

Theoretical studies on the structures and detonation properties of nitramine explosives containing benzene ring

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Abstract The nitramine compounds containing benzene ring 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), energy gap ($\Delta E_{\text{LUMO-HOMO}}$), charge on the nitro group ($-Q_{\text{NO}_2}$), detonation velocity (D) and detonation pressure (P), estimated using Kamlet–Jacobs equations, showed that the detonation properties of these compounds were excellent. It is found that there are good linear relationships between density, heat of formation, detonation velocity, detonation pressure and the number of nitro group. The simulation results reveal that molecule **G** performs similarly to famous explosive HMX, and molecule **H** outperforms HMX. According to the quantitative standard of energetics as an HEDC (high energy density compound), molecule **H** essentially satisfies this requirement. These results provide basic information for molecular design of novel high energetic density compounds.

Keywords Benzene · Density · Density functional theory (DFT) · Detonation performance · Nitramine

Introduction

High energy density compounds (HEDC) have been attracting considerable attention because of their superior explosive performances [1–4]. In order to meet the future

civil and military requirements, continuous research efforts have been received by explosives chemists to develop new energetic materials with good thermal stability, insensitivity, better performance, economic and eco-friendly syntheses [5–9]. Good thermal stability and low impact and shock sensitivities are of equal importance to detonation performance. But these requirements are somewhat reciprocally exclusive, with improved insensitivity bringing inferior performance and vice versa. Therefore, the foremost objective is to find the molecule having better detonation performance and thermal stability. The nitramine compounds are the classic organic explosives. The most prominent member of this class are RDX [10–13] and HMX [14–17]. Nitroguanidine [18, 19] and tetryl [20, 21] are also significant nitramines.

Many papers reveal that benzene based compounds have attracted renewed attention due to their high detonation performance, density, and good thermal stability [22–25]. As a benzene based compound, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is an explosive material with a remarkably low detonation sensitivity to impact, friction and spark, and an explosive power comparable to that of 2,4,6-trinitrotoluene (TNT) [26–28]. Because of its high heat-resistant and insensitive property, it is the only insensitive explosive authorized by the U.S. Department of Energy. The compound 3,5-dinitro-2,6-bis(picrylamino) pyridine (PYX) [29–31] is reported as an attractive high thermally stable explosive with decomposition temperature 460°C. It can offer higher velocity of detonation (7.50 km s^{-1}) and detonation pressure (30.8 GPa). 2,2',4,4',6,6'-Hexanitrostilbene (HNS) [32, 33], since it was synthesized, has been widely used as a typical secondary explosive in thermally stable charges or perforators, including secondary fillings of detonators for deep boreholes (high temperatures and

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pressures in exploitation of oil and nature gas), because of its structural stability, higher energy, and good detonation properties. Therefore, incorporation of benzene ring to nitramine compounds is an effective approach to enhance thermal stability of explosives.

The insensitive property of explosives containing benzene is combined with the high energy of nitramine explosives, and the concept of new nitramine explosives containing benzene is proposed, into which nitramine group with N–N bonds are introduced as much as possible. This study was motivated by, and based on, the concept of new nitramine explosives containing benzene. Reacting with formaldehyde, benzene-2,3,5,6-tetraamine yields a precursor with two five-membered rings, which provides more N–H sites for introducing nitro substituents, and thus generates a series of new energetic materials (Fig. 1).

Theoretical studies not only make it possible to screen candidate compounds, but also provide understanding in terms of the relationships between molecular structure and property [34–38]. To date, information on the relationships between structure and property of nitramine compounds containing benzene was very sparse, there was no systematic survey covering these compounds. In the present study, the molecular geometries and electronic structure were obtained with density functional theory method (DFT). Based on optimized geometries, molecular volume (V) and theoretical density (ρ) were calculated using Monte–Carlo method. The most important detonation properties, such as detonation velocity (D) and detonation pressure (P) were estimated by using K–J equation. Through calculations of energy gaps ($\Delta E_{\text{LUMO–HOMO}}$) and the nitro group charges (Q_{NO_2}), the thermal stability and sensitivity were 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 [39–41] method with 6-31+G(d) basis set [42]. 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 the optimized structures were characterized to be true local energy minima on potential energy surfaces without imaginary frequencies.

Detonation velocity and pressure are the most important parameters for evaluating detonation characteristics of energetic materials. For the explosives with CHNO ele-

ments, the Kamlet and Jacob empirical equations were used to determine these parameters [43].

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

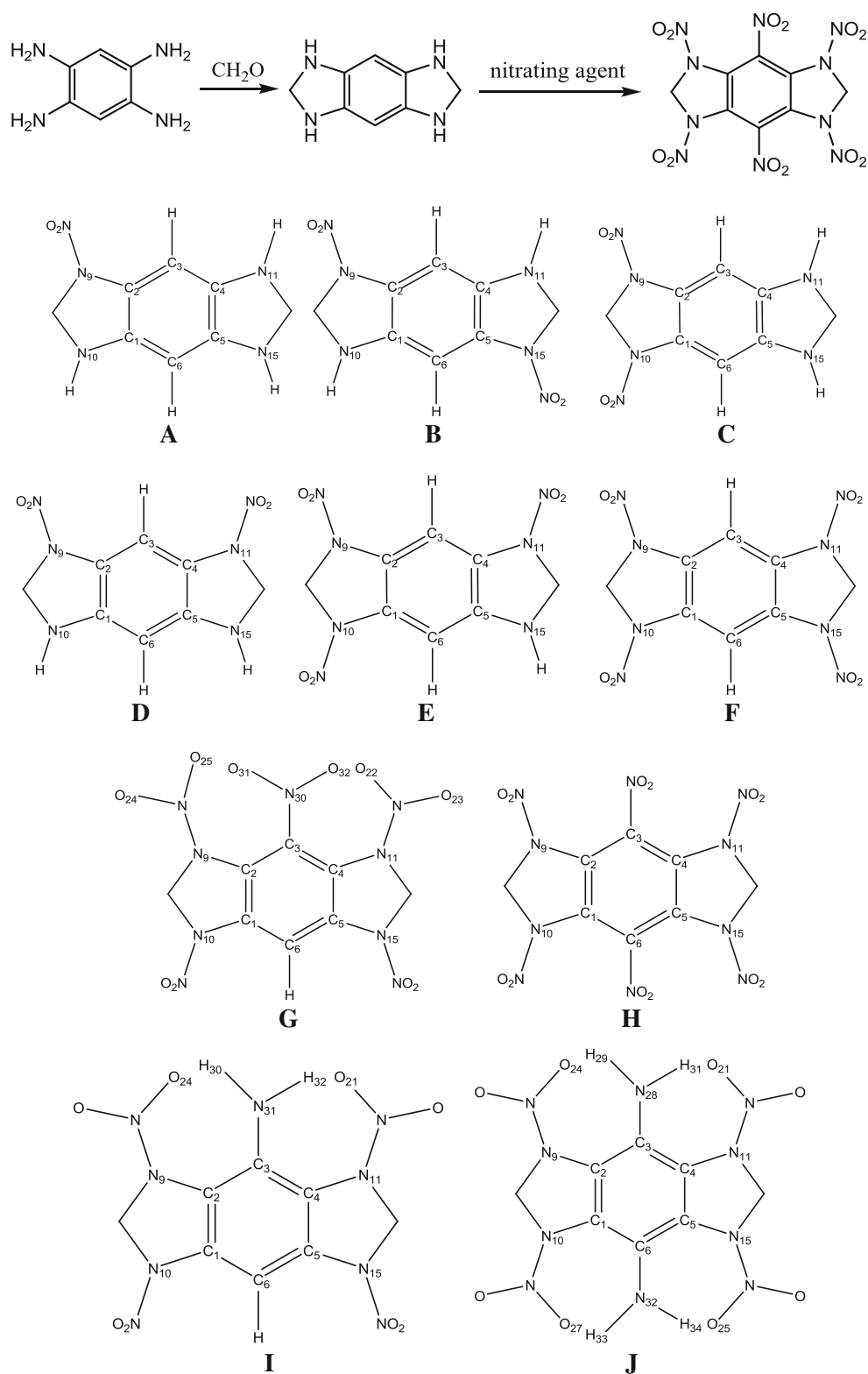
$$D = 1.01\left(NM^{1/2}Q^{1/2}\right)^{1/2}(1 + 1.30\rho) \quad (2)$$

where P is detonation pressure in GPa, D is detonation velocity in km s^{-1} , N is the number of 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 decided according to the largest exothermic principle [44], i.e., for the explosives with CHNO elements, all the N atom convert 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.

For known explosives, their 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}). The detonation properties obtained using gas phase heats of formation will be overestimated in all cases. 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) [45] are precise enough to substitute the experimental data, which has been proven in previous studies [46–49]. A statistics average method was worked out to predict crystalline densities of energetic materials containing C, H, N and O elements. This method is found to be efficient and convenient [50–54]. 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/bohr³ density that was evaluated using Monte–Carlo integration. The molecular volumes thus obtained 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} ($\rho_{\text{theor}} = M/V$, where M is the molecular weight) is very close to the experimental crystal density ρ_{cry} .

The oxygen balance (OB_{100}) is used in all predictive properties related to Q , D and P , detonation products and sensitivity [44]. It also represents the lack or excess of O_2

Fig. 1 Structures and atom numbering of nitramine compounds containing benzene ring



needed to produce the most stable products N_2 , H_2O , CO and CO_2 in explosive compounds. D is a linear function of OB_{100} and it is improved by taking into the consideration of the number of NO_2 groups. The ideal oxygen balance

required for energetic compounds is zero and if energetic compounds have lower amount of oxygen than required for the complete oxidation then it is said to have negative oxygen balance.

Results and discussion

Optimized structures

Optimized bond lengths of nitramine compounds are tabulated in Table 1. It is calculated that the longest C1–N10, C2–N9, C4–N11 and C5–N15 bonds in all molecules corresponds to C2–N9 and C4–N11 bonds of molecule **I**, which are 1.435 Å, while the shortest one due to the C5–N15 bond of molecule **E**, which is 1.396 Å. Thus, all the C1–N10, C2–N9, C4–N11 and C5–N15 bonds in compounds are much shorter than the normal C–N single bond that is referred to 1.49 Å, which confirms these bonds to have some character of double or conjugated bonds. In addition, the bond distances of C3–N28, C6–N32 (molecule **J**) and C3–N31 (molecule **I**) are 1.380, 1.380 and 1.371 Å, respectively. These results suggest that all the nitrogen atoms in NH₂ groups are participating in the hyperconjugation system. In molecule **G**, nitro group (N30O31O32) and benzene ring form molecular plane. However, oxygen (O22 and O23) atoms of N11–NO₂ and oxygen (O24 and O25) atoms of N9–NO₂ are rotated by about ±15° from molecular plane. It is due to the repulsion between the neighboring nitro group, which rotates oxygen atoms from the molecular plane. The interatomic distances of O22–O32 and O25–O31 are 2.804 and 2.821 Å, respectively. The same results are obtained for molecule **H**.

The hydrogen bonds between neighboring nonbonding atoms in nitramine compounds are also investigated. As pointed out [55], in a moderate X–H···Y hydrogen bonding (H–bonding) system, normal Y···H separations are in the range of 1.5–2.2 Å, while the separations between X and Y are within 2.5–3.2 Å. Hence according to these criteria, there are moderate intramolecular H–bonding between neighboring O and H in molecules. For molecule **I**, interatomic distance of O21–H32 and O24–H30 are 2.180 Å and 2.119 Å, respectively, which is substantially shorter

than the sum of van der Waals radii and is known to be a typical distance for N–H···O hydrogen bond. The same result is found for molecule **J**. In molecule **J**, interatomic distance of O21–H31 and O24–H29 are 2.132 Å and 2.128 Å, respectively, distance between atom O25 and H34 is 2.133 Å; distance between atom O27 and H33 is 2.131 Å. Four hydrogen bindings increase stability of molecule **J** and are more insensitive than any other nitramine compounds. Through analyses for the data in Table 1, it is shown that the more H–bonds are formed in a molecule, the more stable it is. Consequently, it could be concluded that H–bonding had contributions to stability of molecules.

Density

In the present study, single-point molecular volume calculations at B3LYP/6-31+G(d) were performed based on geometry optimized structures. The densities were calculated and listed in Table 3. All these data in Table 3 provide some clues about the explosive characters of these molecules. The nitramine compounds with different substituent groups have different ρ values, for example, the largest value and the smallest one is 1.99 g cm⁻³ and 1.50 g cm⁻³, respectively. It is clear that an increase in density is observed with an increase in the number of nitro groups, while density decreases with the introduction of an amino group. Introduction of a nitro group increases the density of molecules and therefore has a significant contribution to detonation velocity (D), and detonation pressure (P). In addition, molecule **G** (or **H**) have higher ρ values than corresponding molecule **I** (or **J**). Molecules **G** and **H** have a density of above 1.90 g cm⁻³, which will be novel potential candidates for HEDC when it is successfully synthesized. Density (ρ) is the essential factor in determining detonation properties of energetic compounds. According to Kamlet and Jacob semi-empirical equations, the D increases with increasing ρ for most energetic compounds. Also, P varies with the square of ρ , when ρ is greater than one.

Table 1 Selected bond lengths^{a)} of nitramine compounds computed at B3LYP/6-31+G(d) level

Bond	A	Bond	B	Bond	C	Bond	D	Bond	E
C3–C4	1.389	C3–C4	1.394	C3–C4	1.390	C3–C4	1.395	C3–C4	1.393
C2–N9	1.420	C2–N9	1.412	C2–N9	1.416	C2–N9	1.418	C2–N9	1.419
C1–N10	1.420	C1–N10	1.409	C1–N10	1.416	C1–N10	1.406	C1–N10	1.410
C4–N11	1.430	C4–N11	1.409	C4–N11	1.401	C4–N11	1.419	C4–N11	1.414
C5–N15	1.405	C5–N15	1.412	C5–N15	1.401	C5–N15	1.400	C5–N15	1.396
Bond	F	Bond	G	Bond	H	Bond	I	Bond	J
C3–C4	1.394	C3–C4	1.402	C3–C4	1.400	C3–C4	1.410	C3–C4	1.408
C2–N9	1.410	C2–N9	1.421	C2–N9	1.416	C2–N9	1.435	C2–N9	1.434
C1–N10	1.414	C1–N10	1.415	C1–N10	1.402	C1–N10	1.421	C1–N10	1.434
C4–N11	1.411	C4–N11	1.414	C4–N11	1.418	C4–N11	1.435	C4–N11	1.434
C5–N15	1.412	C5–N15	1.410	C5–N15	1.419	C5–N15	1.415	C5–N15	1.434

^{a)} Bond lengths in Angstroms.

Table 2 Calculated electronic energies (E_0), zero-point energies (ZPE), thermal correction to enthalpy (H_T) and gas phase heats of formation (HOF)

Compound	E_0 (a.u.)	ZPE (a.u.)	H_T (a.u.)	HOF (kJ/mol)
A	-734.174621	0.184781	0.012751	209.09
B	-938.667464	0.186668	0.015397	261.69
C	-938.664330	0.186612	0.015329	268.41
D	-938.666299	0.186499	0.154620	363.28
E	-1143.152147	0.188581	0.017932	323.68
F	-1347.633041	0.190393	0.020578	391.22
G	-1552.108691	0.192083	0.022767	408.06
H	-1756.584112	0.193870	0.025260	437.33
I	-1402.973793	0.207490	0.021419	396.36
J	-1458.313983	0.224664	0.022543	417.57

Heats of formation and oxygen balance

Heat of formation reflects the energy content of a compound. High positive HOF is usually required for an effective energetic material. The zero point energies (ZPE), thermal correction to enthalpy (H_T) and electronic energies calculated at B3LYP/6-31+G(d) level for nitramine compounds containing benzene ring are listed in Table 2. It is evident from the data listed in Table 2 that all HOFs of nitramine compounds are quite large positive values, which shows that the introduction of nitro groups is the main energy origin of this series. It is also clear from Table 2 that with the number of nitro groups (n) increasing, the HOFs of molecules increase, which may be attributed to repulsion of nitro groups. The correlation equation describes the linear relationship between the number of nitro groups (n) and the corresponding HOF. For the isomers with the same n , the most stable compound with less HOF was chosen for analysis. The correlation coefficient is 0.970, indicating that the HOFs have the property of group additivity.

For molecules **A**, **C**, **E** and **F**, each nitro group addition will increase HOF by 60.71 kJ·mol⁻¹ or so. But for molecules **F**, **G** and **H**, each nitro group addition will increase HOF by 23.06 kJ·mol⁻¹. It indicates that the value

of HOF relates to the nature of C–NO₂ or N–NO₂. The space orientations of nitro groups also affect the HOFs of nitramine compounds. For the isomers with the same number of –NO₂ group (molecules **B**, **C** and **D**), the values of HOF are slightly different, indicating that HOF is a little influenced by the position of –NO₂ group. On the whole, according to n and the relative position of the nitro groups, the relative HOFs order of molecules can be distinguished, which is useful for evaluating the relative thermal stability of nitramine compounds.

Oxygen balance is another one of the most important criterion for selecting potential HEDC. It is found from Table 4 that by and large, the higher oxygen balance is, the larger D and P values are, and the performance of nitramine compounds is better. The –NO₂ group is a good substituent for improving oxygen balance in designing potential HEDC.

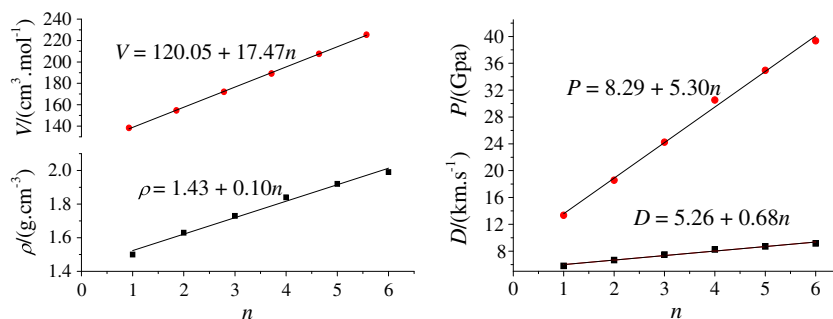
Detonation performance

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

Table 3 Predicted densities and detonation properties of nitramine compounds

Molecule	OB ₁₀₀	$V(\text{cm}^3/\text{mol})$	$\rho(\text{g}/\text{cm}^3)$	$Q(\text{J}/\text{g})$	$D(\text{km}/\text{s})$	$P(\text{Gpa})$
A	-1.43	138.31	1.50	799.87	5.81	13.35
B	-1.02	158.31	1.59	1165.65	6.55	17.63
C	-1.02	154.66	1.63	1172.02	6.67	18.58
D	-1.02	153.85	1.64	1262.00	6.83	19.52
E	-0.73	172.05	1.73	1337.45	7.48	24.24
F	-0.52	189.13	1.84	1476.55	8.24	30.53
G	-0.35	207.62	1.92	1536.73	8.71	34.96
H	-0.22	225.40	1.99	1598.08	9.15	39.36
I	-0.52	202.77	1.76	1424.77	7.96	27.72
J	-0.52	211.55	1.76	1395.43	7.98	27.84

Fig. 2 Correlations between V , ρ , D , P and the number of nitro group (n) for nitramine compounds



important parameters to evaluate performances of explosion of energetic materials. Table 3 shows the predicted detonation properties of nitramine compounds containing benzene ring. 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 [56]. Although the error or limitation of calculation method leads the predicted D and P to somewhat deviate from those of experiments, these results are still reliable and meaningful.

It can be found from Table 3 that all nitramine compounds have good detonation properties ($Q=799.87$ – 1598.08 J g⁻¹, $D=5.81$ – 9.15 km s⁻¹, $P=13.35$ – 39.36 GPa). Meanwhile, with the number of nitro groups increasing from one to six, ρ , Q , D , and P of the corresponding compounds increase. Molecule **H** is calculated to have the highest D and P values among nitramine compounds, and replacements of nitro groups of benzene ring by amino groups bring D and P values down in molecule **J**. In terms of the predicted detonation parameters, the most powerful explosive among these compounds is molecule **H**. However, the values of D and P decrease a bit if there are other substituted groups in the molecule.

As for the isomers with the same OB_{100} , no conspicuous discrepancy of their respective Q , V , ρ , D , and P is found. As a whole, V , ρ , D and P linearly increase with the increasing number of $-NO_2$ groups. Figure 2 presents the relationships between V , ρ , D , P and the number of nitro

group (n), which all exist in linear relationships. This may show good group additivity on detonation properties and support the claim that introducing more nitro substituents into a molecule usually helps to increase its detonation performance [44]. The correlation equations are as follows:

$$\begin{aligned} \text{HOF} &= 176.18 + 46.21n & R &= 0.9701 \\ V &= 120.05 + 17.47n & R &= 0.9996 \\ \rho &= 1.43 + 0.10n & R &= 0.9867 \\ D &= 5.26 + 0.68n & R &= 0.9673 \\ P &= 8.29 + 5.30n & R &= 0.9954 \end{aligned}$$

Compared with famous nitramine explosive RDX (1,3,5-trinitro-1,3,5-triazinane) ($\rho = 1.82$ g cm⁻³, $D = 8.75$ km s⁻¹, $P = 34.70$ GPa) [57, 58], they all have better detonation performance when the number of nitro groups is not less than 4, which indicates that they are all potential energetic compounds. Calculation results of detonation velocity and detonation pressure for nitramine compounds indicate that molecule **G** performs similarly to HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) ($\rho = 1.92$ g cm⁻³, $D = 8.96$ km s⁻¹, $P = 35.96$ GPa) [57, 58], molecule **H** outperforms 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, $D \approx 9.0$ km s⁻¹, and $P \approx 40.0$ GPa, it is found from Table 3, that molecule **H** satisfies the requirements.

Table 4 Energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}) and energy gaps ($\Delta E_{\text{LUMO-HOMO}}$) for nitramine compounds

Compound	HOMO (a.u.)	LUMO (a.u.)	$\Delta E_{\text{LUMO-HOMO}}$ (a.u.)
A	-0.29147	-0.06012	0.23135
B	-0.31096	-0.08777	0.22319
C	-0.31528	-0.08525	0.23003
D	-0.30584	-0.07452	0.23132
E	-0.32221	-0.10440	0.21781
F	-0.32684	-0.12114	0.20570
G	-0.33155	-0.14308	0.18847
H	-0.34869	-0.16232	0.18637
I	-0.31413	-0.11647	0.19766
J	-0.33585	-0.11345	0.22240

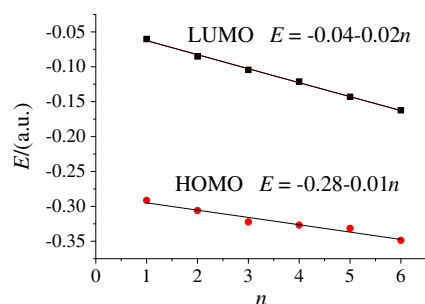


Fig. 3 Variations of HOMO and LUMO energies with the number of nitro group (n)

Therefore, the above prediction indicates that nitramine compounds containing benzene ring appear to be promising candidates comparable to nitramine explosive RDX and HMX.

Thermal stability

Energies (a.u.) of frontier molecular orbitals and their gaps ($\Delta E_{\text{LUMO-HOMO}}$) of nitramine compounds containing benzene ring at B3LYP/6-31+G(d) level are listed in Table 4. It is seen that the $\Delta E_{\text{LUMO-HOMO}}$ values are different with different positions of substituted groups. The $\Delta E_{\text{LUMO-HOMO}}$ of molecule **A** (0.23135 a.u.) is the largest while molecule **H** is the smallest (0.18637 a.u.) indicating the former is more stable than the latter. For molecules **A**, **B**, **E**, **F**, **G**, **H** and **I**, **J**, it can be easily found that $\Delta E_{\text{LUMO-HOMO}}$ decreases when $-\text{NO}_2$ group is attached to the ring. On the contrary, introduction of $-\text{NH}_2$ group will make $\Delta E_{\text{LUMO-HOMO}}$ values increase gradually. This indicates that different substituents exert different effects on $\Delta E_{\text{LUMO-HOMO}}$. The effects of $-\text{NO}_2$ groups on HOMO and LUMO are schematically shown in Fig. 3, and it can be found that HOMO and LUMO energy levels decrease when $-\text{NO}_2$ group is attached to the ring. As is known, LUMO is related to molecular electron affinity, Badders's study showed that impact sensitivity of aromatic explosives will increase with decrease of LUMO energy [59], so incorporation of $-\text{NO}_2$ group will increase sensitivity. It is obvious that only $-\text{NH}_2$ can decrease the sensitivity. The stability here refers to chemical or photochemical processes with electron transfer or electron leap.

The relationship between impact sensitivity and electronic structures of nitramine compounds can be established by charge analysis of nitro group [60, 61]. Because $\text{C}-\text{NO}_2$,

$\text{N}-\text{NO}_2$, and $\text{O}-\text{NO}_2$ bonds are usually the trigger bonds in nitro explosives, the net charges on nitro group (Q_{NO_2}) may reflect the ability of $-\text{NO}_2$ attracting electrons. In the present study, the charge on nitro group ($-Q_{\text{NO}_2}$) is considered for its correlation to impact sensitivity:

$$Q_{\text{NO}_2} = Q_{\text{N}} + Q_{\text{O}_1} + Q_{\text{O}_2}.$$

The charge on nitro group ($-Q_{\text{NO}_2}$) is calculated by the sum of atomic charges on nitrogen (Q_{N}) and oxygen (Q_{O_1} and Q_{O_2}) atoms in nitro group. Computed $-Q_{\text{NO}_2}$ values of molecules are presented in Table 5. The higher the $-Q_{\text{NO}_2}$, the larger the impact insensitivity, and hence, $-Q_{\text{NO}_2}$ can be regarded as the criterion for estimating impact sensitivities. Molecules **B**, **C** and **D** are isomers having two nitro groups attached to the ring. Based on $-Q_{\text{NO}_2}$ values in Table 5, the probable decreasing order of stability is as follows: **D** > **C** > **B**. This shows that molecule **D** is more insensitive than molecules **C** and **B**. This order is consistent with the order based on $\Delta E_{\text{LUMO-HOMO}}$. An increase in the number of nitro groups (from one to six in molecules **A**, **B**, **E**, **F**, **G** and **H**) increase the impact sensitivity. Hence, in the explosive molecule design, incorporation with $-\text{NH}_2$ is an effective means to decrease sensitivity despite its disadvantage to detonation performance. The above investigations provide important theoretic information for molecular design of novel high energetic density nitramine explosives containing benzene ring.

Conclusions

The full geometrical optimizations of nitramine compounds containing benzene ring 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 for the first time. Sensitivity correlations are established for these molecules by analyzing the charge on the nitro groups and energy gaps ($\Delta E_{\text{LUMO-HOMO}}$). For the nitramine compounds containing benzene ring, with the increase in the number of nitro groups, heat of formation, volume, density, detonation velocity and detonation pressure linearly increase, except E_{HOMO} and E_{LUMO} linearly decreasing. Calculation results of detonation velocity and detonation pressure for nitramine compounds indicate that molecule **G** performs similarly to HMX, molecule **H** ($\rho = 1.99 \text{ g cm}^{-3}$, $D = 9.15 \text{ km s}^{-1}$, $P =$

Table 5 Computed nitro group charge (Q_{NO_2}) of molecules **B**, **C** and **D**

Compound	B		C		D	
Bond	N9–NO ₂	N12–NO ₂	N9–NO ₂	N10–NO ₂	N9–NO ₂	N11–NO ₂
Q_{NO_2}	-0.465	-0.465	-0.417	-0.417	-0.412	-0.403

39.36 GPa) outperforms HMX, which essentially satisfies the quantitative criteria for the energy as HEDCs. These results provide theoretical support for molecular design of novel high energetic density compounds and experimental synthesis.

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