

# NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

# Comparative Theoretical Study on Energetic Substituted 1,2,3- and 1,2,4-triazoles: Azido-cyclization Mechanism and Effect of Solvent

Piao He<sup>a</sup>, Jian-Guo Zhang<sup>\*a</sup>, Kun Wang<sup>ab</sup>, Xin Jin<sup>a</sup>, Xin Yin<sup>a</sup>, Tong-Lai Zhang<sup>a</sup>, Shaowen Zhang<sup>c</sup>

<sup>a</sup>State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081 P. R. China;

<sup>b</sup>Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, United Kingdom

<sup>c</sup>School of Chemistry, Beijing Institute of Technology, Beijing 100081 P. R. China

**Abstract:** The hybrid DFT calculations with B3LYP/6-311G\* level of theory have allowed us to gain insight into the azido-cyclization of 4,5-diazido-1,2,3-triazole and 3,5-diazido-1,2,4-triazole and the effect of solvent. The optimized geometry, charges and molecular electrostatic potential, were calculated and results indicate that the cyclization occurs mainly in the conversion azido→tetrazole, in which the molecular and electronic structures change more significantly. Further analysis of the energy parameters indicates that all possible reactions are endothermic and not spontaneous in gas phase, but the first and second azido-cyclization of 3,5-diazido-1,2,4-triazole could be performed theoretically with energy barriers of 26kcal/mol and 33kcal/mol. Again, the rate constants and the Arrhenius experience formulas of azido-cyclization have been obtained between 200-1000K temperature regions. In addition, the solvent effect on azido-cyclization was studied with acetone, trifluoroacetic acid and dimethylsulfoxide. Results show that solvent effect can make the intermediates and products more stable than in gas phase. The energy barriers for the first and second cyclization are lowered more or less especially in the dimethylsulfoxide, and the influence on the azido-cyclization of 4,5-diazido-1,2,3-triazole is a little larger.

**Key words:** Density functional theory (DFT); Substituted triazoles; Cyclization mechanism; Solvent effects; Rate constant

## 1. Introduction

Nitrogen-rich energetic compounds have developed into a unique class of energetic materials and have attracted considerable attention because of their high heat of formation, high density, and

---

\* Corresponding authors: Jian-Guo Zhang, Tel & Fax: +86 10 68918091.

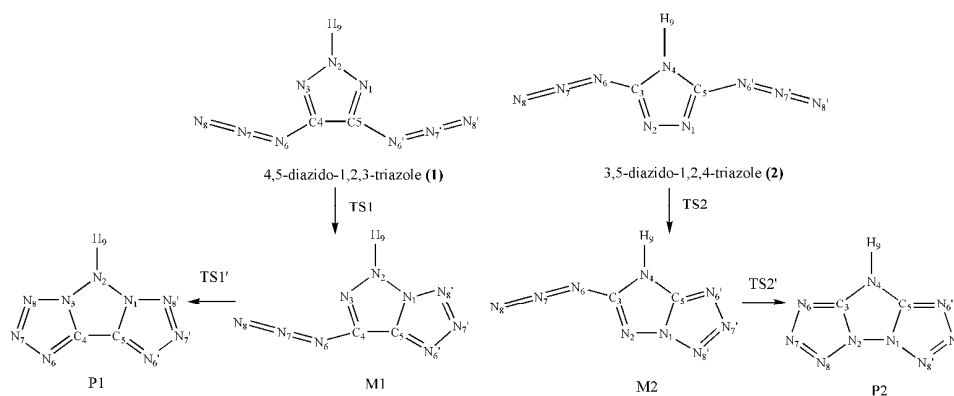
E-mail: zjgbit@bit.edu.cn

good thermal stability.<sup>1-10</sup> They mainly include triazole, tetrazole, furazan, and tetrazine derivatives currently in use for energetic applications.<sup>11-13</sup> These heterocyclic compounds have a large number of N-N and C-N bonds and therefore exhibit large positive heats of formation contributed to high energy densities.<sup>14</sup> Five-membered and nitrogen-rich heterocyclic ring is an efficient fragment to enhance the performance of energetic materials. The dinitrogen being the primary decomposition products will make these energetic compounds may be more environmentally acceptable.<sup>15, 16</sup>

Triazoles are five-membered heterocycles with three nitrogen atoms (molecular formula  $C_2H_3N_3$ ) and two isomers are 1,2,3-triazole and 1,2,4-triazole respectively. Substituted 1,2,3-triazoles can be prepared through the Huisgen cycloaddition reaction of the azide alkyne,<sup>17-19</sup> while 1,2,4-triazoles are obtained using the Einhorn-Brunner or the Pellizzari reaction.<sup>20, 21</sup> There have been many researches on triazole derivatives including their substituted compounds<sup>22-25</sup> and ample ionic salts.<sup>26-31</sup> For example, 3,5-diazido-1,2,4-triazole with a high nitrogen content of 81.8%, has been reported the preparation by Pevzner,<sup>32</sup> then was obtained from 2,5,2',5'-tetrachloro-1,1'-azo-1,3,4-triazole treated with  $NaN_3$ .<sup>33</sup> While only Shafeev reported 4,5-diazido-2-alkyl-1,2,3-triazoles<sup>34</sup> early in 1995 and no relative works were available.

Furthermore, since the azido group is attached to carbon atom adjacent to annular nitrogen, it may spontaneously cyclize to give a tetrazole ring or an equilibrium mixture of both forms. The azido-tetrazole isomerization was defined by Huisgen as a 1,5-dipolar cyclization and has been the subject of many studies.<sup>35, 36</sup> Considering that the azido-cyclization can form delocalized conjugation which makes for stabilizing the molecule and reducing the sensitivity, thus this type of mechanism of azido-cyclization should be known expressly. Klapötke's<sup>37</sup> investigations of the azido-tetrazole isomerism mainly performed in polyazido-1,3,5-triazines, triazido-sheptazine, and diazidotetrazines. But the transformations of triazoles have been little reported up to now.

In the following, we report the results of comparative theoretical study on the isomerism of 4,5-diazido-1,2,3-triazole (**1**) and 3,5-diazido-1,2,4-triazole (**2**). For better investigating the mechanism of conversion between azido and tetrazole forms, the possible reaction pathways of cyclization of diazidotriazoles including the first and second cyclization steps are listed systematically in Scheme 1.



**Scheme 1** The possible pathways of the cyclization of diazidotriazoles

## 2. Computational methods

Density functional theory (DFT)<sup>38</sup> including Beck's three-parameter nonlocal exchange functional along with the Lee-Yang-Parr nonlocal correlation functional (B3LYP) is employed.<sup>39, 40</sup> The geometries have been optimized using B3LYP/6-311G\* and second-order Møller-Plesset perturbation theory (MP2)<sup>41, 42</sup> methods with the 6-311++G\*\* basis sets for comparison. Thermochemical parameters, IR spectrum, natural bond orbital (NBO)<sup>43</sup> charges and electrostatic potential (ESP) of the molecule were obtained. The intrinsic reaction coordinate (IRC)<sup>44</sup> was calculated to confirm whether the transition state (TS) is connecting the reactant and product as two minimum points. The energy parameters such as internal energy ( $U$ ), enthalpy ( $H$ ), free energy ( $G$ ), and the potential energy curve were determined as well. Moreover, the rate constants and Arrhenius empirical formula were evaluated over a wide temperature region from 200 to 1000 K.

The rate constants were evaluated using the conventional transition-state theory (TST)<sup>45</sup>. Here, we give a brief description and rate constant,  $k_{TST}(T)$ , is evaluated using:

$$k_{TST}(T) = \frac{\sigma}{\beta h} \frac{q^{TS}(T)}{q^A(T)q^B(T)} e^{-\beta \Delta E_0^{TS}}$$

Where  $\sigma$  is the reaction symmetry number accounting for the possibility of more than one symmetry related reaction path and can be calculated as the rotational symmetry numbers to that of the transition state. The parameter  $\beta$  meets  $\beta = (k_B T)^{-1}$ , and  $h$  is the Planck constant.  $\Delta E_0^{TS}$  is the classical barrier height, and  $q$  is partition functions.

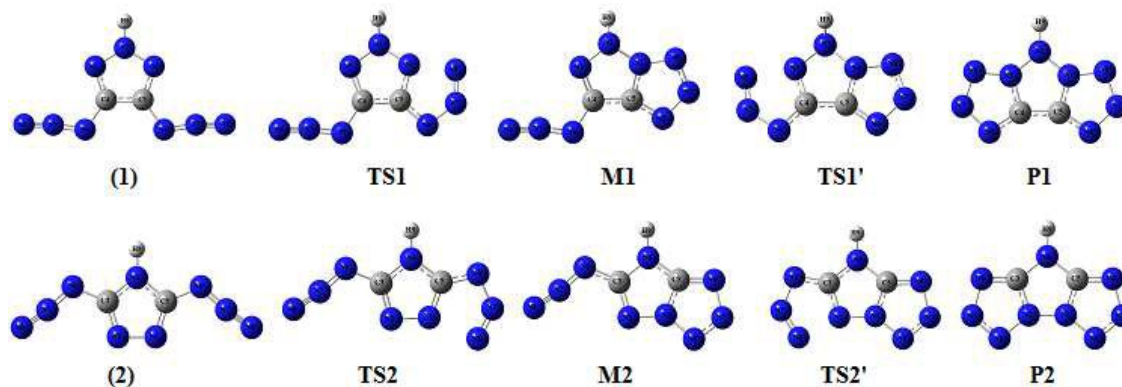
The self-consistent reaction field (SCRF) and the polarized continuum model (PCM)<sup>46-48</sup> have been used to examine solvent effect on the azido-cyclization, and three different continuum environments were acetone, TFA (trifluoroacetic acid) and DMSO (dimethylsulfoxide).

All the calculations involved in this work were carried out using the Gaussian 09 program package.<sup>49</sup> The relevant kinetics of azido-cyclization was performed using the VKLab<sup>50</sup> and POLYRATE 8.2 program package.<sup>51</sup>

### 3. Results and Discussions

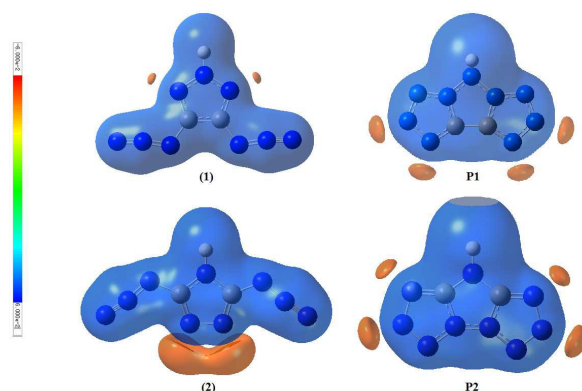
#### 3.1 Molecular Geometry and Electronic Structure

The geometries of title compounds have been optimized using B3LYP/6-311G\* and MP2/6-311++G\*\*. There are small differences of bond length and angle between two methods, but the main structures are coincident. All optimized geometries with a rigid plane are shown in Fig. 1, and detailed structural parameters are listed in SI. 1. Regarding the compound (1) for first and second cyclization, the azido group loses linearity with bends around 60°. And the most relevant changes upon cyclization concern the angles N1-C5-N6' (or N3-C4-N6) and C5-N6'-N7' (or C4-N6-N7). A similar change is observed for the compound (2). As expected, the optimized parameters for the transition state (TS) are intermediate between those of azido and tetrazole. Different events occur as the azido group cyclizes, while the geometric influence exerted by the nature of the ring on the cyclization is very small.



**Fig. 1** The optimized geometry along the reaction paths

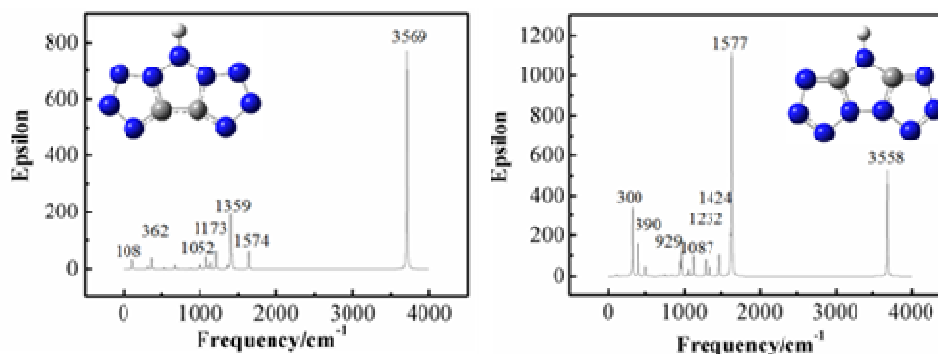
The azido-cyclizations in both (1) and (2) compounds are presumably driven by electronic effects. The NBO charges (e as unit) and the molecular electrostatic potential were calculated to gain insight into the electron redistribution in the cyclization. The calculated NBO charges are listed in the SI. 2 and the molecular electrostatic potentials are shown in the Fig. 2. Most N atoms of both (1) and (2) rings possess negative charges, while the middle N atoms of azido group possess positive charges as a result of electronic repulsion. And the analysis of charge population indicates that most of the electron redistribution occurs in the conversion azido→tetrazole.



**Fig. 2** Molecular electrostatic potential of main compounds

The ESP on the 0.05 a.u. molecular surface with range of -0.06 to 0.06 a.u. is shown in Fig. 2, which provides a visual representation of the comparative changes of ESP along with the azido-cyclization reactions. As can be seen, the nuclei naturally display the positive ESP (shown in blue) on all molecules. Both of compound **(1)** and **(2)** show strong negative region of ESP (shown in orange) associated with the lone pair of the ring nitrogen. Final products P1 and P2 redistribute electrons around the tetrazole rings for structural stability. Again the negative potential occupies mainly on N6 and N7 (N6' and N7'), which may be attracted to the electrophiles.

IR spectrum is an effective method to identify the substances. The characteristic peaks from simulated infrared results are shown in Fig. 3. The calculated IR has been scaled with value of 0.966 from Introduction to Gaussian 09 Package.



**Fig. 3** IR spectra of calculated compounds P1 and P2 (the unit of vertical axis is  $10^{-40}$  esu $^2$ ·cm $^2$ )

The results show that the P1 has one strongest peak at  $3569\text{ cm}^{-1}$ , which is the asymmetrical stretching mode in the bond N-H of triazole ring. The peaks at  $1574\text{ cm}^{-1}$  and  $1173\text{ cm}^{-1}$  refer to the symmetrical stretching on C-C bond and stretching vibration on C-N bond of triazole's skeleton. For the compound P2, the strongest peak at  $1577\text{ cm}^{-1}$  corresponds to the swing vibration of N-H bond and the asymmetrical stretching modes in the ring C-N. The peak at  $3558\text{ cm}^{-1}$  refers to the

strong stretching modes in the bond N-H, while the peak at  $1424\text{ cm}^{-1}$  is stretching vibrations of C-N and N-N bonds belonging to the triazole's skeleton.

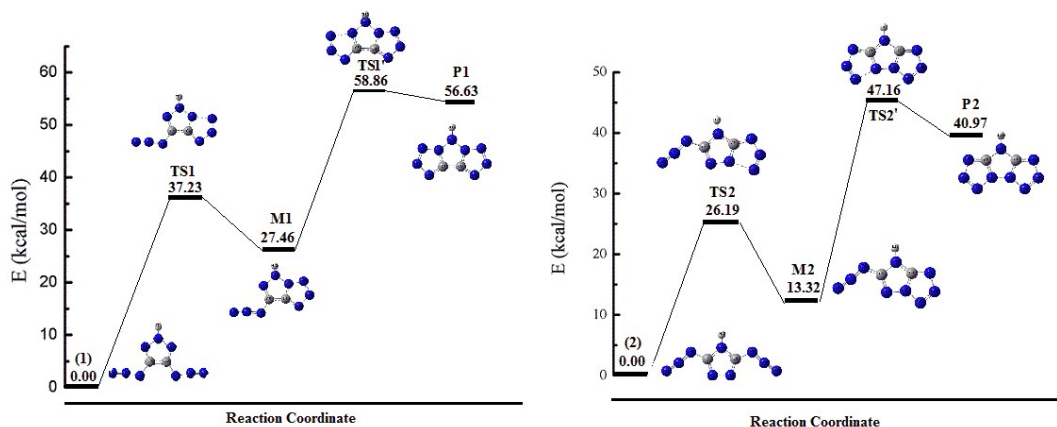
Thermochemistry parameters, including internal energy ( $U$ ), enthalpy ( $H$ ), free energy ( $G$ ), constant volume molar heat capacity ( $C_v$ ) and molar entropy ( $S$ ) of two major products are evaluated and tabulated in Table 1. All these values are at 298.15K, 1.00 atm. and with kcal/mol as unit and kcal/(mol·K) for  $S$  and  $C_v$ . Vibration frequencies are calculated including IR spectrum and thermodynamics to investigate the basic properties of compounds and identify the substances.

**Table 1** Thermochemistry parameters of two major compounds

Species	$U$	$H$	$G$	$S$	$C_v$
P1	45.84	46.43	21.84	82.48	24.56
P2	46.59	47.18	21.35	86.64	26.54

### 3.2 Mechanism of Cyclization

The reaction potential energy curves of possible pathways composed of azido-cyclization (for 4,5-diazido-1,2,3-triazole **(1)**: Reaction11, Reaction12 and for 3,5-diazido-1,2,4-triazole **(2)**: Reaction 21, Reaction 22) are shown in Fig. 4. The corresponding energy parameters of reactions are listed in Table 2. Considering the excited-state, the energies of singlet and triplet have been calculated. And comparative potential energy curves and energy parameters are listed in SI. 3. Results show that the reactions of ground-state occur more easily rather than excited-state.



**Fig. 4** The potential energy curves along the azido-cyclization paths of **(1)** and **(2)**

The energy changes of reaction ( $\Delta E$ ) are positive, which means that products possess higher energy than reactants. Both the enthalpy change ( $\Delta H_{298k}^\ominus$ ) and the Gibbs free energy change ( $\Delta G_{298k}^\ominus$ ) are positive, which imply that all reactions are endothermic and not spontaneous in gas phase. In general, when the energy barrier is under 40kcal/mol, the reaction deemed may occur in

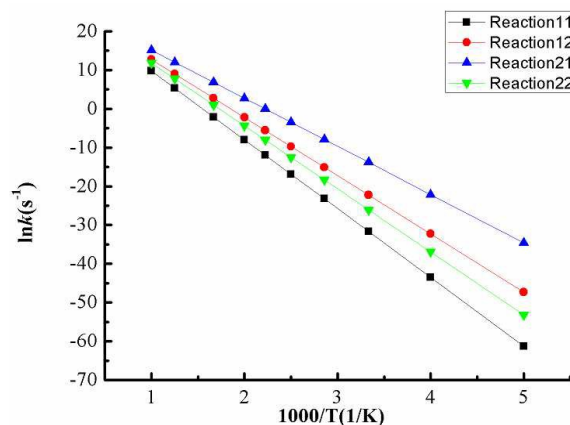
the view of kinetics criterion and the lower value the easier for reaction. In this research, the energy barriers of the first and second cyclization for the compound **(1)** are 37.23kcal/mol and 31.40kcal/mol, and 26.19kcal/mol and 33.83kcal/mol for the compound **(2)**. Therefore, it is predictable that the azido-cyclization of both **(1)** and **(2)** could be performed theoretically. It's worth noting that the energy barriers of **(2)** in the first cyclization are far less than that of **(1)** and the barriers in the second one of **(1)** and **(2)** are similar, which implies compound **(2)** may cyclize relatively easier than compound **(1)** in gas phase.

**Table 2** The energy parameters of all possible azido-cyclization reactions (kcal/mol)

B3LYP/6-311G*	$\Delta E$	$V_{MEP}$	$\Delta H_{298k}^{\circ}$	$\Delta G_{298k}^{\circ}$
Reaction11	26.21	37.23	25.45	27.46
Reaction 12	28.14	31.40	27.42	29.17
Reaction 21	12.23	26.19	11.55	13.32
Reaction 22	27.34	33.83	27.05	27.65

### 3.3 Rate constant

To better understand the azido-cyclization kinetics of compounds **(1)** and **(2)**, the rate constants of reactions have been evaluated between 200-1000K temperature regions. Fig. 5 displays the rate constant  $\ln(k)$  changes linearly with the reciprocal of temperature.



**Fig. 5** The reaction rate constants along the reaction paths

The results in Fig. 5 show that higher temperature makes for accelerating the cyclization reaction, and when it is about 600K the azido-cyclization would occur quickly. For comparison, the slope of rate curves for the first cyclization reaction of **(2)** (Reaction 21) is largest than that of other steps, which indicates activation energy of this reaction is lower and makes for azido-cyclization. As for the high temperature, rate constant curves of cyclization reactions are similar, while the difference is bigger in the lower temperature region. At the same temperature, the rate constant of



the Reaction 21 is bigger than that of others, implying that the temperature effect on promoting the first cyclization reaction of **(2)** is most remarkable.

In addition, the relationship of rate constant and temperature meets the Arrhenius experience formula, and the modified equations are corrected as follows. It is obvious that the ascending order of activation energy is that: Reaction 21 < Reaction 12 < Reaction 22 < Reaction 11, which corresponds to the facility degree of azido-cyclization reactions.

$$k(T) = 6.10 \times 10^{11} \times T^{0.05274} \times e^{-(1.77 \times 10^4 / T)} \text{ s}^{-1} \quad (\text{Reaction 11})$$

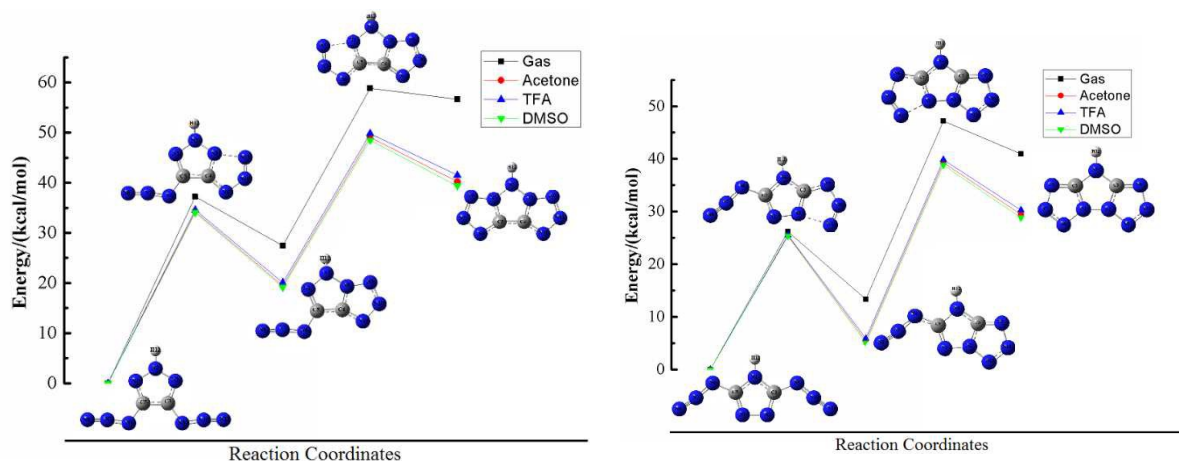
$$k(T) = 1.28 \times 10^{12} \times T^{-0.01193} \times e^{-(1.50 \times 10^4 / T)} \text{ s}^{-1} \quad (\text{Reaction 12})$$

$$k(T) = 1.09 \times 10^{12} \times T^{-0.01858} \times e^{-(1.24 \times 10^4 / T)} \text{ s}^{-1} \quad (\text{Reaction 21})$$

$$k(T) = 1.33 \times 10^{12} \times T^{0.02700} \times e^{-(1.62 \times 10^4 / T)} \text{ s}^{-1} \quad (\text{Reaction 22})$$

### 3.4 Effect of Solvent

To examine the solvent effect on azido-cyclization of compounds **(1)** and **(2)**, the potential energy curves in gas phase and different solvents with acetone, TFA and DMSO have been discussed in Fig. 6. The corresponding energy barriers of reaction are listed in Table 3.



**Fig. 6** The potential energy curves along the azido-cyclization paths in gas phase and different solvents

As can be seen, the solvation effects in acetone, TFA and DMSO lead to notable reduction of the molecular energy, which makes the intermediates and products of **(1)** and **(2)** more stable than in gas phase, especially for P1 and P2. Regarding to the first cyclization reactions of **(1)** and **(2)**, the

energy barriers in the three solvents decrease more or less compared in the gas phase. Particularly in the DMSO solvent, the energy barriers for the first cyclization are lowered by 3.19kcal/mol (Reaction 11) and 0.84kcal/mol (Reaction 21), respectively. These results are similar to the second cyclization reactions. The energy barrier of compound **(1)** is decreased by 2.06kcal/mol (Reaction 12), while the energy barrier of **(2)** is only lowered by 0.03kcal/mol (Reaction 22) in the DMSO solvent. Overall, the energy barriers for the first and second cyclization are lowered more or less especially in the DMSO solvent and the influence on the azido-cyclization of **(1)** is bigger compared with other cyclization reactions.

**Table 3** The energy barriers along the azido-cyclization paths in gas phase and different solvents (kcal/mol)

$V_{MEP}$	Gas	Acetone	TFA	DMSO
Reaction11	37.23	34.25	34.57	34.04
Reaction12	31.40	29.52	29.72	29.34
Reaction21	26.19	25.44	25.50	25.35
Reaction22	33.83	33.90	33.92	33.80

#### 4. Conclusion

Comparative theoretical study on azido-cyclization of 4,5-diazido-1,2,3-triazole **(1)** and 3,5-diazido-1,2,4-triazole **(2)** have been performed at the B3LYP/6-311G\* level of theory. The analysis of molecular geometry and electronic structure indicates that azido-cyclization mainly occurs in the conversion azido→tetrazole where the electronic structures change more significantly. The simulated infrared spectra of final products of azido-cyclization and thermodynamic parameters were calculated for easier assignment and positive identification of the respective isomers.

In addition, the analysis of energy parameters indicates that azido-cyclization reactions are endothermic and non-spontaneous in gas phase. However the energy barriers of **(2)** are about 26kcal/mol and 33kcal/mol for the first and the second cyclization, which implies the reaction path connecting M2 and P2 could proceed theoretically. Again, the rate constants and the Arrhenius experience formulas have been obtained between 200-1000K temperature regions.

Finally, the solvent effect on azido-cyclization has been performed with three different solvents of acetone, TFA and DMSO. On one hand, solvation in acetone, TFA and DMSO can make the intermediates and products of **(1)** and **(2)** more stable than in gas phase, especially for P1 and P2. On the other hand, the energy barriers for the first and second cyclization are lowered more or less especially in the DMSO solvent. And the influence on the azido-cyclization of compound **(1)** is a

little bigger. Solvation certainly has different effect on reactions due to the differences of reactants and solvents.

### Acknowledgments

The support of the National Natural Science Foundation of China (10776002) and the project of State Key Laboratory of Science and Technology (ZDKT12-03 and YBKT16-04) should be gratefully acknowledged.

### References and Notes

1. S. Zhang, X. Liu, Q. Yang, Z. Su, W. Gao, Q. Wei, G. Xie, S. Chen and S. Gao, *Chem Eur J*, 2014, **20**, 7906-7910.
2. Q. Zhang and J. M. Shreeve, *Angew Chem Int Ed Engl*, 2014, **53**, 2540-2542.
3. Q. Zhang and J. M. Shreeve, *Angew Chem Int Ed Engl*, 2013, **52**, 8792-8794.
4. Z. Zeng, H. Gao, B. Twamley and J. n. M. Shreeve, *J. Mater. Chem.*, 2007, **17**, 3819-3826.
5. J.-S. Qin, D.-Y. Du, W.-L. Li, J.-P. Zhang, S.-L. Li, Z.-M. Su, X.-L. Wang, Q. Xu, K.-Z. Shao and Y.-Q. Lan, *Chem Sci*, 2012, **3**, 2114.
6. C. Qi, R.-B. Zhang and S.-P. Pang, *RSC Advances*, 2013, **3**, 17741.
7. M. Le Meur, S. Bourg, S. Massip, M. Marchivie, C. Jarry, G. Guillaumet and S. Routier, *Eur. J. Org. Chem.*, 2014, **2014**, 3704-3714.
8. T. M. Klapötke and J. Stierstorfer, *Eur. J. Inorg. Chem.*, 2008, **2008**, 4055-4062.
9. B. Hirshberg, R. B. Gerber and A. I. Krylov, *Nat Chem*, 2014, **6**, 52-56.
10. K. Karaghiosoff, T. M. Klapotke, P. Mayer, C. M. Sabate, A. Penger and J. M. Welch, *Inorg. Chem.*, 2007, **47**, 1007-1019.
11. J. Stierstorfer, T. M. Klapotke, D. Fischer, M. Volkl and M. Reymann, *New J. Chem.*, 2014.
12. P. He, J.-G. Zhang, K. Wang, X. Yin, S.-W. Zhang and J.-S. Jiao, *RSC Advances*, 2014, **4**, 25302-25309.
13. Q.-L. Yan, S. Zeman, J.-G. Zhang, P. He, T. Musil and M. Bartoskova, *Phys Chem Chem Phys.*, 2014.
14. H. Gao and J. n. M. Shreeve, *Chem. Rev.*, 2011, **111**, 7377-7436.
15. T. M. Klapötke and S. M. Sproll, *Eur. J. Org. Chem.*, 2010, **2010**, 1169-1175.
16. A. Hammerl and T. M. Klapötke, *Inorg. Chem.*, 2002, **41**, 906-912.
17. Z. Y. Yan, Y. B. Zhao, M. J. Fan, W. M. Liu and Y. M. Liang, *Tetrahedron*, 2005, **61**, 9331-9337.
18. V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2002, **41**, 2596-2599.
19. J. Barluenga, C. Valdés, G. Beltrán, M. Escribano and F. Aznar, *Angew. Chem. Int. Ed.*, 2006, **45**, 6893-6896.
20. J. W. Fronbarger, R. D. Chapman and R. D. Gilardi, *Tetrahedron Lett.*, 2006, **47**, 7707-7709.
21. R. G. Child, *J. Heterocycl. Chem.*, 1965, **2**, 98.
22. D. L. Naud, M. A. Hiskey and H. H. Harry, *J. Energ. Mater.*, 2003, **21**, 57-62.
23. S. Buscemi, A. Pace, I. Pibiri, N. Vivona and D. Spinelli, *J. Org. Chem.*, 2002, **68**, 605-608.
24. A. Lauria, R. Delisi, F. Mingoia, A. Terenzi, A. Martorana, G. Barone and A. M. Almerico, *Eur. J. Org. Chem.*, 2014, **2014**, 3289-3306.
25. P. Cardillo, M. Dellavedova, L. Gigante, A. Lunghi, C. Pasturenzi, E. Salatelli and P. Zanirato, *Eur. J. Org. Chem.*, 2012, **2012**, 1195-1201.
26. C. Darwich, T. M. Klapötke and C. M. Sabaté, *Chem Eur J*, 2008, **14**, 5756-5771.

27. K. E. Gutowski, R. D. Rogers and D. A. Dixon, *J. Phys. Chem. B*, 2007, **111**, 4788-4800.
28. T. M. Klapötke, D. G. Piercey and J. Stierstorfer, *Dalton. Trans.*, 2012, **41**, 9451-9459.
29. H. Xue, S. W. Arritt, B. Twamley and J. n. M. Shreeve, *Inorg. Chem.*, 2004, **43**, 7972-7977.
30. M.-J. Crawford, K. Karaghiosoff, T. M. Klapötke and F. A. Martin, *Inorg. Chem.*, 2009, **48**, 1731-1743.
31. J. Catalán, M. Sánchez-Cabezudo, J. L. G. De Paz, J. Elguero, R. W. Taft and F. Anvia, *J. Comput. Chem.*, 1989, **10**, 426-433.
32. M. S. Pevzner and M. N. Martynova, *Khim Geterotsikl Soedin*, 1974, **9**, 1288-1290.
33. S. H. Li, H. G. Shi, C. H. Sun and e. al., *Chinese J. Org. Chem.*, 2008, **28**, 727-729.
34. M. A. Shafeev, V. I. Meshcheryakov, A. A. Al'mukhamedov, G. A. Gareev and L. I. Vereshchagin, *Zhurnal Organicheskoi Khimii*, 1995, **30**, 915-917.
35. R. Huisgen, *Angew. Chem. Int. Ed. Engl.*, 1968, **7**, 321-328.
36. E. Kessenich, K. Polborn and A. Schulz, *Inorg. Chem.*, 2001, **40**, 1102-1109.
37. A. Hammerl, T. M. Klapötke and R. Rocha, *Eur. J. Inorg. Chem.*, 2006, **2006**, 2210-2228.
38. R. G. Parr and W. Yang, *Density-functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.
39. C. Lee, W. Yang and R. G. Parr, *Phys. Rev.*, 1988, **37**, 785.
40. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
41. M. J. Frisch, M. Head-Gordon and J. A. Pople, *Chem. Phys. Lett.*, 1990, **166**, 275-280.
42. M. J. Frisch, M. Head-Gordon and J. A. Pople, *Chem. Phys. Lett.*, 1990, **166**, 281-289.
43. F. Weinhold; and C. R. Landis, *CHEMISTRY EDUCATION: RESEARCH AND PRACTICE IN EUROPE*, 2001, **2**, 91-104.
44. C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.*, 1989, **90**, 2154-2161.
45. D. G. Truhlar, A. D. Isaacson and B. C. Garrett, *Theory of Chemical Reaction Dynamics, vol. 4*, CRC Press, 1985.
46. M. Cossi, V. Barone, B. Mennucci and J. Tomasi, *Chem. Phys. Lett.*, 1998, **286**, 253-260.
47. E. Cancès, B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, **107**, 3032-3041.
48. B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, **106**, 5151-5158.
49. M. J. Frisch, G. W. Trucks, H. B. Schlegel, GAUSSIAN 9 (Revision A.01), Gaussian, Inc, 2009.
50. S. W. Zhang and T. N. Truong, VKLab version1.0 [CP/ CD], Minneapolis: University of Minnesota, Utah: University of Utah, **2001**.
51. Y. Y. Chuang, J. C. Corchado and P. L. Fast, POLYRATE, Program vision 8. 2 [CP/CD], Minneapolis: University of Minnesota, **1999**.

## GRAPHICAL ABSTRACT

Piao He, Jian-Guo Zhang, Kun Wang, Xin Jin, Xin Yin, Tong-Lai Zhang, Shao-Wen Zhang

Comparative Theoretical Study on Energetic Substituted 1,2,3- and 1,2,4-triazoles: Azido-cyclization Mechanism and Effect of Solvent

The azido-cyclization of 4,5-diazido-1,2,3-triazole and 3,5-diazido-1,2,4-triazole and the effect of solvent have been investigated using the hybrid DFT with B3LYP/6-311G\* level.

