Synthesis, Characterization, and Anodic Oxidation of Selected Norbornyl Dithioethers[1]

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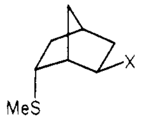
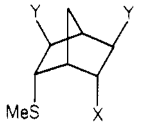
Both 2-*exo*- and 2-*endo*-[(methylthio)methyl]-6-*endo*-(methylthio)bicyclo[2.2.1]heptane (**1a** and **2a**, respectively) were prepared by standard methods. Treatment of episulfide **3** with sulfur dichloride followed by reduction and alkylation afforded 2-*endo*,6-*endo*-bis(methylthio)-3-*exo*,5-*exo*-dichlorobicyclo[2.2.1]heptane (**2d**). The structure of **2d** was unequivocally established by X-ray crystallographic analysis. An interesting feature of the structure of **2d** is the unusually short S···S nonbonded distance of 3.179 (1) Å. Electrochemical oxidation of **1a**, **2a**, and **2d** was studied by using cyclic voltammetric and rotating-disk techniques. Anodic oxidation of **2a** is almost 600 mV easier than that of its isomer **1a** because of intramolecular interaction between the two sulfur atoms in **2a** but not **1a** on oxidation. The vertical ionization potentials for the nonbonding sulfur 3p lone-pair electrons were determined by photoelectron spectroscopy for **1a**, **2a**, and **2d**.

It has been hypothesized that suitable electron-rich groups held proximate to the sulfur atom of a divalent sulfide would facilitate oxidation of the sulfide.[2] Such facilitation by neighboring alcohol and carboxylate groups has been demonstrated for 2-*endo*-substituted 6-*endo*-(methylthio)bicyclo[2.2.1]heptanes.[3] Similarly, certain medium-sized-ring dithioethers, e.g., 1,5-dithiacyclooctane, undergo anodic oxidation with exceptional ease.[4] This has been ascribed to transannular bond formation between the two sulfur atoms. In addition, 1,5-dithiacyclooctane, unlike most aliphatic thioethers, undergoes reversible electrochemical oxidation. Because of the interesting behavior of medium-sized-ring dithioethers, norbornyl derivatives with appended methylthio groups were sought. This paper reports the synthesis of such norbornyl derivatives, their electrochemistry, and photoelectron and charge-transfer spectra. In addition, the crystal and molecular structure of one of these compounds determined by single-crystal X-ray crystallographic techniques is also presented.

Two methods were found for preparing 2-*exo*-[(methylthio)methyl]-6-*endo*-(methylthio)bicyclo[2.2.1]heptane (**1a**). In method A, reduction of the known thiol ester **1b**[5] with chloroaluminum hydride[6] produces **1a** in 23% yield. Similar reductions of thiol esters to the corresponding thioethers have been reported.[7] Method B is based on the procedure for making unsymmetrical sulfides from alcohols and thiols effected by an aminophosphonium salt.[8] By use of this method the known alcohol **1c**[5] was transformed into **1a** in 33% yield.



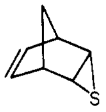
1a, X = CH_2SMe
b, X = COSMe
c, X = CH_2OH



2a, X = CH_2SMe; Y = H
b, X = COSMe; Y = H
c, X = CH_2OH; Y = H
d, X = SMe; Y = Cl

Three methods were investigated for the synthesis of 2-*endo*-[(methylthio)methyl]-6-*endo*-(methylthio)bicyclo[2.2.1]heptane (**2a**). Reduction of the known thiol ester **2b** by method A did not give significant amounts of **2a**. Method B applied to the known alcohol **2c**[5] afforded **2a** in 11% yield. Treatment of alcohol **2c** with dimethyl disulfide and tri-*n*-butylphosphine (method C) produced **2a** in 19% yield. This method has previously been reported for converting alcohols into unsymmetrical sulfides.[9]

The key step in the synthesis of 2-*endo*,6-*endo*-bis(methylthio)-3-*exo*,5-*exo*-dichlorobicyclo[2.2.1]heptane (**2d**) is reaction of the known episulfide **3**[10] with sulfur dichloride.[11] The presumed product of this reaction is disulfide **4** which on reduction with lithium aluminum hydride and methylation afforded **2d** in an overall yield of 18%. The structure of **2d** was unequivocally established by an X-ray crystallographic structure study. A stereoview of the molecule is shown in Figure 1.



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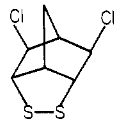

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Some interesting structural features of **2d** were revealed by the X-ray study. The intramolecular S···S nonbonded distance of 3.179 (1) Å is unusually short.[12] Since this separation is considerably less than twice the van der Waals radius of sulfur,[13] there is considerable steric strain in the molecule. A relatively large symmetrical contra twist, C(+−),[5,14] of the norbornyl skeleton minimizes the S···S nonbonded interaction. Viewed down the C(1)–C(4) vector, C(3) is located clockwise (+) from C(2), and C(5) is located counterclockwise (−) from C(6). The C(1)–C(2)–C(3)–C(4) and C(4)–C(5)–C(6)–C(1) torsional angles

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[1] Presented in part at the 181st National Meeting of the American Chemical Society, Atlanta, GA, Apr 1, 1981; Abstract ORGN 146.

[2] Glass, R. S.; Williams, E. B., Jr.; Wilson, G. S. *Biochemistry* **1974**, *13*, 2800.

[3] Glass, R. S.; Duchek, J. R.; Klug, J. T.; Wilson, G. S. *J. Am. Chem. Soc.* **1979**, *99*, 7349.

[4] Wilson, G. S.; Swanson, D. D.; Klug, J. T.; Glass, R. S.; Ryan, M. D.; Musker, W. K. *J. Am. Chem. Soc.* **1979**, *101*, 1040. Ryan, M. D.; Swanson, D. D.; Glass, R. S.; Wilson, G. S. *J. Phys. Chem.* **1981**, *85*, 1069.

[5] Glass, R. S.; Duchek, J. R.; Prabhu, U. D. G.; Setzer, W. N.; Wilson, G. S. *J. Org. Chem.* **1980**, *45*, 3640.

[6] Eliel, E. L. *Rec. Chem. Prog.* **1961**, *22*, 129. Ashby, E. C.; Prather, J. *J. Am. Chem. Soc.* **1966**, *88*, 729.

[7] Bublitz, D. E. *J. Organomet. Chem.* **1966**, *6*, 436. Bublitz, D. E. *J. Org. Chem.* **1967**, *32*, 1630.

[8] Tanigawa, Y.; Murahashi, S.-I.; Moritami, I. *Tetrahedron Lett.* **1975**, 4655.

[9] Nakagawa, I.; Hata, T. *Tetrahedron Lett.* **1975**, 1409.

[10] Lautenschlaeger, F. *J. Org. Chem.* **1969**, *34*, 3998.

[11] McCabe, P. H.; Stewart, A. *J. Chem. Soc., Chem, Commun.* **1980**, 100.

[12] Guru Row, T. N.; Parthasarathy, R. *J. Am. Chem. Soc.* **1981**, *103*, 477.

[13] The van der Waals radius of sulfur is 1.85 Å: Pauling, L. "The Nature of the Chemical Bond"; 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

[14] Altona, C.; Sundaralingam, M. *J. Am. Chem. Soc.* **1970**, *92*, 1995.

0022-3263/82/1947-2761$01.25/0

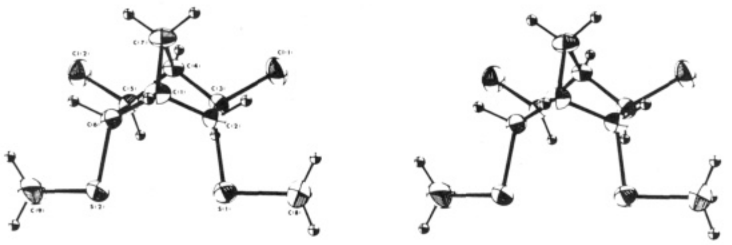

Figure 1. ORTEP[23] stereoview of dithioether **2d**. The hydrogen atoms have been assigned arbitrary thermal parameters. Thermal ellipsoids are drawn to enclose 30% of the probability distribution.

are 8.0° and −8.0°, respectively. This distortion is necessarily symmetrical because C(1), C(4), and C(7) are located in a crystallographic mirror plane. The increased C(2)–C(1)–C(6) bond angle of 114.9 (3)° also lessens S⋯S interaction. The direction of approach of the two closely spaced sulfur atoms is also of interest. One sulfur atom approaches the other approximately 90° from the perpendicular to the C–S–C plane and along the extension of the CH_3–S vector. Because of the crystallographic mirror plane through C(1), C(4), and C(7) the direction of approach of each sulfur atom toward the other is necessarily identical. Thus this compound shows a type IIIa S⋯S contact.[12]

Cyclic voltammetry of **2a** and **2d** show irreversible two-electron diffusion-controlled oxidation at 0.63 and 0.75 V, respectively, at a scan rate of 100 mV/s. Cathodic peaks are seen for both compounds at scan rates greater than 100 mV/s at potentials at least 30 mV negative to the anodic peak. Controlled-potential electrolysis establishes that both compounds undergo two-electron oxidations. Rotating-disk experiments demonstrate that the process is diffusion controlled and gives diffusion coefficients of 9.8 $\times 10^{-6}$ and 8.3 $\times 10^{-6}$ cm^2/s for **2a** and **2d**, respectively. Cyclic voltammetry of **1a** shows two oxidation peaks at 1.21 and 1.36 V. No cathodic peak is seen.

For insight into the electrochemical oxidations the vertical ionization potentials for these compounds were determined by photoelectron spectroscopy. These values for **1a** and **2a** are 8.36 and 8.35 eV, respectively. The photoelectron spectrum of **2d** shows two bands which correspond to ionization potentials of 8.40 and 8.68 eV. This splitting is due to sulfur–sulfur lone-pair interaction. Although the sulfur–sulfur distance in **2d** is unusually short, the sulfur–sulfur lone pair interaction is relatively modest as shown by the 0.28-eV splitting in the photoelectron spectrum.[15] Because the 3p orbital on one sulfur atom is parallel with that of the other sulfur atom, modest overlap results despite their proximity. Previous work[16] has shown that for aliphatic sulfides vertical ionization potentials determined by photoelectron spectroscopy and peak maxima for charge-transfer bands linearly correlate. Therefore, the peak maxima for the charge-transfer band of the complexes formed between **1a**, **2a**, and **2d** with tetracyanoethylene were measured. These peak maxima are 19 460, 19 230, and 20 490 cm^{-1}, respectively.

The vertical ionization potentials for **1a** and **2a**, as determined by photoelectron spectroscopy, are nearly the same. In addition, the peak maxima for the charge-transfer band of their respective complexes with tetracyanoethylene occur at comparable frequencies. Nevertheless, the electrochemical oxidation of **2a** is almost 600 mV easier than that of its isomer **1a**. This result is presumably due to direct intramolecular interaction between the two sulfur atoms in the course of electron transfer involving **2a** and/or the cation radical of **2a** but not **1a** where such interaction is geometrically precluded. Comparable intramolecular bonding between the transannular sulfur atoms in the cation radicals obtained by chemical oxidation of certain mesocyclic dithioethers has been reported.[17] Such bonding between the sulfur atoms in the cation radical of **2a** formed during the photoelectron spectroscopic measurement apparently does not occur. This is expected because, in accord with the Franck–Condon principle, the short time scale of this measurement does not permit the extensive movement of atoms required for such interaction. Interaction between sulfur atoms apparently occurs on anodic oxidation of 2,7-dithiaoctane, the acyclic analogue of **2a**, as surmised from its oxidation potential of 0.67 V.[16] Oxidation of **2d** occurs more easily than that of simple aliphatic sulfides due to intramolecular interaction between the sulfur atoms. However, **2d** oxidizes less readily than its acyclic analogue 2,6-dithiaheptane for which Ep = 0.66 V[16] owing to the electron-withdrawing inductive effect of the chlorine atoms.

Experimental Section

All melting points and boiling points are uncorrected. IR spectra were obtained on a Perkin-Elmer Model 137 spectrometer. ^1H NMR spectra were measured at 60 MHz with a Varian T-60 NMR spectrometer on samples containing tetramethylsilane as an internal standard. A Varian Model 1720 gas chromatograph equipped with a 0.25 in. × 6 ft 10% SE-30 on Chromosorb W column was used for GC studies. Mass spectra were measured with a Varian MAT 311A mass spectrometer equipped with a Varian SS-200 data system. Elemental microanalysis was performed by analysts at Atlantic Microlab, Inc., Atlanta, GA. For preparative layer chromatography, silica gel HF-254 (Type 60), supplied by Brinkmann Instruments, Inc. (E. Merck HF-254), was used. Column chromatography was done by using silica gel (70–230 mesh) supplied by ICN Pharmaceuticals, Inc.

Anhydrous *N*,*N*-dimethylformamide was prepared by distillation of the reagent grade material from calcium hydride. Dry 1,2-dimethoxyethane was secured by distillation of reagent grade material from sodium metal and benzophenone. Spectroquality dichloromethane obtained from Matheson Coleman and Bell was further purified by sequential washing with 5% aqueous sodium carbonate solution and water and then distilled from phosphorus pentoxide. Tetracyanoethylene obtained from Aldrich Chemical Co. was twice recrystallized from dichloromethane and then sublimed at 100 °C (1 mm).

Preparation of 2-*exo*-[(Methylthio)methyl]-6-*endo*-(methylthio)bicyclo[2.2.1]heptane (1a). Method A.[7] A solution (3.15 mL) of anhydrous aluminum chloride (0.226 g, 1.69

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(15) Setzer, W. N.; Coleman, B. R.; Wilson, G. S.; Glass, R. S. *Tetrahedron* **1981**, *37*, 2743.

(16) Coleman, B. R.; Glass, R. S.; Setzer, W. N.; Prabhu, U. D. G.; Wilson, G. S. "Biochemistry of Aliphatic Thioethers"; American Chemical Society: Washington, DC; *Adv. Chem. Ser.*, in press. For determining ionization potentials of aliphatic sulfides from transition energies for charge-transfer complexes with tetracyanoethylene see also: Moreau, W. M.; Weiss, K. *Nature (London)* **1965**, *208*, 1203. Bock, H.; Wagner, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 150.

(17) Musker, W. K.; Wolford, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3055. Musker, W. K.; Wolford, T. L.; Roush, P. B. *Ibid.* **1978**, *100*, 6416. Musker, W. K. *Acc. Chem. Res.* **1980**, *13*, 200.

mmol) in anhydrous ethyl ether was added dropwise to a solution (2.24 mL) of lithium aluminum hydride (64.4 mg, 1.69 mmol) in anhydrous ethyl ether. After this mixture was heated at reflux under a nitrogen atmosphere for 1 h, a solution of thiol ester **1b** (0.304 g, 1.41 mmol) in anhydrous ethyl ether (5 mL) was added and the mixture heated at reflux for 3 h. The mixture was allowed to stand overnight at room temperature. Sufficient 10% aqueous hydrochloric acid solution was cautiously added, with ice-bath cooling, to make the mixture acidic. The layers were separated, and the organic phase was washed successively with water, saturated aqueous sodium bicarbonate solution, water, and brine. Concentration gave a residue which on preparative layer chromatography afforded **1a** (64 mg, 23%) identical with material prepared by Method B by ^{1}H NMR, TLC, and GC analysis.

Method B.[8] A sample of sodium hydride in a mineral oil dispersion (50%, 100 mg, 2.0 mmol) was washed with dried petroleum ether and suspended in anhydrous *N*,*N*-dimethylformamide (4 mL). A solution of alcohol **1c** (310 mg, 1.80 mmol) in anhydrous *N*,*N*-dimethylformamide (8 mL) was then added. The reaction mixture was placed in an oil bath maintained at 60 °C and stirred under a nitrogen atmosphere for 75 min. The heating bath was removed and a solution of (methylphenylamino)triphenylphosphonium iodide[18] (891 mg, 1.80 mmol) in anhydrous *N*,*N*-dimethylformamide (9 mL) was added dropwise. The heating bath was returned and heating continued for 1 h. The reaction mixture was then cooled to room temperature, saturated with methanethiol, and stirred at room temperature for 48 h. After exposure to water aspirator pressure to remove the excess methanethiol, the reaction mixture was diluted with water and extracted several times with ethyl ether. The ether extracts were combined, washed successively with 0.1 M aqueous hydrochloric acid solution and brine, dried with anhydrous sodium sulfate, filtered, and concentrated on a rotary evaporator. The residue was triturated with petroleum ether and filtered, and the filtrate was concentrated and chromatographed on a layer of silica gel by eluting with benzene/petroleum ether (3:1) to give **1a**: 93 mg (26%); IR (neat) 2935, 2910, 2860, 2840, 1470, 1430, 1310, 1240, 960 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.6–3.3 (m with s at 2.07 and 2.13); mass spectrum, *m/e* 202 (P), 155, 154, 139, 107, 106, 61.

Anal. Calcd for $C_{10}H_{18}S_2$: C, 59.35; H, 8.97; S, 31.69. Found: C, 59.55; H, 8.68; S, 31.76.

Preparation of 2-*endo*-[(Methylthio)methyl]-6-*endo*-(methylthio)bicyclo[2.2.1]heptane (2a). Method A.[7] Significant amounts of **2a** were not obtained by treatment of **2b** with the reagent prepared from lithium aluminum hydride and aluminum chloride by using the procedure reported for the preparation of **1a** by method A.

Method B.[8] A sample of sodium hydride in mineral oil dispersion (50%, 25 mg, 0.50 mmol) was washed with dried petroleum ether and suspended in anhydrous *N*,*N*-dimethylformamide (0.5 mL). A solution of alcohol **2c** (52 mg, 0.30 mmol) in anhydrous *N*,*N*-dimethylformamide (1.5 mL) was then added. The reaction mixture was placed in an oil bath maintained at 60 °C and stirred under a nitrogen atmosphere for 1.5 h. The heating bath was removed and a solution of (methylphenylamino)triphenylphosphonium iodide[18] (149 mg, 0.30 mmol) in anhydrous *N*,*N*-dimethylformamide (1.0 mL) added dropwise. The heating bath was returned and heating continued for 1.5 h. The reaction mixture was then cooled to room temperature, saturated with methanethiol, and stirred at room temperature for 60 h. The workup was the same as that reported for the preparation of **1a** by method B and gave **2a** (7 mg, 11%) identical with that prepared by method C by ^{1}H NMR and TLC.

Method C.[9] A sample of endo alcohol **2c** (0.52 g, 3.0 mmol), dimethyl disulfide (2.7 mL, 30 mmol) distilled from calcium hydride, and tri-*n*-butylphosphine (7.5 mL, 30 mmol) were stirred at room temperature for 37 h under a nitrogen atmosphere. Elution of the reaction mixture from a silica gel column (200 g, 24 × 55 cm) with benzene/petroleum ether (3:1) followed by preparative layer chromatography with benzene/petroleum ether (3:1) as the eluant and distillation afforded **2a**: 112 mg (18%); IR (neat) 2955, 2915, 2875, 1460, 1435, 1305, 1240, 1190, 955 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.7–3.4 (m with s at 2.13 and 2.17); mass spectrum, *m/e* 202 (P), 187, 155, 139, 107, 79, 61.

Anal. Calcd for $C_{10}H_{18}S_2$: C, 59.35; H, 8.97; S, 31.69. Found: C, 59.39; H, 8.97; S, 31.62.

Preparation of 2-*endo*,6-*endo*-Bis(methylthio)-3-*exo*,5-*exo*-dichlorobicyclo[2.2.1]heptane (2d). A solution of sulfur dichloride (0.64 mL, 6.2 mmol) in methylene chloride (10 mL) was added dropwise to a well-stirred solution of episulfide **3** (1.24 g, 10.0 mmol), prepared according to the method of Lautenschlaeger,[10] in methylene chloride (20 mL) cooled in a dry ice–acetone bath. After completion of the addition, the cooling bath was removed and the reaction mixture stirred for 1 h after warming to room temperature. The reaction mixture was then poured onto ice–water and extracted with chloroform. The layers were separated, and the organic phase was washed successively with water, saturated aqueous sodium bicarbonate solution, water, and brine. Concentration of the organic layer gave a viscous residue (2.55 g). A portion of this residue (1.36 g) dissolved in dry 1,2-dimethoxyethane (12 mL) was added dropwise to a suspension of lithium aluminum hydride (0.63 g, 16.6 mmol) in dry 1,2-dimethoxyethane (20 mL) under a nitrogen atmosphere and cooled in an ice–water bath. The reaction mixture was allowed to warm to room temperature and was stirred at this temperature for 21 h. The reaction mixture was then placed in an ice–water bath, and methyl iodide (8 mL, 130 mmol) was added carefully. After being stirred for 24 h, the reaction mixture was concentrated on a rotary evaporator and ice-cold 3 M aqueous hydrochloric acid solution added to the residue. The mixture was extracted (2×) with ethyl ether, and the combined organic extracts were washed successively with water, saturated aqueous sodium bicarbonate solution, water, and brine, dried (Na_2SO_4), and concentrated to a yellow viscous liquid. Elution of this material by benzene/petroleum ether (1:1) from a silica gel column gave **2d**: 0.25 g (18%); mp 95–96.5 °C; IR (KBr) 2955, 2915, 1465, 1425, 1310, 1295, 1280, 1210, 950, 930, 885, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.8–2.1 (br, 2 H, H7), 2.20 (s, 6 H, SMe), 2.6–2.7 (br, 1 H, H4), 2.7–3.0 (m, 1 H, H1), 3.20 (dd, $J_1 = J_2 = 4$ Hz, 2 H, H2, H6), 3.70 (d, $J = 4$ Hz, 2 H, H3, H5); mass spectrum, *m/e* (relative intensity) 256 (P, 31), 257 (3.7), 258 (23), 259 (2.6), 260 (5.2), 241 (100), 193, 157, 126, 108, 91, 65.

Anal. Calcd for $C_9H_{14}Cl_2S_2$: C, 42.02; H, 5.49; S, 24.93. Found: C, 42.01; H, 5.50; S, 24.88.

X-ray Single Crystal Structure Study of 2d. Clear, colorless crystals of **2d** were obtained by slow evaporation of a saturated solution of the compound in pentane. A well-formed crystal, sealed in a quartz capillary, was mounted on a Syntex P2$_1$ automatic diffractometer equipped with a scintillation counter and Mo Kα radiation with a graphite monochromator. The automatic centering, indexing, and least-squares routines were carried out on 25 reflections to obtain the cell dimensions which are given in Table I. The θ–2θ scan technique over the range $4° \leq 2\theta \leq 50°$ was used to collect the data of which those with $I \geq 3\sigma(I)$ were considered observed and were used in the calculations. The data were reduced to F_o^2 and $\sigma(F_o^2)$. Lorenz and polarization factors were applied to all reflections.

The structure was solved by the direct-methods program MULTAN.[19] The positions of all nonhydrogen atoms were obtained from an "E map" based on the highest combined figure-of-merit value and the lowest residual index. The structures were refined by full-matrix least-squares techniques[20] by using neutral atom scattering factors for all species,[21] leading to isotropic convergence at $R = 0.151$ and anisotropic convergence at $R = 0.065$. The hydrogen atoms were located from electron-density difference maps and were added to the model in geometrically ideal positions. The hydrogen atom thermal parameters were set according to $B_H = B_N + 1$, where N is the atom to which H is bonded. The hydrogen atom parameters were not refined. Several cycles of

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(18) Tanigawa, Y.; Kanamaru, H.; Sonoda, A.; Murahashi, S.-I. *J. Am. Chem. Soc.* **1977**, *99*, 236, footnote 2.

(19) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

(20) The major programs used during the structure determination were FORDAP (Fourier summation program by A. Zalkin) and NUCLS (structure factor calculations and full-matrix least-squares refinement by J. Ibers, adapted from ORFLS by W. R. Bussing, K. O. Martin, and H. A. Levy).

(21) Scattering factors were obtained from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71–98.

Table I. Crystal Data[a] for 2d

molecular formula	$C_9H_{14}S_2Cl_2$
molecular weight	257.22
space group	*Pnma* (No. 62)[b]
a,[c] Å	9.483 (1)
b,[c] Å	17.879 (3)
c,[c] Å	7.137 (1)
V,[c] Å^3	1210.1 (3)
Z	4
d_{obsd},[d] g cm^{-3}	1.404 (10)
d_{calcd}, g cm^{-3}	1.412
crystal color, shape	colorless, plate
crystal dimensions, mm	0.3 × 0.3 × 0.6
no. of unique data	1040
no. of data used in the calculations	710
abs coef (μ_λ), cm^{-1}	8.20

[a] The standard deviation of the least significant figure is given in parentheses. [b] Based upon systematic absences: $0kl$; $k + l \neq 2n$; $hk0$, $h \neq 2n$; $h00$, $h \neq 2n$; $0k0$, $k \neq 2n$, $00l$, $l \neq 2n$. These systematic absences are also consistent with the space group $Pna2_1$ (No. 33), but the structure could be solved only in the space group *Pnma*. [c] Cell dimensions were obtained from a least-squares refinement of setting angles of 25 reflections in the 2θ range from 4.6° to 28.2°. [d] The density was determined by the flotation method by using aqueous sodium iodide solution.

anisotropic refinement led to convergence with $R = 0.039$, $R_w = 0.051$, and GOF = 2.14.

Cyclic Voltammetry. Voltammograms were measured on solutions approximately 10^{-3} M in **1a**, **2a**, or **2d** and 0.1 M in sodium perchlorate, which served as the supporting electrolyte, in acetonitrile (Matheson Coleman and Bell, spectrograde, water content 0.003%) with a Ag/0.1 M $AgNO_3$ in acetonitrile reference electrode. A 1.0-cm^2 platinum flag, which was heated to incandescence in a flame prior to each run, served as the working electrode. The electrochemical apparatus was assembled and used in a Vacuum Atmospheres Model HE-113-210 drybox equipped with an HE-493 Dri-Train purification system. The electrochemical instrumentation, data acquisition, and data processing systems have been described previously.[22]

Photoelectron Spectroscopy. Photoelectron spectra were measured by using a McPherson 36 spectrometer fitted with a He(I) source chamber. All spectra were measured by using argon (15.76 eV) as a single internal standard. The resolution was less than 30 meV. Calibration with methyl iodide showed the energy scale to deviate less than 10 meV from linearity over a range of binding energies from 9 to 17 eV. Instrument drift was controlled at less than 10 meV. The spectra represent a time-averaged sum of individual scans through a binding energy range of 10 eV stored in 500 data channels. Dithioether **2d** was heated to 60 °C inside the spectrometer to increase volatility.

Charge-Transfer Spectroscopy. An approximately 5-mg sample of **1a** or **2a**, after collection from GC, or **2d**, after recrystallization, was dissolved in a 4.3×10^{-3} M solution of tetracyanoethylene (0.5 mL) in a quartz microcell of 1-cm path length. The visible absorption spectrum (330–700 nm) of each of these solutions was measured by using a Cary 219 recording spectrophotometer.

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Registry No. 1a, 81583-59-7; **1b**, 74080-76-5; **1c**, 64937-43-5; **2a**, 81623-53-2; **2c**, 64887-95-2; **2d**, 81583-60-0; **3**, 22061-73-0; **4**, 81583-61-1.

Supplementary Material Available: Stereoscopic view of the packing of the molecules in the unit cell of **2d** and tables of final atomic positional and thermal parameters, bond lengths, bond angles, and selected torsion angle data for **2d** (5 pages). Ordering information is given on any current masthead page.

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(22) Langhus, D. L.; Wilson, G. S. *Anal. Chem.* **1979**, *51*, 1139.

(23) Johnson, C. K. "ORTEP"; Oak Ridge National Laboratory: Oak Ridge, TN.