ORIGINAL PAPER

Theoretical investigation on detonation performances and thermodynamic stabilities of the prismane derivatives

Wei-Jie Chi · Lu-Lin Li · Bu-Tong Li · Hai-Shun Wu

Abstract Based on DFT-B3LYP/6-311G** method, the molecular geometric structures of polynitramineprismanes are fully optimized. The detonation performances, energy gaps, strain energies, as well as their stability were investigated to look for high energy density compounds (HEDCs). Our results show that all polynitramineprismanes have high and positive heat of formation. To construct the relationship between stabilities and structures, energy gaps and bond dissociation energies are calculated, and these results show that the energy gaps of prismane derivatives are much higher than that of TATB (0.1630). In addition, the C-C bonds on cage are confirmed as trigger bond in explosive reaction. All polynitramineprismanes have large strain energies, and the strain energies of all compounds are slightly smaller than prismane, which indicated that the strain energies were somewhat released compared to prismane. Considering the quantitative criteria of HEDCs, hexanitramineprismane is a good candidate of high energy compounds.

Keywords Detonation performance · High energy density compounds · Isodesmic reaction · Nitramine group · Prismane derivatives · Strain energies

Introduction

In the field of high-energy materials, the synthesis and development of new energetic materials continues to focus on new heterocycles and cage compounds with high density, high heats of formation and good oxygen balance [1–5].

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Combined with the development of solid propellants and explosives, improving the energetic level of the solid propellants and explosives becomes the main research orientations and the key step of technology in the future. Properties are often manipulated by making structural modifications. The optimization of molecules with high energy and density is the primary step for searching and synthesizing high energy density compounds (HEDCs). As the HEDCs, experimental synthesis is not only dangerous but also hazardous to humans and the environment. However, computer simulation, an effective way in screening promising explosives without these shortcomings, has been used to design various new energetic materials.

Polysubstituted cage compounds are investigated as an important category of HEDCs due to high strain energies, compact structures and self-oxidizability [6–8]. The typical characteristics of these kind of compounds are their heats of formation (HOFs) which can produce high explosive energies. On the other hand, compounds with compact structure usually have higher densities and can also release additional energies upon detonation as a consequence of cage strain in these systems. Among various types of HEDCs, the well-know CL-20 (hexanitrohexaazaisowurtzitane) [9] and ONC (octanitrocubane) [10, 11] are typical examples of the cage compounds and their successful synthesis is regarded as a breakthrough in the history of explosives. Recently, highly symmetrical polyhedral hydrocarbons have attracted special interest from chemists because of their highly strained structures. Such molecules are important with regard to both their fundamental chemistry as well as possible technological applications.

Prismane is a hydrocarbon with a large ring strain energy of 606.9 kJmol^{-1} [12], which is an important requirement as HEDCs. Therefore, we selected the cage compounds prismane C_6H_6 - D_{3h} to design new energy compounds. Lately, many prismane derivatives have been studied in detail as

high-energy compounds, such as polyisocyanoprismanes [13] and polyazidoprismanes [14], besides the azaprismanes have been studied by Politzer et al. [15, 16]. Currently, we also theoretically researched the polynitroprismanes's characters systematically, and some potential HEDCs have been found [17].

Nitro compounds, as an important class of HEDCs, have attracted continuous attention due to their ability to endure the high temperature and low pressure encountered in space environments [18]. However, studies have shown that another nitrogen-containing group, which is nitramine (−NHNO₂) [19, 20], can also lead a molecule to a good potential high energy compound. The main difference between a nitro and a nitramine group is the nitrogen and hydrogen content. The superiority of nitramine is found that the high nitrogen content can lead to high crystal density and heats of formation, which is associated with increased denotation performance. In addition, in polynitramineprismanes derivatives, the hydrogen of content kept unchanged compared to prismane. So, the heat of combustion values of polynitramineprismanes can not decline.

In our work, the simplest approach is used to generate the prismane derivatives—the nitramine group replaced the hydrogen atom on the prismane skeleton. For these polynitramineprismanes, many properties are studied in detail at the DFT-B3LYP/6-311G** level. It is expected that our results could provide some useful information for laboratory synthesis of polynitramineprismanes and the development of new novel HEDCs.

Computation details

All geometries were optimized using G03 program package [21] on a desktop computer. All the molecules and the related radical species were fully optimized without any symmetry restrictions at the DFT-B3LYP/6-311G** level. To characterize the nature of stationary point and determine the zero-point vibrational energy corrections, harmonic vibrational analyses were performed subsequently.

Based on the obtained total energy (E_0), zero-point energy (ZPE) and thermal correction from 0 K to 298 K (ΔH_T). The isodesmic reaction [22–24] was used to obtain the HOFs of the polynitramineprismanes at 298 K:

$$C_6H_{6-n}(NHNO_2)_n + nCH_4 = C_6H_6 + nCH_3NHNO_2 (n = 1 - 6).$$
$$(1)$$
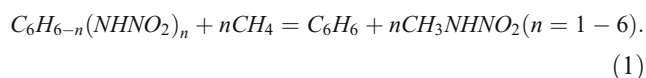
For the isoseismic reaction, enthalpy of reactions ΔH_{298} at 298 K can be calculated from the following equation:

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

where $\Delta H_{f,p}$ and $\Delta H_{f,R}$ are the HOFs of the reactants and products at 298 K respectively. The experimental HOFs of reference compound CH_4 and C_6H_6 are available from NIST Chemistry Book Website. However, the experimental HOFs of CH_3NHNO_2 is not available. So, another isodesmic reaction is used to get the HOF of CH_3NHNO_2.

$$CH_3NHNO_2 + CH_4 = CH_3NH_2 + CH_3NO_2$$
$$(3)$$

Thus, the HOFs of the polynitramineprismanes can be deduced when the heat of reaction ΔH_{298} is known. The ΔH_{298} can be calculated using the following formula.

$$\Delta H_{298} = \Delta E + \Delta ZPE + \Delta H_T + \Delta nRT$$
$$(4)$$

ΔE is the change in total energy between the reactants and products at 0 K. ΔZPE is the difference between the zero-point energy of reactants and products. The ΔH_T is the thermal correction from 0 to 298 K. ΔnRT is the work term, which equals zero here.

Base on the HOFs, the enthalpy of combustion can be obtained easily according to Eq. (5):

$$C_6H_{6-n}(NHNO_2)_n + (7.5 - n)O_2 = 6CO_2 + 3H_2O + nN_2.$$
$$(5)$$
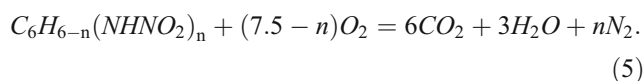
The enthalpy of formation of carbon dioxide and water were also obtained from the NIST Chemistry Book Website, and these values are −393.52 and −285.83 kJmol⁻¹, respectively. Division of the enthalpies of combustion obtained from reaction (5) by the mass of the molecule give the specific enthalpies of combustion.

The bonding strength, which could be evaluated by bond dissociation energy (BDE), is fundamental to understanding chemical processes. The energy required for bond cleavage at 298 K and 1 atm corresponds to the enthalpy of reaction (6).

$$A - B(g) \rightarrow A \bullet (g) + B \bullet (g)$$
$$(6)$$
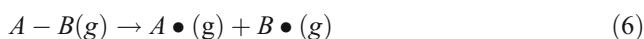
For many organics, "the bond dissociation energy" and "the bond dissociation enthalpy" is almost numerically equivalent. Therefore, the bond dissociation energy can be given in terms of Eq. (7).

$$BDE(A - B) = E(A\bullet) + E(B\bullet) - E(A - B)$$
$$(7)$$

The BDE with zero-point energy (ZPE) correction can be calculated via Eq. (8)

$$BDE(A - B)_{ZPE} = BDE(A - B) + \Delta ZPE,$$
$$(8)$$

where ΔZPE is the difference between the ΔPEs of the products and the reactions.

Strain is an important concept in structural organic chemistry. The concept of strain energy (SE) provides a basis that helps to correlate structures, stabilities and reactivities of molecules [25]. The method of homodesmotic reaction has

been employed very successfully to calculate SE from total energies (E0) and the zero-point energies(ZPE) obtained from *ab* initio calculations [26, 27]. In the homodesmotic reaction, not only are the number of bonds of various types conserved, but the valence environment around each atom is preserved as well. The homodesmotic reaction used to derive the SE of the title compounds are as follows:

$$C_6H_{6-m}(NHNO_2)_m + 9CH_3CH_3$$
$$\rightarrow (6-m)(CH_3)_3CH + m(CH_3)_3CNHNO_2, \qquad (9)$$
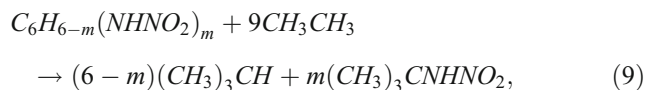
where m is the number of substituent groups in prismane derivatives molecules $C_6H_{6-m}(NO)_m$. The change of energies, with correction of zero-point vibrational energy (ZPE), in this homodesmotic reaction is:

$$\Delta E_n = \sum E_{product} - \sum E_{reac\,tant} + \Delta ZPE. \qquad (10)$$

We wish to define SE as a positive quantity. Therefore, we relate SE with $-\Delta E_n$ from Eq. (10) [28].

Detonation velocity (D), and detonation pressure (P) are the important parameters to evaluate the explosive performances of energetic materials. For the explosives with CHNO elements, these parameters can be calculated using the Kamlet–Jacbos (K–J) equations [29]:

$$D = 1.01\left(N\overline{M}^{1/2}Q^{1/2}\right)^{1/2}(1 + 1.30\rho_0) \qquad (11)$$

$$P = 1.558\rho_0^2 N\overline{M}^{1/2}Q^{1/2}. \qquad (12)$$

N is the moles of gaseous detonation products per gram of explosives; $\overline{M}$ is the average molecular weight of gaseous products. Q is the chemical energy of detonation ($cal\,g^{-1}$) defined as the difference between the heats of formation of the products and reactants of the most exothermic reactants. Where ρ is the density of explosives ($g\,cm^{-3}$).

As known to all, accurate prediction of crystal density is very difficult for the unknown explosives. "Group or volume additivity" method [30], although simple and rapid, cannot give reliable results owing to its inherent drawbacks; while the "crystal packing" method [31, 32], which is more reliable, has its limitation in routine calculation due to its extensive requirement in computational resources. However, previous studies have indicated that the theoretical density, which was calculated from the molar weight (M) divided by the average value molar volume (V), which was gained from the arithmetic average value of 100 singe point molar volumes, defined as the volume of 0.001 electrons Bohr^{-3} electron density [33] envelope and computed by Monte Carlo integration. However, the procedure used to estimate densities can lead to significant errors. Politzer [34,

35] and coworker considered that the solid density can be corrected by the electrostatic potential. The method is shown by Eqs. (13)–(17).

$$\text{Crystal density } (\rho_0) = \alpha(M/Vm) + \beta\left(\nu\sigma^2_{tot}\right) + \gamma \qquad (13)$$

$$\sigma^2_{tot} = \sigma^2_+ + \sigma^2_- = \frac{1}{m}\sum_{i=1}^{m}\left[V^+(r_i) - \overline{V}_s^+\right]^2$$
$$+ \frac{1}{n}\sum_{j=1}^{n}\left[V^-(r_j) - \overline{V}_s^-\right]^2 \qquad (14)$$

$$\nu = \sigma^2_+\sigma^2_-/\sigma^2_{tot}{}^2 \qquad (15)$$

$$V_S^+ = \frac{1}{m}\sum_{i=1}^{m}V^+(r_i) \qquad (16)$$

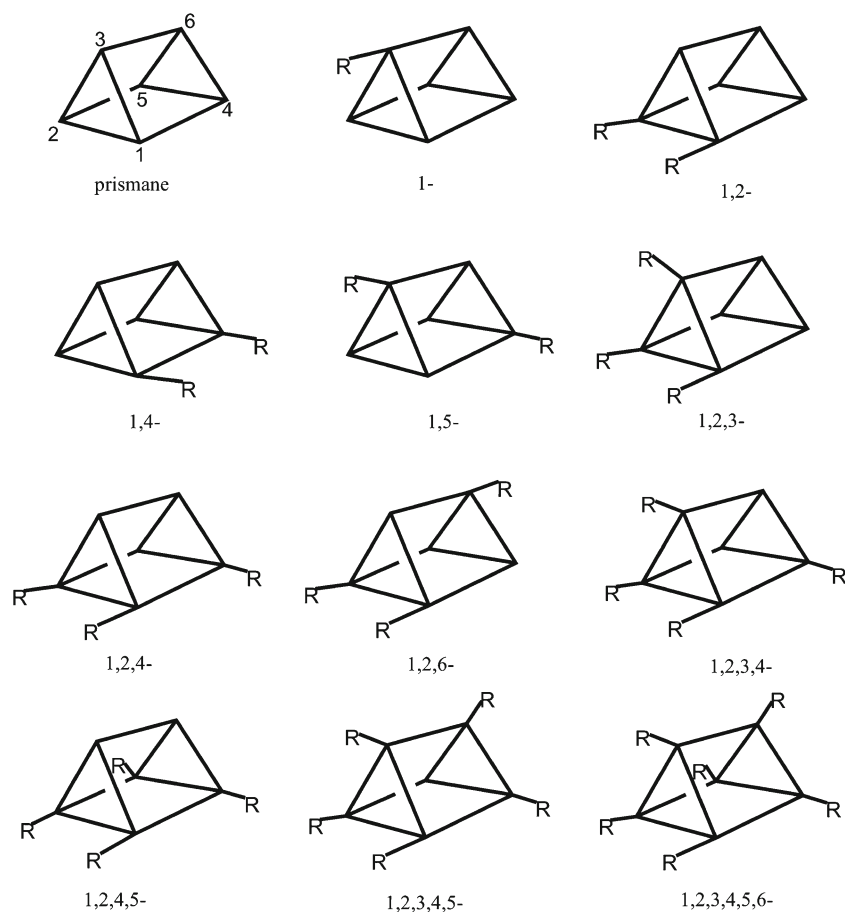$$V_S^- = \frac{1}{n}\sum_{j=1}^{n}V^-(r_j), \qquad (17)$$

where ν is balance parameter, V(r) is electrostatic potential, V(r_i) is the value of V(r) at any point r_i on the surface, $V_S^+(r_i)$ and $V_S^-(r_j)$ represent the positive and negative value of V(r) on the surface. $\overline{V}_S^+$ and $\overline{V}_S^-$ are their averages, σ^2_{tot} is the total variance.

Results and discussion

Heats of formation

Before discussing the results on polynitramineprismanes, all molecular structures are presented in Fig. 1. HOF is a prerequisite paramater for obtaining the detonation property, and it is usually the indicator of the 'energy content' of a HEDCs. The higher the HOF, the greater the energy stored in the molecule. Therefore, it is of great importance to predict HOFs accurately. However, obtaining HOFs of HEDCs experimentally is an extremely hazardous and difficult task. So, theoretical studies of HOFs are particularly important and necessary [36]. The use of isodesmic reactions, in which some of the bonds and electron pairs are effectively "swapped" during the reaction, leads to a much lower error in the calculated. Table 1 listed the total energy, zero-point energy, thermal corrections and HOFs of the reference compounds. Some calculated thermodynamic data (HOF and enthalpy of combustion) are listed in Table 2.

Fig. 1 Molecular frameworks of prismane and prismane derivatives [R=−NHNO$_2$]

The sixth column in Table 2 shows values for the enthalpy of combustion. It is found that more and more heat released with the number of nitramine group growing. The reason is that the number of carbon dioxide and water remain unchanged in the products. The seventh column in Table 2 shows values of the specific enthalpy of combustion, which is the molar enthalpy of combustion divided by the molar mass of the substance. We can find that as the number of nitramine groups in the molecule increases, the specific enthalpy of combustion values decreases. This is because the enhancing of the specific enthalpies of combustion of title molecules is more prominent than enthalpies of combustion as the substitution increasing.

Electronic structure

Table 3 listed the highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies, and the energy gaps ($\Delta E_{LUMO–HOMO}$) at the B3LYP/6-311G** level. From Table 3, it is interesting to note that all prismane derivatives decrease the $\Delta E_{LUMO–HOMO}$ of the unsubstituted prismane. Also, it is found that the HOMO energy levels decrease with the numbers of substitute group increasing, and there is a good linear relationship between the HOMO energy level and the number of nitramine group (n):

Inspecting the HOFs in Table 2, it is found that all polynitramineprismanes have high and positive HOF values, which is one of the necessary characteristics of high-energy compounds, consistent with previous reports in which high-nitrogen compounds have high HOFs. In addition, it is clear that there is a strong linear relationship between HOFs and number of nitramine groups (n): $HOF = 35.271n + 544.51 (R = 0.994, n = 1−6)$. It should be pointed out that the average HOFs are used for isomers. Thus, the contributions from the nitramine groups to the HOFs of the polynitramineprismanes clearly comply with the group additivity rule, and introducing an extra nitramine group increases the HOF by 35.271 kJmol^{-1}. It is noteworthy that there is little difference between HOFs despite the different location of substituent group for isomers.

Table 1 Calculated total energies (E$_0$, a.u), thermal corrections (H$_T$, a.u), zero-point energies (ZPE, a.u), and HOFs (kJmol^{-1}) for the reference compounds at B3LYP/6-311G** level

Compound	E$_0$	ZPE	H$_T$	HOF
C$_6$H$_6$	−232.11118	0.09670	0.00504	567.7
CH$_4$	−40.53374	0.04460	0.00382	−74.6
CH$_3$NHNO$_2$	−300.43445	0.06722	0.00622	−18.53

Table 2 Calculated total energies (E_0, a.u), thermal corrections (H_T, a.u), zero-point energies (ZPE, a.u), HOFs (kJmol^{-1}), enthalpies of combustion (H, kJmol^{-1}) and the specific enthalpies of combustion (H_c kJg^{-1}) for polynitramineprismances at B3LYP/6-311G** level

1-and 1,2-denote 1-nitramineprismane and 1,2-dinitramineprismane, respectively; the others are similar

Compounds	E_0	ZPE	H_T	HOF	H	Hc
1-	−492.02360	0.11635	0.00869	588.51	−3807.12	−27.59
1,2-	−751.93577	0.13601	0.01235	610.03	−3828.64	−19.34
1,4-	−751.93135	0.13571	0.01254	621.34	−3839.95	−19.39
1,5-	−751.93430	0.13581	0.01247	613.68	−3832.29	−19.36
1,2,3-	−1011.84813	0.15505	0.01633	630.26	−3848.87	−14.92
1,2,4-	−1011.84226	0.15514	0.01634	645.93	−3864.54	−14.98
1,2,6-	−1011.84518	0.15531	0.01623	638.43	−3857.04	−14.95
1,2,3,4-	−1271.75380	0.17425	0.02029	668.42	−3887.03	−12.22
1,2,4,5-	−1271.74253	0.17419	0.02030	697.88	−3916.49	−12.32
1,2,3,4,5-	−1531.65386	0.19341	0.02422	721.13	−3939.74	−10.42
1,2,3,4,5,6-	−1791.55844	0.21271	0.02811	762.24	−3980.85	−9.09

$HOMO = -0.0092n - 0.2526 (R = 0.959, n = 1-6)$. It is noteworthy that $\Delta E_{LUMO-HOMO}$ is small for the compounds with different number of substituted groups. In addition, we can find that the energy gaps of prismane derivatives are much higher than that of TATB (0.1630), which means prismane derivatives may be more sensitive. However, it is also worth noting that this stability refers to the photochemical processes with electron transfer or leap.

Bond dissociation energies

To find the relationship of impact sensitivity with the electronic structure properties of materials, many studies [37–41] have been carried out at the molecular level. The later works suggest that the dissociation energy of the weakest bond of the explosive molecule may play an important role in initiation events. BDE provides useful information for understanding the stability of the title compounds.

Table 3 Calculated, HOMO, LUMO energies (a.u), energy gaps ($\Delta E_{LUMO-HOMO}$) of the title compounds at B3LYP/6-311G** level

Compounds	E_{LUMO}	E_{HOMO}	ΔE
C_6H_6	0.05360	−0.23150	0.28510
1-	−0.05571	−0.25473	0.19902
1,2-	−0.07787	−0.27143	0.19356
1,4-	−0.06516	−0.27466	0.20950
1,5-	−0.06855	−0.27463	0.20608
1,2,3-	−0.08219	−0.28779	0.20560
1,2,4-	−0.08781	−0.28592	0.19811
1,2,6-	−0.08553	−0.28679	0.20126
1,2,3,4-	−0.09049	−0.29903	0.20854
1,2,4,5-	−0.08509	−0.28448	0.19939
1,2,3,4,5-	−0.09512	−0.29916	0.20404
1,2,3,4,5,6-	−0.10995	−0.30283	0.19288
TATB	−0.10280	−0.26480	0.16210

Generally, the smaller the energy for breaking a bond is, the weaker the bond is, and the easier the bond becomes a trigger bond; that is to say, the corresponding compound is more unstable, and its sensitivity is larger. Previous studies [42] on the BDE for the nitro compounds have shown that there is a parallel relationship between the BDE of the weakest $R-NO_2$ or $N-NO_2$ bond in the molecule and its sensitivity. However, this is only applicable to the molecules in which the $R-NO_2$ or $N-NO_2$ bond is the weakest one.

Bond order is a theoretical index of bonding capability between two atoms, and can be used as a measure of overall bond strength between two atoms. A high bond order value denotes a covalent bond, while a low bond order shows an ionic nature. The principle of the smallest bond order (PSBO) [43] points out that the chemical bond with the smallest bond order may be first ruptured in thermal decompositions. As you can find in literature, it is very successful to estimate the trigger bond with bond order. So, in this paper, the pyrolysis mechanism is predicted by PSBO. However, we also must be aware that the mechanism for the pyrolysis of cage compounds is linked to their molecular structure, and is not estimated by bond order simply in practice. For time saving, two possible bond dissociation locations have been considered: (1) the $C-NHNO_2$ bond on the side chain; (2) the $N-NO_2$ bond on the side chain; (3) the C-C bond in the cage. The BDEs of two kind of bonds are listed in Table 4.

Comparing BDE_{C-C} with BDE^0_{C-C}, it can be found that the BDE^0_{C-C} value shifts to the lower side by ca. 6 kJmol^{-1} when the ZPE is included. However, for BDE_{C-NHNO_2} and $BDE^0_{C-NHNO_2}$, we find that the BDE_{C-NHNO_2} values without zero-point energy corrections are larger than those including zero-point energy corrections by about 22 kJmol^{-1}. For the BDEs of N-NO2, BDE_{N-NO_2} are larger than $BDE^0_{N-NO_2}$ by about 23 kJmol^{-1}. Inspecting the values in Table 4, we can find that all bond orders of $C-NHNO_2$ and $N-NO_2$ bond are larger than that of C-C bond, which shows that bond

Table 4 Calculated bond dissociation energies (kJmol^{-1}) and bond order (B) for the possible rupture of the weakest C-NHNO$_2$, C-C and N-NO$_2$ bond at UB3LYP/6-311G** level

Compounds	B_{N-NO2}	BDE_{N-NO2}	BDE^0_{N-NO2}	$B_{C-NHNO2}$	$BDE_{C-NHNO2}$	$BDE^0_{C-NHNO2}$	B_{C-C}	BDE_{C-C}	BDE^0_{C-C}
1-	0.9976	228.29	203.84	1.0122	399.11	376.93	0.9384	107.12	100.98
1,2-	1.0024	223.17	198.53	1.0140	402.35	379.89	0.9075	80.58	76.39
1,4-	0.9831	218.77	194.54	1.0253	390.37	369.32	0.8970	186.54	180.54
1,5-	0.9931	227.08	203.21	1.0133	396.53	374.65	0.9369	113.19	106.78
1,2,3-	1.0170	234.81	211.16	1.0216	412.75	391.84	0.9129	99.66	95.46
1,2,4-	0.9776	215.31	191.84	1.0150	402.70	380.57	0.8913	196.36	189.81
1,2,6-	0.9947	229.76	206.31	1.0158	398.93	376.92	0.9118	97.25	93.12
1,2,3,4-	0.9806	220.84	197.52	1.0230	412.68	391.45	0.8856	198.02	191.37
1,2,4,5-	0.9678	215.84	192.22	1.0208	384.68	364.11	0.8891	168.43	160.12
1,2,3,4,5-	0.9618	188.12	164.96	1.0197	383.30	362.41	0.8828	206.47	200.14
1,2,3,4,5,6-	0.9648	206.67	183.04	1.0211	381.65	360.28	0.8746	206.02	199.79

BDE^0_{C-C} and BDE_{C-C} denotes the bond dissociation energy of C-C bond without and with zero-point correction, respectively; the same is with $BDE^0_{C-NHNO_2}$ and BDE_{C-NHNO_2}, BDE^0_{N-NO2} and BDE_{N-NO2}

strength of C-NHNO$_2$ and N-NO$_2$ bond are stronger than that of C-C bond. The result is consistent with BDE mentioned above. In other words, BDE of C-NHNO$_2$ and N-NO$_2$ bond are larger than that of C-C bond. These indicated that the C-C bond in cage can be seen as the trigger bond in explosive reaction. This is very similar with the pyrolysis mechanism of octanitrocubane [44]. It is noteworthy that the change of BDE is a bit confusing with the number of nitramine group growing. The main reason of such a situation is that a difference number of hydrogen bonds exist in the title compounds. According to the suggestion from Chung et al. [45], a molecule with dissociation barriers larger than 20 kcalmol^{-1} (83.68 kJmol^{-1}) can be considered as a viable candidate of HEDCs. Thus, we can conclude that most prismane derivatives meet the standard except 1,2-dinitramineprismane. However, we should be aware that BDE is a factor, but not the only one [46].

Strain energies

Strain energies can be defined as the difference between energies for a process that release strain as determined by experiment and as obtained from a model that does not involve strain. The advantage of using homodesmotic reaction is cancellation of errors, associated with truncation of the basis set and incomplete electron correlation recovery, present to a large extent. The method, which has been used in obtaining the strain energies of cubane and its derivatives, is very successful. The relevant values of reference compounds are listed in Table 5. SE values of the title compounds are listed in Table 6. In order to verify methods are reliable for prismane derivatives, we calculated the SE value of prismane at the B3LYP/6-311G** level via homodesmotic reaction at first, which is 619.52 kJmol^{-1}. The value

is in good agreement with 606.9 kJmol^{-1} from ref. [12]. From Table 6, it is found that all polynitramineprismanes have larger SE, ranging from 595.28 to 616.81 kJmol^{-1}, and there is not significant change with the number of substitute group increasing. So, the large SE is considered to be one of the factors for the high HOFs of prismane derivatives. To our astonishment, the SE of all compounds are slightly smaller than prismane, which indicated that the SE is somewhat released for prismane derivatives as compared to prismane itself. In addition, we should notice that the SE of the title compounds may be underrated due to the intermolecular interactions which have not been considered in homodesmotic reaction, such as hydrogen bond.

Explosive performance

For each title compound, explosive reaction is designed in terms of the maximal exothermal principle, that is, all the N atoms turn into N$_2$, the O atoms react with H atoms to give H$_2$O at first, and then form CO$_2$ with the C atom. If the number of O atoms is more than what is needed to oxidize H and C atoms, redundant O atoms will convert into O$_2$. If the number of atoms is not enough to satisfy full oxidation of the H and C atoms, the remaining H atoms will convert into H$_2$O, and the C atoms will exist as solid-state C. Halogen

Table 5 Calculated total energy (E$_0$, a.u) and zero-point energy (ZPE) of the reference compounds at the B3LYP/6-311G** level

Compounds	E_0	ZPE
CH$_3$CH$_3$	−79.85626	0.07437
(CH$_3$)$_3$CH	−158.50589	0.13095
(CH$_3$)$_3$CNHNO$_2$	−418.41238	0.15103

Table 6 Calculated strain energies (SE, kJmol^{-1}) of the title compounds at the B3LYP/6-311G** level via homodesmotic reactions

Compounds	SE
C$_6$H$_6$	619.90
1-	609.09
1,2-	595.28
1,4-	607.67
1,5-	599.66
1,2,3-	582.60
1,2,4-	597.77
1,2,6-	589.66
1,2,3,4-	587.06
1,2,4,5-	616.81
1,2,3,4,5-	606.36
1,2,3,4,5,6-	613.42

atoms form hydrogen halide with hydrogen atoms. Detonation velocity (D) and detonation pressure (P) are two important parameters for deciding the performance of the energetic materials. The Kamlet-Jacobs approach has been applied to estimate the detonation performance. Table 7 presents the calculated oxygen balance (OB$_{100}$), chemical energy of detonation (Q), D, and P. The experimental detonation parameters of the benchmark explosives like RDX (hexahydro-1,3,5-trinitro-1,3,5-trizine) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) are also listed in Table 7 for comparison. The oxygen balances (OB$_{100}$) are calculated using formula (13) [47], which can be used to roughly predict the impact sensitivities of the explosives.

$$OB_{100} = 100(2n_O - n_H - 2n_C - 2n_{COO})/M, \quad (13)$$

where n$_O$, n$_H$, and n$_C$ represent the numbers of O, H, and C atoms, respectively; n$_{COO}$ is the number of COO-, and

here n$_{COO}$=0 for the polynitramineprismanes; M is the molecular weight.

As shown in Table 7, all ρ are larger than ρ_0 by about 0.02–0.10 gcm^{-3}. In addition, ρ_0, D and P increase with the increasing number of nitramine groups generally. And there are good linear relationships between detonation performances and the numbers of substituent group (n), respectively: $\rho_0 = 0.069n + 1.404 (R = 0.991, n = 1 - 6)$, $D = 0.510n + 6.275 (R = 0.986, n = 1-6)$, and $P = 4.166n + 13.35 (R = 0.994, n = 1 - 6)$. That is to say, when one additional –NHNO$_2$ is introduced, ρ_0, D and P increase by about 0.069 gcm^{-3}, 0.510 ms^{-1} and 4.166 GPa, respectively. These show good group additivity on the detonation properties. It should be pointed out that the average values of ρ_0, D and P are used for isomers. Furthermore, we can also find that the positions of nitramine group have little influence on detonation property for isomers. Oxygen balance is another important criteria for selecting potential HEDCs. Table 7 shows the performance (D and P) of the polynitramineprismanes increase with the increasing OB. It is suggested that OB can be used to roughly predict the impact sensitivity of the explosives. The larger the OB, the higher the impact sensitivity. Therefore, it can be deduced roughly that the impact sensitivities of these prismane derivatives increase with the increasing nitramine groups. After comparing the D and P of all molecules in Table 7 each other, the detonation performances of tetranitramineprismanes, pentanitramineprismane approximate that of RDX, however, to our regret, except hexanitramineprismane, energy properties of other compounds are inferior compared to HMX. Considering the quantitative criteria of HEDC, that is, $\rho \approx 1.9 g/cm^3, D \approx 9.0 km/s, P \approx 40.0 GPa$, from Table 7, hexanitramineprismane approximates the standard and can be considered as potential HEDC. However, we must notice that that detonation pressure and velocity are

Table 7 Predicted detonation properties of the polynitramineprismanes at B3LYP/6-311G** level

Compounds	OB$_{100}$	ρ(g.cm^{-3})	ρ_0(g.cm^{-3})	Q(cal.g^{-1})	D(km.s^{-1})	P(Gpa)
1-	−10.15	1.46	1.44	1856.91	16.81	6.59
1,2-	−5.05	1.61	1.53	1849.61	21.62	7.34
1,4-	−5.05	1.61	1.54	1863.26	21.78	7.37
1,5-	−5.05	1.62	1.54	1854.01	21.69	7.35
1,2,3-	−2.33	1.73	1.62	1802.74	26.19	7.94
1,2,4-	−2.33	1.71	1.63	1817.25	26.54	7.98
1,2,6-	−2.33	1.72	1.62	1810.31	26.32	7.95
1,2,3,4-	−0.63	1.80	1.69	1787.03	30.50	8.45
1,2,4,5-	−0.63	1.80	1.72	1809.18	31.86	8.59
1,2,3,4,5-	0.53	1.85	1.75	1785.52	33.36	8.74
1,2,3,4,5,6-	1.37	1.90	1.83	1778.08	38.04	9.22
RDX[a]	0.00	1.78(1.82)		1591.03	8.87(8.75)	34.67(34.00)
HMX[a]	0.00	1.88(1.91)		1633.90	9.28(9.10)	39.19(39.00)

[a] The values of RDX and HMX taken from ref [20]

D and P are calculated based on ρ_0

overestimated if gas phase heats of formation instead of solid phase values are used. For instance, the solid phase heats of formation of high energy compounds have been predicted using the Politzer approach [48].

Conclusions

In this work, eleven prismane derivatives are designed and investigated using DFT-B3LYP method with 6–311G** basis set. The results show that all prismane derivatives possess large and positive HOFs. Large strain energies exist in this system, and the SE of all compounds are slightly smaller than parent prismane. The predicted detonation velocities and detonation pressures indicated that the nitramine group is an effective substituent for increasing the detonation performance, and hexanitramineprismane can become a candidate of high energy material.

The thermal stability and pysroysis mechanism of the title compounds are evaluated using the bond dissociation energies. The C-C bonds are the trigger bond in explosive reaction in the gas phase. The bond dissociation energies of prismane derivatives are over or near 80 kJmol^{-1}, which satisfies the requirement of HEDCs. The results of frontier orbital energy gaps show that all nitramine prismane derivatives may be lower sensitive than TATB.

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