

Angular Dependence of Proton Hyperfine Splittings in the Electron Spin Resonance Spectrum of the Methylsulfinyl Radical^{1a,b}

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Abstract: The methylsulfinyl radical ($\text{CH}_3\dot{\text{S}}\text{O}$) has been identified in a γ -irradiated single crystal of dimethyl sulfoxide. Its electron spin resonance spectrum above -100° shows coupling to three equivalent protons (isotropic quartet hfs = 11.6 G) and to one sulfur atom. The principal values of the g tensor [2.023, 2.011, 2.003] and the ^{33}S hfs tensor [-14 , -21 , 59 G] confirm this assignment to a sulfur-centered π radical which is isoelectronic with $\text{SO}_2^{\cdot-}$. The spectrum is temperature dependent such that below -185° there is coupling to sulfur and only two equivalent protons (isotropic triplet hfs = 17.3 G). This result shows that the methyl group, which is freely rotating at high temperature, adopts a fixed conformation at low temperature in which one proton lies in the nodal plane of the sulfur $3p$ orbital which is occupied ($\rho_s = 0.91$) by the unpaired electron. The conformational dependence of these isotropic proton hyperfine splittings is exactly interpretable by a $\rho_s B \cos^2 \theta$ relation with $B = 25.4$ G.

Few sulfur-containing organic radicals have been thoroughly characterized by esr despite much indirect evidence that these species play an important role in the chemistry of organosulfur compounds. In general, the low natural abundance (0.74%) of the ^{33}S ($I = 3/2$) isotope has meant that ^{33}S satellite spectra are difficult to observe and consequently organosulfur radicals are often identified on the basis of their ^1H spectra. Such identifications can be erroneous, however, if there is no reliable guide as to the magnitude of the ^1H hfs to be expected in a given case. Illustrative of the problem is the apparent lack of agreement in the literature concerning the angular dependence of the isotropic hfs for β protons in methyl or methylene groups attached to a sulfur atom bearing a π spin density.²⁻⁷ In fact, the expected $\cos^2 \theta$ relationship analogous to that which obtains for β protons in carbon-centered radicals has been questioned.⁵ This unsatisfactory situation prompts us to report briefly on our findings for the prototype $\text{CH}_3\dot{\text{S}}\text{O}$ radical produced in a γ -irradiated single crystal of dimethyl sulfoxide (DMSO).

Experimental Section

Single crystals of dimethyl sulfoxide (mp 18.6°) were grown in glass tubes of varying diameter by slow immersion of liquid samples into an ice bath. The sample tubes were γ irradiated at -196° for doses up to 4 Mrads and then annealed for 10 min at -20° . ESR studies were made directly on the crystals grown in narrow Suprasil quartz tubes (i.d. 2-4 mm), the reference axes being the tube z axis and arbitrarily chosen x and y axes. On the other hand, the large crystals prepared in wider Pyrex tubes (i.d. 7 mm) were removed

from the glass container after γ irradiation and specially mounted with reference to the crystallographic axes for the esr measurements. In the latter case, crystal samples of the desired shape and size could be readily cleaved from the original crystal. That the cleavage planes coincide with the crystallographic planes was verified through a detailed study of the angular dependence of the $\text{CH}_3\dot{\text{S}}\text{O}$ spectrum. Since no site splitting was observed for any direction of the magnetic field in one particular cleavage plane, this was taken to be the ac plane perpendicular to the b axis of a monoclinic crystal. Dimethyl sulfoxide crystals are known to be monoclinic, space group $P2_1/c$, with four molecules in the unit cell.⁸

The esr spectra were recorded on a Varian V-4502-15 X-band spectrometer and the temperature of the crystal was controlled in the range between -185 and -60° by means of the V-4557 accessory. Experimental details connected with the mounting and orientation of crystals will be discussed in a separate publication concerned with the determination of the hfs (^{33}S and ^1H) and g tensors for the $\text{CH}_3\dot{\text{S}}\text{O}$ radical. The magnetic field was calibrated by recording simultaneously the reference spectrum of Fremy's salt in aqueous solution ($a_N = 13.05$ G; $g = 2.0055$) using a dual-cavity arrangement.

Results and Discussion

We begin by presenting evidence that the methylsulfinyl radical is the main residual paramagnetic species in a γ -irradiated single crystal of DMSO after annealing at -20° . Figure 1 shows the esr spectrum recorded at -90° . The central portion consists of two 1:3:3:1 quartets from different sites whose g factors are well separated at this orientation, the hfs being 11.6 G in each case. In addition, two groups of weak lines displaying the same quartet structure are centered about the main spectrum with the smaller g factor and these satellites have integrated absorption intensities which are about 500 times less than those of the corresponding lines in the main spectrum. No additional quartets were revealed on a wider sweep of the magnetic field and consequently the observed satellites can be assigned to the outer $m_I = \pm 3/2$ components of the ^{33}S spectrum present in natural abundance.⁹ A study of the angular

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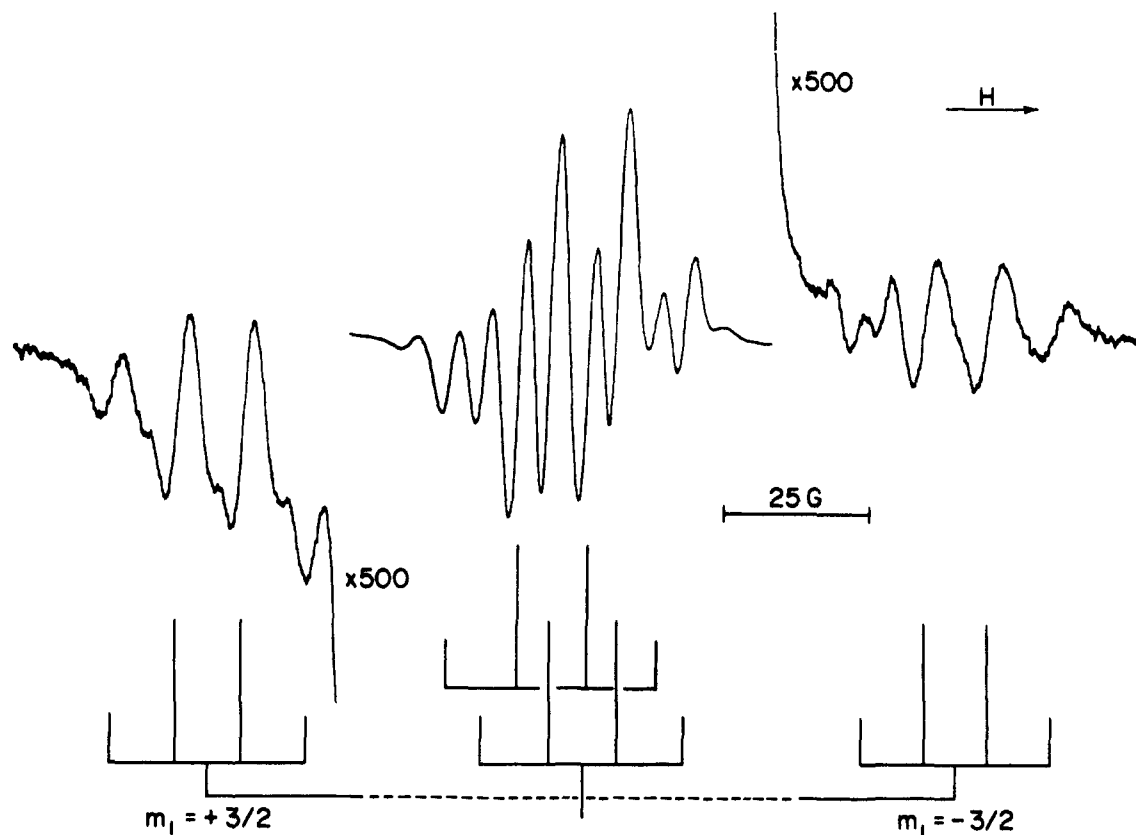


Figure 1. First-derivative esr spectrum of a γ -irradiated crystal of dimethyl sulfoxide at -90° after annealing at -20° . The site splitting revealed in the central spectrum is due to the presence of magnetically nonequivalent sites. The outer lines consisting of the ^{33}S satellites ($m_I = \pm 3/2$) are correlated with one of the central quartets as indicated in the stick diagram.

dependence of the spectra indicates that the ^{33}S satellites corresponding to the other sites are hidden beneath the intense inner spectrum, as are the $m_I = \pm 1/2$ components from both sites. Additional proof of the ^{33}S interaction was obtained from the observation of the $m_I = -1/2$ lines, as well as the $m_I = \pm 3/2$ components, in the corresponding spectra obtained from a single crystal of $\text{DMSO}-d_6$ where the main spectrum is narrowed considerably. These observations show that the radical contains sulfur and three equivalent hydrogens, so the spectrum is assigned to the MeSO radical formed by the net loss of a methyl group from the parent molecule.

This assignment to a sulfur-centered π radical iso-electronic with $\text{SO}_2 \cdot^-$ is strongly supported by the marked anisotropy of the ^{33}S hfs and g tensors, the principal values derived from measurements at low temperature (-185°) being with signs assumed $[-14, -21, 59 \text{ G}]$ and $[2.023, 2.011, 2.003]$. We also find that the directions corresponding to the principal values of 59 G and $g = 2.003$ almost coincide with each other. These results are strikingly similar to those for $\text{SO}_2 \cdot^-$ for which the largest component (58 G) of the ^{33}S hfs tensor and the smallest component (2.002) of the g tensor have the same principal axis perpendicular to the molecular plane. From the ^{33}S hfs anisotropy of the CH_3SO radical, a spin density of 0.91 is calculated to reside in a sulfur 3p orbital. Thus the unpaired electron occupies a π^* orbital largely concentrated on the sulfur atom, a description which also applies to the other 19 valence-electron radicals OSCl and OSBr .¹⁰

As expected for a methyl group attached to a spin-bearing atom, the ^1H hfs of 11.6 G showed little or no anisotropy. From detailed measurements on the spectra corresponding to the locked conformation of the methyl group at low temperature (*vide infra*), the total ^1H anisotropy was found to be less than 3 G. However, this spread would be reduced by the free rotation of the methyl group which results in the above spectrum for three equivalent hydrogens. Therefore, our results clearly disagree with the isotropic ^1H hfs of 6.57 G reported previously for a 1:3:3:1 spectrum tentatively attributed to this radical in solution.⁶ We conclude that the identification in this latter case is suspect since no ^{33}S splittings were obtained and the chemical method of preparation cannot be regarded as unambiguous.⁶

The esr spectrum of the methylsulfinyl radical changed markedly with temperature, as shown in Figure 2. For this study, the central spectra from the two sites were first brought into sharp coincidence by suitable orientation of the crystal. On lowering the sample temperature from -58 to -139° , the relative heights of the two central lines in the original 1:3:3:1 quartet (hfs = 11.6 G) decreased significantly. At -163° these inner lines have coalesced into a single broad line, and at -185° the spectrum approaches a 1:2:1 triplet (hfs = 17.3 G), the spacing between the outer lines remaining approximately constant throughout. This change in the hyperfine structure with temperature was reversible and the corresponding effect was observed for the ^{33}S satellites.

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Spectrum a at the highest temperature is characteristic of a freely rotating methyl group for which all three protons are equivalent. On the other hand, spectrum d implies that the methyl group conformation is locked at low temperature such that, within the uncertainty of the line width, two protons have equivalent hfs and the hfs of the third proton is zero. This interpretation is supported by examination of the intermediate spectra b and c which show line width alternation effects similar to those originally observed for methyl group rotation in the $\text{CH}_3\dot{\text{C}}(\text{H})\text{COOH}$ radical.¹¹ Analysis and simulation of these temperature-dependent spectra through the use of the modified Bloch equation¹² leads to a calculated barrier height of 2.6 kcal mol⁻¹ for the hindered internal rotation of the methyl group. This value is similar to the barrier of 2.88 kcal mol⁻¹ for ethane¹³ and appears to be typical of those obtained for molecules which have threefold symmetry about the axis of internal rotation. Further discussion about the dynamics of methyl group rotation in the $\text{CH}_3\dot{\text{S}}\text{O}$ radical will be given elsewhere.

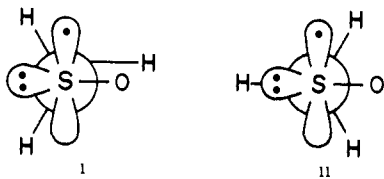
It is well known¹⁴ that the isotropic hfs of β protons in carbon-centered π radicals is described by a relation of the form

$$A_{\beta}(\text{H}) = \rho(B_0 + B_1 \cos^2 \theta)$$

where ρ is the spin density in the p orbital of the α carbon atom, $B_0 = 3\text{--}5$ G, $B_1 = 40\text{--}45$ G, and θ is the dihedral angle between the axis of the p orbital and the projection of the $\text{C}_{\beta}\text{--H}$ bond on the plane perpendicular to the $\text{C}_{\alpha}\text{--C}_{\beta}$ bond. The second term in this equation is generally considered to be due largely to a hyperconjugative mechanism. A similar equation might therefore be expected to hold for the proton splittings in the $\text{CH}_3\dot{\text{S}}\text{O}$ radical and for present purposes this can be reduced to the simpler expression

$$A(\text{H}) = \rho_s B \cos^2 \theta$$

where ρ_s is the spin density in the 3p orbital of the sulfur atom. Accordingly, the triplet spectrum at low temperature is uniquely interpretable in terms of a preferred conformation in which the two equivalent protons have dihedral angles of 30 and 150° and the noninteracting third proton lies in the nodal plane ($\theta = 270^\circ$). Two such conformations are possible, as illustrated by structures I and II, depending on whether the hydrogen atom



in the nodal plane is eclipsed by the oxygen atom or by the orbital containing the unshared pair of electrons on the sulfur atom. We cannot distinguish experimentally

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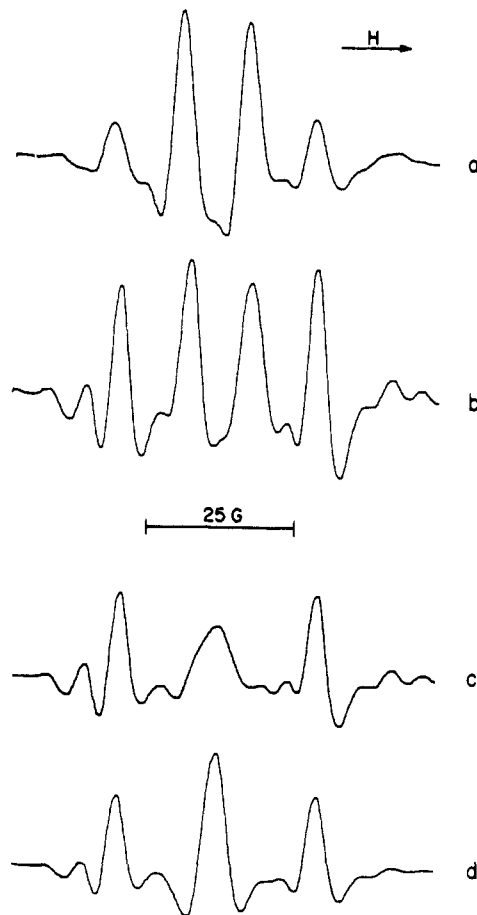


Figure 2. Second-derivative esr spectra showing the main spectrum of the $\text{CH}_3\dot{\text{S}}\text{O}$ radical at -58° (a), -139° (b), -158° (c), and -185° (d). The spectra were recorded at different gains.

between these alternatives and a theoretical choice would require information about the nonbonded forces¹⁵ in the $\text{CH}_3\dot{\text{S}}\text{O}$ radical.

From the isotropic hfs of 17.3 G for the ^1H triplet spectrum at low temperature and the spin density of 0.91 on the sulfur atom, B in the above equation is calculated to be 25.3 G. Similarly, a B value of 25.5 G is obtained from the 11.6 G splitting observed for the quartet spectrum corresponding to the free rotation of the methyl group ($\langle \cos^2 \theta \rangle = 1/2$). The excellent agreement between these results constitutes a direct proof of the $\cos^2 \theta$ relation for the coupling of β protons in the $\text{CH}_3\dot{\text{S}}\text{O}$ radical. Moreover, despite the disagreement in the literature noted in the introduction,¹⁶ there are two independent results which are consistent with the present value of B for sulfur π radicals. First, the β -proton hfs of 2.70 G in the room-temperature esr spectrum (13 lines) of the tetrakis(methylthio)ethylene cation radical⁴ leads to a value of $B\Sigma\rho_s$ equal to 21.6 G for this radical. Taking B equal to 25.4 G as obtained in the present work, $\Sigma\rho_s$ becomes 0.85 for this cation radical. This result is reasonable since it is anticipated that most of the

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(16) Apart from the problem of erroneous assignments, two obvious difficulties have stood in the way of arriving at a generally applicable $\rho_s B \cos^2 \theta$ relation for β protons from results on different sulfur radicals. In each case the spin density ρ_s must be determined, and secondly, the dihedral angle θ needs to be established in the case of radicals with a locked conformation. Thus the failure to agree on a general value of B probably reflects uncertainties in the values of ρ_s and θ rather than the breakdown of the $\cos^2 \theta$ relation as such.

spin density is concentrated on the four sulfur atoms. The second example is for the radical derived by the loss of a hydrogen atom from thiodyglycolic acid.^{7a} In this case B has been estimated to be 22.5 G, but since the spin density on the sulfur atom was calculated indirectly from the β -proton anisotropy, the value is probably subject to an error of at least 10%. Thus it can be

concluded that a $\cos^2 \theta$ relation is indeed applicable to sulfur-centered π radicals such that B is approximately 25 G, *i.e.*, about 60% of the corresponding value for carbon-centered π radicals.

Acknowledgment. Earlier studies on γ -irradiated crystalline dimethyl sulfoxide were carried out in this laboratory by Dr. Y. J. Chung.

Quenching of the First Excited Singlet State of Substituted Benzenes by Diolefins in the Vapor Phase

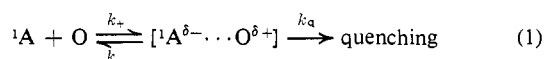
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Abstract: Rate constant data for the quenching of the first excited singlet states of a series of aromatic compounds by *trans*-1,3-pentadiene and 1,3-butadiene are presented. A strong correlation between the quenching rate constant and the estimated electron affinity of the aromatic is found, as would be expected on the basis of formation of an encounter complex stabilized by charge transfer from diolefin to excited aromatic.

The effect of additives on the fluorescence quantum yield of benzene and substituted benzenes in the gas phase has been of interest for some time and has recently been reviewed.¹ The additives chosen usually contain π electrons, although a report has been published in which saturated halogenated compounds were used to quench the $^1B_{2u}$ excited state of benzene.² Until recently, however, there has been little attempt to correlate quenching parameters with properties of quenchers relating to a particular quenching mechanism.

Breuer and Lee³ have investigated the relative contributions of the dipole-dipole and exchange mechanisms of electronic energy transfer to the quenching of the fluorescence of various substituted benzenes by cyclopentanone and 1-pyrazoline, but these electronic energy transfer mechanisms are thought not to be operative for quenching moieties such as olefins, diolefins, and molecular oxygen.⁴ Instead, the formation of a charge-transfer complex is postulated.^{4,5} This has been investigated for the quenching of singlet states of substituted benzenes by molecular oxygen^{6,7} in which case the encounter complex is stabilized by donation of charge from the aromatic compound to the oxygen.⁵ In the case of quenching by olefins,⁴ the charge transfer is proposed to be in the opposite direction as shown in eq 1, where 1A is the aromatic in its



first excited singlet state, O is the olefin and $[^1A^{\delta-} \cdots$

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$O^{\delta+}$] represents an encounter complex between excited-aromatic and olefin which is stabilized by charge transfer from the olefin to the aromatic.

On the basis of this scheme, measured quenching rate constants (k_Q) are given by the expression

$$k_Q = k_+k_q/(k_- + k_q) \quad (2)$$

The stability of the complex, and hence the quenching rate constant, will be determined by the free energy changes associated with complex formation. In solution, strong correlations between the reduction potentials of a series of excited molecules and rate constants for quenching by a variety of additives have been found.⁸⁻¹⁰ To date, such phenomena have not been investigated in the vapor phase, and the present research was directed toward this end.

Experimental Section

The apparatus, experimental technique, and purity of all the aromatic compounds used have been described elsewhere.¹ The *trans*-1,3-pentadiene was obtained from Fluka chemicals with a stated purity of greater than 99%. This was confirmed by vapor phase chromatography on a silver nitrate/ethylene glycol column and the compound was used without any attempt at further purification. The *n*-pentane was obtained from May and Baker Ltd. and vapor phase chromatography on a 5% OV1 column showed it to have 5% isopentane as an impurity. It was considered that isopentane would have a virtually identical effect on the fluorescence quantum yields of the aromatic molecules and hence no attempt was made to remove it.

Results

The quenching by *trans*-1,3-pentadiene of the aromatic compounds used in this study was analyzed in terms of the familiar Stern-Volmer equation

$$\Phi_0/\Phi_p = 1 + k_{QT}[Q] \quad (3)$$

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