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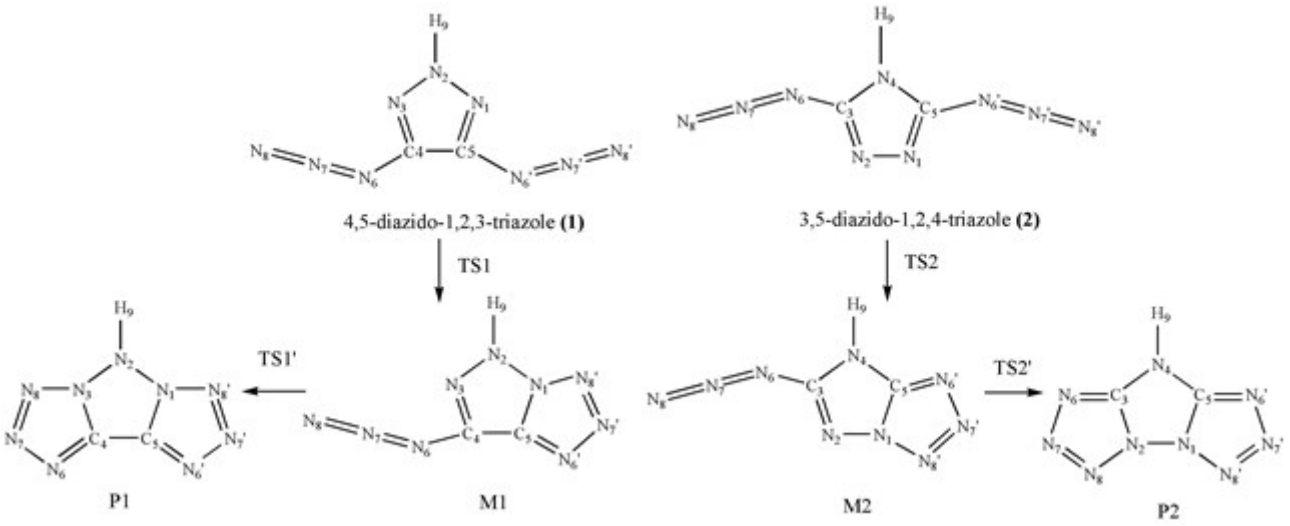
Comparative Theoretical Study on Energetic Substituted 1,2,3- and 1,2,4-triazoles: Azido-cyclization Mechanism and Effect of Solvent

Piao He[a], Jian-Guo Zhang**[a], Kun Wang[ab], Xin Jin[a], Xin Yin[a], Tong-Lai Zhang[a], Shaowen Zhang[c]

7 Figures and 3 Tables



Scheme 1 The possible pathways of the cyclization of diazidotriazoles

* Corresponding authors: Jian-Guo Zhang, Tel & Fax: +86 10 68918091.
E-mail: zjgbit@bit.edu.cn

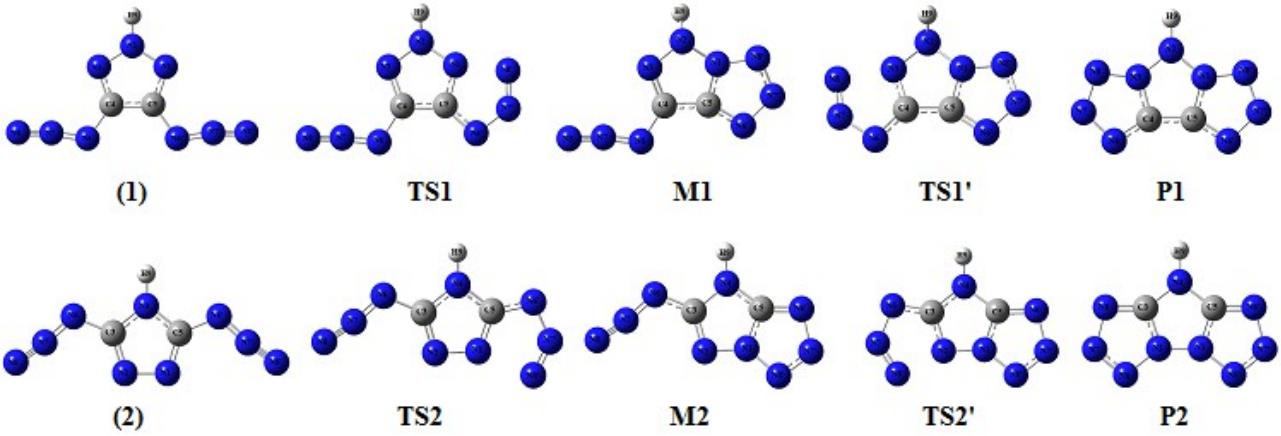


Fig. 1 The optimized geometry along the reaction paths

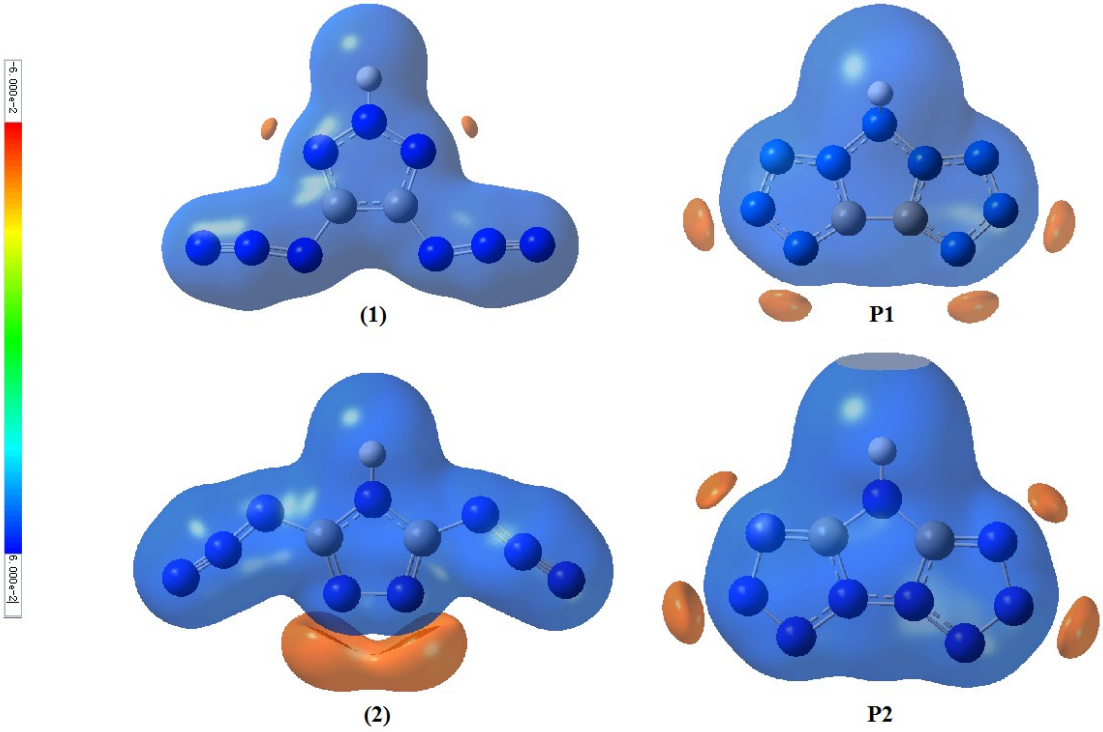


Fig. 2 Molecular electrostatic potential of main compounds

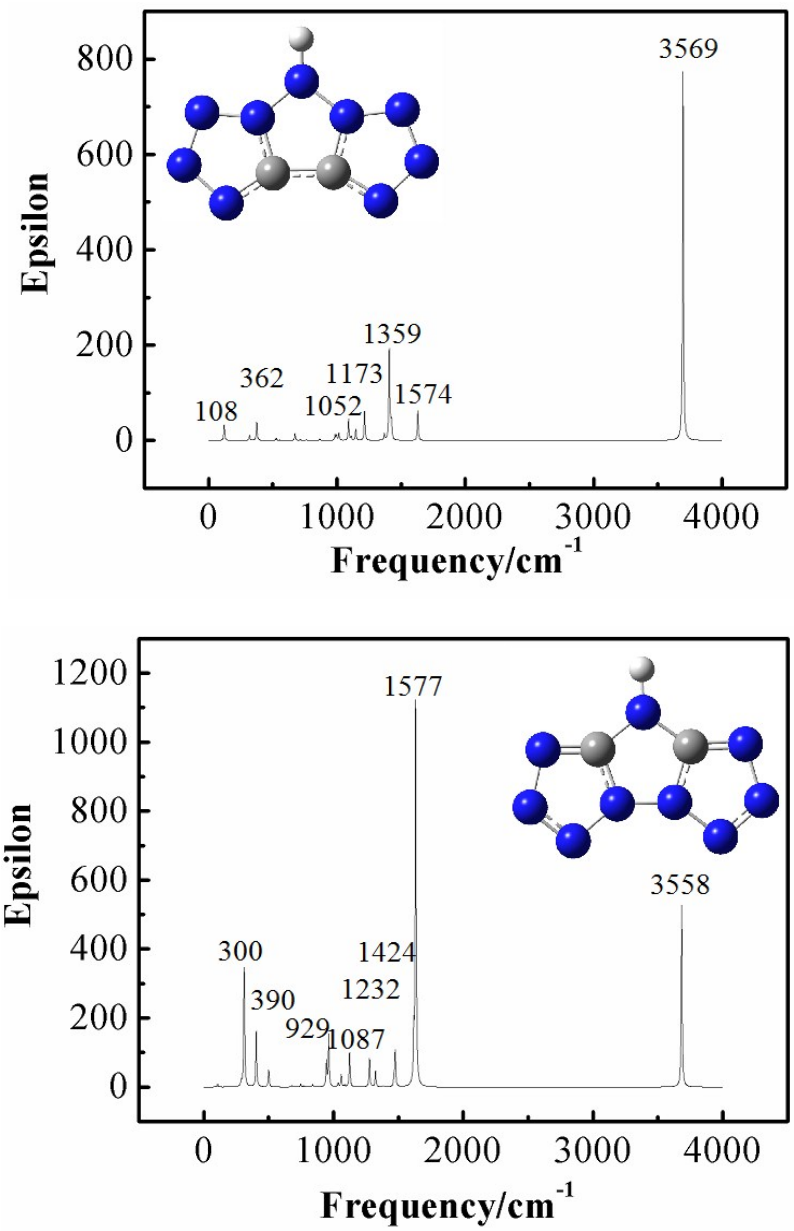


Fig. 3 IR spectra of calculated compounds (the unit of vertical axis is 10^{-40} esu^2•cm^2)

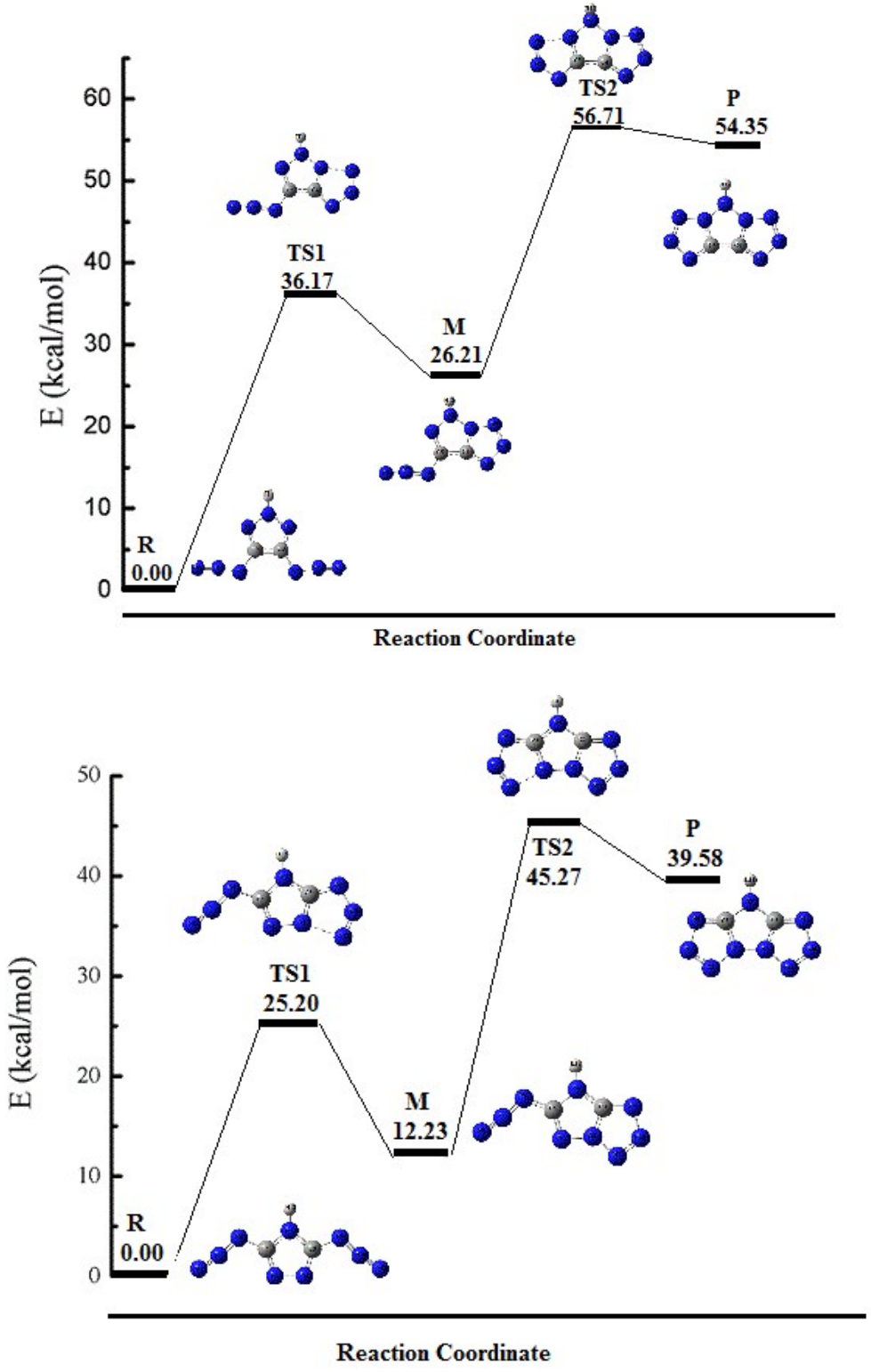


Fig. 4 The potential energy curves along the azido-cyclization paths of **(1)** and **(2)**

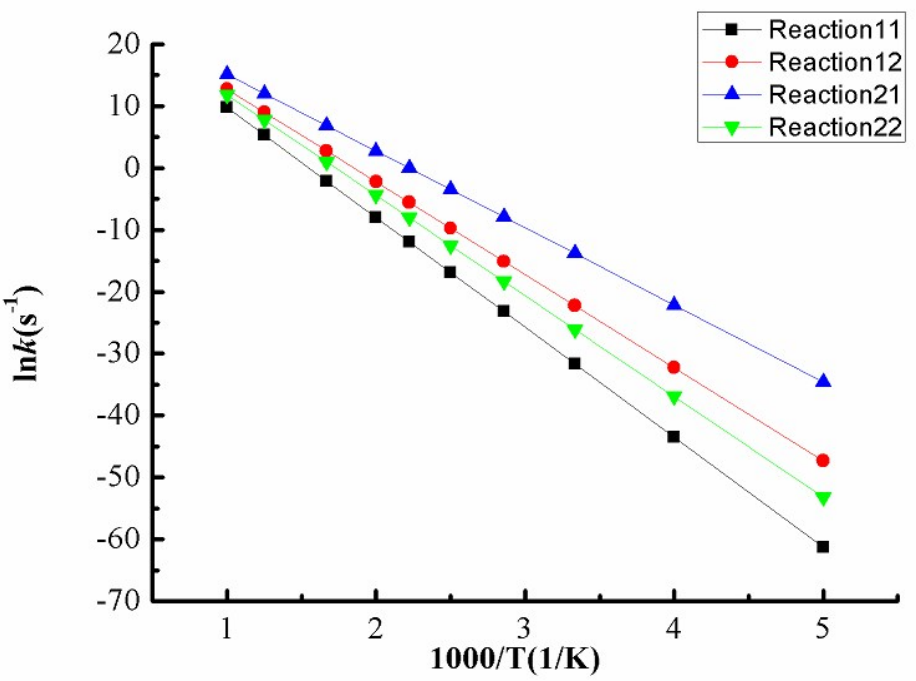
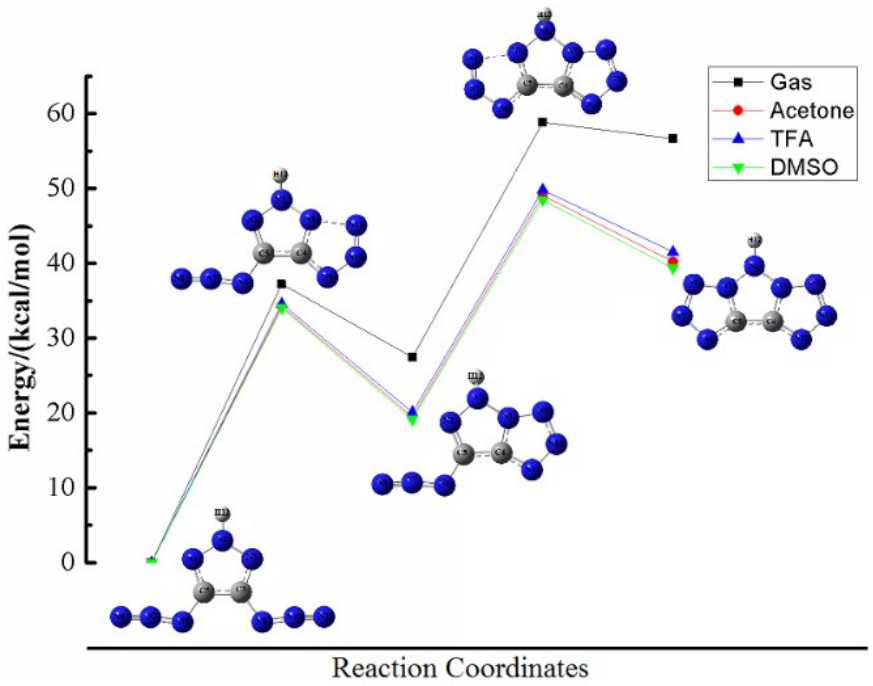


Fig. 5 The reaction rate constants along the reaction paths



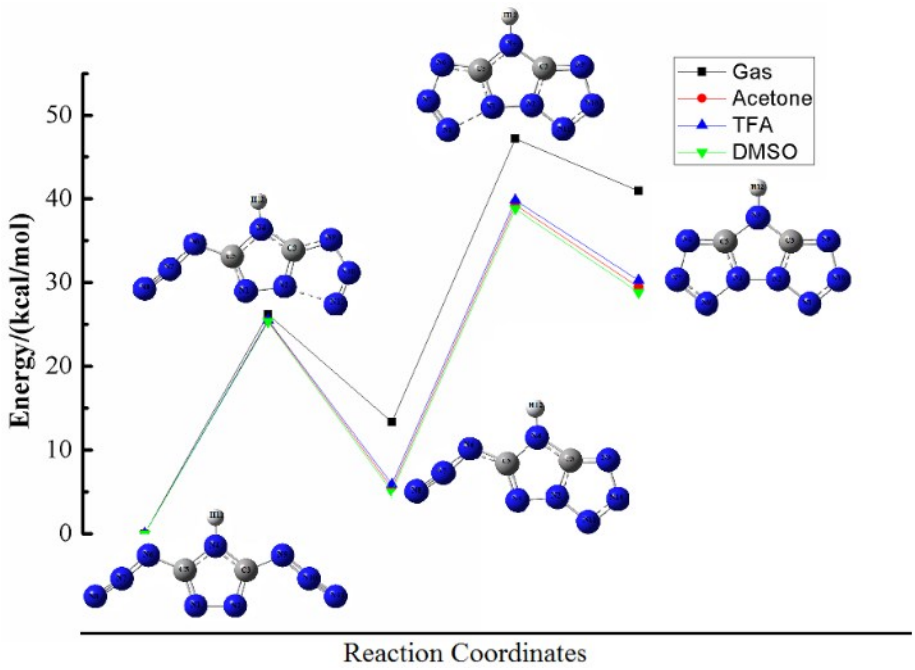


Fig. 6 The potential energy curves along the azido-cyclization paths in gas phase and different solvents

Table 1 Thermochemical parameters of two major compounds (kcal/mol)

Species	*ZPE*	*U*	*H*	*G*	*S*	*Cv*
P1	41.762	45.838	46.430	21.838	82.482	24.557
P2	42.037	46.592	47.184	21.353	86.638	26.539

Table 2 The energy parameters of all possible azido-tetrazolo tautomerizations (kcal/mol)

B3LYP/6-311G*	ΔE	V_{MEP}	ΔH_{298k}^{θ}	ΔG_{298k}^{θ}
Reaction11	26.21	36.17	25.45	27.46
Reaction 12	28.14	30.50	27.42	29.17
Reaction 21	12.23	25.20	11.55	13.32
Reaction 22	27.34	33.04	27.05	27.65

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	36.17	34.25	34.57	34.04
Reaction12	30.50	29.52	29.72	29.34
Reaction21	26.19	25.44	25.50	25.35
Reaction22	33.83	33.90	33.92	33.80