BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1472—1475 (1969)

Molecular Orbital Treatment of Nitric Oxide Radicals. III. Spin Distributions and g Factors of Aromatic Nitric Oxide Radicals

Osamu Kikuchi

Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo

(Received July 25, 1958)

The spin distributions and g factors have been calculated for several aromatic nitric oxide radicals. The spin distributions calculated by the open-shell SCF method with configuration interaction, and by the unrestricted SCF method with the annihilation of the quartet component from the single determination wave function, agreed with the experimental values estimated from the ESR spectra. The contributions of the lone-pair orbital of the oxygen and of the N–O σ-bonding orbital to the g factor were calculated, the calculated g factors in solution being in the range of 2.005—2.006; these values were then discussed on the basis of the electronic structures of nitric oxide radicals.

In preceding papers,[1,2] the electronic structure and the spectrum of the H_2NO radical, and the ESR spectra of aliphatic nitric oxide radicals were discussed quantitatively on the basis of a SCF MO method in which all the valence electrons were explicitly considered. One purpose of this paper is to calculate the spin distributions for the phenyl nitric oxide, the diphenyl nitric oxide, and the carbazole *N*-oxide radicals by the open-shell SCF procedure of Longuet-Higgins and Pople[3] with configuration interaction, and also by the unrestricted Hartree-Fock method,[4] and to compare the calculated spin distributions with the experimental values estimated from the ESR spectra. The π-electrons of aromatic molecules delocalize upon a large conjugated system; nevertheless, some experimental results have shown that the aromatic nitric oxide radical reveals a g factor

---

[1] O. Kikuchi, This Bulletin, **42**, 47 (1969).

[2] O. Kikuchi, *ibid.,* **42**, 1187 (1969).

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

[4] J. A. Pople and R. K. Nesbet, *J. Chem. Phys.,* **22**, 571 (1954); A. Brickstock and J. A. Pople, *Trans. Faraday Soc.,* **50**, 901 (1954); A. T. Amos and L. C. Snyder, *J. Chem. Phys.,* **41**, 1773 (1964).

similar to that of the aliphatic nitric oxide radical.[5] The second purpose of this note is to estimate the g factor of the aromatic nitric oxide from the spin density on the N–O group and the orbital energy of the odd π-orbital. The results will be discussed on the basis of the electronic structures of aromatic nitric oxides.

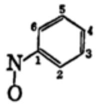
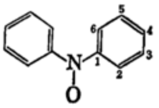
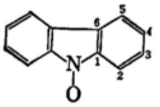
Calculation Procedure

The calculation procedure and all the parameters except the core resonance integrals were the same as those reported elesewhere.[6] The g factor was calculated by means of the equation presented by Stone.[7] The core resonance integrals were computed by the relations:[8]

$$\left.\begin{aligned}\beta_{rs} &= -0.4172S_{rs}(I_r+I_s) \quad (R_{rs} \leq 3\text{Å}) \\ &= 0 \qquad\qquad\qquad\qquad\quad (R_{rs} > 3\text{Å})\end{aligned}\right\} \tag{1}$$

where R_{rs} is the distance between the rth and sth atoms; S_{rs}, the overlap integral between two $2p_z$ Slater-type atomic orbitals, and I_r, the ionization potential for the valence atomic orbital, r. For all the C–C and C–N bonds, the bond lengths were assumed to be 1.40 Å, while for the N–O bonds, they were assumed to be 1.23 Å.[9] The bond angles were also assumed to be 120° and 108° for the benzene rings and the pyrol ring respectively. The overlap integrals were computed using the formula given by Mulliken, Rieke, Orloff, and Orloff[10] with the effective nuclear charges determined from the electron densities by

TABLE 1. CALCULATED AND EXPERIMENTAL[5,11] SPIN DISTRIBUTIONS IN AROMATIC NITRIC OXIDE RADICALS

		Exp.[*1]	Calcd[*2]			
			I	II	III	IV
Phenyl nitric oxide						
	O		0.3402	0.5186	0.4792	0.4658
	N		0.2566	0.3310	0.3837	0.3751
	1		0.0155	−0.0368	−0.1472	−0.0424
	2	0.107	0.1250	0.0855	0.1725	0.0972
	3	−0.036	0.0007	−0.0336	−0.1088	−0.0348
	4	0.107	0.1293	0.0800	0.1550	0.0780
	5	−0.036	0.0000	−0.0302	−0.1072	−0.0345
	6	0.107	0.1327	0.0855	0.1728	0.0955
Diphenyl nitric oxide						
	O		0.3077	0.5119	0.4771	0.4587
	N		0.2000	0.2547	0.3020	0.2958
	1		0.0099	−0.0184	−0.1157	−0.0336
	2	0.068	0.0765	0.0528	0.1362	0.0749
	3	−0.030	0.0010	−0.0061	−0.0858	−0.0276
	4	0.068	0.0756	0.0644	0.1232	0.0608
	5	−0.030	0.0002	−0.0199	−0.0853	−0.0256
	6	0.068	0.0830	0.0439	0.1378	0.0758
Carbazole *N*-oxide						
	O		0.3127	0.5301	0.5066	0.4903
	N		0.1733	0.2302	0.2579	0.2606
	1		0.0202	−0.0053	−0.0717	−0.0147
	2	0.083	0.0676	0.0400	0.1076	0.0620
	3	−0.025	0.0112	0.0007	−0.0531	−0.0153
	4	0.083	0.0674	0.0592	0.0941	0.0488
	5	−0.025	0.0140	−0.0123	−0.0520	−0.0145
	6		0.0765	0.0375	0.0928	0.0584

[*1] The values estimated from the relation $a_{\text{H}}=27\times\rho_{\text{C}}$; M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 1350 (1965).

[*2] The values calculated by the following methods;[6]

I) The open shell SCF method

II) The open shell SCF method with CI

III) The unrestricted SCF method

IV) The unrestricted SCF method with annihilation

---

5) Y. Deguchi, This Bulletin, **35**, 260 (1962); P. H. H. Fischer and F. A. Neugebauer, *Z. Naturforchg.*, **18a**, 1514 (1964); T. Kawamura, S. Matsunami, T. Yonezawa and K. Fukui, This Bulletin, **38**, 1935 (1965); O. Kikuchi and K. Someno, *ibid.*, **40**, 2549 (1967); G. Chapelet-Letourneux, H. Lemaire and A. Rassat, *Bull. Soc. Chim. France,* **1965**, 3283.

6) O. Kikuchi and K. Someno, This Bulletin, **40**, 2972 (1967).

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

8) The numerical constant was chosen so that the value of β_{rs} for benzene calculated by Eq. (1) using $R=$ 1.39Å and $Z=3.25$ fits the empirical value, -2.39 eV.

9) A. W. Hanson, *Acta Cryst.*, **6**, 32 (1953).

10) R. S. Mulliken, C. R. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

each iteration.

Results and Discussion

The spin densities calculated for the phenyl nitric oxide, the diphenyl nitric oxide, and the carbazole *N*-oxide radicals are listed in Table 1. The spin densities of the phenyl nitric oxide agree well with the experimental values; the II and IV methods give a better agreement. From the theoretical point of view, the spin distributions calculated either by the method with configuration interaction (II) or by the annihilation of the quartet component of a single Slater-determinant (IV) are satisfactory. The ESR study of some substituted phenyl nitric oxide radicals has shown that the hyperfine splitting constants of two protons at the 2 and 4 positions differ from each other.[12] The present results (IV) show that $\rho_2 > \rho_4$; this is the relation observed in the experiment. The spin densities of the carbazole *N*-oxide radical also agree with the experimental values. The nitrogen hyperfine splitting constant (3.5—7.0 gauss[11]) of the carbazole *N*-oxide, small in comparison with that of the diphenyl nitric oxide (9.5 gauss[5]), can be explained by the calculated spin densities on the nitrogen and oxygen atoms of these two radicals.[13]

It has been shown that, in nitric oxide radicals, the deviation of the *g* factor from the value of the free spin is caused mainly by the lone-pair orbital of the oxygen atom and by the N–O σ-bonding orbital.[2] In the calculation of the *g* factor, it is necessary to estimate not only the spin distribution, but also the excitation energies from the σ-orbitals to the odd π-orbital. It is troublesome to calculate the electronic structure for the valence electron system of an aromatic radical. In the present investigations, therefore, these excitation energies were estimated by employing some assumptions based on the electronic structure of aliphatic nitric oxide radicals. The excitation energy from the σ-orbital to the odd π-orbital is given by:

$$\Delta E_{\sigma\to\pi^\circ} = \varepsilon_{\pi^\circ} - \varepsilon_\sigma - J_{\sigma\pi^\circ} + \frac{1}{2}J_{\pi^\circ\pi^\circ} + \frac{1}{2}K_{\sigma\pi^\circ} \tag{2}$$

where ε_{π° and ε_σ are the molecular orbital energies for the odd π-orbital and for the σ-orbital respectively. The LCAO approximation and the zero-differencial overlap approximation reduce the two-electron integrals in Eq. (2) to:

$$\left.\begin{aligned} J_{\sigma\pi^\circ} &= \sum_{r,s} C^2{}_{r\sigma} C^2{}_{s\pi^\circ}(r_\sigma r_\sigma|ss) \\ J_{\pi^\circ\pi^\circ} &= \sum_{r,s} C^2{}_{r\pi^\circ} C^2{}_{s\pi^\circ}(rr|ss) \\ K_{\sigma\pi^\circ} &= 0 \end{aligned}\right\} \tag{3}$$

These equations show that the integral values depend largely on the spin distribution of a radical, while for the nitric oxide radical the contribution of the spin density on the N–O group to the integral value is most important. The problem is treated as a "three-atom problem" in which the spin desnity $(1-\rho_{NO})$ is on the third atom, X, bonded to the nitrogen atom, where ρ_{NO} is the sum of the spin densities on the nitrogen and oxygen atoms. The localization of the lone-pair electrons on the oxygen atom is assumed;[14] we then obtain:

$$\begin{aligned} J_{n\pi^\circ} = {} & \rho_O(nn|OO) + \rho_N(nn|NN) \\ & + (1-\rho_{NO})(nn|XX) \end{aligned} \tag{4}$$

The one-center integral of the nitrogen, (NN|NN), is taken to be approximately equal to that of the oxygen, (OO|OO);[15] the value of the two-center integrals, γ, in this equation are taken to be approximately a half of the one-center integral.[15] Therefore,

$$J_{n\pi^\circ} = \gamma(1+\rho_O) \tag{5}$$

Similarly,*1

$$J_{\pi^\circ\pi^\circ} = \gamma(1 + \rho_O{}^2 + \rho_N{}^2) \tag{6}$$

From Eqs. (5) and (6), the excitation energy for the $n\to\pi$ excitation is given by:

$$\Delta E_{n\to\pi^\circ} = \varepsilon_{\pi^\circ} - \varepsilon_n - \frac{\gamma}{2}(1+2\rho_O - \rho_O{}^2 - \rho_N{}^2) \tag{7}$$

A simpler relation between the excitation energy and the spin density on the N–O group is obtained by setting $\rho_N = \rho_O = \frac{1}{2}\rho_{NO}$:

$$\Delta E_{n\to\pi^\circ} = \varepsilon_{\pi^\circ} - \varepsilon_n - \frac{\gamma}{4}(2+2\rho_{NO} - \rho_{NO}{}^2) \tag{8}$$

When the electrons in the N–O σ-bonding orbital are shared equally on the nitrogen and the oxygen atoms,[16] the same relation (8) is obtained for the excitation from the N–O σ-bonding orbital to the odd π-orbital. For the values of ε_n and $\varepsilon_{\sigma(N-O)}$, the preceding results concerning the H_2NO radical were used: $\varepsilon_n = -14.75$ eV and $\varepsilon_{\sigma(N-O)} = -19.20$ eV.[1] The value of the two-center integral, γ,

---

[11] H. R. Falle and G. R. Luckhurst, *Mol. Phys.*, **12**, 493 (1967).

[12] Th. A. J. W. Wajer, A. Mackor, Th. J. de Boer and J. D. W. van Voorst, *Tetrahedron Letters*, **20**, 1941 (1967).

[13] A nitrogen hyperfine splitting constant of an aromatic nitric oxide radical can be estimated by the relation,

$$a_N = \rho_N|Q_N| - \rho_O|Q_O|.$$

[14] Strictly speaking, the lone-pair electron of the oxygen atom is not completely localized on the oxygen atom (see Ref. 1.)

[15] In the calculation for the H_2NO radical, the electron repulsion integrals were $\gamma_{NN}=19.3$, $\gamma_{OO}=22.5$, and $\gamma_{NO}=11.3$ eV (see Ref. 1).

*1 Equation (3) is expanded as:

$$\begin{aligned} J_{\pi\pi} = {} & \rho_N{}^2(NN|NN) + \rho_O{}^2(OO|OO) \\ & + 2\rho_N\rho_O(NN|OO) + c(1-\rho_{NO}{}^2) \end{aligned}$$

where the constant, *c*, corresponds to the mean value of (tt/uu) (t=C, u=C, N, O); this value is approximately equal to the two-center integral, γ.

[16] For the H_2NO radical, this is correct (see Ref. (1)).

TABLE 2. CALCULATED *g* FACTORS FOR AROMATIC NITRIC OXIDE RADICALS

	Odd orbital energy*1 (eV)	Excitation energy (eV)		$\Delta g_{xx}\times 10^{-5}$	$\Delta g_{yy}\times 10^{-5}$	*g*, Factor*2		
		$n\to\pi^\circ$	σ(N-O)$\to\pi^\circ$			g_{xx}	g_{yy}	g_{av}*3
H_2NO radical	−3.63	2.77	7.22	388	678	2.0062	2.0091	2.0059
Phenyl nitric oxide	−4.94	1.89	6.34	265	674	2.0050	2.0091	2.0055
Diphenyl nitric oxide	−5.18	1.87	6.32	225	617	2.0046	2.0086	2.0051
Carbazole *N*-oxide	−5.64	1.47	5.92	226	798	2.0046	2.0103	2.0057

*1 Obtained from the calculation I

*2 The most important excited states correspond to the excitations from the non-bonding orbital to the odd π-orbital and from the N-O σ-bonding to the odd π-orbital and only these excitations were considered. The contributions from the other excited states are small.[2] N-O axis taken as y axis; z axis perpendicular to molecular plane.

*3 Obtained by $g_{av}=\frac{1}{3}(g_{xx}+g_{yy}+g_{zz})$ with $g_{zz}=2.0023$

is determined so that the $n\to\pi$ excitation energy of the H_2NO radical calculated from Eq. (8) agrees with the experimental $n\to\pi$ transition energy of the aliphatic nitric oxide radical (2.76 eV[17]). The relations obtained are:

$$\left.\begin{aligned}\Delta E_{n\to\pi^\circ}(\text{eV}) &= \\ &\varepsilon_{\pi^\circ}+14.75-2.79(2+2\rho_{\text{NO}}-\rho_{\text{NO}}{}^2) \\ \Delta E_{\sigma(\text{N-O})\to\pi^\circ}(\text{eV}) &= \\ &\varepsilon_{\pi^\circ}+19.20-2.79(2+2\rho_{\text{NO}}-\rho_{\text{NO}}{}^2)\end{aligned}\right\} \qquad (9)$$

Using the spin density on the N–O group and the orbital energy of the odd π-orbital, the excitation energies and the *g* factors of aromatic nitric oxide radicals were calculated; they are tabulated in Table 2. The averaged *g* factors for aromatic nitric oxide radicals were in the range of 2.005—2.006; they agree with the experimental values in solution.[5] It may be concluded that, in aromatic nitric oxide radicals, the spin density on the N–O group is smaller than that for the aliphatic nitric oxide radical, but the excitation energy from the σ-frame to the odd π-orbital is lower than that for the aliphatic nitric oxide, mainly because of the lower energy of the odd π-orbital. As a result, aromatic nitric oxide radicals reveal *g* factors similar to those of aliphatic nitric oxide radicals.

The author wishes to express his thanks to Professor Keizo Suzuki, Tokyo Kyoiku University, and to Dr. Kazuo Someno, Government Chemical Industrial Research Institute, Tokyo, for their helpful suggestions and encouragement during the course of this work. Thanks are also due to the Matsunaga Science Foundation for financial support.

---

17) R. Briere, H. Lemaire and A. Rassat, *Bull. Soc. Chim. France,* **1965**, 3273.