The Electron Spin Resonance and Electronic Absorption Spectra of the 3-Nitropyridine Anion Radical

By Michiya ITOH and Saburo NAGAKURA

(Received October 23, 1964)

In a previous paper,[1] the present authors and Okamoto studied the ESR and electronic absorption spectra of the 4-nitropyridine anion radical. In the present paper, a similar study has been made of the 3-nitropyridine anion radical.

Experimental

Material.—3-Nitropyridine was prepared by the oxidation of 3-aminopyridine by Caro's acid, and it was purified by repeated recrystallizations. The melting point (41°C) was in good agreement with that reported in the literature.[2]

The Preparation of the Anion Radical and Measurements.—The 3-nitropyridine anion radical was prepared at room temperature by the reduction of the parent compound with potassium metal in 1, 2-dimethoxy ethane (DME). The details of the preparation of the anion radical and of the measurements of its ESR and electronic absorption spectra are the same as those reported in the previous paper.[1]

Experimental Results

The ESR spectrum observed with the DME solution of the 3-nitropyridine anion radical is shown in Fig. 1. From the spectrum, the hyperfine coupling constants associated with the nitrogen and hydrogen atoms were determined to be as shown in Table I.

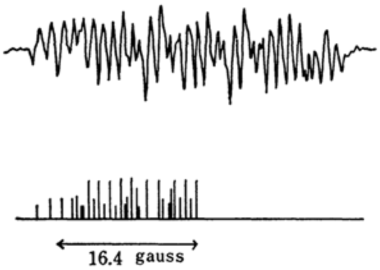


Fig. 1. The ESR spectrum (first derivative) of 3-nitropyridine anion and the reconstruction based on the coupling constants.

The electronic absorption spectrum of the DME solution of the 3-nitropyridine anion has also been measured; the results are shown in Fig. 2. The absorption bands at 304 and 460 mμ can safely be ascribed to the 3-nitropyridine anion, since the intensities of these bands change in parallel with that of the ESR spectrum.

TABLE I. THE COUPLING CONSTANTS AND SPIN DENSITIES OF THE 3-NITROPYRIDINE ANION

	3-Nitropyridine anion			4-Nitropyridine anion	
		Spin density		Spin density	
Position	Coupling const.	Obs.[a]	Calcd.[b]	Obs.[a]	Calcd.[b]
N (NO_2)	10.11 gauss	0.253	0.301	0.218	0.261
N (ring)	2.65	0.098	0.107	0.101	0.124
6-H (C)			0.024	0.133	0.052
5-H (C)	(4.44)*×2 (1.33)*×2	(0.199)*×2 (0.059)*×2	0.040	0.024	0.033
4-H (C)			0.133	—	—
2-H (C)			0.024	0.133	0.052

* No attempt was made to assign the observed proton coupling constants to individual hydrogen atoms.

a) Estimated from the ESR coupling constants.

b) Calculated by the molecular orbital method.

---

[1] M. Itoh, T. Okamoto and S. Nagakura, This Bulletin, 36, 1665 (1963).

[2] F. Friedl, *Ber.*, **45**, 429 (1912).

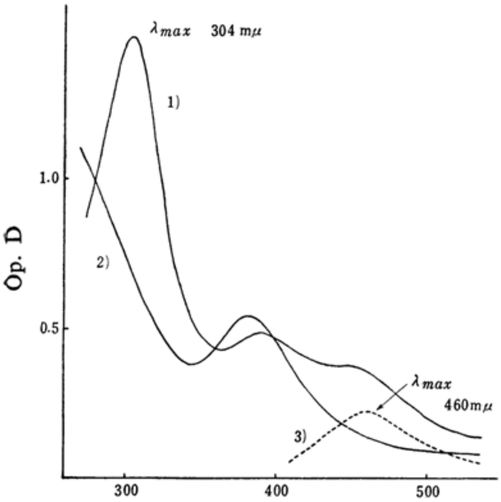


Fig. 2. The electronic absorption spectrum of 3-nitropyridine anion. (The scale factor of vertical axis is arbitrary.)
1) The spectrum of DME solution of the anion.
2) The spectrum of the solution exposed to air.
3) 1)−2).

Theoretical

Molecular orbital calculation has been carried out with the π-electron system of the 3-nitropyridine anion radical in order to ascertain the assignment of the observed electronic spectrum and to obtain some knowledge about the electronic structure of this anion. The present calculation of the 3-nitropyridine anion has been performed by a method similar to that employed in the case of the 4-nitropyridine anion.[1] The anion radical was separated into two components, the pyridine anion as an electron donor and the nitro group as an electron acceptor. The interaction between the components was considered by the aid of the configurational interaction among ground, locally excited and charge-transfer configurations. The electron configurations and energies of these configurations are given in Table II. The procedure for evaluating these energies is not described in the present paper, since the details have been mentioned in the previous paper.[1]

TABLE II. THE π-ELECTRON CONFIGURATIONS OF THE 3-NITROPYRIDINE ANION

Wave function	Energy
Ground configuration[a]:	
$\psi_1=\Phi_1\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	−0.716 eV.
Locally excited configurations within the pyridine ring[a]:	
$\psi_2=\Phi_2\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	−0.231
$\psi_3=\Phi_3\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	2.860[b]
$\psi_5=\Phi_5\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	8.375
$\psi_8=\Phi_8\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	8.877
$\psi_9=\Phi_9\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	9.278
Locally excited configurations within the nitro group[c]:	
$\psi_{4a}=\frac{1}{\sqrt{2}}(\psi_4{}^1-\psi_4{}^2)$	6.303
$\psi_{4b}=\frac{1}{\sqrt{6}}(\psi_4{}^1+\psi_4{}^2-2\psi_4{}^3)$	
$\psi_{6a}=\frac{1}{\sqrt{2}}(\psi_6{}^1-\psi_6{}^2)$	5.877
$\psi_{6b}=\frac{1}{\sqrt{6}}(\psi_6{}^1+\psi_6{}^2-2\psi_6{}^3)$	
Charge-transfer configuration:	
$\psi_7=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\varphi_c\rvert$	$A_P-A_N+\Delta E=$ −0.885

a) The Φ_1, Φ_2, …… are the wave functions of locally excited configurations within the pyridine anion which were shown in the previous paper.[1]

b) The energy of this configuration was estimated by combining the experimental value of locally excited energy within the pyridine ring (3, 5-lutidine: 3.54 eV.) with the electrostatic interaction energy.

c) The φ_a, φ_b and φ_c are the molecular orbitals of the nitro group (J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 1643 (1957)).

d) The $\psi_4{}^1$, $\psi_4{}^2$, …… are as follows:

$$\psi_4{}^1=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_4\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_c\rvert$$
$$\psi_4{}^2=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_4\varphi_a\bar{\varphi}_a\bar{\varphi}_b\varphi_c\rvert$$
$$\psi_4{}^3=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\bar{\varphi}_4\varphi_a\bar{\varphi}_a\varphi_b\varphi_c\rvert$$
$$\psi_6{}^1=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_5\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_c\rvert$$
$$\psi_6{}^2=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_5\varphi_a\bar{\varphi}_a\bar{\varphi}_b\varphi_c\rvert$$
$$\psi_6{}^3=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\bar{\varphi}_5\varphi_a\bar{\varphi}_a\varphi_b\varphi_c\rvert$$

TABLE III. THE OFF-DIAGONAL MATRIX ELEMENTS (IN UNITS OF eV.) USED IN THE CALCULATION OF THE 3-NITROPYRIDINE ANION

$H_{17}=0.573$
$H_{34a}=0.089$
$H_{36a}=-0.412$
$H_{37}=-0.845$
$H_{84a}=0.071$
$H_{86a}=-0.016$
$H_{87}=-0.215$
$H_{24a}=-0.002$
$H_{26a}=0.078$
$H_{27}=1.044$
$H_{54a}=0.234$
$H_{56a}=0.009$
$H_{94a}=0.029$
$H_{96a}=-0.020$

The other off-diagonal elements are zero.

The off-diagonal matrix elements, H_{ij}'s, of the total electronic Hamiltonian were evaluated by the aid of the method presented by Pople[3] and by Murrell and Longuet-Higgins.[4] The results are shown in Table III. The repulsion integrals necessary for the evaluation of the interaction energies between locally

---

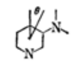
[3] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
[4] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A 68**, 601 (1955).

TABLE IV. THE LOWEST FOUR ENERGY LEVELS AND THEIR WAVE FUNCTIONS OF THE 3-NITROPYRIDINE ANION

Energy	
$W_1=-1.942$ eV.	$\Phi_1=0.367\Psi_1-0.138\Psi_3-0.479\Psi_2+0.785\Psi_7$
$W_2=-0.616$ eV.	$\Phi_2=0.893\Psi_1+0.419\Psi_2-0.155\Psi_7$
$W_3=0.517$ eV.	$\Phi_3=-0.256\Psi_1-0.203\Psi_3+0.767\Psi_2+0.551\Psi_7$
$W_4=3.006$ eV.	$\Phi_4=0.958\Psi_3+0.078\Psi_2+0.135\Psi_{6a}+0.234\Psi_7$

TABLE V. THE CALCULATED AND OBSERVED RESULTS FOR THE LOWEST THREE ELECTRONIC TRANSITIONS OF THE 3-NITROPYRIDINE ANION

Transition	λ_{max}, eV. calcd.	obs.	Calcd. oscillator strength	Direction of transition moment
$W_1 \rightarrow W_2$	1.32	—	3.60×10^{-2}	$\Theta=30°27'$
$W_1 \rightarrow W_3$	2.46	2.69	4.33×10^{-1}	$\Theta=40°39'$
$W_1 \rightarrow W_4$	4.94	4.04	3.29×10^{-1}	$\Theta=40°17'$



excited configurations were obtained in the same way as in the case of the 4-nitropyridine anion studied in the previous paper.[1] The core resonance integral between 2pπ atomic orbitals of the carbon atom on the 3-position and the neighboring nitrogen atom of the nitro group was estimated to be -3.0 eV.[1,6]

The energy levels and wave functions can be evaluated by solving the secular equation constructed by the diagonal and off-diagonal matrix elements given in Tables II and III. The actual calculation was made by the aid of a Facom 202 electronic computer in our Institute. The four lowest energy levels and wave functions of the 3-nitropyridine anion are given in Table IV. Oscillator strengths were calculated for the three longest wavelength absorption bands by the method mentioned in the previous paper.[1] The calculated transition energies and oscillator strengths are shown in Table V.

Discussion

The ESR hyperfine coupling constants associated with the nitrogen atom in the aromatic ring and with that of the nitro group depend not only on the spin densities on the respective atoms, but also on the spin densities on the adjacent atoms via indirect polarization.[7] Fraenkel et al.[8] proposed the following equation for the coupling constant due to the nitrogen nucleus of the nitro group:

$$A_N=Q_N\rho_N+Q_O\rho_O+Q_C\rho_C \qquad (1)$$

where the ρ_N, ρ_O and ρ_C are the spin densities of the nitrogen and oxygen atoms of the nitro group, and that of the carbon atom attached to the nitro group, respectively. Q_N, Q_O and Q_C are constants; they were determined as follows:

$$Q_N=\pm(99.0\pm10.2) \quad Q_O=\mp(35.8\pm5.9) \quad Q_C\doteqdot0$$

from a comparison of the observed nitrogen coupling constants of a the anions of several nitro compounds with the spin densities on the nitro groups calculated by the simple Hückel molecular orbital method.

According to our calculations, the ratio of the ρ_N to ρ_O is always constant, because the molecular orbital wave functions for the nitro group are fixed in the present calculations. Furthermore, we can reasonably assume that the ρ_C term in Eq. 1 may be negligibly small, Thus, Eq. 1 can be reduced to the following equation:

$$A_N=Q_N'\rho_N \qquad (1')$$

where Q_N' is constant. The value of Q_N' was taken to be 40 gauss in the previous paper.[1] The same value has also been adopted in the present paper.

Now let us turn to the coupling constant associated with the nitrogen nucleus of the hetero aromatic ring. Carrington and Santos-Veiga proposed the following equation for the nitrogen-coupling constant, A_N^{ring}, and the spin density, ρ_N^{ring}, on the nitrogen atom, and estimated the value of Q_N^{ring} to be 25.3 gauss:[9]

$$A_N^{ring}=Q_N^{ring}\rho_N^{ring} \qquad (2)$$

By the aid of Eqs. 1′ and 2, the spin densities on the two nitrogen atoms were evaluated from the observed coupling constants; they are shown in Table I. Furthermore, the spin densities on the ring carbon atoms were obtained by the

---

[5] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

[6] A. Ishitani, K. Kuwata, H, Tsubomura and S. Nagakura, This Bulletin, **36**, 1357 (1963).

[7] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

[8] P. H. Rieger and G. K. Fraenkel, ibid., **39**, 609 (1963).

[9] A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

use of the following well-known relation for the proton coupling constant:[10] $A_H=Q_H\rho_C$ ($Q_H=-22.5$ gauss). The theoretical values of the spin densities evaluated by the aid of the ground state wave function are also given in Table I for purposes of comparison. It may be said that the spin densities on the two kinds of nitrogen atoms of the 3-nitropyridine anion as estimated from the ESR coupling constants are in good agreement with the calculated values.

As is shown in Table I, the spin density on the nitrogen atom of the nitro group is larger in the 3-nitropyridine anion than in the 4-nitropyridine anion. This result is consistent with the theoretical conclusion that the contribution of the charge-transfer configuration caused by the electron transfer from the pyridine anion ring toward the nitro group increases in the 3-nitropyridine anion in comparison with that in the 4-nitropyridine anion.

The electronic absorption spectrum of the 3-nitropyridine anion shows two absorption bands at 304 and 460 mμ which can be ascribed to the $W_1 \rightarrow W_4$ and $W_1 \rightarrow W_3$ transitions respectively. Since, in the wave function of the W_4 state, the contribution of the locally excited configuration within the pyridine ring amounts to 92%, the 304 mμ band corresponding to the $W_1 \rightarrow W_4$ transition can be interpreted as the shifted band of the 355 mμ band of the 3, 5-lutidine (pyridine) anion.(1) This blue shift is caused by the fact that the ground configuration is largely stabilized by resonance interaction with the charge-transfer configuration. Furthermore, from the wave functions, Φ_1 and Φ_3, it can easily be seen that the 460 mμ band corresponding to the $W_1 \rightarrow W_3$ transition may be regarded as the intramolecular charge-transfer band. The absorption band corresponding to the $W_1 \rightarrow W_2$ transition could not be observed despite careful experimentation. This may be because the $W_1 \rightarrow W_2$ transition band is weak, as is revealed by the calculated oscillator strength value, and is, therefore, covered by other absorption bands due to reaction products.

The authors wish to express their deep thanks to Mr. Koichi Itoh of this Institute for his kind help in measuring the ESR spectra. One of the authors (M. I.) also gratefully acknowledges the encouragement of Professor Toshihiko Okamoto, Faculty of Pharmaceutical Sciences, the University of Tokyo.

The Institute for Solid State Physics
The University of Tokyo
Azabu, Tokyo

---

[10] S. I. Weissman, T. R. Tuttle and E. J. de Boer, *J. Phys. Chem.*, **61**, 28 (1957).