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ESR Study of Phenyl Nitric Oxide Radical

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ESR spectra were obtained for phenyl nitric oxide radicals derived from phenyl hydroxylamines by oxidation with benzoyl peroxide, and the variation of hyperfine splitting constants with solvent was examined. Hyperfine splitting constants of nitrogen and NH proton varied with the polarity and hydrogen-bonding nature of solvent. This variation was explained by molecular orbital theory where the Coulomb integral of oxygen atom is assumed to vary with solvent. The sigma-pi parameters, Q_{NH} (in $a_{H(NH)}=\rho_N Q_{NH}$), Q_N and Q_O (in $a_N=\rho_N Q_N+\rho_O Q_O$), were determined from experimental splitting constants of nitrogen and NH proton and the spin density calculated by McLachlan's method. The values $Q_{NH}=27.5$, $Q_N=30.5$ $Q_O=-13.6$ were obtained and the latter two values could be used to calculate the nitrogen hyperfine splitting constant for diphenyl nitric oxide radical.

Diphenyl nitric oxide (DPNO) is one of the most typical neutral radical, and has been studied by ESR method.[1,2] Phenyl nitric oxide (PNO) has a simpler molecular structure than DPNO and its ESR spectrum has been obtained,[3,4] but there have been a few reports on PNO. PNO has N–O group and it will be expected that the nitrogen hyperfine splitting constant changes with solvent like DPNO. Moreover, PNO has a hydrogen atom bonded to nitrogen unlike DPNO, the solvent effect on the splitting constant of NH hydrogen also will be expected.

As well known, the hyperfine splitting constant of a ring proton in aromatic molecule is explained by the spin density on the adjacent carbon atom, and for the nitrogen, its splitting is explained by the spin densities on the nitrogen atom and the atoms bonded to it. PNO is a proper example to

1) Y. Deguchi, This Bulletin, **35**, 260 (1962).
2) J. Pannell, *Mol. Phys.*, **7**, 317 (1964).
3) Buchachenko, *Akad. Nauk S. S. S. R., Otdel. khim. Nauk,* 1120 (1963).
4) C. J. W. Gutch and W. A. Waters, *Proc. Chem. Soc.*, **1964**, 230.

study the relation between the splitting constant of NH proton and the spin density on nitrogen atom.

In the present paper, ESR spectra of PNO were obtained in several solvents and the solvent effect on the ESR spectrum of PNO was explained by molecular orbital theory, and the relations between observed hyperfine splitting constants and calculated spin densities will be discussed for nitrogen atom and proton bonded to it.

Experimental

PHA, *p*-tolyl hydroxylamine (*p*-THA) and *m*-tolyl hydroxylamine (*m*-THA) were prepared by reduction of corresponding nitro-compounds with zinc powder. Benzoyl peroxide (BPO) used as an oxidizer was recrystallized from chloroform. Benzene, toluene, *p*-dioxane, tetrahydrofuran (THF), diethyl ether (DEE), chloroform, methanol and ethanol were used as solvents in ESR measurements, and they were purified by the usual method. Purified PHA was dissolved in the solvent containing a small amount of BPO in a sample tube and ESR spectrum of the generated free radical was obtained at room temperature.

When the free radical is generated by the reaction of PHA with BPO, the reactants and the reaction products remain in the solution and these species may contribute to the hyperfine splitting constants of PNO. This effect was examined and it was found that the hyperfine splitting constants of PNO depend on the concentrations of PHA and BPO used. If the amount of reactants are much smaller than that of solvent, this kind of contribution may be neglected and the splitting constants of the free radical in the pure solvent can be obtained. From the splitting constants of PNO at several concentrations of PHA and BPO, the values extrapolated to zero concentrations of reactants were determined. In the present work, all the hyperfine splitting constants of PNO and its methyl-derivatives were obtained by this method.

ESR spectrometer used was an X-band Varian model V-4500 with 100 kc/s field modulation. For magnetic field strength measurements, proton NMR signals were used as a standard.

Results and Discussion

The ESR Spectra of PNO. The ESR spectrum, shown in Fig. 1, was obtained when PHA was oxidized with a small amount of BPO in benzene. The signal intensity decreased gradually if the reaction took place in open air, but it was almost constant under vacuum for about 10 hr. This spectrum has four large groups with intensity ratio approximately 1 : 2 : 2 : 1 arising from hyperfine interactions with one nitrogen and one proton having similar splitting constants. The free radical is expected to be PNO by comparison with the results of DPNO derived from diphenyl hydroxylamine, and the spectrum can be reconstructed from the following hyperfine splitting constants; 11.95 gauss for one proton, 9.07 gauss for one nitrogen, 2.88 gauss for three equivalent protons, and 0.98 gauss for two equivalent protons, as shown in Fig. 1-(b). By analogy with the results for DPNO, the three equivalent protons can be assigned to ortho-, and para-protons and the two equivalent protons to meta-protons. This assignment was confirmed from the ESR spectra of *p*-tolyl nitric oxide (*p*-TNO) and *m*-tolyl nitric oxide (*m*-TNO). Namely, ESR spectra obtained from oxidation of *p*-, and *m*-THA with BPO and shown in Fig. 2-(a) and 2-(b) respectively, were compared with that of Fig. 1-(a). The effect

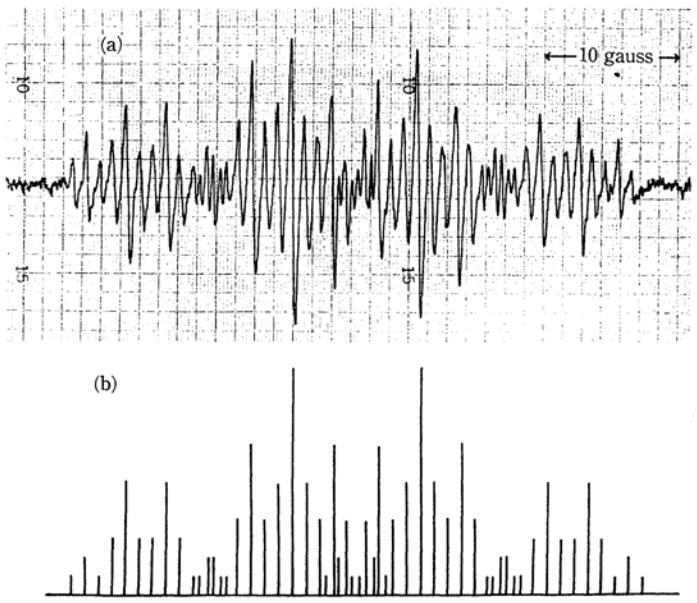


Fig. 1. The observed (a) and the calculated (b) ESR spectra of PNO.

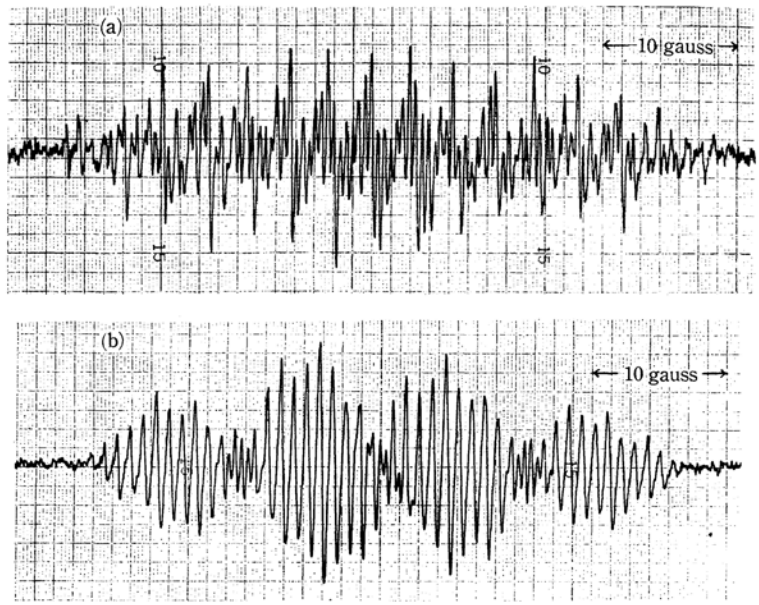


Fig. 2. ESR spectra of *p*-TNO (a) and *m*-TNO (b).

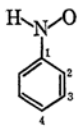
of substituted methyl group on the spectrum was very large for the case of *p*-TNO in comparison with *m*-TNO. This shows that the samallest hyperfine splitting constant corresponds to that of *m*-proton.

The spin densities for PNO were calculated by Hückel and McLachlan's methods. According to McLachlan,[5] the spin density ρ_r on the carbon atom r is written as

$$\rho_r = C_{or}^2 - \lambda \sum_s \pi_{rs} C_{os}^2 \qquad (1)$$

where C_{or} and C_{os} are the Hückel coefficients of the odd electron orbital on atom r and s, π_{rs} is the mutual polarizability of atom r and s, and λ is a numerical constant. The spin distribution calculated is shown in Table 1, and this also supports the present assignment.

Table 1. Calculated spin density of PNO*

	Pnsition	Hückel's	McLachlan's
	O	0.2686	0.4320
	N	0.3132	0.4180
	1	0.0521	−0.0544
	2	0.1092	0.1117
	3	0.0066	−0.0583
	4	0.1344	0.0977

* Parameters used are as follows[6]

$$C\text{—}\underset{\alpha_C+1.5\beta_{CC}}{\overset{\beta_{CC}}{}}N\text{—}\underset{\alpha_C+1.2\beta_{CC}}{\overset{0.7\beta_{CC}}{}}O$$

5) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).
6) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York (1961), p. 117.

Splitting Constants of PNO in Various Solvents. The hyperfine splitting constants of PNO in several solvents are shown in Table 2.

Table 2. Splitting constant of PNO in several solvents (in gauss)

Solvent	$a_{H(NH)}$	a_N	$a_{H(o)}$, $a_{H(p)}$	$a_{H(m)}$
DEE	11.71	8.81	2.92	1.01
THF	11.86	8.92	2.94	1.00
Benzene	11.95	9.07	2.88	0.98
Toluene	11.95	9.05	2.87	1.01
Dioxane	11.96	9.04	2.96	0.97
Chloroform	12.48	9.51	2.99	1.03
Ethanol	12.59	9.55	3.12	1.05
Methanol	12.70	9.65	3.14	1.06

The splitting constants of proton attached to nitrogen atom, $a_{H(NH)}$, and of nitrogen, a_N, considerably depend on solvent species. The fact that a_N is large in the alcohols and changes in the solvents containing the ether type oxygen atom depending on their dipole moment, is the same tendency as that obtained for DPNO.[7] These solvent effect on ESR spectra is revealed in general by the interactions between hetero-atoms in the group substituted to benzene ring and the solvent, these interactions have been thought to be hydrogen bonding of alcohol with hetero-atoms and the polarization effect of polar solvent.[8] From this

7) H. Nishiguchi and Y. Deguchi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 1366 (1965).
8) J. Gendell, J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2837 (1962).

point of view, the present experimental results for PNO were treated by molecular orbital theory assuming that above interactions affect on the Coulomb integral of oxygen and nitrogen. Thus, the spin distribution in PNO was calculated by McLachlan's method as only function of the Coulomb parameter of oxygen, h_O (in $\alpha_O = \alpha_C + h_O\beta_{CC}$), and the variation of spin densities on nitrogen and oxygen atom with h_O were examined. In this calculation, the other Coulomb and resonance integrals were fixed at the values shown in Table 3. From the calculated spin distribution in PNO, it was found that there is an increasing tendency in the spin density ρ_N on the nitrogen atom as h_O increases, and a decreasing tendency in the spin density ρ_O on the oxygen atom as h_O increases, and these relations correspond to the large a_N value and the large $a_{H(NH)}$ value of PNO in polar solvents and the alcohols.

The Values of Q_{NH}, Q_N and Q_O. The relation between the splitting constant of nitrogen in nitrobenzene anion and the spin distribution has been discussed by Rieger and Fraenkel.[9] The molecular structure of PNO is different from nitrobenzene anion, and it is interesting to discuss not only the nitrogen splitting constant but also the splitting constant of NH proton. If the hybridization of nitrogen atom in PNO is assumed to be sp^2, a relation between $a_{H(NH)}$ and ρ_N is given by

$$|a_{H(NH)}| = \rho_N Q_{NH} \tag{2}$$

where Q_{NH} is a sigma-pi parameter. For a_N, Karplus and Fraenkel[10] have proposed the following relation

$$|a_N| = \rho_N Q_N + \sum_i \rho_i Q_i \tag{3}$$

where ρ_i is the spin density on the atom i attached to the nitrogen atom, and Q_N and Q_i are parameters. If the small spin density on the carbon atom attached to the nitrogen atom in PNO is neglected, the relation (3) comes to

$$|a_N| = \rho_N Q_N + \rho_O Q_O \tag{4}$$

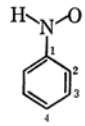
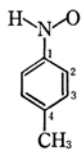
Then the values of Q_{NH}, Q_N and Q_O are estimated from the observed hyperfine splitting constants, $a_{H(NH)}$ and a_N, and the calculated spin densities ρ_N and ρ_O for PNO by the relations (2) and (4). The spin densities of PNO and *p*-TNO were calculated from the relation (1) with parameters which were adjusted in an attempt to fit the calculated spin densities on the ring carbon atoms with the hyperfine splitting constants of ring protons obtained from PNO in benzene. Calculated spin densities are shown in Table 3. The sigma-pi parameters obtained were as follows;

$$Q_{NH} = 27.5 \text{ gauss}, \quad Q_N = 30.5 \text{ gauss},$$

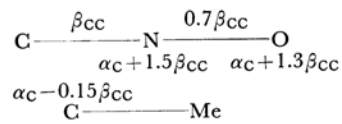
and $$Q_O = -13.6 \text{ gauss}.$$

The relation between a proton hyperfine splitting constant and the spin density on the carbon or nitrogen atom bonded to it is very useful to analyze unknown ESR spectra, but it is difficult to determine sigma-pi parameters like Q_{NH}, Q_N and Q_O, because it is difficult to calculate the precise spin distribution for free radical containing hetero-atoms. For the value of Q_{NH} in Eq. (4), McLachlan[11] used a value of $Q_{NH} = 25$ gauss for the interpretation of hyperfine interaction of amine-proton of cation radicals of aniline derivatives based on Hückel MO calculation, and Melchior and Maki[12] has shown, using the value of $Q_{NH} = 25$ gauss, that the spin density on nitrogen atom calculated by Hückel MO method agrees with experimental one for *p*-phenylenediamine positive ion. But Hückel MO method is clearly insufficient to explain spin distribution in the free radicals which have negative spin densities. This defect can be removed by the more strict methods like semi-empirical open shell calculation with configuration interaction or unrestricted Hartree-Fock SCF method, but these methods are much more complicated than Hückel MO and McLachlan's ones. McLachlan's method is convenient to calculate the spin distribution for free radicals like PNO, and then the value of $Q_{NH} = 27.5$ gauss obtained above may be

Table 3. Spin density of PNO and *p*-TNO

	Position	Calcd*1	Exp.*2
	O	0.3272	
	N	0.4425	
	1	−0.0353	
	2	0.1298	0.128
	3	−0.0592	−0.043
	4	0.1246	0.128
	O	0.2969	
	N	0.4359	
	1	−0.0198	
	2	0.1313	0.127
	3	−0.0539	−0.043
	4	0.1323	0.116

*1 Parameters used are



*2 $Q_{H(CH)} = 22.5$, and $Q_{H(CH_3)} = 28$ gauss were used.

9) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).
10) M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).
11) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).
12) M. T. Melchior and A. H. Maki, *J. Chem. Phys.*, **34**, 471 (1961).

one criterion to estimate the spin density on ni-nitrogen atom in nitric oxide radicals from the experimental hyperfine splitting constant of NH proton.

In order to confirm the values of $Q_N=30.5$ and $Q_O=-13.6$ for nitric oxide radicals, the nitrogen splitting constant of DPNO was calculated from the relation (4) using the values of $Q_N=30.5$ and $Q_O=-13.6$. Spin density for DPNO was obtained by the same method those for PNO. The calculated value of a_N for DPNO was 9.47 gauss and agreed with experimental one.[1)] Sigma-pi parameters given above will be applied to all aromatic nitric oxide radicals.