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Effect of chemical structure on the liquid crystallinity of banana-shaped molecules

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Banana-shaped molecules having two side wings attached to a bent core may exhibit liquid crystallinity. The most studied material is 8-OPIMB that comprises 1,3-dihydroxybenzene as a central core, a Schiff's base moieties as the wing groups and octyloxy tail groups. To clarify the effect of chemical structure on the liquid crystallinity of such a molecule, we have prepared several banana-shaped molecules, with side wings and central cores different from those of 8-OPIMB and examined their liquid crystallinity, which is sensitive to change in chemical structure. Especially, changing the position of the carbonyl group of the ester function linking the central core to the wing and the position of the nitrogen atom in the Schiff's base moiety caused a loss of liquid crystallinity. On the other hand, smectic liquid crystallinity was maintained for five new types of banana-shaped molecule with different central cores. Although all these smectic phases have liquid-like association of the molecules within the smectic layers, they showed unconventional smectic textures through the separation of spiral, fractal and germ textures from the isotropic melt. Moreover, a frustrated smectic phase and chiral smectic phases were found. Several possible smectic structures for those phases will be discussed.

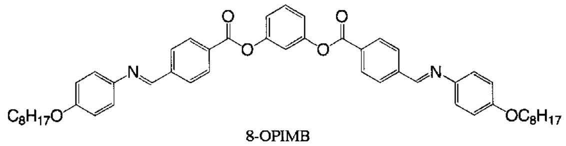
1. Introduction

Since chemical structure has been understood to have a most significant effect on the mesophases formed by a liquid crystal material, it has become clear what type of molecule should be able to form a mesophase. Obviously, a molecule which possesses a linear structure seems to have an advantage in the formation of mesophases. Moreover, flexibility is also likely to have an important effect on the packing of the molecules. However, recently many new materials with non-linear structures have been found to exhibit mesophases. Vorländer was in fact the first to discover a mesogenic compound of non-linear molecular structure, and the mesophase of this was reported by Demus [1, 2]. Later, interesting examples of unconventional molecular structure which can form mesophases were studied and reported, and of these the banana-shaped molecule is the most typical. Such a compound was first synthesized by Matsunaga and co-workers [3–5], and mesophases were clearly identified, even though the molecules have a critical bend at the centre.

Through the study of main chain liquid crystalline polymers, Watanabe *et al.* first proposed that molecules with a bent conformation may form liquid crystalline phases with unusual properties [6–10], and found that banana-shaped molecules may form ferroelectric and antiferroelectric liquid crystals [11–16]. In addition, these achiral materials can form chiral mesophases [17–20]. This very important discovery of ferroelectricity and chirality has attracted many research groups in the chemical and physical fields to study such kinds of banana-shaped molecule [21, 22].

The most common banana-shaped molecule, 1,3-phenylene bis[4-(4-octyloxyphenyliminomethyl)benzoate (8-OPIMB), is shown in scheme 1.

As with 8-OPIMB, most banana-shaped molecules studied basically have a bent central core which is linked with linear side wings via some linkage group [23–25]. According to this criterion, banana-shaped molecules can be prepared in many different ways. In order to further understanding of the relationship between chemical structure and liquid crystalline properties in such



8-OPIMB

$$B_4 \xleftarrow{139.7} B_3 \xleftarrow{151.9} B_2 \xleftarrow{173.9} \mathrm{Iso}$$

Scheme 1.

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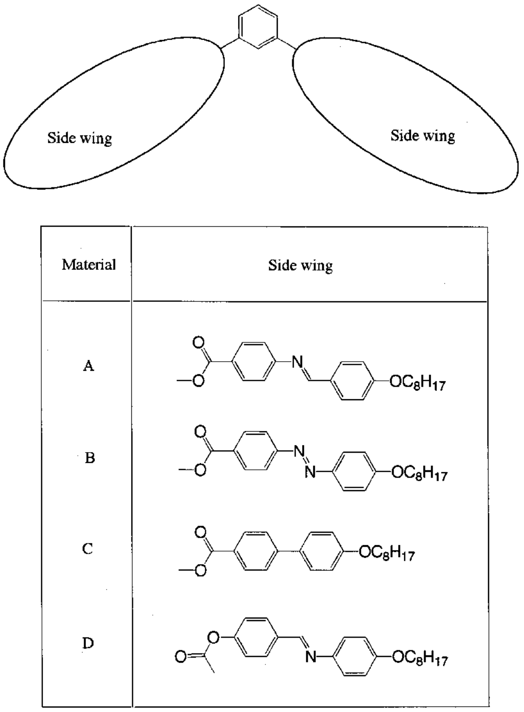
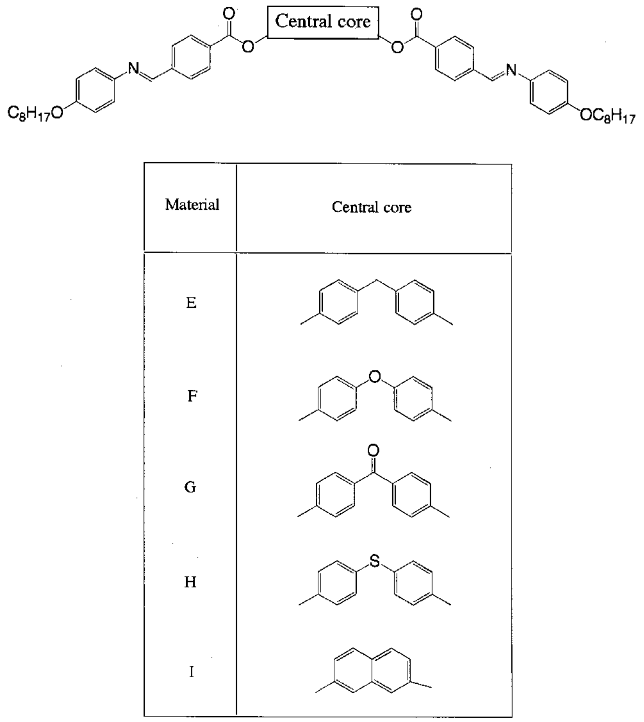
systems, we synthesized nine compounds, A–I, as shown in schemes 2 and 3, and examined their mesomorphic properties in comparison with 8-OPIMB.



Scheme 2.



Scheme 3.

2. Experimental

Synthesis of the materials has been reported elsewhere [19, 26].

The optical microscopic textures of the materials were examined using a polarizing microscope (Olympus, BX50) equipped with a hot stage (Mettler Toledo FP 90 HT). DSC thermograms were obtained using a Perkin Elmer DSC-II differential scanning calorimeter. X-ray diffraction measurements were made using a Rigaku-R-AXIS (CuK$_\alpha$, 40 kV, 100 mA) and circular dichroism data were obtained using a JASCO, J-720WI circular dichroic spectrometer.

3. Results

In 8-OPIMB, the central group is based on a 1,3-dihydroxybenzene unit having two wings composed of a Schiff's based moiety. Among the materials prepared here, A, B and C have different structures for the side wings from that of 8-OPIMB (see scheme 2). In A, a similar Schiff's base moiety is used but the position of the nitrogen atom is switched. In B and C, the Schiff's base moiety in the side wings is replaced by azobenzene and biphenyl groups, respectively. In D, only the orientation of the ester linkage connecting the central groups with the two side wings is different from 8-OPIMB (scheme 2). For compounds E, F, G, and H, the central bent core group is changed to *p*-disubstituted phenylene rings linked via small groups or atoms while the side wings remain the same as in 8-OPIMB (see scheme 3). In I, 2,7-dihydroxynaphthalene is used as the central group (scheme 3).

Thermodynamic data for the materials with altered wings, A, B, C and D, are summarized in table 1. Figure 1 compares the transition temperatures and phase behaviour of these compounds with those of 8-OPIMB. It can be seen that none of them exhibits a mesophase; only crystal phases were observed. From a comparison of 8-OPIMB and compound A, it is clear that the position of the nitrogen in the Schiff's base moiety plays an important role in the mesomorphic behaviour for such a system of molecules. Pelzl *et al.* have also observed this result for compound A [27]. From computer calculations, the number of conformations is significantly

Table 1. Transition temperatures and enthalpies for compounds A, B, C and D.

Compound	Transition temperature/°C (enthalpy, kJ mol^{-1})
A	Cr 143.3 (13.3) I
B	Cr 116.2 (10.4) I
C	Cr 92.6 (26.3) I
D	Cr$_1$ 122.3 (3.19) Cr$_2$ 217.4 (19.9) I

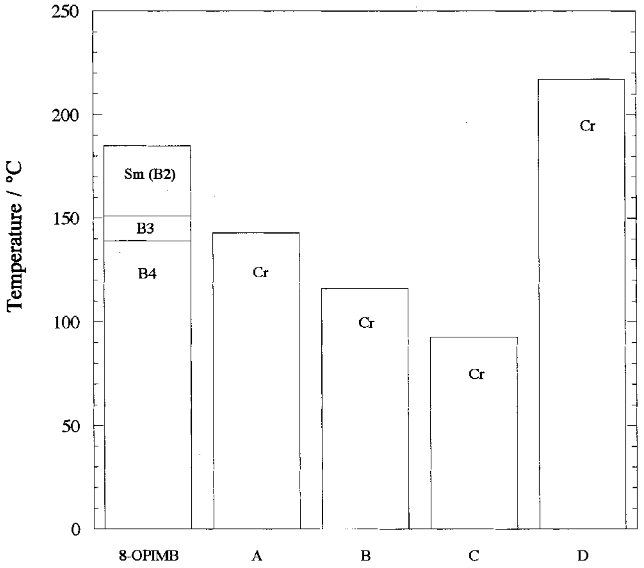


Figure 1. Comparison of phase transition temperatures for 8-OPIMB and compounds A, B, C and D. The data are based on DSC cooling curves.

increased when the position of the nitrogen atom in the Schiff's base is reversed, so causing a loss of colinearity of the side wings and decreased transition temperatures [28]. According to the previous report by Matsunaga [5], however, other homologues of compound A can form liquid crystals, for example when the number of carbon atom in the alkyloxy chains is 1, 2, 3, 4 and 5. For compound B, lost ability to form a liquid crystal phase may be due to the same reason as for compound A. Vorländer observed mesophases in a material similar to compound B, but with the C–O bond reversed [29]. For compound C, the side wing may be reasoned to be too short to form mesophases. In compound D where the position of the carbonyl group of the ester is switched, two crystal phases are formed. It is interesting that in this compound the isotropization point (Cr–I) is appreciably increased in comparison with the clearing point of the smectic phase of 8-OPIMB. Thus, the reversal of the position of the C–O bond of the ester group tends to stabilize the crystal phase.

We will now examine the effect of the central group on the mesomorphic behaviour in the compounds E, F, G, H and I. All of these materials, like 8-OPIMB, exhibit smectic mesophases. Table 2 summarizes the thermodynamic data for these compounds and figure 2 compares their smectic transition temperatures.

Compound E has a liquid crystal phase in the temperature range from 182 to 238°C. From the isotropic melt, spherulitic domains appear and coalesce to fan-shaped domains characteristic of smectic liquid crystals, see figure 3(*a*). X-ray data for this material support a conventional smectic layer structure with layer spacings of 46.9 and 23.5 Å. Moreover, an outer broad reflection with a spacing of about 4.5 Å indicates a liquid-like association within the smectic layers.

Table 2. Transition temperatures and enthalpies for compounds E, F, G, H and I.

Compound	Transition temperature/°C (enthalpy, kJ mol^{-1})
E	Cr 182 (8.7) Sm 238 (6.1) I
F	Cr$_1$ 211 (3.3) Cr$_2$ 216 (10.6) Sm 247 (4.7) I
G	Cr$_1$ 239 (14.5) Cr$_2$ 249 (15.1) Sm 264 (10.3) I
H	Cr 221 (12.1) Sm 229 (5.1) I
I	Smblue (B$_4$) & Cr 205 (14.6) Sm 232 (8.3) I

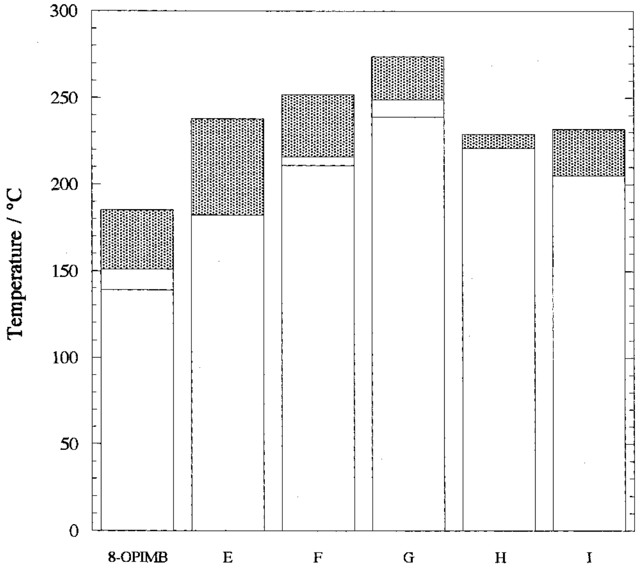
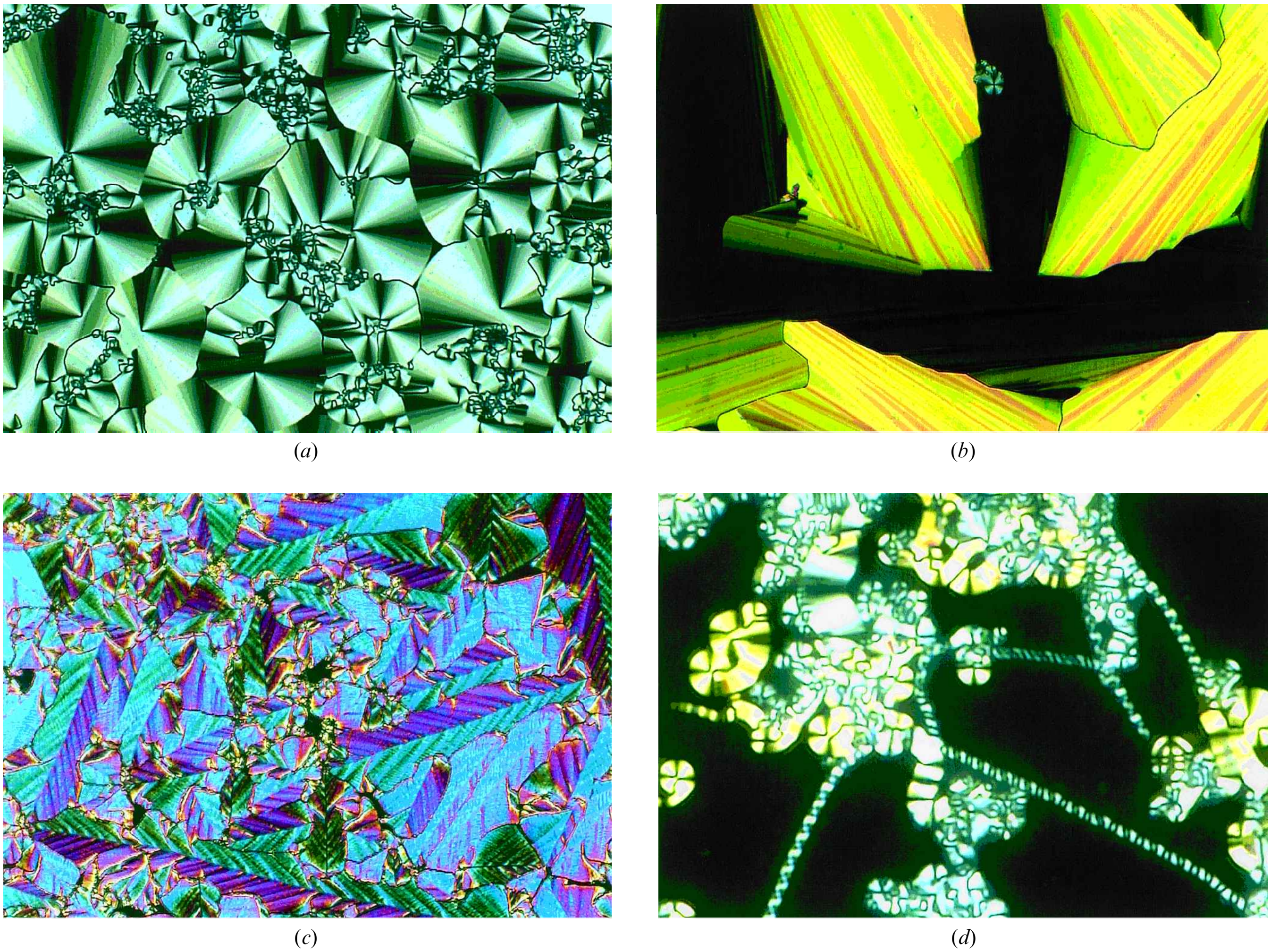


Figure 2. Comparison of the highest temperature smectic phase ranges (hatched regions) for 8-OPIMB and compounds E, F, G, H and I. The data are based on DSC cooling curves.

Compound F exhibited a smectic phase in a narrower temperature range than compound E and formed rather large fan texture domains as shown in figure 3(*b*) as a result of association of large bâtonnets. The smectic phase was also confirmed by the X-ray observation of inner reflections of 47.3, 31.5 and 23.9 Å and an outer broad reflection of 4.5 Å. The 31.5 Å reflection cannot be assigned to a (0 0 *l*) layer reflection and suggests frustration in the smectic layer. This frustrated smectic structure, however, seems to have a different structure from those observed in our previous reports [7–9, 14, 16].

Compound G exhibits a somewhat higher melting temperature than the other materials. This may be caused by an increase in the polarity of the molecule by the central carbonyl group. If the cooling rate is slower than 1°C min^{-1}, herring bone-striped domains can be


(*a*) (*b*)

(*c*) (*d*)

Figure 3. Photomicrographs of the textures of the smectic phases using crossed polarizers: (*a*) compound E, (*b*) compound F, (*c*) compound G, and (*d*) compound H.

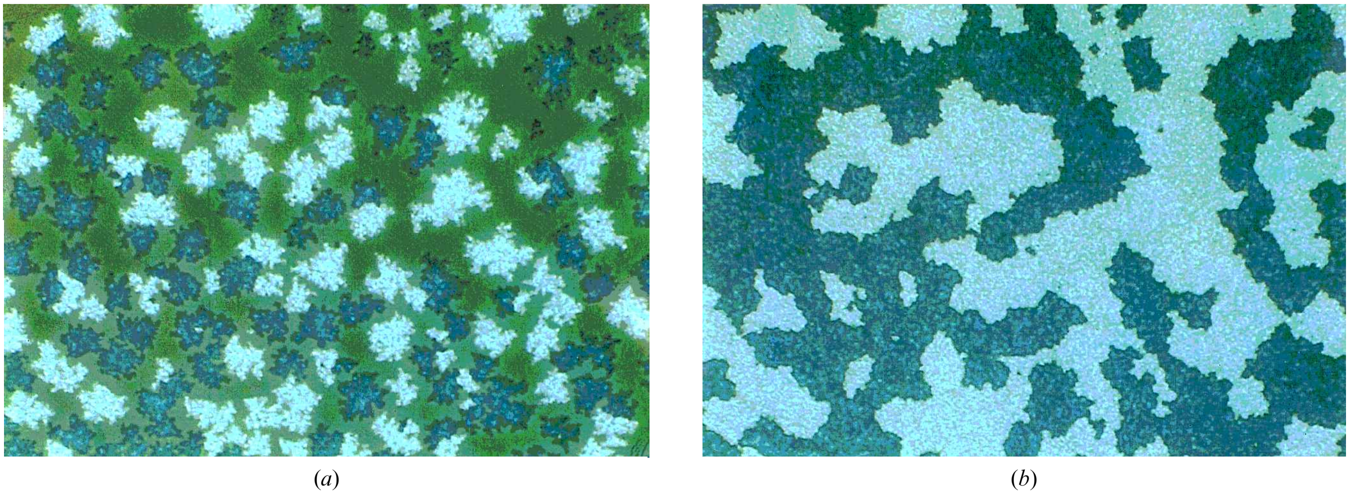

(*a*) (*b*)

Figure 4. Photomicrographs of the texture of the smectic phase of compound I. (*a*) Formation of many fractal smectic domains in the isotropic melt on cooling; (*b*) unidentified texture formed by coalescence of the fractal domains. The photographs were taken with the polarizer and analyser slightly uncrossed to distinguish the two domains with different optical rotation.

observed at the isotropic to smectic transition temperature followed by their association into large domains, suggesting a helical structure in the phase, figure 3 (*c*). Moreover, the texture occasionally exhibited the coexistence of schlieren and fan-like textures depending on sample preparation. X-ray data for this material supported a conventional smectic layer structure with layer spacings of 42.6 and 21.6 Å as observed in compound E. It should also be noted that a relatively large enthalpy was observed at the transition which might be caused by the large polarity of the carbonyl group at the centre of the molecule.

Compound H shows an extraordinary texture. When the isotropic liquid is cooled, the smectic phase nucleates as elongated particles with a clear spiral and double-spiral character as reported by Weissflog *et al.* [30], figure 3 (*d*). We found roughly an equal number of right- and left-handed helices. These finally coalesced to form fan-like or circular domains. Occasionally, in these domains, a fringe pattern can be observed as reported in the smectic phase of 8-OPIMB [18]. The X-ray pattern for this phase is characteristic of a smectic phase with liquid-like association within the smectic layers. The spacings of the inner reflections are 44.7 and 22.6 Å. The smectic phase existed in a very narrow temperature range, and crystallized on further cooling.

Compound I, having a central naphthalene group, exhibited an unconventional smectic texture initiated by the growth of small-fractal domains that finally coalesced into several large domains [19]. The texture is shown in figures 4 (*a*) and 4 (*b*). Rotation of the analyser or polarizer makes it clear that there are two regions which exhibit the opposite sign of optical rotation. Also, each of these regions shows a remarkably large circular dichroism (CD) of opposite sign, indicating a helicoidal structure [19]. On further cooling (10°C min^{-1}), at 205°C a transparent phase with a blue colour, named by us Smblue phase (corresponding to the B_4 phase in 8-OPIMB) was observed with no change of texture and birefringence; this was accompanied by the growth of crystals in some regions of the texture. On the other hand, crystallization did not occur and only the Smblue phase was observed if the cooling rate was 20°C min^{-1} or faster. The higher temperature smectic phase shows layer reflections of 40.9 and 19.4 Å which can be indexed to a series of $(0\,0\,l)$ layer reflections, while relatively large spacings 48.7, 24.2 and 16.4 Å were observed for the Smblue phase. A diffuse scattering in the wide angle region at about 4.5 Å was observed in the higher temperature smectic phase, but it intensified in the Smblue phase, indicating the highly ordered nature of this phase.

4. Discussion

By changing the side wings, central cores and the linkage groups, we have prepared nine banana-shaped molecules and examined the effect of chemical structure on the liquid crystal mesophases. Unfortunately, only five molecules, E–I, prepared by changing the central core, can form smectic liquid crystal phases. Among these, the central core of compounds, E, F, G and H, is based on *p*-disubstituted phenylene rings (Ph) linked via atoms or small groups with the form Ph–X–Ph. The bond linkage between Ph and X can allow somewhat free rotation, although in the conformation with the lowest energy, the twist angles of the phenyls are 30° to 50° when $X = $ –O–, –CO– and –S–, and 90° for $X = -\mathrm{CH}_2-$ [31]; therefore several conformations are allowed in the liquid crystalline region. In this aspect, these central cores are essentially different from those based on 1,3-dihydroxybenzene in 8-OPIMB and 2,7-dihydroxynaphthalene in compound I. All these central cores must surely result in bent molecules and so the packing freedom would be confined in the smectic phase.

It is interesting that the textures exhibited by the highest temperature smectic phases appearing from the isotropic melt vary significantly from sample to sample. For E and F, spherulites and bâtonnets appear, while herringbone-striped domains and spiral entities appear and coalesce to form some kinds of spherical domain in G and H. Compound I shows unconventional fractal domains. We thus have to consider the possibility of various types of smectic liquid crystal. At first, it should be stated that all these smectic phases show similar X-ray patterns which include an inner sharp reflection and an outer broad reflection. Thus, the X-ray patterns indicate that all of these compounds form smectic phases which are liquid-like within the smectic layers, similarly to conventional smectic A and C phases. The smectic layer thickness sometimes reflects the chain conformation and its association into the layer. On this point, it is notable that the smectic layer spacing for all the materials is considerably reduced in comparison with that for the crystalline phase (table 3). A similar reduction has also been observed for banana-shaped molecular systems with 1,3-dihydroxybenzene as the central core and initially explained by a change in conformation [18]. However, according to Link *et al.* [21], the effect should be attributed to tilting of the molecules relative to the layer normal. Link *et al.* observed antiferroelectricity in freely suspended films and thin homogeneous cells in the smectic phase of 8-OPIMB. They showed that the molecules tilt with respect to the layer normal, that the direction of the polarization alternates from layer to layer, and that there are two types of domain, homogeneously chiral and racemic domains. The tilt direction in the homogeneous domains is anticlinic, and in the racemic domains the tilt direction is synclinic in the ground state. The tilt angle was determined to be 34° [20, 21]. It is interesting that this value agrees with that

Table 3. Layer spacings of the smectic and crystal phases for compounds 8-OPIMB, E, F, G, H and I.

Compound	Layer spacing/Å
8-OPIMB	B_2: 38.3 18.9 B_3: 44.1 22.1 Smblue (B_4): 46.5 22.2 14.8
E	Sm: 46.9 23.5 Cr: 50.5 26.3 17.3
F	Sm: 47.3 31.5 23.9 Cr: 52.4 26.4 17.6
G	Sm: 42.6 21.6 Cr: 51.2 26.6 17.6
H	Sm: 44.7 22.6 Cr: 52.9 26.1 17.3
I	Sm: 40.9 19.4 Smblue (B_4): 48.7 24.4 16.4

evaluated from the layer spacings on the assumption that the molecular length is the same in both situations and its axis in the crystal is perpendicular to the layer [20]. In the present systems, the tilt angles were approximately calculated making the same assumptions. In compounds E and F, the tilt angle is around 25°, while in compounds G, H and I, it is considerably larger, around 35°, similar to that in 8-OPIMB.

All these molecules have a banana-shape so that they should be packed with a polar C_{2v} or C_2 symmetry in the smectic layer. Hence, the smectic phase should be ferroelectric and antiferroelectric as initially reported for the smectic phase of 8-OPIMB by Watanabe *et al.* [7, 10, 11]. Relevant measurements were attempted to clarify this point, but unfortunately none gave a satisfactory result since the high temperature nature of the phases interfered with precise measurements.

Chirality in the smectic phases of banana-shaped molecules is another topic, and this was also proposed by Watanabe *et al.* [17, 18]. The observation of fringe patterns in the highest temperature smectic phases was originally explained in terms of a helical structure along the layer normal as in the chiral SmC phase. Link *et al.* [21], however, later suggested that such a fringe pattern may be due to the alternation of racemic domains with domains of opposite tilt sense. Furthermore, chirality is also observed here in the lowest temperature phase (Smblue phase). Strong circular dichroism indicates the existence of left- and right-handed helices. Several reasons can be considered for the origin of the helicity in the present achiral system. Twist conformations [18, 32], tilting of molecules [21, 22] and escape from the spontaneous polarization [14, 33] are all possibilities that should be taken into account to explain the origin of the helix in achiral systems. In this series, compounds G, H and I all show fringe patterns and a strong tendency to form a helix and/or chiral domains as described above. It should be noted that these compounds exhibit a large tilt angle of about 35°. It is therefore assumed that the large tilt angle is important for the formation of these chiral phases.

5. Conclusion

We have prepared two series of banana-shaped molecules. In the first series, the chemical structure of the two side wings was altered while in the second series the bent core was modified. None of the materials in the first series forms mesophases, while all the materials in the second series have smectic liquid crystal phases. Compounds E and F show typical fan textures similar to those found in SmA and SmC, but from X-ray data a frustrated structure of the smectic phase was detected in compound F. In Compounds G and H, the separation of herringbone-striped and spiral textures was observed on cooling the isotropic melts. Occasionally, the materials exhibited fringe patterns. In compound I, the small fractal domains formed on cooling the isotropic melt gradually coalesced to form large domains. These textures may suggest the formation of a helix or a highly ordered structure in these smectic phases. Furthermore, in the texture of compound I, two different domains of distinct right- and left-handed helicity were distinguished by microscopy and found to have opposite signs of the circular dichroism [19]. These results suggest miscellaneous types of smectic phase in these compounds. X-ray diffraction however showed that all the materials had a typical layer structure with liquid-like association within each layer. Again tilting of the molecules with respect to the layer normal in the smectic phases must be taken into account and might invoke the formation of chiral and/or helical domains, especially when the tilt angle is ~35°. It is clear that these bent-shape molecules are very sensitive to change in chemical structure in relation to 8-OPIMB. The reversal of the position of the C–O group of the ester bond linking the wings to the central core and the position of the nitrogen atom in the Schiff's base moiety in the first series caused the loss of liquid crystallinity, but the smectic mesophase is preserved on using various types of bent-core groups in the second series. We are now proceeding with a study of the structures and properties of mesophases in each homologous series of compounds E–I with various tail lengths.

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