

Conformational study of the (z)-[(2-iminoethylidene)silyl]amine at the MP2, DFT and G2MP2 levels

Heidar Raissi, Mehdi Yoosefian*, Samaneh Khoshkhou

Chemistry Department, Birjand University, Birjand, Iran

ARTICLE INFO

Article history:

Received 30 August 2011
Received in revised form 2 December 2011
Accepted 3 December 2011
Available online 20 December 2011

Keywords:

(z)-1-(2-Iminoethylidene) silane amine
Molecular conformation
AIM
NBO
HOMO and LUMO

ABSTRACT

(z)-[(2-Iminoethylidene)silyl]amine has been studied extensively as a model involved in intramolecular hydrogen bonding (HB) assisted by π -electrons resonance. In order to evaluate the stability and the nature of intramolecular HB, all of its possible tautomeric structures (imine and amine) were probed at B3LYP/6-311++G**, MP2/6-311++G**, and G2MP2 levels of theory. The calculated geometrical parameters and conformational analysis in gas phase and water solution indicated that the (z)-1-(2-iminoethylidene) silane amine conformers of this compound were more stable than the others. This stability is mainly due to the formation of an N \cdots H–N intramolecular HB and the position of Si atom in these conformers. The “atoms in molecules” theory of Bader was used to analyze critical points and to study the nature of hydrogen bond in these systems. Natural bond orbital (NBO) analysis was also performed for better understanding the nature of intramolecular interactions. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) with frontier orbital gap are presented. The result showed that N \cdots H–N intramolecular HB in the mentioned compound possesses a bonding character.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

HB is undoubtedly the most vital and interesting interaction force. It strongly affects the structure and properties of many participating molecules. For example, the anomalous properties of water, the basic secondary structural elements of polypeptides and proteins (such as α -helix and β -sheet) as well as the double helical structure of DNA and RNA all are consequences of HB interactions [1–3]. These interactions also play a crucial role in crystal engineering [4], enzymatic catalysis [5], molecular recognition [3], proton transfer reactions [6] and many other chemical and biochemical processes. In recent years quantum mechanical calculations of HB have attracted the attention of theoretical chemists, physicists and biologists [3,7–9]. The importance of hydrogen bonded systems has long been known, although the understanding of its nature is not yet complete. Indeed, HB is responsible for remarkable changes in the properties of solids, liquids or large clusters [3,10]. However, most theoretical studies have concentrated in relatively small hydrogen bonded systems in order to be able to perform high level quantum chemical calculations. There is a wide range of phenomena involving hydrogen bonded systems, which can be probed by quantum mechanical calculations. For example, chirality on the intermolecular interaction [11], cooperativity or non additivity factors [12] and solvatochromic shift in

adsorption transition [13] have been consistently investigated in the domain of HB.

In this work, (z)-1-(2-iminoethylidene)silane amine (IESA) was chosen, because it contains N \cdots H–N intramolecular HB and has a relatively simple structure. IESA is resembled to the 3-imino-propenylamine [14] except replacement of C by Si. Unlike the case of carbon, which easily forms strong π bonds through sp^2 hybridization, the π bond in silicon compounds is fairly weak. Furthermore, our studies will also provide useful information on replacement effect of a CH group by a less electronegative SiH group leading to the nature of the intramolecular HB strength. Theoretically, three classes of tautomers namely, imino ethyl silanimine (ISI), imino silyl ethylene amine (SEA) and imino ethylidene silane amine (ISA) have been demonstrated in Fig. 1. Our theoretical calculations confirm that the HB strength increases from ISA to ISI and SEA.

The main goals of this work were (i) to determine the order of stability of the various IESA conformations, (ii) to predict the most stable structure in the gas phase and in solution, and (iii) to evaluate the intramolecular HB strength in more stable conformers. Here, the exact values of the intramolecular HB energies were estimated by the Espinosa method [15].

2. Analysis method

All the computations in the present study were performed by Gaussian 03 series of programs [16]. The geometry optimization was carried out at B3LYP, MP2 methods with 6-311++G** (160

* Corresponding author. Tel.: +98 5612502064; fax: +98 5612502065.
E-mail address: myoosefian@yahoo.com (M. Yoosefian).

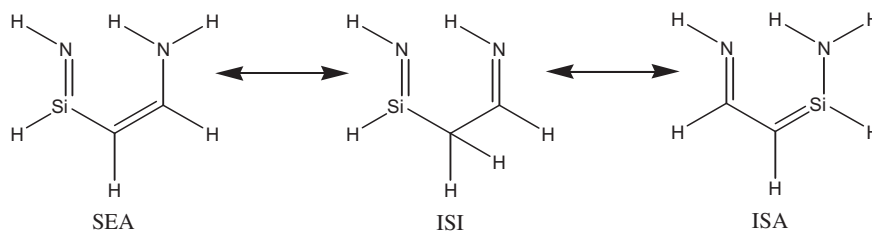


Fig. 1. Tautomery equilibrium in IESA.

basis function, 248 primitive Gaussians) basis set. To have more reliable energetic, their total energies were computed at the G2MP2 level, which yields energies of an effective QCISD(T)/6-311G(d, p) quality. We have presented DFT data here, the rest has been provided as [supplementary Tables](#). The optimized structures were used to obtain the appropriate wave function files for AIM analyses. The nature of the intramolecular HB was studied using the AIM theory of Bader by mean of AIM2000 software [17]. Additionally, the natural bond orbital's (NBO) analysis was performed at the same wave function using the NBO package included in Gaussian 98 suite of program [18]. Furthermore, harmonic vibration frequencies were calculated at B3LYP/6-311++G** and MP2/6-311++G** levels of theory in order to confirm the nature of stationary points found and to account for the zero-point vibrational energy (ZPVE) correction. We have also examined the solvent effect on the relative stability of the most stable conformers. The solute–solvent interactions which were initially taken into account by Onsager model, later were described by polarized continuum model (PCM).

3. Results and discussion

On the basis of the conformer's standard definition, theoretically, IESA has 24 stable conformers. Based on functional groups, these conformers can be classified into three tautomeric classes: 2-(iminosilyl) ethylene amine (SEA), 1-(2-iminoethylidene) silane amine (ISA) and 1-(2-imino ethyl) silane imine (ISI). They have 8, 8, and 8 rotamers respectively. Our theoretical calculations on IESA show that its 1-(2-imino ethylidene) silane amine conformers are more stable than the other conformers. Probing all hydrogen-bonded and non-hydrogen-bonded systems in all conformers by mean energies calculations illustrate that the following stability orders for IESA conformers.

ISA > SEA > ISI

The extra stability of ISA conformers is due to the existence of strong Si=C, Si–N and C=N bonds and more π -electron delocalization in their frameworks. Moreover, the stability order in H-bonded and non H-bonded conformers fairly depend on theoretical level and electron correlation.

3.1. The ISA group

The possible structural conformations and their relative energies with respect to the most stable conformer are given in [Fig. 2](#). Their structural parameters are available upon request as [supplementary Tables](#). Additionally, we calculated the zero-point energy. The results taking ZPVE into account show the same stability order. The absence of imaginary frequency for these conformers proves that each of these forms is stable and has a particular local minimum on the potential energy surface (PES). The dependency of stability order ISA conformers on the applied computational method was observed when the consequent energy orders at all the computational levels were compared. The present results predict

that the heavy atom skeletons of the eight conformations of the ISA tautomer ([Fig. 2](#)) are fully planar. The comparison of the relative energies of the different ISA conformers shows that ISA-1 is more stable than all the other conformers (ISA-2-ISA-8). This stability is mainly due to the formation of a relatively strong N··H–N intramolecular HB, which is assisted by π -electron resonance. Here, the strength of the intramolecular HB was calculated by the Espinosa method [15].

Obviously, HB and the π -electrons resonance strongly affect the stability order of conformers. Indeed, geometrical parameters showed that in ISA-1 conformer, both C=N and C=Si bond lengths have increased, whereas C–C and Si–N bond lengths have decreased with regard to the other ISA conformers. These behaviors are induced by HB formation causing an increase in the π -electron resonance of the chelated ring. Analysis of geometrical parameters provides evidence that bond angles in the ISA-1 chelate ring are closer to the standard sp^2 hybridization values compared with other conformers. This is due to the presence of a relatively strong N··H–N HB. Additionally, comparing the relative energies of all conformers, we find that the ISA-1 is the most stable one, indicating the ISA-1 conformer is a global minimum.

3.2. The SEA group

ISEA has eight possible SEA conformers ([Fig. 3](#)), all of them on average, are less stable than the ISA conformers and their stabilities are related to the existence of the N··H–N HB and π -electron resonance in the chelated ring. Because of π -electron delocalization, all of them have planar structures. The lack of imaginary frequency proved that all were stable and had particular local minima on PES.

It was found out that the ZPVE correction could not considerably change the energy orders being an insensitive parameter. The relative energies show that the trans orientation of NH₂ and C=C bonds has greater stability vis-a-vis the cis orientation. The comparison between the N··H–N HB in ISA-1, SEA-1 and ISI-1 conformers illustrate that the N··H–N HB in SEA-1 conformer is stronger than ISA-1 or ISI-1. This is due to position of Si in SEA structure. Furthermore, the value of N··H distances in SEA-1, ISI-1 and ISA-1 are about 1.985, 2.209 and 2.265 Å respectively, supporting our reason.

On the other hand, the ISA conformers are about 4–19 kJ/mol more stable than the SEA analogues. They contain systematic C=Si and C=C bonds translating to more stability than those containing C–Si and C=C bonds. Relative stabilities of both the ISA-1 and the SEA-1 conformers indicate their almost degeneracy. At the B3LYP/6-311++G** level, the ISA-1 conformer was found to be 0.4 kJ/mol more stable than the SEA-1 one. At the MP2/6-311++G** level, this energy gap becomes 3.6 kJ/mol. However, at the G2MP2 level, the latter was predicted to be only slightly (0.05 kJ/mol) more stable than the former. Therefore, these results confirmed that both conformers are nearly degenerated. The small energetic gap between SEA-1 and ISA-1 is a direct consequence of the stronger intramolecular HB of the former. A topological

Download English Version:

<https://daneshyari.com/en/article/5394830>

Download Persian Version:

<https://daneshyari.com/article/5394830>

[Daneshyari.com](https://daneshyari.com)