

# Computational studies on polynitropurines as potential high energy density materials

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**Abstract** As part of a search for high energy density materials (HEDMs), a series of purine derivatives with nitro groups were designed computationally. The relationship between the structures and the performances of these polynitropurines was studied. Density functional theory (DFT) at the B3LYP/6-311G\*\* level was employed to evaluate the heats of formation (HOFs) of the polynitropurines by designing anisodesmic reaction method. Results indicated that the HOFs were influenced by the number and positions of substituent groups. Detonation properties were evaluated using the Kamlet–Jacobs equations, based on the theoretical densities and heats of formation of the polynitropurines. The relative stabilities of the polynitropurines were studied via the pyrolysis mechanism and the UB3LYP/6-311G\*\* method. Homolysis of the ring–NO<sub>2</sub> bond is predicted to be the initial step in the thermal decomposition of these purine derivatives. Considering their detonation properties and relative stabilities, the tetranitropurine (D1) derivatives may be regarded as potential candidates for practical HEDCs. These results may provide useful information for further investigations.

**Keywords** Polynitropurines · Density functional theory (DFT) · Heats of formation · Isodesmic reactions · Detonation properties · Bond dissociation energies

## Introduction

High energy density materials (HEDMs) have recently received considerable attention because their explosive performances are superior to those of conventional explosive

materials [1–5]. The search for novel HEDCs to meet future demands has been, and continues to be, one of the most active areas of research [6, 7]. It is well known that heterocyclic nitramines are energetic organic compounds that have long played important roles in civil and military applications [8–12]. A series of nitrated products, namely 2,4,6-trinitrotoluene (TNT), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), hexanitrohexaazaisowurtzitane (CL-20), TNAZ (1,3,3-trinitroazetidene), octanitrocubane (ONC), ammonium dinitramide (AND), and hydrazinium nitroformate (HNF), are key high energy density materials (HEDMs).

At present, a commonly used method of obtaining HEDCs is to add highly energetic groups (such as nitro, nitrate, and nitramine groups) as substituents to a compound or polymer chain in order to increase its energetic character and improve its oxygen balance [13–15]. We are interested in the fundamental thermodynamic properties of simple molecules that have been modified slightly to make them more interesting as HEDCs, either by including inherently unstable substituents or by adding additional oxygen atoms to make the new compounds autooxidize. Since the experimental synthesis of HEDCs is not only dangerous but also hazardous to humans and the environment, computer modeling and quantum simulation have been used extensively as tools of theoretical chemistry to facilitate molecular design.

Recently, purines, another group of organic nitramine compounds, have become of interest to us. Purine has a nitrogen content of >46 %, and it is also fascinating because there are four hydrogen atoms on the ring that can be replaced with functional groups. Studies have shown that nitro groups are essential to combustion, and they have been extensively studied as components of propellants and explosives [16, 17]. The presence of nitro groups tends to increase the heat of formation of a compound, and it markedly

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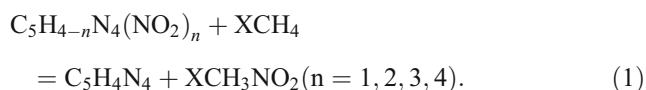
improves the overall energetic performance. Also, nitro groups enhance both the oxygen balance and the density, which improves the detonation performance. In the work described in this article, therefore, 15 purine derivatives were designed by replacing the hydrogen atoms in purine with nitro groups, and their geometries, thermodynamic properties, and detonation performances were calculated in detail using the B3LYP method with the 6-311G\*\* basis set.

The remainder of this paper is organized as follows. In the next section, we describe our computational methods. We then report and discuss our results in the following section, before providing a summary of our conclusions.

## Computational methods

In this work, we used a density functional theory (DFT) [18, 19] method based on Becke's functional with nonlocal correlation provided by the Lee, Yang, and Parr functional (LYP), designated B3LYP [20, 21], along with the 6-311G\*\* basis set [22]. Calculations were performed in the Gaussian 03 software package [23]. Each optimized structure was checked to ensure that it was a local energy minimum on the potential energy surface using vibrational analysis. Based on these structures, Wiberg bond orders were calculated using natural bond orbital (NBO) analyses.

The heats of formation (HOFs) of the title compounds were needed to calculate their detonation energies. To obtain the HOFs, we used the method of isodesmic reactions [24], which has already been employed very successfully to estimate standard gas-phase heats of formation ( $\Delta_f H_{\text{gas}}^\circ$ ) [25–27]. Isodesmic reaction progress must comply with the bond separation reaction (BSR) rule, in which the numbers of all kinds of bonds must remain constant. In other words, the molecule is broken down into heavy-atom molecules containing the same component bonds. Additionally, the utilization of isodesmic reactions allows the error resulting from electronic correlation energies to be accounted for, and also significantly reduces calculation errors. In this work, the isodesmic reactions used were



The heats of formation for these reactions at 298 K were deduced as follows:

$$\begin{aligned} \Delta_r H_{(298)}^0 &= \sum \Delta_f H_{(g,p)}^0 - \sum \Delta_f H_{(g,r)}^0 \\ &= \sum E(298\text{K}, p) - \sum E(298\text{K}, r) + \Delta(PV) \end{aligned} \quad (2)$$

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

Here,  $\sum \Delta_f H_{(g,p)}^0$  and  $\sum \Delta_f H_{(g,r)}^0$  are the heats of formation of the products and the reactants at 298 K, respectively. The values of the experimental thermodynamic parameters for  $\text{C}_5\text{H}_4\text{N}_4$  and  $\text{CH}_4$  were taken from [28, 29]. An accurate value for the  $\Delta H_f$  of  $\text{CH}_3\text{NO}_2$  was obtained from [30]. The data mentioned above are listed in Table 2.  $\sum E(0\text{K}, p)$  correspond to the energies of the sum of the products at 0 K, whereas  $\sum E(0\text{K}, r)$  is the sum of the energies of the reactants at 0 K.  $\Delta\text{ZPE}$  is the sum of the zero-point correction energies of the products and reactants.  $\Delta\text{HT}$  is the thermal correction value, and  $\Delta(PV)$  equals  $\Delta nRT$  for an ideal gas, which is zero here because  $\Delta n$  is zero in an isodesmic reaction.

The solid-phase enthalpies of formation [ $\Delta H_f(\text{s})$ ] were obtained from the gas-phase enthalpies of formation using Hess's law of constant heat summation [31, 32]:

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

Here,  $\Delta H_{\text{sub}}$  is the sublimation enthalpy evaluated using the following equation suggested by Politzer et al. [32]:

$$\begin{aligned} \Delta H_{\text{sub}}(298\text{K}, \text{kcal/mol}) &= 0.000475(\text{SA})^2 \\ &+ 2.1194(v\sigma_{\text{tot}}^2)^{0.5} - 2.25, \end{aligned} \quad (5)$$

where SA is the area of the isosurface of electron density 0.001 e/Bohr<sup>3</sup> of a molecule calculated using a self-compiled program. All values were calculated by us, and the final results are listed in Table 3.

The bond dissociation energy (BDE) is the energy that must be supplied to achieve the homolytic cleavage of a chemical bond. The energy required for bond homolysis at 298 K and 1 atm corresponds to the enthalpy of the reaction  $\text{A-B}_{(\text{g})} \rightarrow \text{A}\cdot_{(\text{g})} + \text{B}\cdot_{(\text{g})}$ , which is the bond dissociation enthalpy of the molecule A–B by definition. For many organic molecules, the terms “bond dissociation energy” and “bond dissociation enthalpy” often appear interchangeably in the literature. Therefore, at 0 K, the homolytic BDE can be given in terms of Eq. 4 [33]:

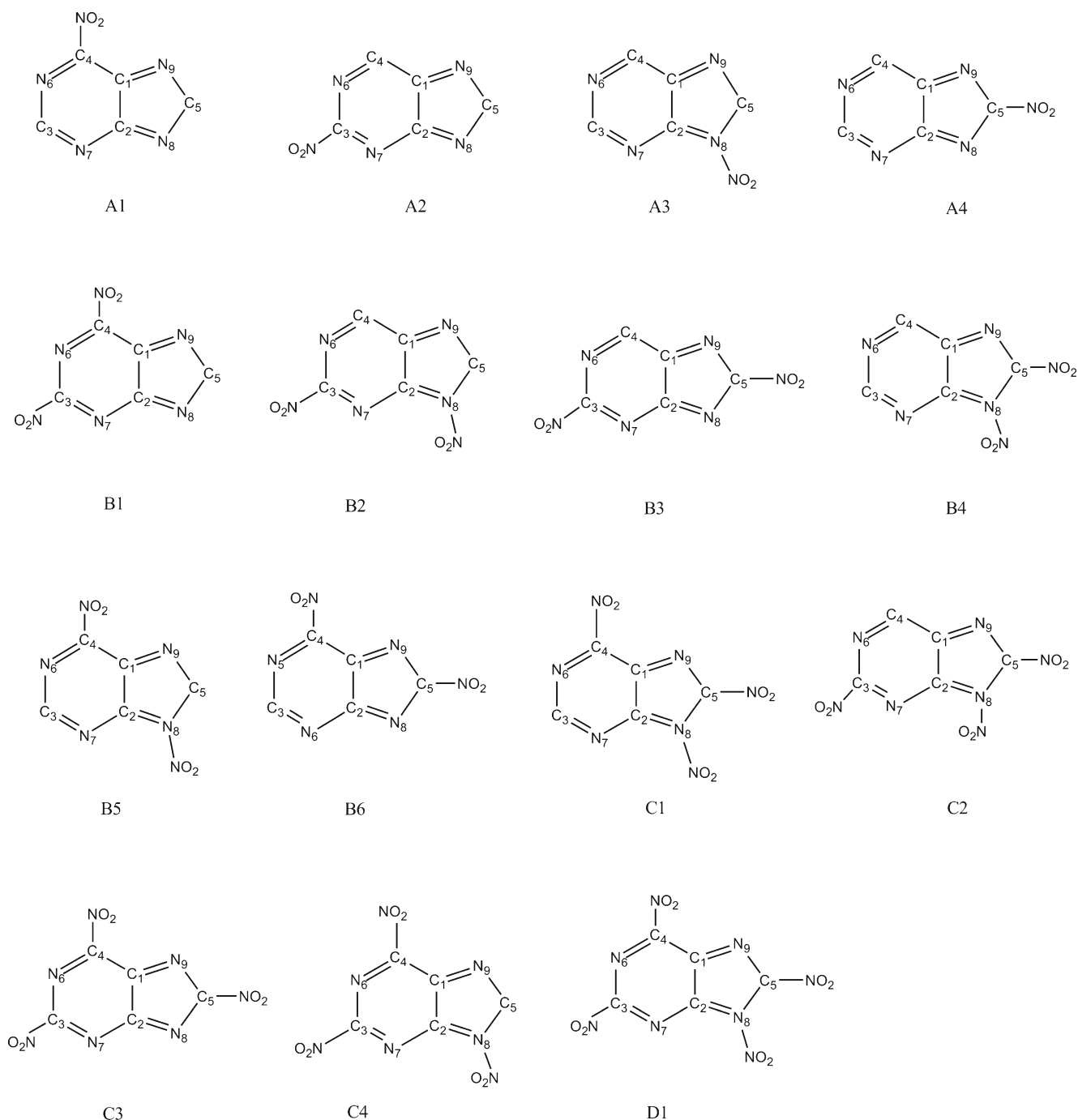
$$\text{BDE}_0(\text{A} - \text{B}) = E_0(\text{A}\cdot) + E_0(\text{B}\cdot) - E_0(\text{A} - \text{B}). \quad (6)$$

The bond dissociation energy corrected for the zero-point energy (ZPE) can be calculated as follows via Eq. 5:

$$\text{BDE}(\text{A} - \text{B})_{\text{ZPE}} = \text{BDE}_0(\text{A} - \text{B}) + \Delta\text{ZPE}. \quad (7)$$

$\Delta\text{ZPE}$  is the difference between the ZPEs of the products and the reactants.

For each compound of interest, the explosive reaction was identified by applying the “most exothermic principle;”



**Fig. 1** Optimized geometries for the polynitropurines considered in this work, as calculated at the B3LYP-6-311G\*\* level

that is, all of the N atoms end up in  $N_2$  molecules, while the O atoms initially react with H atoms to give  $H_2O$  before 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  $O_2$  molecules. 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. Halogen atoms form hydrogen halides with hydrogen atoms. For explosives with the elements C, H, N, O, and F, the detonation velocity ( $D$ ) and the detonation pressure ( $P$ ) are very important parameters for evaluating the explosive performances of the materials. These parameters can be calculated using the

**Table 1** Calculated HOMO and LUMO energies (in a.u.) as well as the energy gaps ( $\Delta E_{\text{LUMO-HOMO}}$ ) for the title compounds, as calculated at the B3LYP/6-311G\*\* level

Compound	$E_{\text{LUMO}}$	$E_{\text{HOMO}}$	$\Delta E_{\text{LUMO-HOMO}}$
C <sub>5</sub> H <sub>4</sub> N <sub>4</sub>	-0.05496	-0.25743	0.20247
A1	-0.08006	-0.28321	0.20315
A2	-0.08308	-0.28129	0.19821
A3	-0.11246	-0.27959	0.16713
A4	-0.12781	-0.28352	0.15571
B1	-0.12746	-0.30026	0.17280
B2	-0.13052	-0.29733	0.16681
B3	-0.14732	-0.30133	0.15401
B4	-0.13888	-0.29733	0.15845
B5	-0.12872	-0.30204	0.17332
B6	-0.14588	-0.30606	0.16018
C1	-0.15471	-0.31767	0.16296
C2	-0.15546	-0.31108	0.15562
C3	-0.16496	-0.31886	0.15390
C4	-0.14718	-0.31377	0.16659
D1	-0.17175	-0.32724	0.15549
TATB	-0.10280	-0.26480	0.16210

Kamlet–Jacobs (K-J) formula [34]. The formula (8) and (9) are listed as the following.

$$D = 1.01 \left( N \bar{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30\rho) \quad (8)$$

$$P = 1.558 \rho^2 N \bar{M}^{1/2} Q^{1/2}. \quad (9)$$

Here,  $D$  is the detonation velocity (in km/s) and  $P$  is the detonation pressure (in GPa).  $N$  is the number of moles of detonation gases per gram of explosive, and  $\bar{M}$  is the average molecular weight of these gases.  $Q$  is the heat of detonation (in cal/g) and  $\rho$  is the molecular crystal density (in g/cm<sup>3</sup>). The parameters  $N$ ,  $\bar{M}$ , and  $Q$  were calculated based on the chemical composition of each explosive, as listed in Table 3. In detail, the density of each compound was predicted from 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 Carlo integration [35].  $Q$  was evaluated by determining the difference between the HOFs of the products and the HOF of the explosive according to the principle of exothermic reactions. The  $D$  and  $P$  values were evaluated using the  $\rho$  and  $Q$  values. Moreover, an electrostatic-interaction correction method for improved crystal density prediction provided by

Politzer et al. [36, 37] was utilized (see the equations below):

$$\rho_{\text{crystal}} = 0.9183 \left( \frac{M}{V_m} \right) + 0.0028 (v \sigma_{\text{tot}}^2) + 0.0443 \quad (10)$$

$$\sigma_{\text{tot}}^2 = \sigma_+^2 + \sigma_-^2 = \frac{1}{m} \sum_{i=1}^m \left[ V^+(r_i) - \bar{V}^+ \right]^2 + \frac{1}{n} \sum_{j=1}^n \left[ V^-(r_j) - \bar{V}^- \right]^2 \quad (11)$$

$$v = \frac{\sigma_+^2 \sigma_-^2}{[\sigma_{\text{tot}}^2]^2} \quad (12)$$

$$\bar{V}^+ = \frac{1}{m} \sum_{i=1}^m V^+(r_i) \quad (13)$$

$$\bar{V}^- = \frac{1}{n} \sum_{j=1}^n V^-(r_j) \quad (14)$$

Here,  $v$  is the balance parameter,  $V(r)$  is the 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 values of  $V(r)$  on the surface, respectively,  $\bar{V}^+$  and  $\bar{V}^-$  are their averages, and  $\sigma_{\text{tot}}^2$  is the total variance. In this paper,  $A$ ,  $\bar{V}^+$ , and  $\bar{V}^-$  for the purine derivatives were obtained at the B3LYP/6-311G\*\* level.

## Results and discussion

### Electronic structure

The basic structures and the atom numbering schemes used for the polynitropurines are presented in Fig. 1. Table 1 lists the energies (eV) of the frontier molecular orbitals for the polynitropurines optimized at the B3LYP/6-311G\*\* level, as well as their HOMO–LUMO energy gaps ( $\Delta E$ ). Many studies

**Table 2** Calculated total energies ( $E_0$ , a.u.), zero-point energies (ZPE, a.u.), thermal correction values ( $H_T$ , a.u.), and heats of formation (HOF, kJ/mol) of the reference compounds

Compound	$E_0$	ZPE	$H_T$	HOF
CH <sub>3</sub> NO <sub>2</sub>	-245.08167	0.04868	0.00539	-74.3
C <sub>5</sub> H <sub>4</sub> N <sub>4</sub>	-412.04628	0.09494	0.00664	18.00
CH <sub>4</sub>	-40.53374	0.04371	0.00382	-74.40

**Table 3** Total energies ( $E_0$ , a.u.), zero point energies (ZPE, a.u.), thermal correction values ( $H_T$ , a.u.), and heats of formation of the purine derivatives considered in this work, as calculated at the B3LYP/6-311G\*\* level

Compound	$E_0$ (a.u.)	$E_{ZPE}$ (a.u.)	$H_T$ (a.u.)	$\Delta H_f(g)$ (kJ/mol)	$\Delta H_f(s)$ (kJ/mol)
A1	-616.58902	0.09690	0.00856	24.58	10.95
A2	-616.59152	0.09684	0.00853	17.77	4.26
A3	-616.55611	0.09617	0.00928	110.95	101.74
A4	-616.59087	0.09705	0.00919	21.78	10.98
B1	-821.13165	0.09880	0.01207	35.45	22.60
B2	-821.09909	0.09806	0.01200	118.79	106.65
B3	-821.13400	0.09892	0.01190	29.15	17.69
B4	-821.08273	0.09779	0.01208	161.28	153.48
B5	-821.09634	0.09808	0.01207	126.25	115.34
B6	-821.13056	0.09899	0.01196	38.51	27.03
C1	-1025.62038	0.09960	0.01493	183.24	173.73
C2	-1025.62313	0.09951	0.01490	175.68	165.14
C3	-1025.66902	0.10067	0.01476	57.89	48.15
C4	-1025.63492	0.09926	0.01487	143.98	133.48
D1	-1230.15685	0.10113	0.01783	214.12	205.65

have indicated that the HOMO–LUMO energy gap is an indicator of chemical stability [38, 39]: the smaller the energy gap, the lower the chemical stability. From Table 1, it is clear that the  $\Delta E_{LUMO-HOMO}$  values decrease as the number of nitro groups increases. The stability generally decreases as the number of substituents increases. If we consider the four mononitropurine isomers,  $\Delta E$  is larger for A1 than for A2, A3, and A4, indicating that A1 is slightly more stable than other three isomers. The  $\Delta E_{LUMO-HOMO}$  value for B5 is the largest among the values for the six dinitropurine isomers. It

should be pointed out that “stability” refers here to any chemical or photochemical process involving an electron transfer or jump [40, 41], so the thermodynamic stability of the title compound cannot be judged solely based on  $\Delta E_{LUMO-HOMO}$ .

#### Heats of formation

The heat of formation is usually considered an indicator of the “energy content” of an HEDM. Effective energetic materials usually have highly positive HOFs, so HOFs are of great importance in thermochemical research. Table 2 lists the total energies, the zero-point energies, and the thermal correction values calculated at the B3LYP/6-311G\*\* level for three reference compounds utilized in the isodesmic reactions. Previous studies have shown that theoretically predicted HOFs agree well with the corresponding experimental values when appropriate reference compounds are chosen for the isodesmic reactions. Table 3 lists the total energies, the zero-point energies, the thermal correction values, and the HOFs calculated at the B3LYP/6-311G\*\* level for the polynitropurines of interest in this work.

We can see from Table 3 that the HOFs are all highly positive values, which is one of the requirements for HEDCs. The molecules with the highest HOFs store the most energy. HOF values for isomers with the same number of nitro groups are different, indicating that the HOF is affected by the positions of the nitro groups. For instance, for the four mononitropurine isomers, the HOFs of A1, A2, and A4 are similar, while the HOF of A3 is larger than those of the other three isomers by about 86.37, 93.18, and 89.17 kJ/mol, respectively, when calculated at the B3LYP/6-311G\*\* level. For the six dinitropurine isomers, the HOF values of B2, B4, and B5 are larger than those of B1, B3, and B6. This indicates that B2, B4, and B5 are less stable than B1, B3, and B6. Among the

**Table 4** Calculated bond dissociation energies (BDE, kJ/mol) for the rupture of the weakest bond, calculated at the UB3LYP/6-311G\*\* level

Compound	Trigger bond	Bond order	BDE	BDE <sub>ZPE</sub>
A1	C <sub>4</sub> –NO <sub>2</sub>	0.8458	234.42	219.17
A2	C <sub>3</sub> –NO <sub>2</sub>	0.8294	252.27	236.44
A3	N <sub>8</sub> –NO <sub>2</sub>	0.9243	156.09	136.16
A4	C <sub>5</sub> –NO <sub>2</sub>	0.9041	276.09	259.77
B1	C <sub>3</sub> –NO <sub>2</sub>	0.8386	249.34	233.78
B2	C <sub>3</sub> –NO <sub>2</sub>	0.8361	248.96	233.07
B3	C <sub>3</sub> –NO <sub>2</sub>	0.8358	248.83	232.99
B4	N <sub>8</sub> –NO <sub>2</sub>	0.6634	144.94	124.14
B5	C <sub>4</sub> –NO <sub>2</sub>	0.8570	230.05	214.84
B6	N <sub>8</sub> –NO <sub>2</sub>	0.8558	228.07	212.88
C1	N <sub>8</sub> –NO <sub>2</sub>	0.8120	125.69	107.15
C2	N <sub>8</sub> –NO <sub>2</sub>	0.8074	123.71	105.58
C3	C <sub>3</sub> –NO <sub>2</sub>	0.8370	242.68	227.36
C4	C <sub>3</sub> –NO <sub>2</sub>	0.8378	243.39	229.35
D1	N <sub>8</sub> –NO <sub>2</sub>	0.7751	148.08	129.10
RDX <sup>a</sup>	–	–	166.19	145.62
HMX <sup>a</sup>	–	–	178.77	160.41

<sup>a</sup> Calculated values for RDX and HMX were taken from [49]

**Table 5** Predicted detonation properties of the purine derivatives of interest in the present work, together with those of RDX and HMX<sup>b</sup>

Compounds	OB <sub>100</sub>	<i>V</i> (cm <sup>3</sup> /mol)	$\rho$ (g/cm <sup>3</sup> )	<i>Q</i> (cal/g)	<i>D</i> (km/s)	<i>P</i> (GPa)
A1	-1.82	101.72	1.69	683.81	5.95	15.10
A2	-1.82	103.46	1.66	674.13	5.86	14.51
A3	-1.82	101.85	1.61	815.32	6.02	15.02
A4	-1.82	101.00	1.65	683.87	5.85	14.39
B1	-1.68	120.13	1.79	972.74	7.14	22.54
B2	-1.68	119.94	1.78	1068.41	7.28	23.34
B3	-1.68	117.59	1.80	967.16	7.16	22.72
B4	-1.68	119.65	1.72	1121.70	7.19	22.29
B5	-1.68	118.35	1.78	1078.30	7.30	23.46
B6	-1.68	119.55	1.77	977.78	7.10	22.18
C1	0.39	137.53	1.83	1290.43	8.03	28.88
C2	0.39	137.59	1.85	1282.38	8.06	29.26
C3	0.39	138.61	1.82	1172.73	7.81	27.24
C4	0.39	138.11	1.84	1252.70	7.99	28.71
D1	2.00	156.24	1.88	1417.83	8.53	33.09
RDX <sup>a</sup>	0.00	–	1.78 (1.82)	1591.03	8.87 (8.75)	34.67 (34.00)
HMX <sup>a</sup>	0.00	–	1.88 (1.91)	1633.90	9.28 (9.10)	39.19 (39.00)

<sup>a</sup>The calculated values for RDX and HMX were taken from [2]

<sup>b</sup>Data in parentheses are experimental values taken from [6]

four trinitropurine isomers, the HOF of C3 is lower than those of C1, C2, and C4, indicating that the latter three are less stable than C. This shows that when the nitro group attaches to the N atom of a derivative, the HOF value of the resulting compound is larger than that of the compound obtained when the nitro group attaches to the C atom of that compound; in other words, it is easier to destabilize a molecule when the nitro group attaches to the N atom of the derivative. Similar situations occur in the A series and C series.

#### Pyrolysis mechanism and thermal stability

The sensitivity and stability are very important parameters of energetic compounds. Therefore, work aimed at predicting the impact sensitivities of energetic materials has been carried out at the molecular level. For example, Owens et al. [42, 43] was the first to note that there is a correlation between sensitivity and electrostatic potential (ESP) at the midpoint of the C–NO<sub>2</sub> bond, and Politzer and coworkers established correlations between the ESP around an isolated molecule and many of its condensed-phase properties [44, 45]. Research has shown that the bond dissociation energy (BDE) of the trigger bond may play an important role in initiation reactions of nitro compounds [46, 47]. In the present work, we calculated the bond dissociation energies (BDE) for various possible initial steps in the pyrolysis of the purine derivatives of interest. Generally, the smaller the BDE, the easier it is to break the bond. The BDE can be calculated by subtracting the combined energy of the reactants from that of the products. We obtained the bond orders of the polynitropurines by performing NBO analyses.

According to the principle of the smallest bond order (PSBO) [48], the ring–NO<sub>2</sub> bonds are the weakest and thus easiest to break. The bond orders, BDEs, and BDE<sub>ZPE</sub> values of the ring–NO<sub>2</sub> bonds are listed in Table 4.

From Table 4, we can see that the calculated BDE and BDE<sub>ZPE</sub> values are larger than 120 kJ/mol, except for those of C1 and C2. The BDE and BDE<sub>ZPE</sub> values that are not corrected for the zero-point energy are larger than those that include this correction. In a comparison with commonly used explosives, it was found that A1, A2, A4, B1, B2, B3, B5, B6, C3, and C4 have higher BDE values than those of RDX (152.09 kJ/mol) and HMX (166.48 kJ/mol), meaning that they are more stable than RDX and HMX. In addition, we found that the BDE values are consistent with the bond order values of the polynitropurines, because the BDE value increases as the bond order increases. This implies that the thermal stability of an HEDC is dependent on its BDE.

#### Detonation properties

The detonation velocity (*D*) and detonation pressure (*P*) are important parameters for evaluating the explosive performance of an energetic material. These parameters can be computed using the Kamlet–Jacobs empirical equations on the basis of the theoretical density ( $\rho$ ) and calculated gas-phase heat of formation of the material. The Kamlet–Jacobs equations have already proven to be reliable for predicting the explosive properties of polynitropurines. Table 5 presents the predicted detonation properties of the polynitropurines considered in this work. For comparison, the detonation performances of two well-known explosives, RDX and HMX, are also listed in this table.



Table 5 shows that  $\rho$  is in the range 1.61–1.88 g/cm<sup>3</sup>,  $Q$  is in the range 674.13–1424.58 cal/g,  $D$  is in the range 5.85–8.53 km/s, and  $P$  is the range 14.39–33.09 GPa for the 15 purine derivatives. The densities as well as the detonation velocities and pressures of the title compounds increase as the number of substituents increases. Unfortunately, the tetranitropurines do not show dramatically improved detonation performances compared to conventional explosives: their performances are similar to that of RDX, while they have higher  $\rho$  values and lower  $D$  and  $P$  values than HMX. This is because they contain too few O atoms to allow full oxidation of the C atoms, so the remaining C atoms exist as solid-state carbon after the oxidation process has completed. They also do not contain enough oxygen to completely oxidize the other atoms in the molecule, which means that a large amount of energy remains untapped during the explosive decomposition of these purine derivatives. This information should prove useful when searching for HEDMs derived from polynitropurines.

## Conclusions

We have carried out computational molecular design based on purine. When the H atoms of the parent compound were replaced with nitro groups, a series of novel molecules were obtained. Using DFT methods, it was possible to study their geometries, heats of formation, and their bond dissociation and detonation properties in detail. Based on this theoretical study, the following conclusions can be drawn:

- (1) The  $\Delta E_{\text{LUMO-HOMO}}$  values of the polynitropurines decrease as the number of nitro groups increases. All of the polynitropurines have positive HOFs. Differences in HOF among isomers are caused by differences in the relative positions of the nitro groups in the isomers. Among isomers, the HOF of the isomer that contains an N–nitro bond is larger than that of the isomer containing a C–nitro bond.
- (2) The calculations of bond dissociation energies (BDE) suggest that the ring–NO<sub>2</sub> bond is the trigger bond for the initiation of polynitropurine pyrolysis. The BDE values range from 105.58 to 259.77 kJ/mol. Aside from the polynitropurines A3, B4, C1, C2, and D1, the BDEs of the polynitropurines are higher than those for RDX and HMX, which implies that the sensitivities of the polynitropurines are lower than those of RDX and HMX.
- (3) The detonation velocity ( $D$ ), detonation pressure ( $P$ ), and molecular density ( $\rho$ ) also increase as the number of nitro groups increases. It is well known that a superior HEDC possesses not only excellent detonation properties but also high stability. Based on the above results, we can conclude that only D1 can be considered a potential candidate for an HEDM. These

compounds present good explosive performance and are worthy of synthesis and further investigation. Our results should also provide some useful information for the molecular design of novel HEDCs.

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