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Distinct Formation of a Chiral Smectic Phase in Achiral Banana-Shaped Molecules with a Central Core Based on a 2,7-Dihydroxynaphthalene Unit

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Abstract: We have prepared a novel series of banana-shaped molecules with a central bent core based on a 2,7-dihydroxynaphthalene group, the side wings containing a Schiff's based moiety, and alkoxy flexible tails with carbon numbers $n = 6$, 8, 10, 12, 14, and 16. Among these, the molecules with $n = 8-16$ formed a novel smectic phase. Its smectic layer possessed a liquidlike association of the molecules similar to the SmA or SmC phase, although the texture that developed from the isotropic melt was unconventional. Small fractal domains initially grew and then coalesced into several large domains. Very weak birefringence and fine structure without any anisotropy are characteristic of this phase. It is interesting to note that two different domains exist showing the opposite sign of optical rotation. Strong circular dichroism (CD) with a peak at 430 nm was also observed for each domain with the opposite sign. The results suggest a natural occurrence of the helix in these materials. The right-handed and left-handed helices were formed with equal probabilities, but the left-handed helix was selectively formed by the introduction of a chiral dopant. The molecule with $n = 6$ formed a frustrated smectic phase, which exhibited a simple fan-shaped texture.

Introduction

Bent-shaped molecules have been generating much interest in the field of liquid crystals since Watanabe et al.[1−6] first found ferroelectricity, helicity, and frustration in several B phases in the homologous series of bent molecules, P-*n*-O-PIMB. The nomenclature "B phase" was used after discussion at the "Banana-Shaped Liquid Crystals" workshop.[7] At the beginning, from an optical microscope observation of the characteristic fringe pattern, Watanabe et al.[8] described the B_2 phase (SmAb phase[9]) as a helical structure with the helical axis lying perpendicular to the smectic layer similar to the chiral S_C phase. The ferroelectric properties were also similar. Later, the structure of the B_2 phase was investigated by many research groups because of its exclusive behavior.[10] Link et al.[11] demonstrated the polar chiral structure of the B_2 phase by using the freely suspended films and thin homogeneous cells. Moreover, antiferroelectricity of the B_2 phase was found in their study. Finally, the B_2 phase was found to be an antiferroelectric phase by much appropriate evidence.[12−16]

In addition to the B_2 phase, the compounds of the P-*n*-O-PIMB series also exhibited lower temperature smectic phases, the so-called Hexb and Smblue phases. They were subsequently designated B_3 and B_4 phases, respectively. Interestingly, the lowest temperature smectic phase (B_4) showed an unidentified texture.[8,17] It seems to possess a glassy state characteristic and shows a transparent blue color. Such a color may be due to a helical structure with the helical axis lying parallel to the smectic layer as in the twisted grain boundary (TGB) phase.[17,18] This helical structure may possibly be formed from a spontaneous breaking of the mirror symmetry in this bent shape molecule. However, there is yet no evidence to clarify the structure of the B_4 phase. Thus, the helicity and chirality in achiral bent shape molecules have been the topic of much interest in the liquid crystal field.

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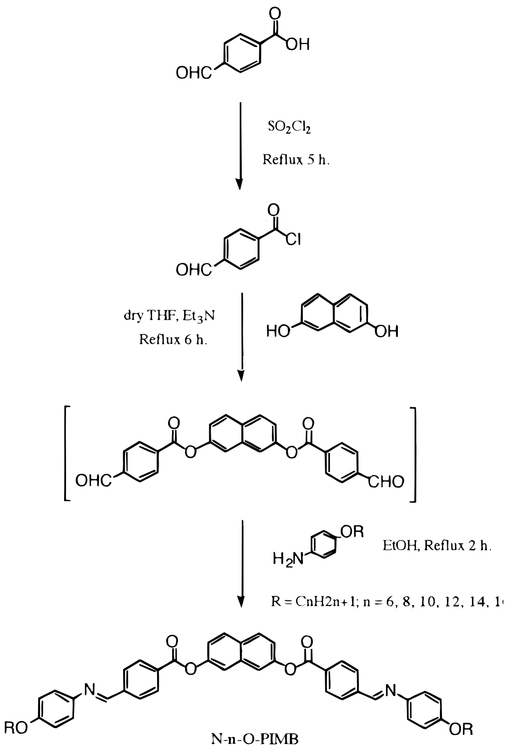
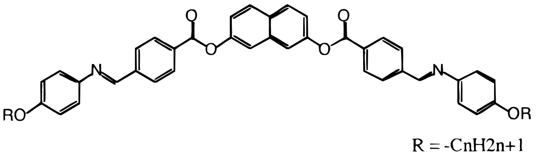
Scheme 1



This prompted us to extensively investigate other types of banana-shaped molecular systems with different mesogenic cores as shown below. These materials named 2,7-naphthalene bis[4-(4-*n*-alkoxyphenyliminomethyl) benzoate] (N-*n*-O-PIMB), have a central core based on the naphthalene group, the side wings containing a Schiff's based moiety, and alkoxyl flexible tails with carbon numbers $n = 6, 8, 10, 12, 14$, and 16. It is interesting that the molecules with $n = 8-16$ possessed high-temperature smectic phases with an extraordinary texture, as well as a low-temperature smectic phase.[19] In this report, we demonstrate the appearance of a helical structure in the smectic phases by means of optical microscope and circular dichroism measurements.



N-*n*-O-PIMB

Experimental Section

The synthesis of the materials used is shown in Scheme 1. 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 thermogram data were obtained using a Perkin-Elmer DSC-II differential scanning calorimeter. X-ray diffraction measurements were performed using a Rigaku-Rint-2000 diffractometer with Cu Kα radiation. Circular dichroism (CD) and optical rotation (ORD) were observed using a JASCO J-720WI spectrometer.

Results and Discussion

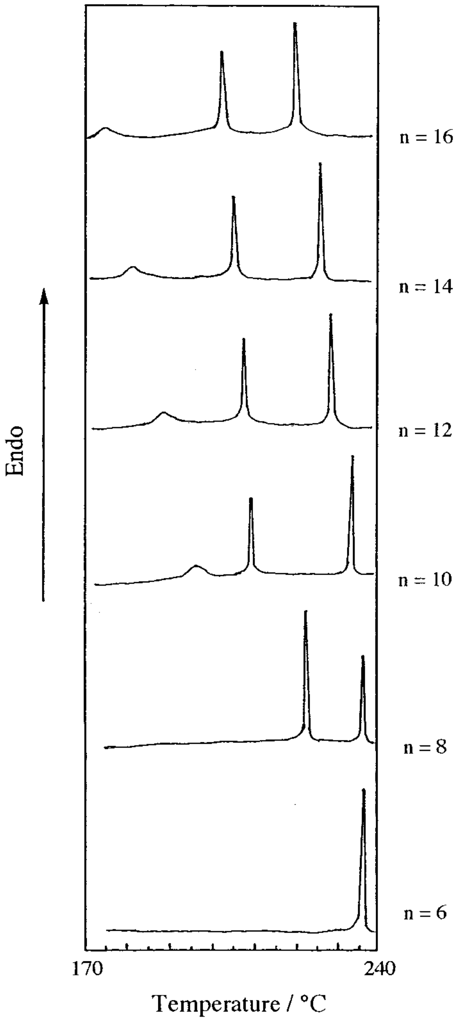


Figure 1. Heating DSC thermograms of the homologous N-*n*-O-PIMB compounds.

Table 1. Transition Temperatures and Enthalpies for the N-*n*-O-PIMB Series

n	transition temperature °C (enthalpy, kJ/mol)
6	Cr 237 (12.6) I[a]
8	Sm3 + Cr 222 (10.2) Sm1 237 (5.3) I
10	Sm3 197 (1.4) Sm2 209 (5.1) Sm1 234 (5.1) I
12	Sm3 187 (1.3) Sm2 207 (5.0) Sm1 229 (4.3) I
14	Sm3 179 (1.6) Sm2 204 (5.1) Sm1 225 (4.0) I
16	Sm3 172 (0.7) Sm2 201 (6.5) Sm1 220 (4.9) I

[a] Cr 219 (7.9) $Sm1_f$ 232 (3.6) I: On cooling.

Thermotropic Behavior of N-*n*-O-PIMB. DSC thermograms are shown in Figure 1. Thermodynamic data of the homologous compounds are summarized in Table 1. As shown in Table 1, four smectic phases, Sm1, $Sm1_f$, Sm2, and Sm3 are established. Well-defined crystallization takes place for only N-6-O-PIMB. N-8-O-PIMB exhibits a crystalline phase on slow cooling (<10 °C/min). On the other hand, no crystalline phases could be attained for the other materials under any conditions nor N-8-O-PIMB when it was subjected to fast cooling. In these materials, hence, the lowest temperature phase is Sm3. Phase behavior is shown in Figure 2.

Structural Characteristics of the Sm1 and $Sm1_f$ Phases. Let us consider the highest temperature Sm1 phase (refer to Figure 2). This phase was observed for the N-*n*-O-PIMB series with $n = 8-16$. The X-ray patterns exhibited sharp inner reflections corresponding to the (*00l*) reflections and an outer broad reflection corresponding to a spacing of 4.5 Å. Thus, the X-ray pattern indicates a smectic layer structure similar to the

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Table 2. Layer Spacings for the N-*n*-O-PIMB Series

	N-6-O-PIMB			N-8-O-PIMB			N-10-O-PIMB			N-12-O-PIMB			N-14-O-PIMB			N-16-O-PIMB		
$Sm1_f$	34.8 (101)	22.0[a] (002)																
Sm1				40.0	19.8		42.2	20.6		44.8	22.3		47.3	23.2		54.1		
Sm2							47.3 (101)	32.9 (301)	27.2[c] (002)	53.2 (101)	34.9 (301)	29.2[d] (002)	55.9 (101)	36.0 (301)	31.0[e] (002)	58.3 (101)	37.9 (301)	32.9[f] (002)
Sm3				48.7	24.4	16.4	54.4	27.2	17.7	57.3	29.2	18.9	63.0	31.0	20.5	65.0	32.9	21.7
Cr	34.8 (101) 14.1 (202)	22.0 (002) 11.1[a] (004)	17.3 (103)	40.0 (101)	23.8 (002)	15.7[b] (103)												

[a–f] The indicies are based on the frustrated structures with the two-dimensional lattices: (*a*) $a = 59$ Å, $c = 45$ Å; (*b*) $a = 71$ Å, $c = 47$ Å; (*c*) $a = 66$ Å, $c = 54$ Å; (*d*) $a = 67$ Å, $c = 58$ Å; (*e*) $a = 67$ Å, $c = 62$ Å; (*f*) $a = 71$ Å, $c = 66$ Å. For other reflections, they can be indexed into the 00*l* series.

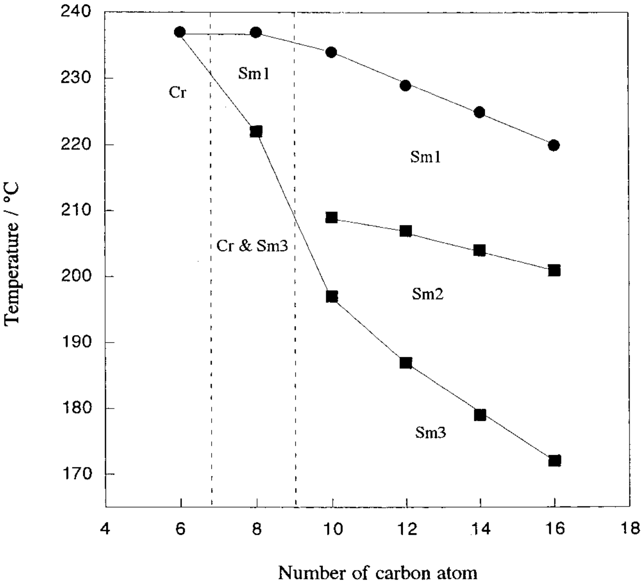

Figure 2. Phase behavior of the homologous compounds. The transition temperatures are based on heating DSC data. N-6-O-PIMB forms the $Sm1_f$ phase only on cooling (refer to Table 1).

SmA or SmC phases, which consist of a liquidlike association of bent molecules within a layer. The $Sm1_f$ phase was formed from N-6-O-PIMB only on cooling from the isotropic liquid (refer to Table 1). It is also composed of a liquidlike association of molecules within a layer, but has a frustrated structure with a layer undulation.[4,6] A two-dimensional lattice with $a = 59$ Å and $c = 45$ Å was established. The spacings of the inner reflections are listed in Table 2. It should be noted here that the similar diffraction profile has also been assigned to the columnar phase with two-dimensional rectangular lattice.[10]

The Sm1 phase shows an unconventional texture. As depicted in Figure 3, several small fractal nuclei[20] initially appear from the isotropic melt on cooling. They gradually associate into several large domains (Figure 3b,c). The texture of each domain exhibits a very weak birefringence and no anisotropy. It looks somewhat like a sandy or foggy texture with a fine structure. In contrast to the unusual texture of the Sm1 phase, the frustrated $Sm1_f$ merely displays a normal fan-shaped texture (see Figure 3d).

Interestingly, the neighboring domains of the Sm1 phase separated by a clear boundary show opposite optical rotations (see Figure 4a,b). This can be recognized by rotation of the polarizer or analyzer from the cross-polarization position. Transmittance of light from one domain is increased by a clockwise rotation of the analyzer (see Figure 4a), while from the other domain the transmittance is increased by a counterclockwise rotation (see Figure 4b). Using crossed polarizers, there is no way to distinguish the two domains, except for the fact that they are separated by a dark boundary (see Figure 3c). When the texture development was carefully observed by rotating the analyzer by 5° from the cross-polarization position, it was found that one fractal nucleus with a specific sign of optical rotation developed into a large domain with preservation of the sign of optical rotation. The coalescence of two domains with the same sign of optical rotation yielded no boundary, while the coalescence of domains with opposite signs gave a clear boundary (see Figure 3c). These results suggest the formation of a helix or chirality.

To confirm the occurrence of a helical or chiral domain, a circular dichroic (CD) measurement was carried out. Figure 5 shows the CD spectrum observed for the N-12-O-PIMB sample with several small domains. A small but clear CD peak was observed with a maximum peak around 430 nm. Since the absorption position of the material was in the wavelength region less than 360 nm, this peak is not due to an induced circular dichroism,[21] but from reflection of the circularly polarized light.[3] We note that the sign of the CD was altered from positive to negative, depending on the preparation of sample. For this reason, the CD spectra measurements were repeated after heating the sample into the isotropic liquid. After 20 runs, the average of the intensity became almost zero although the maximum wavelength scarcely changed as shown in Figure 6a. This indicates an equal occurrence of the right-handed and left-handed helices; the observed CD effect comes from an unbalanced formation of the two domains.

The size of the domains varied according to the preparation condition. It increased with a decrease in the cooling rate because the number of nuclei is decreased. Large domains with a size larger than 2 mm can be prepared by the gradual development of a few nuclei attained by very slow cooling from isotropic melt (less than 1 °C/min). Thus, we can focus the light on each domain. The result is shown in Figure 7. It is clearly seen that domains A and B showing opposite signs of optical rotation give large CD peaks with opposite signs of dichroic ratio. The CD intensity is comparable with those observed for the chiral SmC* and chiral nematic phases, indicating selective reflection of the circularly polarized light due to a certain helical structure.

Structural Characteristics of the Sm2 and Sm3 Phases. In the lower temperature region, two other phases, Sm2 and

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[20] In fact, the fractal dimension *D* of 1.8 was successfully determined with the box-counting technique (Harrison, A. *Fractals in Chemistry*; Oxford University Press: Oxford, 1995; p 16); Thisayukta, J.; Kawauchi, S.; Watanabe, J. To be submitted for publication.

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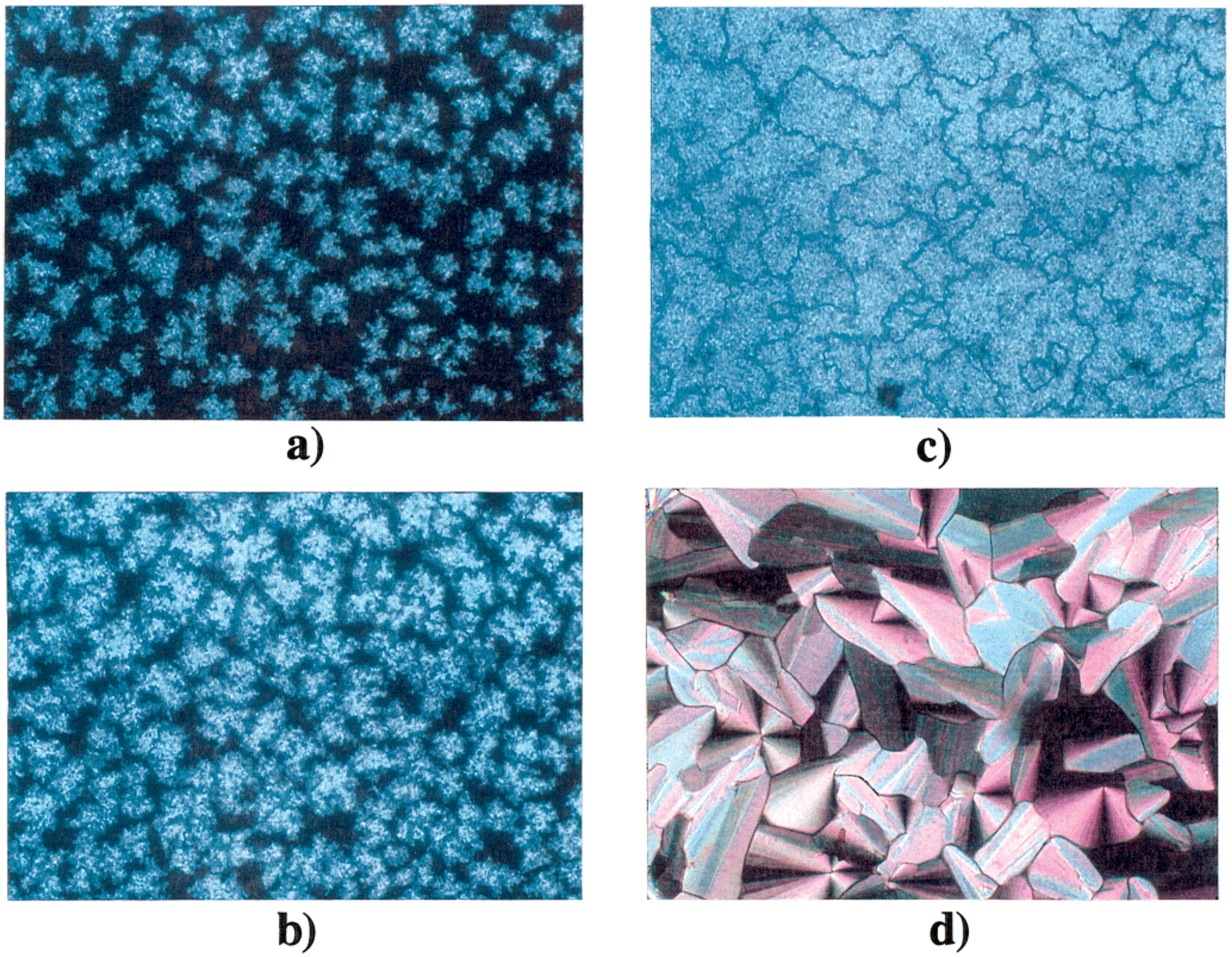


Figure 3. Photomicrographs of the textures observed for the highest temperature Sm1 phase of N-12-O-PIMB at 210 °C under crossed polarizers. Initially, the small fractal nuclei appear in (a), grow up with the similar shape in (b), and finally coalesce to the large fractal domain with clear boundary in (c). In a comparison, the typical fan texture observed for the $\mathrm{Sm1_f}$ phase of N-6-O-PIMB is shown in (d).

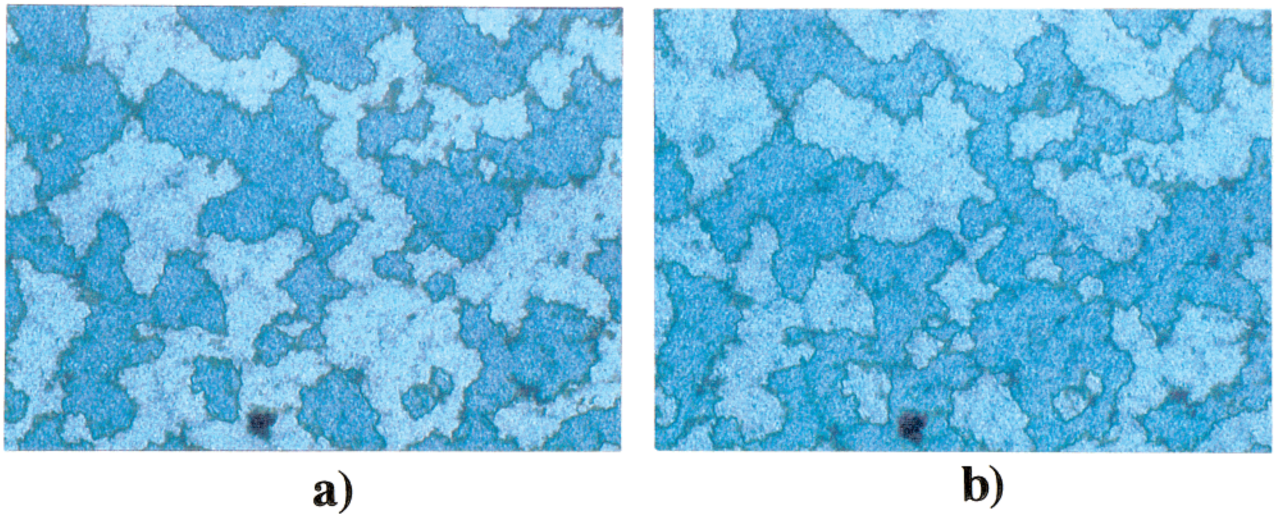


Figure 4. The texture of the Sm1 phase observed at the same position as in Figure 3c, but by the rotation of analyzer from the cross-polarization position. Two different domains with opposite sign of optical rotation can be detected by (a) the clockwise rotation and (b) counterclockwise rotation. The rotation angle is 5°.

Sm3, are observed (refer to Figure 2). These phases have a transparent blue color similar to the Smblue (B_4) phase in the P-*n*-O-PIMB series.[3] The DSC thermogram shows a clear transition from Sm1 to these phases, but the overall domain texture and fine texture inside the domains are not altered at all from those of the Sm1 phase. Only a slight blue shift of the color was observed. Similar CD spectra were also observed; the shape of the CD peak scarcely changes, but the peak

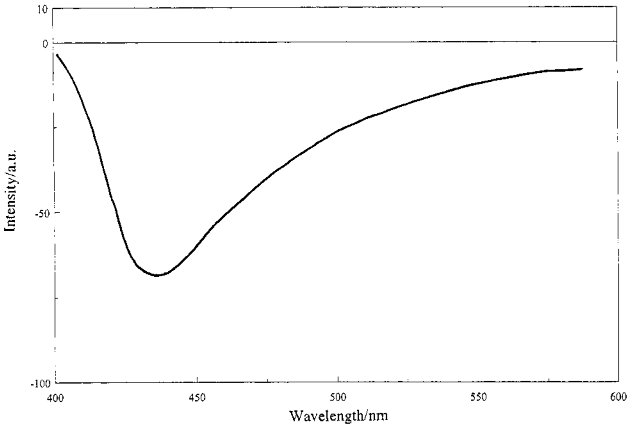


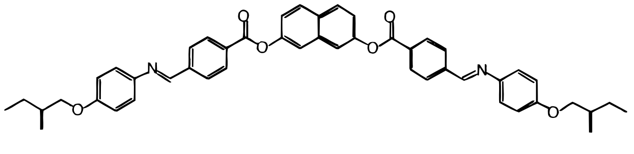
Figure 5. Typical CD spectrum observed in the Sm1 phase composed of the small fractal domains.

maximum was shifted slightly to the blue side. The maximum wavelength was around 400 and 420 nm for the Sm3 and Sm2 phases, respectively. Thus, a preservation of the macroscopic chiral structure is likely in these phases.

Three smectic phases, Sm1, Sm2, and Sm3 phases, can be clearly distinguished from the X-ray patterns. The X-ray diffraction data of these phases are summarized in Table 2. As mentioned above, the Sm1 phase shows a typical smectic layer structure with liquidlike association within the smectic layer, while in the Sm2 and Sm3 phases a few outer reflections appear, suggesting two-dimensional positional ordering within a layer. It is interesting that the layer spacing of the Sm3 phase is somewhat larger than that of the Sm1 phase. This suggests that the molecules in the Sm1 phase are appreciably tilted to the layer. Under the assumption that a similar conformation and molecular length are maintained in these phases, and that the molecules in the Sm2 and Sm3 phases lie perpendicular to the layer, a tilt angle of the molecules was elucidated as approximately 40°. According to this argument, no tilting of the molecules is observed in the frustrated Sm1$_f$ phase.

A difference in the X-ray patterns between the Sm2 and Sm3 phases was observed for the inner reflection profiles; the inner reflections of the Sm3 phase can be indexed to a series of *00l* reflections, but other *h0l* reflections are observed for the Sm2 phase, which can be explained by frustration of the layer.[4] The two-dimensional lattice data of the frustrated structure is given in Table 2. The small transition enthalpies between the Sm2 and Sm3 phases suggest a small change in their structures (refer to Figure 1 and Table 1).

Effect of Chiral Dopant. To further investigate the occurrence of helical domains, we synthesized the chiral N-4-O-PIMB2* with a terminal (S)-(+)-2-methylbutoxy group as shown below. This chiral compound, however, does not form



N-4-O-PIMB2*

a liquid crystal; the melting temperature of the crystal is 247 °C. Thus, we prepared blended samples of N-4-O-PIMB2* and N-12-O-PIMB with various weight fractions of chiral dopant from 0% to 30%. Figure 8 shows the optical microscopic textures of the Sm1 phase for these blended samples. We found that one of the two different chiral domains, the areas of which are A^+ and A^-, gradually decreases with an increase in the amount of the chiral dopant and the texture becomes composed of a single chiral domain for mixtures with 20−30% chiral content. This trend is clearly observed in Figure 9 where the relative difference between the two areas, $|A^+ - A^-|/|A^+ + A^-|$, is plotted against the chiral content. A similar trend can be detected from the CD measurement. Figure 6b shows a plot of the maximum intensity and wavelength of the CD spectra obtained by 20 observations of the mixture with a chiral content of 20%. It is clear that the intensity of the CD is fairly large and the sign becomes biased to the positive side. In contrast, the wavelength of the CD peak scarcely changes. Thus, we conclude that the chiral dopant does not affect the twisting power of the helix, or in other words, the helical twisting is due to the inherent nature of such banana-shaped molecules. The only effect of the chiral dopant is to dominate the helical sense. A similar effect of chiral dopants on circularly polarized scattered light was made in the B$_4$ phase of P-8-O-PIMB.[17]

Figure 10 shows the typical CD and ORD spectra observed for a single chiral domain of the blended sample with a 20%

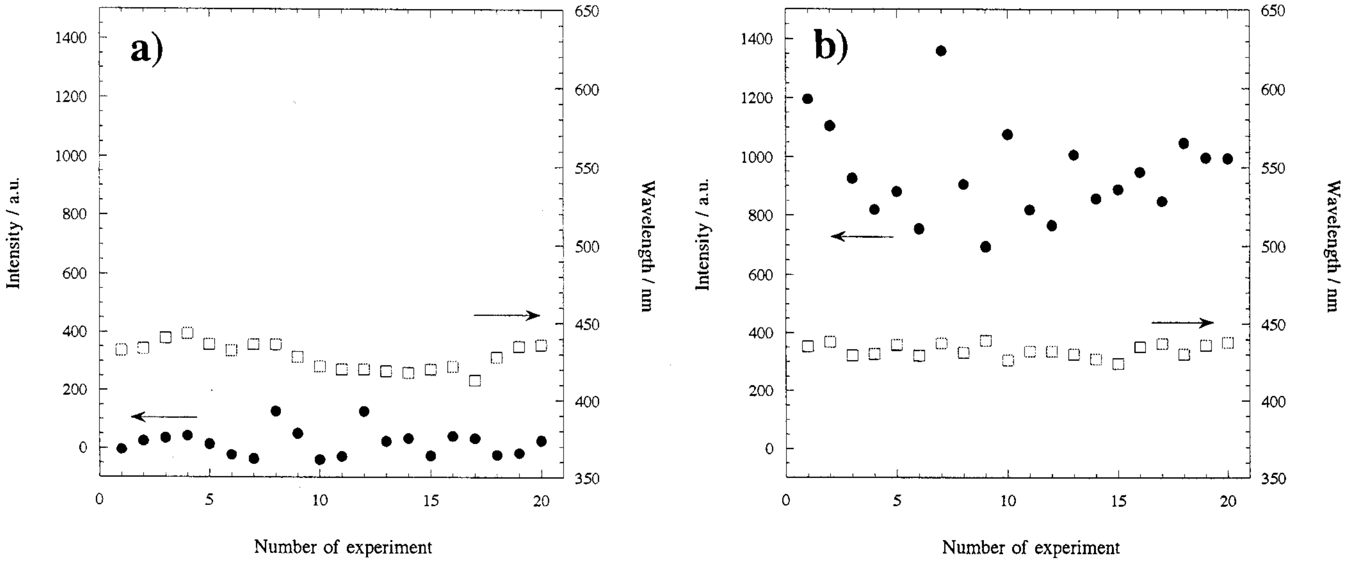


Figure 6. Peak wavelength and intensity of CD collected for the Sm1 phase by 20 runs: (a) pure N-12-O-PIMB and (b) N-12-O-PIMB containing 20% chiral N-4-O-PIMB2*.

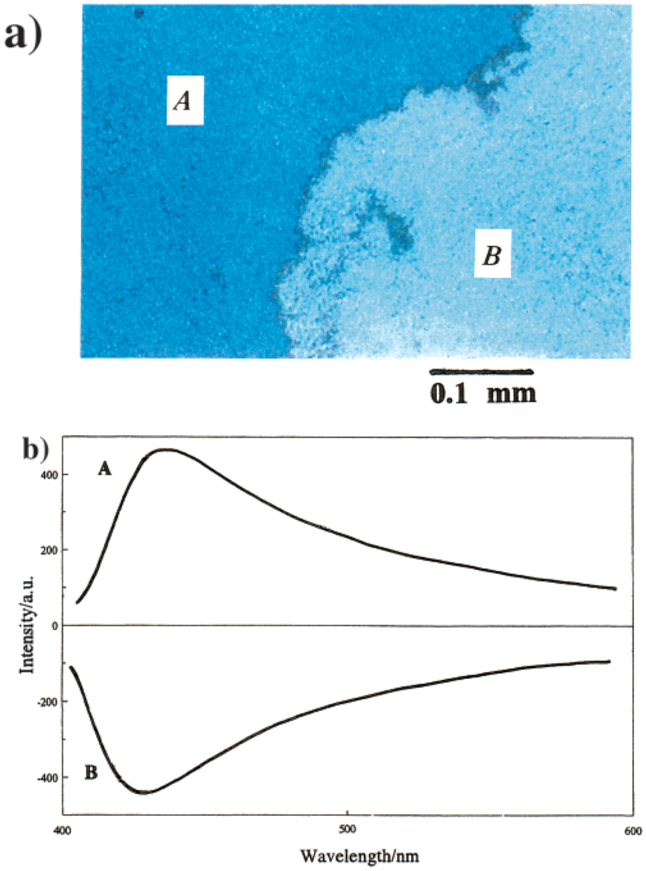


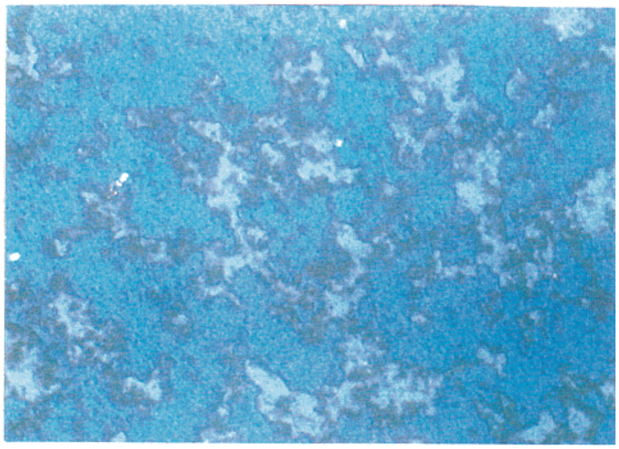
Figure 7. (a) Photomicrographs for large A and B domains of the Sm1 phase of N-12-O-PIMB with the different optical rotation and (b) CD spectra taken by focusing the light on each A or B domain. The texture was observed by rotating the analyzer clockwise by 5° from the cross-polarization position. The different sign of CD can be clearly observed between A and B domains.

chiral content. These are to be expected from a left-handed helical structure.[22,23]

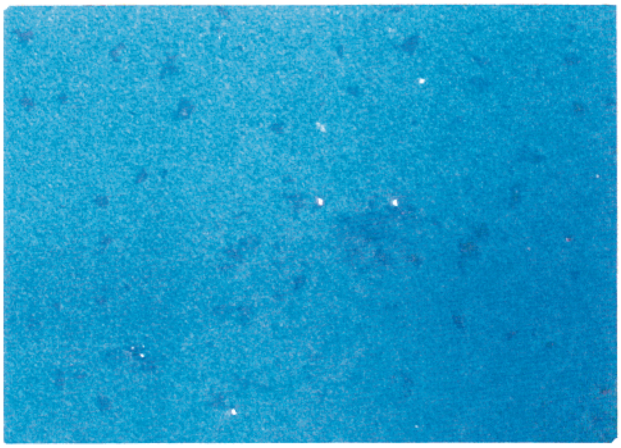
Origin of the Helix. Two basic questions arise with respect to the spontaneous formation of a helix in achiral molecules: (1) What is the structure of the helix? (2) Why can a helical structure be formed from achiral molecules?

In response to the first question, the texture exhibited a very weak birefringence and no anisotropy as mentioned above. This character was the same regardless of the sample preparation, for example, cooling rate, sample thickness, glass surface treatment, etc. Fractral appearance indicates a completely different structure from that of the conventional smectic phase, suggesting the formation of a three-dimensional helical structure like a blue phase or foggy phase.[24,25] We have tried to directly measure the helical structure by means of electron microscopy and atomic force microscopy. Unfortunately, however, we failed to obtain a satisfactory result.

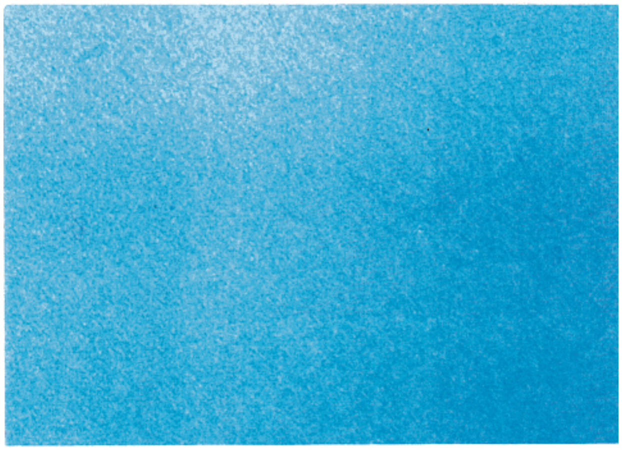
It should be noted here that there are several other examples suggesting the helicity in the smectic phase.[26,27] One of the typical examples is observed in the smectic B_7 phase. This phase appears as elongated germs with a clearly spiral or double spiral character. The germs finally coalesce to form fanlike or circular domains including the fringe pattern.[8,26,27] The texture is



a) 3%



b) 10%



c) 20%

Figure 8. Photomicrographs of the Sm1 phase observed for N-12-O-PIMB with the contents of a chiral dopant of (a) 3%, (b) 10%, and (c) 20%. The texture was observed by rotating the analyzer clockwise by 5° from the cross-polarization position. It can be observed that the area of one domain becomes predominant with the increase of chiral dopant.

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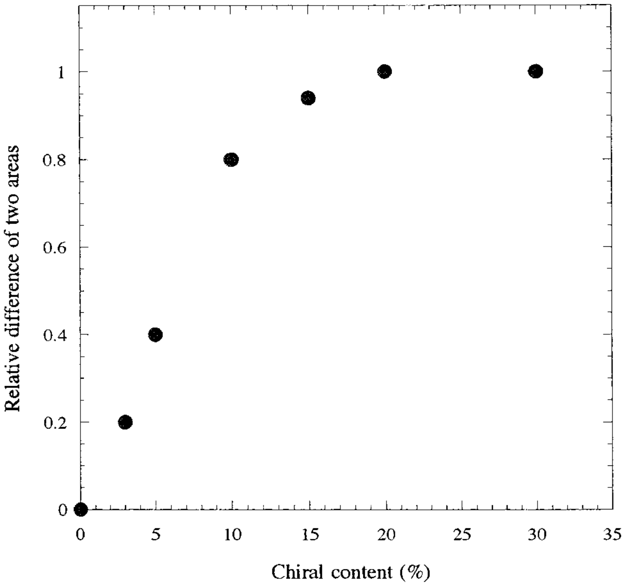


Figure 9. Relative difference in the area between the two domains with opposite optical rotation, $|A^+ - A^-|/|A^+ + A^-|$, plotted against the chiral content. The data are collected from the photomicrographs of Figure 8.

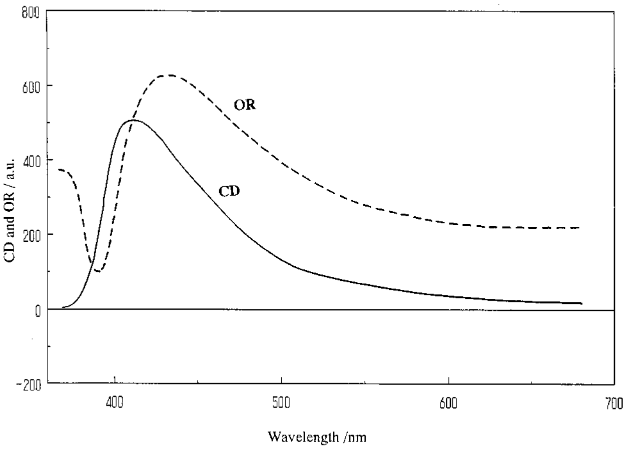
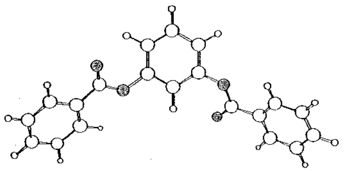


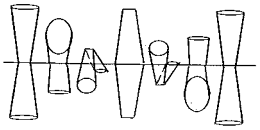
Figure 10. Typical CD and OR curves for the simple chiral domain of the Sm1 phase prepared in the blended sample of N-12-O-PIMB and N-4-O-PIMB2* with the chiral content of 20%.

completely different from the present one, but it is obvious that the helical formation is spontaneously induced. The study is still proceeding in order to clarify the helical structure.

For the second question, there are three possibilities that should be taken into account (Figure 11a−c).

We first consider the molecular chirality that is caused by the twist conformation as in the crystals.[28] This consideration is based on the solid state ^{13}C NMR study of the P-*n*-O-PIMB compounds.[17] In this study, the most remarkable feature was the signal from the carbonyl carbons in the ester linkage. Its signal appeared as a doublet in the SmAb (B_2) phase (164.3 and 164.0 ppm), whereas it appeared as a singlet in the isotropic (164.6 ppm) and crystal phases (162.5 ppm). A similar doublet was also observed in the SmBlue (B_4) phase. Therefore it has been concluded that the two carbonyl groups connecting the central core of the molecule are under different electronic circumstances. In this particular conformation, hence, the two carbonyls have to make different angles with respect to the central phenyl ring, i.e. the molecule should be twisted (conformational chirality). In addition, a significant result was found from the conformational calculation study of a bent-shaped model compound, 1,3-benzenediol dibenzoate in which a 1,3-dihydroxybenzene core was linked to two phenyl rings via an ester bond linkage.[29] The result shows that the most stable conformation was produced as a result of the two carbonyl groups of the two side-wings twisting to each other as illustrated in Figure 11a. This twisted conformation was supported by recent polarizing FT-IR measurements in pure[30] and doped[31] systems. In this study, the 1,3-dihydroxybenzene is altered to the 2,7-dihydroxynaphthalene, but the similar twist conformation can be expected. In general, however, the spontaneous resolution of twist conformation is unlikely since it is contrary to thermodynamic principles in the fluid liquid crystals. Possibly the confined packing of molecules due to their bent shape may enhance the differences in conformation energy as in the solid state.[28]


a) Twist conformation


b) Helical twist

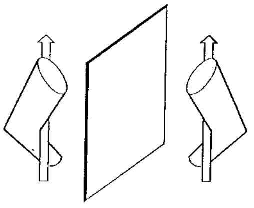

c) Tilting of molecules

Figure 11. Illustration of (a) the most stable twist conformation calculated for the banana-shaped molecule with 1,3-dihydroxybenzene as a core, (b) escape from spontaneous polarization, and (c) tilting of the molecule to the layer normal producing the mirror image.

The twisting power can be induced by an escape from the spontaneous polarization as illustrated in Figure 11b.[19,32] As proposed by Watanabe et al.,[1,33,34] the bent molecules are forced to be packed with the same bent directionality, leading to a spontaneous polarization within each layer. Here, we have to say that the system tends to escape from the resulting polarization. Two ways are observed: one is the antiferroelectric structure which cancels the polarity between layers[12−16,34] and another is the frustrated structure which extinguishes the in-

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plane polarity.[4,6,35−37] Thus, it is reasonable to consider a TGB-like helix as a third type of escape from the polarization.

As reported by Heppke and Moro,[38] an ordering of bent-shaped molecules by tilting with respect to the layer normal can generate a mirror image so that it would be able to build up an enantiomorphic structure by chirality. In other words, the C_{2v} symmetry is altered to C_2 symmetry by tilting as illustrated in Figure 11c. In fact, the chiral phases observed so far are formed by a tilted association of molecules.[11,19,26,38]

Unique determination of the origin of the helicity will be the next important subject.

Conclusion

We have synthesized a series of banana-shaped molecules, N-*n*-O-PIMB with $n = 6-16$ and the 2,7-dihydroxynaphthalene unit, as the mesogenic bent core. They all exhibit the high-temperature Sm1 phase as well as the low-temperature Sm3 phase except for N-6-O-PIMB, which forms only a frustrated $\mathrm{Sm1_f}$ phase (from X-ray data). Moreover, a frustrated Sm2 phase was also observed between the Sm1 and Sm3 phases for the materials where $n = 10$, 12, 14, and 16.

For the Sm1 phases of the $n = 8$, 10, 12, 14, and 16 homologues, an unconventional texture was observed. Initially on cooling from the isotropic liquid, small-fractal nuclei appeared and coalesced to form several large domains. Very weak birefringence and no anisotropy are characteristic of this phase although X-ray data showed a liquidlike packing of molecules in the smectic layers. Most interesting is that two different domains having an opposite optical rotation were observed under uncrossed polarizers. In addition, the circular dichroisms (CD) with a peak around 430 nm and with the opposite signs were observed for these two domains. The results strongly suggest the formation of a helical structure in these phases. Of course, the two domains of right- and left-handed helices are simultaneously formed.

A chiral dopant was used to obtain more information about this helix. We found that the helical sense was naturally affected by the doping agent. However, the doping agent did not influence the twisting power. This would be, therefore, an example of a distinct formation of a helical structure in an achiral molecular system. Many reasons have been considered for this formation of a helix in these achiral materials as discussed above. However, to fully understand this phenomenon we need to collect more significant and decisive data. Our progress will be reported in due course.

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