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Enhancement of Twisting Power in the Chiral Nematic Phase by Introducing Achiral Banana-Shaped Molecules

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Abstract: Achiral banana-shaped molecules with dodecyloxy tail groups, P-12-O-PIMB, N-12-O-PIMB, and S-12-O-PIMB, have exhibited unusual smectic phases which possess chiral and helical structures. In this work, we mixed these banana-shaped molecules with the chiral molecule forming a chiral nematic liquid crystal and found an exclusive effect of the achiral dopant that the twisting power of the chiral nematic phase in the mixtures is significantly increased with the increase of the content of achiral banana-shaped molecules. This characteristic effect in the chiral nematic field seems to offer the rational evidence for the twist conformation of such banana-shaped molecules, since the chirality should be included intrinsically within each chain. The asymmetric twist conformation in the ester linkage group connecting the central core with the side wings is likely to be the origin of enhanced twisting power.

Introduction

Previously, the banana-shaped molecules have been extensively studied, since they exhibit various kinds of smectic phases which possess unusual properties. Particularly, a presence of chiral and/or helical smectic phases is interesting, since the molecules do not have the asymmetric carbon. The most typical phases are the B_2 and B_4 phases in 1,4-phenylene bis[4-(4-*n*-alkoxyphenyliminomethyl)benzoates, P-*n*-O-PIMB, which have been fascinating chemists and physicists in the field of liquid crystals.[1−6] Recently, several other phases formed from various types of banana-shaped molecules were considered to have the chiral or helical structure.[7−11] Thus, chirality in banana-shaped molecular systems becomes an arguably important topic to be studied.

There are three models which are used to describe the origin of chirality in such banana-shaped molecules. One of them is the tilting of molecules in smectic layers that leads to enantiomorphic structure due to the spontaneous breaking of mirror symmetry (see Figure 1a).[5,6] In addition, the twist conformation which will be most stable in such a molecule is also likely as the origin of chirality in these achiral molecules as shown in Figure 1b.[3,7,8] Further, twisting of director to escape from the spontaneous polarization is also a good candidate (Figure 1c).[12−14]

In this work, we will present an unusual effect observed when the achiral banana-shaped molecules are introduced into a typical chiral nematic phase. In general, the chiral nematic helix tends to unwind by introducing the achiral compound, but in this case, the situation is completely opposite so that the introduction of achiral banana-shaped molecules increases the twisting power of the chiral nematic phase. The results strongly support that the achiral banana-shaped molecules possess an intrinsic chirality within each molecule.

Experimental Section

The materials used are shown in Scheme 1. Three banana-shaped molecules as dopants have common side wings connected to different central cores by ester linkage. The synthesis of these molecules was reported in previous papers,[7,8] and their thermal behaviors are described later.

The optical microscopic texture of the materials was examined using a polarizing microscope (Olympus, BX50) equipped with a hot stage (Mettler FP 90 HT). DSC thermogram data were obtained using a Perkin-Elmer DSC-II differential scanning calorimeter. The selective reflection bands from the chiral nematic phases were measured in the wide wavelength region of 300 to 900 nm by a JASCO J-720WI circular

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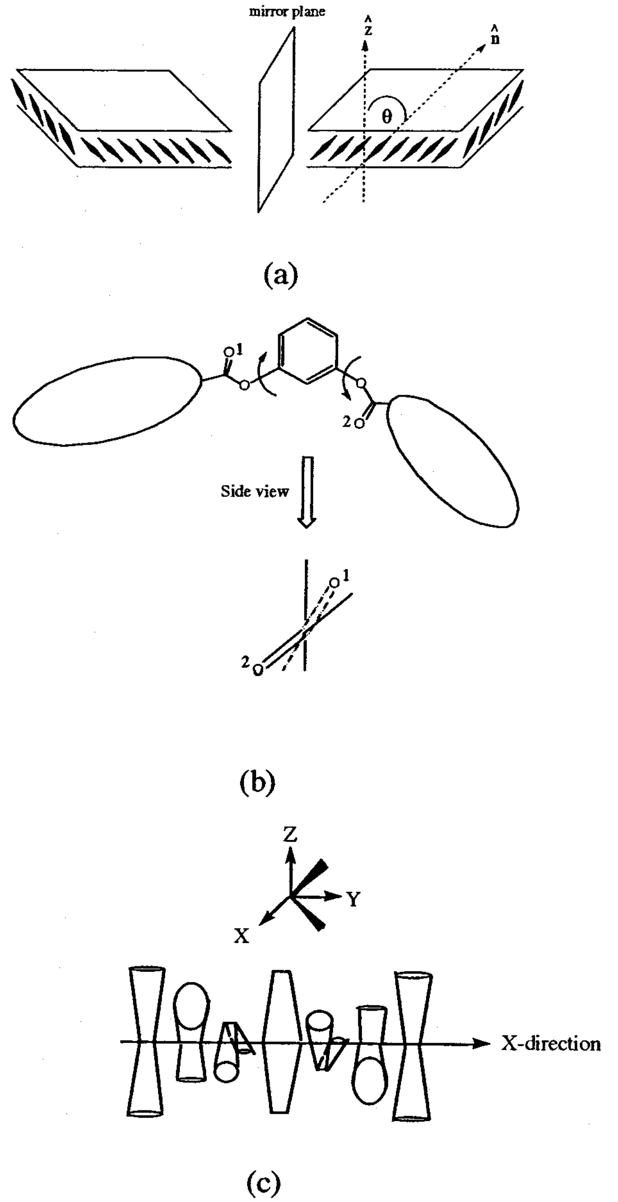

Figure 1. Three possible origins of the chirality in the mesophase of the achiral banana-shaped molecules: (a) the tilting association of molecules into a layer, (b) twisted conformation of the molecule, and (c) two-dimensional helical escape from the spontaneous polarization.

dichroic spectrometer, and the optical helical pitches, *nP*, were determined by an equation $\lambda m = nP$, where *n*, *P*, and λm are respectively the average refractive index, helical pitch, and the maximum wavelength of the reflection band.

Results and Discussion

Thermodynamic data of all materials used are summarized in Table 1.

Compound A (cholesteryl 4-formylbenzoate) exhibits the chiral nematic phase that appears after a melting of crystal at 177 °C on heating and continues up to the isotropitization around 270 °C. On cooling, the chiral nematic phase is sustained up to 150 °C. The helical optical pitch of the chiral nematic phase decreases from 600 to 520 nm with the increase of temperature from 150 to 220 °C. Thus, the range of pitch is convenient to examine the effect of guest banana-shaped molecules by the circular dichroic (CD) measurement that allows us to determine the optical pitches from 300 to 900 nm. This is simply the reason we selected compound A as a host material forming the chiral nematic phase.

Scheme 1

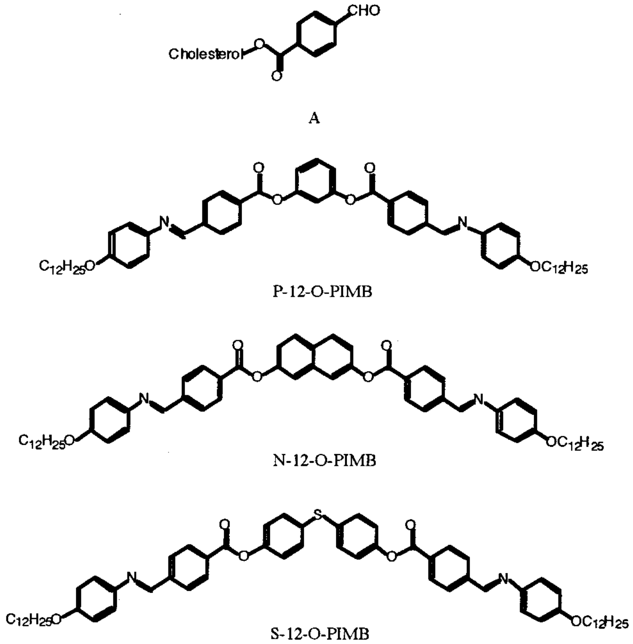

Table 1. Transition Temperatures and Enthalpies for Materials Used

compound	transition temperature °C (enthalpy, kJ/mol)[a]
A	Cr 177 (7.6) Chiral Nematic 270 I
P-12-O−PIMB	B_4 150 (6.2) B_2 172 (4.1) I
N-12-OPIMB	Sm_3 187 (1.3) Sm_2 207 (5.0) Sm_1 229 (4.3) I
S-12-O−PIMB	Cr 215 (14.2) B_7 222 (5.5) I

[a] Transition temperatures are based on heating DSC data.

As one of the banana-shaped molecules, P-12-O-PIMB with a dodecyloxyl tail group was selected from the famous achiral banana-shaped P-*n*-O-PIMB series. This compound exhibited the anti-ferroelectric B_2 and helical smectic B_4 phases in order of increasing temperature. The mesomorphic structures and physical properties have been reported elsewhere.[1−4,15−20]

The second banana-shaped molecule is N-12-O-PIMB that exhibits three chiral mesophases named as Sm1, Sm2, and Sm3.[7,8] The Sm1 phase appeared as small fractal domains on cooling from isotropic liquid and coalesced into several large domains with clear black boundaries. These domains are classified into two distinct chiral domains with opposite optical rotations and circular dichroisms. On further cooling, the Sm2 and Sm3 phases appeared without any change of texture. Only a slight change was observed with respect to the birefringence, and the resulting Sm3 phase displayed a transparent blue color similar to the B_4 phase of the P-*n*-O-PIMB series.[3,4,8]

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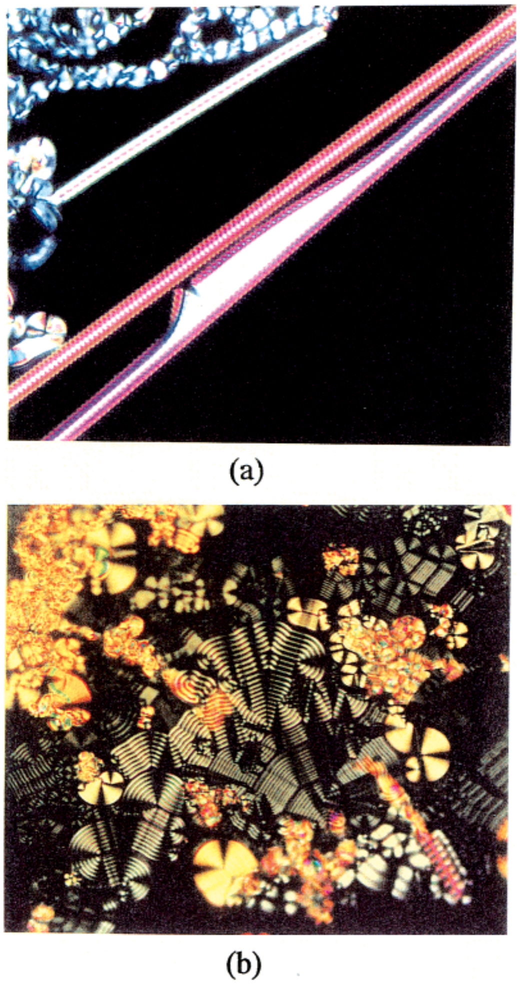
(a)

(b)

Figure 2. Photomicrographs of (a) the spiral domain (×200) and (b) the periodic stripe texture (×100) of the smectic phase of S-12-O-PIMB (at 217 °C) suggesting the helical structure. The texture (b) is preferentially observed for the sample with one surface free from the glass plate.

The third banana-shaped molecule is S-12-O-PIMB with the central core based on 4,4′-dihydroxydiphenylsulfide and with the same side wings and tail groups as two other compounds. The smectic phase of this material is observed in a narrow temperature range from 215 to 222 °C on heating and from 217 to 208 °C on cooling.[7] It exhibits the spiral domain on cooling from isotropic melt as shown in Figure 2a, and so can be classified to the smectic B_7 phase.[7,9−11] Moreover, the periodic stripe texture that may be ascribed to the helicoidal structure is observed (see Figure 2b). The helicoidal structure, if it is the case, is not similar to that of the chiral Sm C, but to that in the TGB phase since the light extinction between crossed polarizers takes place perpendicular to the stripes.[21,22] Thus, three banana-shaped molecules treated here are typical materials which are likely to form the chiral and/or helical phases.

To investigate an effect of the banana-shaped molecules on the helical structure of the chiral nematic phase, we first prepared a contact phase of compound A and P-12-O-PIMB at 180 °C. At this temperature, compound A forms the chiral nematic phase with the planar texture showing the orange reflection color, and P-12-O-PIMB enters into the isotropic phase. Surprisingly, the reflection color in the contact chiral nematic zone is clearly shifted to the blue side on moving to the P-12-O-PIMB side. Thus, it is strongly suggested that the twisting power of the chiral nematic phase is increased through the introduction of the banana-shaped P-12-O-PIMB molecule.

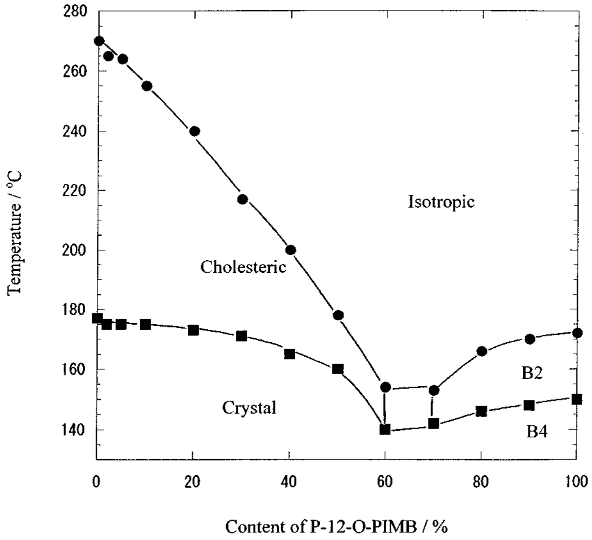

Figure 3. Plot of transition temperature versus the content of P-12-O-PIMB, indicating the temperature region of the chiral nematic phase in the mixtures of compound A and P-12-O-PIMB. The transition temperatures are collected from DSC and optical microscopic data on heating.

For the more detailed analysis of the effect of banana-shaped compounds, we prepared the blended samples of compound A with P-12-O-PIMB in various weight fractions. Their mesophase behavior is shown in Figure 3. As can be seen here, the chiral nematic temperature region of compound A becomes narrower and disappears when the P-12-O-PIMB content is increased. Hence, the homogeneous nematic phase is formed from the mixtures with up to 55% of their contents as P-12-O-PIMB. At contents of 60−70%, the chiral nematic phase coexists with the smectic phases and then turns to the B_2 and B_4 phases above the contents of 80% similarly as in P-12-O-PIMB. Figure 4a and b illustrates the planar textures of chiral nematic phases in the mixtures with 0% and 40% of P-12-O-PIMB contents, respectively. Here, the textures were observed at the same reduced temperature, $T_i - T = 40$ °C, where T_i is the isotropization temperature of the chiral nematic phase. With the increase of the P-12-O-PIMB content from 0% to 40%, the reflection color clearly changes from green to blue, showing the increase of twisting power.

The optical pitches (nP) in individual system were determined from the maximum wavelength of the reflection band by the CD measurement. In Figure 5, *nP* is plotted against the reduced temperature. The temperature dependencies are similar for all the mixtures, but one can find the unusual effect of the achiral dopant on *nP*. The relative value of *nP* decreases, and so the twisting power that is proportional to 1/*nP* increases with the increase of the content of achiral P-12-O-PIMB.

For two other mixtures of the N-12-O-PIMB/compound A and the S-12-O-PIMB/compound A, the chiral nematic phase tends to disappear rapidly with the increase of banana-shaped molecule content. The chiral nematic phase was thus formed from the mixtures with only the limited contents of 0% to 40%, but the similar trend with respect to the twisting power was clearly observed.

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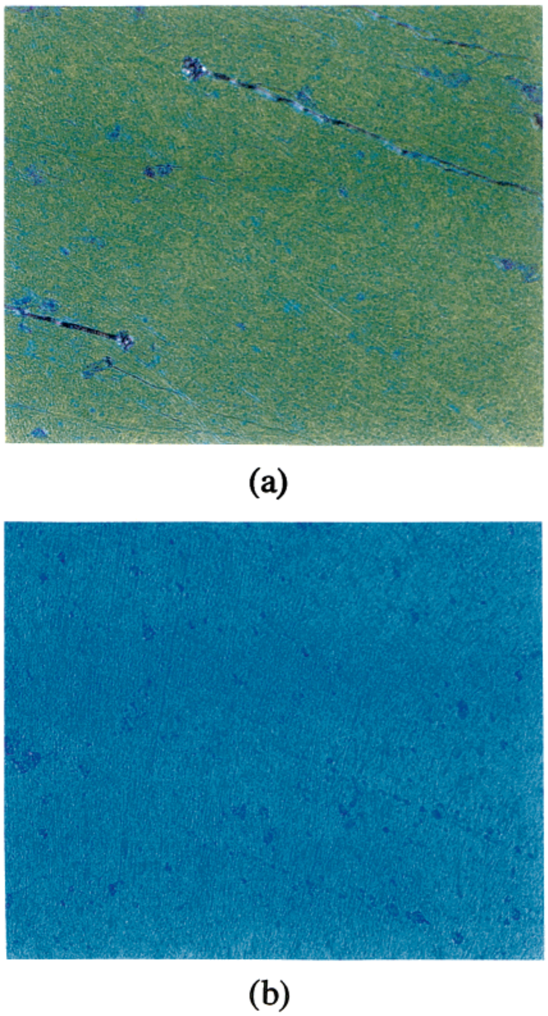

Figure 4. Photomicrographs of the textures observed at $T_i - T = 40$ °C in the chiral nematic phase of compound A/P-12-O-PIMB mixtures with (a) 0% and (b) 40% of P-12-O-PIMB contents.

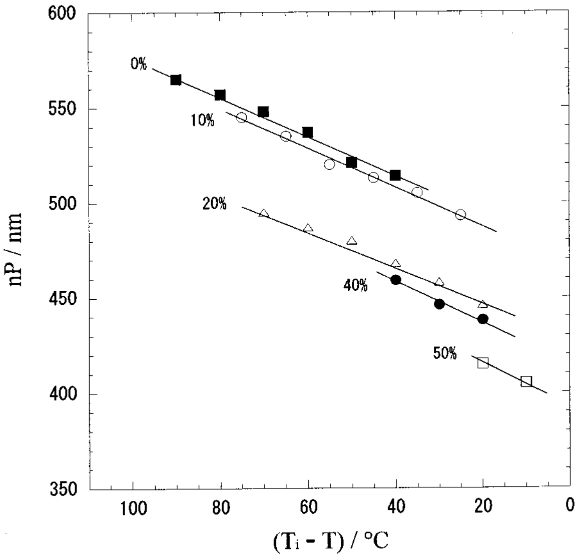

Figure 5. Plot of optical pitch (*nP*) versus reduced temperature in the chiral nematic phases of the compound A/P-12-O-PIMB mixtures with 0%, 10%, 20%, 40%, and 50% of P-12-O-PIMB contents. The data were taken from the wavelength of CD reflection bands which were measured on heating.

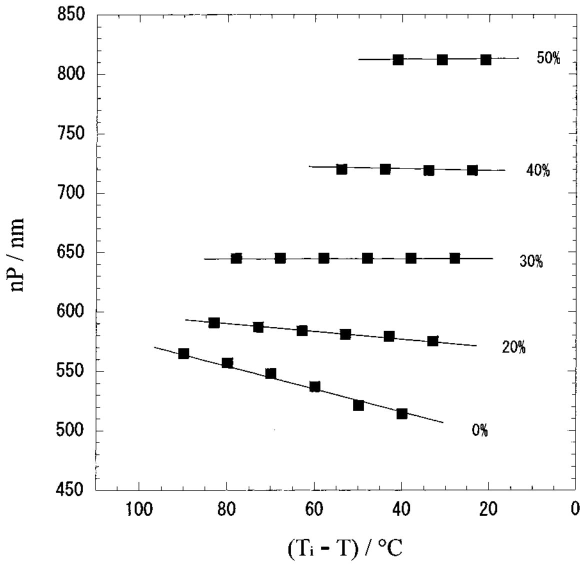

Figure 6. Plot of optical pitch (*nP*) versus reduced temperature of the compound A/TBBA mixtures with 0%, 20%, 30%, 40%, and 50% of TBBA contents. The data were taken from the wavelength of CD reflection bands which were measured on heating.

To ensure that the above results are unusual, we prepared the mixture of compound A and the typical achiral rodlike molecule (terephthalylidene-bis-4-*n*-butylaniline: TBBA)^{23} with the chemical structure similar to the banana-shaped molecules.

TBBA

Figure 6 depicts the reduced temperature dependence of the optical pitches in the TBBA/compound A system. One can understand that the trend is usual in this system. The optical pitch is increased, and so the twisting power is decreased by the introduction of achiral TBBA.

The reciprocal optical pitches (1/*nP*) in all systems which are collected at a certain reduced temperature are plotted against the achiral content in Figure 7. Although an accurate result over the whole content region was interrupted by the disappearance of the chiral nematic phase at high contents of banana-shaped molecules, it is no doubt that all the achiral banana-shaped molecules enhance the helical twisting power in the chiral nematic phase of compound A in a similar way. For example, by the 50% introduction of the achiral P-12-O-PIMB molecule, the twisting power becomes 1.2 times as large as that of the pure chiral compound A. On the other hand, it is not unusual that in the mixtures with the achiral TBBA the twisting power decreases steadily with the increase of achiral content.

Consequently, we reach the conclusion that the achiral banana-shaped molecules behave as the chiral molecule in the chiral nematic liquid crystalline field. This conclusion is very significant since the chirality should not originate from the specific packing of molecules, but from the nature of the individual molecule.

Only one possible molecular chirality is produced by the twisted conformation. With respect to this point, it should be noted that ^{13}C NMR spectra support the existence of the twisted conformation in the P-12-O-PIMB and N-12-O-PIMB.^{3,21} The

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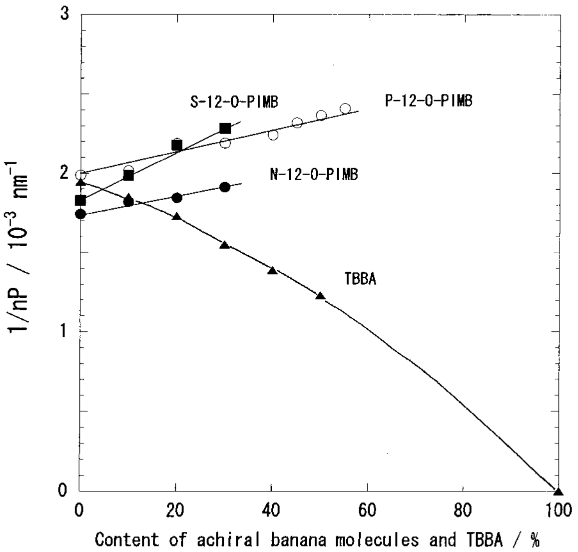

Figure 7. Plot of reciprocal optical pitch (1/*nP*) versus the content of achiral banana-shaped molecules and TBBA molecule in the mixtures. The data at $T_i - T = 30$, 60, 80, and 40 °C were collected for the mixtures with P-12-O-PIMB, S-12-OPIMB, N-12-O-PIMB, and TBBA, respectively.

signal from the carbonyl carbons appears as a doublet, indicating the asymmetric arrangement of the two carbonyls with respect to the central core.[3] Further, the conformation calculation indicates that the most stable conformation is a chiral twisted one in which the two carbonyl carbons are twisted in an opposite direction to the central core.[24] Such a type of twisted conformation was also supported by polarized FTIR measurements.[25,26] For the S-12-O-PIMB, molecular chirality from its specific conformation may be also created by the twisted arrangement of two benzene rings in the diphenylsulfide unit.[27,28]

Of course, two chiral conformations in mirror symmetry arise with the equal probability in achiral fluid systems. Yet if such bent molecules are placed in the chiral field, for example, in the chiral nematic liquid crystalline field, one of the chiral conformations may have the lower potential energy and so be taken up preferentially to the other. This results in the enhancement of the twisting power as illustrated in Figure 8. The detailed analysis is necessary for more information for this unusual phenomenon.

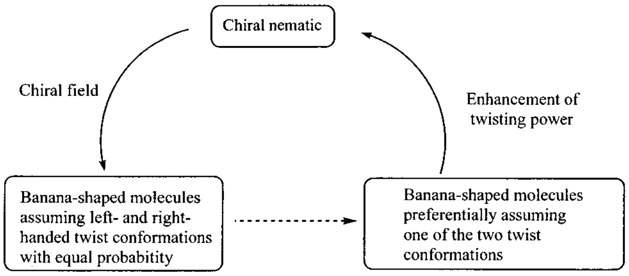

Figure 8. Schematic illustration showing the enhancement of chiral nematic twisting power by the introduction of achiral banana-shaped molecules.

Finally, we note two similar behaviors observed in chiral smectic phases doped with achiral banana-shaped molecules and a chiral nematic phase doped with achiral azobenzene-based molecules. In the former case, the twisting power in chiral smectic C and CA phases was also found to increase by introducing achiral banana-shaped molecules.[29] In the latter case, the optical pitch of the mixture of cholesteryl chloride and cholesteryl nonanoate becomes short (long) linearly with increasing concentration of trans- (cis-) azobenene.[30] In these cases, however, no interpretation for the enhanced twisting power was given.

Conclusion

The banana-shaped molecules used in this work possess 1,3-dihydroxybenzene, 2,7-dihydrox naphthalene, and 4,4′-dihydroxydiphenylsulfide units as the central cores with the same wings. These molecules have obviously formed the chiral and helical mesophases, and the twist conformation, the tilting of molecules in a smectic layer, and the escape from the ferroelectric ordering within a layer have been considered as origins of the chirality or helicity. This work was performed to seek the answer to the simple question which one is a source of chirality in the achiral banana-shaped molecular system. The results represent the distinct fact that the banana-shaped molecules enhance the twisting power in the chiral nematic phase. Thus, we reach the conclusion that the intrinsic chirality is included in each molecule. It is a twisted conformation.

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