Dehydroabietic Acid Esters as Chiral Dopants for Nematic Liquid Crystals

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Dehydroabietic acid esters were prepared as new chiral dopants for the nematic liquid crystals. The magnitude of the helical twisting power (HTP) was good due to simple but rigid three-ring structure and two axial methyl groups. The relationship between the HTP or MHTP (molar helical twisting power) values and the terminal structures was studied. Considering the synthetic accessibility and their miscibility with liquid crystals, the acid was shown to be a good candidate as the scaffold of chiral dopants for the nematic liquid crystals.

Currently, not only lap-top computers but also more and more desk-top computers have a liquid-crystalline display (LCD), which is one of the most important applications of liquid crystals (LCs).¹ The LCs used in the displays are mostly in a nematic phase having chirality, which is therefore called a "chiral nematic phase" (N*). The chiral nematic phase is controlled by an electrical field, and interaction with polarized light is the basic principle of the widely used LCD. Chiral nematic phases can be prepared from optically active liquidcrystalline molecules, like cholesteryl benzoate, which is the first liquid crystal prepared by Reinitzer,² or from non-chiral nematic phases doped with an optically active molecule as a chiral dopant, such as cholesteryl nonanoate (CN).^{1a} Today, all commercial LCDs are composed in the latter style.

The strength of chiral induction by a dopant, i.e., the helical twisting power (HTP), can be estimated by using Eq. $1,^3$

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

where *p* is the pitch of the chiral nematic phase in μ m and *c* is the mass fraction of the dopant. In order to discuss the effect of molecular characteristics on HTP, we have introduced the idea of molar helical twisting power (MHTP) defined by Eq. 2.⁴

$$MHTP = HTP \cdot M_w / 1000 \ (\mu m^{-1} \ mol^{-1} \ kg)$$
(2)

A high HTP value allows for thin LCDs or a low content of the dopant, and the value depends on the molecular structures of both the chiral dopant as well as the host nematic LC. HTP depends on the structure of the chiral dopant as a guest in a certain host nematic LC. Therefore, new chiral dopants with larger values of HTP are still required for new LCs and for further improvement of the LCD performance. However, the relation between the HTP and the molecular structures is not well established.^{5,6}

Chiral dopants are often designed to have similar structures to the host LCs, which usually have rigid "cores" and long flexible chains. At the same time, however, they need to be compact so as not to increase the viscosity of the LC phases, and they must be economical for industrialize. Recently, we have investigated the HTP of chiral chroman derivatives, which are easily synthesized and resolved.⁷ The chroman derivatives have a rigid two-ring structure bearing a quaternary asymmetric center and flexible terminal groups and, as a result, two flexible but short side chains were found to be effective to obtain $11.2 \,\mu\text{m}^{-1}$ for ethyl 6-benzyloxy-2-methylchromane-2-carboxylate.⁷

In the framework of our chiral recognition work, dehydroabietic acid (DAA) (1^*) has been shown to be an effective resolving agent for some 2-aminoalcohols.⁸ Dehydroabietic acid is an interesting natural compound as it is readily available and has three asymmetric carbons. Structurally, DAA has a restricted three-ring structure and a carboxyl group is directly attached to a quaternary asymmetric carbon in a cyclohexyl ring. We expected certain DAA derivatives can be chiral LCs and/ or good chiral dopants for calamitic LC molecules, like cholesterol derivatives.

In this paper, we report new chiral dopants (2^*-8^*) , Chart 1, derived from DAA, and discuss the relation between the HTP or MHTP and the molecular structures of the dopants.

Results and Discussion

Structures of DAA and Its Ester. The crystal structure of DAA was obtained by X-ray single-crystal diffraction analysis and the crystal data are summarized in Table 1. As shown in



Chart 1. Chiral dopants used in this study.

Empirical formula	C40H56O4
Formula weight	600.85
T/K	123(2)
Crystal dimensions/mm ³	$0.45 \times 0.45 \times 0.12$
Crystal color, shape	colorless, prism
Crystal system	Monoclinic
Space group	P2 ₁
a/Å	11.538(2)
b/Å	11.713(2)
c/Å	13.675(3)
$\dot{\beta}/^{\circ}$	108.29
$V/Å^3$	1754.8(6)
Z	2
$D_{ m calcd}/ m Mgm^{-3}$	1.137
μ (Mo K α)/mm ⁻¹	0.071
Reflections collected	12347
Independent reflections	7209 [$R(int) = 0.0188$]
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0572, wR2 = 0.1574
<i>R</i> indices (all data)	R1 = 0.0616, wR2 = 0.1635
GOF	1.262



Fig. 1. Crystal structure of dehydroabietic acid.

Fig. 1, the structure is rather planar, and the carboxyl group is in an equatorial position, while two methyl groups on the asymmetric carbons are in a 1,3-diaxial arrangement (Fig. 1b). These features distinguish the two sides of DAA, and basically, it has the same structure as that of the methyl ester,⁹ except for the conformation of the ester and the carboxylic acid parts. Both AM1 and PM3 calculation using MOPAC¹⁰ on the most stable conformations of methyl, phenyl, and hexyloxyphenyl esters gave the same structures as that shown in Fig. 1, even though DAA forms a dimeric structure due to hydrogen bonding between carboxyl groups.

Synthesis of Chiral Dopants. In order to study the effect of a side chain, the length of an alkyl group was changed from C1 (2^*) to C10 (5^*) , and the effect of an aromatic structure was also investigated using 6^*-8^* .

Dopant 2^* , was derived from (+)-DAA (1^*) by direct esterification with methanol (Scheme 1), and 3^*-8^* were obtained by the reaction of the acid chloride with the corresponding primary alcohols or phenols (Scheme 2). Unexpectedly, no ester Dehydroabietic Acid Esters as Chiral Dopants



Scheme 1. Synthesis of methyl dehydroabietate (2^*) .



Scheme 2. Synthesis of dehydroabietic acid esters (3^*-8^*) .



COO-W-C_nH_{2n+}

Compound	W	n	HTP ^{b)}	MHTP ^{b)}
			$/\mu m^{-1}$	$/\mu m^{-1} \text{ mol}^{-1} \text{ kg}$
2*		1	-11.5	-3.61
3*	_	6	-7.35	-2.83
4*	_	8	-7.00	-2.79
5*		10	-6.53	-2.69
6*	$\langle \bigcirc \rangle$	—	2.89 ^{c)}	1.09 ^{c)}
7*	⊘}-o	6	-8.23	-3.92
8*	@ \ _o	6	-9.00	-4.84

a) Host liquid crystal (ZLI-1132):dopant = 99:1 (by weight). b) The minus sign shows a left-handed helical sense of the nematic phase. c) The handedness was not measurable due to small HTP.

derivatives showed liquid crystallinity, and they were liquid at room temperature except for 2^* , which was obtained as solid. All of the esters were miscible with the host LC (ZLI-1132) and were a good dopants because they did not cause phase separation in or raise viscosity of the LC phase.

Relationship between Structure and Helical Twisting Power of Dehydroabietic Acid Derivatives. The HTP of each chiral dopant was measured as a 1 wt % mixture with the host LC,11 and the results calculated using Eq. 1 are summarized in Table 2 together with the MHTP. Most of them induced a left-handed helicity in CN. The HTP of commercially



Fig. 2. Alkyl chain length of dehydroabietic acid alkyl esters (2^*-5^*) and HTP correlation.

available CN is known to be $4.4 \,\mu m^{-1}$, which is the same as the host LC.^{1a} Comparing the HTP data of 2^*-5^* , the ring structure of DAA should have a good chiral-induction ability, e.g., $11.5\,\mu\text{m}^{-1}$ for 2^{*}, comparable to the chroman derivatives.⁷ However, the HTP values gradually decreased as the alkyl chain length increased: 3^* (n = 6), 7.35 µm⁻¹; 4^* (n = 8), 7.00 μ m⁻¹; and **5**^{*} (*n* = 10), 6.53 μ m⁻¹ (*n* in Table 2). Thus, as shown in Fig. 2, the alkyl chain length of the ester group has a weak negative effect on the HTP. It is in contrast to the relationship reported by Emoto et al. for chiral 4'-(2-alkanovloxypropoxy)biphenyl derivatives.¹² They use chiral alcohols as the terminal moiety, while the present system has an asymmetric center in the acid moiety in a ring structure and the terminal alcohol units are achiral. The positional difference of the chiral center is the major reason for the opposite effect of the alkyl chain length.

On the other hand, introduction of rigid phenyl group without an alkyl chain largely decreased the HTP for 6^* . Although the carboxyl group is equatorial to the ring structure (Fig. 1), the additional bulky phenyl group might reduce the planarity and lessen the affinity or interaction with the host LC molecules. However, introduction of flexible *n*-hexyloxy group increased the HTP for 7^* (8.23 µm⁻¹), and a slight increase in HTP (9.0 µm⁻¹) for 8^* having a biphenyl group was observed. In fact, their MHTP became higher than that of 2^* . The combination of aromatic and aliphatic structures in an alcohol moiety seems promising for further improvement.

Correlations between the molecular structure of a dopant and helicity of induced chiral LC have been investigated and discussed for many systems.^{13,14} Ferrarni, Spada, et al. have presented a model that includes a shape term and a reaction field term to explain the chiral induction and the HTP by chiral biphenyls in nematic LCs.^{14d} The first term is related to the molecular shape, and the second term is related to atomic properties, chemical structures, and flexibility of functional groups or substituents. Recently, it has been reported that the dopant shape, not its chirality, causes the switch in handedness of nematic LCs.13c,14d Considering the present dopants, however, all DAA derivatives are structurally close each other, and the HTP sign does not change. In fact, the stable conformation, simulated with MM215 and MOPAC 2002,10 gave similar structures for 2^* , 3^* , 6^* , and 7^* . As shown in Fig. 3 for 2^* and 6^* , in spite of apparently similar structures, a major



(a) Simulated stable conformations of 2^*



(b) Simulated stable conformations of 6*

Fig. 3. Simulated structures of 2^* (a) and 6^* (b) based on AM1 calculation. Quite similar results were obtained by PM3 calculation and also for 3^* and 7^* .

difference was found in the dihedral angle for $(H_3)C-C-C=O$, that is the direction of a carbonyl dipole, between alkyl esters, 2^* and 3^* , and phenyl esters, 6^* and 7^* . Although the simulated structures may not be the real ones in the nematic LC, it should be the factor of a reaction field model. Further studies are in progress in order to accumulate additional data on electrostatic interactions caused by functional groups and substituents.

In conclusion, it was shown that optically active dehydroabietic acid esters are good chiral dopants with high miscibility to the host LC. By arranging a short alkyl ester group, such as methyl ester, high HTP was induced (HTP = $11.5 \,\mu m^{-1}$, MHTP = $3.61 \,\mu m^{-1} \,mol^{-1} \,kg$) probably because the structure has an appropriate balance of rigidity and bulkiness between the dehydroabietic acid and alcohol moieties. The aromatic core having an alkoxy group at the *para* position effectively to induced helical structure (HTP \cong 9 µm⁻¹, MHTP \cong 4–5 µm⁻¹ mol⁻¹ kg). Although the relation between the ester structure and HTP seems complex, it is similar to that of the chroman derivatives, which also contain a carboxyl group on a quaternary asymmetric carbon.⁷

Experimental

Infrared spectra were recorded on a JASCO FT/IR 400 spectrometer. Melting temperatures were determined on Mel-Temp melting point apparatus (Laboratory Devices, MA) and were reported uncorrected. The measurement of ¹HNMR spectra was performed on Bruker AC300P and AC200, DPX400 spectrometers, and EI-MS spectra were recorded on a JEOL DX303 spectrometer (Molecular Analysis and Life Science (MALS) Center, Saitama University). Specific rotations were measured with a JASCO DIP-370 polarimeter. The computations were performed with MM2 (CAChe ver. 7.5)¹⁵ and MOPAC 2002 (AM1 & PM3, CAChe ver. 7.5).¹⁰

Dehydroabietic Acid (DAA) (1*). Dehydroabietic acid was kindly supplied by Arakawa Chemical Industries Ltd. and purified to >99% purity according to the literature:¹⁶ mp 170–171.5 °C, $[\alpha]_D^{30}$ +61.8° (*c* 1.0, MeOH) (lit.: mp 170–171.5 °C, $[\alpha]_D^{20}$ +62.5°, *c* 2.0, 95% EtOH).^{7,12}

Measurement of HTP and Handedness of the Induced Chirality. The LC sample was prepared by adding 1 wt % of a chiral dopant into the achiral host LC mixture ZLI-1132 (Merck). The helical pitch of the chiral nematic phases were measured using wedge-shaped samples, contained between a convex lens and a plane glass plate (Cano-wedge cell, $\tan \theta = 0.0083$, 0.0140, 0.0194, 0.0288, E. H. C. Ind., Ltd.,) by means of the resulting Cano lines.¹¹ All solvents were used as received except for dry tetrahydrofuran and dry pyridine used in the synthesis of most of the DAA esters.

The handedness of an induced helix was determined by the contact method with the mixture of the achiral host LC and CN (2 wt %), which is known to cause left handedness.^{1a}

Crystal Structure Analysis of DAA (1*). Data collection was performed on a Bruker SMART CCD system (MALS Center) with graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å) at 123 K. The linear absorption coefficient, (μ), for Mo K α was 0.071 mm⁻¹. The crystal structure was solved by a direct method with *SIR97*¹⁷ and refined by full-matrix least-squares using *SHLEXL97*¹⁸ to a final reliability value of 0.0572. The non-hydrogen atoms were refined anisotropically while the hydrogen atoms were located at geometrically calculated positions.

Crystallographic data for DAA have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-299433 for DAA. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 36033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of Methyl Dehydroabietate (2*). A 50-mL roundbottom flask, equipped with a magnetic stirring bar and a reflux condenser topped by a CaCl₂ drying tube, was charged with dehydroabietic acid 1* (125 mg, 0.417 mmol). Methanol (20 mL) and conc. H₂SO₄ (5 drops) was added, and the reaction mixture was heated under reflux for 24 h. The reaction mixture was concentrated under reduced pressure and diluted with ether (15 mL). The mixture was washed with sat. NaHCO₃ aq, water, brine, and dried over anhyd. NaSO₄. The solution was concentrated to dryness, and the residue was purified by chromatography (silica gel, hexane:ethyl acetate = 20:1). The eluent was concentrated to obtain the product as a white solid (99.0 mg, 0.315 mmol, 75.7%): mp 62–62.8 °C, $[\alpha]_D^{34}$ +54.4° (*c* 1.0, MeOH) (lit.: mp 63–64.5 °C, $[\alpha]_D^{20}$ +61°);¹⁹ ¹H NMR (200 MHz, CDCl₃) δ 7.16 (d, *J* = 8.30 Hz, 1H), 6.99 (d, *J* = 8.30 Hz, 1H), 6.88 (s, 1H), 3.66 (s, 3H), 2.97–2.70 (m, 3H), 2.43–2.11 (m, 2H), 1.97–1.35 (m, 10H), 1.27 (s, 3H), 1.22 (d, *J* = 6.84 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 16.48, 18.56, 21.69, 23.96 (2C), 25.08, 29.98, 33.45, 36.63, 36.93, 37.98, 44.84, 47.65, 51.87, 123.88, 124.11, 126.86, 134.68, 145.70, 146.91, 179.12; IR (KBr) 2930, 1718, 1496, 1251, 1176, 822 cm⁻¹.

Synthesis of Hexyl Dehydroabietate (3*). General procedure: A 30-mL, two-necked, round-bottom flask, equipped with a magnetic stirring bar and a reflux condenser protected from moisture by a CaCl₂ drying tube, was charged with dehydroabietic acid 1* (217 mg, 0.723 mmol). Thionyl chloride (2 mL) was added in one portion, and the reaction mixture was heated at reflux for 3 h. Excess thionyl chloride was removed under reduced pressure. The flask was flushed with nitrogen, and dry tetrahydrofuran (THF, 2 mL), dry pyridine (500 µL), and then 1-hexanol (80.5 mg, 0.780 mmol) were added. After stirring at rt for 48 h, the salt was removed by filtration, and the filtrate was concentrated under reduced pressure to dryness. The residue was dissolved in ether, and the solution was poured into a separatory funnel and washed with water (15 mL \times 2). The organic layer was dried over anhyd. NaSO₄. The solution was concentrated under reduced pressure to dryness, and the residue was purified by chromatography (silica gel, hexane: ethyl acetate = 4:1). The eluent was removed to obtain a colorless oil (103 mg, 0.268 mmol, 34.4%). ¹H NMR (300 MHz, CDCl₃) δ 7.17 (d, J = 8.27 Hz, 1H), 7.00 (d, J = 8.27 Hz, 1H), 6.88 (s, 1H), 4.01-3.99 (m, 2H), 2.95-2.70 (m, 3H), 2.42-2.15 (m, 2H), 1.94–1.10 (m, 27H), 0.877 (t, J = 6.80 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 14.08, 16.33, 18.15, 22.96, 23.64, 23.95 (2C), 25.97, 26.09, 28.91, 30.35, 31.56, 33.58, 36.51, 37.05, 37.79, 43.69, 46.51, 60.89, 123.49, 125.04, 128.78, 132.56, 146.91, 153.05, 177.29; IR (neat) 2932, 1724, 1497, 1460, 1244, 1173, 822 cm^{-1} ; $[\alpha]_{D}^{32} + 26.9^{\circ}$ (*c* 1.0, MeOH).

Synthesis of Octyl Dehydroabietate (4*). Prepared as described in the general procedure, **4**^{*} (114 mg, 0.277 mmol) was obtained as colorless oil in 34.4% yield from **1**^{*} (241 mg, 0.803 mmol) and 1-octanol (105 mg, 0.808 mmol). ¹H NMR (300 MHz, CDCl₃) δ 7.17 (d, J = 8.07 Hz, 1H), 7.00 (d, J = 8.07 Hz, 1H), 6.89 (s, 1H), 4.20–3.95 (m, 2H), 3.00–2.78 (m, 3H), 2.40–2.20 (m, 2H), 1.94–1.10 (m, 31H), 0.878 (t, J = 6.60 Hz, 3H); IR (neat) 2925, 1723, 1497, 1467, 1245, 1174, 822 cm⁻¹; $[\alpha]_D^{32} + 35.8^{\circ}$ (*c* 1.0, EtOH). Found: C, 81.34; H, 11.03%. Calcd for C₂₈H₄₄O₂: C, 81.49; H, 10.74%.

Synthesis of Decyl Dehydroabietate (5*). Following the general procedure, **5*** (162 mg, 0.368 mmol) was obtained as colorless oil in 32.7% yield from **1*** (338 mg, 1.13 mmol) and 1-decanol (179 mg, 1.13 mmol). ¹H NMR (300 MHz, CDCl₃) δ 7.17 (d, J = 8.09 Hz, 1H), 7.00 (d, J = 8.09 Hz, 1H), 6.88 (s, 1H), 4.20-3.95 (m, 2H), 2.92–2.70 (m, 3H), 2.39–2.20 (m, 2H), 1.82–1.69 (m, 6H), 1.65–1.55 (m, 1H), 1.40–1.15 (m, 28H), 0.878 (t, J = 6.62 Hz, 3H); IR (neat) 2926, 1724, 1497, 1460, 1245, 1173, 822 cm⁻¹; $[\alpha]_{D^2}^{D^2}$ +30.5° (*c* 1.0, EtOH). Found: C, 81.37; H, 10.91%. Calcd for C₃₀H₄₈O₂: C, 81.76; H, 10.97%.

Synthesis of Phenyl Dehydroabietate (6^{*}). Following the general procedure, 6^{*} (155 mg, 0.412 mmol) was obtained as a colorless oil in 43.4% yield from 1^{*} (269 mg, 0.897 mmol) and phenol (89.3 mg, 0.949 mmol). ¹H NMR (300 MHz, CDCl₃) δ 7.50–7.31 (m, 3H), 7.25–7.13 (m, 3H), 7.00 (d, *J* = 8.09 Hz, 1H), 6.88 (s, 1H), 2.92–2.70 (m, 3H), 2.39–2.20 (m, 2H), 1.95–1.75 (m,

81.97; H, 8.62%. Calcd for C₂₆H₃₂O₂: C, 82.93; H, 8.57%.

Synthesis of 4-Hexyloxyphenyl Dehydroabietate (7*). Following the general procedure, 7* (220 mg, 0.462 mmol) was obtained as a colorless oil in 46.1% yield from 1* (301 mg, 1.00 mmol) and 4-hexyloxyphenol (479 mg, 1.01 mmol). ¹H NMR (300 MHz, CDCl₃) δ 7.52 (d, J = 8.43 Hz, 2H), 7.47 (d, J = 8.43 Hz, 2H), 7.20 (d, J = 8.45 Hz, 1H), 7.06 (d, J = 8.45 Hz, 1H), 6.91 (s, 1H), 3.99 (t, J = 6.62 Hz, 2H), 3.05–2.80 (m, 3H), 2.46 (d, J = 11.4 Hz, 1H), 2.36 (d, J = 12.9 Hz, 1H), 2.10–1.70 (m, 7H), 1.70–1.11 (m, 20H), 0.912 (t, J = 6.96 Hz, 3H); IR (neat) 2931, 1734, 1499, 1459, 994, 821 cm⁻¹; $[\alpha]_D^{34} + 35.6^{\circ}$ (*c* 0.5, CHCl₃).

Synthesis of 4'-Hexyloxybiphenyl-4-yl Dehydroabietate (8*). Following the general procedure, **8**^{*} (260 mg, 0.471 mmol) was obtained as a colorless oil in 45.3% yield from **1**^{*} (312 mg, 1.04 mmol) and 4'-hexyloxybiphenyl-4-ol (281 mg, 1.04 mmol). ¹H NMR (300 MHz, CDCl₃) δ 7.52 (d, J = 8.40 Hz, 2H), 7.47 (d, J = 8.80 Hz, 2H), 7.19 (d, J = 8.00 Hz, 1H), 7.08–6.08 (m, 4H), 6.95 (d, J = 8.00 Hz, 1H), 4.00 (t, J = 8.80 Hz, 2H), 3.03–2.89 (m, 3H), 2.83 (m, 1H), 2.46 (d, J = 12.4 Hz, 1H), 2.36 (d, J = 12.8 Hz, 1H), 2.06–1.40 (m, 7H), 1.38–1.28 (m, 20H), 0.912 (t, J = 7.00 Hz, 3H); IR (neat) 3465, 2950, 1744, 1608, 1497, 1205, 1166, 822 cm⁻¹; EI-MS (70 eV) m/z (rel. intensity) 552 (M⁺; 22), 299 (35), 270 (100); [α]_D³⁴ +34.7° (*c* 0.5, CHCl₃).

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