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Synthesis and properties of new chiral dopants containing a δ-lactone ring for practical ferroelectric liquid crystal mixtures

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A series of new optically active δ-lactones were synthesized as chiral dopants for ferroelectric liquid crystals (FLCs). The response time of an FLC mixture containing 4 mol % (*S*)-2,2-dimethyl-5-[2-fluoro-4-(5-*n*-octylpyrimidin-2-yl)-phenoxy]methyl-δ-valerolactone was 25 μs at 25°C. (0–90 per cent change in light transmission, 10 V μm^{-1}). The synthesis and properties of these materials as practical chiral dopants are reported.

1. Introduction

FLCs have attracted a great deal of attention since surface stabilized FLC (SSFLC) devices were proposed in 1980 [1]. One of the most important properties is the response time because it is related to the number of scanning lines of the *XY*-matrix in SSFLC displays. To realize practical FLC materials, the doping of chiral dopants potentially having a large spontaneous polarization (P_s) to non-chiral smectic C (S_C) mixtures with low viscosity and a wide S_C range is an effective method. In the last few years, chiral compounds containing a ring structure have been studied as chiral dopants because they induce a large P_s [2–6]. However, diasteromer separation or optical resolution was sometimes necessary to synthesize them, and moreover, few of them are known which maintain properties of the non-chiral S_C mixtures such as S_C range, tilt angle and alignment properties. For this reason, we have tried to develop new chiral dopants which satisfy the following basic requirements.

(1) Their synthetic routes should be simple and practical.
(2) They must be chemically stable.
(3) They should induce a large P_s with a small amount of addition.
(4) The helical pitch of the chiral nematic (N*) phase caused by the chiral dopants should be sufficiently long without necessitating other chiral dopants to compensate for it.
(5) They should maintain the phase transition temperatures of the non-chiral mixtures.

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(6) They should maintain the tilt angle of the non-chiral S_C mixtures.
(7) They should maintain the good alignment properties of the non-chiral S_C mixtures.
(8) Miscibility with non-chiral S_C mixtures must be good.

2. Measurement of physical properties

P_s values were measured using the triangular wave method [7] at 25°C. The sign of the P_s was determined by observing the tilt angle direction in the d.c. field as defined by [8]. The helical pitch (ρ) of the N* phase was measured at 63°C using the Cano–Wedge method [9]. The tilt angle (θ) was measured from the scale on the microscope turntable between the two extreme optical states corresponding to the two polarities of the d.c. field applied across the sample cell. Figure 1 shows the components of a standard non-chiral mixture (host 1) and its transition temperatures [10].

3. Synthesis of new chiral dopants

We chose commercially available (*S*)-2,2-dimethyl-4-ethoxycarbonylmethyl-1,3-dioxolane **4** (Wako Pure Chemical Industries Ltd.), which is easily prepared from L-ascorbic acid [11], as the starting material. As shown in scheme 1, reduction of **4** with $LiAlH_4$ was followed by iodination to give **6**. Alkylation of isobutyric acid with **6** in the presence of 2 equivalents of LDA followed by deprotection with hydrochloric acid gave the δ-lactone **7**. The optical purity of **7** was confirmed as 96 per cent by analysing the diasteromer ratio of the corresponding (*S*)-α-methoxy-α-trifluoromethylphenylacetate ((*S*)-MTPA ester) [12] by GLC. Another method to obtain δ-lactone **7** is shown in scheme 2. The alkylating agent **11** was prepared

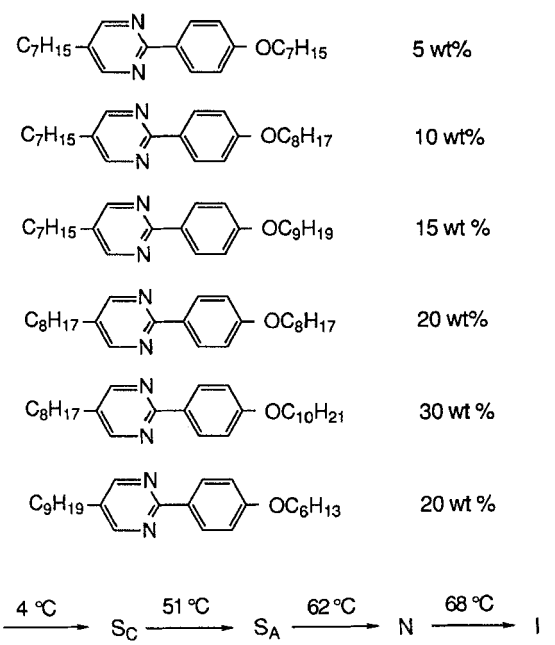
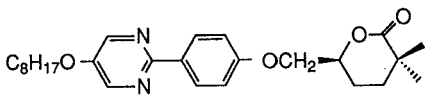
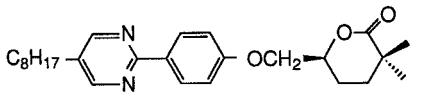


Figure 1. Components of the standard non-chiral base mixture 'host 1'.



1



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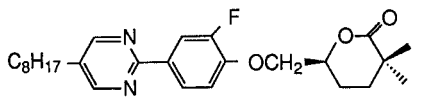
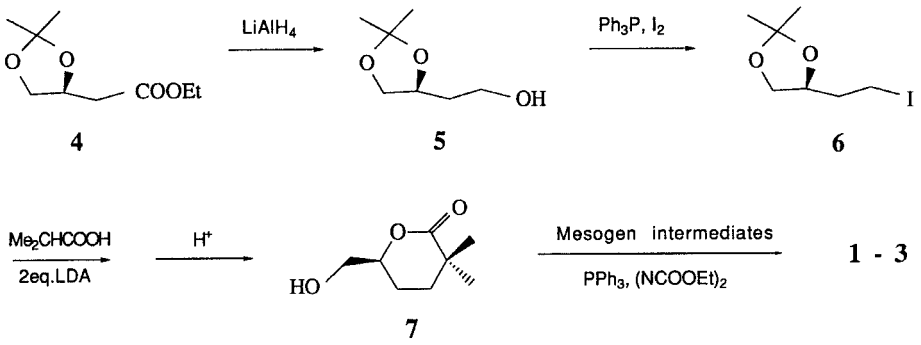
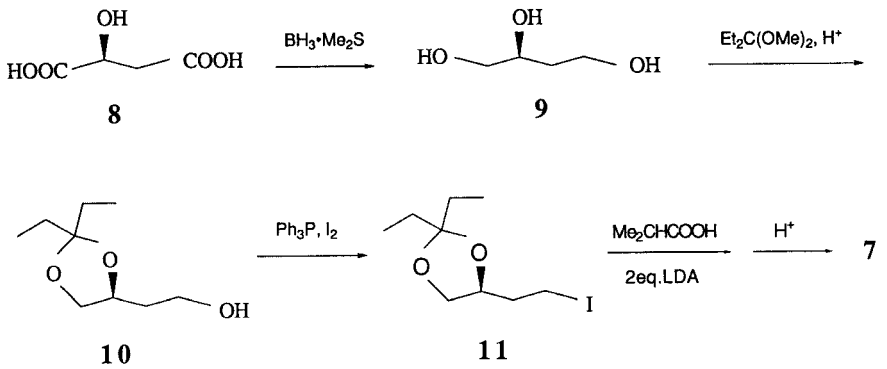


3

Compound **1-3**.



Scheme 1.

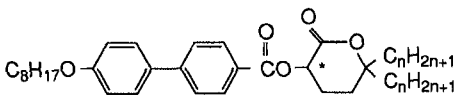


Scheme 2.

according to the known method, that is, the borane reduction of L-malic acid [13] followed by selective ketalization of the triol **9** [14] and iodination of the alcohol **10**. Alkylation of isobutyric acid with **11** followed by deprotection using the same method as described above afforded δ-lactone **7**. Finally, the corresponding mesogen intermediate was treated with **7** under Mitsunobu conditions [15] to give **1**–**3**. The compounds **1**–**3** are chemically stable and their HPLC purities (UV 220 nm, 254 nm) were over 99 per cent even after storage for 1 year at room temperature.

4. Properties of new chiral dopants as FLC mixtures

Recently, we developed chiral dopants **12** and showed that they induce a large P_s



12

Compound **12**.

with a small amount of addition in spite of the fact that they induce a long helical pitch of the N* phase [16]. However, for practical use, it has been found that an increase in the alkyl chain length may have an adverse influence on the alignment properties in the S_C^* phase of the FLC mixtures, while it increases the ability to induce a large P_s. Therefore, the dimethyl ($n=1$) or diethyl derivatives ($n=2$) have been investigated as practical chiral dopants, but as shown in figures 2 and 3, the S_A ranges of the FLC mixtures become narrow with an increase in the concentration of the chiral dopants and it disappears at a concentration of 6 mol % in the case of the dimethyl derivative. The tilt angle in the S_C^* phase also becomes larger with increased dopant concentration. These characteristics are undesirable for practical use because they change the optimized properties of the non-chiral mixtures. It is desired that such chiral dopants which only induce P_s do not influence the properties of the non-chiral base mixtures. So we tried to develop such dopants which do not change temperature properties and tilt angle of the non-chiral base mixtures. We then developed the compounds **1**–**3**.

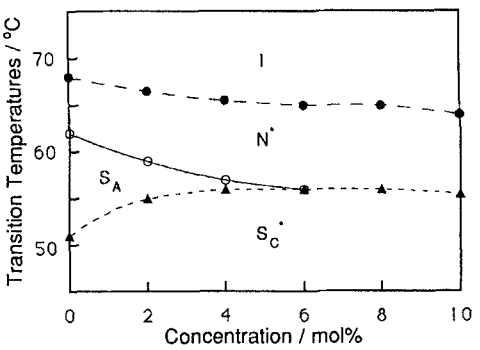


Figure 2. Plots of the transition temperatures versus the concentration of chiral dopant **12** ($n=1$).

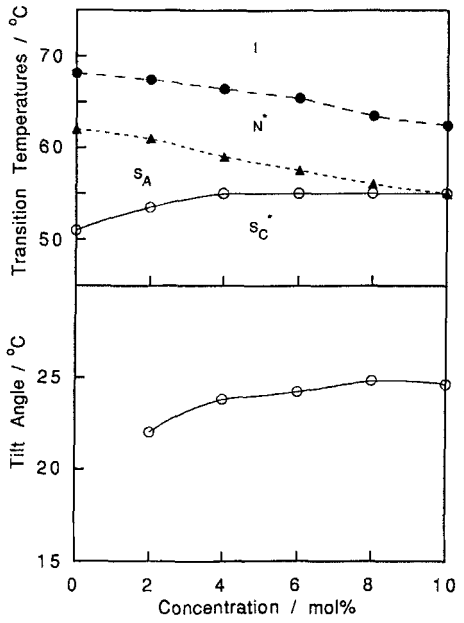


Figure 3. Plots of the transition temperatures and tilt angle at 25°C in the S_C^* phase versus the concentration of chiral dopant **12** ($n=2$).

Comparing compound **1** with compound **12**, decreasing the dipole moment along the molecular axis by changing the linkages between the core and lactone ring from the ester linkage to ether linkage is though to decrease the S_C property [17] of compound **1**, and as a result, S_A ranges are thought to be maintained even when increasing the concentration of the chiral dopants. An additional obvious change is the 'direction' reversal of the lactone ring between compound **1** and compound **12**. However, the lactone ring direction is not thought to influence the S_C property so much, because the values of dipoles are the same and their directions are little different between them. The tilt angle of an S_C phase is known to be related to the phase sequence of a material, that is, it tends to be small when a material shows S_C-S_A-N phase sequence and it tends to be large when a material shows a S_C-N phase sequence [18]. Therefore, the tilt angle is supposed to become large if the S_A range becomes narrow. Another important factor related to the tilt angle is the temperature range between the measured temperature (T) and the S_C-S_A transition temperature (T_{CA}) because the tilt angle is a function of the T_{CA}-T [19]. Considering these two factors, if the S_A ranges and T_{CA} are constant with increasing concentration of the chiral dopants, the tilt angle is expected to be constant at 25°C.

Table 1 shows the melting points of the chiral dopants **1**–**3** and some physical properties of the FLC mixtures containing them. All dopants induced large enough P_s values in spite of the fact that they induced a long helical pitch without compensation with the other dopants having opposite helical sense similar to dopant **12**. Dopants **1** and **2** induced longer helical pitches than **12** ($n=1$). (The induced helical pitch of dopant **12** ($n=1$) was 17 μm under the same conditions [16].)

Figure 4 shows the dependency of transition temperatures and tilt angle of the FLC mixtures against the concentration of dopant **1**. The concentration of the chiral

Table 1. The melting points of the chiral dopants **1**–**3** and some physical properties of the FLC mixtures containing them.

Compound	m.p./°C	Transition temperature/°C C•S_C^*•S_A•N*•I				Response time†/μs	Tilt angle‡ /deg	P_s‡ /nC cm^{-1}	Pitch in N* phase§ /μm
1	150	3	53	62	67	98	22	−4·9	71
2	144	2	53	65	71	108	22	−5·6	72
3	93	2	51	62	68	107	21	−5·4	17

†0–50 per cent transmittance change, $E = \pm 5\,V\,\mu m^{-1}$, 2 μm, 25°C.
‡Measured at 25°C.
§Measured just above the S_A–N* transition temperatures.

dopant has little influence on the properties of the non-chiral base mixtures, as we expected. However, the melting point of compound **1** was high and the miscibility with the base mixture was not good. Though crystallization of the chiral dopant was not recognized in the FLC mixture doped with 2 mol % of the dopant **1**, it occurred in the FLC mixture with 4 mol % dopant **1**. It was the same situation in using dopant **2** whose terminal chain was an alkyl group instead of an alkoxy group. Dopant **3** was developed for the purpose of improving the miscibility with the non-chiral base mixtures while maintaining the properties of non-chiral base mixtures. As a result, crystallization was not observed with an 8 mol % addition of the dopant

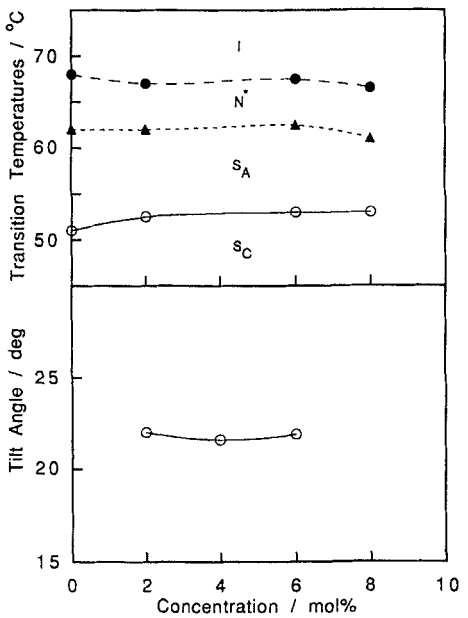


Figure 4. Plots of the transition temperatures and tilt angle at 25°C in the S_C^* phase versus the concentration of chiral dopant **1**.

even when the mixture was left for several weeks at room temperature, and furthermore, the transition temperatures of the non-chiral base mixture and the tilt angle were not influenced even when the concentration of the chiral dopant increased to 10 mol %, as shown in figure 5.

Figure 6 shows the dependency of P_s values versus the concentration of the chiral dopant **3**. P_s values increased in proportion to the concentration of the dopant and reached 25 nC cm^{-2} at a concentration of 10 mol %.

Next, in order to determine the possibility of fast response FLC mixtures using the chiral dopant **3**, host 2 (see figure 7) was prepared as a non-chiral base mixture whose T_{CA} was higher and whose rotational viscosity was lower than those of host 1. Table 2 shows the properties of the FLC mixtures comprised of chiral dopants **3** (4 mol %) and host 2 (96 mol %). The response time (0–90 per cent light-transmission change) of 25 μs was achieved under the practical voltage $\pm$ 10 V μm^{-1}. The P_s value at 25°C was larger than that of the mixture with host 1, because the P_s is an increasing function of T_{CA} and the T_{CA} of host 2 was higher than that of host 1. The tilt angle was also a little larger than that of the mixture with host 1 because the tilt angle is also an increasing function of T_{CA}. Their miscibility was good and no crystallization of the dopant was observed. Alignment properties were also good and only a few zig-zag defects were observed. (But, alignment properties are not thought to be only due to the materials.) However, host 2 cannot be a practical base mixture due to its high melting point and lack of a N* phase. New non-chiral mixtures whose S_C ranges are wide enough and yet whose viscosity are low are under development, and fast response practical FLC mixtures are expected to be realized in the near future.

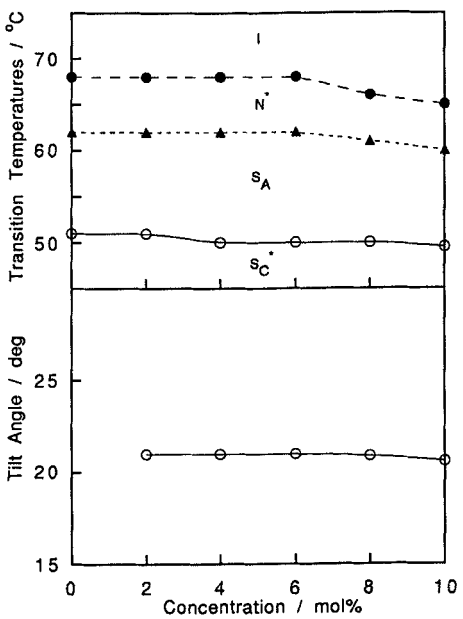


Figure 5. Plots of the transition temperatures and tilt angle at 25°C in the S_C^* phase versus the concentration of chiral dopant **3**.

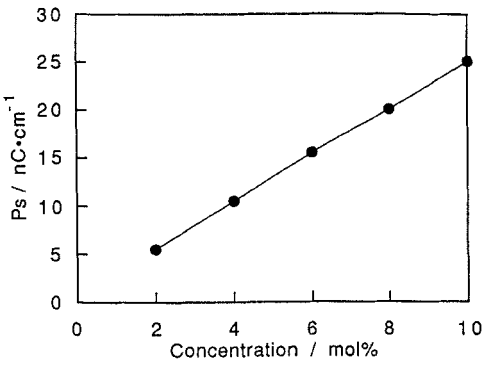


Figure 6. Plots of the P_s values at 25°C in the S_C^* phase versus the concentration of chiral dopant **3**.

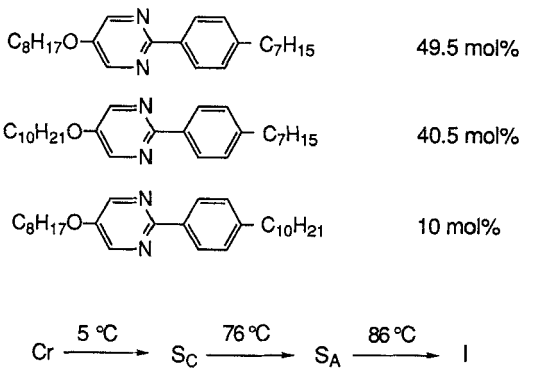


Figure 7. Components of the non-chiral base mixture 'host 2'.

Table 2. Properties of the FLC mixtures comprised of chiral dopant **3** (4 mol %) and host 2.

P_s values	18 nC cm^{-2}
Response time	25 μs ($\pm$10 V μm^{-1}, 0–90 per cent change)
Tilt angle	24·6°

5. Conclusions

A series of new optically active δ-lactones were synthesized. Among these (*S*)-2,2-dimethyl-5-[2-fluoro-4-(5-*n*-octylpyrimidin-2-yl)phenoxy]methyl-δ-valerolactone was found to be an excellent chiral dopant because of the following reasons.

(1) The synthetic routes are simple and practical, and inexpensive optically active compounds are used as starting materials.

(2) It is chemically stable. (HPLC purities did not change even after one year storage.)
(3) It induces a large P_s ($18\,nC\,cm^{-2}$) with a small amount of addition (4 mol %).
(4) Its induced helical pitch of an N* phase is sufficiently long (17 μm with 2 mol % addition).
(5) It maintains the phase transition temperatures of the non-chiral mixtures (even with 10 mol % addition).
(6) It maintains the tilt angle of the non-chiral S_C mixtures (even with 10 mol % addition).
(7) It maintains good alignment properties. Only a few zig-zag defects were observed in the mixture with 4 mol % addition.)
(8) Miscibility with non-chiral mixtures is good. (No crystallization was observed in the mixture with 8 mol % addition.
(9) Fast response (25 μs under $\pm 10\,V\,\mu m^{-1}$) was achieved in the mixture with 4 mol % addition.

6. Experimental

6.1. *Synthesis of (S)-2,2-dimethyl-4-(2-hydroxy)methyl-1,3-dioxolane* **5**

A solution of **4** (10 g) in dry ether (50 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (3·0 g) in dry ether (50 ml) at 0°C. The mixture was stirred for 90 min. The usual alkaline work-up gave an oil, which was chromatographed over SiO_2 (140 g). Elution with *n*-hexane–EtOAc (3:2) gave 7·5 g (97 per cent) of **5**, n_D^{24} 1·4362; $[\alpha]_D^{24}$ −2·1° (c=9·8, MeOH); ν_{max} (neat) 3420 (br), 3000 (s), 2950 (s), 2880 (s), 1370 (s), 1250 (m), 1220 (m), 1160 (m), 1060 (m), 860 (m) cm^{-1}; δ ($CDCl_3$, 90 MHz) 1·37 (3 H, s), 1·43 (3 H, s), 1·82 (2 H, q, J=6 Hz), 3·60 (1 H, t, J=8 Hz), 3·81 (1 H, t, J=5 Hz), 4·09 (1 H, dd, J=6 Hz, J=5 Hz), 4·0–4·4 (1 H, m).

6.2. *Synthesis of (S)-2,2-dimethyl-4-(2-iodo)ethyl-1,3-dioxolane* **6**

To a solution of **5** (6·2 g) in dry benzene (400 ml) was added imidazole (7·3 g), Ph_3P (28·0 g) and I_2 (20·6 g) at room temperature. The mixture was vigorously stirred for 1 h, then it was washed with 10 per cent $Na_2S_2O_3$ solution, saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was repeatedly extracted with a small amount of hexane, and the extract was chromatographed over SiO_2 (150 g). Elution with *n*-hexane–EtOAc (30:1) gave 7·9 g (73 per cent) of **6**, n_D^{24} 1·5040; $[\alpha]_D^{24}$ −24·3° (c=3·0, MeOH); ν_{max} (neat) 3000 (s), 2930 (m), 2860 (m), 1370 (s), 1245 (s), 1215 (s), 1060 (s), 840 (s) cm^{-1}; δ ($CDCl_3$, 90 MHz) 1·36 (3 H, s), 1·42 (3 H, s), 1·95–2·2 (2 H, m), 3·28 (2 H, t, J=7 Hz), 3·5–3·8 (1 H, m), 4·1–4·33 (2 H, m).

6.3. *Synthesis of (S)-2,2-dimethyl-5-hydroxymethyl-δ-valerolactone* **7**

A solution of LDA was prepared by the dropwise addition of *n*-BuLi solution (1·66 M in *n*-hexane, 37 ml) to a stirred and cooled solution of *i*-Pr_2NH (7·0 g) in dry THF (50 ml) at −10°C under Ar. The mixture was stirred for 15 min at −10°C. To a stirred solution of LDA was added dropwise a solution of isobutyric acid (2·5 g) in dry THF (10 ml) at −5°C. The mixture was stirred for 1 h at 0°C. To the stirred mixture was added dropwise a solution of **6** (7·3 g) in THF (10 ml) at 0°C. The stirring was continued for 4 h after the addition with a gradual raise of the reaction temperature to room temperature. The mixture was quenched with water (100 ml).

After the removal of the organic layer, the aqueous layer was neutralized by the addition of N-HCl and extracted with EtOAc. The extract was washed with brine and concentrated under reduced pressure. The residue was dissolved into THF (25 ml) and 4 N HCl (20 ml) was added to the solution at 0°C. The mixture was stirred for 1 h at 0–10°C. It was poured into saturated $(NH_4)_2SO_4$ solution and repeatedly extracted with EtOAc. The extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was then diluted with benzene and concentrated under reduced pressure. The residue was chromatographed over SiO_2 (50 g). Elution with cyclohexane–EtOAc (1:1) gave 2·4 g (53 per cent) of **7**, m.p. 74°C; $[\alpha]_D^{23}$ −9·0° (c = 2·5, MeOH); ν_{max} (neat) 3450 (br), 2950 (s), 2900 (s), 2860 (s), 1720 (s), 1460 (m), 1395 (m), 1290 (m), 1200 (m), 1160 (s), 1140 (s), 1080 (m), 1060 (m), 1020 (m) cm^{-1}; δ ($CDCl_3$, 200 MHz) 1·29 (3 H, s), 1·31 (3 H, s), 1·75–2·06 (4 H, m), 2·83 (1 H, br, -OH) 3·64 (1 H, dd, J = 12 Hz, J = 5 Hz), 3·77 (1 H, dd, J = 12 Hz, J = 3 Hz). (Found: C, 60·76; H, 9·03. Calculated for $C_8H_{14}O_3$: C, 60·74; H, 8·92 per cent.)

6.4. *Determination of the optical purity of 7*

To a solution of **7** (10 mg) and 4-dimethylaminopyridine (2 mg) in dry pyridine (1 ml) was added (*S*)-MTPA chloride (30 mg) at room temperature. The mixture was stirred overnight at room temperature. After conventional work-up, corresponding (*S*)-MTPA ester was isolated by preparative TLC and analysed by GLC (Column, OV-101, 50 m × 0·25 mm, at 220°C; Carrier gas, He, 1·0 kg cm^{-2}) R_f 16·0 min (2·0 per cent), 17·5 min (98·0 per cent). The optical purity of **7** was therefore 96·0 per cent.

6.5. *Synthesis of (S)-2,2-dimethyl-5-[4-(5-n-octyloxypyrimidin-2-yl)phenoxy]-methyl-δ-valerolactone* **1**

To a stirred solution of **7** (0·5 g), 2-(4-hydroxy)phenyl-5-*n*-octyloxypyrimidine (0·95 g) and diethyl azodicarboxylate (0·6 g) was added Ph_3P (0·85 g) at room temperature. The mixture was stirred for 15 h and concentrated under reduced pressure. The residue was chromatographed over SiO_2 (50 g). Elution with $CHCl_3$ gave **1**. This was recrystallized from *n*-hexane–EtOAc to yield 0·88 g (63 per cent) of pure **1**, m.p. 150°C; $[\alpha]_D^{28}$ +13·2° (c = 1·1, $CHCl_3$); ν_{max} (KBr) 2960 (s), 2930 (s), 2860 (m), 1735 (s), 1610 (m), 1590 (m), 1545 (m), 1520 (m), 1440 (s), 1380 (m), 1280 (s), 1260 (s), 1180 (s), 1160 (s), 1130 (s), 1050 (m), 1030 (m), 850 (s), 790 (s) cm^{-1}; δ ($CDCl_3$, 270 MHz) 0·88 (3 H, t, J = 5 Hz), 1·25–1·53 (10 H, m), 1·35 (6 H, s), 1·75–1·88 (4 H, m), 1·98–2·10 (2 H, m), 4·08 (3 H, t, J = 7 Hz), 4·14 (1 H, dd, J = 10 Hz, J = 5 Hz), 4·17 (1 H, dd, J = 10 Hz, J = 4 Hz), 4·64–4·75 (1 H, m), 6·97 (2 H, d, J = 8 Hz), 8·27 (2 H, d, J = 8 Hz), 8·40 (2 H, s). (Found: C, 70·92; H, 8·29; N, 6·36. Calculated for $C_{26}H_{36}O_4N_2$: C, 70·88; H, 8·24; N, 6·36 per cent.)

6.6. *Synthesis of (S)-2,2-dimethyl-5-[4-(5-n-octylpyrimidin-2-yl)phenoxy]methyl-δ-valerolactone* **2**

In the same manner as described for the preparation of **1**, **7** (0·4 g) and 2-(4-hydroxy)phenyl-5-*n*-octylpyrimidine (0·72 g) yielded 0·70 g (65 per cent) of **2**, m.p. 144°C; $[\alpha]_D^{28}$ +12·5° (c = 0·8, $CHCl_3$); ν_{max} (KBr) 2970 (s), 2930 (s), 2850 (m), 1735 (s), 1610 (m), 1590 (m), 1540 (m), 1505 (m), 1430 (s), 1250 (s), 1150 (s), 1120 (m), 1030 (m), 860 (m), 800 (s) cm^{-1}; δ ($CDCl_3$, 270 MHz) 0·88 (3H, t, J = 5 Hz), 1·23–1·40 (10 H, m), 1·34 (6 H, s), 1·57–1·88 (4 H, m), 1·97–2·10 (2 H, m), 2·60 (2 H,

t, $J = 7$ Hz), 4·15 (1 H, dd, $J = 10$ Hz, $J = 5$ Hz), 4·18 (1 H, dd, $J = 10$ Hz, $J = 4$ Hz), 4·65–4·75 (1 H, m), 6·97 (2 H, d, $J = 8$ Hz), 8·33 (2 H, d, $J = 8$ Hz), 8·57 (2 H, s). (Found: C, 73·66; H, 8·57; N, 6·57. Calculated for $C_{26}H_{36}O_3N_2$: C, 73·55; H, 8·55; N, 6·60 per cent.)

6.7. *Synthesis of (S)-2,2-dimethyl-5-[2-fluoro-4-(5-*n*-octylpyrimidin-2-yl)phenoxy]methyl-δ-valerolactone* **3**

In the same manner as described for the preparation of **1**, **7** (0·5 g) and 2-(3-fluoro-4-hydroxy)phenyl-5-*n*-octylpyrimidine (0·96 g) yielded 0·87 g (62 per cent) of **3**, m.p. 93°C; $[\alpha]_D^{28}$ +9·5° ($c = 1·0$, $CHCl_3$); ν_{max} (KBr) 2970 (s), 2930 (s), 2860 (m), 1730 (s), 1620 (m), 1580 (m), 1540 (s), 1530 (s), 1450 (s), 1290 (s), 1140 (s), 1050 (m), 900 (m), 800 (s) cm^{-1}; δ ($CDCl_3$, 270 MHz) 0·88 (3 H, t, $J = 5$ Hz), 1·23–1·40 (10 H, m), 1·35 (3 H, s), 1·35 (3 H, s) 1·60–1·70 (2 H, m), 1·78–1·90 (2 H, m), 2·00–2·18 (2 H, m), 2·61 (2 H, t, $J = 6$ Hz), 4·20 (1 H, dd, $J = 10$ Hz, $J = 5$ Hz), 4·23 (1 H, dd, $J = 10$ Hz, $J = 4$ Hz), 4·68–4·78 (1 H, m), 7·00 (1 H, t, $J = 7$ Hz), 8·16 (2 H, d, $J = 7$ Hz), 8·58 (2H, s). (Found: C, 70·61; H, 7·92; N, 6·32. Calculated for $C_{26}H_{35}O_3N_2F$: C, 70·56; H, 7·97; N, 6·33 per cent.)

References

[1] CLARK, N. A., and LAGERWALL, S. T., 1980, *Appl. Phys. Lett.*, **36,** 899.
[2] DÜBAL, H. R., ESCHER, C., GÜNTHER, D., HEMMERLING, W., INOGUCHI, Y., MÜLLER, I., MURAKAMI, M., OHLENDORF, D., and WINGEN, R., 1988, *Jap. J. appl. Phys.*, **37,** L2241.
[3] NAKAUCHI, J., UEMATSU, M., SAKASHITA, K., KAGEYAMA, Y., HAYASHI, S., IKEMOTO, T., and MORI, K., 1989, *Jap. J. appl. Phys.*, **28,** L1258.
[4] KODEN, M., KURATATE, T., FUNADA, F., AWANE, K., SAKAGUCHI, K., SHIOMI, Y., and KITAMURA, T., 1990, *Jap. J. appl. Phys.*, **29,** L981.
[5] SAKAGUCHI, K., and KITAMURA, T., 1991, *Ferroelectrics*, **114,** 265.
[6] KUSOMOTO, T., NAKAYAMA, A., SATO, K., NISHIDE, K., HIYAMA, T., TAKEHARA, S., SHOJI, T., OSAWA, M., KURIYAMA, T., NAKAMURA, K., and FUJISAWA, T., 1991, *J. chem. Soc. chem. Commun.*, 311.
[7] MIYASATO, K., ABE, S., TAKEZOE, H., FUKUDA, A., and KUZE, E., 1983, *Jap. J. appl. Phys.*, **22,** L661.
[8] LAGERWALL, S. T., and DAHL, I., 1984, *Molec, Crystals liq. Crystals*, **114,** 151.
[9] CANO, R., 1968, *Bull. Soc. fr. Minér. Cristallogr.*, **91,** 120.
[10] KODEN, M., KURATATE, T., and FUNADA, F., Japanese patent, 90-110189.
[11] SAIBABA, R., SARMA, M. S. P., and ABUSHANAB, E., 1989, *Synth. Commun.*, **19,** 3077.
[12] DALE, J. A., and MOSHER, H. S., 1973, *J. Am. chem. Soc.*, **95,** 512.
[13] KOCIEŃSKI, P. J., YEATES, C., STREET, S. D. A., and CAMPBELL, S. F., 1987, *J. chem. Soc. Perkin Trans. 1*, 2183.
[14] MASAMUNE, S., MA, P., OKUMOTO, H., ELLINGBOE, J. W., and ITO, Y., 1984, *J. org. Chem.*, **49,** 2837.
[15] MITSUNOBU, O., 1981, *Synthesis*, 1.
[16] SAKASHITA, K., IKEMOTO, T., NAKAODA, Y., TERADA, F., SAKO, Y., KAGEYAMA, Y., and MORI, K., 1993, *Liq. Crystals*, **13,** 71.
[17] GOODBY, J. W., and LESLIE, T. M., 1984, *Molec. Crystals liq. Crystals*, **110,** 175.
[18] PATEL, J. S., and GOODBY, J. W., 1987, *Opt. Engng*, **26,** 37.
[19] DURAND, G., and MARTINOT-LAGARDE, PH., 1980, *Ferroelectrics*, **24,** 89.