

Extensive theoretical studies of polynitrotriprismanes $C_6H_{6-n}(NO_2)_n$ ($n=1\sim 6$): stability, detonation properties, and pyrolysis mechanisms

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To further test whether polynitrotriprismanes can be capable of being potential high energy density materials (HEDMs), extensive theoretical calculations have been carried out to investigate on a series of polynitrotriprismanes (PNNPs): $C_6H_{6-n}(NO_2)_n$ ($n=1\sim 6$). Heats of formation (HOFs), strain energies (SE), and disproportionation energy (DE) are obtained using B3LYP/6-311+G (2df, 2p)//B3LYP /6-31G* method by designing different isodesmic reactions, respectively. Detonation properties of PNNPs are obtained by the well-known Kamlet-Jacobs equations, using the predicted densities (ρ) obtained by Monte Carlo method and HOFs. It is found that they increase as the number of nitro groups n varies from 1 to 6, and PNNPs with $n\geq 4$ have excellent detonation properties. The relative stability and the pyrolysis mechanism of PNNPs are evaluated by calculated bond dissociation energy (BDE). The comparison of BDE suggests that rupturing the C-C bond is the trigger for thermolysis of PNNPs. The computed BDE for cleavage of C-C bond ($21.08\text{kcal.mol}^{-1}$) further demonstrates that only the hexanitrotriprismane can be considered to be the target of HEDMs.

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1. Introduction

In recent years, there has been considerable interest for synthesis and characterization of highly strained molecules [1-4]. Especially for those compact organic cage compounds, they are usually investigated as promising candidates for high energy density materials (HEDMs) when attached to optimum numbers of nitro groups [3,5-8], due to their superior energetic performances over conventional energetic materials.

A few attempts [5,8] have been made to demonstrate that triprismane (C_6H_6) (see Fig. 1) can be regarded as a possible candidate for HEDMs when all the hydrogen atoms have been replaced by nitro groups, just from the calculated thermochemical properties of the polynitrotriprismanes (PNNPs) series $C_6H_{6-n}(NO_2)_n$ ($n=1\sim 6$). However, to be a candidate as HEDMs, not only should the detonation properties meet the criteria of HEDMs [9] (the density ($\rho\geq 1.9\text{ g.cm}^{-3}$), detonation velocities ($D\geq 9.0\text{ km.s}^{-1}$), and detonation pressure ($P\geq 40\text{ GPa}$)), but also the pyrolysis mechanism and thermal stability should be taken into account [7]. To the best of our knowledge, none of these studies have focused on the pyrolysis mechanism and explosive properties of the polynitrotriprismanes (PNNPs), except for the predicted density and strain energy of the hexa-nitrotriprismane from empirical group additivity method by Gilbert and his

co-workers [5].

The aim of this work is to further test whether hexanitrotriprismane can be capable of being potential HEDMs and which kind of other PNNPs has such properties, through systematical evaluating the heats of formation (HOFs), strain energies (SE), disproportionation Energies (DE), density (ρ), detonation performances and pyrolysis mechanism of PNNPs.

HOF is a key thermodynamic property in chemistry [3,7], especially important for investigation of explosive performances for energetic materials. Because it is impractical and dangerous for investigating the HOFs of energetic materials and unstable compounds, computational derived accurate value of HOFs is required. The density functional theory (DFT) B3LYP method using suitable basis sets, can not only produce reliable geometries and accurate energies, but also save much computer resources as those from high level theoretical methods. Therefore, the HOFs of all PNNPs have been calculated at B3LYP/6-311+G (2df, 2p)//B3LYP /6-31G* level of DFT theory by designing isodesmic reaction.

Strain energy (SE) is the difference between the observed heat of formation and that expected for a strain free molecule with the same number of atoms [10]. It has proven to be very valuable quantities with which to examine the balance of stabilization and destabilization effects that manifest themselves in the "measured" strain

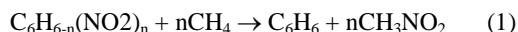
energy of cyclic molecules [11]. The SE of PNNPs is obtained using the reference of triprismane as a criterion by means of isodesmic reaction.

Repulsion interactions among nitro groups are predicted by calculated disproportionation energies (DE). In addition, D and P are obtained by using empirical Kamlet-Jacobs equation [12] with the density functional theory derived density (ρ) and HOFs, which are essential for evaluating the detonation properties of energetic compounds. Bond dissociation energies for C-C and C-N bond are calculated and compared to investigate the pyrolysis mechanism and thermal stability.

2. Computational methods

All calculations are carried out with the Gaussian 03 system of programs [13]. The full optimized geometries and zero-point energy corrections (ZPE) are calculated at Bech3-Lee-Yang-parr (B3LYP) hybrid density functional level of theory, with 6-31G* basis. Single-point energy calculations on the optimized geometries are performed by the use of the relative much higher level B3LYP/6-311+G (2df, 2p). The thermal corrected values and the zero-point energies (ZPE) are scaled by 0.98.

The isodesmic reaction approach [14], in which the HOFs can be estimated by simply calculating the reaction energy or reaction enthalpy with quantum chemical methods, has been employed very successfully to derive the HOFs [15]. The heats of formation (HOFs) of all PNNPs ΔH_{298} at 298K are evaluated by the following expresses:

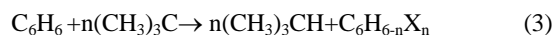


$$\begin{aligned} \Delta H_{298}^0 &= \sum \Delta H_{f,p} - \sum \Delta H_{f,R} = \Delta E_{298} + \Delta PV \\ &= \Delta E_0 + \Delta ZPE + \Delta H_T^0 + \Delta nRT \end{aligned} \quad (2)$$

Where $\sum \Delta H_{f,p}$ and $\sum \Delta H_{f,R}$ are the sums of the heats of formation of the products and the reactants, respectively. ΔH_{298}^0 is the enthalpy change of the reaction between the products and reactants at 298 K. ΔE_0 , ΔZPE , and ΔH_T^0 are the changes in the total energy, the zero-point energies, and thermal correction on going from 0 to 298 K between the products and reactants, respectively. It should be noted that ΔPV equals ΔnRT for the reaction in gas phase, and for the isodesmic reaction (1), $\Delta n = 0$, so $\Delta PV = 0$.

The SE can be regarded as the relative SE of PNNPs plus the known SE value of triprismane. Because of the lack of the experimental value, the SE of the reference compound for triprismane (606.9 kJ.mol⁻¹) is derived from the reference [16], which was calculated by G3/B3LYP method based on the isodesmic reaction. In addition, the relative SE of PNNPs are calculated via the

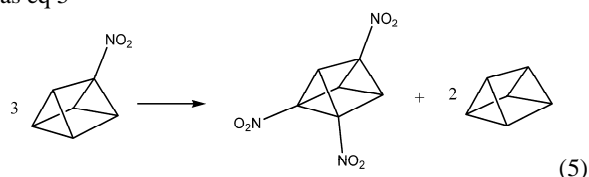
known SE values of triprismane as a criterion [16], i.e., the available SE of triprismane is taken as a reference compound, and the Ring strain energy is computed according to the total energies change of the following isodesmic reactions, with correction of zero-point vibrational energy (ZPE).



$$\Delta E_n = \sum E_{product} - \sum E_{reactant} \quad (4)$$

Where n is the number of nitro groups in PNNPs, from the isodesmic reaction (3), the relative SE of PNNPs can be calculated using the eq (4).

Isodesmic disproportionation reactions [17] are designed to quantitatively investigate on the strength of the interactions among the nitro groups. N-Molecules of mono-nitrotriprismane can be disproportionated to triprismane (NO₂)_n Plus (n-1) molecules of triprismane. For example, the 1,2,4-trinitrotriprismane can be obtained as eq 5



Eq. 5. Isodesmic disproportionation reactions 3-Molecules of mono-nitrotriprismane can be disproportionated to triprismane (NO₂)_n Plus 2 molecules of 1, 2, 4- trinitrotriprismane.

The disproportionation energy is defined as total energies changes in eq 6, corrected by zero-point energy between products and reactants.

$$\Delta E = \Delta E_0 + \Delta ZPE \quad (6)$$

Where ΔE_0 and ΔZPE are the changes in total energy and zero-point energy of the products and reactants at 0 K.

The empirical Kamlet-Jacobs equations are used to estimate the values of D and P for the explosive compounds containing C, H, O, and N as following:

$$P = 1.558\rho_0^2\phi, \quad \phi = NM^{1/2}Q^{1/2} \quad (7)$$

$$D = 1.01\phi^{1/2}(1+1.30\rho_0) \quad (8)$$

Where P, D, N, M, and ρ_0 denote detonation pressure [GPa], detonation velocity [km/s], moles of detonation gases per gram of explosive, average molecular weight of these gases, and density of explosive (g.cm⁻³), respectively. Q, chemical energy of detonation (kJ.mol⁻¹), is defined as the difference of the HOFs between the products and reactants, based on the most exothermic principle [12]; the

theoretical density of each PNNPs was obtained from the molecular weight divided by the average molecular volume (V). The average mole volume of each compound was obtained from the statistical mole volume of 100 molar volumes [18]. The mole volume of each molecule, defined as the volume inside a contour of 0.001e/Bohr³ density, was computed by Monte Carlo method in the Gaussian 03 program package. It has been demonstrated that the theoretically derived density is in good agreement with experimental density and describe the explosive phenomena well [7].

The hemolytic bond dissociation energy [19] at 0k can be obtained in terms of eq 9

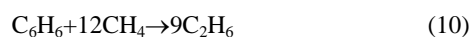
$$D_0(AB)=E_0(A)+E_0(B)-E_0(AB) \quad (9)$$

Where $E_0=E_{elec}+ZPE$ (E_{elec} and ZPE denote electronic energy and zero-point energy, respectively).

3. Results and discussion

3.1. Heats of Formation

To calculate HOFs for PNNPs, the HOF of a reference compound for parent triprismane C₆H₆ should be known in the isodesmic reaction (1). However, to the best of our knowledge, there is no available experimental HOF. In this work, the isodesmic reaction eq (10), in conjunction with the calculated enthalpy H_T values from the high-level ab initio G3 method for the reference compound (listed in the last column of Table 1), is designed to calculate its HOF.



The calculated HOF of parent triprismane, with a large value of 560.7 kJ.mol⁻¹, can be comparable to the previously reported results (559.8 kJ.mol⁻¹ [20] and 565.2 kJ.mol⁻¹[16]). This demonstrates the reliability of the method used for calculation of HOF by combination of the isodesmic reaction and G3 theory.

Table 1. theoretical Total Energies (E_0), Zero-point Energies (ZPE), and Thermal Corrections (H_T^0), experimental HOFs, and enthalpy values from G3 theory for the Reference Compounds^a

Compounds	E_0 (au)	ZPE (kJ.mol ⁻¹)	H_T^0 (kJ.mol ⁻¹)	HOF (kJ.mol ⁻¹)	H _T ^c (au)
C ₆ H ₆	-232.126493	251.67	13.07	560.7 ^b	-231.863814
CH ₄	-40.536842	116.41	10.02	-74.6	-40.453810
CH ₃ NO ₂	-245.106337	129.27	13.86	-81.1	
C ₂ H ₆				-84.04	-79.718915

^a E_0 are calculated at B3LYP/6-311+G (2df, 2p) level, and ZPE and H_T^0 are obtained at B3LYP/6-31G* level scaled with a factor of 0.98. ^bThe HOF of C₆H₆ is obtained by G3 theory for the isodesmic reaction (10) and other experimental HOFs of reference compounds are from reference [23]. ^cH_T are the enthalpy values at 298.15K and 1atm, which were used to calculate HOF of triprismane.

Table 1 lists the theoretical total energies (E_0), zero-point energies (ZPE), and thermal corrections (H_T^0), and experimental HOFs for the reference compounds. Based on the energy properties of the reference compounds given in Table 1, the HOFs of the PNNPs can be obtained by combination with of DFT method and isodesmic reaction, shown in Table 2. It is surprising from Table 2 that the calculated HOF of mono-nitrotriprismane (523.06 kJ.mol⁻¹) is in good agreement with the available theoretical value (523.8 kJ.mol⁻¹) derived from G3/B3LYP method [16]. This implies that the performance of the DFT theory with isodesmic reaction is as good as that computationally demanding G3 theory in the calculation of HOFs. For the first six PNNPs, the HOFs are smaller than that of

triprismane. This is mainly due to the strong electron-withdrawing effect of the nitro groups, which stabilizes the skeleton cage of triprismane; Whereas, from 1,2,3-tritrisprismane to hexanitrotriprismane, the HOFs increase dramatically with the number of nitro groups increasing, which is attributed to the strong interactions among more nitro groups over electron-withdrawing effect. The HOF of hexanitrotriprismane with 697.57kJ.mol⁻¹ is even as large as that of octanitrocubane (726.47 kJ.mol⁻¹) [3], implying that the introduction of nitro groups is the main energy origin of the PNNPs series and the PNNPs are capable of having better energy properties as more energetic compound of octanitrocubane, at least better than other energetic compounds such as TNT, and HMX.

Table 2. Total Energies (E_0), and Zero-point Energies (ZPE), Thermal Corrections (H_T^0), HOF, SE, and DE for the title Compounds^a.

Compounds	E_0 (au)	ZPE (kJ.mol ⁻¹)	H_T^0 (kJ.mol ⁻¹)	HOF (kJ.mol ⁻¹)	DE (kJ.mol ⁻¹)	SE (kJ.mol ⁻¹)
C ₆ H ₆				560.7		606.9 ^a
1	-436.706620	258.52	19.77	523.06 (523.8) ^b		604.26 (617.5) ^b
1,6-	-641.271236	264.59	26.89	525.73	39.91	635.01
1,2-	-641.269215	264.30	26.95	530.77	44.93	640.83
1,5-	-641.278624	264.81	26.84	506.46	20.73	619.74
1,2,5-	-845.829765	270.04	34.26	543.94	95.19	684.74
1,2,4-	-845.835712	270.01	34.30	528.43	79.54	670.54
1,2,3-	-845.821203	269.79	34.29	566.21	117.41	705.92
1,2,3,4,-	-1050.379411	275.08	41.90	585.36	172.87	755.85
1,2,5,6-	-1050.378094	275.03	41.80	588.53	176.77	758.25
1,2,4,5-	-1050.384375	274.92	41.88	572.15	160.17	742.98
1,2,3,4,5-	-1254.925893	279.76	49.54	635.21	259.47	833.56
1,2,3,4,5,6-	-1459.467233	284.39	57.13	697.57	359.04	925.05

^a E_0 are calculated at B3LYP/6-311+G (2df, 2p) level, and ZPE and H_T^0 are obtained at B3LYP/6-31G* level scaled with a factor of 0.98. ^bThe values in the parentheses are from reference 16.

The relative distance of nitro groups also has some effect on the HOFs of PNNPs, and thus influences the stability of the compounds, especially apparent for the isomers with the same number of substitutions. The shorter the distance between nitro groups a compound is, the stronger the repulsive energy (DE) is (see Table 2), the larger the corresponding HOF of the compound is, and the less stability the PNNPs will be. For example, as for the isomers with two nitro groups, the HOF of 1,2-dinitrotriprismane is larger than those of 2,0- and 1,5-, due to the relative shorter distance between nitro groups in 1,2- compared to those of other two isomers. Therefore, the relative HOFs order of PNNPs can be distinguished, based on the number and relative position of substitutions, which is very useful for estimating the relative thermal stability of PNNPs for isomers.

3.2. Strain energy

Actually, the strain energy is also a very important parameter for the choice of the HEDMs, due to the fact that it is directly related to the stability and energetic performance of title compound.

Table 2 also shows the SE of PNNPs predicted at B3LYP/6-311+G (2df, 2p)/B3LYP /6-31G* level by designing isodesmic reaction (3). The SE value of mono-substituted nitro compound (604.26 kJ.mol⁻¹) can be comparable to that derived from G3/B3LYP method (617.5 kJ.mol⁻¹) [16]. The difference between them is only about 13 kJ.mol⁻¹, which can be attributed to the more accuracy of the G3/B3LYP method compared to the DFT theory in

calculation of total energies. However, the G3/B3LYP calculations are computationally demanding for large systems when more nitro-substituents are attached to the triprismane. The SE increase very slightly at the beginning, but then increase rapidly as the number of the substituted groups increases. This further demonstrates that NO₂ groups are more electronegativity and withdraw electrons from C atom of triprismane, first reducing the repulsion between C-C bonds and resulting in the release of the strain of the skeleton, but then, with the more numbers of H atoms substituted by NO₂ groups, the repulsion interactions become predominant and repulsions energies increase sharply, leading to large strains of the skeleton. The SE of hexanitrotriprismane (SE=925.05kJ.mol⁻¹) can be comparable to that of octanitrocubane 1075.09 kJ.mol⁻¹ (SE=257.2 kcal.mol⁻¹) [21], which indicates that the hexanitrotriprismane is capable of being the candidates of HEDMs.

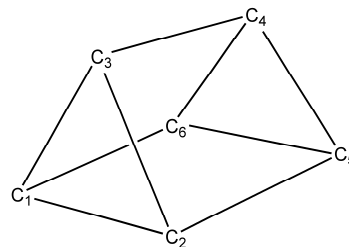


Fig. 1. Molecular structure and atomic numbering of triprismane (C₆H₆).

3.3. Detonation properties

Table 3 presents calculated average Molecular Volume (V), density (ρ), chemical energy of detonation (Q), detonation velocities (D), and detonation pressure (P) of the PNNPs. It has been demonstrated [7] that the derived density in the present study has been successful for evaluating theoretical densities for such molecular systems. Furthermore, the calculated density ($\rho=2.147 \text{ g.cm}^{-3}$) and detonation pressure ($P=52.9393 \text{ GPa}$) for hexanitrotriprismane in this work can be compared with the previously reported values [6] $\rho=2.138 \text{ g.cm}^{-3}$ and

$P=49.3 \text{ GPa}$, respectively, obtained by empirical group additivity method, in which the relative errors for calculated density is only 0.4%. This further confirms the applicability of the present method, which can be applied to evaluate explosive properties for these molecular systems. However, there may be some deviations from the experimental data, to some extent, but they are the most reliable theoretical method available currently for estimating the explosive properties, which are very important properties for characterization on energetic materials.

Table 3. Average Molecular Volume (V), Densities (ρ), Detonation Velocities (D), and Pressures (P) for polynitrotriprismanes.

compounds	V ($\text{cm}^3.\text{mol}^{-1}$)	ρ (g.cm^{-3})	Q (J.g^{-1})	D (km.s^{-1})	P (GPa)
C ₆ H ₆	62.130	1.2554			
1	91.912	1.3382	1956.20	5.8357	12.4096
1,6	98.766	1.7010	1995.84	7.6252	24.9156
1,2	102.040	1.6464	2003.01	7.4613	23.3836
1,5	103.470	1.6237	1968.43	7.3611	22.5461
1,2,5-	120.857	1.7624	2010.87	8.3117	30.2568
1,2,4-	112.564	1.8923	1993.47	8.7192	34.7301
1,2,3-	121.264	1.7565	2035.85	8.3182	30.2407
1,2,3,4-	132.959	1.9404	2042.16	9.2384	39.5548
1,2,5,6-	134.895	1.9126	2045.09	9.1469	38.4571
1,2,4,5-	132.013	1.9544	2029.92	9.2722	40.0071
1,2,3,4,5-	153.281	1.9768	2070.80	9.6041	49.1983
1,2,3,4,5,6-	162.076	2.1471(2.138) ^a	2100.63	10.3957	52.9393

^aThe values in the parentheses are from reference [5].

From Table 3, it can be seen that with the number of nitro groups increasing from n=1 to 6, V, ρ , Q, D, and P of all corresponding PNNPs increase. Moreover, V, ρ , Q, D, and P are in good linear relationship with the number of the nitro substitutions, respectively. Fig 2. (A-E) display the corresponding correlations with coefficients of 0.9968, 0.9815, 0.977, 0.9824 and 0.995, respectively. It is worth noting that, for the isomers with the same number of substituted groups, the most stable compound with the least detonation values were chosen as for analysis.

The density of all PNNPs (shown in Table 3) have larger values ($\rho=1.6237\sim 2.1471 \text{ g.cm}^{-3}$) compared to that of parent triprismane ($\rho=1.2554 \text{ g.cm}^{-3}$), except for the mono-substitution compound. Particularly, PNNPs with $n \geq 4$ have excellent detonation performances ($\rho \geq 1.9126 \text{ g.cm}^{-3}$, $Q \geq 2029.92 \text{ J.g}^{-1}$, $D \geq 9.1469 \text{ km.s}^{-1}$, $P \geq 38.4571 \text{ GPa}$), which meet the standard as HEDMs, and most likely become the candidates for HEDMs.

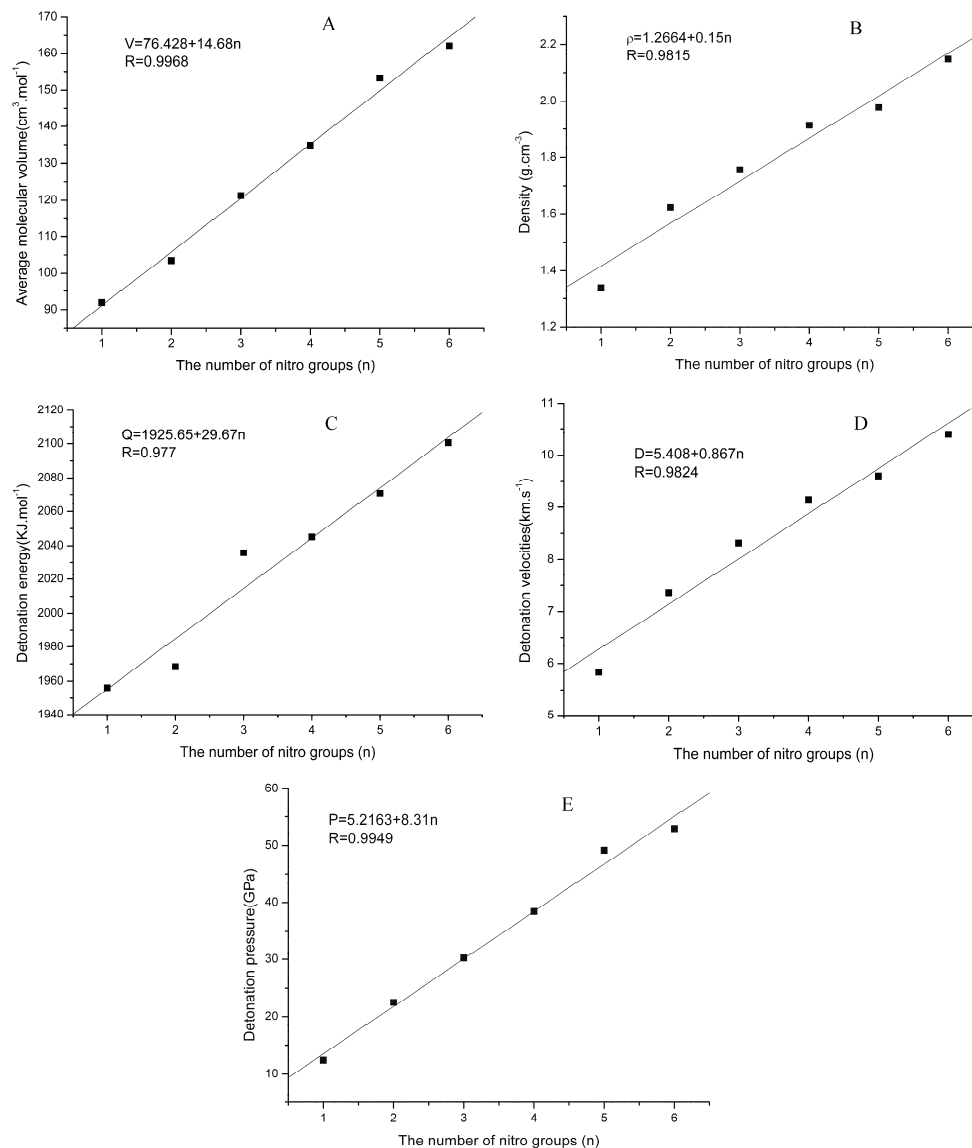


Fig. 2. The linear relationship between the number of nitro groups and (A), Average molecular volume, and (B), Densities, and (C), Detonation Energy, and (D), Detonation velocities, and (E), Detonation pressures, respectively, for PNNPs.

3.4. Pyrolysis mechanism and thermal stability

Besides the discussed above, the bond dissociation energies (BDE) for each possible trigger bond are used to investigate the pyrolysis mechanism and thermal stability for PNNPs. Generally speaking, the smaller the BDE for breaking a bond is, the more easily the bond is broken. In

this work, the BDE for two possible initial steps in the pyrolysis route are calculated (Table 4): (1) breaking a C-NO₂ bond and (2) breaking the C-C bond on the cage skeleton. It should be noted that the weakest C-C or C-NO₂ bonds based on the Mulliken population analyses are chosen as the initially breaking bond.

Table 4. The total energies and bond dissociation energies (BDE) for C-C (E_{C-C}) and C-N (E_{C-N}) bonds at 0 K^a

Compounds	E_R (a.u)	E_{MCC} (a.u)	E_{MCN} (a.u)	E_{C-C} (kJ.mol ⁻¹)	E_{C-N} (kJ.mol ⁻¹)
1	-436.608214	-436.572291	-436.507594	94.31	264.17
1,6-	-641.170507	-641.147767	-641.079115	59.70	239.95
1,2-	-641.168607	-641.14867	-641.081283	52.34	229.27
1,5-	-641.177829	-641.148073	-641.087188	78.12	237.97
1,2,5-	-845.726974	-845.699602	-845.641011	71.86	225.69
1,2,4-	-845.732933	-845.702074	-845.648518	81.02	221.63
1,2,3-	-845.718505	-845.697036	-845.637195	56.36	213.47
1,2,3,4,-	-1050.274703	-1050.24668	-1050.192742	73.57	215.18
1,2,5,6-	-1050.273403	-1050.25872	-1050.191305	38.55	215.54
1,2,4,5-	-1050.279725	-1049.87368	-1050.198357	37.69	213.63
1,2,3,4,5-	-1254.819405	-1254.78868	-1254.740148	80.66	208.08
1,2,3,4,5,6-	-1459.358979	-1459.32541	-1459.282465	88.13	200.88

^a E_R denotes the total energies corrected by zero-point energies for the ground state, and E_{MCC} and E_{MCN} (a.u) are the intermediates for initial C-C and C-N cleavage, respectively.

It is found, from Table 4, that BDE for dissociation of C-NO₂ bond for each PNNPs bonds are much larger than those for breaking C-C cage skeleton, indicating that the rupture of C-C bonds should be the trigger bond during the thermolysis initiation process. This is the same as the pyrolysis process of octanitrocubane, but it is different from those of other energetic compounds such as TNT, RDX, and HMX, in which initial dissociation reaction occurs between the ring and NO₂.

It has been recommended by Chung et al. [22] that, to be candidates for potential HEDMs, the energy barriers to decomposition and bimolecular destruction should be more than 20 kcal.mol⁻¹. It can be seen from Table 4 that the hexanitrotriprismane meets the needs, with the BDE of 21.08 kcal.mol⁻¹ (BDE=88.13 kJ.mol⁻¹). Therefore, from the mentioned above, only the hexanitrotriprismane of all PNNPs satisfied the standard as candidates for HEDMs, although other PNNPs with more than four nitro groups have better detonation properties.

4. Conclusion

From the calculated results above and analyses, the following conclusions can be drawn.

(1) The calculated HOFs, SE, and DE suggest that the introduction of NO₂ groups to the triprismane is indeed the source of the energy. They are correlated with each other, respectively, which reflect the relative stability of PNNPs, especially useful for identifying the isomers with same nitro groups.

(2) The detonation properties of PNNPs increase with the number of nitro groups increasing from $n=1$ to 6, and moreover, they are in good linear relationship with the number of the nitro substitutions, respectively. However, only when $n \geq 4$ can PNNPs can be regarded as energetic compounds.

(3) The comparison of BDE shows that homolysis of the C-C bond is predicted to be the trigger bond during thermolysis.

(4) The BDE obtained from B3LYP/6-311+G (2df, 2p)//B3LYP /6-31G* calculations, in conjunction with the detonation properties, further confirmed that only the

hexanitrotriprismane can be considered to be the target of HEDMs.

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