*Electron Paramagnetic Resonance Study of Diphenyl Nitric Oxide in Single Crystals**

By Yasuo DEGUCHI

(Received December 27, 1960)

The study of organic free radicals by electron paramagnetic resonance has been developed during the last several years. Most of these studies were done in liquid states[1]. However, Kittel et al.[2], Weissman et al.[3], Cohen and Kikuchi[4], Gordy et al.[5], McConnel et al.[6] and Whiffen et al.[7], reported the study of organic free radicals in solid state.

Cohen and Kikuchi[4] measured the angular variation of g-value and half-power width of single crystals of pure diphenylpicrylhydrazyl. Weissman et al., observed the maximum hyperfine splitting of crystals of peroxylamine disulfonate ion ($(SO_3)_2NO^{2-}$) diluted with $K_2(SO_3)_2NOH$.

We investigated the angular variation of the line width and the hyperfine splitting in EPR spectra of single crystals of pure diphenyl nitric oxide and of the ones diluted with benzophenone which is diamagnetic.

Preparation of the Single Crystals

Following the method of Wieland and Roth[8], we synthesized diphenyl nitric oxide. From saturated ether solutions of diphenyl nitric oxide, we obtained single crystals of pure diphenyl nitric oxide as large as 6×1.5×0.5mm.

In order to make magnetically diluted single crystals, the saturated ether solutions with various mixing ratios of diphenyl nitric oxide to benzophenone were made. The concentration** of mixed crystals were pure, 4.4, 3.3, 2.9, 1.9, 0.84, 0.51, 0.41, 0.35, 0.1, 0.01, 0.001 and 0.0005 mol./l., most of which crystallized in prismatic form. The largest crystal thus obtained was 8×4×3 mm.

---

* This work was supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract. Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

[1] D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance", Academic Press (1958), p. 168.

[2] A. N. Holden, C. Kittel, F. R. Merritt and W. A. Yager, *Phys. Rev.*, **77**, 147 (1950).

[3] S. I. Weissman and D. Banfill, *J. Am. Chem. Soc.*, **75**, 2534 (1953).

[4] C. Kikuchi and V. W. Cohen, *Phys. Rev.*, **93**, 394 (1954).

[5] A. Roggen, L. Roggen and W. Gordy, ibid., **105**, 50 (1957).

[6] H. M. McConnel, C. Heller, T. Cole and R. S. Fessenden, *J. Am. Chem. Soc.*, **82**, 766 (1960).

[7] N. M. Atherton and D. H. Whiffen, *Mol. Phys.*, **3**, 1 (1960).

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

** These concentrations were calculated from the values of weight mixing ratio regarding benzophenone as solvent.

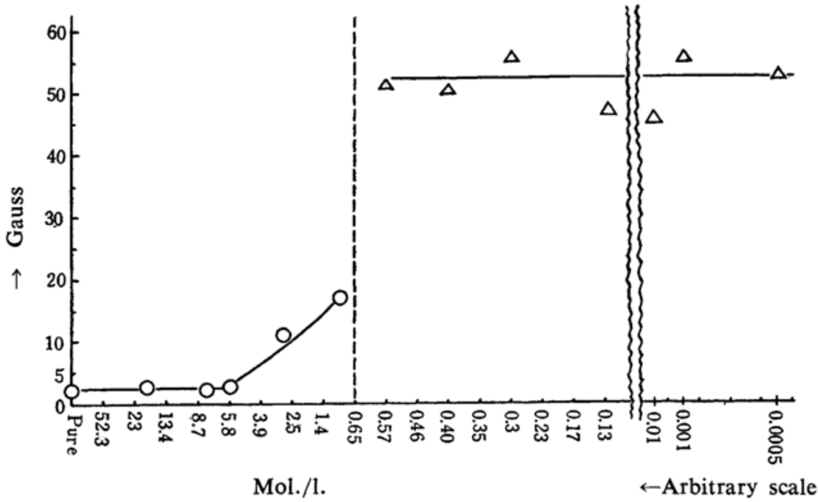

Fig. 1. The variation of half-widths and hyperfine splitting with changing concentrations. The left hand-side region of the broken line is the single line region and the right-hand-side region is the hyperfine splitting region. In the right hand-side region of the wavy line, the concentration scale is taken arbitrarily.

Experimental

The EPR spectrometer employed in this work was constructed by Professor J. Townsend, Washington University, St. Louis. The details of this spectrometer will be described elsewhere.

The crystal structure of diphenyl nitric oxide has not been determined yet, but the crystal structure of benzophenone has been investigated by Banrajee and Haque[9]. According to their result, it is orthorhombic with $a=10.30\,\text{Å}$, $b=12.11\,\text{Å}$ and $c=8.04\,\text{Å}$. Its unit cell contains 4 molecules and its space group belongs to $D^4_2-P_{2_1 2_1 2_1}$. But, as Lonsdale pointed out[10] the above crystal symmetry description is not the definite one but the possible one guessed from the static magnetic susceptibility measurement results.

As each single crystal forms with a broad face and a long edge, an axis normal to the broad face was designated as the c-axis, the one parallel to the long edge, a-axis, and the one perpendicular to both a and c, the b-axis. To rotate the crystal about these mutually perpendicular axes in the cavity, the crystal was mounted at the end of a quartz rod with oil clay.

In each measurement one of these axes was set parallel to the applied static magnetic field. Then we obtained the absorption spectra at every 15 degrees of rotation from 0 to 180°. The g-value was determined comparing the spectra thus obtained with the one of peroxylamine disulfonate in dilute aqueous solution. The g-value and separation between the outside lines and the center line of the peroxylamine disulfonate were well confirmed by Weissman et al.[11] as $g=2.0054$ and the separation is 13 gauss.

The concentration of mixed crystal was determined by comparing the optical absorption intensities of the cyclohexane solutions of mixed crystals in various mixing ratios with those of solutions containing a known amount of pure diphenyl nitric oxide which show the absorption peaks at 3680 and 3030 Å respectively.

Results and Discussion

The relation between half-width of the absorption line and the concentration is shown in Fig. 1 where $\Delta H_{1/2}$ is the width between the steepest deflection points of the resonance absorption line and is measured at the orientation of crystal with respect to the static magnetic field; that is, the long axis a is perpendicular and the c-axis is parallel to the static magnetic field.

But the attempt to maintain the same orientation of the crystals at all concentrations may not have been successful because of the uncertainty over the structure of the concentrated crystals. When the mixing ratio of diphenyl nitric oxide to benzophenone becomes less than 0.1, the spectra no longer show a single line, but instead show hyperfine structures due to the interaction of the unpaired electron with the nuclear moment of nitrogen (^{14}N). In Fig. 1, within the single line region where the exchange narrowing effect is dominant, the more the content of benzophenone increases i. e. the less the mixing ratio becomes, the wider the line becomes.

After passing over the single line region, the hyperfine lines are not well resolved but overlap each other. This overlapping structure, however, turns out to be well resolved by decreasing

---

[9] K. Banrajee and A. Haque, *Indian J. Phys.*, **12**, 87 (1938).

[10] K. Lonsdale, *Proc. Roy. Soc.*, **A171**, 562 (1939).

[11] G. E. Pake, J. Townsend and S. I. Weissman, *Phys. Rev.*, **85**, 682 (1952).

the mixing ratio $((C_6H_5)_2NO)/((C_6H_5)_2CO)$. Finally well-resolved hyperfine lines can be obtained. And the half-width of each component line does not change by varying the mixing ratio.

In the concentration region where the hyperfine lines appear, not only three but also four or five lines appear at certain rotation angles as shown in Fig. 2.

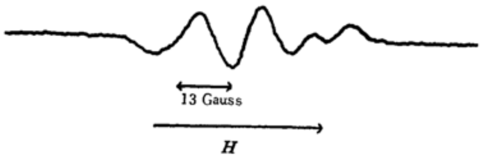

Fig. 2. The spectrum of the intermediate concentration region where four or five lines appear. The concentration of crystal is 0.1 mol./l.

The remarkable feature of the extra lines is that they never appear symmetrically with respect to the three main lines and their relative intenstities compared with the main lines are one third or one fourth and they do not change with varying concentrations of crystal.

The analysis of the spectrum in terms of the hyperfine interaction Hamiltonian

$$\begin{aligned}H=a\vec{I}\cdot\vec{S}+b\Big[&S_zI_z(1-3\cos^2\theta)\\&-\frac{3}{2}(S_+I_z+S_zI_+)\sin\theta\cos\theta e^{-i\varphi}\\&-\frac{3}{2}(S_-I_z+S_zI_-)\sin\theta\cos\theta e^{i\varphi}\Big]\end{aligned}$$

reveals that the weak lines which accompany simultaneous electron and nuclear spins transitions should be about 4% of the strong allowed lines. So this is not the case.

Another possible explanation for the appearance of extra lines may be as follows.

In the very concentrated region where the strong exchange interaction is dominant, the crystal structure of single crystals will be exclusively the one of diphenyl nitric oxide. On the other hand, the crystal structure of the very diluted single crystals will be the one of benzophenone. But in the intermediate concentration region, diphenyl nitric oxide and benzophenone may not be completely miscible. Then the crystals will no longer be perfect but rather contain misoriented crystallites in them. Thus these misoriented crystallites will show those extra lines in spectra.

In case of 0.0005 mol./l. mixed crysal, there appear three lines at certain rotation angles but still they do not show any hyperfine lines because of the protons adjacent to the ring carbon atoms. On the other hand well-resolved proton hyperfine splittings are obtained in oxygen-free solutions with low viscosity[12].

The higher the viscosity of the solutions are raised, the broader the proton hyperfine lines become and finally all proton hyperfine lines are broadened out and only three broad lines due to the nitrogen nuclear moment hyperfine interaction remain.

Thus we could not expect well-resolved proton hyperfine lines in diluted crystals.

Exchange Narrowing Effect in the Concentrated Crystals. — Many authors[13-19] have studied the theory of the line shape in the magnetic resonance. Kubo and Tomita[19] have developed the general theory of the line shape rigorously based on the quantum mechanics. Yokota and Koide[16] applied their theory to the absorption spectra of paramagnetic inorganic crystals, and Kivelson[20,21] extended it to the calculation of the line shape of organic free radicals.

In this paper we shall follow Kivelson's calculation.[21] According to his calculations, in case of strong exchange $J \gg A^2$ where J and A are defined below, the frequency of the resonance line is equal to

$$\omega_0-\Delta$$

where

$$\omega_0=\left[\gamma+\frac{\Delta\gamma}{3}(3\cos^2\beta-1)-\delta\gamma\sin^2\beta\cos^2\gamma\right]B_0$$

$$\Delta=T_1'^{-1}\,(IS)\int_0^{\omega_0/\omega_e}\exp(u^2/2)\,\mathrm{d}u$$

Δ: non-secular shift due to the electron and nuclear spin interaction

B_0: static magnetic field

γ: gyromagnetic ratio tensor i.e. $(1/3)\,T_r\vec{\gamma}$

$$\left.\begin{aligned}\Delta\gamma&=\gamma_s-\frac{1}{2}(\gamma_r+\gamma_s)\\ \delta\gamma&=\frac{1}{2}(\gamma_p-\gamma_r)\end{aligned}\right\}\text{where } p,r,s:\ \text{x, y, z coordinates in the molecule fixed frame}$$

β: the angle between the molecular s-axis and the crystal b-axis

γ: the angle of rotation about the molecular s-axis

---

[12] Y. Deguchi, to be published; Y. Deguchi, *J. Chem. Phys.*, **32**, 1584 (1960).

[13] M. H. L. Pryce, *Nature*, **162**, 538 (1948).

[14] J. H. Van Vleck, *Phys, Rev.*, **74**, 1168 (1948).

[15] N. Bloembergent, E. M. Purcell and R. V. Pound, ibid., **73**, 679 (1948).

[16] M. Yokota and S. Koide, *J. Phys. Soc. Japan*, **9**, 953 (1954).

[17] P. W. Anderson and P. R. Weisse, *Rev. Mod. Phys.*, **25**, 269 (1953).

[18] P. W. Anderson, *J. Phys. Soc. Japan*, **9**, 316 (1954).

[19] R. Kubo and K. Tomita, ibid., **9**, 884 (1954).

[20] D. Kivelson, *J. Chem. Phys.*, **27**, 1087 (1957).

[21] D. Kivelson, ibid., **33**, 1094 (1960).

α: the angle of rotation about the crystal b-axis

$\omega_e{}^2=(2/3)S(S+1)J^2$, J: exchange integral

$A_\lambda{}^2=\{(\Phi_{zz}^{(\lambda)}-a_\lambda)^2+4|\Phi_{z+}^{(\lambda)}|^2\}$ (see Appendix)

And the total line width $2T_2{}^{-1}$ is equal to the sum of the secular line width $2T_2'{}^{-1}$ and the non-secular line width $2T_1'{}^{-1}$

$$2T_2{}^{-1}=2T_2'{}^{-1}+2T_1'{}^{-1}$$

where

$$T_2'{}^{-1}(IS)=\frac{\pi^{1/2}}{2[3S(S+1)]^{1/2}J}\sum_\lambda n_\lambda I_\lambda(I_\lambda+1)$$
$$\times[(\Phi_{zz}^{(\lambda)}-a_\lambda)^2+4|\Phi_{z+}^{(\lambda)}|^2]$$

$$T_1'{}^{-1}(IS)=\frac{\pi^{1/2}}{2[3S(S+1)]^{1/2}J}\sum_\lambda n_\lambda I_\lambda(I_\lambda+1)$$
$$\times\left[\left(\frac{1}{2}\Phi_{zz}^{(\lambda)}+a_\lambda\right)^2+2|\Phi_{z+}^{(\lambda)}|^2+4|\Phi_{++}^{(\lambda)}|^2\right]$$
$$\times\exp(-\omega_0{}^2/2\omega_e{}^2)$$

For the extreme exchange case which is analogous to the extreme motional narrowing, $(J^2\gg\gamma^2B_0{}^2\gg A^2)$

$$T_2{}^{-1}(IS)=\frac{\pi^{1/2}}{2[3S(S+1)]^{1/2}J}\sum_\lambda n_\lambda I_\lambda(I_\lambda+1)$$
$$\times\left[\frac{4}{5}|\Phi_{zz}^{(\lambda)}|^2-a_\lambda\Phi_{zz}^{(\lambda)}+2a_\lambda{}^2+6|\Phi_{z+}^{(\lambda)}|^2+4|\Phi_{++}^{(\lambda)}|^2\right]$$

In organic free radicals, we can assume

$$\delta\gamma=0$$
$$c_\lambda=d_\lambda=0$$

Then for the strong exchange case $(J^2\gg A^2)$

$$\omega=\gamma+\frac{\Delta\gamma}{3}(3\cos^2\beta-1)-\Delta$$

$$T_2'{}^{-1}(IS)=\frac{\pi^{1/2}}{2[3S(S+1)]^{1/2}J}\sum_\lambda n_\lambda I_\lambda(I_\lambda+1)$$
$$\times\Big\{[(3\cos^2\beta-1)(b_\lambda{}^2/4-b_\lambda a_\lambda)+b_\lambda{}^2/2+a_\lambda{}^2]$$
$$+\Big[(1-3\cos^2\beta)\left(\frac{1}{3}b^2-\frac{1}{2}a_\lambda b_\lambda\right)$$
$$+b_\lambda{}^2/2+a_\lambda{}^2\Big]\Big\}\exp(-\omega_0{}^2/2\omega_e{}^2)$$

and for the extreme exchange case

$$T_2'{}^{-1}(IS)=\frac{\pi^{1/2}}{2[3S(S+1)]^{1/2}J}\sum_\lambda n_\lambda I_\lambda(I_\lambda+1)$$
$$\times\left[(3\cos^2\beta-1)\left(\frac{1}{8}b^2-\frac{1}{2}b_\lambda a_\lambda\right)+b_\lambda{}^2+2a_\lambda{}^2\right]$$

In case of diphenyl nitric oxide, we have three different equivalent groups of nuclei, that is, one nitrogen, six protons at para- and ortho-positions and four protons at meta-positions in two benzene rings.

As shown in the Appendix, we obtain the following isotropic and anisotropic hyperfine splitting factors, that is,

Nitrogen isotropic hyperfine splitting factor

$$a_N=-9.5\text{ gauss}$$

Nitrogen anisotropic hyperfine splitting factor

$$b_N=-13.92\text{ gauss}$$

Para- and ortho-proton isotropic splitting factor

$$a_{p,o}=+1.96\text{ gauss}$$

Para- and ortho-proton anisotropic splitting factor

$$b_{p,o}=-1.564\text{ gauss}$$

Meta-proton isotropic splitting factor

$$a_m=-0.98\text{ gauss}$$

Meta-proton anisotropic hyperfine splitting factor

$$b_m=-0.782\text{ gauss}$$

and the total electron spin $S=1/2$.

Then

$$T_2{}^{-1}(\mathrm{IS})=\frac{\pi^{1/2}}{3J}\Big[2\Big\{(3\cos^2\beta-1)\left(\frac{1}{8}b_N^2-\frac{1}{2}b_Na_N\right)$$
$$+b_N^2+2a_N^2\Big\}$$
$$-\frac{9}{2}\Big\{(3\cos^2\beta-1)\left(\frac{1}{8}b_{p,o}^2-\frac{1}{2}b_{p,o}a_{p,o}\right)$$
$$+b_{p,o}^2+2a_{p,o}^2\Big\}$$
$$-3\Big\{(3\cos^2\beta-1)\left(\frac{1}{8}b_m^2-\frac{1}{2}b_ma_m\right)$$
$$+b_m^2+2a_m^2\Big\}\Big]$$

At $\beta=0°$, $\Delta H_{1/2}$ at the maximum slope is equal to 2.3 gauss from the measurement. Then assuming the Gaussian line shape for the spectra, we have

$$J=284.96\text{ gauss }(0.0262\text{ cm}^{-1})$$

that is, if we consider J as an adjustable parameter[16] and choose the above value for J, a good agreement with the experiment will be obtained.

This exchange integral value is about ten times smaller than the one obtained in inorganic paramagnetic salts[17,18].

The angular variations of g-value and half-width are shown in Figs. 3 and 4.

As mentioned before, things are rather complicated in the intermediate concentration region.

According to Kubo and Tomita's theory[19] EPR spectra in this region should show a

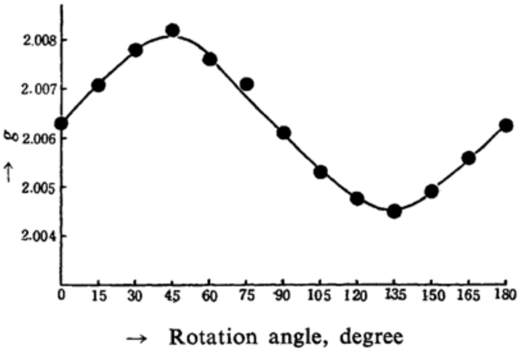

Fig. 3. The angular variation of *g*-values rotated around the a-axis for the pure crystal.

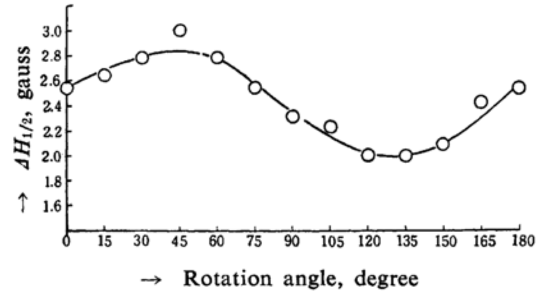

Fig. 4. The angular variation of half-widths rotated around the a-axis for the pure crystal.

microwave frequency dependence. Unfortunately, the apparatus we employed is a fixed microwave frequency one. Thus we shall not discuss it here.

The Weak Exchange Interaction Case in Single Crystals Diluted with Benzophenone.—As stated at the beginning of this section, the hyperfine spectra consist of the three broad but well-separated lines at a certain orientation of crystal. Since the exchange interaction in diluted crystals is reduced to small magnitude, the main contribution to the line broadening comes from the magnetic dipolar interaction due to an electron spin and protons in molecules in the crystal.

As shown in Appendix, the resonance frequency is given as follows:

$$\left[\gamma+\frac{\Delta\gamma}{3}(3\cos^2\beta-1)\right]B_0+\sum_{\lambda}A_{\lambda}M_{\lambda}-\frac{S(S+1)}{3}K$$

where

$$A_{\lambda}^2=\left[-a_{\lambda}+\frac{b}{2}(1-3\cos^2\beta)\right]^2$$

$$+\frac{9}{4}b_{\lambda}^2\sin^2\beta\cos^2\beta$$

$$K=J^2\sum_{\lambda}g_{M'}\Big[\sum_{M_{\lambda}'\neq M_{\lambda}}A_{\lambda}(M_{\lambda}-M_{\lambda}')\Big]^{-1}$$

$$NJ^2=\sum_{j}\sum_{i\neq j}J^2{}_{ij}$$

$$g_M=\Pi W(n_{\lambda},M_{\lambda},I_{\lambda})(2I_{\lambda}+I)^{-n\lambda}$$

Using the above formula, we can obtain the expression for the separation between the center line and the outside one, i.e.

$$\Delta H_{ab}=\Delta H_{bc}=A_{\mathrm{N}}$$

where *K* term is neglected, since it is actually a very small quantity. Comparing with the experimental results.

$$-(a_{\mathrm{N}}+b_{\mathrm{N}})=23.42 \text{ (gauss) at } \beta=0^{\circ}$$

$$-a_{\mathrm{N}}+b_{\mathrm{N}}/2=2.54 \text{ (gauss) at } \beta=90^{\circ}$$

Then one obtains

$a_{\mathrm{N}}=-9.5$ gauss (isotropic splitting coeff.)

$b_{\mathrm{N}}=-13.92$ gauss (anisotropic splitting coeff.)

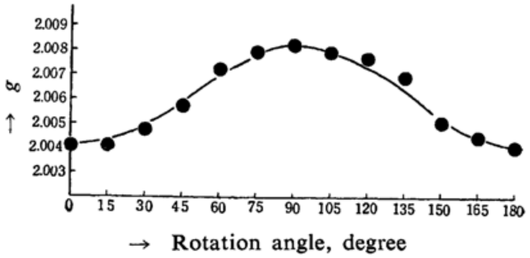

Fig. 5. The angular variation of *g*-values rotated around the a-axis for the 0.0005 mol./l. crystal.

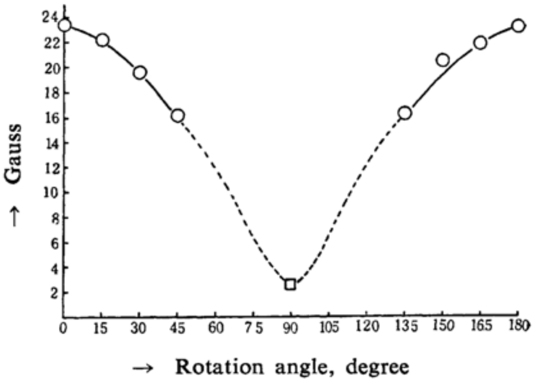

Fig. 6. The angular variation of the hyperfine splittings rotated around the a-axis for the 0.0005 mol./l. crystal where the open circles are the measured widths and the square is the graphically obtained one.

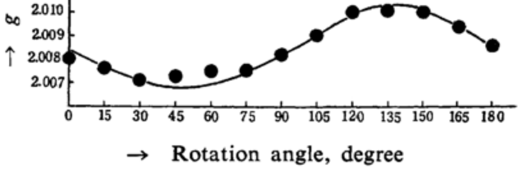

Fig. 7. The angular variation of *g*-values rotated around the b-axis for the 0.0005 mol./l. crystal.

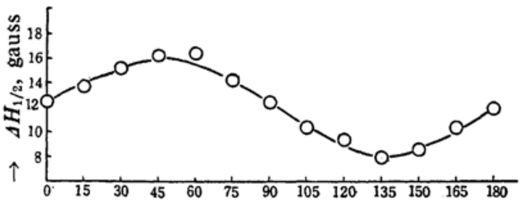

Fig. 8. The angular variation of half-widths rotated around the b-axis for the 0.0005 mol./l. crystal. In this direction there appear only single lines.

The angular variations of the separation between the two successive lines are shown in Figs. 5—8.

From Fig. 6, above 60° rotation of the crystal, the spectrum collapses into a single line. Then we can not measure the separations directly. In order to avoid this difficulty we employed the graphical method, that is, assuming a Gaussian shape for each line, we tried the graphical composition to obtain a composed single line changing the relative distance between the centered line and the outside ones. Thus 2.5 gauss was obtained for the separation at 90° rotation of the crystal.

The anisotropic splitting coefficient b_N will be exressed as

$$b_N = -(4/5)\gamma\gamma_N\hbar(0|r^{-3}|0)$$

where

γ, γ_N: the gyromagnetic ratio for an electron and a nitrogen respectively.

$\hbar$: Planck's constant divided by 2π

$(0|r^{-3}|0)$: the expectation value of the enclosed operator between $2p\pi$ wave functions.

Hence one can obtain

$$(0|r^{-3}|0) = 8.54 \times 10^{24}\ \mathrm{cm}^{-3}$$

Accoeding to Dousmanis' calculation[20], the "best" theoretical value is

$$(0|r^{-3}|0) = 22.5 \times 10^{24}\ \mathrm{cm}^{-3}$$

Then the ratio of our result to the Dousmanis' will be

$$(0|r^{-3}|0)/(0|r^{-3}|0) = 0.38$$

This ratio means that in diphenyl nitric oxide the electron distribution amplitude of $2p\pi$ wave function expanded in the series of an orthonormal set of A. O. functions may be 0.38. In other words, this value is the probability of finding an unpaired electron on the nitrogen atom. As mentioned before, the spectra of very diluted single crystals do not give well-resolved proton hyperfine lines but show nitrogen hyperfine lines. Thus we can not apply the results of the weak exchange case in Kivelson's theory.

From Figs. 5—8, the angular variation of g-values about a certain axis is larger than the one about another axis perpendicular to the former. Furthermore, in the former case, there appear three well-resolved hyperfine lines and these collapse into a single line by 90° rotation, but in the latter case, the hyperfine line is single and stays in a single line during a rotation.

From these results and the crystallographic orientation of the benzophenone molecules, we might conclude that the p-orbital of a nitrogen atom in diphenyl nitric oxide molecule would be almost parallel to one crystal axis of the bulk crystal.

Summary

Electron paramagnetic resonance experiments of diphenyl nitric oxide single crystals were performed. Variation of exchange narrowed line were measured by changing the magnitude of magnetic dilution in crystals. Angular variations of g-value and of hyperfine spectra were investigated. The value of the exchange integral in pure crystal and the spin density on ^{14}N atom in the molecule were determined.

The author wishes to thank Professor S. I. Weissman for his helpful discussions and suggestions; special thanks are due to Professor J. Townsend for offering the chance to used the EPR apparatus which was constructed by him.

Department of Chemistry
Washington University
*St. Louis, Mo., U. S. A.****

Appendix

Determination of the Isotropic and Anisotropic Hyperfine Splitting Factors for Nitrogen, para-, ortho- and meta-Protons in Benzene Rings of Diphenyl Nitric Oxide.

Kivelson[20,21] applied the Kubo and Tomita's theory[19] to the organic free radicals in both cases of liquid and solid. We shall summarize the results of his calculation briefly.

In case of weak exchange (i. e. in case of diluted mixed crystals) the resonance frequency of each hyperfine line is

$$\omega = [\gamma + (1/3)\Delta\gamma(3\cos^2\beta - 1) - \delta\gamma\sin^2\beta\cos^2\gamma]B_0$$

*** On leave from Kyoto University; Fulbright Scholar 1958-1959. Present address: Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto.

$$+\sum_{\lambda} A_{\lambda} M_{\lambda} - \frac{S(S+1)K}{3} \qquad (1)$$

where

$$A_{\lambda}{}^{2} = \{(\Phi_{zz}^{(\lambda)} - a_{\lambda})^{2} + 4\,|\,\Phi_{z+}^{(\lambda)}\,|\,^{2}\} \qquad (2)$$

$$K = J^{2} \sum_{M' \neq M} g_{M'} [\sum_{\lambda} A_{\lambda} (M_{\lambda} - M_{\lambda}')]^{-1} \qquad (3)$$

$$NJ^{2} = \sum_{j} \sum_{i \neq j} J^{2}{}_{ij} \qquad (4)$$

$$g_{M} = \prod_{\lambda} W(n_{\lambda}, M_{\lambda}, I_{\lambda}) (2I_{\lambda}+1)^{-n_{\lambda}} \qquad (5)$$

$$\Phi_{zz}^{(\lambda)} = \frac{b_{\lambda}}{2}(3\cos^{2}\beta - 1) - \sin^{2}\beta(c_{\lambda}e^{-2i\gamma} + c_{\lambda}{}^{*}e^{2i\gamma}) + \sin 2\beta(id_{\lambda}e^{-i\gamma} - id_{\lambda}{}^{*}e^{i\gamma}) \qquad (6)$$

$$\Phi_{z+}^{(\lambda)} = \{(3/8)b_{\lambda} i \sin 2\beta - (1/2) i \sin\beta \times [c_{\lambda}(1+\cos\beta)e^{-2i\gamma} - c_{\lambda}{}^{*}(1-\cos\beta)e^{2i\gamma}] - (1/2)[d_{\lambda}(2\cos^{2}\beta + \cos\beta - 1)e^{-i\gamma} + d_{\lambda}{}^{*}(-2\cos^{2}\beta + \cos\beta + 1)e^{i\gamma}]\}e^{-i\alpha} \qquad (7)$$

where J_{λ} and M_{λ} are the total and the z-component of angular momentum, respectively, for the λ'th group of equivalent nuclei in a molecule. There are one nitrogen, 6 para- and ortho-protons and 4 meta-protons in case of diphenyl nitric oxide. $W(n_{\lambda}, M_{\lambda}, I_{\lambda})$ is the degeneracy of an M_{λ} spin state which is composed of n_{λ} equivalent nuclei with spin I_{λ}. In our case we have 3 different $W(n_{\lambda}, M_{\lambda}, I_{\lambda})$'s, i. e. $W(n_{\mathrm{N}}, M_{\mathrm{N}}, I_{\mathrm{N}})$, $W(n_{\mathrm{p,o}}, M_{\mathrm{p,o}}, I_{\mathrm{p,o}})$ and $W(n_{\mathrm{m}}, M_{\mathrm{m}}, I_{\mathrm{m}})$. And $N_{\mathrm{N}}=1$, $M_{\mathrm{N}}=0, \pm 1$, $I_{\mathrm{N}}=1$; $n_{\mathrm{p,o}}=6$, $M_{\mathrm{p,o}}=0, \pm 1, \pm 2, \pm 3$, $I_{\mathrm{p,o}}=1/2$; $n_{\mathrm{m}}=4$, $M_{\mathrm{m}}=0, \pm 1, \pm 2$, $I_{\mathrm{m}}=1/2$. γ, $\Delta\gamma$, $\delta\gamma$, β, γ and B_0 have been explained in the preceding section. Then we shall obtain 105 absorption lines corresponding to the combinations of M_{N}, $M_{\mathrm{p,o}}$ and M_{m}. However, in the crystal of diphenyl nitric oxide case only three rather broad absorption lines wese observed.

In order to determine the anisotropic hyperfine splitting coefficients, one inserts the experimental results into the Eq. 1 and calculates the A_{λ}'s. The isotropic hyperfine splitting coefficients were determined by direct measurements from the spectra of degassed and vacuum sealed ether solution of diphenyl nitric oxide.

Since a detailed explanation will be given in the forthcoming paper, a brief description of the calculation method of the isotropic and anisotropic hyperfine splitting factors of proton in diphenyl nitric oxide will be presented below.

From the direct measurement of diphenyl nitric oxide spectra, one can obtain the isotropic hyperfine splitting coefficients for para-, ortho- and meta-position protons respectively, i. e.

$$a_{\mathrm{p,o}} = +1.96 \text{ gauss}$$

$$a_{\mathrm{m}} = -0.98 \text{ gauss}$$

where we assumed that the spin density at ortho- and para-position ($\rho_{\mathrm{p,o}}$) is about twice as large as the one at meta-position (ρ_{m}) and $\rho_{\mathrm{p,o}}$ is negative and ρ_{m} is positive.

The anisotropic hyperfine splitting coefficients will be evaluated as follows[21]

$$b_{\mathrm{p,o}} = -\gamma\gamma_{\mathrm{H}}\hbar(0.6) \times 10^{24} \rho_{\mathrm{p,o}}$$

$$b_{\mathrm{m}} = -\gamma\gamma_{\mathrm{H}}\hbar(0.6) \times 10^{24} \rho_{\mathrm{m}}$$

where γ and γ_{H} are the gyromagnetic ratios of an electron and a proton, respectively.