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Liquid Crystal Materials with Sulfur Atoms Incorporated in the Principal Structure 1. New Liquid Crystal Compounds with 1,3-Dithiane Ring

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2-(*p*-Substituted phenyl)-5-alkyl-1,3-dithianes, new liquid crystals, were synthesized by the thioacetalization of the corresponding aldehydes and dithiols. These compounds have characteristic supercooling states, exhibit monotropic liquid crystal phases even in the case of long terminal alkyl substituents. The mesomorphic characteristics of these compounds were different from those of the corresponding 1,3-dioxanes, this must originate in the difference in the molecular width caused by the difference in the atomic volume between sulfur and oxygen.

In a previous communication,[1)] 2,5-disubstituted 1,3-dithianes and 1,3-oxathianes as novel types of liquid crystal were reported. Since only 2,5-disubstituted 1,3-dioxanes are known as structurally related liquid crystal materials,[2)] we wish to report here in more detail the synthesis and properties of these novel 1,3-dithiane type liquid crystals prepared by us.

Results and Discussion

2-(*p*-Substituted phenyl)-5-alkyl-1,3-dithianes were synthesized *via* the following route.

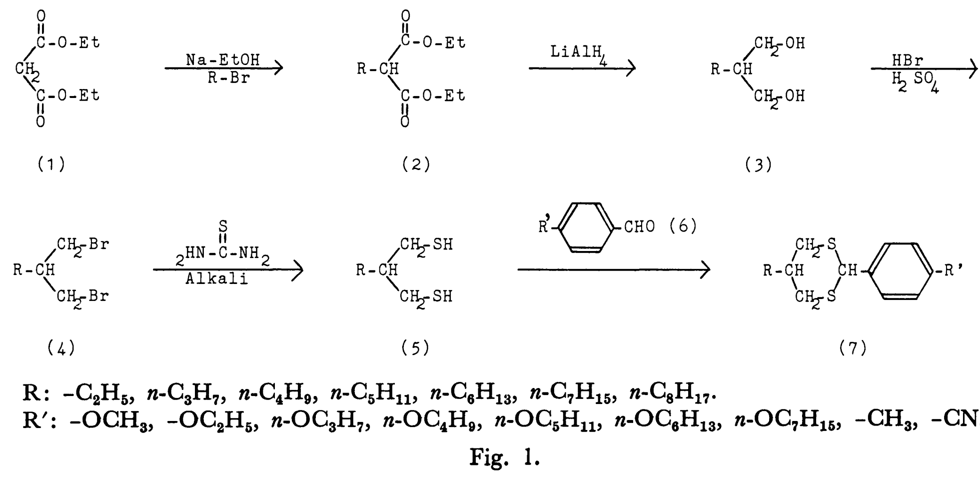
Compounds **2** and **3** were obtained in good yields. In step **3**→**4**, the reaction temperature was crucial. If the reaction temperature was 70—75 °C, the main product was a mono substituted bromide contrary to our purpose. Therefore, the reaction temperature must be kept at 95—100 °C. As compound **5** was susceptible to oxidation, step **4**→**5** required a nitrogen atomosphere. In **5**→**7**, both axial (cis) and equatorial (trans) isomers were produced differing at the C-5 position of the 1,3-dithiane ring. Repeated recrystallization was necessary to obtain the purified equatorial isomers. In the case of 2-(*p*-cyanophenyl)-5-alkyl-1,3-dithianes, the production ratios of the axial isomers were higher than those for other 1,3-dithianes, so that purification of the equatorial isomers by recrystallization was unsuccessful.

Centrifugal liquid chromatography and T.L.C. were used to purify these compounds. As the axial and equatorial isomers exhibited different patterns of ^{1}H-NMR, the existance of the axial isomer can be detected by the examination of proton signals at δ=2.3—3.5: proton signals of the equatorial isomer are located only in a narrow range of ^{1}H-NMR chemical shift (δ=2.6—2.9), whereas those of the axial isomer cover a wide range (δ=2.3—3.5). Synthesized compounds **7** are all colorless and odorless crystals or powders, which are soluble in common organic solvents. They all exhibited remarkable supercooled states (about 15—70 °C below the melting point). This property seems to originate from the steric structure of the 1,3-dithiane ring bearing bulky sulfur and its dominant role in the lateral interactions between molecules, since the corresponding 1,3-dioxane-type compounds mostly indicate enantiotropic liquid crystal behavior. (Table 1)

Mesomorphic ranges determined for compounds **7** are given in Table 1, together with those for the corresponding 1,3-dioxanes.

Measurement of the mesomorphic ranges and assignment of the mesophases were carried out by means of a differential scanning calorimeter (D.S.C.) and a micro melting point apparatus equipped with polarizers.

In the alkyl-chain length ranging from R=C_2 to C_4 (**7-1**—**7-17**), any mesomorphic phases could not be observed under the polarization microscope. These compounds only exhibited the supercooled state. In the alkyl chain length from R=C_5 to C_7 (**7-18**—**7-32**), monotropic nematic phases were observed under the

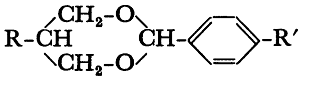


R: -C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11}, *n*-C_6H_{13}, *n*-C_7H_{15}, *n*-C_8H_{17}.
R′: -OCH_3, -OC_2H_5, *n*-OC_3H_7, *n*-OC_4H_9, *n*-OC_5H_{11}, *n*-OC_6H_{13}, *n*-OC_7H_{15}, -CH_3, -CN.

Fig. 1.

TABLE 1. TRANSITION TEMPERATURE OF COMPOUNDS **7** AND THE CORRESPONDING 1,3-DIOXANES

	R	R′	Transition temp./°C[a]
7—1	C_2H_5	OCH_3	$C \underset{34}{\overset{69}{\rightleftarrows}} I$
7—2	C_2H_5	n-OC_4H_4	$C \underset{10}{\overset{50}{\rightleftarrows}} I$
7—3	C_2H_5	CH_3	$C \underset{55}{\overset{95}{\rightleftarrows}} I$
7—4	C_2H_5	CN	$C \underset{90}{\overset{130}{\rightleftarrows}} I$
7—5	n-C_3H_7	OCH_3	$C \underset{34}{\overset{97}{\rightleftarrows}} I$
7—6	n-C_3H_7	n-OC_4H_9	$C \underset{25}{\overset{46}{\rightleftarrows}} I$
7—7	n-C_3H_7	CH_3	$C \underset{45}{\overset{87}{\rightleftarrows}} I$
7—8	n-C_3H_7	CN	$C \underset{78}{\overset{133}{\rightleftarrows}} I$
7—9	n-C_4H_9	OCH_3	$C \underset{35}{\overset{85}{\rightleftarrows}} I$
7—10	n-C_4H_9	OC_2H_5	$C \underset{35}{\overset{75}{\rightleftarrows}} I$
7—11	n-C_4H_9	n-OC_3H_7	$C \underset{32}{\overset{65}{\rightleftarrows}} I$
7—12	n-C_4H_9	n-OC_4H_9	$C \underset{27}{\overset{68}{\rightleftarrows}} I$
7—13	n-C_4H_9	n-OC_5H_{11}	$C \underset{33}{\overset{64}{\rightleftarrows}} I$
7—14	n-C_4H_9	n-OC_6H_{13}	$C \underset{40}{\overset{70}{\rightleftarrows}} I$
7—15	n-C_4H_9	n-OC_7H_{15}	$C \underset{37}{\overset{65}{\rightleftarrows}} I$
7—16	n-C_4H_9	CH_3	$C \underset{42}{\overset{67}{\rightleftarrows}} I$
7—17	n-C_4H_9	CN	$C \underset{30}{\overset{88}{\rightleftarrows}} I$
7—18	n-C_5H_{11}	OC_2H_5	$C \underset{35}{\overset{57}{\rightleftarrows}} I$
7—19	n-C_5H_{11}	n-OC_3H_7	$C \underset{40}{\overset{55}{\rightleftarrows}} I$
7—20	n-C_5H_{11}	n-OC_4H_9	$\begin{array}{c} C \xrightarrow{46} I \\ {}^{26}\nwarrow\swarrow{}^{43} \\ N \end{array}$
7—21	n-C_5H_{11}	n-OC_5H_{11}	$\begin{array}{c} C \xrightarrow{61} I \\ {}^{40}\nwarrow\swarrow{}^{45} \\ N \end{array}$
7—22	n-C_5H_{11}	CN	$C \underset{28}{\overset{98}{\rightleftarrows}} I$
7—23	n-C_6H_{13}	OC_2H_5	$\begin{array}{c} C \xrightarrow{61} I \\ {}^{32}\nwarrow\swarrow{}^{43} \\ N \end{array}$
7—24	n-C_6H_{13}	n-OC_3H_7	$C \underset{38}{\overset{75}{\rightleftarrows}} I$
7—25	n-C_6H_{13}	n-OC_4H_9	$\begin{array}{c} C \xrightarrow{55} I \\ {}^{34}\nwarrow\swarrow{}^{44} \\ N \end{array}$
7—26	n-C_6H_{13}	n-OC_5H_{11}	$\begin{array}{c} C \xrightarrow{60} I \\ {}^{38}\nwarrow\swarrow{}^{47} \\ N \end{array}$
7—27	n-C_6H_{13}	CN	$C \underset{36}{\overset{90}{\rightleftarrows}} I$
7—28	n-C_7H_{15}	OC_2H_5	$\begin{array}{c} C \xrightarrow{70} I \\ {}^{48}\nwarrow\swarrow{}^{57} \\ N \end{array}$
7—29	n-C_7H_{15}	n-OC_3H_7	$\begin{array}{c} C \xrightarrow{60} I \\ {}^{35}\nwarrow\swarrow{}^{50} \\ N \end{array}$
7—30	n-C_7H_{15}	n-OC_4H_9	$\begin{array}{c} C \xrightarrow{59} I \\ {}^{42}\nwarrow\swarrow{}^{56} \\ N \end{array}$
7—31	n-C_7H_{15}	n-OC_5H_{11}	$\begin{array}{c} C \xrightarrow{67} I \\ {}^{52}\nwarrow\swarrow{}^{58} \\ N \end{array}$
7—32	n-C_7H_{15}	CN	$C \underset{43}{\overset{98}{\rightleftarrows}} I$
7—33	n-C_8H_{17}	n-OC_3H_7	$\begin{array}{c} C \xrightarrow{56} I \\ {}^{31}\nwarrow\swarrow{}^{56} \\ S \end{array}$
7—34	n-C_8H_{17}	n-OC_4H_9	$\begin{array}{c} C \xrightarrow{57} I \\ {}^{26}\nwarrow\swarrow{}^{57} \\ S \end{array}$
7—35	n-C_8H_{17}	n-OC_5H_{11}	$\begin{array}{c} C \xrightarrow{55} I \\ {}^{34}\nwarrow\swarrow{}^{55} \\ S \end{array}$
7—36	n-C_8H_{17}	CN	$C \underset{39}{\overset{93}{\rightleftarrows}} I$


(8)

b)

	R	R′	Transition temp./°C
8—1	n-C_5H_{11}	n-OC_4H_9	$C \xrightarrow{40} N \xrightarrow{53} I$
8—2	n-C_5H_{11}	n-OC_5H_{11}	$C \xrightarrow{38} N \xrightarrow{50.5} I$
8—3	n-C_6H_{13}	n-OC_4H_9	$C \xrightarrow{35.5} S \xrightarrow{44} N \xrightarrow{50} I$
8—4	n-C_6H_{13}	CN	$\begin{array}{c} C \xrightarrow{47} I \\ \nwarrow\swarrow{}^{40.5} \\ N \end{array}$
8—5	n-C_7H_{15}	n-OC_4H_9	$C \xrightarrow{49} S \xrightarrow{59.5} I$
8—6	n-C_7H_{15}	n-OC_6H_{13}	$C \xrightarrow{37.5} S \xrightarrow{62} I$
8—7	n-C_7H_{15}	CN	$\begin{array}{c} C \xrightarrow{54} I \\ \nwarrow\swarrow{}^{52} \\ N \end{array}$
8—8	n-C_8H_{17}	n-OC_5H_{11}	$C \xrightarrow{38} S \xrightarrow{60} I$

a) C=crystal; N=nematic; I=isotropic; S=smectic. b) Cited from Ref. 2.

polarization microscope. In compounds of $R=C_8$ (**7-33—7-35**), monotropic smectic phases were observed.

In the case of 2-(*p*-alkoxyphenyl)-5-butyl-1,3-dithianes (**7-9—7-15**), increasing the carbon number of the *p*-alkoxyl group (R′) did not afford any mesophases, but in 2-(*p*-butoxyphenyl)-5-alkyl-1,3-dithianes, increasing the length of the alkyl group (R) brought about the appearance of mesophases (**7-20**, **-25**, **-30**, **-34**). Therefore, the effect of the chain length of the alkyl substituent (R) at the C-5 position of the 1,3-dithiane ring on the appearance of mesophases is more marked than that of the *p*-alkoxyl substituent (R′) of the 2-phenyl group.

While, for $R=C_5$ to C_8, all 1,3-dithiane compounds indicated monotropic liquid crystal behavior, the corresponding 1,3-dioxane compounds became enantiotropic liquid crystals.

This suggests that the increased width of the 1,3-dithiane molecule caused by the bulky sulfur atoms decreases attractive interactions between the molecules. This strong tendency to exhibit monotropic mesophases is a feature of this 2-(*p*-substituted phenyl)-5-alkyl-1,3-dithiane liquid crystal group.

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. Centrifugal liquid chromatography was made with a Hitachi CLC-5 apparatus. Mesomorphic phases and transition temperatures were determined more precisely and in detail than in the communication[1)] by means of both a Mitamura Riken micro melting point apparatus equipped with polarizers and D.S.C., with satisfactory coincidences of the results. The rate of cooling was fixed to 1 °C/min.

Diethyl n-*Alkylmalonates (2).* A conventional procedure[3)] was used for the syntheses of **2**. Yields ranged from 80 to 90%. Bp: 82—84 °C/3—5 mmHg[†] ($R=C_2H_5$), 90—92 °C/3—5 mmHg ($R=C_3H_7$), 94—97 °C/3—5 mmHg ($R=C_4H_9$), 110—113 °C/4—6 mmHg ($R=C_5H_{11}$), 113—115 °C/3—5 mmHg ($R=C_6H_{13}$), 120—123 °C/3—5 mmHg (C_7H_{15}), 124—128 °C/3—5 mmHg ($R=H_8H_{17}$). IR ($CHCl_3$) 2800—3000 (Alkyl), 1740 (C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$) $\delta=0.7$—2.1 (m, Alkyl), 3.25 (t, 1H, CH), 4.2 (q, 4H, $2CH_2$-O).

2-Alkyl-1,3-propanediol (3). $LiAlH_4$-reduction of 2 in ether at 35 °C for 18 h provided **3**. Yields ranged from 90 to 95%. IR ($CHCl_3$) 3600 (OH), 2800—3000 (Alkyl) cm^{-1}. ^{1}H-NMR ($CDCl_3$) $\delta=0.6$—2.1 (m, R-CH), 3.1—4.3 (m, 6H, $2CH_2$-OH).

2-Alkyl-1,3-dibromopropane (4). To a solution of 48% HBr (50g) and conc. H_2SO_4 (15 g) cooled in an ice bath were added successively compound **3** (0.1 mol) and conc. H_2SO_4 (25g). The solution was kept at 95—100 °C, for 18 h. The reaction mixture was then poured into ice water (200g). The mixture was stirred and extracted twice with ether (each 400 ml). The extract was washed with cold 10% aq $NaHCO_3$, and concentrated on a rotary evaporator at 30 °C. The residue was distilled *in vacuo* to afford transparent liquid in a 30—50% yield. Bp: 60—65 °C/1—2 mmHg ($R=C_2H_5$), 65—69 °C/1—2 mmHg ($R=C_3H_7$), 73—74 °C/1—2 mmHg ($R=C_4H_9$), 76—79 °C/1—2 mmHg ($R=C_5H_{11}$), 91—92 °C/2—3 mmHg ($R=C_6H_{13}$), 97—100 °C/1—2 mmHg ($R=C_7H_{15}$), 105—108 °C/1—2 mmHg ($R=C_8H_{17}$). IR ($CHCl_3$) 2800—3000 (Alkyl) cm^{-1}. ^{1}H-NMR ($CDCl_3$) $\delta=0.7$—2.1 (m, R-CH), 3.45—3.75 (m, 4H, $2CH_2$-Br).

2-Alkyl-1,3-propanedithiol (5). To a solution of thiourea (0.064 mol, 4.9 g) in triethylene glycol (8 ml) kept at 75 °C was added compound **4** (0.016 mol) in a nitrogen atmosphere, followed by stirring at 75 °C for 18 h.

Tetraethylenepentamine (0.016 mol, 3.03 g) was then added, and the mixture was stirred at 75 °C for 2 h under a nitrogen atmosphere. The reaction mixture was fractionated *in vacuo* to afford a transparent oily product in a 70—80% yields. Bp: 55—57 °C/1—2 mmHg ($R=C_2H_5$), 64—66 °C/1—2 mmHg ($R=C_3H_7$), 82—85 °C/1—2 mmHg (C_4H_9), 95—98 °C/1—2 mmHg ($R=C_5H_{11}$), 108—110 °C/1—2 mmHg ($R=C_6H_{13}$), 109—113 °C/1 mmHg ($R=C_7H_{15}$, 116—121 °C/1—2 mmHg ($R=C_8H_{17}$). IR ($CHCl_3$) 2800—3000 (Alkyl) cm^{-1}. ^{1}H-NMR ($CDCl_3$) $\delta=0.7$—2.1 (m, R-CH, 2SH), 2.5—2.9 (m, 4H, $2CH_2$-S).

*2-(*p*-Substituted phenyl)-5-alkyl-1,3-dithiane (7).* To a solution of compound **5** (0.004 mol) and *p*-substituted benzaldehyde **6** (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, 1/5; 3g). 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% $NaHCO_3$(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 recrystallizations from hexane–ether (5:1, v/v), then if necessary, by centrifugal liquid chromatography to separate the trans isomers.

*2-(*p*-Alkoxyphenyl)-5-Alkyl-1,3-dithianes.* IR ($CHCl_3$) 2800—3000 (Alkyl), 1600 (Ar), 1240 (Ether) cm^{-1}. ^{1}H-NMR ($CDCl_3$) 7-1, 7-5, 7-9: $\delta=0.7$—2.1 (m, R–CH), 2.6—2.9 (m, 4H, CH_2–S), 3.8 (s, 3H, OCH_3), 5.05 (s, 1H, $\genfrac{}{}{0pt}{}{S}{S}{>}CH-$), 6.7—7.5 (q, 4H, ArH); Others: $\delta=0.7$—2.1 (m, R–CH, O–CH_2–C_n–$\underline{H}_{2n+1}$), 2.6—2.9 (m, 4H, $2CH_2$–S), 3.9 (t, 2H, OCH_2, 5.05 (s, 1H, $\genfrac{}{}{0pt}{}{S}{S}{>}CH-$), 6.7—7.6 (q, 4H, ArH).

*[2-(*p*-Methoxyphenyl)-5-ethyl-1,3-dithiane (**7-1**)]*: Yield, 49%.

Found: C, 64.40; H, 8.21. Calcd for $C_{13}H_{18}S_2O_1$: C, 61.37; H, 7.13. MS (*m*/*z*) 254 (M^+).

*[2-(*p*-Butoxyphenyl)-5-ethyl-1,3-dithiane (**7-2**)]*: Yield, 76%.

Found: C, 64.40; H, 8.21. Calcd for $C_{14}H_{24}S_2O_1$: C, 64.82; H, 8.16 MS (*m*/*z*) 296 (M^+).

*[2-(*p*-Methoxyphenyl)-5-propyl-1,3-dithiane (**7-5**)]*: Yield, 70%.

Found: C, 62.32; H, 7.51. Calcd for $S_{14}H_{20}S_2O_1$: C, 62.64; H, 7.51. MS (*m*/*z*) 268 (M^+).

*[2-(*p*-Butoxyphenyl)-5-propyl-1,3-dithiane (**7-6**)]*: Yield, 72%.

Found: C, 65.89; H, 8.59. Calcd for $C_{17}H_{26}S_2O_1$: C, 65.76; H, 8.44. MS (*m*/*z*) 310 (M^+).

*[2-(*p*-Methoxyphenyl)-5-butyl-1,3-dithiane (**7-9**)]*: Yield, 62%.

Found: C, 63.59; H, 7.80. Calcd for $C_{15}H_{22}S_2O_1$: C, 63.78; H, 7.85. MS (*m*/*z*) 282 (M^+).

*[2-(*p*-Ethoxyphenyl)-5-butyl-1,3-dithiane (**7-10**)]*: Yield, 70%.

Found: C, 64.66; H, 8.14. Calcd for $C_{16}H_{24}S_2O_1$: C, 64.82; H, 8.16. MS (*m*/*z*) 296 (M^+).

*[2-(*p*-Propoxyphenyl)-5-butyl-1,3-dithiane (**7-11**)]*: Yield, 62%.

Found: C, 65.96; H, 8.38. Calcd for $C_{17}H_{26}S_2O_1$: C, 65.76; H, 8.44. MS (*m*/*z*) 310 (M^+).

*[2-(*p*-Butoxyphenyl)-5-butyl-1,3-dithiane (**7-12**)]*: Yield, 61%.

Found: C, 66.56 ; H, 8.72. Calcd for $C_{18}H_{28}S_2O_1$: C, 66.62; H, 8.70. MS (*m*/*z*) 324 (M^+).

*[2-(*p*-Pentyloxyphenyl)-5-butyl-1,3-dithiane (**7-13**)]*: Yield,

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[†] 1 mmHg≈133.322 Pa.

69%.

Found: C, 67.49; H, 8.95. Calcd for $C_{19}H_{30}S_2O_1$: C, 67.40; H, 8.93. MS (*m/z*) 338 (M^+).

*[2-(*p*-Hexyloxyphenyl)-5-butyl-1,3-dithiane (**7-14**)]*: Yield, 66%.

Found: C, 68.07; H, 9.21. Calcd for $C_{20}H_{32}S_2O_1$: C, 68.13; H, 9.15. MS (*m/z*) 352 (M^+).

*[2-(*p*-Heptyloxyphenyl)-5-butyl-1,3-dithiane (**7-15**)]*: Yield, 67%.

Found: C, 68.88; H, 9.29. Calcd for $C_{21}H_{34}S_2O_1$: C, 68.80; H, 9.35. MS (*m/z*) 366 (M^+).

*[2-(*p*-Ethoxyphenyl)-5-pentyl-1,3-dithiane (**7-18**)]*: Yield, 63%.

Found: C, 65.80; H, 8.43. Calcd for $C_{17}H_{26}S_2O_1$: C, 65.76; H, 8.44. MS (*m/z*) 310 (M^+).

*[2-(*p*-Propoxyphenyl)-5-pentyl-1,3-dithiane (**7-19**)]*: Yield, 69%.

Found: C, 66.71; H, 8.71. Calcd for $C_{18}H_{28}S_2O_1$: C, 66.62; H, 8.70. MS (*m/z*) 324 (M^+).

*[2-(*p*-Butoxyphenyl)-5-pentyl-1,3-dithiane (**7-20**)]*: Yield, 64%.

Found: C, 67.28; H, 8.95. Calcd for $C_{19}H_{30}S_2O_1$: C, 67.40; H, 8.93. MS (*m/z*) 338 (M^+).

*[2-(*p*-Pentyloxyphenyl)-5-pentyl-1,3-dithiane (**7-21**)]*: Yield, 66%.

Found: C, 68.12; H, 9.29. Calcd for $C_{20}H_{32}S_2O_1$: C, 68.13; H, 9.15. MS (*m/z*) 352 (M^+).

*[2-(*p*-Ethoxyphenyl)-5-hexyl-1,3-dithiane (**7-23**)]*: Yield, 56%.

Found: C, 66.79; H, 8.68. Calcd for $C_{18}H_{28}S_2O_1$: C, 66.62; H, 8.70. MS (*m/z*) 324 (M^+).

*[2-(*p*-Propoxyphenyl)-5-hexyl-1,3-dithiane (**7-24**)]*: Yield, 68%.

Found: C, 67.49; H, 8.92. Calcd for $C_{19}H_{30}S_2O_1$: C, 67.40; H, 8.93. MS (*m/z*) 338 (M^+).

*[2-(*p*-Butoxyphenyl)-5-hexyl-1,3-dithiane (**7-25**)]*: Yield, 71%.

Found: C, 68.19; H, 9.14. Calcd for $C_{20}H_{32}S_2O_1$: C, 68.13; H, 9.15. MS (*m/z*) 352 (M^+).

*[2-(*p*-Pentyloxyphenyl)-5-hexyl-1,3-dithiane (**7-26**)]*: Yield, 68%.

Found: C, 68.64; H, 9.37. Calcd for $C_{21}H_{34}S_2O_1$: C, 68.80; H, 9.35. MS (*m/z*) 366 (M^+).

*[2-(*p*-Ethoxyphenyl)-5-heptyl-1,3-dithiane (**7-28**)]*: Yield, 67%.

Found: C, 67.45; H, 8.92. Calcd for $C_{19}H_{30}S_2O_1$: C, 67.40; H, 8.93. MS (*m/z*) 338 (M^+).

*[2-(*p*-Propocyphenyl)-5-heptyl-1,3-dithiane (**7-29**)]*: Yield, 70%.

Found: C, 68.21 ; H, 9.14. Calcd for $C_{20}H_{32}S_2O_1$: C, 68.13; H, 19.15 MS (*m/z*) 352 (M^+).

*[2-(*p*-Butoxyphenyl)-5-heptyl-1,3-dithiane (**7-30**)]*: Yield, 55%.

Found: C, 68.75; H, 9.32. Calcd for $C_{21}H_{34}S_2O_1$: C, 68.80; H, 9.35. MS (*m/z*) 366 (M^+).

*[2-(*p*-Pentyloxyphenyl)-5-heptyl-1,3-dithiane (**7-31**)]*: Yield, 66%.

Found: C, 69.46; H, 9.69. Calcd for $C_{22}H_{36}S_2O_1$: C, 69.42; H, 9.53. MS (*m/z*) 380 (M^+).

*[2-(*p*-Propoxyphenyl)-5-octyl-1,3-dithiane (**7-33**)]*: Yield, 61%.

Found: C, 68.60; H, 9.38. Calcd for $C_{21}H_{34}S_2O_1$: C, 68.80; H, 9.35. MS (*m/z*) 366 (M^+).

*[2-(*p*-Butoxyphenyl)-5-octyl-1,3-dithiane (**7-34**)]*: Yield, 53%.

Found: C, 69.20; H, 9.60. Calcd for $C_{22}H_{36}S_2O_1$: C, 69.42; H, 9.53. MS (*m/z*) 380 (M^+).

*[2-(*p*-Pentyloxyphenyl)-5-octyl-1,3-dithiane (**7-35**)]*: Yield, 70%.

Found: C, 69.89; H, 9.72. Calcd for $C_{23}H_{38}S_2O_1$: C, 69.99; H, 9.71. MS (*m/z*) 394 (M^+).

*2-(*p*-Methylphenyl)-5-alkyl-1,3-dithianes.* IR ($CHCl_3$) 2800—3000 (Alkyl), 1600 (Ar) cm^{-1}. ^1H-NMR ($CDCl_3$) δ=0.7—2.1 (m, R-CH), 2.25 (s, 3H, CH_3), 2.6—2.9 (m, 4H, $2CH_2$-S), 5.05 (s, 1H, $^{S}_{S}\!>$CH–), 6.95—7.5 (q, 4H, ArH).

*[2-(*p*-Methylphenyl)-5-ethyl-1,3-dithiane (**7-3**)]*: Yield, 63%.

Found: C, 65.58; H, 7.49. Calcd for $C_{13}H_{18}S_2$: C, 65.49; H, 7.60. MS (*m/z*) 238 (M^+).

*[2-(*p*-Methylphenyl)-5-propyl-1,3-dithiane (**7-7**)]*: Yield, 61%.

Found: C, 66.58; H, 7.73. Calcd for $C_{14}H_{20}S_2$: C, 66.61; H, 7.99. MS (*m/z*) 252 (M^+).

*[2-(*p*-Methylphenyl)-5-butyl-1,3-dithiane (**7-16**)]*: Yield, 72%.

Found: C, 67.99; H, 8.25. Calcd for $C_{15}H_{22}S_2$: C, 67.61; H, 8.32. MS (*m/z*) 266 (M^+).

*2-(*p*-Cyanophenyl)-5-alkyl-1,3-dithianes.* IR ($CHCl_3$) 2800—3000 (Alkyl), 2215 (CN), 1600 (Ar) cm^{-1}. ^1H-NMR ($CDCl_3$) Trans: δ=0.7—2.0 (m, R-CH), 2.6—2.9 (m, 4H, $2CH_2$-S), 5.10 (s, 1H, $^{S}_{S}\!>$CH–), 7.60 (s, 4H, ArH). Cis: δ=0.7—2.0 (m, R-CH), 2.4—3.5 (m, 4H, CH_2-S), 5.08 (s, 1H, $^{S}_{S}\!>$CH–), 7.65 (s, 4H, ArH).

*[2-(*p*-Cyanophenyl)-5-ethyl-1,3-dithiane (**7-4**)]*: Yield, 53%.

Found: C, 62.97; H, 6.06; N, 5.64 Calcd for $C_{13}H_{15}N_1S_2$: C, 62.61; H, 6.06; N, 5.62 ^{13}C-NMR ($CDCl_3$). Trans: δ=50.77 (C2 of the 1,3-dithiane ring), 37.06 (C4, C6), 37.22 (C5). Cis: δ=50.15 (C2), 35.27 (C4, C6), 30.83 (C5). MS (*m/z*) 249 (M^+).

*[2-(*p*-Cyanophenyl)-5-propyl-1,3-dithiane (**7-8**)]*: Yield, 52%.

Found: C, 64.03; H, 6.54; N, 5.44 Calcd for $C_{14}H_{17}N_1S_2$: C, 68.83; H, 6.51; N, 5.32. ^{13}C-NMR ($CDCl_3$). Trans: δ=50.77 (C2), 37.38 (C4, C6), 35.22 (C5). Cis: δ=50.06 (C2), 35.60 (C4, C6), 28.88 (C5). MS (*m/z*) 263 (M^+).

*[2-(*p*-Cyanophenyl)-5-butyl-1,3-dithiane (**7-17**)]*: Yield, 50%.

Found: C, 64.80; H, 6.97; N, 5.15. Calcd for $C_{15}H_{19}N_1S_2$: C, 64.94; H, 6.90; N, 5.05. ^{13}C-NMR ($CDCl_3$). *Trans:* δ=50.66 (C2), 37.33 (C4, C6), 36.14 (C5). Cis: δ=49.96 (C2), 35.60 (C4, C6), 29.80 (C5). MS (*m/z*) 277 (M^+).

*[2-(*p*-Cyanophenyl)-5-pentyl-1,3-dithiane (**7-22**)]*: Yield, 56%.

Found: C, 66.00; H, 7.16; N, 4.89 Calcd for $C_{16}H_{21}N_1S_2$: C, 65.93; H, 7.26; N, 4.81. ^{13}C-NMR ($CDCl_3$). Trans: δ=50.82 (C2), 37.38 (C4, C6), 36.46 (C5). Cis: δ=50.01 (C2), 35.49 (C4, C6), 30.12 (C5). MS (*m/z*) 291 (M^+).

*[2-(*p*-Cyanophenyl)-5-hexyl-1,3-dithiane (**7-27**)]*: Yield, 47%.

Found: C, 66.47; H, 7.51; N, 4.69. Calcd for $C_{17}H_{23}N_1S_2$: C, 66.83; H, 7.59; N, 4.59 MS (*m/z*) 305 (M^+).

*[2-(*p*-Cyanophenyl)-5-heptyl-1,3-dithiane (**7-32**)]*: Yield, 42%.

Found: C, 67.58; H, 7.90; N, 4.35. Calcd for $C_{18}H_{25}N_1S_2$: C, 67.66; H, 7.89; N, 4.38. MS (*m/z*) 319 (M^+).

*[2-(*p*-Cyanopenyl)-5-octyl-1,3-dithane (**7-36**)]*: Yield, 49%.

Found: C, 68.72; H, 8.06; N, 4.12. Calcd for $C_{19}H_{27}N_1S_2$: C, 68.42; H, 8.16; N, 4.20. MS (*m/z*) 333 (M^+).

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