Electron-driven proton-transfer channel in the hypothetical prebiotic RNA base pairs

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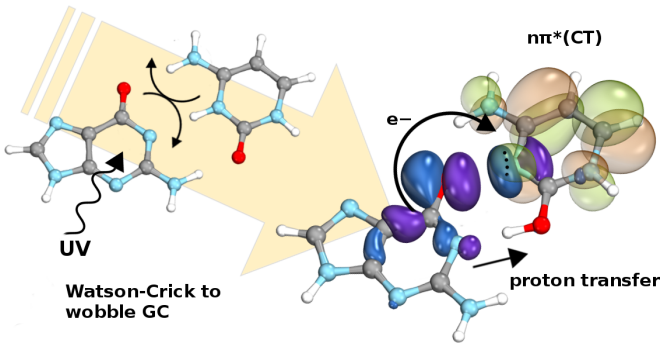
Significant photostability of canonical DNA/RNA nucleobases and their base pairs was one of the main reasons for their selection as building blocks of the informational polymers, due to ultrafast non-radiative deactivation after photoexcitation. This hypothesis seems valid irrespective of whether protonucleotides were indeed assembled from nucleobases, ribose and phosphates or appeared in a direct synthesis from prebiotic feedstock molecules [1]. We do not really know whether RNA and DNA simply appeared in the Archean and remained unchanged since then or, what is more likely, the precursors did undergo a sort of prebiotic evolution. To validate the latter, several groups suggested and investigated in this context a large number of hypothetical prebiotic protonucleobases [2,3]. Since the excited state electron-driven proton-transfer process (EDPT) was suggested as one of the key relaxation channels in canonical base pairs [4] we decided to investigate whether it is also accessible in selected Watson-Crick-like pairs of such alternative nucleobases using state-of-the-art ab initio calculations utilizing adiabatic diagrammatic construction to second order [ADC(2)].

The examined tally contains hydrogen-bonded dimers of perspective proto-RNA analogues, like 8-oxo-guanine as the main product of oxidative damage of DNA, or barbituric acid [2,3]. The potential-energy profiles computed using ADC(2)/cc-pVTZ suggest a quite high probability of the barrierless electron-driven inter-base proton-transfer deactivation proceeding through peaked S1/S0 conical intersections, however, the role of nπ* states in this mechanism is greater than it is commonly recognized. For example, an investigation of guanine-cytosine base pair under UV radiation revealed a significant WC-to-wobble change of pairing, which has not been yet described in the literature.



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