

# Looking for high energy density compounds among polynitraminepurines

Ting Yan · Guangdong Sun · Weijie Chi · Butong Li · Haishun Wu

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**Abstract** A series of purine derivatives with nitramine groups are calculated by using density functional theory (DFT). The molecular theory density, heats of formation, bond dissociation energies and detonation performance are investigated at DFT-B3LYP/6-311G\*\* level. The isodesmic reaction method is employed to calculate the HOFs of the energies obtained from electronic structure calculations. Results show that the position of nitramine groups can influence the values of HOFs. The bond dissociation energies and the impact sensitivity are analyzed to investigate the thermal stability of the purine derivatives. The calculated bond dissociation energies of ring-NHNO<sub>2</sub> and NH-NO<sub>2</sub> bond show that the NH-NO<sub>2</sub> bond should be the trigger bond in pyrolysis processes. The H<sub>50</sub> of most compounds are larger than that of CL-20 and RDX.

**Keywords** Bond dissociation energy · Density functional theory · Detonation performance · Heats of formation · Isodesmic reaction · Polynitraminepurines

## Introduction

Research on new high-energy density compounds (HEDCs) to meet the future usage prospect in the fields of fuel, explosives and propellants has become one of the most activated regions and seems to be never ending in recent years [1–6]. Nitrogen-

rich heterocycles (such as pyrazine, pyrazole, tetrazine, tetrazole, and so on) have become the ideal building blocks for HEDCs owing to their novel properties including high density, high positive heat of formation, high thermal stability and low sensitivity [7, 8]. In addition, nitrogen-rich heterocycles are usually insensitive to the static, friction and impact because  $\pi$  aromatic bonding located in these heterocycles stabilizes the molecule. Typical examples of these well-known explosives are TNT (2,4,6-trinitrotoluene), TATB (1,3,5-triamino-2,4,6-trinitrobenzene), FOX-7(1,1-diamino-2,2-dinitroethylene), LLM-105(2,6-diamino-3,5-dinitropyrazine-1-oxide) and so on. Nowadays, more works have concentrated on purine in biology [9] because it is a mother frame for many important biologic compounds: guanine, xanthine adenine, hypoxanthine, theobromine, and so on. In fact, amino-substituted purine and nitro-substituted purine have been synthesized in experiment [10]. At the same time, it is noticed that purine has a nitrogen content above 46 %, and it is also fascinating because four hydrogen atoms are located at the ring and can be substituted by functional groups. In addition, our previous studies have shown that tetranitropurine is finally recommended as the candidate of HDECs [11]. When purine are designed through substituting the hydrogen atoms on it for nitro and amino groups [12], their performances have been calculated in detail and some derivatives have good explosive performance. These theoretical and experimental results show that purine may be a prominent parent structure in designing high energy molecules. So, it is necessary that purine derivatives are studied more in depth. To obtain novel high-density and high-energy materials, scientists have managed to attach energetic groups (such as nitro, nitrate, and nitramine) in energetic nitrogen-rich compounds. The superiority of nitramine ( $\text{-NHNO}_2$ ) is found in that the high nitrogen content can lead to high crystal density and heats of formation, which is associated with increased denotation performance. Furthermore, nitramine groups have been widely studied as ingredients of propellants and explosives [13–16].

Ting Yan and Guangdong Sun contributed equally to this work.

T. Yan · W. Chi · B. Li (✉) · H. Wu  
School of Chemistry and Material Science, Shanxi Normal University, 041004, Linfen, China  
e-mail: butong.lee@gmail.com

G. Sun  
Department of Nephropathy, Second Hospital of Jilin University, 130041, Changchun, China

In this work, we have managed to attach nitramine groups ( $-\text{NHNO}_2$ ) to look for some new HEDCs candidates in the purine derivatives.

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 HEDCs. The density ( $\rho$ ) of a compound is the most important and decisive parameter in evaluating its performance as an energetic material. In addition, detonation properties, including detonation velocity ( $D$ ) and detonation pressure ( $P$ ), are also important parameters for judging the potential of a compound to be an HEDC. Owing to the difficulties in the synthesis of the molecules under consideration, computer tests become an effective and safe way.

In this paper, we report a systematic study of the HOFs and detonation properties of a series of purine derivatives by using density functional theory (DFT). The HOFs of the derivatives were calculated by designing isodesmic reactions. Detonation velocities and pressures were predicted using the calculated HOFs and densities. It is expected that our results can provide useful information for the molecular design of novel HEDCs.

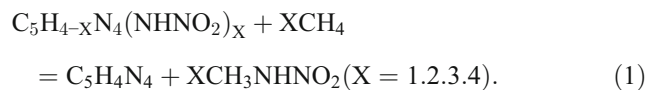
The remainder of this paper is organized as follows. A description of our computational method is given in “Computational methods”. The results and discussion are presented in “Results and discussion”, followed by a summary in “Conclusions”.

## Computational methods

Geometry optimization of the molecular structures was fully optimized without symmetry restriction using density functional theory (DFT) [17, 18] with the Becke's three-parameter exchange functional plus the correlation functional of Lee, Yang, and Parr (B3LYP) [19, 20], along with the 6-311G\*\* basis set [21], in the Gaussian 03 program package [22]. This method/basis set combination has long been considered reliable for predicting thermodynamic properties. Each optimized structure was checked to ensure that there was a local energy minimum on the potential energy surface by vibrational analyses. Figure 1 shows the object molecular.

In this paper, the predictions of HOFs adopt the DFT-B3LYP method with 6-311G\*\* basis set via designed isodesmic reactions. The isodesmic reaction must comply with the bond separation reaction (BSR) rule. That is to say the molecule is broken down into two heavy-atom molecules containing the same component bond. The method of isodesmic reactions has been employed very successfully to decrease the calculation errors, in which the numbers of all kinds of bonds are

kept invariable. These isodesmic reactions that were used to calculate the HOFs of all purine derivatives at 298 K are as follows:



For reaction, the heats of formation at 298 K by Eq. (3) can be deduced from

$$\sum \Delta_f H_{(g,p)}^0 - \sum \Delta_f H_{(g,r)}^0 \quad (2)$$

$$= \sum E(298\text{K}, p) - \sum E(298\text{K}, r) + \Delta(PV)$$

$$= \sum E(0\text{K}, p) - \sum E(0\text{K}, r) + \Delta ZPE + \Delta H_T + \Delta nRT. \quad (3)$$

Where  $\sum \Delta_f H_{(g,p)}^0$  and  $\sum \Delta_f H_{(g,r)}^0$  are the heats of formation of product and reactant at 298 K, respectively. The experimental thermodynamic parameters of  $\text{C}_5\text{H}_4\text{N}_4$  and  $\text{CH}_4$  are taken from reference [23]. In addition, as to the needed reference compounds  $\text{CH}_3\text{NHNO}_2$ , their HOFs were evaluated using the G2 theory. Those data mentioned above are listed in Table 1.  $\sum E(0\text{K}, p)$  corresponds to the energies sum of products at 0 K,  $\sum E(0\text{K}, r)$  is sum of the energies of reactant at 0 K.  $\Delta ZPE$  is sum of the zero point correction energies of products and reactants.  $\Delta H_T$  is the thermal correction value,  $\Delta(PV)$  equal  $\Delta nRT$  for ideal gas, and it will be zero because  $\Delta n$  is zero in an isodesmic reaction.

The HOF in solid state  $[\Delta H_f(s)]$  can then be estimated by Eq. (4) using Hess' law of constant heat summation [24, 25]:

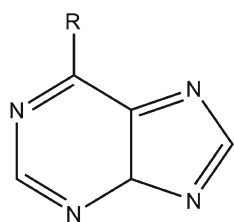
$$\Delta H_f(s) = \Delta H_f(g) - \Delta H_{\text{sub}}. \quad (4)$$

Where  $\Delta H_{\text{sub}}$  is the heat of sublimation evaluated by the Eq. (5) suggested by Rice and Politzer et al. [26, 27]:

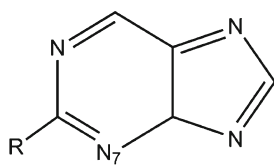
$$\Delta H_{\text{sub}}(298\text{K}, \text{kcal/mol}) = \alpha_1(\text{SA})^2 + \beta_1(\nu\sigma_{\text{tot}}^2)^{0.5} + \gamma_1 \quad (5)$$

Where SA is the surface area of the isosurface of electron density 0.001 e/Bohr<sup>3</sup> molecules calculated using a selfcompiled program. The values of coefficients  $\alpha_1$ ,  $\beta_1$ , and  $\gamma_1$  are taken from ref [26].

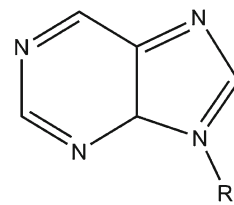
Detonation velocity ( $D$ ) and detonation pressure ( $P$ ), the most important parameters for evaluating the detonation characteristics of HEDCs, were calculated using the Kamlet-Jacobs (K-J) formulas [28, 29] shown as follows, which have been verified by many studies



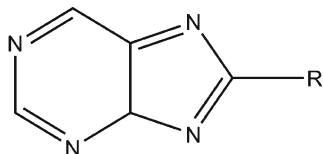
A1. 6-nitramine-purine



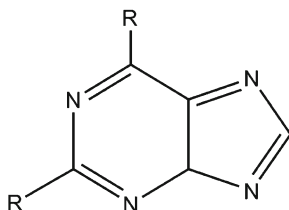
A2. 2-nitramine-purine



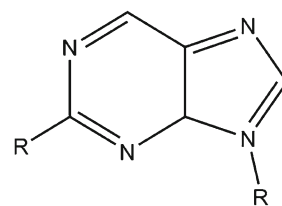
A3. 9-nitramine-purine



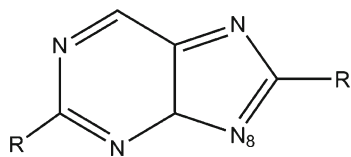
A4. 8-nitramine-purine



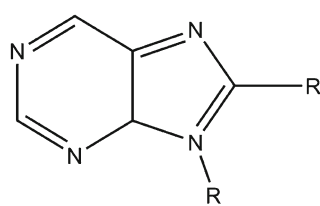
A4. 4-nitramine-purine



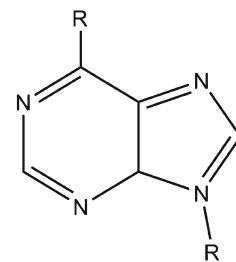
B1. 2,9-dinitramine-purine



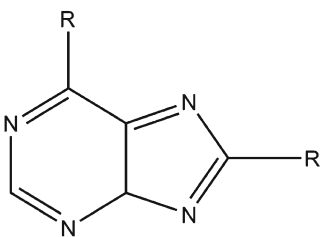
B2. 2,8-dinitramine-purine



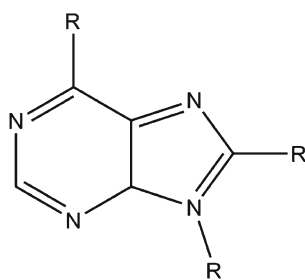
B3. 8,9-dinitramine-purine



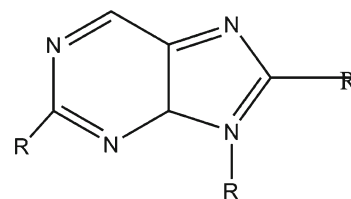
B5. 6,9-dinitramine-purine



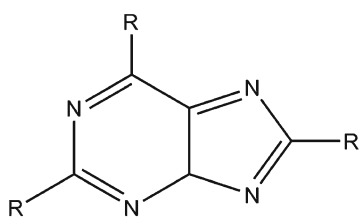
B6. 6,8-dinitramine-purine



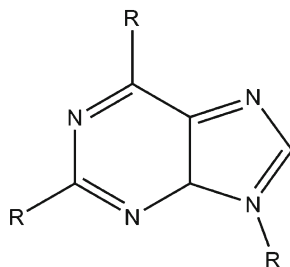
C1. 6,8,9-trinitramine-purine



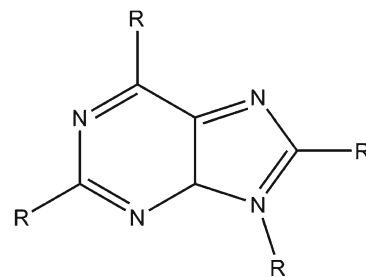
C2. 2,8,9-trinitramine-purine



C3. 2,6,8-trinitramine-purine



C4. 2,6,9-trinitramine-purine



D1. 2,6,8,9-tetranitramine-purine

**Fig. 1** Molecular frameworks of polynitroaminpurines [R=–NHNO<sub>2</sub>]

[16, 30, 31] to be suitable for predicting the detonation properties of CHNO explosives.

$$D = 1.01 \left( N \bar{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30\rho) \quad (6)$$

$$P = 1.558\rho^2 N \bar{M}^{1/2} Q^{1/2} \quad (7)$$

Where each term in Eqs. (6) and (7) is defined as follows:  $D$ , the detonation velocity (km/s);  $P$ , the detonation pressure (GPa);  $N$ , the moles of detonation gases per gram explosive;  $\bar{M}$ , the average molecular weight of these gases;  $Q$ , the heat of detonation (cal/g); Here, the parameters  $N$ ,  $\bar{M}$ , and  $Q$  were calculated according to the largest exothermic principle [32]. That is, all of the  $N$  atoms end up in  $N_2$  molecules, while the  $O$  atoms initially react with  $H$  atoms to give  $H_2O$  bar forming  $CO_2$  with the  $C$  atom. If the number of  $O$  atoms present in the molecule is greater than the number needed to oxidize all of the  $H$  and  $C$  atoms, the redundant  $O$  atoms will combine to form  $O_2$ . On the other hand, if the number of  $O$  atoms is insufficient to allow full oxidation of the  $H$  and  $C$  atoms, the remaining  $H$  atoms will be incorporated into  $H_2O$ , while the remaining  $C$  atoms will exist as solid-state  $C$ .

Moreover, the corresponding  $D$  and  $P$  values can be evaluated on the basis of the  $\rho$  and  $Q$  values. The density of the explosives  $\rho$  was replaced by the crystal theoretical density ( $\rho_c$ ) by the following equation:

$$\rho_c = - \frac{M}{V(0.001)} \quad (8)$$

where the density of each compound was predicted from the molecular volume divided by the molecular volume divided by the molecular weight, which was obtained by finding the arithmetic average of 100 single-point molar volumes, defined as the volume of the 0.001 electrons/Bohr<sup>3</sup> electron density envelope and computed by Monte Carol intergration [33]. However, the results obtained using this equation may lead to significant errors for some systems. To predict their detonation properties, the modified K-J equations based on the calculation results of quantum chemistry were recommended [30, 31, 34]. An electrostatic interaction correction for improved crystal density prediction has also been promoted by Politzer et al. [25, 35]. The method is shown by Eqs. (9) – (13).

$$\rho_{\text{crystal}} = \alpha_1 \left( \frac{M}{V_m} \right) + \beta_1 (v\sigma_{\text{tot}}^2) + \gamma_1 \quad (9)$$

$$\sigma_{\text{tot}}^2 = \sigma_+^2 + \sigma_-^2 = \frac{1}{m} \sum_{i=1}^m \left[ V^+(r_i) - \bar{V}_S^+ \right]^2 + \frac{1}{n} \sum_{j=1}^n \left[ V^-(r_j) - \bar{V}_S^- \right]^2 \quad (10)$$

$$v = \frac{\sigma_+^2 \sigma_-^2}{[\sigma_{\text{tot}}^2]^2} \quad (11)$$

$$\bar{V}_S^+ = \frac{1}{m} \sum_{i=1}^m V^+(r_i) \quad (12)$$

$$\bar{V}_S^- = \frac{1}{n} \sum_{j=1}^n V^-(r_j) \quad (13)$$

Here, the values of coefficients  $\alpha_1$ ,  $\beta_1$ , and  $\gamma_1$  are taken from ref. [36].  $v$  is the degree of balance between the positive and negative charges on the isosurface.  $V(r)$  is electrostatic potential,  $V(r_i)$  is the value of  $V(r)$  at any point  $r_i$  on the surface,  $V^+(r_i)$  and  $V^-(r_j)$  represent the positive and negative value of  $V(r)$  on the surface,  $\bar{V}_S^+$  and  $\bar{V}_S^-$  are their averages,  $\sigma_{\text{tot}}^2$  is the total variance.

The strength of bonding, which can be evaluated by bond dissociation energy (BDE), is fundamental to understanding chemical processes. BDE is the energy required for a bond homolysis and is commonly denoted as the difference between the total energies of the radical products and reactants. At 0 K, the homolytic BDE can be given in terms of Eq. (14).

$$\text{BDE}_0(A-B) = E_0(A\cdot) + E_0(B\cdot) - E_0(A-B) \quad (14)$$

Where  $\text{BDE}_0(A-B)$  is the BDE of the bond  $A-B$ ;  $E_0(A-B)$ ,  $E_0(A\cdot)$  and  $E_0(B\cdot)$  are the total energies of the parent compound and the corresponding radicals, respectively. The characteristic height ( $H_{50}$ ) that can also reflect the impact sensitivity and stability of the compounds was estimated using the Eq. (15) suggested by Politzer et al. [36]:

$$H_{50} = \alpha_2 \sigma_+^2 + \beta_2 v + \gamma_2. \quad (15)$$

Where the values of coefficients  $\alpha_2$ ,  $\beta_2$ , and  $\gamma_2$ , are taken from reference [37].

## Results and discussion

### Heats of formation

The basic structures are presented in Fig. 1. Table 1 lists the total energies, zero-point energies and the values of thermal correction at the B3LYP/6-311G\*\* level for three reference compounds being enlisted in the isodesmic reactions (1). The experimental HOFs of reference compounds CH<sub>4</sub> are taken from reference [38]. The accurate value of  $\Delta H_f$  for CH<sub>3</sub>NHNO<sub>2</sub> is obtained using G2 method from reference [5]. Table 2 presents the calculated total energies, the zero-point energies, and the values of thermal corrections for purine derivatives with -NHNO<sub>2</sub> group, and the values of HOFs obtained via Eq. (2). Previous studies showed that the theoretically predicted values of HOFs were in good agreement with experiments by choosing appropriate reference compounds in the isodesmic reactions. An efficient strategy of reducing errors of HOFs is to keep bonds unbroken as much as possible. This approach has been proven to be reliable. On that basis, data in Table 2 are supposed to be credible, although the experimental values of HOFs are unavailable for comparison.

As shown in Table 2, we find that the -NHNO<sub>2</sub> derivatives of purine have positive HOFs. And with the number of substituted groups increasing, the HOFs of polynitraminepurines derivatives increase, too. In addition, differences can be found between the HOFs of isomers, revealing that the HOF is also affected by the special relative positions of the substituted groups. This can be illustrated by the HOFs of isomers with the same number of -NHNO<sub>2</sub> groups, respectively. For instance, the HOFs of A1, A2 and A4 of four mono-substituent NHNO<sub>2</sub> isomers are close to each other, while the HOF of the A3 is higher than the other three derivatives. The HOFs of six di-substituent -NHNO<sub>2</sub> isomers show that the HOFs values of B2, B4, B5 are larger than B1, B3, and B6. Similar results can be found in the three substituted groups, from which we can find that the HOFs values is larger when the substituents attached to the N atoms than to the C atoms. In other words, the compounds are more stable when the substituents are attached to the C atom of purine than the N atom.

**Table 1** Total energy ( $E_0$ , a.u.), zero-point energies (ZPE, a.u.), values of thermal correction ( $H_T$ , a.u.), and heats of formation (HOF, kJ mol<sup>-1</sup>) of the reference compounds

Compound	$E_0$	ZPE	$H_T$	HOF
CH <sub>3</sub> NHNO <sub>2</sub>	-300.43446	0.06722	0.00611	-15.2 <sup>a</sup>
C <sub>5</sub> H <sub>4</sub> N <sub>4</sub>	-412.04628	0.09494	0.00664	18.00
CH <sub>4</sub>	-40.53375	0.04459	0.00381	-74.40 <sup>a</sup>

<sup>a</sup> Data experimental values taken from refs [5, 38]

### Electronic structure

Many studies indicated roughly that the HOMO-LUMO energy gap is a sign of chemical stability [39, 40]. The smaller the energy gap, the lower the chemical stability. Table 3 lists the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and the energy gaps ( $\Delta E_{\text{LUMO-HOMO}}$ ), which were obtained by NBO analyses at the B3LYP/6-311G\*\* level. From Table 3, it is found that the  $\Delta E_{\text{LUMO-HOMO}}$  values decrease as the number of nitramine group increase. A possible event is the stability possible decreases generally as the number of substituents increase. In addition, all of the polydifluoroaminopurines have lower  $\Delta E_{\text{LUMO-HOMO}}$  values than the purine parent body. It is seen that the  $\Delta E_{\text{LUMO-HOMO}}$  values are different with different positions of substituted groups. For the four mononitraminepurine isomers, the  $\Delta E_{\text{LUMO-HOMO}}$  value of A4 (0.17253 a.u.) is slightly smaller, while that of A1 (0.18626 a.u.) is slightly larger, indicating the latter is more stable than the former. For the six di-nitraminepurine isomers, the  $\Delta E_{\text{LUMO-HOMO}}$  value of B5 is the largest among the six isomers, thus indicating that it is more stable than the other five isomers. For series C, the stabilities of C1, C2, and C3 are more stable than C4. Furthermore, we found that the  $\Delta E_{\text{LUMO-HOMO}}$  value of most polynitraminepurines are much higher than that of (triamino-trinitrobenzene) TATB (0.1621 a.u.), which means most polynitraminepurines are not more sensitive than TATB. It is worth noting that the stability refers here to any chemical or photochemical process involving an electron transfer or jump [41, 42]. So the thermodynamic stabilities of the title compounds are not simply judged via  $\Delta E_{\text{LUMO-HOMO}}$ .

### Pyrolysis mechanism and stability

Another main concern for explosives is whether they are kinetically stable enough to be used practically. Research on the bond dissociation energies (BDE) are important and essential for investigating the pyrolysis mechanism and sensitivity. Generally, a smaller BDE a bond has, more easily the bond is broken.

Previous research works have shown that the bond order may be used as a measure of bonding capability between two atoms, and as a measure of overall bond strength between two atoms [13, 34]. A high value for the bond order indicates a covalent bond, while a low value shows an ionic nature. In this paper, Wiberg bond index (WBI) is chosen as the symbol of the molecular stability. A smaller WBI generally indicates a weaker bond. We obtained the bond orders of the polynitraminepurines by natural bond orbital analyses (NBO). To explore the initial step in the

**Table 2** Total energies ( $E_0$ , a.u.), zero point energies (ZPE, a.u.), thermal correction values ( $H_T$ , a.u.), heat of formation of the derivatives of purine at the B3LYP/6-311G\*\* level

Compound	E	$E_{ZPE}$	$H_T$	$\Delta H_{sub}$	$\Delta H_{f(g)}$	$\Delta H_{f(s)}$
A1	-671.95632	0.11438	0.01042	127.94	48.21	-79.73
A2	-671.95746	0.11413	0.01041	127.46	44.54	-82.92
A3	-671.90651	0.11328	0.01040	120.33	176.07	55.74
A4	-671.94296	0.11292	0.00918	134.62	76.20	-58.42
B1	-931.86496	0.13334	0.01421	156.43	80.88	-75.55
B2	-931.81508	0.13231	0.01425	165.06	209.26	44.20
B3	-931.86846	0.13334	0.01419	156.42	71.63	-84.79
B4	-931.81198	0.13224	0.01438	148.12	217.52	69.40
B5	-931.81494	0.13233	0.01444	161.63	210.16	48.53
B6	-931.86605	0.13333	0.01434	159.76	78.35	-81.41
C1	-1191.72088	0.15201	0.01788	178.46	250.88	72.42
C2	-1191.72594	0.15195	0.01788	194.89	237.43	42.54
C3	-1191.77599	0.15223	0.01831	195.02	107.90	-87.12
C4	-1191.72933	0.15173	0.01810	187.73	228.55	40.82
D1	-1451.62686	0.17015	0.02238	251.97	296.68	44.71

pyrolysis route, two possible initial steps in the pyrolysis route of polynitraminepurines were considered: (1) ring-NHNO<sub>2</sub> bond; (2) the NH-NO<sub>2</sub> bond. It should be pointed out that the weakest bond was selected as the breaking bond following the principle of the smallest bond order (PSBO) among the same kind of bonds [43].

The values of BDE are listed in Table 4. Compared to BDE<sub>NH-NO<sub>2</sub></sub>, the BDE<sup>0</sup><sub>NH-NO<sub>2</sub></sub> values shift downward by ca.

**Table 3** Calculated HOMO and LUMO energies (in a.u.) as well as the energy gaps ( $\Delta E_{LUMO-HOMO}$ ) of the title compounds, calculated at the B3LYP/6-311G\*\* level

Compound	$E_{LUMO}$	$E_{HOMO}$	$\Delta E_{LUMO-HOMO}$
C <sub>5</sub> H <sub>4</sub> N <sub>4</sub>	-0.05496	-0.25743	0.20247
A1	-0.0799	-0.26616	0.18626
A2	-0.07536	-0.2607	0.18534
A3	-0.08815	-0.27148	0.18333
A4	-0.08728	-0.25981	0.17253
B1	-0.09221	-0.26496	0.17275
B2	-0.09612	-0.2735	0.17738
B3	-0.10605	-0.26012	0.15407
B4	-0.10626	-0.28411	0.17785
B5	-0.09479	-0.27586	0.18107
B6	-0.10833	-0.26349	0.15516
C1	-0.10863	-0.28489	0.17626
C2	-0.11757	-0.27815	0.16058
C3	-0.1129	-0.26162	0.14872
C4	-0.10344	-0.27741	0.17397
D1	-0.11524	-0.27134	0.15610
TATB	-0.10280	-0.26480	0.16210

16–19 kJ mol<sup>-1</sup>. For the same molecule, the BDE<sub>NH-NO<sub>2</sub></sub> value is smaller than BDE<sub>Ring-NHNO<sub>2</sub></sub> markedly, and indicates the trigger bond of polynitraminepurines should be the BDE<sub>NH-NO<sub>2</sub></sub> bond in the skeleton. The NH-NO<sub>2</sub> bonds are very weak, particularly the one listed for A4, B4, C4 and D1. This may lead to very sensitive compounds. However, clearly bond dissociation energies are not the only factor in determining sensitivities, but they may play a role, particularly in molecules with very weak trigger linkages. We must mention that bond dissociation energies are a possible factor in determining stabilities and sensitivities, but not the only factor.

The impact sensitivity also reflects the stability of a compound and it can be evaluated by the characteristic height  $H_{50}$ , which has been predicted in this study using the method described in reference [37]. This method is widely studied and seems to be reliable [44, 45]. The predicted  $H_{50}$  of famous RDX (29 cm), HMX (33 cm), CL-20 (12 cm) is found to be in good agreement with the corresponding experimental values [44]. The obtained results of  $H_{50}$  are also collected in Table 4. It is known that greater  $H_{50}$  a compound has, less sensitive the compound is. From Table 4, the values of  $H_{50}$  are in the range of 29–50 cm, most of the title compounds have high  $H_{50}$  except for C1, whose sensitivities are lower than that of RDX. It is found that absolutely most of the title compounds are less sensitive than C1. Moreover, the conclusion from  $H_{50}$  is not very consistent with that from BDE, for example, the BDE of NH-NO<sub>2</sub> bond is the smallest, but it is not the case for  $H_{50}$ , which supports the proposal of Politzer that the correlation between bond strength and impact sensitivity is not general but limited within certain classes of molecules [46].

**Table 4** Calculated Wiberg bond index (WBI) of part bonds, bond dissociation energies (kJ mol<sup>-1</sup>) and characteristic height (H<sub>50</sub>, cm) of the trigger bonds at the UB3LYP/6-311G\*\* level

Compound	P <sub>NH-NO<sub>2</sub></sub>	BDE <sub>Ring-NHNO<sub>2</sub></sub>	BDE <sup>0</sup> <sub>Ring-NHNO<sub>2</sub></sub>	P <sub>NH-NO<sub>2</sub></sub>	BDE <sub>NH-NO<sub>2</sub></sub>	BDE <sup>0</sup> <sub>NH-NO<sub>2</sub></sub>	H <sub>50</sub>
A1	1.0422	406.84	385.32	0.9796	148.39	128.72	49
A2	1.0348	421.12	399.50	0.9987	151.78	132.53	49
A3	1.0508	284.15	258.90	0.9082	122.04	105.08	33
A4	1.0657	408.59	390.23	0.9905	102.14	85.75	32
B1	1.0429	417.08	395.93	0.9696	144.07	124.91	42
B2	1.0461	415.96	394.75	0.9015	120.38	103.56	41
B3	1.0365	420.10	398.61	0.9922	148.53	129.12	50
B4	1.0432	422.70	402.71	0.8905	104.43	88.39	46
B5	1.0497	267.55	244.42	0.9065	122.31	105.47	39
B6	1.0595	449.01	427.49	0.9906	146.71	127.70	49
C1	1.0320	431.46	409.87	0.8711	117.51	100.42	29
C2	1.0328	446.27	423.87	0.8989	131.75	113.73	47
C3	1.0526	419.75	398.72	0.9897	144.65	126.18	42
C4	1.0533	279.41	255.38	0.8647	116.89	100.23	37
D1	1.0542	411.07	390.45	0.8406	107.81	91.55	41

### Explosive performance

Table 5 lists the predicted detonation velocity (D) and pressure (P) of polynitraminepurines combined with the

**Table 5** Predicted detonation properties of the polynitraminepurines and TNT<sup>a</sup>, RDX<sup>a</sup>, and HMX<sup>a</sup> calculated at the B3LYP/6-311G\*\* level

Copmound	ρ (g/cm <sup>3</sup> )	Q	D	P
A1	1.73	215.25	4.97	10.37
A2	1.69	211.01	4.88	9.90
A3	1.64	395.12	5.68	13.31
A4	1.73	243.54	5.07	10.70
B1	1.76	798.31	7.17	22.18
B2	1.76	917.56	7.35	23.08
B3	1.81	789.11	7.31	23.50
B4	1.72	942.65	7.47	24.08
B5	1.76	921.87	7.37	23.24
B6	1.81	792.47	7.27	23.10
C1	1.79	1262.69	8.37	31.11
C2	1.84	1238.89	8.38	31.32
C3	1.83	1135.59	8.20	30.01
C4	1.83	1237.52	8.46	32.16
D1	1.90	1455.66	8.90	35.79
TNT <sup>a</sup>	1.63(1.64)	1376.95	7.06(6.95)	20.78(19.10)
RDX <sup>a</sup>	1.78(1.82)	1591.03	8.87(8.75)	34.67(34.00)
HMX <sup>a</sup>	1.88(1.91)	1633.90	9.28(9.10)	39.19(39.00)

<sup>a</sup>Data in the parentheses are the experimental values taken from ref [47]

<sup>b</sup>The calculated values of RDX and HMX taken from ref [31]

experimental detonation parameters of TNT, RDX and HMX for comparison.

As is evident in Table 5, the ρ values of polynitraminepurines become larger as the number of -NHNO<sub>2</sub> groups increases. The largest ρ value and the smallest one are 1.90 and 1.64 (g cm<sup>-3</sup>), respectively. Furthermore, for the isomers with the same number of substituted groups, the explosive performances are slightly different. Compared to the conventional explosive, when the number of the -NHNO<sub>2</sub> substituent group attains two, the explosive performances of the title compounds would exceed TNT. The explosive properties of four trinitraminepurines isomers are similar to that of RDX. Only one of the proposed compounds (D1) is predicted to have detonation properties superior to RDX.

### Conclusions

From the calculations and analyses mentioned above, the following conclusions can be drawn:

1. The HOFs of the title compound increase almost constantly with each nitramine group attached to the purine skeleton. The HOF discrepancies among isomers are caused by the relative positions of substituent groups, from which we found that when -NHNO<sub>2</sub> attached to the N atom of derivatives, the heat of formation values are bigger than -NHNO<sub>2</sub> attached to the C atom of derivatives.
2. The NH-NO<sub>2</sub> bond is confirmed as the trigger bond during the pyrolysis initiation process of polynitraminepurines through the calculations of bond dissociation energies.

According to the estimated impact sensitivity, absolutely most of the title compounds are more stable than CL-20 and RDX.

- The calculated molecular densities, detonation velocities, and detonation pressures of the polynitraminopurines indicate that nitramino groups play a very important role in enhancing molecular density and detonation performances. The calculated values of D and P for the isomers are close. D and P increase as the number of  $-\text{NHNO}_2$  groups vary from one to four.
- As is well-known, a HEDCs candidate with superior performance not only has excellent detonation properties but also good stabilities. On the basis of our calculations, taking all factors into consideration, HEDCs may be considered as the potential candidates of HEDCs based on good detonation performance (D and P), thermal stability (BDE) and  $H_{50}$  value. These compounds are worthy of further synthesis and investigation. Our results should also provide some useful information for the molecular design of novel HEDCs.

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