



# Canadian Journal of Chemistry

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Journal:	<i>Canadian Journal of Chemistry</i>
Manuscript ID	cjc-2017-0312.R1
Manuscript Type:	Article
Date Submitted by the Author:	02-Jul-2017
Complete List of Authors:	Pan, Yong; Nanjing Polytechnic Institute Zhu, Weihua; Nanjing University of Science and Technology Xiao, Heming; Nanjing University of Science and Technology, Department of Chemistry
Is the invited manuscript for consideration in a Special Issue?:	Not applicable (regular submission)
Keyword:	Azaoxadamantane cage, Density functional theory, Detonation properties, Thermal stability, Impact sensitivity

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# Molecular design on a new family of azaoxadamantane cage compounds as potential high-energy density compounds

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**Abstract**

A new family of azaoxadamantane cage compounds were firstly designed by introducing the oxygen atom into hexanitrohexaazaadamantane (HNHAA) to replace the N-NO<sub>2</sub> group. Their properties including heats of formation (*HOFs*), detonation properties, strain energies, thermal stability, and sensitivity were extensively studied by using density functional theory. All of the title compounds exhibit surprisingly high density ( $\rho > 2.01 \text{ g/cm}^3$ ) and excellent detonation properties ( $D > 9.35 \text{ km/s}$  and  $P > 41.35 \text{ GPa}$ ). In particular, B (4,8,9,10-tetraazadioxaadamantane) and C (6,8,9,10-tetraazadioxaadamantane) have a remarkably high *D* and *P* values (9.70 km/s and 44.45 GPa), which are higher than that of HNHAA or CL-20. All of the title compound have higher thermal stability and lower sensitivity ( $h_{50} > 19.58 \text{ cm}$ ) compared to the parent compound HNHAA. Three triazatrioxadamantane cage compounds, D (6,8,9-triazatrioxadamantane), E (6,8,10-triazatrioxadamantane), and F (8,9,10-triazatrioxadamantane), are expected to be relatively insensitive explosives. All of the title compounds exhibit a combination of high denotation properties, good thermal stability, and low insensitivity.

**Keywords**

Azaoxadamantane cage, Density functional theory, Detonation properties, Thermal stability, Impact sensitivity

## Introduction

With the rapid development of national defense and modern economy, considerable attention has been paid to the development of novel high energy density compounds (HEDCs) that exhibit high density, high detonation properties, good thermal stability, and low sensitivity to external stimuli.<sup>1-4</sup> In recent decades, energetic cage compounds, such as hexanitrohexaazaadamantane (HNHAA), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), octanitrocubane (ONC) etc. (Fig. 1) have been extensively investigated as an important category of HEDCs due to their excellent performance over conventional energetic compounds<sup>4-10</sup>. Among them, polynitro-substituted adamantanes and azaadamantanes have attracted considerable interest as the potentials of HEDCs since 1,3,5,7-tetranitroadamantane was reported to be moderate power output, insensitive, and good thermal stability (m.p. >360 °C).<sup>5,6,11-14</sup> Especially, HNHAA has been forecasted to be a promising HEDM and listed as one of the 21 critical technologies of the Department of Defense Critical Technologies Plan (DCTP, USA) (AD-A234900).<sup>5,11,14</sup> It is found that attaching more substituents such as nitro groups to the adamantane or azaadamantane cage skeleton is helpful to increase the mass density and heat of formation and so enhances effectively detonation performance. However, the introduction of more nitro groups should lead to a dramatic increase in thermal instability and impact sensitive. Moreover, too many nitro groups in the structure increase the difficulty and cost in their synthesis. Therefore, much effort continues to be put into designing novel compounds based on the azaadamantane or adamantane cage skeleton to obtain novel HEDCs with improved energetic properties and reduced sensitivity.

<Fig. 1 about here>

In this work, six azaoxadamantane cage compounds (see Fig. 2) were designed based on the hexanitrohexaazaadamantane (HNHAA) by introducing one to three oxygen atom(s) into the azaadamantane cage to replace the N-NO<sub>2</sub> groups. And their molecular structure, heats of formation (*HOFs*), energetic properties, strain energy, thermal stability, and impact sensitivity were systematically investigated by density functional theory (DFT) method. To our best knowledge, no work devoted to studying the azaoxadamantane cage compounds was reported till now. It is unclear whether the introduction of oxygen atom into azaadamantane cage skeleton would be helpful to improve energetic performance and stability for the parent compound. The study will provide useful information for design or experimental studies of potential HEDCs.

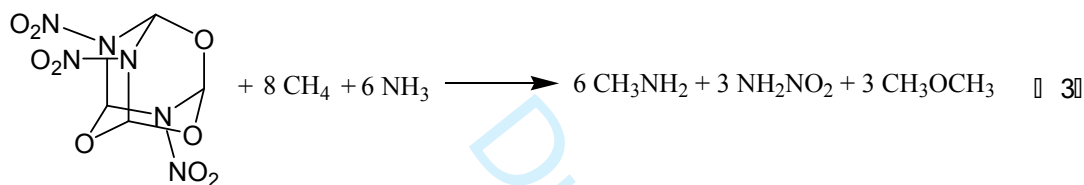
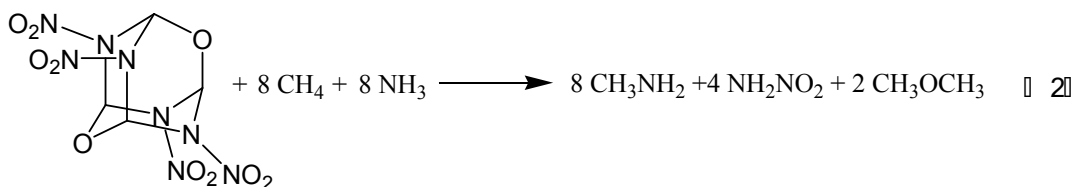
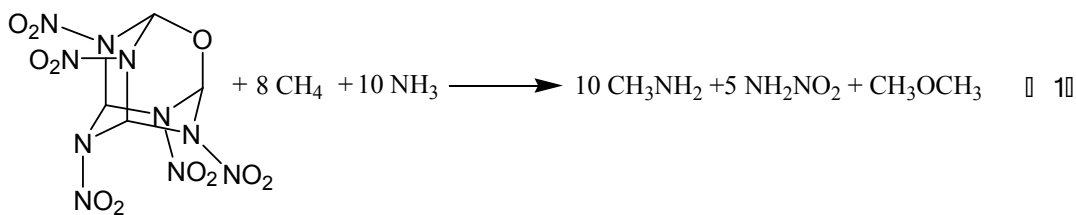
<Fig. 2 about here>

### Computational method

The hybrid DFT-B3LYP method with the 6-311G(d, p) basis set was adopted to optimize the molecular structures and calculate total energy ( $E_0$ ), zero-point energies (*ZPE*), and thermal correction ( $H_T$ ). Previous studies have shown that the basis set 6-311G(d, p) is able to precisely figure out molecular structure and energies of energetic organic compounds.<sup>15-18</sup> The optimizations were performed without any symmetry restrictions using the default convergence criteria in the program. All of the optimized structures were characterized to be true local energy minima on the potential energy surfaces without imaginary frequencies. The calculations were performed with Gaussian 09 package.<sup>19</sup>

The gas-phase *HOF* ( $\Delta H_{f, gas}$ ) were estimated using isodesmic reaction method, which has been demonstrated to evaluate reliably the gas-phase *HOFs* of many organic

systems.<sup>9,15-18,20</sup> The isodesmic reactions are designed to obtain the gas-phase *HOFs* of the title compounds at 298 K are as follows:



For the isodesmic reaction, the heat of reaction  $\Delta H_{298\text{K}}$  at 298 K can be calculated from the following equation:

$$\Delta H_{298\text{K}} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R} \quad (4)$$

where  $\Delta H_{f,R}$  and  $\Delta H_{f,P}$  are the *HOFs* of reactants and products at 298 K, respectively.

Therefore, the  $\Delta H_{298\text{K}}$  can be evaluated using the following expression:

$$\Delta H_{298\text{K}} = \Delta E_{298\text{K}} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (5)$$

where  $\Delta E_0$  is the change in total energy between the products and the reactants at 0 K;  $\Delta ZPE$  is the difference between the zero-point energies (*ZPE*) of the products and the reactants at 0 K;  $\Delta H_T$  is thermal correction from 0 to 298 K. The  $\Delta(PV)$  value equals  $\Delta nRT$  for the reactions of ideal gas.

Since the condensed phase for most energetic compounds is solid, the calculation of detonation properties requires solid-phase *HOF* ( $\Delta H_{f,solid}$ ). According to Hess's law<sup>21</sup>, the

gas-phase *HOF* ( $\Delta H_{f,gas}$ ) and heat of sublimation ( $\Delta H_{sub}$ ) can be used to evaluate their solid-phase *HOF*:

$$\Delta H_{f,solid} = \Delta H_{f,gas} - \Delta H_{sub} \quad (6)$$

The  $\Delta H_{sub}$  can be calculated by the empirical expression suggested by Politzer et al.,<sup>22,23</sup> which can predict reliably  $\Delta H_{sub}$  of many energetic compounds.<sup>24-26</sup> The equation is as follows:

$$\Delta H_{sub} = aA^2 + b(\nu\sigma_{tot}^2)^{0.5} + c \quad (7)$$

where  $A$  is the surface area of the 0.001 electrons/bohr<sup>3</sup> isosurface of electronic density of the molecule,  $\nu$  describes the degree of balance between positive and negative potential on the isosurface, and  $\sigma_{tot}^2$  is a measure of variability of the electrostatic potential on the molecular surface. The descriptors  $A$ ,  $\nu$ , and  $\sigma_{tot}^2$  were calculated using the computational procedures proposed by Bulat *et al.*<sup>26</sup> The coefficients  $a$ ,  $b$ , and  $c$  were determined by Rice *et al.*:  $a = 2.670 \times 10^{-4}$  kcal/mol/Å<sup>4</sup>,  $b = 1.650$  kcal/mol, and  $c = 2.966$  kcal/mol.<sup>24</sup>

For a molecular formula like C<sub>a</sub>H<sub>b</sub>O<sub>c</sub>N<sub>d</sub>, the detonation velocity and detonation pressure were estimated by the Kamlet-Jacobs equations<sup>27</sup> as

$$D = 1.01(N\bar{M}^{1/2} Q^{1/2})^{1/2} (1 + 1.30\rho) \quad (8)$$

$$P = 1.558\rho^2 N\bar{M}^{1/2} Q^{1/2} \quad (9)$$

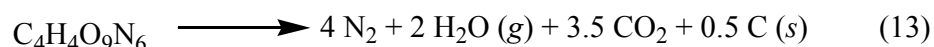
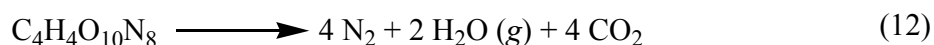
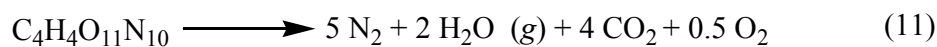
where  $\rho$  is the density of explosives (g/cm<sup>3</sup>),  $D$  is the detonation velocity (km/s),  $P$  is the detonation pressure (GPa),  $N$  is the moles of detonation gases per gram explosive,  $\bar{M}$  is the average molecular weight of these gases, and  $Q$  is the heat of detonation (cal/g). As the  $Q$  and  $\rho$  of some compounds cannot be evaluated from experimental measures, their  $Q$  and  $\rho$  need be firstly calculated.

For the title compounds, the theoretical density was corrected with an improved approach developed by Politzer *et al.*,<sup>28</sup> in which the electrostatic interaction index  $v\sigma_{tot}^2$  was introduced:

$$\rho = \beta_1 \left( \frac{M}{V(0.001)} \right) + \beta_2 (v\sigma_{tot}^2) + \beta_3 \quad (10)$$

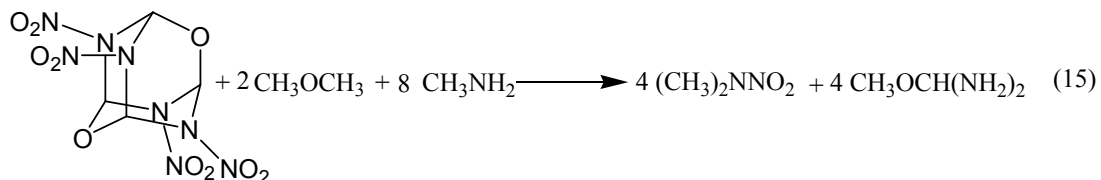
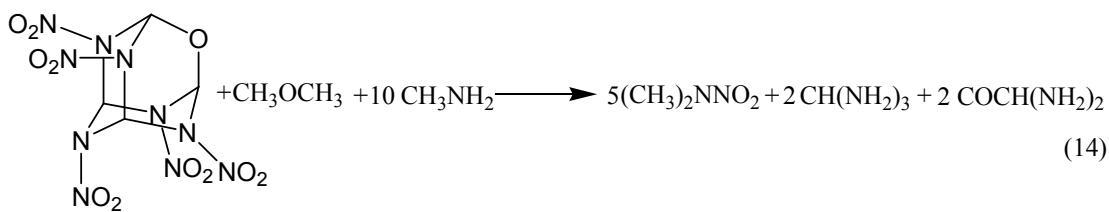
where  $M$  is the molecular mass (g/mol), and  $V(0.001)$  is the volume of the 0.001 electrons/bohr<sup>3</sup> contour of electronic density of the molecule (cm<sup>3</sup>/molecule). The coefficients  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  are 1.0462, 0.0021, and -0.1586, respectively.<sup>29</sup>

The heat of detonation  $Q$  was evaluated by the *HOF* difference between products and explosives according to the principle of exothermic reactions. For the title compounds, all the N atoms turn into N<sub>2</sub>, and oxygen atoms go to H<sub>2</sub>O before CO<sub>2</sub>. The detonation products are supposed to be CO<sub>2</sub> (or C), H<sub>2</sub>O, and N<sub>2</sub>, so released energy in the decomposition reaction reaches its maximum. The detonation reactions of the title compounds are as follows:



Strain energy (*SE*) is an important parameter for evaluating the stability and reactivity of organic cage compounds. The strain energy can be predicted successfully via homodesmotic reaction based on ab initio calculations.<sup>30-34</sup> In this work, strain energies of these azaoxadamantane cage compounds were investigated by the corresponding homodesmotic reactions designed as follows:





The change of energies with zero-point vibrational energy (*ZPE*) correction in the homodesmotic reactions can be obtained from eq. 16:

$$\Delta H_{298\text{K}} = \sum E_{\text{product}} - \sum E_{\text{reactant}} + \Delta ZPE \quad (16)$$

The strength of bonding, which could be evaluated by bond dissociation energy (BDE), is fundamental to understand chemical processes.<sup>35</sup> The energy required for bond homolysis at 298 K and 1 atm corresponds to the enthalpy of reaction  $\text{A-B}(\text{g}) \rightarrow \text{A}\cdot(\text{g}) + \text{B}\cdot(\text{g})$ , which is the bond dissociation enthalpy of the molecule A-B by definition.<sup>36</sup> For many organic molecules, the terms “bond dissociation energy” and “bond dissociation enthalpy” often appear interchangeably in the literature.<sup>37</sup> Therefore, at 0 K, the homolytic bond dissociation energy can be given in terms of eq. (17):

$$BDE_0(\text{A-B}) \rightarrow E_0(\text{A}\cdot) + E_0(\text{B}\cdot) - E_0(\text{A-B}) \quad (17)$$

The bond dissociation energy with zero-point energy (*ZPE*) correction can be calculated by eq. (18)

$$BDE(\text{A-B})_{\text{ZPE}} = BDE_0(\text{A-B}) + \Delta E_{\text{ZPE}} \quad (18)$$

where  $\Delta E_{\text{ZPE}}$  is the difference between the ZPEs of the products and the reactants.

Impact sensitivity is generally characterized through a drop weight test and reported as the height in cm, designated as  $h_{50}$ . For the title compound, impact sensitivity was

predicted by a simple method suggested by Pospíšil et al.<sup>38,39</sup>

$$h_{50} = \alpha\sigma_+^2 + \beta\nu + \gamma \quad (19)$$

where  $h_{50}$  is the height from which the sample is impacted by a 2.5 kg dropping mass and there is a 50% probability of causing an explosion,<sup>40,41</sup>  $\sigma_+^2$  indicates the strengths and variabilities of the positive surface potentials,  $\nu$  is the balance of charges between positive potential and negative potential on the molecular surface, and the coefficients  $\alpha$ ,  $\beta$ , and  $\gamma$  are -0.0064, 241.42, and -3.43, respectively.

## Results and discussion

**Molecular geometry and electronic structure** Table 1 lists some bond parameters of the title compounds along with HNHA for comparison.

*<Table 1 about here>*

Seen from Table 1, all the N-N bonds linked to the cage of the title compounds are shorter than the normal N-N single bond (1.45 Å), which may be due to hyper-conjugation effects between nitrogen atoms and nitro groups in the system. In addition, the average value of the N-N bond length of the title compounds is shorter than that of the parent compound HNHA. On the whole, as the N-NO<sub>2</sub> group in the azaadamantane cage is replaced by the oxygen atom, the average N-N bond length of the title compounds decreases except for F. The average bond lengths of C-N in the cage for the title compounds are smaller than those of HNHA except for E and F, but the differences are not significant.

Table 1 also lists the energies of HOMO, LUMO, and their energy gap ( $\Delta E$ ) of the title compound and HNHA. All of the title compounds have larger  $\Delta E$  than HNHA. It is found that the  $\Delta E$  values of these cage compounds increase generally as the oxygen atom in the azaadamantane cage increases. The 3D plots of HOMO and LUMO for the title

compounds were illustrated in Fig. 3. It is seen in Fig. 3 that all of their C–N orbits or N–N orbits participate in both the HOMO and LUMO levels, in which the positive phase is shown in red while the negative one is shown in green. This means that both removal of an electron from HOMO or addition of an electron to LUMO could weaken their cage skeleton.

<Fig. 3 about here>

<Fig. 4 about here>

Molecular electrostatic potentials (MEPs) of the title compounds for the 0.001 electron/bohr<sup>3</sup> isosurface of electron density are demonstrated in Fig. 4. The colors range from -0.02 to 0.02 Hartree, with red denoting the most negative potential and blue denoting the most positive potential. Previous studies<sup>42</sup> showed that the molecules that are more sensitive to external impact often have a larger electron deficiency within the inner structure than those that are less sensitive. Seen from the MEPs of these cage compounds, the positive potentials locate at the center of the cage skeleton, while the negative potentials appears to be distributed mostly on the N-NO<sub>2</sub> moiety. Obviously, A, B, and C have stronger positive potential focused in the inner cage than other three cage compounds, indicating that A, B, and C exhibit relatively high impact sensitivity.

**Gas-phase and solid-phase heats of formation** Table 2 lists the total energies, *ZPEs*, and thermal corrections for five reference compounds in the isodesmic reactions. The experimental gas-phase *HOFs* of CH<sub>4</sub>, NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub>, NH<sub>2</sub>NO<sub>2</sub>, and CH<sub>3</sub>OCH<sub>3</sub> were taken from Ref. <sup>43</sup>.

<Table 2 about here>

Table 3 presents the total energies, *ZPEs*, thermal corrections,  $\Delta H_{f,gas}$ , and  $\Delta H_{f,solid}$  of

the title compounds. It is seen from Table 3 that the  $\Delta H_{f,gas}$  and  $\Delta H_{f,solid}$  of all of the title compounds are smaller than those of HNHA. As the N-NO<sub>2</sub> group of the hexaazaadamantane cage is replaced by the oxygen atom, the  $\Delta H_{f,gas}$  and  $\Delta H_{f,solid}$  of the cage compounds decrease markedly. Among these azaadamantane cage compounds, A has the highest  $\Delta H_{f,gas}$  and  $\Delta H_{f,solid}$ , whereas E has the smallest ones.

Furthermore, to illustrate the effects of the oxygen atom in the cage on the *HOFs* for the title compounds, the variation of the calculated *HOFs* with the number (*n*) of oxygen atom in the azaadamantane cage are described in Fig. 5. For isomers with the same *n*, the average value of *HOFs* is used. Obviously, there exists a linear relationship with good correlation coefficients (*R*=0.9983 or 0.9980, respectively) between the  $\Delta H_{f,gas}$  or  $\Delta H_{f,solid}$  and the number (*n*) of the oxygen atom in the cage. For the cage compounds, the induction of each oxygen atom will result in the decrease of the gas-phase or solid-phase *HOFs* by 257.0 kJ/mol or 244.9 kJ/mol on average, respectively.

<Table 3 about here>

<Fig. 5 about here>

In addition, the space orientations of oxygen atom also affect the *HOFs* of the title compounds. For the isomer with the same number of oxygen atom, the shorter the distance between the oxygen atoms in the cage of a compound is, the larger the  $\Delta H_{f,gas}$  or  $\Delta H_{f,solid}$  is. e.g., B has a somewhat higher *HOF* than C, while F has higher *HOF* than D or E, when two oxygen atoms were introduced into the azaadamantane cage.

**Detonation properties** Detonation velocity and detonation pressure are two key performance parameters of energetic materials. Table 4 and Fig.6 present the calculated  $\rho$ , heat of detonation (*Q*), Detonation velocity (*D*), detonation pressure (*P*), and oxygen

balance (*OB*) of the title compounds along with HNHA. The semi-empirical Kamlet-Jacobs formula has been proved to be reliable for predicting the explosive properties of energetic high-nitrogen compounds.<sup>44,45</sup> To compare with previous studies, the calculated *D* and *P* values of HNHA based on its uncorrected density (2.064 g/cm<sup>3</sup>) were investigated. It is found that the uncorrected  $\rho$ , *D*, and *P* values of HNHA (9.78 km/s, 45.87 GPa, and 2.064 g/cm<sup>3</sup>) agree well with previous studies (9.95 km/s, and 47.52 GPa, and 2.080 g/cm<sup>3</sup>)<sup>5</sup>, where the uncorrected density is used. This indicates that our calculated results in this section are reliable.

<Table 4 about here>

<Fig. 6 about here>

As an important parameter for selecting potential HEDCs, the oxygen balance (*OB*) is defined as the number of equivalents of the oxygen content per hundred grams of explosive (C<sub>a</sub>H<sub>b</sub>O<sub>c</sub>N<sub>d</sub>) above or under the total oxygen required for converting all the carbon to CO<sub>2</sub> and all the hydrogen to H<sub>2</sub>O. By and large, the higher the *OB* value is, the larger the *D* and *P* values of an explosive are. Our previous studies<sup>34,46</sup> indicate that an explosive with oxygen balance equal to zero or around zero often have outstanding detonation properties. It is seen in Table 4 that the *OB*s of all these azaoxadamantane cage compounds are more close to zero compared with HNHA. Especially, the *OB* of B or C is equal to zero. This indicated that the title compound might present excellent detonation properties.

As shown in Table 4, the densities of all the azaoxadamantane cage compounds are surprisingly high ( $\rho > 2.010$  g/cm<sup>3</sup>) and very close to that of HNHA (2.021 g/cm<sup>3</sup>), which is attributed to the compact azaoxadamantane cage of the molecule to a great extent. On the whole, as the N-NO<sub>2</sub> group of HNHA is replaced by the oxygen atom,

the densities of these cage compounds slightly decrease.

All the title compounds have remarkably high  $D$  and  $P$  values, which are superior to or very close to that of CL-20 (9.40 km/s and 42.00 GPa). Especially, B and C, two tetraazadioxaadamantane cage compounds, have the best  $D$  and  $P$  values (9.65 km/s and 44.04 GPa) among these cage compounds and are higher than that of HNHA. It suggests that all the title compounds can be regarded as potential candidates of HEDCs. In addition, though the triazatrioxaadamantane cage compound (D, E, or F) possess only three nitramine moieties in the structure, these caged compounds exhibit excellent energetic properties ( $\rho > 2.01 \text{ g/cm}^3$ ,  $D > 9.29 \text{ km/s}$  and  $P > 40.81 \text{ GPa}$ ), which significantly exceed that of HMX (1.91 g/cm<sup>3</sup>, 9.10 km/s and 39.00 GPa), a widely used explosive containing four nitramine moieties in the molecule. Therefore, it can be concluded that constructing the azaoxaadamantane cage by introducing oxygen atom(s) is an effective way to obtain energetic compounds with excellent detonation properties.

In Fig. 5, the variation trends of  $D$  and  $P$  of the title compounds are basically the same, which firstly increase and then decrease with the number of the oxygen atom increasing. This is because eliminating three N-NO<sub>2</sub> groups leads to a negative oxygen balance values and decreases  $Q$  greatly.

**Strain energies** The calculated strain energies of the azaoxaadamantane cage skeleton of the title compounds via homodesmotic reactions are listed in Table 5. Obviously, all the title compounds have lower strain energy of the cage skeleton than HNHA. And the strain energy of the azaoxaadamantane cage skeleton decreases when the N-NO<sub>2</sub> groups is replaced by the oxygen atoms. It is found that the introduction of one oxygen atom into the cage decreases the strain energy by 55.37 kJ/mol on average. Therefore, the strain of the azaoxaadamantane cage skeleton is weakened when the N-

NO<sub>2</sub> group is replaced by the oxygen atom, indicating that the introduction of the oxygen atom can improve the stability of the parent cage.

< Table 5 about here >

**Thermal stability** In general, the smaller the energy for breaking a bond is, the easier the bond becomes a trigger bond. For the title compounds, three possible bond dissociations are considered: (1) the N-NO<sub>2</sub> bond linked to the cage; (2) the C-N bond in the cage; (3) the C-O bond in the cage. Table 5 presents the BDEs of the relatively weaker bonds of the title compounds.

It is seen in Table 5 that the N-NO<sub>2</sub> bonds linked to the cage have the lowest *BDE* values for each azaoxadamantane cage compound. It can be inferred that the N-NO<sub>2</sub> bonds for the title compounds are easier to break than other bonds and appears to be the initial step in thermal decomposition or detonation, which is consistent with previous studies on nitramine compounds<sup>15,45,47,48</sup>. In addition, the title compounds have higher *BDE* values of the weakest bond than the parent compound HNHA, which means that the title compounds have higher thermal stability than HNHA. By and large, the *BDE* values of the weakest bonds of these azaoxadamantane cage compounds increase with the number of the oxygen atom increasing except for E. Therefore, the introduction of the oxygen atom may increase thermal stability of the cage compounds, which is agreement with the conclusion from the strain analysis as mentioned above.

According to the suggestion of Chung et al.<sup>49</sup> that the molecule with good stability should have a dissociation barrier of 80-120 kJ/mol, all the title compounds have good thermal stability.

**Impact sensitivity** Table 6 lists the impact sensitivity ( $h_{50}$ ) of the title compounds together with CL-20 and HMX. The predicted  $h_{50}$  value of CL-20 or HMX is quite

consistent with the experimental results,<sup>42</sup> showing that our calculated results are reliable.

< Table 6 about here >

It can be seen that all the title compounds exhibit relatively low sensitivity with their  $h_{50}$  values ranging from 19.58 cm to 34.58 cm. The estimated  $h_{50}$  value of A, B, or C is higher than that of HNHA or CL-20 but close to that of HMX. This indicates that A, B, or C is slightly more sensitive than HMX but more insensitive than HNHA or CL-20. And the  $h_{50}$  values of D, E, and F exceed that of HMX, indicating that these triazatrioxadamantane cage compounds may be relatively insensitive explosives. In addition, as the number of the oxygen atom in the azaoxadamantane cage increases, the  $h_{50}$  values of the title compounds markedly increase. Thus, it can be concluded that the introduction of the oxygen atom by replacing the N-NO<sub>2</sub> group in the cage can effectively decrease the sensitivity of the parent compound.

## Conclusions

In this work, six novel azaoxadamantane cage compounds were designed by properly introducing the oxygen atom into the cage of hexanitrohexaazaadamantane (HNHA) to replace the N-NO<sub>2</sub> group. Then, their structure, energetic properties, strain energy, thermal stability, and impact sensitivity were investigated by DFT method. It is found that all of the title compounds exhibit high density and excellent detonation properties ( $\rho > 2.01$  g/cm<sup>3</sup>,  $D > 9.35$  km/s, and  $P > 41.35$  GPa), close to or even over those of HNHA or CL-20. This indicates that constructing the azaoxadamantane cage in the molecule by introducing oxygen atom(s) is an effective way to obtain high energy compounds.

An analysis of strain energy, thermal stability, and impact sensitivity indicates that



the introduction of the oxygen atom into the cage can effectively increase thermal stability and insensitivity of the parent compound. And all of the title compounds have higher thermal stability and lower sensitivity than the parent compound HNHAA. In particular, D, E, and F are expected to be relatively insensitive explosives with  $h_{50}$  values much higher than that of HMX. In addition, an analysis of *BDE* for several relatively weak bonds suggests that the N–NO<sub>2</sub> bond is the weakest one and is possible to initially rupture in thermal decomposition.

All of the title compounds are very attractive candidates for HEDCs due to outstanding energetic properties and good stability. Especially, both B (4,8,9,10-tetraazadioxaadamantane) and C (6,8,9,10-tetraazadioxaadamantane) have higher detonation performance, better thermal stability, and lower sensitivity than HNHAA and CL-20. Thus, B and C are highly recommended as the potential HEDCs. Our results are expected to provide useful information for future experimental investigations.

### Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 21273115) and was sponsored by Qing Lan Project of Jiangsu Province.

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**Table 1.** Selected bond lengths (Å), energies of HOMO and LUMO, and their energy gap  $\Delta E$  (eV) of the title compounds at the B3LYP/6-311G (d, p) level.

Compd.	N-N linked to the cage	C-N in the cage	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\Delta E$
HNHAA	1.433-1.445 (1.439) <sup>a</sup>	1.460-1.478 (1.468)	-9.37	-3.43	5.94
A	1.430-1.444(1.437)	1.456-1.470 (1.466)	-9.31	-3.25	6.06
B	1.421-1.435(1.429)	1.451-1.473 (1.465)	-9.10	-3.09	6.01
C	1.427-1.439(1.431)	1.461-1.473 (1.467)	-9.16	-3.07	6.09
D	1.416-1.438(1.422)	1.457-1.475 (1.467)	-8.96	-2.89	6.07
E	1.413-1.431(1.424)	1.456-1.478 (1.468)	-9.00	-2.88	6.13
F	1.416-1.426(1.422)	1.462-1.472 (1.468)	-8.95	-2.88	6.07

<sup>a</sup> The values in parentheses are the average one.

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**Table 2.** Calculated total energies ( $E_0$ ), zero-point energies ( $ZPE$ ), thermal corrections ( $H_T$ ), and heats of formation ( $HOFs$ ) for the reference compounds.<sup>a</sup>

Compd.	$E_0$	$ZPE$	$H_T$	$HOF$
NH <sub>3</sub>	-56.5760	0.0343	10.0	-45.9(4) <sup>b</sup>
CH <sub>4</sub>	-40.5337	0.0446	10.0	-74.5(5) <sup>b</sup>
CH <sub>3</sub> NH <sub>2</sub>	-95.8884	0.0638	11.6	-23.4 <sup>b</sup>
NH <sub>2</sub> NO <sub>2</sub>	-261.1138	0.0394	12.3	4.9 <sup>b</sup>
CH <sub>3</sub> OCH <sub>3</sub>	-155.0719	0.0793	14.0	-184.1 <sup>b</sup>

<sup>a</sup>  $E_0$  and  $ZPE$  are in a.u.;  $H_T$  and  $HOF$  are in kJ/mol. The scaling factor is 0.98 for  $ZPE$  [16].

<sup>b</sup> The experimental  $HOFs$  were taken from Reference [43].

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**Table 3.** Calculated total energies ( $E_0$ ), zero-point energies ( $ZPE$ ), thermal corrections ( $H_T$ ), heats of sublimation ( $\Delta H_{sub}$ ), and  $HOFs$  for the title compounds. <sup>a</sup>

Compd.	$E_0$	$ZPE$	$H_T$	$\Delta H_{f, gas}$	A	$\nu$	$\sigma_{tot}^2$	$\Delta H_{sub}$	$\Delta H_{f, solid}$
HNHAA	-1714.2197	0.1828	62.3	682.3	299.38	0.07	124.82	133.6	548.7
A	-1529.5675	0.1692	54.8	407.1	273.27	0.10	115.37	119.1	288.0
B	-1344.9085	0.1551	84.6	196.7	245.74	0.12	126.01	106.8	89.9
C	-1344.9110	0.1551	84.4	190.2	244.87	0.12	126.40	106.8	83.4
D	-1160.2559	0.1410	39.8	-104.6	216.99	0.16	139.00	97.3	-201.9
E	-1160.2561	0.1409	39.8	-105.4	217.00	0.16	137.03	97.4	-202.8
F	-1160.2538	0.1410	39.7	-99.3	216.70	0.16	140.18	97.4	-196.7

<sup>a</sup>  $E_0$  and  $ZPE$  are in a.u.;  $H_T$ ,  $\Delta H_{sub}$  and  $HOFs$  are in kJ/mol;  $\sigma_{tot}^2$  is in kcal/mol and A is in  $\text{\AA}^2$ . The scaling factor is 0.98 for  $ZPE$  [16].

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**Table 4.** Predicted densities ( $\rho$ ), heats of detonation ( $Q$ ), detonation velocities ( $D$ ), detonation pressures ( $P$ ), and oxygen balance ( $OB$ ) for the title compounds. <sup>a</sup>

Compd.	$Q$ (cal/g)	$OB$	$P$ (g/cm <sup>3</sup> )	$D$ (km/s)	$P$ (GPa)
HNHAA	1511.74	7.77	2.021 (2.064 <sup>b</sup> , 2.080 <sup>c</sup> )	9.63 (9.80 <sup>b</sup> , 9.95 <sup>c</sup> )	43.95 (46.03 <sup>b</sup> , 47.52 <sup>c</sup> )
A	1523.20	4.35	2.015	9.60	43.63
B	1583.97	0.00	2.011	9.65	44.04
C	1579.12	0.00	2.014	9.65	44.10
D	1415.85	-5.71	2.010	9.29	40.81
E	1415.15	-5.71	2.011	9.30	40.87
F	1420.32	-5.71	2.011	9.30	40.93
CL-20			2.040 <sup>d</sup>	9.40 <sup>d</sup>	42.00 <sup>d</sup>
HMX			1.910 <sup>d</sup>	9.10 <sup>d</sup>	39.00 <sup>d</sup>

<sup>a</sup> Oxygen balance (%) for  $C_aH_bO_cN_d$ :  $1600 \times (c - 2a - b/2) / M_w$ ;  $M_w$ : molecular weight.

<sup>b</sup> The uncorrected  $\rho$  values were used to calculate the  $D$  and  $P$  values of HNHAA.

<sup>c</sup> The calculated values were taken from Reference [5].

<sup>d</sup> The experimental values were taken from Reference [1].

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**Table 5.** Strain energies (*SE*, kJ/mol) of the azaoxadadamantane cage via homodesmotic reactions and bond dissociation energies (*BDE*, kJ/mol) of the relatively weak bonds for the title compounds.

Compd.	SE	N-NO <sub>2</sub>	C-N	C-O
HNHAA	406.1	143.9(142.65 <sup>a</sup> )	246.5(252.07 <sup>a</sup> )	
A	342.2	150.0	259.1	272.3
B	295.0	152.3	278.8	261.2
C	289.2	151.5	255.2	297.6
D	244.0	156.6	274.6	322.7
E	232.5	149.3	304.9	301.0
F	238.0	154.7	318.9	303.7

<sup>a</sup>The calculated values in parentheses are from Reference [5].

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**Table 6.** Impact sensitivity ( $h_{50}$ ) of the title compounds<sup>a</sup>.

	Compd.	$h_{50}$	Compd.	$h_{50}$	$h_{50}$ is in
<sup>a</sup>	A	19.58	F	34.02	
cm/2.5kg.	B	24.91	HNHAA	13.76	The values
<sup>b</sup>	C	25.98	CL-20	11.94(12 <sup>b</sup> )	Reference
were from	D	33.91	HMX	29.02(32 <sup>b</sup> )	
[42].	E	34.58			

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**Fig. 1.** Molecular structure of HNHAA, CL-20, and ONC.

**Fig. 2.** Molecular frameworks of six designed azaoxadamantane cage compounds.

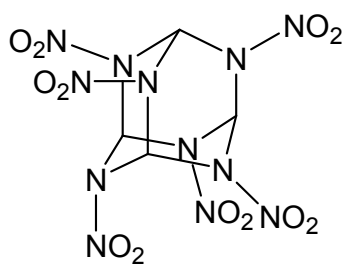
**Fig. 3.** HOMO and LUMO energy level and energy gap of six designed compounds.

**Fig. 4.** Electrostatic potentials mapped for the title compounds. Color coding for MEPs are from red (negative) to blue (positive).

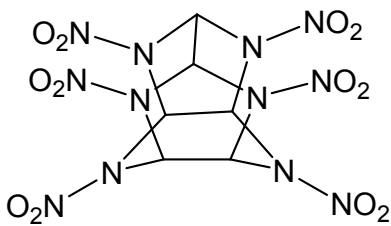
**Fig. 5.** Linear relationship between the number ( $n$ ) of the oxygen atom and HOFs of the title compounds (the average HOFs of isomers with the same  $n$  are used).

**Fig. 6.** Density, detonation pressure, and detonation velocity of the title compounds.

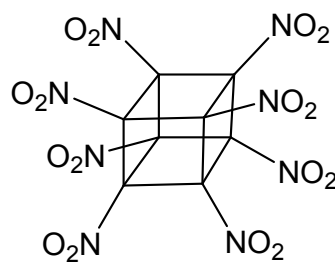
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HNHA

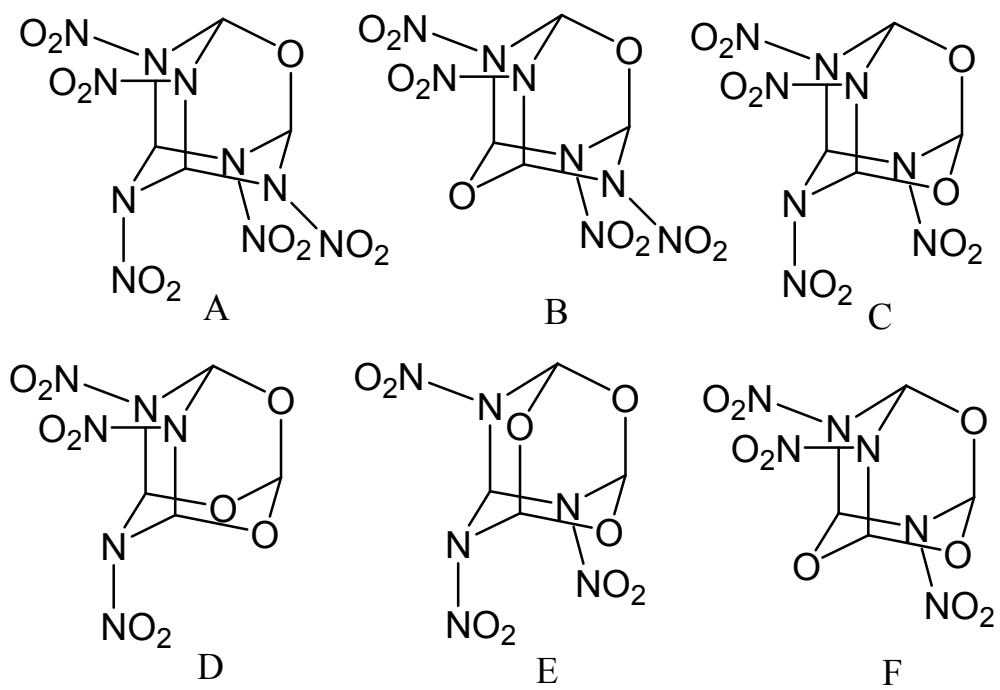


CL-20

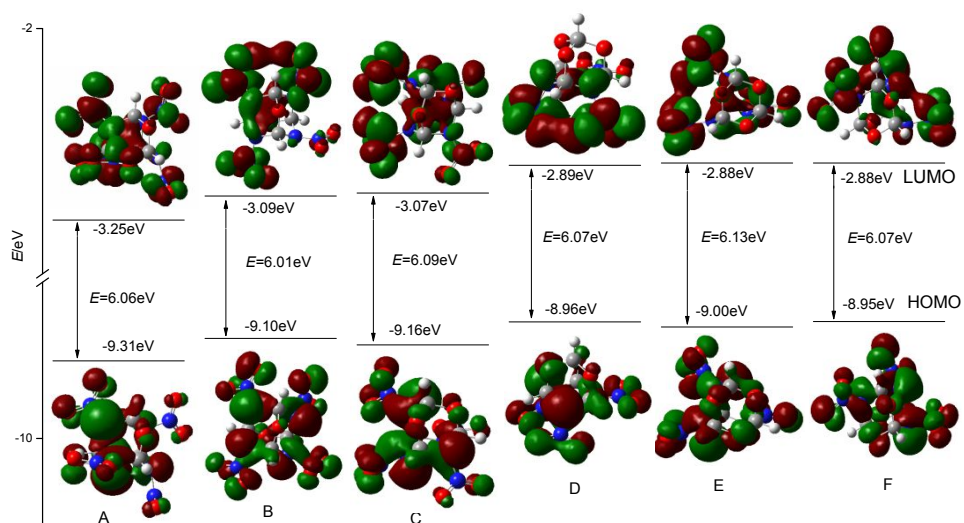


ONC

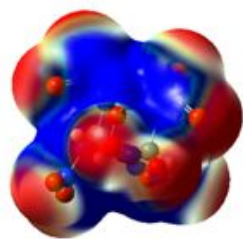
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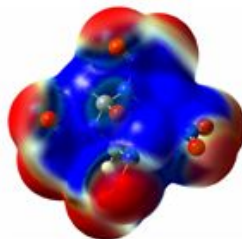
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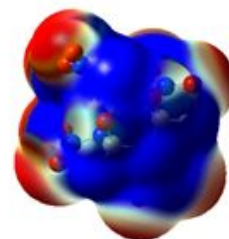
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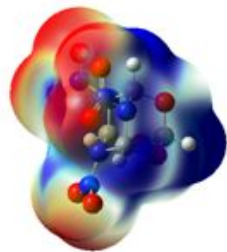
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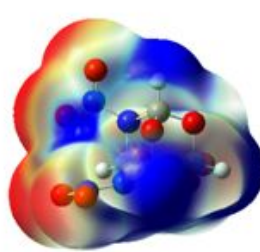
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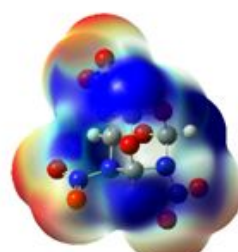
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D

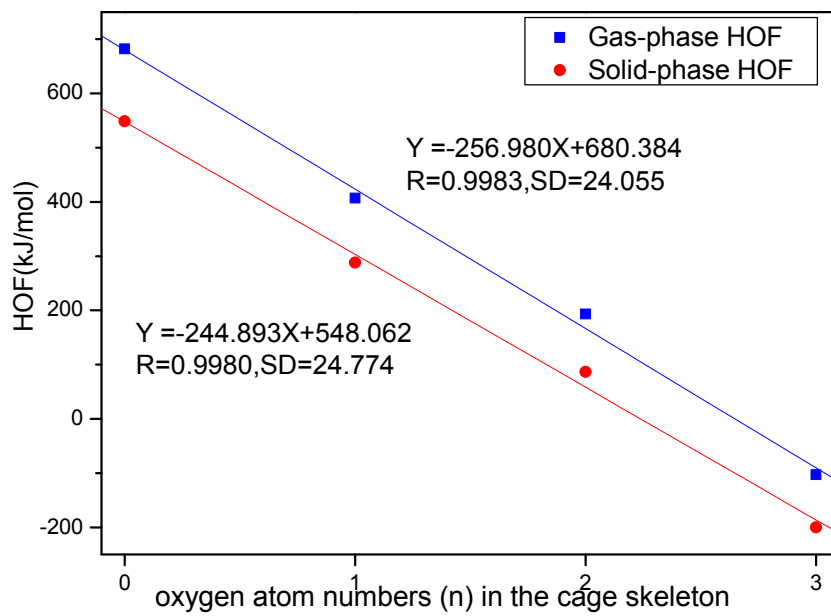


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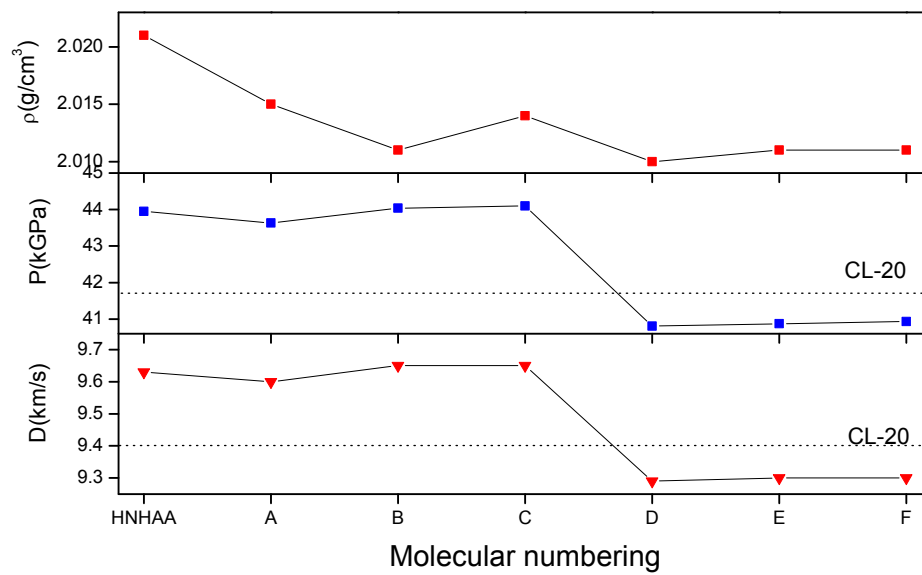
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