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New Ferroelectric Liquid Crystal Materials: (+)-4-(5-Alkyl-1,3-dioxan-2-yl)phenyl 4-(2-Methylbutoxy)benzoates

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(+)-4-(5-Alkyl-1,3-dioxan-2-yl)phenyl 4-(2-methylbutoxy)benzoates (**9**) and their oxathiane (**10**) and dithiane (**11**) analogs have been synthesized. The mesomorphic behavior of these compounds was measured. Compounds **9** exhibited a ferroelectric liquid-crystal behavior (e.g. $R=n\text{-}C_{10}H_{21}$: 51 SmC* 57.5 °C), while the corresponding 1,3-oxathianes (**10**) and 1,3-dithianes did not.

In recent years 2,5-disubstituted 1,3-dioxanes, 1,3-oxathianes, and 1,3-dithianes have been reported as new types of nematic liquid-crystal materials.[1—10]

In view of the increasing attention being paid to new types of liquid-crystal displays using ferroelectric liquid crystals, we have synthesized various ferroelectric liquid-crystal compounds, such as several structural types of optically active liquid-crystal compounds with 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane rings.[11—15] In a previous paper,[13] we reported that (+)-4-(2-methylbutoxycarbonyl)phenyl 4-(5-alkyl-1,3-dioxan-2-yl)benzoates exhibit a ferroelectric liquid-crystal behavior, but (+)-4-(2-methylbutoxy)phenyl 4-(5-alkyl-1,3-dioxan-2-yl)-benzoates (**12**) do not. The title compounds (**9**) were only different from compounds (**12**) regarding the direction of the ester bond. In this paper, we wish to report on the syntheses and mesomorphic behavior of these compounds.

Results and Discussion

(+)-4-(5-Alkyl-1,3-dioxan-2-yl)phenyl 4-(2-methylbutoxy)benzoates (**9**) and the corresponding 1,3-oxathianes (**10**) and 1,3-dithianes (**11**) were synthesized via the following route.

In step **1**→**2**,**3** the reaction temperature was kept within the range 80 to 85 °C in order to obtain compounds **2** and **3** in nearly equal yields.

In step (**2**, **3**) → (**4**, **5**) a mixture of compounds **2** and **3** was used. Compounds **4** and **5** were separated by column chromatography, though which **4** and **5** were eluted with hexane and ether, respectively. During esterification from **6** and **7**, 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) was used as a base. Compounds **9**, **10**, and **11** were synthesized by acid-catalyzed ring-formation reactions of compounds **1**, **4**, and **5** with aldehyde **8**, respectively. Compounds **9**, **10**, and **11** were purified by column chromatography and recrystallized from hexane.

Since each product obtained as a white powder contained about 5—20% cis isomer, these products were chromatographed on preparative thin-layer chromatography (prep. TLC) in order to obtain analytically pure trans isomers. In the ^{1}H NMR data for compounds **9**, **10**, and **11**, the C-2 proton signals of the 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane rings for the trans and cis isomers appeared separately within a range of about 0.05 ppm. For eample, the C-2 proton signals of the trans isomers appeared at $\delta=5.45$ (compound **9-1**,) 5.75 (**10-1**), and 5.20 (**11-1**), and the corresponding signals of the cis isomers appeared at $\delta=5.50$, 5.80, and 5.15, respectively.

Mesomorphic properties were determined suing a

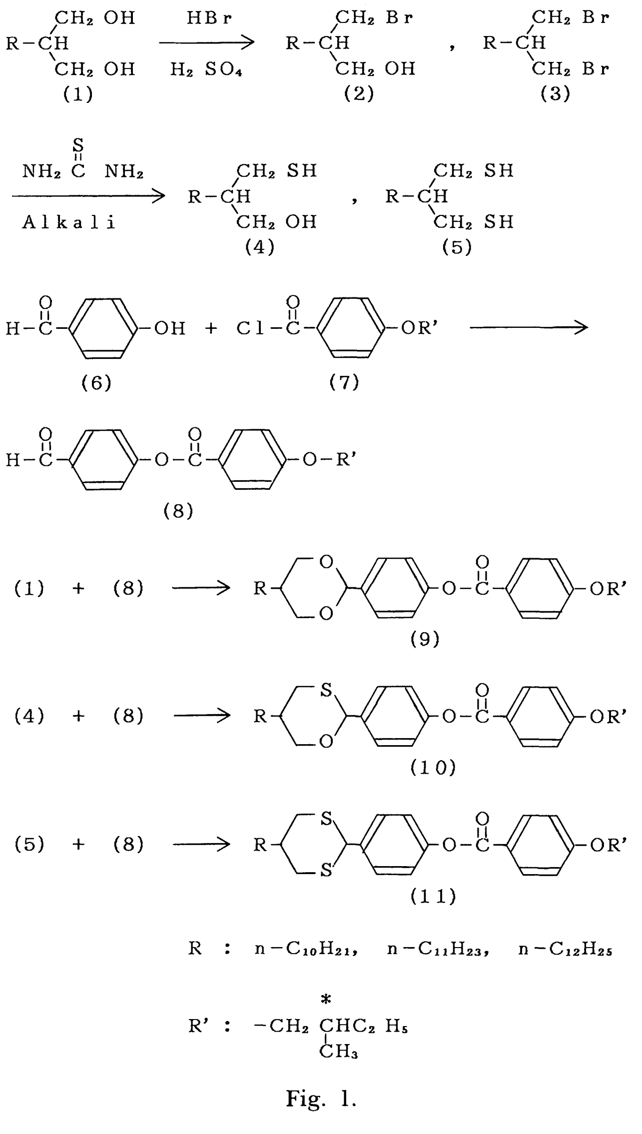
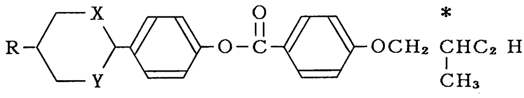
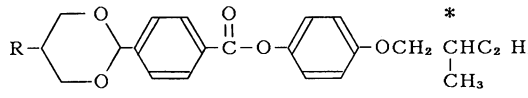


Fig. 1.

Table 1. Mesomorphic Ranges for Compounds **9**, **10**, **11**, and **12**


(**9**, **10**, **11**, **12**)

	R	X Y	Mesomorphic range/°C[a]
9-1	n-$C_{10}H_{21}$	O O	$\mathrm{C}\xrightarrow{69}\mathrm{N^*}\xleftrightarrow{123}\mathrm{I}$ $\mathrm{Sm}\xrightarrow{40}\mathrm{C}$; $\mathrm{N^*}\xleftrightarrow{58}\mathrm{SmC^*}$ $\mathrm{Sm}\xleftrightarrow{51}\mathrm{SmC^*}$
9-2	n-$C_{11}H_{23}$	O O	$\mathrm{C}\xrightarrow{76}\mathrm{N^*}\xleftrightarrow{124}\mathrm{I}$ $\mathrm{Sm}\xrightarrow{35}\mathrm{C}$; $\mathrm{N^*}\xleftrightarrow{63}\mathrm{SmC^*}$ $\mathrm{Sm}\xleftrightarrow{61}\mathrm{SmC^*}$
9-3	n-$C_{12}H_{25}$	O O	$\mathrm{C}\xrightarrow{82}\mathrm{N^*}\xleftrightarrow{118}\mathrm{I}$ $\mathrm{Sm}\xrightarrow{30}\mathrm{C}$; $\mathrm{N^*}\xleftrightarrow{68}\mathrm{SmC^*}$ $\mathrm{Sm}\xleftrightarrow{65}\mathrm{SmC^*}$
10-1	n-$C_{10}H_{21}$	S O	$\mathrm{C}\xrightarrow{88}\mathrm{N^*}\xleftrightarrow{122}\mathrm{I}$ $\mathrm{N^*}\xrightarrow{47}\mathrm{Sm}\xrightarrow{46}\mathrm{C}$
10-2	n-$C_{11}H_{23}$	S O	$\mathrm{C}\xrightarrow{83}\mathrm{N^*}\xleftrightarrow{120}\mathrm{I}$ $\mathrm{N^*}\xrightarrow{61}\mathrm{Sm}\xrightarrow{48}\mathrm{C}$
10-3	n-$C_{12}H_{25}$	S O	$\mathrm{C}\xrightarrow{87}\mathrm{N^*}\xleftrightarrow{114}\mathrm{I}$ $\mathrm{N^*}\xrightarrow{65}\mathrm{Sm}\xrightarrow{23}\mathrm{C}$
11-1	n-$C_{10}H_{21}$	S S	$\mathrm{C}\xrightarrow{92}\mathrm{N^*}\xleftrightarrow{138}\mathrm{I}$ $\mathrm{N^*}\xrightarrow{58}\mathrm{Sm}\xrightarrow{53}\mathrm{C}$
11-2	n-$C_{11}H_{23}$	S S	$\mathrm{C}\xrightarrow{85}\mathrm{N^*}\xleftrightarrow{137}\mathrm{I}$ $\mathrm{N^*}\xrightarrow{71}\mathrm{Sm}\xrightarrow{48}\mathrm{C}$
11-3	n-$C_{12}H_{25}$	S S	$\mathrm{C}\xrightarrow{87}\mathrm{N^*}\xleftrightarrow{135}\mathrm{I}$ $\mathrm{N^*}\xrightarrow{81}\mathrm{Sm}\xrightarrow{35}\mathrm{C}$


(**12**)

	R	Mesomorphic range/°C[a]
12-1	n-$C_{10}H_{21}$	$\mathrm{C}\underset{22}{\overset{66}{\rightleftarrows}}\mathrm{SmB}\xleftrightarrow{100}\mathrm{SmA}\xleftrightarrow{136}\mathrm{I}$
12-2	n-$C_{11}H_{23}$	$\mathrm{C}\underset{94}{\overset{113}{\rightleftarrows}}\mathrm{SmA}\xleftrightarrow{137}\mathrm{I}$
12-3	n-$C_{12}H_{25}$	$\mathrm{C}\underset{22}{\overset{70}{\rightleftarrows}}\mathrm{SmB}\xleftrightarrow{97}\mathrm{SmA}\xleftrightarrow{137}\mathrm{I}$

a) C: crystal, Sm: smectic, N*: chiral nematic, I: isotropic.

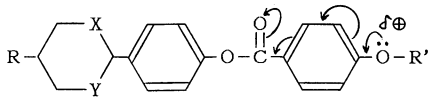


Fig. 2

micro melting-point apparatus equipped with polarizers and a differential scanning calorimeter (DSC). The phase was identified by comparing the observed textures with those found in the literature.[16,17]

Mesomorphic ranges of compounds **9** and **12** are given in Table 1.

Among the smectic phases listed in this table, only SmC* of compounds **9** could be drived in homogeneous cells (d=1.7 μm, applied voltage=10 V). This indicates that only compounds **9** are ferroelectric liquid-crystal compounds. 1,3-Oxathiane and 1,3-dithiane analogues which correspond to compounds **9** did not exhibit the SmC* phase. This must support the previous result[13] that the 1,3-dioxane structure is more favorable for a transition to SmC* than the structures of 1,3-oxathiane or 1,3-dithiane are.

Compounds **12**, having the direction of the ester bond just reversed to that of compounds **9**, did not exhibit the SmC* phase. This seems to originate in the appearance of a chiral nematic phase (cholesteric phase). Generally, there are many examples of a transition from the chiral nematic phase to the SmC* phase.[18] In both the chiral nematic phase and the SmC* phase, the chiral alkoxyl group seems to orient in a way that may be favorable for a transition from the chiral nematic phase to the SmC* phase.

In all compounds **9**, **10**, and **11** the chiral nematic phase (cholesteric phase) appeared. The chemical structural feature of these compounds is that the chiral group (OR′) is conjugated with the phenylcarbonyl group. The *p*-alkoxyphenylcarbonyl group has a dipole moment due to a resonance effect, exhibited as follows (Fig. 2).

Therefore, this chemical structure has a strong dipole moment contiguous to the chiral group. This must be one factor for the appearance of the chiral nematic phase.

The spontaneous polarizations of compounds **9** were too small to detect.

The responses of the optical transmission for compounds **9**-**1**, **9**-**2**, and **9**-**3** were 8, 4, and 7 ms, respectively, values that belong to a large class of ferroelectric liquid-crystal materials. This must originate in the small spontaneous polarization. The tilt angles for compounds **9**-**1**, **9**-**2**, and **9**-**3** are 13°, 21°, and 25°, respectively.

The $\Delta H_{\mathrm{N^*\text{-}I}}$ of compounds **9**-**2**, **10**-**2**, and **11**-**2** were 1.58, 1.73, and 2.12 kJ mol^{-1}, and their $\Delta S_{\mathrm{N^*\text{-}I}}$ were 3.98, 4.40, and 5.16 J K^{-1} mol^{-1}, respectively.

The $\Delta H_{\mathrm{C\text{-}N^*}}$ of these compounds were 28.65, 31.15, and 39.42 kJ mol^{-1}, and their $\Delta S_{\mathrm{C\text{-}N^*}}$ were 87.50, 110.12, and 82.09 J K^{-1} mol^{-1}, respectively.

Experimental

IR, ^{1}H NMR, and mass spectra were obtained with a Hitachi 215 spectraphotometer, a JNM-PMX 60 spectrometer, and a Hitachi M-80B spectrometer, respectively.

Elemental analyses were carried out with a Perkin-Elmer 250 instrument.

The transition temperatures and mesomorphic phases were determined by means of both a Mitamura Rikenn micro melting point apparatus equipped with polarizers and a Rigaku Denki DSC CN8059L1, CN8208A2. Optical studies were performed on an Olympus polarizing microscope in conjunction with a Mettler FP-82 hot stage and a control unit using a function generator on a Hewlett Packard 3310B and a SONY-TECTRONICS 468 oscilloscope.

Mixtures of 2-Alkyl-3-bromo-1-propanol (2) and 2-Alkyl-1,3-dibromopropane (3). The same procedure as that mentioned in a previous paper[11] was used.

2-Alkyl-3-mercapto-1-propanol (4) and 2-Alkyl-1,3-propanedithiol (5). The same procedure as that mentioned in a previous paper[11] was used. Compounds **4** were colorless, tranparent liquids and **5** were yellow, transparent liquids.

(+)-4-Formylphenyl 4-(2-Methylbutoxy)benzoate (8). To a solution of compound **6** (0.03 mol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.03 mol) in anhyd *N*,*N*-dimethylformamide (30 ml) was added compound **7** (0.03 mol) under a nitrogen atmosphere, followed by sterring at 30—40 °C for 18 h. The solution was poured into ice water and extracted twice with ether (each 200 ml). The extract was washed with cold 2% aq. HCl, dried over anhyd Na_2SO_4, and evaporated in vacuo at 40 °C. The residue was extrated with hexane, and concentrated under pressure. Transparent liquid was obtained in 60—70% yield.

IR ($CHCl_3$) 2800—3000 (alkyl), 1720, 1680 (C=O), 1290 (ether) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ=0.7—2.2 (m, 9H, $OCH_2\,C_4\,\underline{H}$), 3.9 (d, 2H, OCH_2), 6.8—8.4 (m, 8H, ArH), 10.05 (s, 1H, CHO).

(+)-4-(5-Alkyl-1,3-dioxan-2-yl)phenyl 4-(2-methylbutoxy)-benzoate (9). To a solution of compound **1** (0.004 mol) and compound **8** (0.004 mol) in anhyd $CHCl_3$ (200 ml) cooled in an ice bath were added $BF_3\cdot(C_2H_5)_2O$ (0.5 g) and Molecular Sieves (3A, 1/15; 3 g). The mixture was stirred at 0—5 °C for 8 h, and then at 20—25 °C for 16 h. The solution was washed with 10% aq. $NaHCO_3$ (400 ml), dried over anhyd. Na_2SO_4, and evaporated in vacuo. The crude product was purified by column chromatography and recrystallized from hexane, and then chromatographed on prep. TLC to give the pure trans isomer.

IR ($CHCl_3$) 2800—3000 (alkyl), 1740 (C=O), 1600 (Ar), 1290 (ether) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ=0.7—2.2 (m, alkyl), 3.3—4.5 (m, 6H, OCH_2), 5.45 (s, 1H, CH), 6.8—8.4 (m, 8H, ArH).

(+)-4-(5-Alkyl-1,3-oxathian-2-yl)phenyl 4-(2-Methylbutoxy)-benzoate (10). Compounds **10** were synthesized according to the same procedure as that for compounds **9**.

IR ($CHCl_3$) 2800—3000 (alkyl), 1740 (C=O), 1600 (Ar), 1280 (ether) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ=0.6—2.2 (m, alkyl), 2.9 (d, 2H, CH_2S), 3.2—4.3 (m, 4H, CH_2O), 5.75 (s, 1H, CH), 6.8—8.4 (m, 8H, ArH).

(+)-4-(5-Alkyl-1,3-dithian-2-yl)phenyl 4-(2-Methylbutoxy)-benzoate (11). Compounds **11** were synthesized according to the same procedure as that for compounds **9**.

IR ($CHCl_3$) 2800—3000 (alkyl), 1740 (C=O), 1600 (Ar), 1280 (ether) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ=0.7—2.2 (m, alkyl), 2.7—2.95 (m, 4H), 3.9 (d, 2H, CH_2O), 5.20 (s, 1H, CH), 6.9—8.4 (m, 8H, ArH).

9-1: Yield, 20%. Found: C, 75.35; H, 9.07%. Calcd for $C_{32}H_{46}O_5$: C, 75.26; H, 9.08%. MS (*m/z*) 510 (M^+).

9-2: Yield, 14%. Found: C, 75.11; H, 9.27%. Calcd for $C_{33}H_{48}O_5$: C, 75.53; H, 9.22%. MS (*m/z*) 524 (M^+).

9-3: Yield, 28%. Found: C, 75.74: H, 9.41%. Calcd for $C_{34}H_{50}O_5$: C, 75.80; H, 9.36%. MS (*m/z*) 538 (M^+).

10-1: Yield, 24%. Found: C, 72.75; H, 8.83%. Calcd for $C_{32}H_{46}SO_4$: C, 72.96; H, 8.80%. MS (*m/z*) 526 (M^+).

10-2: Yield, 19%. Found: C, 72.89; H, 8.99%. Calcd for $C_{33}H_{48}SO_4$: C, 73.29; H, 8.95%. MS (*m/z*) 540 (M^+).

10-3: Yield, 23%. Found: C, 73.61; H, 9.15%. Calcd for $C_{34}H_{50}SO_4$: C, 73.60; H, 9.08%. MS (*m/z*) 554 (M^+).

11-1: Yield, 28%. Found; C, 70.50; H, 8.58%. Calcd for $C_{32}H_{46}S_2O_3$: C, 70.80; H, 8.54%. MS (*m/z*) 542 (M^+).

11-2: Yield, 27%. Found: C, 70.95; H, 8.72%. Calcd for $C_{33}H_{48}S_2O_3$: C, 71.18; H, 8.69%. MS (*m/z*) 556 (M^+).

11-3: Yield, 35%. Found: C, 71.67; H, 8.96%. Calcd for $C_{34}H_{50}S_2O_3$: C, 71.53; H, 8.83%. MS (*m/z*) 570 (M^+).

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