

DFT THEORETICAL STUDY OF ENERGETIC NITROGEN-RICH $C_4N_6H_{8-n}(NO_2)_n$ DERIVATIVES

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Density functional theory (DFT) calculations at the B3LYP/6-31G** theoretical level were performed for a series of guanidine-fused bicyclic skeleton derivatives $C_4N_6H_{8-n}(NO_2)_n$ ($n = 1-6$). The heats of formation (HOFs) were calculated by isodesmic reactions, and the detonation properties were evaluated using the Kamlet–Jacobs equations. The bond dissociation energies were also analyzed to investigate the thermal stability and sensitivity of the compounds. The results show that all of the derivatives have high positive HOFs, compound G has the highest theoretical density, and compound F1 has the highest detonation velocity and detonation pressure. Considering both the detonation properties and thermal stabilities, compounds D1 and D4 (3 nitro substituents), E1–E6 (4 nitro substituents), and G (6 nitro substituents) can be regarded as potential candidates for high-energy density materials.

Keywords: density functional theory; molecular mechanics; guanidine-fused bicyclic skeleton derivatives.

INTRODUCTION

During the last few decades, high-energy density materials (HEDMs) have been widely used for both military and civilian applications.¹⁻⁹ Among the various HEDMs, heterocyclic nitrogen compounds have attracted significant attention, such as the well-known explosives 1,3,4,6-tetranitroglycouril (TNGU),¹⁰ hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX),^{11,12} and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX)^{13,14} and the newer compounds *trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin (TNAD),¹⁵ 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)¹⁶ and *cis*-2,4,6,8-tetranitro-1H,5H-2,4,6,8-tetraazabicyclo[3.3.0]octane (Bicycle–HMX),^{17,18} which are all explosives with high positive HOFs and excellent detonation properties.

Although there are many types of HEDMs, each has different advantages and disadvantages with respect to its stability and detonation properties. For example, TNGU (Figure 1), whose density and detonation properties are superior to the popular explosives RDX and HMX, is moisture sensitive. This molecule has four nitro groups for improved density and detonation properties, but the carbonyl groups at either end of the molecule undergo hydrolytic reaction with water. Thus, to avoid this water sensitivity, the new guanidine-fused bicyclic skeleton $C_4N_6H_8$ (Figure 2, A) was designed as an extension of the glycoluril structure, in which the two $-C=O$ groups were replaced with $-C=N-$ groups.

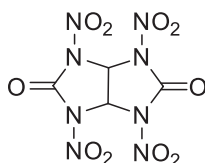


Figure 1. Molecular structure of TNGU

Five-membered and six-membered heterocycles containing nitrogen are typically energetic materials because of their compact structure and the large number of inherently energetic C–N and N–N bonds. Not surprisingly, $C_4N_6H_8$ consists of this type of structure containing six nitrogen atoms. It was therefore selected as the

parent structure for designing new HEDMs. It should be noted that the six N–H bonds can be substituted with nitrogen bonds to other functional groups, such as nitro, isocyano, and azido.¹⁹⁻²² The main difference between the nitro, isocyano, and azido functional groups is the amount of oxygen present. Thus, considering combustion, the nitro group has an advantage. In addition, nitro compounds are an important class of HEDMs, which have long attracted attention from researchers; the addition of a nitro substituent to a molecule can improve its detonation properties more effectively than adding either isocyano or azido groups.²³ Hence, in this study, the hydrogen atoms in the six N–H bonds in the $C_4N_6H_8$ parent structure were replaced with nitro groups, generating a series of cyclic nitramines $C_4N_6H_{8-n}(NO_2)_n$ ($n = 1-6$).

Because new HEDMs with multiple nitro groups can pose substantial danger to humans and the environment during both their synthesis and performance testing, computer simulations have been widely used to effectively screen promising explosives and predict their detonation properties. Recently, many computational chemistry methods have been used to predict the properties of HEDMs, such as semiempirical molecular orbital (MO) theory,²⁴ density functional theory (DFT-B3LYP), and the Gaussian-2 (G2)²⁵ method. However, during the process of estimating the properties of new HEDMs, it has been found that semiempirical MO methods do not produce accurate and reliable results, while the G2 method is more expensive and not yet practical for the calculation of compounds with complicated structures. Thus, the DFT-B3LYP method, not only produces reliable geometries and energies, but also requires less time and computer resources, has been widely employed to predict the properties of HEDMs. In this study, a series of cyclic nitramines $C_4N_6H_{8-n}(NO_2)_n$ ($n = 1-6$) (Figure 2) were designed on the basis of the structure of the guanidine-fused bicyclic skeleton $C_4N_6H_8$ (A). The electronic structures, heats of formation (HOFs), theoretical densities (ρ), and detonation properties, such as the heats of detonation (Q), detonation velocities (D), and detonation pressures (P), were investigated by the density functional theory (DFT) method.²⁶⁻³⁰ In addition, the sensitivity, which can be used to predict whether an energetic material can be stored safely, was also investigated. Rice and Politzer *et al.*³¹⁻³³ recently reported that the explosive sensitivity of nitro explosives exhibits a good linear relationship with the bond dissociation energy (BDE) of the trigger bond. These results indicate that the explosive sensitivity of nitro compounds can be evaluated using the BDE of the

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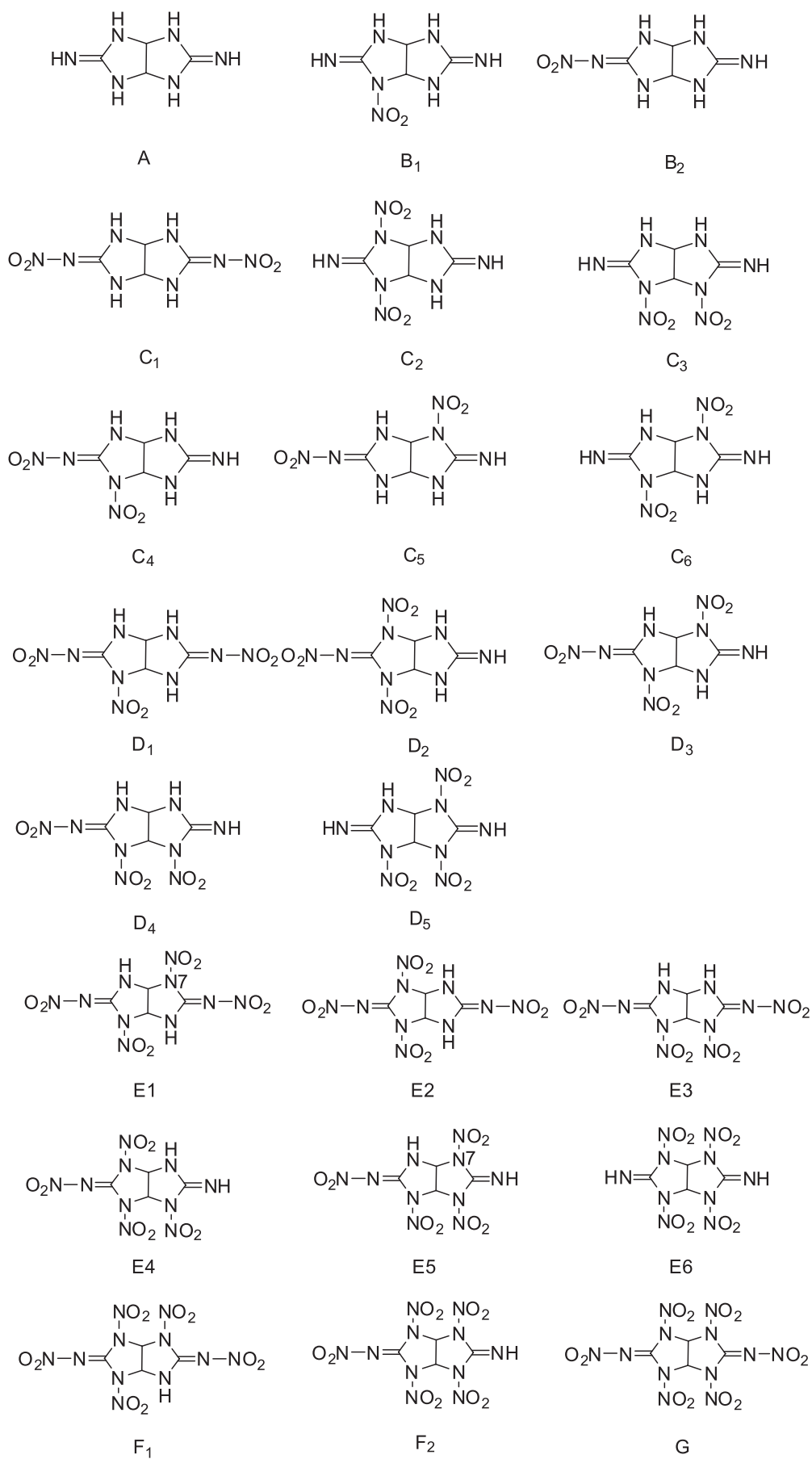


Figure 2. Molecular structures and atomic numbering for $C_4N_6H_8$ and its derivatives

trigger bond; thus, the BDEs of these derivatives were also evaluated in this study. These results may provide useful information for the molecular design and synthesis of novel HEDMs.

COMPUTATIONAL METHOD

All of the computations were performed with the Gaussian 03 package³⁴ at the B3LYP/6-31G** level. The optimizations were performed using the default convergence criteria in the programs. Vibrational analyses at the same level of theory were also performed to confirm that all of the optimized structures correspond to be the local energy minima on the potential energy surfaces.

Calculation of the HOFs of the derivatives is necessary to determine their detonation properties. To obtain accurate HOF values, isodesmic reactions, in which the equivalency of the bonds and electronic pairs in the reactant is not only maintained in both the products and reactants, but also can counterbalance the error in the electronic correlation energies, were designed. The feasibility of this approach for the estimation of accurate HOF of HEDMs has been previously demonstrated.³⁵

The isodesmic reaction that was employed to calculate the HOFs of the title compounds at 298 K can be written as:



where n is the number of substituted nitro groups. Given the isodesmic reaction (1), the HOFs can be calculated from the following equation:

$$\Delta H_{298\text{K}} = \Sigma \Delta H_{f,p} - \Sigma \Delta H_{f,r} \quad (2)$$

where $\Delta H_{f,p}$ and $\Delta H_{f,r}$ are the HOFs of the products and reactants at 298 K, respectively. Thus, the HOFs of the title compounds can be determined when the heat of reaction ΔH_{298} is known. On the other hand, the HOFs at 298 K can be defined by the following equation:

$$\Delta H_{298\text{K}} = \Delta E_{298\text{K}} + \Delta(PV) = \Delta E_0 + \Delta ZPE = \Delta H_T + \Delta nRT \quad (3)$$

where $\Delta E_{298\text{K}}$ and ΔE_0 are the change in total energy between the products and reactants at 298 K and 0 K, respectively; ΔZPE is the difference between the zero-point energy (ZPE) of the products and reactants; and ΔH_T is the thermal correction from 0 to 298 K. For reactions in the gas phase, $\Delta(PV)$ equals ΔnRT , and for isodesmic reactions, $\Delta n = 0$.

The experimental HOFs of the reference compounds NH_3 and NH_2NO_2 are available.^{36,37} Because the experimental HOF of the $\text{C}_4\text{N}_6\text{H}_8$ parent skeleton is unavailable, additional calculations were carried out for the atomization reaction $\text{C}_a\text{H}_b\text{O}_c\text{N}_d \rightarrow \text{C}(\text{g}) + b\text{H}(\text{g}) + c\text{O}(\text{g}) + d\text{N}(\text{g})$ by the G2 theory to accurately predict its HOF. Thus, the HOFs of the target molecules were calculated using Eqs. (1)–(3) in combination with the atomization reaction described above.

However, the condensed phase of most energetic compounds is solid, and thus, the calculation of the detonation properties for such compounds requires solid-phase HOFs ($\Delta H_{f,\text{solid}}$) rather than gas-phase HOFs ($\Delta H_{f,\text{gas}}$). Therefore, $\Delta H_{f,\text{gas}}$ was converted to $\Delta H_{f,\text{solid}}$ according to Hess' law using the following formula:³⁸

$$\Delta H_{f,\text{solid}} = \Delta H_{f,\text{gas}} - \Delta H_{\text{sub}} \quad (4)$$

where ΔH_{sub} denotes the heat of sublimation.

In addition, Politzer *et al.*^{39,40} found that the heat of sublimation of energetic compounds correlates well with the molecular surface area and electrostatic interaction index ($v\sigma_{\text{tot}}^2$) using the following expression:

$$\Delta H_{\text{sub}} = aA^2 + b(v\sigma_{\text{tot}}^2)^{0.5} + c \quad (5)$$

where A is the surface area of the 0.001 e bohr⁻³ isosurface for the electronic density of the molecule; v is the degree of balance between the positive and negative potentials on the isosurface; and σ_{tot}^2 is a measure of the variability of the electrostatic potential on the molecular surface. Byrd and Rice *et al.* calculated the values for ΔH_{sub} of CHNO systems using Eq. (5), and the coefficients a , b , and c were determined to be $a = 2.670 \times 10^{-4}$ kcal mol⁻¹ A⁻⁴, $b = 1.650$ kcal mol⁻¹, and $c = 2.966$ kcal mol⁻¹.⁴¹ The descriptors A , v , and σ_{tot}^2 were calculated using the computational procedures as described by Bulat *et al.*⁴² This approach has been demonstrated to be a reliable method for the prediction of the heats of sublimation of many energetic compounds.^{43,44}

The detonation velocity and detonation pressure were estimated by the empirical Kamlet–Jacobs equations:⁴⁵

$$D = 1.01(N\bar{M}^{0.5}Q^{0.5})^{0.5}(1+1.3\rho) \quad (6)$$

and

$$P = 1.558\rho^2N\bar{M}^{0.5}Q^{0.5} \quad (7)$$

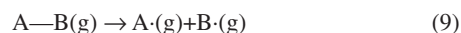
where ρ is the loaded density of the explosive (g cm⁻³); D is the detonation velocity (km s⁻¹); P is the detonation pressure (GPa); N is the number of moles of detonation gases per-gram explosive (mol g⁻¹); \bar{M} is the average molecular weight of these gases (g mol⁻¹); and Q is the heat of detonation (cal g⁻¹). The variables N , \bar{M} , and Q were calculated according to Table 1.^{23,41} The value of ρ can be calculated as M/V , where M is the molecular mass (g mol⁻¹), and V is the volume defined as the space inside a cloud of electron density of 0.001 e Bohr⁻³.

However, the results for ρ obtained using this equation may have significant errors for some systems, such as molecules that can form strong hydrogen bonds. Thus, Politzer *et al.*⁴⁶ suggested that ρ should be corrected to better reflect the effects of intermolecular interactions in crystals, and the modified equation to calculate the ρ of CHNO energetic materials was written as follows:

$$\rho = \beta_1 \left(\frac{M}{V} \right) + \beta_2(v\sigma_{\text{tot}}^2) + \beta_3 \quad (8)$$

where v is the degree of balance between the positive and negative potentials on the isosurface; σ_{tot}^2 is a measure of the variability of the electrostatic potential on the molecular surface; and the coefficients β_1 , β_2 , and β_3 with values of 0.9183, 0.0028, and 0.0443, respectively, were adopted from Politzer's study.

The strength of bonding within a molecule, which can be evaluated using BDEs, plays an important role in understanding its thermal stability.⁴⁷ Most simply, it is defined as the enthalpy change at 298 K, and a value of 1.01×10^5 Pa is assigned for the chemical bond dissociation in a molecule A–B as follows:⁴⁸



and

$$\Delta H_{298}(\text{A—B}) = [\Delta_f H_{298}(\text{A}\cdot) + \Delta_f H_{298}(\text{B}\cdot)] - \Delta_f H_{298}(\text{A—B}) \quad (10)$$

where A–B denotes the neutral molecule, A• and B• represent the corresponding product radicals after bond dissociation; $\Delta H_{298}(\text{A—B})$ is the bond dissociation enthalpy of A–B; and $\Delta_f H_{298}(\text{A}\cdot)$, $\Delta_f H_{298}(\text{B}\cdot)$, and $\Delta_f H_{298}(\text{A—B})$ are the enthalpies of formation for the free radicals and the parent molecule at 298 K, respectively. It can be seen that the

Table 1. Formulas for calculating the values of N , M , and Q for an explosive $C_aH_bO_cN_d$

| Parameters | Stoichiometric ratio | | |
|-------------------|--|--|-------------------------------|
| | $c \geq 2a + b/2$ | $2a + b/2 > c \geq b/2$ | $b/2 > c$ |
| N | $(b + 2c + 2d)/4M$ | $(b + 2c + 2d)/4M$ | $(b + d)/2M$ |
| \bar{M} | $4M/(b + 2c + 2d)$ | $(56d + 88c - 8b)/(b + 2c + 2d)$ | $(2b + 28d + 32c)/(b + d)$ |
| $Q \cdot 10^{-3}$ | $(28.9b + 94.05a + 0.239\Delta H_f)/M$ | $[28.9b + 94.05(c/2 - b/4) + 0.239\Delta H_f]/M$ | $(57.8c + 0.239\Delta H_f)/M$ |

^a a , b , c , and d stand for the number of C, H, O, and N atoms in the explosive molecule, respectively. ^b M in the formula is the molecular weight of the explosive (g mol⁻¹); ΔH_f is the heat of formation of the explosive (kJ mol⁻¹).

reaction enthalpy of the bond homolysis reaction exclusively depends on the relative enthalpies of formation of the reactant and product.

For many organic compounds, BDE(A–B) and $\Delta H_{298}(A-B)$ are nearly equivalent numerically; thus, the terms “bond dissociation energy” and “bond dissociation enthalpy” often appear interchangeably in the literature.⁴⁹ Therefore, the BDEs of the homolytic bond can be calculated by the following equation:

$$BDE_0(A-B) \rightarrow E_0(A\cdot) + E_0(B\cdot) - E_0(A-B) \quad (11)$$

The BDE corrected for the ZPE can be calculated using Eq. (12):

$$BDE(A-B)_{ZPE} = BDE_0(A-B) + \Delta E_{ZPE} \quad (12)$$

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

RESULTS AND DISCUSSION

Electronic structure and stability

The energy gap (ΔE) is one of the most important parameters for predicting the relative stability of compounds. Thus, the highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies, and the energy gaps ($\Delta E_{LUMO-HOMO}$) were calculated at the B3LYP/6-31G** level and are shown in Table 2.

From Table 2, it can be clearly seen that the HOMO energy level of the nitro substituted compounds decreases for each series, and the same is true for the LUMO energy level. On the whole, the $\Delta E_{LUMO-HOMO}$ values for all of the nitro-substituted derivatives are lower than that of the unsubstituted compound A. However, the $\Delta E_{LUMO-HOMO}$ values differ for different isomers with the same number of nitro groups. This result may be due to the different positions of the nitro groups. For example, C3, in which the two nitro groups are located on the same side of the structure, possesses a higher $\Delta E_{LUMO-HOMO}$ than C2, in which the two nitro groups are located on the opposite side of the structure. In other words, C3 may have better thermodynamic stability than C2.

Heats of formation

The HOF, which is a basic property of HEDMs, is usually taken as an indicator of “energy content”. Generally speaking, the higher the HOF, the greater the energy contained by the compound. Thereby, the HOF is frequently considered when HEDMs are designed. However, obtaining accurate HOF values for HEDMs experimentally is an extremely hazardous and difficult task; hence, theoretical studies are employed to calculate accurate HOF values using isodesmic reactions. Table 3 shows the total energies (E_0), thermal corrections (H_T), ZPEs, and HOFs for the reference compounds used in the isodesmic reaction (1).

Table 2. Calculated HOMO and LUMO energies (a.u) and their energy gaps ($\Delta E_{LUMO-HOMO}$)

| Compound | HOMO | LUMO | ΔE |
|----------|---------|---------|------------|
| A | -0.2229 | 0.0526 | 0.2755 |
| B1 | -0.2422 | -0.0749 | 0.1681 |
| B2 | -0.2472 | -0.0553 | 0.1919 |
| C1 | -0.2772 | -0.0721 | 0.2051 |
| C2 | -0.2581 | -0.0999 | 0.1582 |
| C3 | -0.2699 | -0.0685 | 0.2014 |
| C4 | -0.2601 | -0.0980 | 0.1621 |
| C5 | -0.2737 | -0.0924 | 0.1817 |
| C6 | -0.2760 | -0.0901 | 0.1859 |
| D1 | -0.2847 | -0.1114 | 0.1733 |
| D2 | -0.2703 | -0.1203 | 0.1500 |
| D3 | -0.2898 | -0.1097 | 0.1801 |
| D4 | -0.2871 | -0.1021 | 0.1850 |
| D5 | -0.2858 | -0.1093 | 0.1756 |
| E1 | -0.3039 | -0.1192 | 0.1847 |
| E2 | -0.2930 | -0.1333 | 0.1597 |
| E3 | -0.2898 | -0.1156 | 0.1742 |
| E4 | -0.2972 | -0.1277 | 0.1695 |
| E5 | -0.3000 | -0.1160 | 0.1840 |
| E6 | -0.3123 | -0.1125 | 0.1998 |
| F1 | -0.2963 | -0.1378 | 0.1585 |
| F2 | -0.3069 | -0.1297 | 0.1772 |
| G | -0.3158 | -0.1410 | 0.1748 |

Table 3. Calculated total energies (E_0 , au), thermal corrections (H_T , kJ mol⁻¹), zero-point energies (ZPE, kJ mol⁻¹), and heats of formation (HOFs, kJ mol⁻¹) for the reference compounds

| Compound | E_0 | H_T | ZPE | HOF |
|---------------------------------|-------------|----------|----------|--------|
| NH ₃ | -56.557769 | 9.60 | 88.62 | -45.94 |
| NH ₂ NO ₂ | -261.037824 | 11.67 | 101.61 | 6.69 |
| A | -485.757666 | 0.008753 | 0.143898 | 579.23 |

^aThe scaling factor is 0.98 for ZPE and 0.96 for H_T .⁵⁰

Next, the effect of the numbers and positions of the nitro groups on the HOFs of the gas-phase ($\Delta H_{f, \text{gas}}$) and solid-phase ($\Delta H_{f, \text{solid}}$) title compounds were studied. Table 4 summarizes E_0 , H_T , ZPEs, surface areas for the 0.001 electrons/bohr³ isosurfaces of the electronic densities of the molecules (A), degree of balance between the positive and negative potentials on the isosurfaces (v), variability of the electrostatic potentials on the molecular surfaces (σ_{tot}^2), gas-phase HOFs ($\Delta H_{f, \text{gas}}$), and solid-phase HOFs ($\Delta H_{f, \text{solid}}$) of the ($C_4N_6H_{8-n}(NO_2)_n$) derivatives at the B3LYP/6-31G** level.

From Table 4, it can be seen that all of the derivatives have high positive HOFs. Note that the HOF values for all of the nitro-substituted

Table 4. Calculated total energies (E_0 , au), thermal corrections (H_T , au), zero-point energies (ZPE, au), $\Delta H_{f, \text{gas}}$, $\Delta H_{f, \text{sub}}$, and $\Delta H_{f, \text{solid}}$ (kJ mol⁻¹) for the title compounds

| Compound | E_0 | H_T | ZPE | $\Delta H_{f, \text{gas}}$ | A | v | σ_{tot}^2 | ΔH_{sub} | $\Delta H_{f, \text{solid}}$ |
|----------|--------------|----------|----------|----------------------------|--------|------|-------------------------|-------------------------|------------------------------|
| B1 | -690.233172 | 0.011101 | 0.146096 | 640.69 | 188.84 | 0.24 | 272.72 | 108.15 | 532.54 |
| B2 | -690.652886 | 0.011035 | 0.146170 | 604.62 | 193.07 | 0.24 | 351.61 | 117.53 | 487.09 |
| C1 | -894.732447 | 0.013475 | 0.148098 | 639.20 | 219.52 | 0.19 | 372.58 | 124.39 | 514.81 |
| C2 | -894.697017 | 0.013321 | 0.148010 | 731.65 | 211.37 | 0.23 | 241.78 | 113.86 | 617.79 |
| C3 | -894.674640 | 0.013770 | 0.146780 | 785.73 | 212.72 | 0.20 | 371.36 | 122.51 | 663.22 |
| C4 | -894.704884 | 0.013427 | 0.147798 | 710.94 | 216.28 | 0.21 | 317.00 | 121.05 | 589.89 |
| C5 | -894.719296 | 0.013490 | 0.148171 | 672.54 | 215.28 | 0.22 | 327.32 | 126.71 | 545.83 |
| C6 | -894.710239 | 0.013213 | 0.148560 | 698.12 | 210.99 | 0.21 | 192.13 | 106.04 | 592.09 |
| D1 | -1099.186810 | 0.015814 | 0.149865 | 755.06 | 243.21 | 0.17 | 362.89 | 132.78 | 622.28 |
| D2 | -1099.149599 | 0.015804 | 0.149454 | 851.66 | 236.76 | 0.18 | 260.67 | 122.39 | 729.27 |
| D3 | -1099.176023 | 0.015733 | 0.149960 | 783.44 | 238.90 | 0.20 | 252.67 | 125.30 | 658.14 |
| D4 | -1099.165098 | 0.015915 | 0.149331 | 807.94 | 238.46 | 0.16 | 330.09 | 126.17 | 681.77 |
| D5 | -1099.155908 | 0.015746 | 0.149592 | 835.04 | 233.02 | 0.17 | 240.05 | 117.23 | 717.81 |
| E1 | -1303.640367 | 0.018334 | 0.151313 | 872.51 | 266.85 | 0.15 | 304.26 | 138.66 | 733.85 |
| E2 | -1303.629415 | 0.018199 | 0.151542 | 901.63 | 263.92 | 0.15 | 330.22 | 129.96 | 771.67 |
| E3 | -1303.619538 | 0.018368 | 0.151055 | 926.59 | 263.66 | 0.12 | 443.15 | 142.52 | 784.07 |
| E4 | -1303.607261 | 0.018130 | 0.151055 | 931.16 | 258.60 | 0.13 | 278.25 | 128.70 | 802.46 |
| E5 | -1303.621824 | 0.018364 | 0.150983 | 920.13 | 261.13 | 0.16 | 288.24 | 135.52 | 784.61 |
| E6 | -1303.602913 | 0.018364 | 0.150529 | 968.98 | 255.71 | 0.15 | 261.47 | 128.75 | 840.23 |
| F1 | -1508.056391 | 0.021034 | 0.152357 | 1088.18 | 284.74 | 0.10 | 361.10 | 144.54 | 943.64 |
| F2 | -1508.049723 | 0.020988 | 0.151662 | 1103.71 | 280.18 | 0.11 | 311.82 | 140.61 | 963.10 |
| G | -1712.504004 | 0.023460 | 0.153378 | 1219.94 | 307.17 | 0.09 | 366.27 | 155.26 | 1064.68 |

^aThe scaling factor is 0.98 for ZPE and 0.96 for H_T .⁵⁰

derivatives are higher than that of the unsubstituted compound A, and the HOF values are in the order A < B < C < D < E < F < G. This result is consistent with previous reports: the HOFs in high-nitrogen heterocycles increase as the number of nitro groups increases. Isomers with the same number of nitro groups have different HOF values due to the different positions of the nitro groups. It was also found that, in a given molecule, the closer the nitro groups are to each other, the higher the HOF. For example, C3, in which the two nitro groups are located on the same side of the structure, possesses a higher HOF value (663.22 kJ mol⁻¹) than C2 (617.79 kJ mol⁻¹), in which the two nitro groups are located on different sides of the structure, which is in good agreement with the rule.

Detonation Properties

The detonation velocity and detonation pressure are two important parameters for HEDMs. To calculate D and P for an HEDM, ρ must be known first, according to the Kamlet–Jacobs equations. For the derivatives evaluated in this study, the theoretical density was replaced with the loading density, and the detonation properties were calculated. The calculated values ρ , D , and P for the derivatives are listed in Table 5.

From Table 5, it is clear that all of the derivatives with different nitro groups in the ring have different Q , ρ , D , and P values. The largest and smallest Q , ρ , D , and P values are 1898.85 and 1254.13 cal g⁻¹, 2.04 and 1.71 g cm⁻³, 10.06 and 8.00 km s⁻¹, and 47.74 and 27.58 GPa, respectively. In addition, the Q , ρ , D , and P values for the nitro-substituted compounds increase with increasing numbers of nitro groups. It is interesting to note that compound G has the highest value for ρ (2.04 g cm⁻³), while compound F1 has the highest values for D (10.06 km s⁻¹) and P (47.74 GPa) among all of the derivatives. These results are in agreement with a previous study which found that the incorporation of a nitro group into a molecule

Table 5. Predicted densities (ρ), heats of detonation (Q), detonation velocities (D), and detonation pressures (P) for the title compounds

| Compound | Q (cal g ⁻¹) | ρ (g cm ⁻³) | D (km s ⁻¹) | P (GPa) |
|----------|----------------------------|------------------------------|---------------------------|-----------|
| B1 | 1312.85 | 1.71 | 8.00 | 27.58 |
| B2 | 1254.13 | 1.76 | 8.01 | 28.55 |
| C1 | 1493.32 | 1.87 | 8.72 | 34.38 |
| C2 | 1600.33 | 1.83 | 8.72 | 34.02 |
| C3 | 1647.54 | 1.85 | 8.85 | 35.45 |
| C4 | 1571.341 | 1.86 | 8.78 | 34.90 |
| C5 | 1525.56 | 1.85 | 8.68 | 34.02 |
| C6 | 1573.63 | 1.82 | 8.65 | 33.44 |
| D1 | 1664.77 | 1.91 | 9.15 | 39.24 |
| D2 | 1757.70 | 1.89 | 9.26 | 39.47 |
| D3 | 1685.94 | 1.88 | 9.18 | 38.36 |
| D4 | 1716.47 | 1.90 | 9.28 | 39.42 |
| D5 | 1747.80 | 1.88 | 9.21 | 38.62 |
| E1 | 1791.06 | 1.96 | 9.76 | 44.00 |
| E2 | 1819.31 | 1.95 | 9.62 | 43.89 |
| E3 | 1828.57 | 1.96 | 9.76 | 44.67 |
| E4 | 1842.31 | 1.93 | 9.68 | 43.28 |
| E5 | 1828.97 | 1.97 | 9.79 | 44.92 |
| E6 | 1870.52 | 1.93 | 9.62 | 43.61 |
| F1 | 1886.11 | 2.00 | 10.06 | 47.74 |
| F2 | 1898.85 | 1.99 | 9.95 | 47.43 |
| G | 1679.16 | 2.04 | 9.89 | 46.44 |

may increase the density; however, they do not agree with the report from the same study that a greater number of nitro groups affords higher detonation properties.⁵¹ In addition, all of the D1, D4, E, F, and G series compounds possess higher ρ , D , and P values than two famous explosives RDX ($\rho \approx 1.82$ g cm⁻³, $D \approx 8.75$ km s⁻¹, $P \approx 34.00$

GPa) and HMX ($\rho \approx 1.89 \text{ g cm}^{-3}$, $D \approx 9.10 \text{ km s}^{-1}$, $P \approx 39.00 \text{ GPa}$).⁵² Therefore, if these cyclic derivatives can be synthesized in the future, they will have higher exploitable values.

Bond dissociation energies

The bond dissociation energy (BDE) of the trigger bond is another key parameter that can provide useful information for understanding the stability and sensitivity of HEDMs. In general, the smaller the energy that is required for breaking a bond, the weaker the bond is, and the weakest bond becomes the trigger bond when heated or attacked. Thus, to elucidate the thermal stability of HEDMs, the BDE of the trigger bond must be studied.⁵³ On the other hand, a consensus has been reached today that nitro groups often represent the primary cause of initiation reactivity in organic polynitro compounds.⁵⁴⁻⁵⁷ Therefore, the weakest N–NO₂ bonds, which were screened according to the “principle of smallest bond order (PSBO)”, were selected as the breaking bonds for the calculation of the BDEs at the B3LYP/6-31G** level. The PSBO can be defined as follows: for a series of energetic materials with a similar molecular structure and pyrolysis mechanism, the smaller the overlap population of the trigger bond, the larger the impact sensitivity.⁵⁸ It also should be pointed out that the weakest bond was selected as the breaking bond based on the Wiberg bond index. Table 6 presents the bond orders (BO) and BDEs of the weakest N–NO₂ bonds in the title compounds.

From Table 6, it is clear that the highest and lowest BO and BDE values for the derivatives are 1.0805 and 0.8319 and 200.92 kJ mol⁻¹

Table 6. Calculated bond dissociation energies, trigger bond, and bond order for the title compounds

| Compound | N–NO ₂ | | |
|----------|-------------------|--|--|
| | BO | BDE ₀ (kJ mol ⁻¹) | BDE _{ZPE} (kJ mol ⁻¹) |
| B1 | 1.0503 | 161.84 | 140.98 |
| B2 | 1.0805 | 217.34 | 200.92 |
| C1 | 1.0679 | 211.87 | 196.22 |
| C2 | 0.9916 | 139.59 | 120.42 |
| C3 | 0.9333 | 132.35 | 114.22 |
| C4 | 0.9819 | 151.84 | 133.21 |
| C5 | 1.0432 | 151.25 | 130.14 |
| C6 | 1.0440 | 158.92 | 138.65 |
| D1 | 0.9628 | 146.89 | 128.66 |
| D2 | 0.9519 | 142.51 | 126.63 |
| D3 | 0.9718 | 148.32 | 129.94 |
| D4 | 0.9036 | 137.14 | 119.47 |
| D5 | 0.9559 | 120.85 | 102.28 |
| E1 | 0.9560 | 143.91 | 125.84 |
| E2 | 0.9423 | 122.67 | 103.97 |
| E3 | 0.8399 | 131.68 | 114.45 |
| E4 | 0.9258 | 109.31 | 91.28 |
| E5 | 0.9396 | 129.19 | 111.57 |
| E6 | 0.9545 | 128.40 | 109.57 |
| F1 | 0.8665 | 91.95 | 73.09 |
| F2 | 0.8319 | 78.64 | 61.13 |
| G | 0.8510 | 109.05 | 91.47 |

^aBDE_{ZPE} denotes the bond dissociation energies including zero-point energy corrections.

and 61.13 kJ mol⁻¹, respectively. Accordingly, it can be concluded that compound F2 has the highest sensitivity, while compound B2 has the lowest sensitivity. For isomers with the same number of nitro groups, it is fascinating that the BDE value for the N–NO₂ bond in which the nitro group is attached to an $-N=C<$ group is greater than that of the N–NO₂ bond in which the nitro group is attached to the side chain of the ring. For example, B2 has a higher BDE value (200.92 kJ mol⁻¹) than B1 (140.98 kJ mol⁻¹), and thus, compound B2 possesses lower sensitivity than B1. Considering practical requirements and based on the results of these studies, a BDE ≈ 80 –120 kJ mol⁻¹⁵⁹ for the trigger bond is proposed as a quantitative criteria for the stability of HEDCs and was employed to screen the compounds investigated in this study.⁶⁰ Thus, considering both the detonation properties and thermal stabilities, compounds D1, D4, E1–E6, and G can be regarded as potential HEDMs, and the sensitivities of these candidates are in the order of G > E > D4 > D1 according to the BDEs.

CONCLUSIONS

In this study, the electronic structure, HOFs, detonation properties, and thermal stabilities of a series of derivatives based on the guanidine-fused bicyclic skeleton $C_4N_6H_{8-n}(NO_2)_n$ ($n = 1$ –6) were investigated using the B3LYP/6-31G** method of the DFT theory. The following conclusions can be drawn:

(1) All of the $C_4N_6H_{8-n}(NO_2)_n$ derivatives have lower $\Delta E_{\text{LUMO-HOMO}}$ values than the unsubstituted compound $C_4N_6H_8$. In addition, the energy gap of the derivatives is affected by the positions of the nitro groups. The further the two nitro groups are from each other, the higher the $\Delta E_{\text{LUMO-HOMO}}$ values, and thus the better the stability.

(2) All of the $C_4N_6H_{8-n}(NO_2)_n$ derivatives have high positive HOFs, and the HOFs increase with increasing number of nitro groups. For isomers with the same number of nitro groups, the closer the nitro groups are to one another, the higher the HOF.

(3) The predicted detonation velocities and detonation pressures indicate that compounds D1, D4, and E–G, with $\rho > 1.9 \text{ g cm}^{-3}$, $D > 9.0 \text{ km s}^{-1}$, and $P > 39.0 \text{ GPa}$, possess detonation properties superior to those of the famous explosives RDX and HMX. In addition, compound G has the highest theoretical density (ρ , 2.04 g cm⁻³), while compound F1 has the highest values for D (10.06 km s⁻¹) and P (47.74 GPa).

(4) The analysis of the BOs and BDEs of the weakest N–NO₂ bonds indicates that the highest and lowest BO and BDE of the derivatives are 1.0805 and 0.8319 and 200.92 kJ mol⁻¹ and 61.13 kJ mol⁻¹, respectively. Considering both the detonation properties and thermal stabilities, compounds D1, D4, E1–E6, and G can be regarded as potential candidate HEDMs.

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