BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 737—741 (1973)

The Effects of Ion-pair Formation on the ESR Spectra of the Anion Radicals of 4-Nitropyridine *N*-Oxide and 4-Nitropyridine[1]

Yoshiko KAWAMURA(née ŌISHI),[2] Koichi NISHIKIDA, and Tanekazu KUBOTA
Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka 553

(Received June 26, 1972)

The effect of potassium ion-pair formation on the ESR spectra of the anion radicals of 4-nitropyridine and its *N*-oxide (4NPO) was studied at various temperatures lower than room temperature. The hyperfine splitting constant values due to hydrogen, nitrogen, and potassium nuclei were determined by applying the simulation technique. The above value arising from the potassium nucleus, decreased with a decrease in the temperature. Molecular orbital calculations covering the whole system of the $4NPO^{-}$–M^{+} ion pair and employing the McLachlan modification for the spin-density calculation were carried out in order to discuss the configuration of the ion pairs and the temperature dependence of the hyperfine coupling constants. It was reasonably concluded that an alkali metal cation occupies the C_2 axis of the anion radicals and is in contact with the nitro-group oxygen atoms (the symmetry of the ion pairs is C_{2v}.). The temperature dependence of the hyperfine splitting constants was explained using the vibrational model of Atherton and Weissman.

In the foregoing paper we discussed the hydrogen-bonding effects on the electron spin resonance (ESR) spectra of 4-nitropyridine (4NP), 4-nitropyridine *N*-oxide (4NPO), and related *N*-oxide compounds from the experimental and theoretical viewpoints.[3] As part of a series of intermolecular interaction studies of free radicals, the effect of the alkalimetal ion-pair formation on the ESR spectra of the 4NPO and 4NP anion radicals will be reported in this paper.[4] It would be expected that the charge-transfer (CT) force and the electrostatic force may both play important roles[3] in the hydrogen bonding interaction and in the ion-pair formation of radical anions. Therefore, it seemed that it would be valuable to compare and discuss the effects of these two kinds of molecular interactions on the ESR spectra of 4NPO and 4NP anion radicals.

Experimental

Special-grade dimethoxyethane (DME) was carefully rectified and then dried, first with NaH and later with the Na–K alloy *in vacuo* (10^{-4}—10^{-5} mmHg). The solvent turned dark blue. Just before the use of DME as the solvent, degassing was done in the vacuum system by repeated freeze-thaw cycles at about the temperature of liquid nitrogen. In the present experiment, the ESR spectra due to the ion pair formed with the potassium ion alone were successfully obtained with a good resolution. The potassium was first purified by repeated distillation in a vacuum system, and finally a pure K film was prepared in the usual manner.[5,8] To obtain the high-resolution spectrum, the sample solution should be placed in contact with the above K film *in vacuo* as follows. After being placed in contact at room temperature, the glass apparatus, which had been sealed off from the vacuum system, was immersed overnight in liquid nitrogen. Then spectral observation at various temperatures lower than room temperature was carried out the next day. For 4NP, however, it was not necessary to leave the contact solution at the temperature of liquid nitrogen overnight. In turn, the spectra of electrochemically-generated free radicals in the DME solvent were adopted as an example of those where no ion-pair formation occurs.[6]

The ESR spectra were recorded with a Varian V-4502-15X-band spectrometer with a 100 KHz magnetic field modulation, the magnetic field being monitored with a Varian F-8 nuclear fluxmeter and a Takeda Riken TR-5578 frequency counter. The observed spectra were computer-simulated in order to verify the hyperfine coupling constant values.[6,7]

Results and Discussion

A well-resolved hyperfine splitting (hfs) due to the potassium nucleus was obtained at a temperature lower than 0°C. As an example Fig. 1 shows the ESR spectrum and a simulated one of the $4NPO^{\dot{-}}$–K^{+} ion pair obtained at -10°C, all the experimental data being collected in Table 1. The numbering of each atom in 4NPO and in 4NP is shown in Figs. 1 and 4 respectively. Here note that the lower the temperature, the smaller the values of a_K (the hfs value due to the potassium nucleus), $a_N^{NO_2}$, and a_{2H} for the $4NPO^{\dot{-}}$–K^{+} ion pair. However, the values of $a_N^{N\rightarrow O}$ and a_{3H} are almost independent of the temperature variation. By comparing the hfs values of the $4NPO^{\dot{-}}$–K^{+} ion pair with those of the 4NPO anion radical itself (see Table 1),

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[1] Presented in part at the 9th (Tokyo, Oct., 1970) Symposium of Electron Spin Resonance held by the Chemical Society of Japan.

[2] Mrs. Kawamura has already left the Shionogi Research Laboratory. Any correspondence on this paper should be addresed to Dr. Kubota.

[3] T. Kubota, Y. Ōishi, K. Nishikida, and H. Miyazaki, This Bulletin, **43**, 1622 (1970).

[4] The ESR spectra of the anion radicals of 4NPO and 4NP produced by alkali-metal reduction were first reported by Itoh *et al.*, but the spectral resolution was low. Therefore, the effect of the ion-pair formation was not discussed by them. M. Itoh, T. Okamoto, and S. Nagakura, This Bulletin, **36**, 1665 (1963).

[5] a) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956). b) Y. Deguchi *et al.*, "Free Radicals in Solution," in "Electron Spin Resonance and Its Application to Chemistry," Kagaku Zōkan, **17**, ed. by Y. Deguchi, S. Ōnishi, and K. Morokuma (in Japanese), Kagaku Dojin (Kyoto) (1964), p. 43.

[6] T. Kubota, K. Nishikida, H. Miyazaki, K. Iwatani, and Y. Ōishi, *J. Amer. Chem. Soc.*, **90**, 5080 (1968).

[7] K. Nishikida, T. Kubota, H. Miyazaki, and S. Sakata, *J. Mag. Resonance*, **7**, 260 (1972).

[8] N. M. Atherton and S. I. Weissmann, *J. Amer. Chem. Soc.* **83**, 1330 (1961).

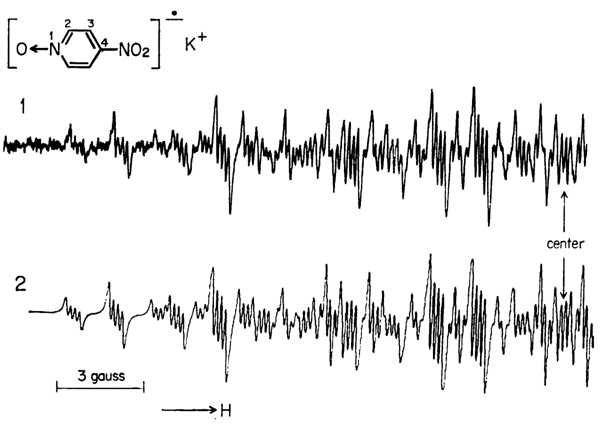

Fig. 1. Recorded (1) and simulated (2) ESR spectra of the potassium ion pair of 4-nitropyridine-*N*-oxide anion radical observed at −10°C. See also Table 1 footnote a.

TABLE 1. HYPERFINE SPLITTING CONSTANTS (IN gauss) OF THE K^+ COMPLEXES OF 4-NITROPYRIDINE *N*-OXIDE AND 4-NITROPYRIDINE ANION RADICALS AT VARIOUS TEMPERATURES

Temp (°C)	$a_N^{NO_2}$	$a_N^{N\to O}$	a_{2H}	a_{3H}	a_K	ΔH[a)]
4-Nitropyridine-*N*-oxide anion radical itself[b)]						
25	6.22	4.69	1.30	3.42	—	—
4-Nitropyridine-*N*-oxide anion radical-K^+ ion pair						
−10	7.35	4.40	1.45	3.51	0.160	0.110
−20	7.35	4.42	1.45	3.51	0.150	0.110
−40	7.23	4.40	1.43	3.51	0.140	0.100
−49	7.25	4.40	1.41	3.51	0.130	0.095
−59	7.22	4.40	1.40	3.51	0.120	0.095
4-Nitropyridine anion radical-K^+ ion pair						
−20	8.43	2.48	0.50	3.16	0.180	0.080
−30	8.31	2.47	0.49	3.13	0.160	0.080
−40	8.27	2.48	0.47	3.10	0.140	0.080
−50	8.23	2.49	0.46	3.10	0.120	0.080

a) Line width which was the most suitable for spectral simulation.
b) Obtained electrochemically in dimethoxyethane. See Fig. 's 1 and 4 for the numbering of each atom.

we can find that when the ion pair is formed, the values of $a_N^{NO_2}$, a_{3H}, and a_{2H} are increased, but the $a_N^{N\to O}$ value is decreased. Theoretically, these results proceed from the previously-reported MHMO calculation,[3)] assuming that the Coulomb integral at the nitro-group oxygen atoms (α_0) comes out deeper[3)] as a reslut of the ion-pair formation compared to that of the anion radical itself. Since the charge transfer may occur from the oxygen atoms to the K^+ ion, the deeper α_0 value seems reasonable. Therefore, it appears likely that the active center for the ion-pair formation is the nitro-group oxygen atoms. This result is in agreement with the active site for the 1 : 1 hydrogen-bonding interaction of $4NPO^{\overset{\cdot}{-}}$ and $4NP^{\overset{\cdot}{-}}$.[3)] Next, it should be noticed that the hfs constants of the two *ortho*-protons and the two *meta*-protons in the ion-paired 4NPO and 4NP free radicals all become equivalent, as may be seen in Table 1. This means that the K^+ ion may, as a time average, lie on the σ_v plane, which contains the C_2 axis but which is vertical for the molecular plane (the symmetry of the ion pair may be C_s or C_{2v}). Summarizing the afore-mentioned discussions, the K^+ ion may occupy the position on the σ_v plane (perhaps on the C_2 axis) and near the NO_2-group oxygen atoms. This result can also explain the temperature dependence of the a_K value resonably in terms of the vibrational model of Atherton and Weissman[8)] (*vide infra*).

Let us now consider quantitatively the structure of the ion pair and its behaviour. There have been reported several papers describing the theoreticl treatments of the structure of radical-ion pairs by applying the charge-transfer model or the electrostatic model, which more or less uses the perturbation technique.[9–12)] Here we have treated the problem using the simple molecular orbital (SMO) method, which covers the whole system of the $4NPO^{\overset{\cdot}{-}}$–$K^+$ ion pair and which employs the McLachlan modification[13)] for the spin density calculation.[14)] The calculation procedure is as follows. The perturbation potential, V, due to a metal cation (the effective charge is Ze) on π or lone-pair orbitals is written by $V=-Ze^2/\varepsilon r_{M\mu}$, where $r_{M\mu}$ is the distance from the metal cation to an electron occupying the atomic orbital, ϕ_μ, in the radical anion. The ε is the dielectric constant of solvents, since the ion pair is embedded in the solvents[17)] (see below). The mutual interaction of the alkali-metal cation with each $2p\pi$ atomic orbital and with the lone-pair orbitals of the nitro-group or *N*-oxide-group oxygen atoms in the anion radical is taken into account. Because the chemical orbital should be employed for the above mutual interaction, we assumed the lone-pair orbitals to be in the sp^2 hybridization. In addition, the charge transfer is considered to take place from the anion radical to the 2s, 3s, 4s, and 5s atomic orbitals of Li^+, Na^+, K^+, and Rb^+ cations respectively. Therefore, these s orbitals have been used for the present computation.

For the actual calculation, a zero-differential overlap approximation was adopted, so that the potential:[9)]

$$V_{\mu\nu}=(-Ze^2/\varepsilon)\langle\phi_\mu|1/r|\phi_\nu\rangle\approx-2Ze^2S_{\mu\nu}/\varepsilon(r_{M\mu}+r_{M\nu})$$

is zero for $\mu\neq\nu$. Here, $S_{\mu\nu}=\langle\phi_\mu|\phi_\nu\rangle$ is the overlap integral. The parameters, k_a, in the form $\alpha+k_a\beta$, for the SMO calculation of the 4NPO anion radical are

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9) B. J. McClelland, a) *Trans. Faraday Soc.*, **57**, 1458 (1961); b) *Chem. Rev.*, **64**, 301 (1964).

10) S. Aono and K. Oohashi, *Progr. Theor. Phys.*, **30**, 162 (1963); **32**, 1 (1964).

11) M. Iwaizumi, M. Suzuki, T. Isobe, and H. Azumi, This Bulletin, **40**, 1325 (1967); **41**, 732 (1968).

12) C. A. McDowell and K. F. G. Paulus, *Can. J. Chem.*, **43**, 224 (1965).

13) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

14) This technique is convenient for the present case, because our previous calculation data[3,6,7)] can extent to this kind of study. After we had presented this paper at the Symposium,[1)] Goldberg and Bolton,[15)] and Takeshita and Hirota[16)] reported the theoretical calculation of several radical ion pairs. Their methods are somewhat similar to ours, but are more simplified than the present treatment.

15) I. B. Goldberg and J. R. Bolton, *J. Phys. Chem.*, **74**, 1965 (1970).

16) T. Takeshita and N. Hirota, *J. Amer. Chem. Soc.*, **93**, 6421 (1971).

17) M. Born, *Z. Phys.*, **1**, 45 (1920).

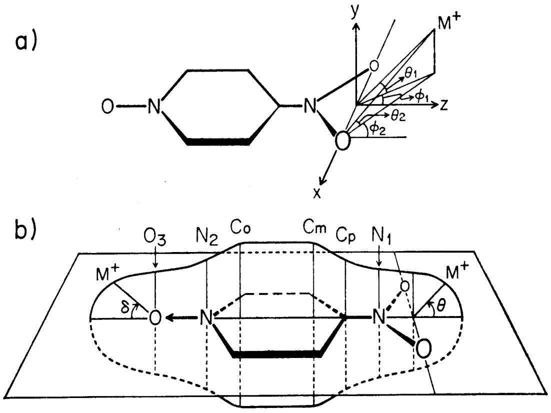

Fig. 2. a) The coordinate which has been used for the molecular orbital calculation of the whole system of the alkali metal ion pairs with 4-nitropyridine *N*-oxide (4NPO) anion radical. b) Each point on the circle, which is in the σ_v plane of 4NPO and drawn by keeping the distance of ion pair contact, is designated by θ, δ, N_1, Cp, *etc.* and employed for the abscissa in Fig. 3A. See text for detailed explanation.

the same as those in the foregoing papers.[3,6] Here we employed the values[18] of $\alpha=-6.31$ eV and $\beta=-2.93$ eV. The electrostatic energies were expressed in β units, *i.e.*, $k_e\beta$. Thus, the total potential at each atom becomes $\alpha+(k_a+k_e)\beta$. The Coulomb integral due to the s orbital of alkali-metal cations is taken to be equal (as the absolute value) to the ionization potential of the neutral atoms;[19] thus, the values are: α_{Li} (-5.39 eV)$=\alpha-0.314\,\beta$, α_{Na} (-5.14)$=\alpha-0.399\,\beta$, α_K (-4.34)$=\alpha-0.672\,\beta$, and α_{Rb} (-4.18)$=\alpha-0.727\,\beta$. In turn, we assumed that the energy of the lone-pair orbitals at the oxygen atoms of the 4NPO anion radical equals that of the corresponding oxygen π Coulomb integral.[20] The resonance integral between a metal cation s orbital and a π atomic orbital or a lone-pair orbital was estimated according to the $(\beta_{M-X}/\beta_{C=C})=(S_{M-X}/S_{C=C})$ relation at various metal positions (*vide infra*). Here note that the overlap integral, S_{K-X}, was obtained by the intrapolation method from the theoretical values using 1s, 2s, 3s, and 5s atomic Slater's orbitals, because $n-\delta=3.7$ in the atomic orbital parameter $\mu=(Z-\sigma)/(n-\delta)$ for the case of the 4s (potassium) orbital. In the present case the contact-ion pair was assumed, so that we take the sum of the ion radius and the Van der Waals radius for the distance[24] between the metal cation and each atom of the 4NPO anion radical, whose dimensions are put equal to those[21] of the neutral molecule.

Now we will solve the secular Eq. (1), to yield the necessary quantities for the discussion of the ion pairs:

$$|H_{\mu\nu}-E\delta_{\mu\nu}|=0 \tag{1}$$

where

$$H_{\mu\nu}=H^0_{\mu\nu}-Ze^2\langle\phi_\mu|1/r\varepsilon|\phi_\nu\rangle\delta_{\mu\nu} \tag{2}.$$

$H^\circ_{\mu\nu}$ is for the SMO parameters of the 4NPO anion radical itself.[3,6] The above-mentioned calculation model represents the adoption of the π electron approximation; *i.e.*, the charge transfer of an odd π electron occurs to the vacant s orbital of alkali metal cations. The value of $<\phi_\mu|1/r_{M\mu}|\phi_\mu>$ was theoretically calculated using the Slater orbital. The lone-pair orbitals in sp^2 hybridization are obtained explicitly in the usual manner; *i.e.*, they are first written out under a suitable coordinate at the oxygen atoms, and then these orbitals are transformed to those which are suitable for the coordinate of the whole molecule (see Fig. 2)[22] and are used for the calculation of S_{M-X} and the values of Eq. (2). Some integrals necessary here are given in the footnote.[23] The stabilization energy due to the ion-pair formation can thus be expressed by the equation:

$$\Delta E=\sum_i^{occ}n_i(E_i-E_i^0)+\sum_a\frac{ZZ_ae^2}{\varepsilon r_{Ma}} \tag{3}$$

Here, n_i is the electron number which occupies the i-th molecular orbital, E_i^0 being the i-th molecular orbital energy of the 4NPO anion radical itself. The last term in Eq. (3) stands for the nuclear repulsion energy between the nuclear cores a's (the core charge of the

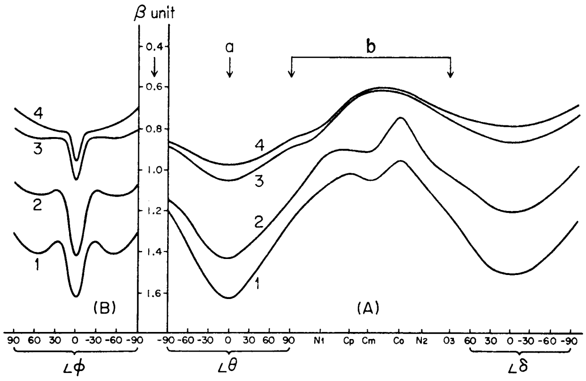

Fig. 3. The stabilization energies of alkali metal ion pairs with 4NPO anion radical. Curves 1, 2, 3, and 4 stand for the ion pairs with Li^+, Na^+, K^+, and Rb^+, respectively. See Fig. 2b and text on the explanation of the meaning of abscissa and "a and b" in the part A, respectively.

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[18] S. Mataga and N. Mataga, *Z. Phys. Chem.*, *N.F.*, **33**, 374 (1962).

[19] C. E. Moore, "Atomic Energy Levels," Natl. Bur. Standards (U. S. A.), Circ. No. 467, Vol. I–III; "American Institute of Physics Handbook, "McGraw-Hill, New York (1957).

[20] Only for the ion pair with K^+ was the calculation made using a deeper Coulomb integral for the oxygen lone-pair orbitals (see below).

[21] E. L. Eichhorn, *Acta Crystallogr.*, **9**, 787 (1956).

[22] a) L. Pauling, "The Nature of the Chemical Bond" (Third Edition), Cornell University Press, Ithaca, New York (1960), p. 120. b) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York (1962), p. 54.

[23]

$$-Ze^2\langle 2p\pi_a|1/r_{Ma}|2p\pi_a\rangle$$
$$=-\frac{Ze^2}{R\rho^2}\left[-\frac{3}{2}+\rho^2+e^{-2\rho}\left(\frac{3}{2}+3\rho+2\rho^2+\frac{1}{2}\rho^3\right)\right]$$
$$-Ze^2\langle 2p\sigma_a|1/r_{Ma}|2p\sigma_a\rangle$$
$$=-\frac{Ze^2}{R\rho^2}\left[3+\rho^2-e^{-2\rho}\left(3+6\rho+7\rho^2+\frac{11}{2}\rho^3+3\rho^4+\rho^5\right)\right]$$
$$-Ze^2\langle 2ps_a|1/r_{Ma}|2ps_a\rangle$$
$$=-\frac{Ze^2}{R}\left[1-e^{-2\rho}\left(1+\frac{3}{2}\rho+\rho^2+\frac{1}{3}\rho^3\right)\right]$$
$$-Ze^2\langle 2p\sigma_a|1/r_{Ma}|2ps_a\rangle$$
$$=-\frac{5Ze^2}{2\sqrt{3}R\rho}\left[1-e^{-2\rho}\left(1+2\rho+2\rho^2+\frac{6}{5}\rho^3+\frac{2}{5}\rho^4\right)\right]$$

In these equations R is the distance in atomic units between the metal cation and each atomic orbital in $4NPO^{\dot{-}}$, and $\rho=\mu_aR$.

atom *a* is $Z_a e$) of the conjugated system and the alkali metal cation (core charge: *Ze*). This term ought to be subtracted from the first electronic stabilization energy term. Here note that $Z_O^{NO_2}$, $Z_N^{NO_2}$, $Z_O^{N\to O}$, $Z_N^{N\to O}$, and Z_C of 4NPO are 5, 2, 5.3, 1.7, and 1 respectively. The calculated results are demonstrated in Fig. 3. In Part A of this figure, each point shown on the abscissa corresponds to that indicated in Fig. 2b. In Part B the ϕ angle is the same as that in Fig. 2a; *i.e.*, the metal cation occupies the $4NPO^{\dot{-}}$ molecular plane and moves between $\phi=90$—$-90°$ by keeping the distance of the ion-pair contact constant.[24] It is now clear that, although the absolute value itself of the stabilization energy is not very accurate,[25] the most stable position of the metal cation is at $\theta=0$ and $\phi=0$; that is, the cation occupies the C_2 axis of the 4NPO anion radical and is in contact with the nitro-group oxygen atoms. In addition, the potential valley arising from the change in the ϕ angle is very narrow and quite deep (see Fig. 3). This may indicate that the metal cation can move more easily along the potential surface derived as a change in the θ angle, *i.e.*, in the direction deviating from the 4NPO molecular plane. These results support the previous qualitative discussions by other authors on the structure of the ion pairs of nitrobenzene, *etc.*[26–29]

Next, the calculated results depicted in Fig. 3 show that the stability of the alkali-metal ion pairs of $4NPO^{\dot{-}}$ is in the order: $Li^+ > Na^+ > K^+ > Rb^+$; the smaller the ion radius, the larger the stability. This conclusion is the same as that reported by Ling and Gendell[26] for the case of the alkali-metal ion pairs of nitrobenzene anion radical. On the other hand, they found a different behaviour in the Li^+ ion pair from the other alkali-metal ion pairs. For example, the hfs value due to the Li^+ nucleus (a_{Li}) has a tenedncy to increase with a decrease in the temperature. This behaviour can not be explained by the present calculations. On the basis of the small size of the Li^+ ion, there occurs more contact complex between Li^+ and the atoms of the nitro group. The terms, such as "spin polarization", other than the assumptions made here for the present calculations should also be taken into account in this kind of calculation.[30]

TABLE 2. CALCULATED HYPERFINE SPLITTING CONSTANTS OF ALKALI METAL-4-NITROPYRIDINE *N*-OXIDE ANION RADICAL ION PAIRS AS A FUNCTION OF THE ANGLE θ[a,b]

θ (°)	M^+	$a_N^{NO_2}$	$a_N^{N\to O}$	a_{2H}	a_{3H}	a_M	(ρ_M)[c]
0	Li	14.38	1.45	1.44	3.09	0.000	(0)
	Na	13.35	2.51	1.40	3.19	0.000	(0)
	K	12.37	3.12	1.34	3.22	0.000	(0)
	Rb	11.93	3.36	1.31	3.22	0.000	(0)
30	Li	15.11	1.01	1.43	3.03	1.079	(0.0075)
	Na	13.82	2.35	1.40	3.15	1.682	(0.0053)
	K	12.41	3.07	1.34	3.20	0.111	(0.0014)
	Rb	11.91	3.31	1.31	3.20	1.085	(0.0009)
45	Li	15.67	0.68	1.42	2.98	1.823	(0.0127)
	Na	14.24	2.16	1.40	3.11	3.105	(0.0098)
	K	12.45	2.95	1.34	3.15	0.442	(0.0054)
	Rb	11.86	3.25	1.31	3.18	2.450	(0.0020)
60	Li	16.03	0.34	1.40	2.90	2.053	(0.0143)
	Na	14.58	1.96	1.39	3.04	4.345	(0.0137)
	K	12.25	2.92	1.34	3.14	0.351	(0.0043)
	Rb	11.71	3.20	1.31	3.14	4.583	(0.0038)
90	Li	14.99	−0.16	1.36	2.72	0.844	(0.0059)
	Na	14.27	1.57	1.34	2.80	5.552	(0.0176)
	K	11.44	2.67	1.33	3.00	0.836	(0.0101)
	Rb	10.74	3.03	1.30	3.01	12.40	(0.0102)

a) For the actual calculations see text.

b) See text and Fig. 2 for the definition of the angle θ.

c) ρ_M indicates calculated spin density on metal cations.

Table 2 shows the calculated hfs values for hydrogen, nitrogen, and metal cations as a function of the θ angle, but at $\phi=0$. The equations combining the spin densities and the hfs values for the $a_N^{NO_2}$, $a_N^{N\to O}$, and a_H were the same as those reported previously.[3,6] The a_M values due to alkali metal cations were obtained using the equation $a_M = Q_M \rho_M$, where the Q_M values are:[31] $Q(^7Li)=143.3$, $Q(^{23}Na)=316.2$, $Q(^{39}K)=82.4$, $Q(^{87}Rb)=1219$. In Table 2 we can see that the increasing θ causes an increase in a_M and $a_N^{NO_2}$, although the $a_N^{NO_2}$ value again shows a tendency to decrease at $\theta > 60°$. Therefore, the decreasing temperature, which corresponds to the decreasing θ, can be expected to bring about the decrease in the a_M and $a_N^{NO_2}$ values, since the metal ion in the ion pair would submerge to the bottom of the potential valley illustrated in Fig. 3.[8] These theoretical results explain well the experimental results previously mentioned, though, in our present treatment, the contributions from the effects of spin polarization, *etc.* to the a_M values were disregarded. Therefore, the spin density on alkali metal cations turns out to be zero when $\theta=0$. Here note that the linear relation is satisfied when the calculated values of $a_N^{NO_2}$ (see Table 2) are plotted against the values of $1/(R_M + C)$, where R_M is the ion radii of Li^+, Na^+, K^+, and Rb^+, and where *C* is a constant (1.4 Å in the present case). This kind of linear relation for radical-ion pairs was suggested by Nakamura[28] and by McClelland;[9a] the former author found this relation experimentally for

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[24] The ion and the Van der Waals radii (Å unit) used are shown in parentheses: Li^+ (0.6), Na^+ (1.0), K^+ (1.3), Rb^+ (1.5), 0 atom (1.4), N (1.5), and $2\pi p$ electron cloud of carbon (1.7).

[25] One main reason for this may be the ε value, for which we used 3.0 as an average of the dielectric constants of ether-like solvents. After we had finished this work, Takeshita and Hirota[16] discussed the physical meaning of the ε value. They used it as an adjustable parameter in intimate correlation with the $r_{M\mu}$ value.

[26] C. Ling and J. Gendell, *J. Chem. Phys.*, **47**, 3475 (1967).

[27] J. M. Gross, J. D. Barnes, and G. N. Pillans, *J. Chem. Soc., A*, **1969**, 109.

[28] K. Nakamura, This Bulletin, **40**, 1 (1967).

[29] Here note that there are two shallow potential minima at $\phi=50°$ and $-50°$ (see Fig. 3b), especially in the case of small-size alkali-metal ion pairs. These positions correspond to those where the lone-pair orbitals at each oxygen atom of the nitro group interact with an alkali ion. Previously, Nakamura[28] indicated the possibility of those potential minima in his qualitative discussion.

[30] G. W. Canters, C. Corvaja, and E. de Boer, *J. Chem. Phys.*, **54**, 3026 (1971). In this paper it was theoretically emphasized that the charge-transfer process from doubly-occupied aromatic π MO's to the atomic orbitals (especially the ns orbital) of an alkali metal cation plays also a very important role in explaining the metal-spin density (particularly the negative spin density) in alkali-radical ion pairs.

[31] H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi, and H. Takaki, *Mol. Phys.*, **9**, 153 (1964).

the $a_N^{NO_2}$ values of alkali-metal ion pairs of halogen-substituted nitrobenzenes.

Now, let us turn to a discussion of the energy level of lone-pair orbitals. The calculation for the $4\text{NPO}^{\cdot-}$—K^+ ion pair indicated that the use of a deeper Coulomb integral for the oxygen lone-pair orbitals (α_l), compared to that of the carbon π orbital resulted in a smaller energy difference between two points, A (σ type ion pair) and B (π type ion pair), in Fig. 3A. The adoption of the deeper α_l value indicates a smaller interaction of lone-pair orbitals with the vacant s orbital of alkali-metal cations. Thus, the charge-transfer effect from the lone-pair orbitals to the s orbital becomes small, resulting in the structure of the above σ-type ion pair becoming unstable.

Last, we would like to add an experimental finding on the K^+ ion pair of the 4-nitropyridine ainon radical ($4\text{NP}^{\cdot-}$), the ESR spectrum of which is shown in Fig. 4 (see also Table 1 for the hfs values of each atom) and which was obtained under almost the same conditions as in the case of the $4\text{NPO}^{\cdot-}$–K^+ ion pair. The temperature dependence of the a_K and $a_N^{NO_2}$ values is quite similar to that of the $4\text{NPO}^{\cdot-}$–K^+ ion pair previously discussed in detail. Therefore, the nature of the $4\text{NP}^{\cdot-}$–K^+ ion pair seems to be the same as that of the $4\text{NPO}^{\cdot-}$–K^+ ion pair; *i.e.*, the K^+ ion would interact with the nitro-group oxygen atoms in the 4NP anion radical. This conclusion is the same as was derived from the study of the hydrogen-bonding effect on the ESR spectra of the 4NP anion radical,[3] where the active sites participating in the hydrogen-bonding interaction are nitro-group oxygen atoms.

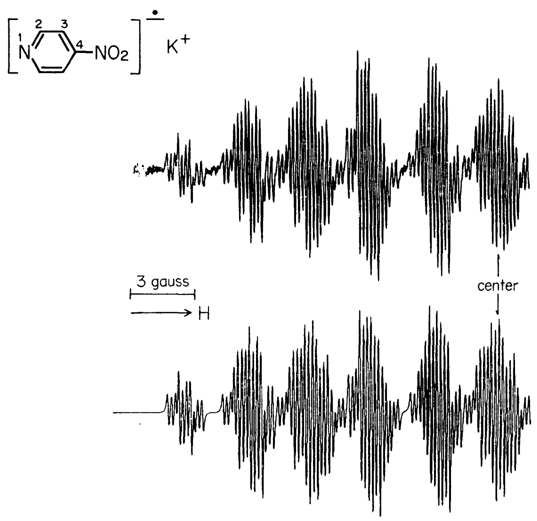

Fig. 4. Recorded (upper) and simulated (lower) ESR spectra of potassium ion pair of 4-nitropyridine anion radical observed at −20°C. See also Table 1 footnote a.