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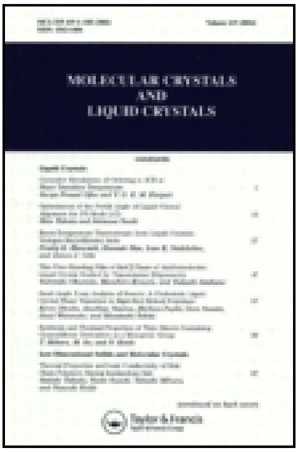

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Optically Active Ketones with Intramolecular Hydrogen Bond

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Optically Active Ketones with Intramolecular Hydrogen Bond

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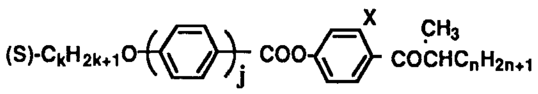
(Received July 25, 1990)

New ferroelectric liquid crystal compounds having an optically active alkanoyl group on one side and a chiral group derived from lactic acid on the other side of the core were synthesized. The new compounds with a three-ring core exhibit very large spontaneous polarization, when the signs of the spontaneous polarization due to the two chiral groups are the same. In particular, the compounds with an intramolecular hydrogen bond show larger spontaneous polarization as high as 1130 nC/cm^2. The spontaneous polarization values are much greater than the sums of the spontaneous polarization for corresponding compounds having one of the two chiral groups. The dopant properties of the new compounds were also studied.

Keywords: ferroelectrics, ketones, hydrogen bond, lactic acid

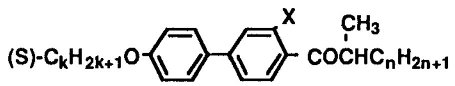
INTRODUCTION

We have discovered that the introduction of a hydroxyl group into the core leads to an increase in spontaneous polarization (Ps) in compounds **1**.[1] This can be



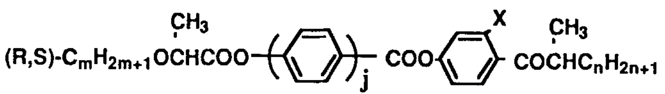
$(S)\text{-}C_kH_{2k+1}O\text{-}(C_6H_4)_j\text{-}COO\text{-}C_6H_3(X)\text{-}COCH(CH_3)C_nH_{2n+1}$

1(j,k,n,X)



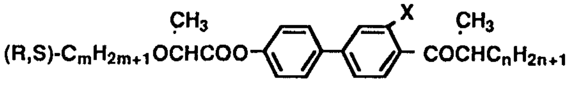
$(S)\text{-}C_kH_{2k+1}O\text{-}C_6H_4\text{-}C_6H_3(X)\text{-}COCH(CH_3)C_nH_{2n+1}$

2(k,n,X)



$(R,S)\text{-}C_mH_{2m+1}OCH(CH_3)COO\text{-}(C_6H_4)_j\text{-}COO\text{-}C_6H_3(X)\text{-}COCH(CH_3)C_nH_{2n+1}$

3(j,m,n,X)



$(R,S)\text{-}C_mH_{2m+1}OCH(CH_3)COO\text{-}C_6H_4\text{-}C_6H_3(X)\text{-}COCH(CH_3)C_nH_{2n+1}$

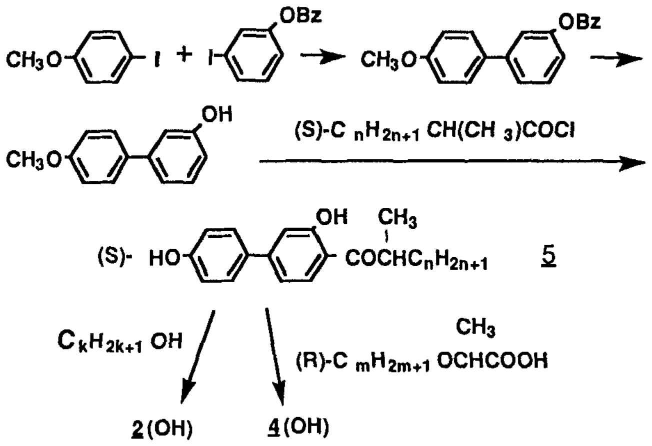
4(m,n,X)

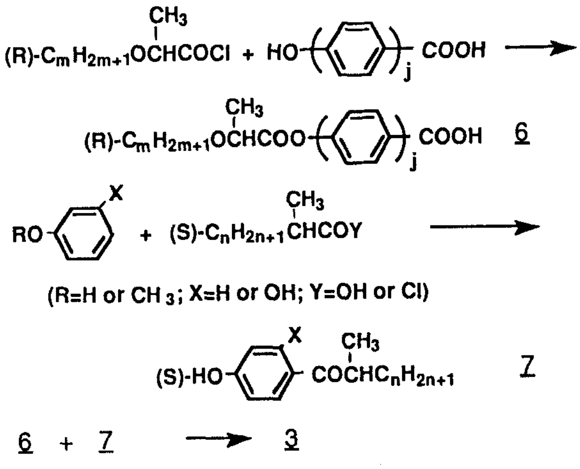
explained by the formation of an intramolecular hydrogen bond between the hydroxyl group and the carbonyl group.

In a study of similar structures, we also synthesized compounds **2** and investigated their dopant properties. Ferroelectric liquid crystal compounds **3** and **4** having another chiral group derived from (R)-lactic acid have been synthesized to increase the Ps value. Their ferroelectric liquid crystal properties and dopant properties will be described.

EXPERIMENTAL

Liquid crystal compounds **2** to **4** were prepared according to Schemes I and II. Phase transition temperatures were determined with a differential scanning calo-


SCHEME I Synthesis of compounds **2** and **4**.


SCHEME II Synthesis of compounds **3**.

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rimeter (Perkin Elmer DSC-7) and a polarized microscope (Nikon XTP-11) with a Mettler FP82 hot stage. The spontaneous polarization was measured by the triangular wave method.[2] Cells used for the measurements were made from two glass plates coated first with transparent indium tin oxide electrodes, and then with rubbed polyimide. The cell spacing was 2.3–10 μm. The electrode area was 1.0 cm^2.

A typical polarization reversal current for compound **3**(2,6,6,OH) is shown in Figure 1. The specific resistance of the compound was measured to be 6×10^9 Ωcm.

RESULTS AND DISCUSSION

Liquid Crystal Properties

Of the compounds we examined, only **3** with a three-ring core, that is j = 2, show liquid crystal phases. Phase transition temperatures, tilt angles (θ), Ps and Ps corrected with regard to θ (Po) are summarized in Table I for **3** and for corresponding compounds having one of the two chiral groups.

As shown in Table I, **3**(2,6,2,X) exhibit an enantiotropic S_A and a monotropic S_C* phase, while **3**(2,6,6,X) show only a monotropic S_C* phase. Although **3** have both structures included in **1** and **8**, **3** with n = 2 show an I-S_A-S_C* phase sequence, analogous to **1**. This means that the effect of the alkanoyl group is predominant in **3** with n = 2. **3** with n = 6, however, show only an S_C* phase, which is common to the two chiral groups. The S_X phase, which appears in **1**, is not observed in **3**.

The presence of a hydroxyl group in **3** causes a considerable decrease in the thermal stabilities of the smectic phases, as is in **1**.[1] The hydroxyl group which forms an intramolecular hydrogen bond increases the molecular width and thus decreases the intermolecular interaction.

The temperature dependences of Ps and θ are shown in Figure 2. The tilt angles

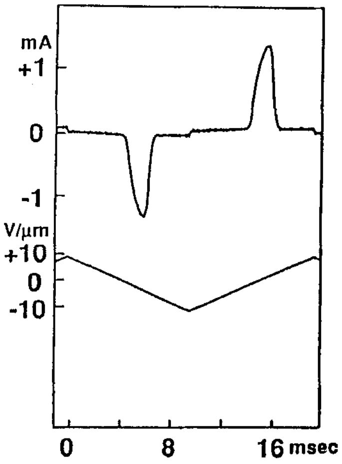


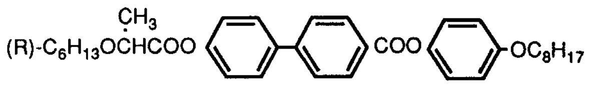
FIGURE 1 Typical polarization reversal current for compound 3(2,6,6,OH) (37°C, 10 μm thick cell).

TABLE I

Phase transition temperatures, Ps, Po and θ for **3** and corresponding compounds

Compound	Cr	S_X	S_C*	S_A	N*	I	θ	Ps	Po
			(°C)				deg	(nC/cm^2)	
3(2,6,2,OH)	•52		(•23)	•63		•	28	-440	-930
3(2,6,6,OH)	•65		(•40)			•	38	-1130	-1830
3(2,6,2,H)	•49		(•49)	•106		•	26	-350	-800
3(2,6,6,H)	•97		(•73)			•	36	-610	-1040
1(2,8,6,OH)	•33	(• 5)	•96	•132		•	20	-146	-427
1(2,8,6,H)	•79	(•65)	•139	•153		•	24	-108	-266
8	•101		•135		•138	•	31	-78	-151

Notes: 1) Ps and θ are measured at 10°C below the S_A-S_C* or I-S_C* transition temperature (Tc). 2) Po = Ps/sinθ.



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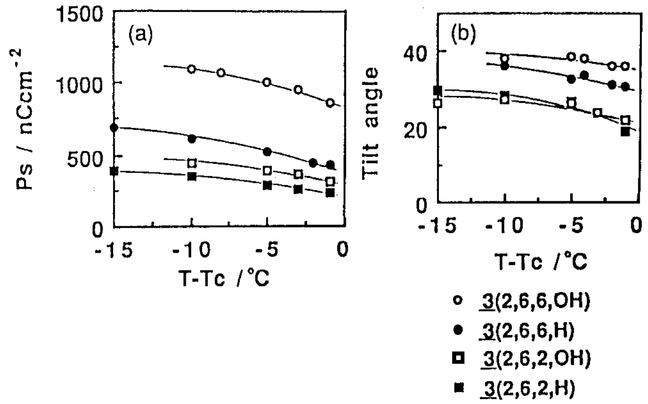

FIGURE 2 Temperature dependences of (a) Ps and (b) tilt angle for **3**.

for **3** are larger than those for **1**, because of the presence of the group derived from lactic acid. The presence of a hydroxyl group in **3** slightly increases the tilt angles.

Compounds **3** with a three-ring core exhibit very large spontaneous polarization. This is attributed to the presence of two chiral groups with the same signs of spontaneous polarization in one molecule. Po for compounds **3** is found to be much larger than the sums of Po for corresponding compounds **1** and **8**. For example, Po for **3**(2,6,6,H) is 1040 and the sum of Po for **1**(2,8,6,H) and **8** is 427 nC/cm^2; Po for **3**(2,6,6,OH) is 1830 and the sum is 578 nC/cm^2. These facts suggest that the dipoles in **3** align more effectively than in **1** or **8**.

Spontaneous polarization values for perfectly ordered compounds **3**(2,6,6,H) and

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3(2,6,6,OH) having a zigzag structure were calculated to be 1520 and 1800 nC/cm^2, respectively, by taking all the dipoles including the central ester groups into consideration. The estimated value for **3**(2,6,6,OH) is almost the same as Po from the measured Ps. This suggests that in this compound the dipoles are almost ideally aligned.

The presence of a hydroxyl group in the core results in an increase in Ps. This is explained by the formation of an intramolecular hydrogen bond, as described above. The increment in Po is 16% for **3** with n = 2, and 76% for **3** with n = 6. This means that the hydroxyl group in **3** with n = 6, as well as a long terminal aliphatic chain,[3] causes damping of the motion around the chiral center.

The largest Ps, which reaches 1130 nC/cm^2 at Tc-T = 10°C, is obtained for **3**(2,6,6,OH). This is the largest value among the ferroelectric liquid crystal compounds ever known.

Dopant Properties

Compounds **1** to **4** are also studied as chiral dopants. A mixture of p-alkoxyphenyl p-alkoxybenzoates showing the transition temperatures, Cr 42°C S_C 69°C S_A 76°C N 88°C I, was used as a base mixture. All mixtures containing 8 mol% of **1** to **4** showed an I-N-S_A-$S_C{}^*$ transition. Ps and θ measured at 10°C below S_A-$S_C{}^*$ transition temperature are shown in Table II. The response times (τ) measured as the time for 0–90% transmission change at a voltage of ±5 V/μm are shown in Figure 3.

The presence of two chiral groups in **3** and **4** causes an increase in Ps of the mixtures. The increment for **3** with j = 2 is much larger than that for **3** with j = 1 or **4**. It is worth noting that the increase in the number of rings in **3** leads to a considerable decrease in response time. This is probably due to the larger Ps. The mixtures containing **3** with j = 2 and a hydroxyl group show the highest S_A-$S_C{}^*$ transition temperatures, though their own S_A-$S_C{}^*$ transition temperatures are lower than that for **1** or **8**. These facts show that **3** with j = 2 have excellent chiral dopant properties.

An increase in the length of the terminal aliphatic chain in the alkanoyl group

TABLE II

Properties of mixtures at Tc − T = 10°C

Compound	Tc/°C	Ps/nCcm^{-2}	θ/°	Po/nCcm^{-2}	τ/μsec
3(2,6,2,OH)	68.0	-8.8	20	25.7	52
3(2,6,6,OH)	66.2	-15.3	22	40.8	47
3(2,6,2,H)	66.0	-7.1	17	24.3	44
3(2,6,6,H)	65.0	-11.7	17	40.0	47
3(1,6,2,OH)	50.4	-4.3	19	13.2	224
3(1,6,2,H)	54.8	-5.4	18	17.5	89
4(6,2,OH)	48.5	-2.6	18	8.4	370
4(6,2,H)	52.8	-3.9	17	13.3	133
1(1,10,2,OH)	54.3	-2.6	14	10.7	113
1(1,10,2,H)	53.4	-1.8	12	8.6	70
2(8,2,OH)	53.4	-2.6	16	9.4	111
2(8,2,H)	51.6	-1.9	13	8.4	110

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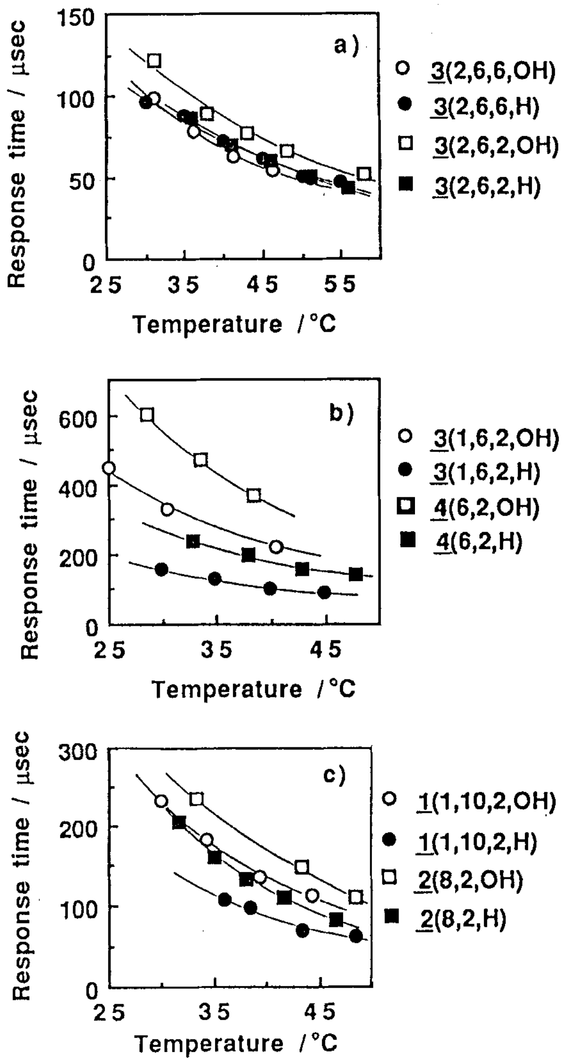

FIGURE 3 Temperature dependences of response time.

considerably increases Ps of the mixture, and results in a decrease in the response time.

The presence of a hydroxyl group in the core in **1** or **2** leads to an increase in Ps, Po and also in response time. In compounds **3** or **4** which have two chiral groups, however, the presence of a hydroxyl group in the core affects the properties of the mixtures in a complicated manner.

The introduction of a hydroxyl group in the compounds having a two-ring core, that is, in **3** with j = 1 and **4**, unexpectedly leads to a decrease in Ps, and to a considerable increase in the response time. The presence of a hydroxyl group in **3** with three benzene rings leads to an increase in Ps and also in θ for all mixtures, although their Po remains unchanged. The effect of a hydroxyl group on response

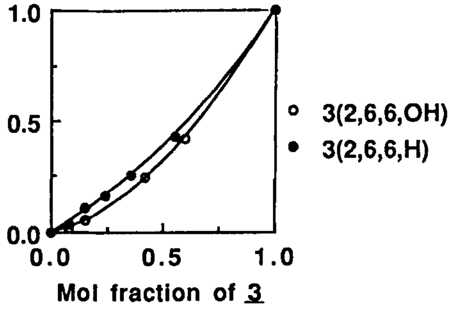

FIGURE 4 Relationship between mole fraction and Po(mixture)/Po(**3**).

time, however, depends on the terminal aliphatic chain length of the alkanoyl group. In **3** with three rings and a short-chain alkanoyl group, the hydroxyl group causes a slight increase in response times. On the other hand, for **3** with three rings and a long-chain alkanoyl group, the hydroxyl group does not cause an increase in response times. In this case, the intermolecular interaction seems to differ from the others.

Figure 4 shows the relationship between mole fraction of **3**($j = 2$) in the mixtures and the ratio of Po for the mixtures to Po for **3** themselves. The curve for **3**(2,6,6,H) is located above that for **3**(2,6,6,OH). As suggested by Dubal,[4] let us suppose that only aggregated dopant molecules contribute to Ps in mixtures. Following the formula,[4] Po(mixture)/Po(**3**) $= x[1 - (1 - x)^j]$, the upper curve indicates that there are more molecules in the aggregates. Thus these curves show that **3**(2,6,6,H) forms aggregates of more molecules than does **3**(2,6,6,OH). If the viscosity increases with increasing number of molecules in aggregates, the difference in the number of aggregated molecules could explain the response time.

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