Research paper

Theoretical Study on Nitroimine Derivatives of Azetidine as High-Energy-Density Compounds

Bu-tong Li*, Lu-lin Li

*School of Chemistry and Materials Science,
Guizhou Education University, Guiyang 550018, China
E-mail: butong.lee@gmail.com

Abstract: A series of derivatives of azetidine were designed by stepwise replacing the hydrogen atoms of azetidine with nitroimine groups. At the G3MP2 level, the heats of formation (*HOFs*), bond dissociation energies (*BDEs*), molecular densities (ρ_0), detonation velocities (*D*), and detonation pressures (*P*) of the nitroimine-substituted azetidines were investigated to look for high-energy-density compounds (HEDCs). It was found that the nitroimine-substituted azetidines have high *HOFs* and large *BDEs*, and sufficient thermal and kinetic stability. Furthermore, the covalent bond strength in the four-membered ring, accompanied by intramolecular hydrogen bonds, are the determining factors for isomer stability. Based on our calculations, derivatives **E** and **F** have better detonation performance than RDX and can be regarded as potential high-energy-density compounds. This work may provide basic information for further study of the title compounds.

Keywords: high-energy-density compounds, Kamlet-Jacobs equations, azetidine derivatives

1 Introduction

The search for new high-energy-density compounds (HEDCs) for use in the fields of both military and civilian applications is the research

topic of many groups [1-5]. In past decades, many high-energy-density molecules have been designed in theory and synthesized in the laboratory, *i.e.* hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), hexanitrohexaazaisowurtzitane (CL-20), and so on [6-10].

Of these species, derivatives of azetidine are important ones. Azetidine has a strained four-membered heterocyclic ring, high-nitrogen-content, and seven hydrogen atoms available for substitution by additional energetic groups. Therefore, it is not surprising that the derivatives of azetidine have excellent energetic parameters, for example 1,3,3-trinitroazetidine (TNAZ) [11]. TNAZ is particularly attractive because of its excellent characteristics, including low sensitivity, easy manufacture, and steam castability. Its melting point is 101 °C and it is solid at room temperature [12]; its density is equal to 1.84 g/cm^3, close to that of RDX; a high detonation velocity (*D*) of 9.56 km/s, better than that of HMX [13]. Its excellent thermal stability causes it to be regarded as a replacement for TNT. Therefore, many studies have been performed on it, including synthetic routes [13, 14], character confirmation [15], and so on.

Considering that only three nitro groups have been introduced to create TNAZ, further improvements in the detonation character and molecular density are still possible for derivatives of azetidine. High-energy-density materials usually have a large content of nitrogen atoms, which causes the molecule to be energetic because of the superior stability of the N$_2$ produced in detonation reactions [16, 17]. Therefore, the introduction of nitro groups [18], nitroso groups [19], or any other groups with high nitrogen content is an effective strategy for raising the detonation performance of a molecule. This is why polynitro-substituted derivatives are an important class of energetic materials [20-24]. Of these energetic groups, the most popular one is the nitro group, but more attractive to us is the nitroimine group ($=NNO_2$). Compared to the nitro group, the nitroimine group contains more nitrogen atoms and same oxygen atoms. A larger nitrogen content should induced better detonation parameters, and a lower oxygen content will result in a more negative oxygen balance, accompanied by a less heat release in a detonation reaction, which may effectively reduce the explosive's sensitivity [25]. Evidently, nitroimine derivatives may be more competitive than nitro derivatives as HEDCs. Therefore, the hydrogen atoms of the azetidine molecule were stepwise substituted by nitroimine groups to design novel energetic compounds. To explore their potential use as HEDCs, the thermal and kinetic stability accompanied by the detonation parameters were calculated in detail using the density functional theory.

2   Computational Methods

All calculations were performed at the G3MP2 level by using the Gaussian 03 program [26]. Harmonic vibrational analyses at the same level were performed to confirm the nature of the potential energy surfaces. All of the object molecules are shown in Figure 1.
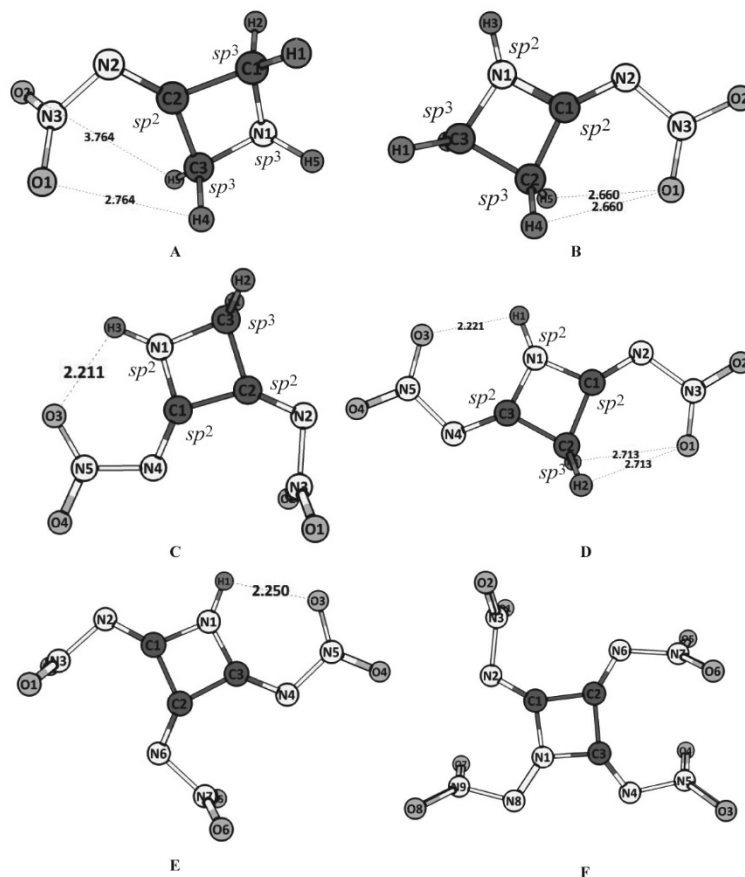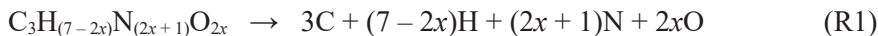

Figure 1. The structures of the azetidine derivatives optimized at the B3MP2 level in this study

The atomization reaction [27] was applied to calculate the heats of formation (*HOFs*) of the title compounds. For **A**, **B**, **C**, **D**, and **E**, reaction R1 was used. For **F**, reaction R2 was used. The *HOFs* were obtained *via* Equations 1-3.

$$C_3H_{(7-2x)}N_{(2x+1)}O_{2x} \rightarrow 3C + (7-2x)H + (2x+1)N + 2xO \tag{R1}$$

where $x = 1\text{-}3$

$$C_3N_8O_8 \rightarrow 3C + 8N + 8O \tag{R2}$$

$$\Delta H_{298}^0 = \sum \Delta_f H_{298,p}^0 - \Delta_f H_{298,M}^0 \tag{1}$$

$$\Delta E_{298} = \sum E_{0,p} - E_{0,M} - ZPE_M - \Delta H_{T,M}^0 \tag{2}$$

$$\Delta H_{298}^0 = \Delta E_{298} + \Delta(PV) = \Delta E_{298} + (\Delta n)RT \tag{3}$$

where ΔH_{298} is the standard enthalpy change of reactions R1 and R2 at 298 K. $\sum \Delta_f H_{298,p}^0$ is the sum of the standard *HOFs* of the product atoms. The experimental *HOF* values of the product atoms were obtained from Ref. [28]. $\Delta_f H_{298,M}^0$ is the standard *HOF* of compound *M*. ΔE_{298} is the energy change between products and reactants in reactions R1 and R2 at 298 K. $\sum E_{0,p}$ is the sum of the calculated total energy of the product atoms. $E_{0,M}$ is the total energy of compound *M*. ZPE_M is the zero point energy of compound *M*. $\Delta H_{T,M}^0$ is the thermal correction from 0 to 298 K for *M*. $\Delta(PV)$ equals $(\Delta n)RT$ and $\Delta n = 10 + 2x$ for reaction R1.

The pyrolysis mechanism and thermal stability can be evaluated by using the bond dissociation energy (*BDE*), which is the difference between the energies of the parent molecule and the corresponding radicals in the unimolecular dissociation reaction [29, 30]. The gas-phase *BDE* for a bond R_1–R_2 is defined as the enthalpy change of the bond homolysis reaction in terms of reaction R3 and Equation 4.

$$R_1\text{–}R_2(g) \rightarrow R_1\bullet(g) + R_2\bullet(g) \tag{R3}$$

$$BDE(R_1\text{–}R_2) = H_{298}(R_1\bullet) + H_{298}(R_2\bullet) - H_{298}(R_1\text{–}R_2) \tag{4}$$

The bond dissociation energy with zero-point energy (*ZPE*) correction can be represented by Equation 5.

$$BDE(R_1\text{–}R_2)_{ZPE} = BDE(R_1\text{–}R_2) + \Delta ZP \tag{5}$$

where ΔZPE is the *ZPE* difference between the products and the reactants.

For each title compound, the explosive reaction was designed in terms of the Kamlet-Jacobs rules, that is, all the N atoms turn into N_2, the O atoms react with H atoms to give H_2O at first, and then form CO_2 with the C atoms. If the number of O atoms is more than that needed to oxidize the H and C atoms, the redundant O atoms will be converted into O_2. If the number of the O atoms is not enough to satisfy full oxidation of the H and C atoms, the remaining of H atoms will be converted into H_2O, and the C atoms will exist as solid-state C. For the CHNO explosives, the detonation velocity and detonation pressure (P) were estimated by the Kamlet-Jacobs equations [31] (Equations 6 and 7).

$$D = 1.01(N\overline{M}^{1/2}Q^{1/2})^{1/2}(1+1.30\rho_0) \tag{6}$$

$$P = 1.558\rho_0^2 N\overline{M}^{1/2}Q^{1/2} \tag{7}$$

where N is the number of moles of detonation gases per gram of explosive, $\overline{M}$ is the average molecular weight of these gases, Q is the heat of detonation, ρ_0 is the loaded density of the explosive. In previous work, the ρ_0 can be replaced by the theoretical density (ρ). In general, ρ was obtained from the molecular weight divided by the average molecular volume. The volume was defined as that inside a contour of 0.001 electrons/bohr^3 density. We performed 100 single-point calculations for each optimized structure to obtain an average volume. Further corrections from the gaseous-state to crystal were also performed following the method from Equations 8-12, which take the electrostatic interaction into account [32].

Crystal density $\rho_0 = \alpha(M/V_m) + \beta(\nu\sigma^2_{tot}) + \gamma$ \hfill (8)

$$\sigma_{tot}^2 = \sigma_+^2 + \sigma_-^2 = \frac{1}{m}\sum_{i=1}^{m}[V^+(r_i)-\overline{V}_s^+]^2 + \frac{1}{n}\sum_{j=1}^{n}[V^-(r_j)-\overline{V}_s^-]^2 \tag{9}$$

$$\nu = \sigma_+^2\sigma_-^2/|\sigma_{tot}^2|^2 \tag{10}$$

$$V_S^+ = \frac{1}{m}\sum_{i=1}^{m}V^+(r_i) \tag{11}$$

$$V_S^- = \frac{1}{n}\sum_{j=1}^{n}V^-(r_j) \tag{12}$$

where ν is a balance parameter, $V(r)$ is the electrostatic potential, $V(r_i)$ is the value of $V(r)$ at any point r_i on the surface, $V_S^+(r_i)$ and $V_S^-(r_j)$ represent the positive

and negative values of $V(r)$ on the surface. $\overline{V}_s^+$ and $\overline{V}_s^-$ are their averages, σ_{tot}^2 is the total variance.

3   Results and Discussion

3.1 Heats of formation

The total energies, zero-point energies, values of thermal correction, and *HOFs* of the nitroimine-substituted derivatives were calculated at the G3MP2 level and are listed in Table 1. In Table 1, all of the azetidine derivatives have positive *HOFs*, which increase with the introduction of more nitroimine groups. Linear regression was performed and the correlation equation between the *HOFs* and the substitution number was:

$$y = 232.83x - 46.183 \tag{13}$$

with $R^2 = 0.94$. Obviously, the correlation meets the group additivity principle and one substituent group can raise the HOF by about 232 kJ/mol. Positive *HOFs* are typically characteristic for high energy density molecules, so the derivatives designed in this paper do have the potential to be used as energetic materials from the view point of the *HOFs*.

Table 1.   Total energy (E_0), zero-point energy (*ZPE*), thermal correction (ΔH_T) and heat of formation (*HOF*) at the G3MP2 level, and *HOF* for the atomization reaction

Compounds	E_0 [a.u.]	*ZPE* [a.u.]	ΔH_T [a.u.]	*HOF* [kJ/mol]
A	−431.27111	0.09294	0.10006	264.5
B	−431.29759	0.09315	0.10032	195.2
C	−689.62783	0.09036	0.10067	399.4
D	−689.65002	0.09044	0.10052	340.6
E	−947.96310	0.08694	0.10058	590.9
F	−1207.99350	0.09059	0.10923	958.9

For the mono-substituted derivatives, the HOF value of **B** is higher than **A** by about 70 kJ/mol, indicating that **A** is more stable than **B**. As shown in Figure 1, the distance of O···H in molecule **A** is 3.764 and 2.764 Å, respectively, a little longer than the 2.660 Å of **B**. Clearly, hydrogen bonding can stabilize **B** somewhat better than **A**. However, the difference between the HOFs of **A** and **B** is so great that it cannot be attributed

entirely to hydrogen bonding, but to the covalent bond strength in the four-membered ring. Furthermore, in the structures of **A** and **B**, the four-membered ring is planar for **B** and twisted for **A**. This indicates that N1 is sp^2 hybridised for **B**, but sp^3 hybridised for **A**. C1 of **B** and C2 of **A** are both sp^2 hybridised. Therefore, the bond N1–C1 of **B** is stronger than the bond N1–C1 (N1–C3) of **A**. Considering that a C–N bond is more energetic than a C–C bond, the C–N bond may be responsible for **B**'s better stability over **A**. We also noticed that the angles in the four-membered ring are all close to 90°, which indicates that the sp^2 hybridised N1 of molecule **B** may induce more ring strain than the sp^3 hybridised N1 of **A**. Therefore, **A** is more stable than **B**, which contradicts the results based on the above covalent bond and hydrogen bonding analysis. Taking our final data on *HOFs* into account, it is concluded that the effect of the covalent bond strength in the four-membered ring accompanied by the hydrogen bonding effects for evaluation of the isomer stability, the covalent bond strength is dominant.

These conclusions can be extended easily to derivatives **C** and **D**. For the disubstituted derivatives, **C** and **D** are both planar, which indicates N1, C1, and C2 of molecule **C** and N1, C1 and C3 of molecule **D** are all sp^2 hybridised. Therefore, the C–N bonds in the four-membered ring are both composed of sp^2-sp^2 bonding for molecule **D**, but sp^2-sp^2 and sp^2-sp^3 bonding for molecule **C**. Because sp^2-sp^2 bonding is stronger than sp^2-sp^3 bonding, molecule **D** is more stable than molecule **C**. More hydrogen bonds are confirmed in molecule **D** compared to molecule **C**, meaning that molecule **D** is stablised further. As regards ring strain, **C** and **D** are both planar and all atoms except for one carbon atom are sp^2 hybridised, so ring strain may be similar in both, without evident influence on the stability.

In summary, the covalent bond strength of the C–N bonds in the four-membered ring accompanied by hydrogen bonding are the determining factors for isomer relative stability.

3.2 Bond dissociation energies

The sensitivity and stability of energetic compounds are directly relevant to the bond strength, which is commonly described by the *BDE* [30, 33]. In general, the stronger the weakest bond is, the more stable the energetic material is. The weakest bond has the least bond order and may initiate the explosion in a detonation reaction, and is accordingly named as the "trigger bond" [34]. Therefore, the bond orders were calculated at the G3MP2 level, and all trigger bonds were located at the N–NO$_2$ position, for which the bond dissociation energy was calculated at the same level. The final results are listed in Table 2.

Table 2.   Bond dissociation energies (*BDE*), bond dissociation energies corrected by zero point energy (*BDE*$_{ZPE}$) and bond order (P_{N-NO2}) of the trigger bonds calculated at the G3MP2 level

Compound	*BDE* [kJ/mol]	*BDE*$_{ZPE}$ [kJ/mol]	P_{N-NO2}
A	165.7	147.6	0.9310
B	227.9	207.4	1.0256
C	142.1	124.8	0.8903
D	183.0	165.0	0.9580
E	156.5	139.4	0.8689
F	157.1	144.8	0.8652

From Table 2, it may be seen that the *BDE* values without zero point energy correction are larger than the *BDE*$_{ZPE}$ values (zero point energies corrected). However, the sequence of dissociation energies is not affected by the zero-point energies. Although the *BDEs* of the trigger bonds are lower than that of TATB (276.93 kJ/mol), the *BDE*$_{ZPE}$ values are over 120 kJ/mol and satisfy the stability needs of an explosive.

The bond order is an important parameter for evaluating the kinetic stability. From Table 2, the sequence of bond orders is mostly consistent with the sequence of bond dissociation energies. However, exceptions exist for **C** and **E**. The bond order for **C** (0.8903) is greater than that for **E** (0.8689), but the *BDE* value for **C** (142.1 kJ/mol) is less than that for **E** (156.5 kJ/mol). Considering the non-observability of bond orders experimentally, the bond dissociation energy is a more reliable parameter for predicting the kinetic stability of a molecule. Further comparison of the thermal stability to the *HOFs* was also performed, and consistency between the thermal stability and the kinetic stability was obtained. In other words, molecules with good thermal stability also have good kinetic stability. Therefore, **B** is more stable than **A**, and **D** is more stable than **C**, not only thermally but also kinetically.

3.3 Detonation performance

Detonation velocity and detonation pressure are two important performance parameters for HEDCs. The Kamlet-Jacobs equations have been proved reliable for predicting these parameters and were used in this study. The calculated molecular densities, heats of detonation, detonation velocities and detonation pressures are listed in Table 3. For comparison purposes, the experimental detonation parameters of the well-known explosive RDX is also included in Table 3.

Table 3. Crystal density (ρ_0), explosive heat (Q), detonation velocity (D) and detonation pressure (P) of the azetidine derivatives, together with those of RDX

Compound	ρ_0 [g/cm³]	Q [kJ/mol]	D [km/s]	P [GPa]
A	1.51	1600.57	7.23	20.71
B	1.57	1456.49	7.26	21.44
C	1.76	1731.66	8.66	32.89
D	1.72	1650.41	8.4	30.43
E	1.77	1855.5	9.03	35.88
F	1.81	1758.23	9.06	36.46
RDXa	1.78	1591.03	8.87	34.67

[a] Experimental data taken from Ref. [25]

In Table 3, the ρ_0 values of the azetidine derivatives become greater with the introduction of nitroimine groups. The correlation equation is:

$$y = 0.1432x + 1.3515 \qquad (14)$$

with $R^2 = 0.937$, which means that one nitroimine group enhances the density by 0.1432 g/cm³. Molecular density is a critical factor for detonation performance. The higher the molecular density, the greater are the detonation pressure and detonation velocity, which has been demonstrated by earlier research [25] and by our calculations. For example, **F** has a higher molecular density (1.81 g/cm³) than that of RDX, consistent with its greater detonation velocity, 9.06 km/s, and greater detonation pressure, 36.46 GPa, compared to those of RDX. This situation is similar for **E**, for which the good molecular density (1.77 g/cm³) results in an excellent detonation pressure (35.88 GPa) and detonation velocity (9.03 km/s). Compared to **E** and **F**, the detonation parameters of the other derivatives are inferior to those of RDX.

4   Conclusions

Based on our calculations, all of these azetidine derivatives possess large positive *HOFs*, which increase with the introduction of nitroimine groups. The thermal stability and pyrolysis mechanism were evaluated using bond dissociation energies. For these azetidine derivatives, the homolysis of the N−NO$_2$ bond is the initial step in explosion reactions. Moreover, the *BDEs* of all of the molecules are over 120 kJ/mol, which meets the criterion for high-

energy-density compounds (HEDCs). The C–N bond strength in the four-membered ring determines the isomer stability, aided by hydrogen bonds. The predicted detonation velocities and detonation pressures indicate that a nitroimine group is an effective substituent group for enhancing detonation performance. Based on our calculations, derivatives **E** ($D = 9.03$ km/s and $P = 35.88$ GPa) and **F** ($D = 9.06$ km/s and $P = 6.46$ GPa) may be promising candidates as HEDCs.

References

[1]   Huynh, M.H.V.; Hiskey, M.A.; Chavez, D.E.; Naud, D.L.; Gilardi, R.D. Synthesis, Characterization, and Energetic Properties of Diazido Heteroaromatic High-Nitrogen C−N Compound. *J. Am. Chem. Soc.* **2005**, *127*: 12537-12543.

[2]   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.

[3]   Zhang, M.-X.; Eaton, P.E.; Gilardi, R. Hepta- and Octa-nitrocubanes. *Angew. Chem. Int. Ed.* **2000**, *39*: 401-404.

[4]   Li, B.; Zhou, M.; Peng, J.; Li, L.; Guo, Y. Theoretical Calculations about Nitro-Substituted Pyridine as High-Energy-Density Compounds (HEDCs). *J. Mol. Model.* **2019**, *25*: 23-28.

[5]   Liu, T.; Jia, J.; Li, B.; Gao, K. Theoretical Exploration on Structural Stabilities and Detonation Properties of Nitrimino Substituted Derivatives of Cyclopropane. *Chin. J. Struct. Chem. (Jiegou Huaxue)* **2019**, *38*: 688-694.

[6]   Smith, G.D.; Bharadwaj, R.K. Quantum Chemistry Based Force Field for Simulations of HMX. *J. Phys. Chem. B* **1999**, *103*: 3570-3575.

[7]   Brill, T.B.; Gongwer, P.E.; Williams, G.K. Thermal Decomposition of Energetic Materials. 66. Kinetic Compensation Effects in HMX, RDX, and NTO. *J. Phys. Chem.* **1994**, *98*: 12242-12247.

[8]   Alavi, G.; Chung, M.; Lichwa, J.; D'Alessio, M.; Ray, C. The Fate and Transport of RDX, HMX, TNT and DNT in the Volcanic Soils of Hawaii: A Laboratory and Modeling Study. *J. Hazard. Mater.* **2011**, *185*: 1600-1604.

[9]   Ariyarathna, T.; Ballentine, M.; Vlahos, P.; Smith, R.W.; Cooper, C.; Bohlke, J.K.; Fallis, S.; Groshens, T.J.; Tobias, C. Tracing the Cycling and Fate of the Munition,

Hexahydro-1,3,5-Trinitro-1,3,5-Triazine in a Simulated Sandy Coastal Marine Habitat with a Stable Isotopic Tracer, (15)N-[RDX]. *Sci. Total Environ.* **2019**, *647*: 369-378.

[10] Eberly, J.O.; Mayo, M.L.; Carr, M.R.; Crocker, F.H.; Indest, K.J. Detection of Hexahydro-1,3-5-Trinitro-1,3,5-Triazine (RDX) with a Microbial Sensor. *J. Gen. Appl. Microbiol.* **2019**, *64*: 139-144.

[11] Archibald, T.G.; Gilardi, R.; Baum, K.; George, C. Synthesis and X-ray Crystal Structure of 1,3,3-Trinitroazetidine. *J. Org. Chem.* **1990**, *55*: 2920-2924.

[12] Thompson, C.A.; Rice, J.K.; Russell, T.P.; Seminario, J.M.; Politzer, P. Vibrational Analysis of 1,3,3-Trinitroazetidine Using Matrix Isolation Infrared Spectroscopy and Quantum Chemical Calculations. *J. Phys. Chem. A* **1997**, *101*: 7742-7748.

[13] Axenrod, T.; Watnick, C.; Yazdekhasti, H.; Dave, P.R. Synthesis of 1,3,3-Trinitroazetidine. *Tetrahedron Lett.* **1993**, *34*: 6677-6680.

[14] Marchand, A.P.; Rajagopal, D.; Bott, S.G.; Archibald, T.G. A Novel Approach to the Synthesis of 1,3,3-Trinitroazetidine. *J. Org. Chem.* **1995**, 60: 4943-4946.

[15] Sućeska, M.; Rajić, M.; Matečić-Mušanić, S.; Zeman, S.; Jalový, Z. Kinetics and Heats of Sublimation and Evaporation of 1,3,3-Trinitroazetidine (TNAZ). *J. Therm. Anal. Calorim.* **2003**, *74*: 853-866.

[16] Hammerl, A.; Klapötke, T.M.; Nöth, H.; Warchhold, M.; Holl, G.; Kaiser, M.; Ticmanis, U. $[N_2H_5]^{+2}[N_4C−NN−CN_4]^{2−}$: a New High-Nitrogen High-Energetic Material. *Inorg. Chem.* **2001**, *40*: 3570-3575.

[17] Chavez, D.E.; Hiskey, M.A. 1,2,4,5-Tetrazine Based Energetic Materials. *J. Energ. Mater.* **1999**, *17*: 357-377.

[18] Li, B.; Chi, W.; Li, L. Theoretical Calculation about the High Energy Density Molecules of Nitrate Ester Substitution Derivatives of Prismane. *Chin. J. Struct. Chem.* **2016**, *35*: 1306-1312.

[19] Ambrose, J.F.; Nelson, R.F. Anodic Oxidation Pathways of Carbazoles: I. Carbazole and N-Substituted Derivatives. *J. Electrochem. Soc.* **1968**, *115*: 1159-1164.

[20] de Vries, L.; Winstein, S. Neighboring Carbon and Hydrogen. XXXIX. Complex Rearrangements of Bridged Ions. Rearrangement Leading to the Bird-cage Hydrocarbon. *J. Am. Chem. Soc.* **1960**, *82*: 5363-5376.

[21] Liebman, J.F.; Greenberg, A. A Survey of Strained Organic Molecules. *Chem. Rev.* **1976**, *76*: 311-365.

[22] Marchand, A.P.; Wu, A. Syntheses of New Substituted Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}] Undecanes: a Novel Synthesis of Hexacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}.0^{5,9}]dodecane (1,3-Bishomopentaprismane). *J. Org. Chem.* **1986**, *51*: 1897-1900.

[23] Nielsen, A.T.; Nissan, R.A.; Vanderah, D.J.; Coon, C.L.; Gilardi, R.D.; George, C.F.; Flippen-Anderson, J. Polyazapolycyclics by Condensation of Aldehydes with Amines. 2. Formation of 2,4,6,8,10,12-Hexabenzyl-2,4,6,8,10,12-Hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}] Dodecanes from Glyoxal and Benzylamines. *J. Org. Chem.* **1990**, *55*: 1459-1466.

[24] Schulman, J.M.; Disch, R.L. Ab Initio Heats of Formation of Medium-sized Hydrocarbons. The Heat of Formation of Dodecahedrane. *J. Am. Chem. Soc.* **1984**, *106*: 1202-1204.

[25] Politzer, P.; Murray, J.S. High Performance, Low Sensitivity: Conflicting or Compatible? *Propellants Explos. Pyrotech.* **2016**, *41*: 414-425.

[26] Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A.; Vreven, J.T.; Kudin, K.N.; Burant, J.C.; Millam, J.M.; Iyengar, S.S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G.A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J.E.; Hratchian, H.P.; Cross, J.B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Ayala, P.Y.; Morokuma, K.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Zakrzewski, V.G.; Dapprich, S.; Daniels, A.D.; Strain, M.C.; Farkas, O.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Ortiz, J.V.; Cui, Q.; Baboul, A.G.; Clifford, S.; Cioslowski, J.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P.M.W.; Johnson, B.; Chen, W.; Wong, M.W.; Gonzalez, C.; Pople, J.A. *Gaussian 03*. Gaussian, Inc., Pittsburgh PA, **2003**, ISBN O-9636769-6-2.

[27] Curtiss, L.A.; Raghavachari, K.; Redfern, P.C.; Stefanov, B.B. Assessment of Complete Basis Set Methods for Calculation of Enthalpies of Formation. *J. Chem. Phys.* **1998**, *108*: 692-697.

[28] 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.

[29] Politzer, P.; Lane, P. Comparison of Density Functional Calculations of $C–NO_2$, $N–NO_2$ and $C–NF_2$ Dissociation Energies. *J. Mol. Struct.: THEOCHEM* **1996**, *388*: 51-55.

[30] Harris, N.J.; Lammertsma, K. Ab Initio Density Functional Computations of Conformations and Bond Dissociation Energies for Hexahydro-1,3,5-trinitro-1,3,5-triazine. *J. Am. Chem. Soc.* **1997**, *119*: 6583-6589.

[31] Kamlet, M.J.; Jacobs, S.J. Chemistry of Detonations. I. A Simple Method for Calculating Detonation Properties of C-H-N-O Explosives. *J. Chem. Phys.* **1968**, *48*: 23-35.

[32] 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.

[33] Owens, F.J. Calculation of Energy Barriers for Bond Rupture in Some Energetic Molecules. *J. Mol. Struct.: THEOCHEM* **1996**, *370*: 11-16.

[34] Li, B.; Li, L.; Chen, S. Thermal Stability and Detonation Character of Nitro-Substituted Derivatives of Imidazole. *J. Mol. Model.* **2019**, *25*: 298-304.