Synthesis and Helical Twisting Power of Optically Active 2-Methylchroman-2-carboxylic Acid Derivatives as New Chiral Dopants for Nematic Liquid Crystals

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Optically active 2-methylchroman-2-carboxylic acid derivatives as new chiral dopants for nematic liquid crystals were prepared from optically active 6-benzyloxy-2-methylchroman-2-carboxylic acid, which was newly synthesized and resolved by diastereomeric salt formation method. The helical twisting power of the dopants was determined and the relationship with their structures were studied.

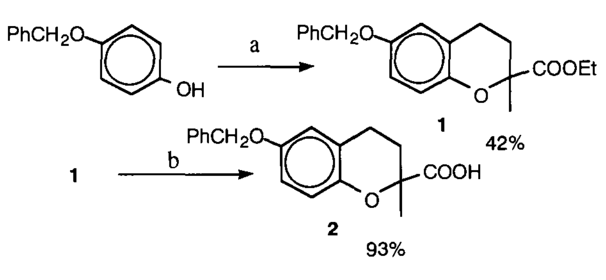
Recently many chiral dopants for nematic liquid crystals have been studied for the application to TN (twisted nematic) and STN (super twisted nematic) display devices.[1] Chiral guest compounds dissolved in a nematic host phase induce cholesteric phases. The strength of this chiral induction can be estimated by the helical twisting power (HTP) (eq. 1)[2]

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

where p is the pitch of the cholesteric phase in μm and c is the mass fraction of the solute.

The HTP depends on the molecular structures of the guest (dopant) and host (nematic phase) molecules. However, knowledge of the relationship between HTP and molecular structures is not clear yet. In this paper, we wish to study this relationship using five optically pure 2-methylchroman-2-carboxylic acid derivatives **1***-**5***. They have a common bulky and restricted cyclic structure at the asymmetric center but different terminal groups. The chiral induction ability was discussed from the comparison of their HTP.

The racemic 6-benzyloxy-2-methylchroman-2-carboxylic acid **2** were prepared by hydrolysis of its ester **1**, which is easily prepared from the reaction of hydroquinone monobenzyl ether (1 mol equiv) with ethyl methacrylate (4.9 mol equiv) and paraformaldehyde (1.1 mol equiv) under reflux conditions in the presence of di-*n*-butylamine (0.1 mol equiv) and acetic acid (0.49 mol equiv) (Scheme 1).[3]



a) $CH_2=C(CH_3)COOEt$, $(HCHO)_n$, n-Bu_2NH, AcOH, 120 °C.
b) NaOH, MeOH, 50°C.

Scheme 1.

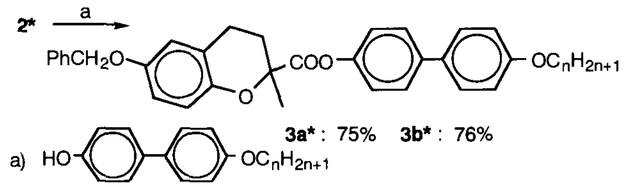
Optical resolution of **2** was performed by fractional crystallization of the diastereomeric salts with optically active *cis*-2-benzylaminocyclohexanemethanol (*cis*-Amine)[4] and the salt was recrystallized from ethyl acetate. Its results and some properties of **2*** are shown in Table 1.

Table 1. Optical resolution of (±)-**2**

Salt[a]		(-)-**2**		O.P.	Yield	Resolving
$[\alpha]_D$[b]	mp /°C	$[\alpha]_D$[b]	mp/°C	/%e.e.[c]	/%[d]	efficiency[e]
-17.8°	142~146	-32.9°	113~117	92.7	51	47

a) (-)-(2)-(+)-*cis*-Amine. b) Solvent: 99% EtOH, c 1.0, 27 °C. c) The optical purity of **2*** was determined as its ethyl ester using HPLC equipped with a chiral column,"CHIRALCEL OJ" (Daicel Chem. Ind., Ltd., 4.6 mm x 250 mm, carrier solvent 35% 2-propanol/hexane). d) The yields were calculated based on half the amount of racemic **2**. e) Resolving Efficiency = Yield x %e.e./100

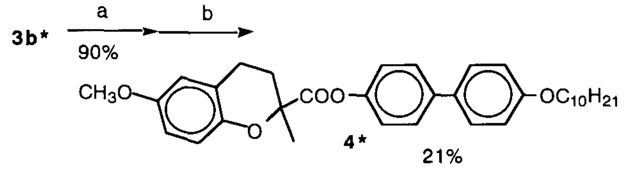
The chiral dopants **3a*** and **3b*** were obtained by esterification of **2*** with corresponding biphenol derivatives (Scheme 2).



(**3a***: n=6, **3b***: n=10), DCC, DMAP, CH_2Cl_2, rt.

Scheme 2.

Debenzylation of **3b*** over palladium-carbon and successive etherification with methyl iodide afforded **4*** (Scheme 3).



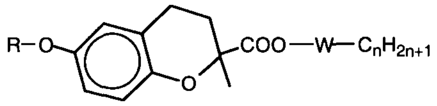
a) H_2, Pd-C, THF, rt. b) CH_3I, K_2CO_3, acetone, 63°C.

Scheme 3.

Biphenyl group was introduced to the aromatic side of **2*** by esterification with 1-butanol, debenzylation, and subsequent esterification with dodecyloxybiphenylcarboxylic acid to obtain **5*** (Scheme 4).

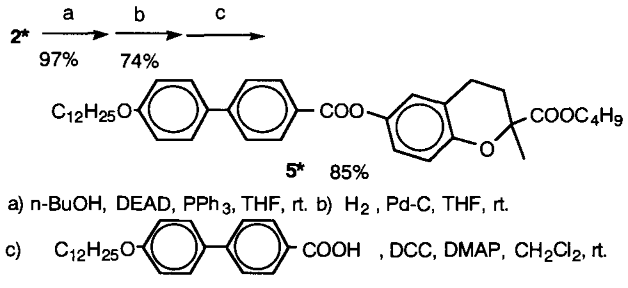
The helical pitch of the cholesteric phase was measured using wedge-shaped samples, contained between a convex lens and a plane glass plate, by means of the resulting Cano lines.[5] The liquid crystal (LC) sample was prepared by adding 1 wt% of a chiral dopant into the achiral host LC mixture ZLI-1132 (Merck). The HTP of LC mixtures and the specific rotations of chiral

Table 2. Helical twisting power (HTP)[a] and specific rotations of chiral dopants



Chiral dopant	R	W	n	$[\alpha]_D{}^b$ / °	HTP / μm^{-1}
1*	$PhCH_2$	-	2	29.5	11.2
3a*	$PhCH_2$	$C_6H_4C_6H_4O$	6	3.3	3.01
3b*	$PhCH_2$	$C_6H_4C_6H_4O$	10	-1.2	4.00
4*	CH_3	$C_6H_4C_6H_4O$	10	8.4	0
5*	$C_{12}H_{25}OC_6H_4C_6H_4CO$	-	4	14.3	8.77

a) Host liquid crystal (ZLI-1132):dopant = 99:1 (by weight).
b) Solvent: $CHCl_3$, c 1.0, 27°C.



a) n-BuOH, DEAD, PPh_3, THF, rt. b) H_2, Pd-C, THF, rt.
c) $C_{12}H_{25}OC_6H_4C_6H_4COOH$, DCC, DMAP, CH_2Cl_2, rt.

Scheme 4.

dopants are summarized in Table 2.

From Table 2, it is clearly shown that 2-methylchroman structure potentially has a good chiral induction ability. However HTP was completely lost by substitution of a benzyl group (**1**, **2a***, and **2b***) in R by a methyl group (**4***). From this drastic change, additional aryl group is requisite for chiral induction at the 6-position of 2-methylchroman. Biphenyl group in R is also very effective considering HTP of **5*** and its molar ratio in the sample. On the other hand, the structure at the asymmetric center has smaller effect. The dopant **1*** having ethyl ester exhibits the highest HTP while **3a*** and **3b*** bearing larger ester terminal have lower HTP. At this aliphatic side, biphenyl group is not as effective as at the aromatic part mentioned above. For larger chiral induction by 2-methylchroman moiety, additional aryl group on its aromatic side and small group in the vicinity of chiral center (W and n in Table 2) is effective. From the synthetic and applicative point of view, the dopant **1*** seems very promising.

In conclusion, it is shown that 2-methylchroman, easily prepared from inexpensive starting materials, becomes a good chiral induction ability, which is as good as (comparable to) some commercial products like (*S*)-4-cyano-4'-(2-methylbutyl)biphenyl (HTP = 9.6 μm^{-1}) and cholesteryl nonanoate (HTP = 4.4 μm^{-1}).[1a] In its design, an additional aryl group at its 6-position and a compact structure at the chiral center are important.

References and Notes

1 a) D. Pauluth and A.E.F. Wachtler, "Synthesis and Application of Chiral Liquid Crystals," in "Chirality in Industry II," ed by A.N. Callins, G.N. Sheldrake, and J. Crosby, Wiley, Chichester (1997), Chap. 13, p. 263. b) H.-G. Kuball, T.H. Müller, H. Brüning, and A. Schönhofer, *Mol. Cryst. Liq. Cryst.*, **261**, 205 (1995).

2 G. Vertogen and W. H. de Jeu, "Thermotropic Liquid Crystals, Fundamentals, " Springer, Berlin (1988).

3 a) E. Nishimura, M. Torihara, and Y. Tamai, Japan Patent 7-97380 (1995). b) H. Shitara, H. Miura, H. Konno, and H. Nohira, Presented at the 72 nd Annual Meeting of the Chemical Society of Japan, Ikebukuro, 1997, Abstr., 2PB081.

4 J. Nishikawa, T. Ishizaki, F. Nakayama, H. Kawa, K. Saigo, and H. Nohira, *Nippon Kagaku Kaishi*, **1979**, 754.

5 R. Cano, *Bull. Soc. Franc. Mineralog. Crystallogr.*, **91**, 20 (1968).