JOC Article

Synthesis, Electrochemistry, and Gas-Phase Photoelectron Spectroscopic and Theoretical Studies of 3,6-Bis(perfluoroalkyl)-1,2-dithiins

Edward D. Lorance,[†] Richard S. Glass,*,[†] Eric Block,*,[‡] and Xiaojie Li[‡]

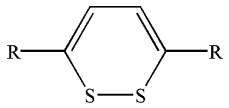
Departments of Chemistry, The University of Arizona, Tucson, Arizona 85721, and State University of New York at Albany, Albany, New York 12222

rglass@u.arizona.edu

Received May 21, 2003

3,6-Bis(trifluoromethyl)- and 3,6-bis(pentafluoroethyl)-1,2-dithiin (**1a**,**b**), the first known perfluoroalkyl-substituted 1,2-dithiins, were synthesized from (*Z*,*Z*)-1,4-bis(*tert*-butylthio)-1,3-butadiene (**2**) to evaluate the effects of electron-withdrawing groups on the ionization and oxidation potentials of 1,2-dithiins. Analysis of the photoelectron spectra of **1a** and **1b** provided a basis for assigning orbital compositions. Ab initio calculations on these compounds showed that they adopt a twist geometry as does 1,2-dithiin (**1c**) itself. Cyclic voltammetric studies on **1a** and **1b** revealed a reversible oxidation followed by an irreversible oxidation at much more positive potentials than for 1,2-dithiin and 3,6-dimethyl-1,2-dithiin (**1d**). The oxidation potentials determined electrochemically do not correlate with the ionization potentials determined by photoelectron spectroscopy. This result supports the previously advanced hypothesis that there is a geometry change on electrochemical oxidation leading to a planar radical cation.

In two previous papers,[1,2] we reported the synthesis, electrochemistry, and gas-phase photoelectron spectroscopic and theoretical studies of 1,2-dithiins and their derivatives containing alkyl groups at the 3,6-positions (**1**), as well as related 1,2-dichalcogenins with selenium in place of sulfur. Analysis of the photoelectron spectra



1a, R = CF_3
b, R = CF_2CF_3
c, R = H
d, R = CH_3

in combination with the theoretical studies provided insight into the compositions of the highest occupied molecular orbitals.[2] The first four filled frontier molecular orbitals of these compounds are associated with orbitals that are primarily carbon π and chalcogen lone pair in character derived from the 1,3-diene and dichalcogen fragments. Orbital assignments of the observed ionization were made on the basis of changes in ionization cross-sections as a function of ionization photon energy[3] and substituent effects. Methyl substituents, in particular, showed a notable effect. Electrochemical studies[1] on these materials revealed an apparently reversible one-electron oxidation. However, an EC mechanism, in which a chemical step follows the electron-transfer step, was required to satisfactorily fit the electrochemical data. In addition, the electrochemical oxidation potentials did not correlate with the lowest ionization potentials obtained from the photoelectron spectroscopic measurements. Theoretical calculations suggested that the chemical step on one-electron oxidation is a change in geometry from the twisted 1,2-dichalcogenin to a planar or flattened cation radical. The extent of the geometry change depended on substituents. Since these previously reported studies involved electron-donating alkyl groups, it was deemed important to determine the effects of electron-withdrawing substituents. This paper presents the synthesis, electrochemistry, and gas-phase photoelectron spectroscopic and theoretical studies on 3,6-bis(trifluoromethyl)- and 3,6-bis(pentafluoroethyl)-1,2-dithiin (**1a** and **1b**, respectively), the first known perfluoroalkyl-substituted 1,2-dithiins.

Results and Discussion

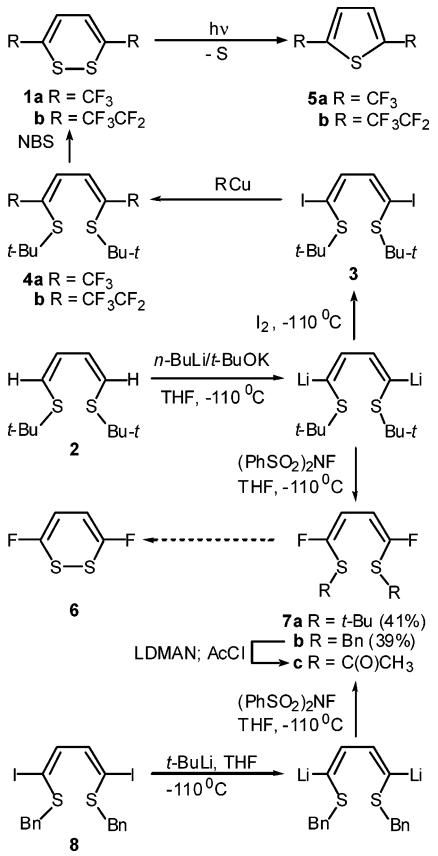
Synthesis. The strongly electron-withdrawing perfluoroalkyl or fluorine groups have not been previously introduced into the 1,2-dithiin ring system. We have succeeded in incorporating the trifluoromethyl and pentafluoroethyl groups into the known[4] 1,2-dithiin precur-

[†] The University of Arizona.
[‡] State University of New York at Albany.

(1) Block, E.; Birringer, M.; DeOrazio, R.; Fabian, J.; Glass, R. S.; Guo, C.; He, C.; Lorance, E.; Qian, Q.; Schroeder, T. B.; Shan, Z.; Thiruvazhi, M.; Wilson G. S.; Zhang, X. *J. Am. Chem. Soc.* **2000**, *122*, 5052−5064.
(2) Glass, R. S.; Gruhn, N. E.; Lichtenberger, D. L.; Lorance, E.; Pollard, J. R.; Birringer, M.; Block, E.; DeOrazio, R.; He, C.; Shan, Z.; Zhang, X. *J. Am. Chem. Soc.* **2000**, *122*, 5065−5074.
(3) Glass, R. S.; Broeker, J. L.; Jatcko, M. E. *Tetrahedron* **1989**, *45*, 1263−1272.
(4) Koreeda, M.; Wang, Y. *J. Org. Chem.* **1997**, *62*, 446−447.

10.1021/jo034683n CCC: $25.00 © 2003 American Chemical Society
Published on Web 09/19/2003

SCHEME 1



sor (*E*,*E*)-1,4-bis(*tert*-butylthio)-1,4-diiodo-1,3-butadiene (**3**) through reaction with the corresponding perfluoroalkylcopper complex. Compound **3** was prepared in 47% yield (along with 8% of the mono-iodo compound) by treatment of (*Z*,*Z*)-1,4-bis(*tert*-butylthio)-1,3-butadiene (**2**) with 4 equiv of superbase (1:1 *t*-BuOK/*n*-BuLi in THF) at −110 °C followed by slow addition of I_2/THF (Scheme 1). Wiemers and Burton[5a] reported the preparation of solutions of CF_3Cu and its thermal transformation to CF_3CF_2Cu, which can be monitored by ^{19}F NMR spectroscopy. Using this methodology, either reagent can be prepared at will and coupled with **3**. In this way, (*Z*,*Z*)-1,4-bis(*tert*-butylthio)-1,4-bis(trifluoromethyl)-1,3-butadiene (**4a**) and (*Z*,*Z*)-1,4-bis(*tert*-butylthio)-1,4-bis(pentafluoroethyl)-1,3-butadiene (**4b**) were formed from in situ generated CF_3Cu and CF_3CF_2Cu in 51 and 61% yield, respectively, after column chromatography. Oxidative deprotection and cyclization of (*Z*,*Z*)-1,4-disubstituted-1,4-bis(*tert*-butylthio)-1,3-butadienes to the corresponding 3,6-disubstituted-1,2-dithiins has been reported.[4] Using this methodology, treatment of **4a** and **4b** with *N*-bromosuccinimide (2 equiv) in CH_3CN afforded 3,6-bis(trifluoromethyl)- and 3,6-bis(pentafluoroethyl)-1,2-dithiin (**1a** and **1b**) as orange, volatile liquids in 68 and 65% yield, respectively, after column chromatography.

Compound **1a** shows a single ^{19}F NMR peak at δ −67.3 ppm while **1b** shows two peaks at δ −84.2 and −111.3 ppm. Compounds **1a** and **1b** show UV λ_{max} at 448 and 452 nm, respectively, which is a bathochromic shift compared to dimethyl derivative **1d** (UV λ_{max} at 422 nm). Furthermore, the bathochromic shift observed on going from **1a** to **1b** is opposite to the trend seen on going from **1d** to compounds with larger alkyl groups at C3/6. The olefinic protons of **1a** and **1b** (^1H NMR δ 6.95−6.96) are significantly deshielded compared to the analogous protons in **1d** (δ 6.05). Irradiation of **1a** with visible light in an NMR tube led to the gradual disappearance of the signal at δ 6.95 ppm while sulfur precipitated on the inner wall of NMR tube. New absorptions at δ 7.43 ppm were seen which belong to 2,5-bis(trifluoromethyl)-thiophene[5b] (**5a**; reported: δ 7.48 ppm; presence confirmed by GC/MS), formed by extrusion of sulfur from **1a**.[1] Weak ^1H NMR signals (δ 7.20, 7.04 ppm (dd)) were also seen corresponding to 2,4-bis(trifluoromethyl)thiophene, from photoisomerism of **5a**.[5c] Irradiation of **1b** gave similar results, although a much longer irradiation time was required to afford 2,5-bis(pentafluoroethyl)-thiophene (**5b**).

TABLE 1. Analytical Representations of Photoelectron Data

label	position[a] (eV)	width (eV)[a]	relative area He I[b]	relative area He II[c]
3,6-Bis(trifluoromethyl)-1,2-dithiin (**1a**)				
1	9.10	0.47	1	1
2	10.57	0.46	1.35	1.12
3	10.87	0.48	0.78	1.22
4	12.44	0.55	0.98	1.05
3,6-Bis(pentafluoroethyl)-1,2-dithiin (**1b**)				
1	9.06	0.46	1	1
2	10.44	0.36	0.70	0.84
3	10.67	0.49	0.93	1.48
4	12.10	-	0.77	1.35
1,2-Dithiin[d] (**1c**)				
1	8.16	0.46	1	1
2	9.82	0.40	0.96	0.86
3	10.06	0.50	0.72	1.05
4	11.51	0.53	0.91	1.26
3,6-Dimethyl-1,2-dithiin[d] (**1d**)				
1	7.78	0.46	1	1
2	9.31	0.42	1.02	1.05
3	9.63	0.36	0.64	0.50
4	10.93	0.52	1.06	1.06

[a] Electron volts (23 kcal/mol). [b] Ionization using monochromatic He I UV radiation (21.22 eV). [c] Ionization using monochromatic He II UV radiation (40.81 eV). [d] Data taken from ref 2.

Attempts to prepare 3,6-difluoro-1,2-dithiin (**6**) were unsuccessful. Treatment of **2** with superbase at −110 °C followed by addition of *N*-fluorobenzenesulfonimide[5d] gave (*Z*,*Z*)-1,4-bis(*tert*-butylthio)-1,4-difluoro-1,3-butadiene (**7a**) in 41% yield (Scheme 1). However all attempts to convert **7a** into **6** (NCS, NBS, NIS, I_2, or SmI_2) led only to decomposition, with formation of a black precipitate. In another attempt to prepare **6**, (*E*,*E*)-1,4-bis(benzylthio)-1,4-diiodo-1,3-butadiene (**8**)[1] was treated in THF at −110 °C sequentially with *tert*-butyllithium followed by *N*-fluorobenzenesulfonimide, giving (*Z*,*Z*)-1,4-bis(benzylthio)-1,4-difluoro-1,3-butadiene (**7b**). Reductive debenzylation of (**7b**) with lithium 1-(*N*,*N*-dimethylamino)naphthalenide (LDMAN) at −45 °C followed by quenching with acetyl chloride gave (*Z*,*Z*)-1,4-difluoro-1,4-bis(acetylthio)-1,3-butadiene (**7c**). Unfortunately, oxidation (I_2) of the hydrolysis product of **7c** failed to give **6**.

Photoelectron Spectroscopy and Theoretical Calculations. The analytical representations of the photoelectron spectroscopic data are shown in Table 1 with those for 1,2-dithiin (**1c**) and 3,6-dimethyl-1,2-dithiin (**1d**)

for comparison. The spectra themselves are in the Supporting Information. The electron-withdrawing perfluoroalkyl groups raise the ionization energies of the four highest occupied molecular orbitals. The effects of the trifluoromethyl and pentafluoroethyl groups on the highest occupied MO are almost the same, resulting in nearly identical lowest ionization energies for **1a** and **1b**. This result is consistent with the similar inductive substituent parameters for the two groups.[6−8] The lowest-energy valence ionizations of 1,2-dithiins are associated with orbitals derived from the butadiene and disulfide fragments.[2] The composition of the MOs can be derived by the changes in relative intensity of the ionizations associated with them because carbon-based orbitals have a higher cross-section than sulfur-based orbitals on going from lower energy monochromatic UV irradiation (He I) to higher energy (He II).[3] Because of the apparent increase of Gaussian 3 relative to Gaussians 1 and 2 in the photoelectron spectrum of **1c** on going from He I to He II as the ionization source, the third highest MO was deduced to have more carbon character than the highest and second highest MOs. The same pattern is seen with both perfluoroalkyl compounds. This is important because in 3,6-dimethyl-1,2-dithiin, Gaussian 2 increases in relative area compared with Gaussians 1 and 3 on going from He I to He II as the ionization source. Since the primary cause of the destabilization of ionization of 3,6-dimethyl-1,2-dithiin is hyperconjugative interaction between the methyl E-symmetry C−H σ-bond orbitals and π-orbitals of the 1,2-dithiin ring, this shows the larger orbital contribution at C3 and C6 for the MOs corresponding to ionizations 1 and 3 than that for ionization 2 (which has a high degree of sulfur character). The observed results with the perfluoroalkyl substituents, in which this effect is not seen, supports the previously proposed suggestions.

Ab initio calculations using MP2/6-31+G* showed that **1a** adopts a twist geometry after energy minimization which is similar to that of **1c**. The geometric parameters for **1a** are given in Table 2. These parameters are very similar to those of **1c**. As examples, the twist in **1c**[9] and **a** is revealed by the CSSC and C=C−C=C torsion angles and they are 53.9°, 29.0° and 57.4°, 29.7°, respectively. The calculated ionization potential for **1a** (8.91 eV) is in reasonable agreement with the experimental value (9.10 eV).

Electrochemistry. The electrochemistry of **1a**,**b** was studied in CH_3CN using the technique of cyclic voltammetry. Satisfactory results were obtained with a glassy carbon electrode but not with a Pt electrode. As with **1c**, a reversible one-electron oxidation followed by an irreversible oxidation at more positive potentials was observed for **1a** and **b**. The peak potential for the reversible oxidation was 1.25 and 1.48 V for **1a** and **b**, respectively, and 1.40 and 1.67 V, respectively, for the irreversible oxidation. All of the peak potentials were measured at a scan rate of 100 mV/s versus a Ag/0.1 M $AgNO_3$ in CH_3CN reference electrode. As expected, it is more difficult to oxidize **1a** and **1b** than **1c**, whose oxidation potentials are 0.65 and 1.21 V,[1] because the lowest ionization potentials for **1a**,**b** are almost 1 eV higher than that for **1c**. On this basis, one would have expected **1a**,**b** to have similar oxidation potentials because their ionization potentials are almost the same. However, the oxidation potential of **1b** is over 200 mV more positive than that of **1a**. Similar discrepancies were reported before and explained in the following way. The chemical step in the EC mechanism for oxidation of 1,2-dichalcogenins was ascribed to a change in geometry from the twist conformation to a planar or planarized radical cation. Because the time scales for electrochemical and photoelectron spectroscopic measurements are different, there is sufficient time for a change in geometry in the electrochemical experiment but not in the adiabatic photoelectron spectroscopic measurement. Therefore, ionization potentials were not found to correlate with oxidation potentials in cases where the oxidized and reduced species possess radically different geometries. This is well-illustrated in the comparison of **1a** and **1b**. These results may also provide clearer insight into the geometric effect because the substituent effect of perfluoroalkyl groups is predominantly inductive in contrast to alkyl groups whose effects are due to hyperconjugation as well as induction. Since inductive effects are geometry independent, they are the same in twist **1a**,**b** as in planar **1a**,**b** radical cations. The electrochemical results show that $[\mathbf{1b}]^{\bullet+}$ is less stable relative to **1b** than is $[\mathbf{1a}]^{\bullet+}$ relative to **1a**. The relative destabilization of $[\mathbf{1b}]^{\bullet+}$ is due to greater steric bulk of the C_2F_5 group relative to the CF_3 group which destabilizes the planar form.[10,11]

TABLE 2. Calculated Geometric Parameters and Ionization Potential for 3,6-Bis(trifluoromethyl)-1,2-dithiin[a] (1a)

parameter	
S−S bond, Å	2.07
S−C bond, Å	1.77
C=C bond, Å	1.36
C−C bond (in ring), Å	1.45
C−C bond (CF_3), Å	1.49
C−F bond, Å	1.36
SSC angle, deg	96.5
SCC angle, deg	122.1
CCC angle, deg	123.1
CCC angle, (CF_3), deg	122.0
CCF angle, deg	110.4
CSSC torsion, deg	57.4
SSCC torsion (in ring), deg	−45.0
SSCC torsion (CF_3), deg	138.5
SCCC torsion, deg	1.4
C=C−C=C torsion, deg	29.7
CCCC torsion (CF_3), deg	177.7
ionization potential, eV	8.91 (9.10)[b]

[a] Calculations were done using MP2/6-31+G*. [b] Experimental value.

Conclusions

Our studies with **1a**,**b** demonstrate the effects of electron-withdrawing groups. They further validate the

(5) (a) Wiemers, D. M.; Burton, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 832−834. (b) Nishida, M.; Fujii, S.; Aoki, T.; Hayakawa, Y. *J. Fluorine Chem.* **1990**, *46*, 445−459. (c) Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine Y. *Tetrahedron Lett.* **1974**, *15*, 2841−2844. (d) Davis, F. A.; Han, W.; Murphy, C. K. *J. Org. Chem.* **1995**, *60*, 4730−4737.

(6) Allen, A. D.; Tidwell, T. T. *Adv. Carbocation Chem.* **1989**, *1*, 1−44.

(7) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

(8) Thompson, M.; Hewitt, P. A.; Wooliscroff, D. S. In *Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy*; Briggs, D., Ed.; Heyden: London, 1977; pp 341−379.

(9) Gillies, J. Z.; Gillies, C. W.; Cotter, E. A.; Block, E.; DeOrazio, R. *J. Mol. Spectrosc.* **1996**, *180*, 139−144.

key conclusions of previous work, namely that the energies of the second and third highest occupied molecular orbitals are inverted in 3,6-dimethyl-1,2-dithiin (**1d**) compared with **1c**. In addition, the studies demonstrate that ionization potentials and electrochemical oxidation potentials for 1,2-dithiins do not correlate because of geometry changes in electrochemical but not in spectroscopic measurements.

Experimental Section

SAFETY WARNING: HMPA is highly toxic and a cancer suspect agent.

Trifluoromethylcadmium.[12] A three-necked round-bottomed flask equipped with magnetic stirrer, thermometer, and dry ice condenser under Ar was charged with anhydrous DMF (4 mL) and activated Cd (acid washed) (0.45 g, 4 mmol). Then CF_2Br_2 (0.42 g, 2 mmol) was added slowly to the suspension, giving an exothermal reaction with a dark brown solution and precipitate. The temperature of the reaction was kept below 90 °C by controlling the rate of addition of CF_2Br_2. After completion of the addition of CF_2Br_2, the reaction mixture was stirred for 1.5 h at room temperature. The cadmium reagent was filtered through a medium-frit Schlenk funnel under argon into a three-necked flask. The precipitate was washed with DMF. The resulting dark brown solution of CF_3Cd (^{19}F NMR (DMF/$CFCl_3$) δ −34.7 (lit.[12] δ −35.7); 0.8−0.95 mmol, estimated 80−95% yield) was utilized immediately in subsequent reactions.

(*Z,Z*)-1,4-Bis(*tert*-butylthio)-1,4-bis(trifluoromethyl)-1,3-butadiene (4a). Following the reported[4] procedure, except that the deprotonation and iodination was carried out at −110 °C instead of −78 °C, with slow addition of I_2 in THF, (*E,E*)-1,4-bis(*tert*-butylthio)-1,4-diiodo-1,3-butadiene (**3**) was prepared in 47% yield from (*Z,Z*)-1,4-bis(*tert*-butylthio)-1,3-butadiene (**2**). In a three-necked flask equipped with a medium-frit Schlenk funnel and argon inlet, CF_3Cd (0.8−0.95 mmol) in anhydrous DMF (4 mL) was mixed with an equal volume of anhydrous HMPA (4 mL) and cooled to −20 °C. CuI (0.19 g, 2.0 mmol) was quickly added followed by the addition of **3** all at once. The reaction mixture was stirred for 1.5 h and then quenched with water. The aqueous solution was extracted with Et_2O, and the organic extracts were combined, washed sequentially with brine and water, dried (Na_2SO_4), and concentrated in vacuo. Chromatography (hexanes) gave **4a** (74 mg, 51%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 9H), 8.04 (s,2H); ^{13}C NMR ($CDCl_3$) δ 31.8 (s), 51.4 (s), 122.8 (q, J = 272 Hz), 132.0 (q, J = 18.5 Hz), 141.6 (q, J = 5.3 Hz); ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ −64.4; IR (neat) ν 2968, 2926, 2901, 2867 1562, 1460, 1368, 1237, 1173, 1134, 931, 743, 658, 595 cm^{-1}; GC−MS *m/z* 366 (M$^+$), 309, 254, 57; HRMS *m/z* 366.0898 (calcd for $C_{14}H_{20}F_6S_2$ 366.0912).

(*Z,Z*)-1,4-Bis(*tert*-butylthio)-1,4-bis(pentafluoroethyl)-1,3-butadiene (4b). In a three-necked flask equipped with a medium-frit Schlenk funnel and argon inlet was added CF_3Cd in DMF−HMPA (8 mL) prepared as described above. To this solution was added CuI (0.38 g, 2.0 mmol) at room temperature and the mixture stirred for 4 h. Compound **3** (0.19 g, 0.40 mmol) was added all at once, and the reaction mixture was stirred overnight. Water was added to quench the reaction, and the aqueous solution was extracted with hexanes. The extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Chromatography (hexanes) yielded **4b** (66 mg, 61%) as a white solid: mp 70−71 °C; ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 9H), 8.11 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 31.8, 51.9, 114.4 (tq, J = 279, 43 Hz), 117.0 (tq, J = 276, 38 Hz), 132.5 (t, J = 2.8 Hz), 144.8 (s); ^{19}F NMR ($CDCl_3$/$CFCl_3$) δ −78.9, −107.9; GC-MS *m/z* 466 (M$^+$), 409, 353, 320, 282, 251, 233, 182, 165, 146, 114, 57; IR (CCl_4) ν 2965, 2925, 1367, 1322, 1209, 1190, 1158, 1060, 1050, 985, 923, 878 cm^{-1}. Anal. Calcd for $C_{16}H_{20}F_{10}S_2$: C, 41.20; H, 4.32. Found: C, 41.16; H, 4.31.

3,6-Bis(trifluoromethyl)-1,2-dithiin (1a). *This procedure was conducted under red light.* In a round-bottomed flask, **4a** (123 mg, 0.33 mmol) was dissolved in CH_2Cl_2 (3 mL) and CH_3CN (3 mL). A solution of NBS (60 mg, 0.33 mmol) dissolved in CH_3CN (3 mL) and CH_2Cl_2 (3 mL) was then added dropwise at room temperature. The resulting mixture was stirred for 1 h and then diluted with pentane (10 mL), washed sequentially with water and brine, dried (Na_2SO_4), and concentrated in vacuo. Chromatography (pentane) afforded **1a** (22 mg, 68% based on recovered **4a**: 39 mg) as a volatile red-orange liquid not easily freed, when working on a small scale, from pentane: ^{1}H NMR (pentane/$(CH_3)_3CBr$/$CDCl_3$) δ 6.96 (s); ^{13}C NMR (pentane/$CDCl_3$) δ 120.2 (q, J = 280 Hz), 130.1 (q, J = 6.0 Hz), 131.9 (q, J = 6.0 Hz); ^{19}F NMR (pentane/$CDCl_3$/$CFCl_3$) δ −67.3; UV ($CHCl_3$) λ_{max} (ϵ) 448 (890), 264 (1330), 242 (1589) nm; GC−MS *m/z* 252 (M$^+$), 233, 232, 213, 183, 139, 114, 69; HRMS *m/z* 251.9489 (calcd for $C_6H_2F_6S_2$ 251.9503). Repetition of this synthesis using 30 mg of **4a** and 2 equiv of NBS gave a higher yield of **1a** with little recovered **4a**. A pentane solution of **1a** was used for measurement of photoelectron (PE) spectra; in the PE spectrometer, the pentane was pumped off first at low temperatures (see below).

Exposure of **1a** to visible light in an NMR tube led to formation of sulfur and appearance of ^{1}H NMR signals corresponding to 2,5-bis(trifluoromethyl)thiophene (**5a**; lit.[5b] δ 7.48 ppm, found δ 7.43 ppm; GC−MS *m/z* 220) and minor signals corresponding to 2,4-bis(trifluoromethyl)thiophene (δ 7.20, 7.04 (dd)).[5c]

3,6-Bis(pentafluoroethyl)-1,2-dithiin (1b). *This procedure was conducted under red light.* A solution of NBS (0.36 g, 2.0 mmol) dissolved in CH_3CN (5 mL) was added dropwise at room temperature to a solution of **4b** (0.47 g, 1.0 mmol) dissolved in CH_3CN (10 mL) in a round-bottomed flask. After the mixture was stirred overnight, pentane (25 mL) was added and the resulting mixture washed sequentially with water and brine. The organic layer was dried (Na_2SO_4), concentrated in vacuo, and chromatographed (pentane) to give **1b** (179 mg, 65% based on recovered **4b**: 163 mg) as a volatile red-orange liquid: ^{1}H NMR (pentane/$CDCl_3$) δ 6.95 (s); ^{13}C NMR (pentane/$CDCl_3$) δ 114.0 (tq, J = 276, 36 Hz), 118.4 (tq, J = 272, 36 Hz), 127.6 (t, J = 18 Hz), 132.8 (t, J = 7.5 Hz); ^{19}F NMR (pentane/$CDCl_3$/$CFCl_3$) δ −84.2, −111.3; UV ($CHCl_3$) λ_{max} (ϵ) 452 (960), 290 (1580), 246 (1105) nm; GC−MS *m/z* 352 (M$^+$), 283, 233, 214, 189, 164, 114, 69; HRMS *m/z* 351.9424 (calcd for $C_8H_2F_{10}S_2$ 351.9439).

Photoelectron Spectroscopy. Gas-phase photoelectron spectra were recorded using an instrument that features a 36-cm, 8-cm gap hemispherical analyzer (McPherson) and custom designed sample cells, discharge source, and detection and control electronics[13] that have been described in more detail elsewhere.[14] The excitation source was a quartz lamp with the ability, depending on operating conditions, to produce He I (21.21 eV), or He II (40.8 eV) photons. For the He I and He II experiments, the ionization energy scale was calibrated using the $^2E_{1/2}$ ionization of methyl iodide (9.538 eV), with the Ar $^2P_{3/2}$ ionization (15.759 eV) used as an internal energy scale lock during data collection. During He I and He II data collection the instrument resolution, measured using the full-width-at-half-maximum of the Ar $^2P_{3/2}$ ionization, was 0.015−0.025 eV. All data are intensity-corrected with an experimentally determined instrument analyzer sensitivity function that

(10) Smart, B. E. In *Organofluorine Chemistry*, Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum: New York, 1994; pp 57−88.

(11) Bégué, J.-P.; Benayoud, F.; Bonnet-Delpon, D.; Allen, A. D.; Cox, R. A.; Tidwell, T. T. *Gazz. Chim. Ital.* **1995**, *125*, 399−402.

(12) Burton, D. J.; Wiemers, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 7, 5014−5015.

(13) Lichtenberger, D. L.; Kellogg, G. E.; Kristofzski, J. G.; Page, D.; Turner, S.; Klinger, G.; Lorenzen, J. *Rev. Sci. Instrum.* **1986**, *57*, 2366.

(14) Westcott, B. L.; Gruhn, N. E.; Enemark, J. H. *J. Am. Chem. Soc.* **1988**, *120*, 3382−3386.

assumes a linear dependence of analyzer transmission (intensity) to the kinetic energy of the electrons within the energy range of these experiments.

All of the spectra were corrected for the presence of ionizations from secondary photons in the discharge sources.[15] The He I spectra were corrected for ionizations from He Iβ photons (1.9 eV higher in energy, and 3% of the intensity of the He Iα photons), the He II spectra were corrected for the He IIβ photons (7.568 eV higher in energy, and 12% the intensity of the He IIα photons).

The compounds studied are light and temperature sensitive and were handled at low temperature to limit self-polymerization. Liquid samples were frozen and loaded into a sample cell that had been cooled in a −40 °C freezer. The cell was then placed in the instrument and allowed to slowly warm, and the spectra were collected at the temperature (monitored using a "K"-type thermocouple passed through a vacuum feedthrough and attached directly to the sample cell) where sufficient sample vapor pressure was achieved.

The valence ionization bands are represented analytically with the best fit of asymmetric Gaussian peaks.[16] The bands are defined with the position, amplitude, halfwidth for the high binding energy side of the peak, and the halfwidth for the low binding energy side of the peak. The peak positions and halfwidths are reproducible to about ±0.02 eV (∼3F level). Confidence limits for the relative integrated peak areas are about 5%, with the primary source of uncertainty being the determination of the baseline, which is caused by electron scattering and taken to be linear over the small energy range of these spectra. The total area under a series of overlapping peaks is known with the same confidence, but the individual peak areas are more uncertain. The fitting procedures used are described in more detail elsewhere.[13]

Computational Methodology. Computations were carried out on an SGI Origin 2000 32-processor mainframe using a single processor under the IRIX64 v6.4 operating system using Gaussian 94 (rev. E.2).[17] Calculations on unsubstituted 1,2-dithiin were performed using the Hartree−Fock method, with second-order Møller−Plesset perturbation corrections. The 6-31G basis set with heavy atom polarization functions (*) and heavy atoms diffuse functions (+) was used.

The neutral species were geometry optimized and single-point calculations were made for the cation radical at the neutral species optimized geometry to obtain ionization potentials (ΔSCF).

Cyclic Voltammetry. Voltammograms were measured on degassed solutions approximately 10^{-3} M in substrate and 0.1 M in tetra-*n*-butylammonium hexafluorophosphate, which served as supporting electrolyte, in CH_3CN as solvent versus a Ag/0.10 M $AgNO_3$ in CH_3CN reference electrode. A 3 mm diameter glassy planar carbon electrode served as the working electrode, and the scan rate was 100 mV/s. A 0.5 mm diameter platinum wire was used as the counter electrode. All electrochemical experiments were performed under rigorously anaerobic conditions in a Vacuum Atmospheres model HE-493 drybox or sealed electrochemical cell under red light. A Cypress Systems electrochemical data acquisition system model CYSY-1 was used to acquire and process the data.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (R.S.G., CHE-9422200; E.B., CHE-9906566; E.D.L., for a Graduate Fellowship), the Petroleum Research Fund, administered by the American Chemical Society (E.B.), and Dr. Nadine E. Gruhn at the Center for Gas-Phase Electron Spectroscopy, The University of Arizona, for helpful discussions and measuring the photoelectron spectra.

Supporting Information Available: General experimental and procedures for the synthesis of **7a**−**c** and attempted preparation of **6**; table of atomic coordinates for optimized geometry of **1a** calculated by using MP2/6-31+G*; photoelectron spectra of **1a** and **1b**; ^{1}H NMR spectra of **1a**,**b** and **4a**; ^{13}C NMR spectra of **1a** and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO034683N

(15) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. *Molecular Photoelectron Spectroscopy*; Wiley-Interscience: London, 1970.

(16) Lichtenberger, D. L.; Copenhaver, A. J. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *50*, 335−352.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, B. B.; Stefanov, A.; Nanayakkara, M.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision E.2.; Gaussian Inc.: Pittsburgh, PA, 1995.