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Liquid Crystal Materials with Sulfur Atoms Incorporated in the Principal Structure. VI. Optically Active New Smectic Liquid Crystal Compounds with 1,3-Oxathiane or 1,3-Dithiane Ring

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(+)-2-Methylbutyl *p*-(5-alkyl-1,3-oxathian-2-yl)benzoate and -cinnamate (**7**) were synthesized. The mesomorphic behavior of these compounds were measured. Though (+)-2-methylbutyl *p*-(5-alkyl-1,3-oxathian-2-yl)-benzoate did not exhibit any liquid-crystal phase, the corresponding 1,3-dithiane compounds (**8-1**, **8-2**, and **8-3**) and compound (**7-4**) having R' of a normal alkyl chain exhibited a smectic phase. This must originate in the wider molecular widths of compounds **7-1**, **7-2**, and **7-3**. Though cinnamate of compounds **7** and **8** exhibited an enantiotropic behavior, the corresponding benzoate did not. This must originate from an increase in the length of the conjugated system and the molecular length.

In recent years, 2,5-disubstituted 1,3-dithianes and 1,3-oxathianes have been reported as new types of liquid-crystal materials.[1-9)]

In proportion to the increase in attention given to new types of liquid-crystal displays using ferroelectric liquid crystals, various optically active smectic liquid-crystal compounds have been synthesized. Thus, the basic structure of optically active new smectic liquid-crystal compounds with a 1,3-oxathiane (**7**) or a 1,3-dithiane ring (**8**) was synthesized.

This paper is related to this synthesis and the mesomorphic behavior of these compounds.

Results and Discussion

(+)-2-Methylbutyl *p*-(5-alkyl-1,3-oxathian-2-yl)benzoate and -cinnamate **7** and the corresponding 1,3-dithiane compounds **8** were synthesized via the following route.

In step **1**→**2**, **3**, the reaction temperature was kept at between 80 and 85 °C so as to produce compounds **2** and **3** at nearly equal rates. A separation between **2** and **3** was not carried out. In step **2**, **3**→**4**, **5**, compounds **4** and **5** could be successfully separated by column chromatography. That is, compound **5** effused in a hexane fraction and **4** in an ether fraction. In steps **4**→**7** and **5**→**8**, cis and trans isomers were produced which differed at the C-5 position of the 1,3-oxathiane and 1,3-dithiane ring, respectively. Repeated recrystallizations (about five to seven times) were required to obtain purified trans isomers. Though for several compounds of **7** and **8**, trans isomers could not be separated by recrystallization, they were gained by using a separative TLC (hexane : ether=5 : 2). In the ^1H NMR data of 1,3-dithiane and 1,3-oxathiane compounds, C-2 proton signals of the 1,3-dithiane or 1,3-oxathiane ring for the trans isomer exhibited about 0.05 ppm with a different magnetic field than those for a cis isomer. For example, in compounds **8-1** and **7-4**, the trans isomer absorbs $\delta=5.2$ (**8-1**) and 5.75 (**7-4**) but the cis isomer absorbs at $\delta=5.15$ (**8-1**) and 5.80 (**7-4**), respectively. Therefore, the contamination of the cis isomers can be detected.

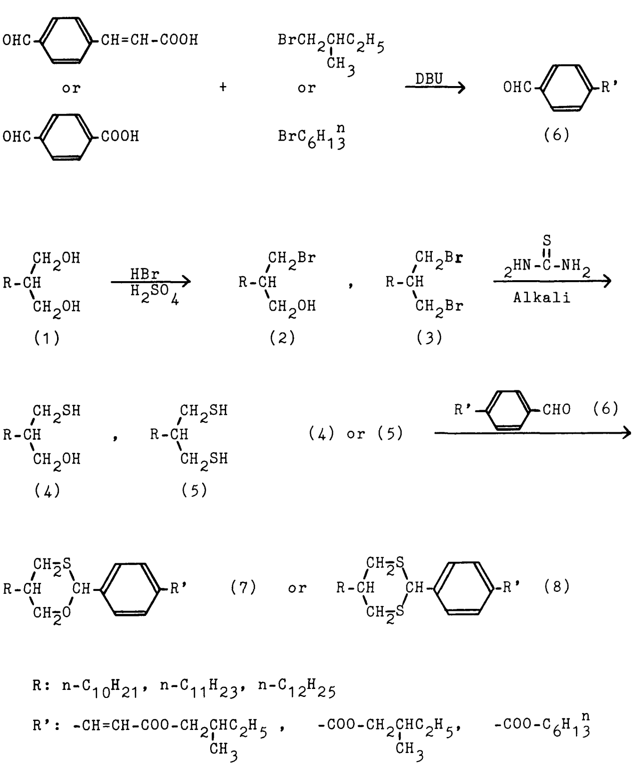


Fig. 1.

The angle of optical rotation was measured for compound **8-1** using a polarimeter; a value of +9.5° was obtained. This must mean that racemization did not occur in this reaction course.

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

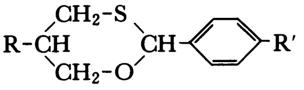
To determine the type of smectic phase, these smectic phases were compared with the color photographs found in the literature.[10)]

A focal-conic fan texture of smectic A was observed.

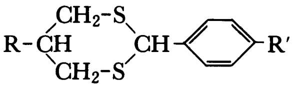
Mesomorphic ranges of the synthesized 1,3-dithianes and 1,3-oxathianes are given in Table 1.

Compounds **7-1**, **7-2**, and **7-3** did not exhibit any

Table 1. Transition Temperature of Compounds **7** and **8**


(**7**)

	R	R′	Transition temp/°C[a]
7-1	n-$C_{10}H_{21}$	$-COOCH_2CH(CH_3)C_2H_5$	$\mathrm{C}\underset{11}{\overset{35}{\rightleftarrows}}\mathrm{I}$
7-2	n-$C_{11}H_{23}$	$-COOCH_2CH(CH_3)C_2H_5$	$\mathrm{C}\underset{32}{\overset{45}{\rightleftarrows}}\mathrm{I}$
7-3	n-$C_{12}H_{25}$	$-COOCH_2CH(CH_3)C_2H_5$	$\mathrm{C}\underset{28}{\overset{37}{\rightleftarrows}}\mathrm{I}$
7-4	n-$C_{11}H_{23}$	$-COOC_6H_{13}{}^n$	$\mathrm{C}\xrightarrow{48}\mathrm{I}\underset{43}{\rightleftarrows}\mathrm{S_A}\xrightarrow{12}\mathrm{C}$
7-5	n-$C_{10}H_{21}$	$-CH=CH-COOCH_2CH(CH_3)C_2H_5$	$\mathrm{C}\underset{-50}{\overset{35}{\rightleftarrows}}\mathrm{S_A}\underset{71}{\overset{71}{\rightleftarrows}}\mathrm{I}$
7-6	n-$C_{11}H_{23}$	$-CH=CH-COOCH_2CH(CH_3)C_2H_5$	$\mathrm{C}\underset{-19}{\overset{50}{\rightleftarrows}}\mathrm{S_A}\underset{74}{\overset{74}{\rightleftarrows}}\mathrm{I}$


(**8**)

	R	R′	Transition temp/°C[a]
8-1	n-$C_{10}H_{21}$	$-COOCH_2CH(CH_3)C_2H_5$	$\mathrm{C}\xrightarrow{46}\mathrm{I}\underset{23}{\rightleftarrows}\mathrm{S_A}\xrightarrow{-15}\mathrm{C}$
8-2	n-$C_{11}H_{23}$	$-COOCH_2CH(CH_3)C_2H_5$	$\mathrm{C}\xrightarrow{44}\mathrm{I}\underset{28}{\rightleftarrows}\mathrm{S_A}\xrightarrow{18}\mathrm{C}$
8-3	n-$C_{12}H_{25}$	$-COOCH_2CH(CH_3)C_2H_5$	$\mathrm{C}\xrightarrow{48}\mathrm{I}\underset{39}{\rightleftarrows}\mathrm{S_A}\xrightarrow{27}\mathrm{C}$
8-4	n-$C_{12}H_{25}$	$-COOC_6H_{13}{}^n$	$\mathrm{C}\xrightarrow{56}\mathrm{I}\underset{54}{\rightleftarrows}\mathrm{S_A}\xrightarrow{16}\mathrm{C}$
8-5	n-$C_{10}H_{21}$	$-CH=CH-COOCH_2CH(CH_3)C_2H_5$	$\mathrm{C}\underset{16}{\overset{53}{\rightleftarrows}}\mathrm{S_A}\underset{88}{\overset{88}{\rightleftarrows}}\mathrm{I}$
8-6	n-$C_{11}H_{23}$	$-CH=CH-COOCH_2CH(CH_3)C_2H_5$	$\mathrm{C}\underset{18}{\overset{54}{\rightleftarrows}}\mathrm{S_A}\underset{82}{\overset{82}{\rightleftarrows}}\mathrm{I}$

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

liquid-crystal phases. However, the corresponding 1,3-dithiane compounds (**8-1**, **8-2**, and **8-3**) exhibited a smectic phase. Also, compound **7-4** having a normal alkyl chain in substituent R′ exhibited a smectic phase. From these results, the main factor for the formation of the mesophase must be the molecular width; thus, compounds **7-1**, **7-2**, and **7-3**, having wider molecular widths, can not exhibit any mesophases. That is, the bend at the 1,3-oxathiane ring due to a difference in the atomic size between sulfur and oxygen and the side chain included in R′ increase the molecular width of compounds **7-1**, **7-2**, and **7-3**; this must weaken interactions among the molecules.

Though compounds **7-5**, **7-6**, **8-5**, and **8-6** exhibited an enantiotropic-type behavior, corresponding benzoate compounds (**7-1**, **7-2**, **8-1**, **8-2**) did not. The existence of the CH=CH part implies an increase in molecular length and the length of the conjugated system. These two factors must contribute to the appearance on the enantiotropic behavior.

The transition temperatures of isotropic to smectic for 1,3-oxathiane compounds (**7-5**, **7-6**) were lower than those for the corresponding 1,3-dithianes (**8-5**, **8-6**). Generally, in a smectic liquid crystal, the temperature of isotropic to smectic is affected by two factors: the molecular width and interactions of side substituents.[11] In this case, a wider molecular width caused by a bend at the oxathiane ring seems to be the cause.

All of compounds **7** and **8** exhibited supercooling states, especially **7-5** and **7-6** have a wide range.

$\Delta H_{C\text{-}I}$ of compounds **7-1**, **7-5**, **8-1**, and **8-5** are 24.64, 21.25, 23.78, and 26.07 kJ mol^{-1} and $\Delta S_{C\text{-}I}$ of them are 79.9, 68.99, 79.96, and 75.77 JK^{-1} mol^{-1}, respectively. These values are somewhat smaller than those of other common liquid-crystal materials.[12]

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 aparatus equipped with polarizers and a Rigaku Denki DSC CN8059L1, CN8208A2. The rate of cooling was fixed to 1 °C min^{-1}.

Mixture of 2-Alkyl-3-bromo-1-propanol (2) and 2-Alkyl-1,3-dibromopropane (2). To a solution of 48% HBr (50 g) and concd H_2SO_4 (15 g) cooled in an ice bath were added, successively, compound **1** (0.1 mol) and concd H_2SO_4 (25 g). The solution was kept at 80—85 °C for 15 h. The reaction mixture was then poured into ice water (200 g), stirred and extracted twice with ether (each 400 ml). The extract was washed with cold 10% aq $NaHCO_3$ (100 ml), dried over anhyd Na_2SO_4, and concentrated on an evaporator at 30 °C. The residue was distilled in vacuo to afford a transparent liquid in a 50—60% yield.

2-Alkyl-3-mercapto-1-propanol (4) and 2-Alkyl-1,3-propanedithiol (5). To a solution of thiourea (0.2 mol) in triethylene glycol (15 ml) kept at 75 °C was added a mixture of compounds **2** and **3** in a nitrogen atmosphere, followed by stirring at 75 °C for 18 h. Tetraethylenepentamine (0.05 mol) was then added, and the mixture was stirred at 75 °C for 2 h under a nitrogen atmosphere. The reaction mixture was distilled in vacuo to afford a transparent liquid. The separation of compounds **4** and **5** was carried out by column chromatography (Wakogel C-300). Compounds **5** effused in a hexane fraction and **4** in an ether fraction. Compound **4** was a colorless transparent liquid and **5** was a yellow transparent liquid.

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

^{1}H NMR ($CDCl_3$) Compounds **4**: δ=0.6—2.0 (m, R-CH, SH), 2.5—2.8 (m, 2H, CH_2S), 3.3—3.9 (m, 3H, CH_2OH). Compounds **5**: δ=0.6—2.0 (m, R-CH, SH), 2.5—2.9 (m, 4H, -CH_2S).

(+)-2-Methylbutyl *p*-Formylcinnamate (6-1). A solution of *p*-formylcinnamic acid (0.03 mol) and 1,8-diazabicyclo[5.4.0] undec-7-ene (0.03 mol) and (+)-2-methylbutyl bromide (0.03 mol) in anhyd DMF (60 ml) was stirred at 80—90 °C for 18 h under a nitrogen atmosphere. 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 30 °C. The residue was dissolved in hexane (30 ml) and filtered. The filtrate was evaporated in vacuo at 40 °C. A transparent liquid was obtained in 70—80% yields.

IR ($CHCl_3$) 2800—3000 (alkyl), 2730 (CHO), 1680—1720 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.5—2.0 (m, 9H, OCH_2R''), 4.1 (d, 2H, OCH_2), 6.6 (d, 1H, =CH), 7.5—8.1 (q, 5H, CH=, ArH), 10.1 (s, 1H, CHO).

(+)-2-Methylbutyl *p*-Formylbenzoate (6-2). IR ($CHCl_3$) 2800—3000 (alkyl), 2730 (CHO), 1680—1720 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.6—2.1 (m, 9H, $OCH_2\underline{R}''$), 4.25 (d, 2H, OCH_2), 8.2 (q, 4H, ArH), 10.2 (s, 1H, CHO).

Hexyl *p*-Formylbenzoate (6-3). IR ($CHCl_3$) 2800—3000 (alkyl), 2730 (CHO), 1680—1720 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.7—2.1 (m, 11H, $OCH_2C_5\underline{H}_{11}$), 4.4 (t, 2H, OCH_2), 8.1 (q, 4H, ArH), 10.2 (s, 1H, CHO).

Alkyl *p*-(5-Alkyl-1,3-oxathian-2-yl)benzoate or -cinnamate (7). To a solution of compound **4** (0.04 mol) and *p*-substituted benzaldehyde **6** (0.04 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; 3g). The mixture was stirred at 0—5 °C for 8h and then at 20 °C for 15h. The solution was first washed with 10% aq $NaHCO_3$ (400 ml), then with water (400 ml), dried over anhyd Na_2SO_4, and evaporated in vacuo at 40 °C. The crude product was purified by column chromatography and recrystallizations from hexane; then, several compounds which could not be isolated as trans isomers were subjected to separative TLC (hexane:ether=5:2) to isolate trans isomers.

IR ($CHCl_3$) 2800—3000 (alkyl), 1710 (C=O), 1605 (Ar) cm^{-1}. ^{1}H NMR ($CDCl_3$).

(+)-2-Methylbutyl *p*-(5-Alkyl-1,3-oxathian-2-yl)benzoate. δ=0.7—2.1 (m, R-CH, OCH_2R''), 2.8 (d, 2H, CH_2S), 3.3, 4.3 (m, 2H, CH_2O), 4.2 (d, 2H, OCH_2R''), 5.75 (s, 1H, $\overset{S}{\underset{O}{>}}CH$), 7.8 (q, 4H, ArH).

Hexyl *p*-(5-Undecyl-1,3-oxathian-2-yl)benzoate: δ=0.5—2.1 (m, 35H, R-CH, $OCH_2C_5H_{11}$), 2.8 (d, 2H, CH_2S), 3.3, 4.3 (m, 2H, CH_2O), 4.3 (t, 2H, $OC\underline{H}_2C_5H_{11}$), 5.75 (s, 1H, $\overset{S}{\underset{O}{>}}CH$), 7.8 (q, 4H, ArH).

(+) 2-Methylbutyl *p*-(5-Alkyl-1,3-oxathian-2-yl)cinnamate: δ=0.5—2.2 (m, R-CH, OCH_2R''), 2.8 (d, 2H, CH_2S), 3.3, 4.2 (m, 4H, CH_2O), 5.7 (s, 1H, $\overset{S}{\underset{O}{>}}CH$), 6.4 (d, 1H, =CH), 7.5 (s, 4H, ArH), 8.0 (d, 1H, CH=).

Alkyl *p*-(5-Alkyl-1,3-dithian-2-yl)benzoate or -cinnamate (8). Compounds **8** were synthesized according to the same ptocedure as that for compounds **7**.

IR ($CHCl_3$) 2800—3000 (alkyl), 1705 (C=O), 1600 (Ar) cm^{-1}. ^{1}H NMR ($CDCl_3$).

(+)-2-Methylbutyl *p*-(5-Alkyl-1,3-dithian-2-yl)benzoate: δ=0.5—2.1 (m, R-CH, $OCH_2\underline{R}''$), 2.6—2.9 (m, 4H, CH_2S), 4.2 (d, 2H, CH_2O), 5.2 (s, 1H, $\overset{S}{\underset{S}{>}}CH$), 7.8 (q, 4H, ArH).

Hexyl *p*-(5-Dodecyl-1,3-dithian-2-yl)benzoate: δ=0.6—2.1 (m, 37H, R-CH, $OCH_2C_5\underline{H}_{11}$), 2.6—2.9 (d, 4H, CH_2S), 4.3 (t, 2H, CH_2O), 5.2 (s, 1H, $\overset{S}{\underset{S}{>}}CH$), 7.8 (q, 4H, ArH).

(+)-2-Methylbutyl *p*-(5-Alkyl-1,3-dithian-2-yl)cinnamate: δ=0.5—2.2 (m, R-CH, OCH_2R''), 2.6—2.9 (m, 4H, CH_2S), 4.05 (d, 2H, OCH_2), 5.15 (s, 1H, $\overset{S}{\underset{S}{>}}CH$), 6.4 (d, 1H, =CH), 7.5 (s, 4H, ArH), 8.05 (d, 1H, CH=).

7-1: Yield 29%. Found: C, 71.59; H, 9.82%. Calcd for $C_{26}H_{42}O_3S$: C, 71.84; H, 9.74%. (*m/z*) 434 (M^+).

7-2: Yield 28%. Found: C, 71.91; H, 9.92%. Calcd for $C_{27}H_{44}O_3S$: C, 72.27; H, 9.88%. MS (*m/z*) 448 (M^+).

7-3: Yield 32%. Found: C, 72.88; H, 9.99%. Calcd for $C_{28}H_{46}O_3S$: C, 72.68; H, 10.02%. MS (*m/z*) 462 (M^+).

7-4: Yield 26%. Found: C, 72.71; H, 10.02%. Calcd for $C_{28}H_{46}O_3S$: C, 72.68; H, 10.02%. MS (*m/z*) 462 (M^+).

7-5: Yield 28%. Found: C, 72.90; H, 9.70%. Calcd for $C_{28}H_{44}O_3S$: C, 72.99; H, 9.63%. MS (*m/z*) 460 (M^+).

7-6: Yield 37%. Found: C, 72.99; H, 9.82%. Calcd for $C_{29}H_{46}O_3S$: C, 73.37; H, 9.77%. MS (*m/z*) 474 (M^+).

8-1: Yield 28%. Found: C, 68.91; H, 9.44%. Calcd for $C_{26}H_{42}O_2S_2$: C, 69.28; H, 9.39%. MS (*m/z*) 450 (M^+).

8-2: Yield 32%. Found: C, 69.00; H, 9.65%. Calcd for $C_{27}H_{44}O_2S_2$: C, 69.77; H, 9.54%. MS (*m/z*) 464 (M^+).

8-3: Yield 21%. Found: C, 69.83; H, 9.75%. Calcd for $C_{28}H_{46}O_2S_2$: C, 70.24; H, 9.68%. MS (*m/z*) 478 (M^+).

8-4: Yield 30%. Found: C, 70.62; H, 9.83%. Calcd for $C_{29}H_{48}O_2S_2$: C, 70.68; H, 9.82%. MS (*m/z*) 492 (M^+).

8-5: Yield 32%. Found: C, 70.63; H, 9.51%. Calcd for $C_{28}H_{44}O_2S_2$: C, 70.53; H, 9.30%. MS (*m/z*) 476 (M^+).

8-6: Yield 30%. Found: C, 71.28; H, 9.42%. Calcd for $C_{29}H_{46}O_2S_2$: C, 70.97; H, 9.45%. MS (*m/z*) 490 (M^+).

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