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

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(+)-4-(2-Methylbutoxycarbonyl)phenyl 4-(5-alkyl-1,3-dioxan-2-yl)benzoate (**12**), (+)-4-(2-methylbutoxy)phenyl 4-(5-alkyl-1,3-dioxan-2-yl)benzoate (**11**) and the corresponding 1,3-oxathiane (**13, 14**) and 1,3-dithiane compounds (**15, 16**) were synthesized. The mesomorphic behaviors of these compounds were measured. Compounds **12** exhibited the ferroelectric liquid-crystal behavior ($R=n\text{-}C_{11}H_{23}$: -4 SmC* 94 °C), while the corresponding 1,3-oxathiane (**13, 14**) and 1,3-dithiane compounds (**15, 16**) did not exhibit such behavior. Therefore, 1,3-dioxane compounds are more favorable for transition of SmA to SmC* than the 1,3-oxathiane or 1,3-dithiane analogs.

2,5-Disubstituted 1,3-dioxanes, 1,3-oxathianes, and 1,3-dithianes were synthesized recently as new types of nematic liquid crystal materials.[1-10] With increasing interests in liquid-crystal displays using ferroelectric liquid crystals, various ferroelectric liquid crystal compounds have been synthesized: the basic structure of optically active liquid-crystal compounds with a 1,3-dioxane, a 1,3-oxathiane, and a 1,3-dithiane ring have been synthesized.[11,12] In a previous letter,[12] we reported new ferroelectric liquid-crystal compounds with a 1,3-dioxane ring. This paper deals with the synthesis and the mesomorphic behavior of these compounds in detail.

Results and Discussion

(+)-4-(2-Methylbutoxy)phenyl 4-(5-alkyl-1,3-dioxan-2-yl)benzoate (**11**), (+)-4-(2-methylbutoxycarbonyl)phenyl 4-(5-alkyl-1,3-dioxan-2-yl)benzoate (**12**) and the corresponding oxathianes (**13, 14**) and dithianes (**15, 16**) were synthesized via the following route.

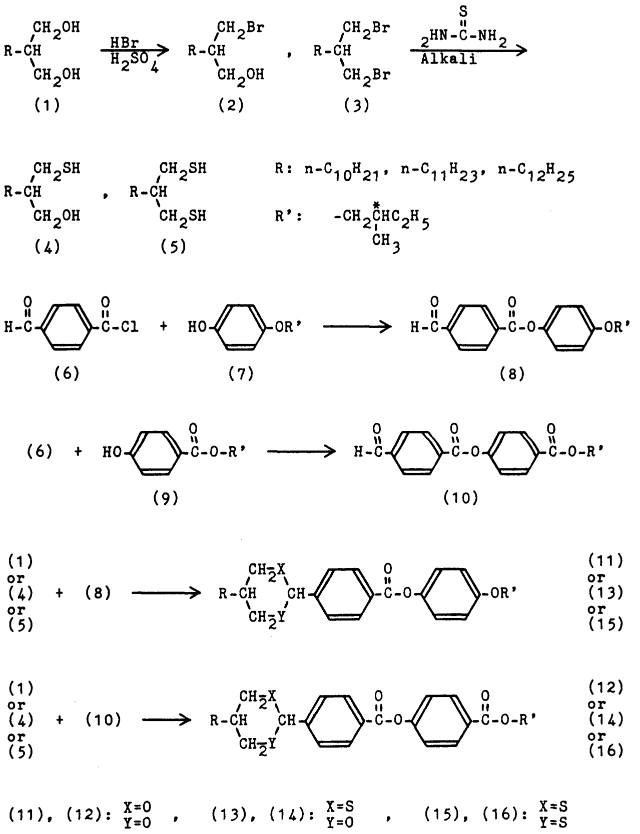


Fig. 1.

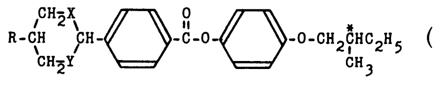
In step **1**→**2**, **3**, the reaction temperature of bromination was kept within the range 80 to 85 °C in order to obtain compounds **2** and **3** at nearly equal yields. In the conversion of **2**, **3** into **4**, **5** respectively, a mixture of compounds **2** and **3** was used. The mixture of compounds **4** and **5**, thus obtained, was separated by column chromatography. Compound **4** was eluted in an ether fraction and **5** in a hexane fraction. Compound **7** was synthesized by the monoetherification of hydroquinone.

Compound **9** was obtained by the esterification of *p*-hydroxybenzoic acid with (+)-2-methyl-1-butanol in the presence of an acid catalyst using a Dean-Stark trap. A two-day reaction is necessary to obtain a sufficient yield.

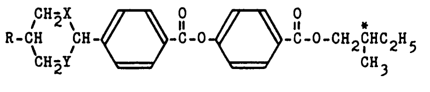
In steps **6**,**7**→**8** and **6**,**9**→**10**, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used as a base. Both compounds **8** and **10** were extracted with hexane.

Compounds **11**—**15**, and **16** were synthesized by ring-formation reactions of compounds **1**, **4**, and **5** with aldehydes (**8**, **10**), respectively. The products, **11**—**16**, were purified by column chromatography and recrystallized from hexane. The trans isomers of **11**, **13**, **15**, **16** were isolated by means of TLC (hexane: ether=5:2) of the cis and trans mixtures. In the ^{1}H NMR data of the 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane compounds, C-2 proton signals of the 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane rings for the trans and cis isomers are separated by about 0.05 ppm. For example, the C-2 proton of the trans isomers absorbs at $\delta=5.50$ (compound **12-1**), 5.75 (**14-1**), and 5.20 (**16-1**) but that of the corresponding cis isomer absorbs at $\delta=5.55$ (**12-1**), 5.80 (**14-1**), and 5.15 (**16-1**), respectively.

Table 1. Mesomorphic Ranges for Compounds **11**, **12**, **13**, **14**, **15**, and **16**


(A)

	R	X Y	Mesomorphic range/°C[a)]
11-1	$C_{10}H_{21}$	O O	$\mathrm{C} \underset{22}{\overset{66}{\rightleftarrows}} \mathrm{SmB} \underset{100}{\overset{100}{\rightleftarrows}} \mathrm{SmA} \underset{136}{\overset{136}{\rightleftarrows}} \mathrm{I}$
11-2	$C_{11}H_{23}$	O O	$\mathrm{C} \underset{94}{\overset{113}{\rightleftarrows}} \mathrm{SmA} \underset{137}{\overset{137}{\rightleftarrows}} \mathrm{I}$
11-3	$C_{12}H_{25}$	O O	$\mathrm{C} \underset{22}{\overset{70}{\rightleftarrows}} \mathrm{SmB} \underset{97}{\overset{97}{\rightleftarrows}} \mathrm{SmA} \underset{137}{\overset{137}{\rightleftarrows}} \mathrm{I}$
13-1	$C_{10}H_{21}$	S O	$\mathrm{C} \underset{-50}{\overset{66}{\rightleftarrows}} \mathrm{SmB} \underset{111}{\overset{111}{\rightleftarrows}} \mathrm{SmA} \underset{134}{\overset{134}{\rightleftarrows}} \mathrm{I}$
13-2	$C_{11}H_{23}$	S O	$\mathrm{C} \underset{-50}{\overset{64}{\rightleftarrows}} \mathrm{SmB} \underset{111}{\overset{111}{\rightleftarrows}} \mathrm{SmA} \underset{132}{\overset{132}{\rightleftarrows}} \mathrm{I}$
13-3	$C_{12}H_{25}$	S O	$\mathrm{C} \underset{-50}{\overset{59}{\rightleftarrows}} \mathrm{SmB} \underset{117}{\overset{117}{\rightleftarrows}} \mathrm{SmA} \underset{132}{\overset{132}{\rightleftarrows}} \mathrm{I}$
15-1	$C_{10}H_{21}$	S S	$\mathrm{C} \underset{54}{\overset{104}{\rightleftarrows}} \mathrm{SmB} \underset{136}{\overset{136}{\rightleftarrows}} \mathrm{SmA} \underset{153}{\overset{153}{\rightleftarrows}} \mathrm{I}$
15-2	$C_{11}H_{23}$	S S	$\mathrm{C} \underset{63}{\overset{109}{\rightleftarrows}} \mathrm{SmB} \underset{140}{\overset{140}{\rightleftarrows}} \mathrm{SmA} \underset{153}{\overset{153}{\rightleftarrows}} \mathrm{I}$
15-3	$C_{12}H_{25}$	S S	$\mathrm{C} \underset{57}{\overset{87}{\rightleftarrows}} \mathrm{SmA} \underset{139}{\overset{139}{\rightleftarrows}} \mathrm{I}$


(B)

	R	X Y	Mesomorphic range/°C[a)]
12-1	$C_{10}H_{21}$	O O	$\mathrm{C} \underset{14}{\overset{59}{\rightleftarrows}} \mathrm{SmC^*} \underset{93}{\overset{93}{\rightleftarrows}} \mathrm{SmA} \underset{137}{\overset{137}{\rightleftarrows}} \mathrm{I}$
12-2	$C_{11}H_{23}$	O O	$\mathrm{C} \underset{-4}{\overset{62}{\rightleftarrows}} \mathrm{SmC^*} \underset{94}{\overset{94}{\rightleftarrows}} \mathrm{SmA} \underset{136}{\overset{136}{\rightleftarrows}} \mathrm{I}$
12-3	$C_{12}H_{25}$	O O	$\mathrm{C} \underset{30}{\overset{66}{\rightleftarrows}} \mathrm{SmC^*} \underset{95}{\overset{95}{\rightleftarrows}} \mathrm{SmA} \underset{135}{\overset{135}{\rightleftarrows}} \mathrm{I}$
14-1	$C_{10}H_{21}$	S O	$\mathrm{C} \underset{-50}{\overset{89}{\rightleftarrows}} \mathrm{SmA} \underset{134}{\overset{134}{\rightleftarrows}} \mathrm{I}$
14-2	$C_{11}H_{23}$	S O	$\mathrm{C} \underset{-50}{\overset{70}{\rightleftarrows}} \mathrm{SmB} \underset{98}{\overset{98}{\rightleftarrows}} \mathrm{SmA} \underset{136}{\overset{136}{\rightleftarrows}} \mathrm{I}$
14-3	$C_{12}H_{25}$	S O	$\mathrm{C} \underset{20}{\overset{68}{\rightleftarrows}} \mathrm{SmA} \underset{133}{\overset{133}{\rightleftarrows}} \mathrm{I}$
16-1	$C_{10}H_{21}$	S S	$\mathrm{C} \underset{94}{\overset{113}{\rightleftarrows}} \mathrm{SmA} \underset{150}{\overset{150}{\rightleftarrows}} \mathrm{I}$
16-2	$C_{11}H_{23}$	S S	$\mathrm{C} \underset{99}{\overset{117}{\rightleftarrows}} \mathrm{SmA} \underset{147}{\overset{147}{\rightleftarrows}} \mathrm{I}$
16-3	$C_{12}H_{25}$	S S	$\mathrm{C} \underset{90}{\overset{107}{\rightleftarrows}} \mathrm{SmA} \underset{141}{\overset{141}{\rightleftarrows}} \mathrm{I}$

a) C: crystal; S: smectic; I: isotropic.

Measurements of the mesomorphic ranges and assignments of the mesophases were carried out by means of a micro melting point apparatus equipped with polarizers and a differential scanning calorimeter (DSC).

To determine the type of smectic phase, the observed smectic phases were compared with color photographs found in the literature.[13,14)] Mesomorphic ranges of the synthesized compounds are given in Table 1. SmA, SmB, and SmC* mean smectic A, smectic B, and chiral smectic C phase, respectively.

Though SmC* of compounds **12** can be driven in homogenious cells (d=2 μm, applied voltage=20 V), other smectic phases can not. Therefore, compounds **12** are ferroelectric liquid-crystal compounds and others are not.

The 1,3-oxathiane and 1,3-dithiane compounds which correspond to compounds **12** did not exhibit a SmC* liquid-crystal phase. This must imply that 1,3-dioxane compounds are more favorable for the transition of SmA to SmC* than the corresponding 1,3-oxathiane or 1,3-dithiane compounds.

Though compounds **12** exhibit an SmC* phase, compounds **11** do not. The difference in these two compounds lies in the number of the carbonyl group. Therefore, a carbonyl group having a dipole moment in a vertical direction to the molecular axis must contribute to the transition from SmA to SmC*.

The transition temperatures of SmA to isotropic ($T_{\mathrm{S-I}}$) for 1,3-oxathiane compounds are lower than those for the corresponding 1,3-dioxanes and 1,3-dithianes. In a smectic liquid crystal, the temperature of the isotropic to smectic transition ($T_{\mathrm{S-I}}$) is affected by two factors: the molecular width and interactions of side substituens.[15)] The 1,3-oxathiane compounds are bent at the 1,3-oxathiane ring, caused by a difference in the atomic size between sulfur and oxygen. Therefore, the width of 1,3-oxathiane compounds is wider than that of the corresponding 1,3-dioxane or 1,3-dithiane compounds. This must make $T_{\mathrm{S-I}}$ for 1,3-oxathiane compounds lower than those for the corresponding 1,3-dioxane or 1,3-dithiane compounds.

The transition temperatures of SmA to isotropic ($T_{\mathrm{S-I}}$) for compounds A are nearly equal to those for the corresponding compounds B. This difference in the terminal group hardly affects the thermal stability of smectic phase.

Textures of SmA and SmB are focal-conic fan texture.

At the transition temperatures of the SmA to SmB phase, pronounced transition bars appeared on the surface of the focal-conic fan texture. Textures of

SmC* are broken focal-conic fan texture.

Several properties as a ferroelectric liquid crystal compound were measured for compound **12-3**; the strength of the spontanious polarization=1.3 nC cm^{-2} (85 °C), helical pich length=14.3 μm (85 °C), the response of the optical transmission=61 μs (85 °C, 20 V), tilt angle=13.5° (85 °C).

Though the strength of the spontanious polarization of compound **12-3** is smaller than that of (S)-2-methylbutyl *p*-(*p*-decyloxybenzylideneamino)cinnamate (DOBAMBC),[16] the helical pitch length of this compounds is longer than that of DOBAMBC.

The most remerkable feature of these new ferroelectric liquid crystal compounds is that, with the appearance of the supercooling state, they exhibit the ferroelectric liquid crystal behavior over a very wide range, including ordinary room temperature (**12-1**: 14 SmC* 93, **12-2**: −4 SmC* 94, **12-3**: 30 SmC* 95).

$\Delta H_{\mathrm{C\text{-}S}}$ of compounds **11-3**, **12-3**, **13-3**, **14-3**, **15-3**, and **16-3** are 25.0, 34.1, 29.5, 19.5, 18.7, and 16.8 kJ mol^{-1}, respectively.

These values are somewhat smaller than those of other common liquid crystal materials.[17]

The $\Delta H_{\mathrm{S\text{-}I}}$ of these compounds are 6.0, 5.8, 6.7, 6.5, 3.0, and 5.2 kJ mol^{-1}, respectively. Nearly the same values have been obtained for other common smectic liquid crystal compounds.[18]

Experimental

IR, ^{1}H NMR, and mass spectra were obtained with a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi M-80B spectrometer, respectively. Elemental analyses were carried out with a Perkin-Elmer 250 instrument. Transition temperatures and mesomorphic phases were determined by means of both a Mitamura Riken micro melting-point apparatus equipped with polarizers and a Rigaku Denki DSC CN8059L1, CN8208A2. The rate of cooling was fixed to 1 °C min^{-1}.

Mixtures of 2-alkyl-3-bromo-1-propanol (**2**) and 2-alkyl-1,3-dibromopropane (**3**) were prepared previously.[11]

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

IR ($CHCl_3$): Compounds **4**; 3600 (OH), 2800—3000 (alkyl) cm^{-1}. Compounds **5**; 2800—3000 (alkyl) cm^{-1}.

^{1}H NMR ($CDCl_3$): Compounds **4**; δ=0.6—2.0 (m, R-CH, SH), 2.5—2.8 (m, 2H, CH_2S), 3.4—4.0 (m, 3H, CH_2OH), Compounds **5**: δ=0.6—2.0 (m, R-CH, SH), 2.5—2.9 (m, 4H, CH_2S).

(+)-4-(2-Methylbutoxy)phenol(7). The Williamson synthesis was applied to hydroquinone and (+)-2-methylbutyl bromide. As the diether was produced as a side product, the crude product was purified by column chromatography. Compound **7** was eluted with benzene and the diether with hexane. Transparent liquid was obtained in a 30—40% yields.

IR ($CHCl_3$) 3600 (OH), 2800—3000 (alkyl), 1600 (Ar), 1260 (ether) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ=0.6—2.3 (m, 9H, $OCH_2C_4\underline{H_9}$), 3.8 (d, 2H, OCH_2), 5.9 (s, 1H, OH), 6.8 (s, 4H, ArH).

(+)-2-Methylbutyl *p*-Hydroxybenzoate (9). A solution of *p*-hydroxybenzoic acid (0.1 mol) and 2-methylbutanol (0.1 mol) and *p*-toluenesulfonic acid (0.3 g) in anhyd. toluene (100 ml) was refluxed for 48 h with a Dean-Stark trap fitted. Then toluene was removed on a rotary evaporator. The residue was dissolved in diethyl ether (300 ml), washed with 5% aq. $NaHCO_3$ (200 ml), dried over anhyd. Na_2SO_4, and evaporated in vacuo.

Transparent liquid was obtained in a 85—90% yields.

IR ($CHCl_3$) 3600 (OH), 2800—3000 (alkyl), 1715 (C=O), 1600 (Ar) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ=0.7—2.2 (m, 9H, $OCH_2C_4\underline{H_9}$), 4.2 (d, 2H, OCH_2), 7.5 (q, 4H, ArH), 8.5 (s, 1H, OH).

(+)-4-(2-Methylbutoxy)phenyl 4-Formylbenzoate (8). To a solution of compound **7** (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 **6** (0.03 mol) in a nitrogen atmosphere, followed by stirring at 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 extracted with hexane, and concentrated under reduced pressure. Light yellow liquid was obtained in a 50—55% yields.

IR ($CHCl_3$) 2800—3000 (alkyl), 1740, 1680 (C=O), 1600 (Ar), 1260 (ether) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ=0.7—2.2 (m, 9H, $OCH_2C_4\underline{H_9}$), 3.75 (d, 2H, OCH_2), 6.7—8.5 (m, 8H, ArH), 10.05 (s, 1H, CHO).

(+)-4-(2-Methylbutoxycarbonyl)phenyl 4-Formylbenzoate (10). The same procedure as that for compound **8** was used for preparation of compounds **6** and **9**. Light yellow liquid was obtained in 50—60% yields.

IR ($CHCl_3$) 2800—3000 (alkyl), 1680—1740 (C=O), 1600 (Ar) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ=0.6—2.2 (m, 9H, $OCH_2C_4\underline{H_9}$), 4.2 (d, 2H, OCH_2), 7.2—8.5 (m, 8H, ArH), 10.2 (s, 1H, CHO).

(+)-4-(2-Methylbutoxy)phenyl 4-(5-Alkyl-1,3-dioxan-2-yl)-benzoate (11). 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 concentrated under reduced pressure at 40 °C. The crude product was purified by column chromatography and recrystallizations from hexane, then separetive TLC was used to remove cis isomer.

IR ($CHCl_3$) 2800—3000 (alkyl), 1730 (C=O), 1600 (Ar), 1260 (ether) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ=0.7—2.3 (m, R-CH, $OCH_2\underline{R}''$), 3.3—4.5 (m, 6H, OCH_2), 5.50 (s, 1H, ${}^{O}_{O}\mathrm{CH}$), 6.7—8.4 (m, 8H, ArH).

(+)-4-(2-Methylbutoxycarbonyl)phenyl 4-(5-Alkyl-1,3-dioxan-2-yl)benzoate (12). To a solution of compound **1** (0.004 mol) and compound **10** (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 8h and then at 20—25 °C for 16h. The solution was washed with 10% aq. $NaHCO_3$ (400 ml), dried over anhyd. Na_2SO_4, and concentrated under reduced pressure at 40 °C. The crude product was purified by column chromatography and recrystallizations from hexane.

IR ($\mathrm{CHCl_3}$) 2800—3000 (alkyl), 1700—1740 (C=O), 1600 (Ar) $\mathrm{cm^{-1}}$.

^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.7—2.2 (m, R-CH, $\mathrm{OCH_2R''}$), 3.3—4.5 (m, 6H, $\mathrm{OCH_2}$), 5.50 (s, 1H, ${}^{\mathrm{O}}_{\mathrm{O}}\mathrm{CH}$), 7.2—8.5 (m, 8H, ArH).

(+)-4-(2-Methylbutoxy)phenyl 4-(5-Alkyl-1,3-oxathian-2-yl)benzoate (13). Compounds **13** were synthesized according to the same procedure as that for compounds **11**.

IR ($\mathrm{CHCl_3}$) 2800—3000 (alkyl), 1730 (C=O), 1600 (Ar), 1270 (ether) $\mathrm{cm^{-1}}$.

^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.6—2.2 (m, R-CH, $\mathrm{OCH_2\underline{R}''}$), 2.85 (d, 2H, $\mathrm{CH_2S}$), 3.2—4.5 (m, 4H, $\mathrm{OCH_2}$), 5.75 (s, 1H, ${}^{\mathrm{S}}_{\mathrm{O}}\mathrm{CH}$), 6.75—8.5 (m, 8H, ArH).

(+)-4-(2-Methylbutoxycarbonyl)phenyl 4-(5-Alkyl-1,3-oxathian-2-yl)benzoate (14). Compounds **14** were synthesized according to the same procedure as that for compounds **12**.

IR ($\mathrm{CHCl_3}$) 2800—3000 (alkyl), 1700—1740 (C=OO, 1600 (Ar) $\mathrm{cm^{-1}}$.

^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.6—2.2 (m, R-CH, $\mathrm{OCH_2\underline{R}''}$), 2.85 (d, 2H, $\mathrm{CH_2S}$), 3.2—4.5 (m, 4H, $\mathrm{OCH_2}$), 5.75 (s, 1H, ${}^{\mathrm{S}}_{\mathrm{O}}\mathrm{CH}$), 7.2—8.5 (m, 8H, ArH).

(+)-4-(2-Methylbutoxy)phenyl 4-(5-Alkyl-1,3-dithian-2-yl)-benzoate (15). Compounds **15** were synthesized according to the same procedure as that for compounds **11**.

IR ($\mathrm{CHCl_3}$) 2800—3000 (alkyl), 1735 (C=O), 1600 (Ar), 1270 (ether) $\mathrm{cm^{-1}}$.

^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.6—2.2 (m, R-CH, $\mathrm{OCH_2\underline{R}''}$), 2.6—2.95 (m, 4H, $\mathrm{CH_2S}$), 3.8 (d, 2H, $\mathrm{OCH_2}$), 5.20 (s, 1H, ${}^{\mathrm{S}}_{\mathrm{S}}\mathrm{CH}$), 6.75—8.5 (m, 8H, ArH).

(+)-4-(2-Methylbutoxycarbonyl)phenyl 4-(5-Alkyl-1,3-dithian-2-yl)benzoate (16). Compounds **16** were synthesized according to the same procedure as that for compounds **11**.

IR ($\mathrm{CHCl_3}$) 2800—3000 (alkyl), 1700—17400 (C=O), 1600 (Ar).

^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.6—2.2 (m, R-CH, $\mathrm{OCH_2R''}$), 2.7—3.0 (m, 4H, $\mathrm{CH_2S}$), 4.2 (d, 2H, $\mathrm{OCH_2}$), 5.20 (s, ^{1}H, ${}^{\mathrm{S}}_{\mathrm{S}}\mathrm{CH}$), 7.2—8.5 (m, 8H, ArH).

11-1: Yield, 25%. Found: C, 75.57; H, 9.04%; $\mathrm{M^+}$, 510. Calcd for $\mathrm{C_{32}H_{46}O_5}$: C, 75.26; H, 9.08%; M, 510.

11-2: Yield, 33%. Found: C, 75.53; H, 9.09%; $\mathrm{M^+}$, 524. Calcd for $\mathrm{C_{33}H_{48}O_5}$: C, 75.53; H, 9.22%; M, 524.

11-3: Yield, 28%. Fond: C, 76.01; H, 9.33%; $\mathrm{M^+}$, 538. Calcd for $\mathrm{C_{34}H_{50}O_5}$: C, 75.80; H, 9.36%, M, 538.

12-1: Yield, 37%. Found: C, 73.96; H, 8.56%; $\mathrm{M^+}$, 538. Calcd for $\mathrm{C_{33}H_{46}O_6}$: C, 73.57; H, 8.61%; M, 538.

12-2: Yield, 36%. Found: C, 73.73; H, 8.76%; $\mathrm{M^+}$, 552. Calcd for $\mathrm{C_{34}H_{48}O_6}$: C, 73.88; H, 8.75%; M, 552.

12-3: Yield, 31%. Found: C, 74.68; H, 8.64%; $\mathrm{M^+}$, 566. Calcd for $\mathrm{C_{35}H_{50}O_6}$: C, 74.17; H, 8.89%; M, 566.

13-1: Yield, 24%. Found: C, 72.88; H, 8.80%; $\mathrm{M^+}$, 526. Calcd for $\mathrm{C_{32}H_{46}O_4S_1}$: C, 72.96; H, 8.80%; M, 526.

12-2: Yield, 27%. Fond: C, 73.33; H, 9.00%; $\mathrm{M^+}$, 540. Calcd for $\mathrm{C_{33}H_{48}O_4S_1}$: C, 73.29; H, 8.95%; M, 540.

13-3: Yield, 23%. Found: C, 73.86; H, 9.05%; $\mathrm{M^+}$, 554. Calcd for $\mathrm{C_{34}H_{50}O_4S_1}$: C, 73.60; H, 9.08%; M, 554.

14-1: Yield, 32%. Found: C, 71.34; H, 8.37%; $\mathrm{M^+}$, 554. Calcd for $\mathrm{C_{33}H_{46}O_5S_1}$: C, 71.44; H, 8.36%; M, 554.

14-2: Yield, 39%. Found: C, 71.41; H, 8.51%; $\mathrm{M^+}$, 568. Calcd for $\mathrm{C_{34}H_{48}O_5S_1}$: C, 71.79; H, 8.51%; M, 568.

14-3: Yield, 34%. Found: C, 72.16; H, 8.64%; $\mathrm{M^+}$, 582. Calcd for $\mathrm{C_{35}H_{50}O_5S_1}$: C, 72.12; H, 8.65%; M, 582.

15-1: Yield, 14%. Found: C, 70.62; H, 8.53%; $\mathrm{M^+}$, 542. Calcd for $\mathrm{C_{32}H_{46}O_3S_2}$: C, 70.80; H, 8.54%; M, 542.

15-2: Yield, 18%. Found: C, 71.35; H, 8.66%; $\mathrm{M^+}$, 556. Calcd for $\mathrm{C_{33}H_{48}O_3S_2}$: C, 71.18; H, 8.69%; M, 556.

15-3: Yield, 22%. Found: C, 71.43; H, 8.79%; $\mathrm{M^+}$, 570. Calcd for $\mathrm{C_{34}H_{50}O_3S_2}$: C, 71.53; H, 8.79%; M, 570.

16-1: Yield, 22%. Found: C, 69.57; H, 8.10%; $\mathrm{M^+}$, 570. Calcd for $\mathrm{C_{33}H_{46}O_4S_2}$: C, 69.43; H, 8.12%; M, 570.

16-2: Yield, 26%. Found: C, 69.83; H, 8.11%; $\mathrm{M^+}$, 584. Calcd for $\mathrm{C_{34}H_{48}O_4S_2}$: C, 69.82; H, 8.27%; M, 584.

16-3: Yield, 25%. Found: C, 70.02; H, 8.44%; $\mathrm{M^+}$, 598. Calcd for $\mathrm{C_{35}H_{50}O_4S_2}$: C, 70.19; H, 8.42%; M, 598.

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