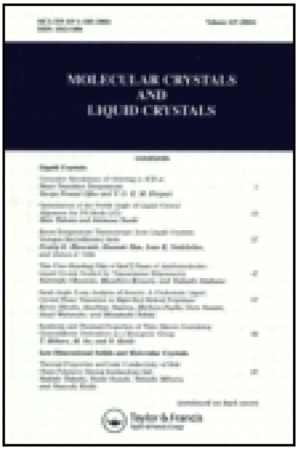

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New Liquid Crystal Compound: (+)-4-Alkoxycarbonylphenyl 4-[5-(2-methylbutyl)-1,3-oxathian-2-yl]benzoate

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New Liquid Crystal Compound: (+)-4-Alkoxycarbonylphenyl 4-[5-(2-methylbutyl)-1,3-oxathian-2-yl]benzoate

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New liquid crystal compound: (+)-4-Alkoxycarbonylphenyl-4-[5-(2-methylbutyl)-1,3-oxathiane-2-yl]benzoates (**11**) was synthesized. The mesomorphic behavior of this compound is compared with those of (+)-4-(2-methylbutoxycarbonyl)phenyl 4-(5-alkyl-1,3-oxathian-2-yl)benzoates (**12**), and (+)-4-alkoxy-carbonylphenyl 4-[5-(2-methylbutyl)-1,3-dioxan-2-yl]-benzoates (**13**), and (+)-4-Alkoxyphenyl 4-[5-(2-methylbutyl)-1,3-oxathian-2-yl]benzoates (**14**). Transition temperatures to the isotropic state for compound **11** were lower than those for the corresponding compounds **12** or **13**. Though compound **11** exhibited the cholesteric phase, compound **12** exhibited the smectic phase. These features seem to originate in the wider molecular width of compound **11**. Transition temperatures to the isotropic state for compound **11** are lower than those for **14**. In this case, the difference of partial molecular width caused by carbonyl group seem to be main factor.

Keywords: 1,3-oxathiane, phase transition, liquid crystal.

1. INTRODUCTION

New types of nematic liquid crystal materials having a hetero ring in the molecule, 2,5-disubstituted-1,3-dioxanes, -1,3-oxathianes, and -1,3-dithianes have been reported.[1–10] Recently, new types of liquid crystal displays using ferroelectric liquid crystals have been noticed because of their high speed response. Therefore, various optically active compounds with the 1,3-dioxane, 1,3-oxathiane, or 1,3-dithiane ring have been synthesized.[11–20] In previous papers,[13,18,19] we have reported the synthesis of the compounds **12**, **13** and **14**. The title compound has the chemical structure which is somewhat different from these compounds. In this paper, we wish to report the synthesis of the title compound and the chemical structural factors which influence the mesomorphic behavior of this compound.

2. RESULTS AND DISCUSSION

The (+)-4-Alkoxycarbonylphenyl 4-[5-(2-methylbutyl)-1,3-oxathian-2-yl]benzoates (**11**) was synthesized by the route shown in Figure 1. In the bromination of the

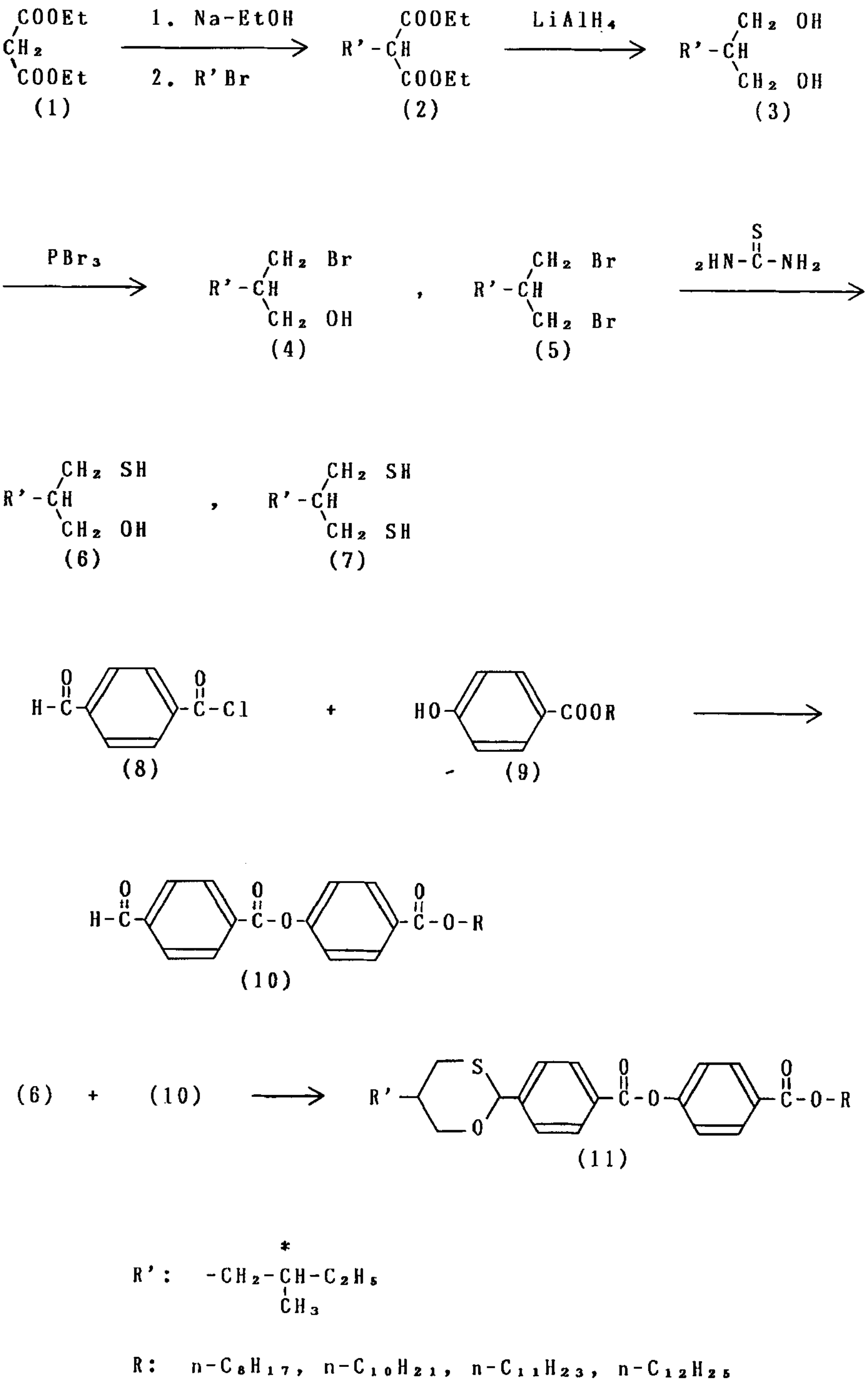

(1)
1. Na-EtOH
2. R'Br
(2)
LiAlH4
(3)
PBr3
(4)
(5)
H2N-C(=S)-NH2
(6)
(7)
(8)
(9)
(10)
(6) + (10)
(11)
R': -CH2-C*H(CH3)-C2H5
R: n-C8H17, n-C10H21, n-C11H23, n-C12H25

FIGURE 1

diol **3**, both **4** and **5** were produced. In this step, the separation of **4** and **5** was not carried out, so that a mixture of **4** and **5** was used in the step (**4**, **5**) → (**6**, **7**). The monothiol **6** and dithiol **7** were separated by column chromatography, in which **6** and **7** were eluted with ether and hexane, respectively. The ester **9** was obtained by esterification of *p*-hydroxybenzoic acid with a *n*-alkyl alcohol in the presence of an acid catalyst using a Dean-Stark trap. A reaction time of 48 hours was necessary to gain a sufficient yield. In the esterification of the acid chloride **8** with the phenol **9**, 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) was used as a base. Oxathiane **11** was synthesized by the acid-catalyzed ring formation reaction of the thiol **6** with aldehyde **10**. This oxathiane was purified by column chromatography, followed by several recrystallizations from hexane. Since the cis isomer could not be removed by recrystallization, preparative thin-layer chromatography was used to obtain the trans isomer. In the ^{1}H-NMR data for compound **11**, the C-2 proton signals of the 1,3-oxathiane ring for the trans and cis isomers appeared at δ = 5.85, and 5.90, respectively. Therefore, the removal of the cis isomer could be checked by the disappearance of the peak for the cis isomer.

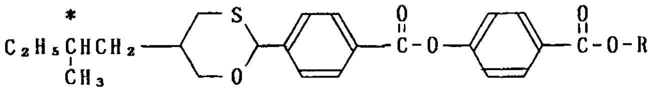
Measurements of the mesomorphic range and assignment of the mesophases were carried out by means of a micro melting point apparatus equipped with polarizers. Phase identification was made by comparing the observed textures with those in the literature.[21,22] Mesomorphic transition temperatures for compound **11** and the corresponding compounds **12**, **13**, and **14** are given in Table I. Although compound **12** exhibited smectic A and B phases on cooling from the isotropic state, **11** exhibited only a cholesteric phase. Compound **11** has a chemical structure in which two terminal substituents of **12** are exchanged. As the (+)-2-methylbutyl group and the 1,3-oxathiane ring of compound **11** hinder each other, the molecular width of **11** seems to be wider than that of **12**. These wider molecular widths would make the molecular side interaction of compound **11** small, so that, in compound **11** the smectic phase does not appear. The transition temperatures to the isotropic state for compound **11** are about 10–20°C lower than those for compound **13**. This must imply that the bent effect of the 1,3-oxathiane ring is influential. That is, in compound **11**, the 1,3-oxathiane ring has a bend caused by the size difference between the sulfur and oxygen atoms. This bend makes the molecular width of compound **11** wider than those of the corresponding 1,3-dioxane compounds.

Transition temperatures of isotropic to liquid crystal for 4-alkoxyphenyl type compound **11** are lower than those for 4-alkoxycarbonylphenyl type compound **14**. This is also true with the case of 1,3-dioxane type compounds **13** and **15**. Generally, the transition temperature of isotropic to liquid crystal phase is affected by molecular width and polarizability. These results may originate in the wider molecular width of compounds **11** and **13** caused by the carbonyl group.

In the case of compounds **12** and **16**, the transition temperatures of isotropic to liquid crystal are nearly equal. This must mean that in this case the molecular width is decided by the 2-methylbutyl group and not by the carbonyl group, making the molecular width of compounds **12** and **16** nearly equal. If the difference in polarizability were the main factor, transition temperatures for **12** and **16** must also differ. Therefore, in this case, molecular width must be the main factor. These

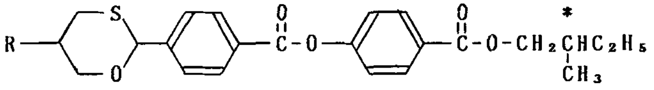
TABLE I

Mesomorphic ranges for compounds **11**, **12**, **13**, **14**, **15**, and **16**



(11)

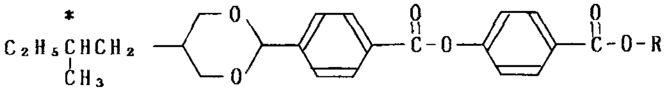
	R	MESOMORPHIC RANGE$^{a)}$ (°C)
11-1	C_8H_{17}	$C \underset{45}{\overset{57}{\rightleftarrows}} Ch \underset{63}{\overset{63}{\rightleftarrows}} I$
11-2	$C_{10}H_{21}$	$C \underset{23}{\overset{39}{\rightleftarrows}} Ch \underset{60}{\overset{60}{\rightleftarrows}} I$
11-3	$C_{11}H_{23}$	$C \underset{31}{\overset{38}{\rightleftarrows}} Ch \underset{62}{\overset{62}{\rightleftarrows}} I$
11-4	$C_{12}H_{25}$	$\begin{tikzcd} C \arrow[rr, "57"] & & I \arrow[dl, shift left, "52"] \\ & Ch \arrow[ul, "38"] \arrow[ur, shift left] & \end{tikzcd}$



(12)

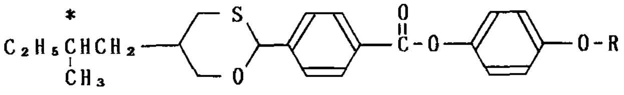
	R	MESOMORPHIC RANGE$^{a)}$ (°C)
12-1	$C_{10}H_{21}$	$C \underset{-50}{\overset{89}{\rightleftarrows}} SmA \underset{134}{\overset{134}{\rightleftarrows}} I$
12-2	$C_{11}H_{23}$	$C \underset{-50}{\overset{70}{\rightleftarrows}} SmB \underset{98}{\overset{98}{\rightleftarrows}} SmA \underset{136}{\overset{136}{\rightleftarrows}} I$
12-3	$C_{12}H_{25}$	$C \underset{20}{\overset{68}{\rightleftarrows}} SmA \underset{133}{\overset{133}{\rightleftarrows}} I$

TABLE I (*continued*)



(13)

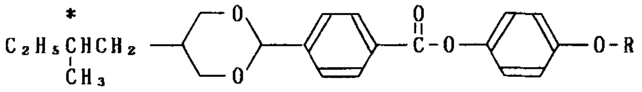
	R	MESOMORPHIC RANGE [a] (°C)
13-1	C_8H_{17}	$\begin{tikzcd} C \arrow[rr, "74"] & & I \arrow[dl, shift left, "66"] \\ & Ch \arrow[ul, "50"] \arrow[ur, shift left] & \end{tikzcd}$
13-2	$C_{10}H_{21}$	$C \underset{48}{\overset{67}{\rightleftarrows}} Ch \underset{81}{\overset{81}{\rightleftarrows}} I$
13-3	$C_{11}H_{23}$	$C \underset{51}{\overset{68}{\rightleftarrows}} Ch \underset{76}{\overset{76}{\rightleftarrows}} I$
13-4	$C_{12}H_{25}$	$\begin{tikzcd} C \arrow[rr, "68"] & & I \arrow[d, shift left, "66"] \\ SmA \arrow[u, "48"] \arrow[rr, shift left] & & Ch \arrow[u, shift left] \arrow[ll, shift left, "61"] \end{tikzcd}$



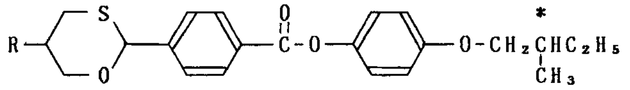
(14)

	R	MESOMORPHIC RANGE [a] (°C)
14-1	C_8H_{17}	$C \underset{46}{\overset{55}{\rightleftarrows}} Ch \underset{99}{\overset{99}{\rightleftarrows}} I$
14-2	$C_{10}H_{21}$	$C \underset{53}{\overset{65}{\rightleftarrows}} Ch \underset{98}{\overset{98}{\rightleftarrows}} I$
14-3	$C_{11}H_{23}$	$C \underset{48}{\overset{65}{\rightleftarrows}} Ch \underset{92}{\overset{92}{\rightleftarrows}} I$
14-4	$C_{12}H_{25}$	$C \underset{55}{\overset{69}{\rightleftarrows}} Ch \underset{91}{\overset{91}{\rightleftarrows}} I$

TABLE I (*continued*)


(15)

	R	MESOMORPHIC RANGE [a] (°C)
15-1	C_8H_{17}	$C \underset{38}{\overset{72}{\rightleftarrows}} Ch \underset{124}{\overset{124}{\rightleftarrows}} I$
15-2	$C_{10}H_{21}$	$C \underset{55}{\overset{75}{\rightleftarrows}} Ch \underset{120}{\overset{120}{\rightleftarrows}} I$
15-3	$C_{11}H_{23}$	$C \underset{70}{\overset{80}{\rightleftarrows}} Ch \underset{119}{\overset{119}{\rightleftarrows}} I$
15-4	$C_{12}H_{25}$	$C \underset{87}{\overset{87}{\rightleftarrows}} Ch \underset{117}{\overset{117}{\rightleftarrows}} I$


(16)

	R	MESOMORPHIC RANGE [a] (°C)
16-1	$C_{10}H_{21}$	$C \underset{-50}{\overset{66}{\rightleftarrows}} SmB \underset{111}{\overset{111}{\rightleftarrows}} SmA \underset{134}{\overset{134}{\rightleftarrows}} I$
16-2	$C_{11}H_{23}$	$C \underset{-50}{\overset{64}{\rightleftarrows}} SmB \underset{111}{\overset{111}{\rightleftarrows}} SmA \underset{132}{\overset{132}{\rightleftarrows}} I$
16-3	$C_{12}H_{25}$	$C \underset{-50}{\overset{59}{\rightleftarrows}} SmB \underset{117}{\overset{117}{\rightleftarrows}} SmA \underset{132}{\overset{132}{\rightleftarrows}} I$

a) C : Crystal, Ch : Cholesteric, Sm : Smectic,
I : Isotropic

results imply that the molecular width of a limited part of a molecule can affect the transition temperatures from isotropic to liquid crystal.

3. EXPERIMENTAL

IR, ^{1}H-NMR, and mass spectra were obtained with a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi M-80 B spectrometer, respectively. Elemental analyses were carried out with a Perkin-Elmer 250 instrument. Transition temperatures and mesomorphic phases were determined by means of a Mitamura Riken micro melting point apparatus equipped with polarizers and a Rigaku Denki DSC CN8059Li, CN8208A2, respectively.

2-(2-Methylbutyl)-3-mercapto-1-propanol (6)

To a solution of thiourea (0.2 mol) in triethylene glycol (15 ml) kept at 75°C was added a mixture of compounds **4** and **5** under 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 poured into cold 5% aq. HCl (100 ml), and extracted twice with ether (each 200 ml). The extract was washed with cold water (50 ml), dried over anhyd. Na_2SO_4, and concentrated on an evaporator at 30°C. The separation of compounds **6** and **7** was carried out by column chromatography (Wakogel C-300). Compound **7** was eluted in a hexane fraction and **6** in an ether fraction. A transparent liquid was obtained. IR ($CHCl_3$) 3600 (OH), 3000–2800 (alkyl) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.5–2.0 (m, 13H, $C_5H_{11}CH$, SH), 2.5–3.0 (m, 2H, CH_2S), 3.5–4.3 (m, 3H, CH_2OH).

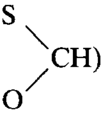
4-Alkoxycarbonyl phenyl 4′-formylbenzoates (10)

To a solution of compound (**9**) (0.015 mol) and 1,8-diazabicycro[5.4.0]undec-7-ene (0.015 mol) in anhyd. *N*,*N*-dimethyl-formamide (30 ml) was added (**8**) (0.015 mol) under a nitrogen atmosphere, followed by stirring at 40°C for 18 h. The solution was poured into ice water and shaken twice with ether (each 200 ml). The extract was washed with cold 5% aq. HCl, dried over anhyd. Na_2SO_4, and evaporated in vacuo at 40°C. The residue was extracted into hexane, and the extract concentrated under reduced pressure. The residue was purified by column chromatography, followed by recrystallization from hexane. The white powder was obtained in a 40–50% yield.

mp: R = C_8H_{17}; 65–66 C, $C_{10}H_{21}$; 71–72°C, $C_{11}H_{23}$; 79–81 C, $C_{12}H_{25}$; 96–97 C. IR ($CHCl_3$) 2800–3000 (alkyl), 1740, 1680 (C=O), 1600 (Ar) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.6–2.1 (m, OCH_2 $\underline{R}$), 4.3 (t, 2H, OCH_2), 7.2–8.5 (m, 8H, ArH), 10.2 (*s*, 1H, CHO).

(+)-4′-Alkoxycarbonylphenyl 4-[5-(2-methylbutyl)-1,3-oxathian-2-yl]-benzoates (11)

To a solution of compounds (**6**) (0.004 mol) and (**10**) (0.004 mol) in anhyd. $CHCl_3$ (200 ml), cooled in an ice bath was added $BF_3(C_2H_5)_2O$ (0.5 g) and molecular sieves (3A, 1/15; 3g). This mixture was stirred at 0–5°C for 8 h and then at 20–25°C for 10 h and then washed with 10% aq. NaHCO$_3$ (400 ml), dried over anhyd. Na$_2$SO$_4$, and concentrated under reduced pressure at 40°C. Purification of the crude product was done by column chromatography, recrystallization from hexane, and preparative T.L.C. (silica gel) to remove the cis isomer. The purified trans isomer **11** was isolated as a white powder.

IR (CHCl$_3$) 3000–2800 (alkyl), 1730 (C=O), 1600 (Ar) cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ 0.7–2.3 (m, R'CH, OCH$_2$ R), 2.9 (*d*, 2H, CH$_2$ S), 3.2–4.5 (m, 4H, CH$_2$ O), 5.85 (s, 1H,  $\genfrac{}{}{0pt}{}{S}{O}\!\!>\!CH$), 6.8–8.3 (m, 8H, ArH).

11-1: Yield, 24%. Elemental Analysis Calcd for $C_{31}H_{42}S_1O_5$: C, 70.69; H, 8.04%. Found: C, 70.90; H, 7.83%. Mass spectrum 526 (M$^+$).

11-2: Yield, 18%. Elemental Analysis Calcd for $C_{33}H_{46}S_1O_5$: C, 71.44; H, 8.36%. Found: C, 71.09; H, 8.00%. Mass spectrum 554 (M$^+$).

11-3: Yield, 31%. Elemental Analysis Calcd for $C_{34}H_{48}S_1O_5$: C, 72.22; H, 8.46%. Found: C, 72.22; H, 8.46%. Mass spectrum 568 (M$^+$).

11-4: Yield, 27%. Elemental Analysis Calcd for $C_{35}H_{50}S_1O_5$: C, 72.03; H, 8.42%. Found: C, 72.03; H, 8.42%. Mass spectrum 582 (M$^+$).

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