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# Quantum Chemical Studies on the Structures and Properties of Nitro Derivatives of Symmetric Pyrazino-dicycloureas

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**Abstract:** The molecular geometries and electronic structures of nitro derivatives of symmetric pyrazino-dicycloureas were obtained by a density functional theory (DFT) method with DFT-B3LYP/6-31G\*\* . Their values of theoretical molecular density ( $\rho$ ) and heat of formation (HOF) were computed by quantum chemical method. The values of detonation velocity ( $D$ ) and detonation pressure ( $p$ ) were estimated using Kamlet-Jacobs equations. Studies on the relationship between structure and property of these nitro derivatives were performed. Results show that the number, positions, surrounding and symmetry of the nitro group within the molecule and the symmetry of the molecular structure are some principal factors affecting the thermal stabilities and detonation properties of nitro derivatives of symmetric pyrazino-dicycloureas. The values of  $\rho$ , HOF,  $D$  and  $p$  for 1,3,5,7-tetra-nitro-5,7-dihydroimidazo[4,5-*b*:4',5'-*e*]pyrazine-2,6(1*H*,3*H*)-dione are 2.03 g · cm<sup>-3</sup>, 265.63 kJ · mol<sup>-1</sup>, 9.08 km · s<sup>-1</sup>, and 39.22 GPa, respectively. The structure of 1,3,5,7-tetra-nitro-2,6-dioxo-1,2,3,5,6,7-hexahydroimidazo[4,5-*b*:4',5'-*e*]pyrazine-4-oxide is unstable. These results obtained provide basic research data for molecular design and synthesis of novel high energetic density compounds (HEDC).

**Key words:** quantum chemistry; detonation performance; cyclourea nitramine; pyrazine ring

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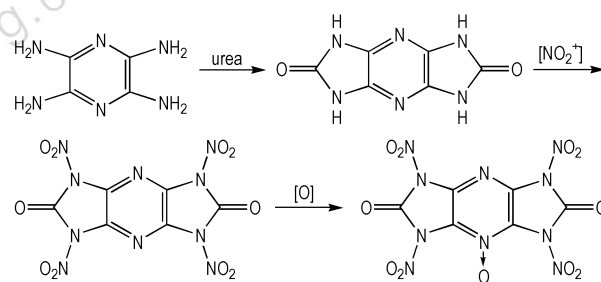
## 1 Introduction

In recent years, the synthesis of energetic, heterocyclic compounds have received a great amount of interest owing to their higher heat of formation, density, and oxygen balance than those of carbocyclic analogues<sup>[1-4]</sup>, especially the nitro derivatives of pyrazines and their analogues for insensitive explosives<sup>[5-11]</sup>. Pagoria et al.<sup>[12-13]</sup> synthesized 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) by reaction 2,6-dichloropyrazine with sodium methoxide to yield 2-methoxy-6-chloropyrazine, following by nitration with mixed acid at 70 °C to yield 2,6-diamino-3,5-dinitropyrazine (ANPZ), and then oxidation to give the target compound, which exhibits a density of 1.918 g · cm<sup>-3</sup><sup>[14]</sup> and decomposition temperature of 354 °C. This work also illustrated that the conversion of tertiary amines to their corresponding *N*-oxides can increase density and oxygen balance in heterocyclic systems<sup>[15]</sup>.

As another class of energetic materials, cyclourea nitramines increasingly gain importance as perspective and highly energetic materials. In general, both the mono- and dinitrourea explosives have very high densities (>1.90 g · cm<sup>-3</sup>) which has been attributed to the inherently high density of the urea framework. However, the dinitrourea explosives suffer from hydrolytic liability, and thus restricting their use. But the mono-nitrourea compounds are fairly stable to hydrolysis and are relatively insensitive to shock<sup>[16-19]</sup>.

With the concept of designing and synthesizing new nitro

derivatives of symmetric pyrazino-dicycloureas, 2,3,5,6-tetraaminepyrazine reacts with urea to yield a precursor with two five-membered rings, which provides a possible conversion of tertiary amines to their corresponding *N*-oxides and more N—H sites for introducing nitro substituents, and thus generates a series of new energetic materials (Scheme 1). Upnow, the study on the relationship between structure and property of nitro derivatives of symmetric pyrazino-dicycloureas is little. Therefore, we report a systematic study on the density, heats of formation, thermal stability, and energetic properties of nitro derivatives of symmetric pyrazino-dicycloureas by density functional theory (DFT) method. Detonation velocities and pressures were predicted using the calculated HOF and densities.



Scheme 1

## 2 Computational methods

Calculations were carried out by using the Gaussian 09 program suite. The geometry optimization of the structures and frequency analysis were carried out by using the B3LYP functional with the 6-31G\*\* basis set<sup>[20-21]</sup>. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. Isodesmic reactions were designed for the prediction of gas

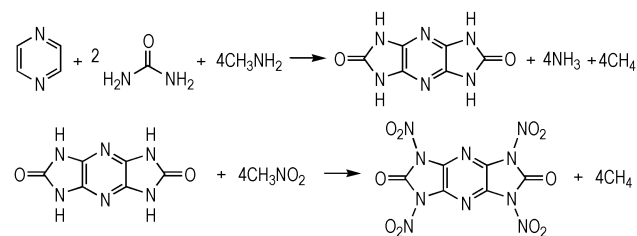
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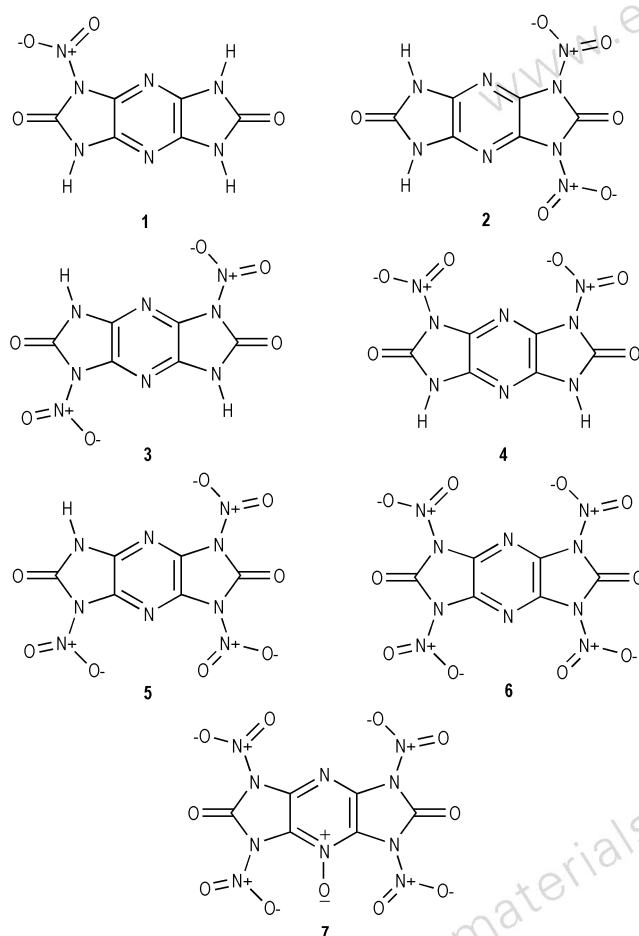
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phase heats of formation. Scheme 2 shows a representative isodesmic reaction for compound **6** (see in Scheme 3).



Scheme 2



Scheme 3 Illustration of the molecular structures of the seven title compounds

For C—H—N—O explosives, the Kamlet and Jacob empirical equations (1) and (2) were used to determine detonation parameters<sup>[22]</sup>.

$$p = 1.558NM^{1/2}Q^{1/2}\rho^2 \quad (1)$$

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (2)$$

where  $p$  is detonation pressure in GPa,  $D$  is detonation velocity in  $\text{km} \cdot \text{s}^{-1}$ ,  $N$  is the number of moles of gaseous detonation products per gram of explosive,  $M$  is the average molecular weight of the gaseous products,  $Q$  is the energy of the detonation reaction of explosive in  $\text{J} \cdot \text{g}^{-1}$  and  $\rho$  is the crystal density in  $\text{g} \cdot \text{cm}^{-3}$ .  $N$ ,  $M$  and  $Q$  are decided according to the

largest exothermic principle, i. e., for C—H—N—O explosives, all the N atom convert into  $\text{N}_2$ , the O atom forms  $\text{H}_2\text{O}$  with H atom first and the remainder forms  $\text{CO}_2$  with C atom. The remainder of C atom will exist in solid state if O atom does not satisfy full oxidation of C atom. The remainder of O atom will exist in  $\text{O}_2$  if O atom is superfluous. Table 1 presents the methods for calculating the parameters  $N$ ,  $M$ , and  $Q$  of  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$  explosives<sup>[23]</sup>.

Table 1 Methods for calculating the  $N$ ,  $M$ , and  $Q$  parameters of  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$  explosives

parameter	stoichiometric ratio		
	$c \geq 2a + b/2$	$2a + b/2 > c \geq b/2$	$b/2 > c$
$N$	$(b + 2c + 2d)/4M$	$(b + 2c + 2d)/4M$	$(b + d)/2M$
$M$	$4M/(b + 2c + 2d)$	$(56d + 88c - 8b)/(b + 2c + 2d)$	$(2b + 28d + 32c)/(b + d)$
$Q \times 10^{-3}$	$(28.9b + 94.05a + 0.239\Delta H_f^\circ)/M$	$[28.9b + 94.05(c/2 - b/4) + 0.239\Delta H_f^\circ]/M$	$(57.8c + 0.239\Delta H_f^\circ)/M$

Note:  $a$ ,  $b$ ,  $c$ , and  $d$  stand for the number of C, H, O, and N atoms in the explosive molecule, respectively;  $M$  in the formula is the molecular weight of explosive ( $\text{g} \cdot \text{mol}^{-1}$ );  $\Delta H_f^\circ$  is the standard heat of formation of the explosive (in  $\text{kJ} \cdot \text{mol}^{-1}$ ).

### 3 Results and discussion

#### 3.1 Optimized structures

At the outset, we have performed structure optimizations of compounds **1–7** in Scheme 3 at the B3LYP/6-31G\*\* level, and selected optimized bond lengths of nitro derivatives of symmetric pyrazino-dicycloreas are in Table 2, and corresponding dihedral angles are listed in Table 3. Investigations on the optimized geometries, variations (i. e. the differences between the maximum and minimum values) of the calculated results for the C—C, C—N, and N—N bond lengths and N—C—N, C—N—C, and C—N—N angles are much more different from all title compounds, indicating that these geometrical parameters are more sensitive to the environmental or molecular structures. The N(11)—N(15) bond length of compound **1** is 1.427 Å which can be used as a original bond length with an introduction of one nitro group. The N—NO<sub>2</sub> bond lengths of compounds **2**, **3**, and **4** are 1.443, 1.432, 1.436 Å, respectively. From the results, both N—C bonds (e. g. N(7)—C(2) of compound **2**) neighboring to the pyrazine ring possess significant double bond character by the lone nitrogen pair, which changes the charge distribution of the heterocyclic ring and leads to, in some cases, an increase in the aromaticity of the heterocyclic ring, thus stabilizing the ring system<sup>[15]</sup>.

However, it appears that two N—NO<sub>2</sub> bonds with bond lengths of 1.517, 1.512 Å break in compound **7** after a formation of pyrazine *N*-oxide, which attributes to the obvious steric hindrance effect. It shows that the high instability of cyclic dinitrourea in the pyrazine *N*-oxide structure. The dihedral angles of the pyrazine ring are almost zero and six atoms can be considered as nearly coplanar. With nitro groups introduced, N—NO<sub>2</sub> should rotate by some degrees from the pyrazine ring to avoid too large space steric effect. It is obvious that there are no intramolecular hydrogen bonds in cyclorea nitramine compounds of the pyrazine ring.

**Table 2** Selected bond lengths<sup>a</sup> of cyclourea nitramine compounds computed at B3LYP/6-31G\*\* level

compound 1	bond lengths/Å
N(11)—N(15)	1.427
N(13)—C(12)	1.390
N(9)—C(8)	1.401
N(7)—C(2)	1.377
compound 2	bond lengths/Å
N(11)—N(15)	1.443
N(13)—N(18)	1.443
N(9)—C(1)	1.38
N(11)—C(4)	1.408
compound 3	bond lengths/Å
N(13)—N(15)	1.432
N(9)—C(18)	1.432
N(13)—C(12)	1.450
N(9)—C(8)	1.450
compound 4	bond lengths/Å
N(9)—N(15)	1.436
N(11)—N(18)	1.436
N(9)—C(8)	1.443
N(11)—C(12)	1.443
compound 5	bond lengths/Å
N(11)—N(15)	1.451
N(7)—N(18)	1.441
N(13)—N(21)	1.457
N(7)—C(8)	1.446
compound 6	bond lengths/Å
N(7)—N(21)	1.456
N(9)—N(18)	1.456
N(11)—N(24)	1.456
N(13)—N(15)	1.456
compound 7	bond lengths/Å
N(9)—N(25)	1.397
N(11)—N(16)	1.461
N(13)—N(19)	1.517
N(7)—N(22)	1.512

### 3.2 Density

In the present study, single-point molecular volume calculations at B3LYP/6-31G\*\* level were performed based on geometry optimized structures. The densities ( $\rho$ ) of compounds **1–6** were calculated and listed in Table 4. It can be seen from Table 4 that the cyclourea nitramine compounds with different numbers or positions of nitro groups have different  $\rho$  values ranging from 1.84–2.03 g · cm<sup>-3</sup>. Compound **6** with four nitro groups has the largest density of 2.03 g · cm<sup>-3</sup> among all nitro derivatives of symmetric pyrido-dicycloureas, while compound **1** with one nitro group has the smallest one, revealing that the density increases as the number of the nitro group increases. There is not much difference in the density for the compounds with the same amount of nitro groups in different positions (comparing compound **2** with compounds **3** and **4**). Their detonation velocities increase with the increasing of density. Thus that compound **6** can be used as a novel po-

tential candidate for HEDC when it is successfully synthesized.

**Table 3** Dihedral angles of cyclourea nitramine compounds computed at B3LYP/6-31G\*\* level

compound 1	dihedral angle/(°)
C(4)—N(11)—C(12)—N(13)	-1.25
O(14)—C(12)—N(13)—C(15)	-177.24
H(18)—N(7)—C(2)—N(6)	-0.36
N(15)—N(11)—C(4)—N(3)	-18.16
compound 2	dihedral angle/(°)
O(16)—N(15)—N(11)—C(4)	165.78
N(13)—C(5)—N(6)—N(18)	8.37
N(15)—N(11)—C(4)—N(3)	-17.83
N(18)—N(13)—C(5)—N(6)	-17.72
compound 3	dihedral angle/(°)
N(15)—N(13)—C(5)—N(6)	-14.78
H(22)—N(11)—C(4)—N(3)	3.22
N(18)—N(9)—C(1)—N(3)	-14.76
C(2)—N(6)—N(7)—H(21)	-177.34
compound 4	dihedral angle/(°)
N(15)—N(9)—C(1)—N(3)	-18.71
H(21)—N(7)—C(2)—N(6)	2.82
C(4)—N(3)—N(11)—N(18)	164.45
H(22)—N(13)—C(5)—N(6)	2.81
N(15)—N(11)—C(4)—N(3)	23.29
N(21)—N(13)—C(5)—N(6)	-27.56
N(18)—N(7)—C(2)—N(6)	-14.18
H(24)—N(9)—C(1)—N(3)	1.51
compound 5	dihedral angle/(°)
N(6)—C(2)—N(7)—N(21)	-15.80
N(9)—N(18)—C(1)—N(3)	167.53
N(3)—C(4)—N(11)—N(24)	-15.64
N(13)—C(5)—N(6)—N(15)	7.45
compound 6	dihedral angle/(°)
N(13)—(C12)—(C5)—N(6)	22.16
N(11)—C(4)—N(3)—N(16)	11.01
N(3)—C(1)—N(9)—N(25)	-6.60
N(7)—C(2)—N(6)—C(8)	12.65

**Table 4** Predicted densities and detonation properties of cyclourea nitramine compounds

compound	OB <sub>100</sub> /%	V /cm <sup>3</sup> · mol <sup>-1</sup>	$\rho$ /g · cm <sup>-3</sup>	Q /J · g <sup>-1</sup>	D /km · s <sup>-1</sup>	p /GPa
<b>1</b>	-43.88	128.55	1.84	1389.71	8.13	29.75
<b>2</b>	-28.37	146.17	1.93	1405.68	8.55	33.78
<b>3</b>	-28.37	145.86	1.93	1401.31	8.56	33.87
<b>4</b>	-28.37	147.36	1.91	1403.56	8.50	33.22
<b>5</b>	-17.13	164.33	1.99	1418.60	8.86	36.89
<b>6</b>	-8.60	183.26	2.03	1434.85	9.08	39.22

### 3.3 Detonation performance

The detonation velocity ( $D$ ) and detonation pressure ( $p$ ) of compounds are computed by Kamlet-Jacobs empirical equations on the basis of their theoretical densities ( $\rho$ ) and calcu-

lated gas phase heats of formation. Table 4 shows the predicted detonation performances of nitro derivatives of symmetric pyrazino-dicycloreas.

It can be found that all nitro derivatives of symmetric pyrazino-dicycloreas have good detonation properties. Compound **6** has the highest  $D$  and  $p$  values among all cycloreas nitramine compounds. With the number of the nitro group increasing from one to four,  $\rho$ ,  $Q$ ,  $D$ , and  $p$  values of the corresponding compounds increase. The above predictions indicate that compound **6** is appearing to be a promising candidate comparable to RDX and HMX.

### 3.4 Heats of formation and oxygen balance

Heat of formation (HOF) reflects to the nature of substances and high positive HOF is usually required for an effective energetic material. The zero point energies ( $ZPE$ ), thermal correction to enthalpy ( $H_T$ ), electronic energies and HOF calculated at B3LYP/6-31G\*\* level for nitro derivatives of symmetric pyrazino-dicycloreas are listed in Table 5. The results show that all HOFs of cycloreas nitramine compounds vary from negative to positive values, revealing that the introduction of the nitro group is the main energy origin of this series. The HOFs of compounds increase when the number of the nitro group increases, which may be attributed to repulsion of the nitro groups. The greater the number of the nitro groups in the same ring (compare compound **2** with compounds **3** and **4**) is, and the better molecular symmetry (compare compound **4** with compound **2**) is, the greater the HOF is. the nitro group is an effective substituent for increasing HOF of the nitro derivatives of symmetric pyrazino-dicycloreas.

**Table 5** Calculated electronic energies ( $E_0$ ), zero-point energies ( $ZPE$ ), thermal correction to enthalpy ( $H_T$ ) and gas phase heats of formation (HOF)

compound	$E_0$ /a. u.	$ZPE$ /a. u.	$H_T$ /a. u.	HOF /kJ · mol <sup>-1</sup>
<b>1</b>	-914.529	0.12314	0.01396	-66.73
<b>2</b>	-1118.973	0.12419	0.01677	39.51
<b>3</b>	-1118.975	0.12422	0.01677	34.35
<b>4</b>	-1118.974	0.12425	0.01675	37.00
<b>5</b>	-1323.416	0.12522	0.01958	147.51
<b>6</b>	-1527.855	0.12586	0.02263	265.63

Oxygen balance ( $OB_{100}$ ) is another one of the most important criterion for selecting potential HEDC, and is a measure of how much oxygen is required for complete combustion of hydrogen to water and carbon to carbon dioxide. A positive or negative oxygen balance signifies that there is an excess of or a deficiency of oxygen in the complete combustion of compound. The oxygen balances are calculated using the formula (3), which can be used to rudely predict the impact sensitivities of the explosives<sup>[24]</sup>.

$$OB_{100} = 100(2n_O - n_H - 2n_C - 2n_{COO}) / M \quad (3)$$

Where  $n_O$ ,  $n_H$ , and  $n_C$  represent the numbers of O, H, and C atoms, respectively;  $n_{COO}$  is the number of  $COO^-$ , and here  $n_{COO} = 0$  for the nitro derivatives of symmetric pyrazino-di-

cycloreas;  $M$  is the molecular weight. It is found from Table 4 that all title compounds have a negative oxygen balance, and when the amount of nitro group increases, the oxygen balance is close to zero, proving that the nitro group is a good substituent for improving oxygen balance in designing potential HEDC.

### 3.5 Thermal stability

Energies (a. u.) of frontier molecular orbital and their gaps of the nitro derivatives of symmetric pyrido-dicycloreas at B3LYP/6-31G\*\* level are listed in Table 6. It can be seen from Table 6 that the  $\Delta E_{LUMO-HOMO}$  values are different from different positions of substituted groups, the  $\Delta E_{LUMO-HOMO}$  of compound **4** is the largest, while compound **2** is the smallest (except compound **7**), indicating that the former is more stable than the latter.

**Table 6** Energy of highest occupied molecular orbital (HOMO), energy of lowest unoccupied molecular orbital (LUMO) and energy gaps ( $\Delta E_{LUMO-HOMO}$ ) for cycloreas nitramine compounds containing pyridine ring

compound	$E_{HOMO}$	$E_{LUMO}$	$\Delta E_{LUMO-HOMO}$
<b>1</b>	-0.22858	-0.08607	0.14251
<b>2</b>	-0.26859	-0.13747	0.13112
<b>3</b>	-0.27220	-0.13487	0.13733
<b>4</b>	-0.27281	-0.12533	0.14748
<b>5</b>	-0.29757	-0.15588	0.14169
<b>6</b>	-0.31806	-0.17409	0.14397
<b>7</b>	-0.28219	-0.22661	0.05559

In nitro compounds, N—NO<sub>2</sub> bond is the weakest in the molecule and the rupture of this bond is the initial step in the decomposition or detonation. The property of N—NO<sub>2</sub> bond, *i. e.*, charge is used to show the relationship with the impact sensitivity of compounds, and may reflect the ability of —NO<sub>2</sub> attracting electrons<sup>[25-26]</sup>. In the present study, the charge on nitro group ( $Q_{NO_2}$ ) is considered for its correlation to impact sensitivity.

$$Q_{NO_2} = Q_N + Q_{O_1} + Q_{O_2} \quad (4)$$

The charge on nitro group ( $Q_{NO_2}$ ) is calculated by the sum of atomic charges on nitrogen ( $Q_N$ ) and oxygen ( $Q_{O_1}$  and  $Q_{O_2}$ ) atoms in nitro group via. Eq. 4. Computed  $Q_{NO_2}$  values of molecules are presented in Table 7. The higher the  $Q_{NO_2}$  is, the larger the impact insensitivity, and hence,  $Q_{NO_2}$  can be regarded as the criterion for estimating impact sensitivities. Compounds **2**, **3** and **4** are isomers having two nitro groups attached to the pyrazine ring. Based on  $Q_{NO_2}$  values in Table 7, the stability of compounds **2**, **3** and **4** decreases in the order of **4**>**3**>**2**. This shows that compound **4** is more insensitive than compounds **2** and **3**. This order is consistent with the order based on  $\Delta E_{LUMO-HOMO}$ . An increase in the number of nitro groups (from one to four in compounds **1**, **2**, **5** and **6**) increases the impact sensitivity (except compound **7**). The above investigations provide important theoretic information for molecular design of novel high energetic density nitramine explosives containing pyrazine ring.

**Table 7** Computed nitro group charge ( $-Q_{\text{NO}_2}$ ) of molecules 1–6

compound	1	2	3	4	5	6		
bond	N—NO <sub>2</sub>	N—NO <sub>2</sub>	N—NO <sub>2</sub>	N—NO <sub>2</sub>	N15—NO <sub>2</sub>	N18—NO <sub>2</sub>	N21—NO <sub>2</sub>	N—NO <sub>2</sub>
$Q_{\text{NO}_2}$	-0.309	-0.351	-0.348	-0.328	-0.371	-0.364	-0.353	-0.398

Note:  $Q_{\text{NO}_2}$  values in compounds 2, 3, 4, and 6 are the same, respectively.

## 4 Conclusions

From the DFT calculations performed in this work, the main conclusions to be drawn are as follows.

(1) The number, positions, surrounding and symmetry of the nitro group within the molecule and the symmetry of the molecular structure are some principal factors affecting the thermal stabilities and detonation properties of compounds 1–6.

(2) With increasing of the number of the nitro group on five-membered rings within molecule, the values of heat of formation of compounds 1–6 increase.

(3) The calculated N(13)—N(19) and N7—N(22) bond lengths in compound 7 are 1.517, 1.512 Å, respectively, which are the longest N—N bonds among all the N—N bonds in compounds 1–7, indicating that the two bonds will be broken first upon heating, so the structure of compound 7 is unstable.

(4) Using  $\Delta E_{\text{LUMO-HOMO}}$  and  $Q_{\text{NO}_2}$  as criterions, the stability of compounds 2, 3 and 4 decreases in the order of 4>3>2.

(5) The calculated theoretical molecular density, heat of formation, detonation velocity and detonation pressure of compound 6 are 2.03 g · cm<sup>-3</sup>, 265.63 kJ · mol<sup>-1</sup>, 9.08 km · s<sup>-1</sup> and 39.22 GPa, respectively, revealing compound 6 might be a promising candidate for HEDC.

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## 对称的吡嗪并环脲硝基衍生物结构和性能的量子化学研究

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**摘要:** 运用密度泛函理论 DFT-B3LYP/6-31G\*\* 方法得到了对称的吡嗪并环脲硝基衍生物的分子几何构型和电子结构。用量子化学方法计算了理论密度和生成热, 用 Kamlet-Jacobs 方程计算了爆速和爆压, 对这些硝基衍生物的结构-性能关系进行了研究。结果表明, 分子中硝基的数量、位置、环境和分子结构的对称性是影响对称吡嗪并环脲硝基衍生物热稳定性和爆轰性能的一些主要因素。1,3,5,7-四硝基-5,7-二氢二咪唑 [4,5-*b*:4',5'-*e*] 吡嗪-2,6 (1*H*,3*H*)-二酮的理论密度为  $2.03 \text{ g} \cdot \text{cm}^{-3}$ , 生成热为  $265.63 \text{ kJ} \cdot \text{mol}^{-1}$ , 爆速为  $9.08 \text{ km} \cdot \text{s}^{-1}$ , 爆压为 39.22 GPa。1,3,5,7-四硝基-2,6-二氧杂-1,2,3,5,6,7-六氢二咪唑 [4,5-*b*:4',5'-*e*] 吡嗪-4-氧化物的结构是不稳定的。这些计算结果为新型高能量密度材料的设计和合成提供了基础研究数据。

**关键词:** 量子化学; 爆轰性能; 环脲硝胺; 吡嗪环

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