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Looking for High Energy Density Compounds among 1,3-Bishomopentaprismane Derivatives with CN, NC, and ONO_2 Groups

Limei Qiu,[†] Xuedong Gong,[†] Guixiang Wang,[†] Jian Zheng,[‡] and Heming Xiao*,[†]

Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China, and China Aerospace Science and Technology Corporation, Beijing, 100048, Peoples' Republic of China

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The paper concentrates on the "molecular design" of 1,3-bishomopentaprismane (BPP) derivatives with CN, NC, and ONO_2 groups as high energy density compounds (HEDCs). The heats of formation (HOFs), densities (ρ), detonation velocities (D), and pressures (P) for a series of BPP derivatives, as well as their thermal stabilities, were calculated using density functional theory. The HOFs are high and increase with the substituted number (n) for BPP derivatives with CN and NC groups while are low and decrease with n for derivatives with ONO_2 group. D and P were estimated by using modified Kamlet−Jacobs equations based on the calculated HOFs and ρ. The BPP derivatives with ONO_2 groups have excellent energetic properties to be HEDCs while the other two kinds of derivatives have relatively low ρ, D, and P, revealing that CN and NC groups are not ideal substituents in the construction of HEDCs. The trigger bond in the pyrolysis process for CN and NC derivatives is the C−C bond in the skeleton, and these derivatives all have good thermal stability. In comparison, the trigger bond in the pyrolysis process for ONO_2 derivatives is the $O-NO_2$ bond, and these compounds are medium-stable. Taking both energetic properties and thermal stability into account, BPP derivatives with 6−8 ONO_2 groups are recommended as potential candidates of HEDCs. These results would provide basic information for the further studies of the title compounds.

1. Introduction

Nowadays, the idea of "molecular design" has been widely applied to search for excellent materials in various fields. With the rapid development in computer technology and theoretical chemistry, computer modeling and quantum simulation have been extensively used to facilitate "molecular design". High energy density compounds (HEDCs) have been receiving heated attention because of their superior explosive performance over traditional energetic compounds.[1−3] Cage compound is investigated as a crucial category of HEDC owing to its high strain energy and compact structure.[4] Typical examples are hexanitrohexaazaisowurtzitane (CL-20) and octanitrocubane (ONC). 1,3-Bishomopentaprismane (BPP, see Figure 1 for the structure), known as birdcage hydrocarbon, is a typical cage compound with good symmetry (C_{2v}) and stability.[5−7] It is well-known that the addition of energy-rich or oxidizing groups such as NO_2, CN, NC, and ONO_2 creates exceptionally dense and powerful explosives, propellants, and fuels with excellent explosive properties. Recently, we have presented papers on the structures and performance of NO_2 derivatives of BPP, and some of them have been recommended as potential HEDCs.[8] Because of difficulties and costs, hitherto there have been few studies on the synthesis and properties of the CN, NC, and ONO_2 derivatives of BPP, either experimentally or theoretically. Therefore, the "molecular design", i.e., the theoretical predictions of structures and explosive performance, is of importance in finding promising candidates for novel HEDCs among these derivatives.

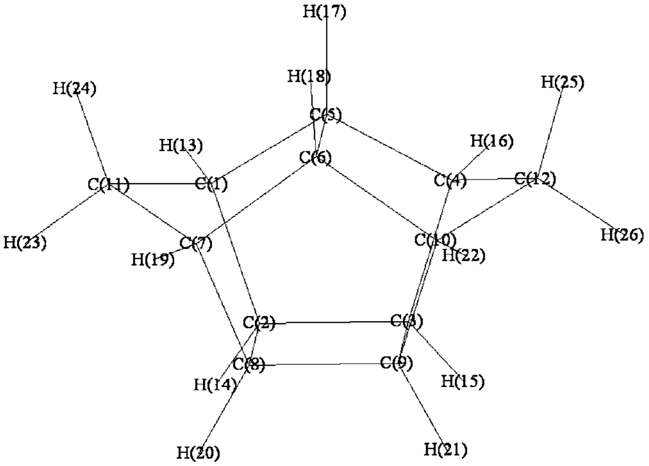

Figure 1. The structure and atomic numbering for BPP.

The density (ρ) of a compound, which is directly related to the energy density, is the most important and decisive parameter in evaluating its performance to be an energetic material. Detonation properties, including detonation velocity (D) and detonation pressure (P), are also important parameters for judging the potential of a compound to be an HEDC, because these properties determine its ability of doing work while outputting energy. However, generally speaking, the thermal stability of a compound decreases with the increasing energy. It is well-known that the thermal stability of a compound is directly relevant to safety, which determines the applicability of an explosive. Therefore, thermal stability is an essential property in evaluating the potential of a compound to be an excellent HEDC. Based on a series of studies,[8−15] quantitative criteria considering both energy (including ρ, D, and P) and stability (bond dissociation energy BDE of the trigger bond)

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* Corresponding author. Fax: +86-25-84303919. E-mail: xiao@mail.njust.edu.cn.
[†] Nanjing University of Science and Technology.
[‡] China Aerospace Science and Technology Corporation.

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TABLE 1: Methods for Calculating the N, $\overline{M}$, and Q_{cal} Parameters for $C_aH_bO_cN_d$ Explosive[a]

	stoichiometric ratio		
parameter	$c \geq 2a + b/2$	$2a + b/2 > c > b/2$	$c \leq b/2$
N (mol·g^{-1})	$(b + 2c + 2d)/4M$	$(b + 2c + 2d)/4M$	$(b + d)/2M$
$\overline{M}$ (g·mol^{-1})	$4M/(b + 2c + 2d)$	$(55d + 88c - 8b)/(b + 2c + 2d)$	$(2b + 28d + 32c)/(b + d)$
Q_{cal} (kJ·g^{-1})	$(28.9b + 94.05a + 0.239\Delta_f H^0_M)/M$	$[28.9b + 94.05(c/2 - b/4) + 0.239\Delta_f H^0_M]/M$	$(57.8c + 0.239\Delta_f H^0_M)/M$

[a] M in the formula refers to the molecular weight of the title compound (g·mol^{-1}); $\Delta_f H^0_M$ is the standard heat of formation of the title compound (kJ·mol^{-1}).

TABLE 2: Experimental Standard Heats of Formation ($\Delta_f H^0_{atom}$)[22] and Calculated Total Energy (E_0) for C, H, N, and O Atoms at the B3LYP/6-31G* Level

$\Delta_f H^0_{atom}$ (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

requirements have been put forward to filter the candidates and identify potential HEDCs, i.e., $\rho \approx 1.9$ g·cm^{-3}, $D \approx 9$ km·s^{-1}, $P \approx 40$ GPa, and BDE ≈ 80−120 kJ·mol^{-1}.[15] The present paper focuses on the potential for BPP derivatives possessing CN, NC, and ONO_2 groups as HEDCs. Consequently, the densities, detonation properties, and thermal stabilities for the title compounds were investigated and discussed using density functional theory (DFT). Besides, the heat of formation (HOF) is a key thermodynamic property for a compound and directly related to the detonation energy (Q) and thus D and P. Consequently, HOF is also calculated and discussed for the studied system. Because there are many isomers for the derivatives, only certain kinds of derivatives reflecting the typical relative position of substitution and with good molecular symmetry are chosen as the targets.

2. Computational Methods

A series of BPP derivatives with CN, NC, and ONO_2 groups were studied using Gaussian 03 program.[16] All the molecules in Tables 3−5 and the related radical species generated from the ChemBats3D software were fully optimized without any symmetry restrictions at the DFT-B3LYP level[17,18] with the 6−31G* basis set.[19] Harmonic vibrational analyses at the same level of theory were performed subsequently to confirm that the located structures correspond to minima and to determine the zero-point vibrational energy corrections. A scaling factor of 0.96 was used to approximately correct the systematic overestimation of vibrational frequencies in the B3LYP/6−31G* calculation.[20]

The theoretical density (ρ_{cal}) of each compound is computed from the average molecular volume divided by the molecular

TABLE 3: Total Energy (E_0), Zero-Point Energy (ZPE), and Thermal Correction (ΔH^0_T) for CN Derivatives of BPP at the B3LYP/6-31G* Level, ΔnRT for the Atomization Reaction 3, $\Delta_f H^0_{298}$ Calculated from Reaction 3 and Formulas 5−7, and $\Delta_f H^0_{298,corrected}$ Obtained from the Correction Equation 6

		(kJ·mol^{-1})				
compd[a]	E_0 (a.u.)	ZPE	ΔH^0_T	ΔnRT	$\Delta_f H^0_{298}$	$\Delta_f H^0_{298,corrected}$
1-	−557.919662	584.83	25.15	64.44	488.20	402.64
2-	−557.921569	584.99	25.20	64.44	483.40	397.94
5-	−557.919806	584.60	25.18	64.44	487.62	402.08
11^{23}-	−557.917302	585.18	25.02	64.44	494.61	408.93
11^{24}-	−557.917338	585.23	24.99	64.44	494.54	408.86
1,3-	−650.161251	580.37	30.40	66.92	641.14	552.53
1,9-	−650.162371	580.52	30.40	66.92	638.35	549.79
$1,12^{26}$-	−650.158462	581.00	30.20	66.92	648.89	560.12
5,6-	−650.155498	579.53	30.40	66.92	655.40	566.51
$11^{23},12^{26}$-	−650.156444	581.50	30.09	66.92	654.58	565.70
$11^{24},12^{25}$-	−650.156081	581.58	29.99	66.92	655.51	566.61
1,3,6-	−742.398975	575.37	35.72	69.40	803.76	711.90
1,4,8-	−742.397421	575.53	35.72	69.40	808.00	716.05
$3,11^{23},12^{26}$-	−742.393879	577.02	35.35	69.40	818.42	726.26
5,6,9-	−742.395204	575.03	35.72	69.40	813.32	721.26
11^{23},12,12-	−742.384081	576.30	35.28	69.40	843.35	750.70
1,3,8,10-	−834.633562	570.65	41.09	71.88	974.94	879.66
1,4,7,10-	−834.628761	570.49	41.05	71.88	987.35	891.81
$5,6,11^{23},12^{26}$-	−834.624812	571.15	40.68	71.88	998.01	902.26
11,11,12,12-	−834.609695	570.85	40.56	71.88	1037.28	940.74
$3,6,8,11^{23},12^{26}$-	−926.860589	566.72	46.06	74.35	1166.37	1067.25
$2,3,8,9,11^{23},12^{26}$-	−1019.077802	560.39	51.60	76.83	1381.73	1278.31
$2,5,6,9,11^{23},12^{26}$-	−1019.086909	560.75	51.51	76.83	1358.09	1255.14
$2,3,5,8,9,11^{23},12^{26}$-	−1111.307039	554.57	57.07	79.31	1565.96	1458.85
1,2,3,4,7,8,9,10	−1203.527682	546.60	63.06	81.79	1771.12	1659.91
$2,3,5,6,8,9,11^{23},12^{26}$-	−1203.530232	548.44	62.57	81.79	1765.78	1654.68
$2,3,5,6,8,9,11^{24},12^{25}$-	−1203.528478	548.44	62.56	81.79	1770.38	1659.18
$1,2,3,4,7,8,9,10,11^{23},12^{26}$-	−1387.962530	535.59	73.76	86.75	2202.01	2082.18

[a] 1- denotes 1-cyanobishomopentaprismane; 1,3- denotes 1,3-dicyanobishomopentaprismane; 11^{23}- denotes the H23 atom bonded to C11 is replaced by a CN group; $11^{23},12^{26}$- denotes the H23 atom bonded to C11 and H26 atom bonded to C12 are replaced by a CN group, respectively; the others are similar.

TABLE 4: Total Energy (E_0), Zero-Point Energy (ZPE), and Thermal Correction ($\Delta H^0{}_T$) for NC Derivatives of BPP at the B3LYP/6-31G* level, ΔnRT for the Atomization Reaction 3, $\Delta_f H^0{}_{298}$ Calculated from Reaction 3 and Formulas 5−7, and $\Delta_f H^0{}_{298,\mathrm{corrected}}$ Obtained from the Correction Equation 6

		(kJ·mol^{-1})				
compd[a]	E_0 (a.u.)	ZPE	$\Delta H^0{}_T$	ΔnRT	$\Delta_f H^0{}_{298}$	$\Delta_f H^0{}_{298,\mathrm{corrected}}$
1-	−557.885818	583.18	25.52	64.44	575.78	488.47
2-	−557.887550	583.24	25.55	64.44	571.32	484.10
5-	−557.886686	583.02	25.52	64.44	573.34	486.08
11^{23}-	−557.883601	584.04	25.44	64.44	582.38	494.94
11^{24}-	−557.883457	584.11	25.40	64.44	582.78	495.34
1,3-	−650.094040	577.04	31.13	66.92	815.00	722.91
1,9-	−650.094960	577.17	31.13	66.92	812.72	720.67
$1,12^{26}$-	−650.091276	578.29	30.98	66.92	823.36	731.10
5,6-	−650.090567	576.54	31.05	66.92	823.54	731.28
$11^{23},12^{26}$-	−650.089183	579.24	30.92	66.92	829.75	737.36
$11^{24},12^{25}$-	−650.088671	579.35	30.84	66.92	831.12	738.71
1,3,6-	−742.299469	570.48	36.79	69.40	1061.19	964.18
1,4,8-	−742.297455	570.51	36.82	69.40	1066.54	969.42
$3,11^{23},12^{26}$-	−742.293825	572.86	36.55	69.40	1078.15	980.80
5,6,9-	−742.297040	570.23	36.75	69.40	1067.28	970.14
$11^{23},12,12$-	−742.285725	571.82	36.52	69.40	1098.35	1000.59
1,3,8,10-	−834.501064	563.81	42.58	71.88	1317.47	1215.33
1,4,7,10-	−834.496909	563.95	42.51	71.88	1328.45	1226.09
$5,6,11^{23},12^{26}$-	−834.494032	565.71	42.20	71.88	1337.45	1234.91
11,11,12,12-	−834.480829	564.31	42.17	71.88	1370.68	1267.48
$3,6,8,11^{23},12^{26}$-	−926.696480	558.98	47.99	74.35	1591.43	1483.81
$2,3,8,9,11^{23},12^{26}$-	−1018.887016	551.66	53.93	76.83	1876.24	1762.92
$2,5,6,9,11^{23},12^{26}$-	−1018.892420	551.45	53.78	76.83	1861.69	1748.67
$2,3,5,8,9,11^{23},12^{26}$-	−1111.084928	543.96	59.79	79.31	2141.22	2022.61
1,2,3,4,7,8,9,10	−1203.278991	534.07	66.23	81.79	2414.70	2290.62
$2,3,5,6,8,9,11^{23},12^{26}$-	−1203.278251	536.36	65.61	81.79	2418.32	2294.16
$2,3,5,6,8,9,11^{24},12^{25}$-	−1203.275559	536.38	65.53	81.79	2425.32	2301.03
$1,2,3,4,7,8,9,10,11^{23},12^{26}$-	−1387.656079	520.29	77.92	86.75	2995.46	2859.76

[a] 1- denotes 1-isocyanobishomopentaprismane; 1,3- denotes 1,3-diisocyanobishomopentaprismane; 11^{23}- denotes the H23 atom bonded to C11 is replaced by an NC group; $11^{23},12^{26}$- denotes the H23 atom bonded to C11 and H26 atom bonded to C12 are replaced by an NC group, respectively; the others are similar.

weight while the average volume is obtained from the statistical average value of 100 single-point molar volumes. The molecular volume, defined as the volume inside a contour of electron density of 0.001e·Bohr^{-3}, 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.[15] Previous studies on CHNO energetic compounds have proved that this method is an efficient and convenient way to predict density of CHNO explosives.[9−15]

The modified K−J equations[21] have been verified by many studies to be suitable for predicting the detonation properties of CHNO explosives. Based on the obtained HOFs and ρ_{cal}, D and P for the title compounds were estimated using the modified K−J equations as follows:

$$D = 1.01\left(N\bar{M}^{1/2}Q_{\mathrm{cal}}^{1/2}\right)^{1/2}(1 + 1.30\rho_{\mathrm{cal}}) \qquad (1)$$

$$P = 1.558\rho_{\mathrm{cal}}^{2}N\bar{M}^{1/2}Q_{\mathrm{cal}}^{1/2} \qquad (2)$$

Here, N is the moles of gaseous detonation products per gram of explosive, $\bar{M}$ is the average molecular weight of gaseous products, ρ_{cal} refers to the theoretical density of a compound crystal, and Q_{cal} is calculated as the difference between the HOFs of products and reactants of the detonation reaction. The explosive reaction is designed according to the maximal exothermic principle. 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, H atoms unable to produce H_2O because of insufficiency of oxygen will turn into H_2 gas while C atoms unable to produce CO_2 will exist as solid C. The detailed calculation methods for parameters N, $\bar{M}$, and Q_{cal} for the compounds with different compositions are listed in Table 1.

As has been pointed above, the HOF for the title compounds is needed in the calculation of detonation energy. In the present paper, the atomization reaction[22] was applied to calculate the HOF of the title compounds. For BPP derivatives with CN and NC groups, reaction 3 was used; while for ONO_2 derivatives, reaction 4 was used.

$$C_{12+n}H_{14-n}N_n \rightarrow (12 + n)C + (14 - n)H + nN \qquad (3)$$

$$C_{12}H_{14-n}N_nO_{3n} \rightarrow 12C + (14 - n)H + nN + 3nO \qquad (4)$$

$$\Delta H^0_{298} = \sum \Delta_f H^0_{298,P} - \Delta_f H^0_{298,M} \qquad (5)$$

$$\Delta E_{298} = \sum E_{0,P} - E_{0,M} - \mathrm{ZPE}_M - \Delta H^0_{T,M} \qquad (6)$$

$$\Delta H^0_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_{298} + (\Delta n)RT \qquad (7)$$

In the above expressions, each term is defined as follows: M, $C_{12+n}H_{14\text{-}n}N_n$, or $C_{12}H_{14\text{-}n}N_nO_{3n}$; ΔH^0_{298}, the standard enthalpy change of reaction 3 or 4 at 298 K; $\sum\Delta_f H^0{}_{298,P}$, the sum of experimental standard HOFs of product atoms, which are known and listed in Table 2;[23] $\Delta_f H^0_{298,M}$, the standard HOF of the

TABLE 5: Total Energy (E_0), Zero-Point Energy (ZPE) and Thermal Correction (ΔH^0_T) for ONO_2 Derivatives of BPP at the B3LYP/6-31G* level, ΔnRT for the Atomization Reaction 3, $\Delta_f H^0_{298}$ Calculated from Reaction 4 and Formulas 5−7, and $\Delta_f H^0_{298,corrected}$ Obtained from the Correction Equation 6

		(kJ·mol^{-1})				
compd[a]	E_0 (a.u.)	ZPE[b]	ΔH^0_T[b]	ΔnRT	$\Delta_f H^0_{298}$	$\Delta_f H^0_{298,corrected}$
1-	−745.356011	604.09	29.89	64.44	273.60	192.33
2-	−745.359823	604.16	29.87	64.44	263.64	182.57
5-	−745.360003	604.31	29.79	64.44	263.23	182.18
11^{23}-	−745.358967	605.71	29.77	64.44	267.34	186.20
11^{24}-	−745.358732	605.75	29.73	64.44	267.95	186.80
1,3-	−1025.035685	619.52	39.92	66.92	208.05	128.10
1,9-	−1025.041249	619.72	39.84	66.92	193.56	113.90
$1,12^{26}$-	−1025.038716	621.23	39.71	66.92	201.59	121.77
5,6-	−1025.031307	619.19	39.78	66.92	219.07	138.90
$11^{23},12^{26}$-	−1025.039852	622.52	39.64	66.92	199.83	120.04
$11^{24},12^{25}$-	−1025.039486	622.61	39.54	66.92	200.78	120.97
1,3,6-	−1304.712918	633.61	50.14	69.40	147.76	69.01
1,4,8-	−1304.716879	634.37	49.99	69.40	137.97	59.42
$3,11^{23},12^{26}$-	−1304.709736	636.56	49.88	69.40	158.80	79.83
5,6,9-	−1304.710740	634.11	49.87	69.40	153.71	74.84
$11^{23},12,12$-	−1304.714108	635.68	49.78	69.40	146.34	67.63
1,3,8,10-	−1584.388798	648.82	60.22	71.88	92.00	14.37
1,4,7,10-	−1584.384651	648.72	60.12	71.88	102.69	24.84
$5,6,11^{23},12^{26}$-	−1584.373836	650.03	60.23	71.88	132.50	54.06
11,11,12,12-	−1584.387581	648.72	60.04	71.88	94.91	17.23
$3,6,8,11^{23},12^{26}$-	−1864.071774	665.11	70.33	74.35	18.72	−57.44
$2,3,8,9,11^{23},12^{26}$-	−2143.715512	664.37	81.81	76.83	32.80	−43.65
$2,5,6,9,11^{23},12^{26}$-	−2143.724127	677.63	80.99	76.83	22.62	−53.62
$2,3,5,8,9,11^{23},12^{26}$-	−2423.382603	688.69	91.29	79.31	8.63	−67.33
1,2,3,4,7,8,9,10	−2703.032120	702.35	101.58	81.79	20.75	−55.46
$2,3,5,6,8,9,11^{23},12^{26}$-	−2702.955855	702.35	101.58	81.79	220.98	140.77
$2,3,5,6,8,9,11^{24},12^{25}$-	−2703.054811	702.35	101.58	81.79	−38.83	−113.84
$1,2,3,4,7,8,9,10,11^{23},12^{26}$-	−3262.383377	729.65	122.16	86.75	−84.70	−158.80

[a] 1- denotes 1-bishomopentaprismanenitrate; 1,3- denotes 1,3-bishomopentaprismanedinitrate; 11^{23}- denotes the H23 atom bonded to C11 is replaced by an ONO_2 group; $11^{23},12^{26}$- denotes the H23 atom bonded to C11 and H26 atom bonded to C12 are replaced by an ONO_2 group, respectively; the others are similar. [b] ZPE and ΔH^0_T for PNBPPs of $n \geq 7$ were derived from equations ZPE = 593.13 + 13.65n and ΔH^0_T = 19.24 + 10.29n, respectively.

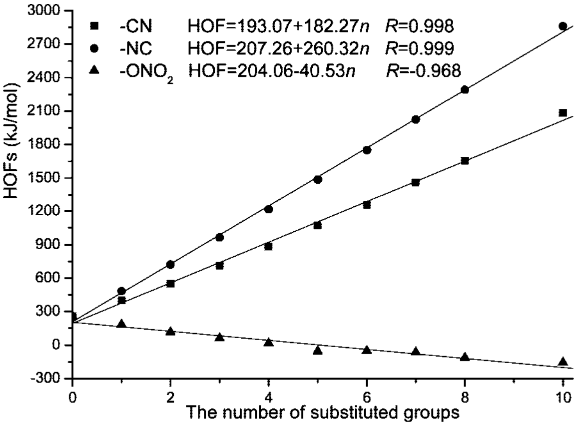

Figure 2. The relationship between $\Delta_f H^0_{298,M,corrected}$ (the lowest one for isomers) and the number of substitution groups (n = 0−10).

compound M; ΔE_{298}, the energy change of reaction 3 or 4 at 298 K; $\sum \Delta E_{0,P}$, the sum of calculated total energy (E_0) of product atoms; $E_{0,M}$, the total energy of compound M; ZPE_M, zero point energy of M; $\Delta H^0_{T,M}$, the thermal correction from 0 to 298 K of M. In addition, the $\Delta(PV)$ value in eq 7 is the PV work term and it equals ΔNRT for the reactions of an ideal gas; for the reactions 3 and 4, ΔN equals 25 + n and 25 + 3n, respectively. 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.[24] By comparing the experimental and calculated results, a correction equation was obtained with a good linear correlation coefficient (R = 0.990):

$$\Delta_f H^0_{298,M,corrected} = -75.79 + 0.98\Delta_f H^0_{298,M} \qquad (8)$$

The thermal stabilities of the title compounds were evaluated by calculating BDE of the trigger bond. BDE is originally defined as the enthalpy change at 298 K and 1 atm for the chemical bond dissociation in a molecule as follows:[23]

$$A - B(g) \rightarrow A\cdot(g) + B\cdot(g) \qquad (9)$$

where A−B denotes the neutral molecules while A· and B· stand for the corresponding product radicals after the bond dissociation. In the present paper, the BDE is computed as the difference between the ZPE corrected total energies at 0 K according to 9:

$$BDE = [E(A\cdot) + E(B\cdot)] - E(A - B) \qquad (10)$$

Equation 10 has been successfully and frequently used to determine the bond strength and relative stability of the compounds and corresponding radicals.[25−28] Therefore, we use BDE calculated from eq 10 based on (U)B3LYP/6−31G* results to determine the thermal decomposition mechanism of the title compound.

TABLE 6: Predicted Detonation Properties of Title Compounds[b]

	CN				NC				ONO_2			
compds[a]	ρ	Q	D	P	ρ	Q	D	P	ρ	Q	D	P
1-	1.34	525.13	3.63	4.80	1.37	637.07	3.86	5.53	1.53	1000.58	5.49	12.08
2-	1.31	519.00	3.57	4.59	1.35	631.37	3.82	5.35	1.51	989.94	5.42	11.61
5-	1.35	524.40	3.64	4.87	1.35	633.95	3.82	5.34	1.53	989.52	5.47	11.94
11^{23}-	1.34	533.33	3.64	4.84	1.36	645.51	3.85	5.45	1.49	993.90	5.39	11.42
11^{24}-	1.32	533.24	3.61	4.69	1.35	646.03	3.84	5.42	1.49	994.55	5.39	11.44
1,3-	1.40	634.08	4.05	6.19	1.38	829.61	4.29	6.84	1.68	1346.78	6.46	17.76
1,9-	1.40	630.94	4.05	6.16	1.37	827.04	4.26	6.72	1.68	1334.67	6.44	17.62
$1,12^{23}$-	1.38	642.79	4.02	6.00	1.39	839.00	4.32	6.99	1.65	1341.38	6.38	17.15
5,6-	1.38	650.12	4.03	6.05	1.41	839.21	4.36	7.17	1.68	1355.99	6.48	17.91
$11^{23},12^{26}$-	1.38	649.19	4.03	6.03	1.36	846.07	4.27	6.70	1.65	1339.90	6.38	17.10
$11^{24},12^{25}$-	1.37	650.24	4.02	5.98	1.38	847.74	4.31	6.93	1.66	1340.70	6.40	17.26
1,3,6-	1.44	729.38	4.33	7.20	1.40	987.86	4.59	7.96	1.75	1462.29	7.32	23.36
1,4,8-	1.41	733.63	4.28	6.93	1.41	993.22	4.62	8.10	1.75	1455.57	7.31	23.29
$3,11^{23},12^{26}$-	1.39	744.09	4.26	6.82	1.40	1004.88	4.61	7.99	1.79	1469.86	7.44	24.45
5,6,9-	1.42	738.97	4.30	7.01	1.42	993.96	4.65	8.23	1.74	1466.37	7.30	23.19
$11^{23},12,12$-	1.41	769.13	4.34	7.12	1.42	1025.16	4.68	8.35	1.77	1461.32	7.37	23.89
1,3,8,10-	1.45	813.99	4.48	7.72	1.39	1124.60	4.73	8.38	1.86	1545.41	8.07	29.48
1,4,7,10-	1.46	825.23	4.52	7.89	1.42	1134.56	4.81	8.80	1.84	1551.63	8.02	28.91
$5,6,11^{23},12^{26}$-	1.44	834.90	4.50	7.79	1.42	1142.72	4.82	8.85	1.85	1568.99	8.07	29.34
11,11,12,12-	1.49	870.51	4.65	8.48	1.45	1172.86	4.91	9.27	1.85	1547.11	8.04	29.15
$3,6,8,\ 11^{23},12^{26}$-	1.48	900.39	4.66	8.48	1.46	1251.82	5.01	9.72	1.93	1597.78	8.61	34.27
$2,3,8,9,\ 11^{23},12^{26}$-	1.50	990.97	4.80	9.13	1.49	1366.64	5.18	10.59	1.95	1676.99	8.95	37.25
$2,5,6,9,\ 11^{23},12^{26}$-	1.50	973.00	4.76	8.94	1.47	1355.60	5.11	10.16	1.97	1672.44	9.02	38.02
$2,3,5,8,9,\ 11^{23},12^{26}$-	1.53	1046.07	4.89	9.57	1.52	1450.31	5.28	11.10	2.07	1724.38	9.55	43.74
1,2,3,4, 7,8,9,10-	1.54	1107.16	4.95	9.85	1.52	1527.84	5.33	11.32	2.12	1775.98	9.90	47.70
$2,3,5,6,8,9,\ 11^{23},12^{26}$-	1.53	1103.67	4.93	9.74	1.50	1530.20	5.29	11.06	2.10	1775.69	9.86	47.13
$2,3,5,6,8,9,\ 11^{24},12^{25}$-	1.53	1106.67	4.94	9.79	1.55	1534.79	5.39	11.69	2.10	1754.39	9.83	46.86
$1,2,3,4,7,8,9,\ 10,11^{23},12^{26}$-	1.59	1218.69	5.10	10.68	1.55	1673.81	5.43	11.88	2.13	1570.20	9.73	46.15

[a] See Figure 1 for the atomic numbering. 1- denotes H atom bonded to C1 is substituted; 1,2- denotes H atoms bonded to C1 and C2 are substituted; 11^{23}- denotes the H23 atom bonded to C11 is replaced by a nitro group; $11^{23},12^{26}$- denotes the H23 atom bonded to C11 and H26 atom bonded to C12 are replaced by nitro groups; the others are similar. [b] Unit: ρ: $g \cdot cm^{-3}$; Q: $kJ \cdot g^{-1}$; D: $km \cdot s^{-1}$; P: GPa.

3. Results and Discussion

3.1. Heats of Formation. Tables 3−5 present calculated $\Delta_f H^0_{298,M}$ for BPP derivatives with CN, NC, and ONO_2 groups obtained using the method of atomization reactions. For ONO_2 derivatives of BPP with $n \geq 7$, the vibrational analyses are difficult to fulfill because of their structural complexity. Fortunately, there exists a good linear relationship between ZPE and n or ΔH^0_T and n for bishomopentaprismanenitrate: ZPE $= 593.13 + 13.65n$ ($R = 0.994$, $n = 1-6$); $\Delta H^0_T = 19.24 + 10.29n$ ($R = 1.000$, $n = 1-6$). It should be pointed out that the average values of ZPE and ΔH^0_T were used for the isomers. Therefore, the values of ZPE and ΔH^0_T for PNBPPs with $n \geq 7$ were computed using the above equations.

Inspecting the values of $\Delta_f H^0_{298,M,corrected}$ in Tables 3−5, we can find that the CN and NC derivatives of BPP have quite large positive HOFs; in comparison, the HOFs of ONO_2 derivatives are low and some of them are even negative. Besides, the value of HOF relates to the number of substituted groups. To illustrate this, the related curves of the calculated HOFs with n were presented in Figure 2. For the isomers with the same kind and number of substituted group, the most stable compound with the lowest HOF was chosen for analysis. It can be seen that they all have a linear relationship with good correlation coefficients (R). Obviously, the contributions of the substituted groups on the HOFs of BPP derivatives meet the group additivity rule. It is noticeable that the influencing degree of the substituted groups on HOF differs a lot for different groups. The HOFs increase by 182.27 and 260.32 $kJ \cdot mol^{-1}$, respectively, if one more CN or NC group is attached; while for ONO_2 derivatives, one more substitution group leads to the decrease of HOF by 40.53 $kJ \cdot mol^{-1}$. Also noteworthy is that the introduction of NC group makes the largest increment of HOF, which has also been observed in HOFs of derivatives of cubane and hexaazaadamantane.[13,29] For the ONO_2 derivatives of BPP, the attachment of ONO_2 makes the HOF shift to the lower side.

In addition, differences can be found between the HOFs of the isomers, revealing that the HOF is also affected by the special relative position of the substituted groups. Generally speaking, the closer the substituted groups, the more the repulsion energy, thus the higher the HOF. As far as the isomers with four substituted BPP derivatives with CN or NC groups are concerned, 1,3,8,10- substituted BPPs, whose substituted groups are not bonded to the same ring and are farthest separated, have the lowest HOFs, and the 1,4,7,10- BPP derivatives, whose substituted groups are not bonded to adjacent C atoms, also have relatively small HOFs. For $5,6,11^{23},12^{26}$- derivatives, the HOFs keep increasing with distances between the bonded C atoms decreasing; while for 11,11,12,12- derivatives, where two substituted groups are bonded to the same C atom, their HOFs are the largest of the isomers. Similar phenomena also exist for other isomers of CN and NC derivatives. Therefore, the relative order of the HOF values can be estimated according to the relative position of the substituted groups in the isomeric molecule and further identifies the relative stabilities of the isomers for CN and NC derivatives of BPP. For ONO_2 derivatives of BPP, the influence of the substituted position on the HOFs has no absolute rule. For example, comparison of derivatives with four substituted groups shows that the HOF of 11,11,12,12-bishomopentaprismanenitrate is smaller than that of 1,4,7,10- and $5,6,11^{23},12^{26}$- bishomopentaprismanenitrates. This is probably caused by the unique space and electronic interactions between the ONO_2 groups in the molecules. On the one hand, the −O− linkage in the ONO_2 group makes the substituted groups stretch more freely and

TABLE 7: Bond Dissociation Energies (kJ·mol^{-1}) of the Trigger Bonds for the Title Compounds Computed without ZPE Corrections (BDE^0) at the (U)B3LYP/6-31G* Level[a]

	CN		NC		ONO_2	
compd[b]	C−CN	C−C	C−NC	C−C	$O-NO_2$[b]	C−C
1-	563.16	295.91	474.30	294.43	163.99(124.24)	
2-	560.98	289.35	471.66	289.12	82.58(41.17)	
5-	551.63	240.56	464.67	245.88	165.21(125.51)	
11^{23}-	547.06	288.46	456.45	286.37	183.60(141.36)	283.79
11^{24}-	547.15	287.08	456.42	287.73	181.82(140.69)	
1,3-	554.77	197.10	465.22	296.92	168.83(128.93)	
1,9-	557.69	197.39	467.39	296.74	87.26(45.70)	
1,12^{23}-	557.95	297.76	469.91	294.34	166.96(127.02)	
5,6-	536.08	181.89	454.58	195.12	162.80(120.81)	
11^{23},12^{26}-	540.45	290.21	452.40	285.99	182.06(140.62)	
11^{24},12^{25}-	539.50	290.31	451.58	291.02	181.19(140.04)	
1,3,6-	546.79	248.54	461.93	252.53	162.83(123.20)	
1,4,8-	547.64	304.99	460.73	303.09	168.61(129.11)	
3,11^{23},12^{26}-	544.52	290.00	458.66	285.89	179.20(138.84)	263.48
5,6,9-	548.77	183.35	448.54	195.99	157.29(117.89)	
11^{23},12,12-	454.18	289.23	385.21	284.97	137.98(99.05)	
1,3,8,10-	543.00	309.89	452.69	306.76	156.47(116.19)	
1,4,7,10-	539.63	317.42	454.70	316.23	163.26(123.56)	
5,6,11^{23},12^{26}-	524.55	187.02	445.00	194.72	130.84(92.56)	
11,11,12,12-	450.82	291.92	382.75	286.67	139.72(101.33)	
3,6,8, 11^{23},12^{26}-	527.70	243.29	447.78	243.18	155.87(117.01)	
2,3,8,9, 11^{23},12^{26}-	521.74	167.33	447.27	180.87	138.22(115.29)	
2,5,6,9, 11^{23},12^{26}-	516.04	185.54	437.96	192.02	142.35(106.16)	
2,3,5,8,9, 11^{23},12^{26}-	517.59	245.32	443.61	244.66	175.86(144.06)	
1,2,3,4, 7,8,9,10-	518.64	182.00	444.08	182.00	123.30(93.32)	
2,3,5,6,8,9, 11^{23},12^{26}-	509.44	186.82	442.60	192.95	131.41(101.43)	
2,3,5,6,8,9, 11^{24},12^{25}-	518.77	188.90	443.85	198.11	122.24(92.26)	

[a] See Figure 1 for the atomic numbering. 1- denotes H atom bonded to C1 is substituted; 1,2- denotes H atoms bonded to C1 and C2 are substituted; 11^{23}- denotes the H23 atom bonded to C11 is substituted; 11^{23},12^{26}- denotes the H23 atom bonded to C11 and H26 atom bonded to C12 are substituted; the others are similar. [b] Values in parentheses are BDE after ZPE corrections.

therefore have less space hindrance from the substituted groups; on the other hand, the electronic interactions between ONO_2 groups are more complex than that between CN and NC groups. Except for the repulsion energy, the HOF may also be affected by molecular symmetry. However, its influence is smaller than that of the substituted position, which can be deduced from the orderliness between the isomers.

3.2. Energetic Properties. As is pointed out in the first section, ρ, D, and P are the most important parameters in evaluating the explosive performances of energetic materials. Based on the obtained ρ and HOFs, the detonation properties, including Q, D, and P, were estimated using the modified K−J equations as described in Computational Methods. Detailed results are listed in Table 6.

It can be found from Table 6that the magnitudes of ρ, D, and P for BPP derivatives with CN and NC groups are small and do not meet the quantitative criteria of HEDC. In comparison, the corresponding values of BPP derivatives with ONO_2 group are much larger. If only the magnitudes of ρ, D, and P are considered, the studied BPP derivatives with the number of ONO_2 groups more than six can be considered as the candidates of HEDCs. In addition, it can be seen that the values of D and P for 1,2,3,4,7,8,9,10,11^{23},12^{26}- ONO_2-substituted BPP are lower than BPP derivatives with eight ONO_2 groups. Therefore, considering both the energetic properties and the synthesis difficulty, 2,3,8,9,11^{23},12^{26}-, 2,5,6,9,11^{23},12^{26}-, 2,3,5,8,9,11^{23},12^{26}-, 1,2,3,4,7,8,9,10-, 2,3,5,6,8,9,11^{23},12^{26}-, and 2,3,5,6,8,9,11^{24},12^{25}- ONO_2-substituted BPP are considered to be potential HEDC candidates.

In addition, ρ, Q, D, and P all increase with the number of substituted groups for the three types of BPP derivatives in a whole, revealing that the increase of substituted groups benefit the densities and detonation properties of the title compounds. However, the increments of ρ, D, and P for derivatives with CN and NC groups are much smaller than that of derivatives with ONO_2 groups. This is mainly because CN and NC groups contribute less to the crystal densities than ONO_2 group. Although both ρ and Q have influences on D and P, the effect of ρ is far bigger than that of Q, which can also be deduced from expressions 1 and 2. Another important influence factor for the low values of D and P of BPP derivatives with CN and NC groups is that these molecules have no oxygen atom and are “oxygen-balance-negative” in a large scale, which leads to the solid C product instead of CO_2 gas and thus the smaller values of N (the moles of gaseous detonation products per gram of explosive) in expressions 1 and 2. The lower ρ and N values of CN and NC derivatives result in the lower values of their D and P. Besides, it can be found that the difference of ρ, D, and P between the isomers are small, indicating that the space orientations of substitution groups have little influence on the values of ρ, D, and P.

Another noteworthy phenomenon is the relationship between Q and HOF. For derivatives with the same number of CN and NC groups, whose chemical compositions are the same, the order of their Q is directly related to their HOFs. Because of the larger HOFs of derivatives with NC groups, their Q are bigger than that of corresponding derivatives with a CN group. However, for BPP derivatives with ONO_2 groups, although they have relatively lower HOFs than the those of the other two types of derivatives, their Q are higher. Therefore, the value of HOF cannot be used to predict the detonation energy of a compound. The detonation energy is related to both HOF and molecular compositions.

From the above analysis, we find that CN and NC groups are not good substituents of HEDCs, although they have high HOFs. In comparison, the introduction of ONO_2 groups can benefit ρ, D, and P in a large scale, and ONO_2 derivatives are of great potential to meet the demand of ρ, D, and P for HEDC.

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, 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.

As judged from the properties of the title compounds, the breaking of the C−CN bond for CN derivatives, the C−NC bond for NC derivatives, the $O-NO_2$ bond for ONO_2 derivatives, and the C−C bond in the skeleton for the three kinds of derivatives were considered to be the initial step for pyrolysis. In order to simplify the calculation, the bond of each kind with the least Mulliken population at the B3LYP/6−31G* level was studied. It has been pointed out that the consideration of ZPE correction only leads to the BDE value shifting to a higher side; however, the pyrolysis mechanism is not affected by ZPE correction.[8,11] Therefore, Table 7 lists the bond dissociation energy without ZPE correction (ZPE^0) for the possible trigger bonds.

It can be found from Table 7 that BDE^0_{C-C} for both CN and NC derivatives are far smaller than that of $BDE^0_{C\text{-}CN}$ or $BDE^0_{C\text{-}NC}$; accordingly, the C−C bond in the skeleton is the trigger bond for these two kinds of BPP derivatives. The values of BDE^0_{C-C} for CN and NC derivatives are much higher than the stability criteria of HEDC (80−120 kJ·mol^{-1}), revealing that they have good thermal stabilities. Besides, the high values of $BDE^0_{C\text{-}CN}$ and $BDE^0_{C\text{-}NC}$ indicate that the C−CN and C−NC bond are thermally stable and not easily broken.

For the ONO_2 derivatives, $O-NO_2$ is the trigger bond. Since the magnitude of BDE^0_{O-NO2} is equivalent to the stability criteria of HEDC (80−120 kJ·mol^{-1}), the BDE values after ZPE correction (BDE) are given in parentheses so as to be comparable with the criteria. It can be deduced from the BDE that for most of the derivatives, BDE are in the range of 80−120 kJ·mol^{-1}, and these compounds have medium thermal stability. What concerns us most is the BDE for compounds with $n \geq 6$ whose ρ, D, and P achieve the energetic standard of HEDC. It can be found that the BDE values of $n = 6-8$ are in the range of 80−120 kJ·mol^{-1}, revealing that these compounds are comparatively stable and meet the stability requirement of HEDC.

In conjunction with the energetic properties discussed above, the studied BPP derivatives with 6−8 ONO_2 groups meet the demand of HEDC and are the candidates of HEDC. They are 2,3,8,9,11^{23},12^{26}-, 2,5,6,9,11^{23},12^{26}-, 2,3,5,8,9,11^{23},12^{26}-, 1,2,3,4,7,8,9,10-, 2,3,5,6,8,9,11^{23},12^{26}-, and 2,3,5,6,8,9,11^{23},12^{26}- bishomopentaprismanenitrates.

4. Conclusions

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

(1) The NC derivatives of BPP have the largest HOFs among the three kinds of derivatives; while the ONO_2 derivatives have the lowest HOFs. The HOFs of the title compounds have a linear relationship with the substituted number. The values of HOFs for CN and NC derivatives increase with n and are affected by the relative position of the substitution groups while the HOFs of ONO_2 derivatives decrease with n.

(2) The densities and detonation properties of CN and NC derivatives cannot meet the demand of HEDCs, revealing that CN and NC groups are not ideal compositions for the constitution of HEDCs. In comparison, derivatives with more than six ONO_2 groups meet the energy criteria of HEDCs and are considered to be potential candidates of HEDCs. As a whole, ρ, D, and P of the title compounds all increase with n, revealing that the increase of n will benefit the energetic performance. The position of the substituted groups has little influence on the values of ρ, D, and P.

(3) C−C bond in the skeleton is the trigger bond in the pyrolysis process for BPP derivatives with CN and NC groups, and these two kinds of derivatives have good thermal stabilities as judged by the large values of BDE^0_{C-C}. The breaking of $O-NO_2$ bond is the first pyrolysis step for ONO_2 derivatives. The values of BDE_{O-NO2} are mostly in the range of 80−120 kJ·mol^{-1}, revealing that these kinds of compounds have medium thermal stability.

(4) The studied BPP derivatives with 6−8 ONO_2 groups meet the demands of HEDC and are finally recommended as candidates of HEDC. These target compounds with good performances are worthy of synthesis and further investigation.

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