Journal of Hazardous Materials 179 (2010) 581–590

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

DFT study on energetic tetrazolo-[1,5-*b*]-1,2,4,5-tetrazine and 1,2,4-triazolo-[4,3-*b*]-1,2,4,5-tetrazine derivatives

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ARTICLE INFO

Article history:
Received 8 October 2009
Received in revised form 11 March 2010
Accepted 11 March 2010
Available online 17 March 2010

Keywords:
Density functional theory
Tetrazole- and triazole-functionalized tetrazine derivatives
Heats of formation
Bond dissociation energies
Detonation properties

ABSTRACT

The heats of formation (HOFs) for a series of tetrazolo-[1,5-*b*]-1,2,4,5-tetrazine (TETZ) and 1,2,4-triazolo-[4,3-*b*]-1,2,4,5-tetrazine (TTZ) derivatives were studied by using density functional theory. The results show that the substitution of the $-N_3$ or $-N(NO_2)_2$ group in the TETZ or TTZ ring extremely enhances its HOF values. For monosubstituted case, attachment of a substituent to position 8 in the TETZ or TTZ ring will increase its energy gaps except for the derivatives with the $-NO_2$ group. It is also found that the energy gap of TTZ can be tuned by incorporating a substituent into different positions in the parent ring. The substitution of the $-NH_2$ group in the TETZ ring is favorable for enhancing its thermal stability. For the TTZ ring, different substituted positions and number of the substituent might affect its thermal stability. The calculated detonation properties indicate that incorporating the $-NO_2$, $-NF_2$, $-ONO_2$, or $-N(NO_2)_2$ group into the TETZ or TTZ ring is very helpful for enhancing its detonation performance. Considered the detonation performance and thermal stability, four derivatives may be regarded as the promising candidates of high-energy density materials (HEDMs).

1. Introduction

Five- or six-membered nitrogen-containing heterocycles are traditional sources of energetic materials. Triazole, tetrazole, and tetrazine derivatives have been investigated extensively as high-energy density materials (HEDMs) both theoretically and experimentally [1–6] due to their high densities [7,8], high heats of formation [1,2], and high thermal stability (due to aromaticity) [9,10]. Also, increasing interest in the chemistry of 1,2,4,5-tetrazine derivatives has stimulated research on 1,2,4,5-tetrazine-based compounds [11–14]. Among them, 1,2,4-triazolo-[4,3-*b*]-1,2,4,5-tetrazine (TTZ) and its substituted derivatives have been synthesized. The first synthesis of this ring system was reported in 1968 by Ershov and Postovskii [15]. Later, Chavez and Hiskey [11] synthesized the parent TTZ ring and got its 3,6-disubstituted and monosubstituted derivatives: 3,6-diamino-1,2,4-triazolo-[4,3-*b*]-1,2,4,5-tetrazine (AATZ) and 6-amino-1,2,4-triazolo-[4,3-*b*]-1,2,4,5-tetrazine (ATZ). The melting points (mp) of TTZ, ATZ, and AATZ are 210, 217–218, and 332–333 °C, respectively. In addition, parent tetrazolo-[1,5-*b*]-1,2,4,5-tetrazine (TETZ) ring was synthesized and its explosive properties were reported [12–14]. Licht and Ritter [12] reported the friction sensitivity and shock sensitivity of 6-diamino-tetrazolo-[1,5-*b*]-1,2,4,5-tetrazine (ATTZ). Some of them have displayed potential as energetic additives for high explosive/rocket propellant formulations and pyrotechnic ingredients. Despite the growing interest in the TTZ and TETZ derivatives, a systematic design of the TTZ- and TETZ-based compounds with higher performance and less sensitivity is lacking. To meet the continuing demand for improved energetic materials, there is a clear need to continue to design and develop new TTZ- and TETZ-based HEDMs.

Properties are often manipulated by making structural modifications. The optimization of molecules with high energy and density is the primary step for searching and synthesizing HEDMs. Owing to the difficulties in the synthesis of the molecules under consideration, computer tests become an effective way to design high-energy density compounds theoretically. Theoretical studies not only make it possible to screen candidate compounds, but also provide understanding in terms of the relationships between molecular structure and property. Therefore, they can help design better and more efficient laboratory tests [16,17].

In this work, we report a systematic study on the HOFs, thermal stability, and energetic properties of a series of TETZ and TTZ derivatives by using density functional theory (DFT) method. The HOFs of the derivatives were calculated by designing isodesmic reactions. Next their thermal stabilities were evaluated based on their bond dissociation energies. Finally their detonation velocities and pres-

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doi:10.1016/j.jhazmat.2010.03.043

sures were predicted using the calculated HOFs and densities. It is expected that our results can provide useful information for the molecular design of novel HEDMs.

The remainder of this paper is organized as follows. A description of our computational method is given in Section 2. The results and discussion are presented in Section 3, followed by a summary of our conclusions in Section 4.

2. Computational methods

The hybrid DFT-B3LYP and DFT-B3P86 methods with the 6-311G** basis set were adopted for the prediction of HOFs via designing isodesmic reactions. We reported that the basis set 6-311G** may produce relatively satisfactory HOFs compared with the experiment values [18]. The method of isodesmic reactions has been employed very successfully to calculate HOF from total energies obtained from *ab initio* calculations [18–25]. We design isodesmic reactions in which the numbers of all kinds of bonds remain invariable to decrease the calculation errors of HOF. Because the electronic circumstances of reactants and products are very similar in isodesmic reactions, the errors of electronic correction energies can be counteracted, and then the errors of the calculated HOF can be greatly reduced [23]. In these designed reactions, the basic structural unit of the TETZ or TTZ ring skeleton keeps invariable, and the big molecules are changed into small ones too. This approach has been proved to be reliable [18–21]. The object molecules are classed into five groups as shown in Fig. 1.

The isodesmic reaction used to calculate the HOFs of the tile compounds at 298 K may be written as:

$$\text{X-nR} + n\text{CH}_4 \rightarrow \text{X} + n\text{CH}_3\text{R} \quad (n \leq 2) \tag{1}$$

$$\text{Y-R}_1\text{R}_2 + 2\text{CH}_4 \rightarrow \text{Y} + \text{CH}_3\text{R}_1 + \text{CH}_3\text{R}_2 \tag{2}$$

where R = –NH$_2$, –NO$_2$, –N$_3$, –NHNO$_2$, –NF$_2$, –ONO$_2$, and –N(NO$_2$)$_2$. X is TETZ or TTZ, and Y is TTZ. For the isodesmic reactions (1) and (2), the heat of reaction ($\Delta H_{298\,\text{K}}$) at 298 K can be calculated from the following equation:

$$\Delta H_{298\ \text{K}} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R} \tag{3}$$

where $\Delta H_{f,R}$ and $\Delta H_{f,P}$ are the HOFs of reactants and products at 298 K, respectively. The experimental HOFs of reference compounds CH$_4$, CH$_3$NH$_2$, CH$_3$NO$_2$, CH$_3$ONO$_2$, and CH$_3$N(NO$_2$)$_2$ are available. As the experimental HOFs of CH$_3$N$_3$, CH$_3$NHNO$_2$, CH$_3$NF$_2$,

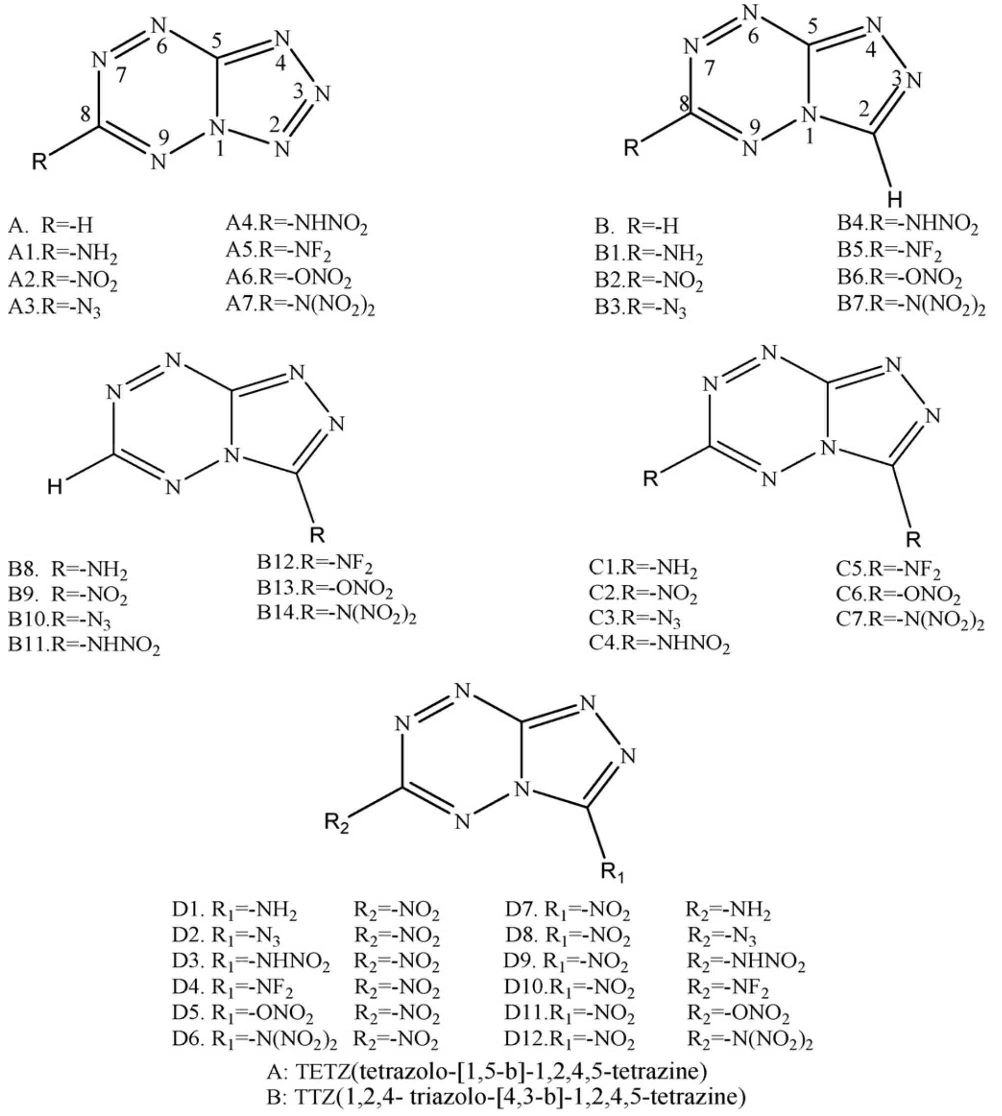

Fig. 1. Molecular frameworks of TETZ and TTZ derivatives.

TETZ, and TTZ are unavailable, additional calculations were performed to get their accurate HOFs by using the complete basis set (CBS-Q) method [26–28]. The CBS-Q approach was used to compute the total energies of the systems. The HOFs for CH_3N_3, CH_3NF_2, TETZ, and TTZ were computed from the atomization reactions (4)–(7), respectively:

$$CH_3N_3(g) \rightarrow C(g) + 3H(g) + 3N(g) \tag{4}$$

$$CH_3NF_2(g) \rightarrow C(g) + 3H(g) + N(g) + 2F(g) \tag{5}$$

$$\text{TETZ}(g) \rightarrow 2C(g) + H(g) + 7N(g) \tag{6}$$

$$\text{TTZ}(g) \rightarrow 3C(g) + 2H(g) + 6N(g) \tag{7}$$

For CH_3NHNO_2, its HOF was calculated from the following isodesmic reaction:

$$CH_3NHNO_2(g) + CH_4(g) \rightarrow CH_3NH_2(g) + CH_3NO_2(g) \tag{8}$$

The HOFs of the TETZ and TTZ derivatives can be evaluated when the heat of reaction $\Delta H_{298\,K}$ is known. Therefore, the principal thing is to compute the $\Delta H_{298\,K}$. $\Delta H_{298\,K}$ can be calculated using the following expression:

$$\Delta H_{298\,K} = \Delta E_{298\,K} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \tag{9}$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (*ZPE*) of the products and the reactants; and ΔH_T is thermal correction from 0 to 298 K. The $\Delta(PV)$ term in Eq. (9) equals ΔnRT for the reactions of ideal gas. For the isodesmic reactions (1) and (2), $\Delta n = 0$, so $\Delta(PV) = 0$.

The strength of bonding, which could be evaluated by bond dissociation energy (BDE), is fundamental to understanding chemical processes [29]. To compare the bond strength and thermal stabilities of the derivatives, their bond dissociation energies were calculated at the UB3LYP/6-311G** level. The energy required for bond homolysis at 298 K and 1 atm corresponds to the enthalpy of reaction $A–B(g) \rightarrow A^\bullet(g) + B^\bullet(g)$, which is the bond dissociation enthalpy of the molecule A–B by definition [30]. For many organic molecules, the terms “bond dissociation energy” (BDE) and “bond dissociation enthalpy” often appear interchangeably in the literature [31]. Therefore, at 0 K, the homolytic bond dissociation energy can be given in terms of Eq. (10) [31]:

$$\text{BDE}^0(A - B) = E_0(A^\bullet) + E_0(B^\bullet) - E_0(A - B) \tag{10}$$

The bond dissociation energy with zero-point energy (*ZPE*) correction can be calculated by Eq. (11):

$$\text{BDE}(A - B)_{ZPE} = \text{BDE}^0(A - B) + \Delta ZPE \tag{11}$$

where ΔZPE is the difference between the *ZPE*s of the products and the reactants.

The detonation velocity and pressure were estimated by the semi-empirical Kamlet–Jacobs formula [32] as:

$$D = 1.01(N\bar{M}^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho_0) \tag{12}$$

$$P = 1.558\rho_0^2\, N\bar{M}^{1/2}Q^{1/2} \tag{13}$$

where D is the detonation velocity (km s^{-1}); P is the detonation pressure (GPa); N is the moles of detonation gases per gram explosive; $\bar{M}$ is the average molecular weight of these gases; Q is the heat of detonation (J g^{-1}); and ρ_0 is the loaded density of explosives (g cm^{-3}). For known explosives, their Q and ρ_0 can be measured experimentally; thus, their D and P can be calculated according to Eqs. (12) and (13). However, for some compounds, their Q and ρ_0 cannot be evaluated from experimental measures. Therefore, to estimate their D and P, we first need to calculate their Q and ρ_0.

In these derivatives, the theoretical density (ρ) could replace the loading density (ρ_0). The ρ needs the datum of the molecular volume. The volume was defined as inside a contour of 0.001 electrons/bohr^3 density that was evaluated using a Monte Carlo integration. This method has been successfully applied to high-nitrogen compounds [33]. We performed 100 single-point calculations for each optimized structure to get an average volume at the B3LYP/6-31G* level. The Q was evaluated by the HOF difference between products and explosives according to the principle of exothermic reactions. Based on the ρ and Q values, the corresponding D and P values can be evaluated. In practice, ρ_0 can only be approximated to a value less than ρ, thus the D and P values obtained from ρ can be regarded as their upper limits (maximum values).

The calculations were performed with the Gaussian 98 package [34]. The optimizations were performed without any symmetry restrictions using the default convergence criteria in the programs. The optimized structure of each molecule corresponds to at least a local energy minimum on the potential energy surface without imaginary frequency.

3. Results and discussion

3.1. Heats of formation

The HOF is frequently taken to be indicative of the “energy content” of a HEDM. Thereby, it is very important to accurately predict the HOF. Table 1 lists the total energies, zero-point energies, thermal corrections, and HOFs for 10 reference compounds in the isodesmic reactions (1) and (2) at the B3LYP/6-311G** and B3P86/6-

Table 1
Calculated total energies (E_0, a.u.), zero-point energies (*ZPE*, kJ/mol), thermal corrections (H_T, kJ/mol), and heats of formation (HOFs, kJ/mol) of the reference compounds[a].

Compound	B3LYP/6-311G**			B3P86/6-311G**			HOF[b]	HOF[c]	HOF[d]
	E_0	*ZPE*	H_T	E_0	*ZPE*	H_T			
A	−460.016800	147.97	17.01	−461.120179	150.05	16.88			787.02
B	−444.008932	180.17	17.46	−445.113374	182.08	17.36			667.49
CH_4	−40.533744	117.09	10.03	−40.713980	117.42	10.04	−74.60	−77.68	−74.02
CH_3NH_2	−95.888439	167.56	11.56	−96.213717	168.31	11.55	−22.50	−23.21	−17.25
CH_3NO_2	−245.081673	130.42	14.15	−245.649164	131.34	14.12	−80.80	−85.96	−81.11
CH_3N_3	−204.148401	131.67	14.41	−204.679787	132.53	14.40		296.50	289.66
CH_3NHNO_2	−300.434462	176.49	16.34	−301.147794	177.78	16.30		−15.20	−18.53
CH_3NF_2	−294.298331	122.75	13.85	−294.895029	123.62	13.75		−110.57	−106.29
CH_3ONO_2	−320.282743	142.24	15.81	−320.991094	143.73	15.65	−122.00	−132.87	−132.71
$CH_3N(NO_2)_2$	−504.942375	179.04	22.95	−506.042839	181.32	22.72	53.50 ± 0.80	68.66	63.69

[a] E_0 is in a.u.; *ZPE*, HOF, and H_T are in kJ/mol. The scaling factor for *ZPE* is 0.98 and the scaling for H_T is 0.96 [35].
[b] Data are the experimental values taken from Ref. [36].
[c] The calculated values are at the G2 level.
[d] The calculated values are at the CBS-Q level.

Table 2
Calculated total energies (E_0, a.u.), zero-point energies (*ZPE*, kJ/mol), thermal corrections (H_T, kJ/mol), and heats of formation (HOFs, kJ/mol) of the TETZ and TTZ derivatives at the B3LYP and B3P86 levels[a].

Compound	B3LYP/6-311G**			HOF	B3P86/6-311G**			HOF
	E_0	*ZPE*	H_T		E_0	*ZPE*	H_T	
A1	−515.409801	191.21	21.68	734.60	−516.659746	193.75	21.44	730.56
A2	−664.546736	152.04	24.26	822.11	−666.037558	154.88	24.07	821.77
A3	−623.646179	155.43	24.10	1108.35	−625.101423	158.10	23.91	1106.51
A4	−719.919270	197.36	27.39	832.75	−721.556253	200.36	27.29	831.46
A5	−713.765894	144.16	24.88	790.78	−715.286650	146.95	24.64	788.54
A6	−739.766803	161.98	27.23	730.51	−741.398014	165.25	26.89	731.25
A7	−924.416959	198.33	34.63	931.51	−926.440706	202.55	34.22	931.29
B1	−499.399738	223.43	22.07	620.78	−500.650688	225.32	22.26	616.83
B2	−648.542094	184.46	24.67	694.29	−650.034022	187.11	24.51	693.82
B3	−607.638062	187.64	24.56	989.50	−609.094406	190.15	24.40	987.57
B4	−703.913112	229.90	27.77	708.99	−705.551187	232.74	27.68	707.61
B5	−697.760274	176.41	25.34	665.40	−699.282044	179.05	25.12	663.31
B6	−723.756484	194.27	27.94	617.75	−725.388904	197.34	27.63	618.09
B7	−908.411672	230.85	34.98	805.42	−910.436498	234.88	34.61	805.14
B8	−499.390966	223.79	21.72	643.82	−500.641524	225.96	21.64	640.90
B9	−648.538627	185.07	24.75	704.07	−650.030458	187.66	24.62	703.83
B10	−607.635163	188.16	24.85	997.91	−609.091223	190.65	24.70	996.71
B11	−703.911139	230.71	27.57	714.77	−705.548699	233.72	27.39	714.82
B12	−697.755774	176.48	25.77	677.71	−699.277000	179.03	25.59	677.00
B13	−723.759121	194.35	28.03	611.01	−725.390647	197.60	27.67	613.81
B14	−908.410695	231.41	35.43	808.98	−910.435211	235.43	35.09	809.54
C1	−554.780888	267.88	25.87	599.79	−556.177881	270.27	25.86	593.12
C2	−853.068323	189.25	32.11	740.00	−854.947580	192.59	31.90	739.44
C3	−771.264697	195.60	32.04	1318.93	−773.072655	198.70	31.83	1315.81
C4	−963.814720	280.03	38.13	757.69	−965.985942	283.98	37.93	756.27
C5	−951.505414	172.78	33.72	680.21	−953.444068	176.05	33.40	677.12
C6	−1003.509999	208.42	38.33	552.33	−1005.669388	212.83	37.76	555.77
C7	−1372.811205	281.55	53.32	952.60	−1375.756052	287.64	52.72	952.99
D1	−703.926875	227.81	29.11	663.32	−705.564973	230.68	28.97	659.74
D2	−812.168440	192.40	32.15	1024.45	−814.011937	195.61	31.95	1022.90
D3	−908.443040	234.76	34.94	744.80	−910.468066	238.49	34.69	744.40
D4	−902.286322	180.80	33.06	711.48	−904.195064	184.05	32.81	710.16
D5	−928.291345	198.42	35.43	640.24	−930.310182	202.36	35.02	642.99
D6	−1112.941232	235.34	42.90	842.58	−1115.353176	240.04	42.52	842.77
D7	−703.932746	228.43	29.37	648.78	−705.571210	231.46	29.14	644.31
D8	−812.169190	192.40	31.99	1022.32	−814.013052	195.62	31.79	1019.82
D9	−908.441056	234.47	35.24	750.02	−910.466486	238.05	35.07	748.50
D10	−902.287602	181.32	32.73	708.30	−904.196837	184.62	32.48	705.74
D11	−928.288574	199.11	35.09	647.85	−930.308211	202.84	34.77	648.38
D12	−1112.936634	235.04	42.72	854.17	−1115.348605	239.74	42.31	854.27

[a] E_0 is in a.u.; *ZPE*, HOF, and H_T are in kJ/mol. The scaling factor for *ZPE* is 0.98 and the scaling for H_T is 0.96 [35].

311G** levels. Thermodynamic properties were obtained from the scaled vibrational frequencies with scaling factors taken from Ref. [35] using Eq. (9). In Table 1, the experimental HOFs of the reference compounds (including CH_4, CH_3NH_2, CH_3NO_2, CH_3ONO_2, and $CH_3N(NO_2)_2$) in the isodesmic reactions (1) and (2) were taken from Ref. [36]. The heat of atomization reaction, $\Delta H_{298\,K}$, for the reactions (4)–(7), and the heat of isodesmic reaction, $\Delta H_{298\,K}$, for the reaction (8) were obtained through Eq. (9) using the CBS-Q theory. The CBS-Q approach was used to compute the total energies of the systems. A precise value of ΔH_f for TETZ, TTZ, CH_3N_3, CH_3NF_2, and CH_3NHNO_2 were then obtained through Eq. (9) as well as the available experimental HOFs for C(g), H(g), N(g), F(g), CH_4(g), CH_3NH_2(g), and CH_3NO_2(g). There are no experimental HOFs values of TETZ, TTZ, CH_3N_3, CH_3NF_2, and CH_3NHNO_2 for comparison. To validate the reliability of these results, we compared the calculated ΔH_f values of 1,2,3-benzotriazole (TETZ and TTZ have similar structural characters with 1,2,3-benzotriazole), CH_4, CH_3NH_2, CH_3NO_2, CH_3ONO_2, and $CH_3N(NO_2)_2$ at the CBS-Q level with their experimental data as well as those at the G2 level. Since the 1,2,3-benzotriazole system is relatively large, we did not obtain its calculated ΔH_f values at the G2 level. The ΔH_f value of 1,2,3-benzotriazole is calculated by the CBS-Q theory to be 343.26 kJ/mol, very close to the experimental ΔH_f of 335.54 kJ/mol [36] with an error of only 7.72 kJ/mol. The mean absolute deviation from the experimental values for the calculated HOFs at the G2 level is 6.996 kJ/mol, while that at the CBS-Q level is 5.408 kJ/mol. The linear relationship between the HOFs from the G2 and CBS-Q levels is very good, $HOF_{CBS\text{-}Q} = 0.9734HOF_{G2} + 0.2041$, $R^2 = 0.9994$. This shows that both methods produce similar HOF for the reference compounds, but the former has relatively higher mean absolute deviation than the latter. We also performed the calculations on TETZ and TTZ at the G2 level, but we cannot succeed. This may be because the sizes of TETZ and TTZ are large and their total energy calculations cannot proceed at the G2 level. Therefore, the CBS-Q theory can not only predict the HOFs for the aforementioned compounds accurately but also deal with relatively large molecules. This is supported by previous reports [27] that the CBS theory has a range of molecular size for which it is the most accurate computational model currently available.

Table 2 summarizes the total energies, zero-point energies, thermal corrections, and HOFs of the TETZ and TTZ derivatives. We also evaluate the dependence of the HOFs on the B3P86 and B3LYP levels with 6-311G**. The results show that the HOFs at the two methods for the same compound are very close. There is a very good linear relationship between the HOFs from the B3P86 and B3LYP methods with 6-311G**: $HOF_{B3P86} = 0.9986HOF_{B3LYP} - 0.1004$ with $R^2 = 0.9998$. This indicates that both the methods produce similar HOFs for the TETZ and TTZ derivatives.

As is evident in Table 2, all the compounds exhibit positive HOFs. C3 has the largest HOF value among the derivatives and is over 1300 kJ/mol. This reflects that the TETZ and TTZ derivatives have

Table 3
Calculated HOMO and LUMO energies (a.u.) and energy gaps ($\Delta E_{\text{LUMO-HOMO}}$) of the TETZ and TTZ derivatives at the B3LYP/6-311G** and B3P86/6-311G** levels[a].

Compound	E_{HOMO}	E_{LUMO}	$\Delta E_{\text{LUMO-HOMO}}$
A	−0.3002(−0.3220)	−0.1576(−0.1804)	0.1426(0.1416)
A1	−0.2853(−0.3088)	−0.1373(−0.1598)	0.1480(0.1490)
A2	−0.3271(−0.3489)	−0.1854(−0.2083)	0.1417(0.1406)
A3	−0.3021(−0.3243)	−0.1582(−0.1813)	0.1439(0.1430)
A4	−0.3117(−0.3335)	−0.1650(−0.1875)	0.1467(0.1460)
A5	−0.3192(−0.3406)	−0.1745(−0.1968)	0.1447(0.1438)
A6	−0.3104(−0.3338)	−0.1662(−0.1900)	0.1442(0.1438)
A7	−0.3217(−0.3437)	−0.1769(−0.1994)	0.1448(0.1443)
B	−0.2805(−0.3021)	−0.1389(−0.1615)	0.1416(0.1406)
B1	−0.2677(−0.2900)	−0.1201(−0.1423)	0.1476(0.1477)
B2	−0.3071(−0.3287)	−0.1675(−0.1903)	0.1396(0.1384)
B3	−0.2845(−0.3064)	−0.1421(−0.1651)	0.1424(0.1413)
B4	−0.2927(−0.3142)	−0.1485(−0.1708)	0.1442(0.1434)
B5	−0.2994(−0.3205)	−0.1564(−0.1784)	0.1430(0.1421)
B6	−0.2895(−0.3121)	−0.1436(−0.1673)	0.1459(0.1448)
B7	−0.3031(−0.3248)	−0.1604(−0.1830)	0.1427(0.1418)
B8	−0.2500(−0.2725)	−0.1261(−0.1484)	0.1239(0.1241)
B9	−0.3031(−0.3250)	−0.1628(−0.1855)	0.1403(0.1395)
B10	−0.2707(−0.2941)	−0.1393(−0.1621)	0.1314(0.1320)
B11	−0.2884(−0.3102)	−0.1474(−0.1701)	0.1410(0.1401)
B12	−0.2972(−0.3186)	−0.1561(−0.1784)	0.1411(0.1402)
B13	−0.2879(−0.3104)	−0.1482(−0.1713)	0.1397(0.1391)
B14	−0.2981(−0.3199)	−0.1572(−0.1800)	0.1409(0.1399)
C1	−0.2350(−0.2572)	−0.1086(−0.1305)	0.1264(0.1267)
C2	−0.3282(−0.3501)	−0.1879(−0.2108)	0.1403(0.1393)
C3	−0.2710(−0.2946)	−0.1418(−0.1650)	0.1292(0.1296)
C4	−0.2972(−0.3196)	−0.1548(−0.1771)	0.1424(0.1425)
C5	−0.3149(−0.3358)	−0.1715(−0.1934)	0.1434(0.1424)
C6	−0.2975(−0.3214)	−0.1570(−0.1809)	0.1405(0.1405)
C7	−0.3168(−0.3388)	−0.1744(−0.1971)	0.1424(0.1417)
D1	−0.2703(−0.2930)	−0.1536(−0.1762)	0.1167(0.1168)
D2	−0.2898(−0.3133)	−0.1653(−0.1883)	0.1245(0.1250)
D3	−0.3119(−0.3340)	−0.1732(−0.1959)	0.1387(0.1381)
D4	−0.3220(−0.3434)	−0.1818(−0.2043)	0.1402(0.1391)
D5	−0.3105(−0.3334)	−0.1731(−0.1965)	0.1374(0.1369)
D6	−0.3214(−0.3433)	−0.1820(−0.2050)	0.1394(0.1383)
D7	−0.2900(−0.3129)	−0.1447(−0.1672)	0.1453(0.1457)
D8	−0.3078(−0.3300)	−0.1639(−0.1869)	0.1439(0.1431)
D9	−0.3134(−0.3353)	−0.1689(−0.1914)	0.1445(0.1439)
D10	−0.3206(−0.3421)	−0.1780(−0.2002)	0.1426(0.1419)
D11	−0.3124(−0.3358)	−0.1698(−0.1938)	0.1426(0.1420)
D12	−0.3224(−0.3449)	−0.1818(−0.2055)	0.1406(0.1394)

[a] The values in parentheses are at the B3P86/6-311G** level.

high positive HOFs, consistent with previous reports that energetic high-nitrogen heterocycles have high positive heats of formation [1,2]. When the substituent is $-NO_2$, $-N_3$, $-NHNO_2$, or $-N(NO_2)_2$, an increase in the HOF values of its substituted TETZ or TTZ is large compared with the unsubstituted case. For the substituent $-NH_2$ or $-ONO_2$, the case is quite the contrary. When the H atom of TTZ is replaced by $-N_3$, its HOF value is the largest one among these derivatives with the same number of substituent. The same is true of TETZ. This is in agreement with previous studies [4,7,18] that the azido group is one of the most energetic functional groups known and its substitution can increase the energy content of a molecule by about 293–320 kJ/mol. It is also seen in Table 2 that the substitution of the group $-N_3$ or $-N(NO_2)_2$ in TETZ or TTZ extremely enhances the HOF values compared to parent ring. This shows that the $-N_3$ or $-N(NO_2)_2$ group plays a very important role in increasing the HOF values of the TETZ and TTZ derivatives. For B series, the HOF values of the TTZ derivatives with single substituent are different as the position of substituent varies. The HOFs of the derivatives with single substituent in position 2 of the parent TTZ ring are larger than those of the ones with single substituent in position 8 except for B6 and B13, indicating different position of the substituent can affect the HOF values. Similar conclusion is also drawn from D series. By comparison of B and C series, we also note that the HOFs of the TTZ derivatives are not satisfactory with the relationship of simple group addition.

3.2. Electronic structure and thermal stability

Table 3 lists the HOMO and LUMO energies and the energy gaps ($\Delta E_{\text{LUMO-HOMO}}$) for the TETZ and TTZ derivatives at the B3LYP/6-311G** and B3P86/6-311G** levels. It can be seen that the E_{HOMO}, E_{LUMO}, and $\Delta E_{\text{LUMO-HOMO}}$ values at the B3P86/6-311G** level are systematically smaller than those at the B3LYP/6-311G** level for most of the derivatives. The variations of $\Delta E_{\text{LUMO-HOMO}}$ are very similar at the two levels. There is a good linear relationship between $\Delta E_{\text{LUMO-HOMO}}$ by B3LYP and $\Delta E_{\text{LUMO-HOMO}}$ by B3P86 with the 6-311G** basis set: $\Delta E_{\text{B3P86}} = 0.9557\Delta E_{\text{B3LYP}} + 0.0056$, with $R^2 = 0.9955$. This shows that both the two methods produce similar energy gaps for the TETZ and TTZ derivatives. When a $-NH_2$ group is attached to the ring, the HOMO energy level increases, whereas attachment of other groups will make HOMO energy level decrease. The same is true of the LUMO energy level for these derivatives. For the 8-substituted TETZ (A1–7), all the derivatives increase the HOMO–LUMO gap as compared to the parent TETZ (A) except the derivative with the $-NO_2$ group (A2). The same is true of the 8-monosubstituted TTZ derivatives (B1–7). It is interesting to note that all the 2-monosubstituted TTZ derivatives (B8–14) decrease the HOMO–LUMO gap of the unsubstituted TTZ (B). Also, for the disubstituted case (D1–12), all the derivatives with $-NO_2$ in position 8 of the TTZ ring (D1–6) decrease the HOMO–LUMO gap of TTZ, while the ones with NO_2 in position 2 (D7–12) increase that compared

Table 4
Calculated bond overlap populations of part bonds of the TETZ and TTZ derivatives at the B3LYP/6-311G** level.

Compound	P_{C-N}	P_{N-N}	P_{C-R}	$P_{C-R'}$	$P_{N-R'}$
A	0.2176	0.1337			
A1	0.2355	0.1672	0.3982		
A2	0.1952	0.1257	0.1546		
A3	0.2226	0.1502	0.4120		0.2019(P_{N-N_2})
A4	0.2097	0.1248	0.2866		0.1511(P_{NH-NO_2})
A5	0.2038	0.1215	0.2267		
A6	0.2091	0.1124	0.3367		0.1395(P_{O-NO_2})
A7	0.2029	0.1317	0.2114		0.1001(P_{N-NO_2})
B	0.2801	0.1252			
B1	0.2960	0.1529	0.3888		
B2	0.2559	0.1211	0.1517		
B3	0.2814	0.1410	0.4009		0.2048(P_{N-N_2})
B4	0.2703	0.1173	0.2784		0.1574(P_{NH-NO_2})
B5	0.2649	0.1153	0.2213		
B6	0.2848	0.1438	0.3187		0.1257(P_{O-NO_2})
B7	0.2629	0.1275	0.2086		0.1089(P_{N-NO_2})
B8	0.2770	0.1189	0.3872		
B9	0.2939	0.1304	0.1527		
B10	0.2857	0.1216	0.4269		0.2768(P_{N-N_2})
B11	0.2965	0.1372	0.3066		0.1814(P_{NH-NO_2})
B12	0.2872	0.1267	0.2184		
B13	0.2982	0.1242	0.4120		0.1280(P_{O-NO_2})
B14	0.3017	0.1345	0.2539		0.0919(P_{N-NO_2})
C1	0.2926	0.1443	0.3819		
C2	0.2721	0.1293	0.1502		
C3	0.2870	0.1378	0.4017		0.2034(P_{N-N_2})
C4	0.2873	0.1300	0.2804		0.1512(P_{NH-NO_2})
C5	0.2727	0.1184	0.2176		
C6	0.2901	0.1052	0.3304		0.1283(P_{O-NO_2})
C7	0.2856	0.1362	0.2039		0.0921(P_{N-NO_2})
D1	0.2540	0.1118	0.1506(P_{C-NO_2})	0.3958(P_{C-NH_2})	
D2	0.2626	0.1202	0.1529(P_{C-NO_2})	0.4346(P_{C-N_3})	0.2892(P_{N-N_2})
D3	0.2736	0.1336	0.1524(P_{C-NO_2})	0.3070(P_{C-NHNO_2})	0.1803(P_{NH-NO_2})
D4	0.2642	0.1254	0.1527(P_{C-NO_2})	0.2166(P_{C-NF_2})	
D5	0.2749	0.1196	0.1521(P_{C-NO_2})	0.4219(P_{C-ONO_2})	0.1281(P_{O-NO_2})
D6	0.2790	0.1319	0.1511(P_{C-NO_2})	0.2535(P_{C-NNO_2})	0.0923(P_{N-NO_2})
D7	0.3071	0.1532	0.1579(P_{C-NO_2})	0.3965(P_{C-NH_2})	
D8	0.2911	0.1206	0.1538(P_{C-NO_2})	0.4212(P_{C-N_3})	0.2927(P_{N-N_2})
D9	0.2845	0.1236	0.1535(P_{C-NO_2})	0.2830(P_{C-NHNO_2})	0.1500(P_{NH-NO_2})
D10	0.2795	0.1212	0.1516(P_{C-NO_2})	0.2228(P_{C-NF_2})	
D11	0.2857	0.1102	0.1524(P_{C-NO_2})	0.3364(P_{C-ONO_2})	0.1400(P_{O-NO_2})
D12	0.2820	0.1555	0.1508(P_{C-NO_2})	0.2052(P_{C-NNO_2})	0.0993(P_{N-NO_2})

with the derivative C2. This shows that attachment of a substituent to position 2 in the TTZ ring will decrease the HOMO–LUMO gap of the parent TTZ, whereas addition of a substituent to position 8 will increase that. Accordingly, the energy gap of TTZ can be tuned by incorporating a substituent into different positions in the parent ring. A1, A3–7, B1, B3–7, C4–5, C7, and D7–11 have higher energy gaps than the unsubstituted molecule TETZ or TTZ, indicating a shift toward higher frequencies in their electronic absorption spectra. But A2, B2, B8–14, C1–3, C6, D1–6, and D12 have lower energy gaps than the corresponding unsubstituted one, reflecting a shift toward lower frequencies in their electronic absorption spectra. Among these derivatives, A1 has the highest ΔE value, whereas D1 has the smallest one. Overall, different substituted molecules present a comparison of the energetics.

Bond order is theoretical index of the degree of bonding between two atoms. It can be used as a measure of the overall bond strength between two atoms. A high value of the bond order indicates a covalent bond, while a low value shows an ionic nature. Table 4 presents the bond overlap populations of the C–N, N–N, C–R (R = $-NH_2$, $-NO_2$, $-N_3$, $-NHNO_2$, $-NF_2$, $-ONO_2$, $-N(NO_2)_2$), and N–R′ (R′ = $-N_2$, $-NO_2$) bonds for the TETZ and TTZ derivatives. It is found that the N–N bonds of all the derivatives have the lowest bond overlap populations among all the bonds except for A7, B7, and B14, showing that the ring cleavage is possible to happen in thermal decomposition. But the $N-NO_2$ bonds of A7, B7, and B14 have the lowest bond order, so their fragmentation pathways may be concerned with NO_2 radical. It is interesting to note that A1 or A3 has higher bond orders of the C–N and N–N bonds in the ring than the parent TETZ, whereas the case is quite the contrary for A2 and A4–7. This indicates that the substitution of the $-NH_2$ or $-N_3$ group increases the strength of the C–N and N–N bonds of TETZ. The same is true of the TTZ derivatives (B1–7). Among the TETZ and TTZ derivatives, the bond orders of the weakest bonds for A7, B7, B14, C7, D6, and D12 are relatively small and are close to 0.1000. The principle of the smallest bond order (PSBO) [19] pointed out that the chemical bond with the smallest bond order may be firstly ruptured in thermal decompositions. According to PSBO, it may be thus inferred that the thermal stability of A7, B7, B14, C7, D6, and D12 is relatively bad. Similar conclusions can also be drawn from the BDE of the derivatives below.

Bond dissociation energy (BDE) provides useful information for understanding the stability of the title compounds. It should be pointed out that we select the weakest bond (N–N or N–R′) as the breaking bond based on the bond overlap populations to calculate BDE at the B3LYP/6-311G** level. The bond overlap populations and bond dissociation energies (BDE) of the weakest bonds for the TETZ and TTZ derivatives are listed in Table 5. From the BDE^0 and BDE_{ZPE} values, it is found that the BDE values without zero-point energy correction are larger than those including zero-point energy corrections. However, the order of the dissociation energies is not affected by the zero-point energies. Most of the derivatives have smaller BDE_{ZPE} values than the unsubstituted molecule TETZ or TTZ except

Table 5
Calculated bond dissociation energies (BDE, kJ/mol) for A–B(g) → A•(g) + B•(g) and bond overlap populations of the weakest bonds for the TETZ and TTZ derivatives together with RDX and HMX at the B3LYP/6-311G** level[a].

Compound	P_{N1-N9}	$P_{N-R'}$	BDE^0	BDE_{ZPE}
A	0.1337		119.53	108.91
A1	0.1672		130.40	121.03
A2	0.1257		106.93	96.55
A3	0.1502		116.77	106.91
A4	0.1248		118.13	108.38
A5	0.1215		113.07	103.11
A6	0.1124		80.26	63.66
A7		0.1001(P_{N-NO_2})	81.48	66.18
B	0.1252		230.44	214.88
B1	0.1529		255.03	241.21
B2	0.1211		223.70	209.30
B3	0.1410		239.88	225.69
B4	0.1173		137.23(239.99)[b]	118.69(225.66)[b]
B5	0.1153		232.96	218.66
B6		0.1257(P_{O-NO_2})	63.40	47.60
B7		0.0994(P_{N-NO_2})	75.88	60.76
B8	0.1189		180.52	165.81
B9	0.1304		213.96	198.93
B10	0.1216		199.28	183.86
B11	0.1372		107.34(212.04)[b]	88.05(195.88)[b]
B12	0.1267		205.37	190.76
B13	0.1242		70.32	54.44
B14		0.0919(P_{N-NO_2})	54.81	39.87
C1	0.1443		201.92	187.51
C2	0.1293		205.22	191.06
C3	0.1378		209.20	194.65
C4	0.1300		106.93(218.29)[b]	87.90(202.69)[b]
C5	0.1184		205.78	192.15
C6	0.1052		22.93	7.51
C7		0.0921(P_{N-NO_2})	56.47	41.41
D1	0.1118		187.90	173.77
D2	0.1202		189.78	175.51
D3	0.1336		106.04(190.23)[b]	86.61(175.52)[b]
D4	0.1254		194.89	181.33
D5	0.1196		25.65	10.13
D6		0.0923(P_{N-NO_2})	57.03	41.82
D7	0.1532		243.20	229.89
D8	0.1206		235.85	221.78
D9	0.1236		139.32(221.98)[b]	120.83(208.14)[b]
D10	0.1212		216.71	202.93
D11	0.1102		82.63	66.47
D12		0.0993(P_{N-NO_2})	74.27	59.58
RDX		0.1376(P_{N-NO_2})	166.19	145.62
HMX		0.1382(P_{N-NO_2})	178.77	160.41

[a] BDE^0 denotes the bond dissociation energies without zero-point energy corrections, while BDE_{ZPE} denotes the bond dissociation energies including zero-point energy corrections.

[b] The values in parentheses are the bond dissociation energies of the bonds with the smallest bond overlap populations.

for A1, B1, B3, B5, D7, and D8. The calculated BDE can be used to measure the relative order of thermal stability for energetic materials [37,38]. Therefore, it can be deduced that incorporating most of the substituents into TETZ or TTZ are unfavorable for increasing its thermal stability. Compared with the commonly used explosives RDX (1,3,5-trinitro-1,3,5-triazinane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane), most of the TTZ derivatives have higher the BDE_{ZPE} values. This implies that they have good thermal stability.

It is interesting to note that the N1–N9 bond in the ring of B4 has relatively low bond order of 0.1173 but higher BDE_{ZPE} value (225.66 kJ/mol) among the weakest bonds of the TTZ derivatives. However, the NH–NO_2 bond of B4 has higher bond order (0.1574) but lower BDE_{ZPE} (118.69 kJ/mol) compared to the N1–N9 bond of B4. The initial step should be via NH–NO_2 cleavage in thermal decompositions. Accordingly, to judge the thermal stability of the TTZ derivatives is not by the bond order simply, but it is necessary to depend on the BDE_{ZPE}. As is evident in Table 5, the B1–7 derivatives basically have higher BDE than B8–14. This indicates that attachment of the substituent to position 2 in the parent TTZ ring is very useful for improving its thermal stability than that to position 8, i.e. the relative position of the substituent affects the stability of the compounds. Similar conclusions are also drawn from D series. Also, we note that A3 and A5 have smaller BDE_{ZPE} than A, while B3 and B5 have higher BDE_{ZPE} than B. This shows that the effect of the $-N_3$ or $-NF_2$ group in the TETZ and TTZ rings on BDE_{ZPE} is different. When the $-NO_2$, $-NHNO_2$, $-ONO_2$, or $-N(NO_2)_2$ group is attached to the TETZ or TTZ ring, the BDE_{ZPE} value decreases. This shows that incorporating these groups into the TETZ or TTZ ring make its stability decrease.

3.3. Predicted detonation performances

Detonation velocity and detonation pressure are two important performance parameters for an energetic material. Table 6 presents calculated detonation velocities (D) and pressures (P) of the TETZ and TTZ derivatives. For a comparison, the experimental detonation performances of two known explosives RDX and HMX are also listed in this table [39]. The semi-empirical Kamlet–Jacobs formula has been proved to be reliable for predicting the explosive properties of energetic high-nitrogen compounds [18,40–42].

Table 6
Predicted detonation properties of the TETZ and TTZ derivatives together with RDX and HMX[a].

Compound	V^b (cm^3/mol)	Q (J/g)	ρ (g/cm^3)	D (km/s)	P (GPa)
A	73.28	1528.89	1.68	8.08	27.77
A1	82.31	1264.88	1.68	7.97	26.95
A2	88.92	1728.74	1.89	9.18	38.45
A3	91.55	1612.23	1.79	8.56	32.39
A4	99.32	1629.04	1.84	8.98	36.26
A5	88.67	1766.80	1.96	9.54	42.46
A6	95.89	1716.45	1.92	9.37	40.42
A7	116.04	1801.14	1.96	9.80	44.85
B	76.53	1307.26	1.59	7.28	21.77
B1	85.87	1075.72	1.60	7.20	21.34
B2	93.94	1588.20	1.78	8.30	30.30
B3	98.06	1447.72	1.66	7.74	25.33
B4	102.38	1504.94	1.78	8.30	30.35
B5	91.87	1635.12	1.89	8.77	35.01
B6	100.11	1686.11	1.81	8.62	33.27
B7	121.34	1686.11	1.87	9.00	36.79
B8	85.11	1117.70	1.61	7.31	22.14
B9	94.77	1602.53	1.76	8.26	29.91
B10	97.35	1461.12	1.67	7.80	25.82
B11	104.36	1514.40	1.74	8.21	29.30
B12	91.64	1654.03	1.89	8.81	35.39
B13	100.91	1601.86	1.81	8.56	32.69
B14	122.20	1690.74	1.86	8.96	36.32
C1	94.36	932.26	1.61	7.19	21.43
C2	109.93	1720.84	1.93	9.22	39.28
C3	116.99	1541.28	1.74	8.16	28.95
C4	132.06	1568.52	1.83	8.85	35.10
C5	109.13	1784.82	2.05	9.84	46.33
C6	127.63	1700.77	1.91	9.30	39.77
C7	166.37	1549.42	2.00	9.49	42.38
D1	102.61	1442.09	1.77	8.20	29.57
D2	115.17	1627.35	1.81	8.58	32.75
D3	119.30	1636.01	1.90	9.11	38.02
D4	107.97	1755.77	2.02	9.64	44.02
D5	120.09	1705.27	1.90	9.19	38.64
D6	139.58	1786.09	1.95	9.61	42.88
D7	102.38	1421.83	1.78	8.19	29.50
D8	114.05	1623.82	1.82	8.64	33.36
D9	119.53	1640.33	1.90	9.10	37.92
D10	108.65	1750.93	2.01	9.59	43.41
D11	136.25	1710.92	1.93	9.29	39.84
D12	123.17	1796.19	2.00	9.79	45.13
RDX[c]	124.91	1591.03	1.78(1.82)	8.87(8.75)	34.67(34.00)
HMX[c]	157.50	1633.90	1.88(1.91)	9.28(9.10)	39.19(39.00)

[a] Data in the parentheses are the experimental values taken from Ref. [39].
[b] Average volume from 100 single-point calculations at the B3LYP/6-31G* level.
[c] The calculated values of RDX and HMX taken from Ref. [18].

As is evident in Table 6, the TETZ and TTZ derivatives with different substituent groups have different ρ values. For the TETZ derivatives, the largest ρ value and the smallest one are 1.96 and 1.68 g cm^{-3}, respectively, whereas, for the TTZ derivatives, the largest ρ value and the smallest one are 2.05 and 1.60 g cm^{-3}, respectively. This makes the derivatives have different D and P values. Most of the derivatives increase the D and P values as compared to the corresponding unsubstituted molecule (TETZ or TTZ) except for the $-NH_2$ substituents. For B and D series, their detonation properties are different when the position of substituent in the TTZ ring is changed. As the number of substituent increases, the ρ, D, and P values of the substituted TTZ enhance except for the derivative with $-NH_2$. It is observed from Table 6 that most of the derivatives have higher ρ values than RDX (1.82 g cm^{-3}) [39], so they have very high D and P values. The derivatives with the $-NO_2$, $-NF_2$, $-ONO_2$, or $-N(NO_2)_2$ group have very high ρ, D, and P values, which are close to 1.9 g cm^{-3}, 9.0 km s^{-1}, and 40.0 GPa, respectively. It is also found that C5, the derivative with two $-NF_2$ groups, has the largest ρ, D, and P values among these derivatives. This shows that the substitutions of the $-NO_2$, $-NF_2$, $-ONO_2$, or $-N(NO_2)_2$ group are useful for increasing the densities and detonation properties of the TETZ and TTZ derivatives.

3.4. Potential candidates for HEDMs

Most of the nitrogen-rich compounds have very high positive heats of formation rather than from oxidation of the carbon backbone, as with traditional energetic materials [43]. However, high heats of formation are usually unfavorable for the stability of a compound. Accordingly, a good nitrogen-rich HEDM candidate not only has excellent detonation properties but also could exist stably. Fig. 2 presents the detonation properties and bond dissociation energies of the weakest bonds for the TETZ and TTZ derivatives together with commonly used explosives RDX and HMX.

It is seen that the derivatives A2, A4–7, B7, B14, C2, C5–7, D3–6, and D9–12 have higher D and P than RDX. But only A5–7, C2, C5–7, D4, D6, and D10–12 have good detonation performance (D and P) over HMX. Also, it is found that B, B1–3, B5, B8–10, B12, C1–3, C5, D1–2, D4, D7–8, and D10 have higher BDE for the weakest bonds as compared to RDX and HMX. On the basis of the BDE for the initial steps in the thermal decompositions, it may be inferred that these derivatives are more insensitive to thermal and impact. On the above suggestions, it may be concluded that only C2, C5, D4, and D10 have good detonation performance

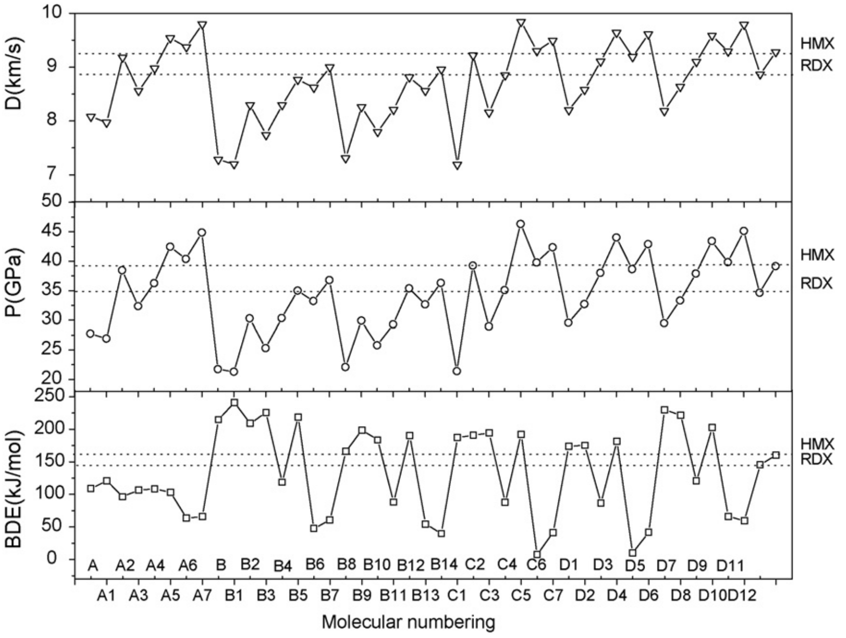

Fig. 2. Detonation properties and dissociation energies of the weakest bonds for the TETZ and TTZ derivatives.

(*D* and *P*) and thermal stability (BDE) over RDX and HMX. Therefore, C2, C5, D4, and D10 may be considered as the potential candidates of HEDMs with less sensitivity and higher performance.

Although A1, B, B1, and C1 have been successfully synthesized, some detonation and thermodynamics properties are still lacking. In addition, the syntheses of other energetic compounds have not been reported yet. Thus, further investigations are still needed.

4. Conclusions

In the present study, we have calculated the heats of formation (HOFs) for a series of TETZ and TTZ derivatives using B3LYP and B3P86 with the 6-311G** basis set. The results show that the HOFs at the two levels for the same compound are very close. The substitution of the $-N_3$ or $-N(NO_2)_2$ group in the TETZ or TTZ ring extremely enhances its HOF values.

For monosubstituted case, attachment of a substituent to position 8 in the TETZ or TTZ ring will increase its HOMO–LUMO gap except for the derivatives with the NO_2 group (A2 and B2). Also, for the TTZ derivatives with two different substituents, attachment of a substituent to position 2 in the TTZ ring will decrease its HOMO–LUMO gap, whereas addition of a substituent to position 8 will increase that. This shows that the energy gap of TTZ can be tuned by incorporating a substituent into different positions in the parent ring.

An analysis of the bond dissociation energies for the weakest bonds indicates that attachment of the NH_2 group to the TETZ ring is favorable for enhancing its thermal stability. For TTZ, different substituted positions and number of the substituent might affect its thermal stability.

The calculated detonation velocities and pressures indicate that incorporating the $-NO_2$, $-NF_2$, $-ONO_2$, or $-N(NO_2)_2$ group into the TETZ or TTZ ring is very helpful for enhancing its detonation performance. Considering the detonation performance and thermal stability, C2, C5, D4, and D10 may be regarded as the potential candidates of HEDMs. These results provide basic information for the molecular design of novel HEDMs.

Acknowledgments

This work was supported by the NSAF Foundation of National Natural Science Foundation of China and China Academy of Engineering Physics (grant no. 10876013), the Specialized Research Fund for the Doctoral Program of Higher Education (200802881043), and the Project-sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

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