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A Molecular Orbital Study of the Conformation and g-Factors of the $HSSH^-$ Radical Anion

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Synopsis. The electronic structure and g-factors of the $HSSH^-$ radical anion were calculated by means of a restricted open-shell SCF MO method with the MINDO/3 approximation, and the dependence of the g-factors upon the conformation was clarified. The most stable conformation predicted agreed well with the experimentally estimated –S–S– geometry of dialkyl disulfide anions, and its g-factors agreed well with the observed values.

Attention has been drawn in recent literature[1,2] to the electronic structures of sulfur-containing radicals and their ESR data. Lin and Lunsford[1] observed the $HSSH^-$ radical anion formed by allowing H_2S to react with trapped electrons on MgO. From the hyperfine splittings and the g-factors ($g_\perp=2.015$, $g_{//}=2.003$), they pointed out that the radical earlier identified as H_2S^- by Bennett *et al.*[3] is $HSSH^-$. Since the principal values of the g-tensor correlate strongly with the electronic structure of a radical, the theoretical analysis of the g-tensor can clarify the electronic structure and conformation of the radical. The purpose of the present note is to investigate the relation between the g-factors and the conformation of $HSSH^-$ by means of restricted open-shell SCF calculations.

The MO's of the spin-restricted doublet state were obtained by the approximate SCF version which has been proposed by Longuet-Higgins and Pople[4] for π-radicals and which has since been applied to all-valence-electron systems by the present author.[5] For the evaluation of the electron integrals involved, the MINDO/3 approximation[6] was employed. The geometry of $HSSH^-$ was first optimized with respect to three parameters; the S–S bond length, the HSS angle, ψ, and the dihedral angle, θ, between two planes containing the HSS′ or SS′H group. The dependence of the g-factors upon ψ and θ was calculated according to Stone's formula,[7] the S–S bond length being fixed at the optimized value, 2.17 Å. A more detailed description of the calculation has been reported elsewhere.[8]

Results and Discussion

The electronic structure and g-factors of a typical conformation (shown in Fig. 1) will be discussed first, since the g-tensor of this conformation is practically diagonal in terms of the axes, x, y, and z. The ground electron configuration of C_2 symmetry is:

$$\cdots(2a)^2(2b)^2(3a)^2(3b)^2(4a)^2(4b)^1\text{:}\ {}^2B$$

where 2a and 2b MO's are bonding S–H σ orbitals and where 3a is the bonding S–S 3pσ orbital directed along the S–S bond. The 3b and 4a orbitals are nearly degenerate and are expressed as $(3p_\alpha(S)+3p_\beta(S'))/\sqrt{2}$ and $(3p_\alpha(S)-3p_\beta(S'))/\sqrt{2}$ respectivley. The half-occupied MO, 4b, is the anti-bonding 3pσ^* orbital directed along the S–S bond. The contribution of each excited configuration to the principal values of the g-tensor is shown in Table 1. The large deviation of g_{xx} from the free-spin value can be understood as resulting from the spin-orbit mixing of the ground state with the 4a→4b excited configuration, and that of g_{zz}, from the mixing with the 3b→4b excited configuration. The contributions of the bonding S–H σ orbitals (2a and 2b) compensate for those of the anti-bonding S–H σ^* orbitals (5a and 5b). The calculated principal values ($g_\perp=2.011$ and $g_{//}=2.002$) are in fair agreement with the observed values.[1]

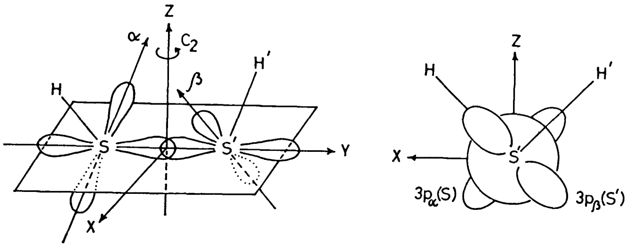

Fig. 1. The coordinate axes and the Newman projection for a typical conformation of $HSSH^-$ viewed in the direction of the S–S bond. The dihedral angle, θ, between two planes containing H–S–S′ and S–S′–H′ is 90° and the HSS′ angle, ψ, is 90°.

Table 1. Calculated Δg_{ii}[a)] values of the $HSSH^-$ of the C_2 symmetry, with $\theta=90°$ and $\psi=90°$

Excited configuration	ΔE (eV)[b)]	Δg_{xx}	Δg_{yy}	Δg_{zz}
1a→4b	16.40	0	0	0
1b→4b	11.46	0	0	2
2a→4b	6.33	77	0	0
2b→4b	6.06	0	0	79
3a→4b	3.98	5	0	0
3b→4b	2.53	0	0	81
4a→4b	2.51	79	0	0
4b→5a	2.26	0	0	−66
4b→5b	2.29	−65	0	0
Total[c)]		96	0	96

a) Deviation from the free-spin value. The value of $\Delta g_{ii}\times10^4$ are listed in each column. b) Energy difference between the ground state and an excited configuration. c) The three principal values calculated from these values are: $g_{xx}=2.0119$, $g_{yy}=2.0023$, and $g_{zz}=2.0119$.

The ground state of the $HSSH^-$ with the C_2 symmetry was calculated to be the ^2B state for any value of ψ or θ. Though the half-occupied MO is always expressed as 3pσ^*, its shape depends considerably upon ψ and θ. This is the reason why the g-factors of $HSSH^-$ depend largely on the conformation of $HSSH^-$. The dependence of $g_{av}=1/3(g_1+g_2+g_3)$ upon ψ and θ is shown in Fig. 2. It can be seen from Fig. 2 that there are many conformations for a given value of g_{av}. The three principal values, however, vary largely with the

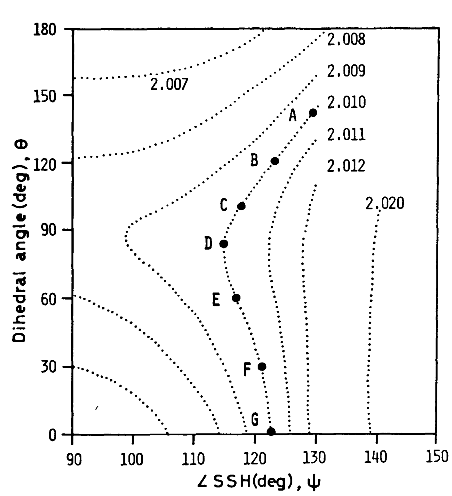

Fig. 2. The conformational dependence of the g_{av} value of HSSH⁻. The bond lengths shown in Fig. 4 were employed.

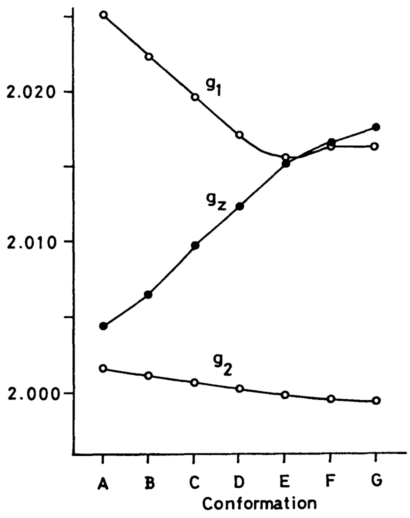

Fig. 3. Variations of three principal values of the g-tensor of HSSH⁻ along A→G cited in Fig. 2.

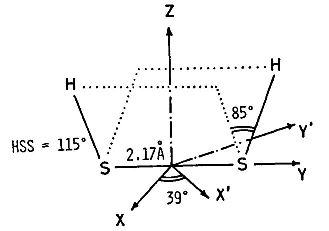

Fig. 4. The most stable conformation of HSSH⁻ and the principal axes, x′, y′, and z, of its g-tensor.

conformation of HSSH⁻. When $g_{av}=2.010$, for example the three principal values of the conformations corresponding to A—G in Fig. 2 vary as is shown in Fig. 3. From a detailed examination of the three principal values, it was found that the conformations whose calculated three principal values agree with the observed ones within ± 0.003 have (i) $\theta=90°$ and $90°<\psi<115°$ or (ii) $60°<\theta<90°$ and $105°<\psi<115°$. The g-factors for the D conformation ($\theta=85°$, $\psi=115°$, SS=2.17 Å, SH=1.358 Å (ass.)) cited in Fig. 4 are worth listing, since this conformation is most stable in the present calculations and closely resembles the estimated –S–S– geometry of dialkyl disulfide anions.[9)] The g-factors calculated ($g_{x'x'}=2.0172$, $g_{y'y'}=2.0003$, $g_{zz}=2.0124$, $g_{av}=2.0010$) agree well with the observed values.[1)]

The radicals which have been attributed to $R_2S_2^-$ are RCH_2-S-S-CH_2R^- ($g_\perp=2.018$, $g_{//}=2.002$),[9)] the n-amyl disulfide anion ($g_\perp=2.022$, $g_{//}=2.003$),[10)] and the dibenzoyldisulfide anion ($g_1=2.014$, $g_2=2.010$, $g_3=2.004$).[11)] In spite of the large substituents in these radicals, their g-factors have the same features as those of HSSH⁻. This indicates that the dependence of the conformation of $R_2S_2^-$ and of the electronic structure of the –S–S– group upon the substituent is relatively small, and that the present analysis of the g-factors gives information not only about HSSH⁻, but also about RSSR⁻.

The spin distribution of HSSH⁻ is worth discussing since the identification of HSSH⁻ has thus far rested on the ^1H and ^{33}S hyperfine coupling constants. The small ^1H coupling constants[1)] suggest that the primary interaction in ^1H coupling is due to spin polarization by an unpaired electron on the sulfur atom. The spin densities were thus calculated by means of the unrestricted SCF version[12)] with the MINDO/3 approximation. The spin density on the 3s(S) AO is almost constant (0.06—0.07) for all the above conformations (i) and (ii). The spin density on the 1s(H) AO depends largely on the HSS angle (−0.050(90°), −0.040(100°), −0.009 (115°), +0.001(120°), with the constant value of $\theta=90°$), while its dependence on θ is small. The calculated spin distribution[13)] and observed ^1H coupling constants (6—9 G)[1)] predict that the HSS angle will be 105°—115°.

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