

Theoretical investigation on the heats of formation and detonation performance in polydinitroaminocubanes

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Abstract A series of polydinitroaminocubanes have been designed computationally. We calculated the heats of formation, the detonation velocity (D) and detonation pressure (P) of the title compounds by density function theory (DFT) with 6-311 G** basis set. The relationship between the heats of formation and the molecular structures is discussed. The result shows that all cubane derivatives have high and positive heats of formation, which increase with increasing number of dinitroamino groups. The detonation performances of the title compound were estimated by Kamlet-Jacobs equation, and the result indicated that most cubane derivatives have good detonation performance over RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane). In addition, we also found that the heat of detonation (Q) is another very important impact in increasing detonation performance except density. The relative stabilities of the title compound are discussed in the terms of the calculated heats of formation, and the energy gaps between the frontier orbitals. The results have not only shown that these compounds may be used as high energy density compounds (HEDCs), but also provide some useful information for further investigation.

Keyword Cubane · DFT · Dinitroamino group · Heats of formation · High energy density compounds

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Introduction

High energy density compounds (HEDCs) have attracted many attentions for their bright usage prospect in the fields of fuel, explosives and propellants [1–7]. The general requirements for 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), and thermal stability [8, 9]. All-nitrogen molecules store abundant energy, but they would have to resist dissociation well enough to be a stable fuel. Theoretical studies [10–12] have shown that all-nitrogen molecules are not sufficiently stable to be practical HEDCs and can be synthesized hardly. Besides the pure-nitrogen cluster, early investigations on this kind of compound indicate that caged alkyl molecules possess high density, high strain energy, and some stability [13–15]. From the 1960s onward, marked progress has been made in synthesized chemistry [16]. This strengthens our interest in cubane (C₈H₈). It and its derivatives have been the subject of numerous investigations since Eaton's synthesis of the parent compound in 1964 [17].

There is some work on cubane as high energy compounds. Octanitrocubane was first synthesized in 2000 in 45–55 % yield from heptanitrocubanes, which is a derivative of strained cubane molecule, have high nitrogen contents, has been found to have a high density, ranging from 1.98 to 2.06 g/cm³ due to nitro group orientation. In the follow-up studies, the tetranitrotetraazacubane [18], polynitrosocubanes, polynitratecubanes, and polydifluoroaminocubanes have been widely studied [19–22]. These results show that these derivatives of cubane may prove a viable alternative high-energy material. High-energy material containing large numbers of nitrogen atoms, so called “high nitrogen” compounds, have been shown to derive energy from the presence of many energetic N–N and C–N bonds [23, 24]. We are

interested in cubane derivatives that contain a high percentage of both oxygen and nitrogen atoms, and lower amounts of carbon and hydrogen atoms. The high nitrogen content can lead to high crystal density, which is associated with increased denotation performance. The high oxygen content has an advantage for combustion reaction. For these reasons, another nitrogen-containing functional group, and the one we are interested in for this study, is the dinitroamino group. The main differences among the dinitroamino group and the nitro group, nitroso group, and the nitrate group are the amount of oxygen present and nitrogen present.

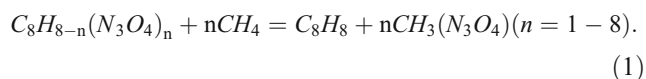
In this paper, we suggested that the replacement of the hydrogen atoms of cubane molecule with dinitroamino groups would make the resulting molecule some new potential HEDCs. It is expected that our results could provide some useful information for laboratory synthesis of polydinitroaminocubanes and development of new novel HEDCs.

Computation details

The Gaussian 03 package [25] was used as the calculation tool. The geometries of polydinitroaminocubanes were fully optimized without symmetry restriction using the density functional theory (DFT) at the B3LYP [26] level with the 6-311 G** [27] basis set. Harmonic vibrational 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.

In previous studies, the heats of formation (HOFs) were predicted via isodesmic reactions [28, 29]. The isodesmic reaction progress must comply with the bond separation reaction (BSR) rule. That is to say the molecule is broken down into two heavy-atom molecules containing the same component bond. Therefore, we design isodesmic reactions in which the numbers of all kinds of bonds are kept invariable to decrease the calculation errors, in addition, for our system, the cage structure can not be broken.

The isodesmic reactions used to obtain the HOFs of the polydinitroaminocubanes at 298 K are as follows Eq. (1):



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

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

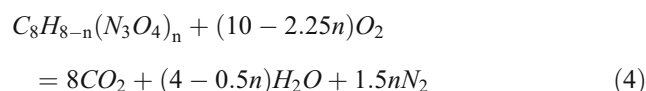
where $\Delta H_{f,p}$ and $\Delta H_{f,R}$ are the heats of formation of the reactants and products at 298 K respectively. The experimental HOFs of reference compounds CH_4 , C_8H_8 , and $CH_3(N_3O_4)$ are available. Thus, the HOFs of the polydinitroaminocubanes can be calculated when the

heat of reaction ΔH_{298} is known. The ΔH_{298} can be calculated using the following formula (3).

$$\Delta H_{298} = \Delta E + \Delta ZPE + \Delta H_T + \Delta nRT \quad (3)$$

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 polydinitroaminocubanes obtained from Eqs. 2 and 3, then it is a straightforward process to determine the enthalpy of combustion using reaction (4).



Enthalpies of formation for the carbon dioxide and water were also obtained from the NIST Chemistry Webbook website. These values are -393.52 and -285.83 kJ mol^{-1} , respectively. In reaction (4), we are assuming these combustion products, as suggested by the modified Kistiakowsky-Wilson rules.

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 atoms is not enough to satisfy full oxidation of the H and C atoms, 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 [30]. The detonation performance is an important factor that be considered when HEDCs were designed. The semi-empirical Kamlet-Jacobs equation [31] was applied in previous work. The formula (5) and (6) was listed as the following.

$$D = 1.01 \left(N \bar{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30 \rho_0) \quad (5)$$

$$P = 1.558 \rho_0^2 N \bar{M}^{1/2} Q^{1/2} \quad (6)$$

D is the detonation velocity (km/s), P is the detonation pressure. N is the moles of gas produced by per gram of explosive, and \bar{M} is the mean molecular weight of the gaseous detonation products. Q is the detonation energy (cal/g). ρ_0 is molecular crystal density (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

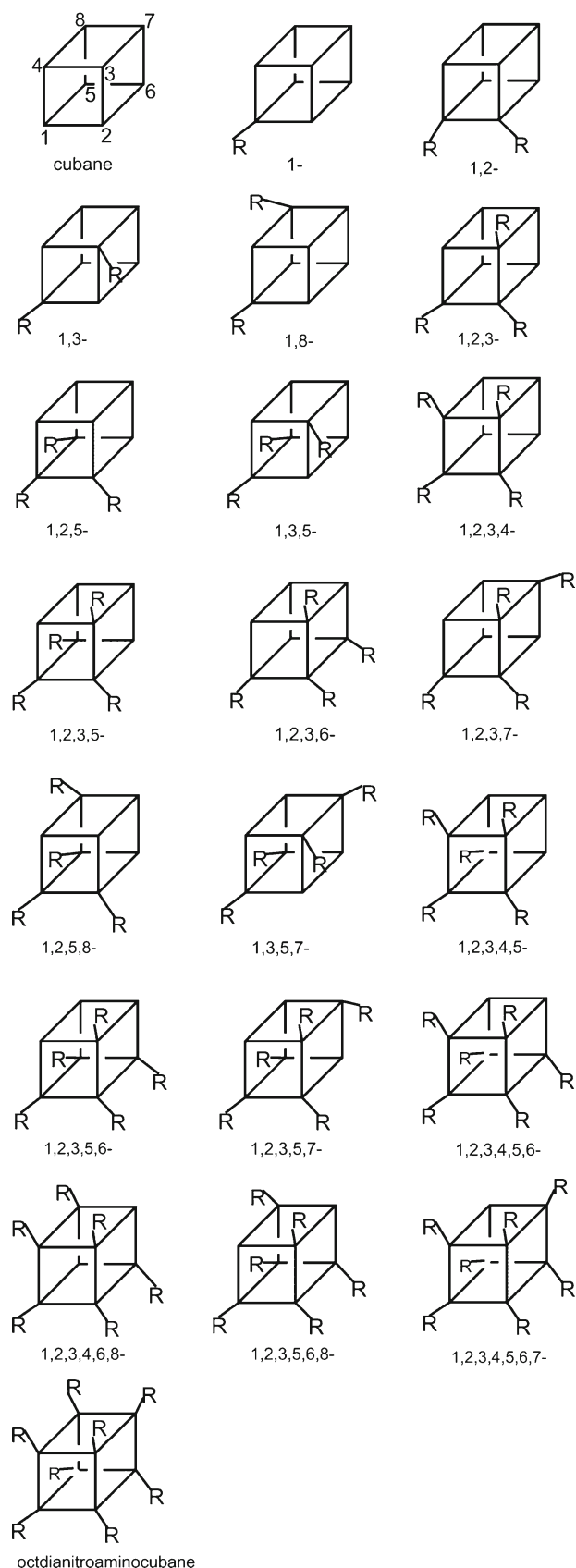


Fig. 1 Molecular frameworks of cubane and cubane derivatives [R = -N(NO₂)₂]

integration. Moreover, an electrostatic interaction correction for improved crystal density prediction also had been studied by Politzer et al. [32], and the result shows that the electrostatic interaction correction has advantageous influence for the crystal density of some high energy compounds. The method is shown by Eqs. 7, 8, 9, 10, and 11.

$$\text{Crystal density } (\rho_0) = \alpha(M/Vm) + \beta(v\sigma^2_{\text{tot}}) + \gamma \quad (7)$$

$$\sigma^2_{\text{tot}} = \sigma^2_+ + \sigma^2_- = \frac{1}{m} \sum_{i=1}^m [V^+(r_i) - \bar{V}_s^+]^2 + \frac{1}{n} \sum_{j=1}^n [V^-(r_j) - \bar{V}_s^-]^2 \quad (8)$$

$$v = \sigma^2_+ \sigma^2_- / |\sigma^2_{\text{tot}}|^2 \quad (9)$$

$$V_s^+ = \frac{1}{m} \sum_{i=1}^m V^+(r_i) \quad (10)$$

$$V_s^- = \frac{1}{n} \sum_{j=1}^n V^-(r_j) \quad (11)$$

Table 1 Calculated *HOMO*, *LUMO* energies (a.u), energies gaps ($\Delta E_{LUMO-HOMO}$) of polydinitroaminocubane at B3LYP/6-311 G** level

Compound	LUMO	HOMO	ΔE
Cubane	0.04369	-0.26324	0.30693
1-	-0.10557	-0.28302	0.17745
1,2-	-0.11687	-0.29397	0.17710
1,3-	-0.11785	-0.29629	0.17844
1,8-	-0.11671	-0.29518	0.17847
1,2,3-	-0.13079	-0.31092	0.18013
1,2,5-	-0.12741	-0.30541	0.17800
1,3,5-	-0.12746	-0.30654	0.17908
1,2,3,4-	-0.13518	-0.30922	0.17404
1,2,3,5-	-0.14102	-0.31768	0.17666
1,2,3,6-	-0.13438	-0.31685	0.18247
1,2,3,7-	-0.13663	-0.31291	0.17628
1,2,5,8-	-0.13610	-0.30851	0.17241
1,3,5,7-	-0.13491	-0.31891	0.18400
1,2,3,4,5-	-0.14257	-0.31370	0.17113
1,2,3,5,6-	-0.14275	-0.32213	0.17938
1,2,3,5,7-	-0.14167	-0.32052	0.17885
1,2,3,4,5,6-	-0.15010	-0.32391	0.17381
1,2,3,4,6,8-	-0.14922	-0.31868	0.16946
1,2,3,5,6,8-	-0.14987	-0.31596	0.16609
1,2,3,4,5,6,7-	-0.15108	-0.32837	0.17729
Octdianitroaminocubane	-0.16017	-0.32648	0.16631

1- and 1,2- denote 1-dinitroaminocubane and 1,2-didinitroaminocubane, respectively; the other are similar

Table 2 Calculated total energies (E_0 a.u), thermal corrections (H_T , kJ mol⁻¹), zero-point energies (ZPE, a.u), and HOFs (kJ mol⁻¹) for the reference compounds at B3LYP/6-311 G** level

Compound	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 N ₃ O ₄	-504.94238	0.06819	22.54	43.1

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 $V_S^-(r_i)$ represent the positive and negative value of $V(r)$ on the surface. $\overline{V_S^+}$ and $\overline{V_S^-}$ are their averages, σ_{tot}^2 is the total variance, in this paper, these parameters of the title compounds were obtained at B3LYP/6-311 G** level.

Results and discussion

Electronic structure

Before discussing the result on polydinitroaminocubanes, the basis structure and atom numbering scheme are presented in Fig. 1. Table 1 listed the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energies, the energy gaps ($\Delta E_{LUMO-HOMO}$) at the B3LYP/6-311 G** level. From the Table 1, it is found that $\Delta E_{LUMO-HOMO}$

values decrease as the dinitroamino group number increase. It is interesting to note that all polydinitroaminocubanes decrease $\Delta E_{LUMO-HOMO}$ of the unsubstituted cubane. It is found that the $\Delta E_{LUMO-HOMO}$ values are affected by the positive of dinitroamino groups. For the isomer, the four dinitroamino groups cubane derivatives, the $\Delta E_{LUMO-HOMO}$ of the 1,2,3,4-tetradinitroaminocubane is slightly smaller, while that of the 1,3,5,7-tetranitroaminocubane is slightly larger. This shows that the 1,3,5,7-tetradinitroaminocubane is more stable than 1,2,3,4-tetranitroaminocubane. Furthermore, we found that the energy gaps of polydinitroaminocubanes are much higher than that of (triamino-trinitrobenzene) TATB (0.1621 eV), which means polydinitroaminocubanes are not more sensitive than TATB. It is worth noting that the stability refers to the stability of the compound to photochemical electron-transfer processes. So the thermodynamic stability of the title compound is not simply judged via $\Delta E_{LUMO-HOMO}$.

Heats of formation

The molecular total energy, 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. To the best of our knowledge, no experimental HOFs values for the designed molecules are available. However, the HOFs can be obtained by theisodesmic reactions. The method has been employed very successfully

Table 3 Calculated total energies (E_0 , a.u), thermal corrections (H_T , kJ mol⁻¹), Zero-point energies (ZPE, a.u), and HOFs (kJ mol⁻¹) for polynitroaminocubane at B3LYP/6-311 G** level

Compound	E_0	ZPE	H_T	HOF	H_c
1-	-773.95257	0.15312	29.22	716.59	-23.27
1,2-	-1238.36535	0.17333	48.55	837.49	-15.42
1,3-	-1238.36912	0.17334	48.41	827.48	-15.39
1,8-	-1238.37142	0.17328	48.79	821.66	-15.37
1,2,3-	-1702.76861	0.19298	65.80	980.14	-11.56
1,2,5-	-1702.78020	0.19326	65.53	948.87	-11.48
1,3,5-	-1702.78238	0.19294	66.14	943.92	-11.48
1,2,3,4-	-2167.15714	0.21292	81.87	1160.44	-9.31
1,2,3,5-	-2167.18102	0.21256	83.69	1098.62	-9.20
1,2,3,6-	-2167.18305	0.21322	82.34	1093.66	-9.19
1,2,3,7-	-2167.16612	0.21251	83.34	1137.26	-9.27
1,2,5,8-	-2167.17743	0.21289	83.18	1108.40	-9.21
1,3,5,7-	-2167.19064	0.21278	83.23	1073.28	-9.15
1,2,3,4,5-	-2631.56433	0.23220	97.89	1290.27	-7.74
1,2,3,5,6-	-2631.57326	0.23248	99.98	1269.65	-7.71
1,2,3,5,7-	-2631.57730	0.23268	99.71	1259.30	-7.69
1,2,3,4,5,6-	-3095.94384	0.25152	116.61	1495.58	-6.72
1,2,3,4,6,8-	-3095.95722	0.25222	116.61	1408.47	-6.60
1,2,3,5,6,8-	-3095.96358	0.25219	116.98	1445.88	-6.65
1,2,3,4,5,6,7-	-3560.32935	0.27162	132.39	1684.25	-5.93
Octdianitroaminocubane	-4024.68001	0.28969	149.32	1960.22	-5.41

1-and 1,2-denote 1-dinitroaminocubane and 1,2-didinitroaminocubane, respectively; the others are similar

Table 4 For the $C_aH_bO_cN_d$ explosives, the values of N , \bar{M} , Q , are calculated following the formula

Parameters	Explosives components conditions		
	$C \geq 2a+b/2$	$2a+b/2 > c \geq b/2$	$b/2 > c$
N	$(b+2c+2d)/4 M$	$(b+2c+2d)/4 M$	$(b+d)/2 M$
\bar{M}	$4 M/(b+2c+2d)$	$(56d+88c-8b)/(b+2c+2d)$	$(2b+28d+32c)/(b+d)$
$Q \cdot 10^{-3}$	$(28.9b+94.05a+0.239\Delta H_f^0)/M$	$[28.9b+94.05(c/2-b/4)+0.239\Delta H_f^0]/M$	$(57.8c+0.239\Delta H_f^0)/M$

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

to estimate HOFs from total energies obtained from *ab initio* calculations. Table 3 listed the total energy, the zero-point energies, the values of the thermal correction and the HOFs value of the title compounds at the B3LYP/6-311 G** level.

According to the data in Table 3, inspecting the values of HOFs, we can find that the polydinitroaminocubanes have high and positive HOFs values, which is one of the necessary characteristics of energetic materials [33], consistent with previous reports that energetic high-nitrogen compounds have high positive heats of formation [34]. In addition, the HOFs values become larger as the number of dinitroamino groups is increased. Obviously, the contributions of dinitroamino group on the HOFs of polydinitroaminocubanes meet the group additivity rule. For the isomers with the same number of nitro groups that have disparate HOFs values, it clearly states that the HOFs are affected by the position of the dinitroamino group. Generally speaking, the closer the dinitroamino group, the higher the HOFs, in other words, the thermodynamic stability is poor. For example, for the four dinitroamino groups cubane derivatives, the 1,2,3,4-tetradinitroaminocubane, the four dinitroamino groups are located on the same four-membered rings and are close, hence, has the higher HOFs. However, for the 1,3,5,7-tetradinitroaminocubane, the distance of the four dinitroamino groups is the farthest in all tetradinitroaminocubanes, so which has the lower HOFs.

The sixth numerical column in Table 3 shows the specific enthalpies of combustion, which is the molar enthalpy of combustion divided by the molar mass of the substance. We can find that as the dinitroamino number of molecular increases, the specific enthalpies of combustion decrease. This is due to the fact that we are replacing hydrogen atoms, each of which contributes to roughly about 8 kJ/g of energy upon combustion by forming water. However, each nitrogen atom forms diatomic nitrogen, which has an enthalpy of formation of 0 kJ mol⁻¹. Steric hindrance compensates for some of the lost 8 kJ/g, but not enough to make an additional dinitroamino group cause the molecule to give off more energy than it did when it had one less dinitroamino group. The result is that the higher substituted molecules give off less energy than the lower substituted molecules.

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. For $C_aH_bO_cN_d$ compounds, N , \bar{M} , and Q are obtained according to Table 4 [35]. Table 5 listed the molecular crystal density (ρ_0), detonation heat (Q),

Table 5 Predicted detonation properties of the polydinitroaminocubane and RDX and HMX at B3LYP/6-311 G** level

Compound	$\rho_0(\text{g/cm}^3)$	$Q(\text{cal/g})$	$D(\text{km/s})$	$P(\text{GPa})$
1-	1.53	1899.89	6.82	18.67
1,2-	1.73	1938.49	8.30	29.94
1,3-	1.73	1930.87	8.30	29.89
1,8-	1.71	1926.43	8.24	29.16
1,2,3-	1.81	1970.15	9.01	36.09
1,2,5-	1.79	1952.31	8.90	35.14
1,3,5-	1.81	1949.49	8.97	35.88
1,2,3,4-	1.91	2006.29	9.67	43.13
1,2,3,5-	1.88	1978.09	9.57	41.52
1,2,3,6-	1.89	1975.83	9.57	41.91
1,2,3,7-	1.92	1995.72	9.71	43.48
1,2,5,8-	1.91	1982.55	9.67	42.86
1,3,5,7-	1.87	1966.53	9.49	40.92
1,2,3,4,5-	1.97	1824.28	9.71	43.96
1,2,3,5,6-	1.96	1816.45	9.68	43.45
1,2,3,5,7-	1.95	1812.52	9.64	42.95
1,2,3,4,5,6-	2.02	1590.80	9.52	42.98
1,2,3,4,6,8-	2.01	1562.43	9.45	42.17
1,2,3,5,6,8-	2.02	1574.61	9.49	42.72
1,2,3,4,5,6,7-	2.05	1411.01	9.33	41.51
Octadinitroaminocubane	2.08	1293.32	9.35	42.20
RDX ^a	1.78(1.82)	1591.03	8.87(8.75)	34.67 (34.00)
HMX ^a	1.88(1.91)	1633.90	9.28(9.10)	39.19 (39.00)

1- and 1,2- denote 1-dinitroaminocubane and 1,2-didinitroaminocubane, respectively; the other are similar

The calculated values of RDX and HMX taken from ref [7]

Date in parentheses are the experimental values taken from ref [7]

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.

From Table 5, it is found that the ρ_0 values become larger as the number of dinitroamino groups is increased. The Q values become larger as the number of dinitroamino groups is increased when the numbers of substituents are less than five, but when the numbers of substituents are more than five, the Q values become smaller as the number of dinitroamino groups is increased. This is because the oxygen balance (BO) [36] plays an important role in increasing Q values. For pentadinitroaminocubanes, hexadinitroaminocubanes, heptadinitroaminocubane and octadinitroaminocubane, their oxygen balances are 6.36 %, 15.26 %, 21.93 % and 27.11 %, respectively. That fact shows that the title compound releases needless oxygen, which takes away a large number of energy in explosive decomposition. For this reason, the oxygen balance impact must be considered when the high energy density compounds were designed. The variation of D and P is consistent with Q. In the previous study, the explosive performances are better as the density is increased. However, in our paper, the octadinitroaminocubane has the largest density, but does not have the best explosive performances in all molecular. The result indicates that Q has another very important impact in increasing detonation performance except density. The viewpoint has been discussed by Politzer and cooperator [37]. As is evident in Table 5, we found that most of the compounds have excellent detonation performance except monodinitroaminocubane. In addition, most of cubane derivatives have good detonation performance over HMX, one of the most widely used energetic ingredients in various high performance explosives and propellant formulations. Furthermore, we also should notice that detonation pressure and velocity are 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 [38]. Furthermore, to obtain potential HEDCs, the thermodynamic stability also must be considered. According to previous research for cubane derivatives, we think that these polydinitroaminocubanes are likely to be very sensitive.

Conclusions

In our work, we have studied the electronic structure, heats of formation, the specific enthalpies of combustion, and detonation performances at B3LYP/6-311 G** level. On the basis of the theoretical studied, the following conclusions are drawn:

1) All cubane derivatives have high and positive heats of formation, which increase with increasing number of

dinitroamino groups. For the isomers, the HOFs are affected by the position of the dinitroamino group. For the specific enthalpies of combustion, we can find that as the dinitroamino number of molecular increases, the specific enthalpies of combustion decrease. Furthermore, the energy gaps of polydinitroaminocubanes are much higher than that of TATB.

2) Most of cubane derivatives have good detonation performance over HMX. Especially 1,2,3,4,5-pentadinitroaminocubane, the detonation performance ($D=9.71$ km/s, $P=43.96$ GPa) would range up to CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) [39]. We also found that the BO plays an important role in increasing the Q value. When BO value is greater than zero, the title compound releases needless oxygen, which takes away a large amount of energy in explosive decomposition. In addition, Q is another very important impact in increasing detonation performance except density.

To sum up, our study has shown that polydinitroaminocubanes may be used as high energy density compounds if they have excellent thermodynamic stability. According to the difficulty of the synthesis, we recommend pentadinitroaminocubanes studied as HEDCs in the future. Our work can provide some useful information for further works.

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