Theoretical design of high-nitrogen energetic molecules: Performance prediction of pentazole-based derivatives

Hao-Ran Wang

Nanjing University of Science and Technology

Chong Zhang

Nanjing University of Science and Technology

Cheng-Guo Sun

University of Science and Technology Liaoning

Bing-Cheng Hu

Nanjing University of Science and Technology

Xue-Hai Ju (✉ xhju@njust.edu.cn)

Nanjing University of Science & Technology <https://orcid.org/0000-0002-9668-3066>

Research Article

Keywords: Energetic compounds, Density functional theory, Pentazole, Excellent density

Posted Date: August 23rd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-825139/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License. [Read Full License](#)

Abstract

High nitrogen energetic compounds have always been a hot spot in energetic materials. In this work, we provide a new approach for the design of promising energetic molecules containing pentazole. Attractive energetic compounds include 5-amino-3-nitro-1*H*-1,2,4-triazole (ANTA) and 5-nitro-1,2,4-triazol-3-one (NTO) are used to effectively combine with pentazole to form a series of pentazole derivatives. Then, the NH₂, NO₂ or NF₂ groups were introduced into the system to further adjust the property. Herein, the structures and densities of designed compounds as well as the heats of formation, detonation properties and impact sensitivities were predicted based on density functional theory (DFT). The results show that all ten designed molecules have excellent densities (1.81 g/cm³ to 1.97 g/cm³) and high heats of formation (621.66 kJ/mol to 1374.63 kJ/mol). Furthermore, detonation performances of compounds **A3** ($P = 41.16$ GPa and $D = 9.45$ km/s) and **A4** ($P = 43.90$ GPa and $D = 9.69$ km/s) are superior to 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and lower impact sensitivity than HMX. It exhibited that they could be taken as promising candidates of high-energy density materials. This work provides a worthy way to explore the energetic compounds with excellent performance based on pentazole.

Introduction

Due to the superior performances over conventional explosives, high-energy density materials (HEDMs) have been a hot topic of interest and play a major role in the field of military and civilian in recent years. With the increasing demand for HEDMs, researchers have continuously sought for new HEDMs to store significantly more chemical energy than the energetic materials currently used, which can release energy safely and have minimal impact on the environment. HEDMs can be achieved with the help of traditional chemistry, with novel chemistry dealing with polynitrogen compounds, or exotic physics such as metallic hydrogen. Potential HEDM can be applied in both explosives and propulsion systems. The decomposition of HEDMs releases lots of energy and produces environmentally friendly gas products (non-toxic in nature). In order to meet the above requirements, there should not be any metal atoms in the structure of HEDM. Nitrogen-rich high-energy materials are a kind of important HEDMs [1–7]. High-nitrogen energetic materials (HNEMs) are becoming a research hotspot in the field of advanced HEDMs aimed at futuristic defense and space sector needs. The high energy content of HEDMs results from the existence of adjacent nitrogen atoms, which are ready to form nitrogen ($N \equiv N$). This transition is accompanied by a huge energy release, since the average bond energies of N–N (159 kJ/mol) and N = N (419 kJ/mol) are tremendously different from that of $N \equiv N$ (946 kJ/mol) [8]. Due to the natural result of their chemical structures, HNEMs also produce large amounts of gas (N₂) per gram of high energetic materials projecting them as a good candidates for potentially environmentally friendly energetic materials [9–11]. Triazoles, tetrazoles [12], pentazoles (PZ) [13–19], triazines and tetrazines [20, 21] are the nitrogen-rich organic compounds currently in use for energetic applications.

The pentazole compounds, which are regarded as having enormous energy, are receiving significant attention in the field of energetic materials. The *cyclo*-N₅[−] was first identified in aryl pentazoles in the late 1950s. Eventually, Zhang et al. reported the first synthesis of the *cyclo*-N₅[−] in the solid phase (N₅[−])₆(H₃O⁺)₃(NH₄⁺)₄Cl[−], which is highly stable with an initial thermal decomposition temperature of 390.15 K in 2017 [15]. Subsequently, a series of *cyclo*-N₅[−] salts were successfully synthesized with good detonation properties. These studies indicate that the pentazole is a new generation of energetic compounds as well as one of the promising precursors in the family of full nitrogen compounds. Currently, there are few N₅-based compounds in existence and more research is needed to design and investigate the structure and properties of N₅-based energetic compounds further.

In 1979, Pevzner et al. [22] synthesized 5-amino-3-nitro-1*H*-1,2,4-triazole (ANTA) for the first time as a raw HNEM containing triazole ring. It has the following characteristics: (1) the nitrogen content in the molecule is high (54%), relatively low carbon and hydrogen content, thereby improving the oxygen balance and increasing the energy density of

the compound, (2) intermolecular hydrogen bond is formed between the hydrogen atom in the molecule and the oxygen atom in the nitro group, which increases the stability of the compound, (3) There are two reaction sites, -NH and -NH₂, in the molecule, which can participate in a variety of chemical reactions, and a series of novel insensitive energetic compounds based on ANTA can be obtained. It is reported in the literature [23] that the sensitivity of high-energy insensitive explosive ANTA is similar to that of TATB, and its detonation performance is 7% higher than TATB. Thus, ANTA is an important insensitive explosive and rocket propellant. On account of ANTA containing acidic protons, its application is limited. However, there are active sites in the structure of ANTA, which has the basic characteristics of being a reaction intermediate in chemical synthesis and can eliminate the influence of acidic hydrogen. In order to obtain high-energy insensitive materials with better performance, the synthesis of new high-energy insensitive compounds using ANTA as intermediate has become a research hotspot at home and abroad.

In 1905, von W. Manchot et al. [24] first synthesized 5-nitro-1,2,4-triazol-3-one (NTO) by nitrifying 1,2,4-triazole-5-one (TO). In 1966, the Soviet Union summarized the method of direct nitrification and synthesis of NTO, and developed a two-step synthesis of NTO from semicarbazide hydrochloride and formic acid through condensation and nitration [25]. The method was used by later researchers since it was easier to get raw materials and more industrially friendly. In fact, the detonation performance of NTO is close to that of RDX, and its sensitivity is low, which is close to that of TATB. Moreover, NTO is similar to TNT in that only burns in case of fire but does not explode [26], making it an ideal choice for high energy density and low sensitivity explosives. NTO has been as another high-energy insensitive compound with better performance.

In short, pentazoles, ANTA and NTO are greatly attractive and valuable HEDMs. If combined, are likely to form a new type of high-energy compound with good properties. Hence, in the work, a suite of HNEMs were designed by combining different numbers of PZ with ANTA and NTO (as shown in Fig. 1). Then, their structures and performance were theoretically predicted via using different methods including electrostatic potential (ESP) and the density functional theory (DFT).

Computational Methods

The optimizations of the molecular structures and the predictions of heat of formation (HOF) were performed by Gaussian 09 [27] package under the DFT-B3LYP method with the 6-311++G(d,p) basis set. All of the optimized structures have the local energy minimum on potential energy surfaces without imaginary frequencies.

The density of the compounds can be obtained by the following equation [28],

$$\rho = \alpha \frac{M}{V} + \beta v(\sigma_{tot}^2) + \gamma \quad (1)$$

in which M indicates the molecular mass (g/mol). V is the volume of the molecule. The coefficients α , β and γ are 0.9183, 0.0028 and 0.0443, respectively [28].

The gas-phase HOFs of ten novel compounds at 298 K were estimated on the basis of the following isodesmic reactions, respectively.

The heat of reaction ΔH_{298} at 298 K can be calculated as the following equation,

$$\Delta H_{298} = \Delta H_{f,P} - \Delta H_{f,R} \quad (2)$$

Meanwhile, the ΔH_{298K} can be calculated via the following expression,

$$\begin{aligned}
\Delta H_{298} &= \Delta E_{298} + \Delta(PV) \\
&= \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (3)
\end{aligned}$$

where ΔE_0 denotes the total energy difference between the products and the reactants at 0 K, ΔZPE stands for the difference between the zero-point energies of the products and the reactants at 0 K. ΔH_T shows thermal correction from 0 to 298 K.

According to Hess's law of constant heat summation, the gas-phase HOF ($\Delta H_{f,gas}$) and heat of sublimation (ΔH_{sub}) are used to evaluate the solid-phase HOF ($\Delta H_{f,solid}$),

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

ΔH_{sub} can be obtained by the empirical expression suggested by Politzer et al. [29],

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

in which a, b, and c are 4.4307, 2.0599 and - 2.4825, respectively [29]. A denotes Overall surface area of the molecule.

The detonation velocity (D) and detonation pressure (P) were acquiring using the empirical Kamlet – Jacobs [30] by the following equation,

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (6)$$

$$P = 1.558\rho^2NM^{1/2}Q^{1/2} \quad (7)$$

where N is the moles of detonation gases per gram explosive, Q shows the heat of detonation.

The available free space per molecule in the unit cell (ΔV) were calculated by using the ESP methods proposed by Politzer group [31] as the following,

$$\Delta V = V_{\text{eff}} - V_{\text{int}} \quad (8)$$

where V_{eff} is zero free space, V_{int} stands for the intrinsic gas phase molecular volume. In above equation, V , A and $v(\sigma_{\text{tot}}^2)$ were obtained through the Multiwfn program [32].

Results And Discussion

3.1 Molecular geometry and electronic structure

The molecular structures of **A1** to **A5** and **B1** to **B5** were optimized via the method introduced above. As can be seen in Fig. 2, The combination of pentazole and ANTA, pentazole and NTO have not changed the original structures. The target molecules have the C1 point group by calculation. The order of dipole moment of the designed molecules are as follows: **A2** > **A1** > **A4** > **A3** > **A5** (9.44 to 4.26 Debye) and **B2** > **B1** > **B5** > **B3** > **B4** (4.45 to 3.14 Debye), that is, NH₂ group has a positive correlation to the molecular dipole moment, while NF₂ and NO₂ group are reversed.

Table 1 displays the predicted bond lengths of relevant structures. As shown in Table 1, the N-N bond length in the triazole ring is between 1.342 Å and 1.369 Å, and the C-N bond length is 1.280 ~ 1.435 Å. In other words, the bond length of the triazole ring is between the corresponding N-N and C-N single bond (~1.41 Å and ~1.45 Å, respectively) and double bond (~1.23 Å and ~1.27 Å respectively) [33], indicating that the triazole rings of ANTA, NTO and their derivatives have certain aromaticities. Similarly, PZ has aromaticity, where the N-N bond length in the ring ranges from 1.278 Å to 1.377 Å. According to research findings, in the derivative (**A1**) consisting of an ANTA and a PZ ring, the difference of bond lengths in PZ ring is smaller than that of parent PZ, reflecting that the combination of PZ and ANTA enhances the conjugate effect in PZ. The same phenomenon occurs when the NH₂ or NO₂ group is introduced to **A1**. However, for the corresponding NTO derivatives, an opposite trend occurs, showing that the introduction of groups could weaken the conjugation effect of PZ. Overall, the derivatives bound by ANTA and PZ are more insensitive than those bound by NTO and PZ.

Table 1. The predicted bond lengths (Å) of ANTA, NTO and designed compounds.

Comp.	C-N in ANTA (C-N in NTO)	N-N in triazole	N _{ANTA} -NH ₂ /NO ₂ /NF ₂ (N _{NTO} -NH ₂ /NO ₂ /NF ₂ /PZ)	N _{ANTA} -N _{PZ} (N _{NTO} -N _{NH-PZ})	N-N in PZ
ANTA	1.311-1.364	1.362	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$
NTO	1.291-1.403	1.358	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$
PZ	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	1.294-1.354
A1	1.310-1.365	1.357	$\frac{3}{4}$	1.366	1.303-1.334
A2	1.319-1.360	1.342	1.374	1.365	1.303-1.333
A3	1.305-1.399	1.355	1.443	1.367	1.299-1.339
A4	1.303-1.378	1.369	1.368	1.360	1.280-1.374
A5	1.303-1.375	1.367	$\frac{3}{4}$	1.353-1.365	1.278-1.377
B1	1.288-1.415	1.363	$\frac{3}{4}$	1.394	1.284-1.368
B2	1.291-1.400	1.365	1.403	1.393	1.284-1.368
B3	1.283-1.427	1.365	1.487	1.390	1.283-1.370
B4	1.280-1.435	1.367	1.383	1.390	1.283-1.370
B5	1.281-1.424	1.363	1.351	1.389	1.278-1.375

For the designed compounds, the energies of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and energy gaps (ΔE) were illustrated in Fig. 3. The energy of HOMO and LUMO decreases with the increase of the number of PZ attached to nitrogen in ANTA or NTO, showing that the addition of PZ could make the electron acceptance of ANTA or NTO easier and the electron loss more difficult. Since NH₂ is an electron-donor group and NO₂ and NF₂ are electron withdrawing groups, the introduction of NH₂ group increases the energy of HOMO and LUMO, while the introduction of NO₂ and NF₂ groups has an opposite effect. Conceptual density functional theory is a significant theory for the study of chemical reaction activities and sites. In this framework, there is a quantity called softness. Softness does not refer to the rigidity of the system, but reflects the activity of electrons and the distribution of easy deformation degree. For a series of similar systems, it is generally believed that the softer the molecule is, the more active its reactivity is. The softness is approximately equal to the reciprocal of HOMO-LUMO gap. In the chemical or photochemical process of electron transfer or transition, the energy gap is an important parameter to evaluate the reactivity. Thus, the smaller the Energy gap, the higher the reactivity. As shown in Fig. 3, all of the designed compounds have relatively large energy gaps, ranging from 4.14 eV to 5.31 eV, which indicates that these molecules show good stability in the chemical process. Moreover, **A3** has the largest energy gap, while **A5** has the smallest one among these compounds.

3.2 Density and heat of formation

For high-energy materials, density plays a significant role in detonation performance, since higher density means more energy per unit volume. Specifically, the density can directly affect the detonation performance shown in the Kamlet-Jacobs equation. In this part, based on the combination of PZ and ANTA (**A1** to **A5**)/NTO (**B1** to **B5**), the effect of introducing different substituents on the density of energetic compounds with appropriate positions were studied. The density of the designed compounds ranges from 1.81 g/cm³ to 1.97 g/cm³ (Table 2). In view of the second substitution

site of NTO is adjacent to C-NO₂, while that of ANTA is meta-substitution. When the same substituent is introduced, the repulsive force between substituents of series **B** derivatives is larger, and the corresponding substituents contribute more to the volume, so that the densities of series **B** derivatives are slightly lower than those of series **A** derivatives. It is found that the density increases in the order of **A1** to **A4**, exhibiting that the introduction of NH₂, NO₂ and NF₂ into the system increases the density. Since the above groups can significantly increase the molar mass of the compound, but have relatively little effect on the molecular volume. One should note that **A5** (consisting of an ANTA and two PZ rings) has lower density, compared with **A1**, as a result of less coplanarity of its structure, reducing the packing regularity and increasing the spatial volume of the molecule with the addition of another PZ ring. In short, its contribution to volume is much greater than that to molecular weight. The change trend of the density of **B** and **A** series compounds is similar (except **B2**). Obviously, the influence of the introduction of amino group on the volume is greater than that on molecular weight for **B2**.

Nitrogen content and oxygen balance (OB) are two momentous parameters for screening energetic compounds. The higher the nitrogen content of energetic materials is, the better the detonation performance is. Explosive reactions can release maximum heat when the oxygen balance is zero. Lower OB stands for more oxygen being needed from external surroundings during combustion transitioning to detonation, which could result in the decrease of detonation performance. Therefore, the energetic compounds with high nitrogen content and zero oxygen balance would have better detonation performance. For the designed molecules, the nitrogen content is higher than 58%, and the oxygen balance is between -26.29 % and 3.09 %. This displays that these molecules have good detonation properties.

Table 2. The calculated values of solid-phase HOF, density, N-content and OB.

Properties	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5
ρ (g/cm ³)	1.90	1.91	1.92	1.97	1.85	1.83	1.81	1.89	1.96	1.85
HOF _g (kJ/mol)	876.92	1027.14	981.98	940.76	1524.38	737.42	870.63	902.98	870.10	1432.21
ΔH_{sub} (kJ/mol)	130.24	145.71	134.27	134.96	149.75	115.75	124.76	130.81	131.12	151.47
HOF _s (kJ/mol)	746.68	881.43	847.71	805.81	1374.63	621.66	745.86	772.17	738.98	1280.74
OB (%) ^a	-24.24	-26.29	-3.29	-12.85	-14.98	-14.95	-17.47	-3.09	-6.04	-8.48
N-content (%)	70.71	72.30	63.37	61.85	78.65	65.42	67.25	59.46	58.11	74.20

^a OB (%) for C_aH_bO_cN_dF_e: $16 \times (c - 2a - b/2 - e)/M \times 100\%$; M is molecular weight of the title compounds.

Heat of formation (HOF) is one of the most crucial quantities used to evaluate the energetic properties of HEDMs. To demonstrate the reliability of the calculated HOFs, the gas-phase HOF, solid-phase HOF and heat of sublimation of NTO, being -14.18 kJ/mol, -95.31 kJ/mol and 81.13 kJ/mol respectively, were calculated (see **Computational methods** for details). The calculated value of solid-phase HOF is comparable to the experimental values of -100.8 kJ/mol [34]. Thus, the methods we chose are reasonable. The range of solid-phase HOF is from 621.66 kJ/mol to 1374.63 kJ/mol. According to research findings, the addition of another PZ ring could increase the solid-phase HOF of the system by about 640 kJ/mol. For **A** series compounds, the solid-phase HOF of **A2**, **A3**, **A4** or **A5** is larger than **A1**, indicating that the introduction of the NH₂, NO₂, NF₂ groups or consisting of an ANTA and two PZ rings could enhance HOF. While this positive influence of NH₂, NO₂ or NF₂ group is weaker than that of addition of another PZ ring, since **A2** to **A4** all have

lower solid-phase HOFs than **A5** to varying degrees. An analogical situation occurs in series **B** derivatives. Meanwhile, the similar solid-phase HOF values of series **A** and **B** show that the introduction of NF_2 (**A4** and **B4**) cannot significantly increase the HOF. Therefore, in the formation of such compounds, in order to obtain high HOF, the introduction of NH_2 or NO_2 group as a substituent or combining with two PZ rings is a good choice.

3.3 Energetic properties

The detonation heat (Q), detonation pressure (P), and detonation velocity (D) of the title compounds have been assessed by the semi-empirical Kamlet-Jacobs formula, which has been proved to be applicable for predicting the explosive properties of energetic high-nitrogen compounds based on the predicted density and heat of formation. P and D are the most important parameters for evaluating energetic materials.

The P and D for two known explosives RDX and HMX were also calculated by above method. The calculated values (RDX: $P = 34.8$ GPa, $D = 8.9$ km/s; HMX: $P = 39.2$ GPa, $D = 9.3$ km/s) are comparable to the experimental values (RDX: $P = 34.7$ GPa, $D = 8.8$ km/s; HMX: $P = 39.0$ GPa, $D = 9.1$ km/s) [35]. Hence, our predictions for the designed compounds are reliable. For the purpose of comparison, the experimental detonation performances of RDX and HMX were also showed in Fig. 4a. Since densities and HOFs play a crucial role for detonation performances, it is pleasant to see that the trends of Q , P and D are basically the similar. Therefore, combined with the above analysis of the density and HOF of **A** and **B** series derivatives, it is reasonable that the detonation performances of **A** series is larger than those of **B** series on the whole. Judged by the Q , P and D values, all of the designed compounds have good detonation performances.

For molecules **A1** to **A4** and **B1** to **B4**, with increasing sequence number, both corresponding P and D increases gradually, indicating that the introduction of NH_2 , NO_2 or NF_2 is beneficial for improving energetic properties. What's more, the molecule with NF_2 group (**A4** or **B4**) has the best detonation performances while the compound with the NH_2 substituent (**A2** or **B2**) has the worst detonation performances, indicating that the contribution of NF_2 group to the detonation performance of an energetic compound is greater than that of NH_2 group. When an NTO is combined with two PZ rings, both P and D are larger than those of **B1** and **B2**. The reason is that the density and HOF of **B5** advantage over those of **B1** and **B2**. It is further proved that density and HOF are the decisive factors for evaluating the detonation performance of energetic materials. Both P and D of compounds **A3**, **A4** and **B4** are superior to HMX, **A2**, **A5**, **B3** and **B5** have approximate or exceeded P and D over HMX, whereas those of **B1** and **B2** are approximate or inferior to RDX, exhibiting that they can be taken as promising candidates of HEDMs apart from **B1** and **B2**. These predictions further verify that modifying energetic molecules with appropriate substituents is a meritorious method to improve the energetic properties.

3.4 Sensitivity

The core problem in designing new explosives is to achieve the desired balance between high performance and low sensitivity. Therefore, in order to further investigate the practical application, an admissible sensitivity value is essential for a new high-energy compound. It is therefore significant to have some means of evaluating the likely sensitivities of compounds that have not yet been synthesized. In this part, the free space per molecule in the unit cell, designated ΔV , has been used to evaluate sensitivity of the proposed compounds, which has been proved to be reliable for predicting the sensitivity of energetic compounds [31, 36]. The smaller value of ΔV is, the lower sensitivity of the explosive is.

In Fig. 4b, the second substitution site of NTO is adjacent to C-NO_2 , whereas that of ANTA is the meta-position from C-NO_2 . When the same substituent is introduced, the repulsive force between substituents of **B** series derivatives is larger, resulting in the sensitivities of **B** series derivatives being slightly higher than those of **A** series derivatives. Compared with **A1** ($43.51 \text{ \AA}^3$) and **A5** ($56.26 \text{ \AA}^3$), **B1** ($45.73 \text{ \AA}^3$) and **B5** ($58.07 \text{ \AA}^3$), the ΔV values are significantly increased, showing that merging two PZ rings into one structure increases the sensitivity. The increased sensitivity is probably caused by the

weakening interactions between the ring of PZ and ANTA/NTO. ΔV values of **A5**, **B3**, **B4** and **B5** were larger than HMX (49.20 Å^3) [36], indicating that they are more sensitive than HMX. When PZ of the second site in **A5** or **B5** is replaced by NH_2 , NO_2 or NF_2 groups, the ΔV value is significantly reduced. It displays that NH_2 , NO_2 or NF_2 groups can effectively adjust the sensitivity properties of the compounds to an acceptable level. Among them, the addition of NH_2 group reduced the sensitivity of compounds significantly. The reason is that NH_2 is an electron-donating group, which can offset the imbalance of surface potential caused by electron-withdrawing components. Secondly, the existence of NH_2 substituent can generate intermolecular and intramolecular hydrogen bonds, thus stabilizing the system. Moreover, Compounds **A1**, **A2**, **A3**, **A4** and **B2**, all have exceed or approximate P and D to RDX, lower or approximate sensitivity to HMX, indicating that these five novel compounds have good performance, which reveals the great potential of the parent compounds (formed by PZ and ANTA/NTO) used as HEDMs. Additionally, both molecules **A3** and **A4** are superior to HMX in detonation performance and are good candidates to HEDMs.

Conclusion

The connection of PZ with ANTA and NTO form **A1** and **B1**, respectively. In order to adjust the property further, different substituents (NH_2 , NO_2 and NF_2) were introduced to form two series compounds **A** and **B**. The results showed that the formation heat of ANTA or NTO bonding two PZ rings increases by $\sim 640 \text{ kJ/mol}$ compared to those of ANTA or NTO bonding one PZ ring. In addition, better detonation performance and higher sensitivity are achieved when **A1** or **B1** combine with another PZ ring. Meanwhile, the second substitution site of NTO is adjacent to C-NO_2 , which has larger steric hindrance than ANTA, when introducing the same group into the frame. As a result, **A**-series derivatives have larger densities and lower sensitivities than **B**-series. The NH_2 , NO_2 and NF_2 groups increase the densities and HOFs, especially for the NO_2 and NF_2 groups. Moreover, all the compounds have high densities, heats of formation and great detonation performances. Among them, molecules **A3** and **A4** not only have better detonation performances than HMX, but also have comparable sensitivities, which further demonstrate that both NO_2 and NF_2 groups can availably regulate the energetic properties. The excellent energetic properties of **A3** ($P = 41.16 \text{ GPa}$ and $D = 9.45 \text{ km/s}$) and **A4** ($P = 43.90 \text{ GPa}$ and $D = 9.69 \text{ km/s}$) make them be potential candidates for HEDMs.

Declarations

Funding: This work was supported by the National Natural Science Foundation of China (No. 21975128, 21903044, 11972178).

Conflicts of Interest/Competing interests: The authors declare no conflict of interest.

Availability of data and material: The work described is original that has not been published previously, and the data is available.

Code availability: Not applicable.

Author Contributions: Conceptualization, Bing-Cheng Hu and Xue-Hai Ju; Data curation, Hao-Ran Wang, Cheng Guo Sun and Chong Zhang; Formal analysis, Hao-Ran Wang; Project administration, Bing-Cheng Hu and Xue-Hai Ju; Supervision, Xue-Hai Ju; Writing – original draft, Hao-Ran Wang; Writing – review & editing, Xue-Hai Ju.

Ethics approval: Not applicable.

Consent to participate: The manuscript and associated personal data can be shared with Research Square.

Consent for publication: The manuscript is approved by all authors for publication.

References

1. Chen D, Yang H, Yi Z, Xiong H, Zhang L, Zhu S, Cheng G (2018) $C_8N_{26}H_4$: An environmentally friendly primary explosive with high heat of formation. *Angew Chem Int Edit* 57:2081–2084
2. Wang Q, Pang F, Wang G, Huang J, Nie F, Chen F-X (2017) Pentazadiene: a high-nitrogen linkage in energetic materials. *Chem Commun* 53:2327–2330
3. Chavez DE, Hiskey MA, Gilardi RD (2000) 3,3'-azobis(6-amino-1,2,4,5-tetrazine): A novel high-nitrogen energetic material. *Angew Chem Int Edit* 39:1791–1793
4. Joo YH, Twamley B, Garg S, Shreeve JnM (2008) Energetic nitrogen-rich derivatives of 1,5-diaminotetrazole. *Angew Chem Int Edit* 47:6236–6239
5. Klapoetke TM, Piercey DG (2011) 1,1'-azobis(tetrazole): A highly energetic nitrogen-rich compound with a N-10 chain. *Inorg Chem* 50:2732–2734
6. Xiao M, Jin X, Zhou J, Hu B (2021) 1,2,5-Oxadiazole-1,2,3,4-tetrazole-based high-energy materials: molecular design and screening. *Struct Chem* 32:1619–1628
7. Manna MS, Das CK, Ghanta S (2021) Design of C-H-N-O based new hetero-cyclic high energy density molecules: a theoretical survey. *Struct Chem* 32:1095–1104
8. Christe KO (2007) Recent advances in the chemistry of $N_5^+N_5^-$ and high-oxygen compounds. *Propell Explos Pyrot* 32:194–204
9. Klapoetke TM, Martin FA, Stierstorfer J (2011) C_2N_{14} : An energetic and highly sensitive binary azidotetrazole. *Angew Chem Int Edit* 50:4227–4229
10. Klapoetke TM, Sabate CM (2008) Nitrogen-rich tetrazolium azotetrazolate salts: A new family of insensitive energetic materials. *Chem Mater* 20:1750–1763
11. Shlomovich A, Pechersky T, Cohen A, Yan QL, Kosa M, Petrutik N, Tal N, Aizikovich A, Gozin M (2017) Energetic isomers of 1,2,4,5-tetrazine-bis-1,2,4-triazoles with low toxicity. *Dalton T* 46:5994–6002
12. Guo Y, Tao G-H, Zeng Z, Gao H, Parrish DA, Shreeve JnM (2010) Energetic salts based on monoanions of N,N-Bis(1H-tetrazol-5-yl)amine and 5,5'-Bis(tetrazole). *Chem-Eur J* 16:3753–3762
13. Xu Y, Wang P, Lin Q, Lu M (2017) A carbon-free inorganic-metal complex consisting of an all-nitrogen pentazole anion, a Zn(II) cation and H_2O . *Dalton T* 46:14088–14093
14. Xu Y, Wang Q, Shen C, Lin Q, Wang P, Lu M (2017) A series of energetic metal pentazolate hydrates. *Nature* 549:78–81
15. Zhang C, Sun C, Hu B, Yu C, Lu M (2017) Synthesis and characterization of the pentazolate anion $cyclo-N_5^-$ in $(N_5)_6(H_3O)_3(NH_4)_4Cl$. *Science* 355:374–376
16. Zhang C, Yang C, Hu B, Yu C, Zheng Z, Sun C (2017) A symmetric $Co(N_5)_2(H_2O)_4 \cdot 4H_2O$ high-nitrogen compound formed by cobalt(II) cation trapping of a $cyclo-N_5^-$ anion. *Angew Chem Int Edit* 56:4512–4514
17. Steele BA, Stavrou E, Crowhurst JC, Zaug JM, Prakapenka VB, Oleynik II (2017) High-pressure synthesis of a pentazolate salt. *Chem Mater* 29:735–741
18. Laniel D, Weck G, Gaiffe G, Garbarino G, Loubeyre P (2018) High-pressure synthesized lithium pentazolate compound metastable under ambient conditions. *J Phys Chem Lett* 9:1600–1604
19. Yang C, Zhang C, Zheng Z, Jiang C, Luo J, Du Y, Hu B, Sun C, Christe KO (2018) Synthesis and characterization of cyclo-pentazolate salts of NH_4^+ , NH_3OH^+ , $N_2H_5^+$, $C(NH_2)_3^+$, and $N(CH_3)_4^+$. *J Am Chem Soc* 140:16488–16494
20. Chavez DE, Parrish DA, Mitchell L (2016) Energetic trinitro- and fluorodinitroethyl ethers of 1,2,4,5-tetrazines. *Angew Chem Int Edit* 55:8666–8669

21. Wei T, Zhu W, Zhang J, Xiao H (2010) DFT study on energetic tetrazolo-[1,5-b]-1,2,4,5-tetrazine and 1,2,4-triazolo-[4,3-b]-1,2,4,5-tetrazine derivatives. *J Hazard Mater* 179:581–590
22. Pevzner MS, Kulibabina TN, Povarova NA, Kilina LV (1979) Nitration of 5-amino-1,2,4-triazole and 5-acetamidotriazole with acetyl nitrate and nitroium salt. *Chem Heterocycl Com +* 15:929–932
23. Pagoria PF, Lee GS, Mitchell AR, Schmidt RD (2002) A review of energetic materials synthesis. *Thermochim Acta* 384:187–204
24. Manchot von W, Noll R (1905) 1,2,4-triazol-5-ones[J]. *Justus Liebig's Annalen der Chemie* 343:1–42
25. Chipen GI, Bokalder RP, Grinshtein VY (1966) 1,2,4-triazol-3-one and its nitro and amino derivatives. *Chem Heterocycl Com +* 2:79–83
26. Lee KY, Chapman LB, Cobura M (1988) 3-nitro-1,2,4-triazol-5-one, a less sensitive explosive. *J Energ Mater* 5:27–33
27. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA (2009) Gaussian 09, Rev A.1
28. Politzer P, Martinez J, Murray JS, Concha MC, Toro-Labbe A (2009) An electrostatic interaction correction for improved crystal density prediction. *Mol Phys* 107:2095–2101
29. Politzer P, Ma YG, Lane P, Concha MC (2005) Computational prediction of standard gas, liquid, and solid-phase heats of formation and heats of vaporization and sublimation. *Int J Quantum Chem* 105:341–347
30. Kamlet MJ, Jacobs SJ (1968) Chemistry of Detonations. I. A simple method for calculating detonation properties of C–H–N–O explosives. *J Chem Phys* 48:23–35
31. Politzer P, Murray JS (2014) Impact sensitivity and crystal lattice compressibility/free space. *J Mol Model* 20:2223–2230
32. Lu T, Chen F (2012) Multiwfn: A multifunctional wavefunction analyzer. *J Comput Chem* 33:580–592
33. Allen FH, Kennard O, Watson DG, Brammer L, Orpen AG, Taylor R (1987) Tables of bond lengths determined by X-ray and neutron diffraction. Part 1. Bond lengths in organic compounds. *J Chem Soc Perkin Transactions* 2:S1–S19
34. Cronin MP, Day AI, Wallace L (2007) Electrochemical remediation produces a new high-nitrogen compound from NTO wastewaters. *J Hazard Mater* 149:527–531
35. Talawar MB, Sivabalan R, Mukundan T, Muthurajan H, Sikder AK, Gandhe BR, Rao AS (2009) Environmentally compatible next generation green energetic materials (GEMs). *J Hazard Mater* 161:589–607
36. Pospisil M, Vavra P, Concha MC, Murray JS, Politzer P (2011) Sensitivity and the available free space per molecule in the unit cell. *J Mol Model* 17:2569–2574

Figures

Figure 1

Molecular structures of designed compounds.

Figure 2

Optimized structures of designed of compounds.

Figure 3

HOMO and LUMO energy levels and energy gaps of ten compounds.

Figure 4

A comparison of Q, P, D (a) and ΔV (b) of compounds.