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Electronic Spectra of the 2-Oxypurine Isomers

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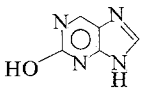
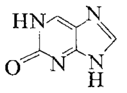
The Pariser-Parr-Pople type calculations were carried out for tautomeric isomers of 2-oxypurine. The calculated transition energies for the keto form (III) of this compound are in a good agreement with the observed absorption spectrum.

In a previous paper [1] the SCF MO CI method was applied to the study of the electronic spectra ($\pi \rightarrow \pi^*$ type) of some monosubstituted purines including 2-substituted molecules. The calculated singlet-singlet transition energies were found to be in a good agreement with the observed absorption spectra with one exception. Namely, the great difference (0.7 eV) between experimental and theoretical values for the first singlet transition energy was obtained in the case of 2-hydroxypurine.

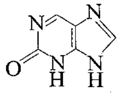
An examination of the bathochromic effect of substituents places in the 2-position of the purine nucleus shows that the 2-OH substituent has the stronger bathochromic effect on the first absorption band of purine than the both 2-OCH_3 and 2-NH_2 groups. This fact was discussed by Mason [3]. According to his opinion the differences between the spectra of 2-oxypurine and 2-methoxypurine suggest that the former compound exists in the keto form (II or III). Therefore, we do not consider the discrepancy between calculated and experimental results mentioned above as unexpected.



I



II



III

The purpose of the present communication is an attempt to apply the Pariser-Parr-Pople method to interpret the electronic spectra of various isomers of 2-oxypurine. The method of calculation is the same as that used in our previous papers [1, 2]. The detailed values of the empirical parameters used in the present calculation may be found in the papers mentioned above (see e.g. Tables 1 and 2 of Ref. [2]; the VI-K set of the β_{pq} values). The valence state data for the oxygen atom of the keto type were taken from the paper by Hinze and Jaffé [4] and the value of -2.40 eV was adopted for the $\beta_{C=O}$ ($r_{C=O} = 1.24$ Å) resonance integral.

The results of calculation for the keto forms of 2-oxypurine are summarized in Table 1. For comparison we give the same theoretical quantities calculated for the enol form (I) of 2-oxypurine [1]. As seen from the figures presented in the Table, the values of the transition energies calculated for the keto form (III) of the compound are in excellant agreement with the experimental spectrum measured by Mason [3]. Thus, the present calculations seem to corroborate suggestion of Mason [3] that the 2-oxypurine in aqueous solution exists principally in the keto form.

Table. *The singlet-singlet transition energies, ΔE (in eV), oscillator strenghts, f, and transition polarizations, θ (in degrees), calculated for tautomeric isomers of 2-oxypurine. Comparison with experiment*

Enol form[a]			Keto forms					
I			II			III		
ΔE	f	θ[b]	ΔE	f	θ[b]	ΔE	f	θ[b]
4.63	0.098	+62	2.99	0.139	−12	3.80	0.136	+76
5.34	0.102	+48	4.72	0.008	+87	5.11	0.265	−65
5.97	0.937	−65	5.01	0.244	−43	5.71	0.343	−70
6.56	0.195	+77	5.43	0.562	+86	5.88	0.378	−53
6.77	0.582	+31	5.97	0.619	−71	6.13	0.033	−69

Experiment [3], ΔE: 3.94, 5.21

[a] Theoretical results taken from Ref. [1].

[b] The polarization direction (angle θ) is measured positive towards C_6 with respect to an axis from C_4–C_5 (see [2]).

References

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