

Synthesis and Electro-Optical Properties of Silicon-Containing Chiral Cyanocyclopropanes and  $\gamma$ -Lactones  
as Dopants for Ferroelectric Liquid Crystals

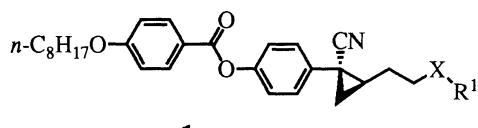
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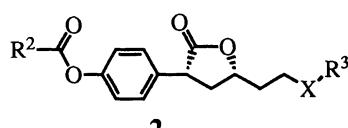
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Starting with (S)-1-chloro-2,3-epoxypropane optically active cyanocyclopropanes and *cis*- $\gamma$ -lactones having a trialkylsilyl group in an alkyl side chain were synthesized and ferroelectric liquid crystals mixture containing one of these as a chiral dopant exhibited large spontaneous polarization.

Ferroelectric liquid crystals (FLCs) are materials expected to be applicable to high speed display device.<sup>1)</sup> In general, FLC materials are made of achiral host liquid crystals mixture of low viscosity and a chiral compound having large spontaneous polarization (Ps) as a chiral dopant. Recently, many chiral dopants have been designed and synthesized which allow to achieve rapid switching.<sup>2-4)</sup> We have disclosed that optically active cyanocyclopropanes (e.g. **1d**) and *cis*- $\gamma$ -lactones (e.g. **2c**) show extremely large Ps's.<sup>5-8)</sup> In order to study the steric effect of the alkyl side chain of these on Ps and response time, we have prepared chiral dopants **1a-1c**, **2a**, **2b**, **2d**, **2e**, and **2g** containing such a bulky side chain as trialkylsilyl. In this paper their synthesis and electro-optical properties are reported.

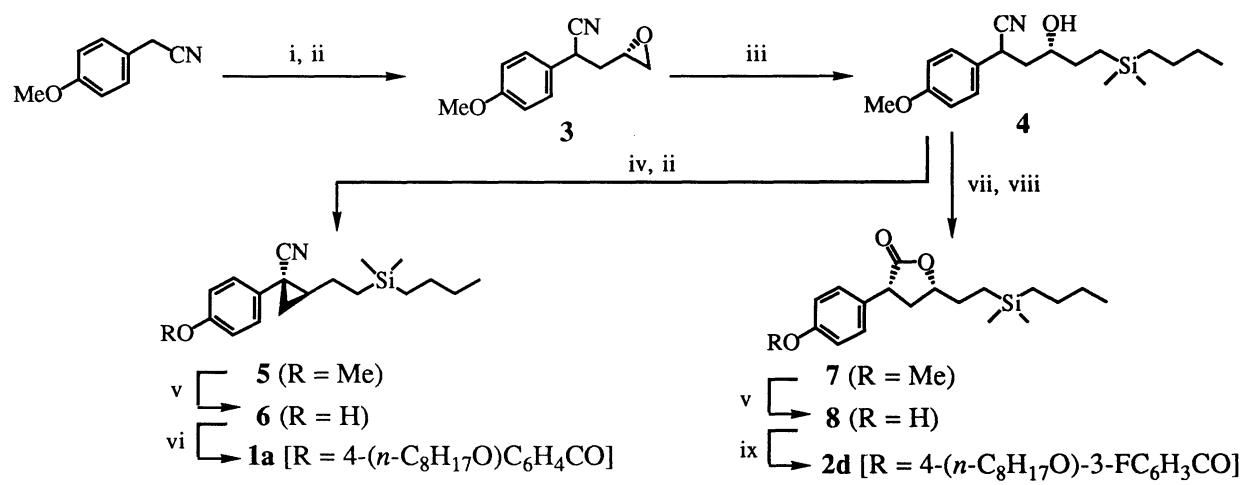


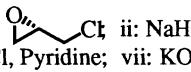
**a:** X = SiMe<sub>2</sub> R<sup>1</sup> = n-C<sub>4</sub>H<sub>9</sub>  
**b:** SiMe<sub>2</sub> Me  
**c:** CMe<sub>2</sub> Me  
**d:** CH<sub>2</sub> Me



**a:** R<sup>2</sup> = n-C<sub>8</sub>H<sub>17</sub>O-phenyl X = SiMe<sub>2</sub> R<sup>3</sup> = Me  
**b:** " CMe<sub>2</sub> Me  
**c:** " CH<sub>2</sub> n-C<sub>3</sub>H<sub>7</sub>  
**d:** n-C<sub>8</sub>H<sub>17</sub>O-phenyl SiMe<sub>2</sub> n-C<sub>4</sub>H<sub>9</sub>  
**e:** " SiMe<sub>2</sub> Me  
**f:** " CH<sub>2</sub> n-C<sub>3</sub>H<sub>7</sub>  
**g:** n-C<sub>6</sub>H<sub>13</sub> SiMe<sub>2</sub> n-C<sub>4</sub>H<sub>9</sub>  
**h:** " CH<sub>2</sub> n-C<sub>3</sub>H<sub>7</sub>

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i: *n*-BuLi,  ii: NaH; iii: ClMgCH<sub>2</sub>SiMe<sub>2</sub>(*n*-C<sub>4</sub>H<sub>9</sub>), CuI; iv: 4-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl; v: AlCl<sub>3</sub>, Me<sub>2</sub>S; vi: 4-(*n*-C<sub>8</sub>H<sub>17</sub>O)-C<sub>6</sub>H<sub>4</sub>COCl, Pyridine; vii: KOH; viii: 4-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H; ix: 4-(*n*-C<sub>8</sub>H<sub>17</sub>O)-3-FC<sub>6</sub>H<sub>3</sub>COOH, DCC

Scheme 1.

Silicon-containing cyanocyclopropane **1a** was prepared according to the route shown in Scheme 1. Cyanogen oxide **3**, obtained in 77% yield (*ca.* 1:1 mixture of diastereomers) through the reaction of the carbanion of 4-methoxy-phenylacetonitrile with (*S*)-1-chloro-2,3-epoxypropane<sup>9</sup>) followed by ring-closure, was allowed to react with ClMgCH<sub>2</sub>SiMe<sub>2</sub>(*n*-C<sub>4</sub>H<sub>9</sub>) in the presence of CuI to give an adduct **4** (68% yield). Tosylation of **4** (65% yield) followed by treatment with NaH stereoselectively afforded cyanocyclopropane **5** (67% yield)<sup>5</sup> which was demethylated using AlCl<sub>3</sub>-Me<sub>2</sub>S reagent system to give phenol **6** (99% yield). Esterification of **6** with 4-octyloxybenzoyl chloride (98% yield) afforded **1a**. Use of ClMgCH<sub>2</sub>SiMe<sub>3</sub> or BrMgCH<sub>2</sub>CMe<sub>3</sub> at step iii gave **1b-1d**. Silicon-containing  $\gamma$ -lactone **2d** was prepared through the same intermediate **4**. Hydrolysis of the cyano group of **4** followed by lactonization afforded *cis*- $\gamma$ -lactone **7** (51% yield) and its *trans*-isomer (29% yield). These two isomers were easily separated by column chromatography. Demethylation of **7** was effected as above and gave **8** (74% yield) which was esterified with 3-fluoro-4-octyloxybenzoic acid by the use of dicyclohexylcarbodiimide (DCC) to give **2d** (94% yield). In a similar manner, lactones **2a**, **2b**, **2e**, and **2g** were obtained. Using (*R*)-1,2-epoxyoctane in lieu of chiral epichlorohydrin we prepared lactones **2c**, **2f**, and **2h**.<sup>6</sup> Each of **1a-1d** or **2a-2h** was added to an achiral host liquid crystal mixture A,<sup>10</sup> and the electro-optical properties of the resulting mixtures were measured as summarized in Table 1. The mixture containing 5 wt% of silicon-containing dopant **1a** or **1b** exhibited large Ps (6.8 nC cm<sup>-2</sup> each), about 2.7 times larger than that of **1d** (2.5 nC cm<sup>-2</sup>), and hence short response times (107 or 118 vs 243  $\mu$ s respectively). Worthy to note is that a carbon analog **1c** also was proved to enhance of Ps (8.0 nC cm<sup>-2</sup>) and decrease of response time (118  $\mu$ s). As mixture containing **1a** exhibited higher phase transition temperature of SmC\*  $\rightarrow$  SmA than those of **1b**, **1c** or **1d** (57 °C vs 48, 47 or 46 °C), **1a** appears to be the best chiral dopant in the series of cyanocyclopropanes **1**. Among the dopants of phenyl benzoate type  $\gamma$ -lactones **2a-2c**, **2b** induced the largest Ps, but there was observed little difference in response time. Although 2 wt% mixture of 3-fluorobenzoate type  $\gamma$ -lactone **2d** or **2e** showed large Ps as compared with **2f** (9.3 or 9.9 vs. 6.2 nC cm<sup>-2</sup>), the shortest limit of response time seems to be 100  $\mu$ s, since doping 3 or 4 wt% of **2e** in Host A did not improve response time to any further extent. Cyclohexane-

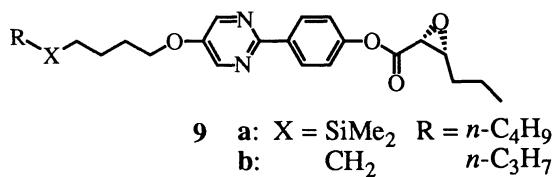
carboxylate type  $\gamma$ -lactone **2g** exhibited double Ps, twice as much as **2b** at 2 wt% level, but at 4 wt% level no increase of Ps was observed any more.

As was observed in cases of 2-arylalkanenitriles<sup>11)</sup> and aryl alkyl sulfoxides,<sup>12)</sup> chiral dopant having 1-methylalkyl side chain exhibit larger Ps's than the linear alkyl derivatives, probably because free rotation of the side chain is restricted by branching near a polar group to fix the dipole of the polar group. However, this effect is absent in *cis*- $\gamma$ -lactones **2**, since Ps of mixtures containing **2** was more affected by core structures and/or the concentration of the chiral dopants rather than a buky alkyl side chain. Similar observation was reported in the case of chiral dopants **9**.<sup>13)</sup> FLC mixture containing **9a** exhibits larger Ps than **9b**. Herein no intramolecular interaction is anticipated between the polar epoxy ester moiety and the silyl group. Thus, intermolecular interaction should be considered between a chiral dopant and host liquid crystal molecules or between the polar group of one dopant molecule and the silyl group of another dopant through host molecules in the liquid crystal phase. This effect is apparently remarkable in the case of *cis*- $\gamma$ -lactones **2**.

Table 1. Phase transition temperature and electro-optical properties of **1a-1d** and **2a-2h** in Host A at 25 °C a)

Chiral dopant (wt%)		Phase transition temperature/°C				Ps <sup>c)</sup> /nC cm <sup>-2</sup>	Response time <sup>d)</sup> /μs	Tilt angle/deg
		SmC*	SmA	N*	Iso <sup>b)</sup>			
<b>1a</b>	(5)	57	66	69		+6.8	107	18
<b>1b</b>	(5)	48	66	68		+6.8	118	19
<b>1c</b>	(5)	47	66	67		+8.0	118	18
<b>1d</b>	(5)	46	62	66		+2.5	243	18
<b>2a</b>	(2)	55	63	68		+4.2	149	23
<b>2b</b>	(2)	56	63	69		+6.6	150	25
<b>2c</b>	(2)	57	64	70		+4.5	162	25
<b>2d</b>	(2)	57	63	69		+9.3	110	26
<b>2e</b>	(2)	57	63	69		+9.9	120	25
	(3)	57	60	68		+14.1	104	26
	(4)	57	59	68		+27.0	101	28
<b>2f</b>	(2)	57	64	70		+6.2	129	27
<b>2g</b>	(2)	56	63	69		+8.1	117	25
	(4)	54	61	68		+9.7	110	25
<b>2h</b>	(2)	55	64	70		+4.2	142	25
	(4)	57	63	69		+13.5	94	27

a) The liquid crystal mixture was sealed in a polyimide rubbing cell of 2  $\mu$ m thickness, and a square wave of 10 V<sub>p-p</sub>/ $\mu$ m was applied to the cell. b) SmC\*: chiral smectic C phase; SmA: smectic A phase; N\*: chiral nematic phase; Iso: isotropic liquid phase. c) Ps was measured by the triangular wave method. d) The change of transmittance (from 0 to 90%) of light was observed.



In summary, we synthesized new chiral dopants having a silycon-containing side chain as well as a side chain containing a quarternary carbon and demonstrated these exhibited larger Ps's than those having a linear side chain. These observations must be important not only for the design of new chiral dopants of large Ps's but also for the investigation of the intra- and intermolecular interactions of liquid crystalline molecules.

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- 9) (S)-1-Chloro-2,3-epoxypropane (>96% ee) was purchased from Daiso Co. Ltd and used directly.
- 10) Host A consists of 2-(4-nonyloxyphenyl)-5-heptylpyrimidine (30 wt%), 2-(4-octyloxyphenyl)-5-octylpyrimidine (20 wt%), 2-(4-decyloxyphenyl)-5-octylpyrimidine (30 wt%), and 2-(4-octyloxyphenyl)-5-nonylpyrimidine (20 wt%). The phase transition temperatures (T/°C) were Cr 13 SmC 56 SmA 65 N 70 Iso (Cr: crystal phase; SmC: smectic C phase; N: nematic phase).
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