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The Electronic Structures of Aminopyridines and Their Mono- and Di-Protonated Cations

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Using a semi-empirical ASMO SCF method for valence electron systems previously proposed by the present authors, the electronic structures of aminopyridines and their mono- and di-protonated cations are calculated. It is explained that the mono-protonation occurs on the ring nitrogen atoms and the di-protonation takes place on the nitrogen atoms both in the ring and the amino group. The electron migration to the added protons are calculated to be about 0.7 e for all the cations treated. The calculated results for $n-\pi^*$ and $\pi-\pi^*$ singlet transitions of aminopyridines and their protonated cations show fairly good agreement with the experimental results. The electronic structures of pyridone imines, the tautomeric isomers of aminopyridines, are also briefly discussed.

Mittels eines semiempirischen ASMO SCF-Verfahrens wird die Elektronenstruktur von Aminopyridinen und ihrer mono- und diprotonierten Kationen berechnet. Die erste Protonierung findet am N-Atom im Ring und die zweite an der Aminogruppe statt. Für die Elektronenverschiebung zu den angelagerten Protonen ergibt sich in allen Fällen etwa 0,7 e. Die berechneten $n-\pi^*$- und $\pi-\pi^*$-Singulettübergänge zeigen befriedigende Übereinstimmung mit dem Experiment. Schließlich wird noch die Elektronenstruktur von Pyridoniminen diskutiert.

Calcul des structures électroniques des aminopyridines et de leurs cations mono- et di-protonés, en utilisant une méthode semi-empirique ASMO SCF pour les électrons de valence proposée précédemment par les auteurs. On explique la mono-protonation sur les atomes d'azote du cycle et la di-protonation sur les atomes d'azote du cycle et du groupe amine. Le transfert d'électron sur les protons supplémentaires est de l'ordre de 0,7 e pour tous les cations étudiés. Les résultats calculés pour les transitions singulets $n\rightarrow\pi^*$ et $\pi\rightarrow\pi^*$ des aminopyridines et de leurs cations sont en bon accord avec l'expérience. Les structures électroniques des pyridone imines, tautomères des aminopyridines, sont brièvement discutées.

Introduction

Theoretical studies on the electronic structures of aminopyridines (AP's) have been done by the several authors [15, 14, 13, 18, 10, 3, 23]. pk_a values of AP's have been discussed by means of π electron calculations by Nakajima and Pullman [15]. Transition energies of 4-AP, its tautomeric isomer (4-pyridone imine) and their protonated compounds have been studied by Morita [14]. Afterwards the transition energies and the charge distribution of AP's have been calculated [13, 18, 10, 3, 23] and also the equilibrium between the tautomers by Polansky and Grassberger [18]. However, the di-cations of AP's have not been treated by the theoretical study.

In our previous paper, a theoretical treatment of the effects of protonation on the electronic structures of pyridine and diazines was presented [9]. In the present paper, using a semi-empirical ASMO SCF method for valence electron

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systems previously proposed by the present authors [25], the protonation sites of AP's will firstly be discussed. Then, the calculated results of charge distribution and the transition energies of AP's and their protonated cations will be presented. Finally, the tautomerism between AP's and pyridone imines (PI's), and the electronic structures of PI's will be examined.

Theoretical

In the present paper, calculations are made by a semi-empirical ASMO SCF method for valence electron systems previously proposed by the present authors [25]. This is a modified method of our previous one [26] in which the zero-differential overlap approximation except for the one-center exchange integrals are introduced. The one-center integrals[1] are estimated with an aid of empirical values [8] and the two-center Coulomb integrals are evaluated by the Ohno approximation [16].

The protonation energy, ΔE, is defined as follows:

$$\Delta E = E_{\text{total}}(\text{free}) - E_{\text{total}}(\text{protonated}),$$

where E_{total} is the sum of the total electronic energy of the valence electrons, $E_{\text{electronic}}$, and the repulsion energy between cores, E_{core}, as,

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{core}}\,.$$

If ΔE is calculated on the basis of the point charge model, the calculated protonation energy becomes too small, while it becomes rather large when the positive hole approximation [17, 19] is adopted. Thus in the present treatment, an intermediate approximation, a modified one of Dewar and Klopman's proposal [6], is adopted.

$$E_{\text{core}} = \sum_{A<B} \left(C_{AB} + (Z_A Z_B e^2/R_{AB} - C_{AB}) \exp(-\alpha_{AB} R_{AB}^2)\right)$$

$$C_{AB} = \sum_{r}^{\text{on A}} \sum_{s}^{\text{on B}} n_r n_s (rr \mid ss)$$

$$\alpha_{AB} = \sqrt{\alpha_{AA}\alpha_{BB}}$$

where Z_A is the number of the valence electrons belonging to the neutral atom A; R_{AB}, the distance between the atoms A and B; n_r, the number of the valence electrons occupying the rth atomic orbital (AO) in the valence state; $(rr \mid ss)$, the two-center Coulomb repulsion integral; and $\sum_{r}^{\text{on A}}$ denotes the summation over all the valence orbitals belonging to the A atom.

The atomic parameter α_{AA} is chosen to give the heats of formation for molecules in a similar manner as Dewar and Klopman's [6]. Reproducing the heats of

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[1] The following one-center Coulomb repulsion integral is revised in the present paper.

$$(pp \mid p'p') = (pp \mid pp) - 2(pp' \mid pp')$$

where p and p' are the different p orbitals centered at the same atom and $(pp' \mid pp')$ is the one-center exchange integral.

formation of benzene and pyridine [22, 11], one obtains 0.376 (Å)$^{-2}$ for α_{HH}, 0.539 (Å)$^{-2}$ for α_{CC}, and 1.229 (Å)$^{-2}$ for α_{NN}.

Their ring structures are assumed tentatively to be equal to that of pyridine [21]. The C–N bond length in the amino group and the N–H bond lengths are taken respectively as 1.37 Å and 1.01 Å, and the CNH angle is taken as 120°. For AP's, PI's and the products obtained from them by protonation of the ring nitrogen atom, the planarity is also assumed. The protonated amino group is taken to be tetrahedral. The N–H$^+$ bond distance is taken as 1.032 Å, as in the NH_4^+ ion. The numbering of ring atoms follows the chemical use; the nitrogen atom of the amino group has number 7.

Protonation Sites of Aminopyridines and pK_a

The calculated protonation energies of AP's are presented in Table 1 for both 1-mono-protonated (1-MP) and 7-mono-protonated (7-MP) AP's. For each pair of cations, the calculated values indicate that 1-MP-cation is more stable than 7-MP-cation. This is compatible with the experimental result by the ultraviolet spectra of mono-protonated 3-AP which shows the protonation occuring on the ring nitrogen atom [1].

The basicity of aromatic heterocycles can be related to the protonation energy, ΔE, of a base so far as the entropy of protonation is assumed to be a constant or proportional to the protonation energy [12, 5, 24]. Thus the following relations are obtained:

$$pK_{a1} \propto \Delta E_{\mathrm{MP}},$$

$$pK_{a2} \propto (\Delta E_{\mathrm{DP}} - \Delta E_{\mathrm{MP}}).$$

Table 1 shows no agreement between the calculated ΔE_{MP} values and the observed pK_a values for the mono-protonation. This discrepancy is a defect of the present treatment which may be caused partly by the parametrization and partly by the assumption on the molecular geometry of the ion, since Elliott and Mason reported that the variation in the pK_a value is primarily due to enthalpy changes rather than entropy changes [7].

Table 1. *pK_a values (in water at 20° C) and the calculated protonation energies (ΔE) of aminopyridines (in eV unit)*

	Mono-Protonation ΔE_{MP}			Di-Protonation		
	1-MP-	7-MP-	pK_{a1}	ΔE_{DP}	$\Delta E_{\mathrm{DP}} - \Delta E_{\mathrm{MP}}$	pK_{a2}
2-AP	3.82	1.71	6.86[a]	0.22	−3.60	−7.6[b]
3-AP	3.99	1.73	5.98[a]	1.24	−2.75	−1.5[c]
4-AP	4.03	1.30	9.17[a]	0.92	−3.11	−6.3[b]

[a] Albert, A., Goldacre, R. J., Phillips, J.: J. chem. Soc. **1948**, 2240.

[b] Bender, M. L., Chow, Y.-L.: J. Amer. chem. Soc. **81**, 3929 (1959).

[c] Ref. [1].

However, on the case of the di-cations, the orders of magnitude are the same in both series. Moreover, the negative values of pK_{a2} indicate that the dissociated side is predominant at the equilibrium. This is in accord with the calculated results that the di-protonated cations are all unstable compared with the 1-mono-protonated cations.

Charge Distribution of Aminopyridines and Their Protonated Cations

The calculated charge densities (for both the σ and π AO's) of AP's and the difference of charge densities between the protonated cations and free compounds are presented in Table 2. For each AP, the π electron densities in the present calculation run almost parallel to those in the SCF calculation of π electrons by Kwiatkowski [10]. The formal π charge of the ring nitrogen atom, however, is more negative in the present treatment than that in the treatment of Kwiatkowski.

The electron migrations to the added protons are calculated to be about 0.7 e for every cations (in Table 2). In every 1-MP-cation, about the half of the electron density on the added hydrogen atom is supplied by the ring nitrogen atom, where the σ electron density decreases largely with slight increase of the π electron

Table 2. *Charge densities of aminopyridines and the differences of charge densities between the protonated cations and free compounds*

i) 2-AP and their protonated cations

		2-AP	1-MP-	7-MP-	DP-
N_1	σ	4.370	−0.506	−0.043	−0.528
	π	1.465	+0.163	−0.079	+0.102
C_2	σ	2.515	+0.070	+0.066	+0.114
	π	0.686	+0.023	+0.214	+0.255
C_3	σ	3.094	−0.028	−0.020	−0.037
	π	1.213	−0.060	−0.118	−0.197
C_4	σ	2.959	+0.039	−0.002	+0.052
	π	0.838	−0.067	+0.008	−0.093
C_5	σ	3.096	−0.038	+0.014	−0.023
	π	1.181	−0.086	−0.133	−0.189
C_6	σ	2.721	+0.075	+0.016	+0.098
	π	0.738	+0.062	−0.015	−0.006
N_7	σ	3.872	−0.032	−0.501	−0.512
	π	1.879	−0.035	+0.018	+0.007
H_3		0.948	−0.045	−0.013	−0.059
H_4		1.006	−0.057	−0.049	−0.103
H_5		0.949	−0.044	−0.038	−0.084
H_6		1.041	−0.078	−0.046	−0.120
H_7^1		0.703	−0.007	$+0.003_{av.}$[a]	$-0.024_{av.}$[a]
H_7^2		0.725	−0.040		
H_1		—	+0.693	—	+0.683
H_7^3		—	—	+0.717	+0.690

[a] The average value.

Table 2 (continued)

ii) 3-AP and their protonated cations

		3-AP	1-MP-	7-MP-	DP-
N_1	σ	4.341	−0.529	−0.040	−0.510
	π	1.342	+0.173	+0.002	+0.177
C_2	σ	2.765	+0.077	−0.014	+0.054
	π	0.866	+0.056	−0.118	−0.083
C_3	σ	2.834	−0.035	+0.073	+0.032
	π	0.991	−0.069	+0.242	+0.168
C_4	σ	3.006	+0.048	−0.027	+0.020
	π	0.969	−0.080	−0.111	−0.181
C_5	σ	3.068	−0.039	+0.006	−0.032
	π	1.083	−0.071	−0.006	−0.072
C_6	σ	2.747	+0.082	+0.026	+0.098
	π	0.830	+0.025	−0.136	−0.110
N_7	σ	3.758	−0.001	−0.623	−0.565
	π	1.919	−0.034	+0.046	+0.020
H_2		1.026	−0.076	−0.016	−0.086
H_4		0.989	−0.056	−0.013	−0.068
H_5		0.959	−0.045	−0.047	−0.090
H_6		1.030	−0.076	−0.043	−0.113
H_7^1		0.740	−0.028	$+0.019_{av.}$	$-0.022_{av.}$
H_7^2		0.738	−0.032		
H_1		—	+0.709	—	+0.667
H_7^3		—	—	+0.758	+0.717

iii) 4-AP and their protonated cations

		4-AP	1-MP-	7-MP-	DP-
N_1	σ	4.362	−0.512	−0.032	−0.493
	π	1.433	+0.173	−0.117	+0.072
C_2, C_6	σ	2.718	+0.073	+0.022	+0.086
	π	0.738	+0.043	−0.008	±0
C_3, C_5	σ	3.113	−0.037	−0.028	−0.059
	π	1.221	−0.074	−0.113	−0.163
C_4	σ	2.730	+0.038	+0.072	+0.098
	π	0.765	−0.055	+0.223	+0.139
N_7	σ	3.826	−0.004	−0.532	−0.502
	π	1.886	−0.059	+0.020	−0.001
H_2, H_6		1.039	−0.073	−0.051	−0.117
H_3, H_5		0.943	−0.042	−0.013	−0.057
H_7		0.727	−0.024	+0.007	−0.028
H_1		—	+0.697	—	+0.662
H_7^3		—	—	+0.734	+0.699

density. As Table 3 shows this decrease of the σ electron densities are due mostly to the lone pair orbitals of the ring nitrogen atom. These features remarkably resemble the protonated cations of pyridine and diazines [9].

The π bond orders of the bonds between the nitrogen atom in the amino group and the ring carbon atom are not so large as those of the other bonds in AP's

Table 3. AO *charge densities of the ring nitrogen atoms*

	$2s$	$2p_n$[a]	$2p_\sigma$	$2p_\pi$
2-AP	1.542	1.720	1.108	1.465
1-MP-	1.434	1.209	1.222	1.628
DP-	1.434	1.211	1.196	1.567
3-AP	1.549	1.707	1.085	1.342
1-MP-	1.431	1.187	1.194	1.515
DP-	1.463	1.216	1.180	1.519
4-AP	1.547	1.710	1.105	1.433
1-MP-	1.432	1.202	1.215	1.606
DP-	1.439	1.225	1.205	1.505

[a] Lone pair orbital.

Table 4. π *Bond orders of aminopyridines and their differences between protonated cations and free compounds*

	Bond	AP	1-MP-	7-MP-	DP-
2-AP	1–2	0.562	−0.058	+0.023	−0.060
	2–3	0.585	+0.011	+0.106	+0.152
	3–4	0.691	+0.009	−0.069	−0.105
	4–5	0.631	−0.048	+0.055	+0.038
	5–6	0.680	+0.070	−0.040	−0.014
	6–1	0.597	−0.101	+0.031	−0.030
	2–7	0.396	+0.060	−0.203	−0.199
3-AP	1–2	0.631	−0.074	+0.004	−0.062
	2–3	0.638	+0.017	+0.003	+0.054
	3–4	0.642	−0.045	−0.040	−0.043
	4–5	0.661	+0.007	+0.041	+0.013
	5–6	0.669	+0.010	−0.039	−0.002
	6–1	0.625	−0.048	−0.002	−0.058
	3–7	0.284	+0.066	−0.053	−0.079
4-AP	1–2	0.597	−0.084	+0.036	−0.022
	2–3	0.689	+0.064	−0.044	−0.014
	3–4	0.597	−0.051	+0.056	+0.050
	4–7	0.373	+0.092	−0.162	−0.171

Table 5. *Dipole moments of aminopyridines (in Debye unit)*

		2-AP (Direction)[a]	3-AP (Direction)[a]	4-AP (Direction)[a]
Calcd.	$\mu_Q(\pi)$	1.44 (6°)	2.18 (54°)	2.79 (90°)
	$\mu_Q(\sigma)$	1.70 (112°)	1.05 (135°)	0.33 (90°)
	μ_{atom}	0.59 (49°)	0.99 (71°)	1.16 (90°)
	μ_{total}	2.47 (61°)	3.55 (76°)	4.29 (90°)
Obsd.[b]	μ	2.17	3.19	3.79

[a] The direction of the dipole is represented by the angle measured from the x axis toward y axis, both in the plane of the molecule, the y axis bisecting the atoms N_1 and C_4.

[b] Morino, Y.: see Ref. [20].

(Table 4). The π bond order of the C–N (amino) bond is the smallest in 3-AP. This shows that the conjugation of these C–N bonds are not so tight, especially the C–N (amino) bond of 3-AP is the weakest. It is also found from Table 4 that the conjugation of these bonds increase by the protonation on the ring nitrogen atoms and decrease by the protonation on the nitrogen atoms in the amino group.

The calculated dipole moments of AP's are larger by about 0.4 Debye than the experimental values for all AP's (Table 5). The components of the calculated values are also presented in terms of the contribution from the formal charge, μ_Q, and that from the atomic dipole, μ_{atom}.

Energy Changes of MO's by Protonation

The energy levels of π (the full lines) and some lone pair (n) or σ (the dotted lines) molecular orbitals (MO's) for 4-AP and its protonated cations are shown in Fig. 1 to reveal the change in energy of MO's by protonation. The dotted lines connect the MO's which have similar charge distributions and belong to the same irreducible representation. The occupied π MO's of the MP-cations are more stable than those of the free compounds by about 5 eV. The lone pair MO of 4-AP is stabilized about 13 eV by the protonation upon the ring nitrogen atom and plays so an important role in the formation of the N–H$^+$ bond. It is also found from the figure that the stabilization energies of the occupied MO's by the di-protonation are nearly equal to the sum of those by the protonations on the nitrogen atoms in the ring and the amino group.

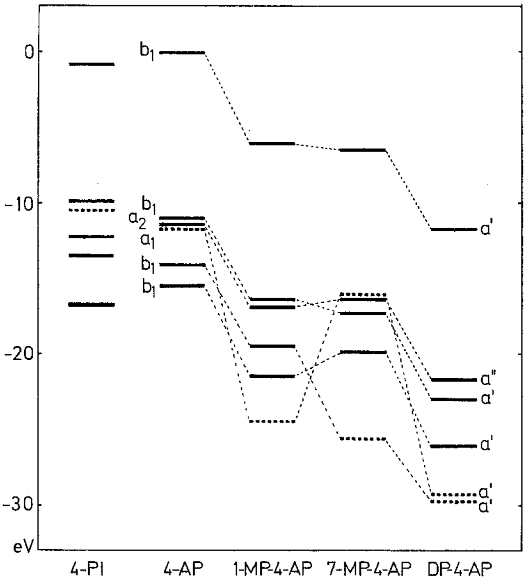

Fig. 1. Molecular orbital energy diagram for 4-aminopyridine, its protonated cations and 4-pyridone imine. (The full lines indicate the π MO levels and the dotted lines are the lone pair or σ MO levels.)
* This is a π-type orbital contributing to the N–H bonds in the $-N^+H_3$

Table 6. *Singlet-singlet transition energies of aminopyridines and their protonated cations (ΔE), and the oscillator strengths (f) and the polarization directions of the transition*

Compd.	Transition	State	Calcd.			Obsd.	
			ΔE_{eV}	f	Polarization direction[a]	ΔE_{eV}	ε
2-AP	$n-\pi^*$	A''	4.64	0.0001	z	4.14^{b}	—
	$n-\pi^*$	A''	5.57	0.0001	z	—	
	$\pi-\pi^*$	A'	4.76	0.16	$(17^{\circ})_{xy}$	4.32^{c}	3800
	$\pi-\pi^*$	A'	5.48	0.02	$(121^{\circ})_{xy}$	5.41^{c}	9400
	$\pi-\pi^*$	A'	7.14	0.79	$(127^{\circ})_{xy}$	—	
1-MP-2-AP	$\pi-\pi^*$	A'	4.51	0.24	$(5^{\circ})_{xy}$	4.13^{c}	5700
	$\pi-\pi^*$	A'	5.31	0.03	$(113^{\circ})_{xy}$	5.41^{c}	8900
	$\pi-\pi^*$	A'	6.93	0.95	$(106^{\circ})_{xy}$	—	
7-MP-2-AP	$n-\pi^*$	A''	4.29	$\sim 10^{-6}$	z	$(4.13)^{d}$, $(4.31)^{e}$	
	$n-\pi^*$	A''	5.25	$\sim 10^{-5}$	z	—	
	$\pi-\pi^*$	A'	4.69	0.12	$(155^{\circ})_{xy}$	$(4.75)^{d}$, $(4.66)^{e}$	
	$\pi-\pi^*$	A'	5.10	0.01	$(25^{\circ})_{xy}$	$(6.17)^{d}$	
	$\pi-\pi^*$	A'	6.57	0.35	$(99^{\circ})_{xy}$	—	
DP-2-AP	$\pi-\pi^*$	A'	4.57	0.18	$(170^{\circ})_{xy}$	—	
	$\pi-\pi^*$	A'	5.19	0.009	$(23^{\circ})_{xy}$	—	
	$\pi-\pi^*$	A'	6.78	0.85	$(89^{\circ})_{xy}$	—	
3-AP	$n-\pi^*$	A''	4.21	0.0003	z	4.09^{b}	—
	$n-\pi^*$	A''	5.37	$\sim 10^{-5}$	z	—	
	$\pi-\pi^*$	A'	4.50	0.13	$(156^{\circ})_{xy}$	4.31^{c}	3000
	$\pi-\pi^*$	A'	5.03	0.02	$(47^{\circ})_{xy}$	5.37^{c}	8200
	$\pi-\pi^*$	A'	6.98	0.77	$(59^{\circ})_{xy}$	—	
1-MP-3-AP	$\pi-\pi^*$	A'	4.08	0.19	$(155^{\circ})_{xy}$	3.94^{c}	3600
	$\pi-\pi^*$	A'	4.84	0.01	$(40^{\circ})_{xy}$	4.96^{c}	7600
	$\pi-\pi^*$	A'	6.34	0.50	$(55^{\circ})_{xy}$	5.90^{c}	—
7-MP-3-AP	$n-\pi^*$	A''	4.34	$\sim 10^{-5}$	z	$(4.31)^{d}$, $(4.30)^{e}$	
	$n-\pi^*$	A''	4.54	0.0008	z	—	
	$\pi-\pi^*$	A'	4.88	0.08	$(29^{\circ})_{xy}$	$(4.75)^{d}$, $(4.63)^{e}$	
	$\pi-\pi^*$	A'	5.20	0.02	$(47^{\circ})_{xy}$	$(6.17)^{d}$	
	$\pi-\pi^*$	A'	6.49	0.32	$(33^{\circ})_{xy}$	—	
DP-3-AP	$\pi-\pi^*$	A'	4.76	0.12	$(13^{\circ})_{xy}$	4.77^{f}	—
	$\pi-\pi^*$	A'	5.29	0.02	$(76^{\circ})_{xy}$	5.28^{f}	—
	$\pi-\pi^*$	A'	6.94	0.66	$(58^{\circ})_{xy}$	—	
4-AP	$n-\pi^*$	B_1	4.82	0.0005	z	—	
	$n-\pi^*$	A_2	5.13	0	—	—	
	$\pi-\pi^*$	B_2	5.01	0.0*b*8	x	4.68^{c}	2400
	$\pi-\pi^*$	A_1	5.35	0.03	y	5.15^{c}	14000
	$\pi-\pi^*$	A_1	6.94	1.13	y	—	
	$\pi-\pi^*$	B_2	6.97	0.78	x	—	
1-MP-4-AP	$\pi-\pi^*$	B_2	4.84	0.02	x	—	
	$\pi-\pi^*$	A_1	5.10	0.17	y	4.72^{c}	16500
	$\pi-\pi^*$	B_2	6.51	0.49	x	—	
	$\pi-\pi^*$	A_1	6.67	1.01	y	—	

Table 6 (continued)

			Calcd.			Obsd.	
Compd.	Transition	State	ΔE_{eV}	f	Polarization direction[a]	ΔE_{eV}	ε
7-MP-4-AP	$n-\pi^*$	A'	3.89	0.0003	$(89°)_{yz}$	$(4.31)^d$, $(4.36)^e$	
	$n-\pi^*$	A''	4.95	$\sim 10^{-6}$	x	—	
	$\pi-\pi^*$	A''	4.62	0.15	x	$(4.75)^d$, $(4.75)^e$	
	$\pi-\pi^*$	A'	5.20	0.02	$(9°)_{yz}$	$(6.17)^d$	
	$\pi-\pi^*$	A''	6.77	0.04	x	—	
	$\pi-\pi^*$	A'	6.81	0.79	$(4°)_{yz}$	—	
DP-4-AP	$\pi-\pi^*$	A''	4.59	0.20	x	—	
	$\pi-\pi^*$	A'	5.31	0.003	$(15°)_{yz}$	—	
	$\pi-\pi^*$	A'	7.06	1.14	$(2°)_{yz}$	—	
	$\pi-\pi^*$	A''	7.54	0.34	x	—	

[a] $(\alpha)_{xy}$ indicates the direction represented by the angle α measured from the x axis toward y axis, defined in footnote a, Table 5.

[b] Misra, T. N.: Indian J. Physics **35**, 420 (1961).

[c] Mason, S. F.: J. chem. Soc. **1960**, 219.

[d] The data of pyridine. Innes, K. K., Byrne, J. P., Ross, I. G.: J. molecular Spectroscopy **22**, 125 (1967).

[e] The datum of picolines. Sponer, H., Rush, J. H.: J. chem. Physics **20**, 1847 (1952).

[f] Ref. [1].

Transition Energies of Aminopyridines and Their Protonated Cations

The calculated singlet-singlet transition energies of AP's and their protonated cations, and the oscillator strengths and the polarization directions of transitions are presented in Table 6 together with experimental results. The calculated energies are obtained by considering the configuration interactions of limited numbers of configurations which include all the $\pi-\pi^*$ and $n-\pi^*$ singly-excited states with the lower transition energies than 10 eV.

Though the calculated oscillator strengths of the two lower $\pi-\pi^*$ transitions of 2- and 3-AP's do not agree with experimental results, the calculated transition energies of three AP's are in fair agreement with the experimental values. The calculated polarization directions of the two lower $\pi-\pi^*$ transitions of AP's in the present treatment are very similar to the results of Kwiatkowski by means of the π electron approximation [10].

The calculated transition energies of the 1-MP-cations are also in accord with experimental results. The red shifts and the increasing of transition probability of the lowest $\pi-\pi^*$ transitions of 2- and 3-AP's by protonation on the ring nitrogen atoms are found in both calculated and experimental results of the 1-MP-2- and 3-cations. Because the electronic spectra for the protonated aniline are found to be similar to those for benzene or toluene [20], the experimental data for both pyridine and corresponding picolines are listed to be compared with the calculated results for the 7-MP-cations. The fair agreements between the calculated energies of the lowest $n-\pi^*$ and $\pi-\pi^*$ transitions of the 7-MP-cations and the experimental data of pyridine and the corresponding picolines show the same features as in the case of aniline. In the DP-3-cation, satisfactory results are also contained for the $\pi-\pi^*$ transition energies.

Electronic Structures of Pyridone Imines

PI's are known as the tautomeric isomers of AP's [13, 18], so the electronic structures of PI's will be briefly discussed here. The total energies of AP's and PI's presented in Table 7 suggests that PI's are more unstable than corresponding AP's, especially unstable is 3-PI which is not observed experimentally [2]. So the AP's are indicated to be the predominant isomers by both the calculation and the experiment, but the order of magnitude of the total energy differences is the reverse for that of the tautomeric equilibrium constants. This discrepancy may be ascribed to the reason stated above. The predominance of the amino form in the present amine-imine tautomerism is the same as in the case of DNA bases as pointed out by Berthod and Pullman [4].

The calculated charge densities of PI's are shown in Table 8. The charge densities on the ring nitrogen atoms of PI's resemble closely those on the ring

Table 7. *Total energies of aminopyridines and pyridone imines (in eV unit) and the tautomeric equilibrium constant,* $K_{\mathrm{taut.}}$

	AP	PI[a]	$k_{\mathrm{taut.}}$[b]
2-Isomer	−1113.70	−1112.36 (+1.34)	2×10^5
3-Isomer	−1113.09	−1111.18 (+1.91)	—
4-Isomer	−1113.43	−1111.80 (+1.63)	2×10^3

[a] The values in parentheses are the differences between PI's and AP's.
[b] $K_{\mathrm{taut.}}$ = AP/PI. Ref. [2].

Table 8. *Charge densities of pyridone imines*

		2-PI	3-PI	4-PI
N_1	σ	3.876	3.793	3.817
	π	1.668	1.518	1.693
C_2	σ	2.543	2.901	2.777
	π	0.665	0.981	0.863
C_3	σ	3.103	2.739	3.125
	π	1.140	0.808	1.145
C_4	σ	2.985	3.090	2.704
	π	0.859	0.944	0.687
C_5	σ	3.043	3.022	3.109
	π	1.163	1.027	1.127
C_6	σ	2.789	2.811	2.781
	π	0.839	0.997	0.874
N_7	σ	4.396	4.322	4.389
	π	1.666	1.725	1.612
H_1		0.701	0.755	0.729
H_2		—	0.965	1.009
H_3		0.929	—	0.926
H_4		0.991	0.941	—
H_5		0.947	0.960	0.915
H_6		1.007	0.991	1.006
H_7		0.689	0.709	0.698

Table 9. *Calculated dipole moments of pyridone imines (in Debye unit)*

		2-PI (Direction)[a]	3-PI (Direction)[a]	4-PI (Direction)[a]
Calcd.	$\mu_Q(\pi)$	6.29 (174°)	9.95 (45°)	9.90 (90°)
	$\mu_Q(\sigma)$	2.55 (50°)	2.31 (39°)	2.85 (69°)
	μ_{atom}	0.39 (110°)	1.82 (82°)	1.56 (122°)
	μ_{total}	5.59 (148°)	9.21 (53°)	8.76 (102°)

[a] See footnote a in Table 5.

Table 10. *Singlet-singlet transition energies of pyridone imines* (ΔE)

			Calcd.			Obsd.
	Transition	State	ΔE_{eV}	f	Polarization direction[a]	ΔE_{eV}
2-PI	$n-\pi^*$	A''	4.26	0.0001	z	—
	$n-\pi^*$	A''	5.58	0.002	z	—
	$\pi-\pi^*$	A'	4.01	0.23	$(13°)_{xy}$	(3.91)[b]
	$\pi-\pi^*$	A'	5.30	0.21	$(131°)_{xy}$	(4.94)[b]
	$\pi-\pi^*$	A'	6.15	0.06	$(79°)_{xy}$	—
3-PI	$n-\pi^*$	A''	3.54	0.001	z	—
	$n-\pi^*$	A''	4.64	0.004	z	—
	$\pi-\pi^*$	A'	2.78	0.10	$(149°)_{xy}$	—
	$\pi-\pi^*$	A'	4.36	0.15	$(35°)_{xy}$	—
	$\pi-\pi^*$	A'	5.44	0.23	$(11°)_{xy}$	—
4-PI	$n-\pi^*$	A''	3.81	0.001	z	—
	$n-\pi^*$	A''	5.31	0.002	z	—
	$\pi-\pi^*$	A'	4.34	0.01	$(4°)_{xy}$	—
	$\pi-\pi^*$	A'	4.71	0.53	$(89°)_{xy}$	(4.63)[b]
	$\pi-\pi^*$	A'	5.90	0.14	$(175°)_{xy}$	—

[a] See the footnote a in Table 6.

[b] The data of 1-methyl-2-pyridone imine or 1-methyl-4-pyridone imine. See the footnote c in Table 6.

nitrogen atoms of the corresponding 1-MP-cations. The total $(\sigma+\pi)$ charge densities on the imino nitrogen atoms of PI's are larger than those on the amino nitrogen atoms of AP's, but the reverse is for the π electron densities because of the larger conjugation with the ring in PI's than in AP's. Namely, the values of the π bond orders of PI's are as follows: 0.657 for 2-PI, 0.562 for 3-PI, 0.688 for 4-PI.

The calculated dipole moments of PI's (in Table 9) are twice or more times larger than those of AP's (in Table 5). The greater part of these large values dues to the π charge components, $\mu_Q(\pi)$.

The calculated results for the singlet-singlet transitions of PI's are presented in Table 10 together with experimental results for those of corresponding 1-methyl-PI's. The lowest $n-\pi^*$ and $\pi-\pi^*$ transition energies of PI's are calculated to have smaller values than AP's.

The calculations are carried out on a HITAC 5020 E computer at the computation center of Tokyo University.

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