Helical Twisting Power of Optically Active Spiro Compounds with a 3,3′-(4*H*,4′*H*)-Spirobi(2*H*-naphtho[1,2-*b*]pyran) Skeleton

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New chiral dopants for nematic liquid crystals, containing a (*S*)-3,3′-(4*H*,4′*H*)-spirobi(2*H*-naphtho[1,2-*b*]pyran) skeleton, were synthesized and their helical twisting powers (HTP) were evaluated. A chiral dopant with two terphenyl structures showed the highest molar HTP value of 50.3 μm^{-1} mol^{-1} kg.

Chirality is one of the most interesting subjects in the field of liquid crystals. Chiral nematic liquid crystals with a macro helical structure are currently used in liquid crystal display (LCD) devices. Generally, chiral nematic materials consist of a mixture of achiral host nematic liquid crystals and a chiral dopant with large helical twisting power (HTP).[1,2] A helical structure is induced in the chiral nematic liquid crystals by the interaction between the host liquid crystalline molecules and the chiral dopant. Many optically active compounds with asymmetric carbons have been synthesized and used as dopants to induce chiral nematic phases.[1–8] It has been reported that biaryl chiral dopants with axial chirality show large HTP values.[2,9–12] In particular, conformational fixation of 1,1′-binaphthyl-2,2′-diol (BINOL) derivatives has been shown to be effective in achieving large HTP values. In previous studies, conformational fixation was found to increase the molar HTP value of BINOL derivatives from 0.38 to 21 μm^{-1} mol^{-1} kg.[2,12]

Optically active spiro compounds have a more rigid structure than axially chiral compounds. Therefore, optically active spiro compounds have been used as chiral ligands for asymmetric synthesis[13] and as chiral dopants for smectic liquid crystalline mixtures.[14] However, the subject of optically active compounds with a spiro structure remains largely unexplored in the field of chiral dopants for nematic liquid crystals.

We recently reported the synthesis of a novel optically active spiro carboxylic acid, 3,3′-(4*H*,4′*H*)-spirobi(2*H*-naphtho-[1,2-*b*]pyran)-6,6′-dicarboxylic acid (**1***, Figure 1).[15] The two naphthalene rings of **1*** are fixed by the spiro structure. The compounds may easily be converted to its ester derivatives. In this paper, we report the HTP values of derivatives of **1*** and discuss their potential as chiral dopants for nematic liquid crystals (**2***–**4***, Figure 2). The rigid structure of the spiro part is thought to suppress conformational changes. Based on the interaction of the aromatic rings of the chiral dopants with those of the host liquid crystalline molecules, these novel dopants were expected to show large HTP values.

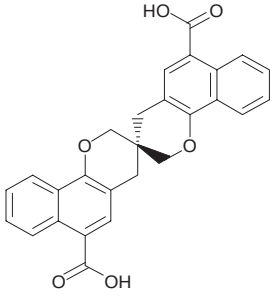
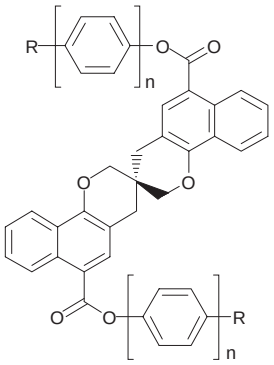


Figure 1. Structure of (*S*)-(−)-**1***.

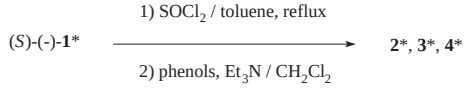


2*: n = 1, R = $-OC_8H_{17}$

3*: n = 2, R = $-OC_8H_{17}$

4*: n = 3, R = $-C_7H_{15}$

Figure 2. Structures of novel chiral dopants **2***–**4***.



Scheme 1. Synthesis of novel chiral dopants **2***–**4***.

The novel chiral dopants **2***–**4*** were derived from (*S*)-(−)-**1*** and phenols (Scheme 1).[16] The chiral nematic liquid crystalline mixtures were prepared by adding the chiral dopant (1 wt %) to the host nematic liquid crystal (ZLI-1132, Merck).[17] The helical pitch of the chiral nematic phase was measured using Cano wedge cells.[18] The HTP values were calculated based on eq 1, where p is the pitch of the chiral nematic phase (in μm) and c is the mass fraction of the chiral dopant. In order to describe HTP per molecule, we used the value of molar helical twisting power (MHTP), as defined in eq 2, where Md is the molecular weight of the chiral dopant.[6]

$$\mathrm{HTP} = (pc)^{-1} \quad (1)$$

$$\mathrm{MHTP} = \mathrm{HTP} \times \mathrm{Md} \times 10^{-3} \quad (2)$$

The helical senses of the chiral nematic phases were determined by the contact method using a reference mixture of the host liquid crystal and cholesteryl nonanoate, which features a left-handed helix (minus sense). The helical pitch, HTP and MHTP values of the new chiral dopants are summarized in

Table 1. HTP and MHTP values of **2***–**4***

Chiral dopant	n	R	Optical purity/%	Helical pitch[a] /μm	HTP[b] /μm^{-1}	MHTP[c] /μm^{-1} mol^{-1} kg
2*	1	$-OC_8H_{17}$	97.9	−4.63	−21.1	−17.9
3*	2	$-OC_8H_{17}$	>99.9	−2.42	−38.2	−38.2
4*	3	$-C_7H_{15}$	>99.9	−2.14	−46.1	−50.3

[a]Measurement method: Cano wedge cell; measurement temperature: room temperature. [b]HTP (μm^{-1}) = $(pc)^{-1}$; p: helical pitch (μm), c: weight ratio of chiral dopant (c: 0.01). [c]MHTP (μm^{-1} mol^{-1} kg) = HTP × Mr × 10^{-3}; Mr: molecular weight of the chiral dopant, host L.C.: ZLI-1132 (Merck).

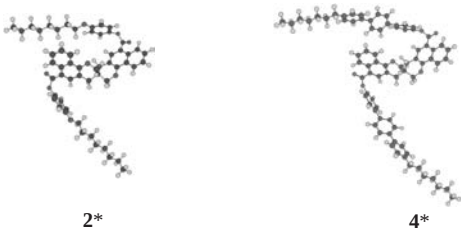


Figure 3. PM3-optimized conformations of **2*** and **4***.

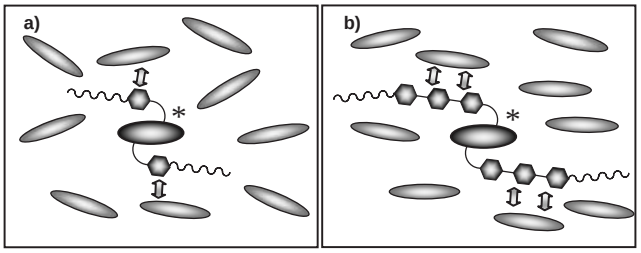


Figure 4. Image of the interaction between the chiral dopant molecule and the host liquid crystalline molecule. a) In the case of **2***. b) In the case of **4***.

Table 1. All the novel chiral dopants derived from (*S*)-(−)-**1*** induced a minus-sense helix and showed large MHTP values. The absolute MHTP values of the new chiral dopants were in the order **4*** > **3*** > **2***. The value of **4*** was the largest, at 50.3 μm^{-1} mol^{-1} kg; this is larger than those generally observed for chiral dopants with asymmetric carbons,[1–8] and was comparable with or larger than those of chiral dopants with axial asymmetric chirality.[2,9–12,19] It is thought that the large MHTP values are due to conformational fixation of asymmetric chirality by the spiro structure. It is suggested that the phenyl rings of the chiral dopants interact with the aromatic rings of the host liquid crystalline molecule via π–π interactions. As biphenyl and terphenyl moieties are rigid, rod-like structures, it is expected that chiral dopants with rod-like moieties readily align in the same direction as the host liquid crystalline molecules, resulting in efficient interaction between the chiral dopants and the host liquid crystalline molecules (Figure 3 and 4). Therefore, the absolute MHTP value was proportional to the number of phenyl rings.

In conclusion, novel chiral dopants with a (*S*)-3,3′-(4*H*,4′*H*)-spirobi(2*H*-naphtho[1,2-*b*]pyran) skeleton induced minus-sense helices and showed large MHTP values. It was also found that the MHTP values of the chiral dopants were proportional to the size of their aromatic moieties. We have indicated that these optically active spiro compounds can be used as chiral dopants for nematic liquid crystals.

References and Notes

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16 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp./journals/chem-lett/index.html.
17 The host liquid crystalline mixture (ZLI-1132, Merck) consists of 4-(4-propylcyclohexyl)benzonitril (24 wt %), 4-(4-pentylcyclohexyl)benzonitril (36 wt %), 4-(4-heptylcyclohexyl)benzonitril (25 wt %), and 4-{4-(4-pentylcyclohexyl)phenyl}benzonitril (15 wt %). The host liquid crystalline mixture shows a nematic liquid crystal phase in the range −6 to 70 °C.
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19 For example, the MHTP values of the imine chiral dopant with two (*R*)-naphthylethylamine moieties[3] is 40.0 μm^{-1} mol^{-1} kg, that of the tetrasubstituted BINOL derivative[9] is 19.7 μm^{-1} mol^{-1} kg, and that of the optically active biphenol derivative[10] is 50.0 μm^{-1} mol^{-1} kg.

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