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Computational Studies on Polynitrohexaazaadmantanes as Potential High Energy Density Materials

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Polynitrohexaazaadamantanes (PNHAAs) have been the subject of much recent research because of their potential as high energy density materials (HEDMs). The B3LYP/6-31G* method was employed to evaluate the heats of formation (HOFs) for PNHAAs by designing isodesmic reactions. The HOFs are found to be correlative with the number (n) and the space orientations of nitro groups. Detonation velocities (D) and detonation pressures (P) were estimated for PNHAAs by using the well-known Kamlet−Jacobs equations, based on the theoretical densities (ρ) and HOFs. It is found that D and P increase as n ranges from 1 to 6, and PNHAAs with 4−6 nitro groups meet the criteria of an HEDM. When n is over 6, ρ of PNHAAs slightly increases; however, the chemical energy of detonation (Q) decreases so greatly that both D and P decrease. The calculations on bond dissociation energies suggest that the N−N bond be the trigger bond during the pyrolysis initiation process of each PNHAA, and with increasing n, N−N bond dissociation energy ($E_{\mathrm{N-N}}$) decreases on the whole, that is to say, the relative stability of PNHAAs decreases. All $E_{\mathrm{N-N}}$(s) of PNHAAs are more than 30 kcal·mol^{-1}, which further proves that four PNHAAs with 4−6 nitro groups can be used as the candidates of HEDMs. Considering the synthesis difficulty and the performance as an energetic compound, we finally recommended 2,4,6,8,10-pentanitrohexaazaadamantane as the target HEDM for PNHAAs.

1. Introduction

High energy density materials (HEDMs) have been attracting considerable attention[1−15] owing to their superior explosive performances over conventional energetic compounds.[16−21] Due to strain energies and compact structures, organic cage compounds are investigated as an important category of HEDMs. Typical examples of these compounds are hexanitrohexaazaisowurtzitane (CL-20) and octanitrocubane (ONC). Recently another two types of organic cage compounds, nitro derivatives of hexaazaadamantane (HAA) and adamantane series, have also been investigated as promising candidates of HEDMs.[4,22]

Theoretical studies have been performed to investigate the performances and structures of polynitroadamantanes (the nitro derivatives of adamantane, PNAs) systematically.[23,24] Conventionally, a compound is considered to be an HEDM if its density (ρ) is larger than 1.9 g·cm^{-3}, detonation velocity (D) greater than 9 km·s^{-1}, and detonation pressure (P) higher than 40 Gpa. Accordingly, our previous studies predicted that the PNAs with 8 or more nitro groups meet the criteria. Considering the thermal stability, three PNAs may be selected as candidates for potential HEDMs.[24]

When the six secondary C atoms of adamantane are all replaced with N atoms, hexaazaadamantane (HAA, see Figure 1 for the structure, where all the H atoms are omitted) is formed. Correspondingly, polynitrohexaazaadamantanes (the nitro derivatives of HAA, PNHAAs) are formed when the H atoms of HAA are substituted with different numbers of nitro groups. It is worth mentioning that 2,4,6,8,9,10-hexanitrohexaazaadamantane has drawn much attention, and been forecasted to be a promising HEDM.[8,10,17] In this work, the performances of PNHAAs as energetic compounds, including heat of formation (HOF), ρ, D, P, and the thermal stability, were systematically investigated to look for potential HEDMs with the theoretical method.

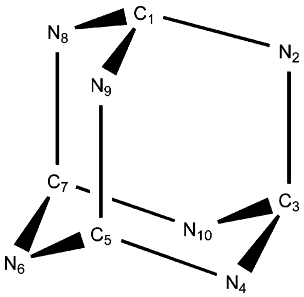

Figure 1. The structure and atomic numbering of HAA.

HOF is a key property for a compound and particularly important in the area of energetic materials, because it is an essential factor in determining detonation or propellant performance.[25] But it is impractical or dangerous to measure HOF for an energetic material or a compound experimentally. In these cases, quantum chemical methods are widely used to solve this problem. The parametrized semiempirical MO methods, such as MINDO/3, MNDO, AM1, and PM3, are able to figure out HOFs directly and rapidly, but they often cause large HOFs errors from various groups and skeletons. As to the small molecules, their HOFs can be obtained by high accuracy calculations, such as G2,[26] G3,[27] and complete basis set (CBS).[28−30] Ab initio MO methods are employed to calculate HOFs, too. For this purpose, certain reactions need to be

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designed and accurate energies are required. The density functional theory (DFT) methods, especially the B3LYP[31,32] hybrid model, not only can produce reliable geometries and energies, but also require less time and computer resources. In this paper, the B3LYP method in combination with the 6-31G*[33] basis set was chosen to evaluate the HOFs for all PNHAAs by designing reasonable isodesmic reactions.

D and *P* are the necessary factors for evaluating the detonation properties of energetic compounds. The *D* and *P* for all PNHAAs were evaluated by using empirical Kamlet−Jacobs equations,[34] based on their theoretical densities (ρ) and calculated HOFs.

In addition, the thermal stability of energetic material determines its applicability. We evaluated the stability of all PNHAAs by calculating the bond dissociation energy (*E*) and predicted the relative stability of these compounds. In section 2 we describe the theoretical methods. Results and discussion are presented in section 3. In section 4, the concluding remarks are given.

2. Computational Methods

The method of isodesmic reaction has been employed very successfully to calculate HOF from total energies obtained from ab initio calculations.[35] Isodesmic reaction processes, in which the number of each kind of formal bond is conserved, are used with application of the bond separation reaction rules. To obtain better calculation accuracy, we did not break down the HAA cage skeleton in all PNHAAs. To be specific, we took HAA as a reference compound when designing isodesmic reactions at the B3LYP/6-31G* level. This method has been proved to be reliable.[23,36−38]

The heats of formation (HOFs) of all PNHAAs were evaluated by eq 2 for the isodesmic reaction 1:

$$C_4N_6(NO_2)_{n+m}H_{10-n-m} + nNH_3 + mCH_4 \rightarrow C_4N_6H_{10} + nNH_2NO_2 + mCH_3NO_2 \qquad (1)$$

$$\Delta H^{\circ}_{298} = \Delta E_0 + \Delta \mathrm{ZPE} + \Delta H^{\circ}_{T} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R} \qquad (2)$$

where n ($n \leq 6$) is the number of the nitro groups combined with the N atoms in the cage skeleton, and m ($m \leq 4$) is the number of nitro groups combined with the C atoms in the skeleton. ΔH°_{298} is the enthalpy change of the reaction at 298 K. ΔE_0, ΔZPE, and ΔH°_{T} are the changes in the total energy, the zero point energy, and the enthalpy change from 0 to 298 K, respectively. $\sum \Delta H_{f,P}$ and $\sum \Delta H_{f,R}$ are the sums of the heats of formation of the products and the reactants, respectively. In addition, as to the reference compound NH_2NO_2, its HOF was evaluated by G3 theory, based on the atomization energies being used by Curtiss etc.[26]

The empirical Kamlet−Jacobs equations are widely applied to estimate the values of *D* and *P* for the explosives containing C, H, O, and N as following:

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho_0) \qquad (3)$$

$$P = 1.558\rho_0^{\,2}NM^{1/2}Q^{1/2} \qquad (4)$$

where each term in eqs 3 and 4 is defined as follows: *D*, detonation velocity [km/s]; *P*, detonation pressure [GPa]; *N*, moles of gaseous detonation products per gram of explosive; *M*, average molecular weight of gaseous products; *Q*, chemical energy of detonation [kJ·mol^{-1}]—defined as the difference of the HOFs between the products and reactants, based on the most exothermic principle; and ρ_0, density of the explosive [g/cm^3]. Here, the theoretical density of each PNHAA was obtained from the molecular weight divided by the average molecular volume. The average mole volume of each compound was obtained from the statistical average value of 100 molar volumes. The mole volume of each molecule, defined as the volume inside a contour of 0.001e/Bohr^3 density,[39] was calculated by Monte Carlo method in the Gaussian98 program package.[40] Our group has ever validated this method by comparing the experimental density with the calculated values for >30 energetic compounds; most of these compounds are nitramines (N−NO$_2$-based), and the average value of ρ_{cal}/ρ_{exp} is more than 0.998.[41]

TABLE 1: Total Energies (E_0), Zero-Point Energies (ZPE), Thermal Corrections (H°_{T}), and HOFs for the Reference Compounds at the B3LYP/6-31G* Level

compds	E_0 (au)	ZPE (kJ·mol^{-1})	H°_{T} (kJ·mol^{-1})	HOF (kJ·mol^{-1})
$(CH_2NH)_3$	−283.96178	347.39	16.55	78.10[a]
CH_4	−40.51838	113.96	10.02	−74.4[42]
HAA	−486.90680	444.96	19.44	236.95[b]
NH_2NO_2	−261.0315	99.87	12.32	6.20[a]
NH_3	−56.54795	87.01	10.00	−45.94[43]
CH_3NO_2	−245.00933	126.49	14.08	−74.3[44]

[a] HOFs were obtained by using the G3 theory. [b] HOF was obtained at the B3LYP/6-31G* level for the isodesmic reaction 5.

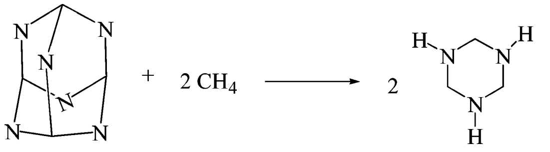
Furthermore, we evaluated the thermal stability of the title compounds by calculating bond dissociation energy. Each of the bond breaks leads to an intermediate with a triplet ground state. Spin-restricted wave functions were used for all PNHAAs compounds, and spin-unrestricted wave functions were employed for the obtained intermediates.

All calculations were performed on a Pentium IV personal computer in our laboratory. The default convergence criteria given in the programs were used throughout the computations.

3. Results and Discussion

This section presents and discusses the results, including the HOFs, *D*, *P*, and thermal stability for all PNHAAs at the B3LYP/6-31G* level.

3.1. Heats of Formation. To calculate HOFs for PNHAAs, the HOF of a reference compound HAA should be known in the isodesmic reaction 1. However, to the best of our knowledge, no experimental HOF has been reported. Due to its large size, we could not evaluate its HOF using the high accuracy method, thus we designed isodesmic reaction such as eq 5 to resolve this problem at the B3LYP/6-31G* level.



(5)

The experimental HOF of CH_4 is −74.4 kJ·mol^{-1},[42] and the HOF of triazacyclohexane $(CH_2NH)_3$ was evaluated by using the G3 theory, based on the atomization energies.[26] Thus the HOF of HAA was evaluated as 236.95 kJ·mol^{-1}. The HOF of NH_2NO_2 in the isodesmic reaction 1 was obtained in the same way as that for $(CH_2NH)_3$. The related data are listed in Table 1.

From Table 1, it can be seen that the HOF of HAA (236.9 kJ·mol^{-1}) is much larger than that of adamantane (−136.5 kJ·mol^{-1}),[22] which indicates that the nitro derivatives of HAA may have better energy performances than those of adamantane.

TABLE 2: Total Energies (E_0), Zero-Point Energies (ZPE), Thermal Corrections (H°_{T}), and HOFs for PNHAAs at the B3LYP/6-31G* Level[a]

compds	E_0 (au)	ZPE ($kJ\cdot mol^{-1}$)	H°_{T} ($kJ\cdot mol^{-1}$)	HOF ($kJ\cdot mol^{-1}$)
2-	−691.39564	449.89	26.08	270.95
2,4-	−895.87020	452.72	33.39	341.08
2,6-	−895.88117	454.29	32.87	313.31
2,4,6-	−1100.35126	456.49	40.36	394.70
2,4,9-	−1100.34974	456.47	40.38	398.61
2,4,10-	−1100.34526	455.93	40.42	410.10
2,4,6,8-	−1304.82401	459.36	47.54	469.52
2,4,6,9-	−1304.81843	458.60	47.79	483.67
2,4,6,8,10-	−1509.29297	462.21	54.82	556.97
2,4,6,8,9,10-	−1713.755267	463.90	62.35	665.76
1,2,4,6,8,9,10-	−1918.19593	464.16	63.39	775.78
1,2,3,4,6,8,9,10-	−2122.6311	463.72	76.87	918.51
1,2,3,4,5,6,8,9,10-	−2327.07529	461.68	85.15	1041.73
1,2,3,4,5,6,7,8,9,10-	−2531.50605	460.47	92.70	1150.41

[a] 2- and 2,4- denote 2-nitrohexaazaadamantane and 2,4-dinitrohexaazaadamantane, respectively, the others follow the same pattern.

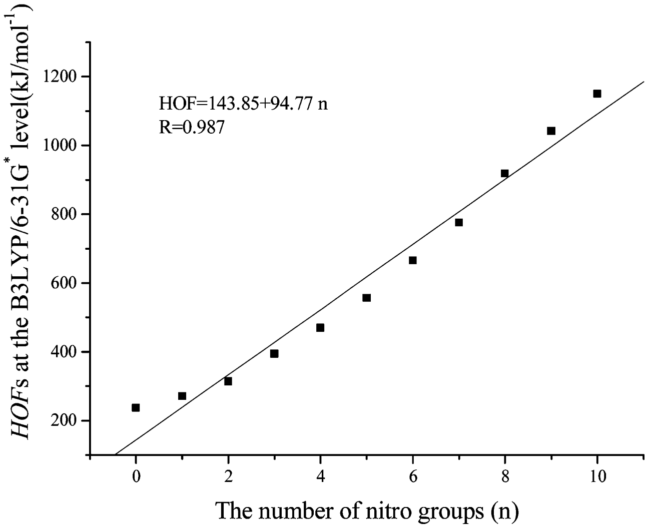


Figure 2. The linear relationship between the number of nitro groups (n) and HOFs for PNHAAs.

TABLE 3: The Calculated Densities (ρ), Chemical Energies of Detonation (Q), Detonation Velocities (D), and Detonation Pressures (P) of PNHAAs[a]

compds	ρ ($g\cdot cm^{-3}$)	Q ($kJ\cdot mol^{-1}$)	D ($km\cdot s^{-1}$)	P (GPa)
2-	1.64	974.10	7.46	23.32
2,4-	1.77	1347.92	8.21	29.64
2,6-	1.79	1319.32	8.23	30.00
2,4,6-	1.87	1495.29	8.90	36.12
2,4,9-	1.87	1498.67	8.94	36.18
2,4,10-	1.92	1508.58	9.11	38.25
2,4,6,8-	1.97	1617.21	9.55	42.66
2,4,6,9-	1.96	1627.71	9.53	42.38
2,4,6,8,10-	2.02	1727.67	9.96	47.11
2,4,6,8,9,10-	2.08 (2.10)[b]	1574.09	9.95	47.52
1,2,4,6,8,9,10-	2.12	1418.62	9.78	46.56
1,2,3,4,6,8,9,10-	2.17	1301.84	9.72	46.51
1,2,3,4,5,6,8,9,10-	2.21	1195.75	9.70	46.04
1,2,3,4,5,6,7,8,9,10-	2.24	1099.91	9.48	45.18

[a] 2- and 2,4- denote 2-nitrohexaazaadamantane and 2,4-dinitrohexaazaadamantane, respectively, the others follow the same pattern. [b] A calculation value from ref 25 is given in parentheses.

On the basis of the energy properties of the reference compounds listed in Table 1 and the isodesmic reaction 1, the HOFs of the PNHAAs obtained with the B3LYP/6-31G* method are given in Table 2.

It is evident from the data listed in Table 2 that all HOFs of PNHAAs are quite large positive values, and far larger than that of the parent HAA, which shows that the introduction of nitro groups is the main energy origin of the PNHAAs series. Compared with PNAs with negative HOFs,[23,24] PNHAAs studied here are proven to have better energy properties than the corresponding PNAs.

It is also clear from Table 2 that with n increasing, the HOFs of PNHAAs increase. Figure 2 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 the least HOF was chosen for analysis. The correlation coefficient is 0.987, indicating that the HOFs have the property of group additivity, and each nitro group addition will increase HOF by 94.77 $kJ\cdot mol^{-1}$ or so.

The space orientations of nitro groups also affect the HOFs of PNHAAs. As usual, for the isomers with the same n, the shorter the distance between the nitro groups a compound is, the stronger the repulsive energy is, and the larger the HOF of the compound is. For example, as for the isomers with two nitro groups, the HOF of 2,6- is smaller than that of 2,4- because the two nitro groups in 2,6- are farther away from each other than those in 2,4-. The ordering of HOFs for the isomers with three nitro groups is as follows: 2,4,6- < 2,4,9- < 2,4,10-. A similar explanation is also true for the isomers with $n = 3$. The three nitro groups in 2,4,6-, not in the same ring, are farther away from each other than those in 2,4,9- and 2,4,10-. Since the three nitro groups in 2,4,9- are in the same ring but separated from each other, and the three $N-NO_2$ bonds of 2,4,10- are connected by the same C3 atom, the nitro groups in 2,4,9- are farther away from each other than those in 2,4,10-. On the whole, according to n and the relative position of the nitro groups, the relative HOFs order of PNHAAs can be distinguished, which is useful for evaluating the relative thermal stability of PNHAAs.

3.2. Detonation Properties. Table 3 presents all the calculated densities (ρ), chemical energy of detonation (Q), detonation velocities (D), and detonation pressures (P) for the PNHAAs. The calculated ρ (2.08 $g\cdot cm^{-3}$) of 2,4,6,8,910- is very close to the previous value (2.10 $g\cdot cm^{-3}$),[45] which further confirms the applicability of the method used to evaluate theoretical densities for these molecular systems. Although these data may slightly deviate from the actual values according to our previous experiences,[41] they will still be of much significance for our studies on them.

It can be found from Table 3 that all PNHAAs have large densities in the range of 1.64−2.24 $g\cdot cm^{-3}$ and good detonation properties ($Q = 974.10-1727.67\ kJ\cdot mol^{-1}$, $D = 7.46-9.96\ km\cdot s^{-1}$, $P = 23.32-47.52$ GPa). PNHAAs with 4−10 nitro groups meet the criteria as an HEDM and can be regarded as candidates of HEDMs.

Meanwhile, with the number of nitro groups increasing from 1 to 6, ρ, Q, D, and P of the corresponding compounds increase. However, as for 1,2,4,6,8,9,10- and 1,2,3,4,6,8,910-, which come into being when one and two nitro groups further replace the H atoms attached to the C atom of 2,4,6,8,9,10-hexanitrohexaazaadamantane, respectively, their D and P decrease. This is because their larger positive oxygen balance values decrease Q greatly and lead ρ to have less influence on D and P. For example, the Q, D, and P of 2,4,6,8,9,10- are 1574.09 $kJ\cdot mol^{-1}$, 9.95 $km\cdot s^{-1}$, and 47.52 GPa, respectively, but those of 1,2,4,6,8,9,10- quickly decrease to 1418.62 $kJ\cdot mol^{-1}$, 9.78 $km\cdot s^{-1}$, and 46.56 Gpa, respectively. Thus, it may be inferred that PNHAAs with over 6 nitro groups are not regarded as potential HEDMs. In addition, it can be easily seen that 2,4,6,8,9,10- has larger ρ than 2,4,6,8,-

TABLE 4: The Total Energies (E_{ZPE}) Corrected by Zero-Point Energies (ZPE) for 1-Nitrocubane and Each Intermediate, and Dissociation Energies (E) for Both C−N and N−N Bonds at the B3LYP/6-31G* Level[a]

1-nitrocubane	intermediate for C−C bond breaking		intermediate for C−N bond breaking	
E_{ZPE}	E_{ZPE}	E_{C-C}	E_{ZPE}	E_{C-N}
−513.83306	−513.77310	157.42	−513.73357	261.21

[a] Units for E_{ZPE} and E are au and kJ·mol^{-1}, respectively.

TABLE 5: Dissociation Energies for the C−N (E_{C-N}) and N−N (E_{N-N}) Bonds at the B3LYP/6-31G* Level[a]

compds[b]	E_{C-N}	E_{N-N}
2-	290.93	172.50
2,4-	254.32	155.47
2,6-	291.67	168.32
2,4,6-	247.28	149.58
2,4,9-	256.64	150.75
2,4,10-	243.39	149.12
2,4,6,8-	256.39	146.93
2,4,6,9-	261.18	143.96
2,4,6,8,10-	268.48	158.97
2,4,6,8,9,10-	252.07	142.65

[a] Unit: kJ·mol^{-1}. [b] 2- and 2,4- denote 2-nitrohexaazaadamantane and 2,4-dinitrohexaazaadamantane, respectively, the others follow the same pattern.

10-, but the Q of 2,4,6,8,9,10- decreases so greatly that its D and P are almost equal to those of 2,4,6,8,10-. Thus considering the synthesis difficulty and the practicability of these compounds, we recommend 2,4,6,8,10- as the target HEDM of these compounds. This information appears to be useful for looking for HEDMs from PNHAAs.

3.3. Pyrolysis Mechanism and Thermal Stability. The dissociation energy (E) for each possible trigger bond is often a key factor in investigating the pyrolysis mechanism for an energetic compound. Generally, the smaller the E for breaking a bond is, the more easily the bond is broken. To break the bond will be the initial step during thermolysis process. First we investigated the pyrolysis mechanism for 1-nitrocubane to testify to the reliability of this method. From Table 4, it can be seen that the dissociation energy for the C−C bond (E_{C-C}) is far smaller than that for C−N (E_{C-N}) at the B3LYP/6-31G* level. Thus the C−N bond was considered to be the trigger bond for 1-nitrocubane during pyrolysis, which is in good agreement with experiment.[46−47]

To elucidate the pyrolysis mechanism and thermal stability of PNHAAs, we calculated the dissociation energies for the two possible initial steps in the pyrolysis route: (1) breaking the N−N bond and (2) breaking the C−N bond on the skeleton. It should be pointed out that, in this work, we selected the C−N or N−N bond with the least mulliken population at the B3LYP/6-31G* level.

From Table 5, comparing E_{C-N} with E_{N-N}, we found that, for each PNHAA, E_{N-N} is much smaller than E_{C-N}, which predicts that the N−N bond should be the trigger bond during the thermolysis initiation process. On the other hand, on the whole, with n increasing, the dissociation energy for the N−N bond (E_{N-N}) decreases except for 2,4,6,8,10-, which indicates that the relative stability of these PNHAAs decreases as n increases but the sensitivity increases. Meanwhile, E_{N-N} of PNHAAs ranges from 142.65 to 172.50 kJ·mol^{-1}, and the small discrepancy among these E_{N-N} values indicates that the relative stabilities of these PNHAAs are close to each other. Certainly, we can also find the discrimination of E_{N-N} for isomers with the same number of nitro groups. For instance, 2,6- has more E_{N-N} than 2,4-, which predicts that 2,6- is more stable than 2,4-. 2,4,6,8- is also found to be more stable than 2,4,6,9-. These are in good agreement with that from the above HOFs. But the relative stability cannot be well distinguished for three trinitrohexaazaadamantanes in this way, in our opinion, which may be due to the B3LYP/6-31G* not always producing such a high calculation accuracy.

It has been suggested by Chung etc. that a molecule should have barriers to decomposition and isomerization of at least 30 kcal/mol to be considered a viable candidate for HEDM.[48] According to this, we can see that all the compounds listed in Table 4 satisfy this standard. In combination with the detonation properties in Table 3, we are certain that four PNHAAs with 4−6 nitro groups are candidates of HEDMs. What is most interesting is that 2,4,6,8,10- has more dissociation energy than the PNHAAs with 3−4 nitro groups, which further confirms that it is the target compound of this series.

4. Conclusions

From the above calculations and analyses, the following conclusions can be drawn:

(1) The HOFs of PNHAAs can be obtained by designing reasonable isodesmic reactions at the B3LYP/6-31G* level, where the skeleton (HAA) has been kept. The results indicate that the HOFs increase with the increasing number of nitro groups (n) in PNHAAs, better reflecting the properties of group additivity. The HOF discrepancies among isomers are caused by the relative positions of nitro groups.

(2) All PNHAAs have quite large D and P. The calculated values of D and P for the isomers are close. D and P increase as n ranges from 1 to 6, and PNHAAs with 4−6 nitro groups satisfy the criteria as an HEDM. When n is over 6, D and P of PNHAAs decrease due to their larger positive oxygen balance values.

(3) The calculations on bond dissociation energies (E) suggest that the N−N bond is the trigger bond during the pyrolysis initiation process of PNHAAs. On the whole, although their relative stabilities decrease with increasing n, all the E_{N-N} values are more than 30 kcal/mol, ranging from 142.65 to 172.50 kJ·mol^{-1}. This further proves that PNHAAs with 4−6 nitro groups are the candidates of HEDMs. Taking detonation properties and relative stability into account, 2,4,6,8,10-pentanitrohexaazaadamantane was finally confirmed to be the best HEDM candidate for PNHAAs.

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