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Liquid Crystal Materials with Sulfur Atoms Incorporated in the Principal Structure 2. New Liquid Crystal Compounds; 2-Substituted-5-(*p*-substituted phenyl)-1,3-dithianes

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2-Substituted-5-(*p*-substituted phenyl)-1,3-dithianes (**8**), new liquid crystals, were synthesized. The mesomorphic properties of these compounds were compared with those of the corresponding 2-(*p*-substituted phenyl)-5-alkyl-1,3-dithianes (**9**). The main difference found between these two liquid-crystal compounds was that some of **8** exhibited both monotropic nematic and smectic liquid-crystal phases but **9** exhibited only the monotropic nematic phase. This difference seems to originate in somewhat increased lateral interactions between molecules. Even for the three-ring compounds, many of them exhibited the monotropic liquid-crystal behavior. This should mean that these 1,3-dithiane compounds strongly tend to exhibit the monotropic liquid-crystal behavior.

In recent years, 2,5-disubstituted 1,3-dithianes and 1,3-oxathianes have been reported as new types of liquid-crystal materials.[1,2] Since these structures are quite novel as liquid crystals, we wish to report information on a further synthesis of 2-substituted-5-(*p*-substituted phenyl)-1,3-dithianes and to compare their liquid-crystal behavior with that of the 2-(*p*-substituted phenyl)-5-alkyl-1,3-dithianes previously reported.

Results and Discussion

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

In the synthesis of **2**, both esterification and etherification were done in one step. In step **2**→**3**, it was necessary to keep the reaction temperature at 190—200 °C for about 30 min under a reduced pressure (15 mmHg (1 mmHg=133.322 Pa)) for the complete evolution of carbon monoxide. This evolution of CO allowed us to check and control the progress of the reaction.

In step **4**→**5**, PBr_3 must be used for *p*-ethoxy compounds to prevent the cleavage of the ether bond, but in the case of *p*-methyl compounds $HBr-H_2SO_4$ could be used under conventional conditions. **8** was purified mostly by means of recrystallizations from hexane. Those compounds which could not be purified by recrystallization were purified first by column chromatography, then by recrystallization from hexane until only a single spot in TLC was obtained.

Thus synthesized **8**, were all colorless and odorless crystals or powders which were soluble in common organic solvents.

Absorption of C2 and C4, C6 carbons of the 1,3-dithiane 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=47.46 and 37.06, respectively, for a 1,3-dithiane ($R=C_2H_5O$, $R'=C_7H_{15}$). According to Eliel, in the 1,3-dithiane substituted at the C2 carbon by the methyl group, the equatorial isomer absorbs at about 5 ppm lower field than the axial isomer does.[3] Since this compound exhibits liquidcrystal phases and any absorption does not exist between δ 47.46 and 63.39, it should be the pure equatorial isomer without contamination with the axial one.

Mesomorphic ranges of the synthesized 2-substituted-5-(*p*-substituted phenyl)-1,3-dithiane **8** and the corresponding 2-(*p*-substituted phenyl)-5-alkyl-1,3-dithiane **9** are given in Table 1.

Measurements of the mesomorphic ranges and the assignment of the mesophases were carried out by means of a micro melting-point apparatus equipped with polarizers. To decide on the type of smectic phase, a comparison was made of these smectic phases with the color photography found in the literature.[4]

The difference between **8** and **9** are : (1) Some of **8** exhibited smectic A, but **9** not at all and (2) **8** exhibited liquid-crystal phases down to temperatures lower than those corresponding to **9**.

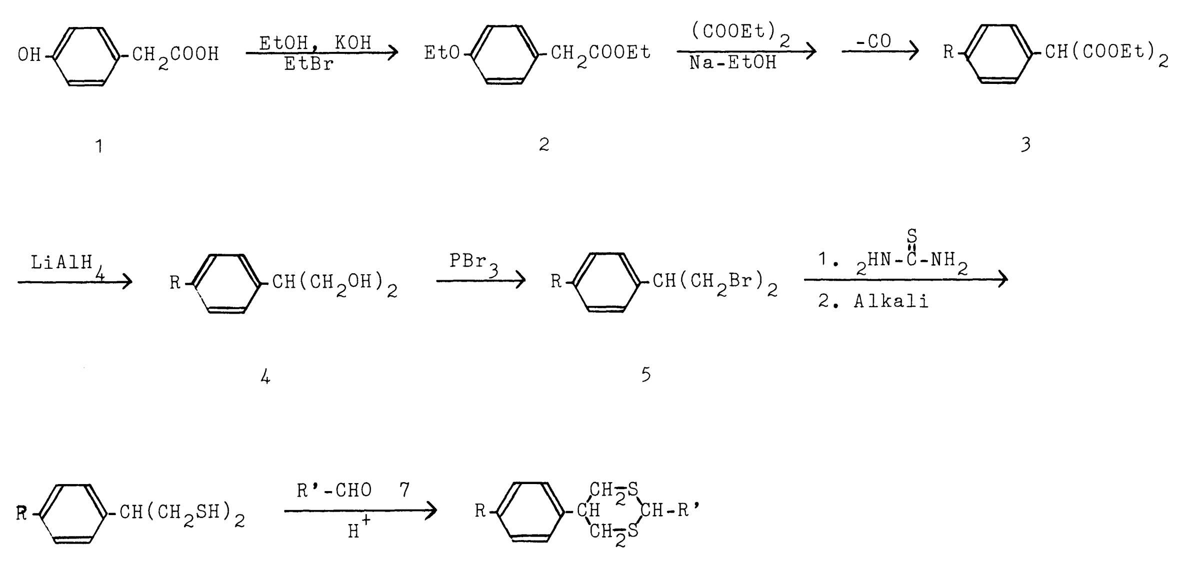
Generally, the smectic phase appears by increasing the attractive side interactions between molecules. The difference in structure between **8** and **9** involves the position of the sulfur atoms. This difference seems to increase side interactions between **8**. That is, in **9**, S-atoms are located more closely to the benzene ring than in **8**, so that the steric effect which decreases lateral interactions seems to become more effective.

Since sulfur atoms are located more closely to the electron-withdrawing benzene ring in **9** than in **8**, this electron withdrawal might be responsible for the lower dipole moment and dispersion force of the C–S bond. In **8**, C–S bonds are more distant from the benzene ring than in the case of **9**, so that this diminishing effect may be very small. Therefore, lateral interactions in **9** should be smaller than those in **8**.

ΔH_{C-I} of the compound **8-5** and **8-6** are 4.97 kcal/mol (1 cal=4.184 J) and 5.90 kcal/mol, and ΔS_{C-I} of them are 15.0 cal/mol/K 17.6 cal/mol/K respectively. These values are somewhat smaller than those of other common liquid-crystal materials.[5]

Even in the three-ring compounds, many of them exhibit the monotropic liquid-crystal behavior. This fact indicates that the 1,3-dithiane compounds of the present study strongly tend to exhibit the monotropic liquid-crystal behavior.

Three-ring compounds having the 5-(*p*-ethoxyphenyl) group (**8-8**, **-10**, **-11**) have a stronger tendency to



R: OC_2H_5, CH_3.
R′: C_2H_5, n-C_3H_7, n-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}, n-C_8H_{17}, $C_6H_4OC_2H_5$(p-), $C_6H_4OC_3H_7{}^n$(p-), $C_6H_4OC_4H_9{}^n$(p-), $C_6H_4OC_5H_{11}{}^n$(p-), $C_6H_4CH_3$(p-), C_6H_4CN(p-).

Fig. 1.

exhibit the enantiotropic liquid-crystal behavior than those having the 5-(p-methylphenyl) group (**8-13**, **-14**, **-15**). All of **8** which do not exhibit any liquid-crystal phases exhibited remarkable supercooling states. This property is common to both **8** and **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. Mesomorphic phases and the transition temperature were determined by means of both a Mitamura Riken micro melting-point apparatus equipped with polarizers and a differential scanning calorimeter. The rate of cooling was fixed to 1 °C/min.

Diethyl p-*Ethoxyphenylmalonate (3).* A conventional procedure was used for the syntheses of **3**.[6] Yield 60—70% Bp 160—163 °C/3—5 mmHg IR ($CHCl_3$) 2850—3000 (alkyl), 1740 (C=O), 1600 (Ar), 1260 (ether) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=1.3 (q, 9H, CH_3), 3.9—4.5 (m, 6H, O-CH_2), 4.6 (s, 1H, CH), 6.8—7.6 (q, 4H, ArH).

Diethyl p-*Methylphenylmalonate (3′).* Yield 50—60% Bp 137—140 °C/5—8 mmHg IR ($CHCl_3$) 2850—3000 (alkyl), 1740 (C=O), 1600 (Ar) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=1.25 (t, 6H, CH_2-CH_3), 2.3 (s, 3H, CH_3), 4.25 (q, 4H, O-CH_2), 4.6 (s, 1H, CH), 7.2 (s, 4H, ArH).

*2-(*p-*Ethoxyphenyl)-1,3-propanediol (4).* $LiAlH_4$-reduction of **3** in ether at 35 °C for 18 h provided **4**. Yields ranged from 90 to 95%. IR ($CHCl_3$) 3600 (OH), 2850—3000 (alkyl), 1605 (Ar), 1250 (ether) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ= 1.4 (t, 3H, CH_3), 2.5—4.3 (m, 9H, CH_2-O, CH, OH), 7.05 (q, 4H, ArH).

*2-(*p-*Methylphenyl)-1,3-propanediol (4′).* Yield 90%. IR ($CHCl_3$) 3600 (OH), 2850—3000 (alkyl), 1600 (Ar) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=2.3 (s, 3H, CH_3), 2.5—4.0 (m, 7H, CH_2-O, OH), 7.2 (s, 4H, ArH).

*2-(*p-*Ethoxyphenyl)-1,3-dibromopropane (5).* To a solution of PBr_3 (0.03 mol), anhyd benzene (10 ml), and pyridine (0.8 g) cooled in an ice bath were added, dropwise, a solution of **4** (0.04 mol), anhyd benzene (10 ml), and pyridine (0.3 g) (30 min.). The solution was kept at 0—5 °C for 1 h, then at 30—40 °C for 15 h. The reaction mixture was poured into ice water (400 ml) and extracted twice with ether (400 ml). The extract was washed with cold water, dried over anhyd Na_2SO_4, and evaporated *in vacuo* at 30 °C.

Yield 53%. IR ($CHCl_3$) 2800—3000 (alkyl), 1600 (Ar), 1250 (ether) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=1.4 (t, 3H, CH_3), 3.0—4.5 (m, 7H, CH_2-O, CH_2-Br, CH), 7.0 (q, 4H, ArH).

*2-(*p-*Methylphenyl)-1,3-dibromopropane (5′).* To a solution of 48% HBr (50g) and concd H_2SO_4 (15 g) cooled in an ice bath were added successively **4′** (0.1 mol) and concd H_2SO_4 (25g). The solution was kept at 95—100 °C for 18 h. The reaction mixture was then poured into water (200g). The mixture was stirred for a while 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 a transparent liquid in a 50% yield.

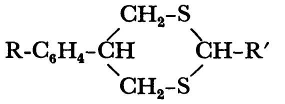
Bp 125—130 °C/1 mmHg. IR ($CHCl_3$) 2850-3000 (alkyl), 1600 (Ar) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=2.3 (s, 3H, CH_3), 2.8—4.0 (m, 5H, CH_2, CH), 7.2 (s, 4H, ArH).

*2-(*p-*Ethoxyphenyl)-1,3-propanedithiol (6).* To a solution of thiourea (0.064 mol, 4.9 g) in triethylene glycol (8 ml) kept at 75 °C was added **5** (0.016 mol) under the nitrogen atmosphere followed by stirring at 75 °C for 18 h.

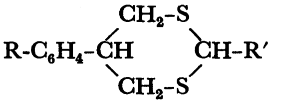
Tetraethylenepentamine (0.016 mol, 3.03 g) was then added, and the mixture was stirred at 75 °C for 2 h under the nitrogen atmosphere. The reaction mixture was poured into ice water (200 g) and extracted twice with ether (each 300 ml). The extract was dried over anhyd Na_2SO_4, and evaporated *in vacuo* at 30 °C.

Yield 55%. IR ($CHCl_3$) 2800—3000 (alkyl), 1600 (Ar), 1250 (ether) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=1.0—1.7 (m, 5H, SH, CH_3), 2.9 (s, 4H, CH_2-S), 3.0—3.6 (m, 1H, CH), 4.05 (q, 2H,

TABLE 1. TRANSITION TEMPERATURE OF COMPOUNDS 8 AND THE CORRESPONDING 2-(*p*-ETHOXYPHENYL)-5-ALKYL-1,3-DITHIANES

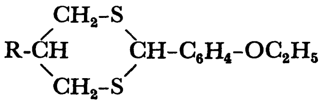


(**8**)



(**8**)

	R	R′	Transition temp /°C[a)]
8-1	OC_2H_5	C_2H_5	$C \underset{21}{\overset{56}{\rightleftarrows}} I$
8-2	OC_2H_5	n-C_3H_7	$C \underset{28}{\overset{96}{\rightleftarrows}} I$
8-3	OC_2H_5	n-C_4H_9	$C \underset{22}{\overset{67}{\rightleftarrows}} I$
8-4	OC_2H_5	n-C_5H_{11}	$C \underset{48}{\overset{55}{\rightleftarrows}} I$
8-5	OC_2H_5	n-C_6H_{13}	$\begin{tikzcd} C \arrow[rrr, "58"] & & & I \arrow[dl, shift left] \\ & S_A \arrow[ul, "12"'] \arrow[r, shift right, "27"'] & N \arrow[l, shift right] \arrow[ur, shift left, "46"'] & \end{tikzcd}$
8-6	OC_2H_5	n-C_7H_{15}	$\begin{tikzcd} C \arrow[rrr, "63"] & & & I \arrow[dl, shift left] \\ & S_A \arrow[ul, "17"'] \arrow[r, shift right, "27"'] & N \arrow[l, shift right] \arrow[ur, shift left, "52"'] & \end{tikzcd}$
8-7	OC_2H_5	n-C_8H_{17}	$\begin{tikzcd} C \arrow[rrr, "66"] & & & I \arrow[dl, shift left] \\ & S_A \arrow[ul, "41"'] \arrow[r, shift right, "43"'] & N \arrow[l, shift right] \arrow[ur, shift left, "53"'] & \end{tikzcd}$
8-8	OC_2H_5	$C_6H_4OC_2H_5(p\text{-})$	$C \underset{176}{\overset{176}{\rightleftarrows}} N \underset{195}{\overset{195}{\rightleftarrows}} I$
8-9	OC_2H_5	$C_6H_4OC_3H_7{}^n(p\text{-})$	$\begin{tikzcd} C \arrow[rr, "173"] & & I \arrow[dl, shift left] \\ & N \arrow[ul, "167"'] \arrow[ur, shift left, "173"'] & \end{tikzcd}$
8-10	OC_2H_5	$C_6H_4OC_4H_9{}^n(p\text{-})$	$C \underset{148}{\overset{148}{\rightleftarrows}} N \underset{182}{\overset{182}{\rightleftarrows}} I$
8-11	OC_2H_5	$C_6H_4OC_5H_{11}{}^n(p\text{-})$	$C \underset{126}{\overset{126}{\rightleftarrows}} N \underset{175}{\overset{175}{\rightleftarrows}} I$
8-12	OC_2H_5	$C_6H_4CH_3$	$\begin{tikzcd} C \arrow[rr, "165"] & & I \arrow[dl, shift left] \\ & N \arrow[ul, "132"'] \arrow[ur, shift left, "165"'] & \end{tikzcd}$
8-13	CH_3	$C_6H_4OC_4H_9{}^n(p\text{-})$	$\begin{tikzcd} C \arrow[rr, "170"] & & I \arrow[dl, shift left] \\ & N \arrow[ul, "110"'] \arrow[ur, shift left, "156"'] & \end{tikzcd}$
8-14	CH_3	$C_6H_4OC_5H_{11}(p\text{-})$	$\begin{tikzcd} C \arrow[rr, "146"] & & I \arrow[dl, shift left] \\ & N \arrow[ul, "121"'] \arrow[ur, shift left, "142"'] & \end{tikzcd}$
8-15	CH_3	$C_6H_4CN(p\text{-})$	$\begin{tikzcd} C \arrow[rr, "180"] & & I \arrow[dl, shift left] \\ & N \arrow[ul, "142"'] \arrow[ur, shift left, "160"'] & \end{tikzcd}$



(**9**)

2-(*p*-Ethoxyphenyl)-5-alkyl-1,3-dithiane

	R	Transition temp /°C[a)]
9-1[b)]	n-C_4H_9	$C \underset{35}{\overset{75}{\rightleftarrows}} I$
9-2	n-C_5H_{11}	$C \underset{35}{\overset{57}{\rightleftarrows}} I$
9-3	n-C_6H_{13}	$\begin{tikzcd} C \arrow[rr, "64"] & & I \arrow[dl, shift left] \\ & N \arrow[ul, "32"'] \arrow[ur, shift left, "43"'] & \end{tikzcd}$
9-4	n-C_7H_{15}	$\begin{tikzcd} C \arrow[rr, "70"] & & I \arrow[dl, shift left] \\ & N \arrow[ul, "49"'] \arrow[ur, shift left, "57"'] & \end{tikzcd}$

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

CH_2-O), 7.0 (q, 4H, ArH).

2-(p-Methylphenyl)-1,3-propanedithiol (6′). Yield 66% IR ($CHCl_3$) 2800—3000 (alkyl), 1600 (Ar) cm^{-1}. ^1H-NMR ($CDCl_3$) δ=0.9—1.5 (m, 2H, SH), 2.3 (s, 3H, CH_3), 2.5—3.7 (m, 5H, CH, CH_2-S), 7.1 (s, 4H, ArH).

2,5-Disubstituted 1,3-Dithianes (8). To a solution of **6** (0.004 mol) and aldehyde **7** (0.004 mol) in anhyd $CHCl_3$ (200 ml) cooled in an ice bath were added BF_3-$(C_2H_5)_2O$ (0.5 g) and Molecular Sieve (3A, 1/15; 3g). The mixture was stirred at 0—5 °C for 8 h and then at 20—25 °C for 18h. 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 alumina column chromatography to collect the hexane-benzene=1 : 1 eluate.

Upon evaporation of the eluate *in vacuo*, the residue was purified by recrystallization from hexane.

2-Alkyl-5-(p-ethoxyphenyl)-1,3-dithianes. IR ($CHCl_3$) 2800—3000 (alkyl), 1600 (Ar), 1250 (ether) cm^{-1}. ^1H-NMR ($CDCl_3$) δ=0.7—2.0 (m, alkyl), 2.6—3.4 (m, 5H, CH_2-S, CH), 3.8—4.3 (m, 3H, CH_2-O, $^{S}_{S}\!\!>$CH-), 7.0 (q, 4H, ArH).

2-Ethyl-5-(p-ethoxyphenyl)-1,3-dithiane (8-1): Yield, 28%. Found: C, 62.51; H, 7.915. Calcd for $C_{14}H_{20}S_2O$: C, 62.71; H, 7.51%. MS (*m/z*) 268 (M^+).

2-Propyl-5-(p-ethoxyphenyl)-1,3-dithiane (8-2): Yield 27%. Found: C, 63.56; H, 7.55%. Calcd for $C_{15}H_{22}S_2O$: C, 63.78; H, 7.85%. MS (*m/z*) 282 (M^+).

2-Butyl-5-(p-ethoxyphenyl)-1,3-dithiane (8-3): Yield, 17%. Found: C, 64.94; H, 8.15%. Calcd for $C_{16}H_{24}S_2O$: C, 64.82; H, 8.16%. MS (*m/z*) 296 (M^+).

2-Pentyl-5-(p-ethoxyphenyl)-1,3-dithiane (8-4): Yield, 16%. Found: C, 65.97; H, 8.70%. Calcd for $C_{17}H_{26}S_2O_1$: C, 65.76; H, 8.44. MS (*m/z*) 310 (M^+).

2-Hexyl-5-(p-ethoxyphenyl)-1,3-dithiane (8-5): Yield, 15%. Found: C, 66.75; H, 8.68. Calcd for $C_{18}H_{28}S_2O$: C, 66.61; H, 8.70%. MS (*m/z*) 338 (M^+). ^{13}C-NMR ($CDCl_3$) δ=47.46 (C2), 37.06 (C4, C6), 42.86 (C5).

2-Heptyl-5-(p-ethoxyphenyl)-1,3-dithiane (8-6): Yield, 15%. Found: C, 67.17; H, 8.96%. Calcd for $C_{19}H_{30}S_2O$: C, 67.40; H, 8.93%. MS (*m/z*) 338 (M^+). NMR ($CDCl_3$) δ=47.46 (C2), 37.06 (C4, C6), 42.86 (C5).

2-Octyl-5-(p-ethoxyphenyl)-1,3-dithiane (8-7): Yield, 21%. Found: C, 68.01; H, 9.17%. Calcd for $C_{20}H_{32}S_2O$: C, 68.13; H, 9.15%. MS (*m/z*) 352 (M^+).

2-(p-Alkoxyphenyl)-5-(p-ethoxyphenyl)-1,3-dithiane. IR ($CHCl_3$) 2800—3000 (alkyl), 1600 (Ar), 1250 (ether) cm^{-1}. ^1H-NMR ($CDCl_3$) δ=0.7—2.0 (m, -OH_2C-$\underline{R}$), 2.8—3.5

(m, 5H, CH_2-S, CH), 4.0 (m, 4H, CH_2-O), 5.25 (s, 1H, $^{S}_{S}{>}$CH-), 6.8—7.7 (m, 8H, ArH).

*2,5-Bis(*p*-ethoxyphenyl)-1,3-dithiane (**8-8**)*: Yield, 28%. Found: C, 66.58 ;H, 6.71%. Calcd for $C_{20}H_{24}S_2O_2$: C, 66.63; H, 6.71%. MS (*m*/*z*) 360 (M^+).

*2-(*p*-Propoxyphenyl)-5-(*p*-ethoxyphenyl)-1,3-dithiane (**8-9**)*: Yield, 47%. Found: C, 67.38; H, 7.16%. Calcd for $C_{21}H_{26}S_2O_2$: C, 67.34; H, 7.00%. MS (*m*/*z*) 374 (M^+).

*2-(*p*-Butoxyphenyl)-5-(*p*-ethoxyphenyl)-1,3-dithiane (**8-10**)*: Yield, 39%. Found: C, 67.70; H, 7.29%. Calcd for $C_{22}H_{28}S_2O_2$: C, 68.00; H, 7.26%. MS (*m*/*z*) 388 (M^+).

*2-(*p*-Pentyloxyphenyl)-5-(*p*-ethoxyphenyl)-1,3-dithiane (**8-10**)*: Yield, 31%. Found: C, 68.36; H, 7.81%. Calcd for $C_{23}H_{30}S_2O_2$: C, 68.61; H, 7.51%. MS (*m*/*z*) 402 (M^+).

*2-(*p*-Methoxyphenyl)-5-(*p*-ethoxyphenyl)-1,3-dithiane (**8-12**)*: Yield, 38%. IR ($CHCl_3$) 2800—3000 (alkyl), 1605 (Ar), 1250 (ether) cm^{-1}. ^1H-NMR ($CDCl_3$) δ 1.45 (t, 3H, OCH_2-C$\underline{H}_3$), 2.4 (s, 3H, CH_3), 2.7—3.5 (m, 5H, CH_2-S, CH), 4.05 (q, 2H, OCH_2), 5.25 (s, 1H, $^{S}_{S}{>}$CH-), 6.8—7.7 (m, 8H, ArH). Found: C, 68.76; H, 7.02%. Calcd for $C_{19}H_{22}S_2O$: C, 69.05; H, 6.71%. MS (*m*/*z*) 330 (M^+).

*2-(*p*-Alkoxyphenyl)-5-(*p*-methylphenyl)-1,3-dithiane.* IR ($CHCl_3$) 2800—3000 (alkyl), 1600 (Ar), 1250 (ether) cm^{-1}. ^1H-NMR ($CDCl_3$) δ=0.7—2.0 (m, OCH_2-$\underline{R}$), 2.3 (s, 3H, CH_3), 2.8—3.5 (m, 5H, CH_2-S, CH), 4.0 (t, 2H, CH_2-O), 5.25 (s, 1H, $^{S}_{S}{>}$CH), 6.8—7.6 (m, 8H, ArH).

*2-(*p*-Butoxyphenyl)-5-(*p*-methylphenyl)-1,3-dithiane (**8-13**)*: Yield, 42%. Found: C, 70.59; H, 7.28%. Calcd for $C_{21}H_{26}S_2O_1$: C, 70.36; H, 7.31%. MS (*m*/*z*) 358 (M^+).

*2-(*p*-Pentyloxyphenyl)-5-(*p*-methylphenyl)-1,3-dithiane (**8-14**)*: Yield, 47%. Found: C, 70.67; H, 7.48%. Calcd for $C_{22}H_{28}S_2O$: C, 70.92; H, 7.58%. MS (*m*/*z*) 372 (M^+).

*2-(*p*-Cyanophenyl)-5-(*p*-methylphenyl)-1,3-dithiane (**8-15**)*: Yield, 15%. IR ($CHCl_3$) 2800—3000 (alkyl), 2220 (CN), 1600 (Ar) cm^{-1}. ^1H-NMR ($CDCl_3$) δ=2.3 (s, 3H, CH_3), 2.5—3.5 (m, 5H, CH_2-S, CH), 5.25 (s, 1H, $^{S}_{S}{>}$CH), 7.2 (s, 4H, Ar$\underline{H}$-CH_3), 7.7 (s, 4H, Ar$\underline{H}$-CN). Found: C, 69.02; H, 5.51; N, 4.53%. Calcd for $C_{18}H_{17}NS_2$: C, 69.41; H, 5.50; N, 4.50%. MS (*m*/*z*) 311 (M^+).

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