

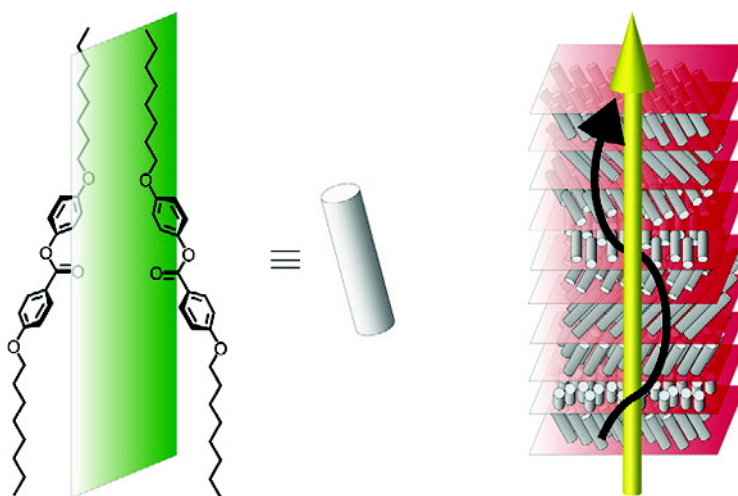
Communication

Generation of a Chiral Mesophase by Achiral Molecules: Absolute Chiral Induction in the Smectic C Phase of 4-Octyloxyphenyl 4-Octyloxybenzoate

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Generation of a Chiral Mesophase by Achiral Molecules: Absolute Chiral Induction in the Smectic C Phase of 4-Octyloxyphenyl 4-Octyloxybenzoate

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Is absolute chiral induction in mesophase generated only by banana-shaped molecules? After the discovery of the chiral mesophase generated by achiral banana-shaped molecules,¹ scientists have been focused on the properties of banana molecules² and the mechanism for the chiral induction. As a result, three possible origins have been proposed based on the banana shape: (1) tilting of the molecule to the layer normal producing the mirror image,^{3,4} (2) twisting of the layers to escape the spontaneous polarization,^{3,5} and (3) a chiral conformation of the ester groups.^{3,6} However, it has not been clarified which is the real origin for the chiral induction, and it has been thought that the banana shape is essential for absolute chiral induction in mesophase. On the other hand, it is well-known that absolute chiral induction in crystal takes place by freezing one chiral conformation of achiral molecules during the crystallizing process in which a banana shape is not essential.⁷ We believe that the realization of this chiral induction process should be also possible in mesophase.

In this communication, we report the first example in which an absolute chiral induction with simple rodlike molecules was observed in mesophase. Compound **1**, 4-octyloxyphenyl 4-octyloxybenzoate, is one of the simplest liquid crystalline compounds that is easily available and has been used for many experiments in past decades.⁸ In an experiment of our dopants, **1** was used as the mother liquid crystalline compound. To our surprise, a chiral induction was observed even without the aid of a dopant.

In the smectic C phase of **1**, plane textures were observed by polarized-light optical microscopy (POM) in the homeotropically aligned sample. The microphotographs are shown in Figure 1. The boundaries between the domains were observed as the bright lines (Figure 1a). The domains were recognized as the difference of brightness which were separated to bright and dark areas by a clockwise rotation (+5°) of the analyzer from the cross-polarization position (Figure 1b), because transmittance of light from one area increased and the other decreased. Then, in the case of a counterclockwise rotation (−5°) of the analyzer from the cross-polarization position (Figure 1c), the bright and dark areas changed with each other. This suggests that the molecules in the neighboring domains generate opposite chirality.

To confirm the chirality of the domains, the CD spectra of **1** in the smectic C phase were measured at room temperature in supercooled state. Figure 2a shows the CD spectra of **1**. The CD spectrum was measured after each cycle in which the sample was heated over the clearing point and then cooled to room temperature. The CD signal was observed as one peak at 300–310 nm in either

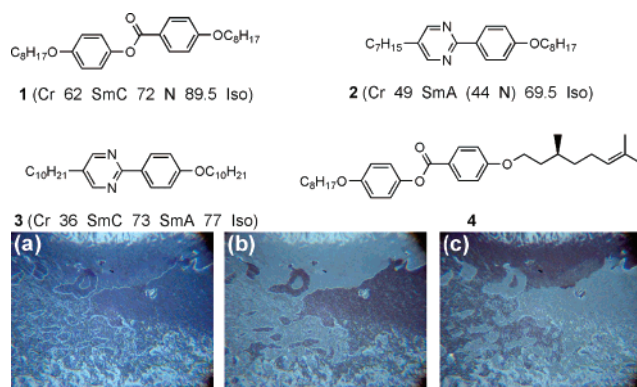


Figure 1. Polarized optical microphotograph of **1** in the smectic C phase at 65 °C (a). Photographs obtained by (b) the clockwise rotation (+5°) of the analyzer from the cross-polarization position and (c) the counterclockwise rotation (−5°) of the analyzer from the cross-polarization position.

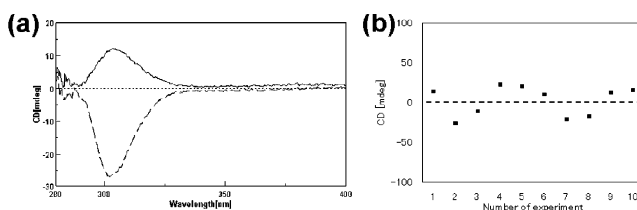


Figure 2. CD spectra of **1** in the smectic C phase at room temperature in supercooled state. (a) The full and dashed lines indicate right- and left-handed helical structures in the smectic C phase. (b) ■ shows the peak intensities of 10 runs.

positive or negative side at random. After 10 runs, the average of the peak intensities was almost zero and the maximum wavelength was almost constant (Figure 2b). This suggested that right- or left-handed helicity was generated in each domain randomly. The result is similar to that of the achiral banana-shaped molecules reported by Thisayukta et al.³

To investigate the dopant effect of **1** on the helicity in the layer structure of a smectic C phase, the following miscibility experiment was performed. A mixture of **2** and **3** (= 1:1) which exhibits a smectic C phase at room temperature was used as the host liquid crystalline compounds. The mixture showed a stable smectic C phase at room temperature up to 30 wt % of **1**. Although the melting points were higher than room temperature at the range of 40–100 wt % contents of **1**, the smectic C phases could be observed at room temperature on cooling in the supercooled state. Figure 3a shows a periodic stripe texture observed in the smectic C phase of the mixture of **1**, **2**, and **3** (30:35:35) in the homogeneously aligned domain. The pitch decreased with decrease in temperature. The observed pitch at constant reduced temperature ($T - T_c = -15$ K)

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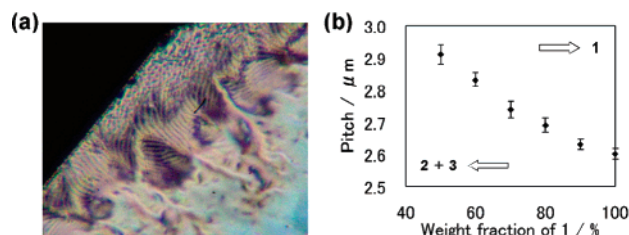


Figure 3. (a) Pitches observed in the smectic C phase of the mixture of **1**, **2**, and **3** (30:35:35) in POM at room temperature. (b) The pitch against the content of **1** in the mixture of **1**, **2**, and **3** in the smectic C phase. The pitches were measured at constant reduced temperature ($T - T_c = -15$ K).

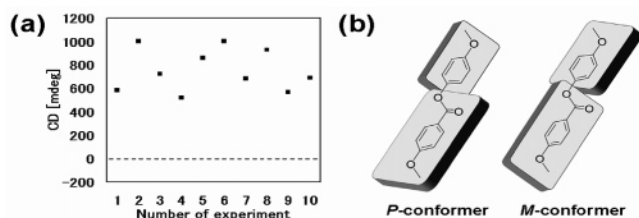


Figure 4. (a) Peak intensities of the CD signals of **1** doped with 10% of **4** (10 runs). (b) Molecular models of the *P*- and *M*-conformers of **1**.

was plotted against the content of **1** in the mixture (Figure 3b). The pitch decreased with increase of the contents of **1**. Accordingly, it was clear that compound **1** generated the periodicity in the smectic C phase. With thinking of the plane textures in the homeotropically aligned sample (Figure 1), it was assumed that the smectic C phase of **1** had a helical layer structure.

To confirm that the two kinds of domains in the plane textures of **1** originated in a chiral induction, a small amount of chiral compound **4** was mixed with **1**, and the optical textures and the CD spectra were investigated. As compared with the result in Figure 1, one kind of domain is observed more predominantly than the other one in the POM observation of **1** with 5 wt % dopant. In Figure 4a, all of the 10 runs in the CD spectrum of **1** doped with 10% of **4** showed only a positive peak at 300–310 nm with strong intensity, 20–30 times stronger than the CD signal of pure **1**. It was assumed that the appearance of the CD signal originated in the helical conformation of the molecule and not in the helical layer structure itself. The fluctuation in the intensity originates in that the chiral induction was not controlled perfectly by the doping.

We propose the mechanism for the chiral induction which is based on intermolecular interaction between the conformers in the smectic C phase. In the AM1 calculation, the angle between the benzoyl plane and the other benzene plane was about 45° in the most stable conformer of **1**, which indicates existence of two chiral conformers, *P*- and *M*-conformers (Figure 4b), although the rotational barrier between them is only 0.3 kcal/mol. The above-mentioned CD signal also suggested existence of the twisted conformation. In each domain, aggregation of conformers with one chirality is preferable than that of racemic conformers. The shape-fitting of one molecule with other molecules is significant during the packing process in liquid crystal as well as that in crystal. Thus, either the *P*- or *M*-conformer becomes the majority in one of the smectic layers, and the chirality of the layer influences the adjacent layers. Finally, one of the chiral conformers exists predominantly in the whole domain.

The results in this study suggest that conformational chirality in the phenyl ester moiety is the origin of the generation of the chiral

smectic phase. In this chiral induction process, it is estimated that dipole–dipole intermolecular interaction between the ester linkages is important to organize the molecules;⁹ however, further study of the intermolecular interactions is necessary.

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Supporting Information Available: The result of miscibility experiment of **1**, **2**, and **3**, synthesis of **4**, details of the CD experiment, and polarized optical microphotographs of **1** doped with **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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