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A Theoretical Study of Highly Nitrated Azacubanes

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*The geometries of highly nitrated azacubanes have been fully optimized at the B3LYP/6-31++G** theory level, and the gas phase enthalpies of formation have been obtained by designing the isodesmic reaction in which the azacubane cage skeleton is not destroyed. An efficient procedure for judging the driving force of detonation products of energetic compounds has been developed from the conservation of energy condition. The MP2/6-31++G**//B3LYP/6-31++G** atom-atom overlap-weighted NAO bond order shows that after the full nitration of 1,4-diazacubane and 1,3,5,7-tetraazacubane the weakest C–N bond on the 1,3,5,7-tetraazacubane cage skeleton strengthens slightly, but on the 1,4-diazacubane cage skeleton it weakens. For highly nitrated azacubanes, the introduction of –NH₂ group results in the destabilization of the neighboring C–N bond on the cage skeleton. The shock stability of 2,4,6,8-tetranitro-1,3,5,7-tetraazacubane (TNTAzC) is superior to that of 2,3,5,6,7,8-hexanitro-1,4-diazacubane (HNDAzC). The detonation velocity and pressure for TNTAzC are predicted to reach 11.10 km/s and 101.7 GPa, respectively. The driving force of detonation products of*

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HNDAzC is close to that of octanitrocubane, and the driving force of TNTAzC is about 4.0 times as large as that of the widely used high explosive HMX, showing that TNTAzC is a potential candidate of super high-energy compound.

Keywords: 2,3,5,6,7,8-hexanitro-1,4-diazacubane, 2,4,6,8-tetranitro-1,3,5,7-tetraazacubane, bond order, density functional B3LYP method, detonation performance

Introduction

Energetic compounds are widely used [1,2]. There is an ongoing need for high-energy compounds. Although examined as an extremely high-energy compound [3,4], N₈ cubane (octaazacubane) is difficult to synthesize because of its instability. However, if some carbon atoms take the place of nitrogen atoms of octaazacubane (equivalently some carbon atoms of cubane are replaced with nitrogen atoms), the new azacubane molecules will be much more stable than octaazacubane, with the C–N bond being stronger than the N–N bond [5]. On the other hand, because the nitrogen atom in azacubane carries significantly more energy than the carbon atom in cubane, the fully nitrated azacubanes will have better detonation performance with respect to octanitrocubane (ONC), which recently has been synthesized by Eaton and coworkers and predicted to have larger detonation velocity and pressure than the polycyclic nitramine CL-20 [6].

For energetic compounds the detonation performance is a fundamental and important property. In the past, the detonation velocity and pressure (which can be calculated with the Kamlet-Jacobs empirical method [7], the BKW equation of state [EOS] semiempirical method [8], the VLW EOS semiempirical method [9], and so forth) have been used to evaluate theoretically the detonation performance of energetic compounds. But the driving force of detonation products of energetic compounds is sometimes concentrated on, which involves the metal acceleration and can be determined experimentally with the cylinder test and the plane flyer test [2]. The present methods,

which use detonation velocity, detonation pressure, or detonation heat to evaluate the driving force of detonation products of energetic compounds, are usually inefficient. Therefore, it is necessary to develop a more efficient theoretical procedure for judging the driving force of detonation products of energetic compounds.

In this article, firstly a procedure for judging the driving force of detonation products of energetic compounds has been developed from the conservation of energy condition. The properties of enthalpy of formation, crystal density, and detonation performance of highly nitrated azacubanes have been investigated from theoretical calculations in order to search for azacubane-based high-energy compounds. Additionally, this work tries to shed some light on the theoretical design of energetic compounds at the ab initio level.

Computational Methods and Details

Molecular and Crystal Structures

The density functional B3LYP method [10] and the 6-31++G** basis set are applied to fully optimize the molecular geometries of 1,4-diazacubane (DAzC), 2,3,5,6,7,8-hexanitro-1,4-diazacubane (HNDaZC), 1,3,5,7-tetraazacubane (TAzC), and 2,4,6,8-tetranitro-1,3,5,7-tetraazacubane (TNTAzC) with the Bery gradient approach [11]. Harmonic vibrational frequency has been performed at the B3LYP/6-31++G** level, and natural bond orbital analysis [12] performed at the MP2/6-31++G**//B3LYP/6-31++G** level. Considering that the introduction of $-\text{NH}_2$ group into 1,3,5-trinitrobenzene can get insensitive compounds 1,3-diamino-2,4,6-trinitrobenzene (DATB) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), compounds 2,7-diamino-3,5,6,8-tetranitro-1,4-diazacubane (DATNDaZC) and 2-amino-4,6,8-trinitro-1,3,5,7-tetraazacubane (ATNTAzC) have also been investigated to discuss the influence of $-\text{NH}_2$ group on the stability of highly nitrated azacubanes. All these calculations have been fulfilled with the GAUSSIAN-03W program [13] using the default Gaussian

convergence criteria. The ab initio crystal structure prediction method proposed by Karfunkel and Gdanitz [14] (hereafter called the Karfunkel–Gdanitz method) contained in the Materials Studio software [15] has been employed to predict the crystal density from molecular structure, which proves to be feasible for the density prediction of polynitropyridines [16].

Detonation Performance

For a detonation wave propagating with velocity D into an energetic material initially at rest, the conservation of energy condition is [17]

$$E_1 - E_0 = \frac{1}{2}(P_1 + P_0)(V_0 - V_1) \quad (1)$$

where E_0 , P_0 , and V_0 are, respectively, the initial internal energy per unit mass, pressure, and specific volume, and E_1 , P_1 , and V_1 are, respectively, the final internal energy per unit mass, pressure, and specific volume. Since $P_1 \gg P_0$, for explosives Eq. (1) can be written as [17]:

$$E_1 - E_0 = \frac{1}{2}P_1(V_0 - V_1) + Q \quad (2)$$

where E_0 is the specific internal energy of the solid explosive and Q is the specific chemical energy released by the explosive detonation. If the detonation products are regarded as polytropic gases $p = AV^{-\gamma}$, where γ is the polytropic exponent, the detonation pressure (P_{CJ}) and the specific volume (V_{CJ}) at the Chapman-Jouguet (CJ) point can be expressed as [17]:

$$V_{CJ} = \frac{\gamma}{\gamma + 1} V_0 \quad (3)$$

$$P_{CJ} = \frac{1}{\gamma + 1} \rho_0 D^2 \quad (4)$$

$$D = \sqrt{2(\gamma^2 - 1)Q} \quad (5)$$

where ρ_0 is the initial density. The substitution of Eqs. (3), (4), and (5) into Eq. (2) yields the change of internal energy per unit

volume at the CJ point:

$$(E_{CJ} - E_{00})\rho_0 = \frac{\gamma}{\gamma - 1} \frac{D^2 \rho_0}{(\gamma + 1)^2} = \frac{(\rho_0 D^2 - P_{CJ})P_{CJ}^2}{(\rho_0 D^2 - 2P_{CJ})\rho_0 D^2} \quad (6)$$

Obviously the value of $(E_{CJ} - E_{00})\rho_0$ can reflect the driving force of detonation products of energetic compounds. Based on the crystal density and the solid-phase enthalpy of formation, the VLW EOS method has been employed to calculate D and P_{CJ} . The detonation velocity has also been calculated using the convenient Stine method [18]:

$$D = 3.69 + \rho_0[13.85n_N + 37.74n_N + 68.11n_O + 3.95n_H + 0.1653\Delta_f H_0(s)]/M \quad (7)$$

where D is in km/s, ρ_0 is in g/cm³, $\Delta_f H^0(s)$ is the solid-phase enthalpy of formation in kJ/mol, and n_C , n_N , n_O , and n_H are, respectively, the numbers of atoms C, N, O, and H, and M is the molecular mass of compound. For CHNO energetic compounds the Stine method is relatively more accurate than the Kamlet-Jacobs empirical method [19].

Results and Discussion

Geometry and Bond Order

Molecular structure has an important influence on susceptibility to shock- and impact-induced reactivity [20]. In fact, for most nitroaromatic compounds it has been confirmed that the C–NO₂ bond is of key importance in determining impact and shock sensitivities [21]. In general, the stronger the C–NO₂ bond, the less sensitive the compound. For highly nitrated azacubanes it is realistically postulated that the C–N bonds on the cage skeleton would be related to impact and shock sensitivities due to the existence of large cage strain energy.

The atomic numberings for the cage skeletons of highly nitrated azacubanes are displayed in Fig. 1, which are consistent with the positions of substituents. Vibrational analysis shows that there are no imaginary frequencies for all optimized

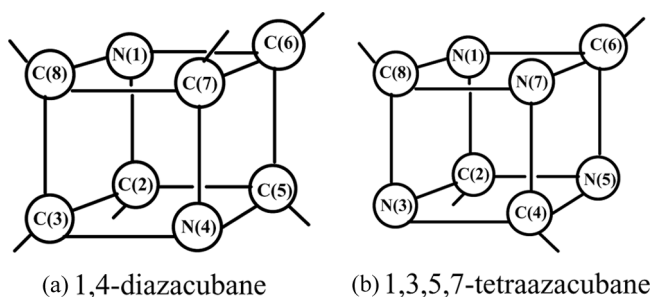


Figure 1. Atomic numberings for the cage skeletons of highly nitrated azacubanes.

structures, which suggests that all the structures obtained are local minima on the potential energy surface. The calculated longest bond length and the least atom–atom overlap-weighted NAO bond order for the C–C and C–N bonds on the cage skeletons are listed in Table 1. It can be seen from Table 1 that after the full nitration of 1,3,5,7-tetraazacubane the longest C–N bond length on the cage skeleton shrinks by 0.0006 nm and the least C–N bond order increases by 0.006. Therefore, the C–N bond on the cage skeleton of TNTAzC is slightly stronger than that of 1,3,5,7-tetraazacubane. But the full nitration of 1,4-diazacubane makes the C–N bond on the cage skeleton weaken and the C–C bond strengthen. It is worth comparing the bond orders of HNDAC and TNTAzC. For TNTAzC the least C–N bond order is 0.746, which is larger than the least C–N bond order (0.704) of HNDAC, implying that the shock stability of TNTAzC is superior to that of HNDAC.

For aromatics and other unsaturated systems, the proper introduction of $-\text{NH}_2$ group can usually get a stable and insensitive molecule. However, for DATNDAC and ATNTAzC the introduction of $-\text{NH}_2$ group makes the neighboring C–N bond on the cage skeleton elongate significantly. For DATNDAC, r_{2-5} reaches 0.1592 nm, and for ATNTAzC, r_{1-2} reaches 0.1591 nm. Consequently, for highly nitrated azacubanes, the introduction of $-\text{NH}_2$ group has a large destabilizing effect on

Table 1

The longest bond length (r/nm) and the least atom-atom overlap-weighted NAO bond order (β) for the C-C and C-N bonds on the cage skeletons for DAzC, TAzC, and their highly nitrated derivatives

Compounds	Parameters	Compounds	Parameters	Compounds	Parameters			
DAzC	r_{1-2}	0.1540	DATNDAzC	r_{4-7}	0.1574	TNTAzC	r_{3-8}	0.1506
	b_{1-2}	0.729		β_{4-7}	0.689		β_{4-5}	0.746
	r_{2-3}	0.1547		r_{2-5}	0.1592	ATNTAzC	r_{1-2}	0.1591
	β_{2-3}	0.805		β_{2-5}	0.790		β_{1-2}	0.665
HNDAzC	r_{1-8}	0.1520	TAzC	r_{1-2}	0.1512			
	β_{1-8}	0.704		β_{1-2}	0.740			
	r_{3-8}	0.1548						
	β_{3-8}	0.829						

the cage skeleton, which is in agreement with a previous ab initio study of nitrocubanes [22]. In summary, for highly nitrated azacubanes it is inappropriate to introduce the $-\text{NH}_2$ group onto the cage skeletons.

Gas Phase Enthalpy of Formation

For energetic compounds the gas-phase enthalpy of formation [$\Delta H_f^0(\text{g})$] is an important thermodynamic property. The calculated gas-phase enthalpies of formation for reference compounds CH_4 , CH_3NH_2 , CH_3NO_2 , cubane, DAzC, and TAzC using the G3(MP2) method [23] and the atomization scheme are listed in the top lines of Table 2. Table 2 shows that

Table 2

Enthalpy and gas-phase enthalpy of formation for CH_4 , CH_3NH_2 , CH_3NO_2 , cubane, DAzC, and TAzC at the G3(MP2) level and for HNDAzC, DAHNDAzC, TNTAzC, and ATNTAzC at the B3LYP/6-31++G** level at $P = 1.013 \times 10^5$ Pa and $T = 298$ K
(1 hartree = 2625.50 kJ/mol)

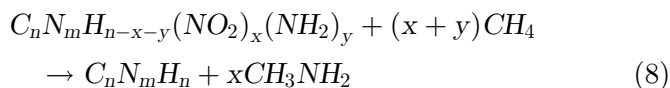
Compounds	(kJ/mol)	(kJ/mol)	(kJ/mol)
CH_4	-106,118.20	-74.3	-74.8 ^a
CH_3NH_2	-259,088.99	-16.8	-23.0 ^a
CH_3NO_2	-642,460.40	-66.1	-74.7 ^a
cubane	-811,032.40	613.9	622.2 ^b
DAzC	-895,219.33	760.2	
TAzC	-979,432.77	880.0	
ONC	-5,107,233.24	857.4	
HNDAzC	-4,117,703.41	929.8	
DATNDAzC	-3,334,670.17	769.6	
TNTAzC	-3,128,177.20	1006.6	
ATNTAzC	-2,736,676.87	910.2	

^aFrom Weast et al. [29].

^bFrom Kybett et al. [30].

the G3(MP2) calculated $\Delta H_f^0(\text{g})$ approaches relatively the corresponding experimental value. The gas-phase enthalpy of formation of azacubane is larger than that of cubane, implying that the replacement of carbon atoms of cubane with nitrogen atoms can boost the energy significantly.

For highly nitrated azacubanes, it is very expensive to use the G3(MP2) method to calculate their enthalpies of formation, so the isodesmic concept has been adopted. The isodesmic reactions are designed as follows, in which the cage skeleton is not destroyed:



where $C_n N_m$ is the cage skeleton and x and y stand for the numbers of $-\text{NO}_2$ and $-\text{NH}_2$ groups, respectively. By employing the B3LYP/6-31++G** calculated enthalpies (H^0) of all reactants and products, which are corrected for the zero-point energy, the isodesmic reaction, the above G3(MP2) calculated $\Delta H_f^0(\text{g})$, and the calculated values of $\Delta H_f^0(\text{g})$ for highly nitrated azacubanes at $P = 1.013 \times 10^5$ Pa and $T = 298$ K are listed in the bottom lines of Table 2. For brevity, the B3LYP/6-31++G** calculated enthalpies for reference compounds CH_4 , CH_3NH_2 , CH_3NO_2 , cubane, DAzC, and TAzC are not displayed in Table 2. It is obvious that highly nitrated azacubanes hold the large enthalpy of formation. Owing to parent contribution, the enthalpy of formation increases greatly from the fully nitrated cubane and diazacubane to tetraazacubane.

Crystal Density

Equations (4), (6), and (7) reveal that the crystal density influences directly the detonation performance. During the ab initio prediction of crystal structure, the Dreiding force field [24], which models carbon, nitrogen, oxygen, and hydrogen accurately, has been adopted, and the 17 most common space groups are considered [25]; the asymmetric unit contains one rigid unit. The calculated crystal density ($\rho_{\text{K-D}}$) and binding

energy (ΔE) by the Karfunkel–Gdanitz method are arranged in Table 3 for the five space groups with lower total energy. For convenient comparison, Table 3 also gives the calculated crystal density (ρ_{add}) by the group additivity method [26].

An energetic compound usually has several polymorphs, which can be obtained from recrystallization with different solvents, and we are interested in the polymorph with the largest density. Table 3 shows that for an energetic compound, generally the larger the crystal binding energy, the larger the crystal density. The largest value of $\rho_{\text{K-D}}$ for ONC is 2.065 g/cm³ with the $P\bar{1}$ space group, which approaches more the experimental (1.979 g/cm³) with respect to the ρ_{add} (2.111 g/cm³). The crystal density for HNDAzC and TNTAzC are predicted to reach 1.975 and 2.156 g/cm³, respectively, implying that the two compounds have very large crystal density.

Table 3

Calculated crystal density and binding energy for HNDAzC, TNTAzC, and ONC

Compounds	ρ_{exp} (g/cm ³)	ρ_{add} (g/cm ³)	Space groups	ΔE (kJ/mol)	$\rho_{\text{K-D}}$ (g/cm ³)
HNDAzC		2.144	P2 ₁	142.3	1.975
			P2 ₁ /c	137.7	1.912
			$P\bar{1}$	133.5	1.896
			P1	133.5	1.897
			C2/c	132.2	1.894
TNAzC		2.199	P2 ₁ 2 ₁ 2 ₁	149.0	2.156
			P2 ₁	149.0	2.155
			Cc	143.5	1.996
			P2 ₁ /c	138.5	2.074
			Pca2 ₁	135.6	2.066
ONC	1.979	2.111	$P\bar{1}$	147.3	2.065
			P2 ₁	134.7	1.954
			P2 ₁ /c	131.0	1.971
			Pna2 ₁	129.7	1.932
			C2/c	128.0	1.930

Detonation Performance

In order to evaluate the driving force of detonation products of highly nitrated azacubanes, the widely used highly explosive HMX is recommended as a reference compound, and from Eq. (6) the relative driving force of detonation products of other energetic compounds is judged by

$$I_e = \frac{(\rho_0 D^2 - P_{CJ}) P_{CJ}^2}{(\rho_0 D^2 - 2P_{CJ}) \rho_0 D^2} \bigg/ \frac{(\rho_{HMX} D_{HMX}^2 - P_{HMX}) P_{HMX}^2}{(\rho_{HMX} D_{HMX}^2 - 2P_{HMX}) \rho_{HMX} D_{HMX}^2} \quad (9)$$

where P_{HMX} is the experimental detonation pressure (39.0 GPa) for HMX, D_{HMX} is the detonation velocity (9.11 km/s), and ρ_{HMX} is the corresponding density (1.894 g/cm³) [2]. The experimental I_e by the cylinder test and the calculated I_e by Eq. (9) are listed in Table 4, in which E_{cyl} is the specific wall kinetic energy at 19 mm wall displacement in the cylinder test and can determine the driving force of detonation products of explosives [2]. Table 4 shows that the calculated I_e by Eq. (9) is very in agreement with the experimental I_e .

In order to calculate the detonation performance of energetic compounds, the solid-phase enthalpy of formation is

Table 4

Experimental detonation performance [2] and relative driving force of detonation products for ordinary explosives

Compounds	ρ_0 (g/cm ³)	D (km/s)	P_{CJ} (GPa)	E_{cyl} (km ² /s ²)	I_e^{exp}	I_e^{cal}
CH ₃ NO ₂	1.130	6.35	12.5	0.745	0.43	0.35
TNT	1.63	6.93	21.0	0.975	0.56	0.58
TATB	1.86	7.66	25.9	1.045	0.62	0.64
PETN	1.765	8.26	33.5	1.575	0.90	0.96
RDX	1.767	8.70	33.8	1.600	0.92	0.88
BTF	1.859	8.49	36.0	1.680	0.96	0.99
HMX	1.894	9.11	39.0	1.745	1.00	1.00

necessary. A procedure for converting gas to solid-phase enthalpy of formation has been developed by Politzer et al. [27] on the basis of the calculated electrostatic potential on the molecular surface. In this work, $\Delta H_f^0(s) = \Delta H_f^0(g) - \Delta E$. Based on ρ_{K-D} and $\Delta H_f^0(s)$, the calculated values of D , P_{CJ} , and I_e for HNDAzC, TNAzC, and ONC are summarized in Table 5. For ONC and HNDAzC, the calculated D by the Stine method is 0.15–0.35 km/s larger than by the VLW EOS method, but for compound TNTAzC is 0.32–0.90 km/s less than by the VLW EOS method. As a whole, the detonation velocities from the two methods are in good agreement. The detonation velocity and pressure of HNDAzC are close to the

Table 5

Calculated solid phase enthalpy of formation, detonation velocity, detonation pressure, and relative driving force of detonation products for HNDAzC, TNAzC, and ONC

Compounds	Space groups	$\Delta H_f^0(s)$ (kJ/mol)	Stine D (km/s)	VLW		
				D (km/s)	P_{CJ} (GPa)	I_e
HNDAzC	P2 ₁	787.5	9.82	9.47	58.2	1.98
	P2 ₁ /c	792.1	9.62	9.37	53.8	1.78
	P $\bar{1}$	796.3	9.58	9.34	52.9	1.75
	P1	796.3	9.58	9.34	52.9	1.75
	C2/c	797.6	9.57	9.34	52.7	1.73
TNTAzC	P2 ₁ 2 ₁ 2 ₁	857.6	10.68	11.10	101.7	4.02
	P2 ₁	857.6	10.67	11.10	101.7	4.02
	Cc	863.1	10.16	11.06	96.7	3.96
	P2 ₁ /c	868.1	10.42	11.08	99.2	3.99
	Pca2 ₁	871.0	10.40	11.08	100.1	4.08
ONC	P $\bar{1}$	710.1	9.91	9.61	60.7	2.00
	P2 ₁	722.7	9.59	9.41	53.6	1.72
	P2 ₁ /c	726.4	9.64	9.44	54.7	1.76
	Pna2 ₁	727.7	9.52	9.37	52.4	1.67
	C2/c	729.4	9.52	9.36	52.3	1.67

corresponding values of ONC . From the three compounds, TNTAzC has the largest detonation velocity and pressure, which are 11.10 km/s and 101.7 GPa, respectively.

The value of I_e shows that HNDazC and ONC both have the close driving force of detonation products, which is 1.7–2.0 times as large as that of HMX, implying that HNDazC is more powerful than the most powerful used nonnuclear explosive CL-20, whose driving force of detonation products exceeds that of HMX by about 14% [28]. The driving force of detonation products of TNTAzC is about 4.0 times as large as that of HMX, showing that TNTAzC is a potential candidate of super high-energy compound.

Conclusions

This work has investigated the geometries, electronic structures, enthalpies of formation, crystal densities, and detonation parameters of highly nitrated azacubanes. An efficient theoretical procedure for judging the driving force of detonation products of energetic materials has been developed from the conservation of energy condition. After the full nitration of 1,4-diazacubane and 1,3,5,7-tetraazacubane, the weakest C–N bond on the 1,3,5,7-tetraazacubane cage skeleton strengthens slightly but on the 1,4-diazacubane cage skeleton weakens. For highly nitrated azacubanes, the introduction of $-NH_2$ group results in the destabilization of the neighboring C–N bond on the cage skeleton. The MP2/6-31++G**//B3LYP/6-31++G** atom-atom overlap-weighted NAO bond order implies that the shock stability of TNTAzC is superior to that of HNDazC. The values of crystal density for HNDazC and TNTAzC can reach 1.975 and 2.156 g/cm³, respectively. The detonation velocity and pressure for TNTAzC are predicted to be 11.10 km/s and 101.7 GPa, respectively. The driving force of detonation products of HNDazC is close to that of ONC , and the driving force of TNTAzC is about 4.0 times as large as that of HMX, showing that TNTAzC is a potential candidate of super high-energy compound.

Acknowledgments

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