BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 923—928 (1969)

Semi-Empirical ASMO SCF Method for the Valence Electron System. The Electronic Structures of Protonated Pyridinium and Diazinium Cations

Hiroshi KATO, Hajime KATÔ,[*1] Hideyuki KONISHI and Teijiro YONEZAWA

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

(Received August 26, 1968)

Using a semi-empirical ASMO SCF method for valence electron systems previously proposed by the present authors, the valence shell electronic structures of various protonated azines are investigated. The compounds treated in the present paper are monoprotonated pyridinium, mono-, and diprotonated diazinium cations. The calculated results show that quite large charge redistributions on both σ and π electron systems in these cations take place in the protonation, while about a 0.7 *e* charge migrates to the attached protons. As to the transition energies, the lowest π–π^* transitions exhibit slight red shifts, while the n–π^* transitions would be expected to cause large blue shifts by means of protonation. Several models for protonated cations are compared, and the configuration where the proton is situated on the bisector of the CNC(N) angle and in the molecular plane is shown to be the most stable one. The changes in Fock's operators upon protonation are also briefly discussed.

Numerous experimental and theoretical studies of the effect of protonation or hydrogen bonding on the electronic structures of nitrogen heterocycles have been presented in the past decade.1) Mataga and Mataga treated the protonated pyridinium cation and pyrazinium diion by a semi-empirical SCF method for π electron systems and showed that their calculation were successful in accounting for the electronic spectra of these ions.2) However, their method is based on the π-approximation and the σ-electronic systems are not taken into account explicitly; that is, the core attraction of the adding proton is considered as a prameter of the perturbation in the π electron systems. Recently, calculations including the π electrons in the compounds containing the nitrogen atoms have been made by several authors, but these treatments have not discussed the electronic spectra and the positions of the added protons.1g,i,j)

In the present paper, the protonated cations of pyridine and three diazines are calculated by the semi-empirical ASMO SCF method for all valence electron systems previously proposed by the present authors.3) The changes in the σ and π electronic distributions, the stabilization of the orbitals, and the shift of the electronic transitions caused by the protonation are discussed. Further, the location of the adding proton and the changes in the Fock's operators are investigated. The compounds studied in the present paper are monoprotonated pyridinium and mono- and diprotonated diazinium cations.[*2] As to the geometries of these cations, it is assumed that the added proton is situated on the bisector of the CNC angle and in the molecular plane of the compound, which has the same configuration as the free molecule.[*2],4,5) The N–H$^+$ bond distance is taken as 1.032 Å, as in the NH$_4^-$ ion, throughout this procedure.2,5)

Results and Discussion

The Change in the Charge Distribution. The calculated atomic populations of an atom A,

---

[*1] Present address: Department of Chemistry, Faculty of Science, Kobe University.

1) *E. g.*, a) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950); b) J. R. Platt, *J. Chem. Phys.*, **19**, 101 (1951). c) F. Halverson and R. C. Hirt, *ibid.*, **19**, 711 (1951). d) H. McConnell, *ibid.*, **20**, 700 (1952). e) V. G. Krishna and L. Goodman, *ibid.*, **33**, 381 (1961); *J. Am. Chem. Soc.*, **83**, 2042 (1961). f) M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.*, **60**, 248 (1964). g) J. Pugmire and D. M. Grant, *J. Am. Chem. Soc.*, **90**, 679 (1968). h) J. D. Vaughan, D. G. Fullerton and C. Chang, *Int. J. Quantum Chem.*, **2**, 205 (1968). i) J. R. Sabin, *ibid.*, **2**, 23, 31 (1968). j) R. B. Hermann, *ibid.*, **2**, 165 (1968).

2) S. Mataga and N. Mataga, *Naturwissenschaften*, **45**, 333 (1958); *Z. physik. Chem. N. F.*, **19**, 231 (1959); This Bulletin, **32**, 521, (1959).

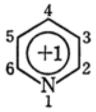
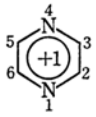
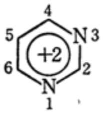
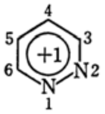
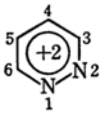
3) T. Yonezawa, K. Yamaguchi and H. Kato, This Bulletin, **40**, 536 (1967); H. Kato, H. Konishi, H. Yamabe and T. Yonezawa, *ibid.*, **40**, 2761 (1967).

[*2] The adopted geometries of free molecules are given in Ref. 4.

4) T. Yonezawa, H. Katô and H. Kato, *Theoret. chim. Acta*, in press.

5) "Tables of Interatomic Distances and Configuration in Molecules and Ions," ed. by L. E. Sutton, The Chem. Soc., London (1956) and (1965).

TABLE 1. THE ATOM POPULATIONS, π AO POPULATIONS AND THEIR DIFFERENCES BETWEEN CATIONS AND FREE COMPOUNDS

Compound*	Position	Q_A**	ΔQ_A	Q_H**	ΔQ_H	$N_{\pi A}$	$\Delta N_{\pi A}$	$\Delta N_{\sigma A}$
	1	5.231	−0.252	0.701	+0.701	1.425	+0.413	−0.665
	2,6	3.784	+0.032	0.896	−0.073	0.879	−0.107	+0.139
	3,5	4.050	−0.068	0.870	−0.043	0.996	−0.021	−0.047
	4	3.966	−0.091	0.881	−0.056	0.824	−0.157	+0.066
	1***	5.148	−0.309	0.709	+0.709	1.381	+0.404	−0.713
	2,6	3.832	+0.010	0.875	−0.075	0.896	−0.115	+0.125
	3,5	3.787	−0.035	0.896	−0.054	0.992	−0.019	−0.016
	4	5.362	−0.095	—	—	0.843	−0.136	+0.041
	1,4	5.135	−0.322	0.645	+0.645	1.276	+0.298	−0.620
	2,3,5,6	3.780	−0.042	0.829	−0.121	0.862	−0.149	+0.107
	1***	5.316	−0.230	0.680	+0.680	1.455	+0.420	−0.650
	2	3.487	+0.026	0.909	−0.072	0.839	−0.115	+0.141
	3	5.456	−0.090	—	—	1.049	+0.014	−0.076
	4	3.630	−0.103	0.897	−0.060	0.780	−0.183	+0.080
	5	4.119	−0.055	0.863	−0.051	1.032	−0.018	−0.037
	6	3.755	+0.022	0.887	−0.070	0.845	−0.118	+0.140
	1,3	4.267	−0.279	0.635	+0.635	1.446	+0.411	−0.690
	2	3.487	+0.026	0.844	−0.137	0.771	−0.243	+0.269
	4,6	3.665	−0.068	0.832	−0.125	0.694	−0.269	+0.201
	5	4.057	−0.117	0.814	−0.100	1.010	−0.040	−0.077
	1***	5.002	−0.261	0.693	+0.693	1.401	+0.386	−0.647
	2	5.283	+0.020	—	—	1.056	+0.041	−0.021
	3	3.676	−0.074	0.907	−0.055	0.914	−0.080	+0.006
	4	4.020	−0.084	0.861	−0.060	0.855	−0.137	+0.053
	5	4.040	−0.060	0.873	−0.048	1.013	+0.021	−0.081
	6	3.764	+0.014	0.883	−0.079	0.761	−0.232	+0.246
	1,2	5.079	−0.184	0.635	+0.635	1.445	+0.430	−0.614
	3,6	3.671	−0.079	0.823	−0.130	0.667	−0.327	+0.248
	4,5	3.965	−0.139	0.816	−0.105	0.889	−0.103	−0.036

* The notation, +1 and +2 indicate to the mono and diprotonated species, respectively. The number for Q_H refers to the position linked with the hydrogen atom.

** The notation, Q_A refers to the atom population of carbon and nitrogen atom, and Q_H to the hydrogen atom. The notation Δ indicates the difference between the values in cation and neutral compound.

*** The protonated nitrogen atom in the monocation.

Q_A and the differences in the charges, ΔQ_A's, in the cation and its neutral molecule are compared in Table 1, where a plus sign indicates an increase in the charge and a minus sign, a decrease in the charge, by protonation. The π atomic orbital (AO) populations and their differences are also listed in the same table, together with σ charge's.

It may be seen from the table that a considerable quantity of the charges migrate to the added proton from the other atoms in the cations, and that the positive charges delocalize in all the positions of the compound. The atomic population of the added proton is equal to the sum of the net charges of the other atoms of its cation. The ratios which

TABLE 2. THE CONTRIBUTION OF VARIOUS TYPE OF ATOMS FOR THE CHARGE OF PROTON (%)

		(%)		
		N	C	H
Monoprotonated	Pyridine	40	25	35
	Pyrazine	58	6	36
	Pyrimidine	47	16	37
	Pyridazine	35	29	35
Diprotonated	Pyrazine	49	13	38
	Pyrimidine	44	18	38
	Pyridazine	29	34	37

are given by the sum of the ΔQ_A's with regard to nitrogen, carbon and hydrogen atoms respectively divided by the atomic population of the proton, are considered to be a measure of the contribution of the transferred charge to the proton from the corresponding atoms. These ratios for the nitrogen, carbon, and hydrogen atoms are listed in Table 2. The results in Table 2 indicate that the charges on the protons in these cations are transferred from all the atoms in the cation; in the monocations, the nitrogen and hydrogen atoms play a important role in the electron transfer, while in the diions, the contribution of the carbon atoms relatively increases. The π electron distributions are also greatly affected by the protonation; for example, the negative charges concentrate on the π AO of the protonated nitrogen atom, and the other carbon atoms almost all bear slightly positive charges. The σ electron redistribution may also be seen in Table 2. Namely, the σ electron populations of the carbon atoms show an alternation of the sign of charge, and at the nearest neighbor carbon its σ electron population increases largely in the cation.

The variations in the AO populations of the nitrogen atoms may be seen in Table 3, where the notation p_n indicates the lone pair 2p AO of the nitrogen atom. The protonation has a remarkable effect on the populations of the p_n and p_π AO's of the nitrogen atom; that is, the p_π AO loses a considerable charge, about 0.7 e, and the p_π AO gains a large negative charge. As a whole, the positive charge on the protonated nitrogen atom is not very large.

TABLE 3. THE AO POPULATIONS IN NITROGEN ATOMS

			s	$p\sigma$	pn	$p\pi$
Pyridine	Neutral		1.85	0.89	1.72	1.01
	Monoion		1.76	1.02	1.00	1.42
Pyrazine	Neutral		1.84	0.89	1.75	0.98
	Monoion	N	1.85	0.92	1.75	0.84
		NH*	1.75	1.00	1.01	1.38
	Diion		1.76	1.02	1.07	1.28

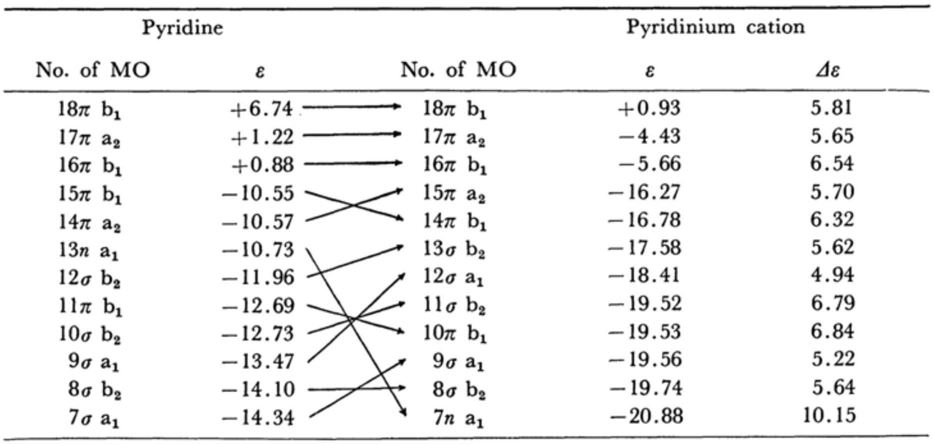
* The protonated nitrogen atom.

Changes in The Total and MO Energies. The proton affinities of these compounds are given as the change in the total energies of the systems, between before and after protonation.[3)] The calculated values are collected in Table 4, together with the observed pK_a values and the hydrogen bonding energies.[1e),*3] Unfortunately, there are no observed data on the proton affinities of these compounds; however, the obtained values may be considered slightly large, in view of the observed values for benzene, about 7 eV, and for NH_3, 8 eV.[6)] The values given in the table indicate that the order of the proton affinities for the monoprotonation agree with those of the observed pK_a values

TABLE 4. THE PROTON-AFFINITIES, ΔW (eV)

	Calcd ΔW		Obsd[1e)]	
	H^{+*}	$2H^{+*}$	pK_a	H.B. energy (kcal/mol)
Pyridine	10.00	—	5.17	—
Pyrazine	9.50	14.07	0.6	4.38
Pyrimidine	9.52	13.96	1.30	4.84
Pyridazine	9.79	13.92	2.33	5.24

* The notations H^+ and $2H^+$ denote to the mono- and diprotonated compounds, respectively.



Pyridine		Pyridinium cation		
No. of MO	ε	No. of MO	ε	$\Delta\varepsilon$
$18\pi\ b_1$	+6.74	$18\pi\ b_1$	+0.93	5.81
$17\pi\ a_2$	+1.22	$17\pi\ a_2$	−4.43	5.65
$16\pi\ b_1$	+0.88	$16\pi\ b_1$	−5.66	6.54
$15\pi\ b_1$	−10.55	$15\pi\ a_2$	−16.27	5.70
$14\pi\ a_2$	−10.57	$14\pi\ b_1$	−16.78	6.32
$13n\ a_1$	−10.73	$13\sigma\ b_2$	−17.58	5.62
$12\sigma\ b_2$	−11.96	$12\sigma\ a_1$	−18.41	4.94
$11\pi\ b_1$	−12.69	$11\sigma\ b_2$	−19.52	6.79
$10\sigma\ b_2$	−12.73	$10\pi\ b_1$	−19.53	6.84
$9\sigma\ a_1$	−13.47	$9\sigma\ a_1$	−19.56	5.22
$8\sigma\ b_2$	−14.10	$8\sigma\ b_2$	−19.74	5.64
$7\sigma\ a_1$	−14.34	$7n\ a_1$	−20.88	10.15

Fig. 1. The changes of MO energies, (ε) by protonation (eV).

[*3] It is noticable that it is necessary to compare the calculated values of proton affinity with those observed in the gas phase, but if the changes in the entropy terms and in the solvent effects by the protonation in these compounds, are constant or are negligibly small, the above comparison is not so unreasonable.

6) F. W. Lampe, J. L. Franklin and F. H. Field, "Progress in Reaction Kinetics," Vol. 1, Pergamon Press, London (1961), p. 67.

TABLE 5. THE SINGLET-SINGLET TRANSITION ENERGIES, ΔE AND OSCILLATOR STRENGTHS, Q

			ΔE_{calcd}			ΔE_{obsd}[2]	Q_{calcd}	
			X*	XH+**	H+XH+**		X*	H+XH+***
Pyridine	π-π^*	B_2	5.10	4.99	—	4.83	0.08	0.090
	π-π^*	A_1	5.05	5.38	—	5.50****	0.02	0.017
	π-π^*	B_2	7.51	7.57	—	—	1.00	0.913
	π-π^*	A_1	7.88	7.33	—	—	1.19	0.695
	n-π^*	B_1	4.29	8·22	—	—	—	—
	σ-π^*	B_1	6.62	6.30	—	—	—	0.008
Pyrazine	π-π^*	B_{3u}	5.08	4.86	4.55	4.35	0.02	0.281
	π-π^*	B_{1u}	5.22	5.94	5.75	6<	0.02	0.009
	π-π^*	B_{3u}	7.42	7.69	8.70	—	0.95	0.935
	π-π^*	B_{1u}	8.25	7.51	8.27	—	1.35	1.329
	n-π^*	B_{2u}	3.17	3.83	7.34	—	—	—
	n-π^*	B_{3g}	4.99	8.22	7.42	—	—	—
	σ-π^*	B_{2u}	8.38	—	5.42	—	—	0.003
Pyrimidine	π-π^*	B_2	4.80	4.75	4.76	—	0.01	0.138
	π-π^*	A_1	5.08	5.11	5.53	—	0.04	0.024
	π-π^*	B_2	7.23	6.91	7.48	—	1.16	1.083
	π-π^*	A_1	7.20	7.40	7.21	—	0.89	0.710
	n-π^*	B_1	3.78	3.73	7.99	—	—	—
	n-π^*	A_2	4.80	8.46	8.70	—	—	—
	σ-π^*	B_1	6.25	—	5.24	—	—	~0
Pyridazine	π-π^*	A_1	5.37	5.43	5.59	—	0.05	0.020
	π-π^*	B_2	5.36	5.01	5.04	—	0.01	0.182
	π-π^*	B_2	7.13	7.28	7.60	—	0.90	0.652
	π-π^*	A_1	7.74	7.41	7.29	—	0.87	0.954
	n-π^*	B_1	3.57	3.72	7.98	—	—	—
	n-π^*	A_2	3.86	8.12	8.60	—	—	—
	σ-π^*	A_2	6.47	—	5.08	—	—	~0

* These calculated values are already given in Ref. 4.

** See note *4.

*** These values are the ones for the monoion (XH^+) in pyridine and for the diion (H^+XH^+) in diazines, respectively.

**** See note *5.

and hydrogen bonding energies, while those for the diprotonation do not. Further, the stabilization energies due to monoprotonation are found to be about twice as large as those of the protonation to a monoprotonated compound. Thus, it may be concluded that the monoprotonations in these diazines occur more easily than do the diprotonations.

The changes in the molecular orbital (MO) energies upon protonation in pyridine are shown in Fig. 1. The pair of MO's in Fig. 1 connected with the arrow line belong to the same irreducible representation and have similar charge distributions. The orbital energy (ε) and the energy difference between these MO's, *i. e.*, the stabilization energy, $\Delta\varepsilon$, are given in Fig. 1. By protonation, all the MO's in a free compound are stabilized about 6 eV; the stabilization of the lone-pair MO (n in Fig. 1) is the largest, 10.12 eV, where the electrons in the MO (n^* in Fig. 1) in cation are mainly localized on the N–H$^+$ σ bond. That is, this large stabilization is due to the nitrogen lone pair in the n MO participating in the formation of the N–H$^+$ bond in the n^* MO. Some crossings of energy levels are seen in Fig. 1; particularly a σ MO belonging to the same symmetry as the n MO in free pyridine comes to exist in the higher-energy region in the cation. This result will be discussed in the next section in connection with the transition energy.

Transition Energy. The calculated transition energies obtained by considering the configuration interactions of limited numbers of configurations for various cations are summarized in Table 5, together with those for free molecules which have already been given in Ref. 4. The symmetry shown in this table indicates an irreducible representation of transitions in free and diprotonated compounds; these notations in the case of monoions correspond to the states in which the charge distributions are similar to those of the free and diprotonated compounds. As may be seen from the table, the lowest π–π^* transitions show a slight red shift, and the n–π^* transitions,[*4] a large blue shift, upon protonation. As was pointed out above, the σ–π^* transitions in the dications which belong to the same symmetries as the n–π^* transitions in the parent molecules appear in the lower-energy regions. It is hoped that these σ–π^* transitions in these ions will be identified experimentally. The observed values for lower π–π^* transitions in pyridinium and pyrazinium cations[2)] are also listed in the same table. The agreements between the calculated and observed values are fairly satisfactory.[*5] The values of the oscillator strength for several π–π^* transitions in several ions were calculated; these values are given in Table 5. The results indicate that the lowest π–π^* transitions in ions are generally intensified by protonation; this finding is in accordance with the experimental results.[2)]

The Orientation of Adding Protons. In the present treatment, it is assumed that the proton is situated in the direction of the lone-pair orbital of a nitrogen atom and lies on the molecular plane of a compound. Here, let us investigate the orientation of adding protons. At first, the proton in the pyridinium cation is oriented above the molecular plane, as is shown in Fig. 2. The calculated total energies for various out-of-plane angles, θ, are given in Table 6. The values in this table indicate that the configuration with $\theta = 0°$ is the most stable. From the obtained potential curve, the N–H$^+$ bending force constant is calculated to be 0.352 md/Å, compared with the observed value, 0.535 md/Å, in the NH_4^+ ion.[7)] Thus, our results seem to be fairly reasonable.

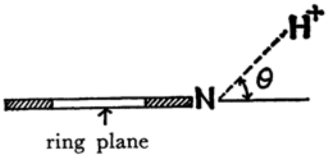
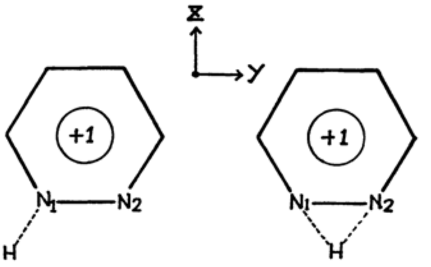


Fig. 2. The orientation of added proton in pyridinium cation.

TABLE 6. THE CONFIGURATION ENERGIES, ΔW FOR VARIOUS θ VALUES

θ	0°	30°	55°
ΔW	0	0.32	1.05

The next calculations are made on the monoprotonated pyridazinium cation, in which the proton is located on the vertical bisector of the N–N bond and is on the moleculer plane (B form). The configuration adopted in the previous sections was referred to the A form. These two configurations are shown in Fig. 3. The total energy obtained for the A form is more stable than that for the B form by about 2.8 eV. This destabilization for the B form is mainly due to the lack of any interaction between the proton and the MO which is constituted from the two nitrogen lone pairs and the anti-bonding type between these two lone pairs. This suggestion is supported by the following consideration. In Table 7 are collected the computed atomic dipole and its bond orders of the nitrogen atoms in pyridazine and its various cations.



A Form B Form

Fig. 3. The two forms in pyridazinium monoion.

TABLE 7. THE ATOMIC DIPOLE VALUES (IN UNIT OF DEBYE) AND ITS BOND ORDER OF NITROGEN ATOM IN PYRIDAZINE AND ITS IONS

		$P_{s_N y_N}$	$P_{s_N z_N}$	$\mu_A(D)$*
Parent	N_1	−0.137	−0.326	1.33
	N_2	0.137	−0.326	1.33
Monoion B	N_1	−0.151	−0.193	0.92
	N_2	0.151	−0.193	0.92
Monoion A	N_1	0.068	0.011	0.26
	N_2	0.151	−0.342	1.41
Diion	N_1	−0.011	−0.006	0.03
	N_2	0.011	−0.006	0.03

* $\mu_A = [(D_N P_{s_N y_N})^2 + (D_N \cdot P_{s_N \cdot z_N})^2]^{1/2}$

$D_N = -e\int \chi_{s_N} \boldsymbol{r} \chi_{Pr_N} d\tau \quad (\boldsymbol{r} = x, y, z)$

The listed values show that the large atomic dipoles in the free molecule are diminished by diprotonation. In the monoprotonated ions, the atomic dipole of the protonated nitrogen atom becomes very small and that of the non-protonated nitrogen becomes, inversely, stronger in the A form, whereas in the B form the atomic dipoles of both the nitrogen atoms have considerably large values and are directed toward the outsides of the N–H$^+$ bonds. The magnitudes of the atomic dipoles may be considered to represent the remaining ability of the corresponding lone pair for the bond forma-

---

[*4] The n^*–π^* one in ion in Table 5 refers to the n–π^* transition in a free molecule.

[*5] Recently, the second-lowest π–π^* transition energy in the pyridinium cation was estimated to be about 6 eV by Nishimoto (private communication). Our value may be somewhat smaller, as in the case of free molecules (see Ref. 4).

7) I. Nakagawa and S. Mizushima, This Bulletin, **28**, 589 (1955).

tion; so, in the B form, the nitrogen lone pairs still possess considerably strong bonding abilities, in spite of protonation. This is one reason for the lower stabilization of the B form. Accordingly, it may be concluded that, in the most stable configurations of these cations, the proton is situated on the bisector of the C=N–N angle and on the molecular plane, a position compatible with our assumed configurations in previous sections. This fact may be evidence that the nitrogen lone pairs in these compounds can be described approximately as sp^2 hybrids.

The Change in Fock's Operator. Lastly, let us examine the effect of protonation on the Fock's operators. The Fock's operator of the rth diagonal element is represented as follows:

$$F_{rr} = H_{rr} + G_{rr} \tag{1}$$

where H_{rr} is the electron-core interaction terms and G_{rr} is the electron-electron interaction term. With the superscript 0 denoting the free molecule and $+$, the monprotonated species, the differences in the quantities in Eq. (1) between the free and protonated compounds are given by:

$$\left.\begin{aligned} \Delta F_{rr} &= F_{rr}{}^{+} - F_{rr}{}^{0} \\ \Delta H_{rr} &= H_{rr}{}^{+} - H_{rr}{}^{0} \\ \Delta G_{rr} &= G_{rr}{}^{+} - G_{rr}{}^{0} = \Delta G_{rr}{}^{\sigma} + \Delta G_{rr}{}^{\pi} \end{aligned}\right\} \tag{2}$$

where $\Delta G_{rr}{}^{\sigma}$ and $\Delta G_{rr}{}^{\pi}$ represent the contributions to the electronic interactions between the other σ and π electrons, and the electron in the rth AO, respectively.

For example, the values of Fock's operators for the π AO's and the valence AO's in a nitrogen atom in pyridine and its cation are listed in Table 8. In the table, the ΔH_{rr} values are equal to the core-attraction energies to the rth AO due to the attached proton, and the ΔG_{rr} values are the changes in the electron interaction energies upon the redistribution which is caused by protonation. Here, $\Delta G_{rr}<0$ means the decrease in the electron-repulsion term and $\Delta G_{rr}<0$ is the increase in its term by protonation. From the table, it may be seen that the absolute values of ΔF_{rr} of the π AO's of the C_1 and C_2 positions (the number is the same in Table 1) do not become as much smaller as the values in C_3, contributed by the negative values of ΔG_{rr} terms. Further, it may be noticed that these negative ΔG_{rr} values are mainly contributed from the σ electronic terms. As to the ΔG_{rr} value in the nitrogen π AO, it is found to be nearly equal to zero; this shows that the redistributions in π and σ electrons around this AO result in mutual cancellation, in spite of the large increase in this AO population, as is shown in Table 1. Finally, it may be noticed that the redistributions in σ electron parts cannot be neglected in treating only the π electron systems in this type of cation.

TABLE 8. THE CHANGES OF FOCK'S OPERATOR (eV) BY PROTONATION IN PYRIDINE

AO**	ΔF_{rr}*	ΔH_{rr}	ΔG_{rr}*	$\Delta G^{\pi}{}_{rr}$	$\Delta G^{\sigma}{}_{rr}$
π_1	-4.67	-3.56	-1.11	-0.20	-0.91
π_2	-5.34	-4.03	-1.31	-0.23	-1.08
π_3	-5.66	-5.97	$+0.31$	$+0.96$	-0.65
π_4	-9.97	-9.47	-0.50	-0.89	$+0.39$
n_4	-5.50	-9.47	$+4.97$	—	—
s_4	-7.72	-9.62	$+1.90$	—	—

* $\Delta F_{rr}=\Delta H_{rr}+\Delta G_{rr}$, $\Delta G_{rr}=\Delta G^{\sigma}{}_{rr}+\Delta G^{\pi}{}_{rr}$

** The number is the same in Table 1.

The calculations were carried out on the HITAC 5020 E computer at the computer center of the University of Tokyo, whose kindness we hereby acknowledge.