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Molecular Orbital Treatment of Nitric Oxide Radicals. II. ESR Spectra of Aliphatic Nitric Oxide Radicals

Osamu KIKUCHI

Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo

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Quantitative discussions of the ESR spectra of aliphatic nitric oxide radicals have been undertaken on the basis of the molecular orbitals of all-valence-electrons, which were evaluated by the approximate SCF method with the CNDO/2 approximation. The spin density on the methyl proton in the dimethyl nitric oxide radical is proportional to $\cos^2\theta$, where θ is the angle between the nitrogen $2p_z$ orbital and the plane containing the C–N and the C–H bonds; the small hyperfine splitting constants of β-protons appearing in some substituted nitric oxide radicals are understood as resulting from the sterically-restricted conformations of substituted groups. The deviation of the g factor of aliphatic nitric oxide from the free spin comes from the large spin densities localized on the nitrogen and the oxygen atoms, and the small excitation energy, from the nonbonding orbital of the oxygen to the odd π-orbital. The electronic structures and g factors of some other radicals are compared to those of aliphatic nitric oxide radicals.

Theoretical treatments have been made by several investigators of the β-proton coupling in free radicals.[1–4] These have mainly been carried out by the perturbation method based on the hyperconjugation model. McLachlan[2] and Lykos[3] have applied the valence bond theory to some alkyl radicals and shown that hyperconjugation takes place between methyl groups and the α-carbon atom. Symons[4] has pointed out that the theory of hyperconjugation affords the best explanation of the large hyperfine coupling of β-protons in alkyl radicals. The hyperconjugation model corresponds to the delocalization of an odd electron onto the β-protons in the molecular orbital theory. The recently-developed molecular orbital theory, in which all valence electrons are explicitly considered, will make clear the mechanism of the β-proton coupling.

Stone[5] has presented a theory which can be used to calculate the g factors of aromatic molecules and has shown that the results for hydrocarbon and semiquinone ions calculated according to the theory agree well with the experimental results. This theory has since been used for a study of the solvent effect on the g factor of the diphenyl nitric oxide radical.[6] However, there have been few theoretical investigations of the correlation between the g factor and the molecular electronic structure, perhaps because it is difficult to calculate the electronic structures for all the valence electrons of large molecules.

In the present study, the approximate self-consistent molecular orbital method of Longuet-Higgins and Pople[7] is applied to the all-valence-electron system of several nitric oxide radicals, and the hyperfine splitting constants of β-protons and the g factors for aliphatic nitric oxide radicals are discussed.

Methods

The ground configuration of the free radical is a doublet, and its antisymmetrized wave function can be described by:

$$\Psi_g = |\phi_1\bar{\phi}_1 \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_m| \tag{1}$$

where $2m-1$ is the number of the valence electrons considered. The molecular orbital, ϕ_i, is obtained using the LCAO MO approximation:

$$\phi_i = \sum_r C_{ri}\chi_r \tag{2}$$

where χ_r is the valence atomic orbital: 1s for hydrogen and 2s, $2p_x$, $2p_y$, and $2p_z$, for carbon, nitrogen, and oxygen atoms. The LCAO coefficients and the orbital energy, ε_i, are calculated by the approximate SCF method, which has been applied to the discussion of the electronic structure

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[1] R. Bersohn, *J. Chem. Phys.*, **24**, 1066 (1956); J. P. Colpa and E. de Boer, *Mol. Phys.*, **7**, 33 (1964); D. B. Chesnut, *J. Chem. Phys.*, **29**, 43 (1958).

[2] A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

[3] P. G. Lykos, *J. Chem. Phys.*, **32**, 625 (1960).

[4] M. C. R. Symons, *Tetrahedron*, **18**, 333 (1962).

[5] A. J. Stone, *Proc. Roy. Soc.*, **A271**, 424 (1963); A. J. Stone, *Mol. Phys.*, **6**, 509 (1963).

[6] T. Kawamura, S. Matsunami, T. Yonezawa and K. Fukui, This Bulletin, **38**, 1935 (1965).

[7] H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc.*, **68**, 591 (1955).

and spectra of the H_2NO radical in a previous paper.8)

The spin density on the valence atomic orbital, *r*, can be simply computed by:

$$\rho_r = C_{rm}^2 \tag{3}$$

The diagonal components of the *g* factor are obtained by;5)

$$g_{aa} = 2.00232 + \Delta g_{aa} \tag{4}$$

$$\Delta g_{aa} = 2\sum_{i=1}^{m-1} \frac{\langle \phi_m | \sum_t l_a^t | \phi_i \rangle \langle \phi_i | \sum_t \zeta_t l_a^t | \phi_m \rangle}{E_{i\to m} - E_0} - 2\sum_{j=m+1}^{2m-1} \frac{\langle \phi_m | \sum_t l_a^t | \phi_j \rangle \langle \phi_j | \sum_t \zeta_t l_a^t | \phi_m \rangle}{E_{m\to j} - E_0} \tag{5}$$

where l^t is the angular momentum about the *t*th nucleus and where ζ_t is the spin-orbit coupling constant for the *t*th atom; the values of 29 cm^{-1}, 76 cm^{-1}, and 151 cm^{-1} were used for carbon, nitrogen, and oxygen atoms respectively.9) $E_{i\to m}$ and $E_{m\to j}$ are the energies of the following antisymmetrized wave functions:

$$\Psi_{i\to m} = |\phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_m \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_m| \tag{6}$$

$$\Psi_{m\to j} = |\phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_i \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_j| \tag{7}$$

then the energy differences in Eq. (5) are computed by the following equations:

$$\left.\begin{aligned} \Delta E_{i\to m} &\equiv E_{i\to m} - E_0 = \varepsilon_m - \varepsilon_i - (mm|ii) \\ &\quad + \frac{1}{2}(mm|mm) + \frac{1}{2}(mi|im) \\ \Delta E_{m\to j} &\equiv E_{m\to j} - E_0 = \varepsilon_j - \varepsilon_m - (mm|jj) \\ &\quad + \frac{1}{2}(mm|mm) + \frac{1}{2}(mj|jm) \end{aligned}\right\} \tag{8}$$

The two-electron integrals were evaluated by the method described by Pople *et al.*10) The *g* factor of the free radical in solution was estimated by:

$$g_{av} = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz}) \tag{9}$$

Results and Discussion

β-Proton Coupling Constants. A simple nitric oxide radical, $(CH_3)_2NO$, was adopted for discussing the β-proton coupling; the calculations were performed using the following assumptions for bond lengths and bond angles: 1.23, 1.41, and 1.10 Å11) for N–O, N–C, and C–H bonds respectively, and 120° for the CNO and CNC bond angles. The spin distributions have been obtained for a number of conformations of two methyl groups in the $(CH_3)_2NO$ radical. The results for a particular conformation of methyl groups ($\theta=90°$, $\phi=90°$) are presented in Table 1. In this table, the spin distribution calculated by the unrestricted Hartree-Fock method10) is also presented. The odd electron is accommodated into the orbital constructed mainly by the $2p_z$ atomic orbitals of nitrogen and oxygen, and the delocalization of the odd electron onto the methyl-protons is clearly

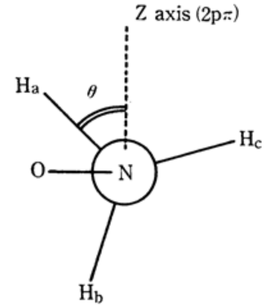

Fig. 1. CH_3–NO group in dimethyl nitric oxide radical.
The angle ϕ is defined as θ between the 2pπ orbital and the other methyl group.

Table 1. The spin distribution in the $(CH_3)_2NO$ radical*1

Atomic orbital*2	Calculated spin density I	Calculated spin density II*3
2s(C)	0.0000	−0.0019
$2p_x$(C)	0.0000	0.0002
$2p_y$(C)	0.0000	−0.0032
$2p_z$(C)	0.0000	−0.0109
2s(N)	0.0000	−0.0001
$2p_x$(N)	0.0000	−0.0002
$2p_y$(N)	0.0000	0.0000
$2p_z$(N)	0.4341	0.2284
2s(O)	0.0000	0.0000
$2p_x$(O)	0.0000	−0.0001
$2p_y$(O)	0.0000	−0.0004
$2p_z$(O)	0.4528	0.7505
$1s(H_a)$	0.0000	−0.0006
$1s(H_b)$	0.0283	0.0138
$1s(H_c)$	0.0283	0.0138

*1 Methyl groups were fixed at $\theta=90°$ and $\phi=90°$.
*2 The N–O axis is taken as y axis and z axis is perpendicular to the molecular plane (CNO plane).
*3 Method II is the unrestricted SCF method.

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8) O. Kikuchi, This Bulletin, **42**, 47 (1969).

9) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York (1967), p. 138.

10) J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); J. A. Pople and G. H. Segal, *ibid.*, **44**, 3289 (1966).

11) A. W. Hanson, *Acta Cryst.*, **6**, 32 (1935).

indicated. The unrestricted SCF method shows that there are actually negative spin densities on some atomic orbitals. In the present calculation of the spin distribution on the valence atomic orbitals, the angular dependence of the spin distribution on the methyl protons is discussed on the basis of the results obtained by the I method.

The methyl groups will rotate freely in solution, and the isotropic hyperfine splitting observed will be an average one. When the methyl group is not rotating freely, the proton splitting depends on the angle, θ, between the nitrogen $2p_z$ orbital and the plane containing the C–N and C–H bonds. In the molecular orbital treatment, this angular dependence of the hyperfine splitting constants can be resolved by the direct calculation of the spin densities on the 1s orbitals of the methyl protons, which are fixed at any angle. The $(CH_3)_2NO$ radical has two methyl groups; the splitting constant (spin density) for the proton in one methyl group (CH_3(I)) depends not only on the θ angle, but also on the conformation of the other methyl group (CH_3(II)). The variation in the spin density on the methyl protons with the conformation of the other methyl group was about 0.002 (5%); this corresponds to 1 gauss of the proton hyperfine splitting constant. The spin distribution on the methyl protons fixed at the θ angle was obtained on the assumption of free rotation for the other methyl group. The results are listed in Table 2.

TABLE 2. ANGULAR DEPENDENCE OF THE SPIN DENSITY OF THE METHYL-PROTON IN $(CH_3)_2NO$

θ°	ρ_H	$\rho_H/\rho_H(\theta=0)$	$\cos^2\theta$
−90	0.0000	0.000	0.000
−75	0.0026	0.068	0.067
−60	0.0097	0.255	0.250
−45	0.0193	0.506	0.500
−30	0.0288	0.754	0.750
−15	0.0356	0.933	0.933
0	0.0381	1.000	1.000
15	0.0356	0.934	0.933
30	0.0287	0.753	0.750
45	0.0192	0.504	0.500
60	0.0096	0.253	0.250
75	0.0026	0.067	0.067
90	0.0000	0.000	0.000

According to Symons,[4] if the hyperfine coupling occurs purely by hyperconjugation, it varies between zero when the β-C–H bond lies in the nodal plane of the unpaired electron and a maximum when it lies on a plane at right angles to this, while the splitting constants for intermediate positions vary according to the $\cos^2\theta$ law:

$$a_{\beta\text{-H}} = B\cos^2\theta \qquad (10)$$

The present finding regarding the angular dependence of the β-proton coupling coincides with that obtained by the hyperconjugation model, and the $\rho_{\beta\text{-H}} \propto \cos^2\theta$ relation holds strictly (Fig. 2). The spin density on the proton in the CH_3 group rotating freely can be estimated from Table 2 or Fig. 2, taking $\cos^2\theta = 0.5$. The obtained value, ρ (average) $= 0.019$, corresponds to the 9.5 gauss[12] β-proton splitting constant, while the experimental value of the $(CH_3)_2NO$ radical in solution is 13.4 gauss.[13]

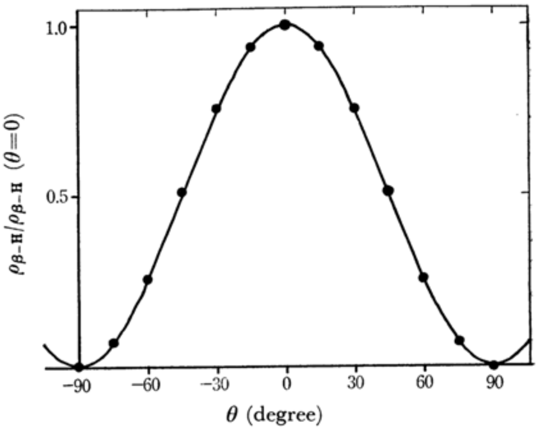

Fig. 2. Angular dependence of spin density on methyl-protons.
solid line: $\cos^2\theta$.
closed circle: calculated spin density.

From Fig. 2 or Table 2, the value of B in Eq. (10) can be estimated. The value of B is equal to $a_{\beta\text{-H}}$ at $\theta=0$. The calculated hyperfine splitting constant at $\theta=0$ was about 19 gauss; this is slightly smaller than the value of 27 gauss which was obtained from the experimental splitting constant, 13.4 gauss,[13] of the $(CH_3)_2NO$ radical in solution. From the calculated spin densities on the β-proton and on the nitrogen $2p_z$ orbital, the magnitude of McConnell's parameter, $Q_{N\text{-}CH_3}$, was estimated to be about 30 gauss.

The present results for the delocalization of the spin density on the β-methyl protons explain some interesting ESR experimental results for nitric oxide radicals. Some nitric oxide radicals reveal small hyperfine splitting constants of the β-protons.[13,14] For example, for di-isopropyl nitric oxide it is about 4 gauss, one third of that of β-protons in a freely-rotating methyl groups. Our results, shown in Fig. 3, indicate that the rotation of the isopropyl groups of this radical is restricted

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12) Hyperfine splitting constants of hydrogen atoms are computed by $a_H = \rho\,(1s) \times 502$ gauss.

13) G. Chapelet-Letourneux, H. Lemaire and A. Rassat, *Bull. Soc. Chim. France*, **1965**, 3283.

14) G. Coppinger and J. Swalen, *J. Am. Chem. Soc.*, **83**, 4900 (1961); J. Q. Adams, S. W. Nicksic and J. R. Thomas, *J. Chem. Phys.*, **45**, 654 (1966).

by the bulky substituents to a structure in which the β-proton oscillates through a small region ($-45° < \theta + 90 < 45°$) close to the N–O molecular plane.

For cyclic nitric oxide radicals, the axial and equatorial β-protons show equal hyperfine splitting constants. This is due to their rapid chair-to-chair conformational interconversion, and a time-averaged splitting constant, $\frac{1}{2}(a_{ax} + a_{eq})$, was observed. For the piperidine nitric oxide radical, it is 11.3 gauss;[13] from this value and the present calculations it can be understood that the equatorial proton in cyclic nitric oxide radicals lies in the region of $\theta = 90°$.

***g* Factors of Aliphatic Nitric Oxide Radicals.** The simplest nitric oxide radical, the H_2NO radical, was used in our attempt to understand the relation between the *g* factor and the molecular structure for the nitric oxide radical. The electronic structure of this radical has been discussed in the previous paper,[8] while the molecular orbital scheme obtained is shown in Fig. 3. In this figure, the atomic orbitals contributing to each molecular orbital are also presented. The odd electron resides in the π-orbital, and since the planarity of the H_2NO radical is assumed, $\Delta g_{zz} = 0$ (see Eq. (5)) and the *z* component of the *g* factor is the value for the free spin, 2.0023. The deviations, Δg_{xx} and Δg_{yy}, from the free spin can be calculated by Eq. (5). In this equation, the first term shows the contribution of the Ψ_{i-m} excited states, while the second term is the contribution of the Ψ_{m-j} excited states. The excitation energies were calculated from Eq. (8). The excitation energies and Δg_{xx} and Δg_{yy} are tabulated in Table 3. The most important excitation for the g_{xx} is the excitation from the N–O σ-bonding orbital (ϕ_4) to the odd orbital, while for g_{yy}, it is the excitation from the lone-pair orbital of the oxygen atom (ϕ_6) to the odd π-orbital. The small contribution of the N–O anti-bonding orbital (ϕ_{10}) is due to the LCAO coefficients of the ϕ_7 and ϕ_{10} molecular orbitals; when the electrons in these orbitals are shared equally by nitrogen and oxygen atoms, the contribution of this orbital is zero. The experimental values of g_{xx}, g_{yy}, and g_{zz} for the di-*t*-butyl nitric oxide radical have been reported as 2.0061, 2.0089, and 2.0027 respectively.[15] The present results show that the large deviations of g_{xx} and g_{yy} for this nitric oxide from the free spin are due to, respectively, the N–O bonding orbital and the lone pair of the oxygen atom. The average *g* factor of the H_2NO radical was 2.0062; this agrees well with the *g* factors (2.0055—2.0061[16]) of many aliphatic nitric oxide radicals in solution.

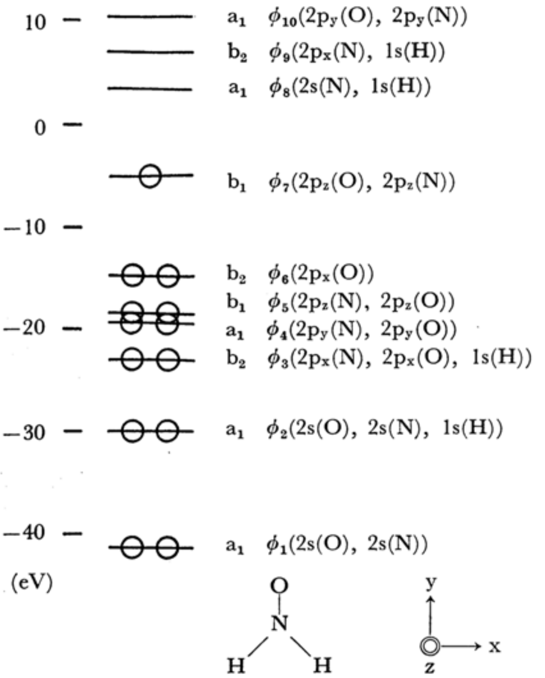

Fig. 3. Molecular orbital scheme for the H_2NO radical.

Table 3. Calculated excitation energies and *g*-factors for the H_2NO radical*1,2

Excitation	$\Delta E_{i \to j}$ (eV)	$\Delta g_{xx} \times 10^{-5}$	$\Delta g_{yy} \times 10^{-5}$
1→ 7	28.54	6	0
2→ 7	18.31	−1	0
3→ 7	12.15	0	0
4→ 7	6.73	352	0
6→ 7	2.32	0	983
7→ 8	4.79	−72	0
7→ 9	8.08	0	−87
7→10	7.56	−13	0
Total		272	896

*1 The choice of the axis is shown in Fig. 3.
*2 $\Delta g_{zz} = 0$

Similar results were obtained for the dimethyl nitric oxide radical. In this radical the lone-pair orbital of the oxygen atom and the N–O σ-bonding orbital mainly contribute to Δg_{yy} and Δg_{xx} respectively, while the contribution of the N–O anti-bonding orbital was again small. $\Delta g_{xx} = 167 \times 10^{-5}$ and $\Delta g_{yy} = 627 \times 10^{-5}$. These values are smaller than those of the H_2NO radical, mainly because of the smaller electron density of the non-bonding orbital and the smaller spin density on the oxygen atom in the dimethyl nitric oxide radical.

It is important to investigate the *g* factors for the other radicals in order to make clear the rela-

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15) O. H. Griffith, D. W. Cornell and H. M. McConnell, *J. Chem. Phys.*, **43**, 2909 (1965).

16) R. Briere, H. Lemaire and A. Rassat, *Bull. Soc. Chim. France*, **1965**, 3273; T. Kawamura, S. Matsunami and T. Yonezawa, This Bulletin, **40**, 1111 (1967).

tion between the g factor and the electronic structure of the free radical. In aromatic nitric oxide radicals such as diphenyl nitric oxide, π-electrons delocalize upon the large conjugate system. Nevertheless, some experimental results have shown that aromatic nitric oxide radicals have g factors similar to those of aliphatic nitric oxide radicals.6,17) It would be difficult to calculate the electronic structure of the all-valence-electron system for aromatic radicals; simple method for estimating the g factor of aromatic radicals is desirable. The relation between the g factor of aromatic nitric oxide and the spin densities on the nitrogen and oxygen atoms has been obtained employing some assumptions based on the electronic structure of aliphatic nitric oxide radicals. The g factor of the diphenyl nitric oxide radical in solution has been calculated by this method to be 2.0051. The details will be reported subsequently.

Another interesting kind of radical is the amino-radical. Unlike nitric oxide radicals, only a few investigations of these radicals by the ESR technique have been presented, perhaps because of their instability. Some of the amino-radicals investigated by the ESR method have been the NH_2 radical,18) the substituted anilino radical,19) and substituted diphenyl aminoradicals.20) In the present investigation, the g factor of the NH_2 radical has been calculated and compared with that for the H_2NO radical. In the NH_2 radical an odd electron occupies the $2p_z$ orbital of the nitrogen atom, and effective lone-pair electrons are on the y axis on the side away from the rest of the molecule.21) As a result, the deviation of g_{xx} from the free spin is expected to be large; the calculated results show that $\Delta g_{xx}=347\times10^{-5}$ and that the contribution of the NH σ-bond is small. The average value was 2.003722); this agrees with the experimental value.17) The main reason for the difference between the g factor of the H_2NO radical and that of the NH_2 radical is the different spin-orbit coupling constants for oxygen and nitrogen atoms.

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17) P. H. H. Fischer and F. A. Neugebauer, *Z. Naturforschg.*, **18a**, 1514 (1964).

18) S. Foner, E. Cochran, V. Bawers and C. Jen, *Phys. Rev. Letters*, **1**, 91 (1958).

19) E. Muller, A. Rieker and K. Scheffler, *Ann. Chem.*, **645**, 92 (1961); N. M. Atherton, E. J. Land and G. Poryer, *Trans. Faraday Soc.*, **59**, 818 (1963).

20) F. A. Neugebauer and P. H. H. Fischer, *Chem. Ber.*, **98**, 844 (1965).

21) The y axis taken as C_{2v} rotation axis; z perpendicular to the molecular plane.

22) $\Delta g_{yy}=53\times10^{-5}$ (calculated).