Theoretical Exploration about the Detonation Performance and Thermal Stability of the Nitro-substituted Derivatives of Guanine[①]

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ABSTRACT   The nitro-substituted derivatives of guanine are designed and calculated to explore novel high energy density materials. To explore the thermal stability of title molecules, the heat of formation (HOF), bond dissociation energy (BDE), and bond order of the trigger bond are calculated. To predict the possibility used as high energy density compounds, the detonation pressure (P), detonation velocity (D), explosive heat (Q), and crystal density (ρ) are calculated by using the classical Kamlet-Jacobs (K-J) equation. Based on our calculations, **E** ($D = 8.93$ km/s, $P = 37.21$ GPa) is confirmed as the potential high energy density compound.

Keywords: high energy density compounds, Kamlet-Jacobs equation, density function theory, guanine derivatives; DOI: 10.14102/j.cnki.0254–5861.2011–2954

1   INTRODUCTION

High energy density materials are very important for civilian production and the military field[1-3]. In the last twenty years, many new materials with excellent characters have been explored and conducted. In the past few decades, many new high energy density materials have been designed and synthesized[4-7]. However, the existing high energy density materials can't fully meet the needs so far, so we need to further work to search for new high energy density materials with better properties. Generally speaking, such energetic materials should have better stability and better detonation performance.

Guanine is a typical DNA molecule composed of a pyrimidine and an imidazole rings[8]. In addition to being of great significance in the field of life science, the guanine ring has five nitrogen atoms and naturally has the characteristics of high energy density. The nitrogen percent is about 46%, which results in guanine energetic because the product in the dissociation reaction is the nitrogen molecules with super stability. Introducing energetic groups into a parent body with high nitrogen content is the popular strategy to construct high energy density compound and has been proved valuable

extensively by many existing models[9-11]. In this sense, it is possible to obtain a novel high energy density molecule with excellent properties if we introduce high energy density groups to the guanine ring, as shown. However, the research on guanine has been focused on biology, and the application of this molecule in the field of energetic materials is less concerned[12, 13]. Guanine has two isomers including keto and enol forms. The study of hydrogen transport isomerization of the two structures shows that the alcohol structure is more stable[14]. Therefore, in this paper, the enol form guanine is used as the parent structure, and the nitro group with high energy density is introduced into it to construct a new class of molecules. To explore the possibility of applications as energetic materials, their structural stability and energetic properties are studied.
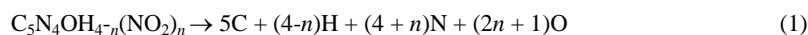
2   COMPUTATIONAL METHODS

The structures of the nitro-substituted derivatives of guanine were fully optimized at the G3MP2 level[15] using the Gaussian 03 program package[16]. The atomization reactions[17-20] are designed to obtain heats of formation (HOFs), and the formula is followed:

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$$C_5N_4OH_{4\text{-}n}(NO_2)_n \rightarrow 5C + (4\text{-}n)H + (4 + n)N + (2n + 1)O \qquad (1)$$

$$\Delta H_{f,0}^{at}(M) = G3MP2_0(M) - \sum_{atom} G3MP2_0(X) + \sum_{atom} \Delta H_{f,0}^{exp}(X) \qquad (2)$$

$$\Delta H_{f,298}^{at}(M) = \Delta H_{f,0}^{at}(M) + \Delta H_{298}(M) - \sum_{atom} \Delta H_{298}(X) \qquad (3)$$

where ΔH_{298} is the difference of enthalpy changing from 0 to 298 K; X refers to the elements; M means the target molecule; $\Delta H_{f,0}^{at}(M)$ is the heat of formation of M at 0 K; $\Delta H_{f,298}^{at}(M)$ is the heat of formation of M at 298 K; $G3MP2_0(M)$ is the enthalpy calculated by the G3MP2 method at 0 K; $\Delta H_{f,0}^{exp}(X)$ is the heat of formation for element X in the experiment and taken from the NIST WebBook[21]. All of the energy values are corrected by the zero-point energies.

To measure the strength of trigger bonds, the bond dissociation energies (BDE) were calculated. BDE is the energy required for the homolytic cleavage of a bond and is commonly denoted as the difference between the total energies of the radical products and reactants. The BDE values of A−B bond were calculated as follows:

$$BDE_{(A\text{−}B)} = E_{(A)} + E_{(B)} - E \qquad (4)$$

The BDE with zero-point energy (ZPE) correction can be calculated via equation (5):

$$BDE(A\text{−}B)_{ZPE} = BDE_{(A\text{−}B)} + \Delta ZPE \qquad (5)$$

where ΔZPE is the difference between the ZPEs of the products and the reactants.

Detonation velocity (D) and detonation pressure (P) are used to evaluate the explosive performances of energetic materials by using the empirical equations[22]:

$$D = 1.01(N\overline{M}^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \qquad (6)$$

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

D is the detonation velocity (km/s); P is the detonation pressure (GPa); N is the moles of gas produced per gram of explosive and $\overline{M}$ is the mean molecular weight of the gaseous detonation products; Q is the detonation energy (cal/g); ρ is molecular theory density (g/cm^3), which was calculated from the molar weight (M) divided by the average value molar volume (V), which was defined as the volume of 0.001 electrons/bohr^3 electron density envelope.

The impact sensitivity is explored by using the characteristic drop height (H_{50}). H_{50} is calculated according to the equations:

$$H_{50} = \alpha\sigma_+^2 + \beta\nu + \gamma \qquad (8)$$

in which α, β, and γ are empirical parameters from Ref. 22.

3   RESULTS AND DISCUSSION

3.1   Heats of formation

HOF is an important factor to reflect the energy content of a compound and molecular stability. High and positive HOF represents highly energetic, but less stable. So, the values of HOFs are calculated according to equations (1), (2) and (3), and the final data are listed in Table 1.

Table 1.   **Heats of Formation Calculated by Using the Atomization Reaction at the G3MP2 Level**

Compound	ZPE (a.u.)	E (a.u.)	H (a.u.)	ΔH_T (a.u.)	HOF (kJ/mol)
A1	0.11503	−746.05218	−746.04067	0.12559	133.95
A2	0.11552	−746.08934	−746.07782	0.12610	36.52
B	0.11819	−950.32206	−950.30730	0.13201	181.11
C1	0.12158	−1154.56912	−1154.55203	0.13773	285.70
C2	0.12153	−1154.56829	−1154.55118	0.13770	287.92
D	0.12373	−1358.81046	−1358.79100	0.14226	405.40
E	0.12485	−136.95821	−1584.63841	0.15263	534.26

From Table 1, the HOF values are all positive, which is a typical feature of high energy density materials. For the single substituted derivatives, the HOF (133.95 kJ/mol) of **A1** is larger than 36.52 kJ/mol of **A2**. From Fig. 1, it is clear that **A1** is derived from the substitution of the nitro group on nitrogen atom but **A2** is derived from the substitution of the carbon atom. On the consideration that the N−C bond is more stable than N−N bond, so our result is reasonable. With the

introduction of nitro groups, the HOF values are increased together. Based on the linear regression, the formula is obtained as $y = 110.56x - 33.688$ with the R^2 value of 0.968. A good linear relationship is confirmed. So, the group addition principle is suitable for title molecules.

The largest HOF is obtained for **E** (534.26 kJ/mol), which represents **E** has the largest energetic content here but indicates the worst thermodynamic stability. In terms of

thermodynamic stability, energetic materials are usually poor. Dynamic stability is a more important parameter for energetic materials, such as RDX[23], CL-20[24], and so on. Therefore,

in the next chapter, we calculate the dissociation energies of these molecules to investigate the kinetic stability of these molecules.
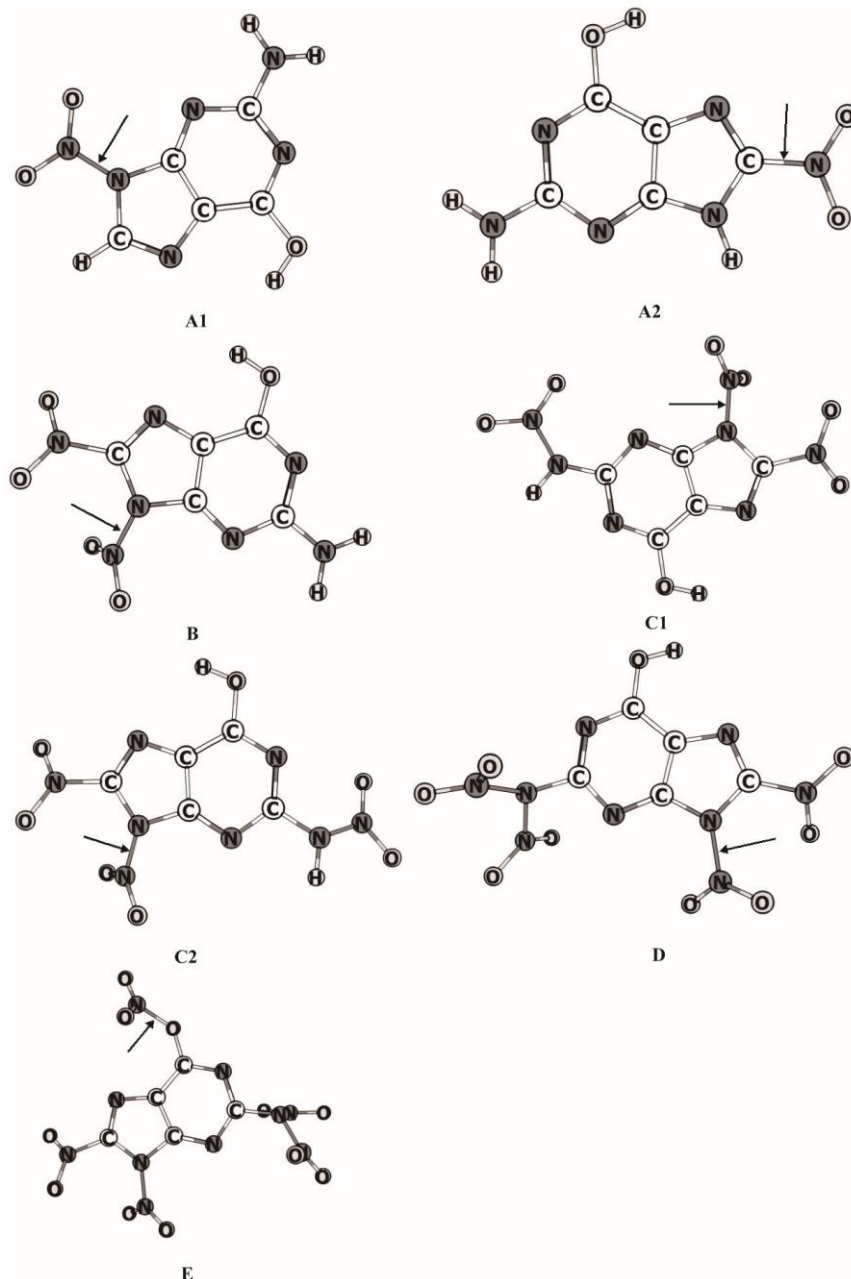

Fig. 1.   Nitro-substituted derivatives of Guanine designed explored in this paper with the arrow pointing to the trigger bond

3. 2   Bond dissociation energy

Bond dissociation energy can be used to indicate the dynamic stability of high energy density compounds[9, 25]. In theory, bond dissociation energy can be obtained by calculating the enthalpy change of the homolytic cleavage reaction. So, the bond dissociation energies are calculated according to equation (4) and listed in Table 2. The bond order is predicted at first to confirm the trigger bond, which is determined by the least bond order and considered to initiate

the dissociation reaction. To save the calculation cost, the calculation about the bond dissociation energy is only performed focused on the trigger bond.

As a measure of bond strength, bond order is less reliable than bond dissociation energy. For instance, the bond dissociation energy 163.46 kJ/mol of A1 is less than 300.63 kJ/mol of **A2**, but 0.9453 of **A1** is larger than 0.9383 of **A2**. So, bond dissociation energy is used to predict the dynamic stability of title molecules. The bond dissociation energies

obtained here are all more than 120 kJ/mol[26], which indicates that these molecules have sufficient kinetic stability and exist stably at ambient temperature. With the introduction of groups, the dissociation energy is generally reduced. The smallest bond dissociation energy is located in the molecular **E**, which is mainly due to the nitro group being attached to the oxygen atom, while the N−O bond energy is lower than the N−C bond.

Table 2.   Bond Dissociation Energies Calculated by Using the Homolytic Cleavage Reaction at the G3MP2 Level

Compound	ZPE (a.u.)	E (a.u.)	HOF (kJ/mol)	Bond order
A1	0.11778	−746.81968	163.46	0.9453
A2	0.11905	−746.85735	300.63	0.9383
B	0.12029	−951.27593	123.72	0.8523
C1	0.12253	−1155.71216	139.65	0.8042
C2	0.12267	−1155.71083	137.29	0.8352
D	0.12337	−1360.13528	147.99	0.8121
E	0.12405	−1564.55312	112.33	0.6978

3. 3   Detonation characters

Detonation properties are the most important properties of energetic materials. Generally speaking, explosion velocity (D) and explosion pressure (P) are the two most important indexes. So, both of them are calculated by using the classical K-J equation accompanied by the molecular density and detonation heat. The insensitivity of high energy density materials is predicted by the characteristic height (H_{50}). The final data are listed in Table 3.

**Table 3.   Detonation Pressure, Detonation Velocity, Explosive Heats,
and Crystal Density Calculated by Using the Kamlet-Jacobs Equation**

Compound	$\rho(g/cm^3)$	Q(cal/g)	D(km/s)	P(GPa)	H_{50}(cm)
A1	1.6767	1053.38	6.91	20.26	49
A2	1.6762	1053.38	6.91	20.24	46
B	1.7822	1224.51	7.76	26.52	35
C1	1.8600	1341.81	8.36	31.59	33
C2	1.8620	1341.81	8.36	31.66	36
D	1.9237	1427.23	8.82	35.90	14
E	1.9661	1367.19	8.93	37.21	18

From the data in Table 3, the detonation pressure and detonation velocity are rising with the introduction of nitro groups. Based on the linear regression between the detonation parameters and the substitution number, a good linear relationship is obtained as $y = 4.5357x + 16.743$ with the R^2 value of 0.9591 for detonation pressure and $y = 0.5432x + 6.5328$ with the R^2 value of 0.9367 for detonation velocity. The group addition principle is appropriate for the detonation parameters. The most excellent detonation parameters are attributed to molecule E ($D = 8.93$ km/s, $P = 37.21$ GPa), which is better than the famous energetic RDX. Except for the energetic characters, the H_{50} of **E** is confirmed to be 18 cm, which is comparable with the RDX. So, **E** is confirmed as the potential high energy density compounds for its comparable molecular insensitivity and better detonation characters.

4   CONCLUSION

In this paper, seven derivatives of Guanine are designed by the introduction of nitro groups to substitute the hydrogen atom and explored by using the G3MP2 method. The HOF values are all confirmed to be positive, which indicates the energetic nature of title molecules. Furthermore, **E** is confirmed with the largest BDE value of 534.26 kJ/mol. The bond dissociation energy of all molecules is confirmed above 120 kJ/mol, which is the benchmark to scale the dynamic stability of high energy density compounds. Furthermore, the bond dissociation energy is more reliable than a bond order to predict the stability of title molecules. The detonation

parameters are rising with the introduction of the nitro groups, and the most excellent parameters are located at **E** (D = 8.93 km/s, P = 37.21GPa), which has the characteristic height value of 18 cm comparable to RDX. Finally, molecule **E** is found to be the potential high energy density compound for further research.

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