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Synthesis of Ferroelectric Liquid Crystals Having Chiral Nitrodihydrobenzofuran Structure

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SYNTHESIS OF FERROELECTRIC LIQUID CRYSTALS HAVING CHIRAL NITRODIHYDROBENZOFURAN STRUCTURE

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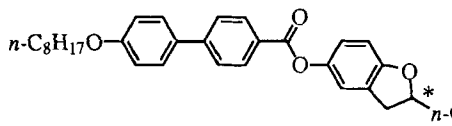
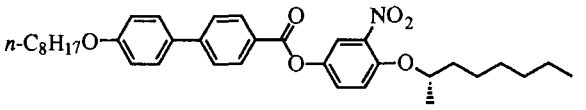
Abstract Optically active 2-alkyl-6(or 7)-nitro-2,3-dihydrobenzofurans were designed and synthesized as chiral dopants for ferroelectric liquid crystals and nonlinear optical materials. The mixtures containing 7-nitro-2,3-dihydrobenzofuran derivative exhibited large spontaneous polarization, and the second-harmonic generation intensity of 7-nitro-2,3-dihydrobenzofuran derivative was slightly smaller than that of (1-methylheptyloxy)-2-nitrobenzene derivative.

INTRODUCTION

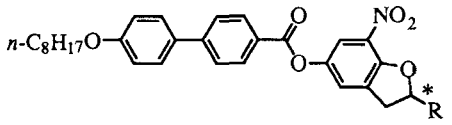
In order to explore ferroelectric liquid crystals (FLC) that exhibit large spontaneous polarization (Ps) and short response time, we designed and synthesized various kinds of optically active compounds useful for chiral dopants.[1] Of the compounds we prepared, dihydrobenzofuran **1** exhibited stable chiral smectic C (S_C*) phase, but Ps value was not large enough.[2] As ferroelectric liquid crystals having nitro group (*cf.* **2**) exhibit not only large Ps but also large second order nonlinear susceptibility,[3,4] we designed nitrated 2,3-dihydrobenzofurans **3-6** which we considered might exhibit large Ps and good second-harmonic generation (SHG), because dipole of the nitro group should be fixed by chiral 2-alkyl-2,3-dihydrobenzofuran ring structure.



1
Cr 115 S_C* 140 S_A 183 N* 185 I
Ps +64 nC/cm^2 (100 °C)
[+1.4 nC/cm^2 (10 wt% in host, 25 °C)]

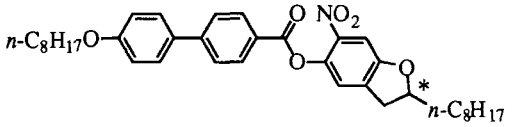


2 Cr 80 S_C* 82 S_A 118 I

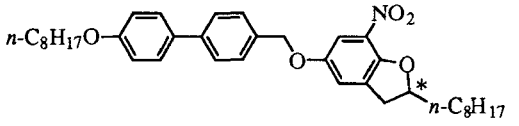


3a R = *n*-C_8H_{17}
Cr 108 S_C* 130 S_A 179 I

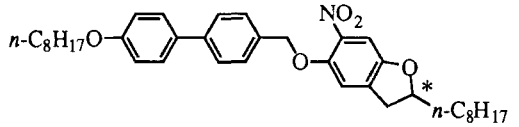
3b R = *n*-C_6H_{13}
Cr 111 S_C* 112 S_A 180 I



4 (Cr, S_C*, N*, I) dec



5 Cr 142 Iso



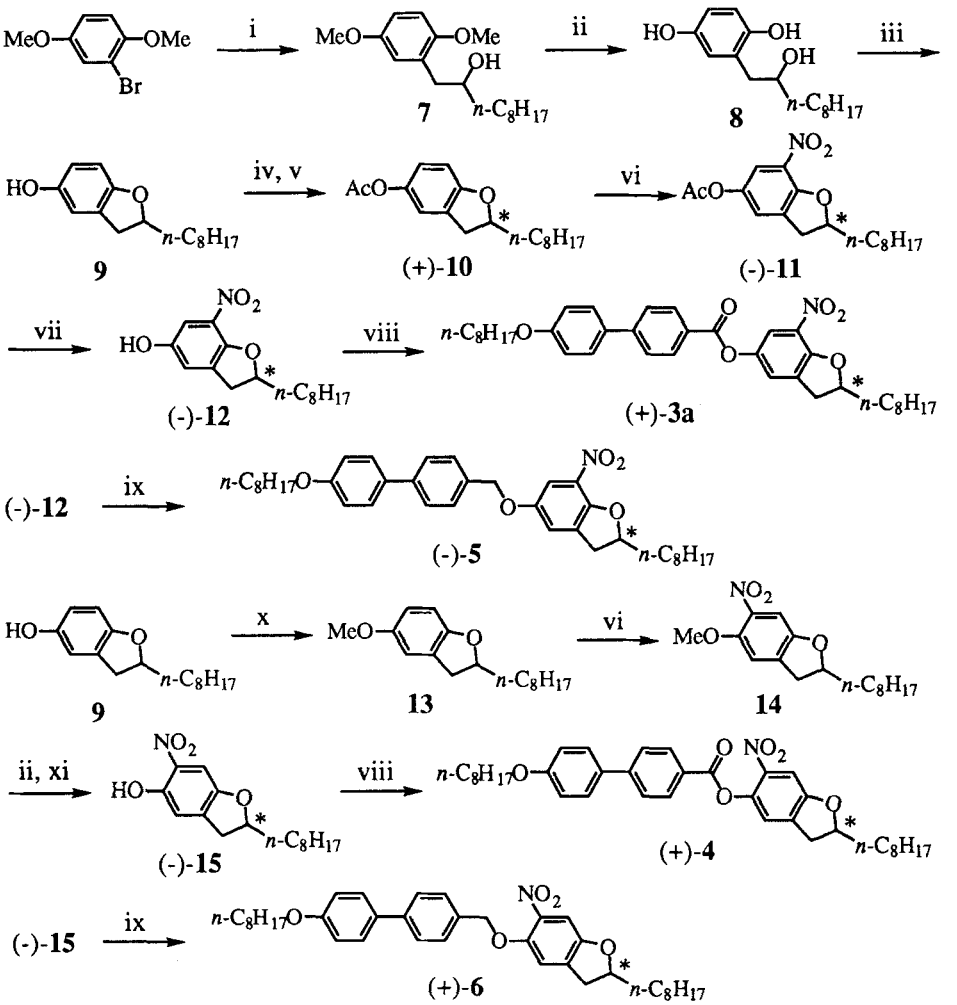
6 Cr 99 S_C* 115 I

SYNTHESIS

Optically active nitro-2,3-dihydrobenzofurans (+)-**3a**, (+)-**4**, (-)-**5**, and (+)-**6** were prepared according to the route shown in Scheme 1. 5-Hydroxy-2,3-dihydrobenzofuran **9** was easily prepared from 2-bromo-1,4-dimethoxybenzene in 3 steps.[2] Although optically active dihydrobenzofuran was obtained by use of a chiral 1,2-epoxyalkane, the optical purity was low and reproducibility was poor. Each enantiomer of **9** and **10** could be resolved by preparative HPLC (CHIRALCEL OD). Nitration of acetoxydihydrobenzofuran (+)-**10** followed by hydrolysis of the resulting 7-nitrodihydrobenzofuran (-)-**11** afforded (-)-**12**. Esterification of (-)-**12** with 4-(4-octyloxyphenyl)benzoic acid using dicyclohexylcarbodiimide (DCC) gave (+)-**3a**. In a similar manner, we synthesized (+)-**3b** using 1,2-epoxyoctane instead of 1,2-epoxydecane.

Regioselective nitration of 5-methoxydihydrobenzofuran **13**, prepared by methylation of **9**, gave 6-nitrodihydrobenzofuran **14**. Demethylation of **14**, followed by separation of the resulting (±)-**15** by preparative HPLC (CHIRALPAC AD), afforded (+)- and (-)-isomers. Esterification of (-)-**15** with 4-(4-octyloxyphenyl)benzoic acid gave (+)-**4**.

Synthesis of 4-(4-octyloxyphenyl)phenylmethyl ether (-)-**5** and (+)-**6** was carried out starting with (-)-**12** and (-)-**15**, respectively, by alkylation of an appropriate benzyl alcohol.



i: n-BuLi, CuI, 1,2-epoxydecane; ii: $AlCl_3$, Me_2S; iii: TsOH; iv: Ac_2O, pyridine; v: HPLC (CHIRALCEL OD); vi: HNO_3, Ac_2O, H_2SO_4; vii: NaOH; viii: n-$C_8H_{17}O$-$C_6H_4C_6H_4COOH$, DCC; ix: n-$C_8H_{17}OC_6H_4C_6H_4CH_2OH$, $(NCOOEt)_2$, PPh_3; x: MeI, NaH; xi: HPLC (CHIRALPAC AD)

SCHEME 1

PROPERTIES

Of the compounds prepared, (+)-**3a**, (+)-**3b**, (+)-**4**, (+)-**6** exhibited S_C^* phase. Although hexyldihydrobenzofuran **1** exhibited stable S_C^* phase (Cr 115 S_C^* 140 S_A 183 N* 185 I), the temperature range of nitro derivative (+)-**3b** was very narrow (Cr 111 S_C^* 112 S_A 180 I). This may suggest that nitro group tends to stabilize S_A phase. In case of 6-nitro derivative (+)-**4**, phase sequence (Cr S_C^* N* I) was observed on first heating and cooling, but phase transition temperatures could not be measured due to

thermal decomposition. On the other hand, an ether analog (-)-**6** was stable to exhibit S_C^* phase. 7-Nitro derivative (+)-**5** did not exhibit mesophase.

Each of **1** and **3b** was added to an achiral host liquid crystal mixture, and electro-optical properties of the resulting mixtures were measured as summarized in Table 1. The mixture containing 10 wt% of dihydrobenzofuran **1** exhibited very small Ps (1.4 nC/cm^2). The mixture containing 10 wt% of nitrodihydrobenzofuran (+)-**3b** showed large Ps (7.2 nC/cm^2) and short response time (162 μs). SHG was measured on the compounds **2**, **3a**, and **3b** by Maker fringe method. The χ_{eff} values of **3a** (0.05 pm/V at 128 °C, 0.088 pm/V at 118 °C, and 0.097 pm/V at 108 °C) were nearly equal to **2** (0.096 pm/V at 74 °C). The χ_{eff} value of **3b** (0.02 pm/V at 110 °C) was smaller than those of **2** and **3a**. We could not measure SHG of **3b** at lower temperatures owing to crystallization. These results suggest that the nitro group on chiral dihydrobenzofuran ring structure of **3a** is well fixed in S_C^* phase and dipole is aligned to exhibit large Ps and SHG.

TABLE 1. Thermal and electro-optical properties of a mixture of **1** or (+)-**3b** at 25 °C.

Chiral dopant (wt%)		Phase transition temperatures (°C)				Ps	Response time	Tilt angle
		S_C^*	S_A	N*	I	(nC/cm^2)	(μs)	(°)
1	(10)	• 51	• 68	• 75	•	+1.4	341	18
(+)-**3b**	(5)	• 55	• 68	• 72	•	+3.7	230	21
	(10)	• 49	• 72	• 74	•	+7.2	162	20

In summary, we have demonstrated new FLC materials having a chiral nitorodihydrobenzofuran structure exhibit large Ps and SHG. These observations allow us not only to design new chiral dopants of large Ps's but also to prepare new second-order nonlinear optical materials.

EXPERIMENTS

SYNTHESIS OF **3a** AND **6**

1,4-Dimethoxy-2-(2-hydroxydecyl)benzene (**7**). To the solution of 2-bromo-1,4-dimethoxybenzene (4.34 g, 20 mmol) in diethyl ether (30 ml), *n*-BuLi (1.55 M in hexane, 12.9 ml) was added at -78 °C. The mixture was stirred for 30 min and was added to copper(I) iodide (1.91 g, 10 mmol) suspended in 1,2-epoxydecane (1.56 g, 10 mmol) and diethyl ether (5 ml). The reaction mixture was stirred for 6 h at 0 °C and then poured into sat. NH_4Cl *aq* solution. Resulting mixture was filtered through a Celite layer and extracted with diethyl ether. The ethereal extracts were washed with sat.

NH_4Cl *aq* solution and then with sat. NaCl *aq* solution, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (toluene-ether = 10 : 1) to give **7** (1.20 g, 41% yield) as a colorless oil. Bp 200 °C/0.6 Torr. ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.1 Hz, 3 H), 1.17-1.58 (m, 14 H), 2.12 (d, J = 3.8 Hz, 1 H), 2.65 (dd, J = 13.5 and 8.2 Hz, 1 H), 2.86 (dd, J = 13.5 and 3.7 Hz, 1 H), 3.77 (s, 3 H), 3.79 (s, 3 H), 3.71-3.92 (b, 1 H), 6.73-6.86 (m, 3 H); IR (neat) 3439, 2928, 2854, 1591, 1500, 1466, 1224, 1051, 800, 710 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 294 (M^+, 7), 152 (100), 137 (58), 121 (21), 91 (11), 41 (32). Found: C, 73.47; H, 10.22%. Calcd for $C_{18}H_{30}O_3$: C, 73.43; H, 10.27%.

1,4-Dihydroxy-2-(2-hydroxydecyl)benzene (**8**). Dimethyl sulfide (2.29 ml, 31.3 mmol) and anhydrous aluminium chloride (2.22 g, 16.6 mmol) were added to dichloromethane (20 ml) solution of **7** (0.92 g, 3.1 mmol). The mixture was stirred overnight at room temperature, concentrated and then diluted with diethyl ether. The whole was poured into 2 M HCl, and the organic layer was separated. The aqueous layer was extracted with diethyl ether. The combined ethereal extracts were dried (Na_2SO_4), and concentrated under reduced pressure. Purification by column chromatography (hexane- ethyl acetate = 2 : 1, R_f 0.3) gave **8** which was recrystallized from dichloromethane and ethyl acetate (10 : 1) to give pure **8** (0.80 g, 96% yield) as colorless powder. Mp 118 °C. ^1H NMR ($CDCl_3$-CD_3OD) δ 0.88 (t, J = 6.1 Hz, 3 H), 1.12-1.65 (m, 14 H), 2.66-2.78 (m, 2 H), 3.40-3.50 (br, 3 H), 3.80-3.94 (m, 1 H), 6.52-6.67 (m, 3 H); IR (KBr) 3340-3150, 2917, 2851, 1607, 1504, 1468, 1206, 1015, 814 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 266 (M^+, 9), 248 (14), 149 (10), 138 (44), 124 (100). HRMS; Found: *m/z* 266.1882. Calcd for $C_{16}H_{26}O_3$: M, 266.1880.

5-Hydroxy-2-octyl-2,3-dihydrobenzofuran (**9**). *p*-Toluenesulfonic acid (145 mg, 0.78 mmol) and **8** (690 mg, 2.60 mmol) were dissolved in toluene (20 ml), and the mixture was heated to reflux for 3 h. The whole was poured into 2 M HCl and extracted with ethyl acetate. The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. Purification by column chromatography (hexane-ethyl acetate = 5 : 1, R_f 0.4) and recrystallization from hexane-ethanol (200 : 1, 5 ml) gave **9** (441 mg, 69% yield) as colorless powder. Mp 61 °C. ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.1 Hz, 3 H), 1.07-1.93 (m, 14 H), 2.81 (dd, J = 15.6 and 8.0 Hz, 1 H), 3.21 (dd, J = 15.5 and 8.6 Hz, 1 H), 4.48 (br, 1 H), 4.72 (quintet, J = 6.5 Hz, 1 H), 6.51-6.67 (m, 3 H); IR (KBr) 3289, 2920, 2851, 1622, 1476, 1385, 1280, 1215, 847, 816 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 248 (M^+, 48), 163 (6), 149 (22), 136 (28), 123 (100), 107(21). Found: C, 77.16; H, 9.52%. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74%.

(+)-5-Acetoxy-2-octyl-2,3-dihydrobenzofuran ((+)-**10**). Acetic anhydride (0.92 ml, 9.8 mmol) and pyridine (0.79 ml, 9.8 mmol) were added to the solution of **9** (405 mg, 1.63 mmol) in dichloromethane (5 ml). The resulting mixture was stirred overnight at room temperature, then poured into 2 M HCl, and extracted with diethyl ether. The organic layer was separated, washed with sat. $NaHCO_3$ *aq* solution, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (hexane-ethyl acetate = 10 : 1, R_f 0.3) and resolved into (+)- and (-)-**10** by preparative HPLC (CHIRALCEL OD, 20 mmϕ × 300 mm × 2, hexane-2-propanol = 200 : 1). (+)-**10** (171 mg, 36%, 100% *ee*). Bp 215 °C/2 Torr; $[\alpha]_D^{20}$ +32.9 ° (*c* 1.28, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.1 Hz, 3 H), 1.16-1.96 (m, 14 H), 2.27 (s, 3 H), 2.85 (dd, J = 15.7 and 8.1 Hz, 1 H), 3.26 (dd, J = 15.6 and 8.8 Hz, 1 H), 4.78 (quintet, J = 6.6 Hz, 1 H), 6.67-6.87 (m, 3 H); IR (neat) 2928, 2855, 1763, 1609, 1483, 1370, 1190, 1125, 1011, 947, 889, 814 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 290 (M^+,·10), 248 (100), 149

(11), 136 (12), 123 (46). Found: C, 77.25; H, 8.92%. Calcd for $C_{18}H_{26}O_3$: C, 77.45; H, 9.02%.

(-)-5-Acetoxy-7-nitro-2-octyl-2,3-dihydrobenzofuran ((-)-**11**). To (+)-**10** (317 mg, 1.09 mmol) in acetic anhydride (5 ml), a mixture of fuming nitric acid (0.1 ml), acetic anhydride (1 ml) and sulfuric acid (1 drop) was added dropwise at 0 °C until the starting material was consumed. Sat. NaCl *aq* solution was added to the reaction mixture, and resulting mixture was extracted with diethyl ether. Organic layer was dried (Na_2SO_4), and concentrated under reduced pressure. Purification by column chromatography (hexane-ethyl acetate = 5 : 1, R_f 0.2) and by recrystallization (hexane (1 ml)-ether (1 drop)) gave (-)-**11** (327 mg, 89% yield, 100% *ee*) as pale yellow powder. Mp 44-45 °C; $[\alpha]_D^{20}$ -20.1 ° (*c* 0.924, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3 H), 1.23-1.69 (m, 12 H), 1.69-1.80 (m, 1 H), 1.88-1.98 (m, 1 H), 2.30 (s, 3 H), 2.95 (ddt, J = 16.2, 7.5, and 1.0 Hz, 1 H), 3.38 (ddt, J = 16.2, 9.0, and 0.9 Hz, 1 H), 5.08 (quintet, J = 6.8 Hz, 1 H), 7.17 (m, 1H), 7.64 (m, 1H); IR (KBr) 2922, 2851, 1766, 1533, 1466, 1372, 1343, 1321, 1196, 1019, 947, 908, 864 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 335 (M^+, 6), 293 (100). Found: C, 64.42; H, 7.51; N, 4.01%. Calcd for $C_{18}H_{25}NO_5$: C, 64.46; H, 7.51; N, 4.18%.

(-)-5-Hydroxy-7-nitro-2-octyl-2,3-dihydrobenzofuran ((-)-**12**). The solution of (-)-**11** (292 mg, 0.87 mmol) in acetone (3 ml) was added dropwise to 0.7 M NaOH *aq* solution (2.2 ml) and water (4 ml). The whole was stirred for 45 min, poured into 2 M HCl, and extracted with ethyl acetate. The combined extracts were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (hexane-ethyl acetate = 3 : 1, R_f 0.3) and by recrystallization from hexane-ether (10 : 1, 4 ml) to yield (-)-**12** (210 mg, 82% yield, 100% *ee*) as pale yellow needle; mp 80-81 °C; $[\alpha]_D^{20}$ -39.3 ° (*c* 1.04, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.9 Hz, 3 H), 1.20-1.56 (m, 12 H), 1.67-1.76 (m, 1 H), 1.87-1.96 (m, 1 H), 2.90 (ddt, J = 16.1, 7.4, and 1.0 Hz, 1 H), 3.33 (ddt, J = 16.1, 9.0, and 1.0 Hz, 1 H), 5.00 (quintet, J = 6.7 Hz, 1 H and br, 1 H), 6.99 (m, 1H), 7.32 (m, 1H); IR (KBr) 3549, 3351, 2919, 2849, 1603, 1535, 1464, 1385 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 293 (M^+, 33), 176 (14), 168 (20), 134 (25). HRMS; Found: *m/z* 293.1631. Calcd for $C_{16}H_{23}NO_4$: M, 293.1625.

(+)-7-Nitro-2-octyl-5-[4-(4-octyloxyphenyl)phenylcarboxyl]-2,3-dihydrobenzofuran ((+)-**3a**). To the suspension of 4-(4-octyloxyphenyl)benzoic acid (212 mg, 0.65 mmol) in dichloromethane (5 ml), DCC (174 mg, 0.85 mmol) was added, and the mixture was stirred for 30 min at room temperature. To the resulting solution, (-)-**12** (190 mg, 0.65 mmol) and 4-dimethylaminopyridine (40 mg, 0.33 mmol) were added. The mixture was stirred overnight at room temperature, filtered through Celite. The filtrate was washed with dil $NaHCO_3$, dried (Na_2SO_4), concentrated under reduced pressure. Purification by column chromatography (first with chloroform, second with hexane-ethyl acetate = 5 : 1, R_f 0.4) and by recrystallization (hexane-ether-dichloromethane = 10 : 1 : 1, 40 ml) gave (+)-**3a** (187 mg, 48% yield, 100% *ee*) as pale yellow needle. Cr 108 S_C^* 130 S_A 179 I; $[\alpha]_D^{20}$ +1.56 ° (*c* 1.02, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.86-0.94 (m, 6 H), 1.23-1.55 (m, 22 H), 1.72-1.86 (m, 3 H), 1.92-2.02 (m, 1 H), 3.00 (dd, J = 16.2 and 7.6 Hz, 1 H), 3.42 (dd, J = 16.2, and 9.3 Hz, 1 H), 4.02 (t, J = 6.6 Hz, 2 H), 5.11 (quintet, J = 6.9 Hz, 1 H), 7.01 (dt, J = 8.6 and 2.8 Hz, 2 H), 7.33 (dt, J = 2.4 and 1.3 Hz, 1 H), 7.60 (dt, J = 8.8 and 3.0 Hz, 2 H), 7.70 (dt, J = 8.7 and 1.9 Hz, 2 H), 7.79 (d, J = 2.5 Hz, 1 H), 8.20 (dt, J = 8.6 and 1.9 Hz, 2 H); IR (KBr) 2920, 2851, 1736, 1605, 1537, 1466, 1290, 1273, 1256, 1082, 934, 831 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 601 (M^+, 1), 309 (100), 197 (10). Found: C, 73.85; H, 7.92; N, 2.28%. Calcd for $C_{37}H_{47}NO_6$: C, 73.85; H, 7.87; N, 2.33%.

5-Methoxy-2-octyl-2,3-dihydrobenzofuran (**13**). Methyl iodide (0.69 g, 4.8 mmol) and sodium hydride (0.19 g, 4.8 mmol) were added to DMF (50 ml) solution of **9** (1.2 g, 4.8 mmol). The mixture was stirred for 5 h at 0 °C and then poured into 2 M HCl. Workup followed by column chromatography (hexane-ethyl acetate = 10 : 1), gave **13** (0.98 g, 77% yield). Bp 205 °C/2.5 Torr; R_f (hexane-ethyl acetate = 5 : 1) 0.7. ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.9 Hz, 3 H), 1.19-1.53 (m, 12 H), 1.59-1.70 (m, 1 H), 1.76-1.87 (m, 1 H), 2.83 (dd, J = 15.5 and 8.0 Hz, 1 H), 3.23 (dd, J = 15.5 and 8.8 Hz, 1 H), 3.75 (s, 3 H), 4.68-4.77 (m, 1 H), 6.63-6.66 (m, 2 H), 6.73-6.76 (m, 1 H); IR (neat) 2928, 2855, 1489, 1206, 1138, 1034 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 262 (M^+, 100), 163 (19), 150 (15), 137 (98), 91(10). Found: C, 77.71; H, 10.00%. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99%.

5-Methoxy-6-nitro-2-octyl-2,3-dihydrobenzofuran (**14**). This (400 mg, 43% yield) was prepared according to the same procedure for **11** from **13** (790 mg, 3.02 mmol) as pale yellow powder. Mp 49 °C; R_f (hexane-ethyl acetate = 5 : 1) 0.3. ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.1 Hz, 3 H), 1.25-1.37 (m, 12 H), 1.61-1.71 (m, 1 H), 1.76-1.86 (m, 1 H), 2.90 (ddd, J = 16.5, 7.7 and 1.0 Hz, 1 H), 3.31 (ddd, J = 16.5, 8.9 and 0.8 Hz, 1 H), 3.90 (s, 3 H), 4.79-4.87 (m, 1 H), 6.92 (s, 1 H), 7.22 (s, 1 H); IR (neat) 2910, 2840, 1590, 1530, 1480, 1460, 1330, 1260, 1190, 1140, 990, 850, 820 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 307 (M^+, 100), 195 (15), 183 (22), 153 (15), 69 (15), 55 (14), 41 (16). Found: C, 66.44; H, 8.47; N, 4.41%. Calcd for $C_{17}H_{25}NO_4$: C, 66.43; H, 8.20; N, 4.56%.

(-)-5-Hydroxy-6-nitro-2-octyl-2,3-dihydrobenzofuran ((-)-**15**). To dichloromethane (25 ml) solution of **14** (744 mg, 2.42 mmol), dimethyl sulfide (1.8 ml, 24 mmol) and anhydrous aluminium chloride (1.0 g, 7.3 mmol) were added at -10 °C. The reaction mixture was stirred for 2 h at -10 °C, then concentrated and diluted with diethyl ether. The whole was poured into 2 M HCl, and the organic layer was extracted with diethyl ether. The ethereal extracts were dried (Na_2SO_4) and concentrated under reduced pressure. Purification by column chromatography (hexane-ethyl acetate = 10 : 1, R_f 0.5) gave (±)-**15** (377 mg, 53 % yield) as yellow powder. Resolution into (+)- and (-)-isomers was carried out by preparative HPLC (CHIRALPAC AD, 20 mmϕ × 300 mm × 2, hexane-2-propanol = 150 : 1) to give (-)-**15** (162 mg, 23 % yield, >99 % ee). Mp 62-63 °C; $[\alpha]_D^{20}$ -3.19 ° (*c* 1.00, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.7 Hz, 3 H), 1.24-1.38 (m, 12 H), 1.61-1.71 (m, 1 H), 1.76-1.86 (m, 1 H), 2.89 (ddd, J = 17.2, 7.6 and 1.3 Hz, 1 H), 3.31 (ddd, J = 17.2, 8.6 and 1.1 Hz, 1 H), 4.77-4.85 (m, 1 H), 6.95 (t, J = 1.2 Hz, 1 H), 7.36 (s, 1 H), 10.62 (s, 1 H); IR (KBr) 3372, 2920, 2852, 1593, 1530, 1481, 1469, 1439, 1317, 1217, 1152, 1134, 961 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 293 (M^+, 100), 181 (42), 169 (32), 134 (15), 123 (23), 83 (34), 69 (70), 55 (56), 41 (58), 29 (42). Found: C, 65.67; H, 8.06; N, 4.56%. Calcd for $C_{16}H_{23}NO_4$: C, 65.51; H, 7.90; N, 4.77%.

(+)-6-Nitro-2-octyl-5-[4-(4-octyloxyphenyl)phenylmethoxy]-2,3-dihydrobenzofuran ((+)-**6**). To the ethereal (20 ml) solution of (-)-**12** (100 mg, 0.34 mmol) were added successively triphenylphosphine (89 mg, 0.34 mmol), 4-(4-octyloxyphenyl)phenylmethanol (106 mg, 0.34 mmol), and diethyl azodicarboxylate (54 μl, 0.34 mmol). The mixture was stirred for 30 h at room temperature before quenching with sat $NaHCO_3$ *aq* solution. Workup followed by column chromatography (first with chloroform, second with hexane-ethyl acetate = 5 : 1) and by recrystallization (diethyl ether-ethanol = 1 : 1) afforded (+)-**6** (117 mg, 61 % yield, 100 % ee) as pale yellow powder. Cr 99 S_C^* 115 I; R_f (hexane-ethyl acetate = 5 : 1) 0.3; $[\alpha]_D^{20}$ -18.6 ° (*c* 1.01, $CHCl_3$). ^1H NMR

($CDCl_3$) δ 0.85-0.93 (m, 6 H), 1.24-1.53 (m, 22 H), 1.60-1.70 (m, 1 H), 1.76-1.86 (m, 1 H), 2.87 (dd, J = 16.6 and 7.7 Hz, 1 H), 3.28 (dd, J = 16.6 and 8.8 Hz, 1 H), 4.00 (t, J = 6.6 Hz, 2 H), 4.78-4.86 (m, 1 H), 5.17 (s, 2 H), 6.94-6.99 (m, 3 H), 7.22 (s, 1 H), 7.46-7.59 (m, 6 H); IR (KBr) 2955, 2922, 2855, 1599, 1533, 1503, 1246, 1188, 963, 810 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 587(M^+, trace), 295 (100), 183 (29), 43 (18). Found: C, 75.46; H, 8.55; N, 2.39%. Calcd for $C_{37}H_{49}NO_5$: C, 75.61; H, 8.40; N, 2.38%.

MEASUREMENTS OF Ps

Host S_C mixture (Cr 13 S_C* 67 N* 70 I) consisting of 2-(4-nonyloxyphenyl)-5-heptylpyrimidine (30 wt%), 2-(4-octyloxyphenyl)-5-octylpyrimidine (20 wt%), 2-(4-decyloxyphenyl-5-octylpyrimidine (20 wt%), and 2-(4-octyloxyphenyl-5-nonyl-pyrimidine (20 wt%) was doped with **3b**, and the resulting mixtures were sealed in a polyimide rubbed cell of about 2 μm thickness. Response time was measured as 0-90% transmittance change when 50 Hz rectangular wave of 10 Vp-p/μm was applied, and Ps was measured by the triangular method both at 25 °C.

MEASUREMENTS OF SHG

Compound **2**, **3a**, or **3b** was sandwiched between two glass plates which were treated with a silane coupling agent for homeotropic alignment. Two sheets of aluminum foil were used for spacers as well as for electrodes to apply an electric field parallel to the smectic layer. The thickness was about 40 μm and the electrode gap was 1.2 mm. The helix was unwound by applied a dc electric field (100 V/mm). The cell was rotated around the axis parallel to the field direction. SHG measurements were performed using an polarized fundamental beam of an Nd:YAG laser as a light source (8 ns duration, 10 Hz and 1-0.1 mJ/pulse). The p-polarized SH light was detected through an IR-cut filter and an interference filter in the transmitted direction, by a photomultiplier tube. The signal was sent to a boxcar integrator and was processed by a microcomputer.

REFERENCES

1. T. Kusumoto, T. Hiyama, and S. Takehara, *Liquid Cryst.*, in press; T. Kusumoto, T. Hiyama, and S. Takehara, *Dyestuffs & Chemicals*, **38**, 57 (1993); T. Kusumoto, T. Hiyama, and S. Takehara, *Nippon Kagaku Kaishi*, **1992**, 1401; T. Kusumoto, T. Hiyama, S. Takehara, and T. Shoji, *Yuki Gosei Kgaku Kyokaishi*, **49**, 467 (1991).
2. S. Takehara, M. Osawa, K. Nakamura, T. Kusumoto, K. Sato, A. Nakayama, T. Hiyama, *Liquid Cryst.*, in press.
3. D. M. Walba, M. B. Ros, N. A. Clark, R. Shao, M. G. Robinson, J. Y. Liu, K. M. johnson, and D. Doroski, *J. Am. Chem. Soc.*, **113**, 5471 (1991); D. M. Walba, M. B. Ros, N. A. Clark, R. Shao, K. M. Johnson, M. G. Robinson, J. Y. Liu, and D. Doroski, *Mol. Cryst. Liq. Cryst.*, **198**, 51 (1991); D. M. Walba, M. B. Ros, T. Sierra, J. A. Rego, N. A, Clark, R. Shao, M. D. Wand, R. T. Vohra, K. E. Arnett, and S. P. Velsco, *Ferrroelectrics*, **121**, 247 (1991); D. M. Walba, M. B. Ros, N. A. Clark, R. Shao, K. M. Johnson, M. G. Robinson, J. Y. Liu, and D. Doroski, Ferroelectric Liquid Crystals Designed for Electronic Nonlinear Optical Applications. In *Materials for Nonlinear Optics: Chemical Perspectives*; Ed. G. D. Stucky, American Chemical Society, Washinton, DC, Vol. 455, pp484-496 (1991).
4. K. Schmitt, R.-P. Herr, M. Schadt, J. Fünfschilling, R. Bucheker, X. H. Chen, and C. Benecke, *Liquid Cryst.*, **14**, 1735 (1993).