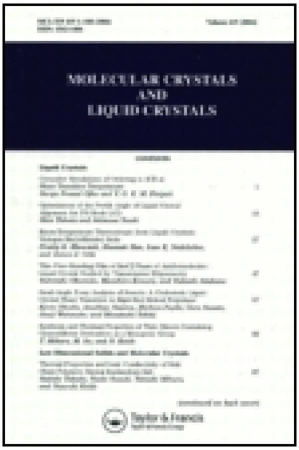

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Ferroelectric Liquid Crystals with Chiral Groups on Each Side of the Core

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To cite this article: S. Kobayashi & S. Ishibashi (1992): Ferroelectric Liquid Crystals with Chiral Groups on Each Side of the Core, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 220:1, 1-17

To link to this article: http://dx.doi.org/10.1080/10587259208033424

Mol. Cryst. Liq. Cryst., 1992, Vol. 220, pp. 1–17
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Printed in the United States of America

Ferroelectric Liquid Crystals with Chiral Groups on Each Side of the Core

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(Received November 13, 1991; in final form December 16, 1991)

The syntheses and properties of a series of ferroelectric liquid crystals with two chiral groups, one on each side of the core, are described. One of the chiral groups is an optically active alkanoyl group and the other is a group derived from one of three kinds of optically active carboxylic acids. The mesomorphic properties and spontaneous polarization of these dichiral compounds are compared with those of monochiral compounds having one of the two chiral groups. These properties and polarization values are discussed in terms of the core and the chiral structure. The dichiral compounds all exhibit very large spontaneous polarization and the maximum value (11.3 mC/m^2) was obtained for a compound with a hydroxyl group in the core.

INTRODUCTION

Since the discovery[1] of a ferroelectric liquid crystal (FLC), many studies have been devoted to synthesis of ferroelectric liquid crystal compounds that have a large spontaneous polarization Ps. The Ps of a liquid crystal compound is induced by the dipole perpendicular to the molecular long axis. Ps can be increased by using a larger dipole or by placing the dipole close to an asymmetric carbon atom. Although the dipoles of esters and ethers have been used to form many ferroelectric liquid crystals, recent works[2,3] have shown that liquid crystals with a carbonyl group adjacent both to the core of the liquid crystal and to an asymmetric carbon atom have a larger Ps than corresponding esters or ethers.

Another way to increase Ps is by introducing two or more dipoles near the chiral center in such a way that their components perpendicular to the molecular long axis are increased.[4] One example of this is the introduction of a hydroxyl group ortho to a carbonyl group[3,5] or an ester group[6] attached to an asymmetric carbon atom. The formation of an intramolecular hydrogen bond between the hydroxyl and the carbonyl group increases the dipole components perpendicular to the molecular long axis, increasing the Ps of the molecule.

The introduction of two or more chiral groups into one molecule has also been studied as a way of enhancing Ps.[7] The most important factor in this case is that the signs of the Ps due to each of the chiral groups are the same. We have already synthesized FLC compounds that have an optically active alkanoyl group on one side of the core and a chiral group derived from lactic acid on the other side, and we have shown that these compounds exhibit markedly large Ps.[8,9] In the present work we have extended this study by synthesizing analogous compounds with a different core or a different terminal group or both. Their ferroelectric liquid crystal properties will be described here.

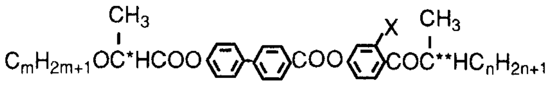
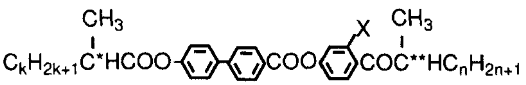
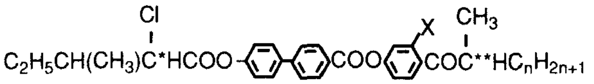
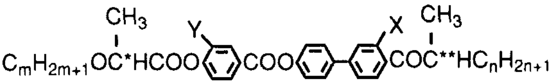
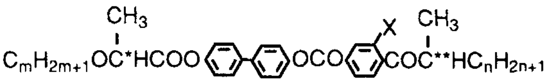
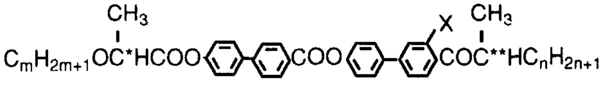
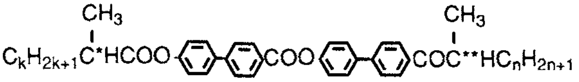
MATERIALS AND THEIR PREPARATION

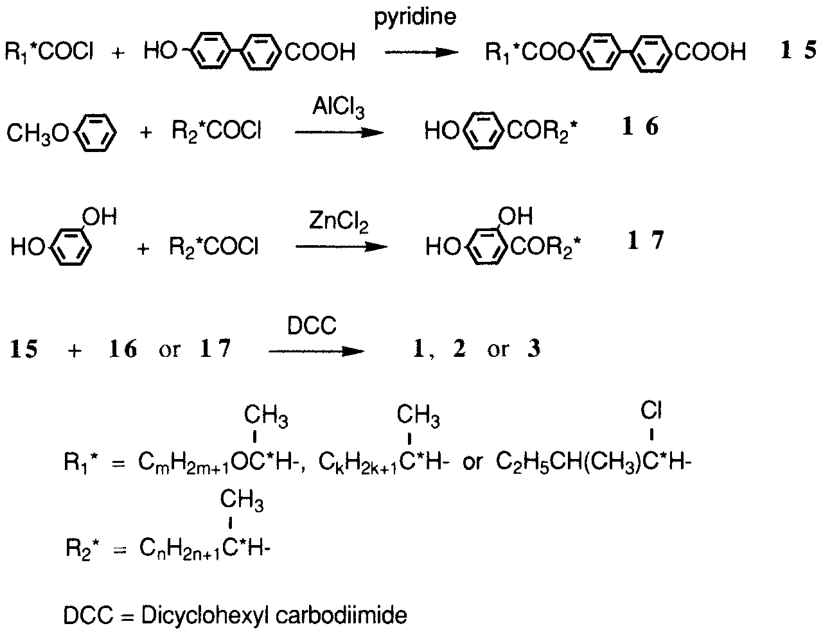
The compounds examined are shown in Table I. The absolute configurations of the two chiral groups in each compound were selected so that the signs of Ps due to each of them are the same.

Compounds **1**, **2** and **3** were prepared according to Scheme I, and compounds

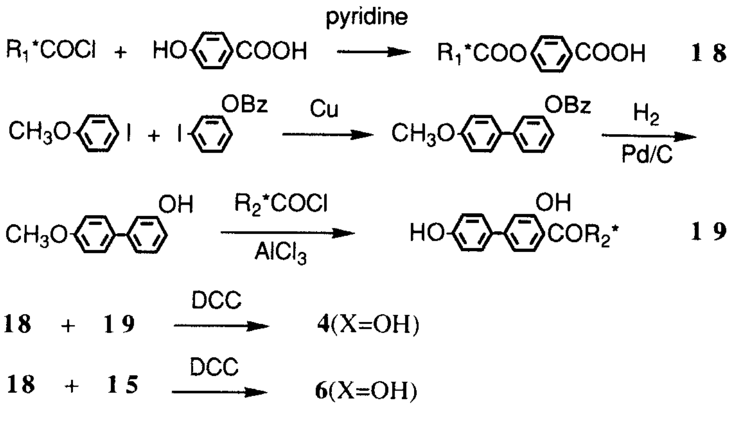
TABLE I

Compounds with two chiral groups

Comp. No.	Chemical Structure	Absolute Configuration	
		C*	C**
1(m,n,X)		R	S
2(k,n,X)		S	S
3(n,X)		S	S
4(m,n,X,Y)		R	S
5(m,n,X)		R	S
6(m,n,X)		R	S
7(k,n)		S	S



SCHEME I Synthesis of compounds **1**, **2** and **3**.

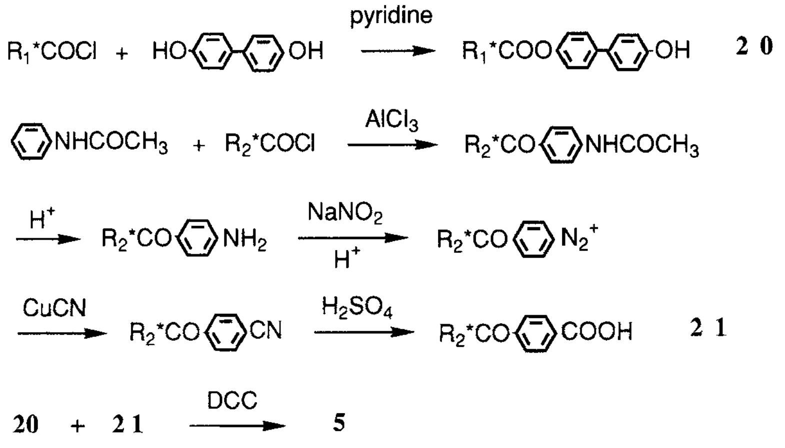


Bz = Benzyl

SCHEME II Synthesis of compounds **4**(X = OH) and **6**(X = OH).

4(X = H), **6**(X = H) and **7** were prepared by using an analogous process. Compounds **4**(X = OH) and **6**(X = OH) were synthesized according to Scheme II. Compounds **5** were prepared according to Scheme III.

Compounds **1**, **2**, **3**, **6** and **7** were compared with compounds **8** to **14** (Table II), each of which have one chiral structure.



SCHEME III Synthesis of compound **5**.

RESULTS AND DISCUSSION

Specific rotations are listed in Table III for compounds **1** to **7** and in Table IV for compounds **8** to **14**. Transition temperatures, Ps, tilt angles θ and Po (= Ps/sinθ) are summarized in Table V for compounds **1** to **7** and in Table VI for compounds **8** to **14**.

Mesomorphic Properties

The mesomorphic properties of liquid crystals are affected by the structure of the chiral center, the core structure, the type and length of the terminal chains, and the presence of a substituent in the core.

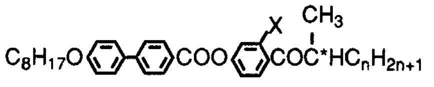
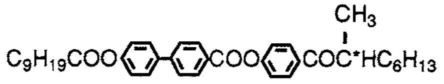
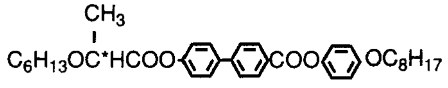
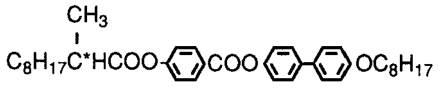
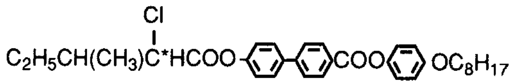
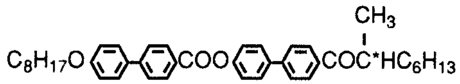
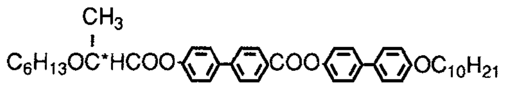
Phase transition temperatures for compounds **1** are plotted against the terminal chain carbon number m in Figure 1 and n in Figure 2. As m increases in compounds **1** with $n = 6$, the thermal stabilities of smectic phases decrease; at the same time, the S_A phase narrows, disappears when $m = 6$, and appears again when m is greater than 6 (Figures 1c, 1d). The thermal stabilities of smectic phases for compounds **1** with $n = 2$, on the contrary, do not vary with increasing m and the S_A phase remains wide (Figures 1a, 1b). The variation of n in compounds **1** with $m = 6$ causes a change of mesomorphic properties (Figure 2) similar to that for compounds **1** with $m = 6$ due to the variation of m (Figure 1c, 1d). This implies that, except when m or n is very small, both the terminal chains in compounds **1** play a similar role in determining mesomorphic properties.

Whereas compounds **1** with $n = 2$ exhibit an enantiotropic S_A and a monotropic S_C^* phase, compounds **1** with n greater than 2 show monotropic S_A and S_C^* phases. Compounds **1** with X = H and certain combinations of m and n, however, show enantiotropic S_A and S_C^* phases. For example, compounds **1**(8,4,H) and **1**(10,6,H) exhibit enantiotropic S_A and S_C^* phases.

The thermal stabilities of the liquid crystal phases for dichiral compounds **1** are considerably lower than those of the monochiral compounds **8**, **9** and **10**. This implies that the molecular packing or the superposition of the cores or both in

TABLE II

Compounds with one chiral group

Comp. No.	Chemical Structure	Absolute Configuration
8(n,X)		S
9		S
10		R
11		S
12		S
13		S
14		R

compounds **1** is considerably depressed because of the presence of two branched chiral groups on both sides of the core.

Dichiral compounds **2** have an I-S_A-S_C^* transition sequence, as do the monochiral compounds **8** and **9** containing the ketone structure. This means that the mesomorphic properties of compounds **2** are mainly governed by the ketone structure. Both the melting points and the thermal stabilities of smectic phases for compounds **2** are lower than those of compound **9**. This is attributed to the presence of a methyl group in the fatty acid residue in compounds **2**. The methyl branch causes the depression of the molecular packing and the superposition of the cores.

Compounds **1**(6,2,H), **4**(6,2,H,H) and **5**(6,2) all show an I-S_A-S_C^* transition sequence (Figure 3). They have the same chiral groups on both sides of three-ring cores but their core structures differ: compound **1** is a derivative of phenyl 4-biphenylcarboxylate, compound **4** is a derivative of biphenyl benzoate and compound **5** has a core similar to that in compounds **1** but that differs in the direction

TABLE III

Specific rotation of dichiral compounds **1** to **7**

Compound	$[\alpha]_D^{25}$	c(g/100ml)
1(3,2,H)	+44.4	0.52
1(4,2,H)	+48.1	0.34
1(5,2,H)	+46.7	0.27
1(6,2,H)	+47.9	0.29
1(6,2,OH)	+42.0	1.0
1(6,4,H)	+35.3	0.54
1(6,4,OH)	+39.2	0.22
1(8,4,H)	+33.9	0.41
1(6,5,OH)	+39.7	0.22
1(2,6,OH)	+32.7	0.25
1(3,6,OH)	+36.4	0.22
1(4,6,H)	+34.4	0.52
1(4,6,OH)	+33.8	0.20
1(5,6,OH)	+33.2	0.25
1(6,6,H)	+32.9	1.0
1(6,6,OH)	+30.7	1.0
1(8,6,H)	+29.4	0.21
1(8,6,OH)	+33.9	0.22
1(10,6,H)	+29.6	0.62
1(10,6,OH)	+29.6	0.42
1(6,8,OH)	+31.7	0.62
1(8,8,OH)	+29.7	0.36
2(8,6,H)	+17.3	0.41
2(8,6,OH)	+18.6	0.22
3(6,H)	+6.4	0.33
3(6,OH)	+7.4	0.33
4(6,2,H,H)	+38.9	0.57
4(6,2,OH,H)	+41.9	0.82
4(6,6,H,H)	+45.6	0.4
4(6,6,OH,H)	+34.2	0.5
4(6,6,H,F)	+34.2	0.31
4(6,6,H,Cl)	+42.3	0.62
4(6,6,OH,Cl)	+34.2	0.63
5(6,2)	+42.1	0.35
6(6,2,OH)	+36.8	0.24
6(6,6,H)	+27.7	0.42
6(8,6,H)	+24.8	0.41
7(8,6)	+12.2	0.42

Solvent: chloroform

of the central ester group. The thermal stabilities of the smectic phases of these compounds are almost the same despite their different cores. The thermal stabilities of the S_C^* phases, however, are influenced by the core structures: the most stable S_C^* phase can be obtained for compound **5**, followed by compounds **1**.

Compounds **6** and **7**, which have a four-ring core, show enantiotropic S_A and S_C^* phases. The thermal stabilities of the liquid crystal phases for compounds **6** and **7** are higher than those for analogous compounds with three-ring cores.

TABLE IV

Specific rotation of monochiral compounds **8** to **14**

Compound	$[\alpha]_D^{25}$	c(g/100ml)
8(2,H)	+12.8	1.0
8(2,OH)	+12.3	1.0
8(6,H)	+4.8	1.0
8(6,OH)	+7.1	0.49
9(H)	+4.2	0.66
10	+28.8	0.4
11	+10.9	0.3
12	+1.8	0.33
13	+0.9	0.31
14	+24.4	0.34

Solvent: chloroform

Introduction of a substituent, such as a hydroxyl group or a halogen atom, into a side position within the core considerably decreases the thermal stabilities of the smectic phases (Figure 3). This is the same as the effect already described for compounds **8**[3] and is attributed to an increase in the intermolecular distance. In general, hydroxyl groups considerably enhance intermolecular cohesion by forming intermolecular hydrogen bonds. In this work, however, a hydroxyl group is introduced into the core at the position ortho to the alkanoyl group so that an intramolecular hydrogen bond is formed to suppress intermolecular interaction. Formation of an intramolecular hydrogen bond was confirmed by IR and NMR spectroscopy.[3,5]

Figure 3 shows that the effect of a hydroxyl group on the mesomorphic properties is larger for compounds **4** than for compounds **1**. For example, the introduction of a hydroxyl group into compounds **4** leads to disappearance of liquid crystal phases for $n = 2$, and a marked depression of the smectic phases (by 55°C) for $n = 6$, whereas the presence of a hydroxyl group in compounds **1** depresses the smectic phase by 43°C for $n = 2$ and by 33°C for $n = 6$. This implies that a hydroxyl group in the biphenyl structure more strongly interferes with the superposition of the cores than does a hydroxyl group in the phenyl ring.

Spontaneous Polarization

The Ps of compounds having two chiral groups, with the same signs of Ps, on both sides of the core is very large. In particular, compounds **1** show extremely large Ps. The largest value reaches 11.3 mC/m^2 at $T_c - T = 10$°C for compound **1**(6,6,OH). This is the largest value ever reported for FLC's.

If the signs of the two chiral groups are different, the compounds show a remarkably smaller Ps. For example, the optical isomer of compound **1**(6,6,H) whose absolute configuration is (S,S) shows a Ps of -0.40 mC/m^2, and the Ps of the (S,S) isomer of compound **1**(6,6,OH) is only -0.46 mC/m^2.

Dichiral three-ring compounds **1** to **3** exhibit larger Ps than corresponding compounds with one of the two chiral groups. The Po values for compounds **1** to **3** are compared with those for the corresponding compounds (Table VII). The Po for

TABLE V

Properties of dichiral compounds **1** to **7**

Compound	Phase transition temperature/°C					#1	Ps#2 /mCm^{-2}	θ#2	Po#3 /mCm^{-2}
	Cr	Sx	Sc*	S_A	N*	I			
1(3,2,H)	•94		(•64)	•108		•	2.85	26	6.46
1(4,2,H)	•55		(•54)	•98		•	3.10#4	-	-
1(5,2,H)	•55		(•53)	•104		•	2.90	27	6.50
1(6,2,H)	•52		(•49)	•106		•	3.50	30	8.00
1(6,2,OH)	•52		(•23)	•63		•	4.40	28	9.40
1(6,4,H)	•79		(•63	•79)		•	4.57	34	8.17
1(6,4,OH)	•47		(•32	•40)		•	7.70	35	13.40
1(8,4,H)	•43		•65	•80		•	4.07	33	7.47
1(6,5,OH)	•45		(•31	•40)		•	6.50	34	11.60
1(2,6,OH)	•37			•68		•	-	-	-
1(3,6,OH)	•62		(•9	•44)		•	-	-	-
1(4,6,H)	•92		(•70	•76)		•	-	-	-
1(4,6,OH)	•45		(•28	•42)		•	6.63	-	-
1(5,6,OH)	•37		(•35)	•49		•	6.60	34	12.0
1(6,6,H)	•97		(•73)			•	6.10	36	10.40
1(6,6,OH)	•65		(•40)			•	11.30	38	17.90
1(8,6,H)	•80		(•73	•75)		•	5.12	36	8.80
1(8,6,OH)	•43		(•36)	•44		•	6.65	29	13.70
1(10,6,H)	•64		•70	•75		•	4.18	33	7.67
1(10,6,OH)	•56		(•37	•47)		•	-	-	-
1(6,8,OH)	•47		(•35	•43)		•	5.60	34	10.0
1(8,8,OH)	•40		(•39)	•46		•	5.85	39	9.20
2(8,6,H)	•79		(•67	•75)		•	3.60	35	6.30
2(8,6,OH)	•46		(•15	•27)		•	4.70	37	7.90
3(6,H)	•99		(•72		•78)	•	4.40	30	8.80
3(6,OH)	•62	(•2		•55)		•	-	-	-
4(6,2,H,H)	•88		(•31)	•103		•	4.05	26	9.14
4(6,2,OH,H)	•54					•	-	-	-
4(6,6,H,H)	•67		(•63	65)		•	6.65#4	-	-
4(6,6,OH,H)	•63		(•12)			•	11.0#4	-	-
4(6,6,H,F)	•44		•45	•51		•	2.78	36	4.73
4(6,6,H,Cl)	•32		(•25	•31)		•	2.87	36	4.85
4(6,6,OH,Cl)	•51					•	-	-	-
5(6,2)	•73		(•71)	•100		•	3.25	27	7.16
6(6,2,OH)	•49	(•17)	•115	•176		•	2.00	25	4.60
6(6,6,H)	•103	(•97)	•172	•193		•	2.75	36	4.70
6(8,6,H)	•97	(•86)	•169	•187		•	2.50	31	4.90
7(8,6)	•106	(•79)	•166	•190		•	1.78	33	3.25

Note #1 Cr, Sx, Sc*, S_A, N* and I are abbreviations for crystal, unidentified smectic, chiral smectic C, smectic A, chiral nematic and isotropic liquid phases, respectively. ( ) indicates monotropic transition.

#2 Ps and tilt angles (θ) were measured at 10 C below the SA-Sc* or I-Sc* transition temperature (Tc). Ps were all minus.

#3 Po=Ps/sinθ.

#4 Obtained by extrapolating the values measured for the mixtures exhibiting an enantiotropic Sc* phase with compound **8**(6,OH).

TABLE VI

Properties of monochiral compounds **8** to **14**

Compound	Phase transition temperature/°C #1 Cr	 S_X	 S_C*	 S_A	 N*	 I	Ps#2 /mCm-2	θ#2	Po#3 /mCm-2
8(2,H)	•78	(•65)	•126	•184		•	-0.53	18	-1.72
8(2,OH)	•49	(•12)	•96	•155		•	-0.77	18	-2.49
8(6,H)	•79	(•65)*	•139	•153		•	-1.08	24	-2.66
8(6,OH)	•33	(•5)	•96	•132		•	-1.46	20	-4.27
9(H)	•84	(•61)	•133	•157		•	-0.97	22	-2.59
10	•101		•135		•138	•	-0.78	31	-1.51
11	•107		•133			•	-0.23	38	-0.37
12	•39		•135	•159	•161	•	-0.60	25	-1.42
13	•132		•209	•251		•	-0.80	23	-2.05
14	•135		•230		•237	•	-0.70	30	-1.40

Note : #1, #2, #3 ; See the note in Table V. * Antiferroelectric S_C* phase[10].

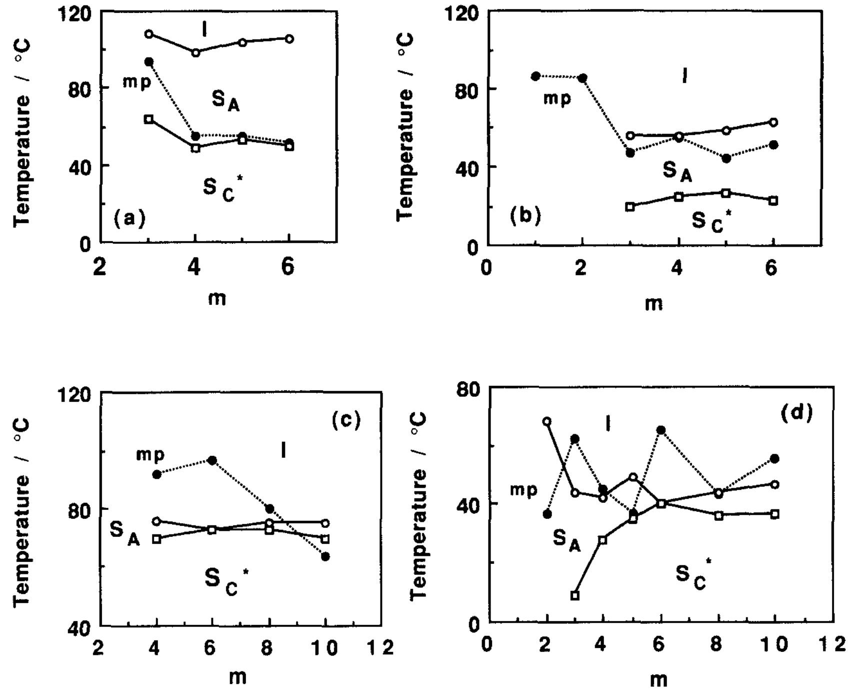


FIGURE 1 Dependences of transition temperatures on m for compounds **1** with (a) $n = 2$, X = H; (b) $n = 2$, X = OH; (c) $n = 6$, X = H; (d) $n = 6$, X = OH.

the compounds with two chiral groups is considerably greater than the sums of the Po for the corresponding compounds.

On the other hand, dichiral four-ring compounds **6** and **7** exhibit smaller Ps than their three-ring analogues, **1** and **2**. The dichiral four-ring compound **6**(6,6,H) shows a Ps of only 2.75 mC/m^2, whereas its three-ring analogue, **1**(6,6,H), shows a Ps of 6.10 mC/m^2. The Po of compound **6**(6,6,H) is larger by 36% than the sum of the

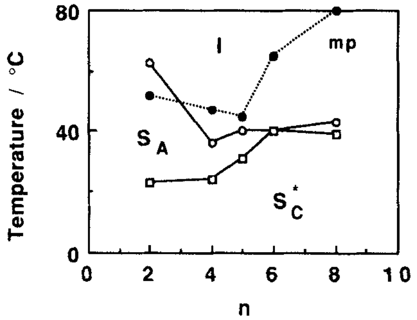


FIGURE 2 Dependences of transition temperatures on *n* for compounds **1**.

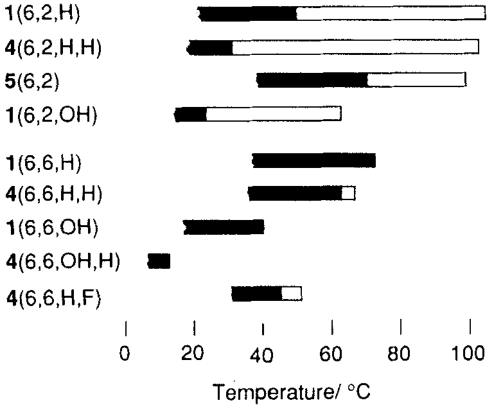


FIGURE 3 Effect of the core structure on phase transition, ■ S_C^*; □ S_A.

TABLE VII

Comparison of Po of dichiral compounds **1**, **2**, **3** and **6** with Po of the corresponding monochiral compounds

Dichiral compound		Monochiral compound				Po_1+Po_2
No.	Po	No.	Po_1	No.	Po_2	
1(6,2,H)	8.0	**10**	1.51	**8**(2,H)	1.72	3.23
1(6,2,OH)	9.4	**10**	1.51	**8**(2,OH)	2.49	4.00
1(6,6,H)	10.4	**10**	1.51	**8**(6,H)	2.66	4.17
1(6,6,OH)	17.9	**10**	1.51	**8**(6,OH)	4.27	5.78
2(8,6,H)	6.3	**11**	0.37	**8**(6,H)	2.66	3.03
3(6,H)	8.8	**12**	1.42	**8**(6,H)	2.66	4.08
6(6,6,H)	4.7	**14**	1.40	**13**	2.05	3.45

Po for the corresponding monochiral compounds **13** and **14**, whereas the Po of compound **1**(6,6,H) is about 2.5 times the sum of the Po for compounds **8**(6,H) and **10** (Table VII). This suggests that marked enhancement of Ps by the introduction of two chiral groups on both sides of the core can be achieved only for compounds with a three-ring core, irrespective of the core structure.

This implies that the motion around the chiral centers in the dichiral compounds with a three-ring core is more effectively damped than it is in the monochiral compounds and in the dichiral compounds with a four-ring core. This damping is probably caused by intermolecular interaction associated with the specific alignment of molecules. Another explanation for the effective damping of the motion may be that the dichiral compounds with a three-ring core show an S_C^* phase at much lower temperatures than do the monochiral compounds and the dichiral compounds with a four-ring core.

The Ps of compounds **1** is plotted in Figure 4 against *m* and *n*. The increase in the terminal aliphatic chain length of the alkanoyl group and of the alkoxy group attached to the lactic acid residue in compounds **1** leads to an increase in Ps. This can be explained by damping of the motion around the chiral centers.[11] The Ps values, however, reach maxima and then decrease with increasing *m* or *n*.

The effect on Ps of the chiral group located at the opposite side of the alkanoyl group is shown in Figure 5. The Ps of compounds **1** is larger than that of compounds **2**. This means that the alkoxy group in compounds **1** plays an important role in enhancing Ps.

Comparison of Ps between compounds **1**, **4** and **5** having the same chiral groups (Figure 6) leads to the conclusion that the effect of the core structure on Ps is not so large.

The presence of a hydroxyl group ortho to the alkanoyl group in the dichiral compounds **1**, **2** and **4** results in a considerable increase in Ps. This can be explained,

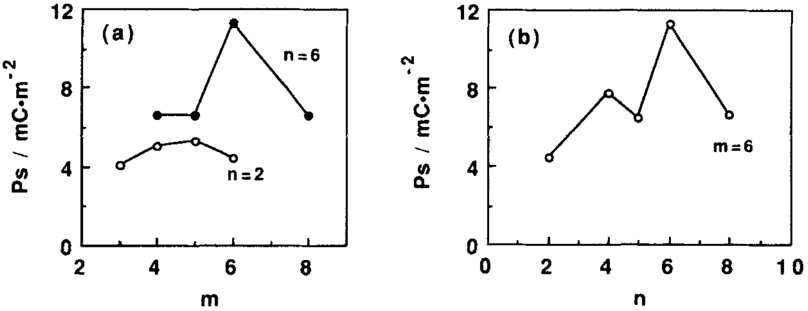


FIGURE 4 Relation between spontaneous polarization and (a) m, and (b) n for compounds 1 with X = OH (measured at $T - T_c = -10°C$).

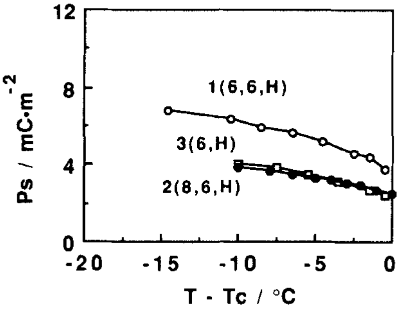


FIGURE 5 Spontaneous polarization of dichiral compounds with different chiral groups.

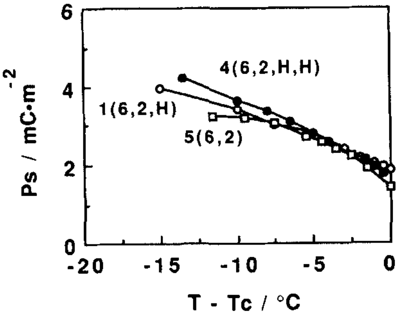


FIGURE 6 Effect of core structure on spontaneous polarization.

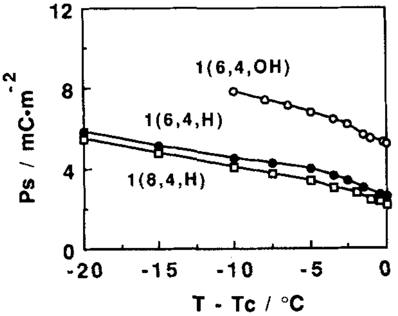


FIGURE 7 Temperature dependences of spontaneous polarization for compounds **1**.

in a manner similar to that for monochiral ketone compounds **8**,[3] by the formation of an intramolecular hydrogen bond between the hydroxyl and the carbonyl group.

The introduction of a halogen atom ortho to the lactic acid residue in the core of compounds **4** leads to a significant decrease in Ps. This is explained by the compensation of dipoles of the ester group and the halogen atom. Steric hindrance and electrostatic repulsion cause the halogen atom to be located on the side opposite to the ester group.

As shown in Figures 5 and 6, the temperature dependences for compounds **1**, **2**, **4** and **5**, which show an I-S_A-S_C^* transition sequence on cooling, are characterized by a steep rise in Ps immediately after the S_A-S_C^* transition. This is also true for other dichiral compounds **1** to **5** exhibiting an I-S_A-S_C^* transition sequence (Figure 7). The steep rise of Ps immediately after the S_A-S_C^* transition is characteristic of the first order S_A-S_C^* transition.[12] The curves of temperature dependences of Ps for the dichiral compounds with a four-ring core (**6** and **7**), on the other hand, show a slow rise from zero (Figure 8). This is characteristic of the second order transition and these curves resemble those of the monochiral ketone compounds **8** (Figure 9).

Electric field-induced S_A-S_C^* transition is observed for the dichiral compounds which show a first order S_A-S_C^* transition. The phenomenon is under investigation and the results will be reported elsewhere.

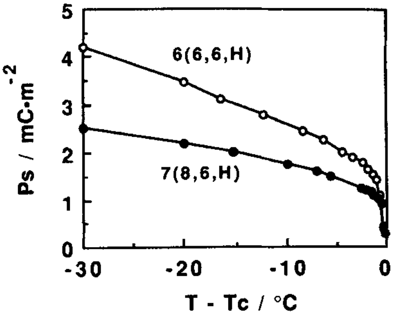


FIGURE 8 Temperature dependences of spontaneous polarization for dichiral compounds with a four-ring core.

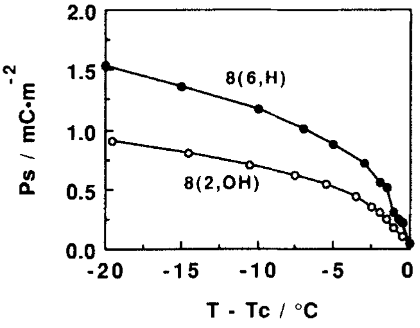


FIGURE 9 Temperature dependences of spontaneous polarization for monochiral ketone compounds **8**.

EXPERIMENTAL

Synthesis of Compounds

(1) (R)-4-(2-n-Hexyloxypropanoyloxy)-biphenyl-4′-carboxylic acid **15**[R_1^* = (R)-$C_6H_{13}OC^*H(CH_3)$-]. To a solution of 4-hydroxy-biphenyl-4′-carboxylic acid (2.61 g) in carbon tetrachloride (50 ml) and pyridine (10 ml), a solution of (R)-2-n-hexyloxypropanoyl chloride (2.35 g) in carbon tetrachloride (20 ml) was added dropwise and the mixture was then refluxed for 3 hours. After cooling, the resultant mixture was taken up in dilute hydrochloric acid and extracted with ethyl ether. The organic extract was washed twice with dilute hydrochloric acid, washed three times with water and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was recrystallized from ethanol to yield 2.30 g of the title compound as white crystals. $[\alpha]_D = +43.8°$ ($CHCl_3$, $c = 0.96$). IR cm^{-1}(KBr): 1756(COO), 1678(COOH), 1186, 772.

(2) (S)-4-(2-Methylbutyroyl)phenol **16**[R_2 = (S)-$C_2H_5C^*H(CH_3)$-]. Anisole (8.25 g) was added dropwise to a suspension of aluminium chloride (9.2 g) in dry 1,2-dichloroethane (100 ml) at 0°C, and then a solution of (S)-2-methylbutyroyl chloride (8.2 g) in dry 1,2-dichloroethane (50 ml) was added dropwise to the mixture over 1 hour while stirring. The resultant mixture was stirred for 3 hours at room tem-

perature, and then aluminium chloride (9.2 g) was added in a small portion to the mixture. The stirring was continued for 2 hours under reflux. After cooling to room temperature, the mixture was poured into dilute hydrochloric acid (200 ml) and extracted twice with diethyl ether (200 ml). The organic extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The residue (10.1 g) was purified by chromatography on silica gel with chloroform as eluent to give 8.37 g of the title compound as a viscous liquid. $[\alpha]_D$ = +40.9° ($CHCl_3$, c = 1.0). IR cm^{-1}(neat): 3305, 1651(C═O), 1602, 1578, 1221. ^1H NMR δppm($CDCl_3$): 0.91(3H, t, $CH_2C\underline{H}_3$), 1.18(3H, d, $C*HC\underline{H}_3$), 1.49 and 1.82(2H, m, $C*HC\underline{H}_2CH_3$), 3.36(1H, m, C*H), 6.03(1H, s, OH), 6.90(2H, d, arom. H ortho to OH), 7.92(2H, d, arom. H ortho to CO).

(3) (S)-3-Hydroxy-4-(2-methyloctyloyl)phenol **17**[R_2 = (S)-$C_6H_{13}C*H(CH_3)$-]. Anhydrous zinc chloride (10.0 g) was dissolved in 10.0 g of (S)-(+)-2-methyl octanoic acid by heating to 110°C. Resorcinol (8.8 g) was added to the mixture and the resultant mixture was then heated to 150°C over a period of 30 minutes while stirring. After cooling to room temperature, hydrochloric acid (25 ml) and water (25 ml) were added to the mixture. Then the mixture was extracted three times with diethyl ether (50 ml) and the organic extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The residue (10.4 g) was purified by chromatography on silica gel with chloroform as eluent to give 7.3 g of the title compound as an orange viscous liquid. $[\alpha]_D$ = +15.2° ($CHCl_3$, c = 0.84). IR cm^{-1}(neat): 3361, 1635(C═O), 1601, 1514, 1383, 1234. ^1H NMR δppm($CDCl_3$): 0.93(3H, t, $CH_2C\underline{H}_3$), 1.20(3H, d, $C*HC\underline{H}_3$), 1.51–1.83(10H, m, CH_2), 3.33(1H, m, C*H), 5.67(1H, s, OH para to CO), 6.38(1H, d, arom. H ortho to CO), 6.39(1H, s, arom. H between OH's), 6.93(1H, d, arom. H meta to CO).

(4) (S)-4-(2-Methylbutyroyl)phenyl (R)-4-(4-(2-n-hexyloxypropanoyloxy)phenyl)-benzoate **1**(6,2,H). To a solution of (R)-4-(2-n-hexyloxypropanoyloxy)biphenyl-4-carboxylic acid (0.37 g) and (S)-4-(2-methylbutyroyl)phenol (0.20 g) in dry methylene chloride, dimethylaminopyridine (0.02 g) and dicyclohexyl carbodiimide (0.23 g) were added, and the reaction was continued for 20 hours at room temperature with stirring. After filtration to remove any insoluble material, the filtrate was diluted with diethyl ether (100 ml), the organic layer was washed twice with dilute hydrochloric acid and three times with water, dried over anhydrous Na_2SO_4, and then evaporated. The resultant residue (0.55 g) was chromatographed on silica gel with n-hexane/ethyl acetate (9:1) as eluent and then recrystallized from n-hexane to give 0.12 g of the title compound as white crystals. $[\alpha]_D$ = +47.9° ($CHCl_3$, c = 0.3). IR cm^{-1}(KBr): 2936, 1764(C*-COO), 1728(PhCOO), 1680(C═O), 1602, 1274, 890, 766. ^1H NMR δppm ($CDCl_3$): 0.88–0.96(6H, m, $CH_2C\underline{H}_3$), 1.22(3H, d, $COC*HCH_2CH_3$), 1.25–1.86(13H, m, $CH_3(C\underline{H}_2)_4CH_2O$ + $COC*HC\underline{H}_3$ + $COC*HC\underline{H}_2CH_3$), 3.40(1H, q, $COC*\underline{H}CH_3$), 3.52(1H, m) and 3.70(1H, m)[$C_5H_{11}C\underline{H}_2O$], 4.22(1H, q, $C_6H_{13}OC*\underline{H}(CH_3)COO$); 7.24(2H, d), 7.35(2H, d), 7.67(2H, d), 7.72(2H, d), 8.06(2H, d) and 8.27(2H, d)[arom. H].

(5) (R)-4-(2-n-Hexyloxypropanoyloxy)benzoic acid **18**[R_1 = (R)-$C_6H_{13}OC*H$-(CH_3)-]. To a solution of p-hydroxybenzoic acid (2.15 g) in methylene chloride (30 ml) and pyridine (10 ml), a solution of (R)-2-n-hexyloxypropanoyl chloride

(3.0 g) in methylene chloride (20 ml) was added dropwise and then the mixture was then refluxed for 5 hours. After cooling, the mixture was poured into dilute hydrochloric acid, and extracted with diethyl ether. The organic extract was washed twice with dilute hydrochloric acid and three times with water and then dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was recrystallized from n-hexane to yield 2.13 g of the title compound as white crystals with a mp. of 67.0°C. $[\alpha]_D = +45.2°$ ($CHCl_3$, $c = 2.1$). IR cm^{-1}(KBr): 1775(COO), 1685(COOH), 1210, 1170, 1123.

(6) (S)-4,3′-Dihydroxy-4′-(2-methylbutyroyl)biphenyl **19**[R_2 = (S)-$C_2H_5C^*H$-(CH_3)-]. A mixture of 3-benzyloxyiodobenzene (119 g) and p-iodoanisole (89.9 g) was heated to 55–65°C. To this mixture, copper powder (210 g) was added and stirring was continued for 10 hours at 200–210°C. After cooling, the reaction mixture was poured into toluene (500 ml), filtered to remove any inorganic material, and evaporated. The residue was chromatographed on silica gel with n-hexane/ethyl acetate (20:1) as eluent to give 64.8 g of 3′-benzyloxy-4-methoxybiphenyl as white crystals with a mp. of 78.5°C.

The 3′-benzyloxy-4-methoxybiphenyl (29.0 g) obtained above was reduced with hydrogen in the presence of Raney nickel (2 g) in ethyl acetate/tetrahydrofuran (300 ml) at 90–110°C. After reaction, the catalyst was filtered off, the solvent was evaporated, and the residue was chromatographed on silica gel with n-hexane/ethylacetate as eluent to give 15.1 g of 3′-hydroxy-4-methoxybiphenyl as white crystals with a mp. of 76.5°C.

To a solution of 3′-hydroxy-4-methoxybiphenyl (15 g) in pyridine (40 ml), (S)-2-methylbutyroyl chloride (9.1 g) was added dropwise and then stirring was continued for 2 hours at room temperature. The reaction mixture was neutralized with dilute hydrochloric acid and extracted with ethyl acetate. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and then evaporated. The pale yellow oily residue was chromatographed on silica gel with n-hexane/ethyl acetate (5:1) as eluent to give 20.5 g of (S)-3′-(2-methylbutyroyloxy)-4-methoxybiphenyl as a pale yellow oil. $[\alpha]_D = +12.0°$ ($CHCl_3$, $c = 2$). IR cm^{-1}(neat): 2930, 1745(COO), 1605.

To a suspension of aluminium chloride (5.7 g) in nitrobenzene (15 ml), (S)-3′-(2-methylbutyroyloxy)-4-methoxybiphenyl (10 g) obtained above was added dropwise at 70°C and stirring was continued for 3 hours at 115–125°C. After cooling, the reaction mixture was poured into dilute hydrochloric acid and extracted with ethyl acetate. The organic layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was chromatographed on silica gel with n-hexane/ethyl acetate (10:1) as eluent to give 3.7 g of (S)-3′-hydroxy-4′-(2-methylbutyroyl)-4-methoxybiphenyl as a pale yellow viscous oil. $[\alpha]_D = +19.5°$ ($CHCl_3$, $c = 2$).

(S)-3′-Hydroxy-4′-(2-methylbutyroyl)-4-methoxybiphenyl (2.8 g) and aluminium chloride (1.7 g) in toluene (300 ml) were stirred for 3 hours under reflux. After cooling, the reaction mixture was poured into dilute hydrochloric acid and extracted with ethyl acetate. The organic layer was washed and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel with n-hexane/acetone (10:1) as eluent to give 1.7 g (S)-4,3′-

dihydroxy-4′-(2-methylbutyroyl)biphenyl as a pale yellow viscous oil. $[\alpha]_D = +18.5°$ ($CHCl_3$, $c = 2$). ^1H NMR δppm ($CDCl_3$): 0.96(3H, t, $CH_2C\underline{H}_3$), 1.25(3H, d, $C^*HC\underline{H}_3$), 1.50–1.93 (2H, m, CH_2), 3.41–3.50(1H, m, COC*H), 5.34(1H, bs, 4-OH), 6.90(2H, d, arom. 3- and 5-H), 7.11(1H, d, arom. 6′-H), 7.18(1H, d, 2′-H), 7.53(2H, d, arom. 2- and 6-H), 7.82(1H, d, arom. 5′-H), 12.70(1H, s, 3′-OH).

(7) (S)-4-(3-Hydroxy-4-(2-methylbutyroyl)phenyl)phenyl (R)-4-(2-n-hexyloxypropanoyloxy)benzoate **4**(6,2,OH,H). Using (R)-(2-n-hexyloxypropanoyloxy)-benzoic acid (0.5 g) and (S)-4,3′-dihydroxy-4′-(2-methylbutyroyl)biphenyl (0.46 g), the reaction was carried out in the same manner as described in (4) above to give 0.3 g of the title compound as white microneedles with a mp. of 50.0°C. $[\alpha]_D = +41.9°$ ($CHCl_3$, $c = 0.82$). IR cm^{-1}(KBr): 1772(C*-COO), 1738(Ph-COO), 1636(C=O), 1604, 1264, 1204, 1162, 1120, 1072, 798. ^1H NMR δppm($CDCl_3$): 0.87–0.99(6H, m, $C\underline{H}_3(CH_2)_5O$- and C^*-$CH_2C\underline{H}_3$), 1.26–1.92(16H, m, $CH_3(C\underline{H}_2)_4CH_2O$- and C^*-$C\underline{H}_2CH_3$), 3.43–3.74(3H, m, $C\underline{H}_2O$- and $COC^*\underline{H}$-), 4.18–4.26(1H, m, -$OC^*\underline{H}COO$-), 7.13–7.36(6H, m, 3- and 5-H in Ph and 3-, 5-, 2′- and 6′-H in Biph), 7.69(2H, d, 2- and 6-H in Biph), 7.85(1H, d, 5′-H in Biph), 8.27(2H, d, 2- and 6-H in Ph), 12.71(1H, s, OH).

(8) (R)-4-Hydroxy-4′-(2-n-hexyloxypropanoyloxy)biphenyl **20**[$R_1 = C_6H_{13}OC^*H(CH_3)$-]. To a solution of 4,4′-dihydroxybiphenyl (3.9 g) in methylene chloride (40 ml) and pyridine (40 ml), a solution of (R)-2-n-hexyloxypropanoyl chloride (3.9 g) in methylene chloride (20 ml) was added dropwise and the mixture was stirred for 2 hours at room temperature. The reaction mixture was poured into dilute hydrochloric acid (150 ml) and extracted twice with methylene chloride. The organic extract was washed twice with dilute hydrochloric acid and three times with water and then dried over anhydrous $MgSO_4$. The solvent was removed and the resultant residue was chromatographed on silica gel with n-hexane/ethyl acetate (5:1) as eluent to give 3.2 g of the title compound as white crystals with a mp. of 91.0°C. $[\alpha]_D = +39.4°$ ($CHCl_3$, $c = 0.97$). ^1H NMR δppm ($CDCl_3$): 0.89(3H, t, $CH_2C\underline{H}_3$), 1.23–1.73(11H, m, $C^*HC\underline{H}_3$ and $CH_3(C\underline{H}_2)_4$-), 3.60(2H, m, $C\underline{H}_2OC^*$), 4.21(1H, m, C*H), 6.02(1H, bs, OH), 6.82(2H, d, arom. H ortho to OH), 7.12(2H, d, arom. H ortho to OCO), 7.36–7.46(4H, m, other arom. H).

(9) (S)-4-(2-Methylbutyroyl)benzoic acid **21**[R_2 = (S)-$C_2H_5C^*H(CH_3)$-]. Aluminium chloride (107 g) was added in a small portion to a solution of acetanilide (27.0 g) in dry 1,2-dichloroethane (500 ml), and then a solution of (S)-2-methylbutyroyl chloride (36.2 g) in 1,2-dichloroethane (50 ml) was added dropwise to the mixture under stirring. The resultant mixture was refluxed for 3 hours. After cooling, the mixture was poured into dilute hydrochloric acid (500 ml), and the separated organic layer was washed with water and evaporated. The residue was then dissolved in 6N hydrochloric acid (200 ml), and the solution was refluxed for 4 hours. After cooling, the mixture was neutralized with 20% NaOH aqueous solution and extracted twice with methylene chloride (100 ml). The organic extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The residue was purified by chromatography on silica gel with n-hexane/ethyl acetate (3:1) as eluent to give 10.3 g of (S)-4-amino-(2-methyl)butyrophenone as a pale yellow

liquid. $[\alpha]_D = +21.5°$ ($CHCl_3$, $c = 0.98$). IR cm^{-1}(neat): 3370, 3280, 2940, 2850, 1660, 1605.

To a solution of (S)-4-amino-(2-methyl)butyrophenone (8.9 g) in concentrated hydrochloric acid (20 ml) and water (20 ml), a solution of sodium nitrate (4.3 g) in water (10 ml) was added dropwise at 0–5°C while stirring. After stirring for 1 hour at the same temperature, the mixture was neutralized, poured into a solution of CuCN (14.1 g) in water (200 ml), and refluxed for 30 minutes. After cooling, the mixture was extracted twice with ethyl ether. The organic extract was washed with water and evaporated. The residue was dissolved in an aqueous solution containing 40% sulfuric acid (100 ml) and the solution was refluxed for 3 hours. After cooling to room temperature, the precipitate was separated, washed with water, and recrystallized from ethanol/water to give the title compound as white crystals with a mp. of 101.0°C. $[\alpha]_D = +21.8°$ ($CHCl_3$, $c = 1.0$). IR cm^{-1}(KBr): 2950, 2870, 2650, 2540, 1680, 1605. ^{1}H NMR δppm ($CDCl_3$): 0.91(3H, t, $CH_2C\underline{H}_3$), 1.18(3H, d, $C^*HC\underline{H}_3$), 1.46–1.90(2H, m, CH_2), 3.42(1H, m, C*H), 8.03(2H, d, arom. H ortho to CO), 8.21(2H, d, arom. H ortho to COOH).

Measurements of Properties

Phase transition temperatures were measured by using a differential scanning calorimeter (Perkin Elmer DSC-7) and a polarized microscope (Nikon XTP-11) with a Mettler FP82 hot stage. Values of Ps were measured by the triangular wave method[13] using cells made from two glass plates coated first with a transparent ITO electrode and then with rubbed polyimide. The cell spacing was 10 μm and the area of the electrode was 1.0 cm^2. The resistivities of the compounds examined were more than $6 \times 10^9\ \Omega$ cm.

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