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Solvent Effects in the Electron Spin Resonance Spectra of Some Phenoxyl, Nitroxide, and Anilino Radicals*[1]

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The electron spin resonance spectra of 2, 6-di-*t*-butyl-4-methylphenoxyl (I) and 2, 4, 6-tri-*t* butylphenoxyl (II) have been observed under high resolution, and it has been shown experimentally that the para methyl proton hyperfine splitting ($a^{\mathrm{H}}_{\mathrm{CH_3}}$) in the radical (I) increases, while, inversely, the meta proton hyperfine interaction decreases, as the dipole moment of the solvent (μ) increases. The relationship between these two variables can be written as:

$$a(\mu_{\mathrm{solv}}) = a(\mu_{\mathrm{solv}}=0) + K\cdot\mu_{\mathrm{solv}},$$

where μ_{solv} is the dipole moment of the solvent and where K is the constant of proportionality. Further study of diphenyl nitric oxide (DPNO) (IV) and di-*p*-anisyl nitric oxide (DPANO) (V) radicals has shown this to be a general form of the solvent effect. However, in the case of various kinds of solvents with OH or NH groups, it has been found that a^{N} deviates from the equation. This phenomenon has been explained qualitatively by the effect of hydrogen bonding. Therefore, the variation in the coupling constants has generally been explained by two effects, that is, the μ dependence described above and the electron delocalization arising from hydrogen bonding. Similar experiments performed with 2, 4, 6-tri-*t*-butylphenoxy (II) and 2, 4, 6-tri-*t*-butylanilino (III) radicals have shown that the variation in the hyperfine splitting constants is small because of the steric hindrance of tertiary butyl groups in these molecules.

In recent electron spin resonance studies, it has been found that the hyperfine splittings of some organic free radicals in a solution vary with the solvents.[1-5] Piette *et al.*[6] have shown that the nitrogen splittings of a nitro group in nitrobenzene, *p*-, and *o*-nitro aniline anions in acetonitrile increase with the addition of water to each solution. In order to account for the solvent dependence of the hyperfine splittings for the semiquinone anions, Gendell *et al.*[7] have proposed a simple model stating that the change in splittings arises entirely from a redistribution of the π-electron spin density caused by the formation of local complexes between polar solvents and polar groups in the radical such as that of ion pairs, or of a hydrogen bond between solvent and radical. Further experimental studies[8,9] have shown that this proposal gives a satisfactory explanation of the above-mentioned mixed solvent effect for nitrobenzene anions and nitric oxide radicals. Recently, similar experiments[10,11] have been performed with the fluorenone anion and *p*-benzosemiquinone-1-^{13}C in mixed solvents.

On the other hand, one of the present authors (Y. D.)[12] has previously reported on an ESR study of diphenyl nitric oxide (DPNO) in various kinds of solvents; he found that nitrogen splittings are approximately linearly proportional to the dielectric constants of the solvents. Similar results were also found for di-*p*-anisyl nitric oxide by Umemoto *et al.*[13]

Previous investigations of the solvent effect of free radicals in a solution have dealt exclusively with the variation in hyperfine splittings in mixed solvents including alcohol. As yet no experiment

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*[1] Parts of this work were presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964, and at the 18th Annual Meeting, Osaka, April, 1965.

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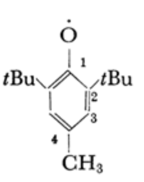
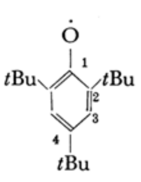
has been made drawing a clear distinction between the electrostatic interaction effect*2 and the hydrogen bond formation effect, which occur simultaneously in the interaction between radical and solvent.

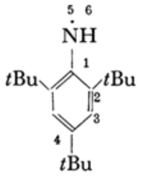
First of all, we will briefly discuss the proton hyperfine splittings of the phenoxyl radicals, especially those of the tertiary butyl group. The oxidation of 2, 6-di-*t*-butyl-4-methylphenol, 2, 4, 6-tri-*t*-butylphenol, or 2, 4, 6-tri-*t*-butylaniline with lead dioxide produces the corresponding phenoxyl or anilino radical. The radicals (II) and (III) are very stable because of resonance and steric hindrance against dimerisation or attack on the benzene nucleus. The electron spin resonance spectra of the radicals (I), (II) and (III) have been reported on by several investigators.[14-17] In recent papers, Atherton *et al.*[18] and Hausser *et al.*[19] have reported on the tertiary butyl proton hyperfine splittings after studying the radicals (II) and (III) under a high resolution.



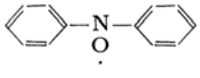
(I)



(II)



(III)



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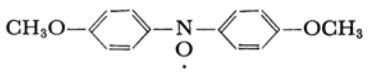

(V)

The second purpose of the work reported on here is to determine how the solvent affects the redistribution of the π-electron density if hydrogen bonding occurs between radical and solvent molecules in addition to the electrostatic interaction effect. We have measured the variation in the hyperfine splitting constants in many solvents using several neutral radicals (*e. g.*, the radicals (I), (II), (III), (IV) and (V)). These stable radicals are suitable for the solvent-effect studies in that one can use many kinds of solvents for the radicals, unlike the cases of the anion radicals or electrolytically-generated radicals.

Experimental

2, 6-Di-*t*-butyl-4-methylphenol was obtained commercially. 2, 4, 6-Tri-*t*-butylphenol[20] and 2, 4, 6-tri-*t*-butylaniline[21-23] were prepared according to the procedures described previously. The radicals (I), (II), and (III) were prepared under a vacuum by the oxidation of substituted phenols and aniline with lead dioxide in the various kinds of organic solvents (including some alcohols and amines) listed in Table 1. On the other hand, nitric oxide radicals were synthesized following the similar method of Wieland and Roth[24] and were prepared under a vacuum in the many solvents listed in Tables 4 and 5. These solvents were well purified and dehydrated by the usual method. An aqueous solution of peroxylamine disulfonate was used as the standard, and the value of 13.00 gauss was taken for the nitrogen splittings.[25] The recorded splitting constants were usually determined by taking the average of two or three spectra. All the ESR spectra were obtained with a JES-3B type apparatus of the Japan Electron Optics Co., equipped with a 100 KC field modulation. Its maximum resolution was about 30 milligauss.

Results and Discussion

Proton Hyperfine Splittings of Phenoxyl Radicals. Becconsall *et al.*[16] and Stone *et al.*[26] have observed the ESR spectra of several kinds of alkyl-substituted phenoxyl radicals. The consistency of the splitting constants in their experiments has shown that the distribution of the unpaired spin density in the ring is similar in all the phenoxyl radicals. Therefore, it may be appropriate to assume that this is also true for the substitution of the tertiary butyl group. The experimental data of the splitting constants for phenoxyl radicals in cyclohexane obtained by Becconsall *et al.* lie in the neighbourhood of:

$$\begin{aligned} a^{\mathrm{H}}_{\mathrm{CH_3}}\ (\text{ortho}) &= 6.5\ \text{gauss} \\ a^{\mathrm{H}}_{\mathrm{CH_3}}\ (\text{para}) &= 11.0\ \text{gauss} \end{aligned} \qquad (1)$$

Using the formula $a^{\mathrm{H}}_{\mathrm{CH_3}} = Q_{\mathrm{CH3}}\rho$, which relates the

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*2 We define this effect as the redistribution of π-electron spin density in a radical molecule induced by the electric dipolar interaction between radical and solvent molecules.

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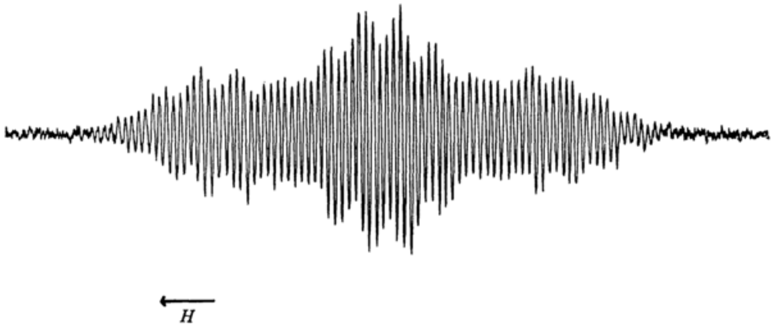


Fig. 1. ESR spectrum of 2, 4, 6-tri-*t*-butylphenoxyl (II) in *n*-hexane.

$a_{\mathrm{CH_3}}^{\mathrm{H}}$ for a ring methyl proton to the spin density, ρ, on the aromatic carbon atom, and the experimental value of $Q_{\mathrm{CH_3}}=25\mathrm{G}$, the spin densities on ortho and para aromatic carbon atoms of the phenoxyl radical can be calculated as:

$$\rho(\text{ortho})=0.26, \qquad \rho(\text{para})=0.44 \tag{2}$$

From Tables 1 and 2, the experimental values of the tertiary butyl hyperfine splitting constants of the radicals (I) and (II) in *n*-hexane, measured under high resolution (see Fig. 1), can be seen to give:

$$\begin{aligned} a_{t\mathrm{Bu}}^{\mathrm{H}}\ (\text{ortho}) &= 0.073 \text{ gauss} \\ a_{t\mathrm{Bu}}^{\mathrm{H}}\ (\text{para}) &= 0.370 \text{ gauss} \end{aligned} \tag{3}$$

If we employ the values of (2) and (3), the Q-value which relates the proton hyperfine splitting constants of the tertiary butyl to the π-distribution of the odd electron in aromatic free radicals becomes:

$$\begin{aligned} Q_{t\mathrm{Bu}}(\text{ortho}) &= 0.28 \text{ gauss} \\ Q_{t\mathrm{Bu}}(\text{para}) &= 0.84 \text{ gauss} \end{aligned}$$

TABLE 1. HYPERFINE SPLITTING CONSTANTS FOR 2,6-DI-*t*-BUTYL-4-METHYLPHENOXYL (in gauss)

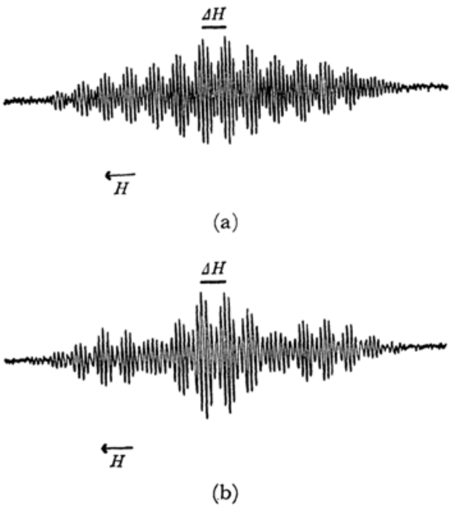
Number (see Fig. 5)	Solvent	$a_4^{\mathrm{CH_3(H)}}$	a_3^{H}	$a_2^{t\mathrm{Bu(H)}}$
1	Cyclohexane	10.93	1.71	
2	$\mathrm{CCl_4}$	11.05	1.69	0.06_9
3	*n*-Hexane	11.07	1.70	0.07_3
4	$\mathrm{C_6H_5CH_3}$	11.10	1.66	0.07_3
5	$\mathrm{(C_2H_5)_2O}$	11.15	1.71	
6	$\mathrm{CH_2Cl_2}$	11.24	1.62	
7	T.H.F.*	11.27	1.65	0.07_4
8	$\mathrm{CH_3COCH_3}$	11.43	1.64	
9	$\mathrm{CH_3NO_2}$	11.44	1.60	
10	$\mathrm{CH_3CN}$	11.50	1.63	
11	$\mathrm{CH_3OH}$	11.36	1.63	
12	$\mathrm{C_2H_5OH}$	11.31	1.63	
13	*iso*-$\mathrm{C_3H_7OH}$	11.30	1.64	
14	*n*-$\mathrm{C_4H_9OH}$	11.29	1.65	
15	$(n\text{-}\mathrm{C_3H_7})_2\mathrm{NH}$	11.14	1.66	

* Tetrahydrofuran

TABLE 2. HYPERFINE SPLITTING CONSTANTS FOR 2, 4, 6-TRI-*t*-BUTYLPHENOXYL (in gauss)

Solvent	a_3^{H}	$a_4^{t\mathrm{Bu(H)}}$	$a_2^{t\mathrm{Bu(H)}}$
$\mathrm{CS_2}$	1.72	0.37_6	0.07_3
Benzene	1.70	0.37_8	0.06_9
n-Hexane	1.70	0.37_0	0.07_3
$\mathrm{C_6H_5CH_3}$	1.72	0.38_5	0.07_6
$\mathrm{CH_3OH}$	1.74	0.39_0	0.07_5
T.H.F.	1.69	0.37_8	0.07_4

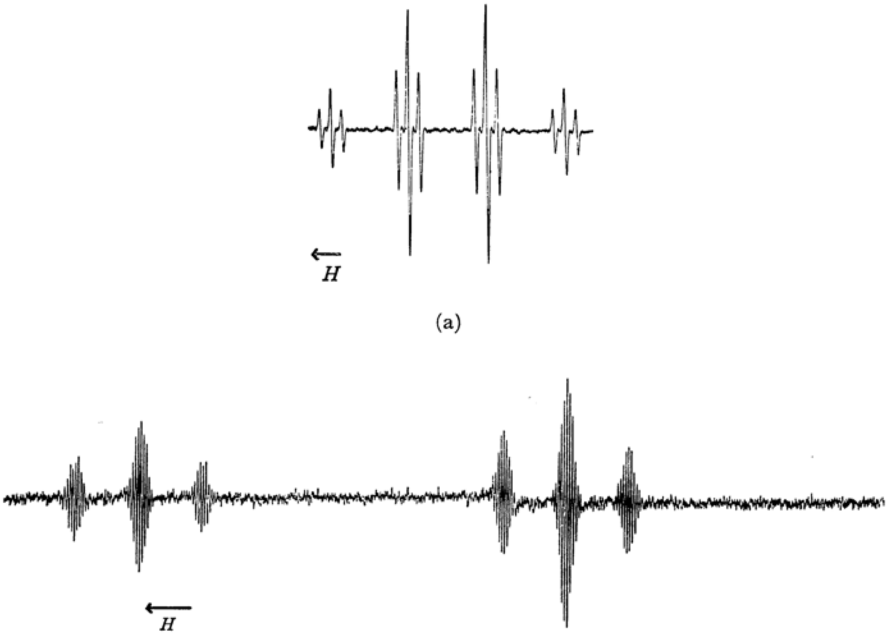
Because the spin polarization of an electron on an ortho tertiary butyl by the unpaired electron in a π-orbital is considerably affected by the oxygen atom in the phenoxyl group, the deviation in Q-value between ortho and para will be large. Therefore, we shall take the value of unaffected $Q_{t\mathrm{Bu}}(\text{para})$ as the Q-value of the tertiary butyl



(a)

(b)

Fig. 2. The ESR spectrum of 2, 4, 6-tri-*t*-butylphenoxyl in THF solution.
(a) at room temperature (20°C)
(b) at −5°C



(a)

(b)

Fig. 3. (a) ESR spectrum of 2, 6-di-*t*-butyl-4-methylphenoxyl (I) in THF solution under low resolution. (b) One half of the spectrum under high resolution.

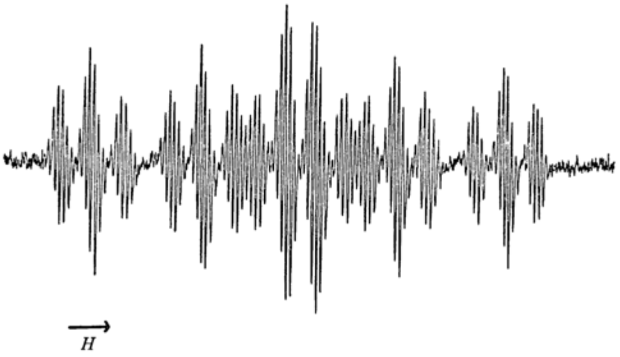


Fig. 4. ESR spectrum of 2, 4, 6-tri-*t*-butylanilino (III) in diethyl ether.

group. That is,

$$Q_{t\mathrm{Bu}} = 0.84 \text{ gauss}$$

We have measured the ESR spectrum of 2, 4, 6-tri-*t*-butylphenoxyl (II) in THF by varying the temperature from 20°C to −20°C. The temperature variation in the spectra is shown in Fig. 2.

From the results of our analysis of the spectrum of the radical (II) in *n*-hexane shown previously (Fig. 1), we can see that each tertiary butyl group rotates freely at room temperature. When the temperature was lowered from 20°C to −20°C, the hyperfine splitting constants of the para tertiary butyl proton and the meta proton were not changed, but those of the ortho tertiary butyl proton changed from 0.074 to 0.063 gauss. This is apparent from Fig. 2, where, though the separation, ΔH (equivalent to $a^{\mathrm{H}}_{t\mathrm{Bu}}$ (para)) is constant, the number of spectral lines involved in it changes from 4 to 5. This suggests that Fermi contact interaction between unpaired electron in the ring π-orbit and the nuclear spin of the ortho tertiary butyl proton undergoes a small change upon temperature variation. When the same experiment was performed in a CS_2 solution, the results were similar.

Solvent Effect. The observed proton hyperfine splittings of the radicals (I), (II), and (III) in various kinds of organic solvents under a high resolution are summarised in Tables 1, 2, and 3. Figures 1, 3, and 4 show the ESR hyperfine spectra of these radicals. From Tables 2 and 3, it can be

TABLE 3. HYPERFINE SPLITTING CONSTANTS FOR 2, 4, 6-TRI-*t*-BUTYLANILINO (in gauss)

Solvent	a_6^{H}	a_5^{N}	a_3^{H}	$a_4^{t\mathrm{Bu(H)}}$
Cyclohexane	11.75	6.70	1.89	0.27_1
$(C_2H_5)_2O$	11.88	6.75	1.89	0.27_0
CH_3OH	11.68	6.83	1.86	0.28_7
T.H.F.	11.85	6.72	1.89	0.28_0
CH_3COCH	11.80	6.70	1.88	0.27_9
CH_3CN	11.85	6.80	1.93	0.28_6

seen that the variation in meta proton splittings (a_3^{H}) of the radical (II) and in the proton, and the nitrogen splittings (a_6^{H} and a_5^{H}) of the radical (III), is comparatively small, and that the variation does not always depend on the polarity of the solvent. The results presented in Fig. 5, however, show that the para methyl proton hyperfine splittings in the radical (I) increase from 10.92 to 11.50 gauss with the dipole moment of the solvent, which corresponds to the polarity of the solvent, while, on the contrary, the meta proton hyperfine splittings decrease. For the radical (I), the hyperfine splittings, $a_4^{\mathrm{CH_3}}$ and a_3^{H}, can be written as:

$$a_4^{\mathrm{CH_3}}(\mu) = 11.1 + 0.11\mu \doteqdot 11.1(1+0.01\mu)$$

$$a_3^{\mathrm{H}}(\mu) = 1.7 - 0.02\mu \doteqdot 1.7(1-0.01\mu)$$

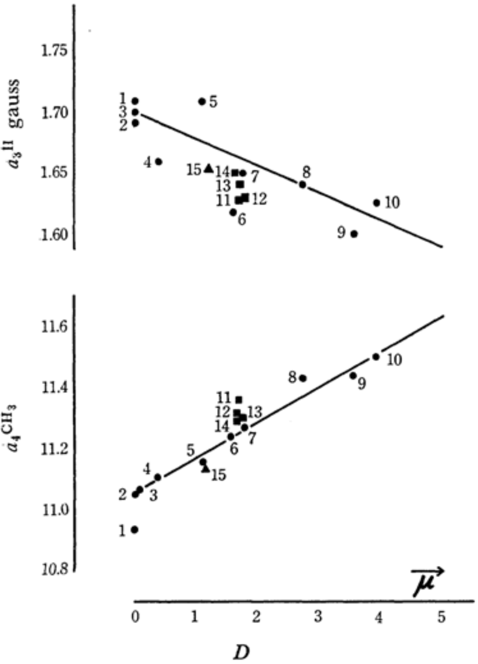


Fig. 5. The variation of the para-methyl and meta-proton coupling constants in 2, 6-di-*t*-butyl-4-methylphenoxyl radical as a function of the dipole moments (in Debye Units) of the solvents (includes some alcohols and amine). The line is a fit of the data by inspection.

●: Solvents having no OH or NH group
■: Solvents having OH group
▲: Solvents having NH group

From these equations one can readily imagine that the unpaired electron on the π-orbital in the radical (I) is not completely isolated from the solvent; therefore, the π-electron spin density at the position 4 can be changed by the electrostatic interaction between the radical and solvent molecules. On the other hand, the π-systems of the radicals (II) and (III) are isolated from the solvent because of the presence of three tertiary butyl groups (steric hindrance). The clear difference between the two cases is in good accordance with the known stability of radicals caused by the steric hindrance of tertiary butyl groups. Here, it should be noted that, though several alcohols were used as solvents, no effect of hydrogen bonding was observed in the present cases. Probably the oxygen atom of the phenoxyl radical is not influenced by the solvent because of the steric hindrance arising from the ortho tertiary butyl groups, as will be discussed in the next section.

In order to confirm the above results, we have measured the nitrogen hyperfine splitting constants a^{N} of diphenyl nitric oxide (DPNO) in various kinds of solvents. Similarly, a^{N} varied linearly with the dipole moments of the solvent molecules (μ), ranging from 0 to 4 D by a factor of about 0.22, although it may deviate from constancy in the presence of certain solvents. The splittings may be written as:

$$a^{\mathrm{N}}(\mu) = 9.24 + 0.22\mu$$

This equation was derived from the results shown in Fig. 6, where the nitrogen splitting, a^{N}, is plotted against the solvent dipole moment, μ. The linear relation holds well within the range of experimental error over the dipole-moment range studied, up to 4 D in DPNO. These results are consistent with the case of 2, 6-di-*t*-butyl-4-methylphenoxyl. In view of the above facts, one may reasonably conclude that the following relationship holds:

$$a(\mu_{\mathrm{solv}}) = a(\mu_{\mathrm{solv}}=0) + K\cdot\mu_{\mathrm{solv}} \qquad (4)$$

where μ_{solv} is the dipole moment of the solvent and K is a proportional constant which expresses the degree of the polarizability of the radical.

In Fig. 6 it should be noted that, in solvents possessing an OH group or an NH group, Eq. (4) is not adequate to explain the observed values of the nitrogen hyperfine splitting constants, a^{N}. In these cases it will be appropriate to assume that the NO group of DPNO forms a hydrogen bond with the OH group of the solvent, $\text{-O-H}\cdots\text{O-N}\langle$. Let us discuss, for example, the case of water (μ= 1.84 D) as a solvent. In Fig. 6, as the point B shows the value of the hyperfine splitting constant at μ=1.84 D due to the electrostatic interaction only, a gross deviation BC (1.83 gauss) from the

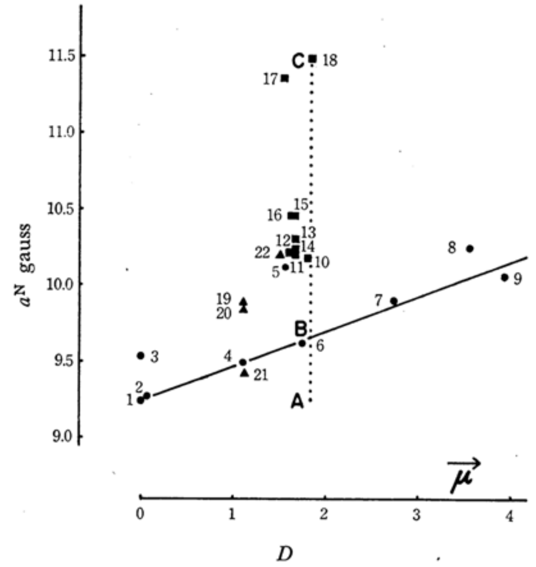


Fig. 6. The variation of the nitrogen hyperfine coupling constants in DPNO as a function of the dipole moments (in Debye Units) of the solvents.

The line is a fit of the data by inspection.
●: Solvents having no OH or NH group
■: Solvents having OH group
▲: Solvents having NH group

point B may reflect the redistribution of the π-orbital electron due to hydrogen-bond formation exerted by water molecules.

Let us next consider why the deviation, that is, the increase in the hyperfine splitting of nitrogen, a^N, arises from the formation of the hydrogen bond. The coordination of the NO group of DPNO and the OH group of the solvents may be represented as in (i):[27,28]

$$\left.\begin{array}{lll}(\text{A}) & O_1\text{—}H\cdots O_2\text{—}N & \text{pure covalent}\\ (\text{B}) & O_1{}^-H^+\cdots O_2\text{—}N & \text{pure ionic}\\ (\text{C}) & O_1{}^-H\text{—}O_2{}^+\text{—}N & \text{charge transfer}\end{array}\right\}\qquad (\text{i})$$

Structures (A) and (B) correspond closely to what would occur in the isolated O_1-H bond. Structure (C) represents the delocalization effect. The greater part of the electrostatic interaction in (A) and (B) may be due to the interaction between an electric dipole in O_1-H and an electric dipole due to the lone paires of the O_2 atom, pointing towards O_1. Therefore, this interaction arising from the structures (A) and (B) may cause a variation similar to that of the hyperfine coupling constants (a^N), depending on the solvent dipole moment (μ), as is represented in Eq. (4).

In order to explain a large deviation from the variation of the hyperfine splittings following Eq. (4), however, the contribution of the charge transfer structure (C) should also be considered in this system. This may cause the electronic charge to move away from the O_2 non-bonding σ orbitals to the O_1H group of the solvent, resulting in the increment in the electronegativity of the O_2 atom. Thus, the unpaired electron density, $\rho_{O_2}{}^\pi$, on the O_2 π-orbital decreases, while the unpaired electron density, $\rho_N{}^\pi$, on the N π-orbital increases, in terms of Ayscough's calculations.[29]

The hyperfine splittings arising from the nitrogen nucleus of the NO group in DPNO can be formulated in terms of the theory of Karplus and Fraenkel[30] as:

$$a^N = (S^N + Q^N_{NO} + 2Q^N_{NC})\rho_N{}^\pi + Q^N_{ON}\rho_O{}^\pi + 2Q^N_{CN}\rho_C{}^\pi \qquad (5)$$

where $\rho_N{}^\pi$, $\rho_O{}^\pi$, $\rho_C{}^\pi$ are the pi-electron spin densities at the nitrogen and oxygen atoms and at the adjacent carbon atoms respectively, and where S and the Q's are constants defined much as in their paper. Neglecting the contribution from the carbon to which the nitrogen ^{14}N is bonded, and using the value for S and the Q's given by Rieger and Fraenkel,[31] Eq. (5) becomes:

$$a^N = 134.8\rho_N{}^\pi - 35.8\rho_O{}^\pi \qquad (6)$$

This equation shows that the decrease in the O_2 unpaired π-electron density, $\rho_O{}^\pi$, and the increase in the N unpaired π-electron density, $\rho_N{}^\pi$, cause the increase in the nitrogen hyperfine splittings, a^N. Alternatively, the increase in a^N caused by the formation of a hydrogen bond with a solvent may be easily explained by assuming various resonance structures, as is shown in Fig. 7. One of the present authors (Y. D.)[12] has proposed the structures (I) and (II), and has suggested that the ionic structure (II) will be favored by the presence of polar solvents. In the case of hydrogen bond formation between DPNO and the solvent, the charge transfer structure (III) in Fig. 7 must be considered.

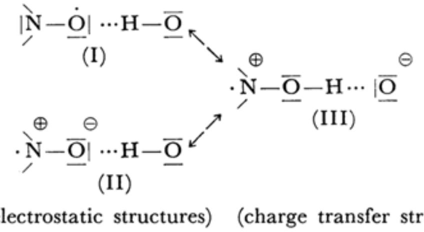


Fig. 7. Various resonance structures between DPNO and solvent possessing OH group.

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in addition to the non-charge transfer structures (I) and (II), which may apparently attribute to an increase in a^N.

Using water as a solvent, AC (2.24 gauss) in Fig. 6 is five or six times larger than AB (0.41 gauss). This may imply that the change in the hyperfine splittings (a^N) is mainly due to the effect of the charge transfer. The same may be said for *m*-cresol. However, it is apparent from Fig. 6 that, in the case of several alcohols, *i. e.*, methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, and *n*-amylalcohol, the AC variation in π-orbital unpaired spin density arising from the hydrogen bond is not larger than in the case of water and *m*-cresol. In Table 4 we list the ratios (AC′/AB) for solvents with OH groups. At the same time, we list the ratio of the force of the hydrogen bond formation, AC′(certain solvent): AC(water), in the last column of the table.

DPNO was examined in amines; the measured nitrogen splitting constants of the nitric oxide radical also show an appreciable deviation from the solid line (depending on the dipole moment), as in Fig. 6. This solvent effect may also be due to the hydrogen bonding between the ON group of DPNO and the NH group of amines. The deviation may be explained by analogy with the case of the solvents with OH groups.

The same measurements for DPANO were carried out in order to confirm the results obtained for DPNO. The observed values for the nitrogen hyperfine coupling constants of DPANO solutions

TABLE 4. HYPERFINE SPLITTING CONSTANTS FOR DPNO (in gauss)

Number (see Fig. 6)	Solvent	μ (D)	a^N	$\frac{AC'}{AB}$	AC′/AC (water) ×100%
1	Cyclohexane	0.00	9.24		
2	*n*-Hexane	0.08	9.27		
3	CCl_4	0.00	9.53		
4	$(C_2H_5)_2O$	1.15	9.48		
5	CH_2Cl_2	1.55	10.12		
6	T.H.F.	1.75	9.62		
7	CH_3COCH_3	2.72	9.89		
8	CH_3NO_2	3.54	10.25		
9	CH_3CN	3.94	10.06		
10	*n*-$C_5H_{11}OH$	1.80	10.18	2.29	41.9
11	*n*-C_4H_9OH	1.67	10.22	2.65	43.8
12	*n*-C_3H_7OH	1.60	10.21	2.62	43.3
13	*iso*-C_3H_7OH	1.68	10.30	2.86	47.4
14	C_2H_5OH	1.68	10.21	2.62	43.3
15	CH_3OH	1.66	10.45	3.18	54.0
16	$C_6H_5CH_2OH$	1.63	10.45	3.27	54.0
17	*m*-$CH_3C_6H_4OH$	1.54	11.36	5.89	94.6
18	H_2O	1.84	11.48	5.46	100.0
19	$(C_2H_5)_2NH$	1.11	9.88	2.56	28.5
20	$(n\text{-}C_3H_7)_2NH$	1.11	9.85	2.44	27.2
21	$(iso\text{-}C_3H_7)_2NH$	1.12	9.42	0.73	8.0
22	$C_6H_5NH_2$	1.51	10.21	2.85	43.3

TABLE 5. HYPERFINE SPLITTING CONSTANTS FOR DPANO (in gauss)

Number (see Fig. 8)	Solvent	μ (D)	a^N	$\frac{AC'}{AB}$	AC′/AC (water) ×100%
1	Cyclohexane	0.00	9.75		
2	CS_2	0.00	9.85		
3	CCl_4	0.00	9.96		
4	$C_6H_5CH_3$	0.37	10.00		
5	$(C_2H_5)_2O$	1.15	9.96		
6	T.H.F.	1.75	10.20		
7	CH_3COCH_3	2.72	10.34		
8	CH_3NO_2	3.54	10.48		
9	CH_3CN	3.94	10.60		
10	*n*-C_4H_9OH	1.67	10.90	3.14	62.2
11	*iso*-C_3H_7OH	1.68	10.84	2.97	58.9
12	C_2H_5OH	1.68	10.91	3.13	62.7
13	CH_3OH	1.66	11.19	3.96	77.8
14	H_2O	1.84	11.60	4.79	100.0
15	$(iso\text{-}C_4H_9)_2NH$	1.11	9.93	0.72	9.7
16	$(iso\text{-}C_3H_7)_2NH$	1.11	9.94	0.76	10.3
17	$(C_2H_5)_2NH$	1.11	10.03	1.12	15.1
18	*n*-$C_4H_9NH_2$	1.40	10.17	1.33	22.7
19	$(C_6H_5)_2NH$	1.08	10.37	2.48	33.5
20	$C_6H_5NH_2$	1.51	10.87	3.20	60.5
21	Pyrrole	1.80	11.01	5.00	68.2

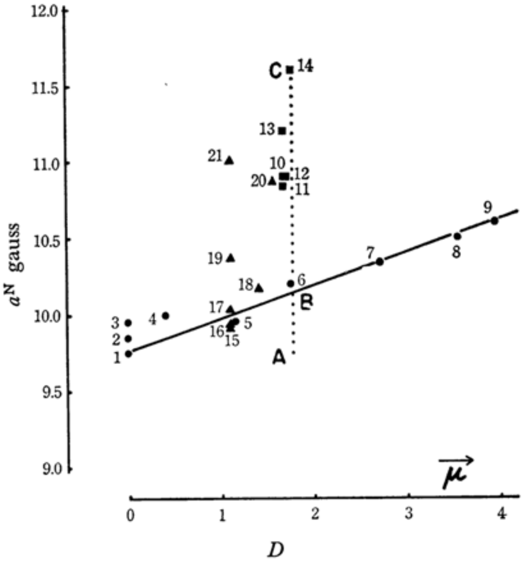


Fig. 8. The variation of the nitrogen hyperfine coupling constants in DPANO as a function of the dipole moments (in Debye Units) of the solvents.

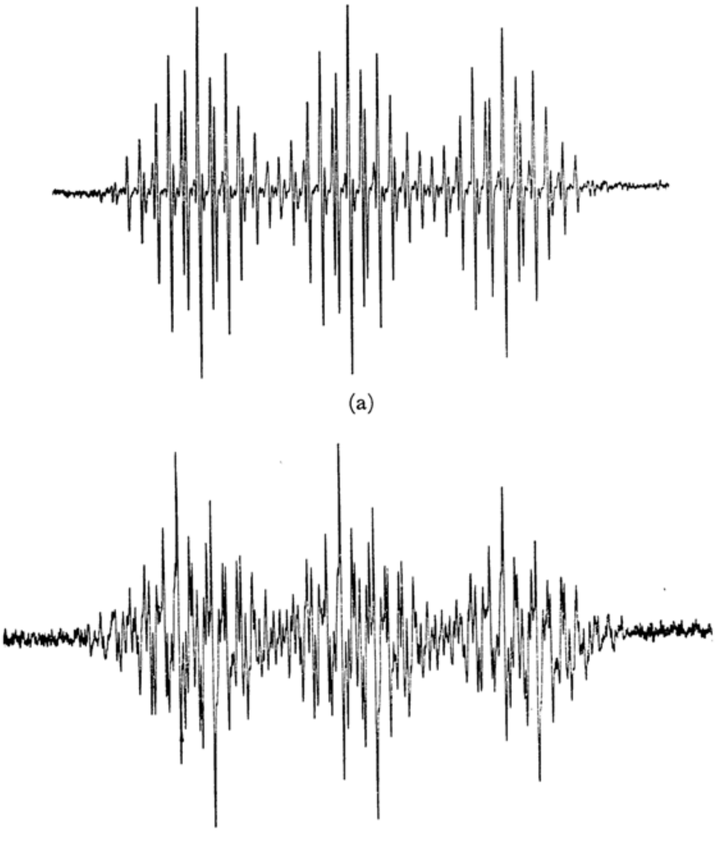
The line is a fit of the data by inspection.
●: Solvents having no OH or NH group
■: Solvents having OH group
▲: Solvents having NH group

are listed in Table 5, while they are plotted against the dipole moments of the solvents in Fig. 8. The agreement between DPNO and DPANO for the variation in the nitrogen hyperfine coupling constant is satisfactory.

From Table 4, it can be seen that the nitrogen splittings in several alcohols are close in magnitude and show values from 10.18 to 10.45 gauss. However, DPNO in *m*-cresol shows a nitrogen coupling of 11.36 gauss; this difference is very pronounced in comparison with the cases of several other alcohols. Furthermore, in the case of DPANO, the hyperfine splitting, a^N, is larger in pyrrole ($a^N=11.01$ gauss, $\mu=1.80$ D) than in diethylamine ($a^N=10.03$ gauss, $\mu=1.11$ D), and larger in aniline ($a^N=10.87$ gauss, $\mu=1.51$ D) than in *n*-butylamine ($a^N=10.17$ gauss, $\mu=1.33$ D).

Here, let us consider the differences between *m*-cresol and methanol, pyrrole and diethylamine, aniline and *n*-butylamine respectively. A property common to the first of each pair is that each has an $-OH$, $\rangle NH$ or $-NH_2$ group bonded directly to the π-system. On the other hand, the second of each pair has the same groups bonded directly to the σ system. In view of the above facts, the most reasonable conclusion to be drawn from the available data is that the contribution of the structure III in Fig. 7 is remarkable; this means that the absolute values of the electron affinity of solvents with an $-OH$, $\rangle NH$, or $-NH_2$ group bonded directly to the σ system are smaller than those of solvents with the same groups bonded directly to the π system.

When diethylamine or di-*n*-propylamine is used as a solvent, each of the $3\times7\times5$ lines due to the one-nitrogen and ten-ring protons splits further into two lines of equal intensity, as is shown in Fig. 9-(b). The magnitude of the splitting was 2.00 gauss for both of the above two solvents. Figure 9-(a) shows the spectrum of DPNO in all the other solvents, including aniline and di-isopropylamine, except diethylamine and di-*n*-propylamine. No splitting could be observed, even in a water solution. Therefore, the spectrum shown in Fig. 9 can not be understood without taking account of the hyperfine coupling of the proton


(a)

(b)

Fig. 9. The ESR absorption for diphenyl nitric oxide (DPNO) (a) in tetrahydrofuran (T.H.F.), (b) in diethylamine at room temperature. Note that in (b) each line of (a) splits further into two lines of equal intensity.

(I=1/2) in the NH group of the amine solvents. These doublet splittings could not be produced by a usual hydrogen bonding (σ bond character), such as the coupling of the NH group with the non-bonding, σ, orbital of the oxygen atom in the nitro group. Further experiments will, however, be necessary in order to confirm the above explanation.

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