BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (11), 2881—2882 (1974)

The ESR of Alkyl Phenyl Nitroxide Radicals Studied as Hindered Rotation

Toshio NISHIKAWA and Kazuo SOMENO

National Chemical Laboratory for Industry, Honmachi, Shibuya-ku, Tokyo 151

(Received May 24, 1974)

Synopsis. The ESR spectra were obtained in the series of *N*-methyl, *N*-ethyl, *N*-*n*-propyl, *N*-isopropyl, *N*-*n*-butyl, and *N*-*tert*-butyl phenyl nitroxide radicals. Two tendencies were found in the hyperfine splitting constants and were explained as hindered rotation.

In *N*-alkyl phenyl nitroxide (*N*-alkyl PNO-) radicals, the ESR spectra would be affected because of the hindered motion with respect to the substituted alkyl group. In these radicals, there may exist the two kinds of hindered rotation, about the σ bond between nitrogen and alkyl carbon and about the π bond between nitrogen and phenyl carbon. It is an interesting question whether the hindered-rotation model is applicable to these rather large molecules.

The hyperfine splitting constants were obtained in the series of *N*-methyl, *N*-ethyl, *N*-*n*-propyl, *N*-isopropyl, *N*-*n*-butyl, and *N*-*tert*-butyl PNO radicals. From these data, two tendencies were apparent for a change of the hyperfine splitting constants; we discussed them as hindered rotation and compared our results with Stone and Maki's calculations.[2)]

Experimental

N-Alkyl PNO radicals were prepared by the oxidation of the corresponding *N*-alkyl-substituted aniline or *N*,*N*-di-alkyl-substituted aniline by perbenzoic acid. For obtaining *N*-alkyl-substituted PNO, care should be taken with regard to the quantity of oxidizing agent, since an excess of perbenzoic acid produces unsubstituted PNO, which is more stable. The ESR measurements were done in an about 10^{-3} mol/l toluene solution.

Results and Discussion

The observed hyperfine splitting constants are shown in Table 1. Two tendencies can be seen from Table 1:

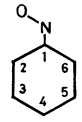
(A) The hyperfine splitting constants of nitrogen (a_N), the *o*- and *p*-protons ($a_{H(o,p)}$) and the *m*-proton ($a_{H(m)}$) are almost all equal except that of *N*-*tert*-butyl PNO, in which a_N is larger and $a_{H(o,p)}$ is smaller.

(B) The hyperfine splitting constants of alkylprotons ($a_{H(CH_3)}$, $a_{H(CH_2)}$, and $a_{H(CH)}$) may be classified into three groups, according to the number of protons.

Table 1. Observed hyperfine splitting constants for *N*-alkyl PNO (in G)

Alkyl	Methyl	Ethyl	*n*-Propyl	*i*-Propyl	*n*-Butyl	*t*-Butyl
a_N	10.65	10.42	10.31	10.65	10.36	12.44
$a_{H(CH_3)}$	9.69					
$a_{H(CH_2)}$		7.84	7.34		7.28	
$a_{H(CH)}$				3.47		
$a_{H(o,p)}$	2.75	2.80	2.58	2.69	2.74	1.90
$a_{H(m)}$	1.01	1.01	0.90	0.90	1.00	0.90

Table 2. Calculated spin densities for PNO and *N*-alkyl PNO



Position	PNO	*N*-Alkyl PNO
N	0.4425	0.4770
O	0.3272	0.3074
1	−0.0353	−0.0474
2	0.1298	0.1313
3	−0.0592	−0.0603
4	0.1246	0.1210

In MO Parameters, such as

$\alpha_N=\alpha_C+h_N\beta_{CC}$

$\beta_{NO}=k_{NO}\beta_{CC}$

and so on, the following values are used,

$h_N=1.5$ for PNO

$h_N=1.4$ for *N*-alkyl PNO

$h_O=1.3$, $k_{NO}=0.7$

$h_1=1.0$, $k_{N1}=1.0$

The data might be considered to reflect the unpaired spin distribution, arising from two types of hindered rotation.

The tendency (A) seems to suggest that the spin densities on the aromatic-ring carbons are constant independent of the kind of substituted alkyl group, except in the case of *N*-*tert*-butyl PNO.

For the purpose of further discussion, McLachlan's spin-density calculation was carried out with substituted and unsubstituted PNO radicals, as is shown in Table 2.

According to our previous calculations on unsubstituted PNO,[1)] an alkyl substitution was treated as the inductive effect on the nitrogen atom as follows:

$$\alpha_{N'}=\alpha_N+h\beta_{CC} \quad (1)$$

while the other MO parameters were taken as having the same values.

On the assumptions that $h=-0.1$, which may be considered acceptable in these cases, and that the same relationship held:

$$\left.\begin{aligned} &a_N=Q_1\rho_N+Q_2\rho_O \\ &a_{H(o)}=Q\rho_2,\quad a_{H(p)}=Q\rho_4 \\ &\text{where}\quad Q_1=30.5,\quad Q_2=-13.6 \\ &\qquad Q=-22.5 \end{aligned}\right\} \quad (2)$$

the splitting constants, a_N, $a_{H(o)}$, and $a_{H(p)}$, were calculated to be 10.37, 2.95, and 2.72 G, respectively.

Thus, the planar structure for *N*-alkyl substitution, except in the case of the *N*-*tert*-butyl group, may be plausible, since the observed splitting constants can be explained by using the same parameters as in *N*-unsubstituted PNO. When the resonance integral between nitrogen and alkyl carbon is decreased, corre-

sponding to the twisting about the bond, the spin densities, ρ_N and ρ_O, are increased, and ρ_2, ρ_4, and ρ_6 are decreased; then the splitting constant, a_N becomes increased and $a_{H(o)}$ and $a_{H(o)}$ are decreased. This seems to imply non-planarity for *N-tert*-butyl PNO.

The (B) tendency was interpreted according to Stone and Maki's treatment[2] on the basis that the hindered rotation about the single bond may be assumed in these cases.

When the alkyl proton internally rotates about the equilibrium angle, θ_0, under the potential function:

$$V = \frac{1}{2}V_0(1-\cos 2\alpha) \tag{3}$$

the hyperfine splitting constants for the alkyl proton can be given as the function of the average value of the overlapping angle and the π-spin density of the adjacent nitrogen atom:

$$a_H = B\langle\cos^2\theta\rangle\rho_N \tag{4}$$

where:

$$\langle\cos^2\theta\rangle = \frac{\sum_i g_i\langle\cos^2\theta\rangle_i \exp(-E_i/kT)}{\sum_i g_i \exp(-E_i/kT)}$$

$$\langle\cos^2\theta\rangle_i = \langle\psi_i(\alpha)|\cos^2(\theta_0+\alpha)|\psi_i(\alpha)\rangle$$

The energy value, E_i, and the corresponding wave function, ψ_i, are calculated in the numerical solution of the Mathieu function for the given potential barrier and the moment of inertia.[3]

The above approximation may be considered to be possible, since the spin density on the nitrogen atom, ρ_N, may be regarded as constant independent of the kind of alkyl group, except in the case of *N-tert*-butyl PNO.

For *N*-methyl PNO, it may be considered that the methyl group freely rotates at room temperature. When $\langle\cos^2\theta\rangle$ is one half for free rotation and when $a_{H(CH_3)}$ is replaced by 9.69 G from Table 1, $B\rho_N$ is given as 19.38. When ρ_N is taken as 0.477 from Table 2, B is obtained as 40.8 G, which is close to the value of 41 ± 6 G in Stone and Maki's calculation. This may show that their method is well applicable to *N*-alkyl PNO radicals.

For *N*-ethyl, *N-n*-propyl, and *N-n*-butyl PNO, which have CH_2 protons, it is evident that the rotation may be restricted, since the observed splitting constants become smaller than that for *N*-methyl PNO. In the case of *N*-ethyl PNO, the splitting constant, $a_{H(CH_2)}$, was calculated as 7.82 G when the potential barrier $V_0=0.78$ kcal/mol, in contrast with the observed value of 7.84 G. Similarly, for *N-n*-propyl PNO, 7.40 G was obtained when $V_0=1.40$ kcal/mol.

For *N*-isopropyl PNO, which has a CH proton, 3.31 G was obtained as $a_{H(CH)}$ when $V_0=2.30$ kcal/mol.

Stone and Maki reported in their paper that the potential barriers are 0.34 and 1.11 kcal/mol for CH_2 and CH protons of nitroalkane radicals respectively. The fact that the ratios of the potential barrier with CH to CH_2 are similar between the present data and theirs (3 and 3.3) suggests a resemblance of the hindered rotational models. The larger values in the present case may result from the increase in steric hindrance and the stabilization of π-conjugation due to the aromatic ring.

For a more detailed discussion, it will be necessary to consider the validity of the 2-fold symmetry or to evaluate the non-bonded interaction; those may be difficult problems.

References

1) O. Kikuchi and K. Someno, This Bulletin, **40**, 2549 (1967).

2) E. Stone and A. Maki, *J. Chem. Phys.*, **37**, 1326 (1962).

3) T. Nishikawa, K. Someno, and M. Kaise, Abstract of the 10th ESR Symposium, the Chemical Society of Japan, (1971), p. 6.