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Liquid Crystal Materials with Sulfur Atoms Incorporated in the Principal Structure. V. New Liquid Crystal Compounds; 2,5-Diaryl-1,3-Oxathianes

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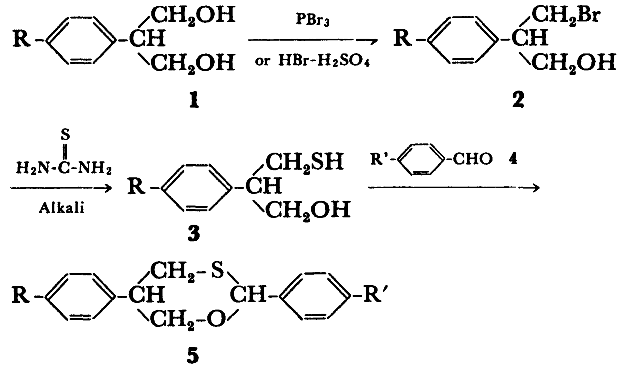
2,5-Bis(*p*-substituted phenyl)-1,3-oxathianes (**5**), new liquid crystal compounds, and some corresponding 1,3-dioxanes were synthesized by the acetal formation reaction. The mesomorphic behaviors of compounds **5** were compared with those of the corresponding 1,3-dioxanes and 1,3-dithianes. Compounds **5** exhibited the lowest transition temperatures between nematic and isotropic phases. This seems to originate in the bend at the 1,3-oxathiane ring containing two heteroatoms, oxygen and sulfur, different in size. Compounds **5** also tend to exhibit supercooling states in nematic phase.

In recent years, 2,5-disubstituted 1,3-dithianes and 2,5-disubstituted 1,3-oxathianes, new types of liquid crystal compounds, have been reported.[1-8] The present study relates to the synthesis and mesomorphic behavior of 2,5-bis(*p*-substituted phenyl)-1,3-oxathianes (**5**). The mesomorphic behavior of **5** were also compared with those of the corresponding 1,3-dioxanes and 1,3-dithianes.

Results and Discussion

2,5-Bis(*p*-substituted phenyl)-1,3-oxathianes (**5**) were synthesized via the route shown in Scheme 1. In step **1**—**2**, PBr_3 must be used for *p*-ethoxy and *p*-methoxy compounds to prevent the cleavage of the ether bond, but in the case of *p*-methyl compounds, $HBr-H_2SO_4$ condition could be used under conventional conditions. The amounts of PBr_3 were controlled so as to effect mainly the monobromination of the diols. Compounds **5** were purified by means of recrystallizations from hexane. Those compounds which could not be purified by recrystallizations were purified first by column chromatography, then by recrystallizations from hexane until only a single spot in TLC was obtained. Compounds **5** thus synthesized were all colorless and odorless powders which were soluble in common organic solvents.



R: OCH_3, OC_2H_5, CH_3.
R′: OC_2H_5, $OC_3H_7{}^n$, $OC_4H_9{}^n$, $OC_5H_{11}{}^n$, CH_3, CN.

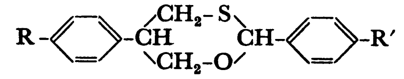
Scheme 1.

Absorption of C2, C4, and C6 carbons of the 1,3-oxathiane ring in ^{13}C-NMR, as determined by ^1H-complete decoupling (COM), ^1H-off resonance decoupling (OFR), and ^1H-selective decoupling (SEL) procedures, are located at δ=84.09, 35.16, and 75.58, respectively ($R=CH_3O$, $R'=OC_4H_9$). These values are almost equal to those of trans isomers of 2-(*p*-substituted phenyl)-5-alkyl-1,3-oxathianes.[6] Therefore, the obtained compounds must be trans isomers. The presence of 1,3-dithianes and 1,3-dioxanes can be detected by the examination of C2 proton signals at δ=5.25 and 5.50, respectively. Measurements of mesomorphic ranges and assignments of mesophases were carried out by means of a micro melting point apparatus equipped with polarizers.

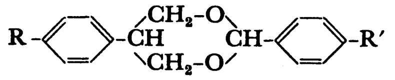
Mesomorphic ranges of the synthesized 2,5-bis(*p*-substituted phenyl)-1,3-oxathianes and the corresponding 1,3-dioxanes and 1,3-dithianes are given in Table 1.

Transition temperatures of isotropic to nematic (Tn-i) for compounds **5** are lower than those for the corresponding 1,3-dioxanes and 1,3-dithianes. It is known generally that the larger the molecular width, the lower Tn-i is.[9] The molecular widths of the heterorings increase in the order: 1,3-dioxane,<1,3-oxathiane<1,3-dithiane. But compounds **5** bent at the 1,3-oxathiane ring due to the difference of atomic size between sulfur and oxygen. Therefore, the actual molecular widths of these three compounds must increase in the order: 1,3-dioxane<1,3-dithiane<1,3-oxathiane. This fact may explain lower values of Tn-i for compounds **5** as compared with those of the corresponding dioxanes and dithianes. However, Tn-i of the dithianes are higher than those of the corresponding dioxanes. This seems to originate from the dispersion force of 1,3-dithiane ring having two sulfur atoms. It is said generally that the main factor affecting Tn-i is molecular width.[10] Concerning the dithianes, however, this rule dose not appear to hold. Namely, the effect of the molecular width

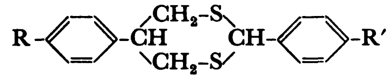
Table 1. Transition Temperature of Compounds **5** and the Corresponding 1,3-Dioxanes and 1,3-Dithianes


(**5**)

	R	R′	Transition temp/°C[a]
5-1	OC$_2$H$_4$	OC$_2$H$_5$	$\mathrm{C} \underset{134}{\overset{144}{\rightleftarrows}} \mathrm{N} \underset{171}{\overset{171}{\rightleftarrows}} \mathrm{I}$
5-2	OC$_2$H$_5$	OC$_3$H$_7$^{n}	$\mathrm{C} \underset{149}{\overset{149}{\rightleftarrows}} \mathrm{N} \underset{159}{\overset{159}{\rightleftarrows}} \mathrm{I}$
5-3	OC$_2$H$_5$	OC$_4$H$_9$^{n}	$\mathrm{C} \underset{106}{\overset{106}{\rightleftarrows}} \mathrm{N} \underset{160}{\overset{160}{\rightleftarrows}} \mathrm{I}$
5-4	OC$_2$H$_5$	OC$_5$H$_{11}$^{n}	$\mathrm{C} \underset{83}{\overset{93}{\rightleftarrows}} \mathrm{N} \underset{152}{\overset{152}{\rightleftarrows}} \mathrm{I}$
5-5	OC$_2$H$_5$	CH$_3$	$\mathrm{C} \underset{109}{\overset{135}{\rightleftarrows}} \mathrm{N} \underset{144}{\overset{144}{\rightleftarrows}} \mathrm{I}$
5-6	CH$_3$	OC$_2$H$_5$	$\mathrm{C} \underset{128}{\overset{139}{\rightleftarrows}} \mathrm{N} \underset{147}{\overset{147}{\rightleftarrows}} \mathrm{I}$
5-7	CH$_3$	OC$_3$H$_7$^{n}	$\mathrm{C} \xrightarrow{135} \mathrm{I}$; $\mathrm{I} \xrightarrow{113} \mathrm{N} \xrightarrow{106} \mathrm{C}$
5-8	CH$_3$	OC$_4$H$_9$^{n}	$\mathrm{C} \xrightarrow{138} \mathrm{I}$; $\mathrm{I} \xrightarrow{133} \mathrm{N} \xrightarrow{109} \mathrm{C}$
5-9	OCH$_3$	OC$_2$H$_5$	$\mathrm{C} \underset{86}{\overset{115}{\rightleftarrows}} \mathrm{N} \underset{163}{\overset{163}{\rightleftarrows}} \mathrm{I}$
5-10	OCH$_3$	OC$_3$H$_7$^{n}	$\mathrm{C} \underset{91}{\overset{132}{\rightleftarrows}} \mathrm{N} \underset{139}{\overset{139}{\rightleftarrows}} \mathrm{I}$
5-11	OCH$_3$	OC$_4$H$_9$^{n}	$\mathrm{C} \underset{68}{\overset{105}{\rightleftarrows}} \mathrm{N} \underset{144}{\overset{144}{\rightleftarrows}} \mathrm{I}$
5-12	OCH$_3$	CN	$\mathrm{C} \xrightarrow{141} \mathrm{I}$; $\mathrm{I} \xrightarrow{106} \mathrm{N} \xrightarrow{100} \mathrm{C}$


(**6**)

	R	R′	Transition temp/°C[a]
6-1	OC$_2$H$_5$	OC$_2$H$_5$	$\mathrm{C} \underset{127}{\overset{127}{\rightleftarrows}} \mathrm{N} \underset{174}{\overset{174}{\rightleftarrows}} \mathrm{I}$
6-2	OC$_2$H$_5$	OC$_3$H$_7$^{n}	$\mathrm{C} \xrightarrow{154} \mathrm{I}$; $\mathrm{I} \xrightarrow{148} \mathrm{S} \xrightarrow{135} \mathrm{C}$
6-3	OC$_2$H$_5$	OC$_4$H$_9$^{n}	$\mathrm{C} \underset{128}{\overset{148}{\rightleftarrows}} \mathrm{S} \underset{149}{\overset{149}{\rightleftarrows}} \mathrm{N} \underset{160}{\overset{160}{\rightleftarrows}} \mathrm{I}$
6-4	OC$_2$H$_5$	CH$_3$	$\mathrm{C} \underset{129}{\overset{136}{\rightleftarrows}} \mathrm{N} \underset{147}{\overset{147}{\rightleftarrows}} \mathrm{I}$


(**7**)

	R	R′	Transition temp/°C[a]	
7-1	OC$_2$H$_5$	OC$_2$H$_5$	$\mathrm{C} \underset{176}{\overset{176}{\rightleftarrows}} \mathrm{N} \underset{195}{\overset{195}{\rightleftarrows}} \mathrm{I}$	b)
7-2	OC$_2$H$_5$	OC$_3$H$_7$^{n}	$\mathrm{C} \xrightarrow{173} \mathrm{I}$; $\mathrm{I} \xrightarrow{173} \mathrm{N} \xrightarrow{167} \mathrm{C}$	
7-3	OC$_2$H$_5$	OC$_4$H$_9$^{n}	$\mathrm{C} \underset{148}{\overset{148}{\rightleftarrows}} \mathrm{N} \underset{182}{\overset{182}{\rightleftarrows}} \mathrm{I}$	
7-4	OC$_2$H$_5$	OC$_5$H$_{11}$^{n}	$\mathrm{C} \underset{126}{\overset{126}{\rightleftarrows}} \mathrm{N} \underset{175}{\overset{175}{\rightleftarrows}} \mathrm{I}$	
7-5	OC$_2$H$_5$	CH$_3$	$\mathrm{C} \xrightarrow{165} \mathrm{I}$; $\mathrm{I} \xrightarrow{165} \mathrm{N} \xrightarrow{132} \mathrm{C}$	
7-6	CH$_3$	OC$_4$H$_9$^{n}	$\mathrm{C} \xrightarrow{170} \mathrm{I}$; $\mathrm{I} \xrightarrow{156} \mathrm{N} \xrightarrow{110} \mathrm{C}$	
7-7	CH$_3$	OC$_5$H$_{11}$^{n}	$\mathrm{C} \xrightarrow{146} \mathrm{I}$; $\mathrm{I} \xrightarrow{142} \mathrm{N} \xrightarrow{121} \mathrm{C}$	
7-8	CH$_3$	CN	$\mathrm{C} \xrightarrow{180} \mathrm{I}$; $\mathrm{I} \xrightarrow{160} \mathrm{N} \xrightarrow{142} \mathrm{C}$	

a) C=crystal; N=nematic; S=smectic; I=isotropic. b) Cited from Ref. 3.

may be smaller than that of the dispersion force of 1,3-dithiane ring having two sulfur atoms.

Compounds **5** having substituent R=CH$_3$ tend to become monotropic liquid crystal in contrast with those having substituent R=C$_2$H$_5$O or R=CH$_3$O. They also exhibited remarkable supercooling states in the nematic liquid crystal phase (R=CH$_3$C, R′=OC$_4$H$_9$:C-N 105 °C, N-C 68 °C).

Tn-i of a series of compounds **5** different only in substituent R decreased in the order: R=OC$_2$H$_5$>R=OCH$_3$>R=CH$_3$, and Tn-i of the compounds different only in substituent R′ exhibited somewhat higher values for those having alkoxyl groups of even carbon number (OC$_2$H$_5$, OC$_4$H$_9$).

Experimental

IR, ^{1}H-NMR, ^{13}C-NMR, and Mass spectra were obtained with a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, a JNM-FX 90Q FT-NMR spectrometer, and a Hitachi RMU-6 MG 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. The rates of heating and cooling were fixed to about 2 °C min^{-1}.

2-(*p*-Alkoxyphenyl)-3-bromo-1-propanols (2). To a solution of 2-(*p*-alkoxyphenyl)-1,3-propanediol (**1**; 0.08 mol), anhyd benzene (150 ml), and pyridine (0.8 g) kept at 30 °C were added, dropwise, a solution of PBr_3 (0.027 mol), anhyd benzene (100 ml), and pyridine (0.3 g) (about 60 min). The solution was kept at 30 °C for 18 h. The reaction mixture was poured into ice water (400 ml) and extracted first with benzene (300 ml), then with ether (400 ml). The extract was washed with cold water (100 ml), dried over anhyd Na_2SO_4, and evaporated in vacuo at 30 °C.

3-Bromo-2-(*p*-methoxyphenyl)-1-propanol (2-1): Yield 50—60%. IR ($CHCl_3$) 3600 (OH), 2800—3000 (alkyl), 1600 (Ar), 1260 (ether) cm^{-1}. ^1H-NMR ($CDCl_3$) δ=2.5—4.2 (m, 9H, CH, CH_2Br, CH_3O, CH_2OH), 6.6—7.3 (q, 4H, ArH).

3-Bromo-2-(*p*-ethoxyphenyl)-1-propanol (2-2): Yield 45—50%. IR ($CHCl_3$) 3600 (OH), 2800—3000 (alkyl), 1600 (Ar), 1260 (ether) cm^{-1}. ^1H-NHR ($CDCl_3$) δ=1.4 (t, 3H, CH_3), 2.5—4.3 (m, 9H, CH, CH_2Br, CH_2OH, $CH_3C\underline{H}_2O$), 6.7—7.4 (q, 4H, ArH).

3-Bromo-2-(*p*-methylphenyl)-1-propanol (2-3): To a solution of 48% HBr (33 g) and concd H_2SO_4 (10 g) cooled in an ice bath were added successively 2-(*p*-methylphenyl)-1,3-propanediol (**1**; 0.065 mol) and concd H_2SO_4 (17 g). The solution was kept at 70—75 °C for 15 h. The reaction mixture was then poured into ice water (200 g). The mixture was stirred and extracted twice with ether (each 300 ml). The extract was washed with cold 10% aq $NaHCO_3$ (100 ml), dried over anhyd Na_2SO_4, and evaporated in vacuo at 30 °C. Yield 50—60%. IR ($CHCl_3$) 3600 (OH), 2800—3000 (alkyl), 1600 (Ar) cm^{-1}. ^1H-NMR ($CDCl_3$) δ=2.3 (s, 3H, CH_3), 3.0—4.2 (m, 6H, CH, CH_2Br, CH_2OH), 7.2 (s, 4H, ArH).

2-(*p*-Substituted phenyl)-3-mercapto-1-propanols (3). To a solution of thiourea (0.064 mol) in triethylene glycol (10 ml) kept at 75 °C was added compound **2** (0.01 mol) in nitrogen atmosphere, followed by stirring at 75 °C for 18 h. Tetraethylenepentamine (0.01 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 water (100 ml) and then extracted twice with ether (each 300 ml). The extract was washed with cold 5% aq HCl (100 ml), dried over anhyd Na_2SO_4, and evaporated in vacuo at 30 °C.

3-Mercapto-2-(*p*-methoxyphenyl)-1-propanol (3-1): Yield 60—65%. IR ($CHCl_3$) 3600 (OH), 2800—3000 (alkyl), 1600 (Ar), 1270 (ether) cm^{-1}. ^1H-NMR ($CDCl_3$) δ=0.9—1.5 (b, 1H, SH), 2.3—4.3 (m, 6H, CH_2OH, CH_3O), 6.5—7.4 (q, 4H, ArH).

2-(*p*-Ethoxyphenyl)-3-mercapto-1-propanol (3-2): Yield 65—70%. IR ($CHCl_3$) 3600 (OH), 2800—3000 (alkyl), 1600 (Ar), 1270 (ether) cm^{-1}. ^1H-NMR ($CDCl_3$) δ=0.9—1.5 (m, 4H, CH_3, SH), 2.4—3.0 (m, 3H, CH_2S, CH), 3.1—4.5 (m, 5H, CH_2O, CH_2OH), 6.5—7.4 (q, 4H, ArH).

3-Mercapto-2-(*p*-methylphenyl)-1-propanol (3-3): Yield 60—65%. IR ($CHCl_3$) 3600 (OH), 2800—3000 (alkyl), 1600 (Ar) cm^{-1}. ^1H-NMR ($CDCl_3$) δ=1.0—1.4 (m, 1H, SH), 2.3 (s, 3H, CH_3), 2.5—4.0 (m, 6H, CH_2S, CH, CH_2OH), 7.1 (s, 4H, ArH).

2,5-Bis(*p*-substituted phenyl)-1,3-oxathianes (5). To a solution of compound **3** (0.004 mol) and *p*-substituted benzaldehyde **4** (0.004 mol) in anhyd $CHCl_3$ (300 ml) cooled in an ice bath were added BE_3-$(C_2H_5)_2O$ (0.5 g) and Molecular Sieve (3A, 1/15; 3 g). The mixture was stirred at 0—5 °C for 8 h and then at 20—25 °C for 18 h. The solution was washed with 10% aq $NaHCO_3$ (400 ml), dried over anhyd Na_2SO_4, and evaporated in vacuo at 40 °C. The crude product was purified by recrystallizations from hexane, if necessary, by column chromatography and recrystallizations.

The spectral properties and analytical data of the synthesized compounds are given below.

2-(*p*-Substituted phenyl)-5-(*p*-ethoxyphenyl)-1,3-oxathianes: IR ($CHCl_3$) 2800—3000 (alkyl), 1600 (Ar), 1280 (ether) cm^{-1}. ^1H-NMR ($CDCl_3$) δ=0.8—2.3 (m, alkyl), 2.5—3.5 (m, 3H, CH, CH_2S), 3.7—4.5 (m, 6H, CH_2O), 5.8 (s, 1H, S-CH-O), 6.7—7.7 (m, 8H, ArH).

2-(*p*-Alkoxyphenyl)-5-(*p*-methylphenyl)-1,3-oxathianes: IR ($CHCl_3$) 2800—3000 (alkyl), 1600 (Ar), 1280 (ether) cm^{-1} ^1H-NMR ($CDCl_3$) δ=0.8—2.1 (m, alkyl), 2.3 (s, 3H, CH_3), 2.5—3.5 (m, 3H, CH, CH_3S), 3.7—4.5 (m, 4H, CH_2O), 5.8 (s, 1H, S-CH-O), 6.7—7.6 (m, 8H, ArH).

2-(*p*-Alkoxyphenyl)-5-(*p*-methoxyphenyl)-1,3-oxathianes: IR ($CHCl_3$) 2800—3000 (alkyl), 1600 (Ar), 1280 (ether) cm^{-1}. ^1H-NMR ($CDCl_3$) δ=0.9—2.1 (m, alkyl), 2.7—4.5 (m, 10H, CH_2S, CH, CH_2O, CH_3O), 5.8 (s, 1H, CH), 6.7—7.6 (m, 8H, ArH).

2,5-Bis(*p*-ethoxyphenyl)-1,3-oxathiane (5-1): Yield 43%. Found: C, 70.07; H, 6.99%. Calcd for $C_{20}H_{24}O_3S_1$: C, 69.73; H, 7.02%. MS (*m/z*) 344 (M^+).

5-(*p*-Ethoxyphenyl)-2-(*p*-propoxyphenyl)-1,3-oxathiane (5-2): Yield 35%. Found: C, 70.18; H, 7.17%. Calcd for $C_{21}H_{26}O_3S$: C, 70.36; H, 7.31%. MS (*m/z*) 358 (M^+).

2-(*p*-Butoxyphenyl)-5-(*p*-ethoxyphenyl)-1,3-oxathiane (5-3): Yield 47%. Found: C, 71.39; H, 7.54%. Calcd for $C_{22}H_{28}O_3S$: C, 71.02; H, 7.58%. MS (*m/z*) 372 (M^+).

5-(*p*-Ethoxyphenyl)-2-(*p*-pentyloxyphenyl)-1,3-oxathiane (5-4): Yield 39%. Found: C, 71.19; H, 7.68%. Calcd for $C_{23}H_{30}O_3S$: C, 71.46; H, 7.82%. MS (*m/z*) 386 (M^+).

5-(*p*-Ethoxyphenyl)-2-(*p*-methylphenyl)-1,3-oxathiane (5-5): Yield 32%. Found: C, 72.31; H, 6.93%. Calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05%. MS (*m/z*) 314 (M^+).

2-(*p*-Ethoxyphenyl)-5-(*p*-methylphenyl)-1,3-oxathiane (5-6): Yield 40%. Found: C, 72.24; H, 7.08%. Calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05%. MS (*m/z*) 314 (M^+).

5-(*p*-Methylphenyl)-2-(*p*-propoxyphenyl)-1,3-oxathiane (5-7): Yield 38%. Found: C, 73.46; H, 7.44%. Calcd for $C_{20}H_{24}O_2S$: C, 73.13; H, 7.37%. MS (*m/z*) 328 (M^+).

2-(*p*-Butoxyphenyl)-5-(*p*-methylphenyl)-1,3-oxathiane (5-8): Yield 44%. Found: C, 72.94; H, 7.72%. Calcd for $C_{21}H_{26}O_2S$: C, 73.64; H, 7.65%. MS (*m/z*) 342 (M^+).

2-(*p*-Ethoxyphenyl)-5-(*p*-methoxyphenyl)-1,3-oxathiane (5-9): Yield 23%. Found: C, 69.21; H, 6.83%. Calcd for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71%. MS (*m/z*) 330 (M^+).

5-(*p*-Methoxyphenyl)-2-(*p*-propoxyphenyl)-1,3-oxathiane (5-10): Yield 30%. Found: C, 69.65; H, 7.09%. Calcd for $C_{20}H_{24}O_3S$: C, 69.73; H, 7.02%. MS (*m/z*) 344 (M^+).

2-(*p*-Butoxyphenyl)-5-(*p*-methoxyphenyl)-1,3-oxathiane (5-11): Yield 35%. Found: C, 70.37; H, 7.31%. Calcd for $C_{21}H_{26}O_3S$: C, 70.36; H, 7.31%. MS (*m/z*) 358 (M^+).

2-(*p*-Cyanophenyl)-5-(*p*-methoxyphenyl)-1,3-oxathiane (5-12): Yield 24%. Found: C, 70.58; H, 5.98; N, 4.89%. Calcd for $C_{18}H_{17}NO_2S$: C, 69.43; H, 5.50; N, 4.50%. MS (*m/z*) 311 (M^+).

2-(*p*-Substituted phenyl)-5-(*p*-ethoxyphenyl)-1,3-dioxanes (6). Compounds **6** were synthesized by following the same procedure as for compounds **5** using **1** instead of **3**. IR

(CHCl$_3$) 2800—3000 (alkyl), 1600 (Ar), 1300 (ether) cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ=0.8—2.4 (m, alkyl), 3.7—4.5 (m, CH, CH$_2$O), 5.5 (s, 1H S-CH-O), 6.8—7.7 (m, 8H, ArH).

2,5-Bis(*p*-ethoxyphenyl)-1,3-dioxane (6-1): Yield 53%. Found: C, 72.81; H, 7.40%. Calcd for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37%. MS (*m/z*) 328 (M$^+$).

5-(*p*-Ethoxyphenyl)-2-(*p*-propoxyphenyl)-1,3-dioxane (6-2): Yield 44%. Found: C, 73.63; H, 7.67%. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65%. MS (*m/z*) 342 (M$^+$).

2-(*p*-Butoxyphenyl)-5-(*p*-ethoxyphenyl)-1,3-dioxane (6-3): Yield 42%. Found: C, 74.03; H, 7.92%. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92%. MS (*m/z*) 356 (M$^+$).

5-(*p*-Ethoxyphenyl)-2-(*p*-methylphenyl)-1,3-dioxane (6-4): Yield 50%. Found: C, 76.39; H, 7.44%. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43%. MS (*m/z*) 298 (M$^+$).

References

1) Y. Haramoto and H. Kamogawa, *J. Chem. Soc., Chem. Commun.*, **1983**, 75.

2) Y. Haramoto, A. Nobe, and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **57**, 1966 (1984).

3) Y. Haramoto, K. Akazawa, and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **57**, 3173 (1984).

4) Y. Haramoto and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **58**, 477 (1985).

5) Y. Haramoto and H. Kamogawa, *Chem. Lett.*, **1985**, 79.

6) Y. Haramoto and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **58**, 1821 (1985).

7) Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **131**, 101 (1985).

8) Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **131**, 201 (1985).

9) G. W. Gray and B. W. Worrall, *J. Chem. Soc.*, **1959**, 1545 .

10) G. W. Gray, *Mol. Cryst.*, **1**, 333 (1966).