

Synthesis and Properties of Optically Active α -Aryl- γ -alkyl- γ -lactones as Chiral Dopants
for Ferroelectric Liquid Crystals

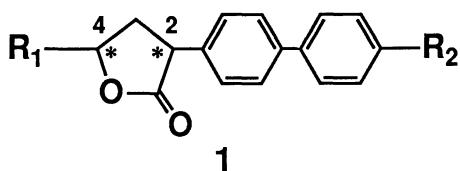
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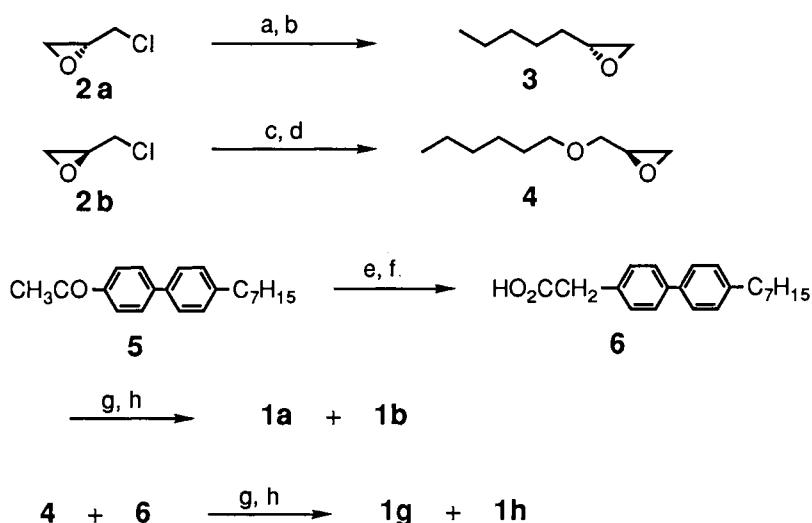
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Optically active α -aryl- γ -alkyl- γ -lactones were synthesized from chiral epichlorohydrin in several steps and found to be good chiral dopants for ferroelectric liquid crystals (FLCs). Relationship between molecular structures and properties is discussed.

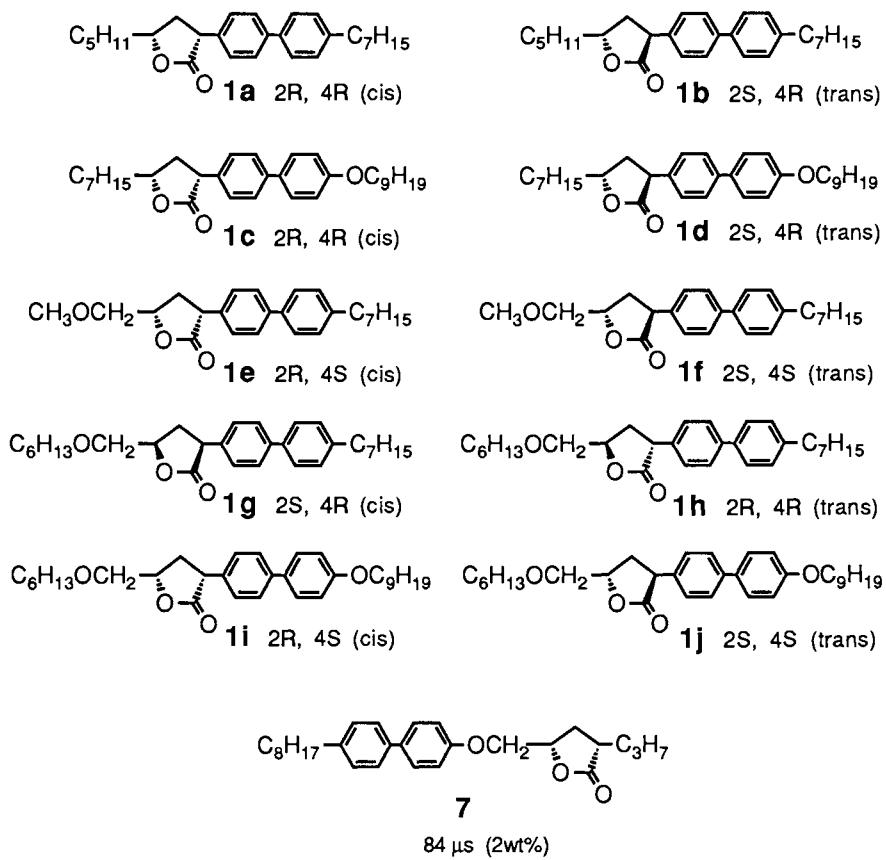
Many FLC materials have been investigated to achieve fast enough response since the proposal of electro-optical devices using FLCs in 1980.¹⁾ Doping of low viscosity smectic C (SmC) liquid crystalline mixtures with chiral compounds having large spontaneous polarization (Ps) is a recent trend for realization of fast response FLC materials. The value of Ps is closely related to partial structures possessing both dipole parts and chiral centers in chiral dopants. We have investigated optically active compounds having chiral γ -lactone ring as chiral dopants^{2,3)} because of their large Ps's⁴⁾ and fast responses.⁵⁾ These excellent properties would be based on the unique γ -lactone structures: 1) two asymmetric carbon atoms are fixed in a rigid 5-membered lactone ring, thereby, free rotation of the dipole moiety (an ester group) is considerably restricted, 2) both the carbonyl group and the ether group are in the same plane⁶⁾ and arranged perpendicular to the long axis of the molecule in the same direction. In this study, we were interested in the properties of optically active α -aryl- γ -alkyl- γ -lactones (**1**) as chiral dopants for FLC. In these molecules, free rotation of the dipole moiety is expected to be restricted because the γ -lactone ring is directly connected with the core aromatic ring. We report herein the synthesis of compounds (**1**) and the effect of the molecular structure on some properties of mixtures doped with them.



The chiral γ -lactones **1** were prepared as shown in Scheme 1. Reaction of butyl magnesium bromide with (R)-epichlorohydrin (**2a**, >99% ee)⁷⁾ in diethylether at -78 °C in the presence of catalytic amount of copper(I) iodide followed by treatment with 48% NaOH at room temperature afforded (R)-1,2-epoxyheptane (**3**) in 78% yield based on **2a**. (S)-Epichlorohydrin (**2b**, >99% ee)⁸⁾ was treated with hexyl alcohol under reflux for 20 minutes in the presence of catalytic amount of concentrated H₂SO₄ followed by treatment with 48% NaOH at 10 °C to afford (S)-hexyl 2,3-epoxypropyl ether (**4**) in 40% yield based on **2b**. Reaction of 4-acetyl-4'-heptylbiphenyl and sulfur in morpholine under reflux for 9 hours followed by hydrolysis using NaOH in aq. ethanol under reflux for 9 hours afforded 4-(4'-heptyl)-biphenylacetic acid (**6**) in 73% yield. Reaction of the



Scheme 1. a) $n\text{-C}_4\text{H}_9\text{MgBr}$, cat. CuI , Et_2O ; b) 48% NaOH aq; c) $n\text{-C}_6\text{H}_{13}\text{OH}$, concd. H_2SO_4 ; d) 48% NaOH aq; e) S , Morpholine; f) NaOH , EtOH , H_2O ; g) 2 equiv. LDA , **3**, THF ; h) concd. H_2SO_4 , Benzene.



dianion of **6** with **3** in tetrahydrofuran at -78°C followed by lactonization using catalytic amount of concentrated H_2SO_4 in benzene under reflux for 30 minutes gave **1a** (36%) and **1b** (41%) as a mixture of diastereomers with high enantioselectivity.⁹⁾ **1g** (40%) and **1h** (47%) were prepared from **4** and **6** in a similar manner. Each diastereomer of **1** was easily separated by silica gel column chromatography.

Table 1. Properties of FLC mixtures containing 2wt% of **1** and 98wt% of the mixture A^{a)}

Chiral dopant	Mp ^{b)} / [°] C	Phase transition temp ^{c)} / [°] C				Response ^{d)} μs	Ps ^{e)} 2wt% (5wt%) nC cm ⁻²	Tilt angle deg
		SmC*	SmA	N*	I			
1a	102	52	61	68		100	+5.3 (+16.6)	21
1b	99	52	61	68		655	+— ^{f)} (+0.8)	17
1c	126	52	62	69		138	+2.9 (+12.5)	21
1d	g)	53	62	69		325	+— ^{f)} (+— ^{f)}	10
1e	68	50	60	68		139	+2.9 (+6.5)	20
1f	66	51	61	68		396	+— ^{f)} (+0.8)	18
1g	71	51	60	67		146	-1.1 (-3.3)	19
1h	48	51	60	67		230	-— ^{f)} (-1.2)	17
1i	92	53	61	68		132	+1.8 (+7.8)	19
1j	64	53	61	68		214	+— ^{f)} (+1.3)	16

a) See Ref. 10. b) Melting point of chiral dopant. c) SmC*: chiral smectic C Phase, SmA: smectic A phase, N*: chiral nematic phase, I: isotropic liquid phase. d) Response time was defined as the 0 to 50% change of transmission of light under the voltage of 10 V_{p-p}/μm at 25 °C. Cells were coated with polyimide rubbed in the same direction and their thickness was 2 μm. e) Measured by the triangular method at 25 °C.¹⁴⁾ f) The absolute value was lower than 0.5. g) This compound showed mesophases. Cr 96 SmC* 114 SmA 118 I (°C).

Table 1 shows melting points of **1**, and some physical properties and electro-optical characteristics of the FLC mixtures comprised of **1** (2 wt%) and the achiral liquid crystalline mixture A (98 wt%).¹⁰⁾ Almost all the γ-lactones (**1**) did not exhibit mesophases. Compounds having alkyloxyethyl groups in R₁ showed lower melting points than those having alkyl groups in R₁. (**1a** vs. **1g**, **1b** vs. **1h**, **1c** vs. **1i**) On the other hand, compounds having alkyloxy groups in R₂ showed higher melting points than those having alkyl groups in R₂. (**1a** vs. **1c**, **1g** vs. **1i**, **1h** vs. **1j**) Almost all the transition temperatures of the mixtures, however, were unaffected by doping of **1** due to the small amount (2 wt%) of doping. The mixture containing cis-γ-lactone **1a** showed a very large Ps (5.3 nC/cm²), a fast response (100 μs) and a suitable tilt angle (21 degrees) at 25 °C. The mixtures containing other cis-γ-lactones (**1c**, **1e**, **1g**, **1i**) showed smaller Ps's and slower responses than the mixture containing **1a**. This result would indicate that the dipoles of the ester groups in γ-lactones and the dipoles of the ether groups in R₁ or R₂ would not be arranged in the same direction in SmC*. All the mixtures containing trans-γ-lactones showed much smaller Ps's (lower than 0.5 nC/cm²) and slower responses than the mixtures containing cis-γ-lactones. This observation would be explained by the conformational difference between cis-γ-lactone and trans-γ-lactone which causes a different interaction with SmC*.^{11,12)} Based on the zig-zag model in SmC*,¹³⁾ the conformations of the cis-γ-lactone **1a** and the trans-γ-lactone **1b** are drawn in Fig. 1. The conformer **cis-A** (Ps>0) is fitted to the zig-zag shape of the host molecules, and the conformer **cis-B** (Ps<0) is far from the zig-zag shape, therefore, the contribution of **cis-A** would be higher than **cis-B** in

SmC*. On the other hand, both the conformer **trans-A** ($Ps > 0$) and the conformer **trans-B** ($Ps < 0$) are not fitted to the zig-zag shape, therefore, there would be almost no contributory difference between them in SmC*.

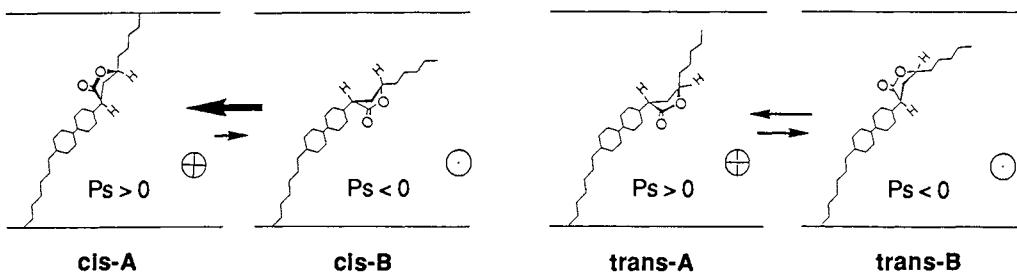


Fig. 1. Molecular conformations of **1a** and **1b** in SmC*.

The present study demonstrates that the α -aryl- γ -alkyl- γ -lactones are good chiral dopants for FLCs. The mixtures containing another type of γ -lactone, i.e. (2S, 4S)-cis- α -propyl- γ -4-(4'-octyl)-biphenylloxymethyl- γ -lactone (7),³⁾ however, showed a little faster responses (84 μ s) than the mixtures containing **1**. These results led to the conclusion that it would not be necessary to design the dipole parts directly connected with the core parts in order to get an excellent chiral dopant having optically active γ -lactone ring.

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- 9) The optical yields were estimated more than 95% by the HPLC analysis using chiral column, "CHIRALCEL OD" produced by Daicel Chemical Industries, Ltd.
- 10) The host liquid crystalline mixture A is composed of 2-(4-heptyloxyphenyl)-5-heptylpyrimidine (5 wt%), 2-(4-octyloxyphenyl)-5-heptylpyrimidine (10 wt%), 2-(4-nonyloxyphenyl)-5-heptylpyrimidine (15 wt%), 2-(4-octyloxyphenyl)-5-octylpyrimidine (20 wt%), 2-(4-decyloxyphenyl)-5-octylpyrimidine (30 wt%), and 2-(4-hexyloxyphenyl)-5-nonylpyrimidine (20 wt%). Cr <rt SmC 51 SmA 63 N 69 I (°C). Cr: crystalline phase, SmC: smectic C phase, SmA: smectic A phase, N: nematic phase, I: isotropic liquid phase.
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