

# Theoretical Investigation on the Structure, Detonation Performance and Pyrolysis Mechanism of 4,6,8-Trinitro-4,5,7,8-tetrahydro-6H-furazano[3,4-f]-1,3,5-triazepine

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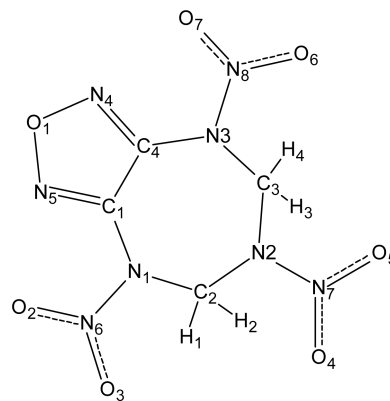
Based on the full optimized molecular geometric structures at B3LYP/cc-pvtz method, a new designed compound, 4,6,8-trinitro-4,5,7,8-tetrahydro-6H-furazano[3,4-f]-1,3,5-triazepine was investigated in order to look for high energy density compounds (HEDCs). The analysis of the molecular structure indicates that the seven-membered ring adopts chair conformation and there exist intramolecular hydrogen bond interactions. IR spectrum and heat of formation (HOF) were predicted. The detonation velocity and pressure were evaluated by using Kamlet-Jacobs equations based on the theoretical density and condensed HOF. The bond dissociation energies and bond orders for the weakest bonds were analyzed to investigate the thermal stability of the title compound. The results show that N<sub>1</sub>-N<sub>6</sub> bond is the trigger bond. The crystal structure obtained by molecular mechanics belongs to Pna2<sub>1</sub> space group, with lattice parameters Z = 4, a = 15.3023 Å, b = 5.7882 Å, c = 11.0471 Å, ρ = 2.06 g cm<sup>-3</sup>. In addition, the analysis of frontier molecular orbital shows the title compound has good stability and high chemical hardness.

**Key Words :** Density functional theory, Thermal stability, Detonation performance, 4,6,8-Trinitro-4,5,7,8-tetrahydro-6H-furazano[3,4-f]-1,3,5-triazepine, Molecular modelling

## Introduction

In recent years, the synthesis of energetic, heterocyclic compounds has attracted an increasing amount of interest because of the higher heat of formation (HOF) and density than their carbocyclic analogues.<sup>1</sup> Cyclic nitramines constitute an important class of organic energetic materials whose synthesis and properties have been widely studied<sup>2,3</sup> and played the important roles in the civil and military fields for a long time.<sup>4-6</sup> In order to study the effect of cyclic size and number of nitro group on energetic properties for nitramines, many four-, five-, six-, seven-, and eight-membered *N*-nitrated azacyclanes were synthesized. For example, RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) were synthesized<sup>7</sup> and their detonation performances were obtained. Polycyclic and caged nitramines compounds such as TNAD (*trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin)<sup>8</sup> and CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane)<sup>9</sup> have higher HOFs, densities and detonation parameters than HMX. *Cis*-2,4,6,8-Tetranitro-1*H*,5*H*-2,4,6,8-tetraazabicyclo[3.3.0]octane, commonly called “bicycle-HMX” exhibits better detonation performance than HMX and becomes another important polycyclic nitramine.<sup>10,11</sup>

However, there are few reports on azole-fused *N*-nitrated azacyclanes. Some researchers investigated furazano<sup>12-14</sup> and tetrazole derivatives,<sup>14,15</sup> which belonged to fused systems



**Figure 1.** The molecular structure of 4,6,8-trinitro-4,5,7,8-tetrahydro-6H-furazano[3,4-f]-1,3,5-triazepine.

with six-membered azacyclanes. Recently, a new designed furazano-fused seven-membered *N*-nitrated azacyclane, 4,6,8-trinitro-4,5,7,8-tetrahydro-6H-furazano[3,4-f]-1,3,5-triazepine was reported.<sup>16</sup> Up to now, there is no report about this compound. Figure 1 gave the molecular structure of the title compound.

In this paper, the structural parameters, thermodynamic properties, density, detonation velocity and pressure, thermal stability have been studied by using density functional theory (DFT). Frontier molecular orbital is also investigated. It is expected that the results could provide useful information for laboratory synthesis and design and development of new

novel energetic materials.

### Computational Details

Geometry optimization of molecular structures were performed without any symmetry restriction by using density functional theory at the B3LYP level with the cc-pvtz basis set in Gaussian 03 package.<sup>17</sup> Vibrational frequency analyses were performed at the same level. All optimized structures were characterized to be the local energy minimum on the potential energy surface by vibrational analysis. This indicates that the structure of each molecule corresponds to a local minimum on the potential energy surface. The  $\langle S^2 \rangle$  values are all very close to 0.75, which shows negligible spin contamination of pure doublets states for fragment open-shell systems.

The structure modifications can make the properties of the compound change drastically, so it is important to predict the properties and performance for a new designed compound. For energetic materials, the detonation velocity  $D$  and the detonation pressure  $P$  are two important parameters. The detonation velocity is the stable velocity of the shock front that characterizes detonation and the detonation pressure is the stable pressure that is development behind the front.<sup>18-20</sup>  $D$  and  $P$  can be calculated according to Kamlet and Jacobs equations.<sup>21</sup>

$$D = 1.01 \times \Phi^{0.5} (1.0 + 1.3\rho) \quad (1)$$

$$\Phi = N\bar{M}^{0.5} Q^{0.5}$$

$$P = 15.58 \times \Phi \rho^2 \quad (2)$$

In Eqs. (1) and (2),  $N$  is the moles of gas produced by per gram of explosives,  $\bar{M}$  is the an average molecular mass of the gaseous products in g/mol,  $Q$  is the estimated heat of detonation in cal/g,  $\rho$  is the density of the explosive in g/cm<sup>3</sup>. Obviously, the density plays a dominant role to determine  $D$  and  $P$ . Density is described as the primary physical parameter in detonation performance by Mader.<sup>22</sup> Higher density can contribute to developing new energetic materials.

Heat of formation (HOF) can be calculated by means of the atom equivalents procedure.<sup>23-25</sup> Since most of energetic materials are in solid, the calculation of detonation properties requires solid phase HOF ( $\Delta H_{f,solid}$ ). According to Hess's law of constant heat summation,<sup>26</sup> the gas-phase HOF ( $\Delta H_{f,gas}$ ) and heat of sublimation ( $\Delta H_{f,sub}$ ) can be used to evaluate their solid phase HOF:

$$\Delta H_{f,solid} = \Delta H_{f,gas} - \Delta H_{f,sub} \quad (3)$$

Politzer *et al.*<sup>27,28</sup> found that the heats of sublimation can correlate well with the molecular surface area and electrostatic interaction index  $\nu\delta_{tot}^2$  of energetic compounds. The empirical expression of the approach is as follows:

$$\Delta H_{sub} = aA^2 + b\sqrt{\nu\delta_{tot}^2} + c \quad (4)$$

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  $\delta_{tot}^2$  is a measure of variability of the electrostatic potential on the molecular surface. The coefficients  $a$ ,  $b$  and  $c$  were determined by Rice and coworker<sup>25</sup>:  $a = 2.670 \times 10^{-4}$  kcal/(mol\*Å<sup>4</sup>),  $b = 1.650$  kcal/mol and  $c = 2.966$  kcal/mol. The descriptors  $A$ ,  $\nu$  and  $\delta_{tot}^2$  were calculated using the computational procedures proposed by Lu.<sup>29</sup>

The possible polymorphs and crystal structure of the title compound is predicted by rigorous molecular packing calculations using polymorph module of Material Studio<sup>30</sup> since high-energy compounds are usually in condensed phases, especially solid form. The compass force-field is used to search the possible molecular packing among the most probable seven space groups (P2<sub>1</sub>/c, P-1, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, Pbc<sub>a</sub>, C2/c, P2<sub>1</sub>, and Pna2<sub>1</sub>).<sup>31-34</sup>

Furthermore, theoretical vibrational spectrum of the title compound was interpreted by means of potential energy distribution (PED) with the version V7.0-G77 of the MOLVIB program written by Sundius.<sup>35,36</sup> The calculated Raman activities ( $S_i$ ) have been converted to relative intensities ( $I_i$ ).

### Results and Discussion

**Molecular Geometry.** It is necessary to study the geometric structures before discussing the other properties. The xyz coordinates of optimized geometry of the title compound are listed in Supplementary Table S1. Some bond lengths and angles obtained from B3LYP/cc-pvtz method are tabulated in Table 1. Obviously, the seven-membered ring adopts chair conformation so that atoms N<sub>3</sub>, C<sub>3</sub>, N<sub>2</sub>, C<sub>2</sub> form central nearly planar fragment. In addition, amino-nitrogen atoms are not planar in all N-NO<sub>2</sub> moieties and all NO<sub>2</sub> groups deviate from the corresponding C-N-C planes in order to come closer to each other. The N-NO<sub>2</sub> groups all depart from the attached ring plane because of the steric hindrance effect and the N<sub>2</sub>-NO<sub>2</sub> moiety has the largest deviation from planarity. Geometry optimization performed on the title compound indicated that there exist intramolecular hydrogen bond interactions. The hydrogen bond lengths and angles are listed in Table 2.

**Table 1.** Selected bond lengths (Å) and angles (°) of the title compound computed at B3LYP level

Bond length		Bond angle	
C <sub>1</sub> -N <sub>1</sub>	1.402	C <sub>1</sub> -N <sub>1</sub> -C <sub>2</sub>	117.85
C <sub>2</sub> -N <sub>1</sub>	1.454	N <sub>1</sub> -C <sub>2</sub> -N <sub>2</sub>	110.93
C <sub>2</sub> -N <sub>2</sub>	1.467	C <sub>2</sub> -N <sub>2</sub> -C <sub>3</sub>	121.38
C <sub>3</sub> -N <sub>2</sub>	1.436	N <sub>2</sub> -C <sub>3</sub> -N <sub>3</sub>	112.86
C <sub>3</sub> -N <sub>3</sub>	1.482	C <sub>3</sub> -N <sub>3</sub> -C <sub>4</sub>	121.07
C <sub>4</sub> -N <sub>3</sub>	1.387	N <sub>3</sub> -C <sub>4</sub> -C <sub>1</sub>	123.37
C <sub>4</sub> -C <sub>1</sub>	1.437	C <sub>4</sub> -C <sub>1</sub> -N <sub>1</sub> -N <sub>6</sub>	167.95
N <sub>4</sub> -C <sub>4</sub>	1.305	N <sub>1</sub> -C <sub>2</sub> -N <sub>2</sub> -N <sub>7</sub>	-74.93
C <sub>1</sub> -N <sub>5</sub>	1.298	N <sub>2</sub> -C <sub>3</sub> -N <sub>3</sub> -N <sub>8</sub>	99.37
O <sub>1</sub> -N <sub>5</sub>	1.387	C <sub>1</sub> -N <sub>1</sub> -C <sub>2</sub> -N <sub>2</sub>	-36.03
O <sub>1</sub> -N <sub>4</sub>	1.344	C <sub>2</sub> -N <sub>2</sub> -C <sub>3</sub> -N <sub>3</sub>	-35.73

**Table 2.** Selected hydrogen bond length (Å) and bond angle (°)

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠DHA
C <sub>3</sub> -H <sub>4</sub> ...O <sub>6</sub>	1.082	2.148	2.628	104.00
C <sub>2</sub> -H <sub>1</sub> ...O <sub>3</sub>	1.085	2.195	2.691	105.14

**Gas- and Solid-phase Heats of Formation.** The gas HOF  $\Delta H_f^0(g)$  of the title compound can be obtained by means of atom equivalent procedure<sup>23-25</sup>:

$$\Delta H_f^0(g) = E(g) - \sum_i n_i x_i \quad (5)$$

In Eq. (5),  $E$  is the quantum mechanically determined electronic energy of the molecule at 0 K,  $n_i$  is the number of atoms of elements  $i$  and  $x_i$  is its atom equivalent energy. Here,  $x_i$  is determined by Rice and Byrd through a least-squares fitting of Eq. (5) to the experimental  $\Delta H_f^0(g)$  of a series of CHNO energetic materials.<sup>23</sup> Using this method, the HOF of the title compound is calculated at B3LYP/cc-pvtz level. Solid-phase HOF,  $\Delta H_{f,solid}$  is an important property to predict the detonation properties of the energetic materials. Table 3 presents the total energies,  $\Delta H_{f,gas}$  and  $\Delta H_{f,gas}$  of the title energetic material.

The crystal density can be calculated by electrostatic potential on the molecular surfaces:

$$\rho = \alpha \left( \frac{M}{V(0.001)} \right) + \beta (v \delta_{tot}^2) + \gamma \quad (6)$$

In Eq. (6),  $M$  is the molecular mass in g/molecule,  $V(0.001)$  is the volume of the isolated gas phase molecule, in cm<sup>3</sup>/molecule. The coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$  were 0.9183, 0.0028, 0.0443, respectively, which are obtained by Politer *et al.*<sup>37</sup> The calculated density is also included in Table 3.

In order to have a comparison, the experimental HOFs of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) were also listed in Table 3. Using the method of Politzer *et al.*,<sup>26,27</sup> the  $\Delta H_{f,sub}$ , the descriptors  $A$ ,  $v$ ,  $\delta_{tot}^2$  and  $\Delta H_{f,solid}$  for the title compound, RDX and HMX<sup>38-40</sup> were all listed in Table 3. It is noted that the experimental  $\Delta H_{f,gas}$  and  $\Delta H_{f,solid}$  of RDX and HMX are agreement with the calculated values of RDX and HMX, which shows that our calculations are reliable.

Density is one of the critical factors that determine the energetic properties of compounds. According to the Kamlet-Jacobs equation,<sup>21</sup> density greatly affects the detonation performance. Detonation pressure is dependent on the square of the density, while detonation velocity is proportional to the density. Densities of the title compound, RDX and HMX

are corrected by the method of Politzer *et al.*<sup>37</sup> and also included in Table 3. For comparisons, the experimental densities and HOFs of HMX, RDX are also listed in this table. It is noted that densities of the studied compounds are slightly higher than those of RDX and HMX. From Table 3, the gas HOF of the title compound is 610.04 kJ/mol and the density is 1.97 g/cm<sup>3</sup>, which is much larger than those of RDX (1.78 g/cm<sup>3</sup>) and HMX (1.89 g/cm<sup>3</sup>).<sup>41,42</sup>

**Detonation Properties.** Based on the condensed HOF and density of the title compound, the detonation properties, including  $Q$ ,  $D$  and  $P$ , were estimated. Table 4 lists the calculated  $D$ ,  $P$ ,  $Q$  and the oxygen balances  $OB(\%)$  of the title compound. For better comparing and evaluating detonation performance of the title compound, the calculated and experimental data<sup>7,41</sup> of RDX and HMX are also listed in Table 4.

In comparison with HMX and RDX, the title compound exhibits much better detonation performance. The detonation velocity and pressure of the title compound are 9.65 km/s and 43.51 GPa, respectively. This shows that the title compound is a promising energetic material. According to energy criterion for high energy density compound,<sup>42</sup> *i.e.*,  $\rho \approx 1.90$  g/cm<sup>3</sup>,  $D \approx 90.0$  km/s,  $P \approx 40.0$  GPa, the title compound satisfies the requirements.

**Infrared Spectrum.** Figure 2 provides the simulated IR spectrum of the title compound based on the scaled harmonic vibrational frequencies. Obviously, there are four main characteristic regions. The modes in 3140-3204 cm<sup>-1</sup> are associated with C-H stretch. In this region, the strongest characteristic peak is at 3180 cm<sup>-1</sup>. The modes in 1604-1700 cm<sup>-1</sup> are associated with the N=O asymmetric stretch of nitro groups and the strong characteristic peak is at 1676 cm<sup>-1</sup>. The modes in 1244-1364 cm<sup>-1</sup> are the complex of C-H bending together with the N-N stretch and the strongest characteristic peak is at 1292 cm<sup>-1</sup>, which corresponds to the N-N stretch. Peaks at less than 1200 cm<sup>-1</sup> such as 980 cm<sup>-1</sup>

**Table 4.** Predicted density and detonation properties of the title compound<sup>a</sup>

Compd	$Q$ (cal/g)	$OB(\%)^a$	$D$ (km/s)	$P$ (GPa)
The title compound (C <sub>4</sub> H <sub>4</sub> N <sub>8</sub> O <sub>7</sub> )	1799.0	-17.4	9.65	43.51
RDX <sup>b</sup>	1597.4	-21.6	8.98(8.75)	35.13(34.00)
HMX <sup>b</sup>	1633.9	-21.6	9.35(9.10)	38.24(39.00)

<sup>a</sup>Oxygen balance (%) for C<sub>a</sub>H<sub>b</sub>O<sub>c</sub>N<sub>d</sub>:  $1600 \times (c-2a-b/2)/M_w$ ;  $M_w$  is molecular weight. <sup>b</sup>Data in parentheses for RDX and HMX are from Ref. [7, 41].

**Table 3.** Calculated total energies ( $E_0$ ), zero-point energies (ZPE), densities and heats of formation (HOFs) for the title energetic material.  $E_0$  and ZPE are in a.u., HOFs are in kJ/mol, densities are in g/cm<sup>3</sup>

Compds.	$E_0$	ZPE	$\Delta H_{f,gas}$	$A$	$v$	$v \delta_{tot}^2$	$\Delta H_{f,sub}$	$\Delta H_{f,solid}$	Density
The title compound	-1119.2007	0.138766	729.78	255.64	0.10	24.88	119.74	610.04	1.97
RDX	-1196.3655	0.192075	175.37(192)	190.34	0.18	30.81	91.16	84.21(79.1)	1.78(1.82)
HMX	-897.2732	0.143296	210.39(250)	254.63	0.17	24.00	118.39	92.00(74.8)	1.89(1.90)

<sup>a</sup>Data in parentheses are the experimental values taken from refs (38-40).

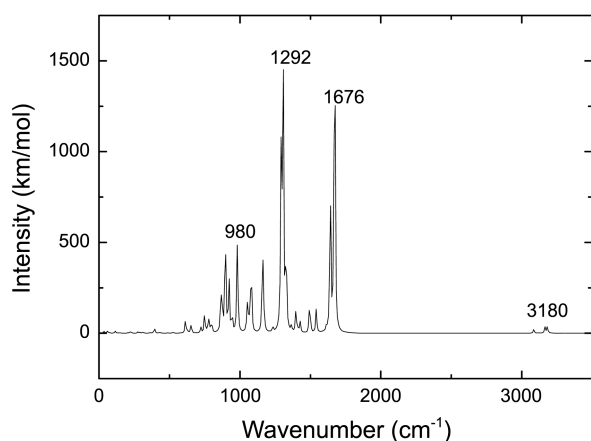


Figure 2. The calculated infrared spectrum for the title compound.

are mainly caused by the deformation of the heterocyclic skeleton, C-H bending and N-NO<sub>2</sub> stretch.

**Electronic Structure and Thermal Stability.** For the energetic material, it is important to understand whether they are stable enough to be of practical interest. A good energetic material should have a high stability. Thus, studies on the bond dissociation or pyrolysis mechanism are important to understand the decomposition process of the energetic materials because they are directly relevant to the sensitivity and stability of the energetic compounds. The bond dissociation energy (BDE) could evaluate the strength of bonding that is fundamental to understand the decomposition process of the energetic materials. Since there may be several bonds of the same kind in a molecule, the Wiberg bond indexes (WBIs) from natural bond orbital (NBO) analysis were used to ascertain the weakest bond. A high WBI value indicates a stronger bond, whereas a low WBI value shows a weaker bond, so the bond with the smallest WBI among all bonds of the same type was considered.

In this paper, two possible initial steps, *i.e.* the breakings of N-NO<sub>2</sub> bond in the side chain and C-N bond in the skeleton are considered. In order to find the weakest bond, natural bond orbital analysis (NBO) has been performed. Table 5 lists some Wiberg bond orders of the title compound. It is noted that C<sub>3</sub>-N<sub>3</sub> in the skeleton and N<sub>1</sub>-N<sub>6</sub> in the side chain have the smaller WBI among the same kind of bonds. The corresponding BDEs were also calculated and listed in

Table 5. Wiberg bond order and BDEs (kJ/mol) of the title compound

Bond	WBI	Bond	WBI	BDE
C <sub>1</sub> -N <sub>1</sub>	0.9913	C <sub>1</sub> -N <sub>5</sub>	1.6085	–
C <sub>2</sub> -N <sub>1</sub>	0.9452	O-N <sub>5</sub>	1.1462	–
C <sub>2</sub> -N <sub>2</sub>	0.9437	O-N <sub>4</sub>	1.0820	–
C <sub>3</sub> -N <sub>2</sub>	0.9836	C <sub>4</sub> -N <sub>3</sub>	1.0504	–
C <sub>4</sub> -C <sub>1</sub>	1.1505	N <sub>3</sub> -N <sub>8</sub>	0.9776	–
N <sub>2</sub> -N <sub>7</sub>	0.9840	C <sub>3</sub> -N <sub>3</sub>	0.9053	221.47
N <sub>4</sub> -C <sub>4</sub>	1.5907	N <sub>1</sub> -N <sub>6</sub>	0.9297	83.39

Table 5.

From Table 5, the BDE of N<sub>1</sub>-N<sub>6</sub> bond is 83.39 kJ/mol, which is weaker than that of C<sub>3</sub>-N<sub>3</sub> bond. This indicates that N<sub>1</sub>-N<sub>6</sub> breaks more easily and may be the trigger bond. The results agree with experimental studies showing dominance of NO<sub>2</sub> fission in the early stages of thermal decomposition.<sup>43,44</sup> According to the stability request of HEDC (BDE ≈ 80-120 kJ/mol), we think that the title compound is a stable compound.

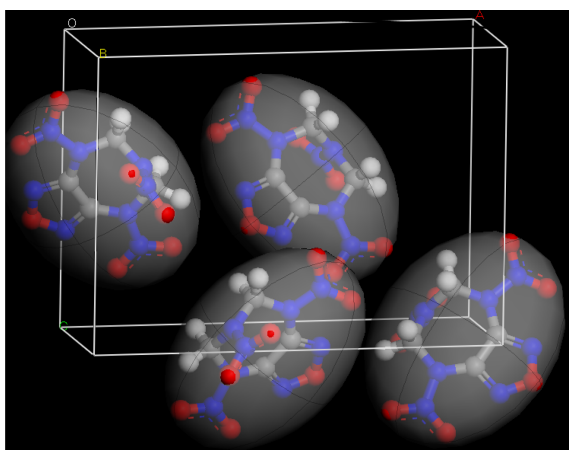
**Molecular Packing Prediction and Density.** The crystal structure of the title compound in this paper is predicted by COMPASS force field,<sup>45</sup> which can produce the gas- and condensed-phase properties reliably for a broad range of systems.<sup>46</sup> Using COMPASS force field, we can pack arrangements in all reasonable space groups to search for the low-lying minima in the lattice energy surface. The structure optimized by B3LYP/cc-pvtz method is considered as input structure for polymorph search. Table 6 lists the lattice parameters in all reasonable space groups.

It is noted from Table 6 that the energies range from -187.2 to -193.0 kJ mol<sup>-1</sup> cell<sup>-1</sup> and the structure with Pna2<sub>1</sub> symmetry has the lowest energy. Most stable polymorphs usually possess the least energy at 0 K, so the title compound tends to exist in the Pna2<sub>1</sub> group. The corresponding lattice parameters are Z = 4, a = 15.3023 Å, b = 5.7882 Å, c = 11.0471 Å, ρ = 2.06 g cm<sup>-3</sup>. Figure 3 gave the molecular packing of the title compound in Pna2<sub>1</sub> space group.

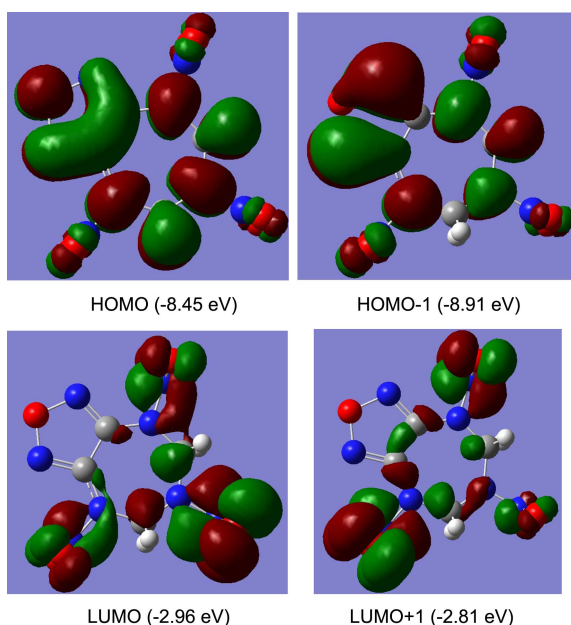
**Frontier Molecular Orbitals.** The frontier molecular orbitals play an important role in the electric and optical properties, as well as in chemical reactions.<sup>47</sup> Figure 4 shows the distributions and energy levels of the HOMO-1, HOMO, LUMO and LUMO+1 orbitals computed at B3LYP/cc-pvtz level for the title compound.

Table 6. Unit cell parameters of the possible molecular packings of the title compound

Space groups	C2/c	P1	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub>	P2 <sub>1</sub> /C	Pna2 <sub>1</sub>	Pbca
Z	8	2	4	2	4	4	8
E (kJ mol <sup>-1</sup> cell <sup>-1</sup> )	-187.3	-187.6	-190.5	-191.6	-189.6	-193.0	-187.2
ρ (g cm <sup>-3</sup> )	1.65	1.68	1.68	1.89	1.56	2.06	1.07
a (Å)	23.4922	7.2551	8.5088	7.5676	7.7185	15.3023	16.8700
b (Å)	7.9285	7.8130	8.5092	12.0096	19.2268	5.7882	17.6208
c (Å)	31.4263	11.1399	12.7352	5.7828	14.4038	11.0471	6.8123
α	90.00	117.12	90.00	90.00	90.00	90.00	90.00
β	161.03	96.00	90.00	126.36	154.10	90.00	90.00
γ	90.00	115.54	90.00	90.00	90.00	90.00	90.00



**Figure 3.** Molecular packing of the title compound in Pna<sub>21</sub> space group.



**Figure 4.** Molecular orbital surfaces and energy levels given in parentheses for the HOMO-1, HOMO, LUMO and LUMO+1 of the title compound computed at B3LYP/cc-PVTZ level.

As seen from Figure 4, LUMO+1 is mainly localized on the nitro groups and the skeleton of seven-membered N-nitrated azacyclane, while LUMO is mainly localized on the nitro groups and the C<sub>2</sub>, C<sub>3</sub> atoms of seven-membered N-nitrated azacyclane. HOMO and HOMO-1 are all mainly localized on the furazan ring, the three nitro groups and the skeleton of seven-membered N-nitrated azacyclane. The value of the energy separation between the HOMO and LUMO is 5.49 eV. This large HOMO-LUMO gap means high excitation energies for many of excited states, a good stability and a high chemical hardness for the title compound.

### Conclusion

In this paper, a new designed polynitro derivative was

investigated by using density functional theory. IR spectrum was also predicted. The results show that there are four main characteristic regions. Detonation properties, HOF and the weakest bond were predicted. The results show the N<sub>1</sub>-N<sub>6</sub> bond is predicted to be the trigger bond during pyrolysis based on the results of bond order and BDE. The most possible packing structure belongs to Pna<sub>21</sub> space group. The detonation velocity and pressure of the title compound are 9.65 km/s and 43.51 GPa, respectively. All the calculation results indicate that the title compound possesses very high HOF, detonation velocity and pressure and is a potential candidate of HEDM.

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### References

- Pagoria, P. F.; Lee, G. S.; Mitchell, A. R.; Schmidt, R. D. *Thermochim. Acta* **2002**, *384*, 187-204.
- Agrawal, J. P.; Hodgson, R. D. *Organic Chemistry of Explosives*; John Wiley & Sons: Chichester, 2007.
- Willer, R. L. *J. Mex. Chem. Soc.* **2009**, *53*, 108-119.
- Xiao, H. M. *Molecular Orbital Theory for Nitro Compounds*; National Defense Industry Press: Beijing, 1993.
- Jalovy, Z.; Zeman, S.; Suceška, M.; Vavra, P.; Dudek, K.; Rajic, M. *J. Energ. Mater.* **2001**, *19*, 219-239.
- Cobbledick, R. E.; Small, R. W. H. *Acta Crystallogr. B* **1972**, *30*, 1918-1922.
- Sasada, Y. *Molecular and Crystal Structures in Chemistry Handbook*; The Chemical Society of Japan: Maruzen, 1984.
- Willer, R. L. *J. Org. Chem.* **1984**, *49*, 5150-5154.
- Simpson, R. L.; Urtiew, P. A.; Ornellas, D. L.; Moody, G. L.; Scribner, K. J.; Hoffman, D. M. *Propellants, Explos., Pyrotech.* **1997**, *22*, 249-255.
- Qiu, L.; Xiao, H. M. *J. Hazard. Mater.* **2009**, *164*, 329-336.
- Koppes, W. M.; Chaykovsky, M. H.; Adolph, G.; Gilardi, R.; George, C. J. *J. Org. Chem.* **1987**, *52*, 1113-1119.
- Willer, R. L.; Moore, D. W. *J. Org. Chem.* **1985**, *50*, 5123-5127.
- Sheremetev, A. B.; Khim, Z. R. *Mendeleev Chemistry Journal* **1997**, *41*, 43-54.
- Ermakov, A. S.; Serkov, S. A.; Tartakovskii, V. A.; Novikova, T. S.; Khmel'nitskii, L. I.; Geterotski, S. K. *Chemistry of Heterocyclic Compounds* **1994**, *30*, 976-978.
- Willer, R. L.; Henry, R. A. *J. Org. Chem.* **1988**, *53*, 5371-5373.
- Aleksei, S. B.; Natal'ya, A. S.; Kyrill, S. Y.; Mikhail, A. Y.; Vladimir, T. A. *Mendeleev Commun.* **2010**, *20*, 249-252.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 03*, Revision B.02, Gaussian Inc.: Pittsburgh PA, 2003.
- Iyer, S.; Slagg, N. *Molecular Aspects in Energetic Materials*, in: *Structure and Reactivity*; VCH Publishers: New York, 1988.
- Dlott, D. D. *Fast Molecular Processes in Energetic Materials*, in:

- Energetic Materials. Part 2. Detonation, Combustion*; Elsevier: Amsterdam, 2003.
20. Meyer, R.; Köhler, J. A. *Homburg, Explosives*; Wiley-VCH: Germany, 2007.
21. Kamlet, M. J.; Jacobs S. J. *J. Chem. Phys.* **1968**, *48*, 23-35.
22. Mader, C. L. *Detonation Performance, in: Organic Energetic Compounds*; Nova Science Publishers: New York, 1996.
23. Rice, B. M.; Pai, S. V.; Hare, J. *Combust. Flame* **1999**, *118*, 445-458.
24. Habibollahzadeh, D.; Grice, M. E.; Concha, M. C.; Murray, J. S.; Politzer, P. *J. Comput. Chem.* **1995**, *16*, 654-658.
25. Byrd, E. F. C.; Rice, B. M. *J. Phys. Chem. A* **2006**, *110*, 1005-1013.
26. Atkins, P. W. *Physical Chemistry*; Oxford University Press: Oxford, 1982.
27. Politzer, P.; Lane, P.; Murray, J. S. *Cent. Eur. J. Energ. Mater* **2011**, *8*, 39-52.
28. Politzer, P.; Murray, J. S. *Cent. Eur. J. Energ. Mat.* **2011**, *8*, 209-220.
29. Lu, T. *Multiwfn Revision 2.5.2*; Beijing Science and Technology: Beijing, 2012.
30. Materials Studio 4.4. Accelrys, 2008.
31. Chernikova, N. Y.; Belsky, V. K.; Zorkii, P. M. *J. Struct. Chem.* **1990**, *31*, 661-666.
32. Mighell, A. D.; Himes, V. L.; Rodgers, J. R. *Acta Crystallogr.* **1983**, *39*, 737-740.
33. Wilson, A. J. C. *Acta Crystallogr A* **1988**, *44*, 715-724.
34. Srinivasan, R. *Acta Crystallogr A* **1992**, *48*, 917-918.
35. Sundius, T. *MOLVIB: A Program for Harmonic Force Field Calculations, QCPE Program No. 807*, 2002.
36. Sundius, T. *Vib. Spectrosc.* **2002**, *29*, 89-95.
37. Politzer, P.; Martinez, J.; Murray, J. S.; Concha, M. C.; Toro-Labbé, A. *Mol. Phys.* **2009**, *107*, 2095-2101.
38. Zhang, X.-H.; Yun, Z.-H. *Explosive Chemistry*; National Defence Industry Press: Beijing, 1989.
39. Talawar, M. B.; Sivabalan, R.; Mukundan, T.; Muthurajan, H.; Sikder, A. K.; Gandhe, B. R.; Rao, A. S. *J. Hazard. Mater.* **2009**, *161*, 589-607.
40. Badgujar, D. M.; Talawar, M. B.; Asthana, S. N.; Mahulikar, P. P. *J. Hazard. Mater.* **2008**, *151*, 289-305.
41. Ghule, V. D.; Jadhav, P. M.; Patil, R. S.; Radhakrishnan, S.; Soman, T. *J. Phys. Chem. A* **2010**, *114*, 498-503.
42. Xiao, H. M.; Xu, X. J.; Qiu, L. *Theoretical Design of High Energy Density Materials*; Science Press: Beijing, 2008.
43. Li, X.-H.; Zhang, R.-Z.; Yang, X.-D.; Zhang, H. *J. Mol. Struct.-THEOCHEM.* **2007**, *815*, 151-156.
44. Li, X.-H.; Zhang, R.-Z.; Zhang, X.-Z. *J. Hazard. Mater.* **2010**, *183*, 622-631.
45. Sun, H. *J. Phys. Chem. B* **1998**, *102*, 7338-7364.
46. Xu, X. J.; Zhu, W. H.; Xiao, H. M. *J. Phys. Chem. B* **2007**, *111*, 2090-2097.
47. Fleming, J. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1976.
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