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## BOOK of ABSTRACTS



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## A HYBRID STATISTICAL MECHANICS – QUANTUM MECHANICAL MODEL FOR PROTON TRANSFER IN 5- AND 6-AZAUACILS IN WATER SOLUTION

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A hybrid statistical physics – quantum mechanical methodology was implemented to study the water-assisted intramolecular proton-transfer processes in 5- and 6-azauracils in aqueous solutions. The solvent effects were included in the model by explicit inclusion of two pairs of water molecules, which model a first hydration shell around the solute. The position of these water molecules was initially estimated by carrying out a classical Metropolis Monte Carlo simulation of dilute water solutions of the title compounds and subsequently analyzing solute-solvent intermolecular interactions in the MC-generated configurations. Sequentially to the statistical physics simulation, *ab initio* quantum mechanical level of theory was implemented. The effects of the water as solvent (at *ab initio* QM level) were introduced at two different levels - using solute-solvent clusters (four water molecules) and using the same clusters embedded in an external continuum. Full geometry optimizations of these complexes were carried out at MP2/6-31G(d,p) and C-PCM/MP2/6-31+G(d,p). Single point calculations were performed at CCSD(T)/6-31+G(d,p)//MP2/6-31+G(d,p) computational level to obtain more accurate energies. According to our calculations hydrated azauracils should exist in three forms: mainly dioxo form and two hydroxy forms. The calculated proton transfer activation energies for tautomeric reactions of 5-azauracil and 6-azauracil show different pictures for these two compounds. According to C-PCM/MP2/6-31+G(d,p) data water-assisted proton transfer in 5-azauracil realizes through two parallel reactions **A**→**B** and **A**→**D**. Tautomeric equilibrium in 6-azauracil in water could occur by two contiguous reactions, **A**→**D** and **D**→**C**. The proton transfer investigated reactions in 5- and 6-azauracils involve concerted atomic movement.

**Keywords:** 5- and 6-azauracils, proton-transfer, solvent effects, Monte Carlo, quantum chemistry

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