*Electron Spin Resonance Hyperfine Spectra of Diphenyl Nitric Oxide**

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Many electron spin resonance spectra of organic free radicals have been reported by many investigators[1]. Hoskins[2], for instance, has reported that he could observe the proton hyperfine spectra of diphenyl nitric oxide (DPNO) during the oxidation of diphenylamine. The spectrum showed that it was composed of three groups, each of which consisted of more than thirteen sharp lines. His explanation of this result was that the separation into three groups was caused by the interaction of the nuclear magnetic moment of nitrogen (^{14}N) with that of electron and that each sharp line in any of the three groups occurred from the proton-electron hyperfine interaction. Thus, he obtained 10.3 gauss as the isotropic hyperfine interaction coefficient of ^{14}N and $g=2.0062$. However, he did not explain the proton hyperfine spectra in detail.

We have synthesized DPNO and studied the exchange narrowing effect and the crystal anisotropy effect on the spectra in crystalline states[3]. In this paper we shall report on the results of electron spin resonance measurements in liquid solutions of DPNO.

Experimental

The synthetic method of DPNO has already been described in a previous paper[3],***. The same compounds, in which either the para- or the meta-position in the two benzene rings was deuterized, were also synthesized.

The ESR spectrometer employed here is the new high-resolution apparatus constructed by Professor J. Townsend, of the Department of Physics of Washington University. The microwave length is 3 cm., and the cavity is a reflex cylindrical type. The static magnetic field is generated by a Varian electro-magnet with 12 pole faces. The magnetic field modulation frequency is 100 kc. An aqueous solution of peroxylamine disulfonate[4] was used as a standard of the g-value and the magnetic field. Especially for the precise measurement of the nitrogen and proton isotropic hyperfine splittings, a glass capillary filled with an aqueous solution of peroxylamine disulfonate was attached to a sample tube, a 2.5 mm. (I. D.) × 200 mm. pyrex glass tube sealed at one end.

Solutions of DPNO were made with various kinds of organic solvents, i. e., cyclohexane, ethyl ether, ethyl alcohol, dimethoxyethane, tetrahydrofurane and mixtures of ethyl alcohol and glycerol[5], either in vacuum-sealed glass tubes[6] or under ordinary pressure atmosphere conditions.

Results and Discussion

The Case of Samples Prepared under the Normal Pressure Atmosphere.—We determined the suitable concentration for obtaining well-resolved hyperfine spectra. Of the different concentrations of cyclohexane solutions, a 0.1 mol./l. solution showed a single absorption line, a 0.01 mol./l. solution began to reveal hyperfine spectra slightly, a 0.001 mol./l. solution had three broad absorption lines due to ^{14}N and a 0.0001 mol./l. solution also had three broad lines but never revealed further splittings due to protons. The measured g-values are 2.0078 for the 0.1 mol./l. solution, 2.0069 for the 0.01 mol./l. solution, 2.0106 for the 0.001 mol./l. solution, and 2.0100 for the 0.0001 mol./l. solution. The isotropic hyperfine splitting coefficient of ^{14}N is 9.55 gauss. In the 0.00001 mol./l. solution, no absorption spectra could be obtained, since at this concentration the noise level of the apparatus was much higher than the signal level. Solutions of ethyl ether, ethyl alcohol, dimethoxyethane and tetrahydrofurane behaved just the same as did the cyclohexane solution. In the case of a mixed solution of ethyl alcohol and glycerol, however, we obtained proton hyperfine spectra similar to those of Hoskins[2]. The remarkable difference between our spectra and Hoskins' is that our spectrum is asymmetric with respect to the center group lines, while Hoskins' is not, as is shown in Fig. 1. In Fig. 1, the absorption lines in the central group

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1) Cf. J. E. Wertz, *Chem. Revs.*, **55**, 828 (1955); D. J. E. Ingram, "Free Radicals", Academic Press (1958).

2) R. Hoskins, *J. Chem. Phys.*, **25**, 788 (1956).

3) Y. Deguchi, This Bulletin, **34**, 910 (1961).

*** The crystals and solutions of DPNO are rather unstable if they are kept at room temperature, but stable if kept in a refrigerator. We synthesized it about a year ago, but it has stayed stable in a refrigerator since.

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

5) K. H. Hausser, *Z. Naturforsch.*, **14A**, 425 (1959).

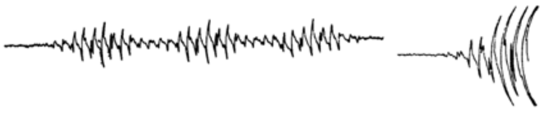
6) Y. Deguchi, *J. Chem. Phys.*, **32**, 1584 (1960).

Fig. 1. ESR proton hyperfine spectrum of DPNO in a mixed solvent of ethyl alcohol and glycerol with a mixed ratio 3 : 2.

are the sharpest compared with the groups in both sides. Also, each line in the lower field side is sharper than the one in the higher field side. Each group overlaps at the tail of the other.

This phenomenon can be explained according to McConnel[7], as the effect of anisotropic hyperfine interaction on the paramagnetic relaxation in liquid. Further experiments will be made and discussed elsewhere in the near future.

The Case of Samples Prepared in Vacuum.— As reported before[6], diphenylpicrylhydrazyl (DPPH) revealed a well-resolved proton hyperfine structure in the ESR spectrum when its sample was prepared in vaccum. DPNO also shows a more detailed proton hyperfine structure when prepared in vacuo, as is shown in Fig. 2.

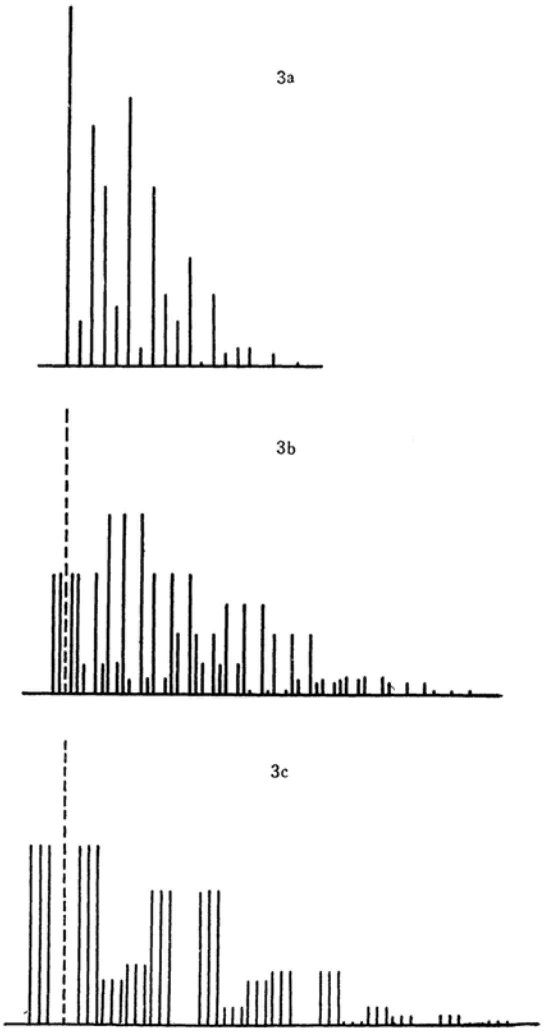


2a 2b

Figs. 2a and 2b. ESR protone hyperfine spectra of DPNO in degassed ethyl alcohol. Fig. 2b. is a half spectrum of the lower magnetic field side group where the concentration of the sample is a little more concentrated than the one in Fig. 2a.

From Fig. 2a, we can not determine exactly the total numbers of lines in each group, because the concentration of the sample is rather small for obtaining the weaker lines in the ends far from the center. Thus, by making a little more concentrated sample, Fig. 2b was obtained. From Figs. 2a and 2b, one could finally find that each group consisted of seventeen lines due to the proton hyperfine interaction.

In other solvents, such as dimethoxyethane, tetrahydrofuran cyclohexane, methylcyclohexane, carbon disulfide, toluene, etc., the same spectra as that of the ethyl alcohol solution have been obtained, except that small variations in the nitrogen and proton isotropic splitting coefficients appear from one solvent to another.



Figs. 3a, 3b and 3c. One halves of calculated intensities of the proton hyperfine spectra of DPNO in one of the three groups: (a) Non-deuterized DPNO; (b) Para-deuterized DPNO; (c) Meta-deuterized DPNO.

In order to explain these spectra, we assume that the odd electron spin densities at the para- and ortho-position carbon adjacent to the proton in the benzene ring are equal to one another and nearly twice as large as the one at the meta-position. The relative intensities thus calculated are shown in Fig. 3a. The measured isotropic splitting coefficients due to the para- or ortho-position spin density and that of the meta-position are 1.89 gauss ($\Delta H_{p,o}$) and 0.83 gauss (ΔH_m) respectively, i. e., $\Delta H_{p,o} \lesssim 2\Delta H_m$. To verify further the validity of our assumption, we observed the ESR spectra of deuterized DPNO, in which one of the para- or meta-protons of the benzene rings was substituted for by a deuterium, as is shown in

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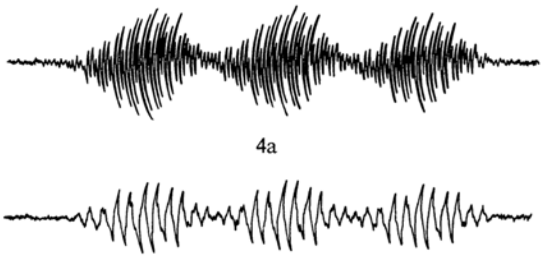
7) H. M. McConnell, ibid., 25, 709 (1956).



4a

4b

Figs. 4a and 4b. ESR spectra of para- or meta-deuterized DPNO in ethyl alcohol. Fig. 4a is the spectrum of the para-deuterized DPNO and Fig. 4b is the one of the meta-deuterized DPNO.

Figs. 4a and 4b. While each hyperfine line splits further into three lines by the substitution for the proton at the para-position of the deuteron ($I=1$) (cf. Fig. 4a), the appearance of the triple splitting in each line is very weak in the case of meta-deuterized DPNO. These results confirm that the aforementioned assumption about spin density is valid. Figures 3b and 3c are the calculated relative intensity diagrams for para- and meta-deuterized DPNO based upon the aforementioned assumption.

Hereafter we shall apply Kivelson's theory[8] to calculate the line width of each hyperfine line in the spectrum of DPNO. As has been described in the preceding paper[3], we will have

$$\omega=\omega_o-\varDelta$$

$$\omega_o=\gamma B_o+\sum_\lambda a_\lambda M_\lambda-\frac{S(S+1)K'}{3}$$

where K' is the same as K as defined in the preceding paper[3] although $A_\lambda=a_\lambda$, a_λ is an isotropic hyperfine splitting factor for the λth nucleus and $\varDelta$ is a nonsecular shift.

The integrated intensity of each line (I) is

$$I=\frac{NS(S+1)\gamma g_M}{3}$$

where N and g_M are defined as in the preceding paper[3].

Assuming $\tau_c{}^2 a_\lambda{}^2 \ll 1$ and $\gamma B_o \gg a_\lambda$, $T_1'(IS)$ and $T_2'(IS)$ are given by

$$\begin{aligned}T_2'{}^{-1}(IS)=&\frac{3\tau_c}{20}\sum_\lambda(2S^2+2S+1)\sigma_{\lambda\lambda'}{}^2\\&\times[\langle\!\langle J_\lambda(J_\lambda+1)\rangle\!\rangle_{M_\lambda}-M_\lambda{}^2]\\&+\tau_c\sum_\lambda\sum_{\lambda'}\{\sigma_{\lambda\lambda'}{}^2M_\lambda M_{\lambda'}\}\\&+\frac{4\tau_c}{15}\left\{\frac{(\varDelta\gamma B_o)^2}{3}+(\delta\gamma B_o)^2\right\}\\&-\frac{4\tau_c}{15}\sum_\lambda\{\varDelta\gamma B_o b_\lambda M_\lambda+2\delta\gamma B_o(c_\lambda+c_\lambda{}^*)M_\lambda\}\end{aligned}$$

$$\begin{aligned}T_1'{}^{-1}(IS)=&\tau_c[1+\omega_o{}^2\tau_c{}^2]^{-1}\left\{\frac{1}{15}(\varDelta\gamma B_o)^2\right.\\&+\frac{1}{5}(\delta\gamma B_o)^2-\sum_\lambda\left[\frac{1}{5}\varDelta\gamma B_o b_\lambda M_\lambda\right.\\&+\frac{2}{5}\delta\gamma B_o(c_\lambda+c_\lambda{}^*)M_\lambda\\&+\frac{7}{40}(8S^2+8S-1)\sigma_{\lambda\lambda}{}^2[\langle\!\langle J_\lambda(J_\lambda+1)\rangle\!\rangle_{M_\lambda}\\&\left.\left.-M_\lambda{}^2]\right]+\sum_\lambda\sum_{\lambda'}\frac{3}{4}\sigma_{\lambda\lambda'}{}^2M_\lambda M_{\lambda'}\right\}\end{aligned}$$

where

$$\begin{aligned}\sigma_{\lambda\lambda'}=&\frac{1}{5}\left[b_\lambda b_{\lambda'}+\frac{8}{3}(c_\lambda{}^*c_{\lambda'}+c_\lambda c_{\lambda'}{}^*\right.\\&\left.+d_\lambda{}^*d_{\lambda'}+d_\lambda d_{\lambda'}{}^*)\right]\end{aligned}$$

If $\delta\gamma=c=d=0$, then

$$\begin{aligned}T_2'{}^{-1}(IS)=&\frac{3\tau_c}{20}\sum_\lambda(2S^2+2S+1)\\&\times\frac{b_\lambda{}^2}{5}[\langle\!\langle J_\lambda(J_\lambda+1)\rangle\!\rangle_{M_\lambda}-M_\lambda{}^2]\\&+\tau_c\sum_\lambda\sum_{\lambda'}\left(\frac{b_\lambda b_{\lambda'}}{5}M_\lambda M_{\lambda'}\right)\\&+\frac{4\tau_c}{45}(\varDelta\gamma B_o)^2-\frac{4\tau_c}{15}\sum_\lambda(\varDelta\gamma B_o b_\lambda M_\lambda)\end{aligned}$$

$$\begin{aligned}T_1'{}^{-1}(IS)=&\tau_c[1+\omega_o{}^2\tau_c{}^2]^{-1}\left\{\frac{(\varDelta\gamma B_o)^2}{15}\right.\\&-\sum_\lambda\left[\frac{1}{5}\varDelta\gamma B_o b_\lambda M_\lambda\right.\\&+\frac{7}{40}(8S^2+8S-1)\frac{b_\lambda{}^2}{25}\\&\left.\times[\langle\!\langle J_\lambda(J_\lambda+1)\rangle\!\rangle_{M_\lambda}-M_\lambda{}^2]\right]\\&\left.+\sum_\lambda\sum_{\lambda'}\frac{3b_\lambda b_{\lambda'}}{100}M_\lambda M_{\lambda'}\right\}\end{aligned}$$

where

$$\langle\!\langle J_\lambda(J_\lambda+1)\rangle\!\rangle_{M_\lambda}=\sum_{I_\lambda=M_\lambda}^{n_\lambda I_\lambda}J_\lambda(J_\lambda+1)\frac{g'_{J_\lambda}-g'_{J_\lambda+1})}{g_M}$$

$$g'_{J_\lambda}=[W(n_\lambda,J_\lambda,I_\lambda)]\prod_\lambda(2I_\lambda+1)^{-n_\lambda}$$

$$g_M=\prod_\lambda W(n_\lambda,J_\lambda,I_\lambda)(2I_\lambda+1)^{-n_\lambda}$$

In the case of diphenyl nitric oxide, we have one nitrogen atom and 6 para- and ortho-protons and 4 meta-protons; i. e.,

$$n_N=1,\qquad I_N=1;\qquad S=\frac{1}{2}$$

$$n_{p,o}=6,\qquad I_{p,o}=\frac{1}{2}$$

$$n_m=4,\qquad I_m=\frac{1}{2}$$

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

Also, as assumed in the preceding section, the electron spin density at the para- or ortho-position is about twice as large as that at the meta-position.

In the formula for ω_o, the term $\sum_{\lambda} a_{\lambda} M_{\lambda}$ gives the hyperfine structure in spectra. In our case, we have three different equivalent groups of niclei, i. e., one nitrogen, 6 para- and ortho-protons, and 4 meta-protons. One nitrogen has I_{zN}: $1, 0, -1$; 6 para- and ortho-protons, $I_{zp,o}$: $\pm 3, \pm 2, \pm 1, 0$; 4 meta-protons, I_{zm}: $\pm 2, \pm 1, 0$. One thus obtains 105 absorption lines, but some of them will be so weak that one can not observe them in the spectra.

It is tedious to calculate the $\ll J_{\lambda}(J_{\lambda}+1) \gg_{M_{\lambda}}$ of all the component lines. Thus we shall calculate only those referred to the three center lines of each group. These lines are given as follows:

1. For $M_N=1$, there exist three different combination of $M_{p,o}$ and M_m, i. e.,

$$\begin{cases} M_{p,o}=0 \\ M_m=2 \end{cases} \quad \begin{cases} M_{p,o}=1 \\ M_m=-2 \end{cases} \quad \begin{cases} M_{p,o}=-1 \\ M_m=2 \end{cases}$$

2. For $M_N=0$ (this corresponds to the center group),

$$\begin{cases} M_{p,o}=0 \\ M_m=0 \end{cases} \quad \begin{cases} M_{p,o}=1 \\ M_m=-2 \end{cases} \quad \begin{cases} M_{p,o}=-1 \\ M_m=2 \end{cases}$$

3. For $M_N=-1$,

$$\begin{cases} M_{p,o}=0 \\ M_m=0 \end{cases} \quad \begin{cases} M_{p,o}=1 \\ M_m=-2 \end{cases} \quad \begin{cases} M_{p,o}=-1 \\ M_m=2 \end{cases}$$

Each combination has its own T_1', T_2' and integrated intensity I, which are given above. In order to evaluate a correlation time (τ_c) for the molecular tumbling, evidently we cannot assume the DPNO molecule as a sphere, but rather must regard it as a prolate ellipsoid. The dimensions thus determined are

$$a=4.84\,\text{Å}$$

$$b=2.10\,\text{Å}$$

where a and b are the longer and the shorter axes. According to Perrin's theory⁹⁾,

$$\frac{\tau_a}{\tau_o}=\frac{2(1-q^4)}{\dfrac{3q^2(2-q^2)}{\sqrt{1-q^2}}\ln\left\{\dfrac{1+\sqrt{1-q^2}}{q}\right\}-3q^2}$$

$$\frac{\tau_b}{\tau_o}=\frac{4(1-q^4)}{\dfrac{3q^2(2q^2-1)}{\sqrt{1-q^2}}\ln\left\{\dfrac{1+\sqrt{1-q^2}}{q}\right\}+3}$$

where τ_a: the correlation time for the molecular tumbling around the b-axis. τ_b: the correlation time for the molecular tumbling around the a-axis. τ_o: the correlation time for a hypothetical sphere with a volume equivalent to that of the actual ellipsoid.

$$\tau_o=\frac{4\pi\eta ab^2}{3KT}$$

q: an axial ratio given by

$$b/a$$

η: the viscosity of a solvent in poise, T: absolute temperature (°K).

In the case of ethyl alcohol at $T=293$°K,

$$\eta=1.20\times 10^{-2}\ \text{poise}^{10)}$$

Thus we get

$$\tau_a=4.608\times 10^{-11}\ \text{sec.}$$

$$\tau_b=4.256\times 10^{-11}\ \text{sec.}$$

The numerical values of a_N, $a_{p,o}$, a_m, b_N, $b_{p,o}$, b_m, $\Delta\gamma$ and H_o have been given in the preceding paper³⁾. The results thus obtained are tabulated in Table I. As can be seen in Table I, the angular quantum number dependency of the spectra for the center line in each group can be explained by this theory, but the two outside lines next to the center line in each group are one-eighth the intensity of the center lines, while their calculated widths are about five times broader than the center lines. Thus we

TABLE I

		Half-width at max. slope gauss	
		Calcd.	Obs.
Lower magnetic field side group	$M_N=1$, $M_{p,o}=0$, $M_m=0$	0.152	0.169
	$M_N=1$, $M_{p,o}=1$, $M_m=-2$	0.764	—
	$M_N=1$, $M_{p,o}=-1$, $M_m=2$	0.751	—
Central group	$M_N=0$, $M_{p,o}=0$, $M_m=0$	0.107	0.122
	$M_N=0$, $M_{p,o}=1$, $M_m=-2$	0.408	—
	$M_N=0$, $M_{p,o}=-1$, $M_m=2$	0.553	—
Higher magnetic field side group	$M_N=-1$, $M_{p,o}=0$, $M_m=0$	0.242	0.203
	$M_N=1$, $M_{p,o}=1$, $M_m=-2$	0.823	—
	$M_N=-1$, $M_{p,o}=-1$, $M_m=2$	0.790	—

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9) J. Perrin, *J. Phys. Radium.*, (7) 5, 497 (1934).

10) "Handbook of Phys. & Chem.", 39th Ed., Chem. Rubber Publishing Co.

can not expect well-resolved absorption lines. This is the case in the actual spectra.

Effect of a Methyl Group Attached to the Benzene Ring either at the para-, meta- or ortho-Position. — Using bromo-toluene instead of bromo-benzene, these radicals were synthesized by the same procedure as has been described above. Among three methylized radicals, the ESR spectra of the para- or meta-methylized ones show that an attached methyl group adds extra proton hyperfine lines to the original spectra of DPNO, while the ortho-methylized one exhibits a drastic modification in the spectra, as is shown in Fig. 5. Only four broad lines instead of seventeen sharp lines appear in each group. From this spectra, one can conclude that the electron spin densities at the nitrogen and methyl groups are much greater than those at the other ring carbons.

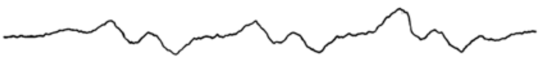

Fig. 5. ESR spectrum of the ortho-methylized DPNO in ethyl alcohol.

In order to clarify this remarkable effect, further investigations, such as optical measurements and ESR measurement of its crystalline state, are now being undertaken.

Effect of Solvents on the Widths of Nitrogen and Proton Hyperfine Splittings. — During the course of the present study, it was found that the widths of nitrogen and proton hyperfine splittings vary from one solvent to other. These results are shown in Fig. 6. In this figure, the magnitudes of the dielectric constants of the solvents were conveniently taken as an abscissa scale. From this diagram, it can be seen that nitrogen and proton isotropic splittings are approximately linearly proportional to the dielectric constants of the solvents. This result can be qualitatively understood if one considers as follows:

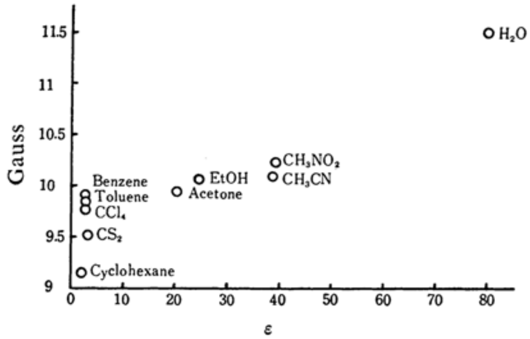

Fig. 6. Dependence of the nitrogen isotropic hyperfine splittings on dielectric constants of various kinds of solvent.

According to the valence bond theory, one will have various kinds of ionic structure besides the covalent bond structure, as is shown in Fig. 7.

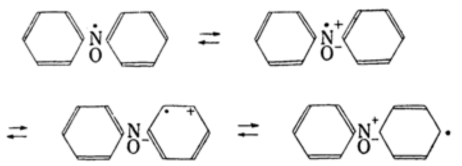

Fig. 7. Various resonance structures of DPNO.

The second structure gives the nitrogen splitting, and the third and fourth structures, the proton splitting. Thus, by the presence of polar solvents, the ionic structures among the above resonant ones will be favored.

In order to put this consideration on a rigorous theoretical basis, a further investigation is now under way.

Summary

Liquid solutions of diphenyl nitric oxide reveal well-resolved proton hyperfine spectra either in mixed solvents of glycerine and ethyl alcohol in a suitable mixed ratio or in vacuum-sealed, degassed solvents.

Assuming odd electron spin densities at the ring carbon atoms and applying Kivelson's theory, one can explain the experimental results. Moreover, the effect on the ESR spectra of the addition of a methyl group to a benzene ring has been reported on.

Finally, the solvent effect on the ESR spectra has been discussed.

The author is much obliged to Professor S. I. Weissman for his helpful discussions and encouragement during the course of this work. He is also indebted to Professor J. Townsend for offering him a chance to use the ESR apparatus. He also appreciates Dr. A. Holtzer's suggestion of the molecular tumbling-correlation time estimation method.

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