41.2, 28.2, 26.4, 23.9, 23.6, 21.7, 21.6, 14.7, 14.6; IR (KBr) 3303, 3272, 1734, 1623, 1470, 1437, 1324, 1306, 1159, 1094, 742 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 224 (4.53), 282 (3.90), 290 (3.82); MS (CI), *m/z* 313 (MH^+), 311.241; ms (EI), *m/z* 312.1486 (100, 312.1474 calcd for $C_{18}H_{20}N_2O_3$), 239 (78), 237 (51), 184 (80). Anal. Calcd for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.97. Found: C, 69.13; H, 6.49; N, 8.94.

(12b*S*)-4-Oxo-1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizine (27). A solution of the ester **26** (100 mg, 0.32 mmol), lithium chloride (27 mg, 0.64 mmol), H_2O (~7 μL), and dimethyl sulfoxide (2.0 mL) was heated at 160 °C for 3.5 h.[42] The reaction mixture was cooled and concentrated in vacuo and the residue was partitioned between H_2O and $CHCl_3$. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (3× 30 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated, and purification of the residue by flash chromatography (HF 254 TLC-grade silica; 3% MeOH–CH_2Cl_2) gave 56 mg (73%) of **27** as a yellow solid. Recrystallization from MeOH afforded pure **27** as pale yellow needles: mp 247–248.5 °C; lit.[19e] mp 250 °C; $[\alpha]^{25}{}_{D}$ −239° (*c* 1.12, $CHCl_3$); lit.[43] $[\alpha]^{25}{}_{D}$ −232° (*c* 1.02, $CHCl_3$).

(12b*S*)-Ethyl 4-Oxo-3-(phenylthio)-1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizine-3-carboxylate (28). To a solution of 0.50 M lithium diisopropylamide (0.50 mL, 0.25 mmol, in THF) and dry THF (1.0 mL) at −78 °C under argon was added a solution of the tetracycle **26** (79.2 mg, 0.25 mmol) and dry THF (1.5 mL), and the resulting solution was maintained at −78 °C for 10 min and then at 0 °C for 20 min. The reaction mixture was then cooled to −45 °C and a solution of benzenethiosulfonate[44] (62.0 mg, 0.25 mmol) and dry THF (1.5 mL) was added dropwise over 10 min. The resulting cloudy mixture was stirred for 2 h and then quenched by addition of saturated aqueous NH_4Cl (20 mL). The aqueous phase was extracted with ethyl acetate (3 × 30 mL), and the combined organic extracts were washed with 1 M aqueous $NaHCO_3$ (50 mL) and brine (50 mL), dried (Na_2SO_4), and concentrated. Purification of the residue by radial chromatography[46] (GF 254 silica gel, 2-mm plate; 0.5% MeOH–0.2% Et_3N–99.3% CH_2Cl_2) afforded 102 mg (98%) of chromatographically pure **28** (a mixture of diastereomers) as a pale yellow solid, which was suitable for use in the next step. For characterization purposes these diastereomers were separated by preparative TLC (silica gel, 1% MeOH–99% CH_2Cl_2, three elutions). Diastereomer A: mp 220–221 °C (from ethyl acetate); $[\alpha]^{25}{}_{D}$ −73.0° (*c* 0.20, EtOH); ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (br s, indole NH), 7.64 (d, *J* = 7.0 Hz, 2 H, aromatic), 7.51 (d, *J* = 7.7 Hz, 1 H, aromatic), 7.40 (d, *J* = 7.3 Hz, 1 H, aromatic), 7.29–7.42 (m, 3 H, aromatic), 7.18 (t, *J* = 7.2 Hz, 1 H, aromatic), 7.13 (t, *J* = 7.2 Hz, 1 H, aromatic), 5.20 (dd, *J* = 11.4, 4.0 Hz, C-6 H_{eq}), 4.62 (dd, *J* = 11.6, 4.3 Hz, C-12_b H_{ax}), 4.13 (q, *J* = 7.1 Hz, OCH_2CH_3), 2.73–2.92 (m, 3 H, C-6 H_{ax} and C-7 H), 2.30–2.40 (m, 2 H), 2.04–2.13 (m, 1 H), 1.72–1.84 (m, 1 H), 1.15 (t, *J* = 7.1 Hz, OCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 166.1, 138.2, 136.9, 133.1, 131.1, 130.4, 129.3, 127.4, 123.0, 120.7, 119.2, 111.6, 110.4, 63.1, 60.7, 55.1, 41.8, 31.5, 27.4, 21.6, 14.6. Diastereomer B: $[\alpha]^{24}{}_{D}$ −8.4° (*c* 0.34, EtOH); ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (br s, indole NH), 7.55 (d, *J* = 7.0 Hz, 2 H, aromatic), 7.52 (d, *J* = 7.7 Hz, 1 H, aromatic), 7.35 (d, *J* = 8.0 Hz, 1 H, aromatic), 7.19–7.33 (m, 4 H, aromatic), 7.15 (t, *J* = 7.4 Hz, 1 H, aromatic), 5.13 (m, 1 H, C-6 H_{eq}), 4.88 (br t, *J* = 7.2 Hz, C-12_b H_{ax}), 4.22–4.32 (m, 2 H, OCH_2CH_3), 2.83–2.96 (m, 2 H, C-7 H), 2.72–2.81 (m, C-6 H_{eq}), 2.45 (ddd, *J* = 13.9, 10.1, 3.8 Hz, 1 H), 2.20–2.35 (m, 2 H), 1.9 (ddd, *J* = 13.8, 6.6, 3.6 Hz, 1 H), 1.30 (t, *J* = 7.1 Hz, OCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 165.6, 137.7, 136.8, 133.2, 131.1, 130.2, 129.3, 127.6, 123.0, 120.7, 119.1, 111.7, 110.8, 63.2, 62.5, 54.8, 42.2, 294, 25.6, 21.6, 14.8. Mixture of diastereomers: $[\alpha]^{25}{}_{D}$ −50.9° (*c* 0.84, EtOH); IR (KBr) 3330, 3296, 3059, 2979, 2920, 2849, 1727, 1624, 1438, 1304, 1220, 1188, 1025, 741, 692 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 224 (4.60), 274 (3.97), 290 (sh, 3.84); MS (CI), *m/z* 421 (MH^+), 314, 313, 311, 111; MS (EI), *m/z* 420.1489 (0.5%, 420.1507 calcd for $C_{24}H_{24}N_3O_3S$), 265 (100%), 184 (21%), 169 (22%). Anal. Calcd for $C_{24}H_{24}N_2O_3S$: C, 68.55; H, 5.75; N, 6.66. Found: C, 67.80; H, 5.82; N, 6.55.

(12b*S*)-Ethyl 4-Oxo-1,4,6,7,12,12b-hexahydroindolo[2,3-*a*]-quinolizine-3-carboxylate (8). To a solution of the sulfide **28** (305 mg, 0.720 mmol) and dry CH_2Cl_2 (20 mL) at −78 °C was added a solution of *m*-chloroperbenzoic acid (197 mg, ~70%, 0.80 mmol) and dry CH_2Cl_2 (10 mL). The cloudy mixture was stirred for 1.5 h at −78 °C and then warmed to −30 °C. After 15 min at −30 °C, freshly distilled Et_3N (147 mg, 1.45 mmol) was added and the cloudy reaction mixture immediately became homogeneous. The resulting solution was then warmed to 0 °C and quenched by pouring into a separatory funnel containing 1 M aqueous $NaHCO_3$ (50 mL) and ethyl acetate (50 mL). The aqueous phase was extracted with ethyl acetate (2 × 50 mL), and the combined organic extracts were washed with 1 M aqueous $NaHCO_3$ (50 mL), dried (Na_2SO_4), and concentrated to a volume of approximately 50 mL. This solution was heated at 80 °C for 45 min and then allowed to cool to room temperature. Concentration of this solution to ~10 mL and immediate flash chromatography (230–400-mesh silica gel, activity IV, 12 g; 24 mm i.d. column; 3:2 ethyl acetate–hexane) yielded 164 mg (74%) of chromatographically pure (−)-**8** as a pale orange glass: mp 233–235 °C. Due to the instability of this intermediate, it must be used immediately if optimum results in the cuprate coupling sequence are to be obtained. Chromatographically purified (−)-**8** showed melting points which ranged from 198 to 233 °C in various runs.

Acknowledgment. This project was supported by NIH Grant GM-30859 and a Senior Scientist Award to L.E.O. from the Alexander von Humboldt Foundation. NMR and mass spectra were determined at Irvine with spectrometers purchased with the assistance of NSF Shared Instrumentation grants. We particularly wish to thank Dr. Thomas A. Malone for his early work on this project, Professor A. B. Smith, III for providing experimental details for the preparation of cuprate **13b**, and Professor E. Winterfeldt for providing a sample of geissoschizine and comparison spectra for methyl geissoschizoate and **18b**.

The Trifulvathiane System

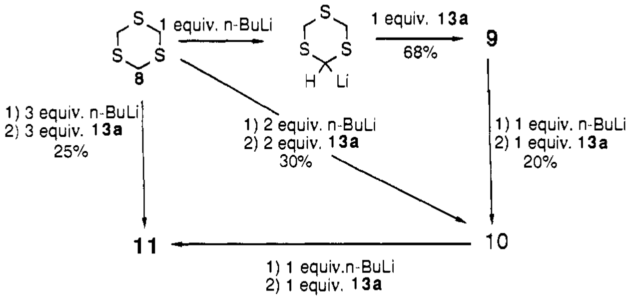
Robert R. Schumaker, Sundaramoorthi Rajeswari, Makarand V. Joshi, Michael P. Cava,* Mohammad A. Takassi, and Robert M. Metzger*

Contribution from the University of Alabama, Department of Chemistry, Tuscaloosa, Alabama 35487-9671. *Received September 30, 1987.*
Revised Manuscript Received August 4, 1988

Abstract: Permethylated monofulvathiane, difulvathiane, and trifulvathiane were synthesized by reacting *s*-trithiane with *N*-butyllithium and 1, 2, or 3 equiv, respectively, of the tetraphenylborate of either 4,5-dimethyl-1,3-dithia-2-imminium or the 4,5-dimethyl-1,3-dithia-2-methylthiolium ions. The MNDO calculated ionization potentials of the fulvathianes support the prediction that they should be as easy to oxidize as tetrathiafulvalene, but cyclic voltammetry (CV) shows significant shifts in the solution redox potentials. EPR solution spectra of the radical ions were obtained.

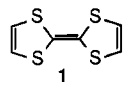
The synthesis of interesting organic one-electron donors and acceptors in the last 30 years has concentrated on flat (or almost flat) molecules of D_{2h} symmetry (or C_i symmetry approaching D_{2h} symmetry). Thus, high conductivity compounds, or quasi-

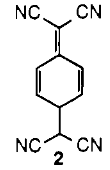
Scheme I



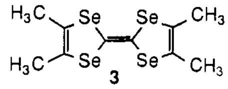
one-dimensional metals,[1] were obtained, e.g., with the 1:1 charge-transfer salt[2] of the donor tetrathiafulvalene[3] (TTF, **1**) and the acceptor 7,7,8,8-tetracyanoquinodimethan[4] (TCNQ, **2**). The first organic superconductors[5] were the so-called Bechgaard salts of the type $TMTSF_2X$, where TMTSF is the almost flat donor tetramethyltetraselenafulvalene, **3** and X is an inorganic anion. The first sulfur-based organic superconductor,[6] the salt ET_2ReO_4, is based on the somewhat nonplanar donor bis(ethylenedithiolene)tetrathiafulvalene[7] (BEDT-TTF, or ET, **4**). The present record-holder in organic superconductivity[8] is $ET_2Cu(SCN)_2$, with critical temperature 10.4 K. The close approach of TTF neutral molecules and TTF^+ cations along one stack (and of TCNQ molecules and $TCNQ^-$ anions along another stack) is the dominant interaction which explains the high conductivity of TTF TCNQ above 60 K; however, below that temperature a Peierls instability causes an incommensurate transition to a semiconducting state. In the Bechgaard salts this transition is suppressed (presumably by Se···Se interactions between neighboring stacks) so that a transition to a superconducting state becomes accessible. In the ET salts the nonplanarity of the donors prevents π–π stack formation, and the dominant interactions that permit high electronic conductivity are thought to be strong interstack S···S interactions (so that even in the normal regime the ET salts are two-dimensional conductors).

A major thrust in the study of such "lower-dimensional" solids has been the search for novel donors and acceptors, in the hope of discovering new and exciting solid-state properties. One intriguing possibility is to break away from the D_{2h} symmetry of donors and/or acceptors. Several years ago Fukunaga[9] synthesized a TCNQ-inspired molecule with D_{3h} symmetry, hexacyanotrimethylenecyclopropane (**5**) in the form of the dianion and the monoanion salts. Similarly, Watson and coworkers[10] have reported **6**, but no mention of electrochemical properties was made. For some cyclic structures containing four, five, and six dithiolidine units, see ref 11–13.

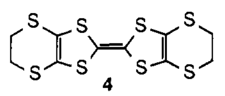

1

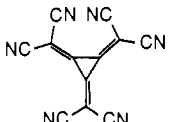


2

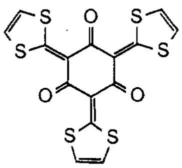


3


4

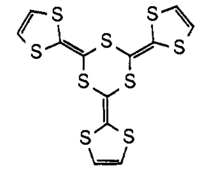


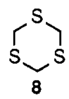
5

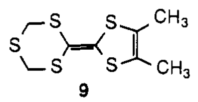


6

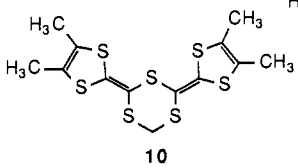
Here we report the first example of a S-π C heterocyclic ring system which can be considered as a tris-dithiafulvalenoid derivative of *s*-trithiane and accordingly could be called 2,4,6-tris(1′3′-dithiol-2′-ylidene)-1,3,5-trithiane or trifulvathiane (TFT, **7**). Starting from the known compound 1,3,5-trithiacyclohexane, or *s*-trithiane (T3, **8**), we have prepared three novel compounds: (i) dimethylmonofulvathiane or 2-(4′,5′-dimethyl-1′,3′-dithiol-2′-ylidene)-1,3,5-trithiane (T5, **9**), (ii) tetramethyldifulvathiane or 2,4-bis(4′,5′-dimethyl-1′,3′-dithiol-2′-ylidene)-1,3,5-trithiane (T7, **10**), and (iii) hexamethyltrifulvathiane or 2,4,6-tris(4′,5′-dimethyl-1′,3′-dithiol-2′-ylidene)-1,3,5-trithiane (T9, **11**). For comparisons of electrochemical properties, we have also prepared 2-(4′,5′-dimethyl-1′,3′-dithiol-2′-ylidene)-1,3-dithiane (T4, **12**). Both **8** and **11** are presumed to have C_{3v} symmetry, and the salts of **11** might be expected to have interesting electronic properties.


7

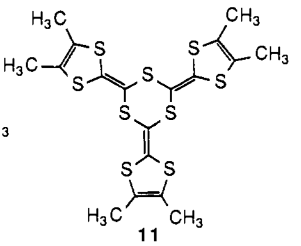

8



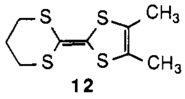
9



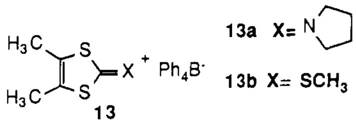
10



11

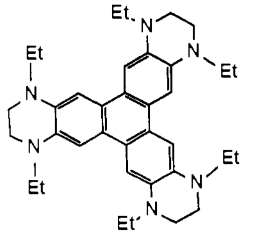


12

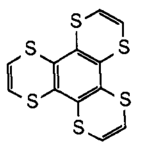


13

Other groups, interested in the possibility of preparing an organic ferromagnet, have prepared several other donor molecules with 3-fold symmetry, e.g., **14**[14] and **15**.[15-16]



14


15

---

[1] For a recent overview of work in this field, see: "Proceedings of the International Conference on Science and Technology of Synthetic Metals, Kyoto, Japan," *Synthetic Metals*; 1987; Vol. 19.

[2] (a) Ferraris, J.; Cowan, D. O.; Walatka, V., Jr.; Perstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948. (b) Miles, M. G.; Wilson, J. D.; Cohen, M. H. U.S. Patent 3 799 814. (c) Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heeger, A. J. *Solid State Commun.* **1973**, *12*, 1125. (d) Thomas, G. A. et al. *Phys. Rev. B* **1976**, *13*, 5105. (e) Cohen, M. J.; Coleman, L. B.; Garito, A. F.; Heeger, A. J. *Phys. Rev. B* **1976**, *13*, 5111.

[3] Wudl, F.; Smith, G. M.; Hufnagel, E. J. *Chem. Commun.* **1970**, 1453.

[4] (a) Acker, D. S.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Melby, L. R.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1960**, *82*, 6408. (b) Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370.

[5] (a) Bechgaard, K.; Jacobson, C. S.; Mortensen, K.; Pedersen, H. J.; Thorup, N. *Solid State Commun.* **1980**, *33*, 1119. (b) Jerome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. *J. Phys. Lett.* **1980**, *41*, L95.

[6] (a) Parkin, S. S. P.; Engler, E. M.; Schumaker, R. R.; Lagier, R.; Lee, V. Y.; Scott, J. C.; Greene, R. L. *Phys. Rev. Lett.* **1983**, *50*, 270. (b) Williams, J. M.; Beno, M. A.; Wang, H. H.; Leung, P. C. W.; Emge, T. J.; Geiser, U.; Carlson, K. D. *Acc. Chem. Res.* **1985**, *18*, 261.

[7] Mizuno, M.; Garito, A. F.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1978**, *18*.

[8] Urayama, T.; Yamochi, H.; Saito, G.; Nozawa, K.; Sugano, T.; Kinoshita, M.; Sato, S.; Oshima, K.; Kawamoto, A.; Tanaka, J. *Chem. Lett.* **1988**, 55.

[9] (a) Fukunaga, T. *J. Am. Chem. Soc.* **1976**, *98*, 601–11. (b) Fukunaga, T.; Gordon, M. D.; Krusic, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 611–613.

[10] Kimura, M.; Watson, W. H.; Nakayama, J. *J. Org. Chem.* **1980**, *45*, 3719–3721.

[11] Sugimoto, T.; Awaji, H.; Misaki, Y.; Yoshida, Z.; Kai, Y.; Nakagawa, H.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 5792.

[12] Sugimoto, T.; Misaki, Y.; Kajita, T.; Yoshida, Z.-I.; Kai, Y.; Kasai, N. *J. Am. Chem. Soc.* **1987**, *109*, 4106–4107.

[13] Sugimoto, T.; Misaki, Y.; Arai, Y.; Yamamoto, Y.; Yoshida, Z.-I. *J. Am. Chem. Soc.* **1988**, *110*, 628–629.

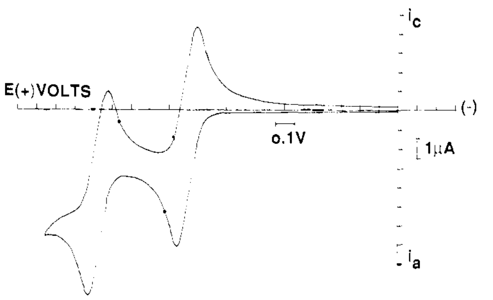


Figure 1. Cyclic voltammogram for **12**(T4): solvent: CH_2ClCH_2Cl; supporting electrolyte: 0.1 M $(n\text{-}C_4H_9)_4NPF_6$; quasi-reference electrode: Ag|0.04 M $(C_4H_9)_4NI$ (DMF)||0.1 M $(n\text{-}C_4H_9)_4NPF_6$ (DMF); sensitivity 1 mA/cm; scan rate 0.050 V/s; for all CV runs the scan was started in the anodic direction. The peak potentials for the oxidation waves are at 1.33 and 1.71 V versus the quasi-reference electrode; the peak potentials for the reduction waves are at 1.64 and 1.25 V. Under similar conditions (but using the solvent CH_3CN instead of CH_2ClCH_2Cl) TTF (**1**) gave peaks in the oxidation waves at 0.96 and 1.35 V and peaks in the reduction waves at 1.28 and 0.89 V.

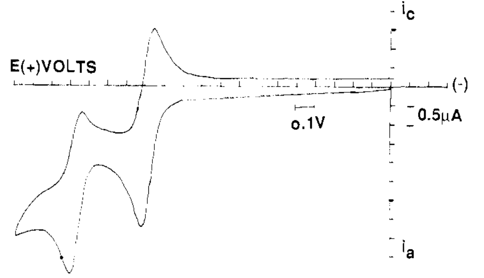


Figure 2. Cyclic voltammogram for **9** (T5): solvent: CH_2ClCH_2Cl; supporting electrolyte: 0.1 M $(n\text{-}C_4H_9)_4NPF_6$; quasi-reference electrode: Ag|0.04 M $(C_4H_9)_4NI$ (DMF)||0.1 M $(n\text{-}C_4H_9)_4NPF_6$ (DMF); sensitivity 0.5 mA/cm; sweep rate 0.050 V/s; the peak potentials for the oxidation waves are at 1.33 and 1.71 V versus the quasi-reference electrode; the peak potentials for the reduction waves are at 1.64 and 1.25 V.

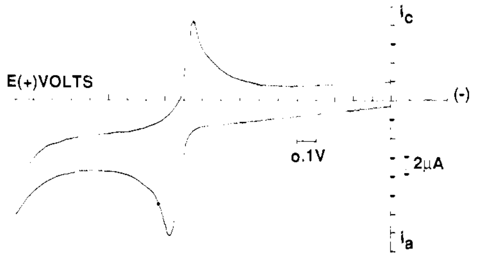


Figure 3. Cyclic voltammogram for **10** (T7): solvent: CH_2iCl_2; supporting electrolyte: 0.1 M $(n\text{-}C_4H_9)_4NPF_6$; quasi-reference electrode: Ag/0.04 M $(C_2H_5)_4NI$(DMF)||0.1 M $(n\text{-}C_4H_9)_4NPF_6$(DMF); sensitivity 2 mA/cm; sweep rate 0.050 V/s; the peak potentials for the reduction wave is at 1.18 V versus the quasi reference electrode; the peak potential for the oxidation wave is at 1.06 V.

Results

Synthesis. Our synthetic method (Scheme I) involved the formation of the anion[17,18] of *s*-trithiane and the reaction with either the 4,5-dimethyl-1,3-dithia-2-imminium cation **13a** or the 4,5-dimethyl-1,3-dithia-2-methylthiolium cation **13b**.[19-22] Spontaneous loss of amine or mercaptan provided the 2-ylidene

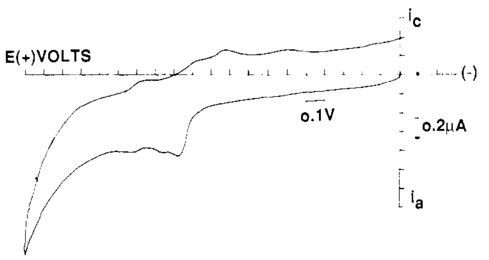


Figure 4. Cyclic voltammogram for **11** (T9): solvent: CH_2ClCH_2Cl; supporting electrolyte: 0.1 M $(n\text{-}C_4H_9)_4NPF_6$; quasi-reference electrode: Ag|0.04 M $(C_4H_9)_4NI$ (DMF)||0.1 M $(n\text{-}C_4H_9)_4NPF_6$ (DMF); sensitivity 0.2 mA/cm; sweep rate 0.050 V/s; the peak potentials for the oxidation waves are at 1.17, 1.26, and 1.40 V versus the quasi-reference electrode; the peak potentials for the reduction waves are at 1.35, 1.06, and 0.92 V.

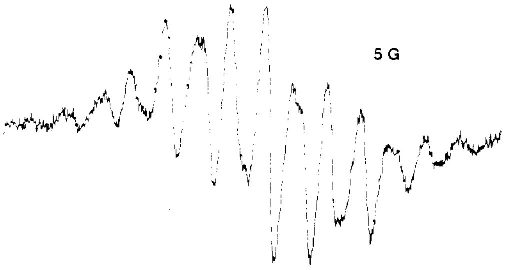


Figure 5. EPR spectrum of T4, molecule **12**.

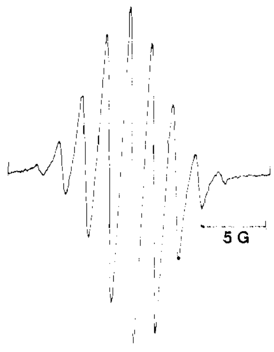


Figure 6. EPR spectrum of T5, molecule **9**.

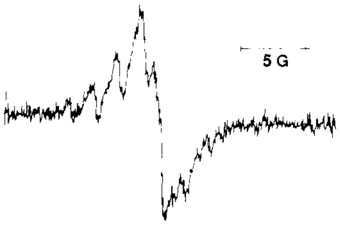


Figure 7. EPR spectrum of T7, molecule **10**.

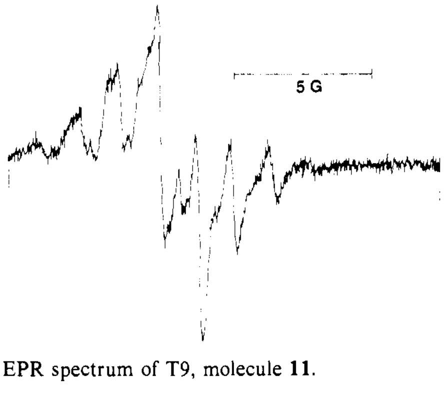


Figure 8. EPR spectrum of T9, molecule **11**.

---

[14] LePage, T. J.; Breslow, R. *J. Am. Chem. Soc.* **1987**, *109*, 6412–6421.

[15] Lapouyade, R.; Morand, J.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 223.

[16] Morand, J.-P.; Brzezinski, L.; Lapouyade, R.; Amiell, J.; Delhaes, P. *Mol. Cryst. Liq. Cryst.*, in press.

[17] Seebach, D.; Corey, E. J.; Beck, A. K. *Chem. Ber.* **1974**, *107*, 367.

[18] Seebach, D.; Beck, A. K. *Org. Synth.* **1970**, *51*, 39.

[19] Campaigne, E.; Jacobsen, N. W. *J. Org. Chem.* **1964**, *29*, 1703.

[20] Hiratani, K.; Shiono, H.; Okawara, M. *Chem. Lett.* **1973**, 867.

[21] Campaigne E.; Hamilton, R. D. *J. Org. Chem.* **1964**, *29*, 1711.

[22] 2-Thiomethyl-1,3-dithiolium iodide is commercially available.

Table I. Electrochemical and Theoretical Data for Fulvathianes[h]

fulvalenoids	oxidn half-wave potntls (V vs SCE) E_1	E_2	E_3	MNDO eigenvalues (eV) I_1	I_2	I_3	ioniztn potntl (eV) I_a, I_v, or I_e
TTF (**1**)	0.38[a]	0.77[a]		−8.08	−9.66	−10.59	8.08[b] 7.66[c] 6.85[d]
ET (**4**)	0.54	0.96					
T3 (**8**)				−10.00	−10.03	−10.05	10.00[b]
T4 (**12**)	0.57	1.03		−8.33	−9.67	−10.00	8.33[b]
T5 (**9**)	0.75	1.13		−8.60	−9.92	−9.98	8.60[b]
T7 (**10**)	0.60	0.60		−8.37	−8.76	−9.74	8.37[b]
T9 (**11**)	0.59	0.68	0.82	−8.15[e]	−8.66[e]	−8.67[e]	8.15[b]
				−8.11[f]	−8.39[f]	−8.71[f]	8.11[b]
				−8.10[g]	−8.41[g]	−8.71[g]	8.10[b]

[a] Measured in CH_3CN. [b] I_v = vertical ionization energy = $-I_1$. [c] I_a = adiabatic ionization energy (see text). [d] I_e = experimental ionization energy (from ref 24). [e] Chair form. [f] Boat form. [g] Boat form, fully symmetrical. [h] The redox half-wave potentials (all measured in CH_2ClCH_2Cl, except for TTF) are computed by subtracting 0.58 V from the oxidation peak potentials of Figures 1–4. The MNDO eigenvalues are the HOMO (I_1) and the second and third highest occupied molecular orbitals (I_2 and I_3). The ionization potentials are the vertical estimate, the adiabatic estimate, and the experimental value.

Table II. EPR Data for Fulvathianes

fulvalenoid radical anions	EPR g value (±0.0001)	no. of hyperfine lines (expected no.)	hyperfine splittings (G)
TTF^+ ($\mathbf{1}^+$)	2.0083,[a] 2.0081[b]	5 (5)[a,b]	1.26,[a] 1.22[b]
$T4^+$ ($\mathbf{12}^+$)	2.0085	11 (7, 7)	1.19
$T5^+$ ($\mathbf{9}^+$)	2.0085	8 (5, 6)	1.75
$T7^+$ ($\mathbf{10}^+$)	2.0075	8? (3, 13)	1.72?, 1.77?
$T9^+$ ($\mathbf{11}^+$)	2.0077	6? (19)	1.43?

[a] From ref 25. [b] From ref 26.

monofulvathiane **9** and, on repetition of the process, difulvathiane **10**. Although this initial stepwise approach via mono- and difulvathianes should have allowed for a mixture of chalcogenide or ring substituents within **7**, in practice it was observed that the intermediate 1,3-dithiol-2-ylidene moieties of **9** and **10** severely retarded subsequent anion formation.

Instead, hexamethyltrifulvathiane **11** was obtained in one synthetic step by treatment of trithiane **8** with 3 equiv of *n*-butyllithium, presumably generating the 1,3,5-trilithio anion which afforded **11** on addition of cations **13**. Although the yield for this process remains modest, Scheme I should make available for study a wide selection of symmetric trifulvathianes.

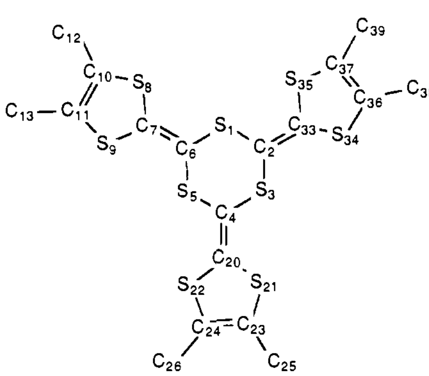
Cyclic Voltammetry. The cyclic voltammograms of T4, T5, T7, and T9 (**9–12**) are shown in Figures 1–4 and listed in Table I, which also gives the results of theoretical MNDO calculations. The EPR spectra of T4, T5, T7, and T9 (**9–12**) are given in Figures 5–8 and are summarized in Table II.

The CV of **12** and **9** consists of two well-separated, reversible waves, similar to the CV of **1**; the oxidation half-wave potentials $E_{1/2}$ are shifted to more positive values relative to **1**, suggesting molecules more difficult to oxidize; however, solubility problems forced the use of different solvents (1,2-dichloroethane for **9–12** but acetonitrile for **1**, since $\mathbf{1}^{2+}$ adsorbs at the electrode in 1,2-dichloroethane and causes a spike in the CV); also, such comparisons are valid only if the solvation enthalpies are comparable for molecules of vastly different sizes and shapes. The distinct increase in redox potentials of **9** (relative to **12**) is probably due to the transannular sulfur atom of **9**. The CV of **10** (Figure 3) shows a single, reversible, two-electron oxidation wave; the two-electron transfer was confirmed by a coulometry experiment. The CV of **11** (Figure 4) is not well resolved, but three quasi-reversible oxidation potentials are identifiable.

The first oxidation half-wave potentials of T4, T7, and T9 are very close to each other, while, as noted above, T5 seems more difficult to oxidize.

Theoretical Calculations. A series of MNDO calculations were performed, with geometry optimization, to calculate the best theoretical geometry of these various molecules. Although recent AM1 calculations in this laboratory have given excellent results,[23] such a calculation is not possible for the present sulfur-containing molecules, for which AM1 parameters do not exist. A judicious use was made of the potential molecular symmetry. Minor but insignificant differences were found between MOPAC 3.13 and MOPAC 4.0 results.

To test the validity of predictions based on MNDO, an effort was made to obtain the adiabatic ionization potential of TTF (known from experiment to be I_e = 6.85 eV):[24] the vertical estimate ($I_v = -I_1$ = 8.08 eV) is 1.23 eV too high; the difference in net energies between TTF and TTF^+ (run as a configuration interaction calculation using a doublet state) is I_a = 7.66 or 0.81 eV too high. Therefore the MNDO estimate of the vertical (or even the adiabatic) ionization energy of these thiafulvenes cannot be considered highly reliable; nevertheless a comparison of the MNDO HOMOs of these molecules may be valid. It is quite clear that the HOMO energy does increase (or the vertical ionization energy decreases) as one adds dithiafulvene rings to *s*-trithiane; in fact, MNDO would have us believe that T9 is almost as easy to ionize as TTF. The closeness of the three oxidation peaks of T9 is mirrored by the closeness of the MNDO eigenvalues.



The most relevant twist angles and dihedral angles are listed in Table III: although one might surmise some pattern of "flattening out" of the T3 ring as dithiafulvene substituents are added, no such pattern emerges from the MNDO calculations. The relative net electronic energies (total + core–core repulsion) of the boat and chair forms of T9 were very close, −4615.882 90 and −4615.877 26 eV; this suggests that the barrier to interconversion between these forms is low.

Electron Paramagnetic Resonance (EPR). The radical cations of dimethylmonofulvathiane (T5) **9**, tetramethyldifulvathiane (T7) **10**, hexamethyltrifulvathiane (T9) **11**, and 2-(4,5-dimethyl-1,3-dithiol-2-ylidene)-1,3-dithiane (T4) **12** generated in 1,2-dichloroethane are all pink and are readily detected by EPR (as is TTF^+[22,23]) (Figures 5–8). Since a three-electrode electrochemical EPR cell was not used, the potential at which the radicals appear could not be monitored. In several, repeated runs, including checks of the background cavity signals, it was found that the EPR signals due to **9–12** were strong and not due to impurities. Not all the expected hyperfine lines were resolved, and no spectral simulation was attempted. The best EPR signals were obtained from $T5^+$. The EPR spectra for the radicals of T7 (**10**) and T9 (**11**) (Figures 7 and 8) are not symmetrical about g = 2, probably because of kinetic effects during the time scale of the EPR scan. Although the electrochemistry suggests that **10** oxidizes to $\mathbf{10}^{++}$ directly, a radical was readily seen by EPR, probably by a disproportionation reaction such as $\mathbf{10} + \mathbf{10}^{++} = \mathbf{10}^{+} + \mathbf{10}^{+}$. It was determined that the EPR signal from **10** was not due to a triplet state (no absorption at half field due to $\Delta m = \pm 2$ transitions was found). The EPR data alone cannot exclude the formation of a noninteracting diradical of **10** (e.g., when both spins are present in $\mathbf{10}^{++}$ but somehow do not interact with each other).

---

(23) Laidlaw, R. K.; Miura, Y.; Grant, J. L.; Cooray, L.; Clark, M.; Kispert, L. D.; Metzger, R. M. *J. Chem. Phys.* **1987**, *87*, 4967–4971.

(24) Gleiter, R.; Schmidt, E.; Cowan, D. O.; Ferraris, J. P. *J. Electron Spectrosc.* **1973**, *2*, 207.

Table III. Salient Features of MNDO Calculated Geometries

	twist angles[a] (deg)						dihedral angles[b] (deg)		
	TA1	TA2	TA3	TA4	TA5	TA6	DA7	DA8	DA9
T3 (**8**) chair	54.9	−57.3	57.1						
T5 (**9**) chair (u)	49.9	−48.3	51.4	137.3			22.0		
chair (s)	49.3	−49.3	49.3	129.8			26.1		
T7 (**10**) chair (u)	52.9	−56.3	56.2	136.4	130.9		26.1	32.1	
T9 (**11**) chair (u)	53.1	−54.3	53.3	135.7	132.6	135.4	25.6	29.5	27.6
boat (u)	−2.6	56.6	−52.8	133.8	−129.7	138.0	30.9	60.9	23.8
boat (s)	4.8	49.6	−49.6	132.4	−133.0	133.0	30.2	60.0	31.1

[a] Twist angle (TA) 1 involves C6–S5–C4–S3; TA 2 involves S5–C4–S3–C2; TA 3 involves C4–S3–C2–S1; TA 4 involves C7–C6–S5–C4; TA 5 involves C33–C2–S1–C6; TA 6 involves C33–C2–S1–C6. [b] Dihedral angle (DA) 7 is between least-squares planes A and B; DA 8 is between least-squares planes A and C; DA 9 is between planes A and D; least-squares plane A includes atoms S1, S3, S5; plane B includes atoms C6, C7, S8, S9, C10, C11, C12, C13; plane C includes atoms C4, C20, S21, S22, C23, C24, C25, C26; plane D includes atoms C2, C33, S34, S35, C36, C37, C38, C39.

Attempts at Crystallization. Unfortunately, the needle-shaped crystals of **9**, **10**, and **11** were too small for X-ray crystal structure determination. In particular, fine needles of **11** were obtained from a variety of solvents such as carbon disulfide, chloroform, benzene, and glyme. When equimolar solutions of **11** and of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, both in 1,2-dichloroethane, were mixed at room temperature, a pink color developed, and two new broad bands were observed at 557 (radical) and 711 nm. Repeated and unsuccessful attempts were made to obtain solid charge-transfer salts of **11** with TCNQ, TCNE, or chloranil. Attempts were also made to prepare conducting radical cation salt crystals of **11**, but they all failed: in an H-tube, under conditions that readily afforded excellent large needles of ET salts, the pink radical of **11** was formed around the Pt electrode, but it proved too soluble in the solvents used, and no crystals large or small ever formed.

Conclusion

We have demonstrated a facile synthetic route to trifulvathianes. Further synthetic possibilities suggested by this work can be gleaned from published preparations of mixed sulfur–selenium[24] and diselenium[25,26] imminium salts, intermediates comparable to **13a**. Furthermore, *s*-triselenane is a known compound which might be expected to react similarly to its sulfur analogue **8**.[27]

The electrochemical evidence shows that T3, T4, T5, T7, and T9 are more difficult to oxidize than TTF (if solvent effects can be neglected); T7 tends to undergo two-electron oxidation; T9 undergoes three oxidations. EPR shows that $T7^{2+}$ must undergo disproportionation to form $T7^{+}$ radicals. The theoretical (MNDO) calculations show no significant conformational consequence of the adding of dithiafulvene rings to T3 but do suggest significant electronic effects: the effect of adding dithiafulvene rings to T3 does indeed decrease the first ionization potential of T3, bringing it very close to that of TTF in the compound T9.

In face of these trends, which bespeak of promise for these molecules, the difficulties encountered in growing adequate crystals of either neutral trifulvathianes or their salts was disappointing.

Experimental Section

Synthesis. The solvent THF was freshly distilled under N_2 over sodium and benzophenone each time before use. The other solvents mentioned were obtained from Fisher Chemical Company and were used without further purification. The chromatography columns were packed with Merck-Kieselgel 60 (0.004–0.063 mm) with 200–400 mesh and eluted with the solvents mentioned in each specific case. Thin layer chromatograms were obtained with Baker SC 250F HC plates, by using the solvent system 1:1 benzene/hexane. Workup means diluting with water, extracting with chloroform, drying the organic phase with Na_2SO_4, and filtering and evaporating the residue to dryness.

Melting points were taken on Thomas Hoover capillary melting point apparatus and are uncorrected. The UV spectra were determined with Perkin-Elmer Lambda 4B spectrophotometer. IR spectra were recorded with a Perkin-Elmer 781 spectrometer. ^1H NMR spectra were recorded on Brucker NT-200 pulsed FT spectrometer. Chemical shifts are reported as ppm downfield from the internal Me_4Si signal. Electron impact mass spectra were recorded on a Hewlett-Packard Model 5985A GC/MS system. Elemental analyses were performed by the Atlanta Microlab Inc., Atlanta, GA.

General Procedure for the Lithiation Reaction. To a solution of *sym*-1,3,5-trithiane (crystallized from refluxing toluene and powdered nicely) in THF (2 mmol in 25 mL of THF) at −70 °C was added *n*-BuLi (2.5 N solution in hexane; 2.2 mmol for monolithiation, 4.4 mmol for dilithiation, and 8.6 mmol for trilithiation; 0.86 mL, 1.72 mL, 2.58 mL, respectively) by means of a syringe, under nitrogen. A yellowish suspension resulted. The temperature of the bath was allowed to rise slowly to −20 °C (this was done in 2.5 h) during which time most of the trithiane went into solution, and a yellow solution was obtained. This was cooled to −70 °C again, and the electrophile **13a**[31] was added as a finely powdered solid from a L-shaped addition tube already fitted to the reaction flask. Immediately after the addition of **13a**/**13b**, triethylamine (0.27 mL, 2.2 mmol for mono-, 0.54 mL for di-, and 0.81 mL for trilithio derivatives) was added, and the resulting mixture was stirred for 1 h at −70 °C, warmed to ambient temperature, and maintained at this temperature for 2 h. During this period the tetraphenylborate salt slowly dissolved, and the whole solution turned dark yellow. Workup of this solution gave a reddish solid which was purified by column chromatography with 4:1 hexane/benzene as the eluting solvent. We routinely used the tetraphenylborate counterion, to avoid the hydrated forms of **13a** (see ref 19 and 20).

2-(4′,5′-Dimethyl-1′,3′-dithiol-2′-ylidene)-1,3-dithiane (T4, 12). 280 mg (57% yield from 1 mmol of 1,3-dithiane and **13a**), red needles, mp 140 °C from EtOAc/hexane; UV-vis spectrum ($CHCl_3$) λ_{max}/nm (log ϵ) = 367 (sh, 3.29), 328 (4.07), 318 (sh, 4.03), 268 (3.55); IR (KBr) ν_{max} = 2850, 1385, 1401, 1260, 900, 865, and 745 cm^{-1}; ^1H NMR (90 MHz) ($CDCl_3$) d 2.86 and 2.20 (6 H, m, $-CH_2-$ × 2), 1.93 (6 H, s, *Me* × 2). Anal. Calcd for $C_9H_{12}S_4$: C, 43.51; H, 4.87. Found: C, 43.48; H, 4.88.

2-(4′,5′-Dimethyl-1′,3′-dithiol-2′-ylidene)-1,3,5-trithiane or Dimethylmonofulvathiane (T5, 9). Column chromatography of the crude reaction product eluted with 4:1 hexane/benzene gave **9** (360 mg; 67.7% from 2 mmol **8** and **13a**; 52% from 2 mol of **8** and **13b**) and some starting material **8** (27.6 mg, 10%). The product **9** was obtained as tan to colorless needles from hexane: mp 168 °C; UV-vis spectrum ($CHCl_3$) λ_{max}/nm (log ϵ) = 355 (sh, 3.78), 330 (4.13), 3.18 (sh, 4.00), 260 (3.61); IR (KBr) ν_{max} = 2890, 1490, 1400, 1260, 900, 865, 745 cm^{-1}; ^1H NMR ($CDCl_3$) d 4.04 (4 H, s, $-CH_2$ × 2), 1.96 (6 H, s, *Me* × 2); MS (EI), m/z = 266 ($M^{\bullet+}$), 268, 220, 180 and 174. Anal. Calcd for $C_8H_{10}S_5$: C, 36.27; H, 3.78. Found: C, 36.15; H, 3.83.

2,4-Bis(4′,5′-dimethyl-1′,3′-dithiol-2′-ylidene)-1,3,5-trithiane or Tetramethyldifulvathiane (T7, 10). Column chromatography of the crude reaction product eluted with 4:1 hexane/benzene gave compounds **9** and **10** as a mixture (the ratio was 60/20 by ^1H NMR) which was separated by repeated crystallization from hexane/chloroform. Compound **10** (20%

---

(25) Bramwell, F. R.; Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 4612–4614.

(26) Bock, H.; Brühler, G.; Henkel, U.; Schlecker, R.; Seebach, D. *Chem. Ber.* **1980**, *113*, 289–301.

(27) Spencer, H. K.; Lakshmikantham, M. V.; Cava, M. P.; Garito, A. F. *J. Chem. Soc., Chem. Commun.* **1975**, 867.

(28) Bechgaard, K.; Cowan D. O.; Bloch, A. N. *J. J. Chem. Soc., Chem. Commun.* **1974**, 973.

(29) Johannsen, Ib; Lerstrup, K.; Henriksen, L.; Bechgaard, K. *J. Chem. Soc., Chem. Commun.* **1984**, 89.

(30) Schmidt, M.; Blaettner, K.; Kochendorder, P.; Ruf, H. *Z. Naturforsch, Part B* **1966**, *21*, 622.

(31) The tetraphenylborate salt of **13a** gave satisfactory elemental analysis. Anal. Calcd for $C_{33}H_{34}NS_2B$: C, 76.29; H, 6.60; N, 2.70; S 12.34. Found: C, 76.15, H, 6.63; N, 2.69; S, 12.40. Much lower yields of **9**, **10**, and **11** were obtained when **13b** was used as the electrophile.

yield from trithiane **8**, and 30% yield from **9** and **13a**) was obtained as colorless needles from acetone/hexane: mp 203 °C; UV–vis ($CHCl_3$) λ_{max}/nm (log ϵ) = 363 (sh, 4.15), 334 (4.39), 322 (sh, 4.34), 264 (3.96); IR (KBr) ν_{max} = 2880, 1520, 1480, 830 cm^{-1}; ^1H NMR ($CDCl_3$) d 3.99 (2 H, d, $-CH_2$) 1.96, 1.93 (12 H, 2 × s, *Me* × 4). MS (EI), *m/z* = 394 ($M^{\bullet+}$), 348, 264, 218, 186 and 174. Anal. Calcd for $C_{13}H_{14}S_7$: C, 39.56; H, 3.58. Found: C, 39.13; H, 3.58.

2,4,6-Tris(4′,5′-dimethyl-1′,3′-dithiol-2′-ylidene)-1,3,5-trithiane or Hexamethyltrifulvathiane (T9, 11). The tan-colored solid after workup was purified by placing it in a Soxhlet thimble and extracting repeatedly with hot chloroform. After 7–8 h the solid remaining in the Soxhlet thimble (120 mg; 25% from 1 mmol of **8** and **13a**; 20% yield using **13b**) was crystallized from carbon disulfide. Compound **11** was obtained as yellow needles from CS_2: mp 216 °C; UV–vis ($CHCl_3$) λ_{max} nm (log ϵ) = 367 (4.11), 334 (4.26), 256 (3.87); IR (KBr) ν_{max} = 2880, 1620, 1485, 1420, 1365, 1180, 1090, 1000, 900, 890, 780 cm^{-1}; ^1H NMR ($CDCl_3$ + CS_2) δ 1.91 (S); MS (EI), *m/z* = 522 (M^+), 264, 218, 201, 186, 174 and 162. Anal. Calcd for $C_{18}H_{18}S_9$: C, 41.35; H, 3.47. Found: C, 41.20; H, 3.49.

Cyclic Voltammetry. A Bioanalytical Systems (BAS) CV-27 cyclic voltammograph was used for cyclic voltammetry measurements. Normal cyclic voltammograms (CV) were recorded on a Houston Instruments Omnigraphic X-Y Recorder; the IR drop was compensated by the built-in positive feedback circuit. All measurements were performed in 1,2-dichloroethane (Aldrich HPLC Grade) with a three-electrode cell, with a platinum disk working electrode, and a platinum wire auxiliary electrode. The supporting electrolyte solution was scanned over the solvent window to ensure the absence of electroactive impurities. In all measurements the sample solutions were bubbled with nitrogen gas for 5 min to remove O_2 prior to measurement; all measurements were performed under a blanket of nitrogen. The quasi-reference electrode used was the half-cell Ag|0.04 M $(n\text{-}C_4H_9)_4NI$ in DMF, connected with an intermediate salt bridge containing 0.1 M TBAHFP in DMF. Relative to this reference electrode, the formal potential of the ferrocene/ferrocenium couple in 1,2-dichloroethane was measured as +1.17 V, while its potential was measured as +0.62 V versus SCE in THF. This implies a difference (offset) of 0.55 V between the two electrode systems. (This offset had been measured[32,33] as 0.511, 0.516, and 0.528 V in DMF for the couples K/K^+, Ru/Ru^+, and Cs/Cs^+, respectively.) That is, we determined that V versus Ag/Ag^+ (CH_2ClCH_2Cl) − 0.55 = V versus aqueous SCE. The oxidation half-wave potentials ($E_{1/2}$) were calculated from the peak voltage for oxidation (E_{ox}) as E_{ox} − 0.030.

Electron Paramagnetic Resonance (EPR) Spectroscopy. The samples were dissolved in dichloroethane (Aldrich HPLC) with 0.20 M TBAHFP as the supporting electrolyte; the solutions were bubbled with nitrogen for 20 min to remove oxygen before transfer to the EPR electrolytic flat-cell. EPR spectra were obtained with a Varian Associates Model E-12 spectrometer during in situ electrolysis in a two-electrode, Pyrex electrolytic flat-cell, with a platinum gauze electrode as the anode and a platinum wire as the cathode. A PAR Model TC 100.2 voltage-current reference source was used to apply the potential, and the current was monitored with a Fluke Model 8024 B multimeter. A Bruker Model ER 035M NMR gaussmeter and a Hewlett-Packard Model 5246L frequency counter were used to measure the magnetic field and the microwave frequency, respectively.

Theory. MNDO calculations were carried out with program MOPAC (version 3.13) on a MicroVAX-II superminicomputer and MOPAC (version 4.0) on the Alabama CRAY X/MP-24. The geometries were optimized. A typical run for T9 (**11**) required 24 h on the MicroVAX and 15 min on the CRAY X/MP-24.

Acknowledgment. We thank the National Science Foundation for Grant CHE8607458 in support of this work. We are grateful to the Office of Naval Research for the purchase of the MicroVAX-II (Grant N00014-86-G-0215), to Chinnarong Asavaroengchai for programming assistance, and to the Alabama Supercomputer Network for a grant of computer time on the Cray X/MP-24.

Registry No. 8, 291-21-4; **9**, 117559-64-5; **10**, 117559-65-6; **11**, 117559-66-7; **12**, 117559-67-8; **13a**, 117559-69-0; **13b**, 117559-71-4; 1,3-dithiane, 505-23-7.

---

(32) Mairanovsky, V. G.; Engovatov, A. A.; Samokhvalov, G. I. *J. Anal. Chem. USSR* **1970**, *25*, 2235.

(33) Mairanovsky, V. G.; Engovatov, A. A.; Ioffe, N. T.; Samokhvalov, G. I. *J. Electroanal. Chem.* **1975**, *66*, 123.