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IONIZATION POTENTIALS AND ELECTRON-DONOR ABILITY OF NUCLEIC ACID BASES AND THEIR ANALOGUES

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The first adiabatic ionization potentials (IP_a) of some purine and pyrimidine bases and their analogues has been measured by photoionization mass-spectrometry in gas phase. The measurements were made on MS-1302 mass-spectrometer (Special Construction Bureau, Academy of Sciences of the USSR)[I] modified by us to increase its sensitivity. A combination of the high-voltage low-pressure hydrogen discharge tube and a Seya-Namioka monochromator with the differential hydrogen pumping technique was used as a source of monochromatic radiation in the vacuum UV region of spectrum. The working spectral area of the instrument was 850-2000 Å. Samples were evaporated directly into ionization chamber at 50-200°C.

The first IP_a have been determined from the initial regions of the photoionization efficiency curves, according to the value of the lowest (threshold) photon energy required for the formation of molecular ions. The estimated accuracy of the IP_a was 0.03÷0.05 eV. The preparations of bases obtained from Chemapol (CSSR), Reanal (Hungary) and Reakhim (USSR) have been used without additional purification, the purity being checked mass-spectrometrically.

Comparison of the IP_a measured in this paper with the vertical ionization potentials (IP_v) published earlier[2] (see Table I) shows that these exceed the IP_a on the average by 0.3 eV. It should be noted that the IP_a for hypoxanthine found in the paper[2] is in agreement with our results.

As can be seen from the Table I, the IP_a of the nucleic bases studied by us increase in the following sequence: guanine - caffeine - 9-methyladenine - 7-methyladenine - adenine - - benzimidazole - 6-methylcytosine - 7-methylhypoxanthine - hypoxanthine - isocytosine - - xanthine - imidazole - cytosine - thymine - purine - uracil - 5,6-dihydrothymine; therefore, their electron-donor ability decreases in this same sequence The IP_v of the nucleic bases are changed in the same order (except for purine).This sequence has been compared with the similar sequences derived by a number of authors by means of theoretical evaluations[3-7]. It should be noted that the sequences obtained by quantum-chemical calculations[3-7] vary within wide range. Nevertheless our experimental data confirm the general conclusion made of these publications that the purine bases are better electron donors than the pyrimidines.

It follows from the analysis of experimental data that the highest occupied orbitals of all the compounds studied **are** π-orbitals. The results obtained for various methyl-substituted purine and pyrimidine bases permit to estimate the relative electron density of the highest π-orbitals of the atoms directly bound with methyl substituents.

TABLE I

IONIZATION POTENTIALS OF NUCLEIC ACID BASES AND THEIR ANALOGUES

Compound	IP$_a$	IP$_v^2$	Compound	IP$_a$	IP$_v^2$
	(in eV)			(in eV)	
5,6-Dihydrothymine	9.68	-	7-Methylhypoxanthine	8.42	-
Uracil	9.32	9.50	6-Methylcytosine	8.38	-
Purine	9.12	9.52	Benzimidazole	8.31	-
Thymine	8.87	9.14	Adenine	8.26	8.44
Cytosine	8.68	8.94	7-Methyladenine	8.18	-
Imidazole	8.67	-	9-Methyladenine	8.04	-
Xanthine	8.55	8.89	Caffeine	7.94	-
Isocytosine	8.44	-	Guanine	7.77	8.24
Hypoxanthine	8.44	8.89 (8.55)^a			

a-adiabatic ionization potential

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