

Density functional theory study of piperidine and diazocine compounds

Xiao-Wei Fan, Xue-Hai Ju^{*}, He-Ming Xiao

Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210094, PR China

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Abstract

Density functional theory calculations at the B3LYP/6-311G** level were performed to predict the heats of formation (HOFs) for three eight-membered ring compounds and four six-membered ring compounds via designed isodesmic reactions. In the isodesmic reactions designed for the computation of HOFs (CH₃CH₂)₂NNO₂ and piperidine were chosen as reference compounds. The HOFs for –NO₂ substituted derivations are larger than those of –NF₂ substituent groups. Thermal stability were evaluated via bond dissociation energies (BDE) at the UB3LYP/6-311G** level. As a whole, the homolysis of C–NF₂ or C–NO₂ bonds is the main step for bond dissociation of the title compounds. Detonation properties of seven title compounds were evaluated by using the Kamlet–Jacobs equation based on the calculated densities and HOFs. It is found that 3,3,7,7-tetrakis(difluoroamino)octahydro-1,5-dinitro-1,5-diazocine (HNFX) and 3,3,5,5-tetrakis(difluoroamino)-1-nitro piperidine (N-nitro TDFAPP), with predicted density of ca. 2.0 g/cm³, detonation velocity (*D*) about 9.9 km/s, and detonation pressure (*P*) of 47 GPa that are larger than those of HMX, are expected to be the novel candidates of high energy density materials (HEDMs). The detonation data of 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane (HNDZ) and TNBDFAPP show that they meet the requirements for HEDMs.
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Keywords: Heats of formation; Density functional theory; Isodesmic reaction; Bond dissociation energy; Detonation properties; Piperidine and diazocine compounds

The nitramines are the most recently introduced class of organic nitrate explosives. The most prominent member of this class is TNAZ (1,3,3-trinitro-azetidene), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (1,3,5,7-tetraazacyclooctane). TNAZ, RDX and HMX are important energetic material extensively used as an explosive and booster charge, and as oxidizer in solid rocket and gun propellants. And the study of structures and characters of TNAZ, RDX and HMX always be interesting [1–5]. The nitramines of four-membered, six-membered and eight-membered ring are suitable to use as a class of explosives. Therefore, to obtain more energetic materials, we are screening of other nitramine compounds.

The nitro is an important group for energetic materials [6]. Another moiety with the similar oxidizing and energetic potential is NF₂ group. Through increasing numbers of these two groups, the compounds' density and the number of mole

gaseous combustion products formed per gram of material can be increased, thereby enhancing propellant performance. Difluoroamino compounds represent a new generation of energetic materials, which are of interest because of their potential high density, energy and properties as solid propellant oxidizers [7–9]. Geminal difluoroamino/nitro compounds are considered toxic and potentially explosive and should be handled with suitable precautions [7]. Alternatively, we employed theoretical investigation of these compounds.

3,3,7,7-Tetrakis(difluoroamino)octahydro-1,5-dinitro-1,5-diazocine (HNFX), 3,3-dinitro-7,7-bis(difluoroamino)octahydro-1,5-dinitro-1,5-diazocine (TNBDFADZ) and 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane (HNDZ) are analogue energetic compounds [10–13]. The ring structures of the title compounds are similar to HMX.

The structures of N-nitro piperidine compounds [7,12] are similar to RDX and the structures of diazocine compounds are similar to HMX. Are their detonation properties similar to those of RDX and HMX? Do the nitramines of four-, six- and eight-membered ring compounds have the similar detonation properties? To answer these, we calculate the heats of formation

^{*} Corresponding author. Tel.: +86 25 84315947x801; fax: +86 25 84431622.
E-mail address: xhju@mail.njust.edu.cn (X.-H. Ju).

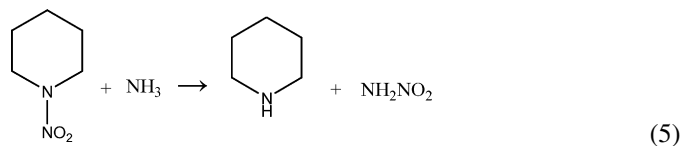
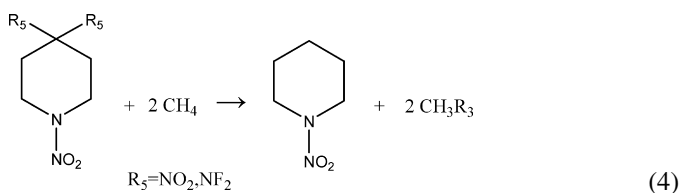
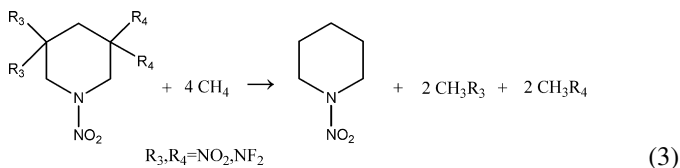
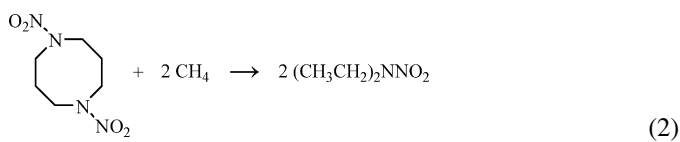
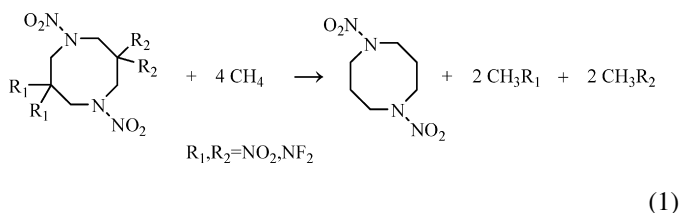
(HOFs), bond dissociation energies (BDE) and detonation properties of seven compounds that are believed to be candidates of novel energetic materials.

The HOFs are well known to evaluate the explosive performances of energetic materials. Computational approaches have shown their great advantages and been employed to obtain HOFs of those demanding materials [8,9,14–16]. Thermal stability was evaluated via BDE [17]. The detonation velocity (D) and detonation pressure (P) are the necessary factors for evaluating the detonation properties of energetic compounds. The D and P for the title compounds were calculated by using empirical Kamlet–Jacobs equations [18,19]. These results provide useful information for the molecular design of novel high energetic density materials.

1. Computational methods

The density functional theory (DFT) [20,21] has emerged as a very reliable theoretical method. Hence, it has been used to evaluate HOFs and BDE of interested molecules. The density functional theory method, especially, the B3LYP [22,23] hybrid DFT that not only produces reliable geometries and energies but also requires less time and computer resources, have been widely employed and have become an important and economical tool to deal with complex electron correlation problems. The predictions of HOFs adopt the hybrid DFT-B3LYP methods with 6-311G** basis set via designed isodesmic reactions [24]. The method of isodesmic reactions has been employed very successfully to calculate HOFs [8,9,14–16].

The enthalpy of formation for the title compounds were derived from the following isodesmic reactions:



For the isodesmic reactions (1)–(5), heat of reaction ΔH_{298} at 298 K can be calculated from the following equation:

$$\Delta H_{298} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R} \quad (6)$$

where $\Delta H_{f,R}$ and $\Delta H_{f,P}$ are the HOFs of reactants and products at 298 K, respectively. As experimental HOFs of CH_3NF_2 is unavailable, additional calculations were carried out for the replacement reaction $\text{CH}_3\text{NH}_2 + \text{F}_2 \rightarrow \text{CH}_3\text{NF}_2 + \text{H}_2$ using the G2 method to get an accurate value of ΔH_f for CH_3NF_2 [8]. All the experimental HOFs of reference compounds CH_4 , CH_3NO_2 , $(\text{CH}_3\text{CH}_2)_2\text{NNO}_2$ and $\text{C}_5\text{H}_{10}\text{NH}$ (piperidine) are available. The HOFs of the title compounds can be figured out when the heat of reaction ΔH_{298} is known. Therefore, the most important thing is to compute the ΔH_{298} . ΔH_{298} can be calculated using the following expression:

$$\Delta H_{298} = \Delta E_{298} + \Delta PV = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (7)$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; ΔH_T is thermal correction from 0 K to 298 K. The ΔPV value in Eq. (7) is the PV work term. It equals ΔnRT for the reactions of ideal gas. For the isodesmic reactions (1)–(5), $\Delta n = 0$, so $\Delta PV = 0$.

The bond strength could be evaluated by the bond dissociation energy [17]. The energy required for homolytic bond cleavage at 298 K and 1 atm corresponds to the enthalpy of reaction (8), $\Delta_{\text{rxn}}H_{298}$ (8), which is by definition [25] the bond dissociation enthalpy of the molecule A–B, $\text{DH}_{298}(\text{AB})$:



By definition, it is the reaction enthalpy of the bond homolysis reaction (8), $\Delta_f H_{298}$ (8), and thus depends exclusively on the relative enthalpies of formation of reactant and product states [26]:

$$\begin{aligned}
 \Delta_{\text{rxn}}H_{298}(8) &= \Delta_f H_{298}(\text{A}^\bullet) + \Delta_f H_{298}(\text{B}^\bullet) - \Delta_f H_{298}(\text{A–B}) \\
 &= \text{DH}_{298}(\text{A–B}) \quad (9)
 \end{aligned}$$

where $\Delta_f H_{298}(\text{A}^\bullet)$ and $\Delta_f H_{298}(\text{B}^\bullet)$ are the enthalpies of formation of the radicals, $\Delta_f H_{298}(\text{A–B})$ is the enthalpy of formation of the molecule.

For many organics, $\text{BDE}(\text{A–B})$ and $\text{DH}_{298}(\text{A–B})$ are almost numerically equivalent, and as a consequence the terms “bond dissociation energy” (BDE) and “bond dissociation enthalpy” often appear interchangeably in the literature [26]. Therefore, the homolytic bond dissociation energy can be given in terms of Eq. (10) [26]:

$$\text{BDE}(\text{A–B}) = E_0(\text{A}^\bullet) + E_0(\text{B}^\bullet) - E_0(\text{A–B}) \quad (10)$$

The bond dissociation energy with ZPE correction:

$$\text{BDE}(A - B)_{\text{ZPE}} = \text{BDE}(A - B) + \Delta\text{ZPE} \quad (11)$$

where ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants.

Detonation velocity (D) and detonation pressure (P) are the important parameters to evaluate the explosive performances of energetic materials and be estimated by using the empirical

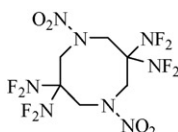
Kamlet formula [18,19] as

$$P = 1.558\rho^2\Phi \quad (12)$$

$$D = 1.01\Phi^{1/2}(1 + 1.30\rho_0) \quad (13)$$

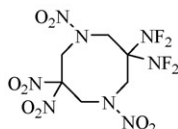
$$\Phi = 0.4889N(MQ)^{1/2} \quad (14)$$

where D is the predicted detonation velocity (km/s) and P is the detonation pressure (GPa), ρ is the density of a compound (g/cm³). Φ , N , M and Q are characteristic parameters of an



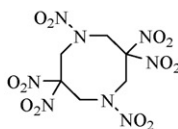
1. 3,3,7,7-tetrakis(difluoroamino)octahydro-1,5-dinitro-1,5-diazocine

(Abbr.HNFX Stoich. C₆H₈F₈N₈O₄)



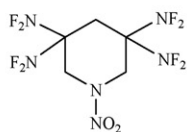
2. 3,3-dinitro-7,7-bis(difluoroamino)octahydro-1,5-dinitro-1,5-diazocine

(Abbr.TNBDFADZ Stoich. C₆H₈F₄N₈O₈)



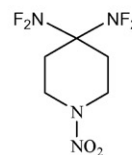
3. 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane

(Abbr.HNDZ Stoich. C₆H₈N₈O₁₂)



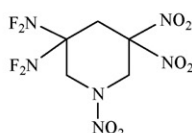
4. 3,3,5,5-tetrakis(difluoroamino)-1-nitro piperidine

(Abbr.N-nitro TDFAPP Stoich.C₅H₆F₈N₆O₂)



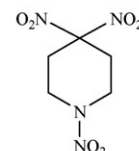
5. 4,4-bis(difluoroamino)-1-nitro piperidine

(Abbr. N-nitro BDFAPP Stoich. C₅H₈F₄N₄O₂)



6. 3,3-bis(difluoroamino)-7,7-dinitro-1-nitro piperidine

(Abbr.TNBDFAPP Stoich. C₅H₆F₈N₆O₂)



7. 4,4-dinitro-1-nitro piperidine

(Abbr. TNPP Stoich.C₅H₈N₄O₆)

Fig. 1. Molecular frameworks and chemical names.

explosive, Q is chemical energy of detonation (kJ/g), M is molecular weight (g/mol) and N is the final number of moles of gas generated by per gram of the explosive (mol/g).

All computations were performed with the Gaussian 98 package [27] at the B3LYP level. The optimizations were performed without any symmetry restrictions using the default convergence criteria in the programs. All of the optimized structures were characterized to be true local energy minima on the potential energy surfaces without imaginary frequencies.

2. Results and discussions

2.1. Heats of formation

Fig. 1 shows the molecular frameworks of seven title compounds. Table 1 lists the total energies, zero-point energies and the values of thermal correction at the B3LYP/6-311G** level for six reference compounds being enlisted in the isodesmic reactions (1)–(5). Thermodynamic information was obtained from scaled vibrational frequencies with scaling factors taken from Scott and Radom [28]. The experimental HOFs of reference compounds CH₄, CH₃NO₂, (CH₃CH₂)₂NNO₂ and C₅H₁₀NH (piperidine) are taken from Refs. [29,30]. The HOF for (CH₃CH₂)₂NNO₂ at 298.15 K in gaseous phase is not available. We derived its HOF of gaseous state at 298.15 K by adding its HOF in solid phase with enthalpy of sublimation (−106.27 kJ/mol and 53.14 kJ/mol, respectively from Ref. [29a]). The HOF value for 1,5-dinitro-diazocine at 298.15 K, that is −3.05 kJ/mol, was obtained from the isodemic reaction (2): C₆H₁₂N₄O₄ (1,5-dinitro-diazocine) + 2CH₄ → 2(CH₃CH₂)₂NNO₂. The HOF of N-nitro piperidine at 298.15 K is −28.70 kJ/mol, was calculated via the isodemic reaction (5): C₅H₁₀NNO₂ (N-nitro piperidine) + NH₃ → C₅H₁₀NH (piperidine) + NH₂NO₂. The accurate value of ΔH_f for CH₃NF₂ and NH₂NO₂ were obtained using G2 method from Refs. [8,31]. Table 2 shows the total energies, zero-point energies and the values of thermal corrections for title compounds, and the values of HOFs obtained via Eq. (7). 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 [8,9,14–16].

Table 1

Calculated total energy (E_0), zero-point energy (ZPE), values of thermal correction to enthalpy (H_T) and heats of formation (HOF) of the reference compounds at the B3LYP/6-311G** level^a

| Compd. | E_0 | ZPE | H_T | HOF |
|--|-------------|--------|-------|---------------------------|
| CH ₄ | −40.533744 | 114.75 | 10.04 | −74.40 [29b] |
| CH ₃ NO ₂ | −245.081672 | 127.82 | 14.14 | −74.30 [29b] |
| CH ₃ NF ₂ | −294.298330 | 120.28 | 13.86 | −115.23 [8] |
| NH ₂ NO ₂ | −261.113787 | 101.39 | 12.33 | 6.69 [31] |
| (CH ₃ CH ₂) ₂ NNO ₂ | −418.407018 | 390.44 | 27.09 | −53.13 ^b [29a] |
| C ₅ H ₁₀ NH | −251.974891 | 415.08 | 17.87 | −47.1 [30] |

^a E_0 is in a.u., ZPE, HOF and H_T are in kJ/mol. The scaling factor for ZPE is 0.98 and the scaling for H_T is 0.96 [28].

^b The value −53.13 kJ/mol is heat of formation at 298.15 K in the solid phase plus the enthalpy of sublimation for (CH₃CH₂)₂NNO₂.

Table 2

Total energy (E_0), zero-point energy (ZPE), values of thermal correction (H_T) and heats of formation (HOF) of the title compounds at the B3LYP/6-311G** level^a

| No. | Compd. | E_0 | ZPE | H_T | HOF |
|-----|----------------|--------------|--------|-------|---------|
| 1 | HNFx | −1770.752499 | 526.98 | 66.58 | −55.09 |
| 2 | TNBDFADZ | −1672.321878 | 543.23 | 66.14 | 19.86 |
| 3 | HNDZ | −1573.890121 | 559.21 | 64.14 | 95.97 |
| 4 | N-nitro TDFAPP | −1471.547856 | 401.72 | 55.58 | −125.55 |
| 5 | N-nitro BDFAPP | −964.047770 | 410.22 | 39.60 | −109.04 |
| 6 | TNBDFAPP | −1373.123139 | 418.53 | 53.80 | −66.88 |
| 7 | TNPP | −865.617829 | 426.80 | 37.90 | 36.80 |

^a E_0 is in a.u., ZPE, HOF and H_T are in kJ/mol. The scaling factor for ZPE is 0.98 and the scaling for H_T is 0.96 [28].

Table 2 shows that the HOFs of HNFx, TNBDFADZ and HNDZ are −55.09 kJ/mol, 19.86 kJ/mol and 95.97 kJ/mol, respectively. The HOFs of gas phase of cyclooctane is −126.49 kJ/mol [29]. The N–NO₂ group, when substituting the methylene group, can increase the HOFs of the compounds. As a result, the HOF of 1,5-dinitro-diazocine at 298.15 K is −3.05 kJ/mol that is somewhat intermediate between those of HNDZ and cyclooctane. The HOFs of title compounds would be reduced with the addition of difluoroamino to the diazocine ring. However, the nitro group can increase the HOFs of title compounds. The experimental HOFs of HNDZ for solid phase is −27.35 kJ/mol [10]. From that we deduced that the enthalpy of sublimation of HNDZ is 123.32 kJ/mol, which is agreeable to the sublimating enthalpy for molecular crystals without strong hydrogen bonding.

For N-nitro piperidine compounds, substituent groups affect the HOFs of title compounds. When the H atom on the N atom was replaced by the NO₂ group, the HOF of N-nitro piperidine is −28.70 kJ/mol, which is more than that of piperidine. When the nitro or difluoroamino groups being attached to the *meta*-position of N-nitro piperidine, the HOF of N-nitro TDFAPP is −125.55 kJ/mol, whereas the HOF of TNBDFAPP is −66.88 kJ/mol since the latter contains two nitro groups. When the nitro or difluoroamino groups being attached to the *para* position of N-nitro piperidine, the HOF of N-nitro BDFAPP is −109.04 kJ/mol. For N-nitro TDFAPP, N-nitro BDFAPP and N-nitro piperidine, the interactions of the substituted group deviate from group additivity, which enables the position of the substituted group determines its substituent effect. TNPP has three NO₂ groups, therefore, the HOF value is 36.80 kJ/mol, which is more than that of N-nitro piperidine.

2.2. Thermal stability

As a high energetic insensitive explosive, the thermal stability of title compounds should be emphasized. To elucidate this, we calculated the dissociation energies for the possible initial steps in the pyrolysis route. It should be pointed out that we select the C–R (R = −NF₂ and −NO₂) bonds, N–NO₂ bond, C–C and C–N bonds on the ring as the possible breaking bond at the UB3LYP/6-311G** level. The values of bond dissociation

Table 3
Bond dissociation energies (BDE, kcal/mol) for A–B (g) → A·(g) + B·(g) at the UB3LYP/6-311G** Level

| No. | Compound | C–N | | C–C | | N–NO ₂ | | C–NF ₂ | | C–NO ₂ | |
|-----|----------------|-------|--------------------|-------|--------------------|-------------------|--------------------|-------------------|--------------------|-------------------|--------------------|
| | | BDE | BDE _{ZPE} | BDE | BDE _{ZPE} | BDE | BDE _{ZPE} | BDE | BDE _{ZPE} | BDE | BDE _{ZPE} |
| 1 | HNFx | 75.61 | 81.61 | 62.93 | 67.62 | 38.69 | 43.40 | 31.98 | 35.99 | | |
| 2 | TNBDFADZ | 72.80 | 78.49 | 71.41 | 77.02 | 36.72 | 41.32 | 33.93 | 37.89 | 32.07 | 36.17 |
| 3 | HNDZ | 69.48 | 75.32 | 70.77 | 75.66 | 37.68 | 42.30 | | | 32.07 | 36.37 |
| 4 | N-nitro TDFAPP | 88.01 | 93.34 | 76.18 | 81.20 | 41.53 | 46.38 | 32.81 | 36.61 | | |
| 5 | N-nitro BDFAPP | 83.51 | 89.30 | 78.43 | 84.38 | 45.05 | 50.02 | 36.39 | 40.44 | | |
| 6 | TNBDFAPP | 85.83 | 91.67 | 78.08 | 83.27 | 40.33 | 44.89 | 35.39 | 39.54 | 36.57 | 40.98 |
| 7 | TNPP | 83.57 | 89.06 | 77.38 | 83.31 | 44.77 | 49.82 | | | 39.51 | 43.79 |

energies (BDE) are listed in Table 3. For the C–N and C–C bonds of title compounds, the BDE_{ZPE} values are ca. 68–93 kcal/mol. Therefore they are relatively stable, not being concerned with the initial fission. The BDE_{ZPE} values of C–NF₂ and C–NO₂ bonds are ca. 36–44 kcal/mol, respectively. These values are smaller than those of the other bonds. Therefore, C–NF₂ or C–NO₂ bonds are easier to break for these compounds. The initial scission step should be the scission of the C–NF₂ or C–NO₂ bonds. The BDE_{ZPE} values of N–NO₂ bond that are ca. 41–50 kcal/mol always are more than that of C–NF₂ or C–NO₂ bonds in the same molecule. So it is not a key to the fragmentation pathway of title compounds.

For the title compounds, the BDE values of N–NO₂, C–NO₂ and C–NO₂ are close to those of earlier works [3,4,32–34]. TNAZ (1,3,3-trinitroazetidene) is the four-membered ring analog for the title compounds. The calculated BDE values are 43.06 kcal/mol, 42.52 kcal/mol, 62.56 kcal/mol and 57.65 kcal/mol before ZPE corrections for the scissions of C–NO₂, N–NO₂, C–C and C–N bonds, respectively [9]. It can be known that the thermal stability of eight-membered ring and six-membered ring are better than that of four-membered ring. But the fissions for the groups attached to eight-membered ring and six-membered ring compounds are easier than that of four-membered ring compounds. The strong repulsion among geminal substituent groups is of importance to the C–NO₂ and/or C–NF₂ bond scissions.

2.3. Detonation properties

Table 4 lists the detonation properties of title compounds and the experimental data of TNAZ, RDX and HMX. HNFx has an experimental density of 1.807 g/cm³, the low density attributed to solvent channels in the crystal structure formed during crystallization [13]. Therefore, the difference of experimental and calculated density is 0.153. HNDZ's experimental density is 1.875 g/cm³. The absolute error is only 0.015. The calculated detonation velocity and detonation pressure are 9.95 km/s and 47.77 GPa for HNFx that is superior to those of HMX. The detonation properties of HNDZ, 9.19 km/s and 38.59 GPa for detonation velocity and detonation pressure, respectively, are similarly to those of HMX. The values of detonation properties of HNFx and HNDZ are larger than those of TNAZ and RDX. Therefore, the two compounds meet the requirements of HEDM.

Table 4
Densities and detonation properties of the title compounds

| No. | Compound | Q (J/g) | ρ (g/cm ³) | D (km/s) | P (GPa) |
|-----|-------------------|---------|---------------------------|----------|---------|
| 1 | HNFx | 7116.30 | 2.06 (1.807) ^a | 9.95 | 47.44 |
| 2 | TNBDFADZ | 6992.96 | 1.96 | 7.92 | 29.27 |
| 3 | HNDZ | 6867.58 | 1.89 (1.875) ^a | 9.19 | 38.59 |
| 4 | N-nitro TDFAPP | 7169.12 | 2.05 | 9.92 | 47.02 |
| 5 | N-nitro BDFAPP | 6294.07 | 1.81 | 8.43 | 31.65 |
| 6 | TNBDFAPP | 6970.43 | 1.95 | 9.45 | 41.55 |
| 7 | TNPP | 6351.65 | 1.68 | 7.97 | 27.02 |
| | TNAZ ^b | | 1.84 | 8.73 | 37.20 |
| | RDX ^c | | 1.81 | 8.75 | 34.70 |
| | HMX ^c | | 1.90 | 9.10 | 39.00 |

^a Data of density for HNFx and HNDZ are from Ref. [13] and Ref. [11], respectively.

^b Data for TNAZ are from Ref. [35].

^c Data for RDX and HMX are from Ref. [36].

But the detonation properties of TNBDFADZ are not as large as those of TNAZ and RDX, only is 7.92 km/s and 29.27 GPa. The small HOF value brings the low detonation velocity and pressure.

For six-membered ring compounds, the values of detonation properties of N-nitro TDFAPP are 9.92 km/s and 47.02 GPa, which are far more than those of HMX. More attentions should concentrate on this compound. At the same time, the 9.45 km/s and 41.55 GPa of TNBDFAPP meet the requirements of HEDM, too. The detonation properties of NBDFAPP, 8.43 km/s and 31.65 GPa for detonation velocity and detonation pressure, respectively, are similarly to those of TNAZ. Therefore, it can be considered for HEDM.

3. Conclusion

Through the DFT study of seven compounds on their HOFs, it indicates that the substituted groups affect the HOFs values of title compounds. The addition of the difluoroamino group to the diazocine ring reduces the HOFs, however, the nitro group increases the HOFs of title compounds. The calculations on BDE suggest that the scission of C–NF₂ or C–NO₂ bond is the initial step among the title compounds. HNFx, HNDZ, N-nitro TDFAPP and TNBDFAPP can be considered for HEDM because of the excellent detonation properties.

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