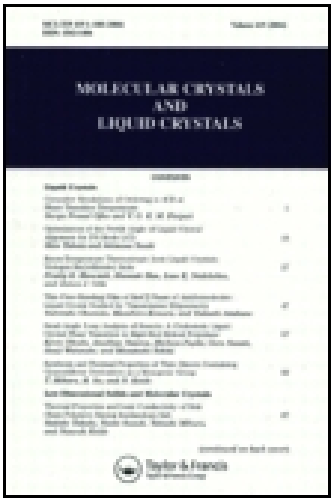

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Helical Twisting Power of New Chiral Dopants Having a Trifluoromethyl Group at the Chiral Center for Nematic Liquid Crystals

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HELICAL TWISTING POWER OF NEW CHIRAL DOPANTS HAVING A TRIFLUOROMETHYL GROUP AT THE CHIRAL CENTER FOR NEMATIC LIQUID CRYSTALS

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New chiral dopants for nematic liquid crystals were synthesized using optically active 4,4,4-trifluoro-3-phenylbutanoic acid. The magnitude of helical twisting power (HTP) was largely influenced by the linkage between the asymmetric frame and the core moiety. The chiral dopant, 4,4,4-trifluoro-1-(4-hexyloxyphenyl)-3-phenyl-1-butanone showed extremely large HTP value (21.0 μm^{-1}).

Keywords: nematic liquid crystal; chiral dopant; helical twisting power; trifluoromethyl

INTRODUCTION

Chirality is one of the most interesting subject in liquid crystals [1,2]. Recently liquid crystals are widely applied to flat panel display devices of mobile computers and TV sets. A liquid crystal display (LCD) is of grater advantage than a CRT for size, thickness, weight and power consumption. Chiral nematic liquid crystals applicable to super twisted nematic (STN) devices are attractive materials [3]. Generally the chiral nematic materials consist of achiral host liquid mixtures, which have low viscosities and the wide range of nematic phase, and a chiral dopant having a large helical twisting power (HTP). Therefore, chiral dopants having a large HTP value are required, and many optically active compounds for application in nematic mixtures have been synthesized [4–6]. We reported simple compounds having a methyl group at the chiral center showed a large HTP value (See Fig. 1) [7].

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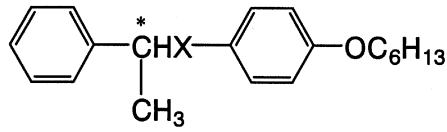


1*:X=COO, HTP=7.8 μm^{-1}, MHTP=2.5$\mu m^{-1}mol^{-1}Kg$
2*:X=CH_2O, HTP=7.2 μm^{-1}, MHTP=2.3 $\mu m^{-1}mol^{-1}Kg$
3*:X=CO, HTP=10.3 μm^{-1}, MHTP=3.19 $\mu m^{-1}mol^{-1}Kg$
4*:X=CH_2, HTP=16.5 μm^{-1}, MHTP=4.88 $\mu m^{-1}mol^{-1}Kg$

FIGURE 1 Chiral dopants derived from 2-phenylpropanoic acid.

In particular, 1-(4-hexyloxyphenyl)-2-phenylpropane (**4***) showed the extremely large HTP value (16.5 μm^{-1}). In this paper, optically active 4,4,4-trifluoro-3-phenylbutanoic acid was synthesized and new chiral dopants were derived from it. A trifluoromethyl group is a strongly polarized group. The relationship between the HTP values and the dipole at the chiral center of the chiral dopants is discussed.

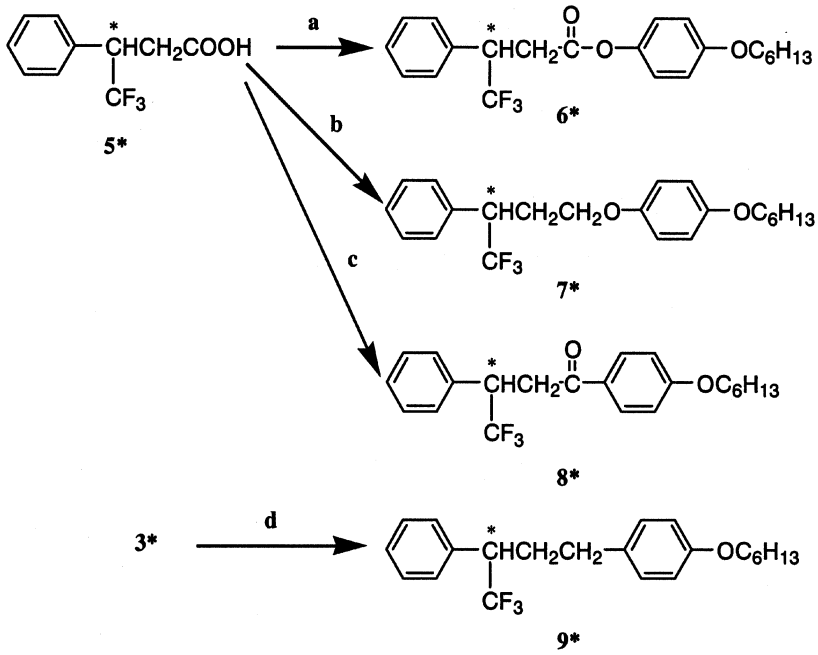
EXPERIMENTS

4,4,4-Trifluoro-3-phenylbutanoic acid (**5**) was synthesized in a usual way [8]. Optically active **1** was prepared by diastereomeric salt formation method using optically active *erythro*-2-amino-1,2-diphenylethanol as a resolving agent. New chiral dopants were synthesized in a usual way (See Scheme 1).

They did not show any liquid crystalline phase, so that only their HTP values were determined. The chiral nematic liquid crystalline mixtures were prepared by adding one weight percent of a chiral dopant to the host liquid crystal (ZLI-1132, Merck). Helical pitches (p) in chiral nematic phases were measured using Cano wedge cell ($\tan\theta = 0.0083$, 0.0140, 0.0194, 0.0288, E.H.C.) [9]. The HTP values were calculated from the pitch of the chiral nematic phase in μm (p) and the weight concentration ratio (c), namely HTP = 1/pc (μm^{-1}). In order to discuss a HTP by a molecule, we suggest molar helical twisting power (MHTP), which is defined as the following equation [7];

$$\mathrm{MHTP} = (\mathrm{pW})^{-1} = \mathrm{HTP} \times \mathrm{Mw} \div 1000(\mu m^{-1}\,\mathrm{mol}^{-1}\,\mathrm{Kg})$$

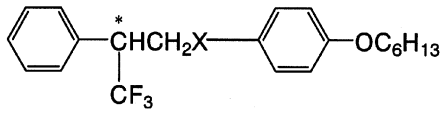
where W is the moles of the chiral dopant per 1 Kg of the mixture, and Mw is molecular weight of the chiral dopant.



a) core, DCC, DMAP b) 1)$LiAlH_4$ 2)TsCl, DABCO c) 1)$SOCl_2$ 2)core, $AlCl_3$ d) Et_3SiH, CF_3COOH

SCHEME 1 Synthesis of new chiral dopants.

TABLE 1 Helical Twisting Power of Chiral Dopants



Chiral dopants	X	HTP/μm^{-1}	MHTP*/$\mu m^{-1}\,mol^{-1}\,kg$
2*	COO	6.5	2.9
3*	CH_2O	15.2	5.8
4*	CO	21.0	7.9
5*	CH_2	5.8	2.1

*MHTP = HTP × Mw ÷ 1000. Mw shows molecular weight of a chiral dopant.

RESULTS AND DISCUSSION

The helical twisting power of new chiral dopants are summarized in Table 1. The HTP values and the MHTP values are largely influenced by the linkage between the asymmetric frame and the core moiety. The order of HTP values in these chiral dopants was **8*** > **7*** > **6*** > **9***. The chiral dopant, 4,4,4-trifluoro-1-(4-hexyloxyphenyl)-3-phenyl-1-butanone (**8***) having a carbonyl group showed the largest HTP value ($21.0\,\mu m^{-1}$), while the chiral dopant **9*** showed the smallest HTP value ($5.8\,\mu m^{-1}$).

The HTP value of **7*** is larger than that of **6***. Along with the case of the derivatives from 2-phenylpropanoic acid (Fig. 1), it is shown that a carbonyl group does not always contribute to increase the HTP value. In the chiral dopant **8***, a carbonyl group is conjugated with a benzene ring, so that these lie on the same plane. This planar structure probably contributes to induce a HTP value. Kuball and coworkers reported chiral induction by optically active aminoanthraquinones [10]. They analyzed the intra- and intermolecular chirality transfer, and concluded that the chiral induction depended on the direction of the orientation axis. It is thought that a structure of **8*** effectively induces a helical structure.

On the other hand, the order of HTP values in the chiral dopants having a methyl group at the chiral center was **4*** > **3*** > **1*** ∼ **2***. The fact **4*** dose not have any strongly polarized groups in the molecule suggests that a steric effect is important to induce a helical macrostructure. Nishiyama and coworkers reported a relationship between chiral compounds and their HTP values, and a certain chiral dimer was found to induce strong helical macrostructures [11,12]. According to their discussion, the present chiral dopants are probably classified into 'a twin molecule' which may exhibit special steric effects on the chirality dependent properties. In order to compare each chiral structure, the MHTP values of the chiral dopants are discussed. The MHTP values of **6***, **7*** and **8*** were greater than those of **1***, **2*** and **3***, respectively. From these data, it is shown that the contribution of a trifluoromethyl group to the MHTP values is larger than that of a methyl group. However, the MHTP value of **4*** was much larger than that of **9***. The chain length between the chiral center and the core moiety largely influences the HTP and the MHTP, because the closer the chiral center to the core, the less the freedom of its movement due to steric hindrance with the rigid core. A helical macrostructure is probably induced by a steric effect and an electronic effect of chiral dopant. However, it is difficult to discuss the effect of steric factor and electronic factor separately. From the present results, we conclude that the dopants having a trifluoromethyl group at the chiral center show the relatively large HTP values, however a strongly polar group at the chiral center does not always induce a large HTP value.

REFERENCES

[1] Goodby, J. W. (1991). *J. Mater. Chem.*, *1*(3), 307.
[2] Goodby, J. W. (1997). *Mol. Cryst. Liq. Cryst.*, *292*, 245.
[3] Scheffer, T. J. & Nehring, J. (1984). *Appl. Phys. Lett.*, *45*(10), 1021.
[4] Pauluth, D. & Wächtler, A. E. F., (1997). Chirality in Industry II, A. N. Collins, G. N. Sheldrake and J. Crosby Eds., John Wiley & Sons Ltd pp. 263–286.
[5] Aoki, Y., Shitara, H., Hirose, T. & Nohira, H., (2001). *Bull. Chem. Soc. Jpn.*, *74*, 2219.
[6] Shitara, H., Aoki, Y., Hirose, T. & Nohira, H., (2000). *Bull. Chem. Soc. Jpn.*, *73*, 259.
[7] Aoki, Y. Nomoto, S., Hirose, T. & Nohira, H., (2000). *Mol. Cryst. Liq. Cryst.*, *346*, 35.
[8] Aoki, Y. & Nohira, H. (1995). *Liq. Cryst.*, *18*(2), 197.
[9] Cano, R. (1968). *Bull. Soc. fr. Minéral. Cristrallogr.*, *91*, 20.
[10] Kuball, H.-G., Müller, T. H., Brüning, H., & Schönhofer, A. (1995). *Mol. Cryst. Liq. Cryst.*, *261*, 205.
[11] Nishiyama, I., Ishizuka, H., & Yoshizawa, A. (1993). *Ferroelectrics*, *147*, 193.
[12] Yoshizawa, A. & Nishiyama, I. (1994). *J. Mater. Chem.*, *4*(3), 307.