



Theoretical studies on polynitro-1,3-bishomopentaprismanes as potential high energy density compounds

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ABSTRACT

Based on the fully optimized molecular geometric structures at the DFT-B3LYP/6-31G* level, the densities (ρ), detonation velocities (D) and pressures (P) for a series of polynitro-1,3-bishomopentaprismanes (PNBPPs), as well as their thermal stabilities, were investigated to look for high energy density compounds (HEDCs). The studied PNBPPs have high values of heats of formation (HOFs) and the magnitude is correlative with the number (n) and the space distance of nitro groups. D and P for PNBPPs were estimated by using modified Kamlet–Jacobs equations based on the calculated HOFs and ρ . It is found that ρ , D and P all increase with n and satisfy the group additivity rule. The calculations on the bond dissociation energies of C–NO₂ and C–C bonds indicate that both bonds can be the trigger bond in the pyrolysis process, and this interesting phenomenon is related with the molecular structure, especially the strain energy of the skeleton. In conjunction with the energetic performances and thermal stabilities, PNBPPs with $n = 8–12$ are recommended as the preferred candidates of HEDCs. These results would provide basic information for the further studies of PNBPPs.

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1. Introduction

Nowadays, high energy density compounds (HEDCs) have been attracting considerable interests because of their superior explosive performances over the currently used materials [1–3]. Looking for HEDCs has become one of the most heated topics and seems to be never-ending to meet with the requirements of national defence and economy. Polynitro-substituted cage compounds are investigated as an important category of HEDCs due to their high strain energies, compact structures and self-contained oxidizability [4]. Typical examples are hexanitrohexaazaisowurtzitane (CL-20) and octanitrocubane (ONC). Recently, our group has carried out theoretical investigations on polynitro-substituted cubane [5], adamantane [6] and hexaazaadamantane [7], and some of them have been recommended as potential candidates of HEDCs. These investigations further indicate that cage skeleton is a good parent structure for HEDCs.

The birdcage hydrocarbon, 1,3-bishomopentaprismane (BPP, see Fig. 1 for the structure), is a typical cage compound with good symmetry (C_{2v}) and stability [8–10]. Ever since its first synthesis in 1960 [8], various kinds of its derivatives have been synthesized and investigated in the following decades [11–17]. Polynitro-1,3-bishomopentaprismanes (PNBPPs), which are formed when parts

of the H atoms in BPP are substituted by nitro groups, have received greater attention for their potentials as HEDCs [15–17]. Nevertheless, due to the difficulties and expenditure, hitherto only PNBPPs with up to four nitro groups have been successfully synthesized [15–17]. Therefore, theoretical predictions of their structures and explosive performances are of important significance in finding promising candidates for novel HEDCs. However, to the best of our knowledge, there are few theoretical studies focused on the performance of PNBPPs. In the present paper, the potentials for a series of PNBPPs as HEDCs are discussed by systematically predicting their densities, detonation properties and thermal stabilities using density functional theory (DFT). Since there are many isomers for PNBPPs with the same number of nitro groups, only certain kinds of PNBPPs reflecting typical relative position of nitro groups or those having experimental data are chosen as the target compounds.

In the past decade, our group has carried out a series of investigations on the “molecular design” of HEDC for many typical categories of energetic compounds [5–7,18–25]. Based on the results of these studies, a quantitative criteria considering both energy (including density ρ , detonation velocity D and detonation pressure P) and stability (bond dissociation energy BDE of the trigger bond) requirements was suggested to be used to predict the potential of a compound as HEDC, i.e., $\rho \approx 1.9 \text{ g cm}^{-3}$, $D \approx 9 \text{ km s}^{-1}$, $P \approx 40 \text{ GPa}$ and $\text{BDE} \approx 80–120 \text{ kJ mol}^{-1}$ [25]. Therefore, the main content of the present paper is to predict the densities, detonation properties and thermal stabilities of PNBPPs so as to search for new high-energy and insensitive explosives among PNBPPs.

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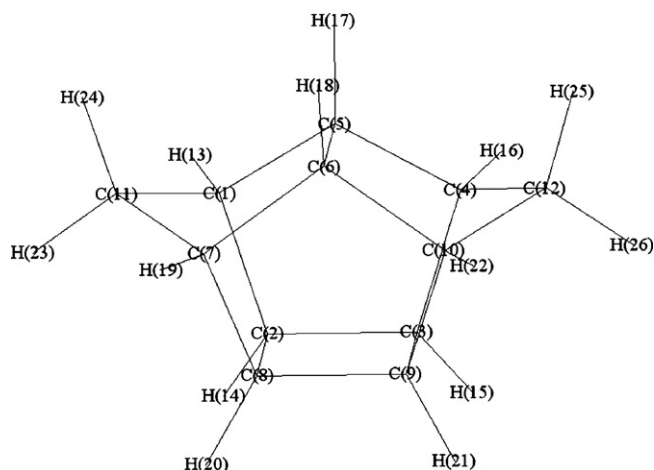
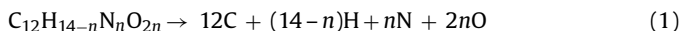


Fig. 1. The structure and atomic numbering for BPP.

2. Computational methods

A series of NPBBPs were studied using Gaussian 03 program [26]. All the molecules and the related radical species were fully optimized without any symmetry restrictions at the DFT-B3LYP level [27,28] with the 6-31G* basis set [29]. The default convergence cut-offs given in the program were used throughout the calculations. To characterize the nature of the stationary points and determine the zero-point vibrational energy corrections, harmonic vibrational analyses were performed subsequently. The computed harmonic vibrational frequencies were scaled uniformly by a factor of 0.96 to take into account the systematic overestimation of vibrational frequencies in the B3LYP/6-31G* calculation [30].

Based on the obtained total energy (E_0), zero-point energy (ZPE) and thermal correction from 0 to 298 K (ΔH_{298}°), atomization reaction (1) was applied to calculate the heat of formation (HOF) [31]:



$$\Delta H_{298}^\circ = 12\Delta_f H_{298,\text{C}}^\circ + (14-n)\Delta_f H_{298,\text{H}}^\circ + n\Delta_f H_{298,\text{N}}^\circ + 2n\Delta_f H_{298,\text{O}}^\circ - \Delta_f H_{298,\text{M}}^\circ \quad (2)$$

where M denotes the title compound $\text{C}_{12}\text{H}_{14-n}\text{N}_n\text{O}_{2n}$; ΔH_{298}° is the standard enthalpy change of reaction (1) at 298 K; the experimental standard HOFs ($\Delta_f H_{298}^\circ$) of C, H, N and O are known and listed in Table 1 [32]. On the other hand, the following relationship exists:

$$\Delta H_{298}^\circ = \Delta E_{298}^\circ + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_{\text{T}}^\circ + (\Delta N)RT \quad (3)$$

where ΔE_0 , ΔZPE , and $\Delta H_{\text{T}}^\circ$ are the change of total energy at 0 K, the change of ZPE and the change of thermal correction from 0 to 298 K between the products and the reactants, respectively. The $\Delta(PV)$ value is the PV work term, and it equals $(\Delta N)RT$ for the reactions of an ideal gas. For reaction (1), it equals $(25+2n)RT$. Besides, the values of ZPE and $\Delta H_{\text{T}}^\circ$ of atom are zero, thus Eq. (3) can be derived into Eq. (4):

$$\Delta H_{298}^\circ = 12E_{0,\text{C}} + (14-n)E_{0,\text{H}} + nE_{0,\text{N}} + 2nE_{0,\text{O}} - E_{0,\text{M}} - ZPE_{\text{M}} - \Delta H_{\text{T},\text{M}}^\circ + (25+2n)RT \quad (4)$$

Table 1

The experimental standard heats of formation ($\Delta_f H_{\text{atom}}^\circ$)³⁴ and calculated total energy (E_0) for C, H, N and O atoms at the B3LYP/6-31G* level.

$\Delta_f H_{\text{atom}}^\circ$ (kJ mol ⁻¹)					E_0 (a.u.)			
	C	H	N	O	C	H	N	O
716.7	218.0	472.7	249.2	-37.84628	-0.50027	-54.58449	-75.06062	

Therefore, based on the calculated results, the standard HOF of the compound M, $\Delta_f H_{298,\text{M}}^\circ$, can be obtained from Eqs. (2) and (4). To decrease the influence of the size and structure of the molecules on the results, the HOFs for 49 energetic compounds whose experimental HOFs are available were calculated at the same theoretical level [33]. By comparing the experimental and calculated results, correction equation was obtained with a good linear correlation coefficient ($R=0.990$):

$$\Delta_f H_{298,\text{M},\text{corrected}}^\circ = -75.79 + 0.98\Delta_f H_{298,\text{M}}^\circ \quad (5)$$

The empirical Kamlet–Jacobs (K–J) equations [34], which were raised by Kamlet and Jacobs in 1968, are widely used to estimate the detonation properties (D and P) of CHNO explosive due to the facility and reliability of the method. The expressions are as follows:

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

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

In the above equations, N is the moles of gaseous detonation products per gram of explosive, \bar{M} is the average molecular weight of gaseous products, Q refers to the detected chemical energy of the detonation reaction, and ρ denotes the experimental loading density of explosive. Obviously, the experimental values of Q and ρ cannot be obtained for energetic compounds that have not been synthesized. In order to predict the detonation properties of potential HEDCs, we recommend that modified K–J equations based on the calculation results of quantum chemistry be used [25]. In detail, ρ can be replaced by the theoretical density of a compound crystal (ρ_{cal}), while Q can be calculated as the difference between the HOFs of products and reactants of the detonation reaction (Q_{cal}). The expressions of the modified K–J equations are as follows:

$$D = 1.01(N\bar{M}^{1/2}Q_{\text{cal}}^{1/2})^{1/2}(1 + 1.30\rho_{\text{cal}}) \quad (8)$$

$$P = 1.558\rho_{\text{cal}}^2 N\bar{M}^{1/2}Q_{\text{cal}}^{1/2} \quad (9)$$

Here, the products for the explosive reaction are N_2 , H_2O , CO_2 and O_2 in turn if the content of oxygen is enough; otherwise, those H atoms that cannot produce H_2O due to the lack of oxygen will turn into H_2 gas, while those C atoms unable to produce CO_2 will exist in the form of solid C. The detailed calculation methods for parameters N , \bar{M} and Q_{cal} for the compounds with different compositions are listed in Table 2 [35].

Considering that crystal is not easy to be compressed and there are vacancies in the loading attachment of actual explosive, ρ_{cal} is always larger than ρ [25]. Besides, since the explosive reaction is designed according to the maximal exothermic principle, Q_{cal} is larger than Q [25]. Therefore, it is comprehensible that the obtained D and P are theoretically the largest values for the title compounds. Previous studies [5–7,18–25] reveal that the modified K–J equations are reliable if the value of ρ_{cal} is close to the experimental one. Therefore, it is noticeable that the reliability of ρ_{cal} is the key factor in the prediction of detonation properties.

As well known, accurate prediction of crystal density is of much difficulty. “Group or volume additivity” method [36,37], although simple and rapid, cannot give reliable results owing to its inherent drawbacks; while the “crystal packing” method [38,39], which is more reliable, has its limitation in routine calculation due to its extensive requirement in computational resources. Recently, an

Table 2
Methods for calculating the N , \bar{M} and Q_{cal} parameters for $C_aH_bO_cN_d$ explosive.^a

Parameter	Stoichiometric ratio		
	$c \geq 2a + b/2$	$2a + b/2 > c > b/2$	$c \leq b/2$
N (mol g ⁻¹)	$(b + 2c + 2d)/4M$	$(b + 2c + 2d)/4M$	$(b + d)/2M$
\bar{M} (g mol ⁻¹)	$4M/(b + 2c + 2d)$	$(55d + 88c - 8b)/(b + 2c + 2d)$	$(2b + 28d + 32c)/(b + d)$
Q_{cal} (kJ g ⁻¹)	$(28.9b + 94.05a + 0.239\Delta_f H_M^\circ)/M$	$[28.9b + 94.05(c/2 - b/4) + 0.239\Delta_f H_M^\circ]/M$	$(57.8c + 0.239\Delta_f H_M^\circ)/M$

^a M in the formula refers to the molecular weight of the title compound (g mol⁻¹); $\Delta_f H_M^\circ$ is the standard heat of formation of the title compound (kJ mol⁻¹).

efficient and convenient way has been worked out to predict the crystalline densities of energetic materials containing C, H, N and O elements [25,40]. The results reveal that the densities of energetic compounds obtained using Monte Carlo method based on the geometrical conformation at the B3LYP/6-31G** (or 6-31G*) level are close to the experimental crystalline densities. Thus, in the present paper, ρ_{cal} of each compound is computed from the average molecular volume divided by the molecular weight, and the average volume is obtained from the statistical average value of 100 single-point molar volume. The molecular volume is defined as the volume inside a contour of electron density of 0.001e Bohr⁻³ and is evaluated by using Monte Carlo method integration as implemented in the Gaussian 03 program based on the geometrical structure at the B3LYP/6-31G* level. It is worth noting that the average volume used here should be the statistical average of at least 100 volume calculations. Previous studies on CHNO energetic compounds have proved that the density obtained using this method is close to the experimental solid-state density and this method is an efficient and convenient way to predict density of CHNO explosive [6,25,40]. Based on the reliable ρ_{cal} , the modified K–J equations have been verified to be suitable for the prediction of the detonation properties for CHNO explosives [6–7,18,25].

Generally speaking, higher energy a compound has, less stable it is. However, the thermal stability of energetic material determines its applicability. Therefore, stability requirement must be considered in the “molecular design” of HEDC besides energy properties. Previous studies [32,41–43] have shown that the value of BDE can be used to evaluate the sensitivity and stability of energetic materials. Thus, we deduce the pyrolysis mechanism and evaluate the thermal stability of PNBPPs according to the BDE value.

BDE is originally defined as the enthalpy change at 298 K and 1 atm for the chemical bond dissociation in a molecule as follows:



where $A-B$ stands for the neutral molecules, A^\bullet and B^\bullet refer to the corresponding product radicals after the bond dissociation. In the present paper, the BDE is calculated as the difference between the ZPE corrected total energies at 0 K according to reaction (10):

$$\text{BDE} = [E(A^\bullet) + E(B^\bullet)] - E(A-B) \quad (11)$$

Eq. (11) has been successfully and frequently used to determine the bond strength and relative stability of the compounds and corresponding radicals [25,44–47]. Therefore, we use BDE calculated from Eq. (11) based on (U)B3LYP/6-31G* results to determine the thermal decomposition mechanism of the title compound.

3. Results and discussion

3.1. Heats of formation

Table 1 lists the experimental HOFs for C, H, N and O atoms [32] and their E_0 calculated at the B3LYP/6-31G* level. By using reaction (1) and formulae (2)–(4), in combination with the calculated E_0 , ZPE and $\Delta_f H_T^\circ$ of PNBPPs at the B3LYP/6-31G* level, $\Delta_f H_{298,M}^\circ$ for the title PNBPPs were obtained and listed in Table 3. Furthermore,

a more reliable HOF, $\Delta_f H_{298,M,\text{corrected}}^\circ$, was computed by using correction Eq. (5). Although we cannot make any comparison due to the absence of the corresponding experimental HOFs of PNBPPs, the reliability of the method can be confirmed by the good correlation coefficient. Therefore, $\Delta_f H_{298,M,\text{corrected}}^\circ$ was used to predict the detonation energy Q_{cal} for each compound. As for PNBPPs with the number of nitro groups (n) ≥ 10 , the vibrational analyses are difficult to fulfill due to their structural complexity. Careful analyses show that the following relationships exist for PNBPPs with n ranging from 0 to 8: $\text{ZPE} = 590.22 + 5.10n$ ($R = 0.997$, $n = 0-8$); $\Delta_f H_T^\circ = 19.97 + 7.26n$ ($R = 1.000$, $n = 0-8$). It should be pointed out that the average values of ZPE and $\Delta_f H_T^\circ$ were used for the isomers. Considering the excellent linear correlation coefficients ($R \geq 0.997$), we believe that there exist good linear relationships for both ZPE and $\Delta_f H_T^\circ$ with n in the present system. Therefore, the values of ZPE and $\Delta_f H_T^\circ$ for PNBPPs with $n \geq 10$ were computed using the above equations.

As can be seen from the values of $\Delta_f H_{298,M,\text{corrected}}^\circ$ in Table 3, all the investigated compounds have quite large positive HOFs, indicating that the PNBPPs have good energy properties to be energetic materials.

Fig. 2 describes the relationship between the calculated HOFs for PNBPPs and n . For the isomers with the same n , the most stable compound with the lowest HOF was chosen for analysis. It can be seen that they have a binomial relationship ($\text{HOF} = 253.55 - 29.67n + 6.00n^2$) with a good R^2 of 0.999 and SD of 7.08, i.e., HOFs decrease with n if $n = 0-3$ and increase with n if $n = 3-12$. Actually, similar phenomena were found in polynitrocubanes [48]. For 1,2,3,4,5,6,7,8,9,10,11,11,12,12-PNBPP, in which all the H atoms are replaced by nitro groups and geminal nitro groups exist, the HOF increases quickly and deviates from the equation. The effect of nitro groups on the HOF of PNBPP is the results of both repulsion and superconjugate energies from nitro groups. When n is not too large, the superconjugate effect of nitro groups can stabilize the BPP skeleton. Therefore, the HOF decreases

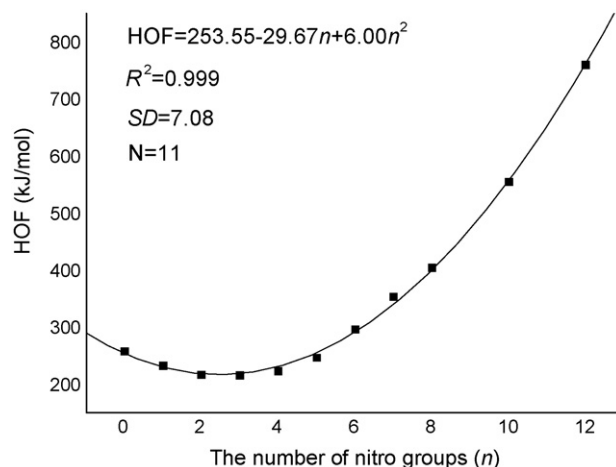


Fig. 2. The relationship between $\Delta_f H_{298,\text{corrected}}^\circ$ (the lowest one for isomers) and the number of nitro groups ($n = 0-12$).

Table 3
Total Energy (E_0), zero-point energy (ZPE) and thermal correction (ΔH_T°) obtained at the B3LYP/6-31G* level, ΔnRT for atomization reaction (1), $\Delta_f H_{298}^\circ$ calculated from reaction (1) and formulae (2)–(4), $\Delta_f H_{298, \text{corrected}}^\circ$ obtained from the correction Eq. (5).

Compound ^a	E_0 (a.u.)	(kJ mol ⁻¹)				
		ZPE ^b	$\Delta H_T^{\circ*}$	ΔnRT	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298, \text{corrected}}^\circ$
BPP	-465.67602	588.66	20.05	61.96	340.16	257.56
1-	-670.17955	594.75	27.50	66.92	319.27	237.09
2-	-670.18141	594.84	27.44	66.92	314.41	232.34
5-	-670.18052	594.77	27.34	66.92	316.59	234.47
11 ²³ -	-670.17653	595.31	25.00	66.92	325.27	242.98
1,2-	-874.67738	600.54	34.75	71.88	312.86	230.82
1,3-	-874.68116	600.56	34.96	71.88	303.27	221.42
1,9-	-874.68159	600.47	35.07	71.88	302.04	220.21
1,10-	-874.68048	600.61	35.10	71.88	215.63	223.23
1,12 ²⁶ -	-874.67762	601.76	34.76	71.88	313.46	231.40
2,6-	-874.68294	600.28	35.00	71.88	298.25	216.50
5,6-	-874.67325	600.42	34.36	71.88	323.19	240.94
11,11-	-874.66186	599.85	34.72	71.88	352.87	270.03
11 ²³ ,12 ²⁵ -	-874.67510	602.96	33.39	71.88	319.90	237.71
11 ²⁴ ,12 ²⁵ -	-874.67398	603.04	33.41	71.88	322.94	240.69
11 ²³ ,12 ²⁶ -	-874.67496	602.64	33.36	71.88	319.92	237.74
1,3,6-	-1079.17874	605.59	42.57	76.83	297.00	215.27
1,4,8-	-1079.17602	605.92	42.52	76.83	304.42	222.54
1,3,12 ²⁵ -	-1079.17628	606.99	42.39	76.83	304.68	222.80
1,4,5-	-1079.16470	606.20	40.25	76.83	332.14	249.70
3,11 ²³ ,12 ²⁶ -	-1079.17219	608.17	40.88	76.83	315.07	232.97
5,6,9-	-1079.17230	605.68	40.75	76.83	312.18	230.14
5,11 ²³ ,12 ²⁶ -	-1079.17388	607.77	40.95	76.83	310.32	228.33
11 ²⁴ ,12,12-	-1079.15815	606.83	40.80	76.83	350.53	267.73
11 ²³ ,12,12-	-1079.15871	606.62	40.86	76.83	348.89	266.13
1,3,8,10-	-1283.67117	610.80	50.32	81.79	304.67	222.79
1,4,7,9-	-1283.66934	610.82	50.33	81.79	309.50	227.52
1,4,7,10-	-1283.66663	610.95	50.04	81.79	316.45	234.33
5,6,11 ²³ ,12 ²⁶ -	-1283.66136	612.44	49.35	81.79	331.09	248.68
7,8,9,10-	-1283.65130	610.90	49.10	81.79	355.72	272.81
11,11,12,12-	-1283.64083	610.60	49.48	81.79	383.27	299.81
3,6,8,11 ²⁴ ,12 ²⁶ -	-1488.15760	617.31	57.27	86.75	328.59	246.22
1,6,7,9,12 ²⁶ -	-1488.15652	616.61	57.34	86.75	330.80	248.39
1,2,3,4,5-	-1488.13135	615.47	55.99	86.75	394.38	310.70
2,5,6,9,11 ²³ ,12 ²⁵ -	-1692.63238	621.54	63.03	91.70	379.63	296.25
1,4,7,10,11 ²³ ,12 ²⁵ -	-1692.63339	621.86	64.75	91.70	379.01	295.64
2,3,8,9,11 ²³ ,12 ²⁵ -	-1692.61798	621.67	63.96	91.70	418.51	334.34
5,6,11,11,12,12-	-1692.60036	619.86	61.73	91.70	460.71	375.70
2,3,5,8,9,11 ²³ ,12 ²⁵ -	-1897.10543	626.46	70.65	96.66	437.77	353.23
1,2,3,4,7,8,9,10-	-2101.56855	628.09	77.16	101.62	517.57	431.43
2,3,5,6,8,9,11 ²³ ,12 ²⁶ -	-2101.58043	630.06	78.26	101.62	489.45	403.87
1,2,3,4,7,8,9,10,11 ²³ ,12 ²⁶ -	-2510.50151	641.26	92.55	111.53	671.83	582.60
1,2,3,5,6,8,9,10,11 ²³ ,12 ²⁶ -	-2510.51242	641.26	92.55	111.53	643.18	554.52
2,3,5,6,8,9,11,11,12,12-	-2510.49561	641.26	92.55	111.53	687.30	597.77
1,2,3,4,5,6,7,8,9,10,11 ²³ ,12 ²⁵ -	-2919.42309	651.46	107.07	121.45	852.10	759.26
1,2,3,4,5,6,7,8,9,10,11,11,12,12-	-3328.05889	661.67	121.59	131.36	1782.72	1671.28

^a 1- denotes 1-nitrobishomopentaprismane; 1,2- denotes 1,2-dinitrobishomopentaprismane; 11²³- denotes the H23 atom bonded to C11 is replaced by nitro group; 11²³,12²⁶- denotes the H23 atom bonded to C11 and H26 atom bonded to C12 are replaced by nitro groups; the others are similar.

^b ZPE and ΔH_T° for PNBPPs of $n \geq 10$ were derived from equations $ZPE = 590.22 + 5.10n$ and $\Delta H_T^\circ = 19.97 + 7.26n$, respectively.

when n increases from zero to three. However, when there are more than four nitro groups on the skeleton, strong repulsion energy is caused and leads to the increase in the total energy and HOF. Further analyses show that HOFs increase quickly with n when $n \geq 4$, indicating that PNBPPs with more nitro groups may be more powerful explosives.

As for the isomers, there exists definite difference between their HOFs, revealing that the HOFs of PNBPPs are also affected by the relative position of the nitro groups. Generally speaking, the closer the nitro groups are, the higher the HOF of the PNBPP is. Taking the isomers with four nitro groups as an example, 1,3,8,10-PNBPP, whose nitro groups are not bonded to the same ring and the farthest separated, has the least HOF (222.79 kJ mol⁻¹); and 1,4,7,9- and 1,4,7,10-PNBPPs, whose nitro groups are not bonded to adjacent C atoms, also have relatively small HOFs (227.52 and 234.33 kJ mol⁻¹, respectively); for 5,6,11²³,12²⁶- and 7,8,9,10-PNBPPs, the HOF keeps increasing with the decrease of distances between the bonded C atoms (248.68 and 272.81 kJ mol⁻¹, respec-

tively); while for 11,11,12,12-PNBPP, where two nitro groups are bonded to the same C atom, its HOF is the highest among the isomers (299.81 kJ mol⁻¹). Similar phenomena were also observed for other isomers. We contribute this to the repulsion energy, which increases with the decreasing distance between nitro groups. 11,11-, 11²⁴,12,12-, 11²³,12,12-, 2,3,5,6,8,9,11,11,12,12- and 1,2,3,4,5,6,7,8,9,10,11,11,12,12-PNBPPs with geminal nitro groups all have extremely higher HOFs than their corresponding isomers. This phenomenon is also originated from the repulsion energy between geminal nitro groups. Therefore, if the relative position of the nitro groups in the isomeric molecule is known, the relative order of the HOF values can be estimated and used to identify the relative stabilities of the isomers for PNBPPs.

3.2. Detonation properties

As is pointed out in the first section, ρ , D and P are the most important parameters in evaluating the explosive performances

Table 4
Predicted detonation properties of PNBPPs.^a

Compounds ^b	ρ (g cm ⁻³)	D (km s ⁻¹)	P (GPa)
BPP	1.30	3.02	3.25
1-	1.46	5.00	9.69
2-	1.48	5.02	9.85
5-	1.46	4.99	9.66
11 ²³ -	1.50	5.08	10.18
1,2-	1.59	5.95	14.56
1,3-	1.58	5.90	14.21
1,9-	1.59	5.95	14.53
1,10-	1.60	5.97	14.70
1,12 ²⁶ -	1.62	6.02	15.02
2,6-	1.57	5.89	14.12
5,6-	1.65 (1.63)	6.11	15.65
11,11-	1.58	5.98	14.64
11 ²³ ,12 ²⁵ -	1.58 (1.58)	5.94	14.43
11 ²⁴ ,12 ²⁵ -	1.59 (1.62)	5.97	14.62
11 ²³ ,12 ²⁶ -	1.58 (1.75)	5.94	14.47
1,3,6-	1.68	6.55	18.28
1,4,8-	1.70	6.61	18.70
1,3,12 ²⁵ -	1.68	6.54	18.18
1,4,5-	1.72	6.67	19.20
3,11 ²³ ,12 ²⁶ -	1.72	6.68	19.29
5,6,9-	1.73 (1.62)	6.70	19.42
5,11 ²³ ,12 ²⁶ -	1.70	6.60	18.66
11 ²⁴ ,12,12-	1.70 (1.69)	6.64	18.88
11 ²³ ,12,12-	1.73 (1.75)	6.73	19.58
1,3,8,10-	1.77	7.25	23.10
1,4,7,9-	1.81	7.37	24.18
1,4,7,10-	1.77	7.27	23.21
5,6,11 ²³ ,12 ²⁶ -	1.80	7.37	24.07
7,8,9,10-	1.78	7.35	23.82
11,11,12,12-	1.77 (1.76)	7.34	23.66
3,6,8,11 ²⁴ ,12 ²⁶ -	1.86	7.89	28.15
1,6,7,9,12 ²⁶ -	1.84	7.82	27.45
1,2,3,4,5-	1.87	7.98	28.92
2,5,6,9,11 ²³ ,12 ²⁵ -	1.92	8.35	32.13
1,4,7,10,11 ²³ ,12 ²⁵ -	1.91	8.35	32.06
2,3,8,9,11 ²³ ,12 ²⁵ -	1.94	8.45	33.05
5,6,11,11,12,12-	1.94	8.48	33.33
2,3,5,8,9,11 ²³ ,12 ²⁵ -	1.97	8.77	35.95
1,2,3,4,7,8,9,10-	2.05	9.24	40.76
2,3,5,6,8,9,11 ²³ ,12 ²⁶ -	2.03	9.17	39.97
1,2,3,4,7,8,9,10,11 ²³ ,12 ²⁶ -	2.11	9.77	46.37
1,2,3,5,6,8,9,10,11 ²³ ,12 ²⁶ -	2.15	9.90	48.06
2,3,5,6,8,9,11,11,12,12-	2.14	9.87	47.64
1,2,3,4,5,6,7,8,9,10,11 ²³ ,12 ²⁵ -	2.23	10.44	54.41
1,2,3,4,5,6,7,8,9,10,11,11,12,12-	2.32	11.03	62.09

^a Data in the parentheses are the experimental values taken from Refs [15–17].^b See the footnote of Table 3 for the meaning of compound name.

of energetic materials. Based on the obtained ρ and HOFs at the B3LYP/6-31G* level, the detonation properties, including D and P , were estimated using the modified K–J equations. Table 4 presents the predicted ρ , D and P for the studied PNBPPs. For eight PNBPPs whose experimental densities are available [15–17], the relative errors of ρ are 1.23%, 0%, –1.85%, –9.71%, 6.79%, 0.59%, –1.14% and 0.57% for 5,6-, 11²³,12²⁵-, 11²⁴,12²⁵-, 11²³,12²⁶-, 5,6,9-, 11²⁴,12,12-, 11²³,12,12- and 11,11,12,12-PNBPPs, respectively. It can be seen that the calculated ρ agree well with the experimental values except that of 11²³,12²⁶- and 5,6,9-PNBPPs. Generally speaking, the discrepancies of the predicted and observed densities may be due to both theoretical and experimental factors. Although the most contribution to the crystal volume comes from the molecular structure, the molecular packing efficiency and intermolecular interactions, which are not considered in the calculations applied here, also affect the crystal density in a certain scale. Besides, the uncertainty of the experimental results is also responsible for the relatively large errors of ρ for 11²³,12²⁶- and 5,6,9-PNBPPs. Although the close-packed structures contribute to the crystal density, we are still amazed of the extremely high density (1.75 g cm⁻³) of 11²³,12²⁶-PNBPP [16], which is even larger than that of PNBPPs with three

Table 5The average values of ρ , D and P and their maximum deviations for PNBPP isomers with the same n .

n	$\bar{\rho}$ ($\pm\%$)	\bar{D} ($\pm\%$)	\bar{P} ($\pm\%$)
1	1.48 ($\pm 1.69\%$)	5.02 ($\pm 1.20\%$)	9.85 ($\pm 3.40\%$)
2	1.59 ($\pm 3.51\%$)	5.97 ($\pm 2.42\%$)	14.63 ($\pm 6.96\%$)
3	1.71 ($\pm 1.54\%$)	6.64 ($\pm 1.44\%$)	18.91 ($\pm 3.54\%$)
4	1.78 ($\pm 4.32\%$)	7.33 ($\pm 1.02\%$)	23.67 ($\pm 2.42\%$)
5	1.86 ($\pm 0.92\%$)	7.90 ($\pm 1.01\%$)	28.17 ($\pm 2.65\%$)
6	1.93 ($\pm 0.91\%$)	8.41 ($\pm 0.86\%$)	32.64 ($\pm 2.11\%$)
7	1.97	8.77	35.95
8	2.04 ($\pm 0.49\%$)	9.21 ($\pm 0.38\%$)	40.37 ($\pm 0.98\%$)
10	2.13 ($\pm 0.78\%$)	9.85 ($\pm 0.78\%$)	47.36 ($\pm 2.08\%$)
12	2.23	10.44	54.41
14	2.32	11.03	62.09

nitro groups. At the same time, the low experimental density of 5,6,9-PNBPP (1.62 g cm⁻³) [17] that is essentially equal to that of 5,6-PNBPP is also susceptible. Anyhow, the reasonable consistency of the predicted densities with the available experimental results reflects the reliability of our calculations.

Table 5 presents the average values of ρ , D and P for PNBPP isomers and also their maximum deviations. It can be found that the maximum deviations of ρ , D and P from their average values are small, indicating that the space orientations of nitro groups have little influence on the values of ρ , D and P . On the other hand, $\bar{\rho}$, \bar{D} and \bar{P} all increase with n , and the linear correlations are $\bar{\rho} = 1.47 + 0.07n$ ($R = 0.977$, $SD = 0.06$, $N = 11$), $\bar{D} = 5.33 + 0.44n$ ($R = 0.978$, $SD = 0.41$, $N = 11$) and $\bar{P} = 7.37 + 3.99n$ ($R = 0.998$, $SD = 1.01$, $N = 11$). The correlation coefficients are 0.977, 0.978 and 0.998 for $\bar{\rho}$, \bar{D} and \bar{P} , respectively. It indicates that they have the property of group additivity. On average, if one more nitro group is attached, $\bar{\rho}$, \bar{D} and \bar{P} increase by 0.07 g cm⁻³, 0.44 km s⁻¹ and 3.99 GPa, respectively. This indicates that introducing more nitro substituents into the BPP molecule will benefit its energetic performances.

From Table 4, it can be concluded that PNBPPs with $n \geq 8$ meet the energy demand of HEDC and can be regarded as potential candidates of HEDC. In addition, in comparison with the famous nitroaromatic explosive trinitrotoluene (TNT) ($\rho = 1.64$ g cm⁻³, $D = 6.95$ km s⁻¹, $P = 19.0$ GPa), PNBPPs with $n \geq 4$ all have better energetic performances than it. Therefore, if PNBPPs can be synthesized successfully, they will have high exploitable values and be worth investigating further.

3.3. Thermal stability and pyrolysis mechanism

Another essential concern for energetic material is its thermal stability and pyrolysis mechanism. BDE is often a key factor in investigating the pyrolysis mechanism. Generally, the smaller the BDE for breaking a bond is, the more easily the bond is broken. Thus, the rupture of the bond with the smallest BDE will be the initial step during thermolysis process, and the magnitude of the smallest BDE is directly relevant to the sensitivity and stability of energetic compounds. Therefore, the smallest BDE is often used to evaluate the thermal stability of a compound.

Previous studies have demonstrated that, in caged nitro compounds such as ONC and polynitroadamantanes [5–6], C–NO₂ or C–C bond is the possible trigger bond of pyrolysis initiation reaction. Similarly, for PNBPPs, the breaking of C–NO₂ bond or C–C bond in the skeleton was considered to be the initial step for pyrolysis. In order to simplify the calculation, the C–NO₂ or C–C bond with the least Mulliken population at the B3LYP/6-31G* level was studied. Table 6 lists the bond dissociation energy without (BDE⁰) and with (BDE) ZPE correction for C–NO₂ and C–C bonds. It should be pointed out the computation for the radical products was carried out at the UB3LYP/6-31G* level. It can be found that the BDE value shifts to

Table 6
Bond dissociation energies (BDE, kJ mol^{-1}) for C–NO₂ and C–C bonds, net charges on nitro groups ($Q_{-\text{NO}_2}$) for the title compounds computed at the (U)B3LYP/6-31G* level.^a

Compound ^b	BDE _{C–NO₂} ⁰	BDE _{C–NO₂}	$Q_{-\text{NO}_2}$	BDE _{C–C} ⁰	BDE _{C–C}
BPP				286.78	270.34
1-	286.71	269.72	−0.370	285.45	268.86
2-	284.41	268.73	−0.383	287.65	270.77
5-	277.34	260.01	−0.354	249.65	236.82
11 ²³ -	268.86	246.07	−0.314	277.91	261.93
1,2-	268.03	251.47	−0.346	293.40	276.62
1,3-	278.26	261.41	−0.349	285.91	269.51
1,9-	277.84	261.27	−0.369	286.13	269.47
1,10-	281.10	264.42	−0.357	283.77	267.74
1,12 ²⁶ -	281.08	264.08	−0.357	278.16	261.44
2,6-	279.9	263.57	−0.372	251.23	238.27
5,6-	252.57	235.87	−0.318	197.03	187.34
11,11-	191.43	174.05	−0.260	195.92	188.16
11 ²³ ,12 ²⁵ -	263.57	243.19	−0.313	277.13	261.80
11 ²⁴ ,12 ²⁵ -	260.56	239.71	−0.308	289.22	274.36
11 ²³ ,12 ²⁶ -	262.19	241.22	−0.310	271.35	255.25
1,3,6-	271.38	255.01	−0.351	248.58	235.68
1,4,8-	270.42	253.97	−0.351	282.50	265.67
1,3,12 ²⁵ -	272.08	255.86	−0.344	287.29	271.17
1,4,5-	254.56	237.76	−0.304	254.45	239.96
3,11 ²³ ,12 ²⁶ -	261.36	243.96	−0.339	268.43	252.16
5,6,9-	271.09	254.82	−0.358	202.58	192.27
5,11 ²³ ,12 ²⁶ -	264.94	248.37	−0.322	241.48	228.68
11 ²⁴ ,12,12-	190.38	173.88	−0.253	282.28	267.48
11 ²³ ,12,12-	190.69	174.20	−0.253	274.20	258.93
1,3,8,10-	261.01	244.75	−0.323	285.67	278.99
1,4,7,9-	263.23	247.00	−0.331	282.17	265.00
1,4,7,10-	261.39	245.28	−0.311	278.99	262.10
5,6,11 ²³ ,12 ²⁶ -	239.76	223.70	−0.286	201.84	191.33
7,8,9,10-	246.21	230.15	−0.290	294.65	277.36
11,11,12,12-	189.87	173.31	−0.244	277.77	262.16
3,6,8,11 ²⁴ ,12 ²⁶ -	255.97	240.28	−0.316	244.11	232.50
1,6,7,9,12 ²⁶ -	252.45	236.84	−0.306	249.50	235.88
1,2,3,4,5-	225.86	209.69	−0.264	261.39	249.25
2,5,6,9,11 ²³ ,12 ²⁵ -	253.13	237.56	−0.306	181.27	169.29
1,4,7,10,11 ²³ ,12 ²⁵ -	246.45	231.10	−0.294	282.57	270.27
2,3,8,9,11 ²³ ,12 ²⁵ -	225.48	209.87	−0.270	275.83	263.73
5,6,11,11,12,12-	212.11	194.58	−0.232	190.91	180.61
2,3,5,8,9,11 ²³ ,12 ²⁵ -	215.38	199.99	−0.253	247.03	236.22
1,2,3,4,7,8,9,10-	196.97	185.93	−0.213	193.72	187.37
2,3,5,6,8,9,11 ²³ ,12 ²⁶ -	211.13	198.12	−0.230	191.98	183.66
1,2,3,4,7,8,9,10,11 ²³ ,12 ²⁶ -	177.07	164.15	−0.179	196.76	189.43
1,2,3,5,6,8,9,10,11 ²³ ,12 ²⁶ -	203.84	190.92	−0.202	214.83	207.50
2,3,5,6,8,9,11,11,12,12-	197.24	184.32	−0.212	148.44	141.11
1,2,3,4,5,6,7,8,9,10,11 ²³ ,12 ²⁵ -	178.45	166.62	−0.185	199.88	194.53
1,2,3,4,5,6,7,8,9,10,11,11,12,12-	90.80	80.05	−0.083		

^a BDE_{C–NO₂}⁰ and BDE_{C–NO₂} denotes the bond dissociation energy of C–NO₂ bond without and with zero-point correction, respectively; the same is with BDE_{C–C}⁰ and BDE_{C–C}.

^b See the footnote of Table 3 for the meaning of compound name.

lower side by ca. 18 kJ mol^{-1} when the ZPE is included. Linear fitting between BDE⁰ and BDE shows that the correlation coefficients are 0.999 and 0.998 for C–NO₂ (SD = 1.88, N = 45) and C–C bonds (SD = 2.12, N = 45), respectively. It is obvious that the pyrolysis mechanism is not affected by ZPE correction. Actually, the same conclusion has been achieved in other systems [18]. Therefore, we suggest that, for the sake of saving computer resources, BDE⁰ may be used to investigate the pyrolysis mechanism for compounds with similar structure to PNBPP. In the present paper, in order to be comparable to the BDE criteria of HEDC (larger than 80–120 kJ mol^{-1}), BDE after ZPE correction is employed to elucidate the pyrolysis mechanism of PNBPPs in the following discussion. First, it can be seen from Table 6 that, except 1,2,3,4,5,6,7,8,9,10,11,11,12,12-PNBPP, all the investigated PNBPPs have BDE_{C–NO₂} and BDE_{C–C} larger than 140 kJ mol^{-1} , in which most of them are larger than 200 kJ mol^{-1} . These values satisfy the stability criteria of HEDC, indicating that all the title PNBPPs have good thermal stabilities except 1,2,3,4,5,6,7,8,9,10,11,11,12,12-PNBPP. In conjunction with the energetic properties discussed above, the studied PNBPPs with $n = 8$ –12 meet the demand of HEDC and are the candidates of HEDC. They are 1,2,3,4,7,8,9,10-, 2,3,5,6,8,9,11²³,12²⁶-, 1,2,3,4,7,8,9,10,11²³,12²⁶-

, 1,2,3,5,6,8,9,10,11²³,12²⁶-, 2,3,5,6,8,9,11,11,12,12-, and 1,2,3,4,5,6,7,8,9,10,11²³,12²⁵-PNBPPs.

Comparing BDE_{C–NO₂} with BDE_{C–C}, we can find that they are essentially equivalent and there is no obvious rule between their magnitudes. Studies have shown that the trigger bond for octanitrocubane is the C–C bond in the skeleton [5], while that for polynitroadamantanes is the C–NO₂ bond [6]. This is because the cubane skeleton has high strain energy (697.64 kJ mol^{-1}); while that of adamantane is low (24.83 kJ mol^{-1}) and thus the skeleton is more stable [49]. The strain energy of BPP is 240.48 kJ mol^{-1} [49], which is between the values of cubane and adamantane. The moderate strain energy of BPP results in the comparative magnitudes of BDE_{C–NO₂} and BDE_{C–C}. Judged from the values of BDE, the ruptures of C–NO₂ and C–C bond can both be the possible pyrolysis initiation step for PNBPP; and considering the small differences between the values of BDE_{C–NO₂} and BDE_{C–C} for the same PNBPP and the calculation discrepancy, the pyrolysis mechanism may be a mixed one. Therefore, it is noticeable that the pyrolysis mechanism for caged nitro compounds is relevant with the molecular structure, including the strain energy of the cage skeleton, the position and number of nitro groups.

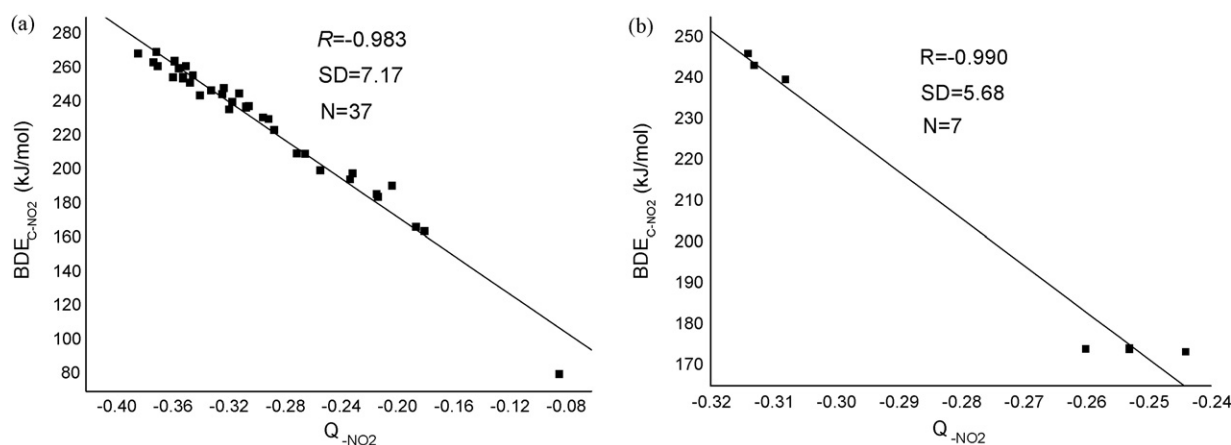


Fig. 3. The relationship between BDE_{C-NO_2} and net charges on nitro group ($C-NO_2$). (a) PNBPPs whose weakest $C-NO_2$ bond is not on C11 or C12; (b) PNBPPs whose weakest $C-NO_2$ bond is on C11 or C12.

On a whole, BDE_{C-NO_2} decreases with n . If the compounds with the largest BDE_{C-NO_2} among the isomers are considered, a linear relationship between BDE_{C-NO_2} and n with a good correlation coefficient of 0.993 can be found: $BDE_{C-NO_2} = 281.69 - 8.73n$, $n = 1-12$ ($SD = 3.96$, $N = 10$). While for BDE_{C-C} , the trend is not so clear. This is because the influence of n is less on the rupture of $C-C$ skeleton than on that of $C-NO_2$ bond, which is understandable.

In addition, it can be seen from Table 6 that there are evident discrepancies between BDE of the isomers, among which the values of PNBPPs with geminal nitro groups are far smaller than others. This is the result of repulsion effect between geminal nitro groups, which leads to the unstability of the molecules and the lower BDE value. The phenomenon is in line with the higher value of their HOFs.

Although it is effective to elucidate the thermal stability of energetic materials using the kinetic parameters such as BDE, it is time-consuming. Studies have revealed that there may be certain relationship between the kinetic parameters and the static electronic structural parameters of the molecules [6,25]. Fig. 3 presents the linear relationship between BDE_{C-NO_2} and the net charge distribution of nitro group ($C-NO_2$). Due to the different circumstances of C11 and C12 from other carbon atoms in BPP, those PNBPPs whose weakest $C-NO_2$ bond is on C11 or C12 have different rules of relationship between BDE_{C-NO_2} and $C-NO_2$. Therefore, these compounds are detached from others and their linear relationship of BDE_{C-NO_2} and $C-NO_2$ is displayed in Fig. 3b. It can be seen from the curve and the corresponding fitting values in Fig. 3 that the linear relationship between BDE_{C-NO_2} and $C-NO_2$ is good. This result enables us to evaluate the strength of $C-NO_2$ bond by the magnitude of $C-NO_2$, which is more feasible.

4. Conclusions

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

- (1) The HOFs of PNBPPs are large and have a binomial relationship with n . The first decrease and then increase rule of HOFs with n is attributed to the repulsion and superconjugate effects of nitro groups. Relative position of nitro groups has influence on the values of HOFs. PNBPPs with geminal nitro groups have larger HOFs and smaller BDE, and therefore lower stability.
- (2) ρ , D and P of PNBPPs all increase with n and satisfy the group additivity rule, revealing that the increase of n benefits the energetic performances. The calculated values of ρ , D and P for the isomers are close, implying that the position of nitro groups has

little influence on these parameters. The consistency of the calculated and experimental densities reflects the reliability of our calculation.

- (3) PNBPPs have good thermal stabilities judged by the large values of BDE. Both $C-NO_2$ and $C-C$ bonds are the possible trigger bond in the pyrolysis process of PNBPPs as derived from the values of BDE_{C-NO_2} and BDE_{C-C} . The unique mechanism of the thermal homolysis for PNBPP is related to the structure of the cage skeleton, as well as the position and number of nitro groups. As a whole, BDE values and thus the thermal stabilities decrease with increasing n for PNBPPs. There exists linear relationship between BDE_{C-NO_2} and $C-NO_2$ for PNBPPs, which makes the evaluation of the strength of $C-NO_2$ bond more feasible.
- (4) Taking both energetic properties and thermal stabilities into account, the studied PNBPPs with $n = 8-12$ are recommended as the candidates of HEDC. PNBPPs with $n \geq 4$ have better energetic performances than TNT. These target compounds with superior performances are worthy of synthesis and further investigation.

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