Why Achiral Rod-like Compound with Ester Group Amplifies Chiral Power in Chiral Mesophase

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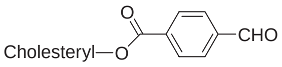
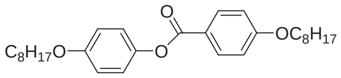
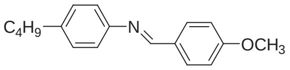
In this work, we carried out ab initio molecular orbital theory calculations for phenylbenzoate and *N*-benzylideneaniline, by which we will interpret unusual phenomenon of compounds 1 and 2.

Generally, chiral twisting power tends to be diminished by introducing achiral molecules without asymmetry carbon(s) in the chiral nematic (cholesteric: Ch) liquid crystal (LC) phase; helical pitch becomes longer by introducing achiral molecules.[1,2] Surprisingly, the exceptions to these general phenomena have been observed in mixtures with achiral molecules possessing ester groups; the helical pitch of ChLCs becomes shorter when ChLC host compound **A** are doped with achiral molecules.[1,2] First, Thisayukta et al.[1] noticed this phenomenon in a ChLC doped with achiral bent-core molecules.[3] Then, very recently, we extended their studies to an achiral rod-like molecule with an ester group.[2] In that work, two different achiral rod-like additives were tested in order to ensure the role of the conformational chirality; compound **1** (4-octyloxyphenyl 4-octyloxybenzoate)[4] with two benzene rings linked in a non-conjugated manner by an ester group and compound **2** [*N*-(4′-methoxybenzylidene)-4-*n*-butylaniline]; MBBA) being a similar, but conjugated Shiff-base.


Compound **A**


Compound **1**


Compound **2**

The unusual phenomenon reported in our previous paper[2] is reproduced in a more intuitive way in Figure 1. The phenomenon is easily recognized by the planar texture observation in the Ch phase, as shown at the top of Figure 1; a mixture with 35 wt % of compound **1** (left), pure compound **A** (center), and a mixture with 35 wt % of compound **2** (right). Here, the textures were observed at the same reduced temperature, $T_\mathrm{i} - T = 40\,°\mathrm{C}$, where T_i is the transition temperature from the isotropic to the Ch phase on cooling. With increasing the fraction of the compound **1** from 0 to 35%, the reflection color clearly changes from green to blue, showing the tightening of the helical pitch. On the other hands, with increasing the fraction of the compound **2** from 0 to 35%, the reflection color clearly changes from green to red, exhibiting the relaxation of the helical pitch, which is a general phenomenon when introducing achiral molecules in the Ch phase.

The CD spectra due to the selective reflection are also shown in Figures 1a (**A**/**1** mixture) and 1b (**A**/**2** mixture). The optical 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.[1] On the other hands, the optical pitch increased by adding the compound **2**, as usually expected when doping the Ch phase with achiral molecules.

The experimental fact observed in the **A**/**1** mixture strongly suggests that the bent core is not a necessary condition, but other molecules with axial chirality are possible to act as a chiral dopant.[2] If such molecules, which have two chiral conformers, P- and M-conformers, are 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, resulting in axially chiral molecules with preferentially chiral conformation despite of no chiral carbon.[5] Then, these axially chiral molecules can lead to chiral amplification in Ch liquid crystalline field. Namely, our results suggest that conformational chirality in molecule itself plays an important role for the above unusual phenomena. According to the conformational analysis by density functional theory calculation, Ph–C(=O)–O and Ph–C=N are confined on the same plane. However, both achiral rod-like additives tested in this work could possess twisted (chiral) conformations.[6] Moreover, the dihedral angle of benzylideneaniline in compound **2** is expected to be nearly the same as that of phenylbenzoate in compound **1**. Yet, the compounds **1** and **2** show opposite tendency; the former tightens the helical pitch and the latter relaxes the pitch, as mentioned above. What are key factors to bring about this difference?

Herein, we carried out ab initio molecular orbital theory calculations[7] for phenylbenzoate and *N*-benzylideneaniline, by which we will interpret the above unusual phenomenon of compounds **1** and **2**. The internal rotation potential was obtained as a function of dihedral angle around C–O bond in Ph–O moiety for phenylbenzoate and that around C–N bond in Ph–N moiety for *N*-benzylideneaniline. First, full optimization was carried out at MP2/6-31+G(d,p) with the fixed dihedral angles around C–O and C–N. Step size for rotation of the dihedral angles was 5 degrees.

Figure 2 shows the relative energy as a function of dihedral angle. Two stable twisted conformations are found in both phenylbenzoate and *N*-benzylideneaniline. There are two paths from one stable conformer to the other stable conformer, as shown in Figure 3. The one is a transition via parallel position between the phenyl rings (dihedral angle = 0 or 180°), and the other via perpendicular (dihedral angle = −90 or 90°). The former path is obstructed by high energy barriers in both

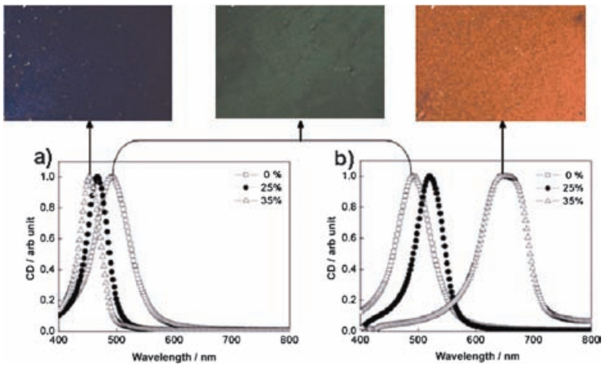


Figure 1. CD spectra due to the selective reflection observed at $T_i - T = 40\,°C$ in the ChLC planar cells of (a) compound **A**/compound **1** and (b) compound **A**/compound **2** mixtures. Some of the corresponding photomicrographs are also shown.

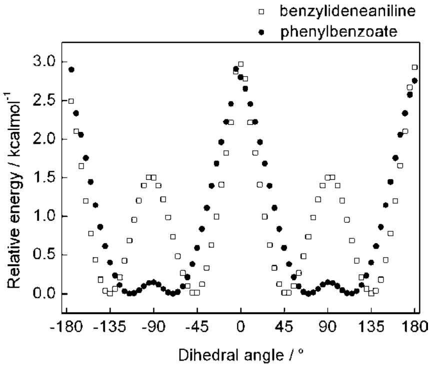


Figure 2. Internal rotation potential against the dihedral angles of phenylbenzoate and *N*-benzylideneaniline at MP2/6-31+G(d,p).

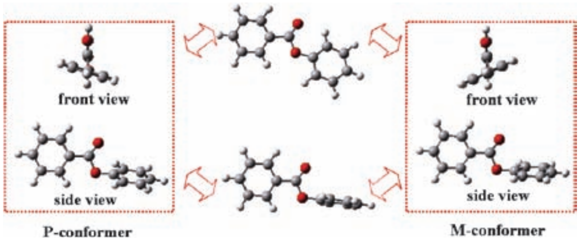


Figure 3. Two transition paths from a conformer to the other conformer of phenylbenzoate.

molecules (2.93 kcal/mol for phenylbenzoate and 2.97 kcal/mol for *N*-benzylideneaniline). By contrast, the potential barriers for the latter path are lower. Particularly, only a very low barrier (0.15 kcal/mol) exists in phenylbenzoate, while *N*-benzylideneaniline has higher barrier (1.52 kcal/mol). This low barrier enables the compound **1** to easily change the conformation to the one consistent with the sense of the external chiral environment. Thus, the compound **1** can possess a preferential twisted conformation and becomes axially chiral, when it is embedded in chiral environment. However, the barrier of the compound **2** cannot explain the experimental observation, because the barrier of the compound **2** is not high enough to prevent from biasing a preferential twisted conformation even in chiral environment.

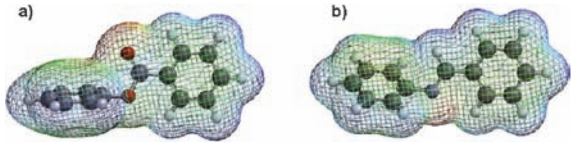


Figure 4. Isoelectron density surface with electrostatic potential of (a) phenylbenzoate and (b) *N*-benzylideneaniline at MP2/6-31+G(d,p). Colors toward red and blue respectively depict negative and positive potentials with intermediate ones by other colors.

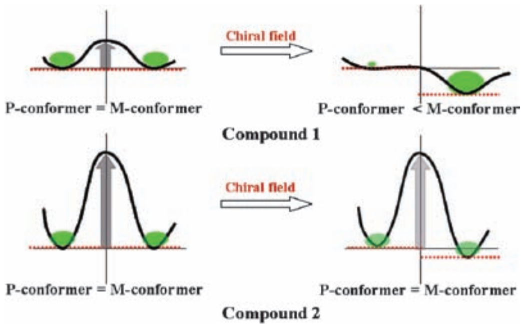


Figure 5. Schematic illustration showing the change of the potential surfaces for compounds **1** and **2** perturbed by chiral field.

Figure 4 displays isoelectron density surface with electrostatic potential of phenylbenzoate and *N*-benzylideneaniline. The molecular shape of phenylbenzoate is sterically bulky, while that of *N*-benzylideneaniline is more planar. In addition, phenylbenzoate has negative electrostatic potential on carbonyl carbon, while *N*-benzylideneaniline seems relatively neutral, as shown by color variation in Figure 4. Based on the potential surface together with these molecular shape and electrostatic properties, one possible explanation for the unusual observation is the distinct perturbation effect of chiral field on the potential surface of conformers with possible axial chirality (Figure 5). The potential surface of compound **1** perturbed by chiral field leads to a preference of one of axially chiral conformers or even to the disappearance of one of the potential minima. By contrast, the potential surface of compound **2** is less influenced by chiral field (at least by the host compound **A**) and keeps two energy minima. Because of small energy difference and low energy barrier between them, preferential chirality never emerges.

References and Notes

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