New Optically Active Liquid Crystal Compounds: (+)-4-Alkoxyphenyl 4-[5-(2-Methylbutyl)-1,3-oxathian-2-yl]benzoates

Yuichiro HARAMOTO* and Hiroyoshi KAMOGAWA
Department of Applied Chemistry, Yamanashi University, Takeda 4, Kofu 400
(Received December 8, 1989)

New liquid-crystal compounds, (+)-4-alkoxyphenyl 4-[5-(2-methylbutyl)-1,3-oxathian-2-yl]-benzoates (**9**), have been synthesized. The mesomorphic behaviors of these compounds were compared with those of (+)-4-(2-methylbutoxy)phenyl 4-(5-alkyl-1,3-oxathian-2-yl)-benzoates and (+)-4-(5-alkyl-1,3-oxathian—2-yl)phenyl-4-(2-methylbutoxy)benzoates; compounds **9** exhibit a cholesteric phase and their transtition temperatures to isotropic were found to be lower those of the corresponding compounds. These properties seem to originate in the wider molecular width caused by both the 2-methylbutyl group at the 5 position of the 1,3-oxathiane ring and the molecular bend in the 1,3-oxathiane ring.

In recent years, 2,5-disubstituted 1,3-dioxanes, 1,3-oxathianes, and 1,3-dithianes have been reported to be new types of nematic liquid crystals.[1,2] Subsequently, optically active liquid-crystal compounds with 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane rings as basic structures have also been synthesized.[3–9]

In previous papers,[5,6] we reported on (+)-4-(2-methylbutoxy)phenyl 4-(5-alkyl-1,3-oxathian-2-yl)benzoate (**10**) and (+)-4-(5-alkyl-1,3-oxathian-2-yl)phenyl 4-(2-methylbutoxy)benzoate (**11**). The title compounds **9** have a chemical structure in which two terminal groups of compound **10** were exchanged. In this paper we report on the synthesis of compounds **9** and the chemical structural factor which exerts influence on the appearance of the mesophase in these three oxathiane liquid-crystal compounds (**9**, **10**, **11**).

Results and Discussion

Syntheses. (+)-4-Alkoxyphenyl 4-[5-(2-methylbutyl)-1,3-oxathian-2-yl]benzoates (**9**) were synthesized via the following route.

Compounds (**2**) were synthesized by the etherification of hydroquinone. Though both mono- and diether were produced, monoether (**2**) could be separated by column chromatography; diether was eluted with hexane and monoether with ether, respectively. In the esterification of **2** with **1**, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used as a base. In the bromination of compound **4**, both **5** and **6** were produced. In this step, since their separation was not carried out, a mixture of **5** and **6** was used in the subsequent step, (**5**, **6**)⟶ (**7**, **8**). Compounds **7** and **8** were separated by column chromatography, in which **7** and **8** were eluted with ether and hexane, respectively. Compounds **9** were synthesized by acid-catalyzed ring-forming reactions of compoounds **3** with **7**. Compounds **9** were purified by column chromatography and subsequent recrystallization.

Since each product was obtained as a white powder containing the cis isomer, it was subjected to prep. T. L. C. (hexane: ether=5:2) to obtain pure trans isomers.

In the ^{1}H NMR data for compounds **9** the C-2 proton signals of the 1,3-oxathiane ring for the trans and cis isomers were separated by a chemical shift of about 0.05 ppm. That is, the C-2 proton signal of the trans isomer is located at 5.80 ppm, and that of cis isomer at 5.85 ppm, respectively.

Properties. Mesomorphic properties were determined using a micro melting-point apparatus equipped with polarizers. Phase identification was achieved

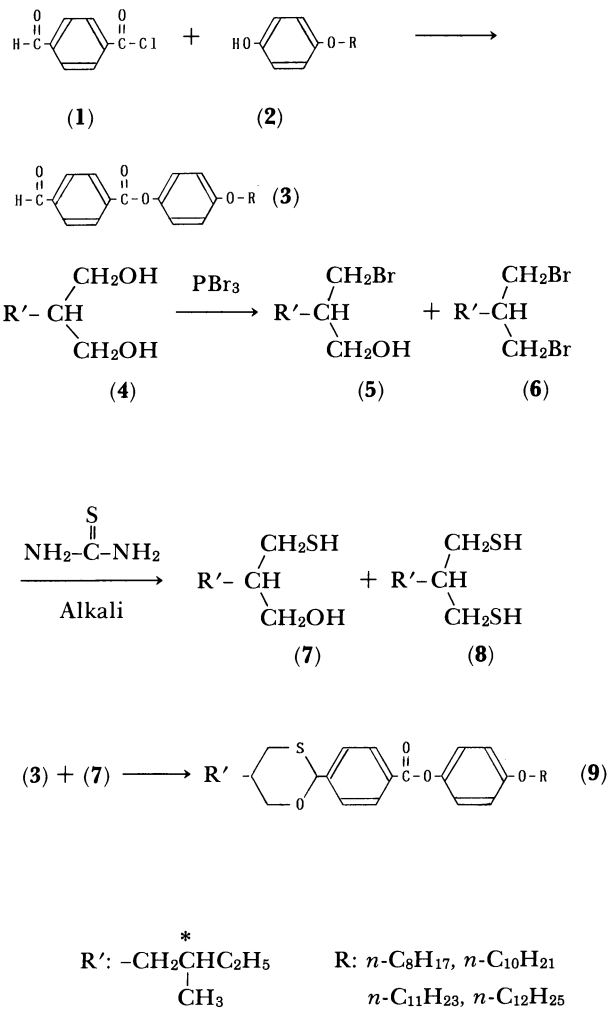


Fig. 1.

by comparing the observed textures with those found in the literature.[10,11]

A discussion concerning molecular structures is possible using molecular models. Our result regarding the X-ray diffraction of the 1,3-dithiane compound indicates that the length of the C-S bond is nearly equal to that of the molecular model. Therefore, a discussion using molecular models seems to be effective regarding compounds of this type; 1,3-dioxane, 1,3-oxathiane, 1,3-dithiane.

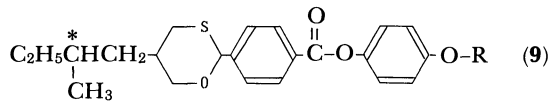
The mesomorphic ranges of synthesized compounds are given in Table 1.

Whereas compounds **10** exhibited smectic A and B phases upon cooling from the isotropic state, **9** exhibited the chole steric phase. Compounds **9** have a chemical structure in which two terminal substituents of **10** are exchanged.

Since the (+)-2-methylbutyl group and the 1,3-oxathiane ring of compounds **9** hinder each other, the molecular widths of **9** appear to be wider than those of **10**. These wider molecular widths are considered to make the molecular side interaction of compounds **9** small, so that, in compounds **9** the smectic phase did not appear.

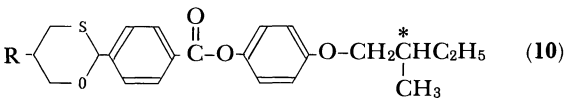
Furthermore, in compounds **9** the dipole moment due to sulfur and oxygen atoms in the 1,3-oxathiane ring may be effective for arranging the chiral 2-methylbutyl group binding at the 5 position of 1,3-oxathiane ring; thus compounds **9** tend to exhibit the cholesteric phase. The transition temperatures to the isotropic form for compounds **9** are lower than those for compounds **10** and **11**. This fact may originate in the wider molecular widths of compounds **9** having the 2-methylbutyl group. These transition temperatures of compounds **9** are about 10—20°C lower than those of the corresponding 1,3-dioxanes **12**, which may imply that the bent effect of the 1,3-oxathiane ring appeared. That is, the 1,3-oxathiane ring of compounds **9** has a bend caused by a size difference between the sulur and oxygen atoms. This bend makes the molecular widths of compounds **9** wider than those of the corresponding 1,3-dioxane com-

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



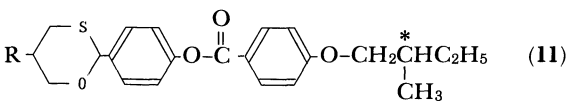
(**9**)

	R	Mesomorphic range/°C[a]
9-1	C_8H_{17}	C $\underset{60}{\overset{55}{\rightleftharpoons}}$ Cho $\underset{99}{\overset{99}{\rightleftharpoons}}$ I
9-2	$C_{10}H_{21}$	C $\underset{53}{\overset{65}{\rightleftharpoons}}$ Cho $\underset{98}{\overset{98}{\rightleftharpoons}}$ I
9-3	$C_{11}H_{23}$	C $\underset{48}{\overset{65}{\rightleftharpoons}}$ Cho $\underset{92}{\overset{92}{\rightleftharpoons}}$ I
9-4	$C_{12}H_{25}$	C $\underset{55}{\overset{67}{\rightleftharpoons}}$ Cho $\underset{91}{\overset{91}{\rightleftharpoons}}$ I



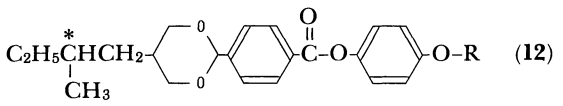
(**10**)

	R	Mesomorphic range/°C[a]
10-1	$C_{10}H_{21}$	C $\underset{-50}{\overset{66}{\rightleftharpoons}}$ SmB $\underset{111}{\overset{111}{\rightleftharpoons}}$ SmA $\underset{134}{\overset{134}{\rightleftharpoons}}$ I
10-2	$C_{11}H_{23}$	C $\underset{-50}{\overset{64}{\rightleftharpoons}}$ SmB $\underset{111}{\overset{111}{\rightleftharpoons}}$ SmA $\underset{132}{\overset{132}{\rightleftharpoons}}$ I
10-3	$C_{12}H_{25}$	C $\underset{-50}{\overset{59}{\rightleftharpoons}}$ SmB $\underset{117}{\overset{117}{\rightleftharpoons}}$ SmA $\underset{132}{\overset{132}{\rightleftharpoons}}$ I



(**11**)

	R	Mesomorphic range/°C[a]
11-1	$C_{10}H_{21}$	C $\overset{88}{\longrightarrow}$ Cho $\underset{122}{\overset{122}{\rightleftharpoons}}$ I; C $\underset{46}{\nwarrow}$ Sm $\underset{47}{\swarrow}$ Cho
11-2	$C_{11}H_{23}$	C $\overset{83}{\longrightarrow}$ Cho $\underset{120}{\overset{120}{\rightleftharpoons}}$ I; C $\underset{48}{\nwarrow}$ Sm $\underset{61}{\swarrow}$ Cho
11-3	$C_{12}H_{25}$	C $\overset{87}{\longrightarrow}$ Cho $\underset{114}{\overset{114}{\rightleftharpoons}}$ I; C $\underset{23}{\nwarrow}$ Sm $\underset{65}{\swarrow}$ Cho



(**12**)

	R	Mesomorphic range/°C[a]
12-1	C_8H_{17}	C $\underset{60}{\overset{70}{\rightleftharpoons}}$ Cho $\underset{120}{\overset{120}{\rightleftharpoons}}$ I
12-2	$C_{10}H_{21}$	C $\underset{65}{\overset{80}{\rightleftharpoons}}$ Cho $\underset{113}{\overset{113}{\rightleftharpoons}}$ I
12-3	$C_{11}H_{23}$	C $\underset{64}{\overset{84}{\rightleftharpoons}}$ Cho $\underset{115}{\overset{115}{\rightleftharpoons}}$ I
12-4	$C_{12}H_{25}$	C $\underset{75}{\overset{93}{\rightleftharpoons}}$ Cho $\underset{112}{\overset{112}{\rightleftharpoons}}$ I

a) C: Crystal, Cho: Cholesteric, Sm: Smectic I: Isotropic.

pounds.

The specific rotatory power (N_D^{30}) for compound **9-1** was about 1. 2.

Experimental

IR, ^{1}H NMR and the mass spectra were obtained with a Hitachi 215 spectrometer, 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 a Mitamura Riken micro melting-point apparatus equipped with polarizers.

4-Alkoxyphenyl 4-Formylbenzoates.(3). To a solution of compound **2** (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 **1** (0.03 mol) in a nitrogen atmosphere, followed by stirring at 40 °C for 18 h. The solution was poured into ice water and the mixture shaken 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 into hexane, and the extract was concentrated under reduced pressure. The residue was purified by recrystallization from hexane, followed by subjection to column chromatograpy. White powder was obtained in a 40—60% yield.

Mp: R=C_8H_{17}; 78—79 °C, $C_{10}H_{21}$; 88—89 °C, $C_{11}H_{23}$; 97—98 °C, $C_{12}H_{25}$; 106—107 °C.

IR ($CDCl_3$) 2800—3000 (alkyl), 1730 (C=O), 1600 (Ar), 1260 (ether) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ=0.7—2.2 (m, $OCH_2\underline{R}$), 4.0 (t, 2H, OCH_2), 6.8—8.5 (m, 8H, ArH), 12.0 (s, 1H, CHO).

Mixtures of 2-(2-Methylbutyl)-3-bromo-1-propanol (5) and 2-(2-Methylbutyl)-1,3-dibromopropane (6). The same procedure as that mentioned in a previous paper[3] was used.

2-(2-Methylbutyl)-3-mercapto-1-propanol (7). The same procedure as that mentioned in a previous paper[11] was used. Transparent liquid was obtained.

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

^{1}H NMR ($CDCl_3$) 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′-Alkoxyphenyl 4-[5-(2-Methylbutyl)-1,3-oxathian-2-yl]benzoate (9). To a solution of compound **3** (0.004 mol) and **7** (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 $NaHCO_3$ and evaporated in vacuo. The crude product was purified by successive column chromatography and recrystallyzations from hexane, then chromatographed on prep. T. L. C. to give pure trans isomer.

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

^{1}H NMR ($CDCl_3$) δ=0.5—2.5 (m, $C_5H_{11}CH$, $OCH_2\underline{R}$), 2.8 (d, 2H, CH_2S), 3.1—4.5 (m, 4H, CH_2O), 5.8 (s, 1H, ), 6.6—8.3 (m, 8H, ArH).

9-1: Yield, 25%. Found: C, 72.97; H, 8.40%. Calcd for $C_{30}H_{42}SO_4$: C, 72.25; H, 8.49%. MS *m/z* 498.

9-2: Yield, 19%. Found: C, 72.89; H, 8.79%. Calcd for $C_{32}H_{46}SO_4$: C, 72.96; H, 8.80%. MS *m/z* 526.

9-3: Yield, 19%. Found: C, 73.34; H, 8.94%. Calcd for $C_{33}H_{48}SO_4$: C, 73.29; H, 8.95%. MS *m/z* 540.

9-4: Yield, 23%. Found: C, 73.96; H, 9.24%. Calcd for $C_{34}H_{50}SO_4$: C, 73.60; H, 9.08%. MS *m/z* 554.

References

1) Y. Haramoto, M. Sano, and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **59**, 1337 (1986). And references cited therein.

2) D. Demus and H. Zaschke, (to V.E.W. Kombinat Mikroelectronic), Japan Patent Appl. No. 54-160916, Dec. (1979).

3) Y. Haramoto, Y. Tomita, and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **59**, 3877 (1986).

4) Y. Haramoto and H. Kamogawa, *Chem. Lett.*, **1987**, 755.

5) Y. Haramoto, K. Kawashima, and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **61**, 431 (1988).

6) Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst., Lett.*, **5**, 117 (1988).

7) Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **173**, 89 (1989).

8) Y. Haramoto and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **63**, 156 (1990).

9) Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **182B**, 195 (1990).

10) D. Demus and L. Richter, "Textures of Liquid Crystals," Verlag Chemie, Weinheim, New York (1978).

11) G. W. Gray and J. W. Goodby, "Smectic Liquid Crystals Textures and Structures," Leonard Hill, Glasgow, and London (1984).