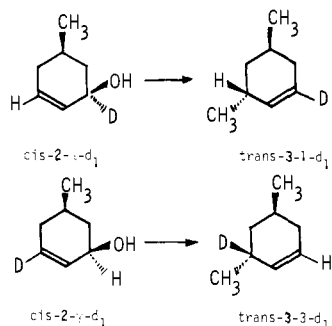


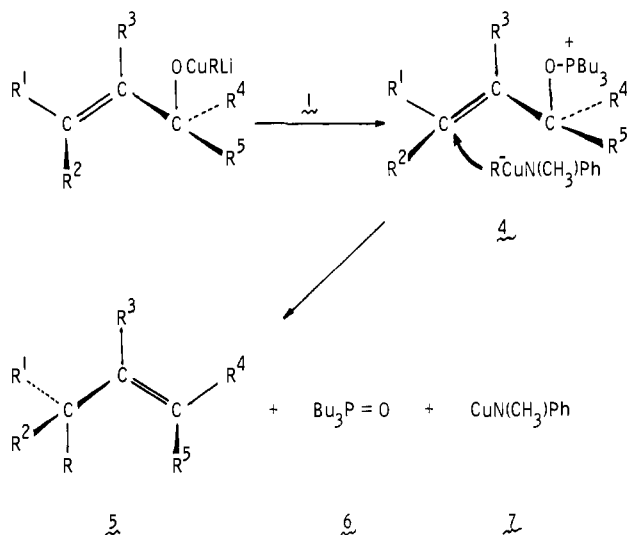
l-*d*₁ (92%) and *trans*-*3-3-d*₁ (8%), while *cis*-*3* consisted of *cis*-*3-1-d*₁ (92%) and *cis*-*3-3-d*₁ (8%). These results clearly show that the transformation from **2** to **3** proceeds predominantly via an S_N2'-type reaction. It is assumed that *trans*-*3-3-d*₁ was formed from *cis*-*2-α-d*₁ via an S_N2 reaction; calculations show that the transformation of **2** to **3** consisted of 86% anti S_N2' and 6% syn S_N2' reactions. Similar methylation



of a mixture of *cis*-*2-γ-d*₁ (92%) and *trans*-*2-γ-d*₁ (8%) gave **3** which consisted of *trans*-*3-3-d*₁ (82%), *trans*-*3-1-d*₁ (4%), *cis*-*3-1-d*₁ (1%), and *cis*-*3-3-d*₁ (13%). These results also show that the reactions proceed as follows: 88% anti S_N2', 7% syn S_N2', and 5% S_N2. Although this system is unbiased with regard to substitution with and without allylic rearrangement, the methylation proceeds with 92% allylic rearrangement (S_N2') in contrast to the nonselective conversion (with and without rearrangement, 50:50) of the acetates of **2** to **3** with lithium dimethylcuprate.^{5b} The predominant anti stereochemistry of the S_N2' reaction (94% anti) may be due to an inconspicuous steric bias, unique to the cyclohexyl system.^{5b,15,16}

The course of the reaction can be rationalized by assuming that the nucleophilic attack of R, from the counterion derived from the aminocuprate, at the γ carbon of allyloxy group of the intermediate **4** gives olefin **5** along with tributylphosphine oxide (**6**) and *N,N*-methylphenylaminocopper (**7**) as shown in Scheme I.

Scheme I



Work is currently in progress on the extension of this reaction to other systems and application to the synthesis of natural products.

Acknowledgment. We appreciate assistance by (the late) Mr. Yoshio Ozawa and Mr. Takashi Yoshioka. This research was supported in part by Grants from the Ministry of Education, Japan (No. 185192, No. 303528).

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- (16) Magid indicated that a cyclohexyl system has certain built-in conformational biases which force syn attack, independent of any stereoelectronic requirement of the S_N2' reaction.¹³

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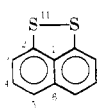
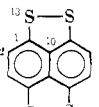
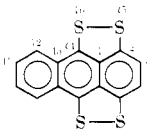
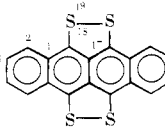

Received March 17, 1978

Electron Spin Resonance Studies of Sulfur-Based Donor Heterocycles: ³³S Couplings

Sir:

Although the theory of low dimensional solids^{1,2} has led to a qualitative understanding of the electronic and magnetic solid-state properties of highly conducting organic donor and

Table I. ESR Spectral Parameters and Calculated Spin Densities

Molecule	Calcd spin density, ρ_S^{\pm}	Calcd hfs	Obsvd hfs
 1^d	C ₁ , -0.006	H ₃ , 4.11	4.56
	C ₂ , -0.003	H ₄ , 1.08	0.96
	C ₃ , 0.152	H ₅ , 4.98	5.52
	C ₄ , -0.040	S ₁₁ , 7.54	7.16
	C ₅ , 0.184		
	C ₆ , -0.038		
	S ₁₁ , 0.228		
 2^b	C ₁ , 0.067	H, 1.53	1.51
	C ₂ , 0.057	S, 4.47	4.37
	C ₁₀ , -0.018		
	S ₁₃ , 0.136		
 3^c	C ₁ , -0.017	H ₃ , 1.76	1.80
	C ₂ , 0.062	H ₁₂ , 0.54	0.55
	C ₃ , 0.065	H ₁₁ , 0.50	0.43
	C ₁₁ , 0.018	S ₁₅ , 3.58	3.70
	C ₁₂ , 0.020	S ₁₆ , 4.04	4.01
	C ₁₃ , 0.015		
	C ₁₄ , 0.105		
	S ₁₅ , 0.108		
S ₁₆ , 0.122			
 4^d	C ₁ , 0.021	H ₂ , 0.45	0.55
	C ₂ , 0.017	H ₃ , 0.55	0.55
	C ₃ , 0.020	S ₁₉ , 3.36	3.30
	C ₁₇ , -0.021		
	C ₁₈ , 0.101		
 5^e	C ₁ , 0.190	H, 1.10	1.26
	C ₃ , 0.041	S, 3.77	4.2
	S ₂ , 0.114		

^a In H₂SO₄/CF₃COOH; $g = 2.0079$, line width = 250 mG. ^b As BF₄⁻ salt in CH₃CN; $g = 2.0094$, line width = 300 mG. ^c Br₂ oxidation in nitrobenzene; $g = 2.0086$, line width = 150 mG. ^d I₂ oxidation in nitrobenzene; $g = 2.0077$, line width = 150 mG. ^e As BF₄⁻ salt in NO₂CH₃; $g = 2.0083$, line width = 400 mG.

acceptor materials, the molecular basis for such effects is not understood. Electron spin resonance (ESR) techniques provide a detailed knowledge of the spin density distribution in such molecules, and may prove useful in revealing qualitative aspects of their dimensionality in the solid state. We report here the results of ESR and electrochemical studies in solution on a series of sulfur-based donor heterocycles including the first natural abundance ³³S hyperfine splitting constants (hfs) derived from planar disulfide compounds.

Radical cations of the following molecules were generated by mild chemical or electrochemical oxidation in an appropriate solvent: 1,8-dithianaphthalene (**1**, DTN),³ 1,4,5,8-tetrathianaphthalene (**2**, TTN),⁴ 1,4,9,10-tetrathiaanthracene (**3**, TTA),⁵ 5,6,11,12-tetrathiatetracene (**4**, TTT),⁶ and tetrathiafulvalene (**5**, TTF).⁷ The results of an analysis of the ESR spectra along with experimental conditions are presented in Table I and are in excellent agreement with theoretical predictions.⁸ Our results represent an advancement upon prior work reported for DTN⁹ and for TTT.¹⁰

A plot of sulfur spin density (ρ_S^{\pm}) vs. observed sulfur hyperfine splitting (a_S) is shown in Figure 1. The results suggest that an equation of the form $a_S = Q_S \rho_S^{\pm}$ with $Q_S = 33.0$ G, adequately describes ³³S hfs for TTF and the planar disulfides, **1**–**4**. The value for Q_S includes contributions from the π spin densities on adjacent carbon and sulfur atoms and from the spin polarization of sulfur inner shell electrons. Our results are in excellent agreement with nonplanar sulfide π systems studied by Sullivan.¹¹

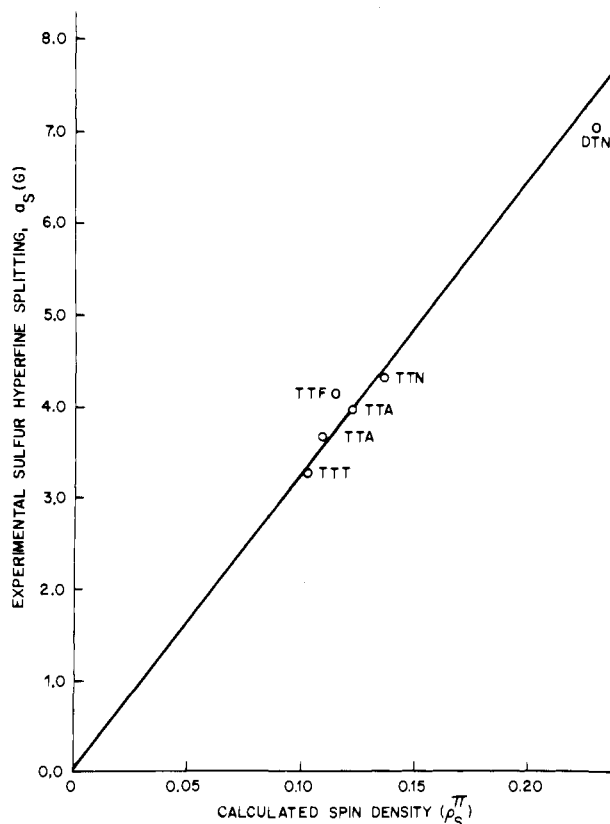


Figure 1. A plot of experimental sulfur hyperfine splittings against calculated spin density ρ_S^{\pm} (cf. ref 8).

Cyclic voltammetry on molecules **1**, **2**, **4**, and **5** was carried out in acetonitrile with 0.1 M *n*-Bu₄NBF₄ as supporting electrolyte, with a platinum working electrode and silver/silver chloride reference electrode. The oxidation potentials are corrected to SCE (-0.02 V) and are shown as a function of ϵ_{HOMO} (the energy of the highest occupied molecular orbital) in Figure 2. This is in agreement with prior work which has suggested a linear relationship between ionization and oxidation potentials.^{12–14} The excellent correlation which is obtained suggests that such calculations may be useful in evaluating the donor properties of sulfur-based donor heterocycles.

Major conclusions based on results shown in Figures 1 and 2 and Table I are enumerated below.

(1) In TTF⁺, the π spin density is localized primarily among the sulfur and central carbon atoms, with the highest spin density at the central carbon atoms. These results may bear upon the Hopkins group's suggestion of significant steric effects determining the increased dimensionality of the hexamethylenetetraselenafulvalene-tetracyanoquinodimethane (HMTSF-TCNQ) complex¹⁵ relative to other charge-transfer derivatives of TTF-TCNQ. Since selenium is more polarizable than sulfur, we would expect more spin (and charge) at the selenium of HMTSF than at the sulfur of the sulfur analogue, HMTTF. The high spin density at the selenium atoms suggests increased interaction between donor and acceptor stacks and hence increased dimensionality. This conclusion is supported in part by the observation that the Se - - N distance of 0.310 nm in HMTSF-TCNQ is shorter than that of the sulfur analogue (S - - N, 0.325 nm).¹⁶ Further support for these conclusions may be found in our calculations¹⁷ on TSF (tetraselenafulvalene), in which we find that the chalcogen atom now has the largest spin density in the molecule. A similar effect was previously invoked by Engler and co-workers¹⁸ to explain the electrochemistry of TTF and TSF.

(2) In TTT⁺, there is considerably higher spin density on the sulfur atoms than on the outer ring carbon atoms (i.e.,

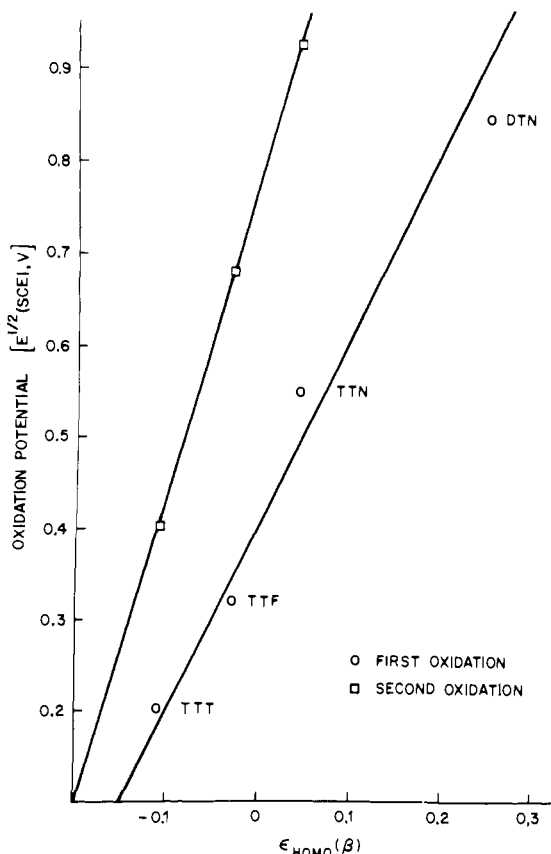


Figure 2. A plot of oxidation potentials (vs. SCE in acetonitrile with $n\text{-Bu}_4\text{NBF}_4$ as supporting electrolyte) against the calculated energy of the highest occupied molecular orbital.

carbons 1, 2, and 3 as shown in Table I and symmetry related atoms). These results are consistent with the higher dimensionality observed in certain TTT and TST (tetraselenatetracene) salts¹⁹ in which the interstack sulfur (or selenium) distances are short and spin may be delocalized across stacks as well as along stacks.

Acknowledgments. We thank S. H. Glarum and D. J. Freed for the use of ESR equipment and for mass spectral analysis of TTA. Also, we thank E. M. Engler of IBM for helpful discussions. F. B. B. acknowledges partial support from the National Science Foundation in the form of Grant No. SMI-077.

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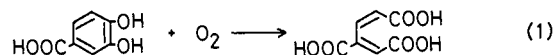
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Received February 16, 1978

Resonance Raman Spectra of Protocatechuate 3,4-Dioxygenase. Evidence for Coordination of Tyrosine Residue to Ferric Iron

Sir:

We wish to report the first well-resolved resonance Raman spectra of a nonheme iron containing dioxygenase, protocatechuate 3,4-dioxygenase (protocatechuate:oxygen 3,4-oxidoreductase, EC 1.13.11.3). The spectroscopic evidence presented in this paper indicates that the tyrosine residue coordinates to the ferric iron, a sole cofactor of the enzyme. This enzyme, isolated from the bacterium, *Pseudomonas aeruginosa*, catalyzes the intradiol cleavage of protocatechuic acid with the insertion of two atoms of molecular oxygen to form β -carboxy-*cis,cis*-muconic acid¹ (eq 1). This enzyme contains



eight atoms of ferric iron per molecule (mol wt 700 000) and consists of eight identical protomers, each of which is composed of two pairs of nonidentical subunits ($\alpha_2\beta_2$).² The enzyme shows a red color with a broad absorption near 450 nm which is attributable to the ferric iron coordinated with some amino acid residues of the polypeptide chains (see the inset of Figure 1). When the substrate (protocatechuic acid) is added anaerobically, the visible spectrum shows an increase in intensity of ~ 480 nm implying the formation of an enzyme-substrate (ES) complex. Upon admission of oxygen a new absorption arises at 520 nm, suggestive of the formation of a ternary complex (ESO₂). When the substrate is consumed, the original spectrum is recovered.³ Apparently the iron atoms play an important role in the activation of oxygen and/or substrate. Elucidation of the coordination environment around the ferric iron is thus of primary importance for understanding the mechanism of the enzymic reaction. A previous report suggested, on the basis of EPR spectroscopy, a tetrahedral arrangement of four cysteinyl sulfur atoms similar to the case of rubredoxin,⁴ while another study based on Mössbauer spectrum claimed coordination of oxygen or nitrogen, but not sulfur, to the ferric iron.⁵ Thus their conclusions are inconsistent with each other. As the resonance Raman scattering