Protonation Effects on the Electronic Spectra of Pyrazine

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In our previous reports[1,2], we have tried to interpret theoretically the characteristics of electronic spectra of hydrogen bonded or protonated nitrogen heterocycles, especially in the case of pyridine. In these reports, semiempirical Hartree-Fock SCF MO's for pyridine interacting with proton have been computed assuming extreme models: (1), there is no transfer of non-bonding electrons on nitrogen toward proton, but bare proton or somewhat shielded proton is located near the nitrogen atom of neutral molecules. In the latter case, the effective charge of proton has been introduced in theory (model I); (2), there is considerable charge transfer from nitrogen atom to proton, leading to covalent binding between them (model II).

The calculated sepectra with model I were in a very good agreement with the experiment. The calculation with model II, however, led to a result which gave rather poor agreement with the experimental values. These results were examined carefully and some discussions on the cause of the superiority of model I and the unsatisfactory result obtained with model II were given.

In the present paper, we shall report another example of our calculations, i.e., the study of the electronic spectra of pyrazinium diion. In this case, the features of spectral change produced by protonation are somewhat different from the case of pyridine.

Method of Calculation

Our method of calculation has already been described in detail elsewhere[2]. Accordingly, the outline of our method will be given briefly as follows.

Model I.—In this case, the complete electronic Hamiltonian may be written as,

$$H=\sum_i H_i^{core'}+\sum_{i<j}^{2m}(e^2/r_{ij}) \tag{1}$$

$$H_i^{core'}=H_i^{core}+H_i^P \tag{2}$$

where H_i^P is the electrostatic potential due to proton

$$H_i^P=-\sum_P\frac{Z_{H^+}e^2}{r_{Pi}} \tag{3}$$

In Eq. 2, r_{Pi} is the distance between proton and i-th electron and $Z_{H^+}e$ is the effective charge of proton. In the present calculation it has been assumed to be $Z_{H^+}=1$. The i-th MO may be written in the LCAO form as,

$$\psi_i=\sum_\mu C_{i\mu}\phi_\mu \tag{4}$$

and the eigenvalue equations become as follows in terms of Hartree-Fock SCF MO with neglect of differential overlap,

$$\sum_\nu F_{\mu\nu}C_{i\nu}=\varepsilon C_{i\mu} \tag{5}$$

where

$$F_{\mu\mu}=\alpha_\mu'+\frac{1}{2}P_{\mu\mu}\gamma_{\mu\mu}+\sum_{\kappa(\neq\mu)}(P_{\kappa\kappa}-1)\gamma_{\mu\kappa} \tag{6}$$

$$F_{\mu\nu}=B_{\mu\nu}-\frac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} \tag{7}$$

$$\alpha_\mu'=\alpha_\mu+V_\mu^P \tag{8}$$

$$V_\mu=-\sum Z_{H^+}e^2\int\frac{\phi_\mu^2(i)}{r_{Pi}}\mathrm{d}v(i) \tag{9}$$

The meaning of the quantities in these equations other than V_μ^P is the same as before[3-5]. Among the molecular integrals that arise, V_μ^P has been computed theoretically employing the usual Slater $2p\pi$ AO's of nitrogen and carbon atoms, and the others have been evaluated by the same procedure as before[3-5]. Because the interatomic distances in pyrazinium diion necessary for the evaluation of molecular integrals are uncertain, C–C and C–N distances have been assumed to be the same as in neutral molecules and the N–H$^+$ distance has been put to be 1.032 Å, which is the value determined by Bersohn and Gutowsky[6] by means of nuclear

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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) N. Mataga and K. Nishimoto, ibid., **13**, 140 (1957).

4) N. Mataga, This Bulletin, **31**, 453, 459, 463 (1958).

5) N. Mataga, *Z. physik. Chem. N. F.*, **18**, 285 (1958).

6) R. Bersohn and H. S. Gutowsky, *J. Chem. Phys.*, **22**, 651 (1954).

magnetic resonance in the case of ammonium chloride.

Model II.—For the calculation to be made by this by this model, the values of the valence state ionization potential I_{N^+} and electron affinity A_{N^+} of N^+ ion are needed. Using the values of valence state energies above the ground state, which have been taken from Pritchard and Skinner[7], the values of I_{N^+} and A_{N^+} are easily obtained considering the processes,

$$N^+(sp_xp_yp_z,\ V_4) \rightarrow N^{++}(sp_xp_y,\ V_3) \text{ and}$$
$$N(sp_xp_yp_z^2,\ V_3) \rightarrow N^+(sp_xp_yp_z,\ V_4),$$

respectively.

With these values the evaluation of molecular integrals has been made in the same manner as before[1-5], and the salf-consistent field calculation has been worked out.

Results and Discussion

The calculated SCF MO's, MO energies, charge and bond orders are collected in Table I.

TABLE I. SCF MO's, MO ENERGIES, CHARGE AND BOND ORDERS OF PYRAZINIUM DIION

Symmetry	ε_i(eV.)	Model I
b_{2u}	-27.0147	$\psi_1=0.3132(\phi_2+\phi_3+\phi_5+\phi_6)+0.5512(\phi_1+\phi_4)$
b_{3g}	-25.4415	$\psi_2=0.2065(\phi_2-\phi_3-\phi_5+\phi_6)+0.6439(\phi_1-\phi_4)$
b_{1g}	-21.4068	$\psi_3=0.5000(\phi_2+\phi_3-\phi_5-\phi_6)$
b_{2u}	-14.1191	$\psi_4=0.3897(\phi_2+\phi_3+\phi_5+\phi_6)-0.4429(\phi_1+\phi_4)$
a_{1u}	-12.0237	$\psi_5=0.5000(\phi_2-\phi_3+\phi_5-\phi_6)$
b_{3g}	$-\ 9.8972$	$\psi_6=0.4553(\phi_2-\phi_3-\phi_5+\phi_6)-0.2920(\phi_1-\phi_4)$

$P_{11}=1.4370$, $P_{22}=0.7815$, $P_{12}=0.6112$, $P_{23}=0.6109$

Symmetry	ε_i(eV.)	Model II
b_{2u}	-20.8925	$\psi_1=0.2038(\phi_2+\phi_3+\phi_5+\phi_6)+0.6457(\phi_1+\phi_4)$
b_{3g}	-20.2163	$\psi_2=0.1425(\phi_2-\phi_3-\phi_5+\phi_6)+0.6778(\phi_1-\phi_4)$
b_{1g}	-10.4320	$\psi_3=0.5000(\phi_2+\phi_3-\phi_5-\phi_6)$
b_{2u}	$-\ 4.6592$	$\psi_4=0.4566(\phi_2+\phi_3+\phi_5+\phi_6)-0.2882(\phi_1+\phi_4)$
a_{1u}	$-\ 1.1677$	$\psi_5=0.5000(\phi_2-\phi_3+\phi_5-\phi_6)$
b_{3g}	0.3512	$\psi_6=0.4792(\phi_2-\phi_3-\phi_5+\phi_6)-0.2015(\phi_1-\phi_4)$

$P_{11}=1.7526$, $P_{22}=0.6237$, $P_{12}=0.4564$, $P_{23}=0.5425$

As shown in Table I, the charge density at nitrogen is increased remarkably by protonation and the features of charge distribution in neutral pyrazine molecule[3] which can be practically regarded as slightly perturbed benzene[5] are lost. With these MO's and MO energies, the electronic spectra of pyrazinium diion are easily calculated. In Table II the calculated spectra are indicated together with the experimental values.

TABLE II. CALCULATED AND OBSERVED SPECTRA OF PYRAZINIUM DIION

Symmetry	Excitation energy (eV.)			Oscillator strength		
	Calcd. I	Calcd. II	Obsd.[a]	Calcd. I	Calcd. II	Obsd.
${}^1B_{3u}({}^1L_b)$	4.2649	3.6205	4.35	0.489	0.723	*
${}^1B_{1u}({}^1L_a)$	6.3592	6.3130	$(6\leq)$[(b)]	0.340	0.504	—
${}^1B_{1u}({}^1B_a)$	8.0161	11.3617	—	0.659	0.286	—
${}^1B_{3u}({}^1B_b)$	9.3522	14.2097	—	0.720	0.368	—

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

(b) There is no indication of the existence of other electronic band than ${}^1L_b$ below 45 *kK*.

* 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 neutral molecule.

In contradistinction to the case of protonated pyridine, ${}^1L_b$ band is somewhat strengthened as well as shifted to red, while the wave length of ${}^1L_a$ band seems to remain almost invariable by double protonation. As shown in Table II, the calculated excitation energy with model I is in good agreement with the experiment. In addition to this, since the calculated oscillator strength of ${}^1L_b$ band in neutral pyrazine molecule is 0.162[3], the calculated value in Table II, 0.489, is correct in its order of magnitude in comparison with the calculated value of the neutral molecule. In contrast with the satisfactory results obtained by model I, the calculation with model II leads to the result which is in rather poor agreement with the experiment, that is, the calculated red shift and increase of intensity in the case of ${}^1L_b$ band are too great compared with the experiment.

As has already been pointed out in the case of protonated pyridine[1,2], the most predominant factor which leads to the unsatisfactory results with model II may be the neglect of the inductive charge displacement in the σ-core, caused by the transfer of non-bonding electrons on the nitrogen atom toward proton. In the case of model II, the core potential is very deep at nitrogen and is the same as

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[7] H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

that in the neutral molecule at the carbon atoms. In the case of model I, however, the difference between the core energies at nitrogen and carbon is not so great as in model II and the displacement in σ-core may be appropriately taken into consideration by the formal use of the electrostatic proton potential.

Moreover, the values of $F_{\mu\mu}$'s which may be regarded as an effective electronegativity of μ atom in the molecule[2,3], show the same tendency as the core energies. They are collected in Table III.

TABLE III. VALUES OF α_μ's AND $F_{\mu\mu}$'s

Model	F_{11}	F_{22}	α_1'	α_2'
I	−22.3721	−16.2897	−29.0877	−21.9661
II	−18.3705	−5.0689	−28.72	−11.42

Although the observed spectra can be satisfactorily reproduced by model I as described above, one should not regard model I as the real state of protonated pyrazine. This model represents the electric interaction between proton and π-electrons rather than the electronic interaction between proton and pyrazine. The strong charge transfer interaction between the nitrogen atom in pyrazine and proton may lead to a fairly strong covalent binding between them. Then, the changes in the core energies produced by protonation may be almost completely contributed by the inductive displacement in σ-core. If this is the case, in view of the short range character of the interactions in σ-core, the $(\alpha_\mu' - \alpha_\mu)$ values used in the calculation with model I may be too large. It seems probable that the protonation effect on the core energies may be almost negligible at the nitrogen atom in the opposite side of that proton. However, if we use $(V_\mu^P - 2V_0^P)$'s instead of V_μ^P's of Eq. 9, where V_0^P is the potential energy due to proton at the nitrogen atom in the opposite side of that proton, it is evident that the MO's calculated by model I stay unchanged although the MO energies are lifted by $2|V_0^P|$ uniformly. Thus, the calculation with model I may still be correct even in this case. One might be able to say that the real changes in core energies due to inductive displacement are approximately represented by $(V_\mu^P - 2V_0^P)$ in the case of doubly protonated pyrazine. We shall give a detailed and critical discussion in a later report[8] about such a statement comparing the results obtained with model I with those obtained by an improved model II which employs the self-consistent electronegativity method as developed by Brown and Heffernan[9].

Summary

The protonation effect on the electronic structure and spectra of pyrazine has been studied theoretically employing quantum mechanical calculation. Semi-empirical Hartree-Fock SCF MO's for pyrazine interacting with two protons have been computed with two different methods, respectively.

i) Electrostatic potential due to proton has been added to the core potential in the total electronic Hamiltonian and nuclear attraction integrals which arise owing to the proton potential have been computed theoretically employing the usual Slater $2p\pi$ AO's.

ii) The doubly protonated pyrazine has been replaced by doubly charged pyrazinium ion and molecular integrals have been evaluated semi-empirically using valence state ionization potential and electron affinity of the N^+ atom.

The calculated spectra with method i are in a very good agreement with the experiment. The calculation with method ii has led to a result which is in rather poor agreement with the experimental observation. On the basis of these results, some discussions about the protonation effect on the electronic structure of this molecule have been given.

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[8] S. Mataga and N. Mataga, to be published elsewhere.

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