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The Electron Spin Resonance and Electronic Spectra of 4-Substituted Pyridinyl Radicals

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The ESR and electronic absorption spectra have been measured with the 1-methyl-4-carbomethoxy-, 1-methyl-4-carbamido-, 1-methyl-4-acetyl- and 1-methyl-4-cyanopyridinyl radicals. From the analysis of their ESR spectra by the aid of a spectrum accumulator, we have been able to determine the nitrogen and hydrogen hyperfine splitting constants of these pyridinyl radicals, from which the spin distributions have then been evaluated. These radicals except for the 1-methyl-4-carbamidopyridinyl radical, have been found to show three absorption bands, at 300—350 mμ, at about 400 mμ and at about 600 mμ. From the results of the ESR and electronic absorption spectra, the electronic structures of these pyridinyl radicals have been concluded to be similar to those of the 4-substituted pyridine anion radicals. The preparation of 1, 2, 6- and 1, 3, 5-trimethyl-4-substituted pyridinyl radicals has been attempted. The latter radicals, except for the 1, 3, 5-trimethyl-4-cyanopyridinyl radical, were not detected by the ESR and electronic absorption spectra, because the steric hindrance of the methyl groups at the 3 and 5 positions prevents them from achieving the resonance stabilization due to the 4-substituent.

Schwarz et al.¹⁾ have reported that the electrochemical reduction of the pyridinium ion in acetonitrile produces a dilute solution of the pyridinyl radical in the presence of tetra-*n*-butylammonium perchlorate as an electrolyte. Kosower et al.²⁾ have reported that a stable free radical can be prepared by bringing 1-ethyl-4-carbomethoxypyridinium iodide into contact with zinc dust in acetonitrile, and that the radical can be isolated in a pure form by distillation under a high vacuum. They proposed that this free radical is the 1-ethyl-4-carbomethoxypyridinyl radical.

The present authors³⁾ have studied the electronic structures of 3- and 4-nitropyridine anion radicals by combining the experimental results of the ESR and electronic spectra with the theoretical studies based on the molecular orbital method.

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1) W. M. Schwarz, E. M. Kosower and I. Shain, *J. Am. Chem. Soc.*, **83**, 2013 (1961).

2) E. M. Kosower and E. J. Poziomek, ibid., **85**, 2035 (1963); **86**, 5516 (1964).

3) M. Itoh, T. Okamoto and S. Nagakura, This Bulletin, **36**, 1665 (1963); M. Itoh and S. Nagakura, ibid., **38**, 825 (1965).

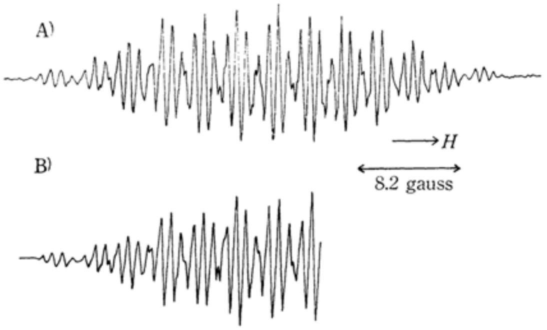

Fig. 1a. A) The ESR spectrum (first derivative) of the acetonitrile solution of 1-methyl-4-carbomethoxypyridinyl radical. B) The theoretically simulated spectrum based on the splitting constants by the aid of the spectrum accumulator. The line width was estimated to be 0.4 gauss and the line shape was considered to be a Lorentzian line.

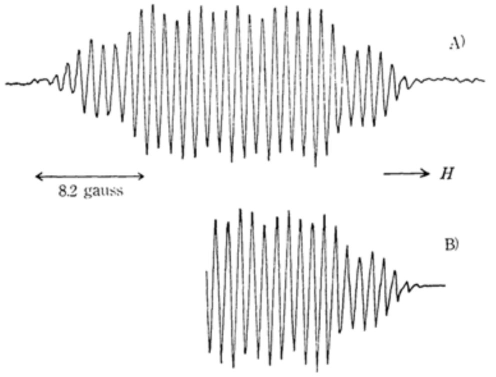

Fig. 1b. A) The ESR spectrum of the acetonitrile solution of the 1-deuteromethyl-4-carbomethoxypyridinyl radical. B) The simulated spectrum based on the splitting constants. The line witdth was estimated to be 0.4 gauss.

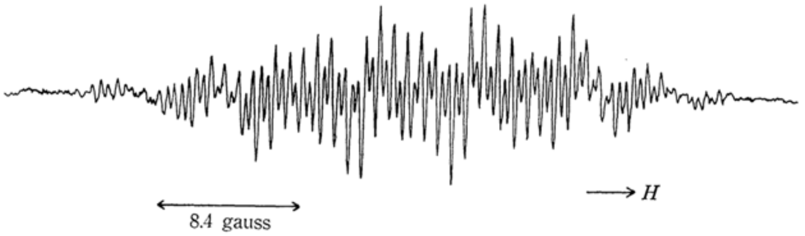

Fig. 1c. The ESR spectrum of the dioxane solution of the 1-methyl-4-carbomethoxypyridinyl radical.

In the course of their investigations, the present authors have attempted to prepare various substituted pyridinyl radicals and to measure their ESR electronic spectra. The present investigation includes the 1-methyl-4-carbomethoxy-, 1-methyl-4-carbamido-, 1-methyl-4-acetyl-, and 1-methyl-4-cyanopyridinyl radicals. The spin distributions and electronic structures of the pyridinyl radicals will be discussed on the basis of the ESR hyperfine splitting constants and the electronic spectra, special attention being paid to a comparison of these results with those concerning the substituted pyridine anion radicals which were reported in previous papers.[3]

Experimental

Materials. — 1-Methyl-4-carbomethoxypyridinium iodide, m. p. 190—191°C,[4] 1-methyl-4-cyanopyridinium iodide, m. p. 197°C,[4] 1-methyl-4-acetylpyridinium iodide, m. p. 172—173°C,[5] and 1-methyl-4-carbamidopyridinium iodide, m. p. 255°C[6], were prepared from the respective 4-substituted pyridines and methyl iodide. Ion exchange resin IRA-410 was used to prepare the 1-methyl-4-carbomethoxypyridinium chloride, m. p. 265—270°C (decomp.). The melting points of these compounds were in good agreement with those reported in the literature.

1-Deuteromethyl-4-carbomethoxy pyridinium bromide was obtained by the treatment of the corresponding substituted pyridines with deuteromethyl bromide (Merck; molecular weight 97.96). 1-Deuteromethyl-4-carbomethoxypyridinium bromide, m. p. 165°C.

Found: C, 40.97, H, (D), 6.04; N, 5.97. Calcd. for $C_8H_7D_3NO_2Br$: C, 40.85; H (D), 5.53; N, 5.95%.

1, 3, 5-Trimethyl- and 1, 2, 6-trimethyl-4-carbomethoxypyridinium iodides, m. p. 218—219°C and m. p. 198°C (decomp.), 1, 3, 5-trimethyl- and 1, 2, 6-trimethyl-4-cyanopyridinium iodides, m. p. 217°C and m. p. 225°C (decomp.), and 1, 3, 5-trimethyl- and 1, 2, 6-trimethyl-4-carbamidopyridinium iodides, m. p. 258°C and m. p. 215°C (decomp.) were prepared from the 2, 6-dimethyl- and 3, 5-dimethyl-4-substituted pyridines which had been obtained from the corresponding dimethyl-4-cyanopyridines.[7,8] The 2, 6-dimethyl-4-cyanopyridine was prepared by the reaction of the 1-methoxy-2, 6-dimethylpyridinium iodide with potassium

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[4] E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

[5] A. R. Katritzky, *J. Chem. Soc.*, **1955**, 2586.

[6] E. M. Kosower and S. W. Bauer, *J. Am. Chem. Soc.*, **82**, 2191 (1960).

[7] T. Okamoto, M. Hirobe and A. Ohsawa, to be published in *Chem. Pharm. Bull.*

[8] T. Okamoto and H. Tani, ibid., **7**, 925 (1959).

cyanide.8) The 3, 5-dimethyl-4-cyanopyridine was obtained from 1-amino-3, 5-dimethylpyridinium iodide and potassium cyanide.9) The melting points of these pyridinium iodides are in good agreement with those reported in the literature.

Solvents.—Acetonitrile was purified by repeated distillation from phosphorus pentoxide. Dimethoxyethane (DME) and dioxane were treated with potassium metal and distilled from lithium aluminum hydride.

The Preparation of Pyridinyl Radicals and Measurements.—The substituted pyridinyl radicals were prepared at room temperature by bringing the corresponding pyridinium salts into contact with zinc mirror in acetonitrile. In DME or doixane, the pyridinyl radicals were prepared by bringing them into contact with sublimated potassium metal. All the solvents were purified and degassed before use. The zinc and potassium metals were purified by repeated sublimation in vacuo. The preparation of the pyridinyl radicals and the measurements of ESR and electronic spectra were performed in vacuo by the method described in previous papers.3) The ESR and electronic spectra were measured with a Hitachi ESR spectrometer, model MPU-2B (X-band 100 kc. modulation) and with a Cary recording spectrophotometer, model 14 M, respectively.

Experimental Results

The 1-Methyl-4-carbomethoxypyridinyl Radical. — The acetonitrile solutions of 1-methyl-4-carbomethoxypyridinium chloride and 1-deuteromethyl-4-carbomethoxypyridinium bromide ($10^{-3}-10^{-4}$ mol./l.) were colored a yellowish green by coming into contact with pure sublimated zinc metal in vacuo. The observed ESR spectra of these solutions are shown in Figs. 1a and 1b.

The DME or dioxane solution of the 1-methyl-4-carbomethoxypyridinium chloride became slightly yellow upon coming into contact with sublimated potassium mirror in vacuo. As is shown in Fig. 1c, the ESR spectrum of the dioxane solution showed an intense hyperfine structure. The ESR spectra of the DME or dioxane solution of the 1-deuteromethyl-4-carbomethoxypyridinyl radical were also measured. Furthermore, 1-methyl-4-carbomethoxypyridinyl radical was prepared by zinc metal in dioxane. The ESR spectrum of the radical prepared by zinc metal in dioxane was exactly the same as that of the radical prepared by potassium metal in the same solvent. Therefore, it may be said that the metal cation does not exert any observable effect upon the hyperfine structure of the ESR spectrum.

The electronic absorption spectrum of the acetonitrile solution of the 1-methyl-4-carbomethoxypyridinyl radical was measured parallel with the ESR spectrum. The results are shown in Fig. 2. The spectrum consists of three absorption bands, at 307, 396 and 650 mμ. The electronic spectra of this pyridinyl radical in the other solvents are similar to those obtained with the acetonitrile solution. The three absorption bands of the radical solution disappeared when the solutions were exposed to air.

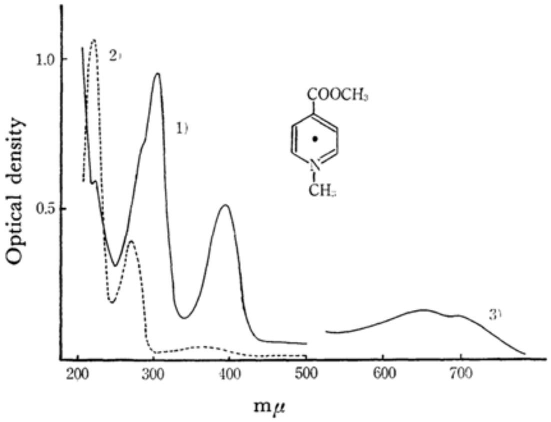

Fig. 2. The electronic absorption spectrum of the 1-methyl-4-carbomethoxypyridinyl radical. (The vertical axis is arbitrary scale.)

1) The acetonitrile solution of the radical.
2) The radical solution exposed to air.
3) The solution about ten times as concentrated as solution 1).

The 1-Methyl-4-acetylpyridinyl Radical.—The acetonitrile solution of the 1-methyl-4-acetylpyridinium iodide turned reddish yellow when it came into contact with sublimated zinc metal in vacuo.* The ESR and electronic absorption spectra of this solution were measured, with the results given in Figs. 3 and 4 respectively.

The 1-Methyl-4-carbamidopyridinyl Radical.—The 1-methyl-4-carbamidopyridinyl radical was prepared by bringing it into contact with zinc mirror in acetonitrile or DME.* The ESR and electronic spectra of this radical are shown in Figs. 5 and 6 respectively. This radical is rather unstable and, therefore, shows an ESR spectrum with a less resolved hyperfine structure.

The 1-Methyl-4-cyanopyridinyl Radical.—The DME solution of 1-methyl-4-cyanopyridinium iodide became an orange yellow when brought into contact with sublimated potassium metal. The observed ESR spectrum of this radical is shown in Fig. 7. The electronic spectrum was also measured with the DME solution of the radical. As is shown in Fig. 8, the spectrum consists of three absorption bands, at 342, 410 and ca. 600 mμ. These bands disappeared when the solution was exposed to air.

The acetonitrile solution of 1-methyl-4-cyanopyridinium iodide became an intense blue-black when brought into contact with zinc metal. The ESR and electronic spectra of the acetonitrile

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9) T. Okamoto, M. Hirobe, C. Mizushima and A. Ohsawa, ibid., **11**, 780 (1963).

* The radicals were prepared by the reaction with potassium metal in DME.

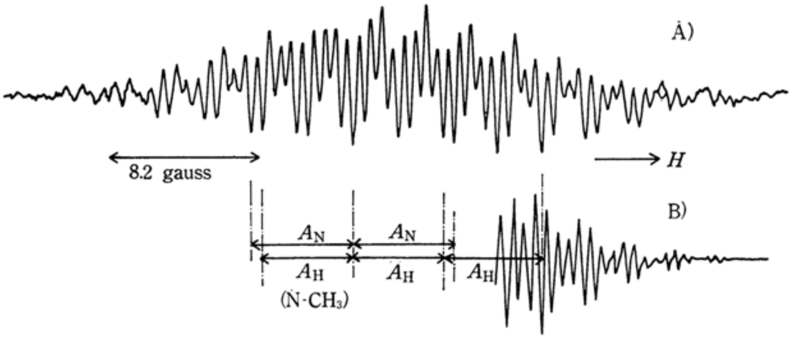

Fig. 3. The ESR spectrum of the acetonitrile solution of 1-methyl-4-acetylpyridinyl radical and a part of the reconstruction based on the splitting constants.

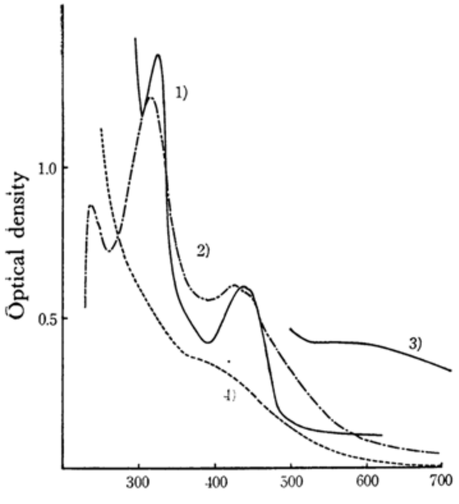

Fig. 4. The electronic spectrum of 1-methyl-4-acetylpyridinyl radical.
1) The acetonitrile solution of the radical.
2) The solution about ten times as concentrated as solution 1).
3) The DME solution of the radical.
4) The acetonitrile solution of the radical exposed to air.

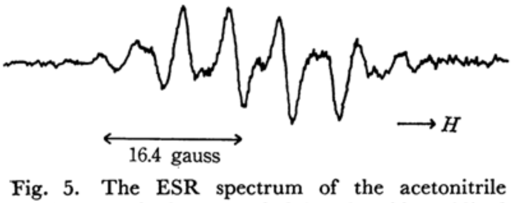

Fig. 5. The ESR spectrum of the acetonitrile solution of the 1-methyl-4-carbamidopyridinyl radical.

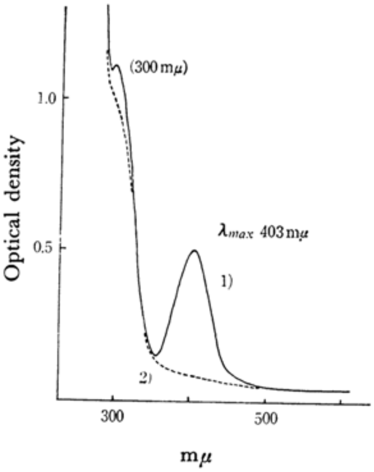

Fig. 6. The electronic absorption spectrum of the 1-methyl-4-carbamidopyridinyl radical. (The vertical axis is arbitrary scale.)
1) The acetonitrile solution of the radical.
2) The radical solution exposed to air.

solution were measured. The observed ESR and electronic spectra were exactly identical with those of the methylviologen cation radical recently reported by Kosower et al.[10] It may be inferred from the present experimental results that the 1-methyl-4-cyanopyridinyl radical easily dimerizes to form the methylviologen cation radical in polar solvents such as acetonitrile, although it is considerably stable in such less polar solvents as DME.

The Determination of the Hyperfine Splitting Constants and Simulated Spectra.— The hyperfine splitting constants associated with the nitrogen and hydrogen (deuterium) atoms of the above-mentioned pyridinyl radicals were determined from the ESR spectra. All the results are summarized in Table I. The theoretical spectra were simulated from the estimated splitting constants by the aid of a spectrum accumulator, JNM-RA-1, of the Japan Electron Optics Laboratory. The simulated spectra match well with the observed spectra, as is shown in Figs. 1, 3 and 7.

The Preparation of the Other Methyl Substituted Pyridinyl Radicals and Their

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[10] E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, **86**, 5524 (1964).

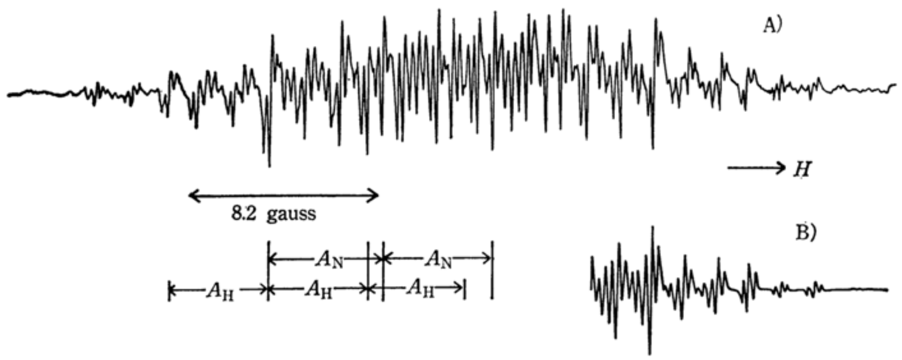

Fig. 7. A) The ESR spectrum of the DME solution of the 1-methyl-4-cyanopyridinyl radical. B) A part of the theoretically simulated spectrum based on the splitting constants. The line width was estimated to be 0.22 gauss. The line shape is considered to be a Lorentzian line.

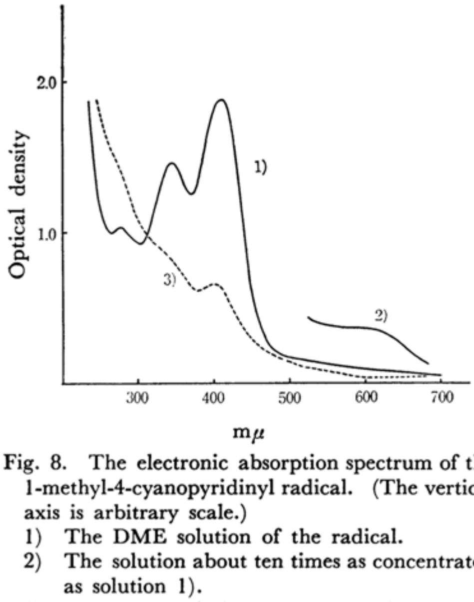

Fig. 8. The electronic absorption spectrum of the 1-methyl-4-cyanopyridinyl radical. (The vertical axis is arbitrary scale.)
1) The DME solution of the radical.
2) The solution about ten times as concentrated as solution 1).
3) The DME solution exposed to air.

Stability.—We also attempted to prepare 1, 2, 6-trimethyl-and, 1, 3, 5-trimethyl-4-substituted (substituents: –COOCH$_3$, –CONH$_2$, and –CN) pyridinyl radicals. The three 1, 2, 6-trimethyl-4-substituted pyridinyl radicals and the 1, 3, 5-trimethyl-4-cyanopyridinyl radical could be obtained from the respective pyridinium iodides. However, the 1, 3, 5-trimethyl-4-carbomethoxy and 1, 3, 5-trimethyl-4-carbamidopyridinyl radicals could not be obtained despite careful and repeated experiments. The stability of these substituted pyridinyl radicals in acetonitrile is summarized in Table II. It seems that the results given in Table II can be explained by considering the steric hindrance of the methyl groups at the 3 and 5 positions. This point will be discussed in a later part of the present paper.

Discussion

The Spin Distribution of Pyridinyl Radicals.

—The hyperfine splitting constant associated with the nitrogen atom of the aromatic ring has been

TABLE I. HYPERFINE SPLITTING CONSTANTS DUE TO NITROGEN AND HYDROGEN ATOMS OF SUBSTITUTED PYRIDINYLS RADICALS (gauss unit)

	4-COOCH$_3$		4-CN*	4-COCH$_3$
A_N (ring)	6.26		6.4±0.2	6.5±0.3
A_H (N-CH$_3$)	5.56	(0.84)**	5.6±0.2	5.16±0.2
A_H (2,6-)	3.56		3.8±0.1	3.2±0.1
A_H (3,5-)	0.84		0.35±0.1	0.6±0.1
	A_H (OCH$_3$) 0.84		A_N (CN) 1.9±0.1	A_H (CH$_3$) 2.63±0.2

* The result of DME solution.
** The result of the 1-deuteromethyl-4-carbomethoxypyridinyl radical.

TABLE II. STABILITY OF SUBSTITUTED PYRIDINYL RADICALS AT ROOM TEMERATURE*

Alkyl substituents	4-COOCH$_3$	4-CONH$_2$	4-CN
None	2—3 days	1—2 hrs.	2—3 days**
3,5-Dimethyl	No radical	No radical	ca. 2 days
2,6-Dimethyl	10—20 min.	ca. 10 min.	1—2 hr.

* Time, until the ESR hyperfine structures disappeared.
** The result of the DME solution.

TABLE III. THE SPIN DENSITIES OF THE NITROGEN AND CARBON ATOMS OF THE PYRIDINYL RADICALS EVALUATED FROM THE ESR SPLITTING CONSTANTS

	Pyridinyl			Anion radical			
	4-COOCH_3	4-CN	4-COCH_3	4-NO_2 [c]	$4\text{-NO}_2\text{N}\rightarrow\text{O}$ [c]	4-CN [d]	4-COCH_3 [e]
Ring N	0.195	0.200	0.203	0.124	0.181	—	0.171
2,6-C	0.158	0.168	0.142	0.052	0.159	0.059	0.021 (0.008)
3,6-C	0.037	0.015	0.026	0.033	0.068	0.110	0.124 (0.143)
N (CN) [a]	—	0.101	—	—	—	0.124	—
C (CO) [b]	—	—	0.095	—	—	—	0.205

a) The spin density on the nitrile-nitrogen, using $Q_N=18.8$ gauss.[13]

b) The spin density on the carbonyl-carbon atom calculated from methyl proton splitting, using $Q^{\text{H}}_{\text{CCH}_3}=27.2$ gauss.[15]

c) The results of the 4-nitropyridine and its 1-oxide anion radicals.[3]

d) The result of the 4-cyanopyridine anion radical obtained by Fraenkel et al.[13]

e) The result of the 4-acetylpyridine anion radical obtained by Fraenkel et al.[15]

considered to depend not only on the spin density of the nitrogen atom, but also, via indirect polarization, on the spin densities of the adjacent atoms. Carrington et al.,[11] however, proposed the following equation for the relationship between the nitrogen splitting constant, A_N, and the spin density on the nitrogen atom concerned, ρ_N, by disregarding the indirect polarization;

$$A_N=Q_N\rho_N \tag{1}$$

They estimated Q_N to be 25.3 gauss for the anion radicals.

Bolton et al.[12] suggested that the hyperfine splitting constant associated with the protonated nitrogen atom in the nitrogen semiquinone cation radical could be represented similarly by Eq. 1. By combining the observed nitrogen splitting constants with the spin densities on the 4,4′-dipyridyl semiquinone cation and the pyrazine semiquinone cation radicals as calculated by the Hückel molecular orbital method, they determined the value of Q_N to be 32—36 gauss[12] for the cation radicals. Rieger and Fraenkel[13] studied the spin density distribution in a number of nitrile anion radicals. They reported that the nitrile-nitrogen splitting, A_N, should be approximately proportional to the spin density, ρ_N, on the nitrogen atom: $A_N=K\rho_N$. Furthermore, they showed that when the least-squares method is applied to the observed nitrile-nitrogen splitting constants, it gives $K=18.8\pm0.7$ gauss for the Hückel spin densities.

In the present paper, the electronic state of the nitrogen atom in the pyridinyl radicals was assumed to be the same as that of the protonated nitrogen atom in the nitrogen semiquinone cation radicals. In other words, the value of Q_N in Eq. 1 was taken to be 32 gauss for the pyridinyl radical. By combining the observed hyperfine splitting constants with the above-mentioned relations for nitrogen splittings and the well-known relation for the proton hyperfine splittings ($A_H=-22.5\rho_C$), we have evaluated the spin densities on the nitrogen and carbon atoms of the substituted pyridinyl radicals. The results are summarized in Table III. The hydrogen splitting constant of the *N*-methyl group is considered to be proportional to the spin density of the nitrogen atom concerned, as in the case of the hydrogen splitting of the methyl group attached to the aromatic carbon atom[14]:

$$A'_H=Q'_H\rho_N \tag{2}$$

According to the present results, the Q'_H value is 28.4 gauss on the basis of the nitrogen spin densities of the pyridinyl radicals and the methyl hydrogen splitting constants shown in Table I.

From the spin densities summarized in Table III, it may be inferred that an odd electron is not localized on the ring nitrogen atom which has a positive formal charge in the pyridinium cation, but is distributed over the pyridinyl radical. This shows that the neutral pyridinyl radicals are of the π-type, as is usual for aromatic anion radicals.

The present authors[3] have reported elsewhere their studies of the ESR and electronic structures of the 4-nitropyridine and its 1-oxide anion radicals. Fraenkel et al.[13,15] have reported on the spin distribution of the electrochemically-generated 4-cyano- and 4-acetylpyridine anion radicals. The spin densities of these anion radicals are also shown in Table III. The results summarized in Table III show that the spin densities on the ring nitrogen and carbon atoms are remarkably larger in the substituted pyridinyl radicals than in the substituted pyridine anions. Furthermore, by comparing the spin densities of the 1-methyl-4-cyano- and 1-methyl-4-acetylpyridinyl radicals with those of the

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

[12] J. R. Bolton, A. Carrington, A. Forman and L. F. Orgel, ibid., **5**, 466 (1962).

[13] H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).

[14] J. R. Bolton, A. Carrington and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

[15] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962).

pyridine anion radicals with the same substituent groups at the 4-position, we can conclude that the spin densities on the nitrile-nitrogen or carbonyl-carbon atoms of the neutral radicals are smaller than those of the anion radicals. This is because the pyridinium ring is more electronegative than the pyridine ring; therefore, the spin density of the pyridinyl ring of these neutral radicals is larger than that of the pyridine ring in the corresponding pyridine anion.

The Electronic Spectra of Pyridinyl Radicals.—As is clearly seen from Figs. 2, 4, 6 and 8, all these pyridinyl radicals in acetonitrile, except for the 1-methyl-4-carbamidopyridinyl radical, show three absorption bands in the visible and ultraviolet regions. The observed maximum wavelengths summarized in Table IV show that the shortest wavelength absorption bands of these neutral radicals shift to longer wavelengths with the increase in the electron-attracting ability of the 4-substituents. The order is as follows: $-CONH_2 < -COOCH_3 < -COCH_3 < -CN$.

TABLE IV. THE ELECTRONIC ABSORPTION BAND OF SUBSTITUTED PYRIDINYL RADICALS

Pyridinyl radical	λ_{max} mμ		
4-$CONH_2$	300	403	—
4-$COOCH_3$	307	396	650*
4-$COCH_3$	326	432	ca. 600*
4-CN**	342	410	ca. 610*

* Very weak band.
** The result of the DME solution.

The present authors³⁾ have also demonstrated elsewhere that the electronic spectrum of the 4-nitropyridine anion showed three absorption bands, at 313, 440 and 640 mμ. The molecular orbital calculation allows us to regard the 440 mμ and 313 mμ bands as the intramolecular charge-transfer band and as the blue-shifted band of the band pertinent to the pyridine anion respectively. The electronic structures of the pyridinyl radicals with the electron-attracting groups, like the carbomethoxy, nitrile or acetyl groups, may be essentially similar to that of the 4-nitropyridine anion, although the valence state ionization potential of the nitrogen atom is considerably greater in the *N*-methyl pyridinyl radical than in the pyridine anion. On this assumption, the 300—350 mμ bands and the 390—440 mμ bands of the pyridinyl radicals may be thought to correspond to the 313 mμ band and the 440 mμ band of the 4-nitropyridine anion radical respectively.

The Effect of the Steric Hindrance of Methyl Groups upon the Stability of the Radicals.—The 1, 3, 5-trimethyl-4-carbomethoxy- and 1, 3, 5-trimethyl-4-carbamidopyridinyl radicals could not be obtained. It seems that this fact can be explained by considering the steric hindrance of the methyl groups at 3- and 5-positions. The $-COOCH_3$ and $-CONH_2$ groups at the 4-position can probably be prohibited by the steric hindrance from coplanarity with the pyridinium ring. This noncoplanarity decreases the resonance stabilization due to the $COOCH_3$ and $CONH_2$ groups.¹⁶⁾ This seems to be a reason why the 1, 3, 5-trimethyl-4-carbomethoxy- and 1, 3, 5-trimethyl-4-carbamidopyridinyl radicals could not be obtained. The above explanation is also supported by the fact that the 1, 3, 5-trimethyl-4-cyanopyridinyl radical can be prepared stably. In this case, the cyano group may reasonably be thought not to be susceptible to the steric hindrance of the methyl groups.

The Metal Cation Effect upon the Hyperfine Splitting Constants.—One electron transfer from zinc or alkali metal into the substituted pyridinium cation results in the formation of the neutral pyridinyl radicals and the metal cations. The alkali metal effect upon the nitrogen and hydrogen hyperfine splittings has been observed for the substituted nitrobenzene or substituted benzophenone anion radical reduced by alkali metal in THF or DME¹⁷,¹⁸⁾ This metal effect has been attributed to the electronic interaction between the anion radical and the metal cation.¹⁹⁾ As for the 1-methyl-4-carbomethoxypyridinyl radical, no metal effect upon the ESR hyperfine splitting was observed. This seems to show that the neutral pyridinyl radicals are different from the usual ion radicals in their interaction with the metal cations.

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16) S. Nagakura, M. Kojima and Y. Maruyama, *J. Mol. Spectroscopy*, **13**, 174 (1964).

17) K. Umemoto, Y. Deguchi and H. Takaki, This Bulletin, **35**, 260 (1962); P. Ludwig, T. Layloff and R. N. Adams, *J. Am. Chem. Soc.*, **86**, (1964).

18) N. Hirota, *J. Chem. Phys.*, **37**, 1884 (1962).

19) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2538 (1964).