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ORIGINAL PAPER

Density functional calculations for a high energy density compound of formula $C_6H_{6-n}(NO_2)_n$

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Abstract A series of polynitroprismanes, $C_6H_{6-n}(NO_2)_n$ (n=1–6) intended for use as high energy density compounds (HEDCs) were designed computationally. Their electronic structures, heats of formation, interactions between nitro groups, specific enthalpies of combustion, bond dissociation energies, and explosive performances (detonation velocities and detonation pressures) were calculated using density functional theory (DFT) with the 6-311 G** basis set. The results showed that all of the polynitroprismanes had high positive heats of formation that increased with the number of substitutions for the prismane derivatives, while the specific enthalpy of combustion decreased as the number of nitro groups increased. In addition, the range of enthalpy of combustion reducing is getting smaller. Interactions between *ortho* (vicinal) groups deviate from the group additivity rule and decrease as the number of nitro groups increases. In terms of thermodynamic stability, all of the polynitroprismanes had higher bond dissociation energies (BDEs) than RDX and HMX. Detonation velocities and detonation pressures were estimated using modified Kamlet–Jacobs equations based on the heat of detonation (Q) and the theoretical density of the molecule (ρ). It was found that ρ, D, and P are strongly linearly related to the number of nitro groups. Taking both their energetic properties and thermal stabilities into account, pentanitroprismane and hexanitroprismane are potential candidate HEDCs.

Keywords Polynitroprismanes · Density functional theory · Heats of formation · High energy density compound

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Introduction

High energy density compounds (HEDCs) have been widely used for both military and civilian applications [1–4]. In the last few decades, extensive theoretical studies have been performed on pure nitrogen clusters, because an all-nitrogen molecule N_x can undergo the reaction $N_x \rightarrow (x/2)N_2$, which can exothermic by 50 kcal mol^{-1} or more per nitrogen atom, making such clusters potential HEDCs [5–7]. However, theoretical studies have shown that many N_x molecules are not easily synthesized and are insufficiently stable to be practical HEDCs [8–10]. Besides these pure nitrogen clusters, some other heterocyclic compounds have also attracted considerable attention as possible HEDCs [11–13]. The characteristic feature of such heterocyclic compounds is that they release a great deal of energy upon the combustion of their carbon backbones or the release of cage strain compared to traditional and modern energetic compounds. Besides the interest in this characteristic of heterocyclic compounds, other unique features of such molecules have also attracted considerable attention, such as high densities and oxygen contents, and good thermal stabilities [14–18]. However, when attempting to identify new HEDCs, experimental synthesis is hazardous to humans and the environment. On the other hand, computer simulation provides an effective way to screen for promising explosives without having to deal with such dangers, so it has been used to design various new energetic materials. Therefore, when searching for new HEDCs, researchers generally perform molecular design via computational methods, and then use the results of that modeling to synthesize new and improved HEDCs.

Among the various types of HEDCs, organic cage compounds have attracted particular attention. CL-20 (hexanitrohexaazaisowurtzitane) [19] and polynitrocubane [20] are some well-known examples of cage compounds, and the successful synthesis of such compounds is generally 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 [21]. Lately, polyisocyanoprismanes and polyazidoprismanes have been studied by Xu Wen-Guo et al. [22, 23]. In addition, azaprismanes were studied by Politzer et al. in 1989 [24, 25]. Their studies show that these compounds could be used as high energy density materials.

Prismane itself has been synthesized and fully characterized, while several substituted derivatives of this hydrocarbon have also been characterized (see Fig. 1 for the structure of prismane and its derivatives). Prismane is a hydrocarbon with a large ring strain energy of 606.9 kJ mol^{-1}, which is an important requirement of HEDCs. Therefore, we selected the cage compound prismane (D_{3h}-C_6H_6) as the basis for designing new high energy density compounds.

Nitro compounds, an important class of HEDCs, have also long attracted attention from researchers due to their ability to endure the high temperatures and low pressures encountered in space [26]. Hence, in the present work, the H atoms in prismane were systematically replaced with nitro groups, generating the series of molecules $C_6H_{6-n}(NO_2)_n$ (n=1–6). The main difference between the nitro, isocyano, and azido functional groups is the amount of oxygen present. As far as combustion is concerned, the nitro group has an advantage. In addition, adding a nitro substituent can improve the detonation pressure, detonation velocity, and molecular density of the compound more effectively than adding either isocyano and azido groups. Thus, in the work described in this paper, the molecular electronic geometries, heats of formation, interactions between nitro groups, bond dissociation energies, specific enthalpies of combustion, and detonation performances of these polynitroprismanes were studied in detail at the B3LYP/6-311 G** level. Our results should provideuseful information for the laboratory synthesis of polynitroprismanes and the development of novel HEDCs.

Computational methods and details

The geometries of the polynitroprismanes were fully optimized without any symmetry restriction using density functional theory (DFT) at the B3LYP level with the 6-311 G** basis set in the Gaussian 03 software package [27]. Harmonic vibrational and natural bond orbital (NBO) [28] analyses were then performed at the same level of theory to confirm that the structures obtained corresponded to minima, and to determine the zero-point vibrational energy corrections.

The heats of formation (HOFs) of the compounds of interest are needed to calculate their detonation energies. In previous papers, isodesmic reactions have been very successfully employed to estimate the HOFs from the total energies obtained from ab initio calculations [29, 30]. Therefore, in our work, we also designed isodesmic reactions in which the basic structural unit of prismane was retained, but big molecules were changed into small ones in order to obtain HOFs.

The isodesmic reactions used to calculate the HOFs of the polynitroprismanes at 298 K were as follows:

$$C_6H_{6-n}(NO_2)_n + nCH_4 = C_6H_6 + nCH_3(NO_2)_n (n = 1-6). \tag{1}$$

For each isodesmic reaction, the HOF of the reaction ΔH_{298} at 298 K can be calculated using the following equation:

$$\Delta H_{298} = \Delta H_{f,p} - \Delta H_{f,R}. \tag{2}$$

Here, $\Delta H_{f,p}$ and $\Delta H_{f,R}$ are the heats of formation of the reactants and products at 298 K, respectively. The experimental HOFs of the reference compounds CH_4, CH_3NO_2, and C_6H_6 are available, which means that the HOFs of the polynitroprismanes can be calculated when the heat of reaction ΔH_{298} is known. ΔH_{298} can be calculated using the following formula:

$$\Delta H_{298} = \Delta E + \Delta ZPE + \Delta H_T + \Delta nRT. \tag{3}$$

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

Using the HOFs of the polynitroprismanes calculated from Eqs. 2 and 3, it is a straightforward process to determine the enthalpy of combustion using Eq. 4:

$$\begin{aligned} &C_6H_{6-n}(NO_2)_n + (7.5 - 1.25x)O_2 \\ &= 6CO_2 + (3 - 0.5x)H_2O + 0.5xN_2. \end{aligned} \tag{4}$$

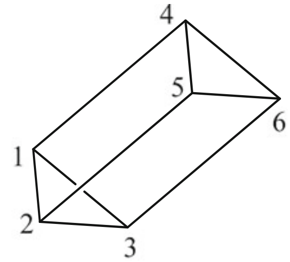
The enthalpies of formation of carbon dioxide and water were also obtained from the NIST Chemistry Book website; these values are −393.52 and −285.83 kJ mol^{-1}, respectively. Dividing the enthalpies of combustion obtained from Eq. 4 by the respective molecular masses yields the specific enthalpies of combustion.

To determine the strength of the interactions between the nitro groups, we computed the energy of disproportionation of the isodesmic reaction:

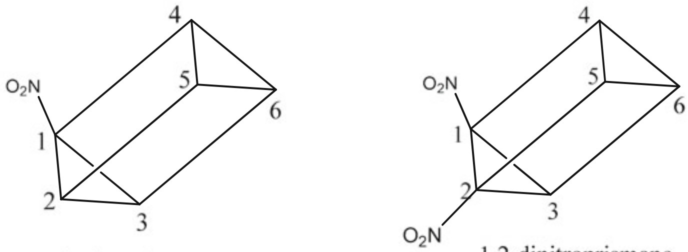
$$mC_6H_5(NO_2) \rightarrow (m-1)C_6H_6 + C_6H_{6-m}(NO_2)_m. \tag{5}$$

The strength of bonding, which can be evaluated using the bond dissociation energy (BDE), is

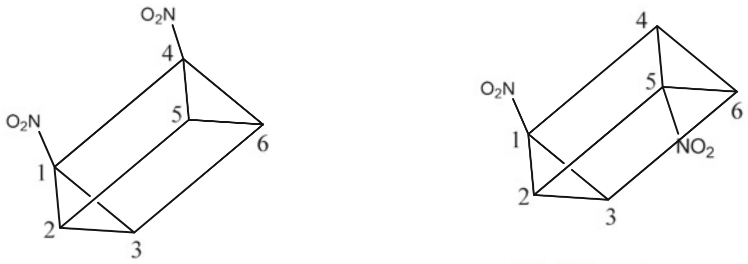
Fig. 1 Molecular framework and atomic numbering for prismane and its derivatives



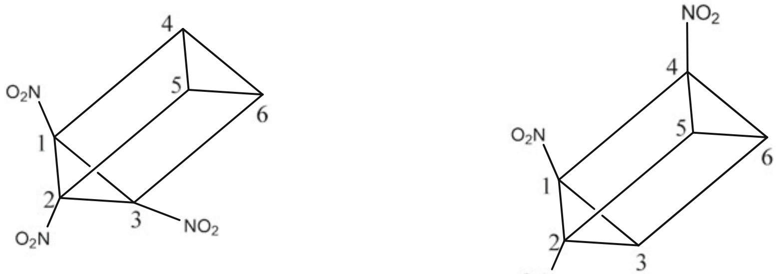
prismane



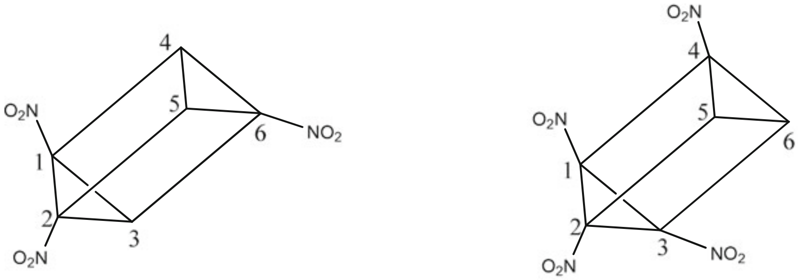
1-nitroprismane 1,2-dinitroprismane



1,4-dinitroprismane 1,5-dinitroprismane



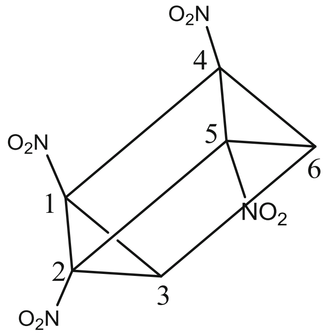
1,2,3-trinitroprismane 1,2,4-trinitroprismane



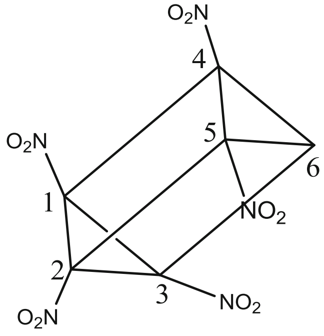
1,2,6-trinitroprismane 1,2,3,4-tetranitroprismane

fundamental to understanding chemical processes [31]. The thermal stabilities of the compounds of interest were evaluated by calculating the BDE of the trigger bond. At 0 K, the homolytic bond dissociation energy

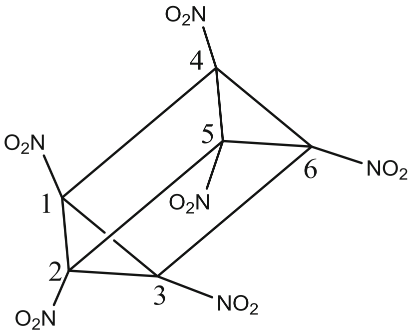
Fig. 1 (continued)



1,2,4,5-tetranotroprismane



1,2,3,4,5-pentanitroprismane



1,2,3,4,5,6-hexanitroprismane

can be obtained using Eq. 6:

$$\mathrm{BDE(A-B)} = E(\mathrm{A}\bullet) + E(\mathrm{B}\bullet) - E(\mathrm{A-B}). \tag{6}$$

The zero-point energy (ZPE) corrected BDE can be calculated via Eq. 7:

$$\mathrm{BDE(A-B)_{ZPE}} = \mathrm{BDE(A-B)} + \Delta\mathrm{ZPE} \tag{7}$$

Here, ΔZPE is the difference between the ZPE of the products and that of the reactants.

The loading density (ρ_0) is an important parameter to consider when HEDCs are designed. However, ρ_0 cannot be obtained for compounds that have not been synthesized. Therefore, in previous studies [32, 33], ρ_0 was replaced by the theoretical density (ρ), because ρ_0 is very close to ρ. Moreover, an electrostatic interaction correction that improves the accuracy of the predicted crystal density was also studied by Politzer et al. [25], and their results showed that the electrostatic interaction correction is useful for improving the accuracy of the crystal density for some high energy density compounds but not all of them. In our work, we needed molecular volume data to calculate the densities of the polynitroprismanes. The molecular volume was defined as the volume inside a contour of density 0.001 electrons/bohr^3, which was evaluated using Monte Carlo integration. This method has frequently been applied to HEDCs in previous studies [34, 35].

For each compound of interest, the explosive reaction was identified by applying the "most exothermic" principle; that is, all of the N atoms turn into N_2, while the O atoms initially react with H atoms to give H_2O before forming CO_2 with the C atom. If the number of O atoms present in the molecule is greater than the number needed to oxidize all of the H and C atoms, the "redundant" O atoms will combine to form O_2. On the other hand, if the number of O atoms is insufficient to allow full oxidation of the H and C atoms, the remaining H atoms will be incorporated into H_2O, while the remaining C atoms will exist as solid-state C. Halogen atoms form hydrogen halides with hydrogen atoms. Using the values of ρ and Q (the heat of detonation, which is evaluated from the difference between the HOFs of the products and the explosive via the principle of exothermic reactions; see Table 5), the fundamental detonation performance (the detonation velocity and detonation pressure) were obtained by the following Kamlet–Jacobs equations:

$$D = 1.01\left(N\overline{M}^{1/2}Q^{1/2}\right)^{1/2}(1 + 1.30\rho) \tag{8}$$

$$P = 1.558\rho^2 N\overline{M}Q^{1/2}. \tag{9}$$

Here, D is the detonation velocity, P is the detonation pressure, N is the moles of gaseous detonation products per gram of explosive, and $\overline{M}$ is the average molecular weight of the gaseous products.

Results and discussion

Electronic structure and stability

Figure 1 shows the numbering scheme for the polynitroprismanes. The numbering system used was such that the nitro groups were labeled with the smallest numbers possible that were still consistent with the numbering pattern shown in Fig. 1. There are a total of 11 structural isomers for these polynitroprismanes. Table 1 lists the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, the energy gaps ($\Delta E_{\mathrm{LUMO-HOMO}}$), and the Wiberg bond indices for C–NO_2 bonds, which were obtained by NBO analyses of prismane and the polynitroprismanes at the B3LYP/6-311 G** level. From Table 1, it is clear that the $\Delta E_{\mathrm{LUMO-HOMO}}$ values decrease as the number of nitro groups increases. It is interesting to note that all of the polynitroprismanes have lower $\Delta E_{\mathrm{LUMO-HOMO}}$ values than the unsubstituted prismane. Note that the $\Delta E_{\mathrm{LUMO-HOMO}}$ value of the 1,2-bisnitroprismane is slightly smaller than that of its isomer 1,5-bisnitroprismane. This shows that the 1,5-disnitroprismane is more stable than the 1,2-bisnitroprismane. It is also worth noting that stability refers to the stability of the compound to photoinitiated electron-transfer processes.

The fifth column in Table 1 shows the Wiberg bond indices for C–NO_2 bonds. This is a theoretical index of the degree of bonding between the two atoms. It can therefore be used as a measure of the overall strength of the bond between two atoms; on the whole, the larger the Wiberg bond index, the stronger the bond. In previous studies [36, 37], the C–NO_2 bond in a nitro derivative was found to have the smallest Wiberg bond index in a of any of the bonds in that derivative. Therefore, we have only listed the C–NO_2 bond indices in Table 1. In addition, the energies of the C–NO_2 bonds were calculated and are listed in this table. From Table 1, 1-nitroprismane has the highest bond order, whereas 1,2,3,4,5,6-hexanitroprismane has the lowest bond order; as the number of nitro groups in the molecule increases, the Wiberg bond index decreases, and thus the stability of the molecule decreases. Hence, according to the "principle of the smallest bond order" (PSBO) [38], hexanitroprismane has the smallest bond order (i.e., bond index) of 0.8876, meaning that it is very sensitive and relatively unstable to thermolysis. It is clear that the energies of the C–NO_2 bonds decrease as the bond index declines. This result also shows that the PSBO is a reliable estimator of the bond dissociation energy.

Table 1 Calculated HOMO and LUMO energies (a.u), energy gaps ($\Delta E_{\mathrm{LUMO-HOMO}}$), average Wiberg bond indices for C–NO_2 bonds ($P_{\mathrm{C-N}}$), and bond energies (kJ mol^{-1}) of polynitroprismanes at the B3LYP/6-311 G** level

Compound[a]	E_{HOMO}	E_{LUMO}	$\Delta E_{\mathrm{LUMO-HOMO}}$	$P_{\mathrm{C-N}}$	Bond energy
1-	−0.2677	−0.0709	0.1968	0.9428	306.68
1,2-	−0.2977	−0.1063	0.1914	0.9204	272.82
1,4-	−0.2930	−0.0967	0.1963	0.9304	278.22
1,5-	−0.3009	−0.0942	0.2067	0.9290	295.50
1,2,3-	−0.3164	−0.1302	0.1862	0.9209	256.83
1,2,4-	−0.3158	−0.1242	0.1916	0.9135	256.80
1,2,6-	−0.3237	−0.1248	0.1989	0.9226	263.78
1,2,3,4-	−0.3318	−0.1407	0.1911	0.9034	245.48
1,2,4,5-	−0.3287	−0.1405	0.1882	0.9025	251.94
1,2,3,4,5-	−0.3439	−0.1572	0.1867	0.8925	241.80
1,2,3,4,5,6-	−0.3556	−0.1726	0.1830	0.8876	240.84
C_6H_5	−0.2315	0.0536	0.2851		

[a] *1-* denotes 1-nitroprismane, *1,2-* denotes 1,2-isocyanoprismane, and so on

Looking at the $\Delta E_{\mathrm{LUMO-HOMO}}$ and Wiberg bond index values, it is interesting to note that the $P_{\mathrm{C-N}}$ of 1,5-dinitroprismane is relatively low (0.9290) but that it has a high $\Delta E_{\mathrm{LUMO-HOMO}}$. On the other hand, 1,4-dinitroprismane has a high bond order of 0.9304 but a lower $\Delta E_{\mathrm{LUMO-HOMO}}$ value than that of 1,5-dinitroprismane. This result shows that the thermal stability of a polynitroprismane is not solely related to its bond index or $\Delta E_{\mathrm{LUMO-HOMO}}$ value.

Heat of formation and enthalpy of combustion

The HOF is the most practical parameter for experimentalists to use to determine the energetic properties of a chemical system. The higher the HOF, the greater the energy stored by the molecule. However, obtaining HOFs of HEDCs experimentally is an extremely hazardous and difficult task, so, theoretical studies of HOFs are particularly important and necessary. The use of isodesmic reactions, in which some of the bonds and electron pairs are effectively "swapped" during the reaction (i.e., no bonds or electron pairs are lost or created overall), leads to a much lower error in the calculated value of the HOF than the error obtained when atomization reactions are considered. The total molecular energies, the zero-point energies, and the values of the thermal correction at the B3LYP/6-311 G** level for three reference compounds are listed in Table 2. Table 3 presents the HOFs of the polynitroprismanes that were calculated at the B3LYP/6-311 G** level.

From Table 3, it is clear that there are strong linear relationships between ZPE and n and between HOF and n for polynitroprismanes: $\mathrm{ZPE} = 5.3474n + 256.48(R = 0.998, n = 1-6)$; $\mathrm{HOF} = 90.912n + 457.02(R = 0.989, n = 1-6)$. It should be pointed out that the average ZPE and HOF values were used for isomers. Inspecting the HOFs, we can see that

Table 2 Total energies (E, a.u.), zero-point energies (E_{ZPE}, kJ mol^{-1}), thermal corrections (H_T, kJ mol^{-1}), and heat of formation (HOF, kJ mol^{-1}) values of the reference compounds, calculated at the B3LYP/6-311 G** level

Compound	E	E_{ZPE}	H_T	HOF
C_6H_6	−232.11118	253.89	13.22	567.7
CH_3NO_2	−245.08167	130.42	14.15	−22.50[a]
CH_4	−40.53374	117.09	10.03	−74.60[a]

[a] Values taken from [22, 23]

the polynitroprismanes have highly positive HOFs, and that the HOFs become larger as the number of nitro groups is increased. Thus, the contributions of the nitro groups to the HOFs of the polynitroprismanes clearly comply with the group additivity rule, and introducing an extra nitro group increases the HOF by 90.912 kJ mol^{-1}. As isomers with the same number of nitro groups have different HOF values, it is also clear that the HOF is affected by the position of the nitro group. Generally speaking, the closer the nitro groups are to one another, the higher the HOF; in other words, the lower the thermodynamic stability. For example, in 1,2,3-trinitroprismane, the three nitro groups are located on the same three-membered ring and are therefore close to each other, leading to a relatively high HOF. However, the three nitro groups of 1,2,6-trinitroprismane are not bonded to the same ring, so they are further apart, leading to a relatively low HOF. In other words, the 1,2,6-trinitroprismane has better thermodynamic stability.

The sixth column in Table 3 shows values for the specific enthalpy of combustion, which is the molar enthalpy of combustion divided by the molar mass of the substance. As the number of nitro groups in the molecule increases, the specific enthalpy of combustion decreases. This is due to the fact that we are replacing hydrogen atoms, each of which contributes roughly about 8 kJ g^{-1} of energy upon combustion through the formation of water. Steric hindrance compensates for some of the lost 8 kJ g^{-1}, but not enough to compensate for the energy lost when a hydrogen is replaced by a nitro group. This means that highly nitro-substituted molecules release less combustion energy than less-substituted molecules.

Table 3 Total energies (E, a.u.), zero-point energies (E_{ZPE}, kJ mol^{-1}), and thermal corrections (H_T, kJ mol^{-1}) for the polynitroprismanes, calculated at the B3LYP/6-311 G** level. The HOF values (kJ mol^{-1}) and ΔH_{comb} values (kJ g^{-1}) were obtained using Eqs. 2, 3, and 4

Compound[a]	E	E_{ZPE}	H_T	HOF	ΔH_{comb}
1-	−436.67041	261.11	19.85	585.84	−29.77
1,2-	−641.21358	267.13	27.04	646.19	−21.30
1,4-	−641.21564	267.42	26.99	641.00	−20.80
1,5-	−641.22222	267.69	26.87	623.89	−21.17
1,2,3-	−845.74625	272.80	34.42	733.95	−16.54
1,2,4-	−845.75453	273.19	34.34	712.53	−16.44
1,2,6-	−845.76026	273.12	34.34	697.41	−16.37
1,2,3,4-	−1050.28516	278.50	41.95	805.52	−13.28
1,2,4,5-	−1050.28385	278.30	41.96	808.77	−13.39
1,2,3,4,5-	−1254.81270	283.34	49.59	906.77	−11.27
1,2,3,4,5,6-	−1459.33505	287.91	57.33	1026.13	−9.73

[a] *1-* denotes 1-nitroprismane, *1,2-* denotes 1,2-isocyanoprismane, and so on

Interactions among the nitro groups in the polynitroprismanes

The disproportionation energies $E_{disproportion}$ of the compounds of interest are shown in Table 4. These values show that the distances between the nitro groups influence the interactions, and the interactions between adjacent groups are much stronger than those between *meta* groups. For the polynitroprismanes, interactions can occur between adjacent groups (vicinal and distal groups) and *meta* groups. For 1,2,3-trinitroprismane, which includes three adjacent nitro groups, a value of 37.30 kJ mol^{-1} is obtained when the disproportionation energy of this compound is divided by 3. For 1,2,4-trinitroprismane, there is one *meta* nitro group and two *ortho* (one vicinal and one distal) nitro groups. The interaction of the *meta* nitro group was estimated from the disproportionation energy of 1,5-dinitroprismane, and the interaction of the distal nitro group was calculated based on the disproportionation energy of 1,4-dinitroprismane. Subtracting their energies from the disproportionation energy of 1,2,4-trinitroprismane yields a value of 33.92 kJ mol^{-1}. A value of 36.16 kJ mol^{-1} is obtained in a similar

Table 4 Disproportionation energies ($E_{disproportion}$, kJ mol^{-1}) of the polynitroprismanes, and average NBO charges on $-NO_2$ groups at the B3LYP/6-311 G** level

Compound[a]	$E_{disproportion}$	Average NBO charge on a nitro group
1-	0	−0.271
1,2-	42.17	−0.213
1,4-	36.76	−0.224
1,5-	19.48	−0.236
1,2,3-	111.90	−0.170
1,2,4-	90.16	−0.187
1,2,6-	75.12	−0.195
1,2,3,4-	165.25	−0.154
1,2,4,5-	168.69	−0.154
1,2,3,4,5-	248.45	−0.132
1,2,3,4,5,6-	345.28	−0.108

[a] *1-* denotes 1-nitroprismane, *1,2-* denotes 1,2-isocyanoprismane, and so on

manner for 1,2,6-trinitroprismane. These values are evidently smaller than that for 1,2-dinitroprismane (42.17 kJ mol^{-1}). This indicates that the vicinal nitro group interaction is influenced by the positions at which the nitro groups are attached to the prismane frame. Steric hindrance is another important factor in this respect.

The energy for the disproportionation of two molecules of trinitroprismane to hexanitroprismane plus prismane was computed in order to evaluate the magnitude of the vicinal nitro group interaction in hexanitroprismane, using the following formula:

$$1{,}2{,}6-\text{Trinitroprismane}+1{,}2{,}6-\text{trinitroprismane}$$
$$=\text{hexanitroprismane}+\text{prismane}.$$

The energy of this isodesmic reaction was calculated to be 195.05 kJ mol^{-1} at the B3LYP/6-311 G** level. The energy change relates to three interactions between distal groups, two interactions between *meta* groups, and four interactions between vicinal groups. According to the above method of estimating the energy, the three distal interactions can be calculated as three times the disproportionation energy of 1,4-dinitroprismane, which gives a value of 110.28 kJ mol^{-1}. A value of 38.96 kJ mol^{-1} is obtained in a similar manner for the two *meta* interactions, which is equal to twice the disproportionation energy of 1,5-dinitroprismane. Subtracting these energies from the disproportionation energy of hexanitroprismane gives a value of 45.81 kJ mol^{-1}, which is the combined total for the four vicinal group interactions in hexanitroprismane. The average energy of each of these interactions is 11.45 kJ mol^{-1}. Note that this value is 30.92 kJ mol^{-1} smaller than the value (42.17 kJ mol^{-1}) for the interaction in 1,2-dinitroprismane, which shows that the vicinal interaction deviates from the group additivity rule in that it decreases as the number of nitro groups increases. The table also shows that the average NBO charge on the NO_2 group decreases as the number of nitro groups increases. There is the same trend for the average charge on the NO_2 group as for the HOF as the number of nitro groups increases. We can therefore deduce that the vicinal group interaction is partly electrostatic.

Bond dissociation energy

The bond dissociation energy (BDE) is a key parameter for estimating the thermodynamic stability, and it can provide useful information for understanding the stability of a compound. Generally speaking, the smaller the BDE, the more labile the bond. Therefore, the BDE is directly related to the stability of energetic compounds. Owens [31] reported that R–NO_2 bond scission is usually the initial step in thermolysis for a number of different families of energetic compounds. However, we also should note that such trigger bonds are not the only possible route to decomposition for some high energy density compounds [39]. The Mulliken net charge on the nitro group (Q_{NO_2}) reflects the ability of the –NO_2 group to attract electrons, and therefore the stability of the molecule. It should be pointed out that we select the weakest bond (R–NO_2) as the trigger bond based on Mulliken population analyses [40–43]. Table 5 lists the BDE and BDE^0 values of the polynitroprismanes at the B3LYP/6-311 G** level. For comparative purposes, the BDE^0 values of RDX (cyclotrimethylenetrinitramine) and HMX (cyclotetramethylene tetranitramine) also are listed in Table 5.

In Table 5, if we contrast the BDE and BDE^0 values, we can see that the BDE values that have not been corrected for the zero-point energy are larger than those that include the correction. However, the trend in the dissociation energy is not affected by the zero-point energy. Compared with the commonly used explosives RDX and HMX, all of the polynitroprismanes have higher BDE^0 values. This implies that they have good thermodynamic stabilities. The BDE^0 value decreases as the number of nitro groups increases, but the Mulliken net charge on a nitro group increases, consistent with the BDE^0 values. Therefore, the thermal stability was estimated via the Mulliken net charge on a nitro group, which is reliable. That results show that the thermodynamic stabilities of the compounds of interest decrease as the number of substituents increases [44]. Nonetheless, the BDE^0 values of all of the compounds shown are over 120 kJ mol^{-1} (the cut-off value for an HEDC), meaning that they can all be considered HEDCs [45].

Table 5 Calculated bond dissociation energies (BDE, kJ mol^{-1}) for the rupture of the weakest bond, and the charge on a nitro group (Q_{NO2}), for various HEDCs of interest, calculated at the B3LUP/6-311 G** level

Compound[a]	Q_{NO2}	BDE	BDE^0
1-	−0.378	306.68	286.10
1,2-	−0.323	272.82	253.31
1,4-	−0.340	278.22	255.09
1,5-	−0.341	295.50	275.43
1,2,3-	−0.285	256.83	237.87
1,2,4-	−0.286	256.80	238.10
1,2,6-	−0.295	263.78	245.02
1,2,3,4-	−0.246	245.48	227.15
1,2,4,5-	−0.266	251.94	233.60
1,2,3,4,5-	−0.236	241.80	223.61
1,2,3,4,5,6-	−0.226	240.84	222.60
RDX[b]			145.62
HMX[b]			160.41

[a] *1-* denotes 1-nitroprismane, *1,2-* denotes 1,2-isocyanoprismane, and so on

[b] Calculated values of RDX and HMX were taken from [46]

Explosive performance

Detonation velocity and detonation pressure are two important performance parameters for high-energy compounds. Several empirical methods have been applied to estimate these parameters. The Kamlet–Jacobs approach has proven to be reliable [46]. N, $\overline{M}$, and Q were obtained using the formulae shown in Table 6. The results calculated at the B3LYP/6-311 G** level using them are listed in Table 7. For comparative purposes, the experimental detonation performances of two known explosives (RDX and HMX) are also listed in this table.

As is evident in Table 7, we found that there are strong linear relationships between ρ and n, D and n, and P and n for polynitroprismanes: $\rho = 0.1014n + 1.42(R = 0.984, n = 1-6)$, $D = 0.7926n + 5.7493(R = 0.984, n = 1-6)$, $P = 6.8946n + 9.2873(R = 0.992, n = 1-6)$. It should be pointed out that the smallest values of the isomers were used. Clearly, ρ, D, and P generally increase as the number of nitro groups increase. Also, the relative positions of the nitro groups influence not only the HOFs but also the Q values. For instance, the two nitro groups are closer together in 1,2-dinitroprismane than in 1,4-dinitroprismane or in 1,5-dinitroprismane, so 1,2-dinitroprismane has the highest Q value among these isomers. The tetranitroprismane, pentanitroprismane, and hexanitroprismane all have higher D and P values than RDX, but only pentanitroprismane and hexanitroprismane show better detonation performance than HMX, one of the most widely used energetic ingredients in various high-performance explosives and propellant formulations. In addition, we also should note that detonation pressures and velocities are overestimated if gas-phase heats of formation are used instead of solid-phase values. For instance, the solid-phase heats of formation of high energy density compounds have been predicted using the approach of Politzer [47] and by Xuedong Gong et al. [48]. Therefore, if the polynitroprismanes were to be synthesized, they would be found to be a class of high energy density compounds.

Table 7 Predicted detonation properties of the polynitroprismanes and RDX and HMX calculated at the B3LYP/6-311 G** level

Compound[a]	ρ (g cm^{-3})	Q (kJ mol^{-1})	D (km s^{-1})	P (GPa)
1-	1.48	2078.17	6.27	15.39
1,2-	1.68	2167.20	7.49	23.88
1,4-	1.68	2159.82	7.49	23.83
1,5-	1.63	2135.47	7.31	22.31
1,2,3-	1.78	2224.07	8.47	31.59
1,2,4-	1.79	2200.03	8.48	31.80
1,2,6-	1.81	2183.06	8.52	32.36
1,2,3,4-	1.83	2246.10	9.04	36.63
1,2,4,5-	1.87	2249.11	9.18	38.25
1,2,3,4,5-	1.93	2285.00	9.90	45.77
1,2,3,4,5,6-	2.00	2326.28	10.15	48.61
RDX[b]	1.78(1.82)	1591.03	8.87(8.75)	34.67(34.00)
HMX[b]	1.88(1.91)	1633.90	9.28(9.10)	39.19(39.00)

[a] *1-* denotes 1-nitroprismane, *1,2-* denotes 1,2-isocyanoprismane, and so on

[b] Calculated values of RDX and HMX taken from [49]

Data in parentheses are experimental values taken from [50]

Conclusions

In this work, we have studied the electronic structures, heats of formation, interactions between nitro groups, specific enthalpies of combustion, thermal stabilities, and detonation performances of polynitroprismanes at the B3LYP/6-311 G** level. On the basis of this theoretical study, the following conclusions can be drawn:

(1) $\Delta E_{\text{LUMO–HOMO}}$ and the Wiberg bond order decrease as the number of nitro groups increases, and all of the polynitroprismanes show lower $\Delta E_{\text{LUMO–HOMO}}$ values than that of the unsubstituted prismane. However, the results also show that the thermal stabilities of the polynitroprismanes cannot be gauged using the bond order or $\Delta E_{\text{LUMO–HOMO}}$ alone.

(2) All of the polynitroprismanes have highly positive HOFs, and these HOFs show a strong linear relationship with the number of nitro groups. The HOFs are also influenced by the positions of the nitro groups in the compounds, leading to different HOFs for different isomers. The closer the nitro groups, the larger the HOFs. Furthermore, as the number of nitro groups increases, the specific enthalpy of combustion decreases, the range of enthalpy of combustion reducing is getting smaller.

Table 6 Formulae for calculating the values of N, $\overline{M}$, and Q for an explosive $C_aH_bO_cN_d$,

Parameters	Conditions (top row) and formulae to determine parameters (final three rows)
	$c \geq 2a + b/2$; $2a + b/2 > c \geq b/2$; $b/2 > c$
N	$(b + 2c + 2d)/4M$; $(b + 2c + 2d)/4M$; $(b + d)/2M$
$\overline{M}$	$4M/(b + 2c + 2d)$; $(56d + 88c - 8b)/(b + 2c + 2d)$; $(2b + 28d + 32c)/(b + d)$
$Q \times 10^{-3}$	$(28.9b + 94.05a + 0.239\Delta H_f^0)/M$; $[28.9b + 94.05(c/2 - b/4) + 0.239\Delta H_f^0]/M$; $(57.8c + 0.239\Delta H_f^0)/M$

M is the molecular weight of the compound (g mol^{-1})

(3) Vicinal group interactions deviate from the group additivity rule; the strength of this interaction decreases as the number of nitro groups increases. Moreover, the average NBO charge on an NO_2 group decreases as the number of nitro groups increases.
(4) In all of the polynitroprismanes, the bond dissociation energy (BDE^0) for the trigger bond is higher than those for RDX and HMX, which implies that the sensitivities of the polynitroprismanes are lower than those of RDX and HMX. The BDE^0 values of all of these compounds are over 120 kJ mol^{-1}, which means that they all meet the requirement for an HEDC.
(5) The calculated molecular densities, detonation velocities, and detonation pressures of the polynitroprismanes indicate that adding nitro groups is a very useful way to enhance their density and detonation performances, and ρ, D, and P all have strong linear relationships to the number of nitro groups. The polynitroprismanes with five or six nitro groups meet the demands of practical HEDCs, and can therefore be recommended as candidates for HEDCs. These compounds present good performance and are worthy of synthesis and further investigation. Our results should also provide some useful information for the molecular design of novel HEDCs.

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