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]

Supporting Information

SI. 1 Optimized parameters

SI. 1 Optimized parameters of title compounds at B3LYP/6-311G* and MP2/6-311++G level of theory**

Compound (1) system

B3LYP/6-311G*	**(1)**	TS1	M1	TS1'	P1	MP2/6-311++G**	**(1)**	TS1	M1	TS1'	P1
C4-N6	1.392	1.387	1.383	1.346	1.324	C4-N6	1.395	1.390	1.387	1.349	1.329
N6-N7	1.238	1.241	1.244	1.340	1.347	N6-N7	1.246	1.249	1.249	1.351	1.358
N7-N8	1.129	1.127	1.125	1.192	1.316	N7-N8	1.151	1.151	1.150	1.189	1.340
C5-N6'	1.392	1.358	1.326	1.320	1.324	C5-N6'	1.395	1.361	1.339	1.334	1.329
N6'-N7'	1.238	1.326	1.350	1.355	1.347	N6'-N7'	1.246	1.338	1.350	1.355	1.358
N7'-N8'	1.129	1.209	1.316	1.313	1.316	N7'-N8'	1.151	1.201	1.348	1.343	1.340
N3-C4-N6	125.7	125.8	125.7	117.2	106.9	N3-C4-N6	125.0	124.6	124.8	118.3	107.4
C4-N6-N7	117.2	117.1	116.7	102.8	105.4	C4-N6-N7	115.1	114.7	114.6	101.5	105.1
N6-N7-N8	172.2	172.0	171.9	126.7	113.3	N6-N7-N8	171.9	171.8	171.8	127.7	112.8
N1-C5-N6'	125.7	115.9	107.9	107.8	106.9	N1-C5-N6'	125.0	117.0	107.5	107.6	107.4
C5-N6'-N7'	117.2	103.0	104.7	104.7	105.4	C5-N6'-N7'	115.1	101.6	104.8	104.8	105.1
N6'-N7'-N8'	172.2	125.7	113.2	113.1	113.3	N6'-N7'-N8'	171.9	127.3	113.1	113.0	112.8

Compound (2) system

B3LYP/6-311G*	**(2)**	TS2	M2	TS2'	P2	MP2/6-311++G**	**(2)**	TS2	M2	TS2'	P2
C3-N6	1.388	1.385	1.381	1.337	1.308	C3-N6	1.393	1.390	1.385	1.339	1.319
N6-N7	1.241	1.242	1.245	1.343	1.375	N6-N7	1.247	1.248	1.250	1.344	1.369
N7-N8	1.126	1.125	1.124	1.207	1.294	N7-N8	1.150	1.149	1.149	1.205	1.334
C5-N6'	1.388	1.357	1.311	1.307	1.308	C5-N6'	1.393	1.359	1.322	1.311	1.319
N6'-N7'	1.241	1.331	1.376	1.376	1.374	N6'-N7'	1.247	1.341	1.370	1.375	1.369
N7'-N8'	1.126	1.183	1.299	1.298	1.294	N7'-N8'	1.150	1.181	1.337	1.309	1.334
N2-C3-N6	129.3	128.9	127.5	116.4	109.1	N2-C3-N6	128.6	128.0	126.7	116.8	108.8
C3-N6-N7	116.3	116.5	116.3	102.6	103.8	C3-N6-N7	113.9	114.1	114.0	102.2	104.1
N6-N7-N8	172.2	172.3	172.2	124.6	114.2	N6-N7-N8	172.2	172.3	172.2	125.0	113.5
N1-C5-N6'	129.3	120.8	110.4	109.7	109.1	N1-C5-N6'	128.6	121.5	110.2	109.6	108.8
C5-N6'-N7'	116.3	101.7	102.9	103.4	103.8	C5-N6'-N7'	113.9	99.9	103.1	103.4	104.1
N6'-N7'-N8'	172.2	125.7	113.2	113.1	113.3	N6'-N7'-N8'	172.2	130.6	113.3	113.6	113.5

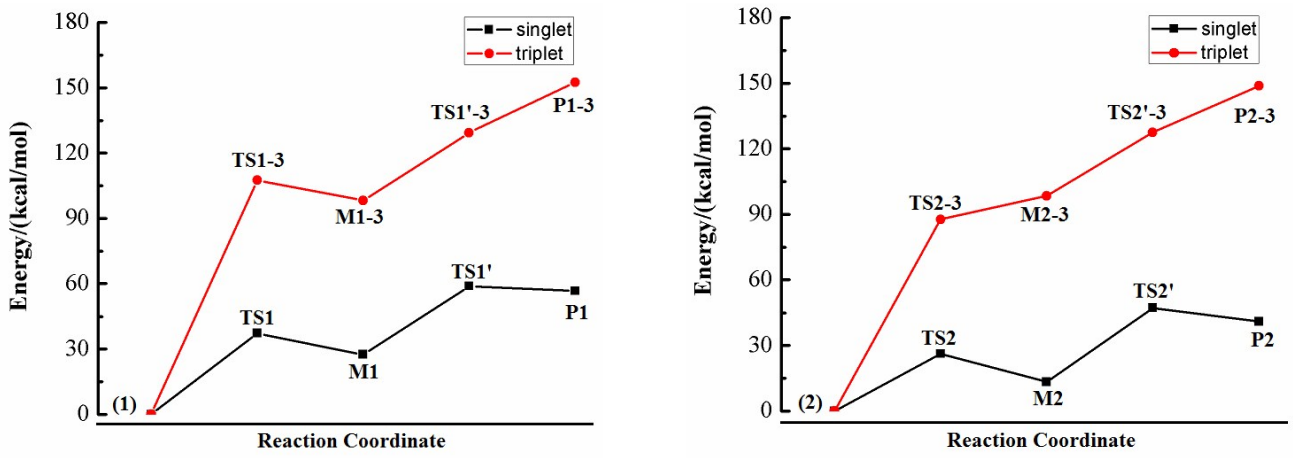
* Corresponding authors: Jian-Guo Zhang, Tel & Fax: +86 10 68918091.
E-mail: zjgbit@bit.edu.cn

SI. 2 NBO charges

SI. 2 NBO charges for all atoms along the reaction paths

Atom	**(1)**	TS1	M1	TS1'	P1	Atom	**(2)**	TS2	M2	TS2'	P2
N1	-0.29	-0.20	-0.02	-0.027	-0.01	N1	-0.33	-0.26	-0.05	-0.04	-0.05
N2	-0.12	-0.15	-0.19	-0.186	-0.20	N2	-0.33	-0.31	-0.32	-0.22	-0.05
N3	-0.29	-0.27	-0.29	-0.237	-0.01	C3	0.50	0.52	0.54	0.56	0.52
C4	0.25	0.28	0.31	0.332	0.27	N4	-0.56	-0.56	-0.57	-0.57	-0.58
C5	0.25	0.29	0.26	0.279	0.27	C5	0.50	0.52	0.49	0.51	0.52
N6	-0.34	-0.33	-0.33	-0.336	-0.27	N6	-0.37	-0.37	-0.37	-0.37	-0.33
N7	0.26	0.26	0.26	0.088	-0.03	N7	0.26	0.26	0.26	0.07	-0.02
N8	-0.02	0.00	0.02	0.063	-0.08	N8	0.01	0.02	0.04	0.05	-0.05
N6'	-0.34	-0.35	-0.28	-0.265	-0.27	N6'	-0.37	-0.41	-0.35	-0.33	-0.33
N7'	0.26	0.06	-0.04	-0.036	-0.03	N7'	0.26	0.09	-0.05	-0.03	-0.02
N8'	-0.02	0.01	-0.08	-0.063	-0.08	N8'	0.01	0.06	-0.07	-0.05	-0.05

SI. 3 Energy of singlet and triplet



SI. 3a The potential energy curves of singlet and triplet for azido-cyclization paths of (1) and (2)

SI. 3b The energy parameters of singlet and triplet for azido-cyclization paths of (1) and (2)

Energy	**(1)**	TS1	M1	TS1'	P1	Energy	**(2)**	TS2	M2	TS2'	P2
E-1[a]	-	-	-	-	-	E-1	-	-	-	-	-
	569.474	569.416	569.432	569.384	569.388		569.492	569.452	569.473	569.420	569.429
	624	983	852	242	000		802	629	307	654	726
G-1[a]	-	-	-	-	-	G-1	-	-	-	-	-
	569.510	569.450	569.466	569.416	569.419		569.527	569.486	569.506	569.452	569.462
	007	672	242	195	751		988	251	749	829	687
E-3[b]	-	-	-	-	-	E-3	-	-	-	-	-
	569.339	569.305	569.319	569.270	569.234		569.353	569.352	569.337	569.292	569.259
	889	999	662	407	786		103	753	799	094	105
G-3[b]	-	-	-	-	-	G-3	-	-	-	-	-
	569.375	569.338	569.353	569.303	569.267		569.385	569.388	569.371	569.324	569.290
	508	676	378	85	057		755	321	072	829	899

[a] E-1 is total energy of singlet and G-1 is sum of electronic and thermal free energies of singlet.

[b] E-1 is total energy of triplet and G-1 is sum of electronic and thermal free energies of triplet.