Effects of Protonation on the Electronic Structure and Spectra of Nitrogen Heterocycles

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In the previous papers[1-3], we have reported detailed theoretical studies about the protonation effects on the electronic spectra of some nitrogen heterocycles. In these reports, the interaction between proton and a nitrogen heterocycle has been treated by various approximations. Among these, the following two are most representative.

i) It has been assumed that there is no transfer of non-bonding electrons on nitrogen toward proton but bare proton is located near the nitrogen atom of neutral molecule. Thus, the electrostatic potential due to proton has been added to the core potential in the total π-electronic Hamiltonian and nuclear attraction integrals which arise owing to this potential have been computed theoretically employing the usual Slater $2p\pi$ AO's.

ii) It has been considered that there is a strong charge transfer from nitrogen atom to proton leading to covalent binding between them and molecular integrals have been evaluated semi-empirically using valence-state ionization potential and electron affinity of N^+ atom.

By means of the semi-empirical Hartree-Fock SCF MO's obtained with these integrals, the electronic spectra of protonated nitrogen heterocycles have been calculated. The calculated spectra by the method i have been in very good agreement with those experimentally obtained. However, the calculation with the method ii has led to a result which is in rather poor agreement with the experimental values. A careful examination of these results has led to the following conclusion. In the case of the later method, the inductive charge displacement in σ-core caused by the charge transfer of non-bonding electrons from nitrogen atom toward proton may not be appropriately accounted, where the core potential is very deep at nitrogen and the same as that in the neutral molecule, at the carbon atoms. In the case of the method i), however, the displacement in σ-core may be appropriately taken into consideration by the formal use of the electrostatic proton potential, which may be the cause of the superiority of this method.

If the unsatisfactory results obtained with the method ii originates from the neglect of the inductive charge displacement in σ-core caused by protonation as described above, one may be able to improve the results by taking into consideration the inductive displacement in σ-core in some appropriate manner. In this respect, we have calculated the electronic structures and spectra of pyridinium ion and pyrazinium diion employing

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[1] N. Mataga and S. Tsuno, *Naturwiss.*, **45**, 333 (1958).

[2] S. Mataga and N. Mataga, *Z. Physik. Chem. N. F.*, in press.

[3] S. Mataga and N. Mataga, This Bulletin, **32**, 511 (1959).

the self-consistent electronegativity method proposed by Brown and Heffernan[4] which may be regarded as an improvement of the method ii. Our calculation procedure is essentially the same as that of Brown and Heffernan but a little different from theirs in some details of actual compution procedures. In the present paper, we shall report the results of this calculation with some discussions. In addition, results of some critical studies about the effects of protonation on the core energies and diagonal elements of Fock's Hamiltonian, $F_{\mu\mu}$'s, will be given comparing the present results with previous ones.

Application of Self-Consistent Electronegativity (SCE) Method

In SCE method, it is assumed that Slater's rules for effective charges of atoms are applicable for continuous variation in electron density. Accordingly, for atoms in the first row of the periodic table the relationship is

$$Z_\mu = N_\mu - 1.35 - 0.35\ (\sigma_\mu + P_{\mu\mu}) \qquad (1)$$

where N_μ is the atomic number of μ atom and σ_μ is the number of σ-electrons associated with μ atom in the molecular framework, e.g. 3 for carbon and positively charged nitrogen in pyridinium ion. $P_{\mu\mu}$ is the π-electron density on μ atom. If this variation of Z_μ with $P_{\mu\mu}$ is included in the SCF MO procedure, in addition to the usual functional dependence of the SCF matrix elements upon the charge distribution, the various molecular integrals become functions of $P_{\mu\mu}$ from their dependence on Z_μ. The methods of allowing for this variation are as follows.

Firstly, the form of the relationship between the valence state ionization potential I_μ and Z_μ should be established.

Various valence-state ionization potentials have been calculated from the experimental term values of atomic spectra. If I_μ's are plotted against Z_μ's for the (sp^3, V_4) valence state of the iso-electronic series, C, N^+, O^{2+} and for the (sp^4, V_3) valence state of the iso-electronic series, C^-, N, O^+, respectively, the curves are accurately parabolic:

$$I_\mu(sp^3,\ V_4) = 3.490\ Z_\mu^2 - 8.541\ Z_\mu + 2.446 \qquad (2)$$

$$I_\mu(sp^4,\ V_3) = A_\mu(sp^3,\ V_4) = 3.730\ Z_\mu^2 - 16.285\ Z_\mu + 14.108 \qquad (3)$$

where A_μ is the valence state electron affinity. These equations are used for evaluating I_{C^+} and I_{N^+}. Then, from these eqs., the mono-centric inter-electronic coulomb repulsion integral, $\gamma_{\mu\mu}$, is easily obtained as,

$$\gamma_{\mu\mu}(sp^3,\ V_4) = I_\mu(sp^3,\ V_4) - A_\mu(sp^3,\ V_4) = -0.240\ Z_\mu^2 + 7.743\ Z_\mu - 11.662 \qquad (4)$$

The two-center electronic coulomb repulsion integral, $\gamma_{\mu\nu}$, was evaluated as in our previous works[2,5-7] from the formula,

$$\gamma_{\mu\nu} = e^2/(a_{\mu\nu} + r_{\mu\nu}) \qquad (5)$$

where parameter $a_{\mu\nu}$ has been determined by the equations:

$$a_{\mu\nu} = 2a_{\mu\mu} \cdot a_{\nu\nu}/(a_{\mu\mu} + a_{\nu\nu}) \qquad (6)$$

$$a_{\mu\mu} = 14.3949/\gamma_{\mu\mu} \qquad (7)$$

The other quantities necessary for the calculation are the values of off-diagonal matrix elements of core Hamiltonian, $\beta_{\mu\nu}$. We have used the same values as before[2] for these quantities.

With the parameters described above, SCE LCAO MO's of pyridinium ion and pyrazinium diion have been obtained by the iterative process in which all integrals except $\beta_{\mu\nu}$ depend on the π-electron distribution.

The results are collected in Table I and

TABLE I. SCE MO'S AND MO ENERGIES OF PYRIDINIUM ION AND PYRAZINIUM DIION

Symmetry	ε_i(eV.)	
		Pyridinium ion
b_2	-18.3382	$\psi_1 = 0.1200(\phi_2+\phi_6) + 0.3272(\phi_3+\phi_5) + 0.0763\,\phi_1 + 0.8667\,\phi_4$
b_2	-13.1857	$\psi_2 = 0.4791(\phi_2+\phi_6) + 0.1121(\phi_3+\phi_5) + 0.6631\,\phi_1 - 0.2758\,\phi_4$
a_2	-11.4409	$\psi_3 = 0.4939(\phi_2-\phi_6) + 0.5059(\phi_3-\phi_5)$
b_2	-3.3504	$\psi_4 = 0.1846(\phi_2+\phi_6) + 0.4811(\phi_3+\phi_5) - 0.5805\,\phi_1 - 0.3632\,\phi_4$
a_2	-1.8341	$\psi_5 = 0.5059(\phi_2-\phi_6) - 0.4939(\phi_3-\phi_5)$
b_2	0.6149	$\psi_6 = 0.4711(\phi_2+\phi_6) - 0.3859(\phi_3+\phi_5) - 0.4663\,\phi_1 + 0.2020\,\phi_4$
		Pyrazinium diion
b_{2u}	-19.7914	$\psi_1 = 0.2637(\phi_2+\phi_3+\phi_5+\phi_6) + 0.6007(\phi_1+\phi_4)$
b_{3g}	-18.6618	$\psi_2 = 0.1781(\phi_2-\phi_3-\phi_5+\phi_6) + 0.6607(\phi_1-\phi_4)$
b_{1g}	-12.1179	$\psi_3 = 0.5000(\phi_2+\phi_3-\phi_5-\phi_6)$
b_{2u}	-5.3902	$\psi_4 = 0.4248(\phi_2+\phi_3+\phi_5+\phi_6) - 0.3729(\phi_1+\phi_4)$
a_{1u}	-2.6605	$\psi_5 = 0.5000(\phi_2-\phi_3+\phi_5-\phi_6)$
b_{3g}	-0.7302	$\psi_6 = 0.4672(\phi_2-\phi_3-\phi_5+\phi_6) - 0.2518(\phi_1-\phi_4)$

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[4] R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958).

[5] N. Mataga and K. Nishimoto, *Z. Physik. Chem. N. F.*, **13**, 140 (1957).

[6] N. Mataga, This Bulletin, **31**, 453, 459, 463 (1958).

[7] N. Mataga, *Z. Physik. Chem. N. F.*, **18**, 19 (1958).

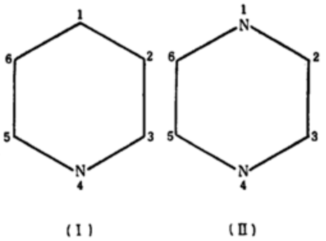

Fig. 1. Numbering of atoms in pyridine (I) and pyrazine (II).

the numbering of atoms is indicated in Fig. 1.

The spectra of these ions calculated with these MO's are given in Table II in comparison with the observed values.

TABLE II. CALCULATED AND OBSERVED SPECTRA OF PYRIDINIUM ION AND PYRAZINIUM DIION

Pyridinium ion

Symmetry	Excitation energy Calcd.	Excitation energy Obsd.*	Calcd. Oscillator strength**
$^1B_1(^1L_b)$	4.7492	4.83	0.346
$^1A_1(^1L_a)$	6.1375	5.50	0.000
$^1A_1(^1B_a)$	7.1336	—	1.108
$^1B_1(^1B_b)$	7.7588	—	0.535

* V. Zanker, *Z. Physik. Chem. N. F.*, **2**, 52 (1954).

** The observed oscillator strengths of pyridinium ion are uncertain. Although ^1L_b band of pyridine is intensified by protonation, the oscillator strength of ^1L_b band may be almost equal to that of ^1L_a band in its order of magnitude, in the case of pyridinium ion.

Pyrazinium diion

Symmetry	Excitation energy Calcd.	Excitation energy Obsd.*	Calcd. Oscillator strength**
$^1B_{3u}(^1L_b)$	4.1412	4.35	0.641
$^1B_{1u}(^1L_a)$	6.5108	$(6\lesssim)$	0.472
$^1B_{1u}(^1B_a)$	9.5635	—	0.454
$^1B_{3u}(^1B_b)$	11.5009	—	0.624

* F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 712 (1951) and S. Mataga, unpublished.

** The observed oscillator strength of pyrazinium diion is uncertain. The oscillator strength of ^1L_b band, however, seems to be two or three times as large as that of a neutral molecule. (The calculated oscillator strength of ^1L_b band in the case of pyrazine molecule is 0.162[5]).

The agreement of the calculated spectra with observed values as given in Table II, is not satisfactory. There is not such nice agreement with experiment as seen in the previous calculation[1-3] with method i as described in the introductory part of this paper, and the present result seems to be only a small improvement of the previous calculation[1-3] with the method ii. Accordingly, the present unsatisfactory results may originate from the same circumstance as in the case of the previous calculation with the method ii, i.e., from the insufficient consideration of the inductive charge displacement in the σ-core caused by the transfer of nonbonding electrons on nitrogen atom toward proton. In this respect, some critical discussions about the effects of protonation on the electronic structure of these nitrogen heterocycles will be given in the next section.

On the Inductive Charge Displacement in the σ-Core Caused by the Protonation

In the method i, the electrostatic potential due to proton is simply added to the core Hamiltonian and the diagonal element of Fock's Hamiltonian in terms of AO's has the following form:

$$F_{\mu\mu}=\alpha_\mu+V_\mu{}^P+\frac{1}{2}P_{\mu\mu}\gamma_{\mu\mu}+\sum_{\kappa(\neq\mu)}(P_{\kappa\kappa}-1)\gamma_{\mu\kappa} \quad (8)$$

where

$$\alpha_\mu=\int\phi_\mu(i)\left\{-\frac{1}{2}\Delta_i{}^2-V_\mu(i)\right\}\phi_\mu(i)\mathrm{d}v(i)=-I_\mu$$

$V_\mu{}^P=-e^2\int\sum_P\frac{\phi_\mu{}^2(i)}{r_{Pi}}\mathrm{d}v(i)$ and r_{Pi} is the distance between proton and i-th electron.

As pointed out before[2,3], the changes in the core energies produced by protonation may be almost completely contributed by the inductive displacement in σ-core. Then, in view of the short range character of the interactions in σ-core, the additional core energy, i.e., $V_\mu{}^P$, used in the method i may be too large. It seems probable $V_\mu{}^P=0$ at the atom in the opposite side of proton. However, if we use $(V_\mu{}^P-V_0{}^P)$'s instead of $V_\mu{}^P$'s where $V_0{}^P$ is the additional core energy at the atom in the opposite side of proton, it is evident that, in our approximation, the MO's calculated by method i stay unchanged although the MO energies are lifted by $|V_0{}^P|$ uniformly. Accordingly, one may be allowed to say that the real changes in core energies due to inductive displacement are represented by $(V_\mu{}^P-V_0{}^P)$, because the calculated spectra with method

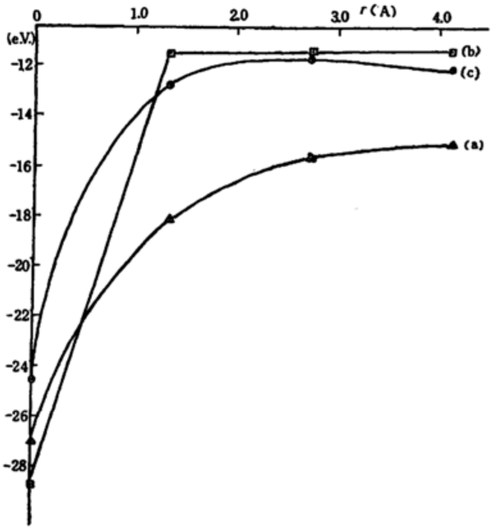

Fig. 2. α_μ's or $(\alpha_\mu + V_\mu^P)$ plotted against the distance r along the bonds between the protonated nitrogen and μ-th atom in the case of pyridine. (a) method i, (b) method ii, (c) SCE method.

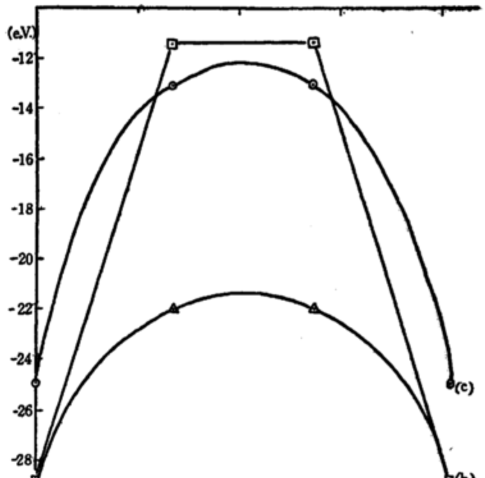

Fig. 3. α_μ's or $(\alpha_\mu + V_\mu^P)$ plotted against the distance r along the bonds in the case of pyrazine. (a) method i, (b) method ii, (c) SCE method.

i are in a very good agreement with experiment[1-3].

Now, the circumstance mentioned at the end of the last section is evident from Figs. 2 and 3 where α_μ's in the method ii and SCE method, and $(\alpha_\mu + V_\mu^P)$'s in the method i are plotted against the distance along the bonds between protonated atom and μ atom. Moreover, $F_{\mu\mu}$'s which may be regarded as a kind of effective electronegativity of μ atom in the molecule[2,5] show the same tendencies as α_μ's and $(\alpha_\mu + V_\mu^P)$'s, respectively, in Figs. 4 and 5.

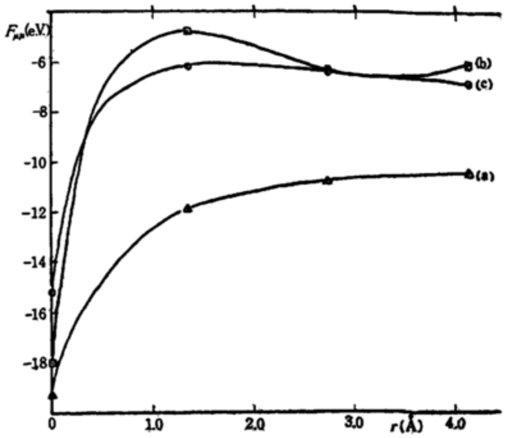

Fig. 4. $F_{\mu\mu}$'s plotted against the distance r along the bonds between the protonated nitrogen and μ-th atom in the case of pyridine. (a) method i, (b) method ii, (c) SCE method.

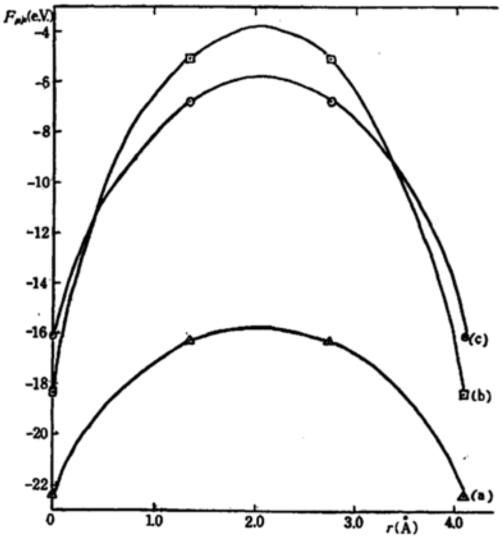

Fig. 5. $F_{\mu\mu}$'s plotted against the distance r along the bonds in the case of pyrazine. (a) method i, (b) method ii, (c) SCE method.

In these figures, the results obtained by the SCE method are rather close to the results obtained by the method ii, which may be the most predominant factor that leads to the unsatisfactory prediction of electronic spectra by the former method.

Now, in the case of protonated pyridine, if we put :

$$\alpha_\mu' - \theta = (\alpha_4' - \theta)/\nu^n \tag{9}$$

where $\alpha_\mu' = (\alpha_\mu + V_\mu^P)$, θ and ν are parameters to be determined semiempirically and n is the number of bonds between nitrogen and μ atom, then the values of α_μ' plotted in Fig. 2 are well reproduced by this equation putting $\theta = 14.86$ eV. and $\nu = 4$.

If we approximate the distances from nitrogen along the bonds by $r = n \cdot \lambda$ where λ is the average bond distance of pyridine, i.e., 1.38 Å, then Eq. 9 becomes

$$\alpha_\mu' - \theta = (\alpha_4' - \theta)/\nu^{r/\lambda} \qquad (10)$$

Actually, Eq. 10 is valid.

Similar equations have been obtained also for $F_{\mu\mu}$'s as follows:

$$(F_{\mu\mu} - 10.50) = (F_{44} - 10.50)/6^n \qquad (11)$$

$$\text{or} \qquad = (F_{44} - 10.50)/6^{r/1.38} \qquad (12)$$

The value of θ in Eqs. 9 and 10 and the corresponding quantity in Eqs. 11 and 12 are very close to α_1' and F_{11}, respectively.

Therefore, these equations may be regarded as representing the inductive displacement caused by protonation and also that the inductive effect due to protonation is practically negligible on the atom which is more than two-bond distance apart from the protonated nitrogen atom.

Then, Eqs. 9 and 10 may be useful in general for the study of the protonation effect on the electronic structure of nitrogen heterocycles, although the behaviour of $F_{\mu\mu}$ may be characteristic of each molecule and Eqs. 11 and 12 can not be used in general. It is customary in the simple MO theory to take into consideration the inductive effect assuming the form of coulomb integral as $\alpha_\mu = \alpha + \delta_\mu \beta$ It has been pointed out[2)] that the SCF MO's and charge distributions calculated by the method i are well reproduced with simple MO's obtained using the values of coulomb integrals $\alpha_4 = \alpha + 2.4\,\beta$, $\alpha_3 = \alpha_5 = \alpha + 0.4\,\beta$ and assuming the all resonance integrals are equal to β. Then $\delta_3 = \delta_5 = \delta_4/6$, which is the same relationship as in the case of $F_{\mu\mu}$, i.e., by Eq. 11 $\Delta F_{33} = \Delta F_{55} = \Delta F_{44}/6$, where $\Delta F_{\mu\mu} = (F_{\mu\mu} - 10.50)$

Although, in the case of the protonated pyrazine, we can not obtain the relationship as Eqs. 9—12, because of the higher symmetry of the molecule, the circumstance may be analogous to the case of protonated pyridine.

Summary

The self-consistent electronegativity method has been applied to calculate the electronic structure and spectra of some protonated nitrogen heterocycles. This method may be regarded as an improvement of our method ii which has led to poor agreement with experiment because of the neglect of the inductive displacement in σ-core caused by protonation. The calculated results with the present method, however, are in rather poor agreement with experiment, and it is only a small improvement of the method ii.

Comparing the present results with the previous ones obtained with method i and ii, some discussions about the nature of the protonation effect on the electronic structure of these molecules have been given. In addition, formulae which represent the magnitude of inductive effect on each atom as a function of the distance or number of bonds from the protonated atom have been given.

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