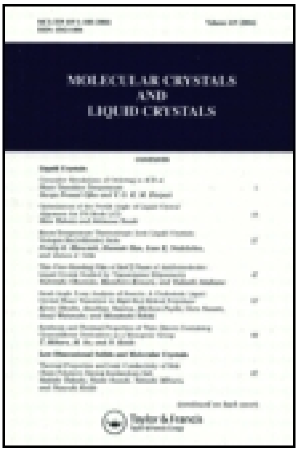

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Interlayer Correlation in Smectic Phases Induced by Chiral Twin Molecules

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INTERLAYER CORRELATION IN SMECTIC PHASES INDUCED BY CHIRAL TWIN MOLECULES

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Abstract Some chiral twin molecules were prepared and the structure-property relationships in the system consisting of chiral twin molecules and achiral host molecules were investigated. The spacer structure was found to have significant effect on the smectic layer strength and the twisting power in the SmC* phase. C-13 NMR measurements revealed that a chiral twin molecule affects motion of host molecules in the SmA phase. The obtained results are discussed in comparison with our proposed model, where chiral twin molecules are intercalated in the SmC-layers formed by achiral host molecules. The chiral twin molecules may produce a strong correlation in host molecules between adjacent layer but decrease the strength of the smectic layer structure.

INTRODUCTION

Smectic liquid crystals[1] have attracted much attention due to their characteristic molecular assembly and their applications in electrooptical devices. Important discoveries concerning chiral smectic phases - ferroelectric phases,[2] "Abrikosov" type twist grain boundary (TGB) phases,[3] and antiferroelectric phases[4] have been reported. Experimental and theoretical works have been performed to understand the apperance of these chiral smectic phases. Nevertheless, some basic problems, i.e., nature in twisting power in the smectic phases and the origin of the smectic layer strength, are not understood very well. We have investigated the microscopic organization of molecules in chiral smectic phases.[5-10] C-13 NMR measurements suggest that: (1) cooperative motion for core parts contributes to orientational order of molecules in each layer, (2) molecular deformation for the core part causes the reorientation of cores near the SmA to SmC* transition, and (3) the interlayer permiation of tails causes the correlation between cores in adjacent layers in SmC* and antiferroelectric SmC* phases. Figure 1 shows the information about dynamics of a molecule in SmA and SmC (SmC*) phases. Correlation of molecular motion bewteen neighbouring molecules has been found to have a significant effect on long range order in the smectic phases.

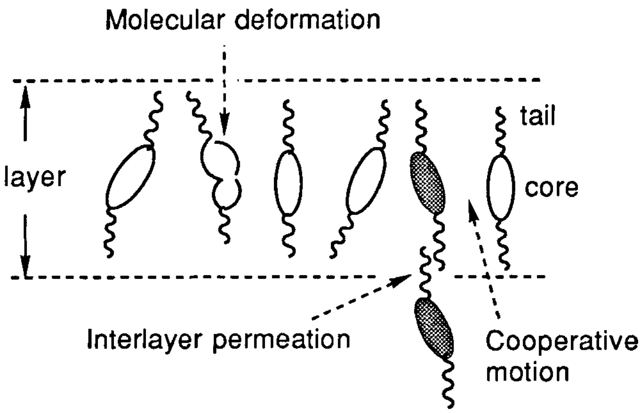


FIGURE 1 Structural model for microscopic organization of molecules in SmA and SmC (SmC*) phases.[10]

In order to study interlayer correlation, some chiral twin molecules, (R)-3-methyladipic acid bis [4-(5-alkyl-2-(pyrimidinyl)phenyl]esters (MAB-n-PYP), were prepared and their physical properties investigated.[11, 12] Some twin materials possessing similar structures to our target materials were already prepared and their ferroelectric properties investigated by Marcos *et al.*[13] Our interest has been focused on the smectic layer structure and the helical macrostructure induced by the chiral twin molecules.

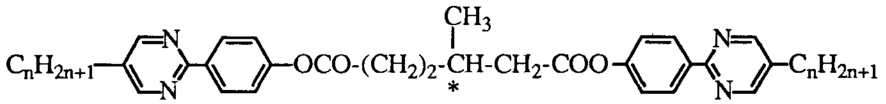


FIGURE 2 Structure of MAB-n-PYP.

Pitch measurements revealed that the twin materials induce stronger helical structures in both cholesteric (Ch) and SmC* phases than the analogous "monomeric" materials. The twin material was found to produce unusual smectic phases of which texture is similar to that reported for the TGB phases, in contact studies with an achiral liquid-crystalline compound.[11] Furthermore, a phase diagram between the twin material (MAB-8-PYP) and an optically active antiferroelectric liquid crystal showed clear discontinuity in phase sequences.[14] Two kinds of effects induced by the chiral twin molecule, i.e., a strong mesophasic helical strucyture and a decrease of the smectic layer strength, have been investigated.

We report here the structure-property relationships in the system consisting of chiral twin molecules and host molecules. The relationships between molecular structure of the twin materials and the twisting power were investigated. The orientation and dynamics of a host molecule in the system were also investigated by solid-state C-13 NMR.

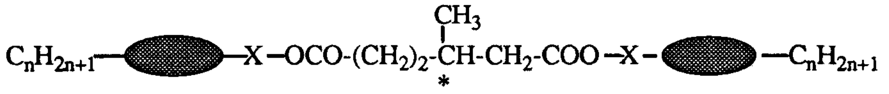


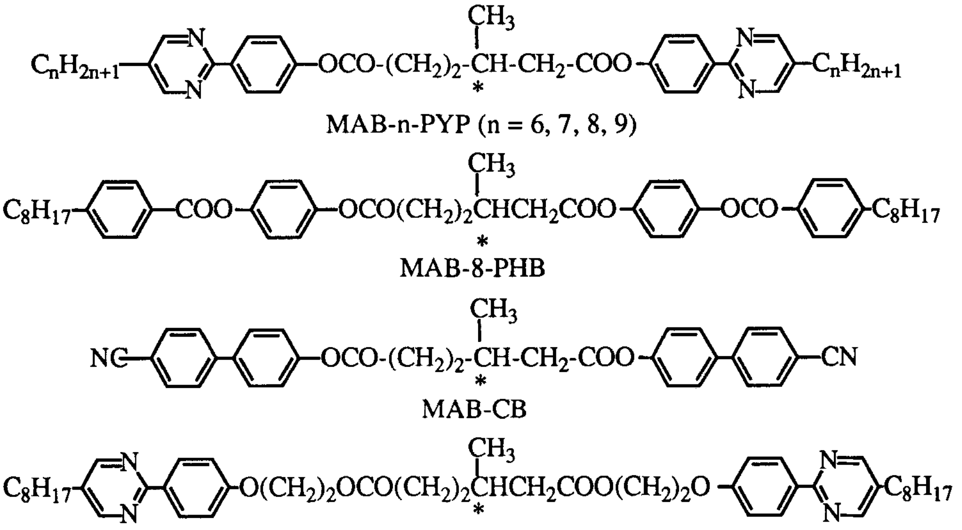
FIGURE 3 A schematic representation of a chiral twin molecule.

The obtained results allow us to discuss nature in the interlayer correlation in SmA and SmC* phases induced by chiral twin molecules.

EXPERIMENTAL

Materials

Structures of chiral twin molecules under investigation are shown in Figure 4.



MAB-n-PYP (n = 6, 7, 8, 9)

MAB-8-PHB

MAB-CB

MAB-8-PYPOE

FIGURE 4 Structures of the chiral twin molecules under investigation.

The chiral twin materials except for MAB-8-PYPOE[15] were prepared by the esterification of a number of 4-substituted phenols with (R)-3-methyl adipic acid using N, N'-dicyclohexylcarbodiimide as an esterification agent, 4-dimethylaminopyrimidine as a catalyst, and dichloromethane as a solvent.[11] MAB-8-PYPOE was obtained by the following method. 5-Octyl-2-(4-hydroxyphenyl)pyrimidine was reacted with

2-bromoethanol in the presence of sodium hydroxide. The obtained 5-octyl-2-[4-(2-hydroxyethyloxy)phenyl]pyrimidine was esterified with (R)-3-methyl adipic acid in the presence of triphenylphosphine and diethyl azodicarboxylate. The final esters were purified by column chromatography and then recrystallized from ethanol ethylacetate mixture. The final products were determined to be pure by reverse-phase high performance liquid chromatography, using a Waters 201 GPC-ALC. The structures of the final products were determined by a combination of IR, NMR, and MS spectral analysis; the results for each compound were found to be consistent with the predicted structures.

Measurements

The initial phase assignments and corresponding transition temperatures for the final products were determined by thermal optical microscopy using a Nikon OPTIPHOTO POL polarizing microscope equiped with a Mettler FP82 microfurnance and FP80 control unit. The heating and cooling rates were 2 °Cmin^{-1}. Temperatures and enthalpies of transitions were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 200 calorimeter. The materials were studied at a scanning rate of 2 °Cmin^{-1} for both heating and cooling cycles.

The helical pitch in the Ch phase was measured by the Cano wedge method.[16] The SmC* helical pitch was obtained directly by measuring the distance between the lines corresponding to the full pitch under the polarized light microscopy for a homogeneously aligned sample in a cell with 200-300 μm spacing. The helical twist senses were measured by using the contact method.[17] The definition of the helical twist senses used in this article is the same as that used by Goodby.[18] The helical pitches and senses for the Ch and SmC* phases were measured at room temperature unless otherwise indicated.

All C-13 NMR spectra were obtained by using a JEOL GSX-270 spectrometer at the magnetic field of 6.34 T. The sample was aligned macroscopically by slow cooling from the isotropic into the liquid-crystalline phase in the magnet. The cooling rate was about 1 °C15min^{-1}. The measurements for C-13 spin-lattice relaxation time in the laboratory frame (T_1) were performed using 180°-τ-90° pulse sequence.

RESULTS AND DISCUSSION

Liquid crystal properties

Transition temperatures and enthalpies of transition for MAB-8-PYP, MAB-8-PHB, MAB-CB, and MAB-8-PYPOE are listed in Table I. Physical properties for MAB-n-PYP were already reported in reference (11).

MAB-8-PYP, MAB-8-PHB, and MAB-CB were found to exibit Ch phases. Typical fan-shaped textures for Ch phases were observed under polarized light microscopy, indicating these compounds have a relatively short Ch pitch.[11] MAB-8-PYPOE exibited a monotropic phase sequence of isotropic liquid-SmA-crystal and the transition temperatures for MAB-8-PYPOE are markedly lower than those for the other twin molecules.[15] The flexible chiral spacer of MAB-8-PYPOE may be thought to cause larger conformational freedom of the molecule than that of MAB-8-PYP. The flexibility of the spacer can be affected by the position of the ester group in the spacer.[15]

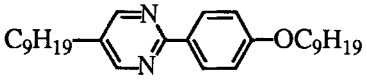
TABLE I Transition temperatures (°C) and enthalpies of transition, ΔH (kJmol^{-1}), for MAB-8-PYP, MAB-8-PHB, MAB-CB, and MAB-8-PYPOE.

	I	Ch	SmA	SmC*	SmX[a]	recryst	mp
MAB-8-PYP	• 127.7	• 122.9				•	130.9
ΔH	7.2	33.6					45.6
MAB-8-PHB[b]	• 140.6	• 113.2		• 110.2	• 108.7	•	116.6
ΔH	5.4	2.1					40.2
MAB-CB	• 210.6	• 136.3				•	157.4
ΔH	5.2	25.7					25.5
MAB-8-PYPOE	• 57.7		• 57.6			•	75.5
ΔH							40.6

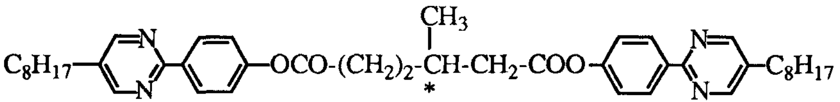
[a] Unidentified smectic phase.

[b] Measured by DSC in an open aluminum pan.

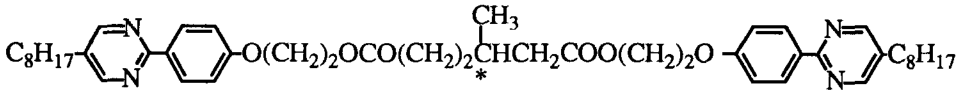
Transition temperatures for MAB-8-PHB strongly depended on experimental conditions, i.e., DSC conditions and cell thickness of a sandwich glass cell.[19] The transition temperatures measured by DSC in an encapsulated pan were 117.8 °C (a broad peak, 3.6 kJmol^{-1}) mesophase I 91.6 °C (12.8 kJmol^{-1}) mesophase II 40.9 °C (2.9 kJmol^{-1}) mesophase III 27.8 °C (18.5 kJmol^{-1}) Cry. However, transition temperatures for a racemic modification did not depend on the experimental conditions. The other chiral twin materials, where the core part is a phenylpyrimidine group or a biphenyl group, did not show unsusal transition behaviour. Optical measurements for MAB-8-PHB indicate that the helical structure in the mesophase I is different from that in the mesophase II. C-13 NMR measurements for MAB-8-PHB and its racemic modification suggest that there is difference in internal motion for cores between the enantiomer in the Ch phase and the racemate in the N phase. Thus, the coupling of the chirality and the internal motion of the phenyl benzoate core of MAB-8-PHB may be thought to produce the unusual phase transition. Our present speculation for the unusal phases is that: (1) the strong correlation of the internal motion between cores of the chiral twin molecule produces a "bend" helical axis in the mesophase I, and then (2) reorganization of the helical axes occurs in the mesophase II. Further experiments are necessary to discuss the unusal phase transition behaviour.



9-PYP-9O



MAB-8-PYP



MAB-8-PYPOE

Mixture A : 9-PYP-9O
Mixture B : 9-PYP-9O (90%) + MAB-8-PYP (10%)
Mixture C : 9-PYP-9O (90%) + MAB-8-PYPOE (10%)

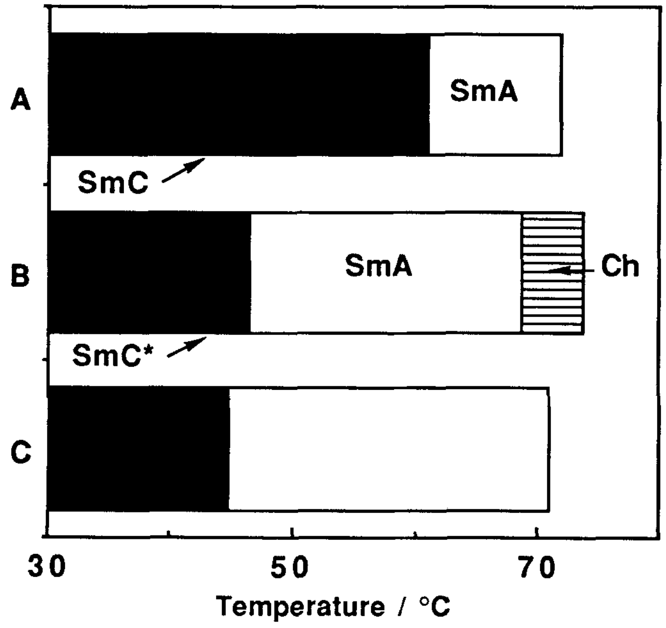


FIGURE 4 Transition temperatures for mixtures A-C.

Phase transition behaviour for a binary mixture between a chiral twin molecule and an achiral smectic host molecule

In order to investigate the effect of a chiral twin molecule on phase transitions for the mixture with a host molecule, the binary mixtures consisting of 5-nonyl-2-(4-nonyloxyphenyl)pyrimidine (9-PYP-9O) and 10% by weight of each twin chiral material were prepared and their transiton temperatures investigated (see Figure 4).

MAB-8-PYP was found to induce a Ch phase in the mixture. The twin molecule is expected to decrease the strength of the smectic layer structure produced by 9-PYP-9O, because the distance between aromatic core parts of the twin molecule may be different from the smectic layer thickness. Due to this mismatching in distance, the twin molecule may not exist happily in the smectic layer, thus , the strength of the layer structure may be decreased, which also contributes to the stabilization of the Ch phase. In the case of MAB-8-PYPOE, the markedly flexible spacer is thought to cause a favorable matching of cores between the twin molecule and the host molecule.[15] Both the chiral twin molecules were found to decrease the stability of the SmC phase of 9-PYP-9O.

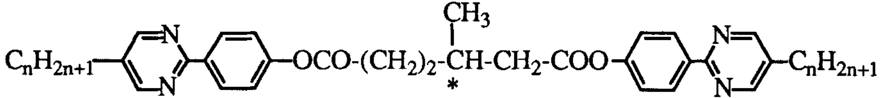
In order to investigate the effect on the smectic layer strength, the binary mixtures of an antiferroelectric liquid crystal, (S)-4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (MHPOBC), and each chiral twin molecule were prepared and their transition behaviour investigated. Smectic layer structure of the antiferroelectric SmC* phase is thought to be strong. A phase diagram between MHPOBC and MAB-8-PYP showed clear discontinuity in phase sequnces.[14] However, a phase diagram between MHPOBC and MAB-8-PYPOE did not show the discontinuity.[20] Thus, the rigid twin molecule (MAB-8-PYP) was found to decrease the smectic layer strength.

Pitch measurements

The helical pitch values in the Ch phases were determined for chiral nematic mixtures of 4-n-hexyl-4'-cyanobiphenyl (6CB) and 2% by weight of each chiral twin material. The SmC* helical pitch values were measured for SmC* mixtures of an achiral SmC host material and 1% by weight of each chiral twin material. The SmC host material (host A) is a mixture of 5-alkyl-2-(4-alkyloxyphenyl)pyrimidines.

Effect of alkyl chain length of a chiral twin molecule on helical structures in the Ch and SmC* phases were investigared.[11] The helical pitch values and their helical twist senses for MAB-n-PYP in the Ch and SmC* phases are listed in Table II. All of the mixtures have a right-handed helix in the Ch and SmC* phases. The twist senses were consistent with Gray-McDonnell rule.[17] The alkyl chain length was found to have little effect on the pitch values in both Ch and SmC* phases.

TABLE II Helical pitches in the Ch and SmC* phases, and the helical senses, i.e., right-handed (RH) or left-handed (LH).[11]

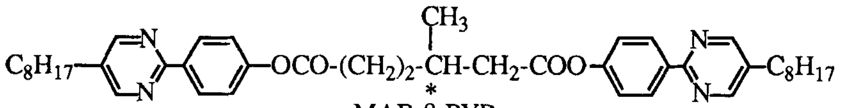


MAB-n-PYP

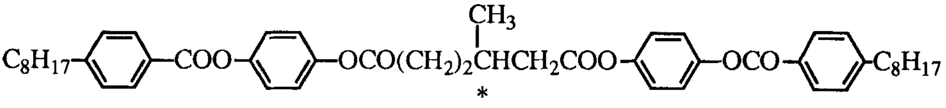
	Ch		SmC*	
	pitch / μm	sense	pitch / μm	sense
MAB-6-PYP	16	RH	8	RH
MAB-7-PYP	19	RH	8	RH
MAB-8-PYP	22	RH	8	RH
MAB-9-PYP	21	RH	8	RH

In order to understand effect of the core structures on twisting power, helical pitch values and helical senses in the Ch and SmC* phases are compared between three related chiral twin materials, MAB-8-PYP, MAB-8-PHB, and MAB-CB (see Table III).

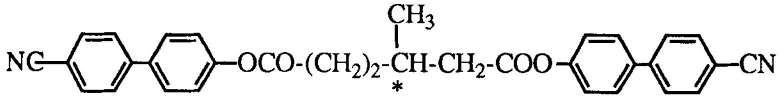
TABLE III Helical pitches (μm) in the Ch and SmC* phases.



MAB-8-PYP



MAB-8-PHB



MAB-CB

	Ch (2 wt%-doped)	SmC* (1 wt%-doped)
MAB-8-PYP	22	8
MAB-8-PHB	13	15
MAB-CB	7	very long[a]

[a]Dechiralization lines corresponding to the pitch did not appear.

All of the mixtures have a right-handed helix in the Ch and SmC* phases. The results are consistent with the Gray-McDonnell rule. MAB-CB induced the shortest pitch in the Ch phase, but dechiralization lines corresponding to the pitch were not observed in the SmC* phase. The core structures were found to have a different effect on helical structures between Ch and SmC* phases.[12]

Then, helical pitch values in Ch and SmC* phases for mixtures with host A are compared between MAB-8-PYP and MAB-CB in Table IV. The host A has a phenylpyrimidine core. The short pitch values in the Ch phases for both systems indicate that core structures have little effect on the helical pitch values in the Ch phase. However, the "matching" of the core structures between a host and a chiral twin material was found to induce a stronger helical structure in the SmC* phase.[12] The results suggest the existence of "core-core" interaction in each layer between the chiral twin molecules and the neighbouring host molecules in the SmC* phase.

TABLE IV Helical pitches (μm) for the mixture consisting of host A and 1 % by weight of each chiral twin material at 64°C in the Ch phase and at room temperature in the SmC* phase.

	Ch	SmC*
MAB-8-PYP	8	8
MAB-CB	5	very long[a]

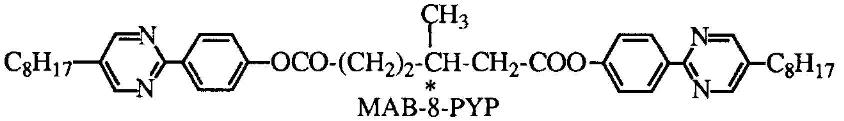
[a]Dechiralization lines corresponding to the pitch did not appear.

In order to understand effect of the spacer structures on the twisting power, the helical pitch values and twist senses in the Ch and SmC* phases are compared between MAB-8-PYP and MAB-8-PYPOE (see Table V). Pitch measurements showed that MAB-8-PYPOE produces a weaker helical structure in the Ch phase and particularly in the SmC* phase than MAB-8-PYP.[15] The flexible chiral spacer of MAB-8-PYPOE may be thought to increase conformational freedom of the molecule, reducing the rigidity of a chiral twin molecule and also reducing the correlation between two core parts of the molecule compared to MAB-8-PYP. The interlayer correlation induced by MAB-8-PYPOE may be weaker than that induced by MAB-8-PYP in the SmC* phase.

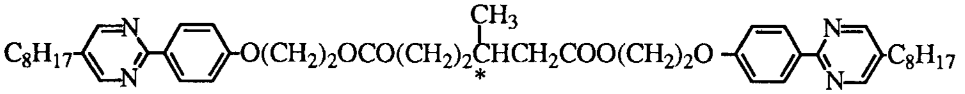
With respect to the helical sense, the Gray-McDonell rule predicts a left-handed helix for MAB-8-PYPOE. The twist sense in the Ch phase induced by MAB-8-PYPOE is left-handed, however, that in the SmC* phase is right-handed. The direction of optical rotation was positive for MAB-8-PYP, whereas negative for MAB-8-PYPOE. The direction of spontaneous polarization was positive for MAB-8-PYP, whereas negative for

MAB-8-PYPOE. These predict a left-handed helix for MAB-8-PYPOE in the SmC* phase. Although the origin of the right-handed helix for MAB-8-PYPOE in the SmC* phase is not understood, the spacer structure was found to have a special effect on the helical sense in the SmC* phase.

TABLE V Helical pitches (μm) in the Ch and SmC* phases for the mixture of a host material and each chiral twin material. A nematic host is 6CB and a SmC host is 5-octyl-2-(4-hexyloxyphenyl)pyrimidine (8-PYP-6O).



MAB-8-PYP

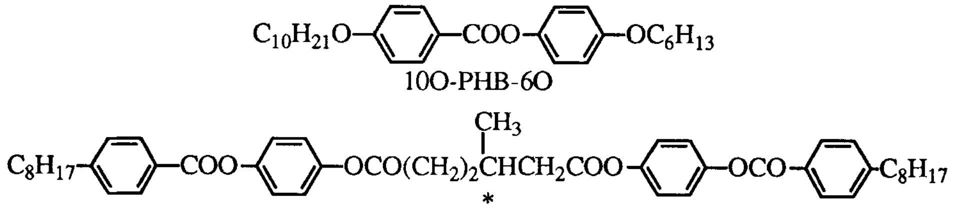


MAB-8-PYPOE

	Ch (2 wt%)		SmC* (5 wt%)	
	pitch	sense	pitch	sense
MAB-8-PYP	22	RH	2	RH
MAB-8-PYPOE	45	LH	8	RH

C-13 NMR measurements

We investigated the effect of a chiral twin molecule on the orientation and dynamics of a host molecule in the mixture by means of C-13 NMR. The mixture of 4-hexyloxyphenyl-4'-decyloxybenzoate (10O-PHB-6O) and 2 % by weight of MAB-8-PHB was used for C-13 NMR measurements (see Figure 5). Transition temperatures for 10O-PHB-6O were Iso 86 °C N 81 SmA 75 SmC. C-13 NMR measurements for 10O-PHB-6O only were also carried out.



10O-PHB-6O

MAB-8-PHB

FIGURE 5 The mixture for C-13 NMR measurements.

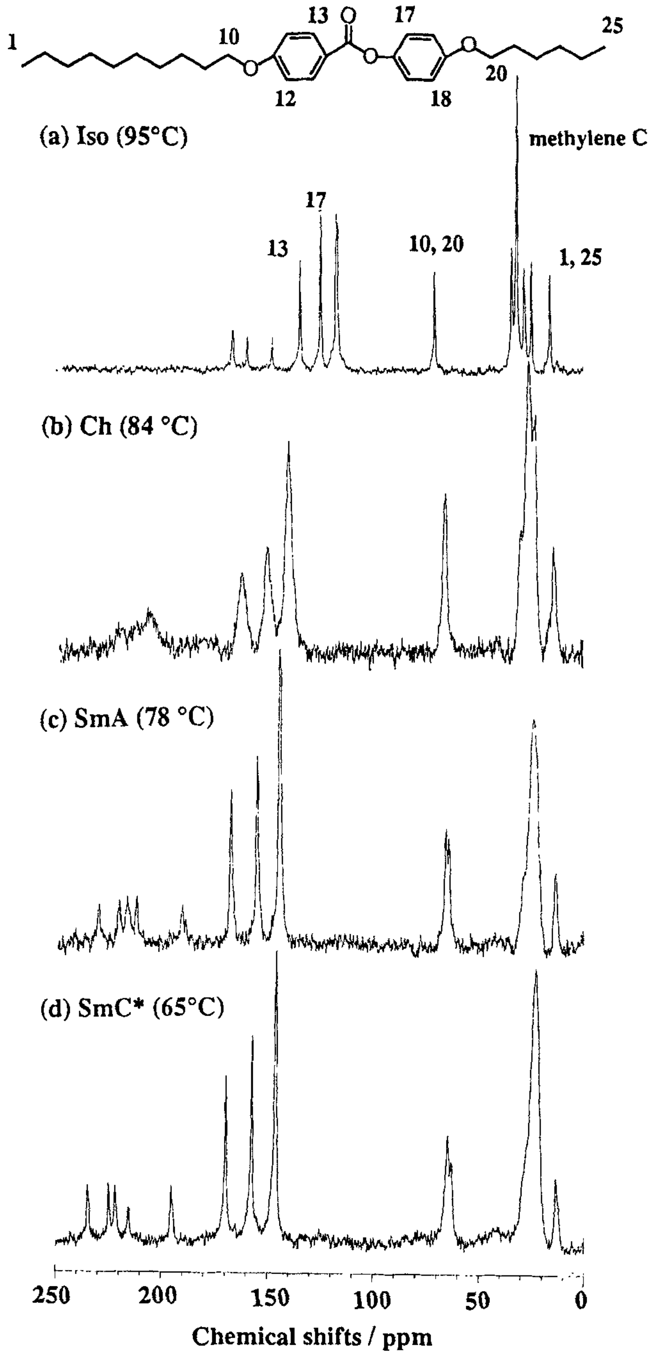


FIGURE 6 The C-13 NMR spectra of 10O-PHB-6O in the mixture of 10O-PHB-6O and 2 % by weight of MAB-8-PHB in the isotropic liquid, Ch, SmA, and SmC* phases without sample spinning.

Figure 6 shows static C-13 NMR spectra of 10O-PHB-6O in the mixture on cooling in the isotropic liquid, Ch, SmA and SmC* phases. The peaks for MAB-8-PHB in the mixture were not detected. Figure 7 shows temperature dependence of chemical shifts for 10O-PHB-6O in the mixture and 10O-PHB-6O only. There was no significant difference in temperature dependent C-13 NMR spectra between 10-PHB-6O in the mixture and 10O-PHB-6O, indicating that helical structures of the mixture were not preserved in magnetic field of 6.34 T. During the phase transition from SmA to SmC*, C-13 chemical shifts of the esters and aromatic carbons of 10O-PHB-6O increase, but those of the other aliphatic carbons decrease. These results suggest that the director is oriented to the direction of the magnetic field, whereas the layer normals are tilted in the SmC* phase.[21] Thus, the results of NMR measurements do not give direct information about the twisting power of the chiral twin molecule in the system.

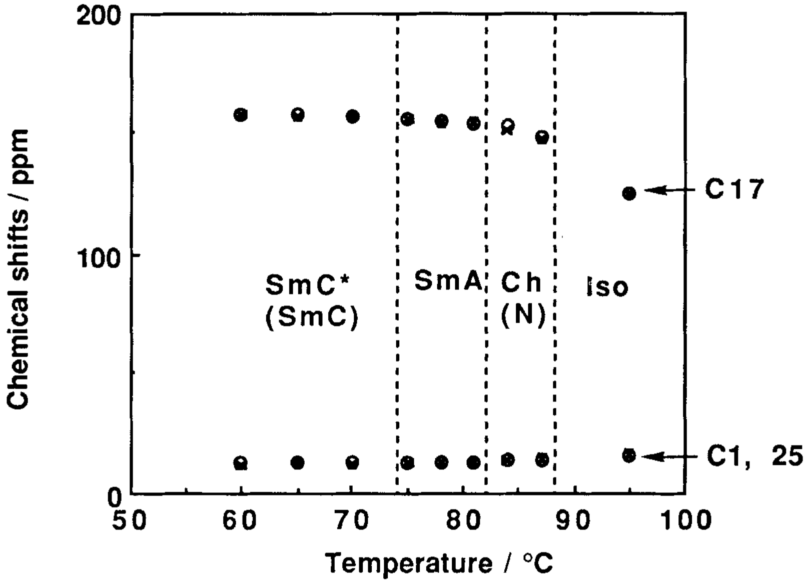


FIGURE 7 Temperature dependence of chemical shifts for 10O-PHB-6O in the mixture and 10O-PHB-6O. The crosses show that for 10O-PHB-6O in the mixtue and the circles show that for 10-PHB-6O only.

We roughly estimate order parameters of a molecular long axis of 10O-PHB-6O in the mixture in the Ch and SmA phases from C-13 chemical shifts of a protonated aromatic carbon. Helical structure for the mixture was not formed in the magnet field, thus the Ch and SmA phases are assumed to be uniaxial phases. The chemical shift σ in a ordered liquid-crystalline phase is related to the isotropic chemical shift σ_i, the components of the chemical shift tensor σ_{jk}, and the order parameters S_{jk} by Eq.(1).[22]

$$\sigma = \sigma_i + (2/3)S_{zz}\{\sigma_{zz} - (1/2)(\sigma_{xx} + \sigma_{yy})\} + (1/3)(\sigma_{xx} - \sigma_{yy})(S_{xx} - S_{yy}) + (2/3)S_{yz}\sigma_{yz} + (2/3)S_{xz}\sigma_{xz} + (2/3)S_{xy}\sigma_{xy} \quad (1)$$

The ordering matrix of the molecule is assumed to be cylindrically symmetric around the molecular long axis so that equation (1) is reduced to

$$\sigma = \sigma_i + (2/3)S(\sigma_{\parallel} - \sigma_{\perp}) \quad (2)$$

where $\sigma_{\parallel} = \sigma_{zz}$ is the chemical shift component along the direction of the molecular long axis, $\sigma_{\perp} = (1/2)(\sigma_{xx} + \sigma_{yy})$ is the average of the components of the chemical shift tensor in the xy plane, and S = Szz is the order parameter associated with the long axis. S is defined as

$$S = <3\cos^2\theta - 1> / 2 \quad (3)$$

where θ describes the orientation of the long axis with respect to the applied magnetic field, < > is a thermal average. For aromatic carbons, the magnetic equivalence of ortho aromatic carbon pairs indicates that the phenyl rings of the core perform flips around each para axis. We can assume that fast molecular motions around the molecular long axis and fast 90 ° flips of the phenyl rings around each para axis occur in the mesophases. The chemical shifts of the aromatic carbons can be written for the ortho carbons as[23]

$$\sigma_{\parallel} = (1/4)(1 + 2\sin^2\Phi)\sigma_{11} + (1/4)(1 + 2\cos^2\Phi)\sigma_{22}$$
$$\sigma_{\perp} = (1/2)\{(1/4)(1 + 2\cos^2\Phi)\sigma_{11} + (1/4)(1 + 2\sin^2\Phi)\sigma_{22} + \sigma_{33}\} \quad (4)$$

where Φ is the angle between the phenyl para axis and the molecular long axis. The order parameters can not be calculated from C-13 chemical shifts without precise values of the chemical shift tensors and the angles between the principal axes of tensor and the moleculare axes. However, both sets of data are difficult to measure. Therefore, we calculate values of S by using the principal values for the chemical shift tensors taken from a model compound. Although the calculations of S may not be accurate, we can get rough values of S to estimate macroscopic ordering of 10O-PHB-6O in the mixture in the unwound Ch and SmA phases. Shielding tensor elements for a protonated aromatic carbon are $\sigma_{11} = -193$ ppm, $\sigma_{22} = -134$ ppm, and $\sigma_{33} = -12$ ppm.[24] Φ is assumed to be 9°. Observed chemical shifts of the protonated aromatic carbon (C17) and calculated order parameters for 10O-PHB-6O in the mixture and 10O-PHB-6O are listed in Table VI.

TABLE VI Observed chemical shifts (ppm) of C17 and calculated order parameters for 10O-PHB-6O in the mixture (A) and 10O-PHB-6O only (B).

	I (95 °C)	Ch (N) (84 °C)		SmA (75 °C)	
	shifts	shifts	S	shifts	S
A (the twin system)	124.2	151.1	0.74	155.5	0.86
B (the host only)	124.2	152.5	0.78	155.8	0.87

There is no significant difference in order parameters in the mesophases between 10O-PHB-6O in the mixture and 10O-PHB-6O, indicating that the chiral twin molecule has little effect on the molecular ordering of the host molecule in the magnetic field.

Table VII shows C-13 T_1 values of typical carbons of 10O-PHB-6O in the mixture and 10O-PHB-6O. In the SmA phase, C-13 T_1 values of the ortho aromatic carbons of 10O-PHB-6O in the mixture are markedly longer than those of 10O-PHB-6O.

TABLE VII C-13 T_1 values (s) of protonated aromatic and methylene carbons of 10O-PHB-6O in the mixture. Values in the parenthese are those for 10O-PHB-6O.

	I	Ch (N)	SmA		SmC* (SmC)	
	95 °C	84 °C	78 °C	75 °C	65 °C	60 °C
aromatic C13	0.44	1.50	0.64	0.73	0.23	0.23
		(1.21)	(0.36)	(0.34)	(0.21)	(0.22)
aromatic C17	0.88	1.49	1.13	1.08	0.45	0.37
	(0.75)	(1.99)	(0.60)	(0.59)	(0.41)	(0.30)
methylene C[a]	0.83	0.92	1.05	0.95	0.90	0.83
	(0.79)	(1.18)	(0.91)	(0.99)	(0.83)	(0.83)

[a]methylene C : unidentified methylene carbons observed at 31.5 ppm in the I phase.

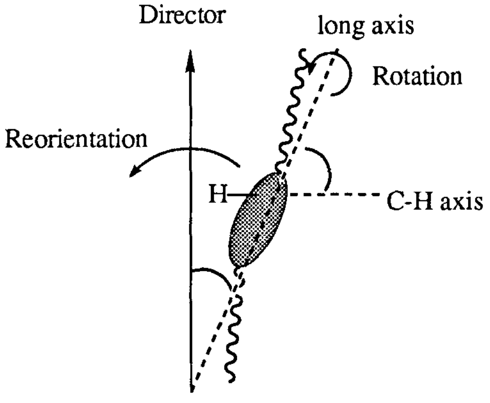


FIGURE 8 The factors that may affect C-13 T1 values of a liquid-crystalline molecule in a SmA phase.

C-13 T_1 values in a SmA phase depend on overall rotation of a molecule around its long axis, reorientation of the long axis around a director, an angle between C-H axis and the long axis, and an angle between the long axis and the director (see Figure 8).[10] There was no difference in chemical shifts of C17 between 10O-PHB-6O in the mixture and 10O-PHB-6O, indicationg that the difference in the C-13 T_1 values does not result from the difference in the angles. Then, there was no significant difference in C-13 T_1 values of the methylene C between the twin system and the host only, indicating that the difference in C-13 T_1 values does not result from the difference in the overall rotation. Thus, the observed longer C-13 T_1 values of the core carbons suggest that the reorientation of the long axis of 10O-PHB-6O in the mixture is faster than that for 10O-PHB-6O in the SmA phase.

Clear discontinuity in C-13 T_1 values for 10O-PHB-6O in the mixture was observed at the SmA-SmC* transition, indicating slowing down of the reorientaion of the long axis around the director at the transition. This dynamic behaviour may be related to the results that the chiral twin materials decreased the stability of a SmC phase of a host material (see Figure 4). Furthermore, the slowing down at the transition may also be related to the strong twist power of the twin molecule in the SmC* phase. But molecules may not be tilted in the SmC* phase for the system in the magnetic field, thus, we do not give further discussion about dynamics of molecules in the SmC* phase.

C-13 NMR measurements for the system in the unwound mesophases indicate that the chiral twin molecules have little effect on the orientation of the host molecules but affect dynamics of the host molecules in the SmA phase.

A possible model for interlayer correlation induced by chiral twin molecules

The obtained results of the structure-property relationships are summarized in Figure 9.

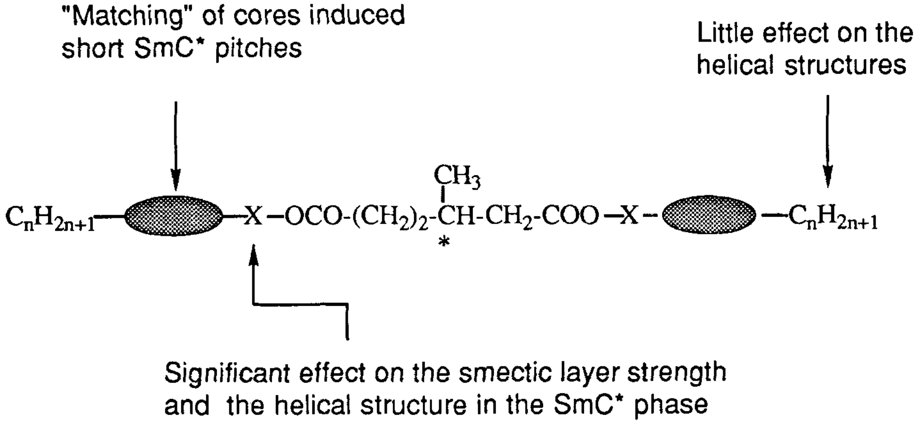


FIGURE 9 The structure-property relationships in the mixture of chiral twin molecules and host molecules.

Let us discuss nature in the interlayer correlation induced by chiral twin molecules. We proposed a possible model for the molecular ordering in the chiral smectic phases, i.e., the chiral twin molecules are intercalated in the SmC-layers formed by the achiral host material as shown in Figure 10.[11] The experimental results presented in this article also support the model.

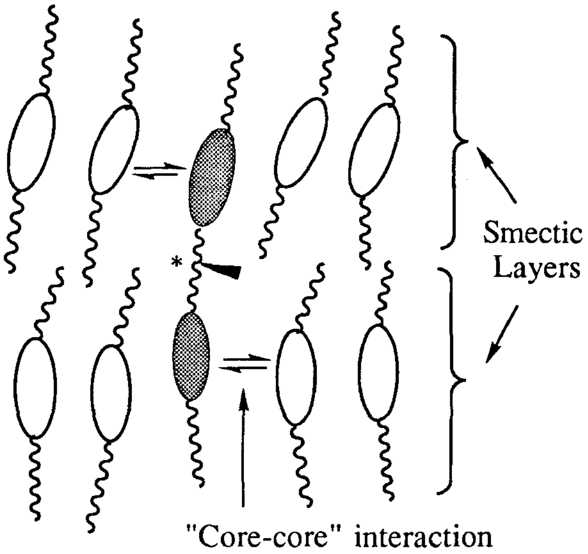


FIGURE 10 Schematic representation of the intercalated chirality produced by the chiral twin molecules in the smectic phases.

In smectic phases for the system of chiral twin molecules and achiral hosts, the chiral twin molecules could be intercalated in the layered structure in such a way that the two core parts exist in adjacent layers. Molecular motion for each core of the twin molecule affect cooperative motion for core parts of the neighbouring host molecules (see Figure 11). The motion of two core parts of the twin molecule is not independent of each other and the relative directions between two core parts depend on the conformation of the chiral spacer. The intercalated chiral twin molecule in the smectic phases may cause a strong correlation between host molecules in adjacent layers. This might be nature in the interlayer correlation induced by chiral twin molecules. Increase of the relationship between two cores of a chiral twin molecule may increase the interlayer correlation but decrease the smectic layer strength.

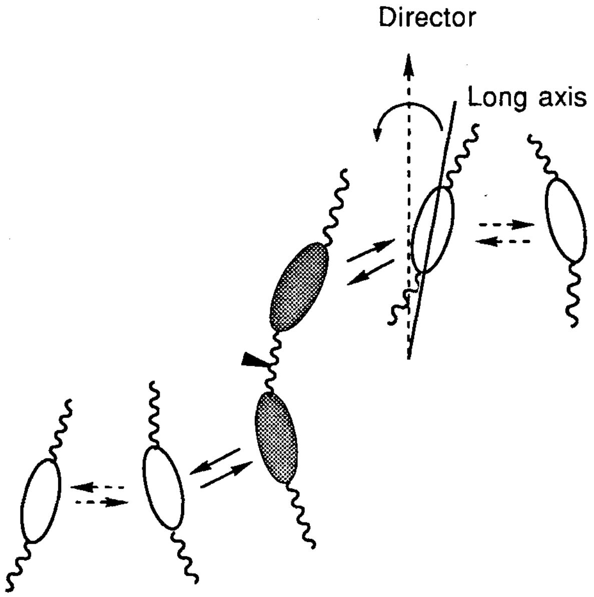


FIGURE 11 A possible model for the "core-core" interaction between chiral twin molecules and host molecules in the SmA phase.

A possible model for the microscopic organization for the system in the I, Ch, SmA, and SmC* phases

Let us discuss about the phase transition behaviour for the system of chiral twin molecules and host molecules. Obtained experimental results allow us to propose a possible model for the microscopic organization of the molecules in the mesophases. Figure 12 shows the schematic representation of the microscopic organization.

The "rigid" chiral twin molecule, i.e. MAB-n-PYP, was found to induce a Ch phase and produce a strong helical structure in a Ch phase. However, the "flexible" chiral twin molecule, i.e., MAB-8-PYPOE, did not induce a Ch phase and produced a weaker helical structure in a Ch phase. A "rigid and long" molecule may disturb the appearence of the smectic layer structure formed by host molecules. With respect to the twisting power of a chiral twin molecule, Allen reported that helical twising power of X shape chiral dopants in a Ch phase depends on the twist angle between two core parts.[25] In our system, although we can not evaluate the twist angle between two cores of the twin molecule, the conformational "rigidity" of a chiral twin molecule and the existence of the ester groups in the chiral spacer are thought to contribute to the helical twisting power in the Ch phase.

In the SmA phase, the "rigid" chiral twin molecule may be thought to induce a strong interlayer correlation and decrease the strength of the smectic layer structure. The coupling of these effects and the helical twisting power of the chiral twin molecule may contribute to the stabilization of the TGB phase.[11] C-13 NMR measurements suggest that the addition of the chiral twin molecule does not change the order parameter for the system but affects molecular motion of each host molecule.

In the SmC* phase, the helical structure induced by a chiral twin molecule depends on structure of its core part and chiral spacer. The "matching" of the core structures between a chiral twin molecule and a SmC host molecule was found to have a significant effect on the production of a strong helical structure.[12] MAB-8-PYPOE with a "flexible" spacer was found to induce a weaker helical structure and induce unexpected twist sense in the SmC* phase.

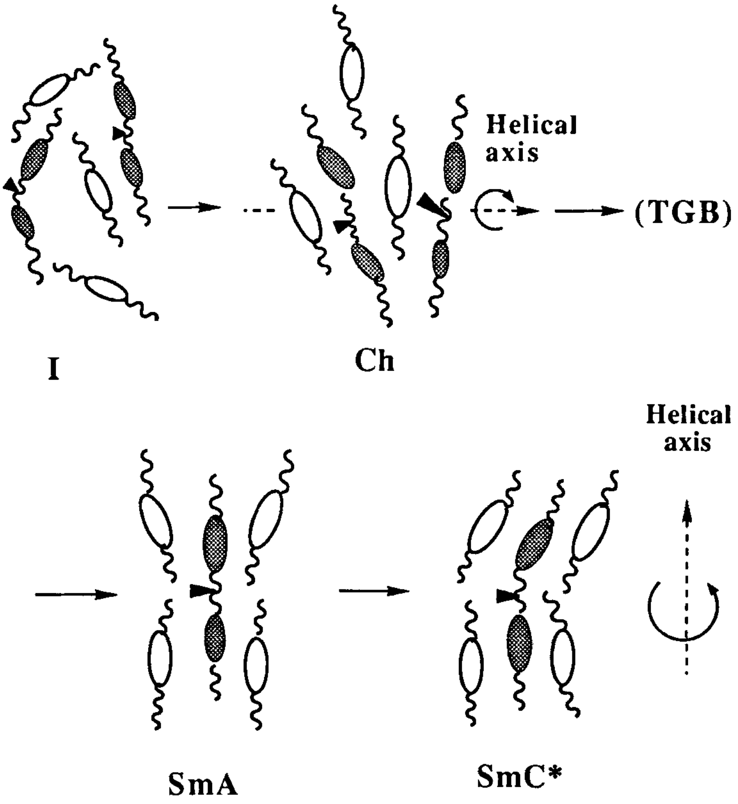


FIGURE 12 A schematic representation of the microscopic organization of chiral twin molecules and host molecules.

Based on our understanding about nature in the twisting power in Ch and SmC* phases, we could control the strength of two kinds of helical structures in the mesophases independently. The "miss matching" of the core structures between a chiral twin molecule and a SmC host molecule, i.e., the system of MAB-CB and a host with a phenylpyrimidine core, induced short pitches only in the Ch phase. On the otherhand, an appropriate mixture of MAB-8-PYP and MAB-8-PYPOE induced a strong helical structure only in the SmC* phase.[15]

CONCLUSIONS

The chiral twin molecules were found to induce a strong interlayer correlation. Molecular design of a chiral twin molecule may allow us to control the strength of the smectic layer structure and chirality-dependent properties for the system. Furthermore, a novel phase transition behaviour can be expected to be observed in the chiral twin system.

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