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Theoretical design of energetic nitrogen-rich derivatives of 1,7-diamino-1,7-dinitrimino-2,4, 6-trinitro-2,4,6-triazaheptane

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Abstract The heats of formation (HOFs), energetic properties, and thermal stability of a series of 1,7-diamino-1,7-dinitrimino-2,4,6-trinitro-2,4,6-triazaheptane derivatives with different substituents, different numbers of substituents, and different original chains are found by using the DFT-B3LYP method. The results show that $-NO_2$ or $-NH_2$ is an effective substituent for increasing the gas-phase HOFs of the title compounds, especially $-NO_2$ group. As the numbers of substitutents increase, their HOFs enhance obviously. Increasing the length of original chain is helpful for improving their HOFs. The substitution of $-NO_2$ is useful for enhancing their detonation performances and the effects of the length of original chains on detonation properties are coupled with those of the substituents. An analysis of the BDE of the weakest bonds indicates that the substitution of the $-NH_2$ groups and replacing the $-NO_2$ groups of $N-NO_2$ by the $-NH_2$ groups are favorable for improving their thermal stability, while the substitution of $-NO_2$ and increasing the length of original chain decrease their thermal stability. Considering the detonation performance and thermal stability, seven compounds may be considered as the potential candidates of high energy density compounds.

Introduction

High energy density compounds (HEDCs) have attracted considerable attention in recent years because of their superior performances over conventional explosives [1–11]. Energetic nitrogen-rich compounds are potential and promising candidates for HEDCs owing to their rather high density, high positive heat of formation (HOF), good oxygen balance, and good thermal stability. To meet the continuing demand for improved energetic materials, there is a clear need to continue to design and develop novel HEDCs.

Properties are often manipulated by making structural modifications. Therefore, the optimization of the candidate compound with high energy and less sensitivity is the primary step for designing and synthesizing new HEDCs. In the past several decades, theoretical studies based on quantum chemical treatment have gained acceptance as a useful research tool to screen the candidates of HEDCs, thereby avoiding expensive and dangerous experimental tests. In addition, they can provide understanding in terms of the relationships between molecular structure and property, which in turn can help design better and more efficient laboratory tests. It can thus be seen that seeking potential HEDCs by theoretical methods is a kind of effective way.

Recently, Altenburg et al. [12] have synthesized an explosive 1,7-diamino-1,7-dinitrimino-2,4,6-trinitro-2,4,6-triazaheptane (APX, as shown in Fig. 1) with a crystal density of 1.911 g/cm³. It decomposes at 174 °C and its experimental impact, friction, and electrostatic discharge sensitivities are over or equal to 3 J, 80 N, and 0.1 J, respectively. APX is a derivative of 1,2-dinitroguanidine and its predicted detonation velocity and detonation pressure are 9540 m s⁻¹ and 39.5 GPa, respectively, which are even better than those of commonly used explosive 1,3,5,7-tetranitro-1,3,5,7-tetraazoctane (HMX). Liu et al. [13] reported that APX possesses good thermal stability. Thus, there is a clear need to do further research on the molecular design and synthesis of APX derivatives to find new potential HEDCs. In addition, many studies reported that $-NH_2$ group is an effective structural unit for enhancing the stability of energetic compounds [4, 6, 7]. The substitution of

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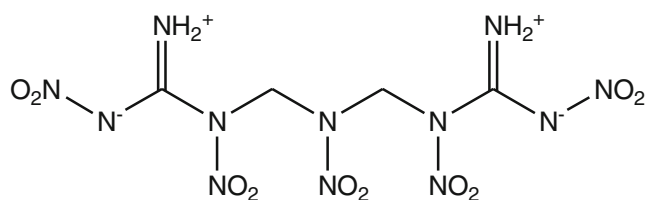of Science and Technology, Nanjing 210094, China
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Fig. 1 The structure of 1,7-diamino-1,7-dinitrimino-2,4,6- trinitro-2,4,6-triazaheptane (APX)

the -NO_2 group is very helpful for enhancing the oxygen balance and detonation performances of energetic materials [3, 6]. A combination of them in a molecule can generates extensive hydrogen bonds and so results in both high energetic performances and good thermal stability. Insensitive explosives: 2,6-dinitro-3,5-diaminopyrazine-1-oxide (LLM-105) and 1,1-diamino-2,2-dinitrorthylene (FOX-7) are two successful examples of the effective combination of -NH_2 and -NO_2.

In this work, we reported a systematic study of the HOFs, energetic properties, and thermal stability of a series of APX derivatives with different substitutent groups (-NH_2 and -NO_2), different numbers of substitutents, and different original chains (as shown in Fig. 2) by using density function theory (DFT). Our main purpose here is to investigate the important role of different substituents, numbers of

substituents and original chains in the design of efficient high-energy density compounds.

The remainder of this paper is organized as follows. A brief description of our computational method is given in the "Computational methods" section; followed by the "Results and discussion" section and summary in the "Conclusions" section.

Computational methods

The DFT-B3LYP [14–21] method with the 6-311G** [22, 23] basis set was very successfully used to predict the HOFs of many organic systems *via* isodesmic reactions [24, 25]. Here, we design isodesmic reactions in which the numbers of all kinds of bonds keep 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 correlation energies can be partially cancelled, and then the errors of the calculated HOF can be greatly reduced [26]. This approach has been demonstrated to predict reliably the HOFs of many organic systems [24, 27].

The isodesmic reactions used to obtain the HOFs of the title compounds at 298 K are as follows:
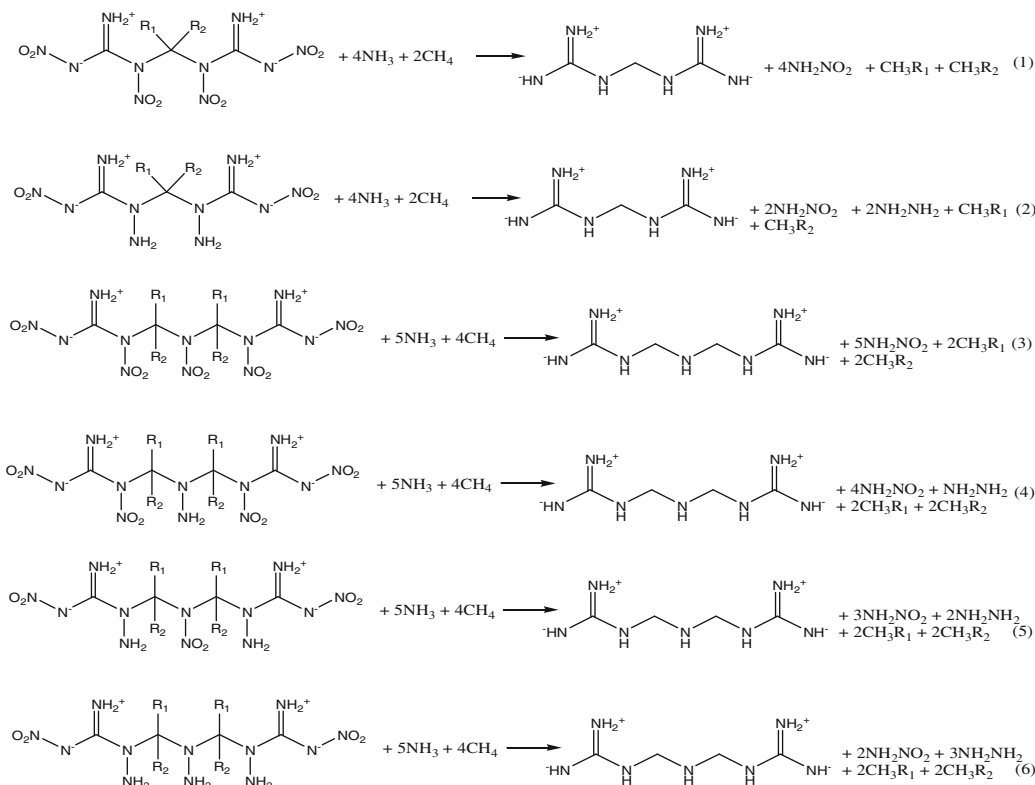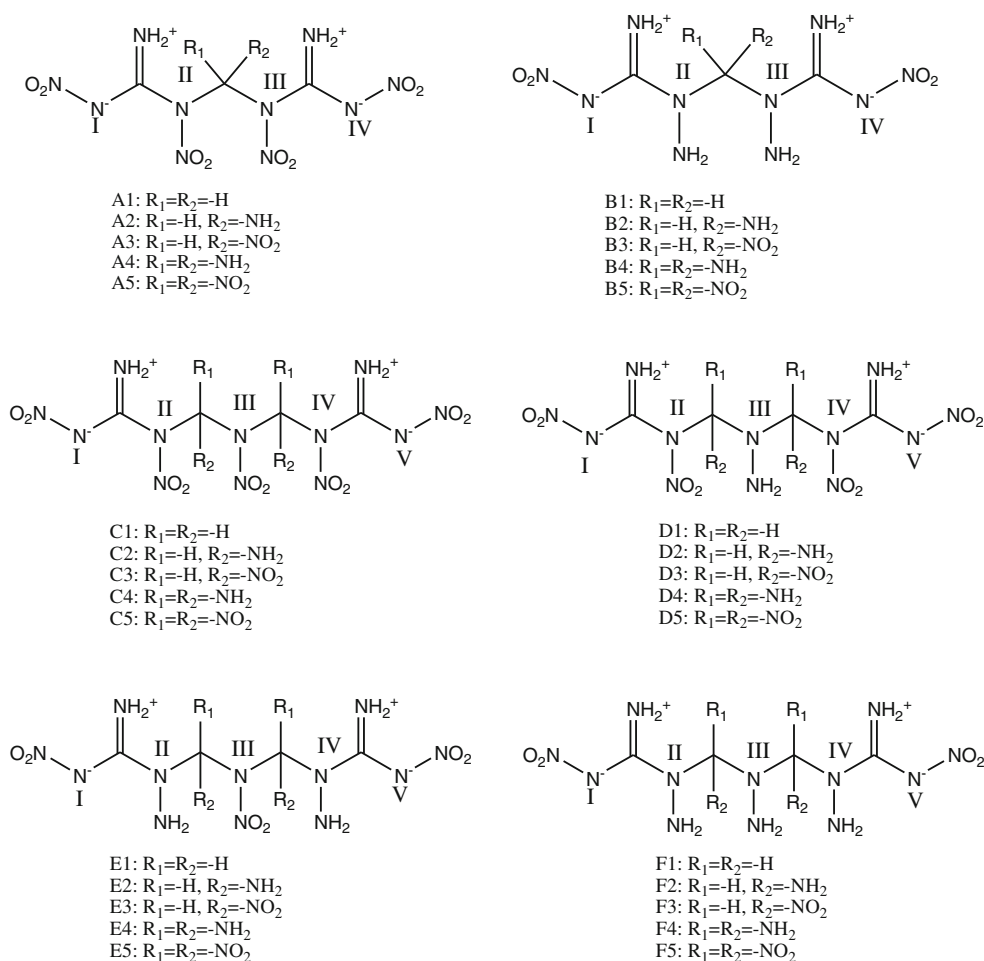
Fig. 2 Molecular frameworks of a series of 1,7-diamino-1,7-dinitrimino-2,4,6- trinitro-2,4,6-triazaheptane derivatives

A1: $R_1=R_2=-H$
A2: $R_1=-H$, $R_2=-NH_2$
A3: $R_1=-H$, $R_2=-NO_2$
A4: $R_1=R_2=-NH_2$
A5: $R_1=R_2=-NO_2$

B1: $R_1=R_2=-H$
B2: $R_1=-H$, $R_2=-NH_2$
B3: $R_1=-H$, $R_2=-NO_2$
B4: $R_1=R_2=-NH_2$
B5: $R_1=R_2=-NO_2$

C1: $R_1=R_2=-H$
C2: $R_1=-H$, $R_2=-NH_2$
C3: $R_1=-H$, $R_2=-NO_2$
C4: $R_1=R_2=-NH_2$
C5: $R_1=R_2=-NO_2$

D1: $R_1=R_2=-H$
D2: $R_1=-H$, $R_2=-NH_2$
D3: $R_1=-H$, $R_2=-NO_2$
D4: $R_1=R_2=-NH_2$
D5: $R_1=R_2=-NO_2$

E1: $R_1=R_2=-H$
E2: $R_1=-H$, $R_2=-NH_2$
E3: $R_1=-H$, $R_2=-NO_2$
E4: $R_1=R_2=-NH_2$
E5: $R_1=R_2=-NO_2$

F1: $R_1=R_2=-H$
F2: $R_1=-H$, $R_2=-NH_2$
F3: $R_1=-H$, $R_2=-NO_2$
F4: $R_1=R_2=-NH_2$
F5: $R_1=R_2=-NO_2$

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

$$\Delta H_{298} = \Delta H_{f,p} - \Delta H_{f,R}, \tag{7}$$

where $\Delta H_{f,R}$ and $\Delta H_{f,P}$ are the HOFs of reactants and products at 298 K, respectively.

As the experimental HOFs of NH_2NH_2, $C_3H_{10}N_6$, and $C_4H_{13}N_7$ are unavailable, additional calculations were carried out for the atomization reaction $C_aH_bO_cN_d \rightarrow aC(g) + bH(g) + cO(g) + dN(g)$ using the G2 and CBS-4M theory to get an accurate value of ΔH_f. Our previous study [28] shows that the CBS-4M theory can more accurately predict the HOFs of azo compounds than G2 or CBS-Q theory when the number of heavy atoms is more than nine in the molecule. Thus, the HOFs of $C_3H_{10}N_6$, and $C_4H_{13}N_7$ are computed by using the CBS-4M theory. The experimental HOFs of reference compounds CH_4, NH_3, CH_3NO_2, CH_3NH_2, and NH_2NO_2 are available. Now the most important task is to compute ΔH_{298}. The ΔH_{298} can be calculated using the following expression:

$$\Delta H_{298} = E_{298} + \Delta(PV) = \Delta E_0 + \Delta E_{ZPE} + \Delta E_T + \Delta nRT, \tag{8}$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔE_{ZPE} is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; ΔE_T is thermal correction from 0 to 298 K. The $\Delta(PV)$ value in Eq. (8) is the PV work term and equals ΔnRT for the reactions of ideal gas. For the isodesmic reactions in this work, $\Delta n=0$, so $\Delta(PV)=0$.

Since the condensed phase for most energetic compounds is solid, the calculation of detonation properties requires solid-phase HOF ($\Delta H_{f,solid}$). According to Hess's law of constant heat summation [29], the solid-phase HOF can be obtained from the gas-phase HOF ($\Delta H_{f,gas}$) and heat of sublimation (ΔH_{sub}):

$$\Delta H_{f,solid} = \Delta H_{f,gas} - \Delta H_{sub}. \tag{9}$$

Recently, Politzer et al. [30–32] reported that the heat of sublimation correlates with the molecular surface area and the electrostatic interaction index $\nu\sigma_{tot}^2$ for energetic compounds. The empirical expression of the approach is as follows:

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

where A is the surface area of the 0.001 electrons/bohr^3 isosurface of the electronic density of the molecule, ν describes the degree of balance between positive potential and negative potential on the isosurface, and $\nu\sigma_{tot}^2$ is a measure of the variability of the electrostatic potential on the molecular surface. The coefficients a, b, and c have been determined by Rice et al.: $a=2.670\times10^{-4}$ kcal·mol^{-1}·Å^{-4}, $b=1.650$ kcal·mol^{-1}, and $c=2.966$ kcal·mol^{-1} [33]. The descriptors A, ν, and $\nu\sigma_{tot}^2$ were calculated by using the computational procedures proposed by Bulat et al. [34]. This approach has been demonstrated to reliably predict the heats of sublimation of many energetic compounds [33, 35].

The detonation velocity and pressure were estimated by the Kamlet-Jacobs equations [36] as

$$D = 1.01\left(N\overline{M}^{1/2}Q^{1/2}\right)^{1/2}(1+1.30\rho) \quad (11)$$

$$P = 1.558\rho^2N\overline{M}^{1/2}Q^{1/2}, \quad (12)$$

where each term in the equations of (11) and (12) is defined as follows: D, the detonation velocity (km s^{-1}); P, the detonation pressure (GPa); N, the moles of detonation gases per gram explosive; $\overline{M}$, the average molecular weight of these gases; Q, the heat of detonation (cal g^{-1}); and ρ, the loaded density of explosives (g/cm^3). For known explosives, their Q and ρ can be measured experimentally; thus their D and P can be calculated according to Eqs. 11 and 12. However, for some compounds, their Q and ρ cannot be evaluated from experimental measures. Therefore, to estimate their D and P, we first need to calculate their Q and ρ.

The theoretical density was obtained by an improved equation proposed by Politzer et al. [37] in which the interaction index $\nu\sigma_{tot}^2$ was introduced:

$$\rho = \alpha\left(\frac{M}{V(0.001)}\right) + \beta\nu\left(\sigma_{tot}^2\right) + \gamma, \quad (13)$$

where the M is the molecular mass (g mol^{-1}) and V(0.001) is the volume of the 0.001 electrons/bohr^3 contour of electronic density of the molecule (cm^3/molecule). The coefficients α, β, and γ are 0.9183, 0.0028, and 0.0443, respectively.

The heat of detonation Q was evaluated by the HOF difference between products and explosives according to the principle of exothermic reactions. The decomposition products are supposed to be only CO_2, H_2O, and N_2, 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. The theoretical density of the compounds in this work is slight greater than practical loaded density. Therefore, according to the Kamlet-Jacobs equations, the D and P values can be regarded as their upper limits.

The strength of bonding, which could be evaluated by bond dissociation energy, is fundamental to understand chemical processes [38]. The energy required for bond homolysis at 298 K and 1 atm corresponds to the enthalpy of reaction A–B(g)→A·(g)+B·(g), which is the bond dissociation enthalpy of the molecule A–B by definition [39]. For many organic molecules, the terms "bond dissociation energy" (BDE) and "bond dissociation enthalpy" usually appear interchangeably in the literature [40]. Thus, at 0 K, the homolytic bond dissociation energy can be given in terms of Eq. (14):

$$BDE_0(A-B) = E_0(A\cdot) + E_0(B\cdot) - E_0(A-B). \quad (14)$$

The bond dissociation energy with zero-point energy (ZPE) correction can be calculated by Eq. (15):

$$BDE(A-B)_{ZPE} = BDE_0(A-B) + E_{ZPE}, \quad (15)$$

where ΔE_{ZPE} is the difference between the ZPEs of the products and the reactants.

The calculations were performed at the B3LYP/6-311G** level with the Gaussian 09 package [41]. The optimizations were performed without any symmetry restrictions using the default convergence criteria in the program. All of the optimized structures were characterized to be true local energy minima on the potential energy surfaces without imaginary frequencies.

Results and discussion

Heats of formation

Here we investigate the effects of different substituents, numbers of substituents and original chains on the gas-phase HOFs ($\Delta H_{f,gas}$) and solid-phase HOFs ($\Delta H_{f,solid}$) of the title compounds. Table 1 lists the total energies, ZPEs, and thermal corrections for eight reference compounds in the isodesmic reactions. As the experimental HOFs of NH_2NH_2, $C_3H_{10}N_6$, and $C_4H_{13}N_7$ are unavailable, additional calculations were carried out for the atomization reaction using the G2 and CBS-4M theory to get their HOFs. The experimental HOFs for the remaining five reference compounds were taken from references [42] and [43]. To validate the reliability of our results, the HOFs of CH_4, NH_3, and CH_3NO_2 were calculated at the G2 level from the atomization reactions. The calculated HOFs are very close to their corresponding experimental values with the relative errors of only 2.04 %, 1.22 %, and 1.25 %, respectively. And the HOF of CH_3NO_2 was also calculated at the CBS-4M level with the relative error of 4.52 %. Thus, our calculated HOFs at the G2 and CBS-4M theory are expected to be reliable.

Table 1 Calculated total energies (E_0), zero-point energies (ZPE), thermal corrections (H_T), and HOFs of the reference compounds

Compd.	E_0	ZPE	H_T	HOF[a]	HOF[b]	HOF[c]
CH_4	−40.5337	0.0446	10.04	−74.6	−76.1	
CH_3NO_2	−245.0817	0.0497	14.06	−80.8	−81.8	−77.2
NH_3	−56.5760	0.0343	10.02	−45.9	−46.5	−46.5
NH_2NO_2	−261.1138	0.0394	12.33	−3.9		
NH_2NH_2	−111.8976	0.0528	12.12		110.4	
CH_3NH_2	−95.8884	0.0638	11.56	−22.5		
$C_3H_{10}N_6$	−448.9756	0.1619	29.20	118.1		
$C_4H_{13}N_7$	−543.6635	0.2082	34.42	104.7		

E_0 and ZPE are in a.u.; 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 [44]

[a] The experimental values are taken from Ref. [42, 43]

[b] The values are calculated at the G2 level

[c] The values are calculated at the CBS-4M level

Table 2 Calculated total energies (E_0), zero-point energies (ZPE), thermal corrections (H_T), molecular properties, heats of sublimation, and HOFs of the title compounds

Compd.	E_0	ZPE	H_T	$\Delta H_{f,gas}$	A	ν	σ^2_{tot}	ΔH_{sub}	$\Delta H_{f,solid}$
A1	−1267.0910	0.1690	55.14	361.8	265.53	0.17	269.85	137.4	224.4
A2	−1322.4669	0.1862	57.64	354.1	266.17	0.22	280.31	145.6	208.5
A3	−1471.6260	0.1710	60.73	383.4	274.87	0.19	280.01	147.7	235.7
A4	−1377.7967	0.2013	62.17	464.1	279.48	0.14	397.45	151.3	312.7
A5	−1676.1206	0.1696	70.17	505.7	293.95	0.17	299.21	158.4	347.3
B1	−968.7229	0.1996	49.04	426.3	243.73	0.24	286.25	135.7	290.6
B2	−1024.1000	0.2172	51.64	416.4	250.95	0.24	257.23	137.0	279.4
B3	−1173.2607	0.2014	55.62	441.0	262.44	0.21	290.72	143.5	297.4
B4	−1079.4640	0.2335	53.90	437.4	255.06	0.24	264.88	140.5	296.9
B5	−1377.7794	0.2024	61.77	502.8	276.10	0.19	317.02	151.1	351.7
C1	−1566.30444	0.2170	68.18	419.5	312.35	0.16	324.05	171.8	247.7
C2	−1677.0454	0.2510	74.46	432.6	325.55	0.18	286.11	180.1	252.5
C3	−1975.3574	0.2199	82.13	506.7	349.83	0.13	346.53	196.0	310.7
C4	−1787.7536	0.2824	81.24	525.5	350.19	0.14	362.93	198.9	326.7
C5	−2384.3622	0.2191	96.90	711.9	366.15	0.16	283.83	208.3	503.7
D1	−1417.1150	0.2321	64.49	464.6	304.04	0.16	293.51	163.6	301.0
D2	−1527.8516	0.2655	72.03	488.9	322.83	0.17	260.13	175.0	314.0
D3	−1826.1877	0.2360	78.19	502.6	344.76	0.17	294.42	193.8	308.8
D4	−1638.5844	0.2977	77.94	518.5	338.97	0.19	307.67	194.3	324.2
D5	−2235.1991	0.2351	93.07	689.9	354.26	0.14	414.08	205.4	484.5
E1	−1267.9250	0.2469	61.70	511.4	301.68	0.19	392.70	173.5	337.9
E2	−1378.6551	0.2818	66.42	553.6	309.38	0.21	456.35	186.3	367.3
E3	−1676.9990	0.2511	74.71	545.8	327.62	0.14	508.80	190.5	355.3
E4	−1489.3646	0.3145	73.61	647.0	340.12	0.24	427.06	212.3	434.7
E5	−2086.0358	0.2528	87.49	671.3	350.09	0.18	310.94	201.3	470.0
F1	−1118.7551	0.2638	56.11	508.0	281.97	0.25	268.20	157.4	350.6
F2	−1229.4839	0.2972	63.97	553.0	297.97	0.24	336.09	173.3	379.7
F3	−1527.8443	0.2677	71.01	513.8	329.31	0.21	375.88	194.8	319.0
F4	−1340.2271	0.3312	68.41	558.3	320.08	0.24	336.59	189.5	368.8
F5	−1936.8742	0.2680	84.54	644.5	338.65	0.17	381.06	195.4	449.1

E_0 and ZPE are in a.u.; $\Delta H_{f,gas}$, ΔH_{sub}, $\Delta H_{f,solid}$, 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 [44]

Table 2 presents the total energies, ZPEs, thermal corrections, and the gas-phase and solid-phase HOFs of the title compounds. It is seen that all the compounds have relatively high gas-phase HOFs, over 350 kJ·mol^{-1}. Among them, C5 possesses the highest HOFs (711.9 kJ·mol^{-1}). It is seen that increasing the length of original chain and replacing the -NO$_2$ group of N(II)-NO$_2$ and N(IV)-NO$_2$ by -NH$_2$ group can improve the gas-phase HOFs of its derivatives. But the cases are different with the increase of the numbers of substitutents, replacing the -NO$_2$ groups of N-NO$_2$ by -NH$_2$ group can increase the gas-phase HOFs of its derivatives, but this effect is coupled with the effects of the numbers of substitutents. In addition, effects of replacing the -NO$_2$ groups of N-NO$_2$ by the -NH$_2$ groups on its gas-phase HOFs are combined with those of the substituted numbers of the -NO$_2$ groups.

Figure 3 presents a comparison of the effects of different substituents and numbers of substituents on the gas-phase HOFs of the title compounds. Among each series, all the substituted compounds have higher gas-phase HOFs than corresponding unsubstituted ones except for A2 and B2. This is attributable to the increase of the number of energetic C-N bonds in the derivatives. It is interesting to note that C2-F2 have higher HOFs than corresponding unsubstituted ones. This indicates that the substitution of -NH$_2$ can enhance the gas-phase HOFs of the title compounds. This is different from our previous studies on energetic nitrogen-rich compounds that the substitution of the -NH$_2$ group decreases the HOF of parent furazan [14], furoxan [18], carbon- and nitrogen-bridged difurazan [12], furazano[3,4-b]pyrazine [19], nitrogen-bridged di-1,3,5-triazine [8], 1,2,4-triazolo-[4,3-b]-1,2,4,5-tetrazine [6], and tetrazolo-[1,3-b]-1,2,4,5-tetrazine [6]. However, our calculated studies [7] on the carbon-bridged diiminotetrazole derivatives found that the substitution of the -ONO$_2$ group increases the HOF of parent carbon-
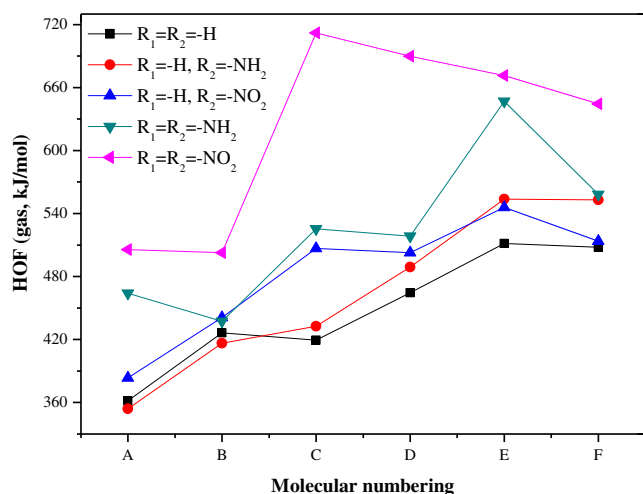
bridged diiminotetrazole ring slightly. This may be because the character of the special chain structure changes the roles of some substituents in affecting the HOF. A3-F3 have higher HOFs than corresponding unsubstituted molecules (A1-F1), showing that incorporating -NO$_2$ group is very useful for improving the HOFs of the title compounds. A4-F4 and A5-F4 have higher HOFs than A2-F2 and A3-F3, respectively. This shows that increasing the numbers of substitutents can enhance the HOFs of the title compounds effectively.

Overall, the -NO$_2$ or -NH$_2$ group are an effective substitutent for increasing the gas-phase HOFs of the title compounds, especially the -NO$_2$ group. As the numbers of substitutents increase, their HOFs enhance obviously. Increasing the length of original chain is helpful for improving their HOFs. The effects of replacing -NO$_2$ groups of N-NO$_2$ by -NH$_2$ groups on gas-phase HOFs are combined with those of the substituted numbers of the -NO$_2$ groups.

A comparison of the gas-phase and solid-phase HOF values for the title compounds is displayed in Fig. 4. It can be found that the calculated solid-phase HOFs reproduce the variation trend of the gas-phase HOFs. This shows that the variation trends of the HOFs of the compounds under the influences of different substituents and the numbers of substituents drawn from the gas-phase results are consistent with those from the solid-phase ones. An exception is that F3 has higher gas-phase HOF than F1, but the former has smaller solid-phase HOF than the latter.

Detonation properties

Table 3 lists the calculated ρ, Q, D, P, and oxygen balance (OB) values of the title compounds together with two well known explosives 1,3,5-trinitro-1,3,5-triazinane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX).
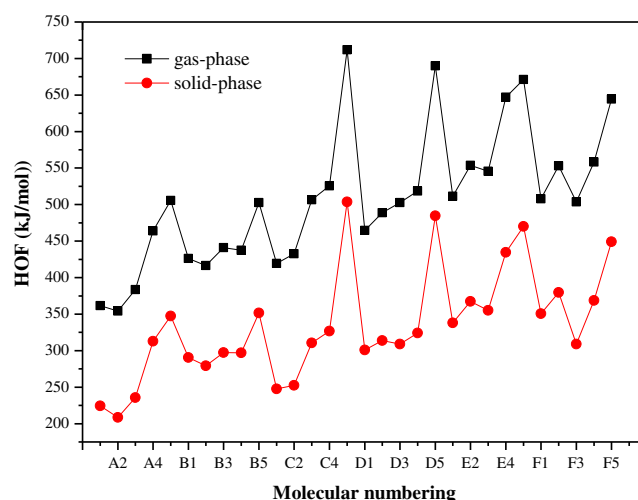

Fig. 3 A comparison of the effects of different substituents and numbers of substituents on the gas-phase HOFs of the title compounds

Fig. 4 A comparison of the gas-phase and solid-phase HOFs of the title compounds

Table 3 Predicted densities (ρ), heats of explosion (Q), detonation velocities (D), detonation pressures (P), and oxygen balance (OB) for the title compounds together with RDX and HMX

Compd.	$\rho(\text{g·cm}^{-3})$	$Q(\text{cal·g}^{-1})$	OB(%)[a]	P(GPa)	$D(\text{km·s}^{-1})$
A1	1.87	1490.6	−5.2	38.4	9.2
A2	1.94	1426.7	−7.4	40.5	9.4
A3	2.00	1360.4	6.8	41.7	9.4
A4	1.89	1452.8	−9.4	39.2	9.3
A5	2.03	1201.9	16.0	40.0	9.2
B1	1.76	1202.1	−44.8	32.9	8.7
B2	1.75	1124.0	−45.3	30.4	8.3
B3	1.84	1361.4	−24.4	35.5	8.9
B4	1.78	1078.7	−45.7	31.2	8.4
B5	1.92	1480.2	−9.4	40.7	9.4
C1	1.90(1.91[b])	1490.9	−8.3	39.2(39.5[b])	9.3(9.5[b])
C2	1.89	1411.5	−11.6	38.3	9.2
C3	1.98	1316.1	10.1	39.9	9.2
C4	1.88	1380.3	−14.4	37.9	9.1
C5	2.09	1085.4	22.7	40.0	9.1
D1	1.81	1417.8	−22.6	34.4	8.8
D2	1.80	1343.1	−25.0	33.5	8.7
D3	1.94	1534.1	0.0	42.0	9.5
D4	1.85	1277.7	−27.1	35.1	8.8
D5	2.08	1246.0	15.0	43.2	9.5
E1	1.80	1319.2	−39.5	32.5	8.6
E2	1.87	1227.2	−40.7	35.4	8.8
E3	1.93	1470.9	−11.6	40.8	9.4
E4	1.91	1180.5	−41.7	37.4	9.0
E5	2.03	1427.9	6.4	44.6	9.7
F1	1.71	1071.0	−59.8	28.6	8.2
F2	1.75	993.2	−59.2	30.0	8.3
F3	1.89	1340.0	−25.0	37.1	9.0
F4	1.79	901.7	−58.7	30.5	8.3
F5	2.00	1530.4	−3.4	45.0	9.8
RDX[a]	1.82	1597.4	−21.6	34.0	8.7
HMX[a]	1.91	1633.9	−21.6	39.0	9.1

The experimental values were taken from Ref. [45]

[a] Oxygen balance(%) for $C_aH_bO_cN_d$: $1600\times(c-2a-b/2)/M_w$; M_w= molecular weight of the titled compounds

[b] The values are taken from Ref. [12]

The compounds with different substituents and numbers of subsitutents have different ρ values, for example, the largest value and the smallest one are 2.09 and 1.71 g/cm^3, respectively. Most of the substituted compounds have higher ρ values than corresponding unsubstituted ones except for B2, C2, C4, and D2. Among all these series, 20 compounds have higher ρ values than RDX and 12 compounds have higher ρ than HMX. This shows that the title compounds possess very good density property. Our calculated ρ value of C1 is 1.90 g/cm^3, which is very close to its experimental value (1.91 g/cm^3). It is seen that replacing the -NO$_2$ groups of N-NO$_2$ by the -NH$_2$ groups decreases density while the substitution of the -NO$_2$ group is a very effective structural unit for enhancing the density of the title compounds. The NO$_2$-substituted molecules have generally

higher ρ than the unsubstituted ones except for B2, C2, and D2, whose ρ values are lower than their unsubstituted molecules slightly. The substitution of the -NH$_2$ group is also helpful to improve the densities of the title compounds. This conclusion differs with previous studies [8, 12, 14, 18] that incorporating the -NH$_2$ group decreases the density of its derivatives. The differences may be because the introduction of the -NH$_2$ group into the title compounds is very helpful for generating a lot of intramolecular and intermolecular H-bonds that can enhance their densities.

It is seen in Table 4 that all the NH$_2$-substituted compounds have lower Q values than corresponding unsubstituted ones. As the numbers of the -NH$_2$ group increase, the Q of the title compounds decrease except for A4. Some of the NO$_2$-substituted compounds (B3, D3-F3,

Table 4 Bond dissociation energies (BDE, kJ·mol^{-1}) of the relatively weak bonds of the title compounds

Compd.	N(I)-NO$_2$ bond	N(II)-NH$_2$/N(II)-NO$_2$ bond	N(III)-NH$_2$/N(III)-NO$_2$ bond	C-NO$_2$ bond
A1	143.6	110.5		
A2	154.8	121.6		
A3	156.9	127.5		131.4
A4	123.9	126.3		
A5	120.7	41.6		59.7
B1	125.6	252.8		
B2	159.6	281.6		
B3	136.4	190.3		112.7
B4	183.5	232.5		
B5	156.7	185.0		57.7
C1	149.5	109.6	142.9	
C2	162.8	129.4	147.1	
C3	109.6	60.3	78.5	76.2
C4	158.4	95.0	90.8	
C5	99.4	98.1	21.6	53.3
D1	163.6	126.1		
D2	169.7	137.5		
D3	119.4	84.0		100.6
D4	175.6	131.1		
D5	125.7	37.8		47.1
E1	143.3		61.7	
E2	157.1		163.6	
E3	102.8		61.3	78.9
E4	148.4		172.4	
E5	110.5		57.5	51.3
F1	170.4			
F2	180.8			
F3	148.8			142.7
F4	184.6			
F5	176.1			75.6

E5-F5) have higher Q values than corresponding unsubstituted ones, while the others (A3, C3, A5-D5) have lower Q values than corresponding unsubstituted molecules.

OB is another one of the most important criterion for selecting potential HEDCs. Generally, the higher the oxygen balance, the larger the D and P values, and the better the performance of the title compound. Our results show that the -NO$_2$ group is a good substituent for improving the OB of the title compounds. However, it is clear that too much oxygen is not favorable for advancing explosive performance of HEDCs. The primary reason is that the excess oxygen will produce O$_2$ groups that take away a great deal of energy. Therefore, one had better keep the OB value around zero in designing HEDCs.

The effects of different substituent, numbers of substitutents, and replacing the -NO$_2$ groups of N-NO$_2$ by the -NH$_2$ groups on the densities make the title compounds have different D and P values. All the substituted compounds have larger D and P values than corresponding unsubstituted ones except for B2, B4, C2, C4, C5, and D2. The NO$_2$-substituted compounds have the highest D and P in the same series. This indicates that the -NO$_2$ group is an effective unit for improving the detonation properties of the title compounds. The effects of replacing the -NO$_2$ groups of N-NO$_2$ by the -NH$_2$ groups on detonation properties are combined with those of the replaced numbers of the -NO$_2$ groups. The effects of the length of original chains on detonation properties are coupled with those of the substituents.

Figure 5 displays the calculated ρ, D, and P values for the title compounds together with RDX and HMX. It is found that with the variation of the molecular numbering, the evolution pattern of ρ is very similar to that of D and P for the title compounds. In addition, some compounds have higher ρ but lower D and P than RDX or HMX, while some others have lower ρ but higher D and P than RDX or HMX.
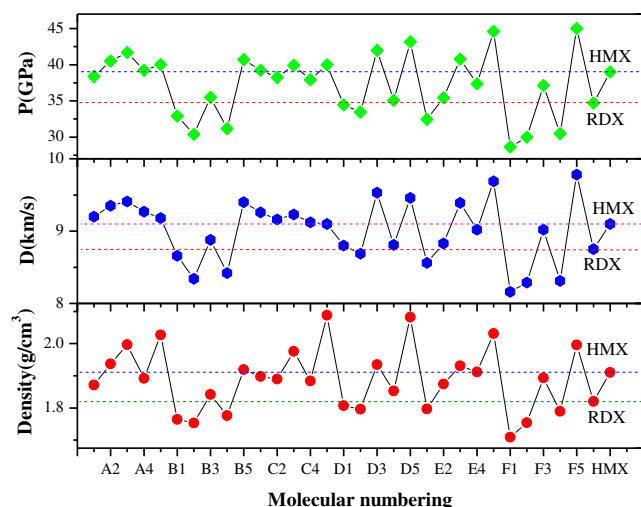
Fig. 5 A comparison of the calculated ρ, D, and P values of the title compounds together with commonly used explosives RDX and HMX

This is because their Q causes ρ to have less influence on D and P. This indicates that the density is not always a key factor for determining detonation properties [31]. It is surprising that 22 compounds have comparable D and P with RDX and 13 compounds (A2-A5, B5, C1, C3, C5, D3, D5, E3, E5, F5) have comparable detonation performance with HMX. If these 22 compounds could be synthesized, they may have good performances. Thus, further investigations are still needed.

Thermal stability

The bond dissociation energy (BDE) can provide very useful information for understanding the stability of energetic materials. In general, the smaller energy for breaking a bond, the weaker the bond, and the easier the bond becomes a trigger bond; that is to say, the corresponding compound is more unstable, and its sensitivity is larger. Therefore, the calculated BDE could be used to measure the relative order of thermal stability for energetic compounds. However, it should be remembered that the BDEs are simply one piece of evidence for molecular stability, but not the conclusive one. The sensitivity of explosives involves many complex factors. The structure of an explosive is the intrinsic factor in determining its sensitivity. Recently, Politzer et al. [46] reported that the available free space per molecule in the unit cell for the explosives can be used as a parameter to estimate their relative sensitivities.

Table 4 lists the BDE values of several relatively weak bonds of the title molecules. Generally, it is found that the substitution of the -NH$_2$ groups improve the stability of the title compounds, while incorporating the -NO$_2$ group has the opposite effect [47]. Then, it is seen that series B has higher BDE values than series A and the order of series (C-F) is as

follows: F > E > D > C, suggesting that replacing the -NO$_2$ groups of N-NO$_2$ by the -NH$_2$ groups enhances the stability of the title compounds, and furthermore their stability improves with the increase of the substituted numbers of the NO$_2$ groups.

Figure 6 presents a comparison of the BDEs of the weakest bonds for the title compounds. Considered the thermal stability and detonation performance, seven compounds (A3, A4, C2, D1, D4, E2, and F3) have good detonation performance (D and P) and thermal stability (BDE). Therefore, seven molecules may be considered as the potential candidates of HEDCs with less sensitivity and higher performance.

Conclusions

In this work, we have studied the HOFs, energetic properties, and thermal stability of a series of 1,7-diamino-1,7-dinitrimino-2,4,6-trinitro-2,4,6-triazaheptane derivatives with different substituents, different numbers of substituents, and different original chains by using the DFT-B3LYP method. The results show that -NO$_2$ or -NH$_2$ is an effective substituent for increasing the gas-phase HOFs of the title compounds, especially -NO$_2$ group. As the numbers of substitutents increase, their HOFs enhance obviously. Increasing the length of original chain is helpful for improving their HOFs. The effects of replacing the -NO$_2$ groups of N-NO$_2$ by the -NH$_2$ groups on its gas-phase HOFs are combined with those of the substituted numbers of the -NO$_2$ groups.

The substitution of -NO$_2$ is useful for enhancing their detonation performances and the effects of replacing the -NO$_2$ groups of N-NO$_2$ by the -NH$_2$ groups on its detonation properties are coupled with those of the substituted numbers
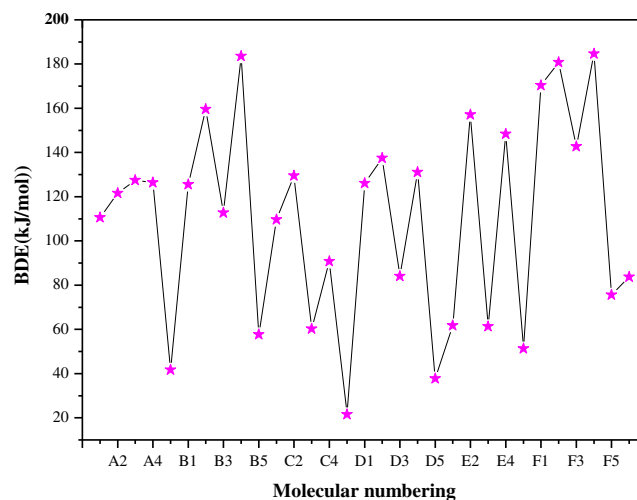

Fig. 6 A comparison of the BDE values of the weakest bonds for the title compounds

of the -NO$_2$ groups. In addition, the effects of the length of original chains on detonation properties are coupled with those of the substituents. An analysis of the BDE of the weakest bonds indicates that the substitution of the -NH$_2$ groups and replacing the -NO$_2$ groups of N-NO$_2$ by the -NH$_2$ groups are favorable for improving their thermal stability, while the substitution of -NO$_2$ and increasing the length of original chain decrease their thermal stability.

Considering the detonation performance and thermal stability, seven compounds (A3, A4, C2, D1, D4, E2, and F3) may be considered as the potential candidates of HEDCs.

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