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Computational study of energetic nitrogen-rich derivatives of 1,4-bis(1-azo-2,4-dinitrobenzene)-iminotetrazole

Qiong Wu · Yong Pan · Weihua Zhu · Heming Xiao

Abstract The heats of formation (HOFs), electronic structure, energetic properties, and thermal stabilities for a series of 1,4-bis(1-azo-2,4-dinitrobenzene)-iminotetrazole derivatives with different substituents and substitution positions and numbers of nitrogen atoms in the nitrobenzene rings were studied using the DFT-B3LYP method. All the substituted compounds have higher HOFs than their parent compounds. As the number of nitrogen atoms in the nitrobenzene ring increases, the HOFs of the derivatives with the same substituent rise gradually. Replacing carbon atoms in the nitrobenzene with nitrogen atoms to form N–N bonds is very helpful in improving their HOFs. Most of the substituted compounds have higher HOMO–LUMO gaps than the corresponding unsubstituted compounds. Substitution of the –NO_2, –NF_2, or –ONO_2 group and an increase in the number of nitrogen atoms in the nitrobenzene rings are useful for enhancing their detonation performance. The substituents' substitution is not favorable for improving thermal stability. Considering detonation performance and thermal stability, five compounds may be considered potential candidates for high energy density compounds (HEDCs).

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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, 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 molecules with high energy and density is the primary step for searching and synthesizing HEDCs. As we know, the iminotetrazole is an azo compound with high nitrogen content (82.4 %), making it of interest for the synthesis of highly energetic materials. Recent studies [12, 13] show that the nitroiminotetrazole-based compounds are of special interest because they have both the energetic nitrogen-rich heterocycle and oxidizer in one molecule. Secondly, incorporating a nitrogen-rich heterocycle into the nitrobenzene makes energetic compounds obtain good detonation performances and outstanding thermal stability at the same time [14–16]. Then, many studies reported that the azo bridge can enhance the heats of formation (HOF) and detonation performances of nitrogen-rich heterocycles efficiently [17, 18]. To combine these advantages into a whole, the connection of an iminotetrazole group with two 2,4-dinitrobeneze groups by two azo bridges in one molecule [named 1,4-bis(1-azo-2,4-dinitrobenzene)-iminotetrazole] thus seems to be a good attempt at designing a novel HEDC.

Some studies have reported that a –NO_2, –NF_2, or –ONO_2 substituent is an effective structural unit for enhancing the performance of energetic compounds [4, 6]. In addition, increasing the number of nitrogen atoms in the 2,4-dinitrobenzene rings by replacing carbon atoms at different positions is a way of increasing the nitrogen content of the molecule.

Here, we report a systematic study using density function theory (DFT) of the HOFs, electronic structure, energetic properties, and thermal stability of a series of 1,4-bis(1-azo-2,4-dinitrobenzene)-iminotetrazole derivatives with different substitutent groups (–NO$_2$, –NF$_2$, –ONO$_2$), different substitution positions and different numbers of nitrogen atoms in the nitrobenzene ring. Our main purpose here was to investigate the important role of different substituents and substitution positions and numbers of nitrogen atoms in the design of efficient HEDCs.

The remainder of the paper is organized as follows. A brief description of our Computational methods is followed by a Results and discussion section, and our findings are then summarized in the Conclusions section.

## Computational methods

Figure 1 displays the molecular frameworks of a series of 1,4-bis(1-azo-2,4-dinitrobenzene)-iminotetrazole derivatives. On the basis of the substitution positions and the numbers of nitrogen atoms in the nitrobenzene ring, the compounds are classified into eight series (molecular numbering of series: A no nitrogen atom in the nitrobenzene ring; B, C, D one nitrogen atom in the nitrobenzene ring; E, F, G two nitrogen atoms in the nitrobenzene ring; H three nitrogen atoms in the nitrobenzene ring).

The DFT-B3LYP [19–26] method with the 6-311G** [27, 28] basis set has been used very successfully to predict the HOFs of many organic systems via isodesmic reactions [29, 30]. Here, we design isodesmic reactions in which the numbers of all kinds of bonds are kept constant 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 thus the errors of the calculated HOF can be greatly reduced [31]. This approach has been demonstrated to predict reliably the HOFs of many organic systems [29, 32].

The isodesmic reactions used to obtain the HOFs of the title compounds at 298 K are as follows:

$$(1)$$
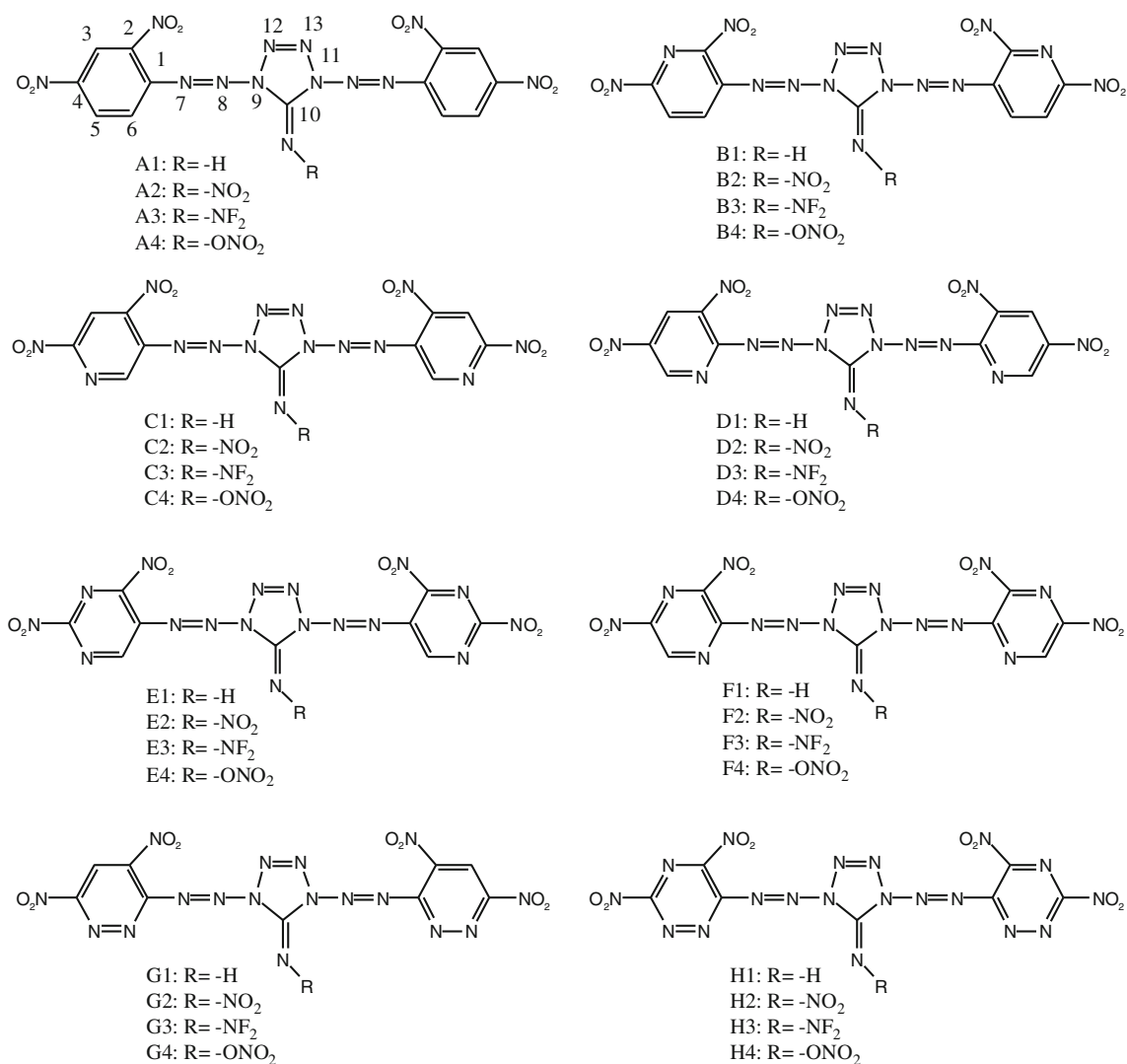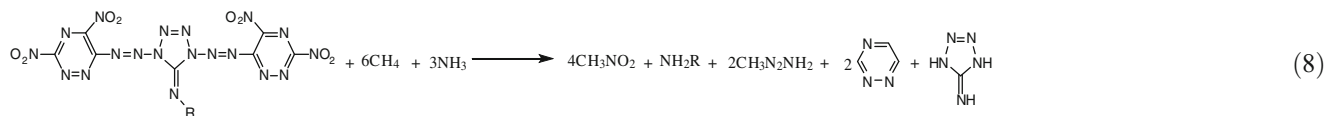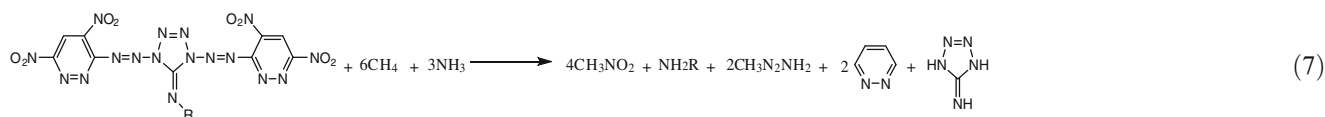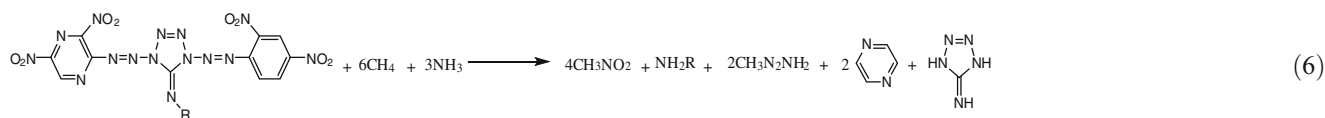

$$(2)$$

$$(3)$$

$$(4)$$

$$(5)$$
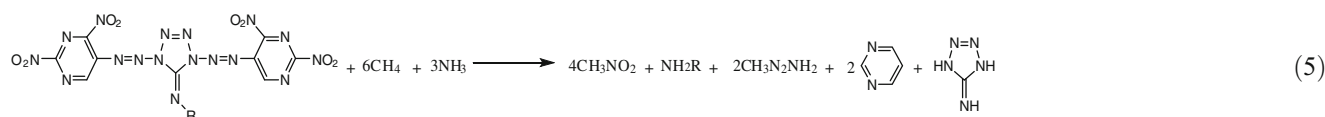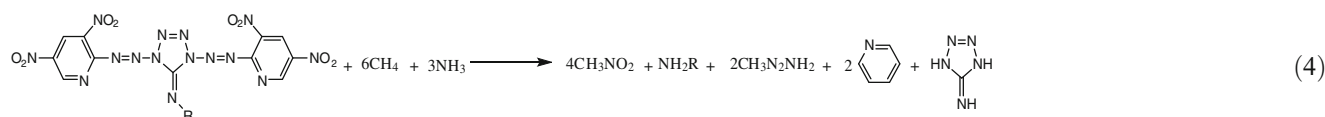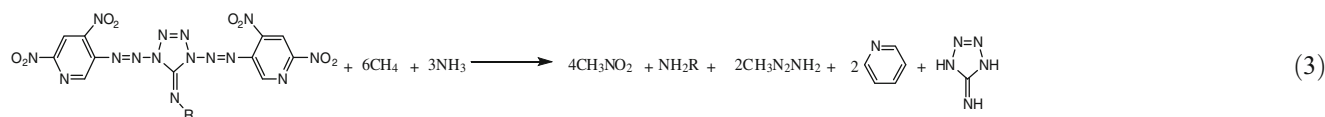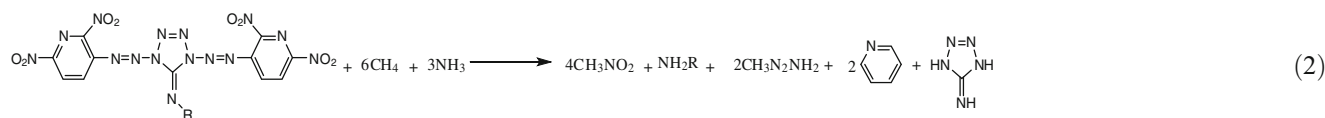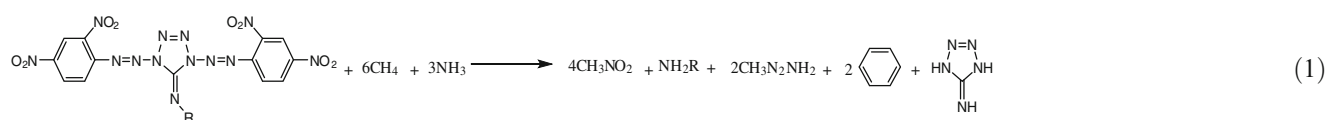
Fig. 1 Molecular frameworks of 1,4-bis(1-azo-2,4-dinitrobenzene)-iminotetrazole derivatives (molecules numbered as A1–A4, B1–B4, C1–C4, D1–D4, E1–E4, F1–F4, G1–G4, and H1–H4)

(6)

(7)

(8)

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

$$\Delta H_{298} = \Delta H_{f,p} - \Delta H_{f,R} \tag{9}$$

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 $CH_3N_2NH_2$, NH_2NF_2, NH_2ONO_2, and iminotetrazole 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 G2 theory to get an accurate value of ΔH_f. The experimental HOFs of reference compounds CH_4, NH_3, CH_3NO_2, C_6H_6, NH_2NO_2, 1, 2, 4-triazine, pyridine, and pyrimidine are available. Now the most important task is to compute ΔH_{298}, which ΔH_{298} can be calculated using the following expression:

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV)$$
$$= \Delta E_0 + \Delta E_{ZPE} + \Delta E_T + \Delta nRT \tag{10}$$

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. (10) 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 [33], the solid-phase HOF can be obtained from the gas-phase HOF ($\Delta H_{f,gas}$) and heat of sublimation (ΔH_{sub}):

$$\Delta H_{f,solid} = \Delta H_{f,gas} - \Delta H_{sub} \tag{11}$$

Recently, Politzer et al. [34–36] 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:

$$\Delta H_{sub} = aA^2 + b\left(\nu\sigma_{tot}^2\right)^{0.5} + c \tag{12}$$

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$^{-1}\cdot$A^{-4}, $b=1.650$ kcal mol^{-1}, and $c=2.966$ kcal mol^{-1} [37]. The descriptors A, ν, and $\nu\sigma_{tot}^2$ were calculated by using the computational procedures proposed by Bulat et al. [38]. This approach has been demonstrated to predict reliably the heats of sublimation of many energetic compounds [37, 39].

The detonation velocity and pressure were estimated by the Kamlet-Jacobs equations [40] as

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

$$P = 1.558\rho^2 N\overline{M}^{1/2}Q^{1/2} \tag{14}$$

where each term in the Eqs. (13) and (14) is defined as follows: D, the detonation velocity (km/s); 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); 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. 13 and 14. 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. [41] in which the interaction index $\nu\sigma_{tot}^2$ was introduced:

$$\rho = \alpha\left(\frac{M}{V(0.001)}\right) + \beta\nu\left(\sigma_{tot}^2\right) + \gamma \tag{15}$$

where M is the molecular mass (g/mol) 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. In the Kamlet-Jacobs equations, the 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 slightly greater than practical loaded density. Therefore, according to the Kamlet-Jacobs equations, the D and P values can be regarded as their upper limits.

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

Compound	E_0	ZPE	H_T	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
$CH_3N_2NH_2$	−205.3669	0.0736	15.40		214.0
NH_3	−56.5760	0.0343	10.02	−45.9	−46.5
NH_2NO_2	−261.1138	0.0394	12.33	−3.9	
NH_2NF_2	−310.3268	0.0354	13.53		−25.0
NH_2ONO_2	−336.2856	0.0424	15.89		18.8
C_6H_6	−232.3085	0.1002	14.44	82.9	
Pyridine	−248.3469	0.0885	14.08	140.4	
Pyrimidine	−264.3881	0.0767	13.80	195.7	
1,2,4-Triazine	−280.3889	0.0640	13.75	334.0	
Iminotetrazole	−313.6808	0.0633			377.9

[a] E_0 and ZPE are in a.u.; 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 [48]

[b] Experimental values taken from Ref. [46, 47]

[c] Values calculated at the G2 level

Table 2 Calculated E_0, ZPE, H_T, molecular properties, heats of sublimation, and HOFs of the title compounds[a]

Compound	E_0	ZPE	H_T	$\Delta H_{f,gas}$	A	ν	σ^2_{tot}	ΔH_{sub}	$\Delta H_{f,solid}$
A1	−1,812.9889	0.251	78.49	1,194.4	427.06	0.23	115.26	251.8	942.6
A2	−2,017.5080	0.252	85.75	1,281.3	449.93	0.21	108.18	271.6	1,009.7
A3	−2,066.7176	0.248	87.13	1,266.7	445.59	0.22	108.97	268.1	998.6
A4	−2,092.6841	0.255	88.60	1,292.3	458.03	0.22	114.08	281.5	1,010.8
B1	−1,845.0572	0.226	78.54	1,214.6	423.53	0.21	165.22	253.6	961.0
B2	−2,049.5724	0.228	85.91	1,426.0	447.08	0.19	169.16	275.0	1,151.0
B3	−2,098.7818	0.223	87.45	1,413.0	443.26	0.19	171.52	271.5	1,141.6
B4	−2,124.7489	0.231	89.05	1,435.8	455.82	0.20	171.52	285.1	1,150.7
C1	−1,845.0530	0.226	78.16	1,225.0	420.50	0.22	136.11	247.8	977.2
C2	−2,049.5671	0.228	85.63	1,439.4	444.74	0.20	142.80	270.4	1,169.0
C3	−2,098.7768	0.223	86.91	1,426.1	440.21	0.20	141.62	265.8	1,160.3
C4	−2,124.7437	0.231	88.47	1,449.2	453.03	0.20	142.41	278.7	1,170.5
D1	−1,845.0592	0.227	77.81	1,209.1	419.04	0.22	111.33	242.9	966.3
D2	−2,049.5740	0.228	85.37	1,421.5	448.51	0.19	114.48	269.5	1,152.1
D3	−2,098.7827	0.224	86.51	1,410.1	443.50	0.19	111.72	264.1	1,146.0
D4	−2,124.7525	0.231	88.22	1,426.5	454.27	0.19	110.54	274.7	1,151.8
E1	−1,877.1178	0.202	78.31	1,496.3	419.19	0.15	182.93	245.0	1,251.3
E2	−2,081.6319	0.204	85.76	1,597.8	443.11	0.14	186.47	267.2	1,330.6
E3	−2,130.8415	0.199	87.18	1,582.6	439.38	0.14	182.53	263.1	1,319.5
E4	−2,156.8086	0.207	88.90	1,605.1	452.00	0.15	183.71	277.0	1,328.0
F1	−1,877.1157	0.202	77.81	1,500.5	415.93	0.19	146.34	242.2	1,258.3
F2	−2,081.6265	0.203	85.40	1,608.2	443.99	0.15	155.00	266.0	1,342.1
F3	−2,130.8347	0.199	86.51	1,598.9	438.97	0.15	236.04	268.9	1,330.0
F4	−2,156.8050	0.206	88.34	1,613.1	450.20	0.17	158.54	274.8	1,338.3
G1	−1,877.0492	0.200	77.94	1,670.7	414.47	0.19	169.16	243.6	1,427.2
G2	−2,081.5576	0.202	85.47	1,785.3	441.73	0.16	177.42	267.3	1,518.0
G3	−2,130.7700	0.197	86.47	1,764.9	438.04	0.15	170.73	261.8	1,503.1
G4	−2,156.7402	0.205	88.90	1,780.1	457.06	0.19	161.68	284.2	1,495.9
H1	−1,909.1051	0.176	77.90	1,808.8	411.88	0.12	180.96	234.2	1,574.6
H2	−2,113.6139	0.177	85.50	1,921.7	440.05	0.09	198.27	258.0	1,663.6
H3	−2,162.8252	0.173	86.45	1,904.4	436.55	0.09	195.12	254.4	1,650.1
H4	−2,188.7928	0.181	88.50	1,925.6	447.01	0.10	188.43	265.7	1,659.9

[a] 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. The scaling factor for ZPE is 0.98 and the scaling for H_T is 0.96 [48]

Fig. 2 Comparison of the effects of different substituents and substitution positions and numbers of nitrogen atoms in the nitrobenzene ring on the gas-phase heats of formation (HOFs) of the title compounds
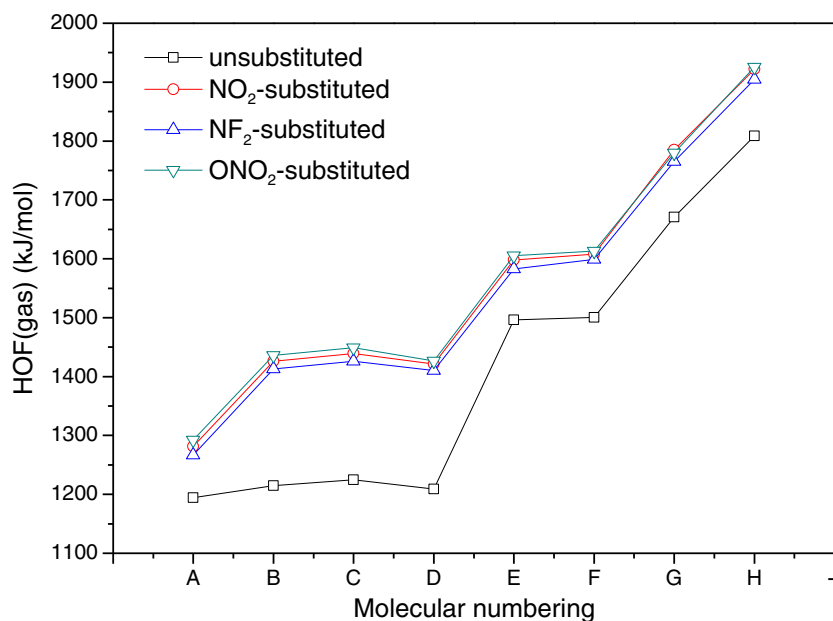
The strength of bonding, which could be evaluated by bond dissociation energy, is fundamental to understanding chemical processes [42]. The energy required for bond homolysis at 298 K and 1 atm corresponds to the enthalpy of reaction A–B (g)→A·(g)+B·(g), which by definition is the bond dissociation enthalpy of the molecule A–B [43]. For many organic molecules, the terms "bond dissociation energy" (BDE) and "bond dissociation enthalpy" usually appear interchangeably in the literature [44]. Thus, at 0 K, the homolytic bond dissociation energy can be given in terms of Eq. (16):

$$BDE_0(A-B) = E_0(A\cdot) + E_0(B\cdot) - E_0(A-B) \quad (16)$$

The BDE with ZPE correction can be calculated by Eq. (17):

$$BDE(A-B)_{ZPE} = BDE_0(A-B) + \Delta E_{ZPE} \quad (17)$$

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 [45]. The optimizations were performed with no symmetry restrictions using the default convergence criteria in the program. All of the optimized structures were characterized to be true local

Fig. 3 Comparison of gas-phase and solid-phase HOFs of the title compounds
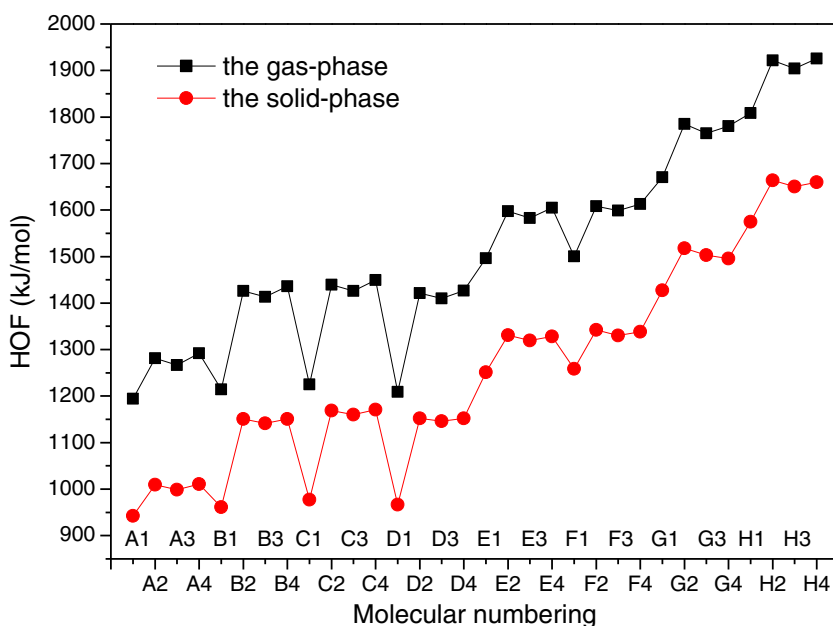
energy minima on the potential energy surfaces without imaginary frequencies.

Results and discussion

Heats of formation

Here, we investigated the effects of different substituents and substitution positions and numbers of nitrogen atoms in the nitrobenzene ring on the gas-phase ($\Delta H_{f,gas}$) and solid-phase ($\Delta H_{f,solid}$) HOFs of the title compounds. Table 1 lists the total energies, ZPEs, and thermal corrections for 12 reference compounds in the isodesmic reactions. As the experimental HOFs of $CH_3N_2NH_2$, NH_2NF_2, iminotetrazole, and NH_2ONO_2 are unavailable, additional calculations were carried out for the atomization reaction using the G2 theory to obtain their HOFs. The experimental HOFs for the remaining eight reference compounds were taken from references 46 and 47. 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 relative errors of only 2.04 %, 1.22 %, and 1.25 %, respectively. Thus, our calculated HOFs at the G2 theory are expected to be reliable.

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 high gas-phase HOFs, over 1,190 kJ mol^{-1}. Among them, H4 possesses the highest HOF value (1,925.6 kJ mol^{-1}). The substitution of $-NO_2$, $-NF_2$, or $-ONO_2$ enhances the HOF value of the unsubstituted compound (A1–H1) extremely. It is interesting to note that the ONO$_2$-substituted derivative has the highest HOF value among the same series except for the G series. In this latter series, the effects of different substituents on the HOF of the parent ring are in the following order: $-NO_2 > -ONO_2 > -NF_2$. This shows that the $-ONO_2$ group is a very good substituent for increasing the HOF of the 1,4-bis(1-azo-2,4-dinitrobenzene)-iminotetrazole and its analogues. In our previous studies on energetic nitrogen-rich compounds, we found that substitution of the $-ONO_2$ group decreases the HOF of parent furazan [19], furoxan [23], carbon- and nitrogen-bridged difurazan [17], furazano[3,4-b]pyrazine [25], nitrogen-bridged di-1,3,5-triazine [8], 1,2,4-triazolo-[4,3-b]-1,2,4,5-tetrazine [6], or tetrazolo-[1,3-b]-1,2,4,5-tetrazine [6]. However, our calculated studies [7] on the carbon-bridged diiminotetrazole derivatives reported that the substitution of the $-ONO_2$ group increases the HOF of parent carbon-bridged diiminotetrazole ring, but the increase in HOF is not apparent. This may be because the = NH bridge between the tetrazole ring and the substituent change the roles of some substituents in affecting the HOF of the diiminotetrazoles. The results

calculated here are different from those in the aforementioned reports, mainly because the ONO$_2$-substituted 1,4-bis(1-azo-2,4-dinitrobenzene)-iminotetrazoles not only have the = N-bridge but also a large number of inherently energetic N–N and C–N bonds. Therefore, it could be concluded that the effect of the $-ONO_2$ groups on the HOFs are determined by the characteristics of the parent molecular framework.

Figure 2 presents a comparison of the effects of different substituents, substitution positions of nitrogen atoms, and numbers of nitrogen atoms in the nitrobenzene ring on the gas-phase HOFs of the title compounds. Among each series, all the substituted compounds have higher gas-phase HOFs

Table 3 Calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and energy gaps ($\Delta E_{LUMO-HOMO}$) of the title compounds[a]

Compound	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	$\Delta E_{LUMO-HOMO}$ (a.u.)
A1	−0.281	−0.147	0.134
A2	−0.293	−0.154	0.139
A3	−0.230	−0.156	0.144
A4	−0.291	−0.151	0.140
B1	−0.292	−0.158	0.134
B2	−0.303	−0.165	0.138
B3	−0.309	−0.167	0.142
B4	−0.301	−0.165	0.136
C1	−0.293	−0.159	0.134
C2	−0.302	−0.165	0.137
C3	−0.308	−0.166	0.142
C4	−0.299	−0.162	0.137
D1	−0.288	−0.154	0.134
D2	−0.294	−0.156	0.138
D3	−0.300	−0.154	0.146
D4	−0.293	−0.156	0.137
E1	−0.301	−0.167	0.134
E2	−0.311	−0.173	0.138
E3	−0.316	−0.175	0.141
E4	−0.301	−0.172	0.129
F1	−0.299	−0.166	0.133
F2	−0.305	−0.169	0.136
F3	−0.312	−0.168	0.144
F4	−0.302	−0.169	0.132
G1	−0.297	−0.164	0.133
G2	−0.303	−0.167	0.136
G3	−0.308	−0.165	0.143
G4	−0.285	−0.163	0.122
H1	−0.310	−0.176	0.134
H2	−0.313	−0.178	0.135
H3	−0.319	−0.174	0.145
H4	−0.309	−0.177	0.132

than corresponding unsubstituted ones. As the numbers of nitrogen atoms in the nitrobenzene ring increase, the HOFs of the derivatives with the same substituent rise gradually. This is attributable to the increase in the number of energetic N–N and C–N bonds in the derivatives. Our observations are in agreement with previous reports that the more N–N bonds a compound has, the higher its HOF [12, 20]. For the series with one nitrogen atom in the nitrobenzene ring (B, C, D), the effect on the HOF of different substitution positions of nitrogen atoms is very small. However, for the series with two nitrogen atom in the nitrobenzene ring (E, F, G), the effects on the HOFs of different substitution positions of nitrogen atoms are obvious. Compounds in the G series have higher HOFs than the corresponding ones in the E or

F series with the same substituent. This is because the former have more N–N bonds than the latter, and N–N bonds contain more energy than C–N or C–C bonds.

Overall, the –NO$_2$, –NF$_2$, or –ONO$_2$ group are an effective substituent for increasing the gas-phase HOFs of the title compounds, and the –ONO$_2$ group is the best one among them. As the numbers of nitrogen atoms in the nitrobenzene increase, their HOFs gradually enhance. Replacing carbon atoms in the nitrobenzene with nitrogen atoms to form N–N bond is very helpful for improving their HOFs.

Figure 3 displays a comparison of the gas-phase and solid-phase HOF values for the title compounds. Qualitatively, the calculated solid-phase HOFs reproduce the variation trend of the gas-phase HOFs. This shows that the

Table 4 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[a]

Compound	ρ(g cm^{-3})	Q(cal g^{-1})	OB(%)[b]	D(km s^{-1})	P(GPa)
A1	1.72	1,351.2	−84.6	7.4	23.3
A2	1.75	1,436.0	−67.9	7.7	25.7
A3	1.78	1,462.2	−61.1	7.9	27.4
A4	1.78	1,481.5	−62.9	7.9	27.2
B1	1.77	1,332.1	−64.0	7.7	26.1
B2	1.81	1,474.7	−49.2	8.1	29.5
B3	1.86	1,501.1	−45.6	8.4	32.1
B4	1.94	1,518.3	−44.8	8.6	34.7
C1	1.76	1,340.3	−64.0	7.7	25.9
C2	1.81	1,483.0	−49.2	8.2	29.6
C3	1.85	1,509.6	−45.6	8.4	31.8
C4	1.96	1,527.1	−44.8	8.7	35.5
D1	1.78	1,334.8	−64.0	7.7	26.4
D2	1.80	1,475.2	−49.2	8.1	29.2
D3	1.83	1,503.1	−45.6	8.3	31.1
D4	1.79	1,518.8	−44.8	8.3	30.6
E1	1.79	1,449.4	−43.6	8.1	29.2
E2	1.83	1,530.7	−30.6	8.5	32.5
E3	1.87	1,555.5	−30.3	8.6	33.6
E4	1.85	1,571.4	−30.3	8.7	33.8
F1	1.79	1,452.9	−43.6	8.2	29.6
F2	1.83	1,535.9	−30.6	8.5	32.5
F3	1.89	1,560.4	−30.3	8.7	34.4
F4	1.86	1,576.0	−26.8	8.7	34.2
G1	1.82	1,537.5	−43.6	8.4	31.4
G2	1.85	1,616.4	−30.6	8.7	34.1
G3	1.89	1,638.6	−30.3	8.8	35.2
G4	1.86	1,646.0	−26.8	8.8	35.0
H1	1.85	1,582.18	−23.4	8.8	34.8
H2	1.88	1,656.2	−12.2	9.1	37.5
H3	1.91	1,678.4	−18.1	9.1	38.3
H4	1.86	1,692.5	−8.9	9.1	37.3
RDX[a]	1.82	1,597.4	−21.6	8.7	34.0
HMX[a]	1.91	1,633.9	−21.6	9.1	39.0

[a]Experimental values taken from Ref. [49]

[b]Oxygen balance(%) for C$_a$H$_b$O$_c$N$_d$: $1,600\times(c-2a-b/2)/M_w$; M_w = molecular weight of the titled compounds

variation trends of the HOFs of the compounds under the influences of different substituents and the numbers of nitrogen atoms drawn from the gas-phase results are consistent with those from the solid-phase ones. An exception is that G4 has higher gas-phase HOF than G3, but the former does smaller solid-phase HOF than the latter.

Electronic structure

Table 3 lists the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and the energy gaps ($\Delta E_{LUMO–HOMO}$) for the title compounds. For each series, the substitution of –NO_2, –NF_2, or –ONO_2 decreases the HOMO energy level except for the compounds G4 and H4. The same is true of the LUMO energy level except for G4 and H3. On the whole, as the number of nitrogen atoms in the nitrobenzene ring increases, the HOMO and LUMO energy levels of the derivatives with the same substituent decrease. For the series with one nitrogen atom in the nitrobenzene ring (B, C, D), the compounds of D series have higher HOMO and LUMO than those of the C series with the same substituent, whose HOMO and LUMO are higher than those of D series. For the series with two nitrogen atoms in the nitrobenzene ring (E, F, G), the HOMO and LUMO energy levels of the compounds with the same substituent increase in the following order: E < F < G. Our observations show that incorporating substituents or nitrogen atoms into the title compounds decreases their HOMO and LUMO.

For each series, the substitution of –NO_2, –NF_2, or –ONO_2 increases the HOMO–LUMO gaps except for the compounds E4, F4, G4, and H4, indicating a shift toward higher frequencies in their electronic absorption spectra.

This indicates that the group –NO_2 or –NF_2 would decrease the reactivity of the title compounds. Incorporating –ONO_2 into compounds of the A, B, C, or D series would decrease the reactivity, whereas for the ONO_2-substituted compound of E, F, G, or H, just the opposite is the case. However, it should be remembered that HOMO–LUMO gaps are suggestive of reactivity only as an approximation. E4, F4, G4, and H4 have lower energy gaps than the corresponding unsubstituted one, indicating a shift toward lower frequencies in their electronic absorption spectra. The NF_2-substituted compound has the largest HOMO–LUMO gap among the same series, while the ONO_2-substituted compound has the smallest gap except for A4. In all, the effects of the substituents on the HOMO–LUMO gap are coupled to those of the substitution positions and numbers of nitrogen atoms in the nitrobenzene ring.

Detonation properties

Table 4 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).

The compounds with different substituent and nitrogen atoms in the nitrobenzene ring have different ρ values. For example, the largest and smallest values are 1.96 and 1.72 g cm^{-3}, respectively. All the substituted compounds have higher ρ values than corresponding unsubstituted ones. Among these series, 19 compounds have higher ρ values than RDX, and three compounds have higher ρ than HMX. This shows that the title compounds possess good density properties. For A, B, and C series, the ONO_2-substituted

Fig. 4 Calculated ρ, D, and P values of the title compounds compared with those of the commonly used explosives RDX and HMX
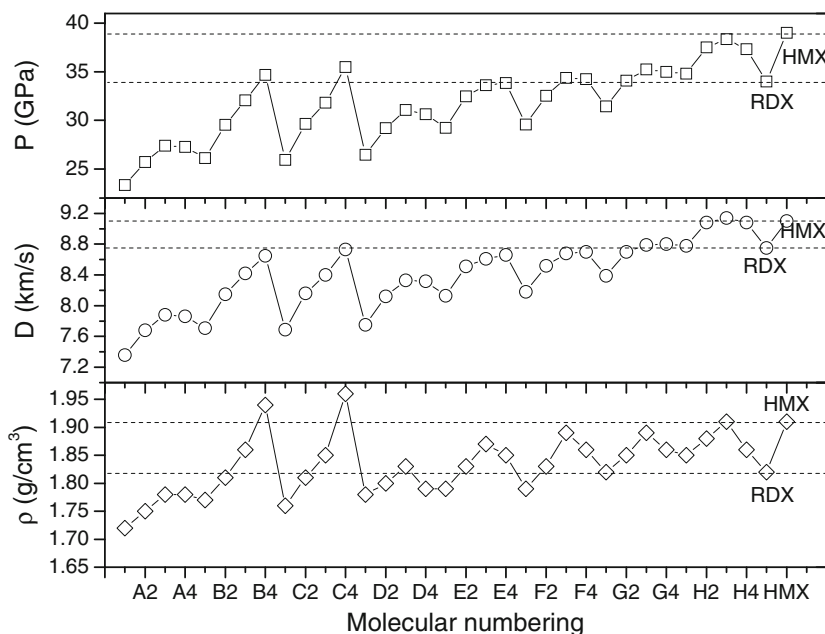
compound has the largest ρ value among the same series, while for D, E, F, G, and H, the NF2-substituted compounds have the highest ρ. This indicates that the effect of the same substituent on ρ of different compounds is determined by the characteristics of the parent molecular framework. As the numbers of nitrogen atoms in the nitrobenzene ring increase, the ρ values of the unsubstituted, NO$_2$-substituted, and NF$_2$-substituted compounds enhance gradually. But for the ONO$_2$-substituted compounds, the situation is complicated. C4 has one nitrogen atom in the nitrobenzene ring, but it has the highest ρ value among the ONO$_2$-substituted compounds. Although H4 has three nitrogen atoms in the nitrobenzene ring, it has a lower ρ value than B4 and C4, and the same ρ as G4 and F4. In addition, the ρ of compounds with different substitution positions of the nitrogen atoms but the same substituent were found to be close to each other, indicating that the substitution positions of the nitrogen atoms do not produce an evident effect on the ρ value.

As seen in Table 4, all the substituted compounds have higher Q values than the corresponding unsubstituted compounds. As the number of nitrogen atoms in the nitrobenzene ring increases, the Q of the title compounds is enhanced, except for B1, C1 and D1. The effects on their Q values of the substitution positions of nitrogen atoms in the nitrobenzene rings are small. OB is another of the most important criterion for selecting potential HEDCs. The values in Table 4 show that, by and large, the higher the oxygen balance is, the larger the D and P values are, and the better the performance of the title compound. Our results show that the –ONO$_2$ group is a good substituent for improving the oxygen balance of the title compounds. However, it is clear that too much oxygen is not favorable for advancing the explosive performance of HEDCs. The primary reason is that the too much oxygen will produce O$_2$, which takes away a great deal of energy. Therefore, it is best to keep the value of oxygen balance at around zero when designing HEDCs.

The effects on their densities of different substituent and nitrogen atoms in the nitrobenzene ring substituents make the title compounds have different D and P values. All the substituted compounds have larger D and P values than the corresponding unsubsituted compounds. The NF$_2$-substituted compounds have the highest D and P in the same series. This indicates that the –NO$_2$, –ONO$_2$, or –NF$_2$ group are an effective unit for improving the detonation properties of the title compounds, especially the –NF$_2$ group. The greater the nitrogen atoms number in the compound is, the higher the D and P values. The effects of substitution positions of nitrogen atoms in the nitrobenzene rings on D and P are small unless two nitrogen atoms are adjacent and form new N–N bonds in the rings. This is because N–N bonds contain more energy than C–C and C–N bonds. This shows that

increasing the number of nitrogen atoms and making them form N–N bonds is an effective way to improve the detonation properties of energetic compounds.

Figure 4 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 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. 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 [35]. It is not surprising that many of the title compounds have relatively poor detonation properties. This is because they do not have a sufficient number of

Table 5 Bond dissociation energies (BDE, kJ mol^{-1}) of the weakest bonds for the title compounds

Compound	BDE^0	BDE$_{ZPE}$
A1	117.5	100.8
A2	115.9	99.6
A3	94.1	81.8
A4	56.6	33.9
B1	343.9	325.2
B2	121.0	104.6
B3	87.8	75.9
B4	75.6	60.8
C1	342.0	323.7
C2	116.0	99.5
C3	102.9	90.2
C4	79.5	67.8
D1	116.7	100.3
D2	98.2	83.0
D3	79.5	67.8
D4	66.0	51.9
E1	346.6	323.9
E2	120.8	104.8
E3	111.9	97.3
E4	72.4	59.5
F1	121.9	104.9
F2	104.0	85.2
F3	75.1	63.1
F4	52.5	38.5
G1	162.6	146.5
G2	101.4	85.2
G3	99.0	84.6
G4	65.0	51.0
H1	333.9	315.9
H2	125.6	108.6
H3	96.6	84.4
H4	72.6	57.4

oxygens to oxidize all of the carbons. Only C4, G2, G3, G4, H1, H2, H3, and H4 have D and P values comparable with RDX. H2, H3, and H4 have comparable detonation performance with HMX. If these eight compounds could be synthesized, they would have good performances. Thus, further investigations are still needed.

Thermal stability

The BDE for each possible trigger bond is often a key factor in investigating the pyrolysis mechanism for an energetic compound. Generally, the smaller the BDE for breaking a bond, the more easily the bond is broken. Therefore, BDE provides useful information for understanding the stability of energetic compounds. It should be pointed out that we select the weakest N8–N9 bond or N9–C10 bond as the breaking bond based on the bond overlap populations to calculate BDE. Table 5 lists the bond overlap populations and BDE of the weakest bonds for the title compounds. It was found that the BDE values without ZPE corrections (BDE^0) are larger than those with ZPE corrections (BDE_{ZPE}). However, the variation order of the BDE is not affected by ZPE corrections. In addition, the BDEs of many compounds indicate that, except for the unsubstituted compounds, their bonds are extremely weak. When the –NO_2, –NF_2, or –ONO_2 groups are attached to the parent compounds, their BDE_{ZPE} values decrease clearly, especially for the –ONO_2 group. Thus, it may be deduced that the substitution of different substituents reduces the stability of the title compounds. The effects of different substitution positions and numbers of nitrogen atoms in the nitrobenzene ring on BDE_{ZPE} are complicated. For example, the number of nitrogen atoms in B2 is more than that of A2 and less than that of E2, but B2 has higher BDE_{ZPE} than both A2 and E2. This indicates that their effects on the stability of the title compounds are coupled with the substituent and parent molecular framework.

It is interesting to note that the N8–N9 bond of A2 has higher BDE_{ZPE} than that of A4, whereas the former has a smaller bond order than the latter. The same is true of A3 and A4. This indicates that the variation trend of BDE_{ZPE} is inconsistent with that of the bond order for the weakest bond in a series under the influence of different substituents. A similar situation is also seen in the other series. The initial step in thermal decompositions should be via ring cleavage. Therefore, to judge the thermal stability of the title compounds not simply by bond order, it is necessary to depend on the BDE. By analyzing the structure of the compounds, it is easy to see that substitution with different substituents would weaken the total electron cloud distribution, thus decreasing the stability of the compounds. As suggested by Chung et al. [50], a molecule should dissociate a barrier of more than 20 kcal/mol (83.72 kJ/mol) in order to be

considered as a potential candidate for HEDCs. Therefore, it can be concluded that A1-2, B1-2, C1-3, D1, E1-3, F1-2, G1-3, and H1-3 are potential candidates for new HEDCs.

Conclusions

In this work, we studied the HOFs, electronic structure, energetic properties, and thermal stabilities of a series of 1,4-bis(1-azo-2,4-dinitrobenzene)-iminotetrazole derivatives with different substituents, different substitution positions and different numbers of nitrogen atoms in the nitrobenzenes using the DFT-B3LYP method. Among each series, all the substituted compounds have higher HOFs than their parent compounds. As the numbers of nitrogen atoms in the nitrobenzene ring increase, the HOFs of the derivatives with the same substituent rise gradually. Replacing carbon atoms in the nitrobenzene with nitrogen atoms to form N–N bonds is very helpful for improving their HOFs.

Most of the substituted compounds have higher HOMO–LUMO gaps than the corresponding unsubstituted ones. The effects of different substituents on the energy gaps are coupled to those of the substitution positions and numbers of nitrogen atoms in the nitrobenzene ring.

The substitution of the –NO_2, –NF_2, or –ONO_2 group and an increase in the numbers of nitrogen atoms in the nitrobenzene rings are useful for enhancing detonation performance. An analysis of the BDE of the weakest bonds indicates that the substituents' substitution is not favorable for improving thermal stability. Considering detonation performance and thermal stability, G2, G3, H1, H2, and H3 may be considered as potential candidates for HEDCs.

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