Experimental and Computational Studies on Aminoguanidine Free Base, Monocation and Dication. Part III: Proton Affinities of Guanidine, Aminoguanidine and Glyoxal Bis(amidinohydrazone)

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The structures of glyoxal bis(amidinohydrazone) (GBG) free base and glyoxal bis(amidinohydrazonium) monocation and dication were calculated quantum chemically by using the density functional hybrid method B3-LYP with the standard basis set 6–31G(d). Proton affinities calculated from these data are 246.4 kcal/mol for the free base and 176.0 kcal/mol for the monocation. The proton affinities of guanidine free base (246.2 kcal/mol), aminoguanidine free base (242.9 kcal/mol), aminoguanidinium monocation (88.6 kcal/mol) were calculated for reference. The B3-LYP functional overestimates the proton affinities for all the species studied. For example, for guanidine the proton affinity at the MP2/6–31G(d) level is 238.3 kcal/mol, the experimental reference value being 233 kcal/mol. However, from the B3-LYP values it can be concluded that in the gas phase all the three bases are nearly equally basic. On the other hand, it is known that in aqueous solution guanidine is a much stronger base than aminoguanidine and glyoxal bis(amidinohydrazone). The results are discussed from the point of view of molecular size, shape and symmetry, and hydrogen bonding in solution.

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