ELECTRONIC STRUCTURE AND SPECTRA OF ORGANIC MOLECULES PART XIII[1]. ELECTRONIC SPECTRA OF PROTONATED DERIVATIVES OF PYRIDINES AND PYRIMIDINES

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The Pariser-Parr-Pople (PPP) type of calculation sare presented to interpret the electronic absorption spectra ($\pi \rightarrow \pi^*$ type) of protonated monooxo, monoamino, and monomethylthio derivatives of pyridine and pyrimidine. The effect of protonation is considered in an electrostatic model in which the appropriate parameters (diagonal core matrix elements) are treated empirically. The calculated spectra for protonated molecules are obtained in a satisfactory agreement with experiment.

Introduction

There have been several theoretical studies on the electronic structures and π-spectra of protonated nitrogen heterocycles including pyridine (Mataga and Tsuno 1958, Mataga and Mataga 1959*a, b*, Brown and Heffernan 1959, Denis and Gilbert 1968, Kato *et al.* 1969, Bailey and Bailey 1970, Nishimoto *et al.* 1969). In particular the shifts in the positions of the electronic absorption bands of N-heterocycles under protonation have been calculated by means of the SCF MO method (π-electron and all-valence-electron calculations). Although the problem of protonation is very interesting theoretically it is, however, still unsettled.

The pyridinium cation spectrum has been used in some papers as the reference data to evaluate the semiempirical parameters of the method. However, all the papers mentioned above (except the paper by Nishimoto *et al.* 1969) have referred to an erroneous absorption maximum of the second transition of the cation. Namely, Zanker (1954) reported the near ultraviolet spectrum of the pyridinium cation with two maxima, 4.8 and 5.5 eV. Authors of theoretical papers have overlooked the next paper by Zanker and Schmid (1957), where the value of 6.0 eV was reported for the second transition. Recently, Nishimoto *et al.* (1969) noticed this disagreement and have measured again the spectra of both neutral and cationic forms of pyridine.

A comparison of the electronic absorption spectra of protonated and neutral pyridine (Nishomoto *et al.* 1969, *DMS-UV* Atlas) shows that there are no great differences between the maxima positions of the first absorption bands, while the second band of pyridine shifts towards longer wavelengths under protonation[2]. On the other hand, protonation leads to changes in intensities of the bands. Namely, the intensity of the first band of the pyridinium cation is stronger compared to that of neutral pyridine, while the second band of the cation is weaker than that of the parent molecule.

It seems that it is necessary to examine all the approaches used in the papers mentioned above, in order to interpret the real effect of protonation on the spectrum of pyridine. In our opinion, however, treating the experimental data of the cationic form of pyridine as the reference data in the PPP method is rather aimless. It is well known that the PPP method is very successful as far as the calculations of the energies of electronic transitions (particularly the singlet-singlet ones) are concerned, but the results are far worse for the oscillator strengths. The shift of the first absorption band of pyridine which takes place under protonation is rather difficult to determine (in energy terms it is of the order 0.0 to 0.05 eV); the shift of the second band is rather small too (in energy terms: 0.1 to 0.2 eV). Therefore, as a first step, we carried out the PPP study on the cation of monosubstituted (oxo, amino, and methylthio) pyridines and pyrimidines, because the spectra of these derivatives undergo distinct changes when protonation occurs.

Results and discussion

The effect of protonation on the π-electrons of the molecule is treated in a manner similar to that of Mataga and Mataga (1959), *i. e.*, the assumption is made that the proton is bound to pyridinic nitrogen lone pair by an electrostatic force. The electrostatic potential due to proton is added to the core Hamiltonian. However, our way of evaluation of the semiempirical parameters (diagonal core matrix elements) is different from that of Mataga and Mataga. The corrections δ_N and δ_C are added to the values of the core integrals for the protonated nitrogen and the carbons bonded to the nitrogen, respectively. The correction values ($\delta_N = -3.5$ eV, $\delta_C = -1.2$ eV) are chosen[3] to fit transition energies for protonated hydroxy (methoxy) and methylthio substituted pyridines and then applied for the other cations under study.

The δ_N and δ_C corrections deserve some comment. It is known that protonation leads to changes in the σ-framework (*e. g.* Emsley 1968), which should be taken into account in the π-electron calculations. In our calculations, the influence of the changed σ-electronic distribution on the π-system is indirectly included in the empirical character of the δ corrections. However, this σ-electronic distribution remains undetermined.

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[2] Unpublished measurements for the pyridinium cation performed by A. Grabowska (Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw) and by A. Bączyński and M. Berndt (our Institute) are in close agreement with the data reported in *DMS-UV* Atlas and by Nishimoto *et al.* (1969).

[3] All the other parameters of the calculations remain unchanged (Berndt and Kwiatkowski 1970, Kwiatkowski *et al.* 1970).

TABLE

Cations of pyridines and pyrimidines — the singlet-singlet transition energies, ΔE(in eV), oscillator strengths, f, logarithms of molar extinction coefficients, log ε, transition polarization θ (in degrees)

Theoretical			Experimental			
ΔE	f	θ^1	ΔE(log ε)			
(1) 2-OH-pyridine						
4.42	0.239	1	4.48(3.84)[2,14]	4.44(3.84)[2,15]	4.51(3.8)[3,14]	
5.71	0.038	−70	5.93(3.56)	5.90(3.55)		
6.57	1.007	−71				
6.95	0.603	24				
(2) 3-OH-pyridine						
4.46	0.186	−16	4.38(3.77)[2,14]	4.37(3.80)[2,15]		
5.48	0.031	−6	5.58(3.57)	5.53(3.63)		
6.44	1.003	61				
6.90	0.680	−26				
(3) 4-OH-pyridine						
4.74	0.089	0	?	?	?	
5.35	0.188	90	5.30(3.99)[2,14]	5.28(3.98)[2,15]	5.28(4.2)[4,14]	
6.47	0.666	0				
6.71	1.058	90				
(4) 2-NH$_2$-pyridine						
4.14	0.288	0	4.13(3.76)[5,6]	4.13(3.6)[7]	4.09(3.8)[8]	**4.12(3.7)[9]**
5.38	0.200	−64	5.41(3.95)	5.39(3.9)	5.37(4.0)	5.34(4.0)
6.32	0.582	−57				
6.51	0.220	74				
(5) 3-NH$_2$-pyridine						
4.11	0.186	−23	3.90(3.5)[7,13]	3.94(3.55)[5]	3.80(3.6)[9]	
5.08	0.090	26	4.96(3.8)	4.96(3.88)	4.88(4.0)	
5.91	0.710	50	~ 5.9			
6.69	0.374	−4				
(6) 4-NH$_2$-pyridine						
4.70	0.038	0	?	?	?	
4.87	0.358	90	4.71(4.22)[5]	4.73(4.3)[7]	4.70(4.2)[9]	
5.94	0.518	0				
6.57	0.841	90				
(7) 2-SCH$_3$-pyridine						
3.91	0.316	−10	3.91(3.90)[10]	3.94(3.97)[11,16]		
5.04	0.228	−60	4.96(3.86)	4.96(3.92)		
5.59	0.019	−71				
6.17	0.298	−67				

Theoretical			Experimental
ΔE	f	θ^1	$\Delta E(\log \varepsilon)$

(8) 3-SCH$_3$-pyridine

3.97	0.146	−18	3.78(3.45)[10]
4.86	0.128	38	4.63(3.94)
5.41	0.392	37	5.44(4.01)
6.26	0.227	34	

(9) 4-SCH$_3$-pyridine

4.48	0.403	90	4.15(4.28)[10]	4.16(4.31)[11,16]
4.64	0.049	0		
5.63	0.331	0	5.41(3.94)	5.49
6.30	0.362	90		

(10) 2-OH-pyrimidine

4.57	0.202	31	4.54(3.70)[2,15]
5.85	0.199	−78	$< 5.9(> 3.95)$
6.75	0.823	−63	
7.28	0.507	14	

(11) 4-OH-pyrimidine (1-NH$^+$)

4.86	0.123	−7	5.17(3.83)[2,15]
5.58	0.118	−4	5.46(3.88)
6.51	0.832	75	
7.02	0.808	1	

(12) 4-OH-pyrimidine (3-NH$^+$)

4.61	0.221	40	
5.76	0.092	−46	
6.79	0.869	−26	
6.91	0.607	59	

(13) 5-OH-pyrimidine

4.49	0.193	−20	4.35(3.67)[2,14]
5.51	0.174	−8?	5.56(3.84)
6.68	0.830	62	
7.29	0.556	−35	

(14) 2-NH$_2$-pyrimidine

4.24	0.211	36	4.13(3.58)[12]	4.11(3.60)[5]
5.46	0.387	−76	5.64(4.10)	5.61(4.17)
6.38	0.204	−64		
6.71	0.360	−57		

TABLE (continued)

Theoretical			Experimental
ΔE	f	θ^1	$\Delta E(\log \varepsilon)$

(15) 4-NH$_2$-pyrimidine (1-NH$^+$)

4.75	0.173	14	?
5.13	0.211	10	5.04(4.27)[5,12]
6.04	0.529	88	
6.75	0.654	18	

(16) 4-NH$_2$-pyrimidine (3—NH$^+$)

4.34	0.281	44	
5.37	0.207	—18	
6.45	0.319	51	
6.56	0.497	—15	

(17) 5-NH$_2$-pyrimidine

4.05	0.179	—17	3.73(3.57)[12]
5.03	0.300	87	4.90(4.16)
6.19	0.326	75	
6.91	0.36?	85	

(18) 2-SCH$_3$-pyrimidine

3.98	0.191	51	4.00(3.54)[12]
4.89	0.396	—77	4.86 (4.16)
5.56	0.075	—23	5.78(3.30)
6.39	0.120	—54	

[1] The polarization direction (angle θ) is measured positive towards C$_4$ with respect to an axis from C$_2$—C$_6$ (in pyridines) or N$_1$—N$_3$ (in pyrimidines). [2] Mason (1959). [3] Hughes (1955). [4] Blizryukov (1953). [5] Mason 1960. [6] Maschka *et al.* (1954). [6] Steck and Ewing (1948). [6] Bayzer (1957). [6] Grammaticakis (1959). [10] Albert and Barlin (1959). [11] Jones and Katritzky (1958). [12] Boarland and McOmie (1952). [13] Albert (1960). Absorption maximum at ~5.9 eV evaluated from the absorption curve. [14,15,16] Data for hydroxy, methoxy, and benzylthio derivative repectively.

As we mentioned above, the calculations reported here are based on the assumption that the cationic forms may be represented by electronic structures with the positive charges concentrated at the pyridinic nitrogen. This assumption is rather evident as far as the cations of methoxy or methylthio derivatives of pyridine and pyrimidine are concerned. Several experimental data indicate that this assumption holds in the cases of cations of hydroxy and amino derivatives of the molecules in question as well (comp. Katritzky and Lagowski 1963, Spinner and White 1966).

The results of the calculations for the singlet-singlet transitions of the cations together with the experimental data are collected in the Table[4]. As we see from the figures presented

[4] In the case of 4-OCH$_3$- and 4-NH$_2$-pyrimidine there are two types of cations considered: one with proton attached to N$_1$ and the other one with proton attached to N$_3$. The results of the calculations are better for the cation of the first type. The π-electron calculations performed here are of rather limited importance because of the approximations applied. On the base of these calculations one cannot conclude what are the actual structures of the cations.

in Table, the calculated values of transition energies are in good agreement with experimental data. For a better illustration, we give diagrams (Figs 1 and 2), where the ΔE values of both neutral and protonated forms of the molecules are compared with experimental data. As it can be seen from the diagrams, the experimentally observed shifts of the first two absorption bands of pyridines and pyrimidines under protonation are, in general, properly reproduced by the present calculations.
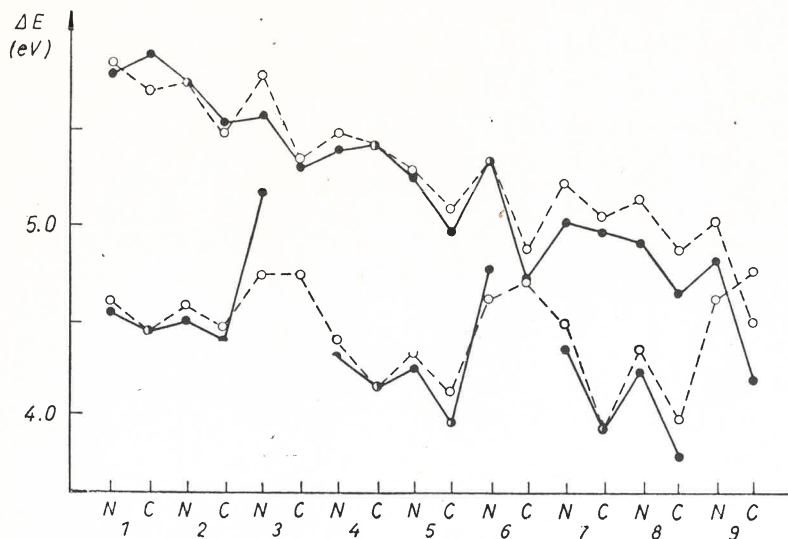

Fig. 1. Monosubstituted pyridines (N — neutral, C — cation) — comparison between observed (—●—●—) and calculated (– – ○ – – ○ – –) singlet-singlet transition energies. Actual data in Table and in our previous papers (Berndt and Kwiatkowski 19.0, Kwiatkowski *et al.* 1970), numbering of the molecules in Table.
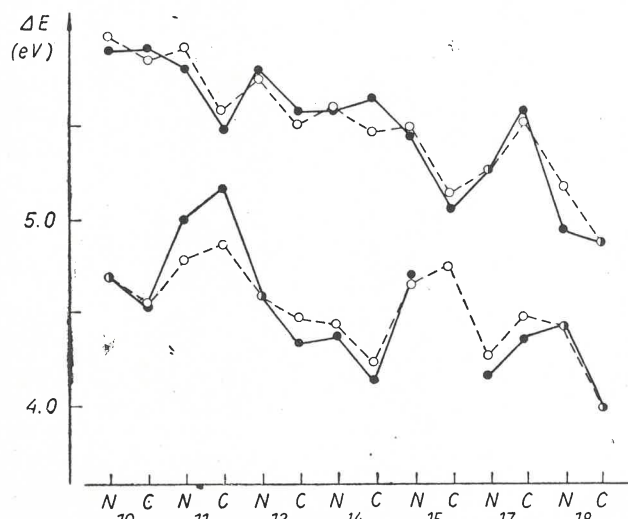

Fig. 2. Monosubstituted pyrimidines — for details see caption to Fig. 1.

We should note that the δ corrections reproduce properly the shifts of the absorption bands of pyridine itself under protonation. The calculated shifts of the first two absorption bands of pyridine, in energy terms, are equal to 0.07 and 0.26 eV respectively which is in agreement with the corresponding experimental shifts (0.0–0.05 and 0.1–0.2 eV, respectively).

It is also worth noting that similar calculations (Kwiatkowski 1971) performed for dioxosubstituted pyridines also provided a correct interpretation of the spectra.

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