

Looking for high energy density compounds among polynitraminecubanes

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

Received: 4 July 2012 / Accepted: 21 August 2012 / Published online: 9 September 2012
© Springer-Verlag 2012

Abstract Based on fully optimized geometric structures at DFT-B3LYP/6-311G** level, we calculated electronic structures, heats of formation, strain energies, bond dissociation energies and detonation performance (detonation velocity and detonation pressure) for a series of polynitraminecubanes. Our results have shown that energy gaps of cubane derivatives are much higher than that of triaminotrinitrobenzene (TATB), which means that cubane derivatives may be more sensitive than TATB. Polynitraminecubanes have high and positive heats of formation, and a good linear relationship between heats of formation and nitramine group numbers was presented. As the number of nitramine groups in the molecule increases, the enthalpies of combustion values are increasingly negative, but the specific enthalpy of combustion values decreases. It is found that all cubane derivatives have high strain energies, which are affected by the number and position of nitramine group. The calculated bond dissociation energies of C-NHNO₂ and C-C bond show that the C-C bond should be the trigger bond in the pyrolysis process. It is found that detonation velocity (*D*), detonation pressure (*P*) and molecule density (ρ) have good linear relationship with substituted group numbers. Heptanitraminecubane and octanitraminecubane have good detonation performance over 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), and they can be regarded as potential candidates of high energy density compounds (HEDCs). The results have not only shown that these compounds may be used as HEDCs, but also provide some useful information for further investigation.

Keywords Bond dissociation energy · Cubane · Detonation performance · Heats of formation · Nitramine group

Introduction

High energy density compounds (HEDCs) have attracted many attentions for their bright usage prospect in the fields of fuel, explosives and propellants [1–6]. The general characteristics of these potential materials include high density and energy, high nitrogen content, high positive heats of formation, low handling hazards (such as low sensitivity and low toxicity), strained rings and cages, and thermal stability [7–10]. Combined with the development of solid propellants and explosives at home and abroad, improving the energetic level of the solid propellants and explosives becomes the main research orientations and the key step of technology for the future. 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. Therefore, to make a breakthrough in HEDCs research, it is a key step to make molecular design and to synthesize new and excellent HEDCs. At present, a practical way to obtain a high energy compound is to substitute a compound or polymer chain with high energetic groups to increase detonation performance. In the past few decades, all-nitrogen molecules can not be a candidate of HEDCs, which had been proved by abundant theory works, owing to unstability [11–15]. Next, cage compounds have been studied widely, such as 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) and octanitrocubane (ONC). The typical characteristic of this kind of compounds is that they contain large numbers of oxygens, and obtain considerable energy from oxidation of carbons. Especially the

Wei-Jie Chi and Lu-Lin Li contributed equally to this work

W.-J. Chi · L.-L. Li · B.-T. Li (✉) · H.-S. Wu
School of Chemistry and Material Science,
Shanxi Normal University,
041004 Linfen, China
e-mail: butong.lee@gmail.com

cubane have made a foray in the area since the 1960s [16]. Cubane and its derivatives have been the subject of numerous investigations ever since Eaton's synthesis of the parent compound in 1964 [17].

There are some works on cubane derivatives as high energy compounds. Synthesized in 2000 from heptanitrocubane [18], octanitrocubane is a cubane derivative having excellent detonation performance. It is found that a larger strain energy and molecular density exist in octanitrocubane depending on the nitro group orientation. Except the polynitrocubane derivatives, polynitrosocubanes [19], polynitratocubanes [20], 2,4,6,8-Tetranitro-1,3,5,7-tetraazacubane [21, 22], and polydifluoroaminocubanes [23] have been widely studied. Some of their performances have been calculated in detail, such as heats of formation, bond dissociation energies, detonation performance and vibrational frequencies, and so on. These theoretical and experimental results show that cubane is a prominent parent structure in designing high energy molecules. So, it is necessary that cubane derivatives are studied more in depth.

Nitro compounds, as an important class of HEDCs, have attracted continuous attention due to their affect to improve detonation properties [24]. However, studies have shown that another nitrogen-containing group, which is nitramine ($-\text{NHNO}_2$), can also lead a molecule to a good potential high energy compound [25, 26]. The main difference of a nitro and nitramine group is the nitrogen and hydrogen of the content of the group. 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 polynitraminecubane derivatives, the hydrogen of content remained unchanged compared with cubane. So, the heat of combustion values of polynitraminecubane can not decline.

In our work, we suggested that the replacement of the hydrogen atoms of cubane molecule with nitramine groups would result in some new potential HEDCs. In addition the 1-nitraminecubane and 1,4-bis-nitraminecubane have been synthesized from the corresponding methylurethanes [27, 28]. For these polynitraminecubanes, many properties are studied in detail at DFT-B3LYP/6-311G** level. It is expected that our results could provide some useful information for laboratory synthesis of polynitraminecubanes and the development of new novel HEDCs.

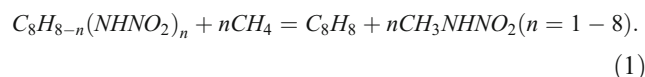
Computational details

All geometries are optimized using G03 program package [29] on a desktop computer. The calculation method used was the density functional theoretical (DFT) method using Beche's 3-parameter exchange functional plus the

correlation functional of Lee, Yang, and Parr (abbreviated B3LYP) [30] along with the standard Gaussian basis set labeled 6-311G** [31]. 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.

The heats of formation (HOFs) are needed in the calculation of detonation energy. The method of isodesmic reactions has been employed very successfully to calculate HOF [32, 33]. In isodesmic reaction, the number of each kind of formal bond is conserved, must comply with the bond separation reaction (BSR) rules. However, for cage compounds, usual bond separation reaction rules can engender large calculated errors of HOFs. Therefore, we design isodesmic reaction in which the numbers of all kinds of bonds remain invariable to decrease the calculation errors of the HOF. For these polynitraminecubane derivatives, the basic unit of cubane skeleton remains invariable, and the big molecules are changed into small ones too. This approach has been proved to be reliable [34].

The isodesmic reaction used to calculate the HOFs of the title compounds at 298 K may be written as:



For reaction (1), the heats of reaction (ΔH_{298}) can be calculated from the following Eq. 2.

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

Where $\Delta H_{f,p}$ and $\Delta H_{f,R}$ are the heats of formation of the reactants and products at 298 K respectively. The experimental HOFs of reference compounds CH_4 , C_8H_8 are available. However, for CH_3NHNO_2 , the experimental values cannot be obtained. So, its HOF was calculated from the following isodesmic reaction:



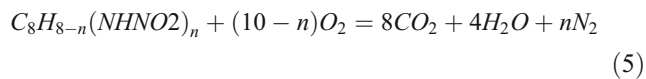
Thus, the HOFs of the polynitraminecubanes can be calculated out when the heat of reaction ΔH_{298} is known. The ΔH_{298} can be calculated using the following formula (3).

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

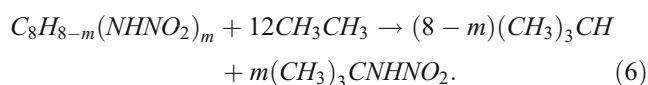
ΔE is the change in total energy between the reactants and products at 0 K. ΔZPE is the difference between the zero-point energy of reactants and products. The ΔH_T is the thermal correction from 0 to 298 K. ΔnRT is the work term, which equals zero here.

Using the HOFs of polynitraminecubanes obtained from Eqs. 2 and 4. Then it is a straightforward process to

determine the enthalpy of combustion using reaction (5). Here, we are following the modified Kistiakowsky-Wilson rules [35].



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. In previous studies, the method of the homodesmotic reaction has been employed very successfully to estimate the SE [36, 37]. 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 following:



Where m is the number of substituent groups in cubane derivatives. The change of energies, with correction of zero-point vibrational energy (ZPE), in this homodesmotic reaction is:

$$\Delta E_n = \sum E_{product} - \sum E_{reactant} + \Delta ZPE. \quad (7)$$

We wish to define SE as a positive quantity. Therefore, we relate SE with $-\Delta E_n$ for Eq. 7.

The strength of bonding, which can be evaluated by bond dissociation energy (BDE), is fundamental to understanding chemical processes. The thermal stabilities of the title compounds were evaluated by calculating BDE of the trigger bond. At 0 K, the homolytic bond dissociation energy can be given in terms of Eq. 8.

$$BDE(A - B) = E(A\bullet) + E(B\bullet) - E(A - B) \quad (8)$$

The bond dissociation energy with zero-point energy (ZPE) correction can be calculated via Eq. 9.

$$BDE(A - B)_{ZPE} = BDE(A - B) + \Delta ZPE \quad (9)$$

Where ΔZPE is the ZPEs difference between the products and the reactants.

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_2O 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 the atoms is not enough to satisfy full oxidation of the H and C atoms, then the remaining H atoms will convert into H_2O , and the C atoms will exist as solid-state C.

Halogen atoms form hydrogen halide with hydrogen atoms. For the C-H-N-O explosives, the detonation velocity (D) and detonation pressure (P) were estimated by empirical Kamlet-Jacobs formula (10) and (11).

$$D = 1.01 \left(N \bar{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30\rho) \quad (10)$$

$$P = 1.558\rho^2 N \bar{M}^{1/2} Q^{1/2} \quad (11)$$

N is the moles of gaseous detonation products per gram of explosives; \bar{M} is the average molecular weight of gaseous products. Q is the chemical energy of detonation (cal/g) 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), 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 single point molar volumes, defined as the volume of 0.001 electrons/Bohr³ electron density envelope and computed by Monte Carlo integration. Moreover, an electrostatic interaction correction for improved crystal density prediction also had been studied by Peter Politzer et al. [38], and the result shows that the electrostatic interaction correction has advantageous influence for the crystal density of some high energy compounds, but not all.

Results and discussion

Electronic structure

Before discussing the results on polynitraminecubanes, all molecular structures are presented in Fig. 1. The band gap of HEDCs is closely related to the molecular orbital energy level in a single molecule. This is the reason for the belief that band gap closing may be the initiation step for the detonation of explosives [39]. Table 1 listed the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energies, and the energy gaps ($\Delta E_{LUMO-HOMO}$) at the B3LYP/6-311G** levels. From Table 1, it is found that $\Delta E_{LUMO-HOMO}$ values decrease as the nitramine group number increase. It is interesting to note that all polynitraminecubanes decrease $\Delta E_{LUMO-HOMO}$ of the unsubstituted cubane. In addition, the energy gaps of cubane derivatives are much higher than that of TATB (0.1630), which means cubane derivatives may be more sensitive than TATB. As for the two nitramine group isomers, the $\Delta E_{LUMO-HOMO}$ value of 1,2-isomer is slightly smaller, while that of 1,8-isomer is larger, indicating the latter may be slightly more stable than the former. It was

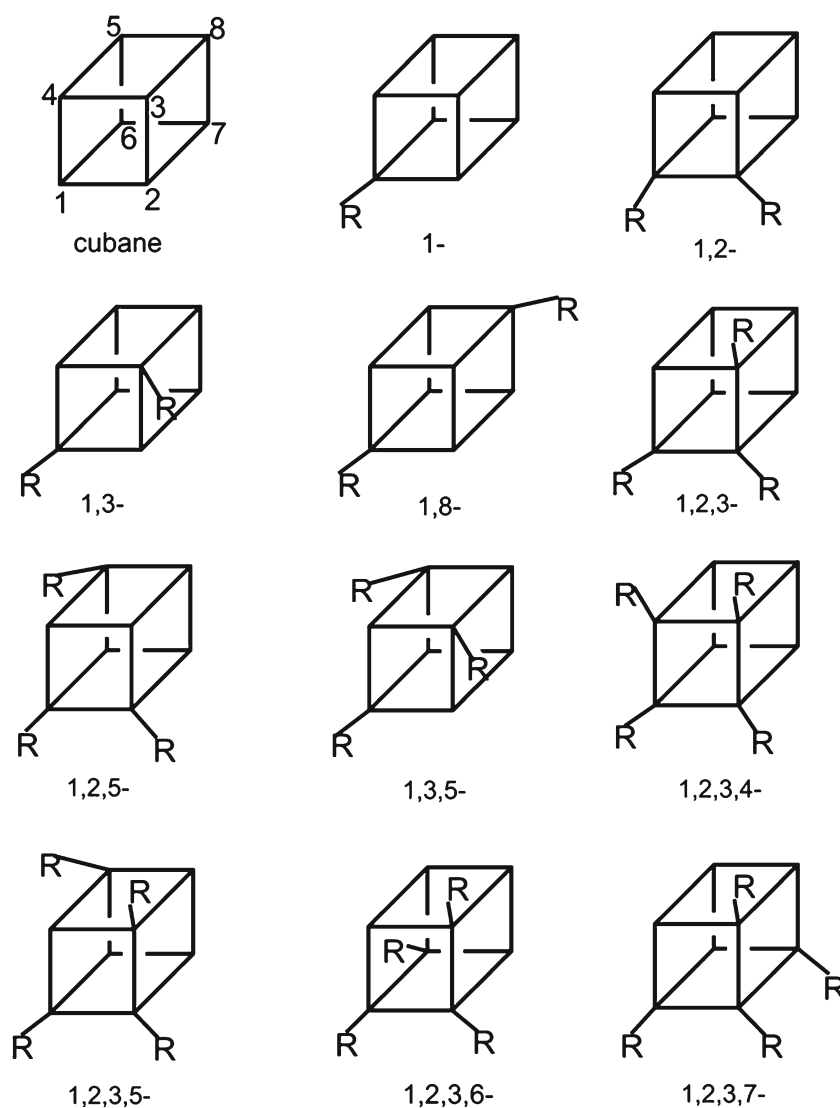


Fig. 1 Molecular frameworks of cubane and cubane derivatives [$R=-NHNO_2$]

proposed that the molecule with a larger energy gap is expected to have a lower reactivity in the chemical or photochemical processes with electron transfer or leap [40]. From the $\Delta E_{LUMO-HOMO}$ values, it can be deduced that the stability generally decreases as the substituent number increases.

Heats of formation

It is well-known that evaluation of the explosive performance of energetic materials requires knowledge of HOFs. Moreover, HOFs are of great importance for the researcher involved in thermochemistry. The molecular total energy, the zero-point energies and the values of the thermal correction at the B3LYP/6-311G** level for three reference compounds are listed in Table 2. Table 3 listed total energies, the zero-point energies, the values of the thermal correction,

HOFs enthalpies of combustion, and the specific enthalpies of combustion of the polynitraminecubanes at the B3LYP/6-311G** level. Previous studies showed that the theoretically predicted values of HOFs were in good agreement with experiments when the appropriate reference compounds in the isodesmic reaction were chosen. An efficient strategy of reducing errors of HOFs is to keep the conjugated bonds or cage skeletons unbroken. So, data in Table 3 are supposed to be credible, although the experimental values of HOFs are unavailable for comparison.

From Table 3, it is found that all cubane derivatives have high positive HOFs. The higher the molecular HOFs, the more the molecule stores energy. In addition, there is a good linear relationship between HOFs and n for polynitroprismanes: $HOFs = 40.892n + 579.98$ ($R = 0.9899, n = 1-8$), which indicated a good group additivity of HOFs for cubane derivatives. It should be pointed out that the minimum values of

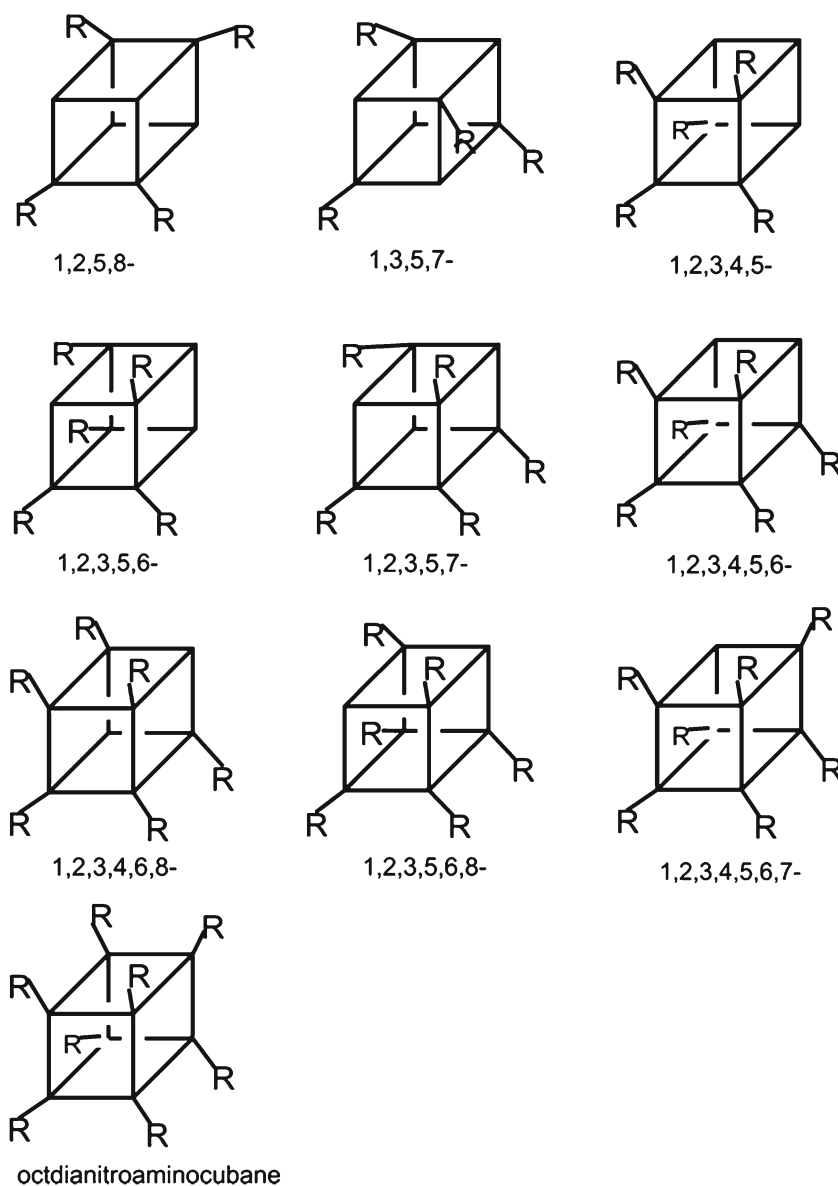


Fig. 1 (continued)

HOFs was used for the isomers. It can be seen that the effect of substituent on *HOFs* are affected by the position of the nitramine groups. Generally speaking, the closer the nitramine groups, the higher the *HOFs*, in other words, the thermodynamic stability is poor. For example, for the two nitramine groups cubane derivatives, the distance between two nitramine groups of 1,2-dinitraminecubane is more distant than that of 1,3- dinitraminecubane and 1,8- dinitraminecubane. So, 1,2-dinitraminecubane has the largest *HOFs* in all dinitraminecubanes.

The sixth numerical column in Table 3 shows enthalpies of combustion (H_{comb}) and the seventh numerical column shows the specific enthalpies of combustion (H_{specific}), which is the molar enthalpy of combustion divided by the molar mass of the substance. As the number of nitramine

groups in the molecule increases, the enthalpies of combustion values are increasingly negative. However, inspecting the specific enthalpies of combustion values, we can find that as the number of nitramine groups in the molecule increases, the specific enthalpy of combustion values decreases in magnitude. This is because the molecule weight increases faster than enthalpies of combustion as the substituted groups increase.

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 [37]. The advantage of using homodesmotic reaction is that the

Table 1 Energies of frontier molecules orbitals and their gaps of the title compounds

Compounds	HOMO	LUMO	ΔE
C ₈ H ₈	-0.044	0.263	0.307
1-	-0.262	-0.054	0.209
1,2-	-0.274	-0.074	0.199
1,3-	-0.269	-0.065	0.204
1,8-	-0.269	-0.064	0.205
1,2,3-	-0.267	-0.083	0.184
1,2,5-	-0.280	-0.077	0.204
1,3,5-	-0.276	-0.079	0.196
1,2,3,4-	-0.280	-0.099	0.180
1,2,3,5-	-0.279	-0.084	0.195
1,2,3,7-	-0.272	-0.094	0.178
1,2,3,8-	-0.275	-0.096	0.180
1,2,5,8-	-0.268	-0.081	0.187
1,3,5,7-	-0.282	-0.087	0.195
1,2,3,4,5-	-0.289	-0.102	0.187
1,2,3,5,6-	-0.276	-0.105	0.172
1,2,3,5,7-	-0.277	-0.097	0.180
1,2,3,4,5,6-	-0.296	-0.110	0.186
1,2,3,4,5,7-	-0.283	-0.105	0.178
1,2,3,5,6,8-	-0.282	-0.110	0.172
1,2,3,4,5,6,7-	-0.287	-0.113	0.173
Octanitraminecubane	-0.295	-0.123	0.172

1- and 1,2- denote 1-nitraminecubane and 1,2-dinitraminecubane, respectively; the others are similar

cancellation of errors, associated with truncation of the basis set and incomplete electron correlation recovery, occurring to a large extent. In addition, the method had been applied for calculating strain energy of cubane derivatives successfully, for example, polynitrocubanes and polynitratecubanes, and so on. So, the SE values of polynitraminecubanes are obtained by homodesmotic reaction. Table 4 lists SE values of the title compound. In order to verify the computational results at the B3LYP/6-311G** level via homodesmotic reaction are reliable for calculated SE values of cubane derivatives, the homodesmotic reaction is added: $C_8H_8 + 12CH_3CH_3 = 8(CH_3)_3CH$, we obtained the SE value of cubane, which is 691.75 kJmol⁻¹. The

Table 2 The total energy (E_0 , a.u), zero point energy (ZPE, a.u), values of thermal correction (H_T , kJmol⁻¹), heats of formation (HOF, kJmol⁻¹) of the reference compounds

Compounds	E_0	ZPE	H_T	HOF
C ₈ H ₈	-309.53146	0.13294	14.46	622.2
CH ₄	-40.52794	0.04484	10.00	-74.9
CH ₃ NHNO ₂	-300.43446	0.06739	16.43	-15.2 ^a

^a value are at the G2 level

value is in agreement with 679.94 kJmol⁻¹ from ref [41]. Inspecting the SE values of polynitraminecubanes, it is found that strain energies slightly changed with the increase of nitramine groups. Octanitraminecubane has the largest strain energy of 695.02 kJmol⁻¹ in the title compounds. For the isomers with same substituent group numbers, generally speaking, the shorter the distance between the nitramine groups, the stronger the repulsive energy, and the larger the SE. Such as in dinitraminecubanes, the SE value of 1,2-dinitraminecubane is slightly larger, while the SE values of 1,3- dinitraminecubane and 1,8-dinitraminecubane are smaller than 1,2-dinitraminecubane. It is indicated that the SE values are affected by the position of substituent groups.

Bond dissociation energies

Another main concern for explosives is whether they are kinetically stable enough to be of practical interest. So, research on the bond dissociation energies (BDE) is important and essential for understanding the decomposition process of high energetic materials. Generally, the smaller the BDE for breaking a bond is, the more easily the bond is broken [42].

Bond order is a measurement of the overall bond strength between two atoms. Previous research on nitro compounds have shown the breaking of R-NO₂ bond is usually the initial step in decomposition processes and there is a parallel correlation between BDE of the weakest R-NO₂ bond and compound's sensitivity [43, 44]. However, this is only applicable to the compound in which the R-NO₂ bond is the weakest one. For octanitrocubane, the pyrolysis initiation reaction is the rupture of the C-C bond in cube cage [45]. Nonetheless, we also should note that such trigger bonds are not a possible route to decomposition for some high energy materials [46]. For these molecules, in which the C-NO₂ bond has been contained or the strength of R-NO₂ bond cannot be used directly as an index of sensitivity, we should consider all bond energies, to determine the weakest one. However to save time, two possible bond dissociations have been considered: (1) the C-NHNO₂ bond on the side chain; (2) the C-C bond in the ring. It should be pointed out that among the same kind of bond, the weakest bond was selected as breaking bond on the principle of the smallest bond order (PSBO). Table 5 lists the bond dissociation energies of possible bonds.

Comparing BDE_{C-C} with BDE^0_{C-C} , it can be found that the BDE^0_{C-C} value shifts to lower side by ca. 5–10 kJmol⁻¹ when the ZPE is included. However, from BDE_{C-NHNO_2} and $BDE^0_{C-NHNO_2}$, it can be found that the BDE_{C-NHNO_2} values without zero-point energy correction are larger than those including zero-point energies correction about 22 kJmol⁻¹. For the same molecule, the BDE_{C-C} value is smaller than BDE_{C-NHNO_2} markedly, which shows that trigger bond for polynitraminecubanes is the C-C bond in the skeleton. In other

Table 3 Calculated total energy (E_0 , a.u), zero point energy (ZPE, kJmol^{-1}), values of thermal correction (H_T , kJmol^{-1}), heats of formation (HOF, kJmol^{-1}), heats of combustion (H_{comb} , kJmol^{-1}), and the specific heats of combustion (H_{specific} , KJ/g) of the title compounds at B3LYP/6-311G** level

Compounds	E_0	ZPE	H_T	HOF	H_{comb}	H_{specific}
1-	-569.44561	400.17	24.36	641.67	-4933.15	-30.08
1,2-	-829.35446	451.75	34.28	675.51	-4966.99	-22.17
1,3-	-829.35832	450.88	34.48	664.71	-4956.19	-22.13
1,8-	-829.35854	450.64	34.64	664.85	-4955.53	-22.12
1,2,3-	-1089.26770	502.91	44.10	697.31	-4988.79	-17.57
1,2,5-	-1089.26189	502.00	44.62	712.18	-5003.66	-17.62
1,3,5-	-1089.26953	501.40	44.62	691.52	-4983.00	-17.55
1,2,3,4-	-1349.17306	553.38	54.40	739.59	-5031.07	-14.63
1,2,3,5-	-1349.16576	551.47	55.34	757.79	-5049.27	-14.68
1,2,3,7-	-1349.17050	553.10	54.36	745.99	-5037.47	-14.64
1,2,3,8-	-1349.17615	552.99	54.50	731.19	-5022.67	-14.60
1,2,5,8-	-1349.16676	550.42	55.71	754.48	-5045.96	-14.67
1,3,5,7-	-1349.17455	551.99	54.86	734.75	-5026.23	-14.61
1,2,3,4,5-	-1609.08047	604.08	64.56	776.58	-5068.06	-12.54
1,2,3,5,6-	-1609.07807	602.85	64.95	782.04	-5073.52	-12.56
1,2,3,5,7-	-1609.08130	603.50	64.57	773.83	-5065.31	-12.54
1,2,3,4,5,6-	-1868.98893	655.99	73.50	810.79	-5102.27	-11.00
1,2,3,4,5,7-	-1868.98345	653.91	74.80	824.40	-5115.88	-11.03
1,2,3,5,6,8-	-1868.97730	653.48	74.95	840.27	-5131.75	-11.06
1,2,3,4,5,6,7-	-2128.88640	704.89	84.68	873.10	-5164.58	-9.86
Octanitraminecubane	-2388.78727	755.26	93.77	925.85	-5217.33	-8.93

words, the C-C bond is an initiator during the thermolysis process. This is because the cubane has high strain energy.

Table 4 Calculated strain energies (SE, kJmol^{-1}) of the title compounds at B3LYP/6-311G** level

Compounds	SE
1-	671.32
1,2-	666.24
1,3-	656.98
1,8-	656.64
1,2,3-	650.06
1,2,5-	666.22
1,3,5-	646.76
1,2,3,4-	655.25
1,2,3,5-	676.33
1,2,3,7-	662.26
1,2,3,8-	647.53
1,2,5,8-	674.76
1,3,5,7-	652.73
1,2,3,4,5-	654.84
1,2,3,5,6-	662.37
1,2,3,5,7-	653.24
1,2,3,4,5,6-	650.46
1,2,3,4,5,7-	666.92
1,2,3,5,6,8-	683.50
1,2,3,4,5,6,7-	677.94
Octanitraminecubane	695.02

Therefore, it is noticeable that the pyrolysis mechanism for cage compounds are relevant with molecular structure, including the strain energy of cage skeleton, the position and the number of substituent group. For all polynitraminecubanes, they have large BDE values, which show that the polynitraminecubanes have good thermodynamic stability. However, we must be aware that bond dissociation energies are a possible factor in determining stabilities and sensitivities, but not the only factor.

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 been proved to be reliable. Table 6 lists the molecular density (ρ), detonation heat (Q), detonation velocity (D) and detonation pressure (P). For a comparison, the experimental detonation performances of two known explosives RDX and HMX are listed in this Table.

As is evident in Table 6, it is found that there are strong linear relationships between ρ and n , D and n , and P and n for polynitraminecubanes: $\rho=0.0679n+1.4696(R=0.9666, n=1-8)$, $D=0.4521n+6.3129(R=0.9750, n=1-8)$, $P=3.8975n+13.93(R=0.9887, n=1-8)$. It should be pointed out that the average values of the isomers were used. The

Table 5 Calculated bond dissociation energies (kJ mol^{-1}) and bond order (P) of C-C bond and C-NHNO₂ bond at UB3LYP/6-311G** level

Compounds	P_{C-C}	BDE_{C-C}	BDE^0_{C-C}	P_{C-NHNO_2}	BDE_{C-NHNO_2}	$BDE^0_{C-NHNO_2}$
1-	0.96	142.1	132.7	0.98	408.3	385.9
1,2-	0.94	103.8	96.3	0.98	395.0	372.2
1,3-	0.96	145.0	135.5	0.98	408.1	385.8
1,8-	0.95	145.5	136.6	0.98	411.8	390.3
1,2,3-	0.90	111.3	103.8	0.99	398.9	376.3
1,2,5-	0.94	104.8	97.1	0.99	404.5	382.2
1,3,5-	0.95	148.4	139.6	0.98	410.2	388.2
1,2,3,4-	0.91	122.7	114.8	0.99	404.9	381.4
1,2,3,5-	0.91	114.6	108.3	0.99	388.8	366.1
1,2,3,7-	0.90	275.2	266.0	0.99	396.0	373.4
1,2,3,8-	0.90	125.1	117.0	0.99	417.0	393.8
1,2,5,8-	0.91	115.0	110.0	1.00	392.8	372.5
1,3,5,7-	0.94	147.6	138.4	0.99	408.6	386.8
1,2,3,4,5-	0.90	84.4	78.2	1.00	398.8	376.1
1,2,3,5,6-	0.90	126.1	117.9	1.00	413.3	389.8
1,2,3,5,7-	0.90	144.7	138.4	0.99	413.7	392.0
1,2,3,4,5,6-	0.91	139.7	130.2	1.00	381.6	359.5
1,2,3,4,5,7-	0.90	121.1	114.0	1.00	390.8	368.5
1,2,3,5,6,8-	0.90	95.9	87.3	1.00	416.4	393.2
1,2,3,4,5,6,7-	0.89	120.9	114.6	1.01	393.6	371.7
Octanitraminecubane	0.93	106.3	99.4	1.00	389.1	366.3

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 $BD E^0_{C-NHNO_2}$ and BDE_{C-NHNO_2}

Table 6 Calculated molecular density (ρ , g/cm^3), heat of detonation (Q , cal/g), detonation velocity (D , km/s) and detonation pressure (P , GPa) for the polynitraminecubanes together with RDX and HMX at the B3LYP/6-311G** level

Compound	ρ	Q	D	P
1-	1.46	1752.89	6.41	15.94
1,2-	1.62	1741.36	7.14	21.18
1,3-	1.61	1740.66	7.10	20.85
1,8-	1.60	1732.07	7.07	20.59
1,2,3-	1.71	1744.58	7.88	26.70
1,2,5-	1.71	1727.19	7.90	26.80
1,3,5-	1.73	1732.74	7.94	27.29
1,2,3,4-	1.79	1745.38	8.44	31.50
1,2,3,5-	1.75	1737.19	8.32	30.22
1,2,3,7-	1.80	1726.90	8.48	31.90
1,2,3,8-	1.79	1743.08	8.43	31.45
1,2,5,8-	1.77	1729.38	8.39	30.90
1,3,5,7-	1.81	1730.08	8.50	32.18
1,2,3,4,5-	1.83	1733.31	8.78	34.51
1,2,3,5,6-	1.84	1728.45	8.82	34.92
1,2,3,5,7-	1.84	1726.68	8.81	34.88
1,2,3,4,5,6-	1.89	1733.69	9.13	38.04
1,2,3,4,5,7-	1.86	1741.86	9.03	36.91
1,2,3,5,6,8-	1.89	1736.87	9.15	38.20
1,2,3,4,5,6,7-	1.93	1741.06	9.40	40.79
Octanitraminecubane	1.97	1752.89	9.63	43.37
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)

^b the calculated values of RDX and HMX taken from ref [49]

Date in parentheses are the experimental values taken from ref [50]

correlation coefficients are 0.9666, 0.9750 and 0.9887 for ρ , D and P , respectively. It indicates that they are the property of group additively. On average, if more nitramine group is attached, ρ , D and P increase by 0.0679 g/cm^3 , 0.4521 km/s , and 3.8975 GPa , respectively. It indicated that introducing more nitramine groups into cubane molecule will benefit its energetic performance. From Table 6, it can be seen that cubane derivatives with $n \geq 7$ meet the request as HEDCs ($\rho = 1.9 \text{ g/cm}^3$, $D = 9.0 \text{ km/s}$, $P = 40.0 \text{ GPa}$) and can be regarded as potential candidates of HEDCs. In addition, heptanitraminecubane and octanitraminecubane have good detonation performance over HMX, one of the most widely used energetic ingredients in various high performance explosives and propellant formulations. In comparison with RDX, cubane derivatives $n \geq 4$ all have better energetic performance than it. Therefore, if the polynitraminecubanes can be synthesized successfully, they will be worth investigating further. However, we also should notice that detonation pressure and velocity are overestimated if gas phase heats of formation instead of solid phase values are used [47]. For instance, the solid phase heats of formation of high energy compounds have been predicted using the Politzer approach [48].

Conclusions

On the basis of the calculated structures and the performance for the polynitraminecubanes, the following conclusions are drawn:

1. The HOMO and LUMO energy levels decrease when nitramine groups are attached to the ring. The energy gaps of polynitraminecubanes are much higher than that of TATB, which means cubane derivatives may be more sensitive than TATB optically. In addition, the energy gaps of polynitraminecubanes can be affected by the position of nitramine group.
2. Polynitraminecubanes have high and positive HOF, and there is good linear relationship between HOF and nitramine group numbers. As the number of nitramine groups in the molecule increases, the enthalpies of combustion values are increasingly negative, but the specific enthalpy of combustion values decreases.
3. All polynitraminecubanes have high strain energies, which are affected by position and number of nitramine group. The calculated bond dissociation energies of C-NHNO₂ and C-C bond show that the C-C bond should be the trigger bond in the pyrolysis process.
4. Detonation velocity (*D*), detonation pressure (*P*) and molecule density (ρ) have good linear relationship with substituted group numbers. Heptanitraminecubane and octanitraminecubane have detonation performance better than HMX, and can be regarded as potential candidates of HEDCs.

Acknowledgments This work is supported by the Natural Science Foundation of Shanxi Province (No. 2010021009-2), the Natural Science Foundation of China (No. 20871077), the Research Project Supported by Shanxi Scholarship Council of China (No. 201063) and the Natural Science Foundation of Shanxi Normal University.

References

1. Korkin AA, Bartlett RJ (1996) Theoretical prediction of 2,4,6-Trinitro-1,3,5-triazine (TNTA). A new, powerful, high-energy density material? *J Am Chem Soc* 118(48):12244–12245
2. Engelke R (1993) *Ab initio* calculations of ten carbon/nitrogen cubanoids. *J Am Chem Soc* 115(7):2961–2967
3. Talawar MB, Sivabalan R, Senthilkumar N, Prabhu G, Asthana SN (2004) Synthesis, characterization and thermal studies on furazan- and tetrazine-based high energy materials. *J Hazard Mater* 113(1–3):11–25
4. Richard R, Ball D (2008) *Ab initio* calculations on the thermodynamic properties of azaborospiropentanes. *J Mol Model* 14(9):871–878
5. Chi WJ, Li LL, Li BT, Wu HS (2012) Density functional calculations for a high energy density compound of formula C₆ H_{6-n} (NO₂)_n. *J Mol Model* 18(8):3695–3704
6. Janning J, Ball D (2010) Nitroborazines as potential high energy materials: density functional theoretical calculations. *J Mol Model* 16(5):857–862
7. Chavez DE, Hiskey MA, Gilardi RD (2000) 3,3'-Azobis(6-amino-1,2,4,5-tetrazine): a novel high-nitrogen energetic material. *Angew Chem Int Ed* 39(10):1791–1793
8. Ciezak JA, Trevino SF (2005) The inelastic neutron scattering spectra of α -3-amino-5-nitro-1,2,4-2H-triazole: experiment and DFT calculations. *Chem Phys Lett* 403(4–6):329–333
9. Levchik SV, Balabanovich AI, Ivashkevich OA, Lesnikovich AI, Gaponik PN, Costa L (1993) The thermal decomposition of aminotetrazoles. Part 2. 1-methyl-5-aminotetrazole and 1,5-diaminotetrazole. *Thermochim Acta* 225(1):53–65
10. Lesnikovich AI, Ivashkevich OA, Levchik SV, Balabanovich AI, Gaponik PN, Kulak AA (2002) Thermal decomposition of aminotetrazoles. *Thermochim Acta* 388(1–2):233–251
11. Chung G, Schmidt MW, Gordon MS (2000) An *ab initio* study of potential energy surfaces for N₈ isomers. *J Phys Chem A* 104(23):5647–5650
12. Shu Li Q, Dong Liu Y (2002) Structures and stability of N₁₁ cluster. *Chem Phys Lett* 353(3–4):204–212
13. Yarkony DR (1992) Theoretical studies of spin-forbidden radiationless decay in polyatomic systems: insights from recently developed computational methods. *J Am Chem Soc* 114(13):5406–5411
14. Gagliardi L, Evangelisti S, Bernhardsson A, Lindh R, Roos BO (2000) Dissociation reaction of N₈ azapentalene to 4 N₂: a theoretical study. *Int J Quantum Chem* 77(1):311–315
15. Schmidt MW, Gordon MS, Boatz JA (2000) Cubic fuels? *Intl J Quantum Chem* 76(3):434–446
16. Marchand AP (1989) Synthesis and chemistry of homocubanes, bishomocubanes, and trishomocubanes. *Chem Rev* 89(5):1011–1033
17. Eaton PE, Cole TW (1964) The cubane system. *J Am Chem Soc* 86(5):962–964
18. Zhang MX, Eaton PE, Gilardi R (2000) Hepta- and octanitrocubanes. *Angew Chem Int Ed* 39(2):401–404
19. Richard RM, Ball DW (2009) Density functional calculations on the thermodynamic properties of a series of nitrosocubanes having the formula C₈H_{8-x}(NO)_x (x=1–8). *J Hazard Mater* 164(2–3):1552–1555
20. Richard RM, Ball DW (2009) B3LYP calculations on the thermodynamic properties of a series of nitroxycubanes having the formula C₈H_{8-x}(NO₂)_x (x=1–8). *J Hazard Mater* 164(2–3):1595–1600
21. Wang F, Du H, Zhang J, Gong X (2011) Computational studies on the crystal structure, thermodynamic properties, detonation performance, and pyrolysis mechanism of 2,4,6,8-Tetranitro-1,3,5,7-tetraazacubane as a novel high energy density material. *J Phys Chem A* 115(42):11788–11795
22. Politzer P, Lane P, Murray JS (2011) Computational characterization of a potential energetic compound: 1,3,5,7-Tetranitro-2,4,6,8-tetraazacubane. *Central Eur J Energ Mater* 8:39–52
23. Hrovat DA, Borden WT, Eaton PE, Kahr B (2001) A computational study of the interactions among the nitro groups in octanitrocubane. *J Am Chem Soc* 123(7):1289–1293
24. Pagoria PF, Lee GS, Mitchell AR, Schmidt RD (2002) A review of energetic materials synthesis. *Thermochim Acta* 384(1–2):187–204
25. Ismail MM, Murray SG (1993) Study of the Blast Wave Parameters from Small Scale Explosions. *Propel Explos Pyrotech* 18(1):11–17
26. Karaghiosoff K, Klapötke TM, Michailovski A, Nöth H, Suter M, Holl G (2003) 1,4-Diformyl-2,3,5,6-Tetranitratopiperazine: a new primary explosive based on glyoxal. *Propel Explos Pyrotech* 28(1):1–6
27. Cunkle GT, Willer RL (1988) SDIO Symposium on Innovative Science and Technology. *SPIE Proc* 872:142
28. Willer RL, Stern AG (1991) ONR Workshop on Advanced Propellants and Processing Science, Chestertown, MD. *CPIA Publ* 574:15
29. Frisch MJ, Trucks GW, Schlegel HB et al (2004) Gaussian 03, Revision C 02. Gaussian Inc, Wallingford
30. Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 37(2):785–789
31. Fan XW, Ju XH, Xiao HM (2008) Density functional theory study of piperidine and diazocine compounds. *J Hazard Mater* 156(1–3):342–347

32. Ju XH, Wang X, Bei FL (2005) Substituent effects on heats of formation, group interactions, and detonation properties of poly-azidocubanes. *J Comput Chem* 26(12):1263–1269
33. Chi W, Li L, Li B, Wu H (2012) Density functional calculation on a high energy density compound having the formula $C_2OH_{4-n}(NO_2)_n$. *Struct Chem*. doi:10.1007/s11224-012-9992-3
34. Chen PC, Chieh YC, Tzeng SC (2003) Density functional calculations of the heats of formation for various aromatic nitro compounds. *J Mol Struct (THEOCHEM)* 634(1–3):215–224
35. Akhavan J (2004) *The chemistry of explosives*, 2nd edn. Royal Society of Chemistry, Cambridge
36. Dill JD, Greenberg A, Liebman JF (1979) Substituent effects on strain energies. *J Am Chem Soc* 101(23):6814–6826
37. Zhao M, Gimarc BM (1993) Strain energies in cyclic oxygen O_n , $n=3-8$. *J Phys Chem* 97(16):4023–4030
38. Bulat F, Toro-Labbé A, Brinck T, Murray J, Politzer P (2010) Quantitative analysis of molecular surfaces: areas, volumes, electrostatic potentials and average local ionization energies. *J Mol Model* 16(11):1679–1691
39. Gilman JJ (1993) Shear-induced metallization. *Philos Mag B* 67(2):207–214
40. Zhou Z, Parr RG, Garst JF (1988) Absolute hardness as a measure of aromaticity. *Tetrahedron Lett* 29(38):4843–4846
41. Kirklin DR, Churney KL, Domalski ES (1989) Enthalpy of combustion of 1,4-dimethylcubane dicarboxylate. *J Chem Thermodyn* 21(11):1105–1113
42. Murray JS, Concha MC, Politzer P (2009) Links between surface electrostatic potentials of energetic molecules, impact sensitivities and C–NO₂/N–NO₂ bond dissociation energies. *Mol Phys* 107(1):89–97
43. Rice BM, Sahu S, Owens FJ (2002) Density functional calculations of bond dissociation energies for NO₂ scission in some nitroaromatic molecules. *J Mol Struct (THEOCHEM)* 583(1–3):69–72
44. Qiu L, Xiao H, Gong X, Ju X, Zhu W (2007) Crystal density predictions for nitramines based on quantum chemistry. *J Hazard Mater* 141(1):280–288
45. Zhang J, Xiao H (2002) Computational studies on the infrared vibrational spectra, thermodynamic properties, detonation properties, and pyrolysis mechanism of octanitrocubane. *J Chem Phys* 116(24):10674–10683
46. Brill TB, James KJ (1993) Kinetics and mechanisms of thermal decomposition of nitroaromatic explosives. *Chem Rev* 93(8):2667–2692
47. Politzer P, Murray JS (2011) Some perspectives on estimating detonation properties of C, H, N, O compounds. *Central Eur J Energ Mater* 8(3):209–220
48. Politzer P, Ma Y, Lane P, Concha MC (2005) Computational prediction of standard gas, liquid, and solid-phase heats of formation and heats of vaporization and sublimation. *Int J Quantum Chem* 105(4):341–347
49. Wei T, Zhu W, Zhang X, Li YF, Xiao H (2009) Molecular design of 1,2,4,5-Tetrazine-based high-energy density materials. *J Phys Chem A* 113(33):9404–9412
50. Talawar MB, Sivabalan R, Mukundan T, Muthurajan H, Sikder AK, Gandhe BR, Rao AS (2009) Environmentally compatible next generation green energetic materials (GEMs). *J Hazard Mater* 161(2–3):589–607