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Solvent Effects on the g-Value of Di-t-butyl Nitric Oxide

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The effects of solvents on the g-value of di-t-butyl nitric oxide (DTBNO) have been examined. Plots of the g-value *vs.* the hyperfine coupling constant of ^{14}N of DTBNO in various solvents formed two different straight lines, for aprotic solvents and for protic solvents. An analysis of the solvent effects on the g-value has also been attempted. The solvent-dependent shifts of the g-value may be divided into three terms, resulting from the blue-shift of the $n—\pi^*$ transition, from the redistribution of the odd electron, and from the delocalization of the lone-pair orbital on the oxygen atom of DTBNO. The first term is calculated from the observed shift of the $n—\pi^*$ absorption in the visible ray spectrum, while the seond one is evaluated from the solvent shift of the g-value of DTBNO in aprotic solvents, where the delocalization of the lone-pair is excepted to be negligible The last term, the difference between the observed shift in the g-value and the sum of the former two terms, is estimated to be in the range from -4×10^{-5} to -10×10^{-5}, which corresponds to the from 2% to 5% delocalization of the lone-pair electron.

It has been reported in a previous paper[1] that the g-value of diphenyl nitric oxide decreases in protic solvents. The decrease in the g-value was there shown to be caused mainly by the decrease in the odd-electron density on the oxygen atom and by the increase in the energy difference between the odd-electron orbital and the lone-pair orbital. This increase in the energy difference should be observed as a blue shift of the $n—\pi^*$ transition in the visible absorption spectrum, but in the case of diphenyl nitric oxide this shift can not be observed since the blue-shifted absorption due to the $n—\pi^*$ transition is hidden by the intense absorption of the $\pi—\pi^*$ transition. Hence, the blue shift of the $n—\pi^*$ transition was estimated from the shift of the g-value.

The purpose of the present study is to examine the relationship between the solvent-dependent shift of the g-value and the solvent-dependent change of the hyperfine coupling constant of di-t-butyl nitric oxide in two kinds of solvents, namely, protic and aprotic solvents, and to make clear experimentally the machanism of solvent effects on the g-value. The relationship between the g-value and the hyperfine coupling constant of di-t-butyl nitric oxide (DTBNO) dissolved in protic solvents shows a different behaviour from that of DTBNO in aprotic solvents. This difference is related mainly to the observed blue shift of the $n—\pi^*$ transition of the radical dissolved in protic solvents.

Experimental

Materials. Di-t-butyl nitric oxide was prepared according to the directions of Brière and Rassat.[2] Carbon tetrachloride, n-hexane, toluene, acetone, and acetonitrile were employed as aprotic solvents, while methanol and water were employed as protic solvents. All the solvents employed here were purified by fractional distillation.

The measurement of the ESR Spectra. The procedure of packing the radical and the solvent into the ESR sample tube was the same as that described in a previous paper.[1] The ESR spectra were run at a temperature of 20 ± 3°C on a JES-3BX-type instrument at 9.4 Gc/sec. For the measurement of the g-value and the hyperfine coupling constant, a glass capillary was attached to a sample. As a reference compound, the capillary was filled with the tetracene radical in concentrated sulfuric acid.[3]

Results

Table 1 summarizes the g-values, the hyperfine coupling constants of ^{14}N (a_N) of DTBNO, and their shifts in the various solvents employed. The differences in the g-values and the coupling constants from those in n-hexane are designated as $\delta\Delta g$ and δa_N respectively, where Δg means the difference in g-value from that of free spins, which is indicated in Eq. (1). When DTBNO is dissolved in the aprotic solvents, the coupling constant of N increases[4] and the g-value of the radical decreases with the increase in the dipole moment of the solvent. When the radical is dissolved in a protic

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

2) R. Brière and Rassat, *Bull. Soc. Chim. France*, **1965**, 378.

3) The g-value and the hyperfine coupling constants have been reported to be $g=2.002604\pm0.000007$, $a_1=5.06$G (four protons), $a_2=1.69$G (four protons), and $a_3=1.03$ G (four protons); B. G. Segal, M. Kaplan and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965); J. S. Hyde and H. W. Brown, *ibid.*, **37**, 368 (1962).

TABLE 1. The g-VALUE AND a_N OF DTBNO DISSOLVED IN PROTIC AND APROTIC SOLVENTS

Solvent	g	a_N, gauss	$\delta\Delta g \times 10^5$	δa_N, gauss
n-Hexane	$2.00614 \pm 2 \times 10^{-5}$	14.85 ± 0.08	0	0
Carbon tetrachloride	$2.00607 \pm 1 \times 10^{-5}$	15.24 ± 0.04	−7	+0.39
Toluene	$2.00606 \pm 1 \times 10^{-5}$	15.26 ± 0.07	−8	+0.41
Acetone	$2.00604 \pm 5 \times 10^{-5}$	15.37 ± 0.13	−10	+0.52
Acetonitrile	$2.00597 \pm 1 \times 10^{-5}$	15.66 ± 0.07	−17	+0.81
Methanol	$2.00579 \pm 2 \times 10^{-5}$	15.85 ± 0.01	−35	+1.00
Water	$2.00556 \pm 1 \times 10^{-5}$	16.75 ± 0.04	−58	+1.90

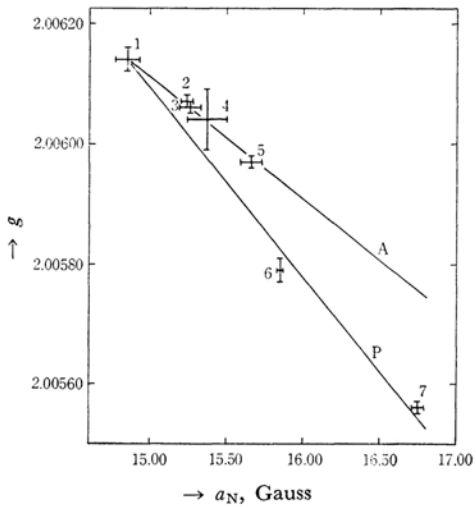

Fig. 1. The relationship between the g-value and a_N of DTBNO. The number at each point designate the solvent employed. 1: n-Hexane, 2: Carbon tetrachloraide, 3: Toluene, 4: Acetone, 5: Aetonitrile, 6: Methanol, 7: Water. The line A shows the g *vs.* a_N plots of DTBNO dissolved in aprotic solvents, the line P that of this radical dissolved in protic solvents.

solvent, the stronger the ability of the proton donation of the solvent, the larger the coupling constant of N[4] and the smaller the g-value of the radical become. In Fig. 1, the g-values in various solvents are plotted against a_N; they form two straight lines. One line represents the relationship between g and the a_N of DTBNO dissolved in aprotic solvents, while the other one represents that in protic solvents. Figure 1 shows that for the same value of a_N the g-value of DTBNO dissolved in a protic solvent is smaller than that of the radical dissolved in a aprotic solvent.

DTBNO in n-hexane displays an absorption in the visible spectrum at $\lambda_{max}=466$ mμ; it has been identified as the n—π^* transition.[5] This absorption peak shows a solvent-dependent shift, especially when this radical is dissolved in protic solvents. The wavelengths of the n—π^* transition of DTBNO dissolved in protic and aprotic solvents are listed in Table 2, together with the shift, $\delta\nu$ (in units of cm^{-1}), of the n—π^* transition energy in several solvents referred to that in n-hexane, where ν designates the absorption energy of the n—π^* transition of DTBNO in units of cm^{-1}.

Discussion

The solvent effects on the electronic structure which cause dominant shifts in the g-value and a_N of DTBNO are as follows; when aprotic solvents are employed, a change in the odd-electron orbital and a lowering of the lone-pair orbital energy take place, while when protic solvents are used, a change in the odd-electron orbital, a more remarkable lowering of the lone-pair orbital energy, and a delocalization of the lone-pair orbital occur according to the formation of a hydrogen bond[6] between the radical and the solvent. The change in the odd-electron orbital causes the shift in the g-value, and also that in the hyperfine coupling constant of N. On the other hand, the lowering of the lone-pair orbital energy and the delocalization of the lone-pair orbital cause the change in the g-value exclusively. As is shown in Fig. 1, the g-value of DTBNO dissolved in protic solvents is smaller than that in aprotic solvents for the same values of a_N. This difference seems to be the effect of the remarkable lowering of the lone-pair orbital energy and the delocalization of the lone-pair orbital caused by the formation of the hydrogen bond. This interpretation will be shown to be reasonable by the following analysis of the solvent effects on the g-value.

The odd electron orbital of DTBNO is localized in the N–O π-orbital. Therefore, the g-value of this radical is given by:[1,7]

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

$$\Delta g = \Delta g_{NO} + \Delta g_n \tag{2}$$

where Δg_{NO} and Δg_n are the contributions to Δg

4) Y. Deguchi and H. Nishiguchi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 54 (1965).

5) R. Briere, M. H. Lemaire and A. Rassat, *Tetrahedron Letters*, **1964**, 1775.

6) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman Comp., San Francisco (1960).

7) A. J. Stone, *Mol. Phys.*, **6**, 509 (1963).

from the NO σ-bond and from the lone-pair(s) on the oxygen atom respectively, and are given as Eqs. (3) and (4). The contribution to Δg from NC σ-bonds is expected to be small and so is neglected here. Throughout this paper, the g and Δg's are averages with respect to three spatial axes.

$$\Delta g_{NO} = \frac{2}{3}\sum_{m}^{a,b}\frac{\left(\begin{array}{l}\zeta_N(C_{NX}^m)^2\rho_N+\zeta_O(C_{OX}^m)^2\rho_O\\ +(\zeta_O+\zeta_N)C_{NX}^mC_{OX}^mP_{NO}^p\end{array}\right)}{\varepsilon^p-\varepsilon^m} \quad (3)$$

$$\Delta g_n = \frac{2}{3}\frac{\zeta_O\{(C_{OX}^n)^2+(C_{OY}^n)^2\}\rho_0}{\varepsilon^p-\varepsilon^n} \quad (4)$$

In Eq. (3), a and b indicate the bonding and anti-bonding orbitals of the NO σ-bond. The coefficient of the $2p_X$ atomic orbital of the oxygen atom in the mth (lone pair, bonding or anti-bonding) σ-orbital is designated as C_{OX}^m, and so on. The energies of the odd electron orbital, of the mth σ-orbital, and of the lone-pair orbital are written as ε^p, ε^m, and ε^n respectively. The notations ζ_N and ζ_O are L–S coupling constants about the nitrogen nucleus and about the oxygen nucleus. The partial bond order of the odd electron orbital between N and O and odd electron densities on N and O are designated as p_{NO}^p, ρ_N, and ρ_O. Here, the three spatial axes, X, Y, and Z, are taken to be as shown in Fig. 2; namely, the NO bond is in the direction of the X axis, and the Z axis is perpendicular to the molecular plane.

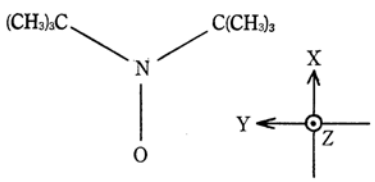

Fig. 2. Three spatial axes X, Y and Z fixed on the DTBNO molecule.

The hyperfine coupling constant ^{14}N of DTBNO can be represented as similar to that of ^{13}C given by Karplus and Fraenkel[8] as follows:

$$a_N = Q_1\rho_N + Q_2\rho_O \quad (5)$$

where the Q's are the sigma-pi parameters.

When DTBNO is dissolved in aprotic solvents, the perturbation exerted upon this radical is mainly the electrostatic field resulting from oriented dipoles of solvent molecules. Since, from Eqs. (3)—(5), $\delta\Delta g$ and δa_N are shown to be proportional to the perturbing electrostatic field, it can be interpreted that $\delta\Delta g$ is proportional to δa_N when this radical is dissolved in aprotic solvents.

When DTBNO is dissolved in protic solvents, the perturbation exerted on this radical is mainly the formation of the hydrogen bonding between this radical and the protic solvent. As has been shown in a previous paper,[1] $\delta\Delta g$ and δa_N are proportional to the strength of the hydrogen bonding; therefore, it can be interpreted that $\delta\Delta g$ is also proportional to δa_N when this radical is dissolved in protic solvents. The formation of the hydrogen bonding accompanies not only the electrostatic interaction, but also the effect of the delocalization of the lone-pair orbital. Therefore, the inclination of the plots of $\delta\Delta g$ *vs.* δa_N of DTBNO in aprotic solvents may be different from that in protic solsolvents; indeed, this difference can actually be observed, as is shown in Fig. 1.

For the analysis of solvent effects on the g-value, the estimation of Δg_n must be attempted. Griffith, Cornell and McConnell[9] have reported that the principal values of the g-tensor of DTBNO are $g^{XX}=2.0089$, $g^{YY}=2.0061$, and $g^{ZZ}=2.0027$. When the lone-pair orbital in the oxygen atom is assumed to be the $2p_Y$ atomic orbital (Case I), Δg_n can be estimated as follows;*1

$$\Delta g_n \simeq \frac{1}{3}(g^{XX}-2.0023) = +220\times10^{-5} \quad (6)$$

while when the lone-pair orbitals on the oxygen atom are assumed to be sp^2 hybrid orbitals (Case II), Δg_n can be evaluated as:*1

$$\Delta g_n \simeq \frac{4}{3}\times\frac{1}{3}(g^{XX}-2.0023) = +290\times10^{-5} \quad (7)$$

The following analysis was performed on the basis of both estimations.

The solvent shift of the g-value, Δg, may be given as:

$$\delta\Delta g \simeq \delta\Delta g_n + \delta\Delta g_{NO} + \delta'\Delta g_n + \delta''\Delta g_n \quad (8)$$

where $\delta\Delta g_n$: solvent effects on Δg_n which come through the redistribution of the odd electron;

$\delta\Delta g_{NO}$: solvent effects on Δg_{NO} due to the change in the odd-electron orbital;

$\delta'\Delta g_n$: solvent effects on Δg_n resulting from the change in the energy difference between the odd-electron orbital and the lone-pair orbital (the blue shift of the n—π^* transition), and the $\delta''\Delta g_n$:

8) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1129 (1959).

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

*1 In Case I, the lone-pair takes part in g^{XX} exclusively. Also, g^{XX} involves a term which is from N–C σ-bonds, but this is expected to be small and so is neglected here. We have defined Δg_n as the average value with respect to the three spatial axes; therefore, Δg_n may be given as Eq. (6). In this case, Δg_{NO} is evaluated as:

$$\Delta g_{NO} \simeq \frac{1}{3}(g^{XX}-2.0023) = +130\times10^{-5}$$

In Case II, two lone pairs contribute to g^{XX} and also to g^{YY}. The ratio of the contribution to g^{XX} to that to g^{YY} is 3/1. Thus Δg_n is given as Eq. (7) and Δg_{NO} becomes:

$$\Delta g_{NO} \simeq \frac{1}{3}(g^{YY}-2.0023) - \frac{1}{4}\Delta g_n = +60\times10^{-5}$$

solvent effects on Δg_n which come through the delocalization of the lone-pair orbital.

Solvent effects on the g-value according to the change in σ-orbitals other than the lone-pair orbital(s) are neglected in this analysis because σ-orbitals are more rigid than the odd-electron orbital and the lone-pair orbital(s).

The value of $\delta'\Delta g_n$ can be estimated by Eq. (9), derived from Eq. (4):

$$\delta'\Delta g_n \simeq -\Delta g_n \times \frac{\delta\nu}{\nu} \tag{9}$$

where ν is the n—π^* transition energy of DTBNO dissolved in n-hexane in units of cm^{-1}, and where

TABLE 2. THE POSITION OF THE n—π^* ABSORPTION OF DTBNO AND ITS SHIFT

Solvent	λ_{max}, mμ	$\delta\nu$, cm^{-1}
n-Hexane	466	0
Carbon tetrachloride	464	+90
Toluene	462	+200
Acetone	460	+300
Acetonitrile	455	+520
Methanol	443	+1100
Water	424	+2100

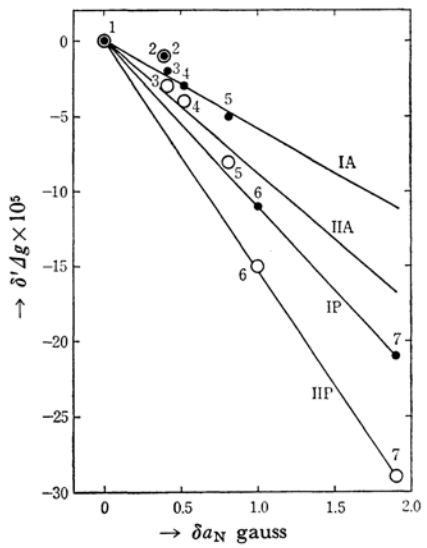

Fig. 3. The graphical representation of the relation between $\delta'\Delta g_n$ and δa_N.
Dots: Plots of $\delta'\Delta g_n^{I}$ *vs.* δa_N
Circles: Plots of $\delta'\Delta g_n^{II}$ *vs.* δa_N
Line IA: The relation between $\delta'\Delta g_n^{I}$ and δa_N of DTBNO dissolved in aprotic solvents
Line IIA: The relation between $\delta' g_n^{II}$ and δa_N of DTBNO dissolved in aprotic solvents
Line IP: The relation between $\delta'\Delta g_n^{I}$ and δa_N of DTBNO dissolved in aprotic solvents
Line IIP: The relation between $\delta'\Delta g_n^{II}$ and δa_N of DTBNO dissolved in aprotic solvents
The no. at each plot has the same significance as in Fig. 1.

$\delta\nu$ is the shift in the n—π^* transition which is shown in the third column in Table 2. The difference between the observed shift of the g-value, $\delta\Delta g$, and $\delta'\Delta g_n$ is equal to $\delta\Delta g_{NO}+\delta''\Delta g_n+\delta\Delta g_n$:

$$\delta\Delta g - \delta'\Delta g_n \simeq \delta\Delta g_n + \delta\Delta g_{NO} + \delta''\Delta g_n \tag{10}$$

The estimated values of $\delta'\Delta g_n$ and $\delta\Delta g_n+\delta\Delta g_{NO}+\delta''\Delta g_n$ are summarized in Table 3, together with the observed shift in the g-value, the superscripts I and II relating, respectively, to the value based upon the estimation of Eq. (6) and to the value based upon the estimation of Eq. (7). Figures 3 and 4 show the relationship between $\delta'\Delta g_n$ and δa_N and that between $\delta\Delta g-\delta'\Delta g_n$ and δa_N respectively. Figure 3 shows that the $\delta\Delta' g_n$ of DTBNO in aprotic solvents is smaller than that in protic solvents for the same value of δa_N.*2

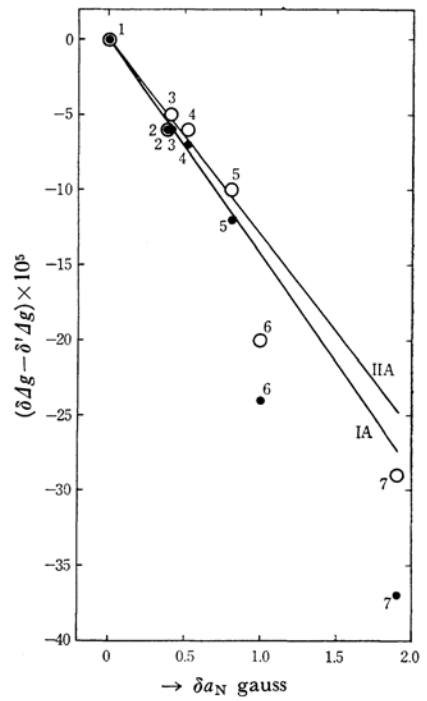

Fig. 4. The relationship between $(\delta\Delta g-\delta'\Delta g_n)$ and δa_N.
Dots: Plots of $(\delta\Delta g-\delta'\Delta g_n^{I})$ *vs.* δa_N
Circles: Plots of $(\delta\Delta g-\delta'\Delta g_n^{I})$ *vs.* δa_N
The relationship between $(\delta\Delta g-\delta'\Delta g_n^{I})$ and δa_N of DTBNO dissolved in aprotic solvents is shown by line IA.
The reiationship between $(\delta\Delta g-\delta'\Delta g'^{II}_n)$ and δa_N of DTBNO dissolved in aprotic solvents is shown by line IIA.
The no. at each plot has the same significance as in Fig. 1.

*2 From Eq. (5), $\delta a_N=Q_1\delta\rho_N+Q_2\delta\rho_O$, where $\delta\rho_N$ and $\delta\rho_O$ present the solvent-dependent redistribution of the odd-electron. Because of the localization of the odd-electron in the N—O π orbital, $\delta\rho_N+\delta\rho_O\simeq 0$; therefore, $\delta a_N\simeq(Q_2-Q_1)\delta\rho_O$. Thus, at the same value of δa_N, $\delta\rho_O$ is the same whether protic or aprotic solvents are employed.

TABLE 3. THE VARIATION OF THE CONTRIBUTION TO Δg FROM THE N–O σ-BOND AND THE LONE PAIR

Solvent	$\delta\Delta g\times10^5$	$\delta'\Delta g_n^{\mathrm{I}}\times10^5$	$(\delta\Delta g_n^{\mathrm{I}}+\delta\Delta g_{\mathrm{NO}}^{\mathrm{I}}+\delta''\Delta g_n^{\mathrm{I}})\times10^5$	$\delta'\Delta g_n^{\mathrm{II}}\times10^5$	$(\delta\Delta g_n^{\mathrm{II}}+\delta\Delta g_{\mathrm{NO}}^{\mathrm{II}}+\delta''\Delta g_n^{\mathrm{II}})\times10^5$
n-Hexane	0	0	0	0	0
Carbon tetrachloride	−7	−1	−6	−1	−6
Toluene	−8	−2	−6	−3	−5
Acetone	−10	−3	−7	−4	−6
Acetonitrile	−17	−5	−12	−7	−10
Methanol	−35	−11	−24	−15	−20
Water	−58	−21	−37	−29	−29

Superscripts I and II relate respectively to the value estimated on the basis of the estimation on Eq. (6), and to the value estimated on the basis of the estimation of Eq. (7).

This leads to the conclusion, through Eq. (9), that the blue shift of the n—π^* transition of DTBNO in protic solvents is greater than that in aprotic solvents when the change in the odd-electron distribution is considered to be the same.*2 The difference observed in Fig. 3 is the major part (50%—75%) in the difference between lines A and P in Fig. 1.

When aprotic solvents are employed, the delocalization of the lone-pair orbital(s) is negligible; therefore, $\delta\Delta g_n+\delta\Delta g_{\mathrm{NO}}+\delta''\Delta g_n$ becomes $\delta\Delta g_n+\delta\Delta g_{\mathrm{NO}}$, which is the contribution to $\delta\Delta g$ from the change in the odd-electron orbital. Plots of $\delta\Delta g-\delta'\Delta g_n$ *vs.* the δa_{N} of this radical in aprotic solvents have formed a stright line, as is shown by the line IA or IIA in Fig. 4. Plots of $\delta\Delta g-\delta'\Delta g_n$ *vs.* the δa_{N} of this radical in protic solvents have distributed below these lines (IA or IIA), as is shown in Fig. 4. This deviation probably is the effect of the delocalization of the lone-pair orbital(s) accompanying the formation of the hydrogen bond. Figure 4 shows that the $\delta''\Delta g_n$ values of DTBNO dissolved in methanol or water are in the range from -4×10^{-5} to -10×10^{-5}, corresponding to about a 2% to 5% delocalization of the lone-pair orbital. Coulson and Danielsson[10] have calculated, with the valence-bond method, the delocalization of the lone-pair in the -OH···O< system to be in the range from 0.7% to 8.0%. Also, Tsubomura[11] has performed the valence-bond calculation of the $H_2O\cdots H\text{-}OH$ system, with the O–O distance of 2.70 A and the O–H bond length of 0.96 A, he has reported the weight of resonance hybrids with the delocalized lone-pair to be 1.5%. Although the analysis in the present work can not avoid some inaccuracies, the estimated value of $\delta''\Delta g_n$ seems passable.

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 Professor Hiroshi Kato for his valuable discussions throughout this work.

10) C. A. Coulson and U. Danielsson, *Arkiv. Fysik.*, **8**, 245 (1954).
11) H. Tsubomura, This Bulletin, **27**, 445 (1954).