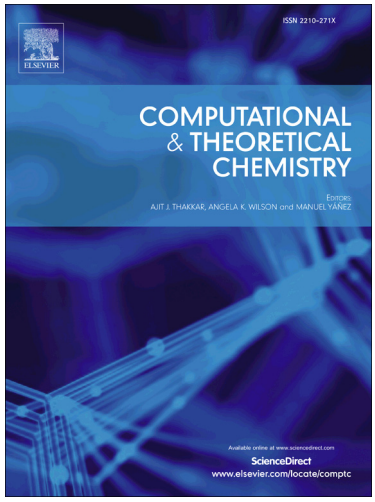

The guanylated bioamine agmatine – A theoretical investigation of its structure and exceptional high basicity in the gas phase

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The guanylated bioamine agmatine – A theoretical investigation of its structure and exceptional high basicity in the gas phase

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Abstract:

The guanylated bioamine agmatine, $H_2N(CH_2)_4–N=C(NH_2)_2 \rightleftharpoons H_2N(CH_2)_4–NH–C(NH_2)=NH$, formed by decarboxylation of the proteinogenic amino acid arginine, plays an important role in the physiological processes of living organisms. Its structure is marked by the flexibility of the four-carbon chain connecting the two potentially basic amino and guanidino sites. Owing to these noteworthy properties and the questionable literature data on its protonated forms, its structure and intrinsic basicity were carefully scrutinized at the B3LYP/6-311+G(d,p) level. Three types of isomerism (prototropy and geometrical isomerism of the guanidino group, and rotational isomerism of the chain) were considered in this structural investigation. Various tautomers, as well as *E*/*Z*-isomers of the free guanidino group, various coiled and open conformations of the alkyl chain, and potential protonation sites (alkylamino and guanidine imino) were analyzed. Due to n-π conjugation in the guanidino group, its amino nitrogen (erroneously taken in the literature as the site of monoprotonation) is the least probable candidate as a protonation site. The $H_2N(CH_2)_4–N=C(NH_2)_2$ tautomer slightly predominates in the tautomeric mixture. One of its coiled conformations, facilitating the formation of