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A Molecular Orbital Study of the Conformation and *g*-Factors of the $H_2SSH_2^+$ and H_2SSH Radicals

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Synopsis. The conformation and *g*-factors of the $H_2SSH_2^+$ and H_2SSH radicals were analyzed by means of a restricted open-shell SCF MO method with the semi-empirical MINDO/3 and INDO approximations, and the observed *g*-factors of the family of radicals consisting of $R_2SSR_2^+$, R_2SSR, and $RSSR^-$ were compared on the basis of their molecular and electronic structures.

Since the principal values of *g*-factors correlate strongly with the molecular structure of a radical, the theoretical analysis of the *g*-factors can clarify the molecular and electronic structure of the radical. We have elucidated the observed *g*-factors of the $HSSH^-$ radical anion in a previous paper.[1] Recently, much attention has been paid to the structure and stability of the S–S cation radicals.[2–4] In the present study, the *g*-factors of the $H_2SSH_2^+$ and H_2SSH radicals were examined, and the $H_2SSH_2^+$, H_2SSH, and $HSSH^-$ radicals are compared in terms of their molecular and electronic structures.

The MO's of the restricted doublet state were obtained by the use of the approximate SCF version proposed by Longuet-Higgins and Pople.[5] In the previous study of the $HSSH^-$ anion,[1] the MINDO/3 approximation was used. It is, however, uncertain whether MINDO/3 correctly predicts the *g*-factors of all of the neutral, anion, and cation radicals. Both the MINDO/3[6] and INDO[7] approximations were, thus, employed independently for the present calculation of $H_2SSH_2^+$ and H_2SSH. A more detailed description of the calculation of the *g*-factors has been reported elsewhere.[8–9]

$H_2SSH_2^+$ Radical. The observed $g_{av}(=(g_1+g_2+g_3)/3)$ values for the $R_2SSR_2^+$ radicals are $\simeq 2.01$;[2–3,10–11] no principal value has been reported. Since the 12 protons in $Me_2SSMe_2^+$ have equivalent hyperfine coupling constants,[10] the symmetric structures are examined. The MINDO/3 optimized $H_2SSH_2^+$ structures are I—IV. In all of the I—IV structures, the singly-occupied MO (SOMO) is the S–S antiboniding σ^* orbital. The large g_y value of the planar structure, I, comes from the contribution of the π(S–S) bonding orbital; the highest occupied π^*(S–S) orbital makes no contribution because of its symmetry property. The other two principal values of I, g_x and g_z, are close to the free-spin value, g_f. The skewed structure, II, has two lone-pair orbitals at the sulfur atoms; these 3p lone-pair orbitals contribute to the large g_y and g_z values of II. These electronic structure and *g*-factors of II are very similar to those of the $HSSH^-$ anion radical.[1] In the bent structures, III and IV, mixing occurs among the σ^* SOMO and the π orbitals. This mixing reduces the g_y value and gives smaller g_{av} values for III and IV.

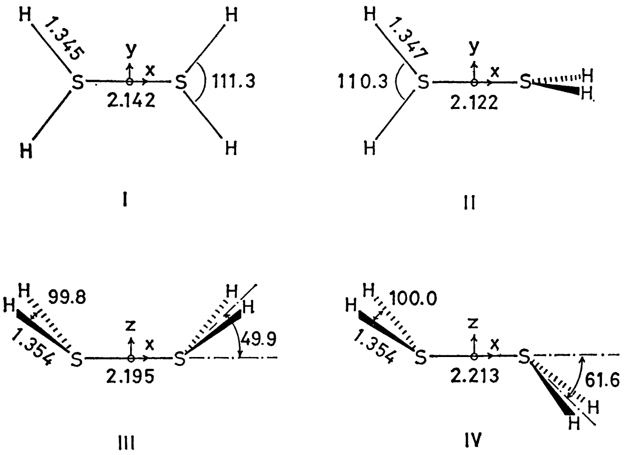

Fig. 1. The MINDO/3 optimized structures of the $H_2SSH_2^+$ radical. Bond lengths are in Å, and angles are in degrees.

Table 1. The MINDO/3 *g*-factors for four optimized structures of the $H_2SSH_2^+$ radical[a)]

	I	II	III	IV
E_{total}/eV	−515.377	−515.483	−515.907	−515.903
g_x	2.0023	2.0023	2.0022	2.0023
g_y	2.0156	2.0125	2.0067	2.0071
g_z	2.0031	2.0125	2.0018	2.0017
g_{av}	2.0070	2.0091	2.0036	2.0037

a) The coordinate axes are shown in the optimized structures in Fig. 1.

The INDO optimized structures are shown in Fig. 2, while their *g*-factors are listed in Table 2. The trend observed in the INDO *g*-factors of I′—IV′ is similar to that in the MINDO/3 *g*-factors.

The electronic structure of the $H_2SSH_2^+$ radical described above indicates that the g_y and g_{av} values depend largely on the S–S distance. The calculation showed that the increase in the g_{av} values of the planar and skewed structures, I and II, with an increase in the S–S distance was larger than that of the bent structures. The bent structure III with $R_{S-S}=2.542$ has $g_{av}=2.0118$. Since the principal values have not been reported for the $R_2SSR_2^+$ radical, it is difficult to derive any ultimate conclusion for the structure of the $H_2SSH_2^+$ radical from the present *g*-factor calculation. However, the present analysis of the *g*-factors suggests that the planar or skewed structure may correspond to the observed $R_2SSR_2^+$ structures. The present calculation shows a large difference in the principal values of the planar and skewed structures; the conformation of the $R_2SSR_2^+$ radicals may be determined if three principal values are determined experimentally.

H_2SSH Radical. The MINDO/3 optimized structure of H_2SSH is V. The calculated principal values of this structure are 2.036, 2.002, and 2.002.

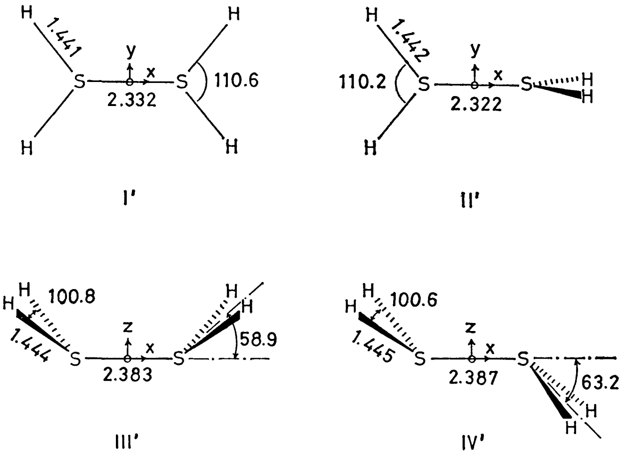

Fig. 2. The INDO optimized structures of the $H_2SSH_2^+$ radical.

Bond lengths are in Å, and angles are in degrees.

Table 2. The INDO g-factors for four optimized structures of the $H_2SSH_2^+$ radical[a)]

	I′	II′	III′	IV′
E_{total}/eV	−609.657	−609.713	−610.136	−610.153
g_x	2.0023	2.0023	2.0023	2.0023
g_y	2.0119	2.0080	2.0068	2.0074
g_z	2.0022	2.0080	2.0010	2.0010
g_{av}	2.0055	2.0061	2.0034	2.0036

a) The coordinate axes are shown in the optimized structures in Fig. 2.

Similar results were obtained by the INDO calculation; the optimized structure is V′, and its g-factors are 2.053, 2.002, and 2.002. The radicals attributed to R_2SSR are H_2SSH (g_1=2.066, g_2=2.025, g_3=2.003),[12)] EtHSSEt (g_1=2.063, g_2=2.027, g_3=1.999),[13)] and RCH_2SSHCH_2R (g_1=2.063, g_2=2.010, g_3=2.000).[12,14)] The two principal values are very large, while only one principal value is close to g_f. Since the two principal values of V and V′ are very close to g_f, the V and V′ structures can not explain the observed g-factors of the R_2SSR radicals. In the solid state, the environment effect may cause a deformation of the molecular structure of the radical. Thus, the dependence of the g-factors upon the conformation of H_2SSH was examined by means of MINDO/3. The g-factors were calculated by changing the S–S distance from 2.05 Å to 2.25 Å, the rotation angle about the S–S bond from −90° to +90°, the S–S–H angle from 100° to 140°, or the bending angle of the H_2S group from 0° to 60°. In all the conformations considered, the second largest principal values was less than 2.007. The results of this examination suggest that the observed principal values are possibly reproduced by the conformation with a very large SSH angle. The structures in Fig. 4 are the conformations for which the best agreement between the calculated and observed values was obtained. The g-factors of VI are 2.066, 2.023, and 2.000. The g-factors of VI′ are 2.067, 2.021, and 2.002. Although the VI and VI′ structures are more unstable than the optimized structures by 80 and 130 kJ mol^{-1} respectively, the present analysis of the g-factors suggests that the SSR* angle of the R_2SSR* radical would be much larger than those to be expected for the $R_2SSR_2^+$ and $RSSR^-$ radicals.

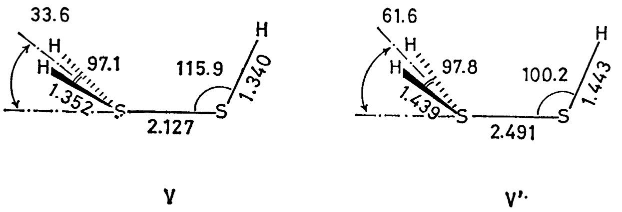

Fig. 3. The MINDO/3(V) and INDO(V′) optimized structures of the H_2SSH radical.

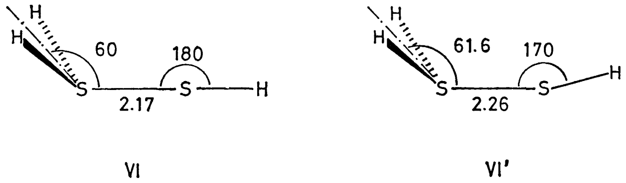

Fig. 4. The MINDO/3(VI) and INDO(VI′) structures of the H_2SSH radical which give the best agreement between the calculated and observed g-factors.

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