Journal of Molecular Structure 1107 (2016) 121–136

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

The effect of deformation and intermolecular interaction on the absorption spectrum of 5-aminotetrazole and hydrazine: A computational molecular spectroscopy study on hydrazinium 5-aminotetrazolate

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ARTICLE INFO

Article history:
Received 15 July 2015
Received in revised form
3 November 2015
Accepted 12 November 2015
Available online 30 November 2015

Keywords:
Deformation
Intermolecular interaction
Absorption
Hydrazinium 5-aminotetrazolate
Hydrazine
SAC-CI

ABSTRACT

In the present work, the UV absorption spectra of seven complexes of hydrazinium 5-aminotetrazolate (HY-5AT), in the range of 4–12 eV, were calculated in both gas and water. The UV absorption spectra of the selected HY-5AT complexes were also calculated in the absence of the intermolecular interaction between 5-aminotetrazole (5AT) and hydrazine (HY) and compared with the calculated UV absorption spectra of isolated HY and 5AT in the gas phase to see the effect of deformation on the electronic structures of the fragments. In addition, the calculated spectra of HY-5AT complexes were compared with the corresponding calculated spectra of HY-5AT complexes in the absence of the interaction between HY and 5AT to see the effect of interaction between two fragments on the absorption spectra of the complexes. Similar studies were performed on the most stable structure of HY-5AT complex in water and different trend was observed for the effect of deformation and interaction on the absorption spectrum of complex compared to the gas phase.

1. Introduction

There are compounds in chemistry which are formed from two or more separate fragments interacting with each other in the structure of a complex. In these molecular systems, the individual parts are held together by forces other than covalent bonds. These include ionic complexes [1] where the dominant attractive force is of electrostatic origin, complexes with hydrogen bonds [2,3], charge-transfer complexes [4], and true van der Waals molecules for which the dominant attractive contribution is the dispersion forces [5].

One of the best examples of this kind of compounds is HY-5AT which has been composed of 5-aminotetrazole (5AT) and hydrazine (HY) interacting with each other in HY-5AT complex and known as one of the most important energetic materials [6–11]. It is often used as a starting material for the synthesis of other tetrazole derivatives, combine several advantages such as smokeless combustion, positive heats of formation, excellent propulsion power, and good specific impulse when it serve as propellants or pyrotechnics [11]. HY-5AT is synthesized from the reaction between 5AT and diluted HY solution in THF [12]. The interaction between 5AT and HY in the complex causes that their molecular geometries and electronic structures become different from their corresponding geometries and electronic structures when they are in their isolated forms. To our knowledge, there is no theoretical paper in literature related to the study of the effect of intermolecular interaction and deformation of fragments in a complex on the spectral properties of fragments. Recently, Farrokhpour et al. studied the effect of van der Waals interaction between Ar and CS_2 molecule on the spectral properties of CS_2 molecule in the gas phase [13,14].

There are seven tautomers for 5AT [15] (see Fig. 1) and, theoretically, can be coupled with HY to form different structures for HY-5AT complexes. Najafi et al. studied the tautomerism of all possible forms of 5AT in the gas phase and different solvents, theoretically [16], and found that 5AT in 2H form (5AT1 in Fig. 1) is the most stable tautomer in both gas phase and solvent. In another study, Najafi et al. studied the interaction of the different tautomers of 5AT with HY and determined the most stable structure of HY-5AT

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http://dx.doi.org/10.1016/j.molstruc.2015.11.027
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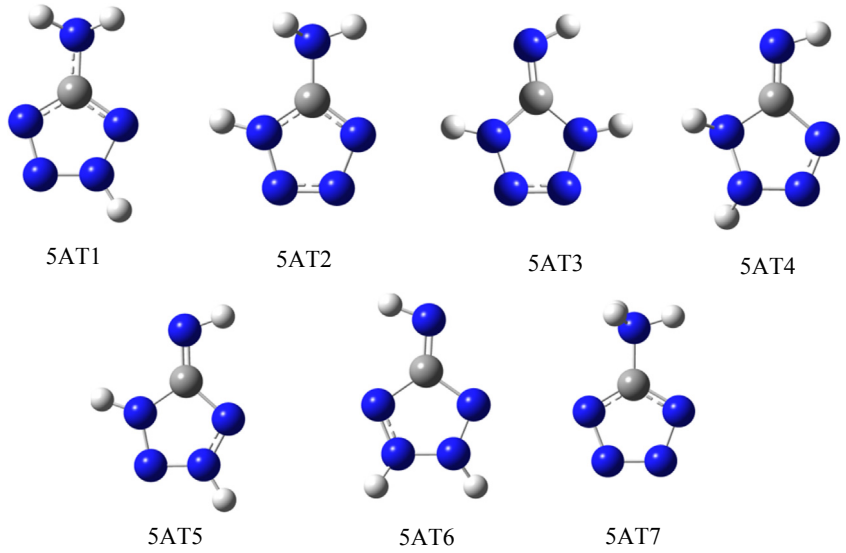

Fig. 1. The optimized structures of the different tautomers of 5AT calculated at the MP2/6-311++G(d,p) level of theory in the gas phase.

in both gas and water [17]. In addition, they determined the standard enthalpy of formation of different structures of HY-5AT in the gas phase.

In this work, the absorption spectra of the different structures of HY-5AT are calculated and studied in both gas phase and water. To our knowledge, there is no theoretical and experimental study on the absorption spectrum of HY-5AT in the range of 4–15 eV in literature. The effects of the structural deformation and

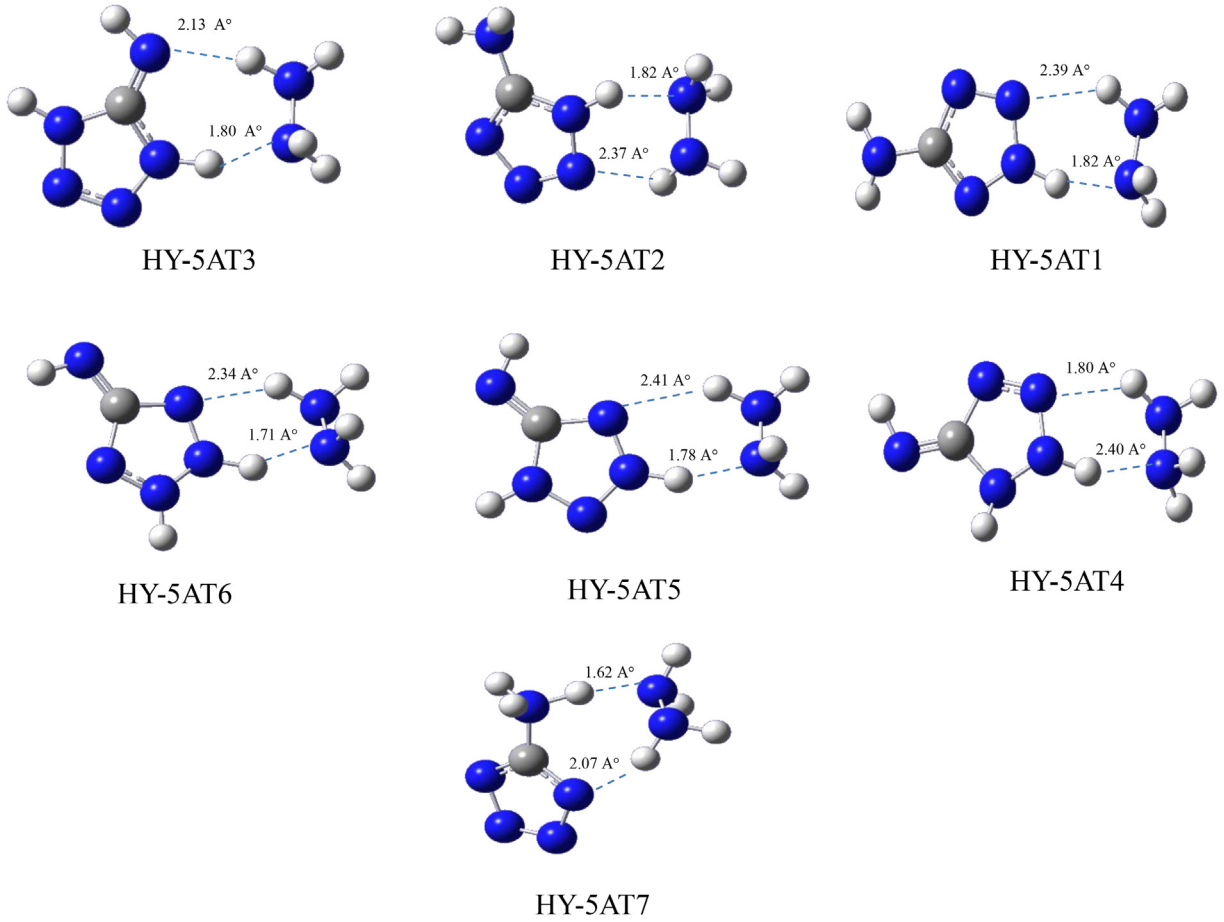

Fig. 2. The optimized structures of different HY-5AT complexes calculated at the MP2/6-311++G(d,p) level of theory in the gas phase.