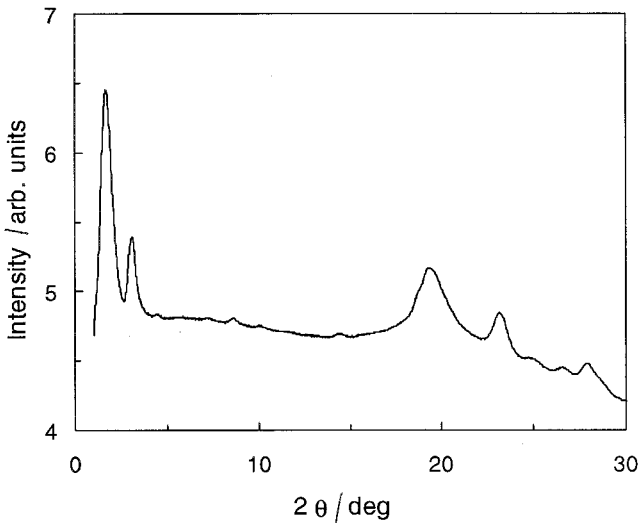


Figure 6. (*a*) X-ray diffraction pattern in the B_7 mesophase (at 220°C) of the compound with $n = 12$. (*b*) χ-averaged one-dimensional intensity vs. 2θ profile derived from (*a*). The three sharp peaks at low angles confirm a two-dimensional structure. The diffuse peak at higher angles is due to liquid-like packing of molecules within the layers.

Bedel *et al.* have reported [8] a series of similar bent-shaped compounds, but with phenyl moieties, see figure 1 (*b*). They observed B_1 and B_2 banana phases. When the phenyl on both ends of the molecule is replaced with biphenyl rings, we observe completely different mesomorphic properties. In the case of figure 1 (*b*) compounds, those with $n \geqslant 10$, exhibit only one type of mesophase, viz. B_2. However, in the present case of 1 (*a*) compounds, that with $n = 10$ shows only one mesophase X_1 (with textural features reminiscent of B_1), whereas those with $n \geqslant 12$ exhibit two types of banana phase, viz. B_4 and B_7. The transition temperatures are of course found to be higher in the case of the compounds 1 (*a*)



(*a*)



(*b*)

Figure 7. (*a*) X-ray diffraction pattern in the B_4 mesophase (at 180°C) of the compound with $n = 12$. (*b*) χ-averaged one-dimensional intensity vs. 2θ profile derived from (*a*). The multiple peak pattern obtained indicates a highly ordered structure for this phase.

when compared with compounds 1(*b*). As already remarked, up to the present only one other compound exhibiting the B_7 to B_4 phase transition has been reported [14].

To summarize, we have synthesized and studied four new bent-core compounds with biphenyl moieties. All exhibit liquid crystalline properties. The compounds with $n = 12$, 16 and 18 exhibit the phase sequence Cr–B_4–B_7–I which is very rare. The significance of this phase sequence lies in the fact that both phases B_4 and B_7 have a helical structure.

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