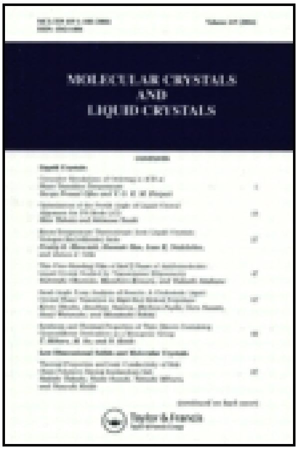

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Novel Chiral Dopants Derived from (2S)-2-(6-Hydroxy-2-naphthyl)propionic Acid for Ferroelectric Liquid Crystal Mixtures

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Novel Chiral Dopants Derived from (2*S*)-2-(6-Hydroxy-2-naphthyl)propionic Acid for Ferroelectric Liquid Crystal Mixtures

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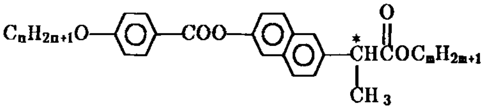
A homologous series of chiral esters **I**(*m*, *n*) derived from (2*S*)-2-(6-hydroxy-2-naphthyl)propionic acid were synthesized as chiral dopants. Some macroscopic properties in ferroelectric liquid crystal mixtures doped with 10% (by mole) of **I**(*m*, *n*) of the above dopants were investigated. Large *Ps* values were obtained in the range of 30.1 nC/cm^2 to 7.5 nC/cm^2 when measured at 10°C below the S_A–Sc^* transition temperature. The *Ps* values are largely dependent on the alkyl chain length at the external side of the chiral centre. The relationship between physical property and the nature of alkyl chain length is discussed.

INTRODUCTION

Since the discovery of ferroelectric liquid crystals (FLC)[1] and the development of surface stabilized ferroelectric liquid crystal display technology,[2] much effort has been carried out in search of new materials having *Sc** phase for use in electro-optical devices. The FLC materials for commercial use, were usually prepared by a guest chiral dopant and a host achiral *Sc* liquid crystal mixture. Accordingly, a chiral dopant with large spontaneous polarization (*Ps*) is required which would allow the use of a low concentration but still maintain most of the properties of *Sc* phase liquid crystals such as low viscosity.

It is generally acknowledged[3,4] that the structure of the chiral tail in a molecule plays an important role in the magnitude of *Ps*. Available evidence indicates that in order to obtain a large *Ps* value for the dopant (1) the chiral centre of the molecule should be in close proximity to the aromatic core,[5–8] (2) a dipolar group with large dipole moment should be introduced to the chiral carbon, preferably directly to the chiral centre,[9] and (3) a relative long terminal aliphatic chain should reside on the external side of the chiral centre to sterically hindered the rotation of the dipole.[10] Based on the above empirical hypotheses, we have synthesized a homologous series of new materials, alkyl (2*S*)-2-(6-(4-alkoxybenzoyloxy)-2-naphthyl)propionates *I*(*m*, *n*) as chiral dopants for FLC mixtures. These materials contain (2*S*)-2-(6-hydroxy-2-naphthyl)propionic acid unit with a chiral centre directly connected to the naphthalene core, a dipolar carbonyl group in the vicinity of chiral centre, and various alkyl chain lengths in the external side of chiral centre. Some macroscopic properties such as *Ps* value, sign of *Ps* and helix twist sense, which characterized these chiral materials in FLC mixtures were measured.

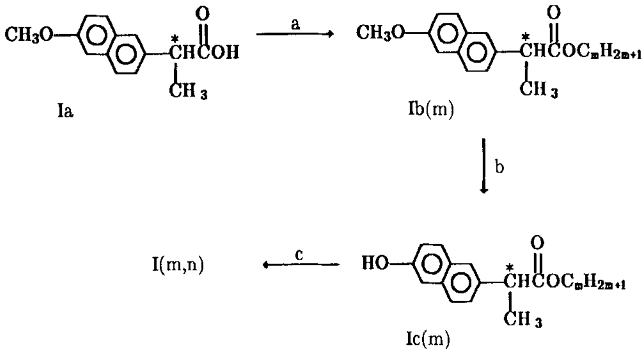


I(m,n): m=4, 6, 8, 10

n=8, 10, 12

SYNTHESIS

The chiral starting material for the synthesis was (2*S*)-2-(6-methoxy-2-naphthyl). propionic acid Ia, purchased from Tokyo Chemical Industry (TCI) Co., Ltd., with optical purity greater than 99% ee. The synthetic route was carried out as outlined in Scheme 1. Esterification of acid group of Ia with *n*-alkanols by the treatment of *N*,*N*′-dicyclohexyl-carbodiimide (DCC) and 4-dimethylaminopyridine (DMAP)[11] gave esters Ib(*m* = 4, 6, 8, 10). Demethylation of methoxy group of esters Ib(*m*) by boron tribromide[12] gave alcohols Ic(*m*). The esterification of alcohols Ic(*m*) with alkoxybenzoic acids (*n* = 8, 10, 12) using DCC and DMAP gave esters I(*m*, *n*). General procedures for the synthesis were given in the experimental section. All materials were isolated using column chromatography and were monitored by TLC. Esters Ib(*m*) were viscous liquids at room temperature. After their structures were characterized by NMR spectra, they were used directly for the follow-up synthesis without purification.



SCHEME 1 a. $C_mH_{2m+1}OH$ (m = 4, 6) DCC, DMAP, CH_2Cl_2; b. BBr_3, CH_2Cl_2; c. $C_nH_{2n+1}O$—⌬—COOH (n = 8, 10, 12), DCC, DMAP, THF.

TABLE 1

Results of Elemental Analysis and Physical Data of Melting Point and Specific Rotation for Alcohols Ic(*m*) and Esters **I**(*m*, *n*)

Compound				Elemental analysis			
	m	*n*		C%	H%	m.p.	$[\alpha]_D^{25.6}$(conc.)
Ic	4		Calc.	74.96	7.42	94–95	+ 37.60 (0.638)
			Found	72.09	7.28		
	6		Calc.	76.00	8.00	74–75	+ 33.47 (0.621)
			Found	75.66	7.85		
	8		Calc.	76.83	8.54	56–57	+ 29.46 (0.620)
			Found	76.48	8.32		
	10		Calc.	77.53	8.99	68–69	+ 26.28 (0.624)
			Found	77.63	8.98		
I	4	8	Calc.	76.19	7.94	64–66	+ 15.75 (0.643)
			Found	76.38	7.90		
	4	10	Calc.	76.69	8.27	55–57	+ 16.02 (0.658)
			Found	76.54	8.38		
	4	12	Calc.	77.11	8.63	52–53	+ 16.10 (0.636)
			Found	76.91	8.68		
	6	8	Calc.	76.69	8.37	60–61	+ 12.26 (0.639)
			Found	76.33	8.40		
	6	10	Calc.	77.11	8.63	49–50	+ 14.40 (0.626)
			Found	77.40	8.75		
	6	12	Calc.	77.51	8.90	48–49	+ 14.22 (0.643)
			Found	77.10	8.96		
	8	8	Calc.	77.11	8.63	62–63	+ 15.02 (0.634)
			Found	76.67	8.67		
	8	10	Calc.	77.51	8.90	50–51	+ 15.44 (0.614)
			Found	77.54	8.88		
	8	12	Calc.	77.88	9.15	45–46	+ 12.46 (0.622)
			Found	78.07	9.23		
	10	8	Calc.	77.51	8.90	68–69	+ 12.34 (0.610)
			Found	76.72	8.89		
	10	10	Calc.	77.88	9.15	53–54	+ 14.44 (0.613)
			Found	77.95	9.15		
	10	12	Calc.	78.22	9.38	44–45	+ 13.80 (0.641)
			Found	78.31	9.27		

Alcohols Ic(*m*) and esters **I**(*m*, *n*) were further purified by crystallization and their structures were confirmed by NMR spectra and elemental analysis. Results of elemental analysis and physical data of melting point and specific rotation are summarized in Table 1. The optical purity of intermediates and products in each synthetic step has not been examined. However, since the esterification using DCC and DMAP[13,14] and the demethylation using boron tribromide[15] have been found to be free from racemization, it can be expected that the esters **I**(*m*, *n*) should possess high enantiomeric purity.

RESULTS AND DISCUSSION

All chiral esters **I**(*m*, *n*) are not mesogenic and are used as chiral dopants. The achiral *Sc* host liquid crystal mixture **IISc** used was a mixture of 4′-hexyloxyphenyl 4-decyloxybenzoate (20.81 mol %), 4′-pentyloxyphenyl 4-octyloxybenzoate (31.49 mol %) and 4′-

TABLE 2

Mesophases and Phase Transition Temperatures of an Achiral *Sc* Mixture **II**(*Sc*)[a] Doped with 10 mol% Chiral Dopants **I**(*m*, *n*)

Dopant		Phase transition temperature[b] (°C)				
m	*n*	K	*Sc**	S_A	*N**	*I*
4	8	· 20.6	· 52.0	· 65.3	· 80.3	·
4	10	· 24.9	· 52.4	· 69.1	· 82.1	·
4	12	· 26.0	· 53.8	· 70.6	· 81.3	·
6	8	· 20.2	· 51.6	· 64.2	· 80.9	·
6	10	· 21.7	· 52.7	· 66.5	· 80.8	·
6	12	· 24.6	· 50.4	· 68.7	· 81.3	·
8	8	· 18.6	· 48.6	· 65.5	· 81.5	·
8	10	· 21.9	· 52.5	· 64.1	· 81.8	·
8	12	· 23.6	· 58.6	· 70.8	· 83.6	·
10	8	· 18.0	· 48.6	· 61.5	· 81.8	·
10	10	· 20.3	· 54.4	· 63.9	· 80.9	·
10	12	· 22.1	· 43.0	· 67.5	· 81.1	·

[a] Mesophases and phase transitions on cooling process of the host **II**(*Sc*) are *I* 86.9, *N* 67.0 S_A 66.7, *Sc* 27.7 K.

[b] Phase transition temperatures of the FLC mixture are reported on cooling process.

hexyloxyphenyl 4-octyloxybenzoate (47.70 mol %), in which the mesophases and the corresponding transition temperatures on the cooling process are: I 86.9 N 67.0 S_A 66.7 *Sc* 27.7 K. The FLC mixtures are prepared by the host IISc doped with 10% (by mole) of chiral dopants I(*m*, *n*). The resulting mesomorphic properties are listed in Table 2. All FLC mixtures show a mesomorphic sequence of I N* S_A SC* K. It is found that an increase in either the chain length of achiral or chiral alkyl group could cause a slightly depressing of thermal stability of *Sc** phase.

Physical properties of chiral dopant induced *Sc** phase such as helix twist sense, apparent tilt angle, and orientation and magnitude of *Ps* are summarized in Table 3. All

TABLE III

Physical Properties of an Achiral *Sc* Mixture **II**(*Sc*) Doped with 10 mol% Chiral Dopant **I**(*m*, *n*) at 10°C below the S_A–Sc^* Transition Temperature

Dopant *m*	*n*	Helix twist sense[a]	*Ps* (nC/cm^2)	Tilt angle (degree)	P_o (nC/cm^2)	Polarization Powder δp (nC/cm^2)	Response Time[b] (μsec)
4	8	LH	+24.2	14.70	94.63	946.3	500
4	10	LH	+30.1	22.73	77.90	779.0	260
4	12	LH	+24.1	23.08	61.22	612.2	219
6	8	LH	+18.2	29.38	37.09	370.9	323
6	10	LH	+14.5	23.53	36.32	363.2	455
6	12	LH	+19.1	19.95	55.97	559.7	821
8	8	LH	+7.6	18.50	23.95	239.5	1102
8	10	LH	+6.8	13.65	28.80	288.0	572
8	12	LH	+9.1	17.75	29.84	298.4	265
10	8	LH	+7.8	18.50	24.56	245.6	3362
10	10	LH	+7.6	14.75	29.85	298.5	431
10	12	LH	+7.5	17.03	25.60	256.0	1596

[a] Helix twist sense of Sc* phase.

[b] The response time was measured by the light transmission from 10% to 90%.

materials exhibit left-handed helix with positive sign of *Ps*. The *Ps* values vary from 30.1 nC/cm^2 to 7.5 nC/cm^2 with largest *Ps* value found in a FLC mixture using **I**(4, 10) as chiral dopant. The apparent tilt angles are in the range of 13.65 to 29.38 degrees.

For the comparison of physical property with respect to the structural change of the chiral molecules, the reduced polarization P_o values were measured by the linear correlation of $Ps(X_G)$ versus $\sin \vartheta(X_G)$ with various mole fraction X_G of chiral molecules in the FLC mixtures according to Equation (1). The obtained transverse dipole moments $P_o(X_G)$ at $X_G = 10$ mole % and the polarization powers δ_p for the corresponding chiral molecules calculated in terms of Equation (2)^{16} at 10°C bellow S_A–Sc^* transition temperature

$$P_o(X_G) = \frac{P_s(X_G)}{\sin \vartheta(X_G)} \tag{1}$$

$$\delta_p = \left[\frac{\partial p_o(X_G)}{\partial X_G}\right]_{\Delta T} \tag{2}$$

are listed in Table 3. The dramatic change in P_o values is obviously due to the variation of alkyl chain length. A plot of P_o values as a function of carbon number *m* of the chiral

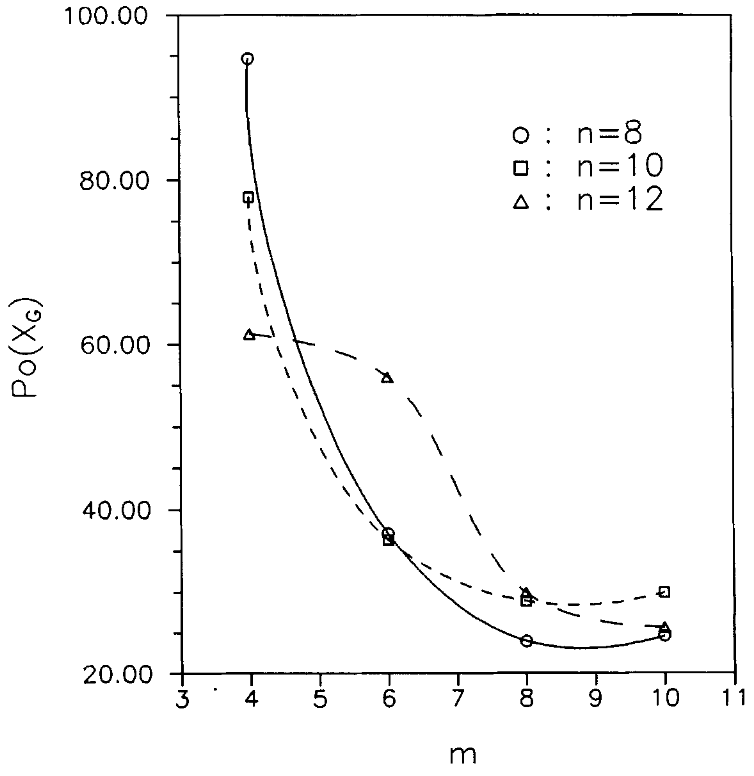


FIGURE 1 Transverse dipole moments of $P_o(X_G)$ where $X_G = 10$ mole% of FLC mixtures measured at 10°C below the S_A–Sc^* transition temperature versus elongated alkyl chain lengths.

end group is shown in Figure 1. It is seen that an increase of *m* from $m = 4$ to $m = 8$ results in a large decrease of P_o. This is evidently implied that the alkyl chain resided in the external side of chiral centre in the molecule contributes a major role in the magnitude of *Ps*. Similar structure-property relationship has also been reported in other related works.[17-19] This declination of P_o values was presumably due to the elongation of the alkyl chain from external side of chiral centre resulting in (1) a reduce of dipole density, in combination with (2) a better alignment of alkyl chain in the direction of the molecular long axis and subsequently reducing its steric influence.[16-19] The P_o values has no longer significant changes as the *m* extended from $m = 8$ to $m = 10$, indicating that the effects of dipole density and the steric hindrance are balanced. Figure 1 also shows that the P_o values are much more sensitive to the variations of *n* at shorter alkyl length *m* than longer ones.

The response times (τ) for the FLC mixtures measured at 10°C bellow the S_A–Sc^* transition temperature by the light transmission from 10% to 90% are listed in Table 3. There is no linear correlation between τ and Ps^{-1} can be found. As the rotation viscosity takes part in the magnitude of τ, this poor correlation is attributed to the variations of the rotation viscosities of the FLC mixtures caused by the doping 10 mole% of chiral materials.

CONCLUSION

Newly synthesized chiral esters **I**(*m*, *n*) possessing large *Ps* values are widely useful as chiral dopants for the FLC mixtures at low concentration. Recent reports[20-22] have shown that naphthalene derived ferroelectric liquid crystal mixtures form a quasi-bookshelf or bookshelf layer structure, and exhibit good electro-optic properties. The potential application of naphthalene-based chiral esters **I**(*m*, *n*) will be investigated in the future.

EXPERIMENTAL

(2*S*)-2-(6-methoxy-2-naphthyl)propionic acid **Ia** purchased from TCI, was used directly for the synthesis. Tetrahydrofuran and dichloromethane were purified by treatment with $LiAlH_4$ and distilled before use. NMR spectra were obtained using a Bruker WP100SY FT-NMR spectrometer. Elemental analysis was performed by a Perkin–Elmer 2400 spectrometer. The magnitudes of specific rotation were measured in dichloromethane using a JASCO DIP-360 digital polarimeter. Transition temperatures were determined by a Du Pont DSC-910 calorimeter at a rate of 2°C/min. Mesophases for the FLC mixtures were identified by observing the textures using a Nikon Microphot-FXA optical microscope under crossed polarizers with a Mettler FP82-HT hot stage. Homogeneously aligned cells with cell thickness of 5 μm were prepared by ITO glass plates coated with rubbed polyimide film. The spontaneous polarization was measured by the Diamant bridge method[23] with voltage 100Vp-p at a frequency of 10 Hz. The apparent tilt angle was derived from the switching angle of the optical director measured in the cell. The response time was measured by the light transmission from 10% to 90%.

Alkyl (2*S*)-2-(6-methoxy-2-naphthyl)propionates Ib(m)

The acid Ia (25 mmol) and *n*-alkanol (27.5 mmol) were dissolved in dry tetrahydrofuran (100 ml). After the addition of DCC (27.5 mmol) and 4-dimethylaminopyridine (DMAP, 2.5 mmol), the solution was stirred at room temperature for 2 days. The precipitates were filtrated and washed with dichloromethane. The filtrate was successively washed with 5% acetic acid, 5% aqueous sodium hydroxide and water, and then dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was purified by column chromatography in silica gel (70–230 mesh) using dichloromethane as eluent. The isolated esters Ib(*m*) with 86–95% yield were identified by NMR spectra and used directly for follow-up reactions. Typical example of chemical shifts for Ib(4) in ^{1}H NMR spectrum is given: δ (ppm, $CDCl_3$) 7.1–7.7 (m, 6H, ArH), 4.1 (t, 2H, OCH_2), 3.9 (s, 3H, OCH_3), 3.8–3.9 (m, 1H, CH), 1.2–1.6 (m, 7H, CH_2), 0.8 (t, 3H, CH_3).

Alkyl (2*S*)-2-(6-Hydroxy-2-naphthyl)propionates Ic(m)

The ester Ib(*m*) (4.36 mmol) dissolved in dry dichloromethane (16 ml) was mixed with tribromoborane (0.8 ml) at −20°C. The mixture was stirred at −20°C for 5 minutes, and at 0°C for 50 minutes. After diluting with dichloromethane (32 ml), the solution was poured into a mixture of saturated ammonium chloride (16 ml) and ice chip (10 g). The organic layer was separated and washed with brine-ice, dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by silica gel (70–230 mesh) column chromatography using dichloromethane as eluent. The alcohols Ic(*m*) with 74–86% yields were collected after recrystallization from hexane. Typical example of chemical shifts for Ic(4) in ^{1}H NMR spectrum is given: δ (ppm, $CDCl_3$) 7.0–7.7 (m, 6H, ArH), 4.1 (t, 2H, OCH_2), 5.7 (s, 1H, OH), 3.9 (m, 1H, CH), 1.2–1.6 (m, 7H, CH_2), 0.8 (t, 3H, CH_3).

Alkyl (2*S*)-2-(6-(4-alkoxybenzoyloxy)-2-naphthyl)propionates I(*m*, *n*)

These esters I(*m*, *n*) were synthesized in the same manner as described for esters Ib(*m*). A mixture of alkoxybenzoic acid (1.87 mmol), alcohol Ic(*m*) (1.7 mmol), DCC (2.04 mmol), DMAP (0.17 mmol) and dry tetrahydrofuran (5 ml) was stirred at room temperature for 2 days. After purification, 70–80% yields of products were obtained. Typical example of chemical shifts for I(4, 8) in ^{1}H NMR spectrum is given: δ (ppm, $CDCl_3$) 6.9–8.2 (m, 10H, ArH), 4.1 (m, 4H, OCH_2), 3.9 (m, 1H, CH), 1.2–1.8 (m, 19H, CH_2), 0.8 (m, 6H, CH_3).

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