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Exploring proton transfer in 1,2,3-triazole-triazolium dimer with *ab initio* method

Ailin Li, Tianying Yan*, Panwen Shen

Department of Material Chemistry, Institute of New Energy Material Chemistry, Nankai University, Tianjin, 300071, China

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ABSTRACT

Ab initio calculations are utilized to search for transition state structures for proton transfer in the 1,2,3-triazole-triazolium complexes on the basis of optimized dimers. The result suggests six transition state structures for single proton transfer in the complexes, most of which are coplanar. The energy barriers, between different stable and transition states structures with zero point energy (ZPE) corrections, show that proton transfer occurs at room temperature with coplanar configuration that has the lowest energy. The results clearly support that reorientation gives triazole flexibility for proton transfer.

1. Introduction

How to promote proton conductivity in polymer electrolyte membrane (PEM) fuel cell is an important issue in designing fuel cells [1]. Since the most widely used PEM, perfluorosulfonic polymer Nafion in hydrated condition, limits its working temperature (less than 80 °C in order to prevent water from evaporating too much) [1,2], growing interests on heterocyclic compounds as proton carriers emerged. In the pioneering work of Kreuer et al. [3,4], pyrrole and imidazole were suggested to be proton conductors. For these nonaquaous proton transfer media, many problems in PEM fuel cells utilizing water as proton transfer media can be hopefully solved at intermediate operation temperature above 100 °C [5,6].

Experimental data showed that imidazole performed well in proton transfer process, and attempts have been made to develop proton-conducting polymers with immobilized, imidazole-based oligomers, in which imidazole moieties were tethered to polymer backbone [1–4,7–9]. In order to investigate the mechanism of proton transfer between imidazoles, theoretical computations were also performed [10–15]. Car-Parrinello molecular dynamics (CPMD) studies on imidazole-based oligomers by Iannuzzi and Parrinello showed that rotational defects, which could be the rate limiting step, were involved in the proton transfer process in imidazole [11,12]. In a recent study, we developed a multi-state empirical valence bond (MS-EVB) model [10] for proton transfer in liquid imidazole, and good agreement was achieved with experimental study for the proton diffusion coefficient as well as proton hopping rate [4]. It is suggested that Grotthuss mechanism [16] plays an important role in proton transfer in imidazole from both experimental [4] and computational studies [10–12].

In later studies, triazole was proposed to be efficient proton transfer media in anhydrous conditions, which can promote working temperature to 120 °C or higher in PEM fuel cells [17]. The experiments showed that triazole was more electrochemically stable than imidazole in cyclic voltammograms (CVs) tests [17,18]. No obivious redox peak was observed for 1*H*-1,2,3-triazole in a wide potential range (0 to +1.8 V). On the contrary, a large irreversible oxidation peak appeared for imidazole [18]. Therefore, 1*H*-1,2,3-triazole is eletrochemically more stable in fuel cell operating conditions. Moreover, polymers with triazoles tethered to backbones have better performance than imidazole-based polymers [19]. Even though the structure and properties of single neutral triazole molecule and two neutral molecules connected by hydrogen bonds have been well discussed [20–24], the interaction between neutral triazoles and triazolium cations, which is important for interpreting the proton transfer mechanism in triazoles, still calls for further studies [25].

In our previous simulation of liquid imidazole utilizing MS-EVB model [10], two protonated structures which could accommodate excess proton were proposed, namely Zundel-type structure by two imidazole molecules (Im...H + ...Im) and Eigen-type structure where excess proton centred on one imidazole molecule (Im...ImH + ...Im). Compared to the single configuration of imidazole-imidazolium dimer, more combinations can be formed via hydrogen bond between different nitrogen atoms among 1*H*(2*H*)-1,2,3-triazole and 1,3-di*H*-or 1,2-di*H*-1,2,3-triazolium cations. Specifically, there are two tautomers for both neutral triazole, 1*H*-1,2,3-triazole (**A**) and 2*H*-1,2,3-triazole (**B**) and protonated triazolium, 1,3-di*H*-1,2,3-

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* Corresponding author.
E-mail address: tyan@nankai.edu.cn (T. Yan).

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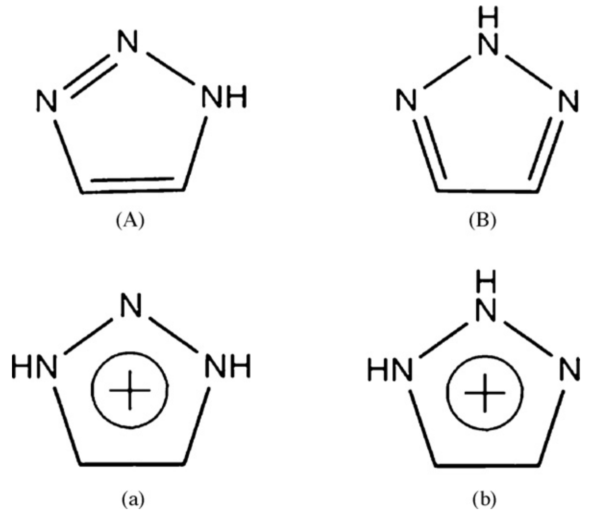

Fig. 1. Triazole and protonated triazolium cations. **A**. *1H*-1,2,3-triazole; **B**. *2H*-1,2,3-triazole; **a**. 1,3-*diH*-1,2,3-triazolium cation; **b**. 1,2-*diH*-1,2,3-triazolium cation.

triazolium (**a**) and 1,2-di*H*-1,2,3-triazolium (**b**) cations (c.f. Fig. 1). Thus, there are four types of neutral/protonated dimers, namely **A-a**, **A-b**, **B-a**, and **B-b**.

In the process of Grotthuss mechanism for the proton hopping among imidazoles, the heterocycles reorientate (or flip) and proton hops along imidazole chains. Adding one more nitrogen atom on the five-membered ring, triazole has three binding sites for proton and thus opens much more proton transfer pathways. In an earlier study by Zhou et al. [25], they found many gas-phase clusters for 1,2,3-triazole-triazolium dimers, and energy difference between the most and least stable triazole-triazolium dimers is about 64.0 kJ mol^{-1} at B3LYP/6-311 + G(d) level of theory. Understanding the proton transfer mechanism in these nitrogen heterocyclic compound, as well as inter-conversion among them, is important in both theoretical aspect and applications. In this study, we performed *ab initio* calculations on triazole-triazolium dimers, aiming at understanding proton transfer mechanism in triazole on the basis of optimized stable dimers and transition state (TS) structures. Since there are many possible pathways for proton transfer in triazole, identifying the most possible pathway and the alternative one associated with it may be helpful on understanding the fast proton transfer in triazole.

2. Computational details

Density functional theory calculations have been performed with the Gaussian 03 program package [26]. The stable structures and TS's were optimized at B3LYP/6-311 + G(d) level of theory, which was also adopted by Zhou et al. for the same system [25]. Harmonic frequencies and zero point energy (ZPE) corrections were calculated at same level of theory. For higher accuracy in terms of energetics, we also calculated single point energies at MP2/cc-pVTZ level of theory based on the B3LYP/6-311 + G(d) optimized structures.

3. Results and discussion

For the tautomers in Fig. 1, the neutral species **B** is more stable than **A** by −20.88 kJ mol^{-1} (−18.95 kJ mol^{-1}) at MP2/cc-pVTZ//B3LYP/6-311 + G(d) level of theory, in which the value in parentheses represents ZPE correction at B3LYP/6-311 + G(d) level. The protonated cation **a** is more stable than **b** by −60.04 kJ mol^{-1} (−57.28 kJ mol^{-1}). The above energy differences are in good agreement with previous studies [21,27]. The "lone pair/lone pair" repulsion disfavars **A** [21,27], while the repulsion between H1 and H2 on **b** makes it more unfavarable comparing to **a**.

Among the various possible configurations of 1,2,3-triazole-triazolium dimers, we found eight distinct stable complexes, which are shown in Fig. 2. All the **B-b** and **B-a** dimers take vertical configuration with the two triazole rings nearly perpendicular to each other, due to the sterical hinder of the two hydrogen atoms, and all

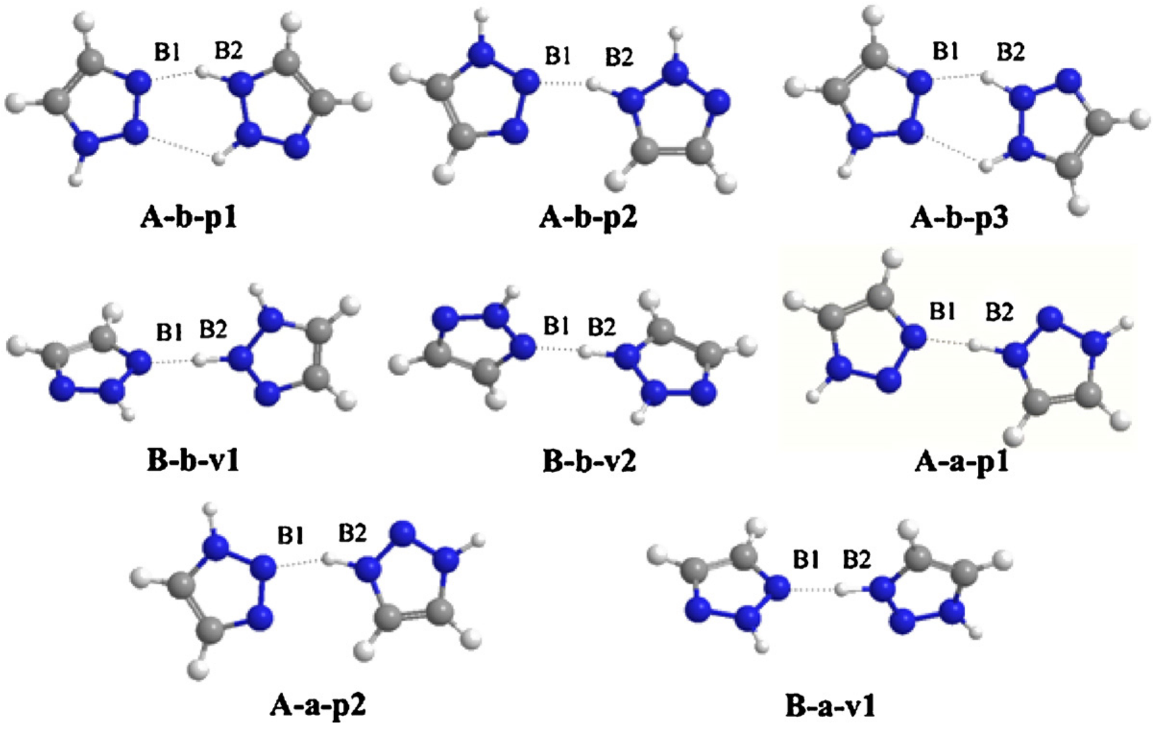

Fig. 2. Stable structures of triazole-triazolium dimers optimized at B3LYP/6-311 + G(d) level of theory.

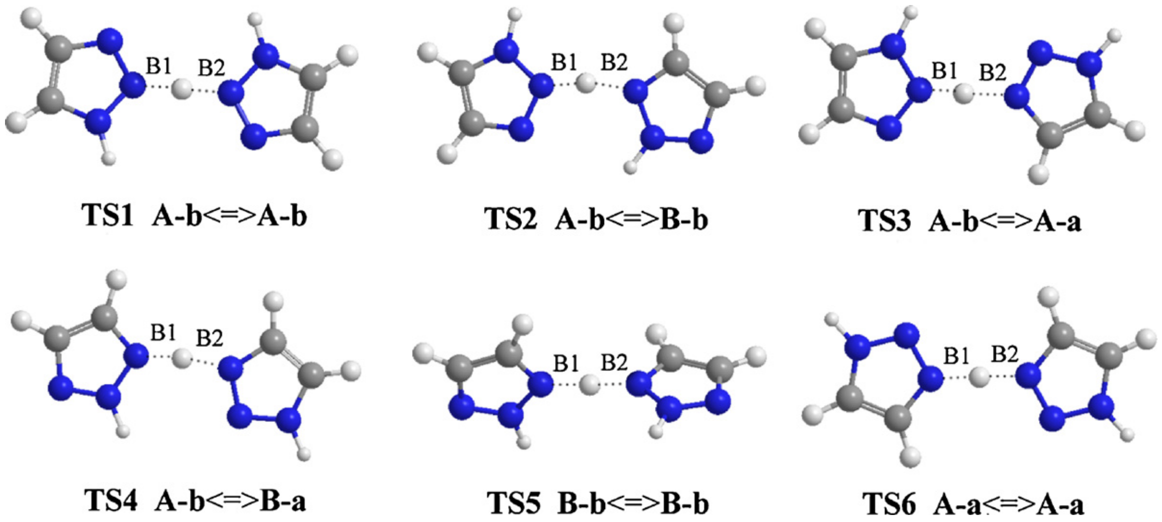

Fig. 3. Optimized transition state structures at B3LYP/6-311 + G(d) level of theory.

the others are coplanar. The stable dimers are similar to previous study by Zhou et al. for the same system [25].

Since reactions **B-a** ⇔ **B-b**, **B-a** ⇔ **A-b**, **A-a** ⇔ **B-b** and **A-a** ⇔ **B-a** are not accessible for the proton transfer process with single step, we found totally six TS structures, as shown in Fig. 3. Important geometrical parameters characterizing the hydrogen bonds in the dimers for both optimized stable and TS structures, including the N-N and N-H distances, N-H-N angles, as well as the relative orientation of the two triazole rings, are listed in Table 1.

It is clearly shown in Table 1 that the N-N bond lengths of the TS are shorter than those in the corresponding stable dimers. The average N-N length is 2.575 Å in transition states, compared with 2.721 Å in stable dimers. This indicates that the bridging proton acts as a bonding atom and strengthens the interaction between the two triazole rings. For the TS structures with higher symmetries, such as **TS1**, **TS5** and **TS6** with C_{2h}, C_2 and C_{2h} symmetries, respectively, and the N-N lengths and N-H-N angles fall in the range of short strong hydrogen bond (SSHB) [28].

Most of the optimized structures of the 1,2,3-triazole-triazolium dimers are planar, in contrast to the imidazole-imidazolium (ImH$^+$-Im) dimer, in which the imidazolium rings of ImH$^+$ and Im are almost orthogonal for the stable and TS structures [13]. Since there are more pathways for proton transfer in triazole, it is easier for triazole to reach the configurations which permit proton to transfer than imidazole, and results in faster proton transport than the imidazole derivatives [18]. Compared with calculations on ImH$^+$-Im dimers by Yan et al. [29] at B3LYP/6-311 + G(d) level of theory, there are certain geometric similarities between triazole dimers and imidazole dimers. Specifically, the lengths of hydrogen bond in the stable ImH$^+$-Im dimers and TS with two rings orthogonal to each other are nearly the same as those in **B-b-v1**, **B-b-v2** and **TS5**, respectively.

In order to represent the potential energy surface of the proton transfer in 1,2,3-triazole-triazolium dimers, harmonic frequencies and zero point energies for the stable and TS structures are calculated at B3LYP/6-311 + G(d) level of theory, and single point calculations are performed at MP2/cc-pVTZ level of theory based on the optimized structures. The relative potential energy for the proton transfer between 1,2,3-triazole and 1,2,3-triazolium cations is presented in Fig. 4, in which the stable dimers (**A-b-p1**, **A-a-p1**, **A-b-p3**, **A-a-p2**, **B-b-v1**, **B-b-v2** and **B-a-v1**) and all the six TS structures are marked.

The stable 1,2,3-triazole-triazolium dimers in Fig. 4 may be devided into three levels in terms of energies. The **B-b** type dimers are all in the highest energy level, and the **A-a** type dimers are low, while the **A-b** type and **B-a** type in between. The lowest energy of the stable dimer is **A-a-p1**, while the highest energy of the stable dimer is **B-b-v1**, in good agreement with the study of the same system by Zhou et al. [25]. Therefore, though **B** and **a** have lower energies than their corresponding tautomers, the sterical hinder of the two hydrogen atoms prevents the dimer from forming the planar configuration, and the **B-a** type of dimers consistantly has higher energy than the **A-a** type.

The energy barriers for the proton transfer between 1,2,3-triazolium cation and 1,2,3-triazole are generally low. For the reactions **A-a-p1** ⇔ **TS6** ⇔ **A-a-p1**, **B-a-v1** ⇔ **TS4** ⇔ **A-b-p1**,

Table 1
Calculated Bond Length (Å) and Angle (deg) of 1,2,3-Triazole in Triazolium-Triazole System.

	B1	B2	Bond$_{N\text{-}N}$	$\theta_{N\text{-}H\text{-}N}$	type
TS1	1.280	1.280	2.560	180	planar
TS2	1.213	1.372	2.569	167.1	planar
TS3	1.182	1.411	2.593	178.4	planar
TS4	1.243	1.338	2.574	171.5	planar
TS5	1.290	1.290	2.579	177.9	vertical
TS6	1.288	1.288	2.575	180	planar
A-b-p1	1.719	1.064	2.701	151.2	planar
A-b-p2	1.718	1.058	2.729	158.5	planar
A-b-p3	1.793	1.051	2.721	145.1	planar
B-b-v1	1.603	1.094	2.696	178.2	vertical
B-b-v2	1.629	1.088	2.716	177.3	vertical
A-a-p1	1.614	1.089	2.699	173.4	planar
A-a-p2	1.755	1.049	2.753	157.4	planar
B-a-v1	1.678	1.073	2.751	177.6	vertical

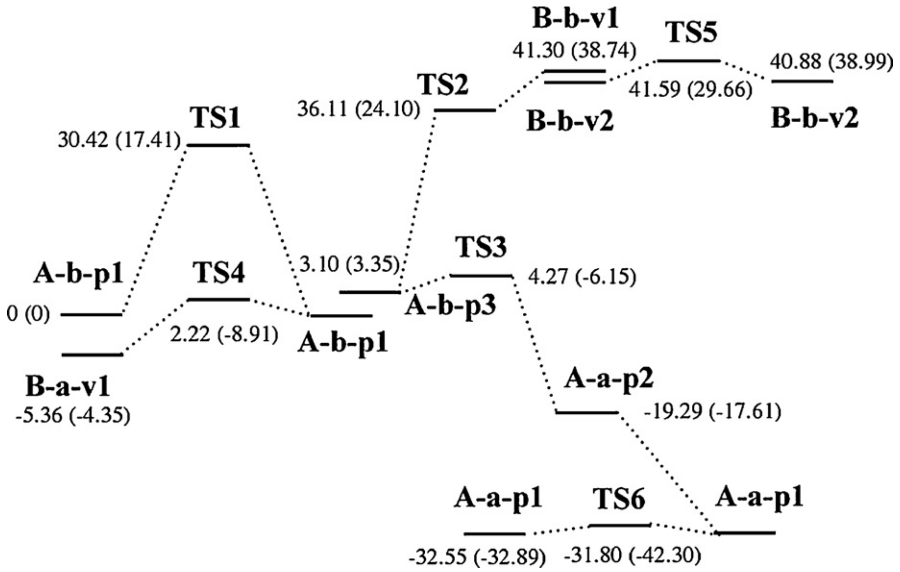

Fig. 4. Energy diagram for proton transfer in triazole-triazolium dimers. The energy barriers are calculated at MP2/cc-pVTZ//B3LYP/6-311 + G(d) level of theory. The values represent relative energies for proton transfer between two triazole molecules in unit of kJ mol^{-1}. The values in parentheses represent energy differences after ZPE corrections.

B-b-v2 $\Leftrightarrow$ **TS5** $\Leftrightarrow$ **B-b-v2**, **A-b-p3** $\Rightarrow$ **TS3** $\Rightarrow$ **A-a-p2**, and **B-b-v1** $\Rightarrow$ **TS2** $\Rightarrow$ **A-b-p3**, the energy barriers become negative if ZPE corrections are included. The negative energy barriers were also found previously by Alkorta and Elguero [30] for the similar systems that inclusion of the ZPE corrections effectively lowered the energy barrier. On the other hand, the energy barriers for the reactions **A-b-p1** $\Leftrightarrow$ **TS1** $\Leftrightarrow$ **A-b-p1**, **A-a-p2** $\Rightarrow$ **TS3** $\Rightarrow$ **A-b-p3**, and **A-b-p3** $\Rightarrow$ **TS2** $\Rightarrow$ **B-b-v1**, are 17.41 kJ mol^{-1}, 20.75 kJ mol^{-1}, and 15.27 kJ mol^{-1}, respectively, with ZPE corrections. These high energy barriers are either due to the torsion of the two rings from coplanar to vertical configuration, or stability of forming intermolecular six-membered ring in the dimer, as shown in Fig. 2. Specifically, The intermolecular six-membered ring decreases energy of **A-b** type dimers, so that **TS1** appears to be with advanced energy as saddle point along the reaction path.

Since the energy of **A-a-p1** dimer is much lower than the other stable dimers, it acts as the main carrier in the process of proton transfer in triazole. On the other hand, these transition states give features of SSHB, in which the existence of proton in the hydrogen bond effectively lowers the energy barriers. The structures of the saddle points **TS4**, **TS5**, and **TS6** appear as the lowest energy point in a single well in potential energy surface. According to Tatara et al. [13], the energy barrier in Im-ImH$^+$ complexes is also negative for the orthogonal configurations. Therefore, in both 1,2,3-triazole and imidazole, proton transfer occurs spontaneously at room temperature. Even though the energy disparity between the highest and lowest dimers is nearly 71 kJ mol^{-1}, some conformational shifts of triazoles may still be achieved through proton transfer among different types of dimer, accompanied by the rotations of the triazole rings.

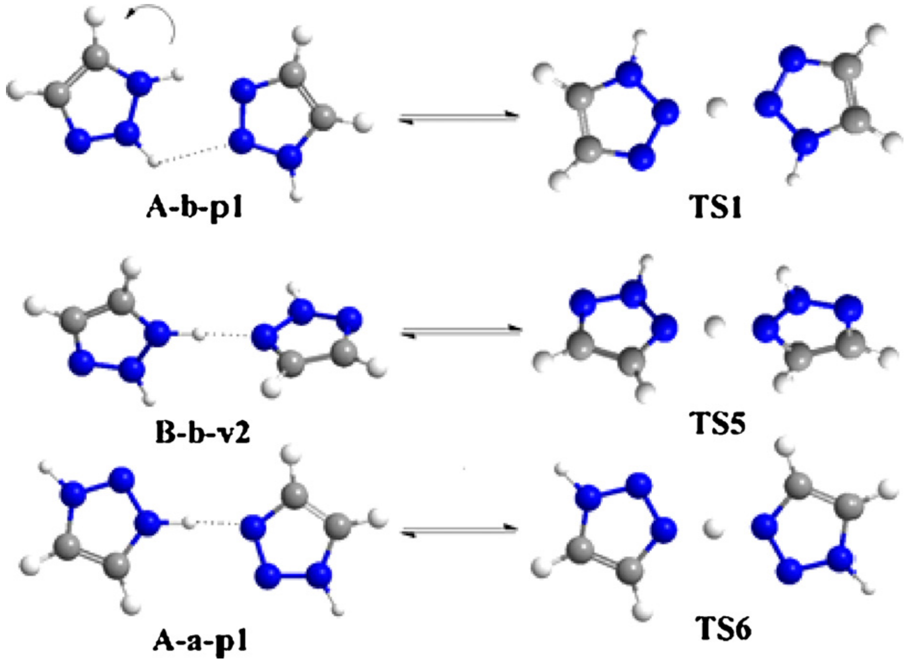

Fig. 5. Proton transfer mechanisms involve **TS1**, **TS5** and **TS6**. The arrow represents the reorientation of the triazole ring.

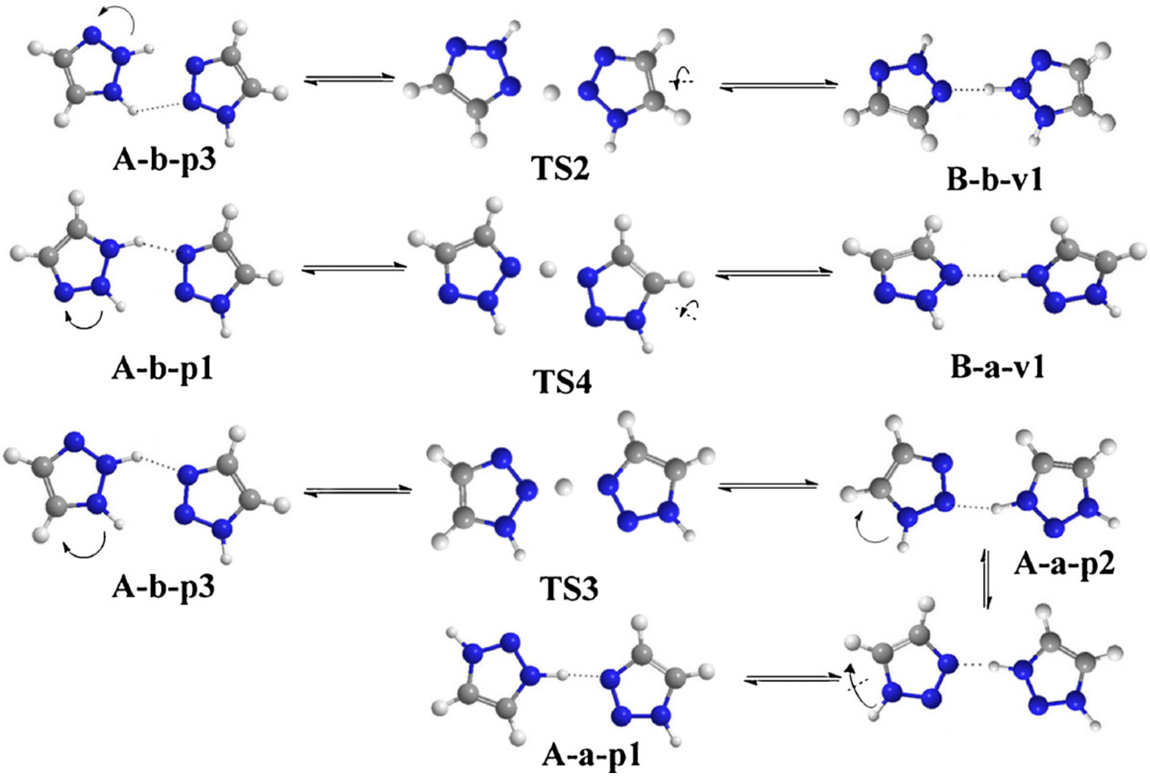

Fig. 6. Proton transfer mechanisms involve **TS2**, **TS3** and **TS4**. The arrow represents the reorientation of the triazole ring.

The proton transfer mechanism between 1,2,3-triazolium cation and 1,2,3-triazole for various pathways is proposed in Figs. 5 and 6. The reactions **B-b-v2** ⇔ **B-b-v2** and **A-a-p1** ⇔ **A-a-p1** can be achieved via one-step reaction that proton migrates from one to the other by passing **TS5** and **TS6**, respectively. For the reaction **A-b-p1** ⇔ **A-b-p1**, one of the hydrogen bonds needs to be broken with triazole ring rotation as shown in Fig. 5. The relatively high energy barrier 17.41 kJ mol^{-1} is the result of the loss of the structure of six-membered ring. Ring reorientation in the plane of 1,2,3-triazole-triazolium dimer and torsion of rings in the dimer almost appear in every proposed mechanism of proton transfer process of **TS2**, **TS3** and **TS4** (shown in Fig. 6). For the reaction **A-b-p1** ⇔ **A-b-p1**, one ring rotates along with the breaking of one hydrogen bond, forming the structure of **TS2**. Then proton migrates from **b** to **A** along with torsion of two rings by the N-H-N axis. The reason that energy of **B-b-v1** is relatively high may lie in the repulsion of two hydrogen atoms on the N1 site of **b** and on the carbon atom of **B** nearest to bridging proton. The reorientation-torsion mechanism is nearly the same in **TS4** process, but a little complicated in TS3 process for the transformation from **A-a-p2** to **A-a-p1**.

According to the energy diagram in Fig. 4, **A-a** group (**A-a-p1**, **A-a-p2** and **TS6**) occupies the lowest energy level, so we may conclude that the dominant proton transfer type for 1,2,3-triazole is **A-a** ⇔ **A-a** due to its low energy level and the rest structures with higher energy tend to transform to **A-a** type via tautomerization and intermolecular proton transfer. One path connecting **A-a** dimer and other stable dimers is **TS3** and possible mechanism consists of reorientation and ring flipping. The process from **A-a-p2** to **A-a-p1** needs the change of proton-accepting site (from N2 to N1 in neutral triazole molecule) and flipping of **A**. This reorientation of neutral triazole verifies the nearly 70° lateral rotation [25] proposed by Zhou et al. Those processes with relative small energy barrier are reversible at room temperature, therefore, shifts among all species of triazole-triazolium dimers can occur via proper paths.

The above analyses have illustrated some features of proton transfer reactions in 1,2,3-triazole, which may help on understanding the mechanism for the proton transfer in triazole. In the study by Alkorta and Elguero [30], the triazolyl residues were tethered to a benzene ring at the N2 site, the geometric impedement prevents triazole rings from being coplanar, and the energy barrier for proton transfer is 10.9–17.2 kJ mol^{-1} at B3LYP/6-31 + G(d,p) level of theory and ring reorientation occurs along with the process. Involving all the three proton-accepting nitrogen atom in triazole ring, more routines may form by reorientation of triazole rings.

4. Summary

In this study, we reported geometries and energies of proton transfer in the 1,2,3-triazole-triazolium dimers with *ab initio* calculations and made a comparison between imidazoles and triazoles. For the totally six TS structures for proton transfer in 1,2,3-triazole-triazolium dimers, five of them are coplanar and one is vertical for the two triazole rings. For the stable structures, the **A-a-p1** is the most stable one, thus it is the main carrier for the proton transfer in triazole. Some of the TS structures are barrierless after ZPE corrections, and thus proton transfer occurs spontaneously. Our calculation clearly supports the mechanism of proton transfer accompanied by the ring reorientation, as proposed by Zhou et al. [25]. After all, 1,2,3-triazole does open many proton transfer pathways. Though the energy disparity between the stable dimers is up to 71 kJ mol^{-1}, certain conformational changes can still be achieved through proton transfer among different dimers, accompanied by certain ring reorientations and flips. With favourable configuration, proton transfer between two triazoles occurs spontaneously with no barrier within the triazole-triazolium dimer investigated in this study. It is important to note that a successful proton transfer depends on many aspects, such as the motion of the second solvation shell, in the condensed phase system. Further study suggested by the current on includes the impact of the ring orientations for the inter-conversion of different dimers, also, in the liquid environment.

Acknowledgements

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