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Synthesis and Helical Twisting Power of Various 6,6'-Substituted Binaphthyl Type Chiral Dopants

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Abstract

Generally, binaphthyl type chiral dopants bridged by alkyl chain at 2,2'-position are known to possess a large ability to twist the molecular alignment in a given nematic host phase, which is expressed by helical twisting power (HTP). Moreover, the 6,6'-fluoronated binaphthyl type chiral dopant exhibited a large HTP value and high solubility in a fluorinated nematic liquid crystal. In this study, we synthesized the non-substituted, 6,6'-halogenated and methylated binaphthyl type chiral dopants and investigated influence of size of their substituents or polarity and polarizability of chiral dopants on their HTP values. The 6,6'-chlorinated chiral dopant was found to show the highest |HTP| value among synthesized chiral dopants. The observed |HTP| values were closely correlated with size of their substituents.

1. Introduction

The lack of mirror symmetry, referred to as chirality, has a remarkable influence on the macroscopic physical properties of materials. The chirality provides liquid crystals with unusual optical properties, ferro- and antiferro-electricity, and even the appearance of exotic phases like blue phases. Because of such unique properties, the chiral liquid crystals have potential applications in low energy consumption displays, fast light shutters, flexible e-papers, and so on[1]. The development of chiral liquid crystals or chiral dopants which enable to form chiral nematic liquid crystals from a nematic liquid crystal, therefore, has attracted considerable attention.

Chiral dopants are asymmetric compounds possessing chirality such as central, axial, and planer chirality and helicity. The ability of a chiral dopant to form the chiral nematic liquid crystal from a host nematic liquid crystal is evaluated by Helical Twisting Power (HTP) expressed as below,

$$\mathrm{HTP} = (P \times c_w)^{-1}$$

where HTP is helical twisting power [μm^{-1}], P is helical pitch of the chiral nematic phase [μm] and c_w is weight percent concentration of the chiral dopant [wt%].

A previous study with respect to a relationship between the HTP value and the chemical structure of chiral dopants suggested that binaphthyl type chiral dopants bridged by alkyl chain at 2,2'-position exhibited a large HTP value[2]. Moreover, we previously synthesized the 6,6'-fluorinated binaphthyl type chiral dopant and reported that it possessed a large HTP value and high solubility in the fluorinated host nematic liquid crystal[3]. However, their chirality transfer mechanism between the chiral dopant and the host nematic liquid crystal has not been understood well. The development of a chiral dopant will be accelerate for practical utilizing electric devices by deep understanding of the mechanism.

In this study, we synthesized various 6,6'-substituted binaphthy type chiral dopants and examined dominant molecular factors like size, polarity and polarizability of their substituents affecting the chirality transfer between the chiral dopant and the host nematics.

2. Experimental Section

2.1. Synthesis

We synthesized non-substituted, 6,6- halogenated and -methylated binaphthyl type chiral dopants (**Figure 1**).

2.2. Measurement of HTP values

Synthesized chiral dopants were dissolved in the host nematic liquid crystal, JC-1041XX (JNC Co.), to prepare 0.5wt% sample solutions. Prepared samples were stirred at a temperature of isotropic phase of the solution for 3 hours and injected in a Grandjean-Cano wedge shaped cell. After cooling to a chiral nematic phase, the interval distances of striped defect lines appeared in the cell were measured at several temperatures below clearing point by means of a polarizing

optical microscope.

2.3. Identification of the helical sense of chiral dopants

The helical sense of synthesized chiral dopants was determined by a contact method with the cholesteryl oleyl carbonate (COC) as a reference material. 0.5wt% samples doped with chiral dopants were injected from the one side of the Grandjean-Cano wedge-shaped cell and COC was injected from the other side of its cell. After static standing for several hours, the helical sense was determined by utilizing polarizing optical microscope.

3. Results and Discussion

Total yields of non-substituted, 6,6'- fluorinated, -chlorinated, -brominated, -iodinated and -methylated binaphthyl type chiral dopants were 58%, 3%, 23%, 47%, 22% and 16% , respectively.

The helical sense of all chiral dopants was left-handed (–) based on the results from the contact method. Generally, the dihedral angle between two naphthyl planes of a binaphthyl type chiral dopant in a host nematic liquid crystal are estimated by comparing differences in the helical sense of its chiral dopant[2]. In case of (*R*)-binaphthyl type chiral dopants, the left-handed sense and the right-handed one correspond to the *cisoid* conformation and the *transoid* conformation, respectively. Therefore, conformations of all synthesized chiral dopants in the host nematic liquid crystal corresponded to the *cisoid* conformation.

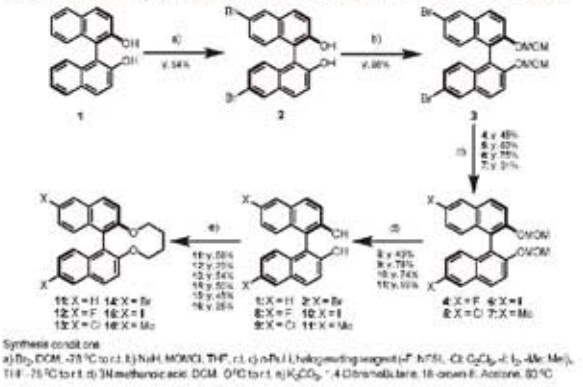

Figure1. Synthesis of various 6,6'-substituted binaphtyl type chiral dopants.

Absolute average values of HTP (|HTP|) of non-substituted, 6,6-fluorinated, chlorinated, brominated and iodinated chiral dopants were 47.5, 51.3, 56.1, 44.9 and 35.3 μm^{-1}, respectively (**Figure 2**).

The 6,6'-chlorinated chiral dopant showed the highest |HTP| value among synthesized chiral dopants. On the other hand, |HTP| values of chiral dopants decreased with increasing the size of halogen groups. We will report the HTP value of the 6,6'-mathylated chiral dopant and relationship between temperature dependence HTP values and effects of their substituents.

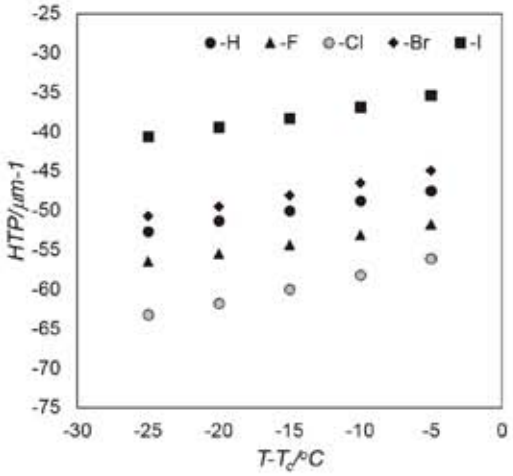

Figure 2. Temperature dependence of HTP values of non-substituted and 6,6'-harogenated binaphyl-type chiral dopants. (Where T_c is clearing point.)

4. Conclusion

Various 6,6'-substituted binaphtyl type chiral dopants were synthesized. Their helical sense and conformations in the host nematic liquid crystal were entirely left-handed (–) and the *cisoid* conformation. |HTP| values of the 6,6'-chlorinated chiral dopant was the highest value (56.1 μm^{-1}) among the synthesized chiral dopants. Moreover, there was a good correlation between the |HTP| values and the size of their substituents.

Acknowledgment

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