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Theoretical Studies on Nitramine Explosives with -NH_2 and -F Groups

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The nitramine explosives with -NH_2 and -F groups were optimized to obtain their molecular geometries and electronic structures at DFT–B3LYP/6-31+G(d) level. The theoretical molecular density (ρ), heat of formation (HOF), detonation velocity (D) and detonation pressure (P), estimated using Kamlet-Jacobs equations, showed that the detonation properties of these compounds were excellent. Based on the frequencies scaled by 0.96 and the principle of statistic thermodynamics, the thermodynamic properties were evaluated, which were respectively related with the temperature. The simulation results reveal that 1,3,5,7-tetranitro-1,3,5,7-tetrazocan-2-amine (molecule **B1**) performs similarly to the famous explosive HMX, and 2-fluoro-1,3,5-trinitro-1,3,5-triazinane (molecule **C1**) and 2-fluoro-1,3,5,7-tetranitro-1,3,5,7-tetrazocane (molecule **D1**) outperform HMX. According to the quantitative standard of energetics and stability as an HEDC (high energy density compound), molecules **C1** and **D1** essentially satisfy this requirement. These results provide basic information for molecular design of novel high energetic density compounds.

Key Words : RDX, HMX, Density functional theory (DFT), Thermodynamic properties, Detonation performances

Introduction

The energy content and power of energetic materials make it very significant for several applications, including advanced conventional weapons, rocket propellants, antiterroist work, demilitarization as well as industrial applications.[1-4] The need for more energetic compounds with better stability and lower sensitivity is one of the main goals of energetic materials research.[5-9] The search for new potential high energy density materials (HEDCs) is on going.[10-14] Good thermal stability and low impact and shock sensitivities are of equal importance to detonation performance.[15-18] Unfortunately, high performance and low sensitivity seem to be mutually exclusive and very energetic compounds tend not to be stable, whereas stable materials are not energetic enough to replace commonly used compounds. Therefore, the foremost objective is to find the molecule with better detonation performance and thermal stability.

Nitramine compounds, as an important class of organic explosives, have received much attention in an energetic materials role due to an advantageous combination of density, heat of formation and oxygen balance. Nitramine compounds are well known by their high positive heats of formation as well as good thermal stability.[19,20] These properties reveal a high performance of energetic materials. 1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX) with advantage of higher melting point (204 °C), is the most important military explosive in modern day use.[21-24] 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX) is reported as an attractive high thermally stable explosive with high melting point 280 °C. It can offer higher density (1.91 g·cm^{-3}) and velocity of detonation (8.96 km·s^{-1}).[25,26] The high brisance exhibited by HMX, its stability on storage and low sensitivity to impact and friction in comparison to many nitrate ester explosives, make it a desirable high explosive.[27,28]

This study was motivated by, and based on, the concept of new nitramine explosives with -NH_2 and -F groups. Reacting with acidic potassium bromide solution and hydrogen peroxide, RDX and HMX yield a precursor, which provides C-Br site for introducing -NH_2 and -F groups, and thus generate a series of new energetic materials (molecules **A**, **B**, **C** and **D**). The experimental synthesis routes of the title compounds are efficient and convenient. Based on the RDX and HMX, molecular structures with -NH_2 and -F groups in the basic skeleton considered are shown in Figure 1.

Theoretical studies make it not only possible to screen candidate compounds, but to provide comprehension of the relationship between molecular structure and property.[29-31] To date, information of the relationship between structure and property of nitramine explosives with -NH_2 and -F groups is very sparse, and much few systematic survey are conducted to cover these compounds. In the present study, the molecular geometries and electronic structures were obtained with the density functional theory (DFT) method. Molecular volume (V) and theoretical density (ρ) were calculated using Monte-Carlo method. Based on calculated vibrational frequencies, thermodynamic properties from 200 to 800 K were evaluated using a statistical thermodynamic method and their relationships with temperature were obtained and would be helpful for further studies on other physical, chemical and energetic properties of these compounds. The most important detonation properties, such as detonation velocity (D) and detonation pressure (P) were estimated by using K-J equations. Through calculations of

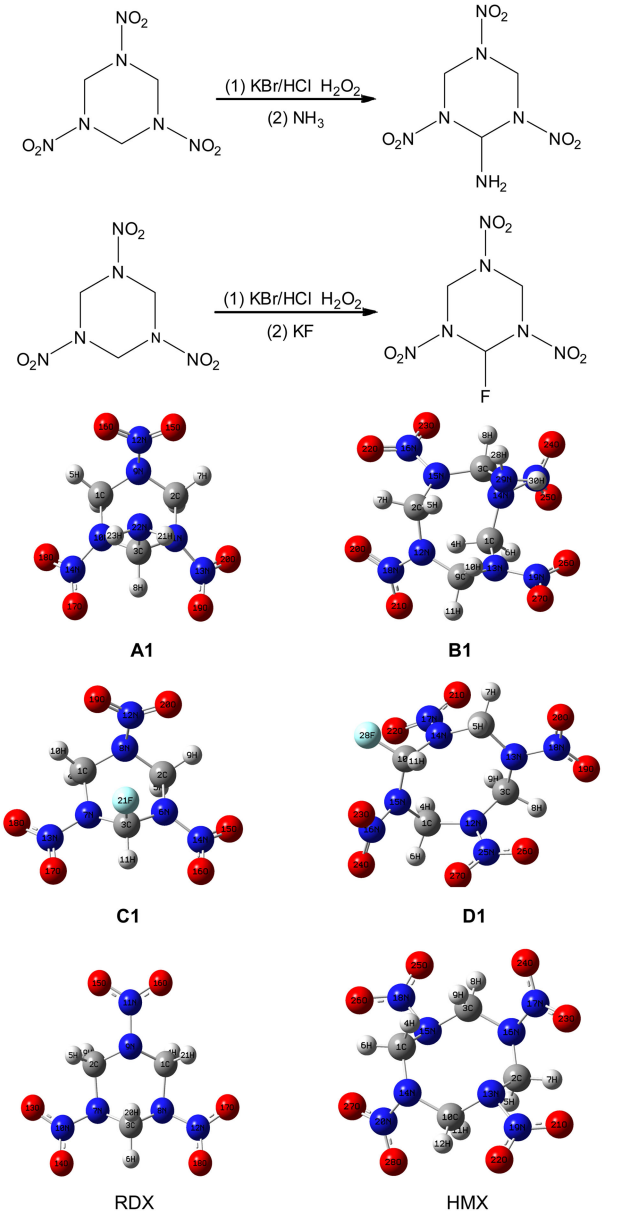

Figure 1. Structures and atom numbering of nitramine explosives with -NH_2 and -F groups, RDX and HMX.

bond dissociation energies (BDE), thermal stability was studied. These results provide theoretical support for molecular design of novel high energetic density compounds.

Computational Methods

Computations were performed with Gaussian 03 package at B3LYP[32-34] method with 6-31+G(d) basis set.[35] The geometric parameters were allowed to be optimized, and no constraints were imposed on molecular structure during optimization process. Vibrational frequencies were calculated for the optimized structures to enable us to characterize the nature of stationary points, zero-point energy (ZPE) and thermal correction (H_T). All of optimized structures were characterized to be true local energy minima on potential energy surfaces without imaginary frequencies. On the basis of the principle of statistical thermodynamics,[36] standard molar heat capacity ($C^{\theta}_{p,m}$), standard molar entropy (S^{θ}_{m}) and standard molar enthalpy (H^{θ}_{m}) from 200 to 800 K were derived from the scaled frequencies using a self-compiled program.

Detonation velocity and pressure are the most important parameters to evaluate detonation characteristics of energetic materials. The Kamlet and Jacob empirical equations were used to determine these parameters.[37,38]

$$P = 1.558NM^{1/2}Q^{1/2}\rho^2 \quad (1)$$

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (2)$$

where P is detonation pressure in GPa, D is detonation velocity in km·s^{-1}, N is the number moles of gaseous detonation products per gram of explosive, M is the average molecular weight of the gaseous products, Q is the energy of explosion in J·g^{-1} of explosive and ρ is the crystal density in g·cm^{-3}. N, M and Q are determined according to the largest exothermic principle,[39] *i.e.*, all the N atom converts into N_2, the O atom forms H_2O with H atom first and the remainder forms CO_2 with C atom. The remainder of C atom will exist in solid state if O atom does not satisfy full oxidation of C atom. The remainder of O atom will exist in O_2 if O atom is superfluous.

As to the known explosives, the Q and ρ can be measured experimentally; thus, their D and P can be calculated according to Eqs. (1) and (2). However, for those unsynthesized explosives and hypothetical compounds, their Q and ρ cannot be evaluated from experimental measures. The loading density of the explosives ρ can be replaced by the crystal theoretical density (ρ_{cry}), while the chemical energy of the detonation reaction Q can be calculated as the difference between the heats of formation (HOFs) of products and those of reactants (Q_{cal}). However, from K-J equations, it is found that Q has much less effect than ρ on D and P. Therefore, Q and HOF estimated using semiempirical molecular orbital (MO) method (PM3)[40] are precise enough to substitute the experimental data, which have been proven in previous studies.[41,42] A statistics average method was worked out to predict crystalline densities of energetic materials. This method is found to be efficient and convenient.[43-46] The densities of nitramine compounds need the datum of molecular volumes. The molecular volume V was defined as inside a contour of 0.001 electrons/bohr^3 density that was evaluated using Monte-Carlo integration. The molecular volumes obtained thus were random digits with normal distribution. We therefore performed 100 single-point calculations at B3LYP/6-31+G(d) level from optimized structure to get an average volume. The theoretical molecular density ρ_{theor} ($\rho_{theor} = M/V$, where M is the molecular weight) is very close to the experimental crystal density ρ_{cry}.

To measure the strength of bonds and relative stabilities of nitramine explosives with -NH_2 and -F groups, the bond dissociation energies of various bonds in molecules are calculated. BDE is the required energy in homolysis of a

Table 1. Calculated energies (a. u.) of the nitramine compounds at B3LYP/6-31+G(d) level[a]

Compound	E_0	ZPE	E_{HOMO}	E_{LUMO}	ΔE
A1	-952.800517	0.159903	-0.30650	-0.10094	0.20556
A2	-952.797232	0.159808	-0.31497	-0.10953	0.20544
B1	-1251.949857	0.208886	-0.33578	-0.10869	0.22709
B2	-1251.949763	0.208865	-0.33586	-0.10891	0.22695
C1	-996.688157	0.134481	-0.33050	-0.11081	0.21969
C2	-996.688156	0.134520	-0.33052	-0.11089	0.21963
D1	-1295.826006	0.183143	-0.34598	-0.12528	0.22070
D2	-1295.823987	0.183121	-0.34576	-0.12511	0.22065

[a]E_0 and ZPE are the total energy and zero-point energy of the nitramine compounds, respectively; E_{HOMO}, E_{LUMO}, and ΔE are the energies of the highest occupied and lowest unoccupied molecular orbitals, and their gap, respectively.

bond and is commonly denoted by difference between total energies of product and reactant after zero-point energy correction. The expressions for the homolysis of A–B bond (3) and for calculating its BDE (4) are shown as follows:[47]

$$\text{A–B(g)} \rightarrow \text{A•(g)} + \text{B•(g)} \quad (3)$$

$$\text{BDE(A–B)}_{ZPE} = E(\text{A•})_{ZPE} + E(\text{B•})_{ZPE} - E(\text{A–B})_{ZPE} \quad (4)$$

where A–B stands for neutral molecules and A•and B• for the corresponding product radicals after bond dissociation; BDE(A–B) is the BDE of bond A–B; $E(\text{A–B})_{ZPE}$, $E(\text{A•})_{ZPE}$ and $E(\text{B•})_{ZPE}$ are zero-point energy corrected total energies of parent compound and corresponding radicals, respectively. Furthermore, basis set superposition error (BSSE) analyses are carried out with the counterpoise method, introduced by Boys and Bernardi.[48] The corresponding BSSE analyses are performed at the same theoretical level.

Results and Discussion

Molecular Structures. Table 1 reports the total energies (E_0), zero point energies (ZPE), energies of the frontier molecular orbitals (*i.e.*, E_{HOMO} and E_{LUMO}) and their gaps (ΔE) for the optimized conformers of nitramine explosives with -NH_2 and -F groups based on the most stable conformations of RDX and HMX. It can be seen from Table 1 that the calculated total energies or the ZPE-corrected relative energies are both in the order: **A1** < **A2**, **B1** < **B2**, **C1** < **C2** and **D1** < **D2**, which suggest that conformers **A1**, **B1**, **C1** and **D1** should be the most stable configurations of the title compounds. The difference in the total energies of various conformers may be attributed to the spacial orientation of -NH_2 and -F groups. Moreover, inspecting the energy gaps (ΔE) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in Table 1, one could deduce that the stability generally decreases in the order: **A1** > **A2**, **B1** > **B2**, **C1** > **C2** and **D1** > **D2**. The stability refers to the chemical or optical processes related with the electron transfer or electron leap, which agrees with the stability order derived from the total energies and further confirms that conformers **A1**, **B1**, **C1** and **D1** are the most stable conformers among nitramine explosives with -NH_2 and -F groups. However, since the energy differences in these isomeric conformations are small, it is not practical to prepare the title compound with only one configuration. Therefore, a crucial question, how to select a proper solvent to prepare the polymorphs of the title compound in a practical way, still requires further

Table 2. Thermodynamic properties of the title compounds at different temperatures

Compound		T (K)							
		200	298.15	300	400	500	600	700	800
A1	$C^{\theta}_{p,m}$	169.19	227.87	228.95	283.69	329.16	365.32	393.94	416.86
	S^{θ}_{m}	407.81	486.35	487.76	561.31	629.68	693.02	751.56	805.72
	H^{θ}_{m}	21.28	40.78	41.20	66.90	97.62	132.42	170.44	211.02
B1	$C^{\theta}_{p,m}$	222.24	300.51	301.94	374.16	433.93	481.40	518.95	549.00
	S^{θ}_{m}	463.82	567.25	569.11	666.13	756.28	839.76	916.90	988.23
	H^{θ}_{m}	27.02	52.70	53.26	87.15	127.67	173.53	223.62	277.07
C1	$C^{\theta}_{p,m}$	163.01	217.56	218.56	269.28	311.11	344.09	369.94	390.40
	S^{θ}_{m}	409.51	484.81	486.15	556.16	620.91	680.67	735.73	786.52
	H^{θ}_{m}	21.04	39.72	40.13	64.58	93.68	126.51	162.26	200.32
D1	$C^{\theta}_{p,m}$	216.58	290.31	291.66	359.64	415.74	460.09	494.97	522.65
	S^{θ}_{m}	459.02	559.34	561.14	654.60	741.11	820.99	894.64	962.60
	H^{θ}_{m}	26.59	51.49	52.03	84.68	123.55	167.43	215.26	266.19

Note: Units: T (K); $C^{\theta}_{p,m}$ (J·mol^{-1}·K^{-1}); S^{θ}_{m} (J·mol^{-1}·K^{-1}); H^{θ}_{m} (kJ·mol^{-1}).

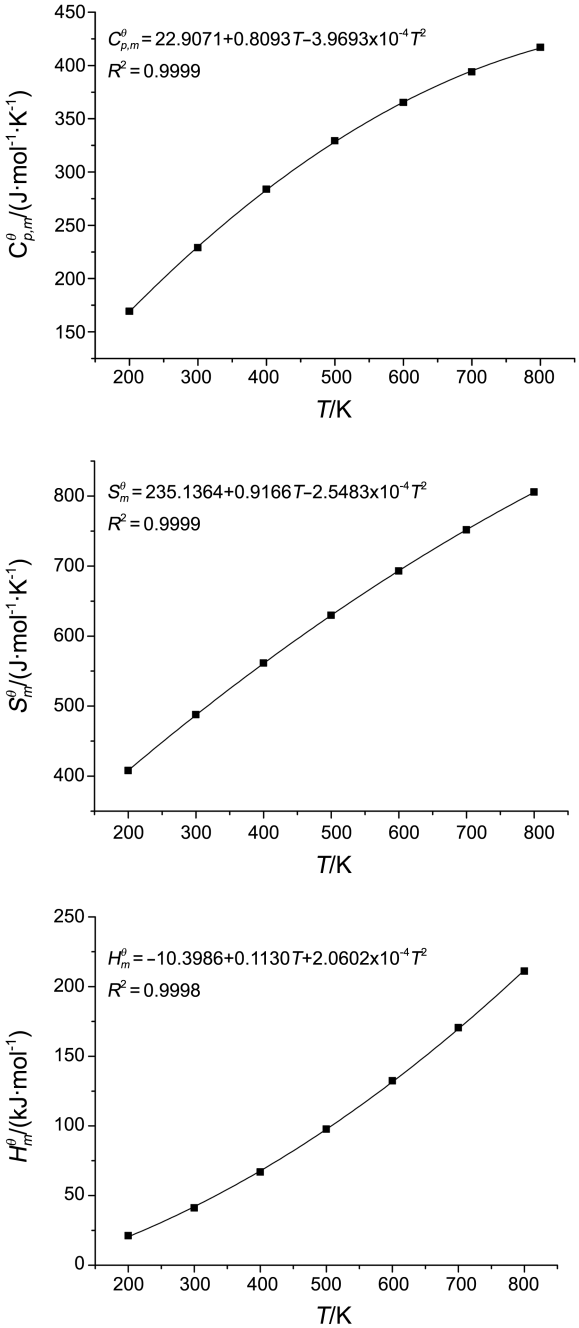

Figure 2. Relationships between the thermodynamic functions of molecule **A1** and temperature (*T*).

studies.

Thermodynamic Properties. Based on the scaled vibrational results, the principle of statistic thermodynamics and self-compiled program, thermodynamic properties ranging from 200 to 800 K were obtained and listed in Table 2. The dependences of thermodynamic functions on the temperature were analysed and would be helpful for further studies on other physical, chemical and energetic properties of nitramine explosives with -NH_2 and -F groups.

From these data, it is found that all the thermodynamic functions increase with temperature evidently. This is because the main contributions to thermodynamic functions are from the translations and rotations of molecules when temperature is low. However, at the higher temperature, the vibrational movement is intensified and therefore makes more contributions to the thermodynamic properties, which lead to the increase in the thermodynamic functions. Taking 1,3,5-trinitro-1,3,5-triazinan-2-amine (molecule **A1**) as an example, the temperature-dependent relations for $C^{\theta}_{p,m}$, S^{θ}_{m} and H^{θ}_{m} in the range of 200-800 K can be expressed as shown in Figure 2 (where R^2 is the correlation coefficients). It is obvious that, as the temperature increases, the gradients of $C^{\theta}_{p,m}$ and S^{θ}_{m} decrease, while that of H^{θ}_{m} increases constantly. Table 3 lists the relationships between the thermodynamic functions ($C^{\theta}_{p,m}$, S^{θ}_{m} and H^{θ}_{m}) and temperature (*T*).

Detonation Performance. The detonation velocity (*D*) and detonation pressure (*P*) of molecules are computed by Kamlet-Jacobs empirical equations on the basis of their theoretical densities (ρ) and calculated gas phase heats of formation, which are the important parameters to evaluate performances of explosion of energetic materials. Table 4 shows the predicted detonation properties of nitramine compounds. Because detonation pressures and detonation velocities are calculated by HOF of gas state, not of crystal, the calculated detonation properties of nitramine compounds have some deviation.[49] Although the error or limitation of calculation method leads to the predicted *D* and *P* somewhat deviate those from experiments, these results are still reliable and meaningful. It can be found from Table 4 that all nitramine compounds have good detonation properties (Q = 1533.24-1713.50 J·g^{-1}, D = 8.74-9.32 km·s^{-1}, P = 33.12-39.19 GPa). Molecule **D1** is calculated to have the highest *D* and *P* values among nitramine compounds and the replacement of -F group by amino groups bring *D* and *P* values down in molecule **B1**. In terms of the predicted detonation parameters, the most powerful explosive among these compounds is molecule **D1**. However, the values of *D* and *P* decrease a bit when there are other substituted groups in the molecule.

Comparing with famous nitramine explosive RDX (1,3,5-trinitro-1,3,5-triazinane) (ρ = 1.82 g/cm^3, D = 8.75 km/s, P =

Table 3. Relationships between thermodynamic functions ($C^{\theta}_{p,m}$, S^{θ}_{m} and H^{θ}_{m}) and temperature (*T*) for the title compounds ($a_0+a_1T+a_2T^2$)

Compd.	$C^{\theta}_{p,m}$			S^{θ}_{m}			H^{θ}_{m}		
	a_0	a_1	a_2	a_0	a_1	a_2	a_0	a_1	a_2
A1	22.9071	0.8093	-3.9693×10^{-4}	235.1364	0.9166	-2.5483×10^{-4}	-10.3986	0.1130	2.0602×10^{-4}
B1	28.4064	1.0746	-5.3119×10^{-4}	236.1050	1.2087	-3.3636×10^{-4}	-14.8164	0.1493	2.7111×10^{-4}
C1	26.5843	0.7565	-3.7798×10^{-4}	243.9729	0.8814	-2.5474×10^{-4}	-9.800	0.1123	1.8906×10^{-4}
D1	33.4614	1.0162	-5.0714×10^{-4}	238.3564	1.1742	-3.3704×10^{-4}	-14.4121	0.1489	2.5401×10^{-4}

Table 4. Predicted densities and detonation properties of nitramine compounds

Molecule	**A1**	**B1**	**C1**	**D1**	RDX	HMX
V (cm^3/mol)	136.81	171.69	128.61	169.56	126.14	160.87
ρ (g/cm^3)	1.73	1.81	1.87	1.85	1.76 (1.82)[a]	1.84 (1.92)
Q (J/g)	1581.04	1591.32	1533.24	1713.50	1623.31	1634.89
D (km/s)	8.74	9.02	9.15	9.32	8.85 (8.75)	9.14 (8.96)
P (Gpa)	33.12	36.18	37.96	39.19	34.26 (34.70)	37.58 (35.96)

[a]The values in parenthesis are experimental values taken from ref. [49, 50].

Table 5. Bond dissociation energies (BDE, kJ/mol)[a] of the weakest bonds for nitramine compounds computed at B3LYP/ 6-31+G(d) level

Compound	**A1**	**B1**	**C1**	**D1**	RDX	HMX
Bond	N9–NO_2	N15–NO_2	N8–NO_2	N15–NO_2	N9–NO_2	N15–NO_2
BDE (kJ·mol^{-1})	135.27	151.81	128.42	111.93	139.86	145.25

[a]BDE include BSSE and ZPE corrections.

34.70 GPa),[50,51] they all have better detonation performance, which indicate that they are all potential energetic compounds. Calculation results of detonation velocity and detonation pressure for nitramine explosives with -NH_2 and -F groups indicate that molecule **B1** performs similarly to HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) (ρ = 1.92 g/cm^3, D = 8.96 km/s, P = 35.96 GPa),[50,51] molecules **C1** and **D1** outperform HMX. Therefore, for the design of molecule, we could adjust detonation properties by changing the substituted group. According to our suggested energy criterion for HEDC, *i.e.*, $\rho \approx$ 1.90 g/cm^3, D ≈ 9.0 km/s, and P ≈ 40.0 GPa, it is found from Table 4, that molecules **C1** and **D1** satisfy the requirements. Then the above prediction indicates that nitramine explosives with -NH_2 and -F groups are appearing to be promising candidates comparable to RDX and HMX.

Thermal Stability. Studies of bond dissociation energies (BDE) provide useful information for understanding stability of nitramine explosives with -NH_2 and -F groups. The stability of compounds is affected by bond dissociation energies, so we select the weakest bonds (N-N bonds that are out of ring) as the breaking bond based on the bond overlap populations to calculate BDE at B3LYP/6-31+G(d) level. The values of bond dissociation energies are listed in Table 5. The calculated BDE values indicate relative stability of energetic materials. Variations of BDE for N-NO_2 are in range of 111.93-151.81 kJ·mol^{-1}. The initial step should be *via* N-NO_2 cleavage in thermal decomposition. The BDE value of molecule **B1** (151.81 kJ·mol^{-1}) is the largest while molecule **D1** is the smallest (111.93 kJ·mol^{-1}) which is less stable than the former. As is evident in Table 5, molecules **A1** and **B1** have higher BDE than molecules **C1** and **D1**, respectively. This indicates that attachment of substituent (-NH_2) to RDX and HMX is very useful for improving thermal stability. When -F group is attached to the ring, BDE value decreases. This shows that incorporating -F group make its stability decrease. Compared with RDX and HMX, the molecule **B1** has higher BDE value. The BDE values of molecules **A1**, **C1** and **D1** are lower than those of RDX and HMX. By analyzing structures of these compounds, it is easy to find that nitramine explosives with -NH_2 and -F groups have symmetric structures. This symmetry can delocalize π electron cloud density of system, which makes BDE of nitramine explosives with -NH_2 and -F groups increase.

Considering the practical requirements and based on the results of these studies, a quantitative criteria associated stability (BDE of the trigger bond) requirement, *i.e.*, BDE ≈ 80-120 kJ/mol, is proposed and employed to filtrate and recommend potential HEDCs.[52] It is found from Table 5, molecules **A1**, **B1**, **C1** and **D1** all satisfy the requirements. In addition, the calculated BDE values of molecules **A1**, **B1** and **C1** are above 120 kJ/mol. This indicates the nitramine explosives with -NH_2 and -F groups have better stability and lower sensitivity. The above investigations provide important theoretic information for molecular design of novel nitramine compounds.

Conclusion

The full geometrical optimizations of nitramine explosives with -NH_2 and -F groups were performed using density functional theory at B3LYP/6-31+G(d) level, without any symmetry restriction. The detailed structure-property studies were performed on these compounds to achieve energetic performance. Thermodynamic properties in the range from 200 to 800 K were obtained. The gradients of $C_{p,m}^{\theta}$ and S_m^{θ} to the temperature decrease, but that of H_m^{θ} increases, as the temperature increases. Stability correlations are established for these molecules by analyzing bond dissociation energies. Calculation results of detonation velocity and detonation pressure for nitramine compounds indicate that molecule **B1** performs similarly to HMX, molecules **C1** and **D1** outperform HMX, which essentially satisfy the quantitative criteria for the energy as HEDCs ($\rho \approx$ 1.90 g/cm^3, $D \approx$ 9.0 km/s, and $P \approx$ 40.0 GPa). These results provide theoretical support for molecular design of novel high energetic density compounds and experimental synthesis.

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