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FUNCTIONAL SUBUNITS IN THE NUCLEIC ACID BASES URACIL AND THYMINE [1]

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Below we present evidence that uracil (1) and thymine (2) contain widely intact dicarboximide and enamine functional subunits.

A combined method based on ab initio [2,3] Koopmans' ionic states [4] and CNDO/S Koopmans' defects [5,6] yields for thymine the ordering of ionization events: $\pi_{C=C-N}$, n_O, π_N, n_O, and $\pi_{C=C-N}$ [7]. Here the ion states are labelled according to the designation of orbitals from which they arise. $\pi_{C=C-N}$ refers to the two possible π enamine ionizations, n_O to the two dicarboximide oxygen lone pair ionization events and π_N denotes the lowest energy π dicarboximide ionization which is mainly a nitrogen lone pair event. CNDO/S CI [5,6] calculations further show that the methyl group in thymine mainly facilitates the $\pi_{C=C-N}$ ionizations whereas the other ionizations stay essentially unaffected.

The aforementioned predicted sequence of ion states for uracil and thymine is in full harmony with the following experimental facts: (i) The photoelectron (pe) spectra of 1 and 2 (Figure) are very similar. The ionization events corresponding to bands ① and ⑤ are facilitated by 0.4 eV for thymine when referenced against uracil whereas the other ionizations occur for both compounds at very similar energies. This observations points to ionizations ① and ⑤ to be connected with the enamine unit. This assignment gets clear support from the observation of the two $\pi_{C=C-N}$ ionizations in the enamines, 2-methyl-2-azabicyclo [3,2,1] octa-3-ene and 2-methyl-2-azabicyclo [3,2,1] octa-3,6-diene [8]. Here, both ionizations are separated by 2.77 and 2.89 eV, respectively. The corresponding separations in 1 and 2 are 3.05 and 3.08 eV [9].

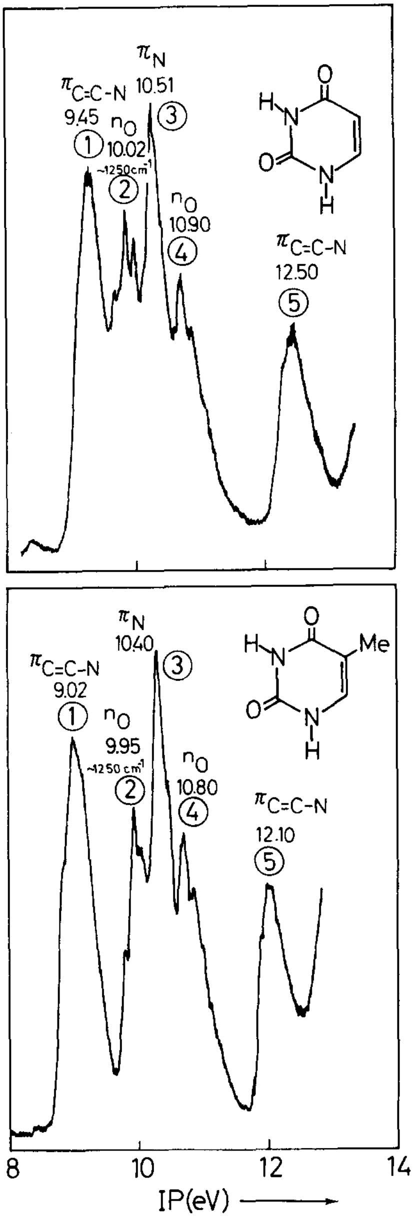


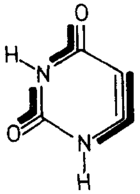
Figure Photoelectron Spectra of uracil and thymine with assignments. The numbers associated with each band refer to vertical ionization potentials in eV.

(ii) Bands ② and ④ exhibit vibrational structure with a spacing of ~1250 cm^{-1}. Such a fine structure very often occurs with oxygen lone pair pe bands, e.g. for acetic acid with 1310 cm^{-1} [10], for acetamide with ~1350 cm^{-1} [10], for ethyl acetate with ~1200 cm^{-1} [10], for thietane-3-one with 1240 cm^{-1} [11] and for cyclopentanone with 1220 cm^{-1} [12], and is quite characteristic for such ionization events. We therefore assign both bands to the two n_O ionization processes. The assignment is further supported by the finding that the corresponding ionizations for succinimide are separated by 0.9 eV [13]. The respective gaps for 1 and 2 are 0.88 and 0.85 eV.

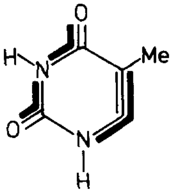
Bands ①, ② , ④ , and ⑤ being assigned the remaining band ③ must be attributed to the π_N ionization process. Interestingly this process is facilitated in 1 and 2 by ~0.4 eV when compared with the same event for succinimide.

The foregoing comparison between the pe spectra of 1 and 2 with those of enamines and succinimide suggests that the uracil and thymine spectra are essentially composite spectra exhibiting well separated enamine (bands ① and ⑤) and dicarboximide (bands ② to ④) substructures.

Therefore we conclude that uracil and thymine must be considered as being composed of widely intact enamine and dicarboximide subunits as illustrated below. It is only the small shift of the π_N band (band ③) towards lower energy mentioned above which points to additional small subunit coupling.



Uracil
1



Thymine
2

The present spectroscopic result might command much chemical interest. So the well-known chemical observations that position 5 in uracil is easily attacked by electrophilic agents [14] or that the biochemical synthesis of thymine from uracil occurs by alkylation [14] can now be understood as typical enamine reactions.

Acknowledgement

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(7) It is interesting to mention that this ordering of ionized states differs from the ab initio Koopmans' states sequence which is $\pi_{C=C-N}$, π_N, n_o, n_o, and $\pi_{C=C-N}$. In consequence, there is a breakdown of Koopmans'theorem for thymine and, by implication, uracil.

(8) The $\pi_{C=C-N}$ ionizations occur at 7.22 and 9.99 eV for 2-methyl-2-azabicyclo [3,2,1] octa-3-ene and at 7.28 and 10.17 eV for 2-methyl-2-azabicyclo [3,2,1] octa-3,6 diene: H.Schmidt, A.Schweig, and A.G.Anastassiou, unpublished results.

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