

Keto-enol tautomerism in 5- and 6-azauracils in water solution

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ABSTRACT

Ab initio quantum chemical investigations on the tautomeric equilibrium in 5- and 6-azauracils in water were performed. The solvent effects were considered by explicit inclusion of two pairs of water molecules, which model a first hydration shell around the solute. The effects of the water as solvent 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 MP2/6-31+G(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 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 the 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 occurs 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-azauracil, 6-azauracil, proton transfer, tautomerism, *ab initio*

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