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SCF MO Calculations of Heteroatomic Systems with the Variable β Approximation

IV. Electronic Structure and Spectra of Protonated N-Heterocycles*

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In order to elucidate the electronic structure of protonated N-heterocycles, we have carried out SCF MO calculations, considering the σ-bond polarizations which are caused by the large net charge on nitrogen atom. Appropriate parametrizations of the valence state energies associated with the σ-bond polarization model have been proposed. Our calculations showed that a conventional covalent model for protonated N-heterocycles failed to explain the experimental electronic spectral data and an extremely polarized σ-core model gave quite good results in the whole. The present theory expected that the nature of electronic spectra of quinoline is considerably changed by the σ-bond polarization due to the protonation.

Um die Elektronenstruktur von protonisierten N-Heterozyklen zu untersuchen, wurden SCF-MO-Rechnungen durchgeführt, bei denen die Polarisierung der σ-Bindung durch die Ladung am N-Atom berücksichtigt wird. Eine geeignete Parametrisierung der Valenzzustands-Energien in Verbindung mit dem Modell der Polarisierung der σ-Bindung wird vorgeschlagen. Die Rechnungen zeigen, daß ein herkömmliches kovalentes Modell für die genannten Verbindungen bei der Erklärung des Elektronenspektrums versagt, während ein Modell mit stark polarisierten σ-Bindungen befriedigende Ergebnisse liefert. Aus der vorliegenden Theorie läßt sich folgern, daß das Elektronenspektrum des Chinolins beträchtlich durch die Polarisierung der σ-Bindung infolge Protonisierung geändert wird.

Afin d'éclaircir la structure électronique d'hétérocycles protonisés sur l'azote, nous avons effectué des calcules SCF MO en considérant la polarization des liaisons σ dûe à la forte charge nette sur l'atome d'azote. Des paramétrisations appropriées à ce modèle polarisé sont proposées pour les énergies des états de valence. Nos calculs ont montré qu'un modèle covalent conventionnel pour les N hétérocycles protonisés ne réussit pas à expliquer le spectre électronique expérimental alors qu'un modèle à forte polarisation du squelette σ donne des résultats dans l'ensemble satisfaisants. Cette théorie prévoit que la nature du spectre électronique de la quinoléine est considérablement modifiée par la polarisation σ dûe à la protonisation.

Introduction

In the previous papers [1–4], it has been shown that the Pariser-Parr-Pople theory with the variable β approximation can be applied successfully to the calculations of the electronic spectra of neutral molecules containing nitrogen

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and oxygen atoms and to some anions of hydroxyaromatics. The electronic structures and spectra of protonated N-heterocycles which are still unsettled, although some work has been carried out on the pyridinium cation [5–10], are very interesting problems for the present theory and for the heterocyclic chemistry from the following reasons.

First of all, the N-heterocycles will form an extreme strong hydrogen bond. The hydrogen bond formed between a N-heterocycle and a polar solvent, HX, can be, in a first approximation, represented by a linear combination of a non-bonded and two ionic configurations [11],

$$\Psi = a\psi(\mathrm{N} \cdots \mathrm{HX}) + b\psi(\mathrm{N} \cdots \mathrm{H}^{+}\mathrm{X}^{-}) + c\psi(\mathrm{N}^{+}\text{–}\mathrm{H} \cdots \mathrm{X}^{-}) . \qquad (1)$$

The contribution of the non-bonded configuration decreases with the increasing proton donating power of HX. The hydrogen bond in a protonated N-heterocycle is considered as an extreme case of the complete neglect of the non-bonded configuration. Secondly, a given protonated N-heterocycle has a net charge $+1$ in the whole molecule and it will be interesting to know how this positive charge delocalizes in the molecule. Thirdly, we inquire whether we can use the semi-empirical parameters for neutral molecules to this kind of cations. Finally, for a neutral molecule in which the π-electrons distribute almost uniformally, we can assume, in a good approximation, a fixed σ-framework. However, in protonated N-heterocycles, we must, perhaps, consider σ-bond polarization. In order to elucidate these interesting problems, we have carried out SCF MO CI calculations based on covalent models.

Calculation

Mataga and Mataga [6] carried out a SCF MO calculation on the pyridinium cation assuming two extreme models; 1. the electrostatic model $(\geqslant\mathrm{N}{:}\mathrm{H}^{+})$ – where the bare proton is bound to the nitrogen lone pair by an electrostatic force and 2. the covalent model $(\geqslant\mathrm{N}^{+}\text{–}\mathrm{H})$ – there is a complete electron transfer from the nitrogen to the proton, leading to covalent binding between them. They concluded that the calculated electronic spectra with the former model were in a good agreement with the experimental observation reported by Zanker [12].

However, they unfortunately refered an erroneous absorption maxima for the second transition. In 1957, Zanker and Schmid [13] reported the near ultraviolet absorption spectra of protonated N-heterocycles and showed that the pyridinium cation has two absorption maxima at about 4.8 eV and 6 eV (not 5.5 eV as given in Ref. [12]). Our measurement for pyridine and pyridinium cations is shown in Fig. 1. Consequently, Mataga's model (electrostatic model) seems to be insufficient to elucidate the electronic structure of the pyridinium cation.

There are some experimental evidences to support the covalent model for that molecule. First of all, the NMR [14] and infrared absorption spectra [15] of ammonium salts confirmed that the $(\mathrm{NH}_4)^+$ ion has a tetrahedral covalent structure. Secondly, with increasing the size of the anion or with decreasing the electrostatic perturbation, the N–H stretching frequency of pyridinium salts [16],

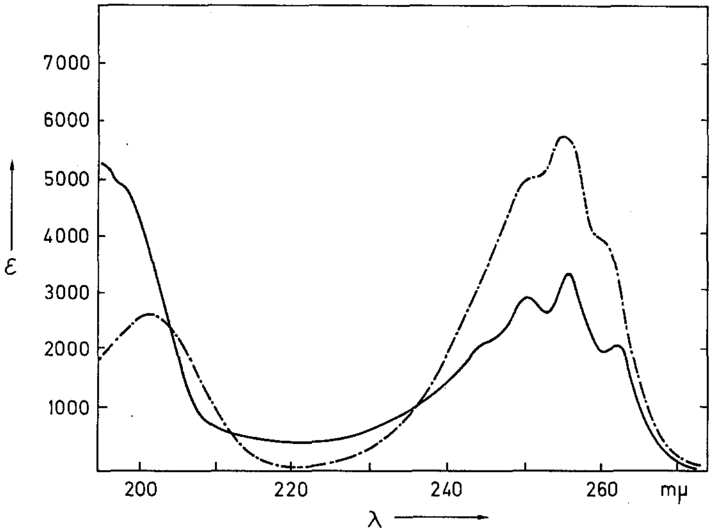


Fig. 1. Near ultraviolet absorption spectra of pyridine (——) and protonated pyridine (-·-·-)

$C_5H_5NH^+X^-$, comes up to that of aniline which has typical covalent N–H bonds. The electron affinity of the proton is 13.6 eV and the ionization potentials of nitrogen lone pairs in N-heterocycles might be near 9 eV [17]. Therefore, this results a strong charge transfer interaction and a fairly strong covalent binding between them.

In the covalent model, we obtain a large amount of positive net charge on the nitrogen atom and we can expect a considerable amount of σ-bond polarization. Therefore, in a more rigorous calculation, we must take into consideration $\sigma - \pi$ interaction in such a manner as proposed by Parr, Lykos, and Parks [18, 19].

According to the facts above, in the present study only the covalent model is considered and we assumed the following two extreme models;

1. Conventional covalent model in which the σ-bond polarization is completely neglected, so that the σ-framework should be represented as Model 1 in Fig. 2.

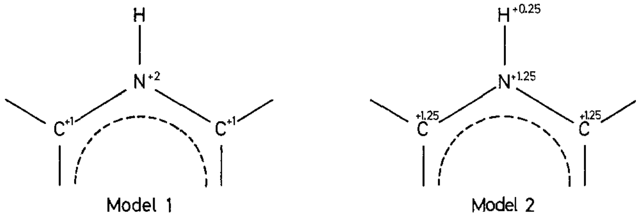


Fig. 2. Assumed σ core frameworks in the neighbourhood of nitrogen atom

2. Equal charge sharing model in which the formal charge on nitrogen in the conventional covalent structure is equally shared with the neighbour carbons and hydrogen. When we assume initially a conventional covalent structure, then the +1 formal charge is concentrated on the nitrogen atom and the electronegativity of this atom might be extraordinarily large. Therefore, the nitrogen

draws strongly σ-electrons from bonded carbons and hydrogen so that the formal charge is apparently spread over on the neighbours. The σ-core skelton of this extreme model is represented by Model 2 in Fig. 2.

Parametrization

In the present calculations, we used variable β approximation and N-gamma [4]. In N-gamma, two center electron repulsion integrals are divided into two classes, upper-upper and upper-lower interaction. They are given by the expressions contained in Ref. [4]. For core integral $\beta_{\mu\nu}$, we used the same expression as given in Ref. [3].

It should be noted that the diagonal $\boldsymbol{H}$ matrix elements associated with the μ-th atom, H_μ, must be expressed as follows;

$$\mathrm{H}_\mu = -I_\mu - \sum_{\nu \neq \mu} CO(\nu) \cdot \gamma_{\mu\nu}$$

where $CO(\nu)$ means the positive charge of ν-th σ-core, I_μ the ionization potential and $\gamma_{\mu\nu}$ the electron repulsion integral.

For Model 2, it is necessary to make a particular parametrization. According to Brown and Heffernan [20] and Klopman [21], the valence state ionization potential can be represented by a quadratic equation of effective nuclear charge or the charge density. In other words, it can be given by a quadratic equation of the core charge, Q, as follows;

$$I(Q) = aQ^2 + bQ + c \tag{2}$$

where a, b and c are the coefficients to be determined. There are three boundary conditions for Eq. (2). These are

$$I(Q=0) = A$$
$$I(Q=1) = I_1$$
$$I(Q=2) = I_2$$

where A, I_1 and I_2 represent the electron affinity, the first and the second ionization potentials associated with the atomic orbital ϕ_μ, respectively. Consequently, we obtain

$$I(Q) = \frac{I_2 - 2I_1 + A}{2} Q^2 - \frac{I_2 - 4I_1 + 3A}{2} Q + A\,. \tag{3}$$

Paoloni [22] showed that the one center electron repulsion integral, $\gamma_{\mu\mu}$, should be proportional to the effective nuclear charge. Therefore, in a good approximation, we can express $\gamma_{\mu\mu}$ by a linear function of Q as

$$\gamma(Q) = mQ + n\,.$$

From the necessary boundary conditions,

$$\gamma(Q=1) = \gamma(1)$$
$$\gamma(Q=2) = \gamma(2)\,,$$

we obtain

$$\gamma(Q) = (\gamma(2) - \gamma(1))Q + 2\gamma(1) - \gamma(2) . \tag{4}$$

The parameters are summarized in Table 1. All bond lengths and angles are set at 1.40 Å and 120°, respectively. The numbering of atoms and the molecular axes are shown in Fig. 3.

Table 1. *Parameters*

Atom	Core charge	Ionization potential I (eV)	Electron affinity A (eV)	Repulsion integral γ (eV)	a (Å)
C	+1	9.6	0.0	9.6	1.500
C	+1.25	12.57	1.15	11.42	1.261
N	+1	12.14	1.53	10.61	1.357
N	+1.25	15.42	2.85	12.57	1.146
N	+2	26.70	8.24	18.46	0.780

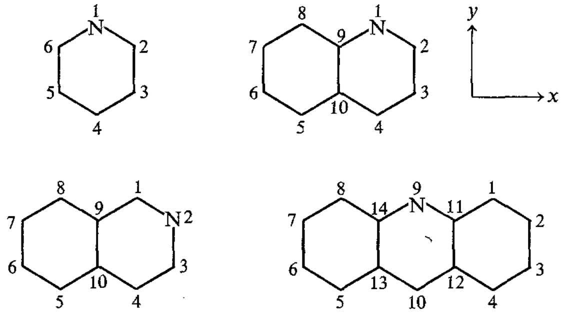


Fig. 3. Numbering of atoms

It is interesting to note that the electronic spectra of protonated aniline and naphthylamines [23] in which the protonations occur at their nitrogen atoms are very similar to those of the parent hydrocarbons. This fact suggests that the electrostatic potential does not have any considerable effect on the electronic spectra. Therefore, we can, to a first approximation, neglect the electrostatic potential due to a small positive charge on the hydrogen atom in Model 2.

A good convergence to SCF MO's is obtained with ten iterations for each of the molecules. The transition energies are calculated by including configuration interaction between all singly excited configurations within 3.0 eV of the lowest excited (singlet or triplet) state.

Results and Discussions

Electronic Spectra

Zanker [12, 13] pointed out that the nitrogen heterocycles have similar electronic absorption spectra with those of the corresponding hydrocarbons. The replacement of $-CH=$ by $-N=$ brings the following characteristic spectral changes;

1. The intensities of ${}^1L_b$ bands are considerably strengthened, but the excitation energies are almost unchanged.
2. The ${}^1L_a$ bands are practically unchanged both their intensities and energies.

The protonation on a N-heterocycle has an effect of enhancement to the above mentioned spectral change 1. Furthermore, the ${}^1L_a$ bands are remarkably shifted to the red and their intensities are decreased.

The calculated results are summarized in Table 2, where the assignment of the transition is made by using a criterion given in the previous paper [26]. The present theory tells us that in a series of pyridine, quinoline, and acridine, their spectral changes are consistent with the Zanker's rule. The increase in ${}^1L_b$ intensity

Table 2. *The effect of protonation on the* UV *spectra of* N-*heterocycles*

Theoretical					Experimental		
Model 1		Model 2		Assignment			
E (eV)	f	E (eV)	f		E (eV)	f	Ref.
Pyridine							
4.81	0.056			${}^1L_b$	4.84		
6.15	0.047			${}^1L_a$	6.36		
6.94	1.081			${}^1B_a$	—		
7.02	1.107			${}^1B_b$	—		
3.67	0			${}^3L_a$	3.68		[26]
Protonated pyridine							
4.72	0.164	4.92	0.036	${}^1L_b$	4.85		
5.86	0.010	6.09	0.003	${}^1L_a$	6.14		
6.92	0.829	7.08	1.131	${}^1B_b$	—		
7.01	1.166	7.09	1.186	${}^1B_a$	—		
3.32	0	3.69	0	${}^3L_a$	—		
Quinoline							
3.99	0.052			${}^1L_b$	3.97		[24]
4.48	0.197			${}^1L_a$	4.43		[24]
5.31	0.636			${}^1B_b$	5.34		[24]
5.78	1.050						
6.19	0.843			${}^1B_a$	—		
2.75	0			${}^3L_a$	2.71		[25]
Protonated quinoline							
3.47	0.100	3.91	0.094	${}^1L_a$	3.97		[24]
3.87	0.114	3.99	0.042	${}^1L_b$	—		
5.07	1.087	5.23	0.958	${}^1B_b$	5.21		[24]
5.73	0.166	5.77	0.375	${}^1B_a$	—		
		5.95	0.521				
6.26	0.798	6.37	1.047				
2.30	0	2.54	0	${}^3L_a$	—		
Isoquinoline							
3.99	0.053			${}^1L_b$	3.86		[24]
4.55	0.212			${}^1L_a$	4.59		[24]
5.51	1.116			${}^1B_b$	5.69		[24]
5.67	0.284						
5.80	0.489						
6.22	0.776			${}^1B_a$	—		
2.70	0			${}^3L_a$	2.63		[25]

Table 2 (Continued)

Theoretical					Experimental		
Model 1		Model 2		Assignment			
E (eV)	f	E (eV)	f		E (eV)	f	Ref.
Protonated isoquinoline							
3.31	0.156	3.78	0.102	^1L_a	3.69		[24]
3.98	0.008	4.05	0.042	^1L_b	4.49		[24]
5.24	1.163	5.31	0.688	^1B_b	5.39		[24]
		5.55	0.488				
5.58	0.505	5.70	0.057	^1B_a	—		
6.05	0.596	6.29	0.888				
2.23	0	2.52	0	^3L_a	—		
Acridine							
3.59	0.129			^1L_b	3.51		[13]
3.61	0.286			^1L_a	3.24		[13]
4.94	2.396			^1B_b	4.96		[13]
5.91	0.708			^1B_a	—		
2.01	0			^3L_a	—		
Protonated acridine							
3.08	0.142	3.27	0.194	^1L_a	3.05		[13]
3.51	0.377	3.63	0.510	^1L_b	3.51		[13]
4.80	1.834	4.81	2.363	^1B_b	4.79		[13]
5.64	0.406	5.91	0.205	^1B_a	—		
1.76	0	1.76	0	^3L_a	—		

Table 3. *Contributions of lower singly excited configurations to the lower excited state functions and the polarizations; quinoline, isoquinoline, and their protonated systems*

Molecule	E (eV)	Coefficients of wave function				Polarization[a]
		$^1\chi(5\to6)$	$^1\chi(4\to7)$	$^1\chi(5\to7)$	$^1\chi(4\to6)$	
Quinoline	3.99	0.0876	0.0306	−0.5932	0.7958	181°
	4.48	0.9487	0.2698	0.0388	−0.0853	88°
Protonated quinoline	3.47	0.9669	0.1798	0.0692	−0.0509	63°
(Model 1)	3.87	0.0864	0.0732	−0.5326	0.8173	2°
Protonated quinoline	3.91	0.7868	0.2053	−0.3678	0.4201	69°
(Model 2)	3.99	0.5424	0.0958	0.5676	−0.5680	94°
Isoquinoline	3.99	0.4660	0.2006	−0.6438	0.5671	109°
	4.55	0.8333	0.2202	0.3903	−0.3210	78°
Protonated isoquinoline	3.31	0.9676	0.1987	0.0102	0.0657	121°
(Model 1)	3.98	−0.0412	0.1180	−0.7293	0.6552	150°
Protonated isoquinoline	3.78	0.7815	0.2491	−0.4051	0.3585	116°
(Model 2)	4.05	0.5464	0.0480	0.6039	−0.5326	92°

[a] Numerical value gives an angle between the transition moment vector and x-axis of the molecule.

is due to the unequal mixing of configurations $^1\chi_{m,m+2}$ and $^1\chi_{m-1,m+1}$. However, as shown in Table 3, in isoquinoline, there is complex configuration interaction and the nature of naphthalene's spectra is considerably lost by the replacement of the β-carbon with a nitrogen.

The effects of protonation on the spectra of N-heterocycles are summarized as follows:

1. In protonated pyridine and acridine, the nature of the parent hydrocarbon's spectra is still preserved by the molecular symmetry in both Models 1 and 2. Namely, the ^1L_a states consist mainly of the configurations $^1\chi_{m,m+1}$ and $^1\chi_{m-1,m+2}$. On the other hand, their ^1L_b states are composed of $^1\chi_{m,m+2}$ and $^1\chi_{m-1,m+1}$. It is interesting to note that in protonated acridine the present theory assigns the weakest and longest wavelength absorption band as ^1L_a species and the medium intensity band near 3.5 eV as ^1L_b species.

2. In quinoline and isoquinoline, there are complex configuration interactions due to σ-bond polarizations caused by the protonation, destroying the nature of the parent hydrocarbon's spectra (see Table 3). In both protonated systems, their longest wavelength absorption bands can be assigned as ^1L_a species, which agrees with the experimental results of Zimmermann and Joop [24].

3. Model 2 gives quite good results in the whole. Therefore, we expect considerable amount of σ bond polarization in a given N-heterocycle by the protonation. For protonated acridine, Model 1 seems to be better than Model 2. However,

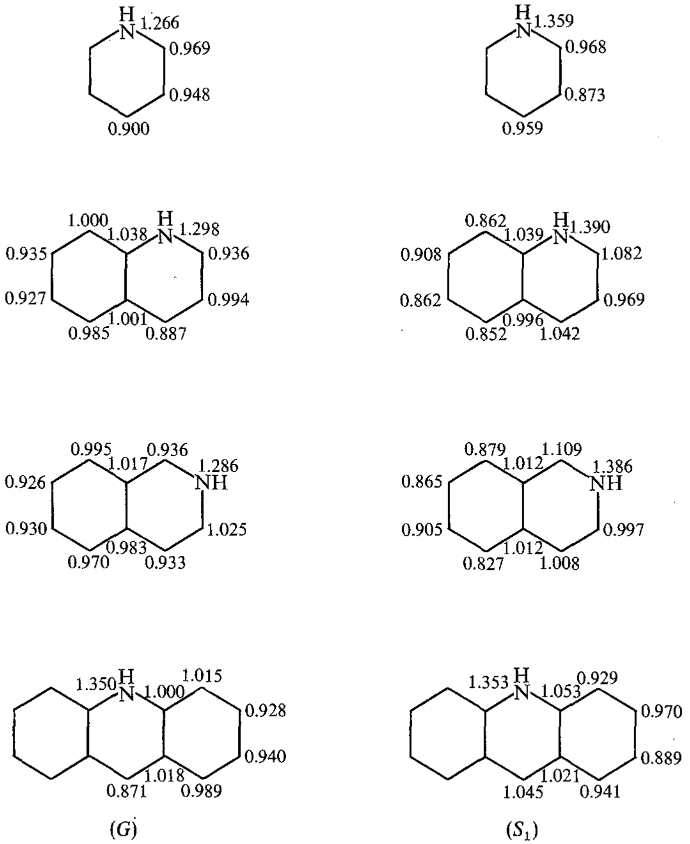


Fig. 4. Charge densities of protonated N-heterocycles in the ground (G) and the lowest excited singlet (S_1) (Franck-Condon state) states

we must compare the spectral change from the reference molecule. From this point of view, Model 2 is also well adapted to this molecule. Model 1 calculates usually too low energies for ^1L_a species.

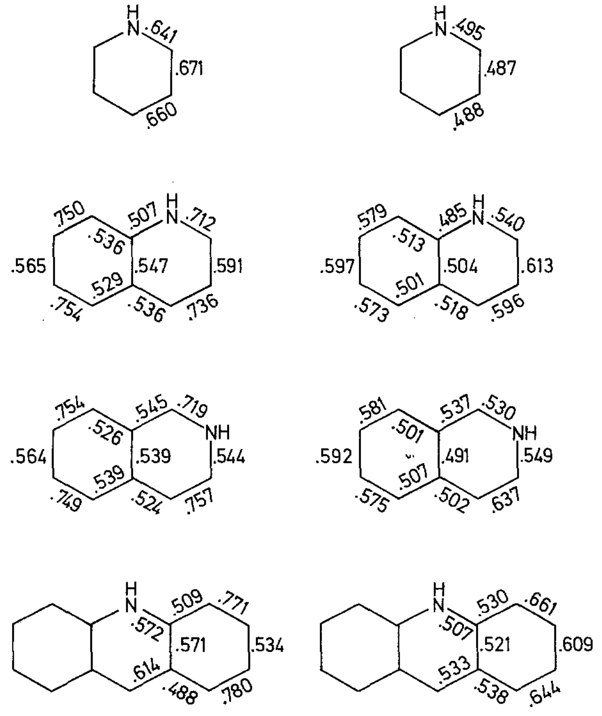
Molecular Diagrams

The calculated molecular diagrams of the ground and lowest excited singlet states of protonated N-heterocycles are shown in Figs. 4 and 5.

Distinctive changes of π-electron population by an excitation are summarized as follows:

a) The charge density on the protonated nitrogen is increased by an excitation, except for protonated acridine. Therefore, the proton releasing power will be decreased in the lowest excited singlet state.

b) In protonated quinoline, isoquinoline, and acridine, the positive charges are almost localized in the pyridine rings at their ground states. On the other hand, at their lowest excited singlet states, considerable amounts of charge transfers occur from benzene rings to pyridine rings. For the ground state protonated quinoline and isoquinoline, it is known [27] that the nucleophilic reactions take place at the pyridine rings, whereas the electrophilic reactions occur at other rings. The present theory expects that for the lowest excited singlet states, the electro-



(G) (S₁)

Fig. 5. Bond orders of protonated N-heterocycles in the ground (*G*) and the lowest excited singlet (S_1) (Franck-Condon state) states

philic reactions occur at the pyridine rings, while the nucleophilic reactions might take place at other rings of protonated quinoline, isoquinoline, and acridine.

c) Bond distances tend to equalize by an excitation from the ground state to the lowest excited singlet state. Therefore, the vibrational mode in the fluorescent state might be somewhat different from that in the ground state.

Schneider *et al.* [28, 29] measured the NMR spectra of pyridine and protonated pyridine. Assuming a simple proportionality between the proton resonance displacement and the charge density on the carbon, a ratio,

$$R = \frac{\text{decrease in the charge density on } \beta\text{-carbon by the protonation}}{\text{decrease in the charge density on } \gamma\text{-carbon by the protonation}},$$

is calculated as 0.88 from their data. The corresponding theoretical value is 0.42 with Model 1 and 0.87 with Model 2, indicating the adequacy of the latter model. This surprising agreement is somewhat, of course, accidental, because there should be complex $\sigma - \pi$ interactions which we can not represent by a simple model. However, it can be said with a confidence that Model 2 is better than Model 1.

Conclusion

The fact that the extremely σ-bond polarized model, Model 2, gives quite good results for near ultraviolet absorption spectra of protonated N-heterocycles confirms that considerable amount of σ-bond polarization occurs in such a molecule by a protonation. When we want to calculate the electronic structure, particularly the electronic spectra of protonated N-heterocycle with a minimum effort, Model 2 of the present theory would be recommended. Our next approach would be the inclusion of σ-electrons explicitly into the theory and express the valence state energies as a function of the total electron density.

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