The Electron Spin Resonance and Electronic Spectra of the Anion Radicals of 4-Nitropyridine and 4-Nitropyridine 1-Oxide

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Recently, both experimental and theoretical studies of aromatic anion radicals have made remarkable progress. Ward and others[1-3] have made electron spin resonance (ESR) studies of various hetero aromatic anion radicals and have determined the coupling constants from proton and nitrogen hyperfine splittings. Furthermore, theoretical studies of odd electron distribution have been carried out with some anion radicals by the aid of a simple molecular orbital method;[4] the results are considerably consistent with the spin densities estimated from the ESR coupling constants.

Hoijtink et al. observed the electronic spectra of the anion radicals of some aromatic hydrocarbons such as benzene and naphthalene, and discussed their electronic structures by comparing the observed results with the theoretical results.[5]

In these circumstances, the present authors have attempted to study the electronic structures of the anion radicals of 4-nitropyridine and its 1-oxide by combining the experimental results of the electronic spectra and electron spin resonance spectra with the theoretical studies based on the semi-empirical molecular orbital method, including "configuration interaction."

Nitrogen hetero aromatic *N*-oxide compounds such as pyridine 1-oxide are known to have some interesting properties.[6,7] The non-bonding electrons of the oxygen atom are strongly conjugated with the π-electron system of the nitrogen hetero aromatic ring. This conjugation usually exerts a predominant effects upon various substitution reactions in the nitrogen hetero aromatic ring, and also upon various physical properties, such as the ultraviolet[8,9] and infrared spectra[10,11] and the nuclear magnetic resonance absorption.[12,13] One of the principal purposes of the present study is to get some knowledge about the conjugation effect in the anion radical of 4-nitropyridine 1-oxide.

In order to analyze exactly the ESR spectra of 4-nitropyridine and its 1-oxide, the measurements were also carried out with the respective compounds containing ^{15}N instead of ^{14}N in the nitro group. Furthermore, for the purpose of getting experimental data necessary for the present semi-empirical calculations, the electronic spectrum of the 3, 5-lutidine[2] anion radical was measured.

1) R. L. Ward, *J. Am. Chem. Soc.*, **84**, 3623 (1962); ibid., **84**, 332 (1962).
2) N. M. Atherton, F. Gerson and J. N. Murrell, *Mol. Phys.*, **5**, 500 (1962).
3) A. Carrington, and J. dos Santos-Veiga, ibid., **5**, 21 (1962).
4) A. Carrington, *Quart. Revs.*, **17**, 67 (1963); P. H. Rieger and C. K. Fraenkel, *J. Chem. Phys.*, **37**, 2735 (1962); ibid., **37**, 2811 (1962).
5) G. J. Hoijtink, *Mol. Phys.*, **2**, 85 (1959).
6) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).
7) D. V. Ioffe and I. S. Efrons, *Uspekhi. Khimii.*, **30**, 1325 (1961).
8) T. Kubota and H. Hirayama, *J. Pharm. Soc. Japan (Yakugaku Zasshi)*, **72**, 1025 (1952); T. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **79**, 930 (1958); ibid., **80**, 578 (1959).
9) M. Ito and S. Mizushima, *J. Chem. Phys.*, **23**, 485 (1956); N. Hatta, This Bulletin, **29**, 82 (1956); M. Ito and N. Hatta, ibid., **28**, 260 (1955).
10) H. Shindo, *Chem. Pharm. Bull. (Japan)*, **4**, 460 (1956); ibid., **6**, 117 (1958).
11) G. Costa and P. Blasina, *Z. physik. Chem. N. F.*, **4**, 24 (1955); R. H. Wiley and S. C. Slaymaker, *J. Am. Chem. Soc.*, **97**, 2233 (1957).
12) L. M. Jackman and J. A. Elvidge, *J. Chem. Soc.*, **1961**, 859.
13) A. R. Katritzky and J. M. Lagowski, ibid., **1961**, 43.
14) E. Ochiai, M. Ishikawa and K. Arima, *J. Pharm. Soc. Japan (Yakugaku Zasshi)*, **63**, 79 (1943).

Experimental

Materials. — 4-Nitropyridine and 4-nitropyridine 1-oxide were prepared by the methods given in literatures[14,15] and were purified by repeating recrystallization before use. The melting points of these nitro compounds were in good agreement with those reported in the literatures.[14,15] 4-Nitropyridine 1-oxide with a heavy nitrogen atom (^{15}N) in the nitro group was prepared by the nitration of pyridine 1-oxide with potassium nitrate ($K^{15}NO_3$) containing the heavy nitrogen atom in sulfuric acid.[14] 4-Nitropyridine with the heavy nitrogen atom in the nitro group was obtained by the deoxygenation of 4-nitropyridine 1-oxide (containing $^{15}NO_2$) with phosphorus tribromide.[15] Commercial 3,5-lutidine was purified by repeating distillation:

The Preparation of Anion Radicals and Measurements.—The 4-nitropyridine, 4-nitropyridine 1-oxide and 3,5-lutidine anion radicals were prepared at room temperature by the reduction of the respective parent compounds with potassium metal in 1,2-dimethoxy ethane (abbreviated hereafter to DME). In order to remove reactive impurities, the solvent was kept in contact with sodium metal and the parent compound in vacuo before use. The potassium metal was purified by repeating sublimation in vacuo.

The preparation of the anion radicals and the measurements of electronic absorption spectra and ESR spectra were performed in vacuo by using a vacuum line system similar to that shown in a previous paper.[16] The ESR and electronic spectra were measured by a Hitachi x-band ESR spectrometer Model MPU-2B and a Cary recording spectrophotometer Model-14 M, respectively.

Experimental Results

The 4-Nitropyridine Anion Radical. — The DME solution of the 4-nitropyridine anion radical was colored yellow. The ESR spectrum observed with this solution is shown in Fig. 1a. The ESR spectrum of the 4-nitropyridine anion radical with the heavy nitrogen atom in the nitro group was also measured with the result shown in Fig. 1b. The heavy nitrogen atom leads to a splitting into doublets since ^{15}N has the nuclear spin of 1/2 (the nuclear magnetic moment, $\mu_N=0.404$), while ^{14}N causes a splitting into triplets.

From these spectra, the coupling constants associated with the nitrogen (^{14}N and ^{15}N) and hydrogen atoms were determined to be as shown in Table I. Reconstructions based on these coupling constants are also shown in Figs. 1a and 1b. The reconstructions match well with the observed spectra. Furthermore, the ratio of the nitrogen coupling constants associated with ^{14}N and ^{15}N of the nitro group is in good agreement with that of the nuclear moments of these two nitrogen isotopes. These facts show the high reliability of the coupling constants determined in the presents study.

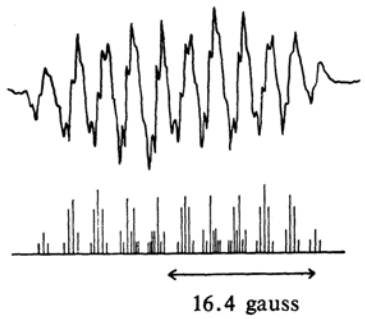


Fig. 1a. The ESR spectrum (first derivative) of 4-nitropyridine anion and the reconstruction based on the coupling constants.

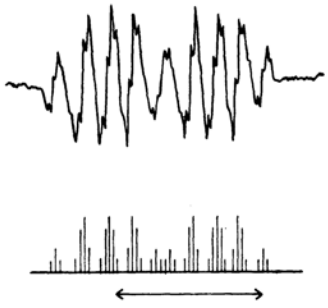


Fig. 1b. The ESR spectrum of the same compound containing ^{15}N in the nitro group and the reconstruction based on the coupling constants.

TABLE I. THE COUPLING CONSTANTS OF THE OBSERVED NITROGEN AND HYDROGEN HYPERFINE SPLITTINGS

Position	4-Nitropyridine anion gauss	4-Nitropyridine 1-oxide anion gauss
$^{14}NO_2$	8.72	7.49
$^{15}NO_2$	12.3	10.32
3-H	0.53*	1.58*
2-H	3.00*	3.58*
Ring N	2.55	4.58

* These assignments were made taking into account spin densities obtained by the molecular orbital calculation.

The electronic absorption spectrum of the DME solution of the 4-nitropyridine anion was measured parallel with the ESR spectrum. The result is shown in Fig. 2. The spectrum consists of three bands at 313, 440 and 640 mμ. It was found that these absorption bands disappeared or decreased remarkably their intensities when the solution was exposed to

15) M. Hamana, ibid., 75, 135 (1955).
16) A. Ishitani, K. Kuwata, H. Tsubomura and S. Nagakura, This Bulletin, 36, 1357 (1963).

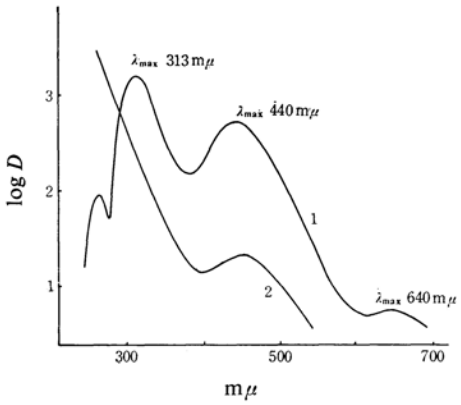


Fig. 2. The electronic absorption spectrum of 4-nitropyridine anion. (The scale factor of vertical axis is arbitrary.)
1) The spectrum of the DME solution of the anion.
2) The spectrum of the solution exposed to air.

air. From this fact, it is inferred that all three bands can be ascribed to the 4-nitropyridine anion. This opinion was also supported by the theoretical consideration based upon molecular orbital calculations which will be described later.

The 4-Nitropyridine 1-Oxide Anion Radical.— When the DME solution of 4-nitropyridine 1-oxide was kept in contact with pure potassium metal in vacuo, the DME solution became yellow after about 2 or 3 days. The ESR spectrum of this colored solution was measured, with the result given in Fig. 3a. The ESR spectrum of the 4-nitropyridine 1-oxide anion containing the heavy nitrogen atom in the nitro group was also measured in order to obtain useful information for the analysis of the hyperfine structure of the ESR spectrum. The result is shown in Fig. 3b. The ESR coupling constants of the 4-nitropyridine 1-oxide anion radical were finally determined to be as shown in Table I. Reconstructions from

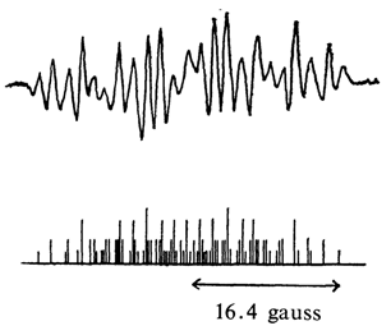


Fig. 3a. The ESR spectrum of 4-nitropyridine 1-oxide anion and the reconstruction based on the coupling constants.

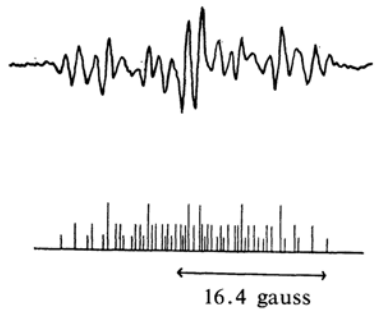


Fig. 3b. The ESR spectrum of the same compound containing ^{15}N in the nitro group and the reconstruction based on the coupling constants.

the coupling constants are also shown in Figs. 3a and 3b for the 4-nitropyridine 1-oxide anion radicals containing ^{14}N and ^{15}N respectively. The reconstructions are well coincident with the observed spectra.

We could not succeed in measuring the electronic absorption spectrum of the DME solution of the 4-nitropyridine 1-oxide anion. This may be because the concentration of the radical is not high enough for the electronic spectrum to be observed.

The Electronic Spectrum of the 3, 5-Lutidine Anion Radical. — The ESR spectrum of the 3, 5-lutidine anion radical was measured by Atherton et al.,[2] but the electronic spectrum has never been observed. Therefore, we measured the electronic spectrum of this anion radical. The DME solution of the 3, 5-lutidine anion shows the electronic absorption band at 355 mμ. This band disappeared parallel with the ESR spectrum by introducing air into the reaction tube.

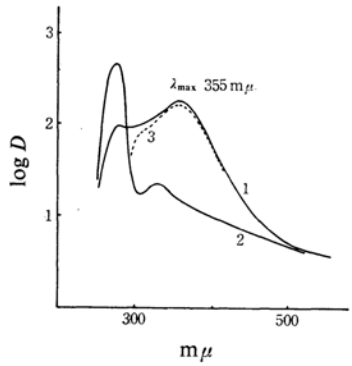


Fig. 4. The electronic absorption spectrum of 3,5-lutidine anion. (The scale factor of vertical axis is arbitrary.)
1) The spectrum of DME solution of the anion.
2) The spectrum of the solution exposed to air.
3) 1)−2).

Theoretical

Molecular orbital calculations were carried out with the π-electron system of the 4-nitropyridine anion in order to ascertain the assignment of the observed electronic spectrum and to obtain some knowledge about the electronic structure of this anion.

In the present calculations, the 4-nitropyridine anion was separated into the two components; the pyridine anion and the nitro group. The interaction between the components was taken into consideration by the aid of the configurational interaction among several π-electron configurations. For accomplishing this theoretical treatment, we need empirical knowledge about the π-electron structure of the pyridine anion radical. Therefore, calculations were first made with the π-electron structure of this anion.

The calculation of the pyridine anion was carried out by taking into account the configurational interaction among the ground and ten excited π-electron configurations which are obtained by putting seven π-electrons into the SCF-molecular orbitals of neutral pyridine.[17] The wave functions and energy values of the electron configurations taken up in the present calculations are shown in Table II. The off-diagonal matrix elements of the total electronic Hamiltonian, H_{ij}'s, are given in Table III. A detailed explanation of the calculation procedure may be omitted since similar calculations have been made for the benzene anion by Hoijtink[5] and by Ishitani et al.[16] In the actual calculation, the approximation of zero-differential overlap was adopted and the one-center Coulomb repulsion integrals of the type of (ii/ii) were calculated from the ionization potentials and electron affinities of the appropriate valence states.[18] The two-center Coulomb repulsion integrals of the type of (ii/jj) were calculated by the aid of quadratic equations* obtained by Pariser and Parr's method.[18]

The finally obtained energy levels and wave functions of the pyridine anion are summarized in Table IV. The transition energy for the transition between the ground and lowest excited states was evaluated to be 3.75 eV. Unfortunately, the electronic absorption of the pyridine anion has never been observed, since it easily converts into the 4, 4'-dipyridyl anion.[1] However, we succeeded in measuring the absorption spectrum of the 3, 5-lutidine anion. Therefore, we compared the calculated transition energy of the pyridine anion with that observed with the 3, 5-lutidine anion.** The calculated transition energy of the former (3.75 eV.) is in good agreement with that of the latter (3.54 eV.).

Table II. The π-electron configurations of the pyridine anion

Wave function	Energy, eV.
$\psi_1=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_4\rvert$	0
$\psi_2=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_5\rvert$	0.416
$\psi_3=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_5\varphi_5\rvert$	10.222
$\psi_4=\lvert\varphi_1\bar{\varphi}_1\varphi_2\varphi_3\bar{\varphi}_3\varphi_5\bar{\varphi}_5\rvert$	10.938
$\psi_5=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\varphi_4\bar{\varphi}_4\rvert$	9.790
$\psi_6=\lvert\varphi_1\bar{\varphi}_1\varphi_2\varphi_3\bar{\varphi}_3\varphi_4\bar{\varphi}_4\rvert$	10.812
$\psi_{7a}=\frac{1}{\sqrt{2}}(\psi_7^1-\psi_7^2)$	10.936
$\psi_{7b}=\frac{1}{\sqrt{6}}(\psi_7^1+\psi_7^2-2\psi_7^3)$	9.895
$\psi_{8a}=\frac{1}{\sqrt{2}}(\psi_8^1-\psi_8^2)$	11.026
$\psi_{8b}=\frac{1}{\sqrt{6}}(\psi_8^1+\psi_8^2-2\psi_8^3)$	9.717
$\psi_9=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_6\rvert$	4.292

In this table, φ_i is the i-th molecular orbital of pyridine obtained by Mataga and Nishimoto,[17] and ψ_7^1, ψ_7^2,..... are as follows:

$$\psi_7^1=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\varphi_4\bar{\varphi}_5\rvert$$
$$\psi_7^2=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\bar{\varphi}_3\varphi_4\varphi_5\rvert$$
$$\psi_7^3=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_4\varphi_5\rvert$$
$$\psi_8^1=\lvert\varphi_1\bar{\varphi}_1\varphi_2\varphi_3\bar{\varphi}_3\bar{\varphi}_4\varphi_5\rvert$$
$$\psi_8^2=\lvert\varphi_1\bar{\varphi}_1\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_4\varphi_5\rvert$$
$$\psi_8^3=\lvert\varphi_1\bar{\varphi}_1\varphi_2\varphi_3\bar{\varphi}_3\varphi_4\bar{\varphi}_5\rvert$$

Table III. The off-diagonal matrix elements (in the units of eV.) used in the calculation of the pyridine anion

$H_{14}=0$	$H_{7a9}=0.629$
$H_{16}=0$	$H_{7b9}=1.245$
$H_{17a}=0$	$H_{23}=0$
$H_{17b}=0.138$	$H_{25}=0$
$H_{19}=0$	$H_{28a}=0$
$H_{46}=0.292$	$H_{28b}=0.247$
$H_{47a}=0.545$	$H_{35}=0.292$
$H_{47b}=-0.651$	$H_{38a}=-0.545$
$H_{49}=-0.900$	$H_{38b}=0.651$
$H_{67a}=0.505$	$H_{58a}=0.228$
$H_{67b}=0.147$	$H_{58b}=-0.276$
$H_{69}=0.957$	$H_{8a8b}=-0.276$
$H_{7a7b}=-0.394$	

17) N. Mataga and K. Nishimoto, *Z. physik. Chem., N. F.*, **13**, 140 (1957).

18) R. Pariser and R. G. Rarr, *J. Chem. Phys.*, **21**, 466, 767 (1953); R. G. Parr, ibid., **20**, 1499 (1952).

* The Actual forms of the quadratic equations are as follows: $(11/22)_{CC}=11.08-2.978r+0.270r^2$ $(11/22)_{CN}=10.72-2.710r+0.228r^2$ $(11/22)_{NN}=12.27-3.634r+0.34r^2$ where r is an appropriate interatomic distance.

** Since the effect of the methyl group on the peak wavelength may conceivably be small, it is not unreasonable to compare the transition energy observed with the 3, 5-lutidine anion with that calculated with the pyridine anion.

TABLE IV. ENERGY LEVELS AND WAVE FUNCTIONS OF PYRIDINE ANION

Wave function	Energy, eV.
$\Phi_1 = 0.9998\phi_1 - 0.0005\phi_4 - 0.0001\phi_6 - 0.0007\phi_{7a} - 0.0145\phi_{7b} - 0.0042\phi_9$	−0.002
$\Phi_2 = 0.9996\phi_2 + 0.0017\phi_3 - 0.0008\phi_5 - 0.0006\phi_{8a} - 0.0267\phi_{8b}$	0.406
$\Phi_3 = -0.0068\phi_1 + 0.1161\phi_4 - 0.1248\phi_6 - 0.0946\phi_{7a} - 0.1860\phi_{7b} + 0.9629\phi_9$	3.757
$\Phi_4 = 0.0052\phi_1 - 0.4419\phi_4 + 0.6891\phi_6 + 0.2859\phi_{7a} + 0.4286\phi_{7b} + 0.2535\phi_9$	11.278
$\Phi_5 = 0.0198\phi_2 - 0.5429\phi_3 + 0.4927\phi_5 - 0.1132\phi_{8a} + 0.6703\phi_{8b}$	9.040
$\Phi_6 = -0.0035\phi_1 + 0.6381\phi_4 + 0.3595\phi_6 + 0.6069\phi_{7a} - 0.3071\phi_{7b} - 0.0300\phi_9$	11.977
$\Phi_7 = 0.0079\phi_2 + 0.6796\phi_3 + 0.4332\phi_5 + 0.5003\phi_{3a} + 0.3163\phi_{8b}$	10.309
$\Phi_8 = 0.0119\phi_1 + 0.4469\phi_4 - 0.3109\phi_6 + 0.1353\phi_{7a} + 0.8240\phi_{7b} + 0.0784\phi_9$	9.542
$\Phi_9 = 0.0153\phi_2 - 0.0136\phi_3 - 0.7509\phi_5 + 0.2953\phi_{8a} + 0.5903\phi_{8b}$	9.923
$\Phi_{10} = -0.0012\phi_1 - 0.4293\phi_4 - 0.5325\phi_6 + 0.7229\phi_{7a} - 0.0902\phi_{7b} + 0.0364\phi_9$	10.321
$\Phi_{11} = -0.0071\phi_2 - 0.4931\phi_3 + 0.0754\phi_5 + 0.8060\phi_{8a} - 0.3185\phi_{8b}$	11.489

Using the above-mentioned results obtained with the pyridine and 3, 5-lutidine anions, the energy levels and wave functions of the 4-nitropyridine anion were calculated by a method similar to that used for the theoretical consideration of the π-electron structures of the nitromethyl anion,[19] the nitrobenzene anion[16] and other neutral nitro compounds.[20] That is to say, the effect of the nitro group on the energy levels of the pyridine anion was considered by means of the configuration interaction between the ground, locally-excited and charge-transfer configurations. In the actual calculations, the geometrical arrangements of the pyridine ring and the nitro group were assumed to be equal to those of neutral pyridine[21] and the nitro group in nitrobenzene[22] respectively.

The energy of the ground configuration was evaluated by taking electrostatic interaction between the benzene anion and the nitro group into account, since there is a large heterogenity in the π-electron distribution of the nitro group with a large positive charge on the nitrogen atom and a negative charge on the oxygen atoms.

We considered the fourteen locally excited configurations whose wave functions and energy values are shown in Table V, together with those of the other electron configurations. Ten of them are brought about by one-electron excitation within the pyridine ring. Except for the lowest locally excited configuration, the energies of the other nine configurations were calculated by adding the electrostatic interaction energies to the calculated excitation energies of the pyridine anion. The energy of the lowest locally excited configuration was estimated by combining the experimental value which had been determined from the peak wavelength of the 3, 5-lutidine anion with the electrostatic interaction energy. The energy of the locally excited configuration within the nitro group was determined from the experimental value of the $\pi \rightarrow \pi^*$ transition energy of the nitromethane[19] and the electrostatic energy.

In addition to these configurations, a charge-transfer configuration which is caused by one electron transfer from the highest-occupied orbital of the pyridine anion toward the lowest vacant orbital of the nitro group was taken into account. The energy of this configuration, E_{CT}, was evaluated by the following equation:

$$\begin{aligned} E_{CT} &= A_P A_N + \Delta E \\ &= -0.4 - 0.4 + \Delta E \\ &= -0.8 + \Delta E \end{aligned}$$

where A_P and A_N are the electron affinities of pyridine and the nitro group respectively, and ΔE is the electrostatic interaction energy between the neutral pyridine ring and the negatively charged nitro group. ΔE was calculated to be −0.1 eV. A_N was determined to be 0.4 eV. for a series of nitro compounds.[16,20] The electron affinity of pyridine has not been determined. Therefore, assuming that it may be almost equal to or a little larger than the value of benzene (−0.54∼−1.62 eV.[23,24]), the authors adopted the two values, −0.4 and 0.1 eV., as the electron affinity of pyridine. The two calculations gave similar results for the transition energies (see Table VIII).

The off-diagonal matrix elements H_{ij}'s of the total electronic Hamiltonian were evaluated by the aid of the method presented by Pople[25] and by Murrell and Longuet-Higgins.[26] The Coulomb repulsion integrals necessary for the evaluation of the interaction energies between

19) S. Nagakura, *Mol. Phys.*, 3, 152 (1960).
20) S. Nagakura, M. Kojima and Y. Maruyama, to be published in *J. Mol. Spectroscopy*.
21) B. Bak, L. Hannsen and J. Rastrup-Andersen, *J. Chem. Phys.*, 22, 2013 (1954).
22) J. Trotter, *Acta. Cryst.*, 12, 884 (1959).
23) N. S. Hush, and J. A. Pople, *Trans. Faraday Soc.*, 51, 600 (1955).
24) R. M. Hedges and F. A. Matsen, *J. Chem. Phys.*, 28, 950 (1958).
25) J. A. Pople, *Trans. Faraday Soc.*, 49, 1375 (1953).
26) H. C. Longuet-Higgins and J. M. Murrell, *Proc. Phys. Soc.*, A68, 601 (1955).

Table V. The π-electron configurations of the 4-nitropyridine anion

Wave function	Energy, eV.
Ground configration :	
$\Psi_1=\Phi_1\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$ [a]	−0.888
Locally-excited configurations within the pyridin ring :	
$\Psi_2=\Phi_2\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	−0.216
$\Psi_3=\Phi_3\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	2.815 [c]
$\Psi_4=\Phi_4\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	10.594
$\Psi_5=\Phi_5\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	8.335
$\Psi_6=\Phi_6\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	11.363
$\Psi_7=\Phi_7\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	9.519
$\Psi_8=\Phi_8\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	8.819
$\Psi_9=\Phi_9\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	9.346
$\Psi_{10}=\Phi_{10}\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	9.607
$\Psi_{11}=\Phi_{11}\lvert\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\rvert$	10.835
Locally-excited configurations within the nitro group : [b]	
$\Psi_{12a}=\frac{1}{\sqrt{2}}(\Psi^1_{12}-\Psi^2_{12})$	9.331
$\Psi_{12b}=\frac{1}{\sqrt{6}}(\Psi^1_{12}+\Psi^2_{12}-2\Psi^3_{12})$	6.331
$\Psi_{13a}=\frac{1}{\sqrt{2}}(\Psi^1_{13}-\Psi^2_{13})$	5.811
$\Psi_{13b}=\frac{1}{\sqrt{6}}(\Psi^1_{13}+\Psi^2_{13}-2\Psi^3_{13})$	5.811
Charge-transfer configuration :	
$\Psi_{14}=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_b\varphi_c\rvert$	$A_P-A_N+\Delta E$

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

b) The Ψ^1_{12}, Ψ^2_{12},..... are as follows :

$$\Psi^1_{12}=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_5\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_c\rvert$$
$$\Psi^2_{12}=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_5\varphi_a\bar{\varphi}_a\bar{\varphi}_b\varphi_c\rvert$$
$$\Psi^3_{12}=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\bar{\varphi}_5\varphi_a\bar{\varphi}_a\varphi_b\varphi_c\rvert$$
$$\Psi^1_{13}=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_4\varphi_a\bar{\varphi}_a\varphi_b\bar{\varphi}_c\rvert$$
$$\Psi^2_{13}=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\varphi_4\varphi_a\bar{\varphi}_a\bar{\varphi}_b\varphi_c\rvert$$
$$\Psi^3_{13}=\lvert\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3\bar{\varphi}_4\varphi_a\bar{\varphi}_a\varphi_b\varphi_c\rvert$$

c) The energy of this configuration was estimated by combining the experimental value which was determined from the peak wavelength of the 3,5-lutidine anion with the electrostatic interaction energy.

locally excited configurations were obtained by the same method as described for the calculation of the pyridine anion. The interaction energies between the charge transfer configuration and the others are calculated through the core resonance integral (β_{CN}) between the carbon atom at the 4-position and the neighboring nitrogen atom of the nitro group. The β_{CN} value was estimated to be −3.0 eV., the same value as that used for the calculation of the nitrobenzene anion.[16] The matrix elements thus evaluated are given in Table VI.

Table VI. The off-diagonal matrix elements (in units of eV.) used in the calculation of the 4-nitropyridine anion

$H_{1.3}=0$	$H_{8.14}=0.018\beta_{CN}$
$H_{1.4}=0$	$H_{10.12a}=-0.007$
$H_{1.6}=0$	$H_{10.12b}=0$
$H_{1.8}=0$	$H_{10.14}=0.011\beta_{CN}$
$H_{1.10}=0$	$H_{12a.12b}=0$
$H_{1.12a}=0$	$H_{12a.14}=0$
$H_{1.12b}=0$	$H_{12b.14}=0$
$H_{1.14}=-0.413\beta_{CN}$	$H_{2.5}=0$
$H_{3.4}=0$	$H_{2.7}=0$
$H_{3.6}=0$	$H_{2.9}=0$
$H_{3.8}=0$	$H_{2.11}=0$
$H_{3.10}=0$	$H_{2.13a}=-0.109$
$H_{3.12a}=0.177$	$H_{2.13b}=0$
$H_{3.12b}=0$	$H_{5.7}=0$
$H_{3.14}=0.281\beta_{CN}$	$H_{5.9}=0$
$H_{4.6}=0$	$H_{5.11}=0$
$H_{4.8}=0$	$H_{5.13a}=0.226$
$H_{4.10}=0$	$H_{5.13b}=0$
$H_{4.12a}=0.194$	$H_{7.9}=0$
$H_{4.12b}=0$	$H_{7.11}=0$
$H_{4.14}=0.071\beta_{CN}$	$H_{7.13a}=-0.115$
$H_{6.8}=0$	$H_{7.13b}=0$
$H_{6.10}=0$	$H_{9.11}=0$
$H_{6.12a}=-0.266$	$H_{9.13a}=-0.098$
$H_{6.12b}=0$	$H_{9.13b}=0$
$H_{6.14}=-0.007\beta_{CN}$	$H_{11.13a}=0.263$
$H_{8.10}=0$	$H_{11.13b}=0$
$H_{8.12a}=0.076$	$H_{13a.13b}=0$
$H_{8.12b}=0$	

The secular equation composed of the matrix elements given in Table VI was solved by the aid of an electronic computer IBM 7090. The evaluated energy levels and wave functions of the 4-nitropyridine anion are given in Table VII. Oscillator strengths were calculated for the three longer wavelength transitions by the following usual equation : $f=1.085\times10^{-5}Q^2\nu$, where Q and ν are the transition moment (in units of Å) and the peak wave number (in units of cm^{-1}) respectively. The calculated transition energies and oscillator strengths for the transitions between the ground level and the lowest three excited levels are shown in Table VIII, together with the observed transition energies.

Discussion

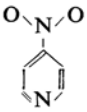
Karplus and Fraenkel proposed that the hyperfine coupling constants for nuclei such as ^{14}N and ^{13}C in aromatic ring depend not only on the spin densities of the respective atoms, but also on the spin densities of the

TABLE VII. THE ENERGY LEVELS AND WAVE FUNCTIONS OF THE 4-NITROPYRIDINE ANION

Energy	Wave function
$W_1 = -2.185$	$\Psi_{W_1} = -0.6716\Psi_1+0.1232\Psi_3+0.0122\Psi_4-0.0012\Psi_6+0.0036\Psi_8+0.0020\Psi_{10}-0.0029\Psi_{12a}+0.7304\Psi_{14}$
$W_2 = -0.218$	$\Psi_{W_2} = 0.9998\Psi_2-0.0005\Psi_5+0.0002\Psi_7+0.0002\Psi_9-0.0004\Psi_{11}+0.0181\Psi_{13a}$
$W_3 = 0.241$	$\Psi_{W_3} = 0.7370\Psi_1+0.2107\Psi_3+0.0133\Psi_4-0.0014\Psi_6+0.0041\Psi_8+0.0023\Psi_{10}-0.0066\Psi_{12a}+0.6419\Psi_{14}$
$W_4 = 3.008$	$\Psi_{W_4} = -0.0748\Psi_1+0.9684\Psi_3-0.0052\Psi_4-0.0011\Psi_6-0.0015\Psi_8-0.0012\Psi_{10}-0.0513\Psi_{12a}-0.2323\Psi_{14}$
$W_5 = 5.773$	$\Psi_{W_5} = -0.0181\Psi_2-0.0877\Psi_5+0.0305\Psi_7+0.0273\Psi_9-0.0516\Psi_{11}+0.9940\Psi_{13a}$
$W_6 = 6.314$	$\Psi_{W_6} = -0.0007\Psi_1+0.0514\Psi_3-0.0454\Psi_4+0.0525\Psi_6-0.0303\Psi_8+0.0021\Psi_{10}+0.9958\Psi_{12a}-0.0044\Psi_{14}$
$W_7 = 8.355$	$\Psi_{W_7} = -0.0011\Psi_2+0.9961\Psi_5+0.0086\Psi_7+0.0086\Psi_9-0.0092\Psi_{11}+0.0869\Psi_{13a}$
$W_8 = 8.822$	$\Psi_{W_8} = 0.0007\Psi_1+0.0017\Psi_3-0.0039\Psi_4+0.0032\Psi_6+0.9995\Psi_8+0.0000\Psi_{10}+0.0300\Psi_{12a}-0.0057\Psi_{14}$
$W_9 = 9.348$	$\Psi_{W_9} = 0.0003\Psi_2-0.0060\Psi_5-0.0183\Psi_7+0.9994\Psi_9+0.0048\Psi_{11}-0.0271\Psi_{13a}$
$W_{10} = 9.522$	$\Psi_{W_{10}} = 0.0004\Psi_2-0.0060\Psi_5+0.9993\Psi_7+0.0174\Psi_9+0.0063\Psi_{11}-0.0313\Psi_{13a}$
$W_{11} = 9.607$	$\Psi_{W_{11}} = -0.0004\Psi_1+0.0003\Psi_3-0.0003\Psi_4-0.0003\Psi_6+0.0000\Psi_8+0.9999\Psi_{10}-0.0021\Psi_{12a}-0.0032\Psi_{14}$
$W_{12} = 10.606$	$\Psi_{W_{12}} = -0.0020\Psi_1+0.0030\Psi_3+0.9987\Psi_4+0.0162\Psi_6+0.0025\Psi_8+0.0003\Psi_{10}+0.0445\Psi_{12a}-0.0189\Psi_{14}$
$W_{13} = 10.849$	$\Psi_{W_{13}} = -0.0005\Psi_2+0.0047\Psi_5-0.0045\Psi_7-0.0034\Psi_9+0.9986\Psi_{11}+0.0523\Psi_{13a}$
$W_{14} = 11.377$	$\Psi_{W_{14}} = 0.0002\Psi_1-0.0013\Psi_3-0.0137\Psi_4+0.9984\Psi_6-0.0016\Psi_8+0.0002\Psi_{10}-0.0532\Psi_{12a}+0.0020\Psi_{14}$

TABLE VIII. THE CALCULATED AND OBSERVED RESULTS FOR THE LOWEST THREE ELECTRONIC TRANSITIONS OF THE 4-NITROPYRIDINE ANION

Transition	λ_{max}, eV. calcd.	λ_{max}, eV. obs.	Calcd. oscillator strength	Direction of transition moment
$W_1 \rightarrow W_2$	1.96 (1.73)*	1.90	1.44×10^{-3}	↔
$W_1 \rightarrow W_3$	2.42 (2.40)*	2.81	6.07×10^{-1}	↕
$W_1 \rightarrow W_4$	5.18 (4.97)*	4.00	8.63×10^{-1}	↕



* The results calculated by assuming the electron affinity of pyridine to be 0.1 eV.

adjacent aromatic ring atoms via indirect polarization and that the coupling constant for the ring nitrogen atom, A_N, can be represented by the following equation:[27]

$$A_N = Q_N\rho_N + \sum_i Q_{C_i}\rho_{C_i} \quad (1)$$

where ρ_N and ρ_{C_i} are the spin densities of the concerned nitrogen and adjacent carbon atoms, respectively, and Q_N and Q_{C_i} are constants. Carrington and Santos-Veiga, however, suggested that the indirect coupling is apparently less important for ^{14}N in hetero aromatic anion radicals.[3] They proposed the following equation for the relationship between A_N and ρ_N:

$$A_N = Q_N\rho_N \quad (2)$$

and estimated the value of Q_N to be 25.3 gauss.

A similar relation is found also for the coupling constant due to the nitrogen nucleus of the nitro group, but the Q_N value is larger for this case than for the above case.[16] In the present study, the Q_N value was tentatively assumed to be 40 gauss for the nitrogen atom of the nitro group. Furthermore, it is well known that the proton coupling constants, A_H's, are related to the spin densities on carbon atoms, ρ_C's, by the following equation:[28]

$$A_H = Q_H\rho_C \quad (3)$$

where Q_H is a constant and is estimated to be 22.5 gauss.

By combining the observed coupling constants with the relations mentioned above, we have evaluated the spin densities on the nitrogen and carbon atoms of the 4-nitropyridine and 4-nitropyridine 1-oxide anions. The results are shown in Table IX, together with the theoretical values evaluated for the 4-nitropyridine anion by the aid of the wave function, Ψ_{W1}, in Table VII. The spin densities on the nitrogen and carbon atoms of the 4-nitropyridine anion estimated from the observed coupling constants are in good agreement with the calculated values except for the 2-carbon atom.

As is shown in Table IX, the spin densities on the ring nitrogen and carbon atoms are undoubtedly larger in the 4-nitropyridine 1-oxide anion than in the 4-nitropyridine anion, while the spin density on the nitrogen atom of the nitro group of the former decreases compared with that of the latter. This seems to be attributed to the resonance and inductive effects of the *N*-oxide group.***

Now let us turn our attention to the problem of the electronic absorption spectrum of

27) M. Karplus and G. K. Fraenkel, ibid., **35**, 1312 (1961).
28) H. M. McConell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

*** The details of this problem will be discussed in a future publication.

Table IX. The spin densities of nitrogen and carbon atoms of the 4-nitropyridine and 4-nitropyridine 1-oxide anions

Position	4-Nitropyridine anion		4-Nitropyridine 1-oxide anion
	Calcd. from molecular orbitals	Fstimated from the coupling const.	Estimated from the coupling const.
$^{14}NO_2$	0.261	0.218	0.187
3-C	0.033	0.024*	0.069*
2-C	0.052	0.133*	0.159*
Ring N	0.124	0.101	0.181

* These assignments were made taking into account spin densities obtained by the molecular orbital calculation.

the 4-nitropyridine anion. As is shown in Table VIII, the 313, 440 and 640 mμ bands can safely be ascribed to the $W_1 \rightarrow W_4$, $W_1 \rightarrow W_3$ and $W_1 \rightarrow W_2$ transitions respectively. From the wave functions Ψ_{W_1} and Ψ_{W_3} given in Table VII, it can be seen that the W_1 and W_3 states are in principle brought about by the resonance between the ground and charge-transfer configurations, and that the 440 mμ band corresponding to the $W_1 \rightarrow W_3$ transition may be regarded as the intramolecular charge-transfer band. Since, in the wave function of the W_4 state, the contribution of the locally excited configuration within the pyridine ring amounts to 94%, the 313 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 (or pyridine) anion. It is noticeable that the 355 mμ band of the 3, 5-lutidine (or pyridine) anion shows a large blue shift upon the introduction of the nitro group. This is because the charge-transfer configuration is rather close to the ground configuration and therefore the ground configuration is largely stabilized by the resonance interaction with the charge-transfer configuration.

A similar blue shift phenomenon was observed with the nitrobenzene anion.[16] The weak 640 mμ band may conceivably correspond to the $W_1 \rightarrow W_2$ transition with a small transition moment.

Summary

The ESR and electronic spectra of the 4-nitropyridine and 4-nitropyridine 1-oxide anions have been measured. The nitrogen and hydrogen hyperfine splitting constants of these two compounds have been determined. In order to analyze the ESR spectra exactly, the measurements have also been carried out with respective compounds containing ^{15}N instead of ^{14}N in the nitro group. The spin densities on the nitrogen and carbon atoms of these two anions have been estimated from the splitting constants. It has thus been found that the spin densities on the ring nitrogen and carbon atoms are undoubtedly larger in the 4-nitropyridine 1-oxide anion than in the 4-nitropyridine anion.

The electronic spectrum of the 4-nitropyridine anion has been measured and three peaks found at 313, 440 and 640 mμ. According to the molecular orbital calculations carried out with the π-electron system of the 4-nitropyridine anion, it has been concluded that the 440 mμ band may be regarded as the intramolecular charge transfer band, and that the 313 mμ band can be interpreted as the blue shifted band of the pyridine anion.

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