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The SCF MO Calculation of the *g* Value for the H_2NO Radical

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In our previous papers,[1] an approximate open shell SCF MO method with the CNDO approximation[2] was proposed and applied to quantitative discussions of the electronic structure and ESR parameters of the aliphatic nitric oxide radicals. The results on the *g* tensor of the H_2NO radical showed that the value of g_{yy}, the principal value of *g* along the N–O bond, was somewhat unsatisfactory. The present note will show that improved results for the g_{yy} of the H_2NO radical can be obtained by a modification of the evaluation of electron repulsion integrals or bonding parameters.

The principal values of the *g* tensor for the H_2NO radical, as calculated by Stone's formula,[3] are listed in Table 1. The results are those obtained by the SCF MO CNDO or INDO[5] approximation, where the values of bonding parameters given in the original papers of Pople and Segal[2] were used.[6] A better agreement with the experimental data was obtained by both these calculation methods than the previous one. The value of g_{yy} could be especially improved by the INDO calculation. This is because of the increase in the excitation energy from the non-bonding orbital of the oxygen atom to the odd-orbital and the decrease in spin density on the oxygen atom.

Table 1. Principal values of *g* tensor for H_2NO

	INDO[a]	CNDO/2[a]	CNDO/2[b]	Exp.[c]
g_{xx}	2.0045	2.0047	2.0050	2.0061
g_{yy}	2.0091	2.0104	2.0113	2.0089
g_{zz}	2.0023	2.0023	2.0023	2.0027
$g_{\mathrm{av.}}$	2.0053	2.0058	2.0062	2.0059

a) Bonding parameters used are those in Ref. 2.
b) Results in Ref. 1.
c) Values for di-*t*-butyl nitric oxide in Ref. 4.

The dependence of the *g* tensor on the molecular geometry of the radical is a subject of importance in the present theoretical study. The g_{yy} of the H_2NO radical is very sensitive to the variation in the N–O bond length and the HNH bond angle, but the g_{yy} is not. The value of g_{yy} obtained by the INDO calculation, for example, changes from 2.0083(1.20 Å) to 2.0119(1.30 Å) at the fixed HNH angle of 120°. This comes from the fact that the oxygen lone-pair orbital, which makes a large contribution to g_{yy}, is very sensitive to these changes in molecular geometry. The theoretical estimation of *g* tensors must, therefore, be carried out on the basis of a careful examination of the molecular geometry of a radical. For the H_2NO radical, the CNDO or the INDO method gives the minimum energy near the assumed structure of this radical, shown in Fig. 1. As was pointed out by Segal,[7] the CNDO method leads to some success in the evaluation of the equilibrium bond length. Therefore, the present results on the *g* tensor for the radical assuming the structure are acceptable.

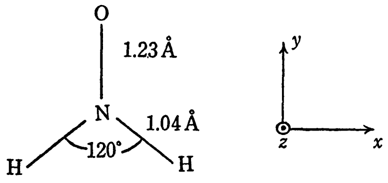

Fig. 1. Assumed stucture of H_2NO.

It may be concluded that the original CNDO/2 and INDO parametrizations give good theoretical results on the *g* value for the aliphatic nitric oxide radical. However, ambiguity still remains as to the applicability of these methods to other radicals. We have, though, applied the methods to several σ-type radicals and observed that the calculated principal values of the *g*-tensors of these σ-type radicals show good agreement with the experimental values.[8] Therefore, the theoretical investigation described here may be applicable to the estimation of *g* values of all other radicals.

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