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Conformational analysis and intramolecular hydrogen bond strength of methyl 3-aminocrotonate

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Introduction

β-Enaminones have been widely studied because they can be found in biological systems such as proteins [1]. Additionally, they are applied as psychoactive drugs [2]. These compounds, theoretically, are capable of forming three different tautomers at equilibrium, i.e., iminoketone, aminoketone, and iminoenol forms. Existence of intramolecular hydrogen bond (IHB) is one of the important characteristics of them. This is an asymmetric hydrogen bond (i.e., N-H⋯O or O-H⋯N) which is significantly weaker than the corresponding homonuclear O-H⋯O bonds in *β*-diketones [3].

The aim of the present work is to investigate the stable conformations of methyl 3-aminocrotonate (MAC) using density functional theory (DFT). The results are compared with the corresponding ones for a simpler molecule, i.e., 4-amino-3-penten-2-one (APO).

Theoretical Methods

The molecular equilibrium geometries of MAC were computed with Gaussian 09W. The B3LYP/6-311++G(d,p) level was used for optimizing the structures. To confirm the stability of the calculated structure, the vibrational wavenumbers were calculated by the same level of DFT (To be sure that one has found a minimum and not a saddle point, it is essential to test the nature of the stationary point found by the geometry optimization. This is done by doing a frequency calculation at the geometry found. For a true minimum, all the calculated frequencies will be real).

AIM2000 software was applied to obtain electron density at hydrogen bond critical points and hydrogen bond strength [4] according to Bader's atoms in molecules (AIM) theory at the MP2/6-311++G(d,p) level.

Results and discussion

All theoretically possible conformers of MAC, considered by rotation of the molecule about its bonds, were optimized using the B3LYP method and 6-311++G(d,p) basis set. The results of full optimization were five stable conformations. All aminoketone conformers were changed to the

corresponding iminoenol ones. Therefore, the iminoenol conformers do not exist for this simple β-enaminone (the same as APO [5]).

The energies of optimized structures are considerably higherthan that of the stable structure (3.56 to 8.42 kcal mol^{-1}). Therefore, the existence of any of these four conformers in the sample is unlikely. According to the AIM results, the IHB strength is about 6.3 kcal mol^{-1}. The corresponding calculated value of APO is about 7.9. Thus, the IHB in APO is stronger than that in MAC.

Conclusions

The conformers of MAC have been studied by means of DFT. The geometry and vibrational wavenumbers of MAC were calculated at the B3LYP level using 6-311++G(d,p) basis set. According to the calculated results, only one structure is the most stable conformer of MAC which is in agreement with the corresponding APO results. On the basis of the AIM theory, the IHB of MAC is weaker than that of APO.

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