by the American Chemical Society, for partial support of this work.

Registry No. **1a**, 64317-99-3; **1b**, 64318-00-9; **3**, 81121-00-8; **4**, 81121-01-9; **5** (M = Mo), 81121-03-1; **5** (M = W), 81121-05-3; **6** (M = Mo), 81120-90-3; **6** (M = W), 81120-91-4; (η^5-C_5H_5)Mo(CO)$_3$Cl, 12128-23-3.

Supplementary Material Available: Listings of atomic positions, thermal parameters, bond lengths, and bond angles (2 pages). Ordering information is given on any current masthead page.

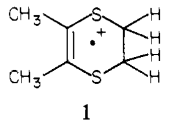
Dithiaethylene Radical Cations and Anions[1]

Glen A. Russell* and Mary Zaleta

Department of Chemistry, Iowa State University
Ames, Iowa 50011

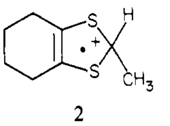
Received November 6, 1981

Hyperfine splittings (hfs) by hydrogen atoms α to a sulfur atom with unpaired spin density in the ESR spectra of tetrathiaethylene ($(RS)_2C{=}C(SR)_2$) radical cations have been interpreted[2,3] as arising mainly or solely from an angle-independent spin polarization ($|a_\alpha{}^H| = 17\rho_S$ G),[3] in contrast to the hyperconjugation mechanism that dominates for carbon-centered radicals.[4] We have tested this interpretation by comparing systems with one and two sulfur atoms with unpaired electron spin density attached to a carbon atom bearing a proton, e.g., **1** and **2**. A spin polarization mechanism with $Q^{\cdot}{}_{SCH}{}^H = 17$ requires $\rho_S(\mathbf{1}) = 0.27$ and $\rho_S(\mathbf{2})$ to have the impossible value of 0.71 ($\rho_S(\mathbf{2}) = 24.2/2\ (17)$). The high value of $a_\alpha{}^H$ for the methine hydrogen of **2** requires a delocalization mechanism. The unpaired electron in the π system is in a symmetric SOMO, which leads to the hyperconjugation predictions;[5] $a_\alpha{}^H(1) = B(c_S)^2\ \langle\cos^2\theta\ (\mathbf{1})\rangle$ and $a_\alpha{}^H(2) = B(2c_S)^2\langle\cos^2\theta\ (\mathbf{2})\rangle$, where c_S is the MO coefficient for the S atom in the SOMO and θs are the dihedral angles between the C–H bonds and the sulfur p orbitals with unpaired electron spin. Utilizing the value of B for $CH_3\dot{S}O$ of 25.4 G[4c] and $a_{\dot{C}CH_3}{}^H = 27\rho_C$ leads to $\rho_S = c_S{}^2 = 0.29$, $\langle\cos^2\theta\ (\mathbf{1})\rangle = 0.5$, $\langle\cos^2\theta\ (\mathbf{2})\rangle = 0.8$. A spin polarization mechanism even with a dihedral angle dependence ($a_\alpha{}^H = nB'\rho_S\langle\cos^2\theta\rangle$; n = 1 or 2) cannot yield reasonable values of $\langle\cos^2\theta\rangle$.



1

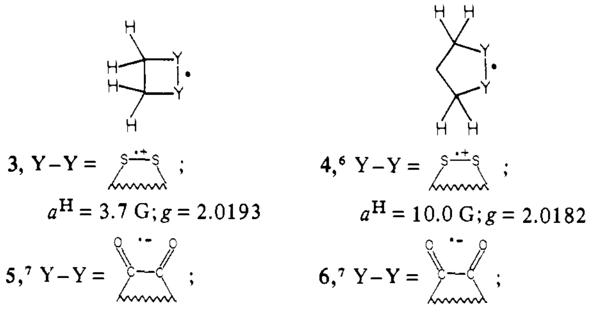
a^H = 5.65 (6 H), 3.50 (4 H) G



2

a^H = 24.2 (1 H), 8.5 (4 H) G

Delocalization also explains a puzzling effect of ring size on $a_\alpha{}^H$ for the radical cations **3** and **4** when compared with the semidiones **5** and **6**. In **3** and **4** the unpaired electron is in an antisymmetric MO ($c_{S(i)} = -c_{S(j)}$), whereas the semidiones possess a symmetric SOMO. The value of $a_\alpha{}^H$ will be determined by the hyperconjugative 1,2 interactions and the homohyperconjugative (W plan) 1,3 interactions[8] and will qualitatively be a function of $(c_i\cos\theta_i + \lambda c_j\cos\theta_j)^2$, where i and j are atoms with π-electron spin density α and β to the C–H bond. In the semidiones the symmetric SOMO leads to a reinforcement of the interactions, whereas in the 1,2-dithia radical cations the two effects are opposed.[9] Apparently **3** possesses a superior geometric arrangement for the 1,3 interaction in **7** ⇄ **8**.



3, Y–Y = ;

a^H = 3.7 G; g = 2.0193

4,[6] Y–Y = ;

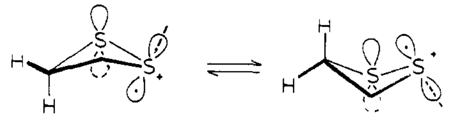
a^H = 10.0 G; g = 2.0182

5,[7] Y–Y = ;

a^H = 13.85 G; g = 2.0051

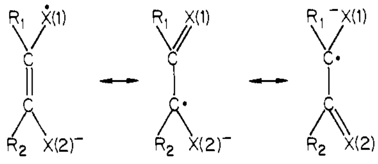
6,[7] Y–Y = ;

a^H = 12.93 G; g = 2.0051



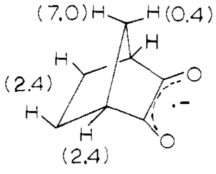
7 **8**

In a related study we have investigated the effect on spin delocalization by replacing semidione oxygen atoms with sulfur atoms (**9** → **10** → **11**). Consistent results were obtained with $R_1 = R_2 = CH_3$, $-(CH_2)_4-$, or *cis*-1,3-cyclopentadiyl and $R_1 = C_2H_5$, $R_2 = CH_3$. Replacement of oxygen by sulfur lowers $\rho_{C=X}{}^C$ by approximately 50% as illustrated by the hfs constants for **12**–**14** (a^H in G in Me_2SO). The spin distribution in **11** favors structure **a** over **b** = **c** when X is changed from O to S, presumably because the π-bond energy of C=S is lower than C=O. In **10**, $\rho_{C=S}{}^C > \rho_{C=O}{}^C$ for the same reason, i.e., structure **b** is preferred to **c**.

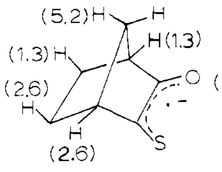


a **b** **c**

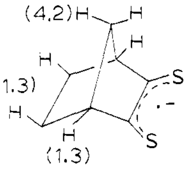
9, X(1) = X(2) = O
10, X(1) = O; X(2) = S
11, X(1) = X(2) = S



12,[8] g = 2.0050



13, g = 2.0100



14, g = 2.0166

Radical cations **1**–**4** were observed upon treatment of 2,3-dihydro-5,6-dimethyl-1,4-dithiin (**1**), 2-methyl-4,5-tetramethylene-1,3-dithiole (**2**), 1,2-ethanedithiol or poly(dithio-1,2-ethanediyl) (**3**), and 1,3-propanedithiol or 1,2-dithiolane (**4**) with concentrated H_2SO_4 at 25 °C. The radical cation **3** was initially observed but upon standing the ESR signal was dominated by the $\Delta^{2,2'}$-bi-1,3-dithiolane radical cation.[2,3] Thiosemidiones were formed by the treatment of the 2-mercapto ketones or generated in situ enedithiols with $KOCMe_3$ in Me_2SO at 25 °C.

Registry No. **1**, 81195-29-1; **2**, 81195-30-4; **3**, 81195-31-5; **4**, 66609-63-0; **13**, 81195-32-6; **14**, 81195-33-7.

---

[1] Applications of ESR Spectroscopy to Problems of Structure and Conformation. 34. This work was supported by Grant CHE-7823866 from the National Science Foundation.

[2] Chambers, J. Q.; Canfield, N. D.; Williams, D. R.; Coffen, C. L. *Mol. Phys.* **1970**, *19*, 581.

[3] Bock, H.; Brähler, G.; Henkel, U.; Schleeker, R.; Seebach, D. *Chem. Ber.* **1980**, *113*, 289.

[4] Other workers had presumed an angle dependence for $a_{SCH}{}^H$: (a) Forbes, W. F.; Sullivan, P. D. *J. Can. Chem.* **1968**, *46*, 317. (b) Geske, D. H.; Merritt, M. V. *J. Am. Chem. Soc.* **1969**, *91*, 6921. (c) Nishikida, K.; Williams, F. *J. Am. Chem. Soc.* **1974**, *96*, 4781.

[5] Whiffen, D. H. *Mol. Phys.* **1963**, *6*, 223.

[6] Previously prepared in CH_2Cl_2: Bock, H.; Stein, U. *Angew. Chem.* **1979**, *92*, 864.

[7] Russell, G. A.; Osuch, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 5979.

[8] Russell, G. A.; Chang, K.-Y. *J. Am. Chem. Soc.* **1965**, *87*, 4381.

[9] For previous applications see: G. A.; Holland, G. W.; Chang, K.-Y.; Keske, R. G.; Mattox, J.; Chung, C. S. C.; Stanley, K.; Schmitt, K.; Blankespoor, R.; Kosugi, Y. *J. Am. Chem. Soc.* **1974**, *96*, 7237. Bauld, N. L.; Farr, F. R. *Ibid.* **1974**, *96*, 5633. Bauld, N. L.; Farr, F. R.; Hudson, C. E. *Ibid.* **1974**, *96*, 5634.

0002-7863/82/1504-2318$01.25/0 © 1982 American Chemical Society