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Electronic Absorption Spectra of 3-Hydroxypyridine and 5-Hydroxypyrimidine

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The electronic absorption spectra ($\pi \rightarrow \pi^*$ type) of the mixture of the enolic and zwitterionic forms of both 3-hydroxypyridine and 5-hydroxypyrimidine are interpreted by means of the Pariser-Parr-Pople type calculations.

It is well known that the hydroxy-derivatives of N-heteroaromatic systems are capable of tautomerism because the labile hydrogen atom may be attached to either a nitrogen or an oxygen atom [1]. The pyridine and pyrimidine compounds can exist under the appropriate conditions in one of the following species: enol, cation, anion and zwitterion or amide. In the previous papers [2, 3] we showed that Pariser-Parr-Pople type calculations can be succesfully used to interpret the electronic absorption spectra of the enolic, anionic and amide forms of monohydroxy substituted pyridines and pyrimidines. It is the purpose of the present note to interpret the ultraviolet spectra of both 3-hydroxypyridine[1] and 5-hydroxypyrimidine which exist in neutral aqueous solution as a mixture of the enolic and zwitterionic forms.

Mason [4] has measured the absorption spectra of spectrally distinct charged species of the molecules under study. The results of his measurements are listed in Table 1. The examination of the measured transition energies for 3-hydroxypyridine shows that the absorption maxima with energies of 3.94 and 5.04 eV are due to the first and second transitions, respectively, in the zwitterion, while the absorption band with the energy of 4.46 eV corresponds to the first electronic transition in the enolic form of the compound. The experimental order of the intensities of the transitions in the enolic and zwitterionic forms shows that 3-hydroxypiridine in aqueous solution is an equilibrium mixture of equal quantites of the enolic and zwitterionic tautomers (compare Ref. [5]).

Similarly, in the case of 5-hydroxypyrimidine, the first absorption band with the energy of about 3.8 eV is due to the first electronic transition in the zwitterionic form of the molecule, while the next bands correspond to the first and second transitions in the enolic form of the compound. However, comparing the observed intensities of the transitions in 5-hydroxypyrimidine we see that the ratio of the

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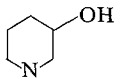
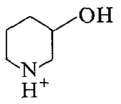
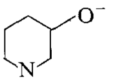
[1] Compare the recent paper [6] in which the results of SCF MO CI calculations for the zwitterionic form of the 3-hydroxypyridine 1-methochloride were reported. Calculated transition energies are in poor agreement with the experiment.

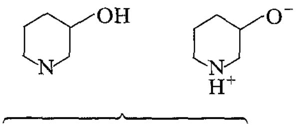
Table 1. *The electronic absorption spectra*[a] *of the enol* (E), *cation* (C), *anion* (A) *and zwitterion* (Z) *of 3-hydroxypyridine and 5-hydroxypyrimidine. All data from Ref.* [4]



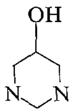


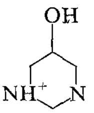


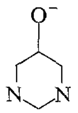
ΔE^b	$\varepsilon_{max}{}^b$	ΔE	ε_{max}	ΔE	ε_{max}
4.49	3960	4.38	5840	4.16	4960
5.74	8320	5.58	3730	5.25	11000



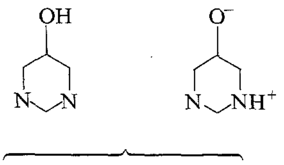
	ΔE	ε_{max}
(Z)	3.94	3060
(E)	4.46	2320
(Z)	5.04	5120







ΔE^c	$\varepsilon_{max}{}^c$	ΔE	ε_{max}	ΔE	ε_{max}
4.49	5330	4.35	4700	4.08	4450
5.59	9970	5.56	6950	5.21	11240



	ΔE	ε_{max}
(Z)	3.81	~107
(E)	4.57	4750
(E)	5.79	9720

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[a] ΔE — transition energy (in eV) corresponding to absorption maximum, ε_{max} — molar extinction coefficient for the absorption maximum. All data measured in aqueous solution unless otherwise indicated.

[b] Experimental data for the methoxy derivative of pyridine.

[c] In ethanol.

enolic form to the zwitterionic one is high. Therefore, no second and next absorption bands in the zwitterion have been measured.

The results of the calculation for the molecules so far considered were obtained by means of the Pariser-Parr-Pople method. For the details of the calculations the reader is referred to our paper [2]. The Coulomb and resonance parameters used are the same as those in the paper mentioned above. The correction of -2.0 eV was added to the value of the core integral for the protonated nitrogen

Table 2. *Enolic* (E) *and zwitterionic* (Z) *tautomers of 3-hydroxypyridine and 5-hydroxypyrimidine – the singlet-singlet transition energies, ΔE (in* eV*), oscillator strengths, f, and molar extinction coefficients, ε*

Theoretical				Experimental [4]		
ΔE	f	ΔE	f		ΔE	ε
3-Hydroxypyridine						
(Z)		(E)				
4.08	0.128			(Z)	3.94	3060
		4.58	0.086	(E)	4.46	2320
5.24	0.216			(Z)	5.04	5120
		5.76	0.129			
6.05	0.507					
		6.74	0.988			
6.79	0.511					
5-Hydroxypyrimidine						
(Z)		(E)				
4.03	0.174			(Z)	3.81	~107
		4.59	0.115	(E)	4.57	4750
5.19	0.359			(Z)	?	?
		5.75	0.229	(E)	5.79	9720
6.34	0.165					
6.94	0.454					
		6.96	0.902			
		7.05	0.754			

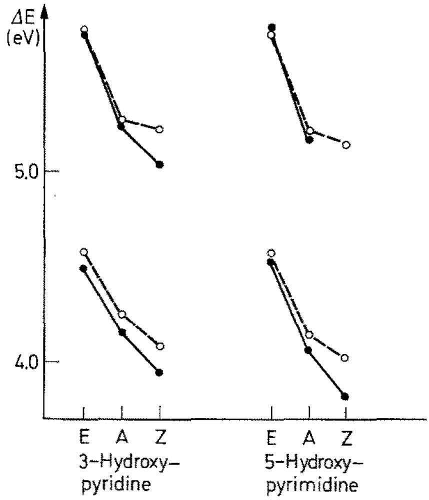

Fig. 1. Comparison between the observed and calculated singlet-singlet transition energies for the enolic (E), anionic (A) and zwitterionic (Z) forms of 3-hydroxypyridine and 5-hydroxypyrimidine. Actual data in Table 2 and Ref. [2]. — ● — ● — observed values, -- ○ -- ○ -- calculated values

of pyridine type. This figure has been determined in our unpublished work on the protonation of N-heterocyclic systems[2].

The comparison of the computed and experimental spectral features of 3-hydroxypyridine and 5-hydroxypyrimidine is shown in Table 2 and Fig. 1. As it can

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[2] A more detailed discussion on this subject will be given elsewhere.

be seen from the figures presented in Table 2, the calculated singlet-singlet transition energies in the zwitterionic forms of the molecules in question are in good agreement with the experimental data. The discrepancies between calculated and experimental transition energies in the zwitterionic tautomers are higher than the corresponding ones for the enolic and anionic forms (see Fig. 1). The differences, however, are of about the same order as those in the experimental values.

References

1. Mason, S. F.: Physical methods in heterocyclic chemistry, ed. by A. R. Katritzky, Vol. 2, p. 1. New York and London: Academic Press 1963.
2. Berndt, M., Kwiatkowski, J. S.: Theoret. chim. Acta (Berl.) in press.
3. Kwiatkowski, J. S., Olzacka, J.: To be published.
4. Mason, S. F.: J. chem. Soc. (London) **1959**, 1253.
5. Metzler, D., Snell, E.: J. Amer. chem. Soc. **77**, 2431 (1955).
6. Evleth, E. M.: Theoret. chim. Acta (Berl.) **11**, 145 (1968).

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