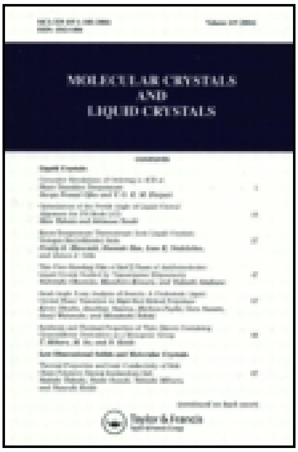

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New Chiral Dopants with an Optically Active Six-membered Ring for Ferroelectric Liquid Crystals. Effect of Direction of the Dipole Moment on Spontaneous Polarization

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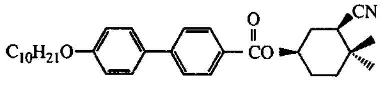
New chiral dopants containing an optically active six-membered ring with a cyano group were synthesized. New chiral dopants containing an optically active six-membered ring with an epoxy group were also synthesized and the effect of the direction of the dipoles on spontaneous polarization were discussed using them. The spontaneous polarization is thought to be influenced by the direction of the dipoles of the chiral moiety.

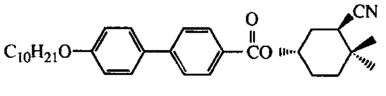
Keywords: Ferroelectric liquid crystals, chiral dopants, spontaneous polarization, chiral smectic C phase, cyano group, epoxy group, six-membered ring.

INTRODUCTION

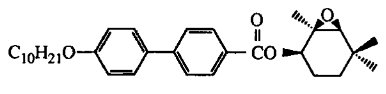
Ferroelectric liquid crystals (FLCs) have attracted a great deal of attention since surface-stabilized FLC (SSFLC) devices were proposed in 1980.[1] One of the important factors for the commercialization of the devices is the response time of the FLC mixtures. To realize practical FLC materials, the doping of chiral dopants potentially having a large spontaneous polarization (Ps) to non-chiral smectic C (Sc) mixtures with low viscosity is an effective method. Therefore, many chiral dopants potentially having a large Ps have been recently investigated. Several researchers mentioned some empirical rules in inducing a large Ps in Sc mixtures, that is, it depends on (1) the magnitude of the dipole near the chiral center, (2) the distance between the chiral center and the dipole, (3) the restriction of the rotational freedom around the chiral center.[2,3] On other hand, it has been known that the component of the molecular dipole moment perpendicular to the molecular axis takes an important role in the generation of Ps since the discovery of FLCs.[4] However, there are only a few examples of practical examination of the effects of the direction of the dipoles on the Ps. One is a discussion by Walba *et al.*, who examined the effects of the component of molecular dipole moments perpendicular to the molecular tilt plane using a "binding site" model.[5,6]



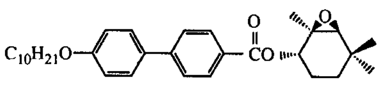
1a



1b



2a

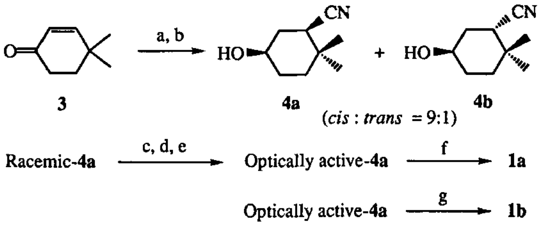


2b

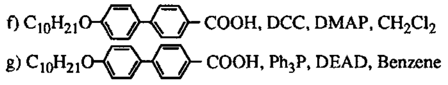
Similar discussion was also done by Kusumoto *et al.* using γ-lactone derivatives.[7] We report herein the influence of the direction of the dipoles of chiral dopants containing a six-membered ring on the spontaneous polarization.

RESULTS AND DISCUSSION

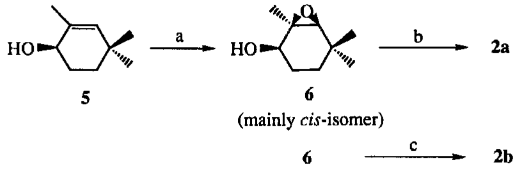
The compounds **1a** and **1b** were synthesized as shown in Scheme 1. Cyanation of 4,4-dimethyl cyclohexen-1-one according to the method of Nagata *et al.*[8] was followed by $NaBH_4$ reduction to afford alcohols **4a** and **4b** (*cis*:*trans* = 9:1). The *cis*-alcohol **4a** separated by silica gel column chromatography was converted to its (S)-α-methoxy-α-trifluoromethylacetate ((S)-MTPA ester) and the diastereomers produced were separated by preparative HPLC. Hydrolysis of the polar isomer gave the optically active



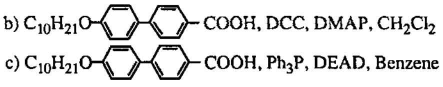
Scheme 1. a) Et_2AlCN, Toluene b) $NaBH_4$, EtOH c) (S)-MTPACl, Pyridine
d) Separation e) LiOH, EtOH, H_2O



f) $C_{10}H_{21}O$–C$_6$H$_4$–C$_6$H$_4$–COOH, DCC, DMAP, CH_2Cl_2
g) $C_{10}H_{21}O$–C$_6$H$_4$–C$_6$H$_4$–COOH, Ph_3P, DEAD, Benzene



Scheme 2. a) mCPBA, $NaHCO_3$, CH_2Cl_2



b) $C_{10}H_{21}O$–C$_6$H$_4$–C$_6$H$_4$–COOH, DCC, DMAP, CH_2Cl_2
c) $C_{10}H_{21}O$–C$_6$H$_4$–C$_6$H$_4$–COOH, Ph_3P, DEAD, Benzene

cis-alcohol **6**. (The absolute configuration has not been determined.) *Cis*-compound **1a** was prepared by esterification with a mesogen using the DCC method, and *trans*-compound **1b** was prepared by using the Mitsunobu esterification.[9] Compounds **2a** and **2b** were prepared as shown in Scheme 2. Epoxidation of optically active allylic alcohol **5**(10) using mCPBA afforded mainly *cis* isomer **6**. Purified **6** was esterified using the DCC method to give **2a**, which was then esterified using Mitsunobu method to give **2b**.

Table 1 shows induced Ps values and the other properties of the FLC mixtures comprised of the new chiral dopants (2 mol%) and non-chiral base mixture A[11] (98 mol%). The FLC properties of an already reported chiral dopant containing δ-valerolactone **7**[12,13] are also shown in Table 1.

We note that the difference in the induced Ps values is caused by the direction of the dipoles on the ring structure, as shown in Figure 1. That is to say, the Ps value is the largest for the δ-lactone derivative **7** whose dipole moment is parallel with respect to the six-membered ring. The Ps value of the cyano derivative **1a** is about two-thirds of the δ-lactone derivative **7**, though the value of the dipole moment of the cyano group is not so different from that of the δ-lactone. This is probably because a component of the dipole moment parallel to the six-membered ring is an effective dipole moment for Ps. That is, cyano derivative **1a** has not only a component of the dipole moment parallel to the six-membered ring but has a component of the dipole moment normal to the six-membered ring, while the dipole moment of δ-lactone is thought to be parallel to the six-membered ring. In compound **1b**, the cyano group is thought to be in an axial position and its direction of the dipole is perpendicular with respect to the cyclohexane ring. Therefore, the effective dipole moment for Ps is thought to be nearly zero when the mesogen is in an equatorial position.

However, actual induced Ps values for compound **1b** is admittedly smaller than that for compound **1a** but not zero. This is probably due to the influence of the ester linkage

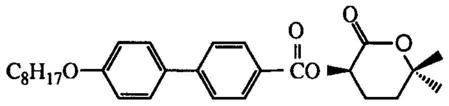


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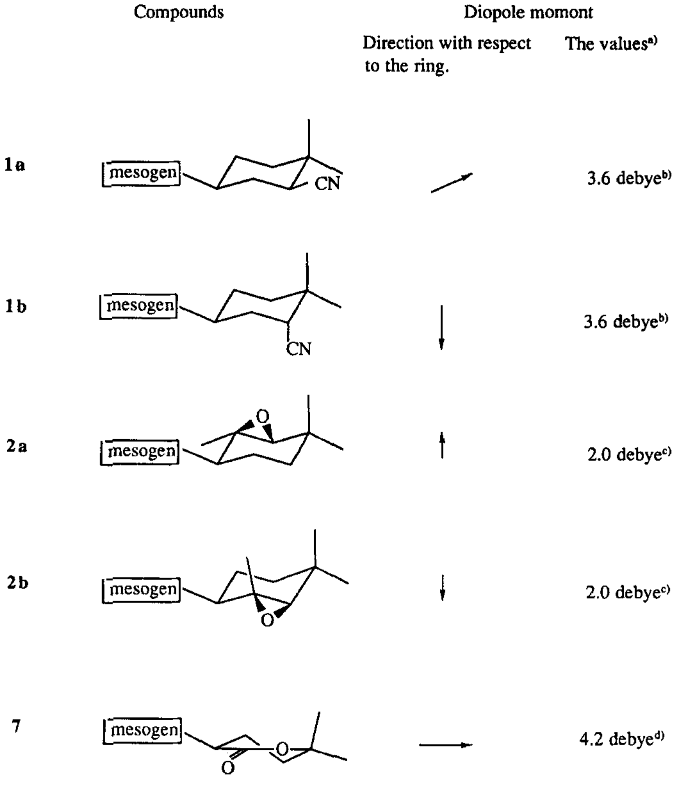
TABLE 1

Some physical properties of chiral doapants and the FLC mixtures containing 2 mol% of the chiral dopants and non-chiral mixture A

Chiral compounds No.	Mp °C	Properties of FLC mixtures Phase transition temp. S_C*	S_A	N*	I	Response time μsec	Ps nC/cm^2
1a	64	47	61	66		98	−3.7
1b	105	43	61	65		145	+1.7
2a	52	47	61	66		1580	<0.1
2b	71	45	62	66		256	+0.6
7	128	52	59	66		92	−5.5



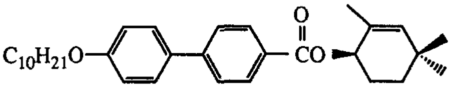
a) Cited from ref.14 and 15. b) the value of isobutyronitrile.
c) the value of propylene oxide. d) the value of δ-valerolactone.

FIGURE 1 Some models of the dipole moment of the chiral moiety.

between the core and the cyclohexane ring, and another reason especially for compound **1b** is that the mesogen does not necessarily lie in the equatorial position. (The effect of the ester linkage on the Ps value is estimated to be 0.7 nC/cm^2, because the induced Ps value containing 2 mol% of compound **8** was -0.7 nC/cm^2).

Next, considering the epoxy derivatives **2a** and **2b**, though the value of the dipole moment originating from the epoxy group is half the values of the cyano group or lactone ring, they should still be expected to show half of the induced Ps value that the lactone compound **7** induces, if the direction of dipole moment is not concerned. However, the actual Ps values of compounds **2a** and **2b** are nearly zero. This would also be because the epoxy group is arranged perpendicular to the cyclohexane ring.

Although we should have essentially discussed the direction of the dipole moment with respect to the tilt plane as indicated by Walba *et al.*,[5,6] we can understand the



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results when the tilt plane of the stable comformer is perpendicular to the cyclohexane ring. Appropriate calculations will be necessary to determine the stable conformers in the Sc phase.

In conclusion, we synthesized new chiral dopants with an optically active six-membered ring and have discussed the influence of the direction of the dipole moment of the chiral moiety in the generation of spontaneous polarization.

EXPERIMENTAL

Measurement of physical properties

FLC mixtures were prepared by adding 2 mol% of the chiral compound into a non-chiral Sc mixture[11] whose transition temperatures (T/°C) were Cr 4 S_c51 S_A 62 N 68 I. Ps values were measured by the triangular wave method [16] at 25 °C. The sign of the Ps was determined by observing the tilt direction in the DC field as defined by Lagerwall *et al.* [17] The response time was defined as the 0 to 50% change in light transmission under a square-wave voltage of $\pm 5\,V/\mu m$ at 25 °C using a polyimide rubbing cell of 2.0 μm thickness. Transition temperatures were determined using a NIKON POH polarizing microscope fitted with a Mettler FP52 heating stage and control unit.

Synthesis of new chiral dopants

3-Cyano-4,4-dimethylcyclohexanone

To a solution of 4,4-dimethyl-2-cyclohexene-1-one **3** (2 g) in dry benzene (20 ml) was added dropwise diethylaluminum cyanide solution (1M in toluene, 32 ml) at 5 °C under Ar. The mixture was stirred for 12 hr after the addition with a gradual rise of the reaction temperature to room temperature. The mixture was quenched with water (30 ml) and N-HCl (10 ml). It was poured into N-NaOH (70 ml) and extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (40 g). Elution with hexane-EtOAc (5:1) gave 1.56 g (64%) of 3-cyano-4,4-dimethylhexanone, m.p. 79 °C; IR (KBr) 2250 (w), 1710 (s) cm^{-1}; ^1H-NMR($CDCl_3$, 90 MHz) 1.20 (3H, s), 1.29 (3H, s), 1.40–2.10 (2H, m), 2.33–2.67 (4H, m), 2.80 (1H, dd, J = 9 Hz, J = 6 Hz).

Racemic-*cis*-3-cyano-4,4-dimethylcyclohexanol **4a**

To a solution of 3-cyano-4,4-dimethylcyclohexanone (1.04 g) in absolute EtOH (30 ml) was added $NaBH_4$ (0.14 g) at 5 °C. the mixture was stirred for 1 hr at 5 °C, then poured into water (100 ml) and extracted with EtOAc. The extract was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was dissolved into pyridine (20 ml) and Ac_2O (1.4 g) was added to the solution at 0 °C. The mixture was stirred for 40 hr at room temperature. It was poured into ice-cooled N-HCl (50 ml) and extracted with Et_2O. The extract was washed with N-HCl and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was analyzed by HPLC (column, Senshu Pack Silica-1301-N (4.6 mm x 25 cm); solvent, *n*-hexane-THF 30:1; 1 ml/min; detector, 220 nm) Rf 37.9 min (*trans*-isomer, 10.1%) Rf 41.6 min (*cis*-isomer, 89.9%). It was chromatographed over SiO_2. Elution with hexane-EtOAc (20:1 → 10:1) gave 0.77 g of *cis*-3-cyano-4,4-dimethylhexyl acetate. To a solution of the acetate (0.70 g) in MeOH (10 ml) was added K_2CO_3 (1.0 g) at room temperature. The mixture was stirred for 16 hr and filtered. The filtrate was concentrated *in vacuo* to give 0.53 g (55%) of racemic-**4a**, IR (neat) 3420 (br), 2250(w) cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) 1.10 (6H, s), 1.10–2.30 (6H, m), 2.38 (1H, dd, J = 9 Hz, J = 4 Hz), 3.40–3.75 (1H, m).

Optically active-*cis*-3-cyano-4,4-dimethylcyclohexanol 4a

To a solution of racemic-**4a** (0.12 g) in dry pyridine (2 ml) was added (S)-α-methoxy-α (trifluoromethyl)phenylacetyl chloride ((S)-MTPACl, 0.30 g) at room temperature. The mixture was stirred for 16 hr, poured into N-HCl (30 ml) and extracted with Et_2O. The extract was washed with N-HCl and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was separated by preparative HPLC (column, YMC-Packed Column-D-SIL-5-06 (2 cm × 25 cm); solvent, hexane-THF 30:1; 16 ml/min) to give (S)-MTPA ester of **4a** (polar fraction, 58 mg). The MTPA ester (50 mg) in EtOH (5 ml) was added $LiOH \cdot H_2O$ (20 mg) at room temperature. The mixture was stirred for 8 hr at room temperature, then poured into water (20 ml) and extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to give 21 mg of optically active-**4a**.

Optically active-*cis*-3-cyano-4,4-dimethylcyclohexyl 4′-*n*-decyloxybiphenyl-4-carboxylate 1a

4-Dimethylaminopyridine (2 mg) was added to a suspension of optically active-**4a** (6.8 mg), 4′-*n*-decyloxybiphenyl-4-carboxylic acid (16 mg) and 1,3-dicyclohexylcarbodiimide (9.3 mg) in CH_2Cl_2 (1 ml) at room temperature. After being stirred overnight, the mixture was concentrated *in vacuo*. The residue was chromatographed over SiO_2 (1 g). Elution with hexane-EtOAc (15:1) gave **1a**. This was recrystallized from hexane-EtOAc to yield 14.2 mg (65%) of pure **1a**, m.p. 64 °C; IR (KBr)2220 (w), 1700 (s) cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) 0.70–2.40 (25H, m), 1.18 (3H, s), 1.21 (3H, s), 2.55 (1H, dd, J = 11 Hz, J = 4 Hz), 4.00 (2H, t, J = 6 Hz), 4.80–5.10 (1H, m), 6.99 (2H, d, J = 8 Hz), 7.57 (2H, d, J = 8 Hz) 7.63(2H, d, J = 8Hz) 8.12 (2H, d, J = 8 Hz).

Optically active-*trans*-3-cyano-4,4-dimethylcyclohexyl 4′-*n*-decyloxybiphenyl-4-carboxylate 1b

Triphenylphosphine (15 mg) was added to a suspension of optically active-**4a** (8.6 mg), 4′-*n*-decyloxybiphenyl-4-carboxylic acid (20 mg) and diethyl azodicarboxylate (10 mg) in benzene (1 ml) at room temperature. After being stirred overnight, the mixture was concentrated *in vacuo*. The residue was chromatographed over SiO_2 (1 g). Elution with hexane-EtOAc (15:1) gave **1b**. This was recrystallized from hexane-EtOAc to yield 15.3 mg (56%) of pure **1b**, m.p. 105 °C; IR (KBr) 2210 (w), 1700 (s) cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) 0.70–2.35 (25H, m), 1.17 (3H, s), 1.22 (3H, s), 2.81 (1H, dd, J = 9 Hz, J = 4 Hz), 4.00 (2H, t, J = 6 Hz), 5.27–5.42 (1H, m), 6.99 (2H, d, J = 8 Hz), 7.57 (2H, d, ,J = 8 Hz) 7.63 (2H, d, J = 8 Hz) 8.12 (2H, d, J = 8 Hz).

(1R,2R,3S)-2,3-Epoxy-2,4,4-trimethylcyclohexanol 6

To a solution of (R)-2,4,4-trimethyl-2-cyclohexen-1-ol (250 mg) and $NaHCO_3$ (300 mg) in CH_2Cl_2 (20 ml) was added 3-chloroperbenzoic acid (800 mg) at room temperature. The mixture was stirred for 15 hr at room temperature, then poured into 10% aq $Na_2S_2O_3$ (50 ml) and extracted with CH_2Cl_2. The extract was washed with aq. $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (10 g). Elution with hexane-EtOAc (7:1) gave 241 mg (87%) of **6**, ^{1}H-NMR ($CDCl_3$, 90 MHz) 0.96 (3H, s), 1.02 (3H, s), 1.05–2.10 (4H, m), 1.41 (3H, s), 2.71 (1H, s), 3.60–3.95 (1H, m).

(1R,2R,3S)-2,3-Epoxy-2,4,4-trimethylcyclohexyl 4′-*n*-decyloxybiphenyl-4-carboxylate 2a

4-Dimethylaminopyridine (45 mg) was added to a suspension of **6** (70 mg), 4′-*n*-decyloxybiphenyl-4-carboxylic acid (160 mg) and 1,3-dicyclohexylcarbodiimide (93 mg) in CH_2Cl_2 (4 ml) at room temperature. After being stirred overnight, the mixture was concentrated *in vacuo*. The residue was chromatographed over SiO_2 (7 g). Elution with hexane-EtOAc (25:1) gave **2a**. This was recrystallized from EtOH to yield 128 mg (58%) of pure **2a**, m.p. 52 °C; ^{1}H-NMR ($CDCl_3$, 90 MHz) 0.70–2.00 (23H, m), 1.08 (3H, s), 1.10 (3H, s), 1.38 (3H, s), 2.72 (1H, s), 4.00 (2H, t, J = 6 Hz), 5.34 (1H, t, J = 7 Hz), 6.98 (2H, d, J = Hz), 7.56 (2H, d, J = 8 Hz), 7.63 (2H, d, J = 8 Hz), 8.13 (2H, d, J = 8 Hz).

(1S,2R,3S)-2,3-Epoxy-2,4,4-trimethylcyclohexyl 4′-*n*-decyloxybiphenyl-4-carboxylate 2b

Triphenylphosphine (120 mg) was added to a suspension of **6** (70 mg), 4′-*n*-decyloxybiphenyl-4-carboxylic acid (160 mg) and diethyl azodicarboxylate (80 mg) in benzene (4 ml) at room temperature. After being stirred overnight, the mixture was concentrated *in vacuo*. The residue was chromatographed over SiO_2 (8 g). Elution with hexane-EtOAc (25:1) gave **2b**. This was recrystallized from EtOH to yield 145 mg (66%) of pure **2b**, m.p. 71 °C; ^{1}H-NMR ($CDCl_3$, 90 MHz) 0.70–2.00 (23H, m), 1.07 (3H, s), 1.13 (3H, s), 1.38 (3H, s), 2.73 (1H, s), 4.00 (2H, t, J = 6 Hz), 5.34 (1H, t, J = 5 Hz), 6.98 (2H, d, J = 8 Hz), 7.57 (2H, d, J = 8 Hz), 7.63 (2H, d, J = 8 Hz), 8.13 (2H, d, J = 8 Hz).

References

1. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
2. J. S. Patel and J. W. Goodby, *Opt. Engineering*, **26**, 373 (1987).
3. M. Koden, T. Kuratate, M. Shiomi, F. Funada, and K. Awane, *Ferroelectrics*, **114**, 259 (1991).
4. R. B. Meyer, L. Liébert, L. Strzelecki, and P. Keller, *J. de Phys.*, **36**, L69 (1975).
5. D. M. Walba, S. C. Slater, W. N. Thurmes, N. A. Clark, M. A. Handschy, and F. Supon, *J. Am. Chem. Soc.*, **108**, 5210 (1986).
6. D. M. Walba, H. A. Razavi, N. A. Clark, and D. S. Parmer, *J. Am. Chem. Soc.*, **110**, 8686 (1988).
7. T. Kusumoto, A. Nakayama, K. Sato, K. Nishide, T. Hiyama, S. Takehara, T. Shoji, M. Osawa, T. Kuriyama, K. Nakamura, and T. Fujisawa, *J. Chem. Soc., Chem. Commun.*, 311, (1991).
8. W. Nagata, M. Yoshioka, and S. Hirai, *J. Am. Chem. Soc.*, **94**, 4635 (1972).
9. O. Mitsunobu, *Synthesis*, 1, (1981).

10. K. Mori and P. Puapoomchareon, *Liebigs Ann. Chem.*, 1053 (1991).
11. T. Ikemoto, K. Sakashita, Y. Kageyama, F. Terada, Y. Nakaoka, K. Ichimura, and K. Mori, *Chem. Lett.*, 567 (1992).
12. K. Sakashita, Y. Nakaoka, T. Ikemoto, F. Terda, Y. Kageyama, M. Shindo, and K. Mori, *Chem. Lett.*, 1727 (1991).
13. K. Sakashita, T. Ikemoto, Y. Nakaoka, F. Terada, Y. Sako, Y. Kageyama, and K. Mori, *Liq. Cryst.*, **13**, 71 (1993).
14. J. A. Riddick and W. B. Burger, *Organic Solvents Third Edition* (1970).
15. J. Nakauchi, M. Uematsu, K. Sakashita, Y. Kageyama, S. Hayashi, T. Ikemoto, and K. Mori, *Jpn. J. Appl. Phys.*, **28**, L1258 (1989).
16. K. Miyasato, S. Abe, H. Takezoe, A. Fukuda, and E. Kuze, *Jpn. J. Appl. Phys.*, **22**, L661 (1983).
17. S. T. Lagerwall, and I. Dahl, *Mol. Cryst. Liq. Cryst.*, **114**, 151 (1984).