The Effect of Hydrogen-Bonding on the *g*-Value of Diphenyl Nitric Oxide

By Takashi Kawamura, Shoichi Matsunami, Teijiro Yonezawa and Kenichi Fukui

(Received March 29, 1965)

The solvent effects on the hyperfine structure of the ESR spectra of semiquinones,[1,2] nitrocompounds[3-5] and aromatic nitric oxides[6,7] have been reported on. However, only a few studies of the solvent effect upon the *g*-value have been reported.[8] Stone has derived the gauge-invariant *g*-tensor[9] and an equation as for calculating the *g*-value of a π-radical.[10] His work suggests that the *g*-value of a π-radical which contains an oxygen atom in conjugated systems would deviate considerably from the *g*-value of a free electron (2.00232) because of the large L-S coupling of oxygen as well as the small difference in energy between the odd-electron orbital and the oxygen lone-pair orbital. This has also been pointed out qualitatively by McConnell and Robertson.[11]

It may be expected that the formation of a hydrogen bond to an oxygen atom in a conjugated system would diminish the contribution of the oxygen atom to the *g*-value through lowering the lone-pair orbital energy and decreasing the odd-electron density on the oxygen atom, thus causing a variation in the *g*-value. In the present paper we will investigate the effect of the hydrogen bond on the *g*-value of diphenyl nitric oxide (DPNO); we will attempt a precise analysis.

Experimental

Materials.—DPNO was synthesized by employing the method of Wieland and Roth,[12] recrystallized from methanol (m. p. 62—63°C), sealed in an ampoule under 10^{-4} mmHg vacuum, and stored in liquid nitrogen.[6] Carbon tetrachloride, chloroform, ethanol and toluene were purified by following the directions described in "Organic Solvents."[13] Phenylacetylene was purified by distillation from Drierite in a vacuum. Phenol was purified by the freezing method.

The Measurement of the ESR Spectra.—Several solvents were employed in preparing a dilute solution of DPNO. The solvents were dried over Drierite for at least one day and then distilled from Drierite under a 10^{-4}—10^{-5} mmHg vacuum into sample tubes which had previously been charged with DPNO. In the case of a phenol-toluene mixed solvent, a dilute solution of DPNO was prepared under ordinary atmospheric conditions, charged into a sample tube, and then degassed. The ESR spectrometer employed was a JES-3BX-type instrument with a 100 kc. modulation, made by the Japan Electron Optics Co. The static magnetic field was generated by a JES electro-magnet with 300 mmϕ pole pieces, with a homogeneity of 1×10^{-5}. For the measurement of the *g*-value and hyperfine splittings, a glass capillary was attached to a sample. The capillary, as in the usual procedure, was filled, as a reference compound, with an aqueous solution of potassium peroxylamine disulfonate, the *g*-value and the hyperfine coupling constant of the ^{14}N of which had been reported to be 2.00550±0.00005 and 13.0±0.1 gauss.[14]

All the measurements of the ESR spectra and the visible spectra were performed at room temperature (10—20°C).

Results

The numbering of the positions in the DPNO molecule is shown in Fig. 1c. The ESR spectrum of DPNO in carbon tetrachloride is shown in Fig. 1a, and a constructed spectrum with coupling constants of $a_{1\text{-H}}=a_{3\text{-H}}=1.845$, $a_{2\text{-H}}=0.810$ and $a_{\text{N}}=9.559$ gauss, in Fig. 1b. Figure 1b shows a good agreement with the observed spectrum in Fig. 1a. The *g*-value of DPNO in carbon tetrachloride proved to be 2.00572 ±0.00005.

The *g*-value and hyperfine coupling constants of 1- and 3-protons are listed in Table I, together with the changes in them caused by

---

[1] W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962).

[2] J. Gendell, J. H. Freed and G. L. Fraenkel, ibid., **37**, 2835 (1962).

[3] L. H. Piette, P. Ludwig and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 4212 (1962).

[4] P. L. Kolker and W. A. Waters, *J. Chem. Soc.*, **1964**, 1136.

[5] C. Corvaja and G. Giacometti, *J. Am. Chem. Soc.*, **86**, 2736 (1964).

[6] Y. Deguchi, This Bulletin, **33**, 260 (1962).

[7] K. Umemoto, Y. Deguchi and H. Takaki, ibid., **36**, 560 (1963).

[8] In the course of our experiments, Zandstra has reported on the solvent effect of the *g*-value of *p*-benzosemiquinone, but his comparison is between in only two solvents, water and dimethylsulfoxide. R. J. Zandstra, *J. Chem. Phys.*, **41**, 3655 (1964).

[9] A. J. Stone, *Proc. Roy. Soc.*, **A271**, 424 (1963).

[10] A. J. Stone, *Mol. Phys.*, **6**, 509 (1963).

[11] H. M. McConnell and R. E. Robertson, *J. Phys. Chem.*, **61**, 1018 (1957).

[12] H. Wieland and K. Roth, *Ber.*, **53**, 216 (1920).

[13] J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," 2nd ed., Interscience Pub. Inc., N. Y. (1955).

[14] J. Q. Adams and J. R. Thomas, *J. Chem. Phys.*, **39**, 1904 (1964).

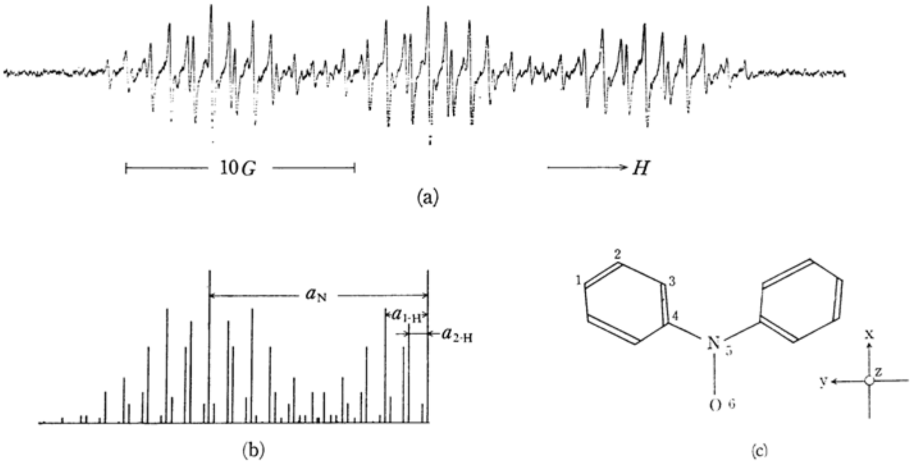

Fig. 1. (a) ESR spectrum of diphenyl nitric oxide in carbon tetrachloride.
(b) Reconstructed spectrum with $a_{1\text{-H}}=a_{3\text{-H}}=1.845$, $a_{2\text{-H}}=0.810$ and $a_{\text{N}}=9.559$ gauss.
(c) Numbering of positions in diphenyl nitric oxide molecule.

TABLE I. THE OBSERVED g-VALUE AND HYPERFINE COUPLING CONSTANTS OF 1- AND 3-PROTONS AND THEIR SHIFTS

Solvent	$(g-g_{\text{POA}})$ $\times 10^5$ a)	$a_{1\text{-H}}=a_{3\text{-H}}$ b) Gauss	$\delta\Delta g$ $\times 10^5$	$\delta a_{1\text{-H}}$ Gauss
Carbon tetrachloride	$+22\pm1$	1.845 ± 0.008	0	0
Phenylacetylene	$+10\pm2$	1.879 ± 0.006	-12	$+0.034$
Chloroform	$+6\pm1$	1.890 ± 0.003	-16	$+0.045$
Ethanol	$+4\pm1$	1.913 ± 0.014	-18	$+0.068$
Methanol	$+0\pm1$	1.917 ± 0.002	-22	$+0.072$
Phenol in toluene (4.4 mol./l. soln.)	-35 ± 1	2.068 ± 0.007	-57	$+0.223$
Water	-42 ± 1	2.105 ± 0.003	-64	$+0.260$

a) The measurement of g-value is performed by employing peroxylamine disulfonate as a reference. The g-value of peroxylamine disulfonate is notated as g_{POA}.

b) Experimentally found values of $a_{1\text{-H}}$ and $a_{3\text{-H}}$ are equal in all solvents employed, although 1- and 3-protons are non-equivalent.

the variation in solvents employed. The differences of these values from those in carbon tetrachloride are denoted by $\delta\Delta g$ and $\delta a_{1\text{-H}}$ respectively, where Δg means the difference in g-value from that of free spins, which is indicated in Eq. 1.

The visible spectra of DPNO in carbon tetrachloride, chloroform, ethanol and methanol are shown in Fig. 2.

In the visible spectrum of DPNO in carbon tetrachloride, the absorptions at 578 mμ (shoulder) ($\log \varepsilon=1.97$), 537 mμ (2.24) and 512 mμ (2.26) are taken to be the n-π^* transition, and the absorptions at 473 mμ (2.66) and 395 mμ (3.17) are taken to be the π-π^* transition, because the former three shift toward blue and the latter two, toward red when dissolved in hydrogen-bond-forming solvents.[15] Although the observed spectra show that the magnitude of the blue shift of the n-π^* transition is parallel with the hydrogen-bonding ability of the solvents, and also with the shift of the g-value and the hyperfine coupling constants, the position of n-π^* absorption in hydrogen-bonding solvents, unfortunately, can not be determined with accuracy.

Discussion

Stone's Theory for the g-Value.—Considering only one-center integrals and using the two-center σ-molecular orbital model, Stone has derived the following equation to give the g-value of a π-radical:[10]

$$g=2.00232+\Delta g \tag{1}$$

$$\Delta g=\sum_i \Delta g_i+\sum_j \Delta g_{\text{n}j} \tag{2}$$

---

[15] H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

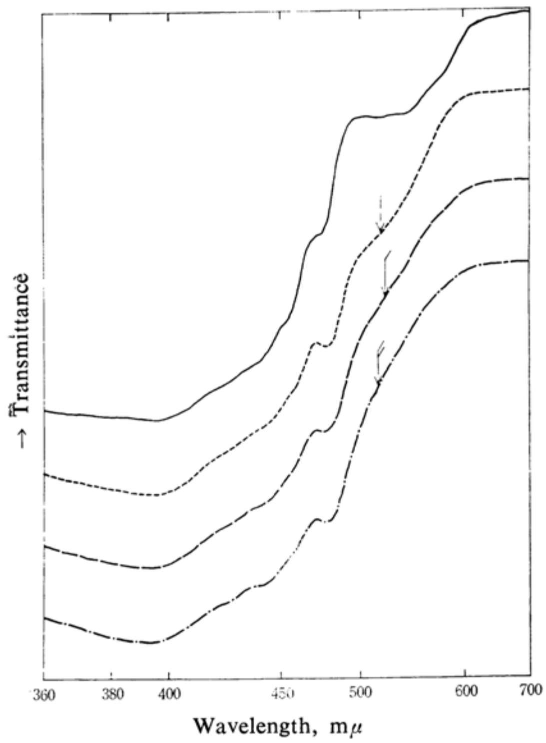

Fig. 2. Visible spectra of DPNO in carbon tetrachloride ——, in chloroform ----, in ethanol — — — and in methanol —·—·—. Arrows ↓, ↙ and ⇙ show the position of *n*-π^* transition of DPNO in chloroform, in ethanol and in methanol calculated from the *g*-value (see text).

$$\Delta g_i = \frac{2}{3}\sum_{m}^{a,\,b} \frac{\zeta_r (C^m{}_{rx})^2 (C^p{}_r)^2 + \zeta_s (C^m{}_{sx})^2 (C^p{}_s)^2 + (\zeta_r+\zeta_s) C^m{}_{rx} C^m{}_{sx} C^p{}_r C^p{}_s}{\varepsilon^p - \varepsilon^m{}_i} + \frac{2}{3}\sum_{m}^{a,\,b} \frac{\zeta_r (C^m{}_{ry})^2 (C^p{}_r)^2 + \zeta_s (C^m{}_{sy})^2 (C^p{}_s)^2 + (\zeta_r+\zeta_s) C^m{}_{ry} C^m{}_{sy} C^p{}_r C^p{}_s}{\varepsilon^p - \varepsilon^m{}_i} \tag{3}$$

$$\Delta g_{nj} = \frac{2}{3}\,\frac{\zeta_j \{(C^n{}_{jx})^2 + (C^n{}_{jy})^2\} (C^p{}_j)^2}{\varepsilon^p - \varepsilon^n{}_j} \tag{4}$$

where Δg_i and Δg_{nj} are the contributions to Δg from *i*th σ-bond and the *j*th lone-pair orbital respectively; the notation $\sum\limits_i$ and $\sum\limits_j$ in Eq. 2 indicate the sums over σ-bonds and over lone-pairs respectively. Throughout this paper, *g* and all the Δg's are the average with respect to three spatial axes. In Eq. 3, *a* and *b* indicate the bonding and the anti-bonding orbitals of the *i*th σ-bond between atoms *r* and *s*. When the nodal plane of the π-orbital is the xy-plane, $C^p{}_r$ is the coefficient of the P_z atomic orbital (AO) of the atom *r* in the odd-electron orbital; $C^m{}_{rx}$ and $C^m{}_{ry}$ are coefficients of the P_x and P_y AO's of the atom *r* in the *m*th σ-orbital, and so on. The notations ζ_r and ζ_s are L-S coupling constants about the *r* and *s* nuclei. The notations $C^n{}_{jx}$ and $C^n{}_{jy}$ in Eq. 4 are the coefficients of the P_x and P_y AO's in the *j*th lone-pair orbital, while $C^p{}_j$ and ζ_j are the coefficient in the odd-electron orbital and the L-S coupling constant of the atom which has the *j*th lone-pair. When many-center integrals are neglected, fully-occupied or vacant π-orbitals do not mix into the half-occupied π-orbital by means of the perturbation of the L-S coupling. Thus, the summation in Eq. 2 is only required over all of the σ-bonds and lone-pair orbitals.

The Calculation of the *g*-Value of DPNO in Carbon Tetrachloride.—The π-orbitals of DPNO were obtained by the Hückel molecular orbital method, with parameters of $\alpha_O = \alpha + \beta$, $\alpha_N = \alpha + 2\beta$, $\beta_{NC} = 0.7\beta$ and $\beta_{NO} = 0.7\beta$.[16] The calculated odd-electron orbital energy, the odd-electron densities, $\rho_r = (C^p{}_r)^2$, and the odd-electron orbital bond-orders, $p^p{}_{rs} = C^p{}_r \times C^p{}_s$, are as follows:

$$\varepsilon^p = \alpha + 0.5090\beta = -8.33\ \text{eV.}^{17)},$$

$$\rho_1 = 0.0551, \qquad \rho_2 = 0.0036,$$
$$\rho_3 = 0.0418, \qquad \rho_4 = 0.0268,$$
$$\rho_5 = 0.2160, \qquad \rho_6 = 0.4389,$$
$$p^p{}_{45} = -0.0761, \qquad p^p{}_{56} = -0.3079$$

To obtain N–O and N–C σ-orbitals, an extended Hückel molecular orbital calculation[18] of $((CH_2)_2C)_2NO$ was performed, on the assumption that all bond angles were 120°, and that the C–H, C–C, C–N and N–O distances were 1.084 Å, 1.397 Å, 1.40 Å and 1.35 Å respectively in the co-planar structure. Then, by slightly modifying the σ-molecular orbitals, which are mainly localized in N–O and N–C bonds obtained by an extended Hückel method, we got:

the N–C anti-bonding orbital and its orbital energy:

$$\varphi^a{}_{NC} = 0.9120\chi_{Ny} + 0.1248\chi_{CS} - 0.3556\chi_{Cx} + 0.6916\chi_{Cy}$$

$$\varepsilon^a{}_{NC} = +4.25\ \text{eV.}$$

the N–C bonding orbital and its orbital energy:

---

[16] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., N. Y. (1961), p. 135. A small β_{NC} is used, because the phenyl ring plane would be somewhat twisted from the nodal plane of N-O π-orbital.

[17] $\alpha = -7.06$ eV. and $\beta = -2.49$ eV. are used. Teijiro Yonezawa, Chikayoshi Nagata, Hiroshi Kato, Akira Imamura and Keiji Morokuma, "Ryōshikagaku Nyūmon (Introduction to Quantum Chemistry)," Kagaku Dōjin Co., Tokyo (1964), p. 130.

[18] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2474, 2480, 2745 (1964).

$$\varphi^{b}_{NC}=0.7777\chi_{Ny}+0.0718\chi_{CS}+0.3627\chi_{Cx}-0.2823\chi_{Cy}$$

$$\varepsilon^{b}_{NC}=-14.33\ \text{eV}.$$

the N–O anti-bonding orbital and its orbital energy:

$$\varphi^{a}_{NO}=0.5456\chi_{OS}+0.7031\chi_{Ox}-0.2846\chi_{NS}+1.0517\chi_{Nx}$$

$$\varepsilon^{a}_{NO}=+0.10\ \text{eV}.$$

the N–O bonding orbital and its orbital energy:

$$\varphi^{b}_{NO}=-0.1804\chi_{OS}+0.8247\chi_{Ox}+0.0555\chi_{NS}-0.3623\chi_{Nx}$$

$$\varepsilon^{b}_{NO}=-19.02\ \text{eV}.$$

Here χ_{NS} and χ_{Ox} are the 2S AO of nitrogen and $2P_x$ AO of oxygen, and so on. These σ-orbitals would not be bad for N–C and N–O σ-orbitals in DPNO. In the present treatment, we assumed that a $2P_y$ AO is a lone-pair orbital of the oxygen atom. We estimated $\varepsilon^{p}-\varepsilon^{n}$ as 18620 cm^{-1} from the observed n-π^* absorption spectrum.

With the above-mentioned orbitals and by putting $\zeta_N=70\ \text{cm}^{-1}$ and $\zeta_O=152\ \text{cm}^{-1}$,[19] Δg_i's and Δg_{nj} were calculated as follows:

$$\Delta g_{NC}=+9.7\times10^{-5}$$

$$\Delta g_{NO}=+53.2\times10^{-5}$$

$$\Delta g_{n}=+238.8\times10^{-5}$$

For the sum of the Δg_i's over the hydrocarbon part, which may be denoted by $\Delta g_{h.c.}$, Stone has proposed formula 5 semiempirically[10]:

$$\Delta g_{h.c.}=\sum_{i}^{\text{carbons}}\rho_i(24.7-19.3\lambda)\times10^{-5} \qquad (5)$$

where λ is the coefficient of the odd-electron orbital energy, $\alpha+\lambda\beta$, and ρ_i is the odd-electron density on the ith carbon. With Eq. 5, $\Delta g_{h.c.}$ of DPNO becomes:

$$\Delta g_{h.c.}=+5.1\times10^{-5}$$

The calculated g-value of DPNO is, therefore:

$$g_{\text{calcd}}=2.00232+2\Delta g_{NC}+\Delta g_{NO}+\Delta g_{n}+\Delta g_{h.c.}=2.00549$$

This value shows a good agreement with the g-value observed in carbon tetrachloride:

$$g_{\text{obs}}=2.00572\pm0.00005$$

The Calculation of the Hydrogen-bond Effect on the *g*-Value.—Bolton[20] has considered the protonation effect on the hyperfine structure of the ESR spectra of semiquinones as a perturbation which causes changes in the coulomb integral of the oxygen atom and the resonance integral of the C–O bond. In a similar way, in explaining the difference in the hyperfine coupling constants of semiquinones in dimethylsulfoxide and in an ethanol-water mixed solvent, Gendell and Fraenkel[2] regarded the solvent effect as a perturbation which causes a change in the coulomb integral of the oxygen atom.

Here we take the hydrogen-bond effect to be a perturbation which increases the coulomb integral of the oxygen atom. In the Hückel molecular orbital theory the perturbation, which increases the coulomb integral of the tth atom from α_t to $\alpha_t+\delta\alpha_t$, also increases the odd-electron density on the rth atom from ρ_r to $\rho_r+\delta\rho_r$, the odd-electron orbital bond order between rth and sth atoms from p^{p}_{rs} to $p^{p}_{rs}+\delta p^{p}_{rs}$, and the odd-electron orbital energy from ε^{p} to $\varepsilon^{p}+\delta\varepsilon^{p}$, as is indicated in Eqs. 6—10.

$$\delta\rho_r=\pi^{p}_{r,t}\times\delta\alpha_t \qquad (6)$$

$$\delta p^{p}_{rs}=\pi^{p}_{rs,t}\times\delta\alpha_t \qquad (7)$$

$$\delta\varepsilon^{p}=\rho_t\times\delta\alpha_t \qquad (8)$$

$$\pi^{p}_{r,t}=2\sum_{k\neq p}\frac{C^{k}_{r}C^{k}_{t}C^{p}_{r}C^{p}_{t}}{\varepsilon^{p}-\varepsilon^{k}} \qquad (9)$$

$$\pi^{p}_{rs,t}=\sum_{k\neq p}\frac{C^{k}_{t}C^{k}_{r}C^{p}_{t}C^{p}_{s}+C^{k}_{t}C^{k}_{s}C^{p}_{t}C^{p}_{r}}{\varepsilon^{p}-\varepsilon^{k}} \qquad (10)$$

Here C^{k}_{r} and C^{p}_{r} are the coefficients of the AO of the rth atom in the kth and the odd-electron π-orbitals. The notations ε^{k} and ε^{p} are the orbital energies of the kth and the odd-electron π-orbitals. Calculated with the parameters mentioned in the preceding section, the values of $\pi^{p}_{r,t}$'s and $\pi^{p}_{rs,t}$'s are tabulated in Table II.

TABLE II. $\pi^{p}_{r,t}$ AND $\pi^{p}_{rs,t}$ (in unit of $1/\beta$)

$\pi^{p}_{1,6}$	$\pi^{p}_{2,6}$	$\pi^{p}_{3,6}$	$\pi^{p}_{4,6}$
+0.1074	+0.0139	+0.0574	+0.0932
$\pi^{p}_{5,6}$	$\pi^{p}_{6,6}$	$\pi^{p}_{45,6}$	$\pi^{p}_{56.6}$
+0.0831	−0.7696	−0.1392	+0.2297

From Eq. 6, in this connection we get:

$$\frac{\delta a_{1\text{-H}}}{a_1}=\frac{\delta\rho_1}{\rho_1}=\frac{\pi^{p}_{1,6}}{\rho_1}\times\delta\alpha_6$$

$$\frac{\delta a_{3\text{-H}}}{a_3}=\frac{\delta\rho_3}{\rho_3}=\frac{\pi^{p}_{3,6}}{\rho_3}\times\delta\alpha_6$$

where a_1 and a_3 are the coupling constants of 1- and 3-protons of DPNO dissolved in carbon tetrachloride respectively, and where $\delta a_{1\text{-H}}$ and $\delta a_{3\text{-H}}$ are their increases in hydrogen-bond solvents. It was observed that $a_1=a_3$ and $\delta a_{1\text{-H}}=\delta a_{3\text{-H}}$. Hence, for the purpose of obtaining the value of $\delta\alpha_6$, we may write approximately:

---

19) D. S. McClure, *J. Chem. Phys.*, 17, 905 (1949).

20) J. R. Bolton, A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, 5, 465 (1962).

$$\delta\alpha_6=(\delta a_{1\text{-H}}/a_1)/\{(1/2)(\pi^{p}_{1,6}/\rho_1+\pi^{p}_{3,6}/\rho_3)\} \tag{11}$$

In this way, we can calculate the increase in the coulomb integral of the oxygen atom, $\delta\alpha_6$, by means of formula 11. The results are listed in Table III.

TABLE III. INCREASE OF THE COULOMB INTEGRAL OF THE OXYGEN ATOM DUE TO HYDROGEN BONDING

Solvent	$\delta\alpha_6$ (β)
Carbon tetrachloride	+0
Phenylacetylene	+0.0111
Chloroform	+0.0147
Ethanol	+0.0222
Methanol	+0.0235
Phenol in toluene (4.4 mol./l. soln.)	+0.0728
Water	+0.0848

The contribution to $\delta\Delta g$ from each σ-bond, the lone-pair and the hydrocarbon part are obtained from Eqs. 3—5 by considering their changes due to the increase in the coulomb integral of the oxygen atom, by considering, that is Eqs. 6—8. The results are as follows:

$$\delta\Delta g_{\text{NC}}=+14.5\times10^{-5}\times\delta\alpha_6/\beta \tag{12}$$

$$\delta\Delta g_{\text{NO}}=-55.3\times10^{-5}\times\delta\alpha_6/\beta \tag{13}$$

$$\delta\Delta g_{\text{h.c.}}=+7.0\times10^{-5}\times\delta\alpha_6/\beta \tag{14}$$

$$\delta\Delta g_{\text{n}}=-418.8\times10^{-5}\times\delta\alpha_6/\beta \tag{15}$$

Using these equations, $\delta\Delta g_i$'s are estimated to be as cited in Table IV.

TABLE IV. THE VARIATION OF CONTRIBUTION TO Δg FROM σ-BONDS AND THE LONE-PAIR

Solvent	$\delta\Delta g_{\text{NO}}$ $\times10^5$	$\delta\Delta g_{\text{NC}}$ $\times10^5$	$\delta\Delta g_{\text{h.c.}}$ $\times10^5$	$\delta\Delta g_{\text{n}}$ $\times10^5$
Carbon tetrachloride	0	0	0	0
Phenylacetylene	−0.6	+0.2	+0.1	−4.6
Chloroform	−0.8	+0.2	+0.1	−6.2
Ethanol	−1.2	+0.3	+0.2	−9.3
Methanol	−1.3	+0.3	+0.2	−9.8
Phenol in toluene (4.4 mol./l. soln.)	−4.0	+1.1	+0.5	−30.5
Water	−4.7	+1.2	+0.6	−35.5

The values of the $\delta\Delta g_i$'s obtained from Eqs. 12—15 are the variations in Δg_i's which are caused by the redistribution of the odd electron through the increase in the coulomb integral of the oxygen atom. Hence, the difference, $\delta'\Delta g_{\text{n}}$, as defined by the equation:

$$\delta'\Delta g_{\text{n}}=\delta\Delta g_{\text{obs}}-(2\delta\Delta g_{\text{NC}}+\delta\Delta g_{\text{NO}}+\delta\Delta g_{\text{h.c.}}+\delta\Delta g_{\text{n}})$$

would be the change in Δg_{n} caused by the increase in the difference between the odd-electron orbital and the lone-pair orbital energies, which brings out the blue shift of the n-π^* transition. The blue shift of the n-π^* transition can be represented by Eq. 16[21]:

$$\delta(\varepsilon^{p}-\varepsilon^{n})=-\frac{\delta'\Delta g_{\text{n}}}{\Delta g_{\text{n}}}\times18620\ \text{cm}^{-1} \tag{16}$$

The value of $\delta'\Delta g_{\text{n}}$ and the blue shift of the n-π^* transition, $\delta(\varepsilon^{p}-\varepsilon^{n})$, are tabulated in Table V.

TABLE V. THE BLUE SHIFT OF THE n-π^* TRANSITION CALCULATED FROM THE g-VALUE

Solvent	$\delta'\Delta g_{\text{n}}$ $\times10^5$	$\delta(\varepsilon^{p}-\varepsilon^{n})$ cm^{-1}
Carbon tetrachloride	0	0
Phenylacetylene	−7	+550
Chloroform	−9	+700
Ethanol	−8	+600
Methanol	−11	+850
Phenol in toluene (4.4 mol./l. soln.)	−24	+1900
Water	−26	+2000

The positions of the n-π^* transition as calculated from the g-value of DPNO in chloroform, ethanol and methanol are shown in Fig. 2. The agreement between the calculated n-π^* transition energy and the observed spectra seems passable. The following factors might cause deviation. The value of $\delta'\Delta g_{\text{n}}$ is very sensitive to parameters in the Hückel calculation. Intermolecular forces other than hydrogen-bonding, orientation forces, inductive forces, dispersion forces and so on, might change the coulomb parameters of the conjugated system, and the solvation might cause a change in the β_{NC} through the distortion of the phenyl ring. Thus, the value of $\delta'\Delta g_{\text{n}}$ obtained is only qualitatively reliable.

Summary

The decrease in the g-value of diphenyl nitric oxide in hydrogen-bonding solvents has been examined. This decrease has been analyzed on the basis of Stone's theory for the g-value of a π-radical. The decrease in the g-value has been shown to be caused mainly by the decrease in the odd-electron density on the oxygen atom and the increase in the energy difference between the odd-electron and lone-pair orbitals. We have also attempted to

---

[21] Thus determined n-π^* transition energy is a weighted mean value of solvated and not solvated DPNO, because when the equilibrium is established with rapid exchange between two states, the observed ESR spectrum is a weighted mean spectrum of ones of the two states. H. M. McConnell, *J. Chem. Phys.*, **28**, 430 (1958).

estimate the blue shift of the n-π^* transition from the g-value.

The authors are indebted to Professor Hideo Takaki and Professor Yasuo Deguchi for offering them a chance to use the ESR spectrometer. They also wish to express their thanks to Dr. Hiroshi Kato and Dr. Keiji Morokuma for their valuable discussions throughout this work.

Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto