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Properties and isomerization mechanism of the singlet state imidazole–imidazolium system

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Abstract

The singlet state complexes of imidazole and imidazolium are optimized using the B3LYP method in conjunction with the 6-311+G* basis set. Totally, four stable complexes are found on the global potential energy surface, and they are classified as: N–H···N mode, C–H···N mode, and C–N mode. The harmonic vibrational frequency and the Mulliken population analyses are carried out. The stability of the isomers are compared, and the most stable complexes are those with N–H···N type H-bonds. Another important finding is that the HOMO electrons of the N–H···N type coupling mode complexes are more difficult to be excited or to be removed for their low HOMO energies as compared with the other isomers, while these complexes are easier to be reduced by the electron attachment for their high LUMO energies. The low barriers for the self-isomerization pathways of C(N)–H···N mode complexes demonstrate that their N–H···N or C–H···N type H-bonds belong to the low barrier hydrogen bond, implying their flexibility for isomerization. The C–N mode complex should be a metastable isomer that has finite lifetime, and upon interconversion, it should transform to C–H···N mode complex and release a lot of energies.

Keywords: Coupling mode; Harmonic vibrational frequency; HOMO and LUMO; Stabilization energy; Isomerization mechanism; Transition state

1. Introduction

The imidazole (Im) and its derivatives are becoming increasingly important in chemical processes because they can form a class of nucleophilic and general base catalysts [1,2]. The possibility of hydrogen bond formation is widely used in pharmaceuticals. The Im ring is a model molecule for more complicated systems, and is of particular interest in biology, where it is involved in nucleic acid bases and amino acids. Im is of importance in biological systems, especially, in enzyme action and protein structure determination [3–5]. As the functional group of histidine residue, Im is commonly associated with protein subunits that act to transport protons from one place to the other [6–10]. The unique ring structure of Im permits the proton to be picked up by one N atom to form a cation and another hydrogen to be released from the other N atom. This action has been proposed to explain the proton conductivity properties [11] of Im in the solid-state and also in the actual biological surrounding where a long H-bond chain is present. Therefore, it is of interest to investigate Im and its ramifications.

Experimental [11–17] and theoretical [18–28] investigations have been carried out for the studying of the properties of imidazole and its ramifications in recent years. In the experiment fields, the vibrations and intra- and intermolecular force constants of crystalline Im [13–15] have been explored. High-pressure infrared spectroscopy is used in probing the C–H···O interaction in aqueous protonated Im [16]. The protonic conduction [17] of Im in solid-state is investigated with NMR study. In theoretical aspect, the cation binding effect [18] on hydrogen bonding of Im, the low-lying electronic states [20] of Im and the proton transfer shuttling [10] with stationary and mobile Im have also been investigated. In our previous [23–25] papers, the coupling character between Im and Im radical cation, the effects of donors and accepters on the energetics and mechanisms of proton, hydrogen, and hydride release from

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Im, and alteration of Im dimer on oxidation or water ligation have been investigated in detail. The calculations [26] about the diffusion mechanism of an excess electron in Im molecule chains have been performed using ab initio molecular dynamics. The harmonic vibrational frequency of Im and its different forms have also been investigated theoretically [27,28].

The significance of the imidazole–imidazolium (Im–ImH$^+$) system has been demonstrated by the investigations about proton transfer and protonic conductivity of the Im chains, furthermore, the Im–ImH$^+$ system can be taken as a model system for investigation on the biomolecular, such as histidine, guanine and adenine, where the Im ring is included in. The importance of Im–ImH$^+$ has intrigued the theoretical investigation about structures, energies, and vibrational spectra of the system, which has been carried out by Tatara et al. [21], but only one complex with the N–H···N coupling mode has been investigated. In order to make-up this insufficiency, the focus of this paper is paid on additional coupling modes of the Im–ImH$^+$ system, the properties, and the isomerization mechanisms of the isomers.

2. Calculation details

The hybrid density functional theory (DFT) methods have been successfully used in the electronic structure determinations, especially they are uniquely successful and computationally inexpensive in describing large free radicals and intermolecular complexes [29–33]. Furthermore, the reliability of the B3LYP/6-311+G* basis set level on the Im system has also been verified in previous papers [23,25]. Therefore, the Im–ImH$^+$ geometry structures are optimized using B3LYP method in conjunction with a 6-311+G* basis set. The harmonic vibrational frequency is determined to confirm that the optimized stable structures correspond to genuine local minima on the global potential energy surface (PES). The HOMO and LUMO of the isomers are investigated for the prediction of the geometry alterations on electron detachment and electron attachment.

It should be noted that although the corrections of the basis set superposition error (BSSE) on the binding enthalpy at 0 K (ΔH_0) could improve the energy quantities, they could not change the relative regularity of the ΔH_0 because the contributions from the BSSE correction is significantly smaller as compared with the corresponding uncorrected values. This point has been illuminated in previous investigations [23–25]. Therefore, the ΔH_0 of these isomers are determined according to the following relationship

$$\Delta H_0(\mathrm{Im-ImH^+}) = H_0(\mathrm{Im-ImH^+}) - H_0(\mathrm{Im}) - H_0(\mathrm{ImH^+}) + \Delta\mathrm{ZPVE} \quad (1)$$

$$\Delta\mathrm{ZPVE} = \mathrm{ZPVE(Im-ImH^+)} - \mathrm{ZPVE(Im)} - \mathrm{ZPVE(ImH^+)} \quad (2)$$

To find the correlations among the isomers, the transition state structure searches are performed, only one imaginary frequency is found in the harmonic vibrational frequency for each transition state. The corresponding state–state isomerization pathways are established using the intrinsic reaction coordination (IRC) method [34,35]. The relative Gibbs free energy of these complexes are also calculated.

Density functional theory calculations are performed using the GAUSSIAN 98 program package [36] throughout this paper.

3. Results and discussion

Three kinds of coupling modes, totally four isomers of the Im–ImH$^+$ system are optimized. These intriguing coupling modes can be classified as N–H···N mode, C–H···N mode, and C–N mode. They are denoted with **I–IV** in short, respectively. These optimized geometries are all collected in Fig. 1, and the corresponding atomic serial numbering is depicted. The harmonic vibrational frequencies of the complexes are exhibited in Fig. 2. The primary vibrational modes of the H-bonds are assigned in the figure. The Mulliken charge populations (*Q*) of the isomers are collected in Table 1. The HOMO and LUMO contour plots are presented at 0.02 e/au^3 isocontour values in Fig. 3, which shows the major distribution of the HOMO and LUMO, the corresponding energies are also depicted in this figure. The calculated binding enthalpies (ΔH_0) of the complexes are given in Table 2. The transition states and the state–state correlations are described in Figs. 4 and 5, respectively. The transition states are denoted with TS1–TS7 in short, respectively.

3.1. Geometry structures

It easily can be seen that the optimized geometry structures of four stable isomers depicted in Fig. 1 can be classified as the following three coupling modes: N–H···N type H-bond coupling mode, which includes **I** and **II** two isomers; C–H···N coupling mode (**III**), and C–N coupling mode (**IV**). The electronic states of all these four isomers are ^{1}A.

I and **II** are two different isomers with N–H···N type H-bond in their structures, and they form a pair of enantiomers. For each isomer, two fragments are in contact with H_9 atom and perpendicular to each other. The length of the N_5–H_9 bond is about 1.086 Å, while the length of the N_{10}–H_9 H-bond is 1.626 Å. The distance between the N_5 and N_{10} atoms in this complex is 2.712 Å, which is shorter as compared with the experimentally measured distance