A Density Functional Theory Study on the Structures and Thermochemical Properties of Azo-bridged Azoles

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Abstract：To find the relationship between the structures and thermochemical properties of energetic compounds, the structures and thermochemical properties of 15 kinds of azo-bridged azoles were studied by density functional theory. Their structures were optimized at B3LYP/6-311+G（d,p）level, their entropies and constant-pressure specific heat capacity were calculated and their enthalpies of formation were estimated via design of the isodesmic reaction. Results show that the N atom and C atom on the heterocyclic ring are sp^2 heterocyclic atoms. All heterocyclic rings are nearly in the same plane. The enthalpy of formation of the compound is proportional to the number of nitrogen atom. For compounds with the same number of nitrogen atoms, the enthalpy of formation of the compound decreases with increasing the distances from the azo-bridge to nitrogen atom on heterocyclic ring and the distances between the nitrogen atoms on heterocyclic ring. The constant pressure specific heat capacity at different temperatures are inversely proportional to the nitrogen content（the number of nitrogen atom on the heterocyclic ring）.

Key words：thermochemical properties；azo-bridged azoles；density functional theory

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1　Introduction

　　Due to the high nitrogen contents and large positive enthalpies of formation, azoles and their derivatives are an important and interesting topic in the field of study of high energetic materials, and are considered as potential propellants and explosives. Huynh[1] synthesized one ditetrazole derivative from 3,6-diazido-1,2,4,5-tetrazine. Abe [2] successfully synthesized 5-azido-（1-dialkylimino）-tetrazole. 1,5-Diamino-4-methyl-tetrazolium dinitramide was synthesized by a metathetical reaction of the corresponding iodide and silver dinitramide[3]. Some derivatives of 4,4′-bis（5-nitro-1,2,3-2H-triazole）were designed, synthesized, and characterized by He[4]. Comparing to the most of current-used propellants, they produced less CO and CO_2, when combustion, which meant more environmental-friendly and might decrease the gun barrel and the rocket nozzle erosion. Among the derivates of azoles, the azo-bridged azoles had been extensively studied recent years, because the azo group could increase the enthalpy of formation remarkably, as an important factor of detonation properties[5-9]. When the azo group attached to the nitrogen atoms of azoles, a long chain of nitrogen would be formed. For example 1,1′-azobis（1,2,3-triazole）[10] and 1,1′-azobis（1,2,3,4-tetrazole）[11], which have been reported and present excellent property, contained nitrogen chains consisted of 8 and 10 nitrogen atoms respectively.

　　The experimental experiences indicated that the nitrogen content, position of nitrogen atoms and decomposition mode of azo-bridged azoles could affect their thermochemical properties remarkably. However, to our knowledge, the thermochemical properties of azo-bridged azoles had never been well-studied by theoretical calculation. To uncover the relationships between their structures and thermochemical properties, we examined the structures and thermochemistries of 15 azo-bridged azoles using DFT method at B3LYP/6-311+G（d,p） level in this work.

2　Computational Methods

　　The structural formulas of azo-bridged azoles are illustrated in Scheme 1.

　　All calculations were performed with the Gaussian 09 suite[12]. B3LYP density functional theoretical method with 6-311+G（d,p）basis set was selected for the geometry optimization and frequency calculation because it provides greater account of electron correlation.

　　Standard enthalpy of formation（$\Delta_f H_{298}^{\ominus}$）was calculated using the isodesmic reaction, which featured same number and type of bonds on each side of the reaction but often lead to cancellation by errors from the bond environments.

For the isodesmic reaction, the enthalpy of formation at 298 K was obtained from the following equation

$$\Delta_r H = \sum \Delta H_{f,p} - \sum \Delta H_{f,R} \qquad (1)$$
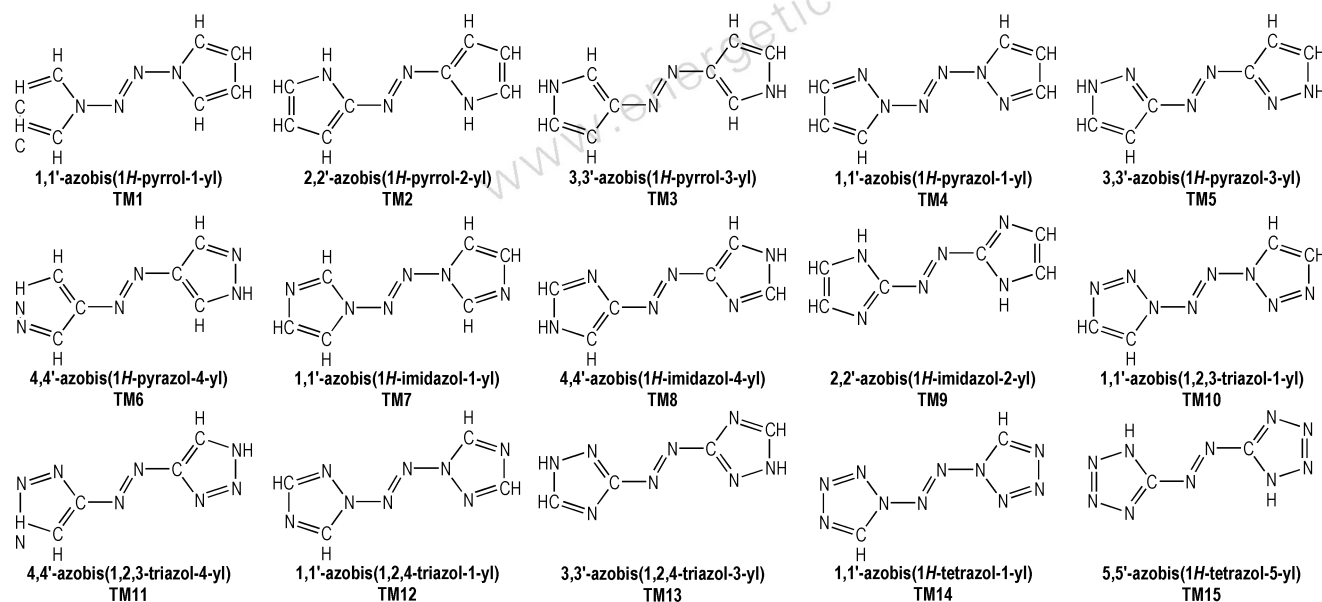
Where $\Delta H_{f,p}$ and $\Delta H_{f,R}$ are the enthalpies of formation for products and reactants at 298 K.

$$\Delta_f H_{298}^{\ominus} = \Delta E_{298} + \Delta(pV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \qquad (2)$$
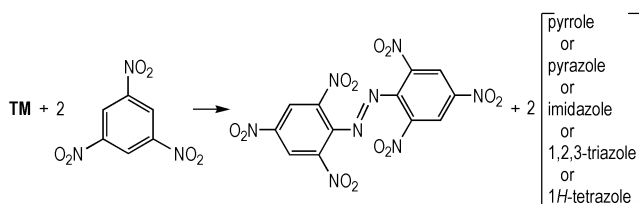
Here ΔE_0 stands for the change in total energy between products and reactants; ΔZPE is the difference between the zero-point energies of products and reactants at 0 K; ΔH_T is the thermal corrections from 0 to 298 K. For the isodesmic reaction, Δn is 0 and $\Delta(pV)$ equals zero.

The accurately-determinated enthalpy of formation data from 1,3,5-trinitrobenzene, 1,1'-azobis(2,4,6-trinitrobenzene), pyrrole, pyrazole, imidazole, 1,2,3-triazole, 1,2,4-triazole, and 1H-tetrazole were used to construct isodesmic reaction for 15 compounds (see Scheme 2).

TM1 1,1'-azobis(1H-pyrrol-1-yl)
TM2 2,2'-azobis(1H-pyrrol-2-yl)
TM3 3,3'-azobis(1H-pyrrol-3-yl)
TM4 1,1'-azobis(1H-pyrazol-1-yl)
TM5 3,3'-azobis(1H-pyrazol-3-yl)
TM6 4,4'-azobis(1H-pyrazol-4-yl)
TM7 1,1'-azobis(1H-imidazol-1-yl)
TM8 4,4'-azobis(1H-imidazol-4-yl)
TM9 2,2'-azobis(1H-imidazol-2-yl)
TM10 1,1'-azobis(1,2,3-triazol-1-yl)
TM11 4,4'-azobis(1,2,3-triazol-4-yl)
TM12 1,1'-azobis(1,2,4-triazol-1-yl)
TM13 3,3'-azobis(1,2,4-triazol-3-yl)
TM14 1,1'-azobis(1H-tetrazol-1-yl)
TM15 5,5'-azobis(1H-tetrazol-5-yl)

Scheme 1 Structural formulas of the azo-bridged azoles

Scheme 2 Isodesmic reaction for calculation of the standard enthalpy of formation

3 Results and Discussion

3.1 Molecular Structures

As the compounds have similar structures excluding the azole rings, our study was focused on them.

The bond lengths, bond angles, and dihedral angles of azoles obtained from the calculation were listed in Table 1. It could be seen from Table 1 that most bonds (C—C, C—N, and N—N) in the azoles had close bond lengths (1.30 – 1.40 Å), which was between the length of typical single bond (1.46 Å) and typical double bond (1.22 Å). At the

same time, the dihedral angles data indicated that all of the azoles were planar. It could be concluded that both the nitrogen and carbon atoms in the azoles were sp^2 hybrid and the azole rings acquired planar aromatic structure as expected.
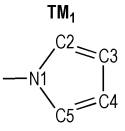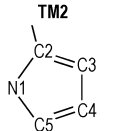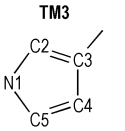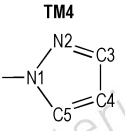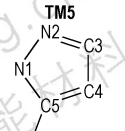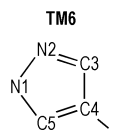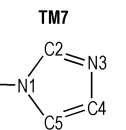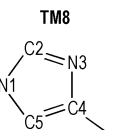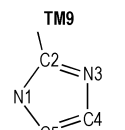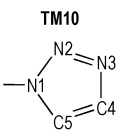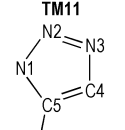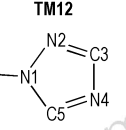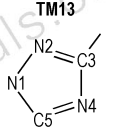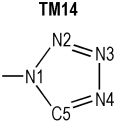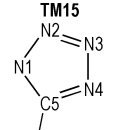
It could be seen that the azo group also had effect on the structure of azoles, especially the atom connected to it. All the bonds consisted of and opposite this atom were elongated. And if the atom is nitrogen, the effect would be enlarged on bonds consisted of same kind atoms (i.e. C—C or N—N bond).

3.2 Enthalpies of Formation

The enthalpies of formation of the 15 compounds were investigated using the isodesmic reaction, which shown in Scheme 2, and the results were listed in Table 2. Enthalpies of formation of reference species acquired from same reactions were shown in Table 3.

It could be observed that the enthalpies of formation of the azo-bridged azoles steadily increased with the increase of nitrogen contents, although some with higher nitrogen contents only had slight higher enthalpy of formation than the lower nitrogen content one.

Table 1   Bond lengths（Å），bond angles（°），and dihedral angles（°）of azoles in the 15 azo-bridged azoles calculated at B3LYP/6-311+G（d，p） level

TM1
N(1)—C(2) 1.39
N(1)—C(5) 1.39
C(2)—C(3) 1.37
C(3)—C(4) 1.43
C(4)—C(5) 1.37
N(1)—C(2)—C(3) 107.47
C(2)—C(3)—C(4) 107.48
C(3)—C(4)—C(5) 108.24
C(4)—C(5)—N(1) 106.80
C(5)—N(1)—C(2) 110.02
N(1)—C(2)—C(3)—C(4) 0.00

TM2
N(1)—C(2) 1.38
N(1)—C(5) 1.37
C(2)—C(3) 1.39
C(3)—C(4) 1.41
C(4)—C(5) 1.39
N(1)—C(2)—C(3) 107.60
C(2)—C(3)—C(4) 107.30
C(3)—C(4)—C(5) 107.40
C(4)—C(5)—N(1) 108.24
C(5)—N(1)—C(2) 109.46
N(1)—C(2)—C(3)—C(4) 0.00

TM3
N(1)—C(2) 1.37
N(1)—C(5) 1.38
C(2)—C(3) 1.39
C(3)—C(4) 1.43
C(4)—C(5) 1.37
N(1)—C(2)—C(3) 107.09
C(2)—C(3)—C(4) 107.46
C(3)—C(4)—C(5) 107.37
C(4)—C(5)—N(1) 107.60
C(5)—N(1)—C(2) 110.49
N(1)—C(2)—C(3)—C(4) 0.00

TM4
N(1)—N(2) 1.35
N(1)—C(5) 1.37
N(2)—C(3) 1.32
C(3)—C(4) 1.42
C(4)—C(5) 1.37
N(1)—N(2)—C(3) 103.72
N(2)—C(3)—C(4) 112.48
C(3)—C(4)—C(5) 104.60
C(4)—C(5)—N(1) 105.99
C(5)—N(1)—N(2) 113.22
N(1)—N(2)—C(3)—C(4) 0.00

TM5
N(1)—N(2) 1.34
N(1)—C(5) 1.34
N(2)—C(3) 1.36
C(3)—C(4) 1.38
C(4)—C(5) 1.42
N(1)—N(2)—C(3) 113.82
N(2)—C(3)—C(4) 105.89
C(3)—C(4)—C(5) 104.66
C(4)—C(5)—N(1) 111.69
C(5)—N(1)—N(2) 103.94
N(1)—N(2)—C(3)—C(4) 0.00

TM6
N(1)—N(2) 1.36
N(1)—C(5) 1.35
N(2)—C(3) 1.33
C(3)—C(4) 1.42
C(4)—C(5) 1.39
N(1)—N(2)—C(3) 104.29
N(2)—C(3)—C(4) 111.66
C(3)—C(4)—C(5) 104.73
C(4)—C(5)—N(1) 105.52
C(5)—N(1)—N(2) 113.81
N(1)—N(2)—C(3)—C(4) 0.00

TM7
N(1)—C(2) 1.39
N(1)—C(5) 1.39
C(2)—N(3) 1.30
N(3)—C(4) 1.39
C(4)—C(5) 1.36
N(1)—C(2)—N(3) 110.55
C(2)—N(3)—C(4) 106.39
N(3)—C(4)—C(5) 110.72
C(4)—C(5)—N(1) 105.00
C(5)—N(1)—C(2) 107.34
N(1)—C(2)—N(3)—C(4) 0.00

TM8
N(1)—C(2) 1.38
N(1)—C(5) 1.37
C(2)—N(3) 1.31
N(3)—C(4) 1.38
C(4)—C(5) 1.38
N(1)—C(2)—N(3) 111.98
C(2)—N(3)—C(4) 105.29
N(3)—C(4)—C(5) 110.46
C(4)—C(5)—N(1) 105.17
C(5)—N(1)—C(2) 107.11
N(1)—C(2)—N(3)—C(4) 0.00

TM9
N(1)—C(2) 1.37
N(1)—C(5) 1.37
C(2)—N(3) 1.32
N(3)—C(4) 1.36
C(4)—C(5) 1.38
N(1)—C(2)—N(3) 111.44
C(2)—N(3)—C(4) 105.39
N(3)—C(4)—C(5) 110.68
C(4)—C(5)—N(1) 105.45
C(5)—N(1)—C(2) 107.04
N(1)—C(2)—N(3)—C(4) 0.00

TM10
N(1)—N(2) 1.37
N(1)—C(5) 1.37
N(2)—N(3) 1.29
N(3)—C(4) 1.38
C(4)—C(5) 1.37
N(1)—N(2)—N(3) 106.73
N(2)—N(3)—C(4) 109.65
N(3)—C(4)—C(5) 109.20
C(4)—C(5)—N(1) 103.06
C(5)—N(1)—N(2) 111.35
N(1)—N(2)—N(3)—C(4) 0.00

TM11
N(1)—N(2) 1.29
N(1)—C(5) 1.37
N(2)—N(3) 1.36
N(3)—C(4) 1.35
C(4)—C(5) 1.39
N(1)—N(2)—N(3) 107.01
N(2)—N(3)—C(4) 111.81
N(3)—C(4)—C(5) 103.20
C(4)—C(5)—N(1) 108.71
C(5)—N(1)—N(2) 109.27
N(1)—N(2)—N(3)—C(4) 0.00

TM12
N(1)—N(2) 1.36
N(1)—C(5) 1.37
N(2)—C(3) 1.31
C(3)—N(4) 1.37
N(4)—C(5) 1.31
N(1)—N(2)—C(3) 101.98
N(2)—C(3)—N(4) 115.26
C(3)—N(4)—C(5) 103.52
N(4)—C(5)—N(1) 108.99
C(5)—N(1)—N(2) 110.25
N(1)—N(2)—C(3)—N(4) 0.00

TM13
N(1)—N(2) 1.36
N(1)—C(5) 1.32
N(2)—C(3) 1.32
C(3)—N(4) 1.37
N(4)—C(5) 1.36
N(1)—N(2)—C(3) 101.53
N(2)—C(3)—N(4) 115.01
C(3)—N(4)—C(5) 102.83
N(4)—C(5)—N(1) 109.72
C(5)—N(1)—N(2) 110.92
N(1)—N(2)—C(3)—N(4) 0.00

TM14
N(1)—N(2) 1.37
N(1)—C(5) 1.36
N(2)—N(3) 1.28
N(3)—N(4) 1.38
N(4)—C(5) 1.30
N(1)—N(2)—N(3) 105.42
N(2)—N(3)—N(4) 112.04
N(3)—N(4)—C(5) 105.76
N(4)—C(5)—N(1) 108.38
C(5)—N(1)—N(2) 108.40
N(1)—N(2)—N(3)—N(4) 0.00

TM15
N(1)—N(2) 1.33
N(1)—C(5) 1.35
N(2)—N(3) 1.30
N(3)—N(4) 1.35
N(4)—C(5) 1.32
N(1)—N(2)—N(3) 106.05
N(2)—N(3)—N(4) 111.40
N(3)—N(4)—C(5) 105.80
N(4)—C(5)—N(1) 108.04
C(5)—N(1)—N(2) 108.72
N(1)—N(2)—N(3)—N(4) 0.00

Table 2 Enthalpies of reaction calculated by the B3LYP/6-311+G(d,p) theoretical method, and enthalpies of formation calculated using the isodesmic reaction $kJ \cdot mol^{-1}$

compound	$\Delta_r H$	$\Delta_f H^\Theta$
TM1	7.579022984	574.1509770
TM2	47.61878945	534.1112105
TM3	35.10016991	546.6298301
TM4	4.810415796	719.3195842
TM5	29.98749620	694.1425033
TM6	33.20384643	690.9261536
TM7	1.598455203	629.5315448
TM8	35.07320499	596.0567950
TM9	43.81234650	587.3176535
TM10	−0.50104579	898.8310458
TM11	33.08407203	865.2459280
TM12	−0.93499282	751.8649928
TM13	21.03138117	729.8986188
TM14	−6.56062704	1025.490627
TM15	25.9383690	992.991631

**Table 3** Enthalpies of formation for the reference species in the isodesmic reactions

compound	$\Delta_f H^\Theta_{298}$ / $kJ \cdot mol^{-1}$
pyrrole	108.4[13]
pyrazole	179.6[14]
imidazole	133.1[15]
1,2,3-triazole [1)]	266.7[16]
1,2,4-triazole	193.0[14]
1H-tetrazole	327.0[17]
1,3,5-trinitrobezene	−37.7[18]
1,2-bis(2,4,6-trinitrophenyl)diazene	289.5[19]

Note：1) represents the value of enthalpy of formation for 1,2,3-triazole is calculated by quantum chemistry method.

As to the azoles with same number of nitrogen atoms, the enthalpies of formation decreased as the distance from azo group to the nitrogen atoms in azole rings increased. The increase of the distance between nitrogen atoms in azole rings had similar effect. Moreover, the effect from the latter was more prominent than the former. However, TM3 was an exception. Its enthalpy of formation was higher than TM2, and the degree of the conjugation might act as an important role (see Fig.1 and Table 1). TM2 had greater conjugation, and then better stability, so its enthalpy of formation was lower than TM3.

a. TM2   **b.** TM3
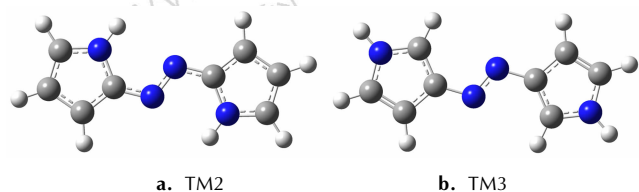
Fig.1 Optimized structures of TM2 and TM3 by B3LYP/6-311+G(d,p) theoretical method

If the 15 azo-bridged azoles were arranged in an order of the nitrogen atoms they contented and then the position connected to the azo group (from 1 to 5), a scatter diagram of enthalpies of formation against the series could be obtained (see Fig.2). It could be observed from the diagram that enthalpies of formation of TM1, TM4, TM10, and TM14 were higher than those of the compounds with same nitrogen content, and there was a good linear relationship. Of the four compounds, all of their nitrogen atoms connected each other to form a continuous nitrogen chain consisted of 4, 6, 8 and 10 nitrogen atoms respectively. So according to above principles, we could guess that 1,1′-azobis(pentazole) might have the largest enthalpy of formation among the azo-bridged azoles.
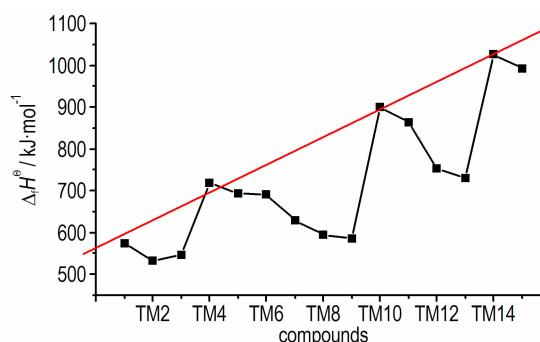
**Fig.2** Enthalpies of formation of the azo-brideged azoles

3.3 Entropies and Specific Heat Capacities

Entropies (S^Θ) and constant pressure specific heat capacity (c_p) for $T=300-1500$ K of 15 compounds were also calculated using B3LYP/6-311+G(d,p) theoretical method, and the results were shown in Table 4. It could be concluded that there was no correlation between the entropies with the nitrogen content, and all of the compounds had close values of $395.36-411.39$ $J \cdot mol^{-1} \cdot K^{-1}$.

Under the calculated temperature, the constant pressure specific heat capacity of the azo-bridged azoles with same nitrogen content were nearly a constant. So four azo-bridged azoles (TM1, TM4, TM10, and TM14) were chosen to represent the ones contented 4, 6, 8 and 10 nitrogen atoms respectively for studying the relationship between the constant pressure specific heat capacity, nitrogen content and temperature. From the obtained scatter diagram (Fig.3), it could be seen that the specific heat capacity decreased while the nitrogen content increased, and the tendency was obvious as temperature rose. According to this principle, it could be drawn that 1,1′-azobis(pentazole) might have the lowest value of specific heat capacity among the azo-bridged azoles.

Table 4　Symmetry point group, entropy and specific heat capacity for the 15 compounds from B3LYP/6-311+G(d,p) calculations　　　$J \cdot mol^{-1} \cdot K^{-1}$

compound	point group	$S^{\ominus}$	c_p					
			300 K	400 K	600 K	800 K	1000 K	1500 K
TM1	$C(2)_h$	402.39	191.04	242.92	319.54	367.64	399.92	446.56
TM2	$C(2)_h$	399.97	191.63	243.29	319.45	367.14	399.09	445.43
TM3	$C(2)_h$	409.30	194.85	245.60	320.54	367.64	399.30	445.39
TM4	$C(2)_h$	397.20	179.82	226.59	296.22	339.51	367.94	407.79
TM5	$C(2)_h$	411.39	182.88	228.68	296.84	339.21	367.06	406.54
TM6	$C(2)_h$	402.14	182.04	227.68	295.92	338.54	366.60	406.25
TM7	$C(2)_h$	403.44	181.29	227.43	296.38	339.42	367.77	407.58
TM8	C_s	406.87	183.42	229.10	296.97	339.21	367.06	406.50
TM9	C_s	399.21	180.20	226.76	295.88	338.75	366.85	406.50
TM10	$C(2)_h$	395.36	173.00	214.66	276.20	313.59	337.41	369.61
TM11	C_s	402.77	174.00	215.20	275.91	312.75	336.24	368.27
TM12	$C(2)_h$	400.63	170.24	210.93	272.77	311.04	335.57	368.73
TM13	$C(2)_h$	400.68	174.42	215.24	275.74	312.59	336.16	368.27
TM14	$C(2)_h$	404.19	167.60	203.48	256.15	287.51	306.81	331.51
TM15	$C(2)_h$	399.59	166.05	201.93	254.85	286.17	305.39	330.13
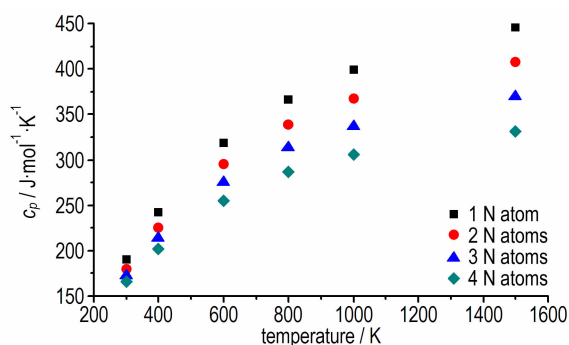
Fig. 3　The c_p of four typical compounds with 1 to 4 nitrogen atoms in the heterocycle as a function of temperature

4　Conclusions

（1）The optimized structures and thermochemical properties of 15 azo-bridged azoles were theoretically obtained via a density functional theory method.

（2）All the nitrogen and carbon atoms of azoles were sp^2 hybrid, and all of the heterocycles were planar aromatic rings.

（3）The enthalpies of formation increased uniformly with the numbers of nitrogen atoms.

（4）For the compounds with same number of nitrogen atoms, the enthalpies of formation decreased uniformly with increasing the distance from azo group to the nitrogen atoms in rings and the distance between the nitrogen atoms in rings.

（5）The constant pressure specific heat capacity at different temperatures are inversely proportional to the nitrogen content (the number of nitrogen atom on the heterocyclic ring).

References：

［1］Huynh M H V, Hiskey M A, Chavez D E, et al. Synthesis char-
acterization and energetic properties of diazido heteroaromatic high-nitrogen C—N compound[J]. *J Am Chem Soc*, 2005, 127 (36)：12537-12543.

［2］Abe T, Tao G H, Joo Y H, et al. Activation of the C＝F bond：transformation of $CF_3N＝N-$ into 5-azidotetrazoles[J]. *Angew Chem.* 2008, 120(37)：7195-7198.

［3］Klapötke T M, Mayer P, Schulz A, et al. 1,5-Diamino-4-methyl-tetrazolium dinitramide[J]. *J Am Chem Soc*, 2005, 127(7)：2032-2033.

［4］He C L, Shreeve J M. Energetic materials with promising properties：synthesis and characterization of 4,4′-bis(5-nitro-1,2,3-2H-triazole) derivatives[J]. *Angew Chem Int Ed*, 2015, 54 (21)：6260-6264.

［5］Chavez D E, Hiskey M A, Gilardi R D. 3,3′-Azobis(6-amino-1,2,4,5-tetrazine)：a novel high-nitrogen energetic material[J]. *Angew Chem*, 2000, 112(10)：1861-1863.

［6］Huynh M H V, Hiskey M A, Hartline E L, et al. Polyazido high-nitrogen compounds：hydrazo- and azo-1,3,5-triazine[J]. *Angew Chem*, 2004, 116(37)：5032-5036.

［7］Hammerl A, Klapötke T M, Nöth H, et al. ［N(2)H₅］²⁺［N(4) C—N＝N—CN(4)］²⁻：A new high-nitrogen high-energetic material[J]. *Inorg Chem*, 2001, 40(14)：3570-3575.

［8］Martin B K, Norbert E, Helmut S, et al. Gas generating mixture containing copper diammine dinitrate：US5663524[P], 1997.

［9］Hammerl A, Hiskey M A, Holl G, et al. Azidoformamidinium and guanidinium 5,5′-azotetrazolate salts[J]. *Chem Mater*, 2005, 17(14)：3784-3793.

［10］Li Y C, Qi C, Li S H, et al. 1,1′-Azobis-1,2,3-triazole：a high-nitrogen compound with stable N8 structure and photochromism [J]. *J Am Chem Soc*, 2010, 132(35)：12172-12173.

［11］Klapötke T M, Piercey D G. 1,1′-Azobis(tetrazole)：a highly energetic nitrogen-rich compound with a N10 Chain[J]. *Inorg Chem*, 2011, 50(7)：2732-2734.

［12］Frisch M J, Trucks G W, Schlegel H B, et al. Gaussian 09[CP], Gaussian Inc, Wallingford CT, 2009.

［13］Scott D W, Berg W T, Hossenlopp I A, et al. Pyrrole：chemical

thermodynamic properties[J]. *J Phys Chem*, 1967, 71(7): 2263-2270.

[14] Jimenez P, Roux M V, Turrion C. Thermochemical properties of N-heterocyclic compounds I enthalpies of combustion vapour pressures and enthalpies of sublimation and enthalpies of formation of pyrazole imidazole indazole and benzimidazole[J]. *J Chem Thermodyn*, 1987, 19(9): 985-992.

[15] Bedford A F, Edmondson P B, Mortimer C T. Heats of formation and bond energies part VI n-butylisobutyraldimine n-butylisobutylamine pyrazole and imidazole[J]. *J Chem Soc*, 1962, 87: 2927-2931.

[16] Gabriel S, Eric E M, Joseph W B. Quantum chemical study of the structure and thermochemistry of the five-membered nitrogen-containing heterocycles and their anions and radicals[J]. *J Phys Chem A*, 2006, 110(51): 13979-13988.

[17] Kabo G J, Kozyro A A, Krasulin A P, et al. Thermodynamic properties and tautomerism of tetrazole[J]. *J Chem Thermodyn*, 1993, 25(4): 485-493.

[18] Stull D R, Westrum E F, Sinke G C. The chemical thermodynamics of organic compounds[M]. New York: John Wiley & Sons Inc. 1969: 807-810.

[19] Bathelt H, Volk F, Weindel M. The ICT-database of thermochemical values 4th ed[M]. 1997.

偶氮桥联氮杂环化合物结构与热化学性能的 DFT 研究

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摘　要: 为了探寻含能化合物结构与热化学性能的关系,用密度泛函理论方法研究了 15 种偶氮桥联氮杂环化合物的结构与热化学性能。在 B3LYP/6-31G(d,p)水平上,优化了它们的结构,计算了它们的熵和等压热容,通过等键反应设计,估算了它们的生成焓。结果表明,杂环上的 N 原子与 C 原子均为 sp^2 杂环原子,所有杂环,几乎在同一平面上。化合物生成焓与氮原子数目成正比,对于氮原子数目相同的化合物,化合物的生成焓随着偶氮桥与杂环上氮原子的距离和杂环上氮原子之间的距离的增加而减小。不同温度下的等压比热容与化合物的氮含量(杂环上的氮原子数)成反比。

关键词: 热性能;偶氮桥联五元氮杂环;密度泛函理论