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Preliminary communication

First observation of double-twisted helical structure in a banana-shaped achiral molecule

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The double-twisted helical structure was confirmed for the first time for the smectic phase of a banana-shaped molecular system from observation of the microscopic pattern. Optically polarized microscopic textures and phase transitions of 1,3-phenylene bis[4-(3-chloro-4-*n*-octyloxyphenyliminomethyl) benzoate (PBCOB) and related compounds are described. The chloro-substituent introduced into the 3-position of the Schiff's base moiety of the banana-shaped molecule destabilized the smectic phase and enhanced new mesomorphic properties. The mesophases exhibited by the octyloxy homologue of the chloro-substituted compound were of the smectic phases, SmX1 and SmX2. The mixing behaviour between chloro-substituted and non-chloro-substituted compounds resulted in the appearance of a wide miscibility gap and enlargement of the SmX1 phase which can be seen in a lateral chloro-substituted compound.

Although classical thermotropic liquid crystals (LCs) are commonly composed of rod-like molecules, many liquid crystals exhibit conventional molecular structures. One new LC molecular architecture is a banana-shaped molecule with a bend in the middle of the mesogenic part [1–4]. Recently, Weissflog *et al.* [5] reported banana-shaped molecules that exhibited ferroelectric properties. The ferroelectricity is attributed to the polar packing of molecules with C_{2v} symmetry where the molecules are packed in the same direction. Niori *et al.* [6] observed ferroelectricity in a smectic phase which was produced from achiral banana-shaped molecules. The existence of such a mesophase depends on the length of the rigid core of molecules as well as on the magnitude of bend and its position. The structure and flexibility of the angled segment are also important [7]. However, the phase is antiferroelectric and has no helix, as Link

et al. [8] point out. Akutagawa *et al.* [9] reported the mesomorphic behaviour of five-ring systems with acute-angled configurations such as 1,2-phenylene bis[4-(4-alkoxybenzylideneamino) benzoates] and the 2,3-naphthylene analogues. The mesophases appearing

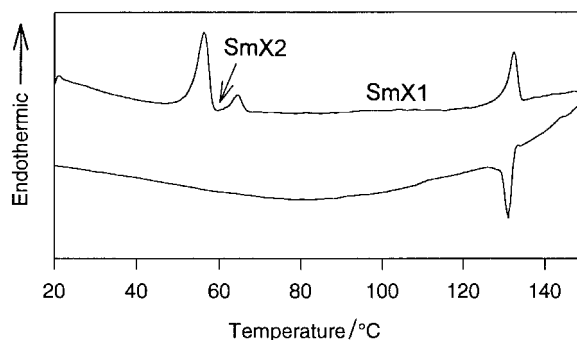


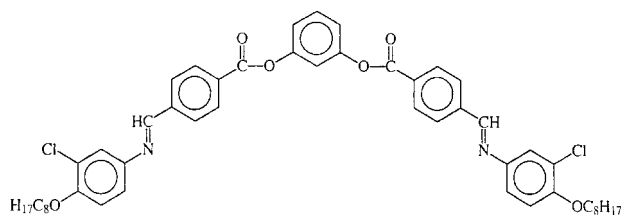
Figure 1. DSC thermogram of PBCOB.

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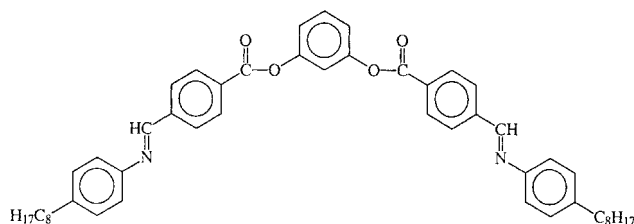
in these compounds were shown to be classical nematic and smectic A, by establishing continuous miscibilities with reference mesophases. Vorlander *et al.* [10] noted that bis[4-(4-methoxyphenylazo)phenyl] isophthalate and 1,3-phenylene bis[4-(4-ethoxyphenylazo) benzoates] are mesogenic, without specifying the phases. The thermal stabilities of these mesophases were shown to be distinctly lower than those of the corresponding 1,4-phenylene compounds. In the banana-shaped molecular system reported here, helical domains of both handedness are spontaneously formed in the smectic phase although the constituent molecules are achiral. The formation of the helical domains observed in banana-shaped molecular systems is unique in the sense that it occurs in a fluid system in which molecular interaction is weak and thermal fluctuation extensive.

It is worth noting that the mixing of chloro-substituted and non-chloro-substituted banana-shaped molecules results in the appearance of a wide miscibility gap and enlargement of the range of the SmX1 phase which can be seen in a lateral chloro-substituted compound. To examine the mesomorphic behaviour and the miscibility between two similar smectic phases, the materials used were two liquid crystals consisting of achiral banana-shaped molecules: 1,3-phenylene bis[4-(3-chloro-4-*n*-octyloxyphenyliminomethyl) benzoate] (PBCOB) and 1,3-

phenylene bis[4-(4-*n*-octylphenyliminomethyl) benzoate] (PBOB), with the following structures.



PBCOB



PBOB

Figure 1 shows the DSC thermogram for PBCOB. Three peaks are observed on heating, indicating the existence of two mesophases such as SmX1 and SmX2.

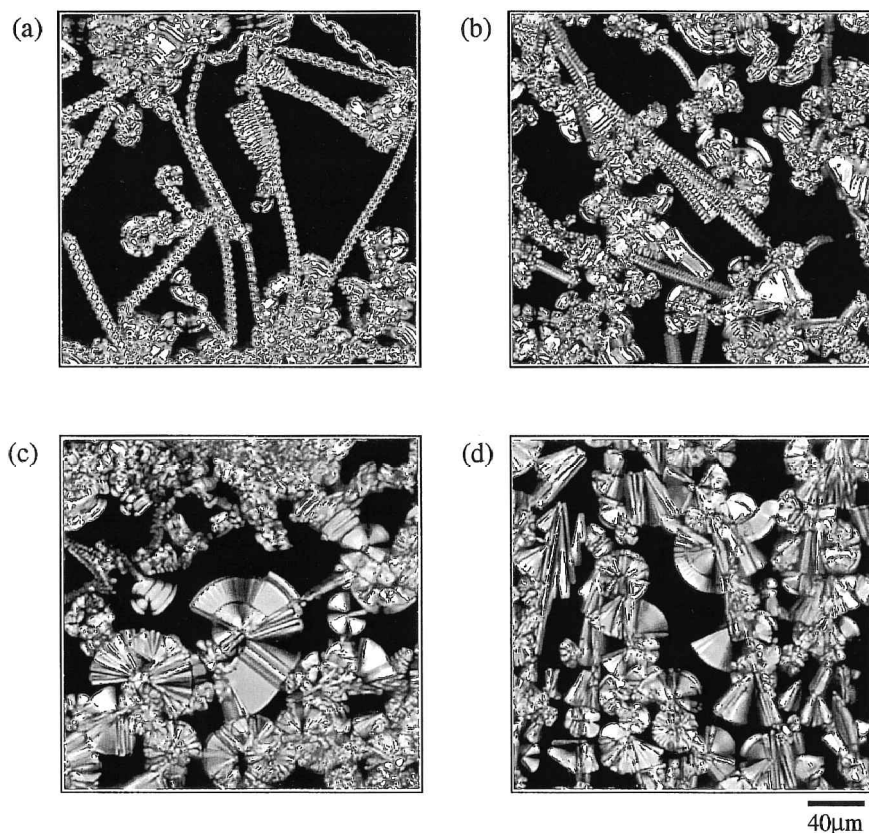


Figure 2. Optical micrographs in the SmX1 phase of pure PBCOB on cooling from the isotropic melt. (a) The SmX1 phase initially appears as double-twisted helices; they tend to transform into fan-shaped textures with a fringe pattern. (b–d) Simultaneously, the homeotropic domains begin to occupy the space between double-twisted helices.

On cooling, a supercooled phase appears from the isotropic phase to -4.8°C . The introduction of a lateral substituent results in the decrease of the smectic thermal stability \dagger [11]. The presence of a lateral chloro-substituent in the 3-position of the Schiff's base moiety prevents the regular stacking of molecules, and the melting and isotropic points are depressed.

Figure 2 shows optical micrographs of pure PBCOB, where the phase transition takes place from the isotropic to SmX1 phase. Upon cooling from isotropic melt, the SmX1 phase appears in several forms, such as double-twisted helices, filaments and fan-shaped textures. They tend to transform into fan-shaped textures with a fringe pattern showing a helical structure, although the system contains only achiral molecules. Figure 3(a) shows an

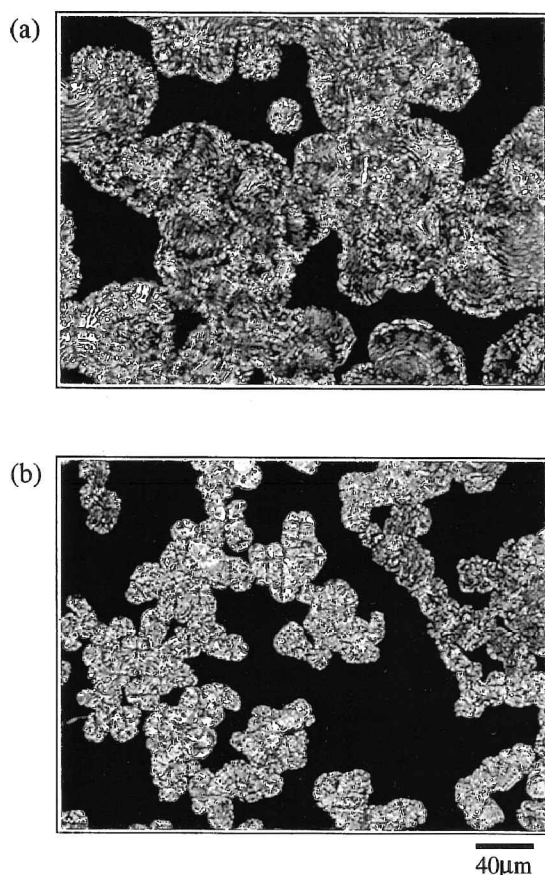


Figure 3. (a) Optical micrograph in the SmX1 phase of PBOB on cooling from the isotropic melt; the SmX1 initially appears as spherulitic domains with a fringe pattern. (b) Optical micrograph in the SmX1 phase of PBCOB with 50 wt % PBOB, showing mesomorphic domains.

\dagger Spectroscopic data: ^1H NMR (CDCl_3 , 200 MHz): $\delta = 0.6$ (6H, T), 1.0–1.9 (24H, m), 4.0–4.1 (4H, T), 6.9–7.5 (10H, m), 8.01–8.05 (4H, d), 8.2–8.3 (4H, d), 8.5 (2H, s).

optical micrograph of PBOB at the I–SmX1 phase transition, where the SmX1 phase appears as spherulites. Figure 3(b) shows the texture of the chloro-substituted compound PBCOB with added non-chloro-substituted compound PBOB (50:50 wt %) at the I–SmX1 phase transition. A different texture from that in pure PBCOB is seen in this mixture. The fan-shaped textures are no longer observable; new mesomorphic domains are observed, although their mesomorphic nature has not yet been confirmed.

Gray [12] concluded that the smectic phase would be affected more than the nematic phase by a lateral chloro-substituent, although the relative effects depend upon the nature of the molecule into which is it introduced. Moreover, banana-shaped molecules prepared from 1,3-phenylene compounds are immiscible among themselves and they have no or only limited miscibility with the phase consisting of rod-like molecules [6]. Thus, we investigated the mixing behaviour between chloro-substituted and non-chloro-substituted compounds to confirm the miscibility and thermal stability of 1,3-phenylene compound with a lateral chloro-substituent.

Figure 4 presents the phase diagram of a binary system composed of the lateral chloro-substituted compound PBCOB and the non-chloro-substituted compound PBOB. In the SmX1 and SmX2 phases, the miscibility gap between the two smectic phases changes according to the weight fraction of the two compounds. In comparison with PBOB, the isotropic points are lowered by the chloro-substituent introduced into the 3-position

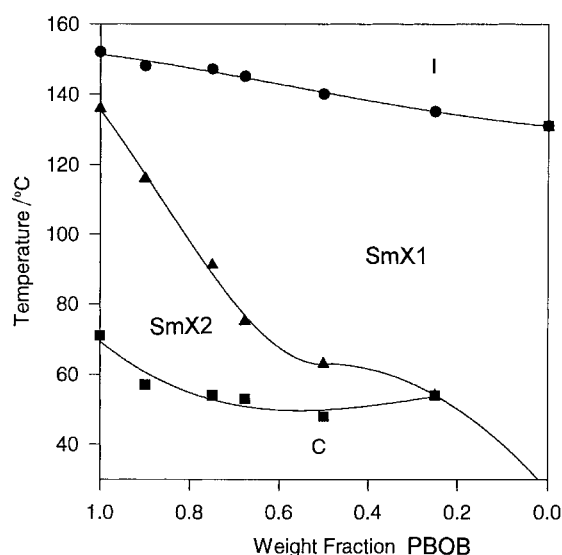


Figure 4. Phase diagram for the binary system PBCOB/PBOB. The transition temperatures are based on DSC cooling data.

of the Schiff's base moiety. Therefore, the effect of steric hindrance appears to outweigh the increased polarization and polarity induced by the lateral substituent. The transition temperatures of the SmX1 and SmX2 phases were confirmed by microscopic observation of the phase changes superimposed on fan-shaped textures.

To obtain 1,3-phenylene bis[4-(3-chloro-4-*n*-octyloxyphenylimino-methyl) benzoate], 3-chloro-4-*n*-octyloxyaniline was first prepared by reaction between 3-chloro-4-*n*-nitrophenol and 1-bromo-octane, followed by hydrogenation with H₂ gas in the presence of palladium on activated carbon [13]. 1,3-phenylene bis(4-formyl benzoate) was then prepared by esterification of resorcinol and 4-carboxybenzaldehyde. This reaction was performed in methylene chloride with dicyclohexylcarbodiimide and a catalytic amount of dimethylaminopyridine. 1,3-Phenylene bis[4-(3-chloro-4-*n*-octyloxyphenylimino-methyl) benzoate] [14] was finally obtained by condensation of 3-chloro-4-*n*-octyloxyaniline and 1,3-phenylene bis(4-formyl benzoate) in 2:1 molar ratio [15]. 1,3-Phenylene bis[4-(4-*n*-octylphenylimino-methyl) benzoate] was synthesized by a similar method.

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