Molecular Design and Property Prediction of High Density Polynitro[3.3.3]–Propellane–Derivatized Frameworks as Potential High Explosives

4 AUTHORS:

Qinghua Zhang
Chinese Academy of Sciences
62 PUBLICATIONS   **1,756** CITATIONS

Jiaheng Zhang
Yokohama National University
56 PUBLICATIONS   **391** CITATIONS

Xiujuan Qi
University of Science and Technology of China
13 PUBLICATIONS   **254** CITATIONS

Jean'ne M Shreeve
University of Idaho
563 PUBLICATIONS   **11,433** CITATIONS

Molecular Design and Property Prediction of High Density Polynitro[3.3.3]-Propellane-Derivatized Frameworks as Potential High Explosives

Qinghua Zhang,*,[†] Jiaheng Zhang,[‡] Xiujuan Qi,[†] and Jean'ne M. Shreeve*,[‡]

[†]Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, China
[‡]Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, United States

**S** *Supporting Information*

ABSTRACT: Research in energetic materials is now heavily focused on the design and synthesis of novel insensitive high explosives (IHEs) for specialized applications. As an effective and time-saving tool for screening potential explosive structures, computer simulation has been widely used for the prediction of detonation properties of energetic molecules with relatively high precision. In this work, a series of new polynitrotetraoxopentaaza[3.3.3]-propellane molecules with tricyclic structures were designed. Their properties as potential high explosives including density, heats of formation, detonation properties, impact sensitivity, etc., have been extensively evaluated using volume-based thermodynamic calculations and density functional theory (DFT). These new energetic molecules exhibit high densities of >1.82 g cm^{-3}, in which **1** gives the highest density of 2.04 g cm^{-3}. Moreover, most new materials show good detonation properties and acceptable impact sensitivities, in which **5** displays much higher detonation velocity (9482 m s^{-1}) and pressure (43.9 GPa) than HMX and has a h_{50} value of 11 cm. These results are expected to facilitate the experimental synthesis of new-generation nitramine-based high explosives.

$\rho = 2.04\ g\ cm^{-3}$ $\rho = 1.99\ g\ cm^{-3}$
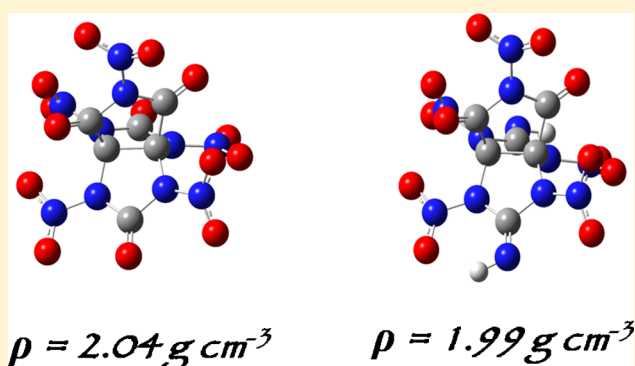
1. INTRODUCTION

Over the past decades, there has been a growing interest in the development of new energetic materials for military and civilian applications.[1−3] In this field, a significant amount of research was directed at the design and syntheses of novel insensitive high explosives (IHEs).[4−7] Major requirements for the ideal IHE include high energy and density, high thermal stability, high positive heat of formation (HOF), good oxygen balance, and good safety (e.g., insensitive to external stimuli such as impact, friction, flame, electrostatic discharge, etc.).[8,9] However, in most cases, the integration of such desired properties in one single molecule is very difficult. Therefore, the challenges in the R&D of new IHEs are heavily concentrated on integration of high energy and low sensitivity in one energetic molecule, that is, designing IHEs with detonation performance comparable to or higher than that of HMX and sensitivity similar to that of TATB. Since World War II, the R&D of high explosives has been focused mainly on those cyclic and caged nitramine derivatives (e.g., RDX, HMX, and CL-20) most of which were discovered many years ago.[10] Because of the high energy density and excellent detonation properties, compounds like TNAZ, RDX, and HMX (Scheme 1), have been widely used as high explosives for a variety of military purposes or industrial applications. However, in spite of outstanding explosive performance, their safety issues still do not measure up to

Scheme 1. Typical Structures of Cyclic or Caged High Explosives Including 1,3,3-Trinitroazetidine (TNAZ), 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX), 1,3,5,7-Tetranitro-1,3,5,7-tetrazocane (HMX), 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), and Octanitrocubane (ONC)
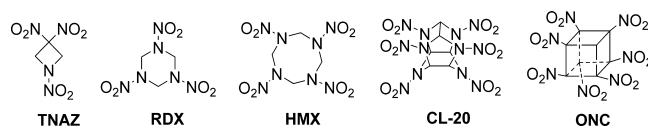
current requirements. Clearly, the search for new IHEs which can meet the criteria for both energy and safety remains an important issue that needs urgently to be addressed to favor the replacement of traditional explosives like RDX and HMX for a large variety of military and civilian applications.[11,12]

From the viewpoint of molecular design, energetic compounds with high densities (ideally higher than 2.0 g/cm^3) are particularly desirable, since the detonation pressure and velocity of the explosives are directly related to their density. In this context, the search for new high explosives, that
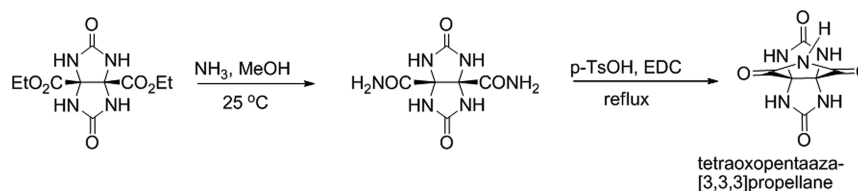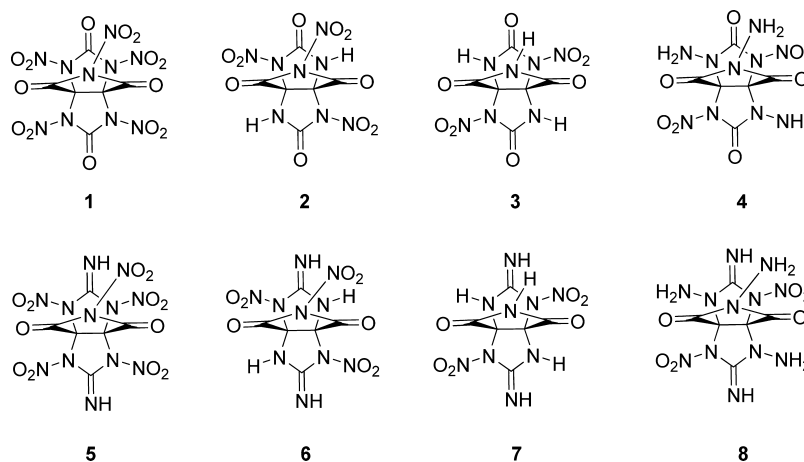
Scheme 2. Synthetic Route of Tetraoxopentaaza[3,3,3]propellane

Scheme 3. Structures of Eight Polynitro[3.3.3]-propellane-Derivatized Frameworks (Compounds 1−8)

is, high density and high velocity of detonation (VOC) explosives, has been one of the most important tasks in the field of energetic materials.[13−16] However, in many cases the syntheses and property tests of such high energy density materials is a dangerous challenge because of their unpredictable stability and safety issues. In the past few years, along with the rapid development of computational chemistry, computer simulation has proven to be an effective and time-saving tool for screening the potential explosive molecules with high performance.[17−19] By virtue of computational modeling, some important properties of explosive molecules, such as density, heats of formation (HOF), detonation velocity, and detonation pressure can be preliminarily evaluated with relatively high precision providing valuable information for experimental work.[20−24] From the discovery history of some typical high-explosives, such as CL-20 and ONC, their molecular structures and property pre-evaluation were achieved by computational chemistry before their experimental syntheses, also demonstrating the effectiveness of this simulation method.[25]

Aiming at exploring new high-performance explosives, we are interested in designing superhigh density energetic structures or frameworks to achieve high detonation performance in the final materials. Recently, a tricyclic skeleton structure, that is, tetraoxopentaaza[3.3.3]-propellane, was reported, in which three five-membered urea heterocycles are connected to a common C−C single bond (so-called a conjoining bond) (Scheme 2).[26] From the view of structural design of new high explosives, this tricyclic compound offers a potentially promising framework for construction of novel nitramine-based energetic materials through different nitration reactions.[27] The advantages of this tricyclic framework include: (1) the presence of urea carbonyls in the skeleton that can significantly increase the density of the resultant energetic materials; (2) the tricyclic structure that can provide additional ring or cage strain, thereby making an active contribution to the high positive HOFs of energetic materials; (3) the replacement
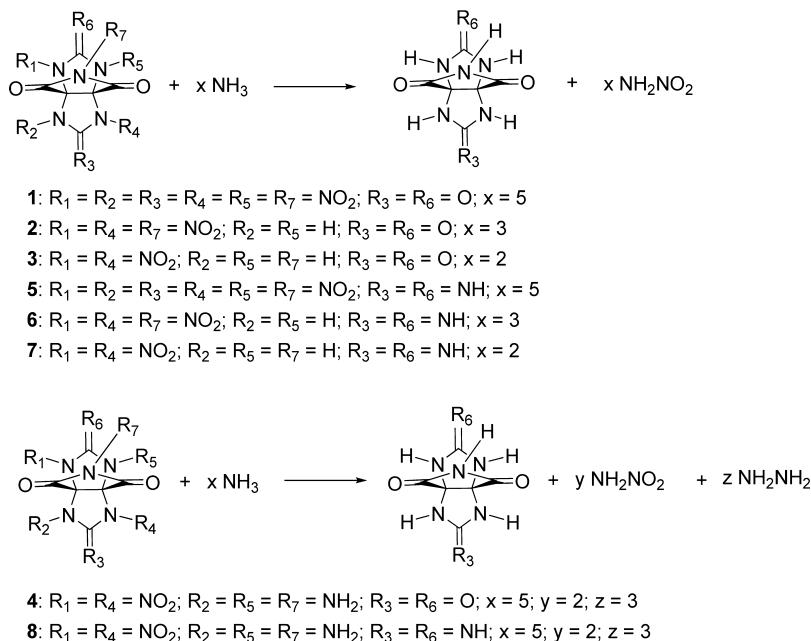
of hydrogen atoms with nitro groups in the urea molecule can greatly increase the oxygen balance and therefore improve the detonation performance of resulting materials. However, there are also some drawbacks to the above propellane structures, for example, (1) the presence of the carbonyls in the structure significantly decrease the heats of formation (HOFs) of the designed energetic molecules and sometimes make the materials hydrolytically unstable; (2) if complete nitration of such a propellane structure is achieved, there will be no hydrogen atoms in the final structure, thereby leading to the poor stability and slightly decreased packing density of the resultant explosive molecule because of the lack of strong hydrogen bonds. This phenomenon has been verified by some representative examples, for example, heptanitrocubane (an example of incomplete nitration that leaves one hydrogen atom) exhibits a higher density than that of ONC (a typical example where complete nitration leaves no hydrogen atoms) mainly due to the existence of stronger hydrogen bond interactions. That is, strong hydrogen bonds in the structures are favorable in the design and synthesis of high energy density materials.

Based on above considerations, in this work eight new nitro-containing tetraoxopentaaza[3.3.3]-propellane molecules with tricyclic structures have been designed through the replacement of hydrogen or oxygen atoms in the urea groups with a nitro or an amino group or both (Scheme 3). Density functional theory (DFT) and volume-based thermodynamics calculations have been employed to predict and evaluate their properties including density, heats of formation, detonation velocity, detonation pressure, as well as sensitivity.

2. COMPUTATIONAL METHODS

The Gaussian 03 program was used to carry out molecular orbital calculations.[28] The DFT-B3LYP methods with the 6-31+g(d,p) basis set[29] and default convergence criteria were

Scheme 4. Designed Isodesmic Reactions for Eight Nitro-Containing Tetraoxopentaaza[3.3.3]-propellane Compounds

1: $R_1 = R_2 = R_3 = R_4 = R_5 = R_7 = NO_2$; $R_3 = R_6 = O$; $x = 5$
2: $R_1 = R_4 = R_7 = NO_2$; $R_2 = R_5 = H$; $R_3 = R_6 = O$; $x = 3$
3: $R_1 = R_4 = NO_2$; $R_2 = R_5 = R_7 = H$; $R_3 = R_6 = O$; $x = 2$
5: $R_1 = R_2 = R_3 = R_4 = R_5 = R_7 = NO_2$; $R_3 = R_6 = NH$; $x = 5$
6: $R_1 = R_4 = R_7 = NO_2$; $R_2 = R_5 = H$; $R_3 = R_6 = NH$; $x = 3$
7: $R_1 = R_4 = NO_2$; $R_2 = R_5 = R_7 = H$; $R_3 = R_6 = NH$; $x = 2$

4: $R_1 = R_4 = NO_2$; $R_2 = R_5 = R_7 = NH_2$; $R_3 = R_6 = O$; $x = 5$; $y = 2$; $z = 3$
8: $R_1 = R_4 = NO_2$; $R_2 = R_5 = R_7 = NH_2$; $R_3 = R_6 = NH$; $x = 5$; $y = 2$; $z = 3$

adopted for structure optimization. The normal-mode analysis for each structure gave true local energy minima on the potential energy surfaces with no imaginary frequencies. Numerous studies showed that the theoretically predicted HOFs of many organic systems via isodesmic reactions were in good agreement with experimental values.[30,31] Isodesmic reaction processes, in which the number of each kind of formal bond is invariable for reactants and products, are designed to decrease the calculation errors of HOFs.[32] Here, the basic tricycle unit of [3.3.3]-propellane remains the same, but target molecules are changed into small ones as in Scheme 4.

For each isodesmic reaction, the heat of reaction ΔH_{298} at 298 K was obtained from the equation

$$\Delta H_{298} = \sum \Delta H_{f,p} - \sum \Delta H_{f,R}$$

where $\Delta H_{f,p}$ and $\Delta H_{f,R}$ are the heats of formation for products and reactants at 298 K, respectively. Since the experimental HOFs of the basic tricycle unit and NH_2NO_2 are unavailable, additional atomization reactions ($C_aH_bN_c \rightarrow aC_{gas} + bH_{gas} + cN_{gas}$) at G2 level[33] were carried out. Following that, the HOFs at 298 K can be calculated from the equation

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

where ΔE_0 stands for the change in total energy between products and reactants at 0 K and ΔZPE is the difference between the zero-point energies of products and reactants at 0K; ΔH_T is the thermal correction from 0 to 298 K. For the isodesmic reactions here, Δn is 0 and $\Delta(PV)$ equals zero. Since the condensed phases of energetic compounds are solids, the heat of formation ($\Delta H_{f,solid}$) for the solid phase is required for the calculation of detonation properties. On the basis of Hess's law of constant heat summation,[34] the calculated gas-phase heat of formation (ΔH_{298}) and heat of sublimation (ΔH_{sub}) are used to evaluate $\Delta H_{f,solid}$:

$$\Delta H_{f,solid} = \Delta H_{298} - \Delta H_{sub}$$

According to Politzer et al.,[35] the heat of sublimation can be computed from the corresponding molecular surface area and electrostatic interaction index $v\sigma_{tot}^2$ for energetic compounds. The empirical expression of this approach is

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

where A describes the surface area of the 0.001 electrons· bohr^{-3} isosurface of the electronic density of the molecule, v is the degree of balance between positive potential and negative potential on the isosurface, and σ_{tot}^2 stands for the variability of the electrostatic potential. The coefficients a, b, and c were reported by Rice et al. as 2.670×10^{-4} kcal mol^{-1} A^{-4}, 1.650 kcal mol^{-1}, and 2.966 kcal mol^{-1}, respectively.[36] In this study, surface area, degree of balance between the positive and negative surface potentials and variability of the electrostatic potential are calculated using the Multiwfn program.[37]

For each polynitro [3.3.3]-propellane derivative, the theoretical density was initially determined from the molecular weight (M) divided by the $V_{0.001}$, where $V_{0.001}$ is defined as the volume of the inside of the density contour of 0.001 electrons· bohr^{-3}, which was obtained from a Monte Carlo integration using the Multiwfn program. By introducing the interaction index $v\sigma_{tot}^2$, the crystal density of energetic compounds can be corrected according to the following equation:[38]

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

where the coefficients β_1, β_2, and β_3 are 1.0462, 0.0021, and −0.1586, respectively.[39]

The calculation of the detonation parameters such as detonation velocity (D), detonation pressure (P), and specific impulse (I_{sp}) was performed with the program package EXPLO5 (version 6.01).[40] The Becker−Kistiakowsky−Wilson equation of state for gaseous detonation products and the Cowan−Fickett equation of state for solid carbon were used in this program.[41] The equilibrium composition of the detonation products is predicted by applying the modified White, Johnson, and Dantzig's free energy minimization technique.[41]The

program is designed to enable the calculation of detonation properties at the CJ point.[41] In this work, these parameters can also be obtained using EXPLO5 6.01.

The oxygen balance value is defined as the ratio of the oxygen content of the energetic compound $C_aH_bN_cO_d$ to the total oxygen required for the oxidation of all carbon, and hydrogen to CO and H_2O, respectively. In this study, it was calculated using the following equation to classify energetic materials as either oxygen rich (positive value) or deficient (negative value)

$$\Omega_{CO} = \frac{\left[d - a - \left(\frac{b}{2}\right)\right] \times 1600}{M}$$

The impact sensitivity (h_{50}) for nitramines can be predicted by the equation

$$h_{50} = \alpha\sigma_+^2 + \beta\nu + \gamma$$

where σ_+^2 is indicator of the strengths and variabilities of the positive surface potentials and ν is the degree of balance between positive potential and negative potential on the isosurface. The coefficients α, β, and γ are −0.0064, 241.42, and −3.43, respectively.[42] To compare with the impact energy, when a 2.5 kg hammer is used, the H_{50} of 100 cm is equivalent to the impact energy of 24.5 J.

The energy of the HOMO measures the electron donating character of a compound and the energy of the LUMO measures its electron accepting character. In the present work, the reactivity of **1−8** within the framework of DFT-B3LYP/6-31+g(d,p) level was studied.[43]

3. RESULTS AND DISCUSSION

3.1. Structural Design and Molecular Geometry. The aim of this study is heavily directed at the molecular design and syntheses of novel high density energetic molecules similar to HMX and CL-20. Therefore, starting with the reported tetraoxopentaaza[3,3,3]propellane[26] as the initial skeleton, the structural design of a series of new polynitro molecules with tricyclic structures has been attempted. In the first design strategy, the replacement of hydrogen atoms with two or more nitro and/or amino groups in the tetraoxopentaaza[3,3,3]-propellane results in the formation of new nitro-containing energetic molecules with a tricyclic framework (Scheme 3, **1−4**), in which at least two nitro groups are introduced with the goal of ensuring the high energy density of the resultant molecules. From Scheme 3, **1** is the product of complete nitration with five nitro groups in the molecule, while **2** and **3** are the incompletely nitrated products that contain two or three nitro groups. Moreover, further replacement of three hydrogen atoms in the structure of **3** with amino groups can yield a new structure **4**, in which both the energy and hydrogen bond interactions are expected to be enhanced. Considering that the carbonyl group in the energetic framework has an unfavorable impact on positive HOFs of materials and also decreases the chemical stability in water, in our second design strategy, partial replacement of oxygen atoms in the carbonyl group of **1−4** with —NH has also been suggested, thereby giving an additional four new energetic frameworks containing the nitro guanidine structure (Scheme 3, **5−8**). From the viewpoint of organic chemistry, the syntheses of such structures are also feasible by using guanidine as the starting material. The feasible synthetic routes are proposed below.

To help understand the stereo structures of polynitro-substituted tetraoxopentaaza[3.3.3]-propellane, the optimized structures of **2** and **6** from different viewpoints are demonstrated in Figure 1. Optimized molecular structures of
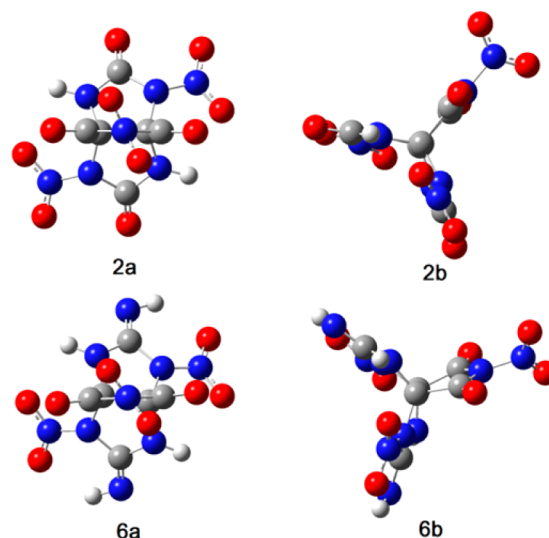

Figure 1. Molecular structures of compounds **2** and **6**. The perspective view of **2a**, **2b**, **6a**, and **6b** are demonstrated from different viewpoints.

other compounds **1**, **3−5**, and **7−8**, as well as their surface analysis are summarized in the Supporting Information (Figure S1−S6). From Figure 1, it can be seen that two of three rings of **2** and **6** remain coplanar after the substitution with nitro groups (Figure1, **2a** and **6a**). However, after nitration of the pyrrolidine-2,5-dione, the nitro group and the ring form a dihedral angle within the scope of 90−120°, which may improve crystal packing (Figure1, **2b** and **6b**).

From a synthetic perspective, the use of different nitrating conditions may result in different nitrated products,[44,45] for example, the completely nitrated compound **1** and partly nitrated compounds **2−4**. Among them, the dinitro-substituted structure (e.g., **3**) is the most common example. Because of the different distribution of two nitro groups in the tricyclic structure, the dinitro-substituted product may have three different isomers, as shown in Scheme 5. The energies of three isomers have been calculated, in which the order of their energy is isomer 3 > isomer 2 > isomer 1. Therefore, the structure of isomer 1 with the minimum energy should be the true molecular geometry of the compound **3** in Scheme 1. Similarly, the dinitro-substituted compound **7** also has three isomers (Scheme 4, **a**), in which the structure of isomer 1 has been calculated to exhibit the minimum energy. Additionally the isomers of the trinitro-substituted compounds (i.e., **2** and **6**) have also been studied (Scheme 4b). The energies of two isomers in **2** and **6** have been calculated, in which the energy gap of the isomers is 1.6 and 2.8 kJ mol^{-1} for **2** and **6**, respectively.

The geometric structures of all eight compounds have been optimized based on the true local energy minima on the potential energy surface without imaginary frequencies. Analyzing the molecular orbitals of a molecule provides valuable information on its electronic structure. Therefore, the HOMO, LUMO, and the molecular electrostatic potentials (MEPs) of all eight compounds have been studied. Figure 2 illustrates HOMO, LUMO, and MEPs of **1** and **5**, the positive

Scheme 5. Relative Energies of Possible Isomers of 2, 3, 5, and 7

a

Dinitro-substituted isomers of **3**

Dinitro-substituted isomers of **7**

b

Trinitro-substituted isomers of **2**

Trinitro-substituted isomers of **5**

HOMO LUMO Electrostatic potential

Compound **1**

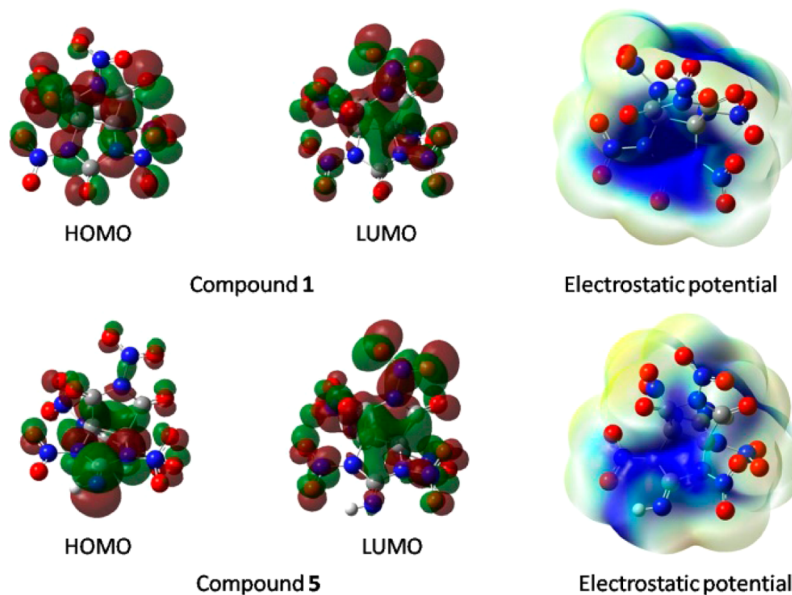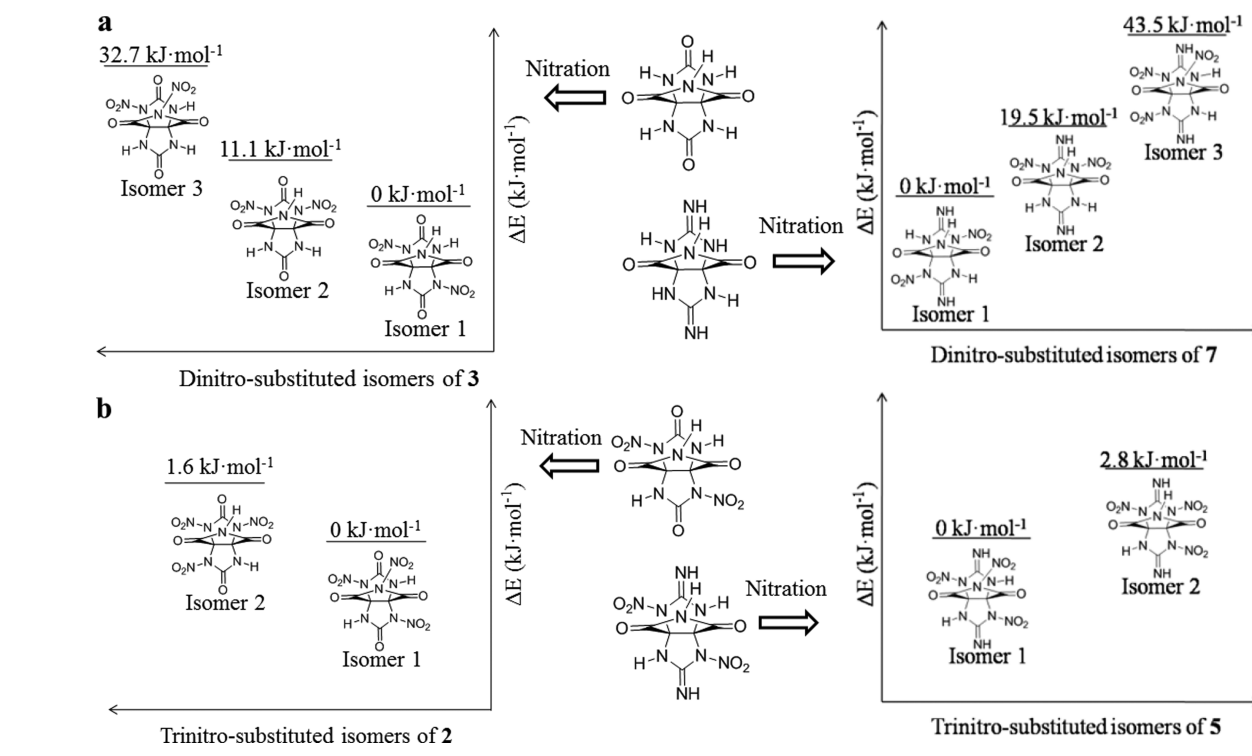HOMO LUMO Electrostatic potential

Compound **5**

Figure 2. HOMO, LUMO, and MEPs of **1** and **5**. Color coding for MEPs are from yellow (negative) to blue (positive).

phase is shown as red and the negative phase is shown as green. It can be seen that, either C−N or N−N orbits in **1** and **5** participate in both the HOMO and the LUMO levels, indicating that the removal of an electron from the HOMO level or addition of an electron to the LUMO level could weaken the skeleton framework. Inspection of the MEPs for two compounds, the very positive potential which indicates the instability of a compound,[38] ranges at the center of the tricyclic skeleton while the negative potential appears to be distributed mostly on the N-NO$_2$ moiety and carbonyl groups.

3.2. Density. Density is an important property for energetic materials because it is a crucial factor that can affect the detonation properties. High density of explosives means that more energy per unit volume can be packed into volume-limited space, thereby yielding the maximum violent explosion. Here, the densities of eight new explosive molecules were defined as molecular weight divided by the average molecular volume and then corrected using interaction index $v\sigma_{tot}^2$. The values of molecular volume, uncorrected densities, and corrected densities are listed in Table 1.

As expected, all the designed polynitro [3.3.3]-propellane-derivatized compounds exhibit densities >1.82 g cm^{-3}, in which the predicted density of **1** (2.04 g cm^{-3}) is even higher than that of ONC (1.98 g cm^{-3}). From Table 1, it can be seen

Table 1. Molecular Volume and Density for Eight Energetic Molecules

compounds	MW (g mol^{-1})	volume (cm^3 mol^{-1})	$\rho_{uncorrected}$ (g cm^{-3})	$\rho_{corrected}$ (g cm^{-3})
1	436.12	210.1	2.08	2.04
2	346.13	173.9	1.99	1.99
3	301.13	155.0	1.94	1.97
4	346.17	183.8	1.88	1.90
5	434.15	215.0	2.02	1.99
6	344.16	181.6	1.89	1.87
7	299.16	163.2	1.83	1.84
8	344.20	190.5	1.81	1.82

clearly that the replacement of hydrogen atoms with the -NO$_2$ group will lead to a greater increase in density than that observed for the corresponding NH$_2$-substituted compounds (compounds 1−4, Table 1). For example, compound 1 which contains five nitro groups exhibits a much higher density (2.04 g cm^{-3}) than that of compound 4 (1.90 g cm^{-3}) with only two nitro groups and three amino groups. This indicates that the introduction of the highly dense nitro group is a very effective method to increase the density of energetic molecules. For compounds 5−8, the densities range from 1.82 to 1.99 g cm^{-3}, in which 5 shows a higher density (1.99 g cm^{-3}) than that of HMX (1.91 g cm^{-3}). However, with similar frameworks that contain the same nitro numbers for comparison (e.g., 1 vs 5, 2 vs 6, 3 vs 7, 4 vs 8), the replacement of oxygen atoms in the carbonyl group with -NH leads to a slight decrease in the density of the latter. An evident example is that 2 has a density of 1.99 g cm^{-3}, whereas the density of 6 is only 1.87 g cm^{-3}. Since the correct method is generalized to take into account possible interactions especially hydrogen bonding, fully substituted 1, 5, and trinitro-substituted 6 are found to be slightly lower than the corresponding uncorrected values. The presence of −NO$_2$ and adjacent N−H bonds in the molecular structures can provide the opportunity for hydrogen bonding which is favorable to the higher packing densities of energetic materials. Hence, 2 and 5, with relatively strong hydrogen bond interactions between the nitro groups and the adjacent NH groups, result in their better densities, that is, 1.99 g cm^{-3} for 2 and 5, respectively. In the structures of 4 and 8, the incorporation of three −NH$_2$ groups may provide additional hydrogen bond interactions but also obviously increase molecular volume when compared to 3 and 7, thereby resulting in the slight decreases in their crystal density. On the whole, the completely nitrated compound 1 exhibited the highest calculated density of >2.0 g cm^{-3}, indicating its high potential as new high energy density material.

3.3. Heat of Formation (HOF). The heat of formation (HOF, ΔH_f) is also a very important property parameter of energetic materials, which is usually taken as the indicator of the "energy content" of an energetic molecule. Therefore, to estimate the detonation velocity and pressure of an explosive molecule through theoretical calculation methods, the ΔH_f value must be first obtained.

In this study, all ab initio calculations were carried out by using the Gaussian 03 (revision D.01) suite of programs. The geometric optimization of the structures and frequency analyses were accomplished by using the B3LYP with the 6-31+G** basis set, and single-point energies were calculated at the MP2/6-311++G** level. Atomization energies were calculated by the G2 method. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The standard gas-phase heats of formation ($\Delta H_{f\ gas}$) of eight new compounds have been calculated by using the method of isodesmic reactions (Scheme 4).

In Table 2, the calculated heats of formation and parameters related to the electrostatic potential of eight designed compounds, including total energies (E0), zero-point energies (ZPE), thermal corrections (HT), gas-phase heats of formation ($\Delta H_{f,\ gas}$), molecular surface area (A), the degree of balance between negative and positive potential (ν), square of the variability of the electrostatic potential (σ^2_{tot}), heats of sublimation (ΔH_{sub}), and heats of formation (HOF), are summarized. It could be seen that compounds 5, 6, and 8 exhibit positive $\Delta H_{f,\ solid}$ values, whereas the other five energetic molecules gave negative $\Delta H_{f,\ solid}$ values varying between −631 and −148.5 kJ/mol because of the negative G2 HOF values of the tricycle units. This is also in agreement with previous studies where the presence of the carbonyl group in the structures is not helpful to obtain highly positive HOFs of energetic molecules. For those compounds that contain four carbonyl groups (1−4, Table 2), the completely nitrated compound 1 shows the highest negative $\Delta H_{f,solid}$ value (−284.6 kJ/mol) compared to the others, mainly because of the presence of five energetic −NO$_2$ groups in its structure. Similarly, for those compounds that have two carbonyl groups in the molecule (5−8), compound 5 with five nitro groups exhibit a higher positive $\Delta H_{f,\ solid}$ value (176.5 kJ/mol) than that of other compounds with two or three nitro groups (6−8, Table 2). Overall, although these new polynitro [3.3.3]-propellane-derivatized compounds exhibit relatively high densities (e.g., > 1.95 g cm^{-3}), their heats of formation were not very high positive, indicating that the carbonyl groups in these materials exhibited both sides of the coin to the

Table 2. Calculated Total Energies (E_0, a.u.), Zero-Point Energies (ZPE, a.u.), Thermal Corrections (H_T, kJ mol^{-1}), Heat of Sublimation (ΔH_{sub}, kJ mol^{-1}), and Solid-Phase Heats of Formation ($\Delta H_{f,solid}$, kJ mol^{-1}) of Eight New High Explosives

compd	E_0	ZPE	H_T	$\Delta H_{f,gas}$	A	ν	σ^2_{tot}	ΔH_{sub}	$\Delta H_{f,solid}$
1	−1824.86	0.14	68.91	−138.0	312.53	0.03	411.14	146.6	−284.6
2	−1416.75	0.52	54.69	−316.7	273.11	0.09	376.27	135.1	−451.8
3	−1212.70	0.14	46.45	−506.9	243.93	0.13	336.46	124.1	−631.0
4	−1378.26	0.19	59.07	−242.6	283.47	0.20	195.68	145.8	−388.4
5	−1785.11	0.17	33.92	330.1	316.30	0.06	281.36	153.6	176.5
6	−1377.00	0.16	68.77	160.9	280.71	0.09	253.00	133.5	27.4
7	−1172.95	0.16	54.45	−22.7	252.28	0.14	262.18	125.8	−148.5
8	−1338.52	0.21	46.71	225.5	283.47	0.20	195.68	145.8	79.7

properties, i.e., the positive side in the high density and the negative side in the high positive HOFs.

3.4. Detonation Properties. Detonation velocity (D) and detonation pressure (P) are two key measures of explosive performance of energetic materials. By using the calculated values of densities and heats of formation, we calculated the detonation pressures (P) and velocities (D) of the eight new explosive molecules on the basis of the traditional Chapman−Jouget thermodynamic detonation theory using EXPLO5 6.01 (Table 3). For these new polynitro tetraoxopentaaza[3.3.3]-

Table 3. Detonation Velocity (D), Detonation Pressure (P), Oxygen Balance (OB), Impact Sensitivity (IS), and Specific Impulse (I_{sp}) of Eight New Nitro-Containing Tetraoxopentaaza[3.3.3]-propellane Molecules

compd	$vD^{[f]}$ [m/s]	$P^{[g]}$ [Gpa]	OB (%)	$IS^{[h]}$ (h_{50}, cm)	$I_{sp}^{[j]}$ (s)
1	8981	36.1	29	3	234
2	8723	33.6	14	17	225
3	8128	28.3	3	27	179
4	8283	29.5	−5	45	196
5	9482	43.9	18	11	269
6	8493	31.2	0	17	228
7	8091	27.0	−13	30	190
8	8325	27.9	−26	45	202
TNT	6881	19.5	−25	100	211
RDX	8748	34.9	0	26	258
HMX	9320	39.6	0	32	266

propellane molecules, the calculated detonation velocities lie in the range between 8091 and 9482 m s^{-1}, which are remarkably higher than that of TNT (6881 m s^{-1}). Among them, **5** gave the highest detonation velocities (9482 m s^{-1}), which exceeds that of RDX (8748 m s^{-1}) and HMX (9320 m s^{-1}). It can also be seen that, in spite of a higher calculated density (2.04 g cm^{-3}) for **1**, its detonation velocity (8981 m s^{-1}) is not superior to that of **5** (9482 m s^{-1}), which may be explained by the larger negative value of the HOF of the former (i.e., −284.6 kJ mol^{-1} for **1**, Table 2) than that of the latter (i.e., 176.5 kJ mol^{-1}, Table 2). The detonation pressures of these explosive compounds range between 27.0 and 43.9 GPa, in which the highest P value of **5** (43.9 GPa) is much higher than that of RDX (34.9 GPa) and HMX (39.6 GPa).

Oxygen balance (OB) is the index of the deficiency or excess of oxygen in a molecule required to convert all carbon into carbon monoxide (or carbon dioxide), and all hydrogen into water. Positive oxygen balance (OB) has significance in explosive molecules, which can be used as oxidizers. In this work, the OB values of eight new compounds (molecular formula $C_aH_bN_cO_d$) have been calculated as follows: OB (%) = $1600 \times (d - a - b/2)/M_w$ (based on carbon monoxide, Table 3). Compounds **1−3** and **5** exhibited positive oxygen balances (3−29%), while the OB value of **6** is zero. Other energetic molecules **4** and **7−8** have negative OB values ranging from −26% to −5%, mainly due to the relatively higher carbon and hydrogen content. In general, incorporation of more -NO$_2$ groups into these tetraoxopentaaza[3.3.3]-propellane molecules substantially improves the heats of formation and the oxygen balance and eventually results in higher exothermicities in the combustion and detonation processes. Hence, those compounds containing more nitro groups (e.g., **1** and **5**) show better detonation velocities and detonation pressures because of their high energy density and oxygen balance (OB).

3.5. Evaluation of Impact Sensitivity. In addition to the energy properties (e.g., density, detonation velocity, and detonation pressure), the sensitivity of high explosives is also an important subject of keen interest to researchers in the field of energetic materials. Theoretical evaluation of impact sensitivity for high explosives has long been considered a challenging task, since the sensitivity of explosive molecules, which is closely related to their decomposition kinetics and thermodynamics, is extraordinarily complex. A series of empirical methods have been proposed to predict the sensitivity of these materials approximately. Specifically, Politzer and co-workers developed a method using crystal volume factors to predict impact sensitivities of nitramine energetic compounds which give acceptable accuracy. Therefore, the impact sensitivities of the designed eight new polynitro [3.3.3]-propellane-derivatized compounds were also studied by using such a calculation equation for h_{50} values and the structure-sensitivity relationships were analyzed.[42]

From Table 3, it can be seen that with the exception of **1**, the other seven explosive molecules exhibit relatively acceptable impact sensitivities with h_{50} values ranging from 11 to 45 cm, which are comparable with that of RDX (26 cm) and HMX (32 cm).[46] It is obvious that the compounds that contain more nitro groups show the higher impact sensitivities. Among them, **1** displays very high impact sensitivity (the h_{50} value is 3 cm), mainly due to its completely nitrated structure and the absence of hydrogen bonding interactions in the molecule. In contrast, dinitro-substituted **4** and **8** show the lowest sensitivity to impact, that is, 45 cm for h_{50} for both. In their structures, the presence of three −NH$_2$ groups may provide additional hydrogen bond interactions, thereby resulting in the significant decrease in their impact sensitivities. Moreover, the specific impulse (I_{sp}, measure of energy content) of eight new explosive compounds are also calculated. Among them, five compounds (**1, 2, 5, 6,** and **8**) displayed I_{sp} values >200 s, in which **5** has a higher I_{sp} value (269 s) compared to RDX (258 s) and HMX (266 s). The properties of moderate sensitivity and high specific impulses coupled with the excellent detonation performance and high density make these new polynitro [3.3.3]-propellane-derivatized compounds attractive candidates for energetic applications.

4. CONCLUSIONS

A new family of high density polynitro tetraoxopentaaza[3.3.3]-propellane molecules with tricyclic structures has been designed, and the properties of these energetic materials including electronic structure, density, heat of formation, detonation velocity and pressure, impact sensitivity, and specific impulse, have been evaluated using volume-based thermodynamics calculations and density functional theory (DFT). Among these energetic compounds, **1** and **5** exhibited high densities ≥1.90 g cm^{-3}, in which especially **1** had the highest density of 2.04 g cm^{-3}. Moreover, especially as a potential explosive, **5** displays excellent integrated performance, that is, a high density of 1.99 g cm^{-3}, higher P (43.9 GPa) and D values (9482 m s^{-1}) than those of HMX, comparable impact sensitivity relative to RDX and HMX, as well as a higher specific impulse than that of HMX. These results are expected to provide useful information for future experimental investigations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Optimized molecular structures of the compounds **1**, **3−5**, and **7−8**, as well as their surface analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: wfqinghua@licp.cas.cn. Fax: (+86)816-2991659. Tel: (+86)816-2991850.

*E-mail: jshreeve@uidaho.edu. Fax: (+1)208-885-9146. Tel: (+1) 208-885-9141.

Author Contributions

The first and second authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Gao, H.; Shreeve, J. M. Azole-Based Energetic Salts. *Chem. Rev.* **2011**, *111*, 7377−7436.

(2) Dippold, A. A.; Klapötke, T. M. A Study of Dinitro-bis-1,2,4-triazole-1,1′-diol and Derivatives: Design of High-Performance Insensitive Energetic Materials by the Introduction of N-Oxides. *J. Am. Chem. Soc.* **2013**, *135*, 9931−9938.

(3) Kettner, M. A.; Klapotke, T. M. 5,5′-Bis-(trinitromethyl)-3,3′-bi-(1,2,4-oxadiazole): A Stable Ternary CNO-Compound with High Density. *Chem. Commun.* **2014**, *50*, 2268−2270.

(4) Fischer, N.; Fischer, D.; Klapotke, T. M.; Piercey, D. G.; Stierstorfer, J. Pushing the Limits of Energetic Materials-the Synthesis and Characterization of Dihydroxylammonium 5,5′-Bistetrazole-1,1′-diolate. *J. Mater. Chem.* **2012**, *22*, 20418−20422.

(5) He, L.; Tao, G. H.; Parrish, D. A.; Shreeve, J. M. Impact Insensitive Dinitromethanide Salts. *Chem. Commun.* **2013**, *49*, 10329−10331.

(6) Klapötke, T. M.; Petermayer, C.; Piercey, D. G.; Stierstorfer, J. 1,3-Bis(nitroimido)-1,2,3-triazolate Anion, the N-Nitroimide Moiety, and the Strategy of Alternating Positive and Negative Charges in the Design of Energetic Materials. *J. Am. Chem. Soc.* **2012**, *134*, 20827−20836.

(7) Zhang, J.; Shreeve, J. M. 3,3′-Dinitroamino-4,4′-azoxyfurazan and Its Derivatives: An Assembly of Diverse N-O Building Blocks for High-Performance Energetic Materials. *J. Am. Chem. Soc.* **2014**, *136*, 4437−4445.

(8) Krause, H. H. In *Energetic Materials*; Teipel, U., Ed.; VCH: Weinheim, Germany, 2005; pp 1−25.

(9) Klapötke, T. M. In *High Energy Density Materials*; Springer: Berlin, 2007; pp 85−121.

(10) Klapötke,T. M. *Chemistry of High-Energy Materials*; Walter de Gruyter: Berlin, 2011.

(11) Pagoria, P. F.; Lee, G. S.; Mitchell, A. R.; Schmidt, R. D. A Review of Energetic Materials Synthesis. *Thermochim. Acta* **2002**, *384*, 187−204.

(12) Singh, R. P.; Verma, R. D.; Meshri, D. T.; Shreeve, J. M. Energetic Nitrogen-Rich Salts and Ionic Liquids. *Angew. Chem., Int. Ed.* **2006**, *45*, 3584−3601.

(13) Song, J.; Zhou, Z.; Dong, X.; Huang, H.; Cao, D.; Liang, L.; Wang, K.; Zhang, J.; Chen, F.; Wu, Y. Super-High-Energy Materials Based on Bis(2,2-dinitroethyl)nitramine. *J. Mater. Chem.* **2012**, *22*, 3201−3209.

(14) Lin, Q. H.; Li, Y. C.; Qi, C.; Liu, W.; Wang, Y.; S. Pang, P. Nitrogen-Rich Salts Based on 5-Hydrazino-1H-tetrazole: A New Family of High-Density Energetic Materials. *J. Mater. Chem. A* **2013**, *1*, 6776−6785.

(15) Dong, H. The Development and Countermeasure of High Energy Density Materials. *Chin. J. Energy Mater.* **2004**, *12*, 1−12.

(16) Liang, L.; Huang, H.; Wang, K.; Bian, C.; Song, J.; Ling, L.; Zhao, F.; Zhou, Z. Oxy-bridged Bis(1H-tetrazol-5-yl)furazan and Its Energetic Salts Paired with Nitrogen-Rich Cations: Highly Thermally Stable Energetic Materials with Low Sensitivity. *J. Mater. Chem.* **2012**, *22*, 21954−21964.

(17) Yan, Q. L.; Zeman, S. Theoretical Evaluation of Sensitivity and Thermal Stability for High Explosives Based on Quantum Chemistry Methods: A Brief Review. *Int. J. Quantum Chem.* **2013**, *113*, 1049−1061.

(18) Zhang, X.; Zhu, W.; Wei, T.; Zhang, C.; Xiao, H. Densities, Heats of Formation, Energetic Properties, and Thermodynamics of Formation of Energetic Nitrogen-Rich Salts Containing Substituted Protonated and Methylated Tetrazole Cations: A Computational Study. *J. Phys.Chem. C* **2010**, *114*, 13142−13152.

(19) Wang, F.; Du, H.; Liu, H.; Gong, X. Hydrogen-Bonding Interactions and Properties of Energetic Nitroamino[1,3,5]triazine-Based Guanidinium Salts: DFT-D and QTAIM Studies. *Chem.—Asian J.* **2012**, *7*, 2577−2591.

(20) Gao, H.; Ye, C.; Piekarski, C. M.; Shreeve, J. M. Computational Characterization of Energetic Salts. *J. Phys.Chem. C* **2007**, *111*, 10718−10731.

(21) Zhu, W.; Yan, Q.; Li, J.; Cheng, B.; Shao, Y.; Xia, X.; Xiao, H. Prediction of the Properties and Thermodynamics of Formation for Energetic Nitrogen-Rich Salts Composed of Triaminoguanidinium Cation and 5-Nitroiminotetrazolate-Based Anions. *J. Comput. Chem.* **2012**, *33*, 1781−1789.

(22) Taylor, D. E.; Rob, F.; Rice, B. M.; Podeszwa, R.; Szalewicz, K. A. Molecular Dynamics Study of 1,1-Diamino-2,2-dinitroethylene (FOX-7) Crystal Using A Symmetry Adapted Perturbation Theory-based Intermolecular Force Field. *Phys. Chem. Chem. Phys.* **2011**, *13*, 16629−16636.

(23) Rice, B. M.; Hare, J. J. A Quantum Mechanical Investigation of the Relation between Impact Sensitivity and the Charge Distribution in Energetic Molecules. *J. Phys. Chem. A* **2002**, *106*, 1770−1783.

(24) Gutowski, K. E.; Rogers, R. D.; Dixon, D. A. Accurate Thermochemical Properties for Energetic Materials Applications. II. Heats of Formation of Imidazolium-, 1,2,4-Triazolium-, and Tetrazolium-Based Energetic Salts from Isodesmic and Lattice Energy Calculations. *J. Phys. Chem. B* **2007**, *111*, 4788−4800.

(25) Eaton, P. E.; Gilardi, R.; Zhang, M. X. Polynitrocubanes: Advanced High-Density, High-Energy Materials. *Adv. Mater.* **2000**, *12*, 1143−1148.

(26) Shin, M.; Kim, M. H.; Ha, T.; Jeon, J.; Chung, K.; Kim, J. S.; Kim, Y. G. Synthesis of Novel 2,4,6,8,10-Pentaaza[3.3.3]propellane Derivatives. *Tetrahedron* **2014**, *70*, 1617−1620.

(27) Shin, M.; Ha, T.; Chung, K.; Kim, J. S.; Kim, Y. G. Nitration of 3,7,9,11-Tetraoxo-2,4,6,8,10-pentaaza[3.3.3]propellane. *Appl. Chem. Eng.* **2014**, *25*, 188−192.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Jr., T. V; Kudin,K. N.; Burant, J. C. et al. *Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.

(29) Bene, J. E. D.; Person, W. B.; Szczepaniak, K. Properties of Hydrogen-Bonded Complexes Obtained from the B3LYP Functional with 6-31G(d,p) and 6-31+G(d,p) Basis Sets: Comparison with MP2/6-31+G(d,p) Results and Experimental Data. *J. Phys. Chem.* **1995**, *99*, 10705−10707.

(30) Wu, Q.; Zhu, W.; Xiao, H. Computer-aided Design of Two Novel and Super-High Energy Cage Explosives: Dodecanitrohexaprismane and Hexanitrohexaazaprismane. *RSC Adv.* **2014**, *4*, 3789−3797.

(31) Wu, Q.; Zhu, W.; Xiao, H. A New Design Strategy for High-energy Low-Sensitivity Explosives: Combining Oxygen Balance Equal

to Zero, A Combination of Nitro and Amino Groups, and N-Oxide in One Molecule of 1-Amino-5-nitrotetrazole-3N-oxide. *J. Mater. Chem. A* **2014**, *2*, 13006−13015.

(32) Wu, Q.; Pan, Y.; Zhu, W.; Xiao, H. Computational Study of Energetic Nitrogen-rich Derivatives of 1,4-Bis(1-azo-2,4-dinitrobenzene)-iminotetrazole. *J. Mol. Model.* **2013**, *19*, 1853−1864.

(33) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. Assessment of Gaussian-2 and Density Functional Theories for the Computation of Enthalpies of Formation. *J. Chem. Phys.* **1997**, *106*, 1063−1079.

(34) Atkins, P. W. *Physical Chemistry*; Oxford University Press: Oxford, U.K., 1982.

(35) Politzer, P.; Murray, J. S.; Grice, M. E.; DeSalvo, M.; Miller, E. Calculation of Heats of Sublimation and Solid Phase Heats of Formation. *Mol. Phys.* **1997**, *91*, 923−928.

(36) Byrd, E. F. C.; Rice, B. M. Improved Prediction of Heats of Formation of Energetic Materials Using Quantum Mechanical Calculations. *J. Phys. Chem. A* **2006**, *110*, 1005−1013.

(37) Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. *J. Comput. Chem.* **2012**, *33*, 580−592.

(38) Politzer, P.; Martinez, J.; Murray, J. S.; Concha, M. C.; Toro-Labbé, A. An Electrostatic Interaction Correction for Improved Crystal Density Prediction. *Mol. Phys.* **2009**, *107*, 2095−2101.

(39) Rice, B. M.; Byrd, E. F. C. Evaluation of Electrostatic Descriptors for Predicting Crystalline Density. *J. Comput. Chem.* **2013**, *34*, 2146−2151.

(40) Sućeska, M. *EXPLO5*, version 6.01; Brodarski Institute: Zagreb, Croatia, 2013.

(41) Gökçmar, E.; Klapötke, T. M.; Kramer, M. O. Computational Study on Nitronium and Nitrosonium Oxalate: Potential Oxidizers for Solid Rocket Propulsion? *J. Phys. Chem. A* **2010**, *114*, 8680−8686.

(42) Pospíśil, M.; Vávra, P.; Concha, M. C.; Murray, J. S.; Politzer, P. A Possible Crystal Volume Factor in the Impact Sensitivities of Some Energetic Compounds. *J. Mol. Model.* **2010**, *16*, 895−901.

(43) Zhu, W.; Zhang, C.; Wei, T.; Xiao, H. Computational Study of Energetic Nitrogen-rich Derivatives of 1,1′- and 5,5′-Bridged Ditetrazoles. *J. Comput. Chem.* **2011**, *32*, 2298−2312.

(44) Vedachalam, M.; T. Ramakrishnan, V.; Boyer, J. H.; Dagley, I. J.; Nelson, K. A.; Adolph, H. G.; Gilardi, R.; George, C.; Flippen-Anderson, J. L. Facile Synthesis and Nitration of *cis*-Syn-*cis*-2,6-dioxodecahydro-1*H*,5*H*-diimidazo[4,5-b:4′,5′-e]pyrazine. *J. Org. Chem.* **1991**, *56*, 3413−3419.

(45) Dagley, I. J.; Flippen-Anderson, J. L. Synthesis of Cyclic Nitramines From Products of the Cyclocondensation Reaction of Guanidine With 2,3,5,6-Tetrahydroxypiperazine-1,4-dicarbaldehyde. *Aust. J. Chem.* **1994**, *47*, 2033−2045.

(46) Guo, C.; Zhang, H.; Wang, X.; Liu, X.; Sun, J. Study on A Novel Energetic Cocrystal of TNT/TNB. *J. Mater. Sci.* **2013**, *48*, 1351−1357.