

Conformation analysis, tautomerism, and vibrational assignment of 1-amino-2-keto-6-cyclohexene

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Introduction

Theoretically, 1-amino-2-keto, 6-cyclohexene (AKC) is capable to form 18 tautomers. This compound is prepared from amination of 1,2-hexanedione. The study of AKC is useful for understanding the nature of intramolecular hydrogen bond in the amino-ketones with 5-membered chelated ring.

The aim of this work is study of Tautomerism, conformational analysis, and predicting the vibrational spectra of AKC and comparing the strength of its intramolecular H-bond with that in 4-amino-pentane-2-one [1], which forms a 6-membered intramolecular H-bond.

Method of calculation

The calculations of geometrical parameters and frequencies were performed using the Gaussian 03 program package [2]. In this work, we applied the DFT method including the hybrid gradient-corrected exchange functional proposed by Becke [3] with the gradient corrected correlation functional of Lee, Yang, and Parr [4], B3LYP, using the basis set 6-31G**. The relative stability of 18 different tautomers of this compound is obtained.

Results and discussion

AKC, theoretically, can exist in three main forms, amino-ketone, imino-ketone, and imino-enol, which with considering all possible conformations one can consider 18 different tautomers.

According to our calculations the aminoketone tautomer engaged in an intramolecular H-bond is the most stable tautomer (AK-1) and theoretical thermodynamics calculations indicate that almost only this tautomer predominantly (about 100%) exists in the sample. There are three



more aminoketones (AK-2, AK-3, and AK-4) which have much higher energy than that of AK-1 (7.4-12.3 kcal/mol). The major difference between these tautomers is position of double bond which changes the π -electron conjugation in the system. AK-4 is about 4 cal/mol more stable than AK-2 and AK-3 tautomers. This energy difference is caused by conjugation between C=O and C=C bonds. Of course, this conjugation can not affect the π -electron delocalization in the H-bonded ring, suggested by Gilli et al. [5]. The imino-ketones are the next stable tautomers, with an energy difference of about 3 kcal/mol for one of this tautomers. However, imino-enols have the highest energy (with an energy difference of 13-26 kcal/mol) and any contribution of them in the sample is unlikely.

References

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