

Characterization of nitrogen-bridged 1,2,4,5-tetrazine-, furazan-, and 1*H*-tetrazole-based polyheterocyclic compounds: heats of formation, thermal stability, and detonation properties

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Abstract The heats of formation (HOFs), thermal stability, and detonation properties for a series of nitrogen-bridged 1,2,4,5-tetrazine-, furazan-, and 1*H*-tetrazole-based polyheterocyclic compounds (3,6-bis(1*H*-1,2,3,4-tetrazole-5-ylamino)-1,2,4,5-tetrazine (TST), 3,6-bis(furazan-5-ylamino)-1,2,4,5-tetrazine (FSF), 3,4-bis(1,2,4,5-tetrazine-3-ylamino)-furazan (SFS), 3,4-bis(1*H*-1,2,3,4-tetrazole-5-ylamino)-furazan (TFT), 1,5-bis(1,2,4,5-tetrazine-3-ylamino)-1*H*-1,2,3,4-tetrazole (STS), and 1,5-bis(furazan-3-ylamino)-1*H*-1,2,3,4-tetrazole (FTF) derivatives) were systematically studied by using density functional theory. The results show that the -N₃ or -NHNH₂ group plays a very important role in increasing the HOF values of the derivatives. Among these series, the SFS derivatives have lower energy gaps, while the TFT derivatives have higher ones. Incorporation of the -NH₂ group into the FSF, SFS, STS, or FTF ring is favorable for enhancing its thermal stability, whereas the substitution of the -NHNH₂ group could increase the thermal stability of the TST, SFS, STS, or FTF ring. The calculated detonation properties indicate that the -NO₂ or -NF₂ is very helpful for enhancing the detonation performance for these derivatives. Considering the detonation

performance and thermal stability, six derivatives may be regarded as promising candidates of high-energy density materials (HEDMs). These results provide basic information for the molecular design of novel HEDMs.

Keywords Bond dissociation energies · Density functional theory · Detonation properties · Heats of formation · Polyheterocyclic systems

Introduction

Over the past decade, high-nitrogen heterocycles have been recognized as one class of useful and promising structures for the design and synthesis of high-energy density materials (HEDMs) [1–10]. Among them, a great deal of effort has been focused on the study of tetrazole, furazan, and 1,2,4,5-tetrazine (or s-tetrazine) derivatives [3–10]. These conditional azo heterocyclic systems have their own advantages and disadvantages as HEDMs. Tetrazine and tetrazole derivatives possess high positive heats of formation (HOFs), crystal densities, thermal stability, and so on [3–7, 11]. In comparison with furazans, tetrazine and tetrazole derivatives have relatively low densities and poor oxygen balance. However, some furazan derivatives exhibit certain disadvantages such as particular chemical instabilities and incompatibilities with the binders and additives presented in propellants and explosives [12]. To make these advantages into a whole, a combination of different nitrogen-rich heterocycles in one molecule thus seems to be an attempt on designing novel high-energy compounds.

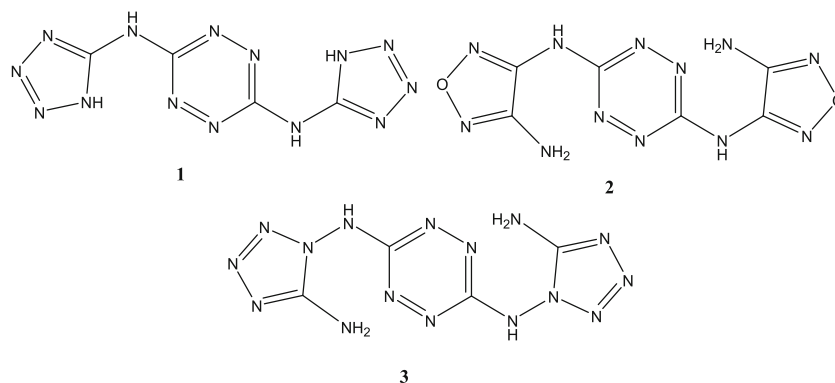
Recently, 3,6-bis(1*H*-tetrazole-5-ylamino)-1,2,4,5-tetrazine (**1**) [6, 13–15], 3,6-bis(3-amino-1,2,5-oxadiazol-4-ylamino)-1,2,4,5-tetrazine (**2**) [16], and 3,6-bis(5-amino-1*H*-tetrazole-1-ylamino)-1,2,4,5-tetrazine (**3**) [17] have been

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Fig. 1 Molecular frameworks of BTATz (1), BAOATz (2), and BATATz (3)



synthesized and their structures are shown in Fig. 1. Compound **1** was measured to have high positive HOF ($+883 \text{ kJ mol}^{-1}$), high density of 1.76 g cm^{-3} , and moderate mechanical sensitivity [15, 18–20]. Because of its high burn rate with low sensitivity with respect to pressure, this material is of great interest to the propellant community. Compound **2** is determined to be very thermally stable and does not begin to decompose until $280 \text{ }^\circ\text{C}$ [16]. **3** possesses exceptionally high positive HOF ($+1289.10 \text{ kJ mol}^{-1}$) and thermal stability. Its decomposition temperature is $209 \text{ }^\circ\text{C}$ [17]. Since they combine two kinds of energetic nitrogen-rich heterocyclic backbone in one molecule and own good performances, the nitrogen-rich polyheterocyclic compounds may be regarded as a new class of energetic materials.

As mentioned above, these heterocyclic compounds and their derivatives are now investigated as potential starting materials for the design and synthesis of new energetic materials. Some of them have displayed potential as energetic additives for high explosive/propellant formulations and pyrotechnic ingredients. Therefore, it is inferred that a hybrid of several nitrogen-containing heterocyclic systems may be another development direction on designing HEDMs. Despite extensive interest in the new class of high-nitrogen heterocyclic systems in recent years, a systematic design of high-nitrogen polyheterocycles with higher performance and less sensitivity is still lacking. To meet the continuing demand for improved energetic materials, there is a clear need to continue to design and develop new high-nitrogen polyheterocycle-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 HEDMs 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. Accordingly, they can help design better and more efficient laboratory tests [21, 22].

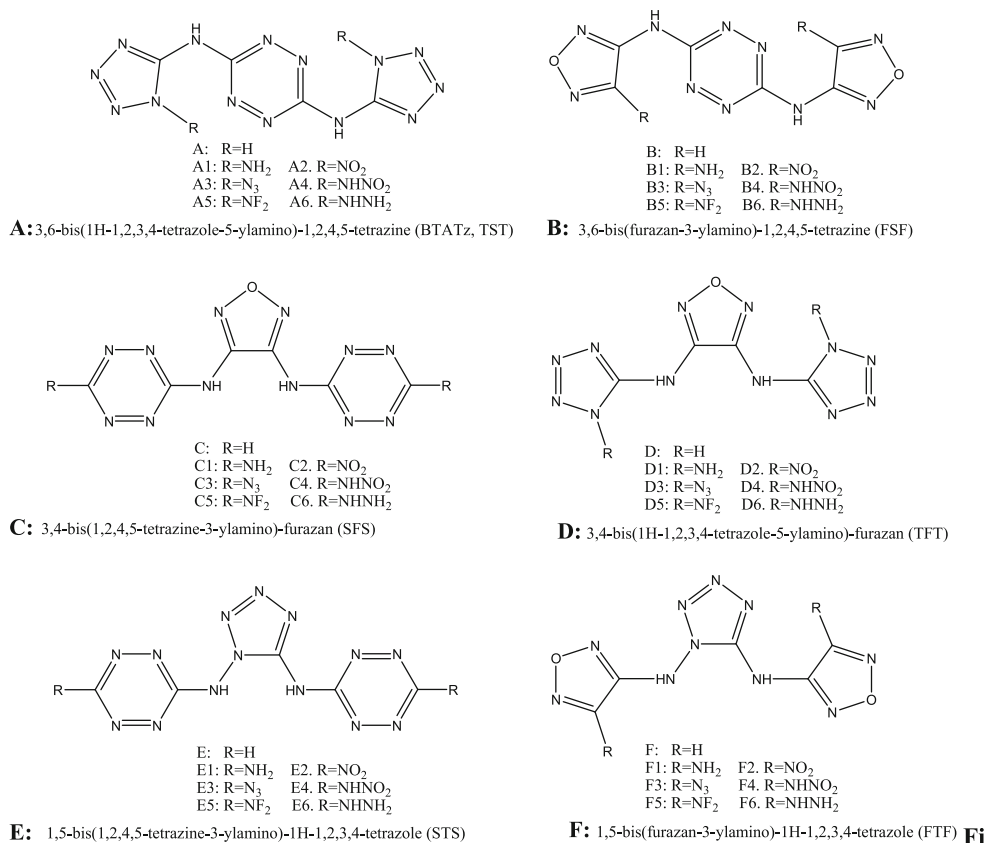
In this work, we report a systematic study on HOFs, thermal stability, and energetic properties of six series of nitrogen-bridged 1,2,4,5-tetrazine-, furazan- and 1*H*-tetrazole-based polyheterocyclic compounds (see Fig. 2) by using density functional theory (DFT) method. The HOFs of the derivatives were calculated by designing isodesmic reactions. Next their thermal stabilities were evaluated based on their bond dissociation energies. Finally their detonation properties 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 brief description of our computational method is given in **Computational methods** section, the **Results and discussion**, and a summary of our **Conclusions** are given in the following.

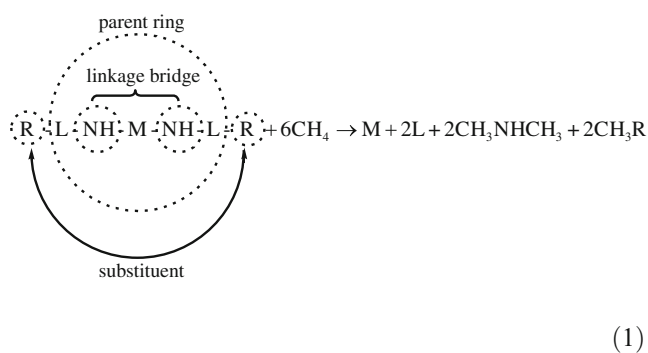
Computational methods

The hybrid DFT-B3LYP and DFT-B3P86 methods with the 6-311 G** basis set were adopted to predict HOFs via designing isodesmic reactions. We reported that the basis set 6-311 G** may produce satisfactory HOFs of nitrogen-rich compounds compared with the experiment values [23]. The method of isodesmic reactions has been employed very successfully to calculate HOF from total energies obtained from *ab initio* calculations [10, 23–30]. 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 [29]. In these designed reactions, the basic structural unit of the 1*H*-tetrazole, 1,2,4,5-tetrazine or furazan ring skeleton keeps unbroken, and the big molecules are changed into small ones too.

Fig. 2 Molecular frameworks of TST, FSF, SFS, TFT, STS, and FTF (A-F series) derivatives



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



where R=H, -NH₂, -NO₂, -N₃, -NHNO₂, -NF₂, or -NHNH₂. M is 1,2,4,5-tetrazine (S), furazan (Fz), or 1H-tetrazole (1H-Tz). L is S, Fz, or 1H-Tz.

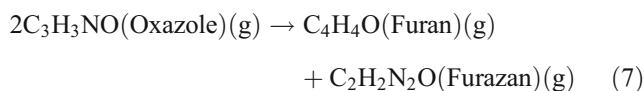
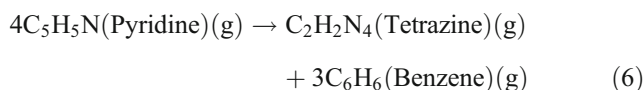
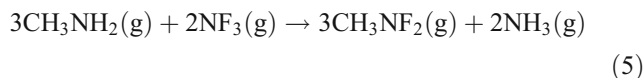
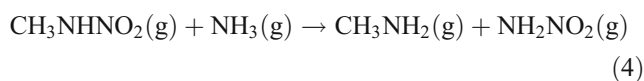
For the isodesmic reaction 1, the heat of reaction (ΔH_{298}) at 298 K can be calculated from the following equation:

$$\Delta H_{298K} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R} \quad (2)$$

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 CH₄, CH₃NHCH₃, CH₃NH₂, CH₃NO₂, CH₃NHNH₂, and 1H-Tz are available. As the experimental HOFs of CH₃N₃, CH₃NHNO₂, CH₃NF₂, S, and Fz are unavailable, additional

calculations were performed to get their accurate HOFs by using G2 method [31, 32]. The G2 approach was used to compute the total energies of the systems. The HOFs for CH₃N₃, CH₃NHNO₂, CH₃NF₂, S, and Fz were computed from the isodesmic reactions 3-7.



The HOFs of the TST, FSF, SFS, TFT, STS, and FTF derivatives can be evaluated when the heat of reaction

ΔH_{298} is known. Therefore, the principal thing is to compute the ΔH_{298} . ΔH_{298} can be calculated using the following expression:

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (8)$$

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. 8 equals ΔnRT for the reactions of ideal gas. For the isodesmic reaction 1, $\Delta n=0$, so $\Delta(PV)=0$.

The condensed phase for most energetic compounds is solid. Therefore, the calculation of detonation properties requires solid-phase heat of formation ($\Delta H_{f,solid}$). According to Hess's law of constant heat summation [33], the gas-phase heat of formation ($\Delta H_{f,gas}$) and heat of sublimation (ΔH_{sub}) can be used to evaluate their solid-phase heats of formation ($\Delta H_{f,solid}$):

$$\Delta H_{f,solid} = \Delta H_{f,gas} - \Delta H_{sub} \quad (9)$$

Politzer et al. [34–38] found that the heats of sublimation can correlate well with the molecular surface area and electrostatic interaction index $\nu\sigma_{tot}^2$ of energetic compounds. The empirical expression of the approach is as follows:

$$\Delta H_{sub} = aA^2 + b(\nu\sigma_{tot}^2)^{0.5} + c \quad (10)$$

where A is the surface area of the 0.001 electrons/bohr³ isosurface of electronic density of the molecule, ν describes the degree of balance between positive and negative potential on the isosurface, and σ_{tot}^2 is a measure of variability of the electrostatic potential on the molecular surface. The coefficients a , b and c were determined by Rice *et al.*: $a=2.670 \times 10^{-4}$ kcal/mol/A⁴, $b=1.650$ kcal mol⁻¹, and $c=2.966$ kcal mol⁻¹ [37]. The descriptors A , ν , and σ_{tot}^2 were calculated using the computational procedures as described by Felipe *et al.* [39]. This approach has been demonstrated to predict reliably the heats of sublimation of many energetic compounds [34, 37].

The strength of bonding, which could be evaluated by bond dissociation energy (BDE), is fundamental to understanding chemical processes [40]. To compare the bond strength and thermal stabilities of the derivatives, their bond dissociation energies were calculated at the UB3LYP/6-311 G** level. The bond dissociation energy can be given in terms of Eq. 11 [41]:

$$\text{BDE}^0(\text{A} - \text{B}) = E_0(\text{A}\cdot) + E_0(\text{B}\cdot) - E_0(\text{A} - \text{B}) \quad (11)$$

The bond dissociation energy with zero-point energy (*ZPE*) correction can be calculated by Eq. 12:

$$\text{BDE}(\text{A} - \text{B})_{\text{ZPE}} = \text{BDE}^0(\text{A} - \text{B}) + \Delta ZPE \quad (12)$$

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

The detonation velocity and pressure were estimated by the semi-empirical Kamlet-Jacobs formula [42] as

$$D = 1.01 \left(N\bar{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30\rho) \quad (13)$$

$$P = 1.558\rho^2 N\bar{M}^{1/2} Q^{1/2} \quad (14)$$

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 is the density of explosives (g·cm⁻³). To estimate their D and P , we first need to calculate their Q and ρ .

The heat of detonation Q was evaluated by the HOF difference between products and explosive according to the principle of exothermic reactions, i.e., all the N atoms turn into N₂, F atoms form HF with H atoms or convert into F₂ without H atoms, and oxygen atoms go to H₂O before CO₂. If the content of O is not enough to satisfy full oxidation of the H and C atoms, the remaining H atoms will convert into H₂, and C atoms will exist as solid-state C [43]. In the Kamlet-Jacobs equations, the detonation products are supposed to be CO₂ (or C), H₂O (or H₂ or HF or F₂), and N₂, so released energy in the decomposition reaction reaches its maximum. Based on the ρ and Q values, the corresponding D and P values can be evaluated.

For the titled compounds, the theoretical density was obtained from the molecular weight divided by the average molecular volume. The volume was defined as inside a contour of 0.001 electrons/bohr³ density that was evaluated using a Monte Carlo integration. We performed 100 single-point calculations for each optimized structure to get an average volume at the B3LYP/6-31 G* level [44]. The crystal density can be improved by the introduction of the interaction index $\nu\sigma_{tot}^2$ [45, 46]:

$$\rho = \beta_1 \left(\frac{M}{V} \right) + \beta_2 (\nu\sigma_{tot}^2) + \beta_3 \quad (15)$$

where M is the molecular mass (g/molecule), and V is the volume of the isolated gas molecule (cm³/molecules). The coefficients β_1 , β_2 , and β_3 are 0.9183, 0.0028, and 0.0443, respectively [44].

The optimization of each molecule was performed without any symmetry restrictions using the default convergence criteria in the programs. Its optimized structure corresponds to at least a local energy minimum on the potential energy surface without imaginary frequency. These calculations were performed with the Gaussian 98 package [47].

Results and discussion

Heats of formation

The HOF is frequently taken to be indicative of the “energy content” of a HEDM. Also, it is one of the most crucial thermodynamic quantities. Thereby, it is very important to accurately predict the HOF. Table 1 lists the total energies, zero-point energies, thermal corrections, and HOFs for eleven reference compounds in the isodesmic reaction 1 at the B3LYP/6-311 G** and B3P86/6-311 G** levels. Thermodynamic properties were obtained from the scaled vibrational frequencies with scaling factors taken from ref [48] using Eq. 8. In Table 1, the experimental HOFs of the reference compounds (including 1*H*-Tz, CH₄, CH₃NHCH₃, CH₃NH₂, CH₃NO₂, and CH₃NHNH₂) were taken from Refs [49] and [50]. The heat of isodesmic reaction, ΔH_{298} , for the reactions 3–7 were obtained through Eq. 8 using the G2 theory. A precise value of ΔH_f for Fz, S, CH₃N₃, CH₃NF₂, and CH₃NHNO₂ were then obtained through Eq. 2 as well as the available experimental HOFs for Pyridine(g), Benzene(g), Oxazole(g), Furan(g), HCl(g), CH₃Cl(g), HN₃(g), NH₃(g), NF₃(g), CH₃NH₂(g), and NH₂NO₂(g) [26, 49].

Table 2 summarizes the total energies, zero-point energies, thermal corrections, and HOFs of the TST, FSF, SFS, TFT, STS, and FTF derivatives. We also evaluate the dependence of the HOFs at the B3P86 and B3LYP levels with 6-311 G**. 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 6-311 G**: $\text{HOF}_{\text{B3P86}} = 0.9999\text{HOF}_{\text{B3LYP}} - 10.0662$ with $R^2 = 0.9998$. This indicates that both the methods produce similar HOFs for the derivatives.

As is evident in Table 2, all the compounds exhibit positive HOFs. A3 and E3 have the largest HOF values

(over 2000 kJ mol⁻¹) among all the derivatives. This reflects that the TST, FSF, SFS, TFT, STS, and FTF derivatives have high positive HOFs, consistent with previous reports [2, 3] that energetic high-nitrogen heterocycles have high positive HOFs. The substituted TST, FSF, SFS, TFT, STS, or FTF derivatives have larger HOFs than the corresponding unsubstituted one except for B1, C1, C5, E1, E5, and F1. When the H atoms of TST are replaced by -N₃, its HOF value is the largest one among the same series. The same is true of the FSF, SFS, TFT, STS, and FTF derivatives. This is in agreement with previous studies [1, 23, 24, 51] 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 300 kJ mol⁻¹. For the A series, when the H atoms of -NH₂ in the TST ring (A1) are replaced by -NH₂ (or -NO₂) to form A4 (or A6), an increase in the HOF value of A4 (or A6) is large compared with the unsubstituted one (A1). The same is true of B, C, D, E and F series. This shows that the -NH- group is an effective linkage for increasing the HOFs of the TST, FSF, SFS, TFT, STS, and FTF derivatives. It is also seen in Table 2 that the substitution of the group -N₃ or -NHNH₂ in TST, FSF, SFS, TFT, STS, or FTF extremely enhances the HOF value of the corresponding parent ring. This indicates that the -N₃ or -NHNH₂ group plays a very important role in increasing the HOF values of the TST, FSF, SFS, TFT, STS, or FTF derivatives. Also, note that the differences between the HOF values of the unsubstituted TST (A) and its substituted derivatives are close to those of the unsubstituted TFT (D) and its unsubstituted ones with the same substituent. Although the parent TST (A) and TFT (D) rings have the same outer ring (tetrazole ring) but have a different center ring, there is a good linear relationship between the differences of the parent ring and its substituted derivatives for A and D series: $y = 1.0037x - 13.0400$, with $R^2 = 0.9991$. This indicates that the substituents produce similar effects on

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

Compd	B3LYP/6-311 G**			B3P86/6-311 G**			HOF ^b	HOF ^c
	E_0	ZPE	H_T	E_0	ZPE	H_T		
S	-296.390906	134.40	13.84	-297.134547	135.41	13.87		493.66
1 <i>H</i> -Tz	-258.316873	122.99	11.79	-258.959350	124.44	11.69	320.00	334.59
Fz	-262.112124	119.67	11.80	-262.749948	120.89	11.72		202.91
CH ₄	-40.533744	117.09	10.03	-40.713980	117.42	10.04	-74.60	-77.68
CH ₃ NHCH ₃	-135.205417	241.47	14.29	-135.676015	242.36	14.27	-18.80	-17.87
CH ₃ NH ₂	-95.888439	167.56	11.56	-96.213717	168.31	11.55	-22.50	-23.21
CH ₃ NO ₂	-245.081673	130.42	14.15	-245.649164	131.34	14.12	-80.80	-85.96
CH ₃ N ₃	-204.148401	131.67	14.41	-204.679787	132.53	14.40		304.39
CH ₃ NHNO ₂	-300.434462	176.49	16.34	-301.147794	177.78	16.30		-10.43
CH ₃ NF ₂	-294.298331	122.75	13.85	-294.895029	123.62	13.75		-97.98
CH ₃ NHNH ₂	-151.222209	213.44	13.74	-151.692042	214.55	13.70	94.70	92.26

^a E_0 is in a.u.; ZPE, HOF, and H_T are in kJ mol⁻¹. The scaling factor for ZPE is 0.98 and the scaling for H_T is 0.96 [48]

^b Data are the experimental values taken from Refs [49] and [50]

^c The calculated values are at the G2 level

Table 2 Calculated total energies (E_0 , a.u.), zero-point energies (ZPE, kJ mol^{-1}), thermal corrections (H_T , kJ mol^{-1}), and heats of formation (ΔH_f , kJ mol^{-1}) of the TST, FSF, SFS, TFT, STS, and FTF derivatives at the B3LYP and B3P86 levels ^a

Compd	B3LYP/6-311 G**			$\Delta H_{f,gas}$	$\Delta H_{f,solid}$	B3P86/6-311 G**			$\Delta H_{f,gas}$	$\Delta H_{f,solid}$
	E_0	ZPE	H_T			E_0	ZPE	H_T		
TST (A) series										
A	-921.403733	368.82	38.59	1110.53	905.17	-923.656840	373.04	38.26	1099.13	893.77
A1	-1032.063695	455.36	46.82	1335.56	1082.16	-1034.606833	460.38	46.41	1324.24	1070.84
A2	-1330.392462	372.62	53.17	1363.33	1066.29	-1333.419293	378.69	52.58	1354.47	1057.44
A3	-1248.537926	375.78	53.88	2103.04	1777.14	-1251.491510	381.46	53.44	2096.74	1770.84
A4	-1441.111291	464.02	59.25	1470.45	1103.96	-1444.428197	470.63	58.72	1465.51	1099.02
A5	-1428.827460	355.68	54.89	1313.22	1013.90	-1431.913357	361.44	54.35	1314.73	1015.40
A6	-1142.729782	544.28	53.21	1573.05	1263.16	-1145.561995	550.17	52.79	1561.98	1252.09
FSF (B) series										
B	-928.982481	361.76	39.28	907.47	701.06	-262.749948	120.89	11.72	897.44	691.02
B1	-1039.736251	452.70	45.77	888.78	640.18	-1042.271819	457.15	45.46	872.84	624.24
B2	-1338.039992	372.85	53.06	986.03	690.59	-1341.058345	378.37	52.65	975.05	679.61
B3	-1256.218666	376.57	54.01	1639.32	1306.99	-1259.164752	381.80	53.66	1628.34	1296.01
B4	-1448.773550	462.40	59.31	1052.83	688.81	-1452.085101	469.39	58.47	1037.99	673.97
B5	-1436.468641	354.34	55.07	963.43	678.72	-1439.545031	359.71	54.60	953.46	668.76
B6	-1150.385132	540.71	53.59	1171.98	860.89	-1153.210054	546.11	53.20	1155.58	844.49
SFS (C) series										
C	-963.258801	376.50	40.99	1204.36	980.87	-965.608534	380.22	40.80	1192.81	969.32
C1	-1074.034705	462.89	49.47	1125.09	846.31	-1076.677062	467.04	49.40	1106.64	827.86
C2	-1372.329838	385.96	55.24	1246.29	912.89	-1375.454681	391.19	54.91	1233.42	900.03
C3	-1290.517869	390.88	55.36	1875.35	1518.72	-1293.571479	395.87	55.03	1859.78	1503.14
C4	-1483.065833	476.44	61.01	1307.12	909.48	-1486.482469	482.39	60.60	1293.69	896.05
C5	-1470.762737	368.78	56.88	1213.45	893.39	-1473.947039	373.86	56.52	1197.91	877.85
C6	-1184.695188	554.04	56.64	1380.26	1041.90	-1187.627557	559.27	56.39	1359.64	1021.29
TFT (D) series										
D	-887.094711	352.68	37.91	899.16	709.44	-889.240583	356.83	37.70	891.44	701.72
D1	-997.756433	441.73	44.58	1120.46	885.07	-1000.192239	446.81	44.16	1113.07	877.69
D2	-1296.086782	358.33	51.58	1144.09	864.73	-1299.006244	364.48	50.96	1139.26	859.90
D3	-1214.230443	360.83	52.68	1888.26	1580.16	-1217.076596	366.60	52.21	1886.18	1578.07
D4	-1406.809565	449.89	57.60	1240.92	887.61	-1410.019085	456.65	57.01	1240.08	886.77
D5	-1394.522386	341.76	53.25	1104.79	823.25	-1397.501024	347.61	52.66	1097.93	816.40
D6	-1108.431709	531.47	51.20	1334.85	1041.61	-1111.156608	537.45	50.74	1327.67	1034.43
STS (E) series										
E	-959.421941	376.49	41.50	1427.96	1201.41	-961.775600	381.11	40.87	1418.55	1192.00
E1	-1070.199191	463.60	49.67	1345.54	1063.09	-1072.845019	468.09	49.58	1330.30	1047.85
E2	-1368.491536	386.00	55.59	1473.54	1136.49	-1371.619731	391.33	55.34	1464.08	1127.03
E3	-1286.681458	391.45	55.51	2097.97	1736.86	-1289.738493	396.63	55.26	2085.68	1724.57
E4	-1479.227371	476.39	61.46	1534.82	1131.65	-1482.647332	482.45	61.16	1524.89	1121.73
E5	-1466.924781	368.98	57.17	1439.91	1115.18	-1470.112478	374.18	56.87	1427.64	1102.91
E6	-1180.859964	554.63	57.03	1600.02	1257.62	-1183.795849	560.12	56.81	1582.48	1240.08
FTF (F) series										
F	-890.840977	348.09	37.52	909.04	713.57	-892.980855	352.36	37.17	905.02	709.55
F1	-1001.602781	439.91	43.58	869.68	639.87	-1004.034999	444.70	43.18	859.43	629.61
F2	-1299.905486	359.55	51.13	969.41	691.82	-1302.820451	365.14	50.64	963.96	686.38
F3	-1218.082788	363.61	52.44	1627.00	1306.48	-1220.925112	368.95	52.08	1622.64	1302.11
F4	-1410.639994	449.79	57.50	1034.52	695.87	-1413.846679	456.05	57.03	1028.74	690.09
F5	-1398.328977	341.36	53.80	961.33	673.93	-1401.302045	346.76	53.40	956.83	669.43
F6	-1112.263837	530.23	51.06	1122.84	830.92	-1114.985449	535.70	50.68	1111.85	819.93

^a E_0 is in a.u.; ZPE, HOF, and H_T are in kJ mol^{-1} . The scaling factor for ZPE is 0.98 and the scaling for H_T is 0.96 [48]

the HOFs of the parent TST and TFT linkages. The same is true of the other series (for B and F series: $y=1.0016x+20.881$, $R^2=0.9966$, for C and E series: $y=1.0026x-0.8261$, $R^2=0.9998$). We also note that the HOFs of the derivatives are not satisfactory with the relationship of simple group addition.

Figure 3 presents a comparison of the HOF values for the TST, FSF, SFS, TFT, STS, and FTF derivatives. The substituted TST derivatives (A series) have higher HOF values than the corresponding FSF ones (B series) with the same substituent. This shows that the TST ring is a more effective linkage for increasing the HOF than the FSF ring. In addition, the HOFs of the STS derivatives (E series) are higher than ones of the FTF derivatives (F series). Also, the HOF values of the substituted SFS derivatives (C series) are close to those of the substituted TFT ones (D series) with the same substituent. This implies that the combination of 1,2,4,5-tetrazine and 1H-tetrazole ring is more helpful for increasing the HOFs than the combination of furazan and 1,2,4,5-tetrazine (or 1H-tetrazole) ring. Among the six series, the substituted TST and STS derivatives have the largest HOF values with the same substituent. This indicates that the linkage TST or STS is a very effective combination for increasing the HOF.

Electronic structure

Table 3 lists the HOMO and LUMO energies and the energy gaps ($\Delta E_{\text{LUMO-HOMO}}$) for the TST, FSF, SFS, TFT, STS, and FTF derivatives at the B3LYP/6-311 G** and B3P86/6-311 G** levels. It can be seen that the E_{HOMO} , E_{LUMO} , and $\Delta E_{\text{LUMO-HOMO}}$ values at the B3P86/6-311 G** level are systematically smaller than those at the B3LYP/6-311 G** level for most of the derivatives. There is a good linear

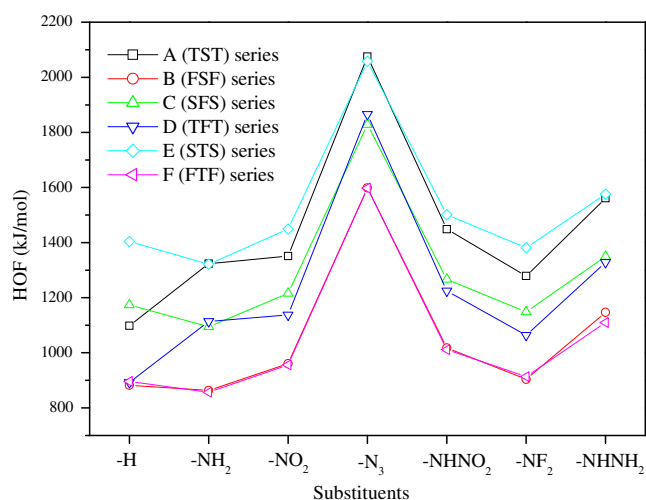


Fig. 3 Comparison of the HOFs of the TST, FSF, SFS, TFT, STS, and FTF derivatives (A-F series) influenced by different substituents

relationship between $\Delta E_{\text{LUMO-HOMO}}$ by B3LYP and $\Delta E_{\text{LUMO-HOMO}}$ by B3P86 with the 6-311 G** basis set: $\Delta E_{\text{B3P86}}=1.0438\Delta E_{\text{B3LYP}}-0.0065$, with $R^2=0.9977$. This shows that both methods produce similar energy gaps for the derivatives. When the $-\text{NH}_2$ or $-\text{NHNH}_2$ group is attached to the TST, FSF, SFS, TFT, or STS parent 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 the SFS, TFT, and STS derivatives. This indicates that different substituents have different effects on the HOMO and LUMO energy levels. As shown in the Table 3, the parent FSF and SFS possess higher HOMO energy levels, while the parent TFT and FTF possess lower ones. In addition, further incorporating of the substituents has almost no effect on the sequence of the HOMO energy level. This indicates that the parent rings interact mainly with the HOMO orbital. However, for the LUMO energy level, the case is different. The LUMO energy level for the six parent rings increases in the order of FTF, TFT, STS, SFS, FSF, and TST; but further introduction of the substituents into the parent rings changes the sequence of the LUMO energy level. This shows that the substituents interact predominately with the LUMO orbital.

Some of the derivatives increase the HOMO-LUMO gaps of the unsubstituted molecules, whereas others decrease them. For TST (A) or TFT (D) series, most of the derivatives increase $\Delta E_{\text{LUMO-HOMO}}$ as compared to the parent A or D except for the derivative with the $-\text{NO}_2$ group (D2). This shows that the same substituent could produce similar effects on the HOMO-LUMO gaps of different parent rings (A and D). It may be because the parent TST (A) and TFT (D) have the same outer ring (1H-tetrazole ring). Additionally, it is interesting to note that A- NH_2 , A- NHNH_2 , D- NH_2 , and D- NHNH_2 have higher HOMO-LUMO gaps than the corresponding unsubstituted molecule. However, the case is quite the contrary for B- NH_2 , B- NHNH_2 , C- NH_2 , or C- NHNH_2 . For C and E series (SFS and STS derivatives), the introduction of the substituents has almost no effect on energy gaps. This further indicates that the effect of the substituent on the HOMO-LUMO gap is closely related to the outer rings of A, B, C, or D. A1-6, B2, B3, B5, C2, C4, C5, D1, D3-6, and E1-5 have higher energy gaps than the unsubstituted molecule A, B, C, D or E, indicating a shift toward higher frequencies in their electronic absorption spectra. However, B1, B4, B6, C1, C3, C6, D2, E6, and F1-6 have lower energy gaps than the corresponding unsubstituted one, reflecting a shift toward lower frequencies in their electronic absorption spectra. Among the derivatives, D5 has the highest energy gap, whereas B6 has the smallest one. Also, among the six series, C series have lower energy gaps, while D series have higher energy gaps. Overall, different substituted molecules present a comparison of the energetics.

Table 3 Calculated HOMO and LUMO energies (a.u.) and energy gaps ($\Delta E_{\text{LUMO-HOMO}}$, a.u.) of the TST, FSF, SFS, TFT, STS, and FTF derivatives at the B3LYP/6-311 G** and B3P86/6-311 G** levels^a

Compd	E_{HOMO}	E_{LUMO}	$\Delta E_{\text{LUMO-HOMO}}$	Compd	E_{HOMO}	E_{LUMO}	$\Delta E_{\text{LUMO-HOMO}}$
TST (A) series				FSF (B) series			
A	-0.2681(-0.2915)	-0.1594(-0.1829)	0.1087(0.1086)	B	-0.2578(-0.2805)	-0.1412(-0.1635)	0.1166(0.1170)
A1	-0.2598(-0.2825)	-0.1405(-0.1642)	0.1193(0.1183)	B1	-0.2467(-0.2681)	-0.1455(-0.1684)	0.1012(0.0997)
A2	-0.2863(-0.3097)	-0.1531(-0.1758)	0.1332(0.1339)	B2	-0.2792(-0.3017)	-0.1440(-0.1659)	0.1352(0.1358)
A3	-0.2741(-0.2972)	-0.1494(-0.1724)	0.1247(0.1248)	B3	-0.2597(-0.2821)	-0.1302(-0.1525)	0.1295(0.1296)
A4	-0.2777(-0.3005)	-0.1493(-0.1726)	0.1284(0.1279)	B4	-0.2821(-0.3067)	-0.1713(-0.1947)	0.1108(0.1120)
A5	-0.2848(-0.3063)	-0.1539(-0.1761)	0.1309(0.1302)	B5	-0.2722(-0.2940)	-0.1397(-0.1620)	0.1325(0.1320)
A6	-0.2555(-0.2777)	-0.1330(-0.1561)	0.1225(0.1216)	B6	-0.2418(-0.2627)	-0.1463(-0.1690)	0.0955(0.0937)
SFS (C) series				TFT (D) series			
C	-0.2456(-0.2658)	-0.1411(-0.1642)	0.1045(0.1016)	D	-0.2768(-0.2993)	-0.0946(-0.1159)	0.1822(0.1834)
C1	-0.2264(-0.2476)	-0.1253(-0.1480)	0.1011(0.0996)	D1	-0.2764(-0.2985)	-0.0884(-0.1101)	0.1880(0.1884)
C2	-0.2808(-0.3012)	-0.1749(-0.1981)	0.1059(0.1031)	D2	-0.2999(-0.3231)	-0.1364(-0.1576)	0.1635(0.1655)
C3	-0.2515(-0.2729)	-0.1487(-0.1723)	0.1028(0.1006)	D3	-0.2836(-0.3063)	-0.1017(-0.1226)	0.1819(0.1837)
C4	-0.2650(-0.2857)	-0.1559(-0.1788)	0.1091(0.1069)	D4	-0.2922(-0.3151)	-0.1056(-0.1253)	0.1866(0.1898)
C5	-0.2703(-0.2902)	-0.1642(-0.1869)	0.1061(0.1033)	D5	-0.3004(-0.3224)	-0.1053(-0.1257)	0.1951(0.1967)
C6	-0.2273(-0.2484)	-0.1295(-0.1523)	0.0978(0.0961)	D6	-0.2709(-0.2925)	-0.0770(-0.0989)	0.1939(0.1936)
STS (E) series				FTF (F) series			
E	-0.2621(-0.2832)	-0.1371(-0.1664)	0.1250(0.1168)	F	-0.2726(-0.2953)	-0.0815(-0.1016)	0.1911(0.1937)
E1	-0.2440(-0.2657)	-0.1181(-0.1408)	0.1259(0.1249)	F1	-0.2496(-0.2711)	-0.0716(-0.0917)	0.1780(0.1794)
E2	-0.2984(-0.3192)	-0.1710(-0.1945)	0.1274(0.1247)	F2	-0.2969(-0.3186)	-0.1606(-0.1823)	0.1363(0.1363)
E3	-0.2695(-0.2909)	-0.1428(-0.1663)	0.1267(0.1246)	F3	-0.2741(-0.2965)	-0.0950(-0.1159)	0.1791(0.1806)
E4	-0.2807(-0.3015)	-0.1516(-0.1749)	0.1291(0.1266)	F4	-0.2776(-0.2998)	-0.1201(-0.1400)	0.1575(0.1598)
E5	-0.2872(-0.3076)	-0.1602(-0.1830)	0.1270(0.1246)	F5	-0.2948(-0.3164)	-0.1197(-0.1388)	0.1751(0.1776)
E6	-0.2441(-0.2659)	-0.1217(-0.1442)	0.1224(0.1217)	F6	-0.2365(-0.2569)	-0.0647(-0.0839)	0.1718(0.1730)

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

Thermal stability

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, O-N, C(N)-R, or N-R') as the breaking bond based on atom-atom overlap-weighted NAO bond order to calculate BDE at the UB3LYP/6-311 G** level. The bond orders and bond dissociation energies (BDE) of the weakest bonds for the TST, FSF, SFS, TFT, STS, and FTF derivatives are listed in Table 4. 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. Saikia [15] found that the activation energy (E_a) for exothermic decomposition of BTATz (A, TST) computed by using ASTM standard method (based on Kissinger correlation) was $212.69 \text{ kJ mol}^{-1}$. As is shown in Table 4, our calculated BDE_{ZPE} of the weakest bond for BTATz was $222.28 \text{ kJ mol}^{-1}$. It means that our result compares well with previous studies [15]. Therefore, our

calculations here should be relatively credible. It is noteworthy that most of the derivatives have smaller BDE_{ZPE} values than the unsubstituted molecule TST, FSF, SFS, TFT, STS, or FTF. The calculated BDE can be used to measure the relative order of thermal stability for energetic materials [52, 53]. Therefore, it can be deduced that introduction of most of the substituents into TST, FSF, SFS, TFT, STS, or FTF 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 FSF, SFS and FTF derivatives have higher BDE_{ZPE} values. This implies that they have good thermal stability.

It is interesting to note that the N-NH₂ bond of A1 has relatively low bond order (0.7881) but the highest BDE_{ZPE} value ($256.53 \text{ kJ mol}^{-1}$) among the weakest bonds of the TST derivatives. However, the N-N bond in the 1H-tetrazole ring of A1 has higher bond order (0.8947) but lower BDE_{ZPE} ($121.81 \text{ kJ mol}^{-1}$) compared to the N-NH₂ bond of A1. A similar situation is also found in C2 and E2. The initial step should be via ring cleavage in thermal decompositions.

Table 4 Calculated bond dissociation energies (BDE, kJ mol^{-1}) for $\text{A-B}(\text{g}) \rightarrow \text{A}\cdot(\text{g}) + \text{B}\cdot(\text{g})$ and atom-atom overlap-weighted NAO bond order of the weakest bonds for the TST, FSF, SFS, TFT, STS, and FTF derivatives together with RDX and HMX at the B3LYP/6-311 G** level^a

Compd	(N-N) _{Tz ring}	O-N	(N-N) _{Bridge}	N-R	C-R	N-R'	BDE ⁰	BDE _{ZPE}
TST (A) series								
A	0.8744						242.06	222.28
A1	0.8947			0.7881			136.49(288.19) ^b	121.81(256.53) ^b
A2				0.6781			99.06	82.19
A3				0.7926			163.36	142.71
A4						0.6736(NH-NO ₂)	112.52	94.63
A5				0.8357			123.36	107.56
A6				0.7583			200.34	177.83
FSF (B) series								
B		0.7475					196.65	186.82
B1		0.7294					201.77	190.33
B2		0.7388					166.79	157.21
B3		0.7438					192.55	182.12
B4						0.7532(NH-NO ₂)	132.09	114.78
B5		0.7494					185.02	174.07
B6		0.7271					162.55	152.05
SFS (C) series								
C		0.7488					190.14	179.47
C1		0.7413					197.78	187.77
C2		0.7552			0.7380		189.98(246.51) ^b	179.35(229.23) ^b
C3		0.7482					190.14	179.37
C4						0.7444(NH-NO ₂)	133.66	114.94
C5		0.7523					200.72	190.30
C6		0.7486					197.38	185.91
TFT (D) series								
D		0.7414					196.03	186.26
D1		0.7326					181.44	169.63
D2				0.6806			97.63	80.78
D3		0.7334		0.7917			114.20(174.91) ^b	96.08(164.00) ^b
D4						0.6880(NH-NO ₂)	116.30	98.69
D5		0.7510		0.8372			123.58(186.58) ^b	107.33(176.50) ^b
D6		0.7438					179.41	167.02
STS (E) series								
E	0.8696		0.8141				90.53(249.23) ^b	83.69(226.75) ^b
E1	0.8712		0.8095				95.04(203.92) ^b	88.05(184.65) ^b
E2	0.8682				0.7370		84.98(246.12) ^b	78.02(228.47) ^b
E3	0.8696		0.8116				91.34(227.15) ^b	83.93(206.79) ^b
E4	0.8694					0.7434(NH-NO ₂)	87.50(136.17) ^b	80.59(117.26) ^b
E5	0.8688		0.8115				84.90(244.17) ^b	77.80(222.81) ^b
E6	0.8701					0.7695(NH-NH ₂)	133.02(275.63) ^b	123.15(243.55) ^b
FTF (F) series								
F		0.7431					179.22	169.27
F1		0.7114					190.32	180.56
F2		0.7185					175.22	165.60
F3		0.7394					190.24	179.79
F4		0.7481				0.7766(NH-NO ₂)	122.82(174.24) ^b	103.30(165.78) ^b
F5		0.7295					169.44	159.63
F6		0.7233					191.87	181.36
RDX				0.7567			166.19	145.62
HMX				0.7812			178.77	160.41

^a BDE⁰ 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 orders

Accordingly, to judge the thermal stability of the derivatives is not by the bond order simply, but it is necessary to depend on the BDE_{ZPE} . As is evident in Table 4, the BDE values of the TST and TFT derivatives are approximately equal except for the molecules with the $-NH_2$ or $-N_3$ group. This indicates that the effect of the substituent on the BDE of TST and TFT is similar. Also, we note that A1 and D1 have smaller BDE_{ZPE} than the corresponding parent ring A or D, while B1, C1, E1, and F1 have higher BDE_{ZPE} than the corresponding parent ring B, C, E, or F. This shows that the effect of the $-NH_2$ group on the BDE_{ZPE} of TST, FSF, SFS, TFT, STS, and FTF is different. When the $-NO_2$, $-N_3$, or $-NHNO_2$ group is attached to the TST, FSF, SFS, TFT, STS, or FTF ring, the BDE_{ZPE} value decreases except for E3 and F3. This implies that incorporating $-NO_2$, $-N_3$, or $-NHNO_2$ groups into the TST, FSF, SFS, TFT, STS, or FTF ring make its stability decreased.

Our calculated BDE values for TST, FSF, SFS, TFT, STS, and FTF show some interesting features. First, the unsubstituted molecules with the center ring of 1*H*-tetrazole often possess lower BDE values than those with the center

ring of furazan or 1,2,4,5-tetrazine. Second, the substituted derivatives with the center ring of 1*H*-tetrazole and the outer ring of 1,2,4,5-tetrazine (STS series) have the lowest BDEs among the six series with the same substituents. Third, the STS derivatives (E series) have lower BDEs than the SFS derivatives (C series) with the same substituents. On the whole, the 1*H*-tetrazole appears to be a relatively poor unit for enhancing the stability of the derivatives.

Predicted detonation performances

Detonation velocity and detonation pressure are two important performance parameters for an energetic material. Table 5 presents the calculated detonation velocities (D) and pressures (P) of the TST, FSF, SFS, TFT, STS, and FTF derivatives together with available experimental data [13]. The detonation properties were evaluated using the semi-empirical Kamlet-Jacobs formula, which was proved to be reliable for predicting the explosive properties of energetic high-nitrogen compounds [23, 24, 54–56]. For a comparison, the experimental

Table 5 Predicted detonation properties of the TST, FSF, SFS, TFT, STS, and FTF derivatives together with RDX and HMX

Compd	Q (J/g)	ρ (g/cm ³)	D (km/s)	P (GPa)	Compd	Q (J/g)	P (g/cm ³)	D (km/s)	P (GPa)
TST (A) series					FSF (B) series				
A	1047.31	1.70(1.76) ^a	7.30(7.52) ^a	22.84(22.30) ^a	B	1306.30	1.65	6.95	20.35
A1	1127.70	1.72	7.67	25.37	B1	1144.13	1.68(1.61) ^c	7.04	21.06
A2	1537.41	1.85	8.53	32.80	B2	1538.08	1.84	8.22	30.29
A3	1498.10	1.76	8.18	29.35	B3	1467.00	1.70	7.54	24.38
A4	1507.18	1.80	8.36	31.02	B4	1476.57	1.79	8.05	28.58
A5	1576.54	1.95	9.01	37.68	B5	1589.59	1.90	8.61	33.92
A6	1202.24	1.68	7.82	26.04	B6	1251.97	1.67	7.39	23.13
SFS (C) series					TFT (D) series				
C	1290.19	1.66	7.14	21.56	D	1140.66	1.73	7.40	23.65
C1	1085.67	1.71	7.14	21.94	D1	1211.03	1.72	7.74	25.87
C2	1523.67	1.79	8.04	28.56	D2	1584.49	1.84	8.59	33.18
C3	1435.93	1.76	7.65	25.61	D3	1582.24	1.77	8.19	29.44
C4	1463.57	1.78	7.97	27.93	D4	1542.42	1.81	8.45	31.76
C5	1564.76	1.87	8.46	32.47	D5	1622.22	1.95	9.09	38.36
C6	1172.74	1.67	7.35	22.83	D6	1261.46	1.64	7.71	24.92
STS (E) series					FTF (F) series				
E	1281.43	1.65	7.38	22.88	F	1392.60	1.65	7.23	21.96
E1	1076.12	1.72	7.40	23.58	F1	1194.52	1.67	7.26	22.31
E2	1551.31	1.79	8.21	29.83	F2	1595.41	1.83	8.44	31.98
E3	1429.39	1.72	7.77	26.03	F3	1527.13	1.77	7.96	27.86
E4	1489.36	1.76	8.07	28.47	F4	1528.22	1.85	8.45	32.16
E5	1590.86	1.92	8.79	35.62	F5	1656.93	1.93	8.95	37.00
E6	1163.47	1.65	7.50	23.64	F6	1277.15	1.68	7.61	24.64
RDX ^b	1591.03	1.71(1.82) ^a	8.42(8.75) ^a	30.47(34.00) ^a	HMX ^b	1633.90	1.82(1.91) ^a	8.81(9.10) ^a	34.69(39.00) ^a

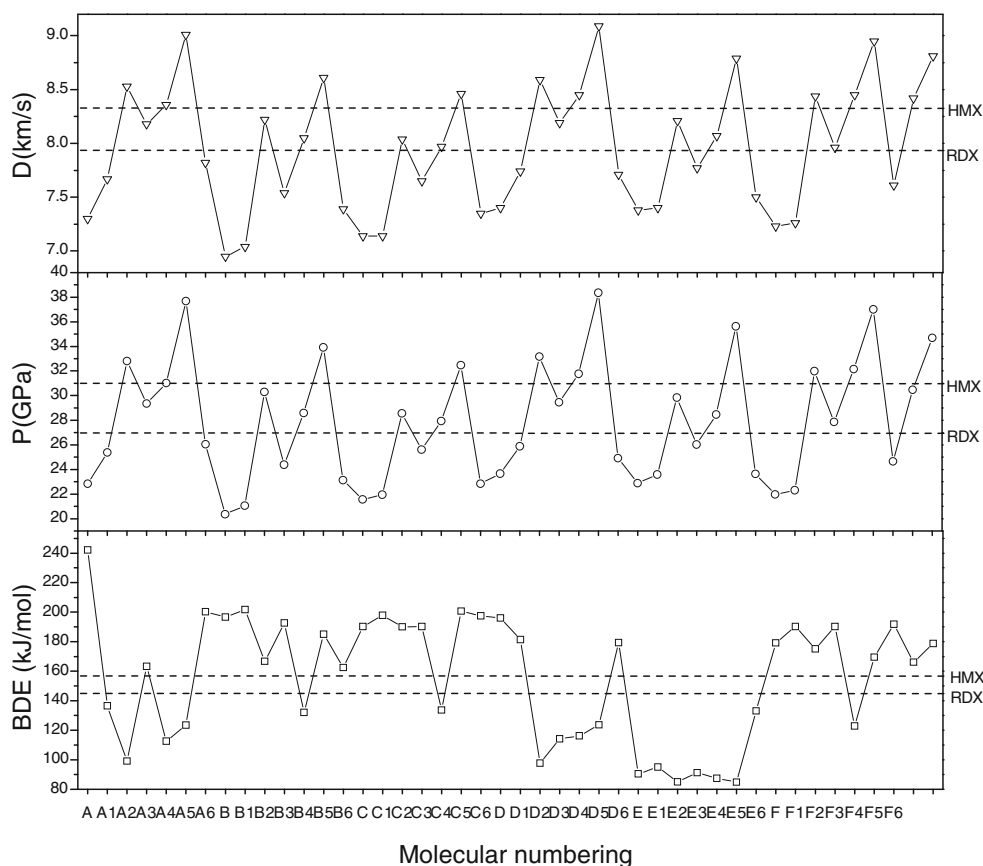
^a Data in the parentheses are the experimental values taken from Refs [13, 16, 54]

^b The calculated values of RDX and HMX are taken from Ref [23]

detonation performances of two known explosives RDX and HMX [57] are also listed in this table.

As is evident in Table 5, the calculated detonation properties of the BTATz (A), RDX, and HMX agree well with available experimental values. Although the error or limitation of the calculation method leads to the predicted D and P somewhat deviating from those from experiment, these results are still reliable and meaningful. The TST, FSF, SFS, TFT, STS, and FTF derivatives with different substituents have different ρ values, for example, the largest ρ value and the smallest one are 1.95 and 1.64 g cm^{-3} , respectively. This makes the derivatives have different D and P values. All the derivatives increase the D and P values as compared to the corresponding unsubstituted molecule. The TST and TFT derivatives (A and D series) possess higher ρ , D , and P values than the other ones; moreover, they nearly have the same D and P . This means that incorporating the substituents have similar effects on the detonation properties of the parent TST and TFT rings even though A and D have different center rings. Additionally, it is found that the difference between D or P of substituted and unsubstituted FSF is close to one between D or P of substituted and unsubstituted FTF. The same is true of C (SFS) and E (STS) series. This indicates that the detonation properties mainly depend on substituents and the outer ring of parent molecule.

Fig. 4 Detonation properties and bond dissociation energies of the weakest bonds for the TST, FSF, SFS, TFT, STS, and FTF (A-F series) derivatives



It is observed from Table 5 that most of the derivatives have higher ρ values than RDX (1.82 g cm^{-3}) [57], so they have very high D and P values. The derivatives with the $-\text{NO}_2$ or $-\text{NF}_2$ have very high ρ , D , and P values. It is also found that D5 (TFT- NF_2), the derivative with two $-\text{NF}_2$ groups, has the largest D , and P values among the derivatives. This shows that the substitutions of the $-\text{NO}_2$ or $-\text{NF}_2$ group are useful for increasing the densities and detonation properties of the TST, FSF, SFS, TFT, STS, and FTF derivatives.

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 [58]. 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. Figure 4 presents the detonation properties and bond dissociation energies of the weakest bonds for the TST, FSF, SFS, TFT, STS, and FTF derivatives together with commonly used explosives RDX and HMX.

It is seen that the D and P values of the derivatives A2-5, B2, B4-5, C2, C5, D2-5, E2, E4-5, F2, and F4-5 are close to

or over RDX, but only A5, D5, and F5 have good detonation performance (*D* and *P*) over HMX. Also, it is found that A, A6, B, B1-3, B5-6, C, C1-3, C5-6, D, D1, D6, F, F1-3, and F5-6 have higher BDE for the weakest bonds as compared to RDX. 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 impact. On the above suggestions, it may be concluded that only B2 (FSF-NO₂), B5 (FSF-NF₂), C2 (SFS-NO₂), C5 (SFS-NF₂), F2 (FTF-NO₂), and F5 (FTF-NF₂) have good detonation performance (*D* and *P*) and thermal stability (BDE) close to or over RDX. Consequently, FSF-NO₂, FSF-NF₂, SFS-NO₂, SFS-NF₂, FTF-NO₂, and FTF-NF₂ may be considered as the potential candidates of HEDMs with less sensitivity and higher performance.

Although A (BTATz), A1 (BATATz), and B1 (BAOATz) have been successfully synthesized, some detonation and thermodynamic properties are still lacking. In addition, the syntheses of other energetic compounds have not been reported yet. Thus, further investigations are still needed.

Conclusions

In the present study, we have calculated the HOFs, thermal stability, and detonation properties for a series of the TST, FSF, SFS, TFT, STS, and FTF derivatives using B3LYP and B3P86 with the 6-311 G** basis set. The results show that the HOFs at the two levels for the same compound are very close. The substitution of the -N₃ or -NHNH₂ group in the TST, FSF, SFS, TFT, STS, or FTF ring extremely enhances its HOF values. For the TST and TFT derivatives, incorporating the substituents into the TST or TFT ring will increase its energy gap except for D2. However, for the FSF and SFS derivatives, attaching the NH₂ or NHNH₂ group to the FSF or SFS ring decreases its energy gap. Among A-F series, the SFS derivatives have lower energy gaps, while the TFT derivatives have higher ones.

An analysis of the bond dissociation energies for the weakest bonds indicates that the introduction of the -NH₂ group into the FSF, SFS STS, or FTF ring is favorable for enhancing its thermal stability, whereas the substitution of the -NHNH₂ group could increase the thermal stability of the TST, SFS, STS, or FTF ring. The 1H-tetrazole appears to be a relatively poor unit for enhancing the stability of the derivatives. The calculated detonation velocities and pressures indicate that incorporating the -NO₂ or -NF₂ group into the TST, FSF, SFS, TFT, STS, or FTF ring is very helpful for enhancing its detonation performance.

Considering the detonation performance and thermal stability, FSF-NO₂, FSF-NF₂, SFS-NO₂, SFS-NF₂, FTF-NO₂, and FTF-NF₂ may be regarded as the potential candidates of HEDMs.

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