Amplification of Twisting Power in Chiral Mesophase by Introducing Achiral Rod-like Compound with Ester Group

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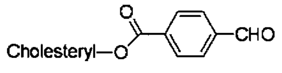
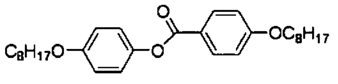
The helical pitch of a chiral nematic (cholesteric: Ch) liquid crystal (LC) became shorter if an achiral compound **1** was added to a chiral host. This unusual behavior characteristic to ester compounds can be explained by the ability of the ester compound **1** to form non-planar conformations.

Self-organization of chiral molecules into helical architectures is of fundamental importance in nature.[1–3] The chirality of the chiral nematic (cholesteric: Ch) liquid crystal (LC) is characterized by the sign and the helical pitch of the chiral organization; i.e., helical structure.[4,5] Generally, the helical pitch tends to become longer by introducing achiral molecules without chiral carbon in the Ch phase.[6] Namely, twisting power is diminished by introducing achiral molecules. Surprisingly, the exception for this general phenomenon can be observed in mixtures with achiral bent-core (banana-shaped) molecules possessing ester groups; the helical pitch of Ch or chiral smectic C (SmC) phases becomes shorter when they are doped with the bent-core molecules.[7–10] Recently, Kajitani et al. reported that even achiral rod-like molecules with an ester group exhibit chiral conglomerates in the SmC phase.[11] Both results suggest that conformational chirality plays an important role for the above unusual phenomena. Recently, Walba and co-workers[12,13] suggested that the occurrence of optically active domains in homeotropic cells of the SmC phase is a result of surface interactions for the phenomenon reported by Kajitani et al.[11] Then, we carried out the doping experiment using rod-like molecules as dopants. The observed phenomena are surprising; whereas the introduction of achiral rod-like molecules with planar conformation to the Ch phase tends to relax the helical pitch, molecules with an ester group, which brings about twisted conformation, tend to tighten the helical pitch.

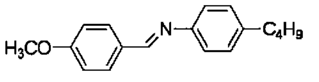
The materials used here are shown in Figure 1. The chiral host compound **A** (cholesteryl 4-formylbenzoate), the same compound used in the advanced work of Thisayukta et al.,[7] exhibits the Ch phase over a wide temperature range. The helical optical pitch in a visible range is convenient to examine the doping effect as the color change and the spectral change due to the Bragg (selective) reflection change. Two different achiral additives are tested; compound **1** (4-octyloxyphenyl 4-octyloxybenzoate) exhibiting two benzene rings linked in a non-conjugated manner by an ester group and compound **2** (*n*-4′-methoxybenzylidene-*n*-butylaniline; MBBA) being a similar, but conjugated Shiff base. Compound **1**, the same compound used in the advanced work of Kajitani et al.,[11] possesses a twisted conformation of the ester groups in molecule itself without chiral carbon, which is referred to as axially desymmetrisationable molecule. Compound **2** is also a typical rod-like compound, but neither chiral carbon nor axial chirality exists in the molecule itself. The mixtures (**A**/**1** and **A**/**2**) showed good miscibility and a stable Ch phase with a wide temperature range (more than 100 °C) on cooling.



Compound A (Iso 250 °C Ch 110 °C Cryst)



Compound 1 (Iso 90 °C N 72 °C SmC 62 °C Cryst)



Compound 2 (Iso 48 °C N 22 °C Cryst)

Figure 1. Chemical structures of materials used in this work.

The helical optical pitches in individual mixture systems were determined from the maximum wavelength of the reflection band in each planar cell. In Figures 2a and 2b, the optical pitch is plotted against the reduced temperature in the cells of

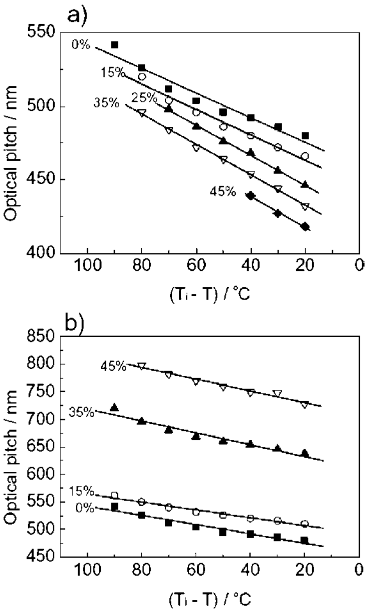


Figure 2. Plots of optical pitch (*nP*, selective reflection wavelength) versus reduced temperature in the Ch phase of the compound **A** with 0–45% of (a) the compound **1** and (b) the compound **2**.

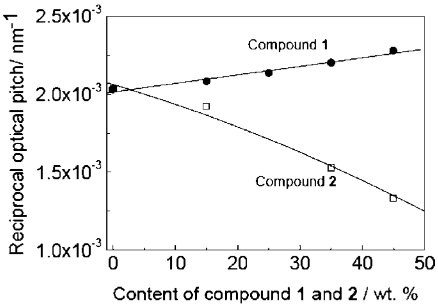


Figure 3. Plots of reciprocal optical pitch ($1/n$P, twisting power) versus the content of rod-like compounds **1** and **2** in the mixtures.

the **A**/**1** and **A**/**2** mixtures, respectively. The pitch decreased with the increase of the content of compound **1**. This surprising phenomenon is similar to that of the achiral bent-core molecules reported by Thisayukta et al.[7] On the other hands, the pitch increased by adding the compound **2**, which is a general trend when doping the Ch phase with achiral molecules.

The reciprocal optical pitch at a certain reduced temperature, $T_\mathrm{i} - T = 40\,^\circ\mathrm{C}$, is plotted against the achiral content in Figure 3. The compound **1** enhances the twisting power, namely, tightens the optical pitch of the compound **A** in the Ch phase. The compound **1** acts as a chiral dopant at the range of concentrations up to 50% or less. For example, in the mixture with **A**:**1** = 55:45, the twisting power becomes 1.12 times as large as that of the pure chiral compound **A**. On the other hands, twisting power decreased steadily with the increase of achiral contents in the mixture with the compound **2**, as usually observed in doping of achiral dopant.

The results of this study suggest that conformational chirality in molecule itself is the origin of the unusual phenomenon. It is no doubt that the rod-like compound **1** with conformational chirality in phenyl ester moiety can behave itself like a chiral species with chiral carbon. According to AM1 calculation, the angle between the benzoyl plane and the other benzene plane was 45° in the most stable conformer of the compound **1**, indicating the existence of two chiral conformers, P- and M-conformers.[11] Of course, the two chiral conformations arise with equal probability in achiral fluid systems. However, if such compound **1** is placed under a chiral field like the Ch liquid-crystalline field, one of the twisted conformations may have the lower potential energy and the degeneracy is lifted. Namely, when compound **1** subjected to the presence of a chiral environment, the equilibrium of conformers is shifted or biased, leading to chiral amplification.[9] Thus, the achiral molecule **1** is now regarded as an axially chiral molecule with preferentially chiral conformation despite of no chiral carbon.

It is important to note that both the bent-core molecule[7] and the present rod-like molecule have ester group(s). This suggests that the bent core is not a necessary condition, but other molecules with axial chirality are possible to act as a chiral dopant. Actually, our preliminary experiments using other rodlike molecules with an ester group also showed the same behavior. The systematic studies are now going on.

Very recently, Walba et al. indicated that the occurrence of optically active domains in homeotropic cells of the SmC phase of compound **1** is a result of pinning of the c-director at the two surfaces, at some relative angle different from 0°, giving twisted configuration.[13] We still cannot conclude whether the phenomenon observed in Ref. 11 is fully attributed to the surface pinning to nucleate twisted geometries or not, as suggested by Walba et al.[13] Even if this is the case, the present result is consistent with the suggestion. Namely, the surface-induced twisted configuration can be also regarded as one of the chiral environments such as cholesteric helical structures used in the present experiment.

In conclusion, a rod-like molecule, compound **1**, with an ester group bearing axially chiral conformations can behave as a chiral dopant in a chiral field like ChLCs. More than 10% increase of the twisting power was found by doping ChLC with the compound **1**. In contrast, the elongation of the helical pitch was observed by adding a rod-like molecule, compound **2**, without axial chirality. The present result together with previous reports by Thisayukta et al.[7] and Kajitani et al.[11] suggests that some molecules with axial conformer can act as chiral molecules in chiral surroundings, even if these molecules are not chiral in their liquid forms.

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