

## Theoretical Studies on High Energetic Density Polynitroimidazopyridines

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Teoria do funcional da densidade (DFT) foi empregada no estudo de poli-nitroimidazopyridinas em nível B3LYP/6-31+G(d). A velocidade ( $D$ ) e a pressão de detonação ( $P$ ) foram avaliadas utilizando as equações Kamlet-Jacobs (K-J) baseadas na densidade molecular teórica ( $\rho$ ) e calor de formação (HOF). A estabilidade térmica dos compostos foi investigada através dos cálculos das energias de dissociação das ligações (BDE) em nível B3LYP/6-31+G(d) irrestrito. Alguns compostos apresentam altas densidades (ca.  $1.95 \text{ g cm}^{-3}$ ) e bons desempenhos. Os resultados das simulações revelam que duas das moléculas atuam similarmente ao 1,3,5,7-tetranitro-1,3,5,7-tetrazocano (HMX), e outras duas moléculas podem ser potenciais candidatas a compostos de alta densidade de energia (HEDCs). Estes resultados fornecem informações básicas para o planejamento molecular de novos compostos de alta densidade energética.

Density functional theory (DFT) was employed to study polynitroimidazopyridines at the B3LYP/6-31+G(d) level. Detonation velocity ( $D$ ) and detonation pressure ( $P$ ) were evaluated using Kamlet-Jacobs (K-J) equations based on the theoretical molecular density ( $\rho$ ) and heat of formation (HOF). Thermal stability of the title compounds was investigated by calculating the bond dissociation energies (BDE) at the unrestricted B3LYP/6-31+G(d) level. Some compounds have high densities (ca.  $1.95 \text{ g cm}^{-3}$ ) and good performance. Simulation results reveal that two molecules perform similarly to 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), and other two molecules may be potential candidates of high energy density compounds (HEDCs). These results provide basic information for molecular design of novel high energetic density compounds.

**Keywords:** density functional theory, polynitroimidazopyridines, heat of formation, detonation property, thermal stability

### Introduction

Energetic materials are more and more widely applied due to their high energy density.<sup>1-4</sup> In order to meet the requirements of future military and space applications, continuous efforts have been made to develop new materials having good thermal stability, impact and shock insensitivity, better performance, economic and environmentally friendly syntheses.<sup>5-7</sup> These properties are essential to improve personnel safety and to reduce warhead vulnerability problems. But these requirements are somewhat reciprocally exclusive, with improved insensitivity bringing inferior performance and *vice versa*. Therefore, the need for more energetic compounds with better stability and lower sensitivity is one of the main goals of energetic material research.<sup>8,9</sup>

Nitramine compounds, an important class of organic explosives, have received much attention as an energetic material due to an advantageous combination of density, heat of formation and oxygen balance. Nitramine compounds are well known by their high positive heat of formation as well as good thermal stability.<sup>10,11</sup> These properties reveal a high performance of these energetic materials. The most prominent members of this class are 1,3,5-trinitro-1,3,5-triazinane (RDX)<sup>12-15</sup> and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX).<sup>16-19</sup> CL-20 [2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (HNIW)] is another new nitramine explosive, which has six N-NO<sub>2</sub> groups in its polycyclic structure, resulting in an increase in both density and detonation properties.<sup>20-25</sup> CL-20 is reported as an attractive high thermally stable explosive with a decomposition temperature at 228 °C. It can offer high velocity of detonation ( $9.38 \text{ km s}^{-1}$ ) and heat of formation ( $410 \text{ kJ mol}^{-1}$ ).<sup>26</sup>

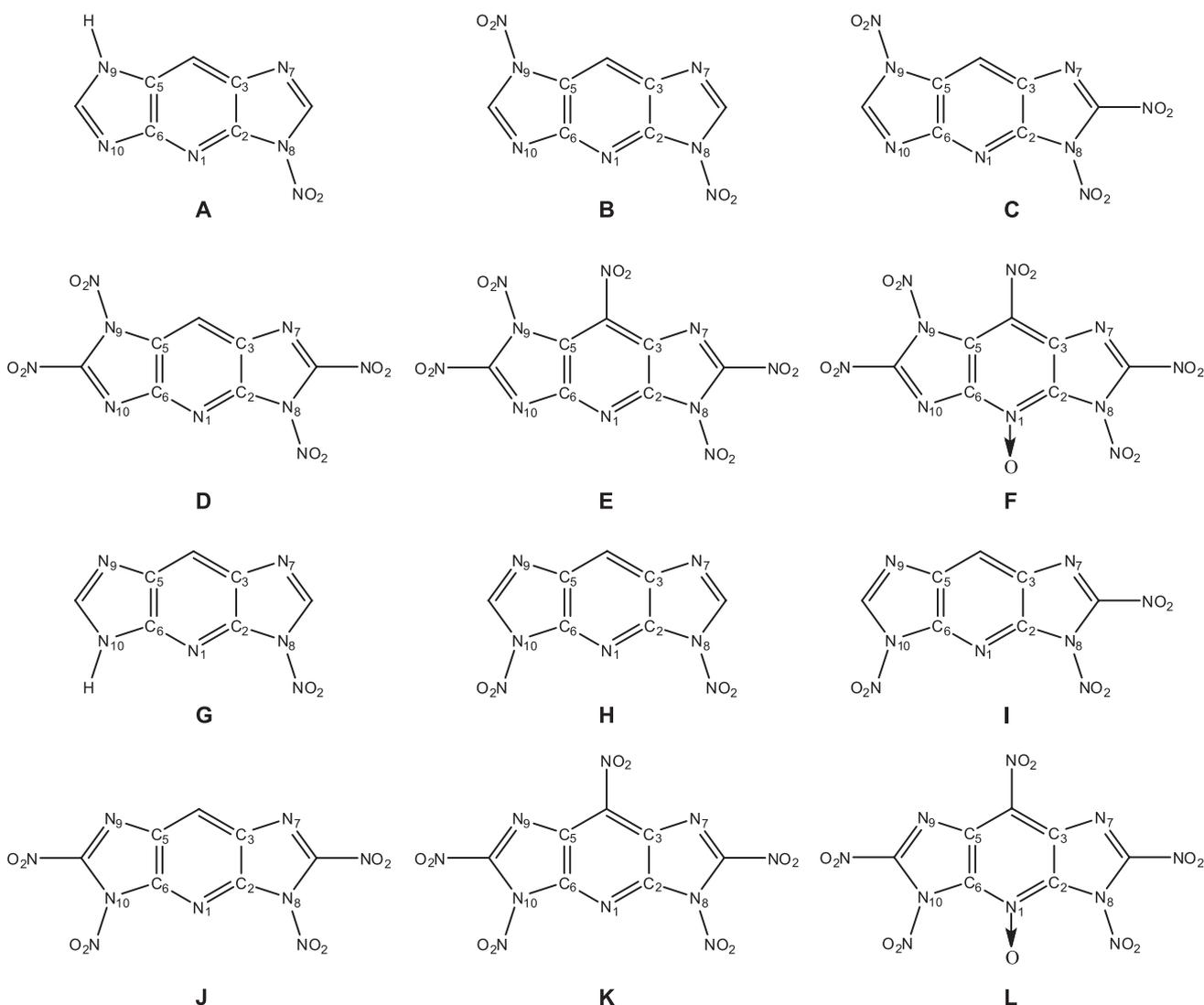
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Compared to carbocyclic analogues, the derivatives of pyridine have higher nitrogen contents and higher densities (e.g., the density of benzene is only  $0.897 \text{ g cm}^{-3}$ , but that of pyridine is  $0.982 \text{ g cm}^{-3}$ ). The presence of pyridine in a molecule is supposed to increase its detonation velocity and pressure. The high energy of nitramine explosives is combined with the insensitive property of explosives containing pyridine, and the concept of new nitramine explosives containing pyridine is proposed, into which nitramine groups with N–N bonds are introduced as much as possible. Introducing a nitramine group (N–NO<sub>2</sub>) into the pyridine derivative can further improve the detonation performance.

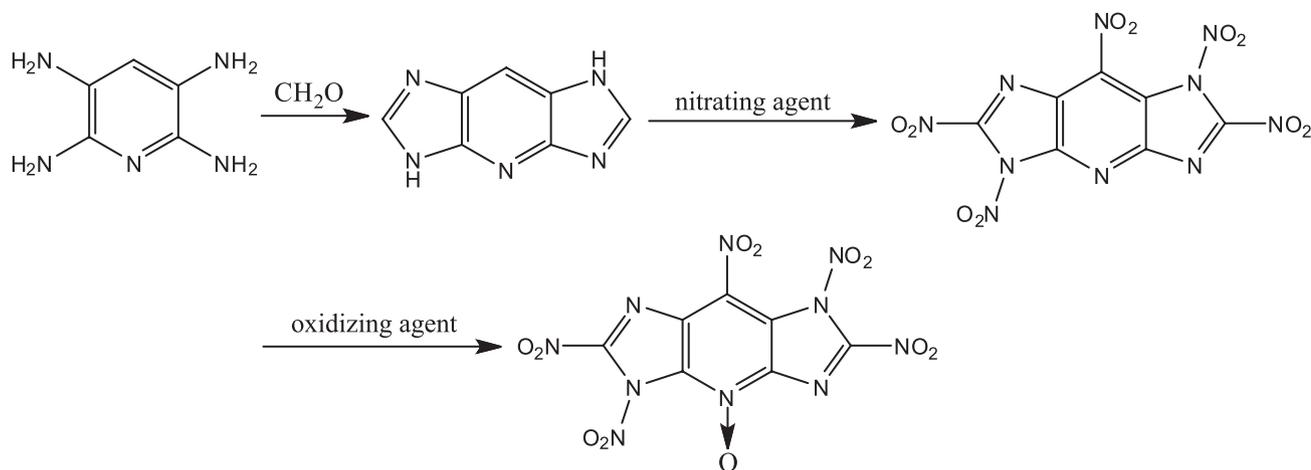
This study was motivated by, and based on, the concept of new nitramine explosives containing pyridine. Reacting with formaldehyde, pyridine-2,3,5,6-tetraamine yields a precursor with two imidazole rings, providing more N–H and C–H sites for introducing nitro substituents, and thus generating

a series of polynitroimidazopyridines (Scheme 1). The energy of polynitroimidazopyridines is derived from the combustion of the carbon backbone, the ring strain and the large number of inherently energetic C–N, C=N and N–N bonds. This shows that polynitroimidazopyridines could ideally store a large amount of energy. On the other hand, the nitrogen content typically leads to high densities and thereby to good performance. Molecular structures with nitro groups at various positions in the basic skeleton considered are shown in Figure 1.

Predicting the detonation performance and thermochemical properties of these energetic materials based on a particular molecular structure, with or without using experimental measurements, has been a prime requirement in the field of explosive research and development.<sup>27–30</sup> In this work, the full geometrical optimizations of nitramine compounds containing a benzene ring at the DFT-B3LYP/6-31+G(d) level were performed. The structure-property studies were performed



**Figure 1.** Structures and atom numbering of polynitroimidazopyridines.



**Scheme 1.** Predicted synthetic route for polynitroimidazopyridines.

to find out potential candidates for high energy density compounds (HEDCs).<sup>4</sup> The B3LYP/6-31G(d) method of density functional theory was used to study the thermodynamic properties and detonation properties of cage-HMX.<sup>31</sup>

To date, information on the relationships between structure and property of polynitroimidazopyridines was very sparse, there was no systematic survey covering these compounds. In the present study, the molecular geometries and electronic structure were obtained with density functional theory (DFT) method. Based on optimized geometries, the molecular volume ( $V$ ) and theoretical density ( $\rho$ ) were calculated using Monte-Carlo method. The most important detonation properties, such as detonation velocity ( $D$ ) and detonation pressure ( $P$ ), were estimated by using the Kamlet-Jacobs (K-J) equations. Through calculations of bond dissociation energies (BDE), the thermal stability was studied. These results provide theoretical support for the molecular design of novel high energetic density compounds.

## Methodology

Computations were performed with Gaussian 03 package at B3LYP<sup>32-34</sup> method with 6-31+G(d) basis set.<sup>35</sup> The geometric parameters were allowed to be optimized, and no constraints were imposed on molecular structure during optimization process. Vibrational frequencies were calculated for the optimized structures to enable the natural characterization of stationary points, zero-point energy (ZPE) and thermal correction ( $H_T$ ). All of optimized structures were characterized to be true local energy minima on potential energy surfaces without imaginary frequencies.

Detonation velocity and detonation pressure are the most important parameters to evaluate detonation characteristics of energetic materials. For the explosives

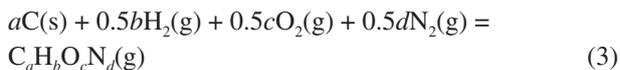
with CHNO elements, the Kamlet-Jacobs empirical equations were used to determine the parameters.<sup>36</sup>

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

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

where  $P$  is the detonation pressure in GPa,  $D$  is the detonation velocity in  $\text{km s}^{-1}$ ,  $N$  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 explosion in J per gram of explosive and  $\rho$  is the crystal density in  $\text{g cm}^{-3}$ .  $N$ ,  $M$  and  $Q$  are decided according to the largest exothermic principle,<sup>37</sup> i.e., for the explosives with CHNO elements, all N atoms convert into  $\text{N}_2$ , the O atoms form  $\text{H}_2\text{O}$  with H atoms first and the remainder forms  $\text{CO}_2$  with C atoms. The remaining C atoms will exist in the solid state if the O atoms do not satisfy full oxidation of C atoms. The remaining O atoms will exist in  $\text{O}_2$  if O atoms are in excess.

The chemical energy of the detonation reaction  $Q$  was calculated as the difference between the heats of formation (HOFs) of products and reactants. In this work, HOFs were calculated using density functional method with the help of the following equations:



The HOF of  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$  in gas phase ( $\Delta H_f(\text{g})$ ) is readily obtained from equation 3 with the experimental HOFs of C(s),  $\text{H}_2(\text{g})$ ,  $\text{O}_2(\text{g})$  and  $\text{N}_2(\text{g})$ , and the calculated enthalpies of all species.

A statistical average method was worked out to predict crystalline densities of energetic materials containing C, H, N and O elements. This method is found to be efficient and

convenient.<sup>38-41</sup> The densities of nitramine compounds need the datum of molecular volumes. The molecular volume  $V$  was defined as inside a contour of 0.001 electrons Bohr<sup>-3</sup> density that was evaluated using Monte-Carlo integration. The theoretical molecular density  $\rho_{\text{theor}}$  ( $\rho_{\text{theor}} = M/V$ , where  $M$  is the molecular weight) is very close to the experimental crystal density  $\rho_{\text{cry}}$ .

To measure the strength of bonds and relative stabilities of polynitroimidazopyridines, the bond dissociation energies of various bonds in molecules are calculated. BDE is the required energy in homolysis of a bond and is commonly denoted by the difference between total energies of the product and reactant after zero-point energy correction. The expressions for the homolysis of the A-B bond (equation 4) and for calculating its BDE equation 5 are shown as follows:<sup>42</sup>



$$\text{BDE(A-B)}_{\text{ZPE}} = E(\text{A}^{\bullet})_{\text{ZPE}} + E(\text{B}^{\bullet})_{\text{ZPE}} - E(\text{A-B})_{\text{ZPE}} \quad (5)$$

where A-B stands for neutral molecules and A<sup>•</sup> and B<sup>•</sup> for the corresponding product radicals after bond dissociation; BDE(A-B) is the BDE of bond A-B;  $E(\text{A-B})_{\text{ZPE}}$ ,  $E(\text{A}^{\bullet})_{\text{ZPE}}$  and  $E(\text{B}^{\bullet})_{\text{ZPE}}$  are zero-point energy corrected total energies of the parent compound and corresponding radicals, respectively.

## Results and Discussion

### Optimized structures

Optimized bond lengths of polynitroimidazopyridines are tabulated in Table 1. The pyridine rings in polynitro-

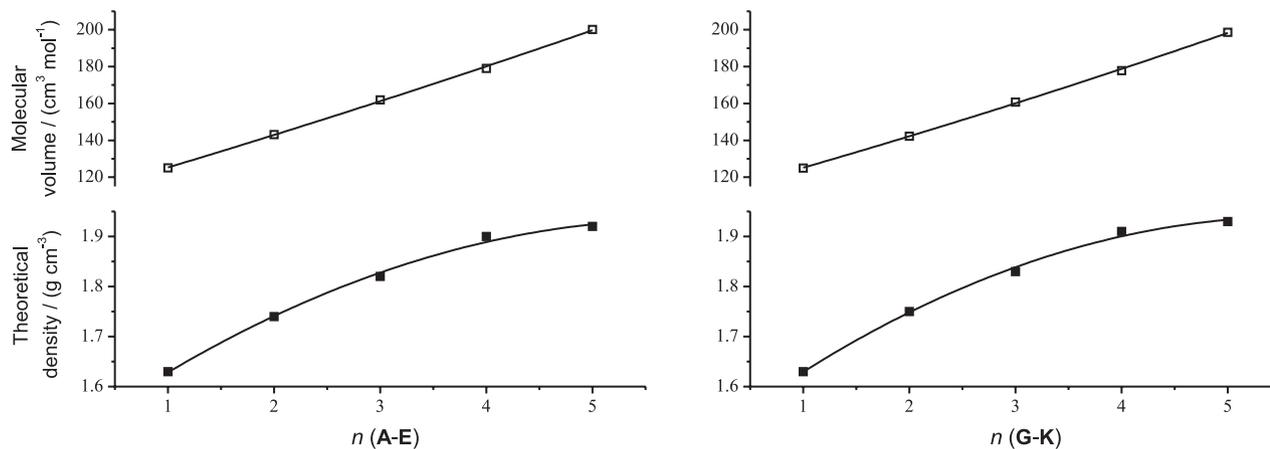
imidazopyridines are basically planar. The imidazole rings are basically planar too but are more distorted than the pyridine rings. The longest C–N bond is calculated to be the C2–N8 bond of molecule **A**, which is 1.414 Å, while the shortest is the C6–N10 bond of molecule **F**, which is 1.358 Å. Thus, all the C1–N7, C3–N8, C4–N10 and C6–N9 bonds are much shorter than a normal C–N single bond (1.49 Å), confirming that these bonds have some character of double or conjugated bonds. The bond lengths of N(8)–NO<sub>2</sub> are in the range of 1.143–1.595 Å and change with the introduction of NO<sub>2</sub> groups in the pyridine ring in the order of **A** < **B** < **C** < **D** < **E** < **F**, which is attributed to the large steric hindrance effect of –NO<sub>2</sub>. The same results are obtained for molecules **G** < **H** < **I** < **J** < **K** < **L**. The corresponding bond lengths of molecules **E** and **F** are close to each other. Some discrepancies are obviously raised by the formation of N→O coordination bond. The lengths of all N–NO<sub>2</sub> bonds in polynitroimidazopyridines are longer than the usual N–N bond lengths (1.35–1.40 Å) in nitramines.<sup>43</sup> The N–NO<sub>2</sub> bonds of molecules **E** and **K** are shorter than those of molecules **F** and **L**, respectively. Obviously, this change is caused by the introduction of the O coordination atom.

### Density

In the present study, single-point molecular volume calculations at B3LYP/6-31+G(d) were performed based on optimized geometries. The densities provide some clue about the explosive character of these molecules. The relationship between  $V$ ,  $\rho$  and the number of nitro groups ( $n$ ) can be expressed as shown in Figure 2. The largest value and the smallest one are 1.95 and 1.63 g cm<sup>-3</sup>, respectively. From **A** to **E**, it is clear that an increase in density is observed

**Table 1.** Selected bond lengths (Å) of polynitroimidazopyridines computed at B3LYP/6-31+G(d) level

		Bond length / Å											
		<b>A</b>		<b>B</b>		<b>C</b>		<b>D</b>		<b>E</b>		<b>F</b>	
N1–C2	1.317	N1–C2	1.320	N1–C2	1.319	N1–C2	1.319	N1–C2	1.318	N1–C2	1.361		
C3–N7	1.395	C3–N7	1.393	C3–N7	1.385	C3–N7	1.385	C3–N7	1.380	C3–N7	1.377		
C2–N8	1.414	C2–N8	1.409	C2–N8	1.404	C2–N8	1.402	C2–N8	1.399	C2–N8	1.372		
C5–N9	1.382	C5–N9	1.400	C5–N9	1.399	C5–N9	1.406	C5–N9	1.400	C5–N9	1.388		
C6–N10	1.382	C6–N10	1.394	C6–N10	1.391	C6–N10	1.391	C6–N10	1.390	C6–N10	1.358		
		Bond length / Å											
		<b>G</b>		<b>H</b>		<b>I</b>		<b>J</b>		<b>K</b>		<b>L</b>	
N1–C2	1.324	N1–C2	1.325	N1–C2	1.324	N1–C2	1.324	N1–C2	1.323	N1–C2	1.359		
C3–N7	1.398	C3–N7	1.395	C3–N7	1.387	C3–N7	1.388	C3–N7	1.383	C3–N7	1.383		
C2–N8	1.409	C2–N8	1.406	C2–N8	1.402	C2–N8	1.398	C2–N8	1.396	C2–N8	1.370		
C5–N9	1.388	C5–N9	1.395	C5–N9	1.395	C5–N9	1.388	C5–N9	1.383	C5–N9	1.383		
C6–N10	1.378	C6–N10	1.406	C6–N10	1.401	C6–N10	1.398	C6–N10	1.396	C6–N10	1.370		



**Figure 2.** Correlations between molecular volume ( $V$ ), theoretical density ( $\rho$ ) and the number of nitro groups ( $n$ ) for polynitroimidazopyridines

with an increase in the number of nitro groups. The same results were obtained for molecules **G**, **H**, **I**, **J** and **K**. The introduction of a nitro group increases the density of molecules and therefore has a significant contribution to the detonation velocity and detonation pressure. Molecules **D**, **E**, **F**, **J**, **K** and **L** have a density of above  $1.90 \text{ g cm}^{-3}$  when it is successfully synthesized.  $\rho$  is the essential factor in determining the detonation properties of energetic compounds.<sup>26</sup> According to Kamlet-Jacobs semi-empirical equations,  $D$  increases with increasing  $\rho$  for most energetic compounds. Also,  $P$  varies with the square of  $\rho$ , when  $\rho$  is greater than one.

#### Heat of formation

Heat of formation reflects the energy content of a compound. High positive HOF is usually required for an effective energetic material. The zero-point energies (ZPE), thermal correction to enthalpy and electronic energies calculated at the B3LYP/6-31+G(d) level for polynitroimidazopyridines are listed in Table 2. It is evident from the data listed in Table 2 that all HOFs of the title compounds are quite large positive values. HOFs of RDX and HMX computed at the B3LYP/6-31+G(d) level are  $216.76$  and  $251.67 \text{ kJ mol}^{-1}$ , respectively. For molecules **A** and **B**, **G** and **H**, each nitro group addition will increase HOF by  $318.68$  and  $340.28 \text{ kJ mol}^{-1}$ , respectively. But for molecules **B** and **C**, **H** and **I**, each nitro group addition will increase HOF by  $296.52$  and  $296.18 \text{ kJ mol}^{-1}$ , respectively. It indicates that the value of HOF relates to the nature of C-NO<sub>2</sub> and N-NO<sub>2</sub>. The space orientations of nitro groups also affect HOFs of the title compounds. For the isomers with the same number of -NO<sub>2</sub> groups, the values of HOF are slightly different, indicating that HOF is a little influenced by the position of -NO<sub>2</sub> group. As a whole, according to the number and

the relative position of the nitro groups, the relative HOF order of molecules can be distinguished, which is useful for evaluating the relative thermal stability of nitramine compounds.

**Table 2.** Calculated electronic energies ( $E_0$ ), zero-point energies (ZPE), thermal correction to enthalpy ( $H_T$ ) and gas phase heats of formation (HOF)

Molecule	$E_0$ / a.u.	ZPE / a.u.	$H_T$ / a.u.	HOF / (kJ mol <sup>-1</sup> )
<b>A</b>	-747.887724	0.125526	0.011301	176.57
<b>B</b>	-952.358263	0.127119	0.013869	495.25
<b>C</b>	-1156.837087	0.128710	0.016665	791.77
<b>D</b>	-1361.312357	0.130218	0.019550	1097.63
<b>E</b>	-1565.788593	0.131711	0.021627	1400.95
<b>F</b>	-1640.932287	0.134883	0.023748	1499.34
<b>G</b>	-747.893184	0.125758	0.011235	162.64
<b>H</b>	-952.355340	0.126913	0.013973	502.92
<b>I</b>	-1156.834296	0.128478	0.016773	799.10
<b>J</b>	-1361.311599	0.129955	0.019621	1099.62
<b>K</b>	-1565.792730	0.131570	0.022712	1390.08
<b>L</b>	-1640.926784	0.134160	0.023152	1513.79

#### Detonation properties

The detonation velocity and detonation pressure of molecules are computed by Kamlet-Jacobs empirical equations on the basis of the theoretical densities and calculated gas phase heats of formation, which are the important parameters to evaluate explosion performance of energetic materials. Table 3 shows the predicted detonation properties of polynitroimidazopyridines. Because detonation pressure and detonation velocity are calculated by HOF of the gas state, not of the crystal,

**Table 3.** Predicted densities and detonation properties of polynitroimidazopyridines

Molecule	OB <sub>100</sub>	V / (cm <sup>3</sup> mol <sup>-1</sup> )	ρ / (g cm <sup>-3</sup> )	Q / (J g <sup>-1</sup> )	D / (km s <sup>-1</sup> )	P / GPa
A	-1.09	125.06	1.63	773.53	5.76	13.84
B	-0.74	143.10	1.74	1295.62	7.25	22.87
C	-0.49	161.96	1.82	1639.99	8.20	30.00
D	-0.31	178.99	1.90	1899.47	8.97	36.81
E	-0.17	200.15	1.92	2096.56	9.44	41.03
F	-0.12	205.48	1.95	2189.04	9.70	43.74
G	-1.09	125.00	1.63	757.21	5.73	13.71
H	-0.74	142.30	1.75	1303.05	7.29	23.20
I	-0.49	160.73	1.83	1645.95	8.25	30.52
J	-0.31	177.82	1.91	1900.88	9.02	37.31
K	-0.17	198.63	1.93	2089.79	9.48	41.59
L	-0.12	207.15	1.94	2197.68	9.66	43.12

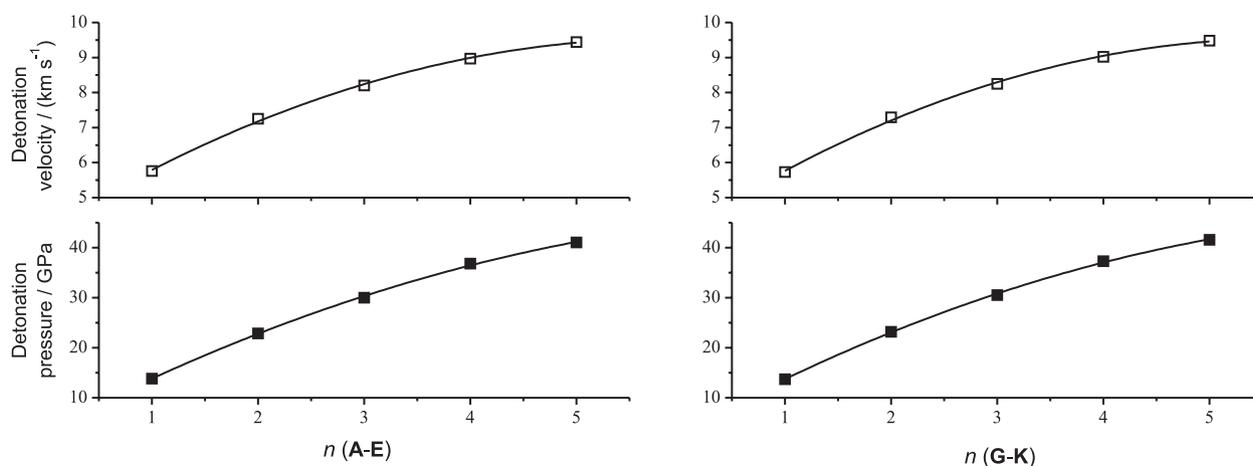
V: molecular volume; ρ: theoretical molecular density; Q: energy of explosion; D: detonation velocity; P: detonation pressure.

the calculated detonation properties of the nitramine compounds have some deviation,<sup>44</sup> but the results are still reliable and meaningful. It can be found from Table 3 that all polynitroimidazopyridines have good detonation properties ( $Q = 757.21\text{--}2197.68\text{ J g}^{-1}$ ,  $D = 5.73\text{--}9.70\text{ km s}^{-1}$ ,  $P = 13.71\text{--}43.74\text{ GPa}$ ). Meanwhile, with the number of nitro groups increasing from one to five,  $Q$ ,  $D$  and  $P$  of the corresponding compounds increase. Molecule **F** is calculated to have the highest  $D$  and  $P$  values among polynitroimidazopyridines. In terms of the predicted detonation parameters, the most powerful explosives among polynitroimidazopyridines are molecules **F** and **L**.

As for the isomers with the same oxygen balance (OB<sub>100</sub>), no conspicuous discrepancy of their respective  $Q$ ,  $D$  and  $P$  is found. As a whole,  $Q$ ,  $D$  and  $P$  increase with the increasing number of  $\text{-NO}_2$  groups. Figure 3 and Table 4 present the relationships between  $D$ ,  $P$  and  $n$ . This may show good group additivity on detonation properties and support the claim that

introducing more nitro substituents into a molecule usually helps to increase its detonation performance.<sup>37</sup>

Compared with the famous nitramine explosive RDX (1,3,5-trinitro-1,3,5-triazinane) ( $\rho = 1.82\text{ g cm}^{-3}$ ,  $D = 8.75\text{ km s}^{-1}$ ,  $P = 34.70\text{ GPa}$ ),<sup>45,46</sup> they have better detonation performance when the number of nitro groups is not less than 4, indicating that they are potential energetic compounds. Calculation results of detonation velocity and detonation pressure for nitramine compounds indicate that molecules **D**, **J**, **E**, **K**, **F** and **L** outperform RDX, molecules **D** and **J** perform similarly to HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) ( $\rho = 1.92\text{ g cm}^{-3}$ ,  $D = 8.96\text{ km s}^{-1}$ ,  $P = 35.96\text{ GPa}$ ).<sup>45,46</sup> According to the energy criterion for HEDC, i.e.,  $\rho \geq 1.90\text{ g cm}^{-3}$ ,  $D \geq 9.0\text{ km s}^{-1}$ , and  $P \geq 40.0\text{ GPa}$ , it is found in Table 3 that molecules **E**, **K**, **F** and **L** satisfy the requirements as novel high energy density compounds. Therefore, in the molecular design, detonation properties by changing the substituted group

**Figure 3.** Correlations between detonation velocity ( $D$ ) and detonation pressure ( $P$ ) and the number of nitro groups ( $n$ ) for polynitroimidazopyridines.

**Table 4.** Correlation equations between  $V$ ,  $\rho$ ,  $D$ ,  $P$  and the number of nitro groups ( $n$ ) for the title compounds

A-E		G-K	
$V = 108.23 + 16.72n + 0.32n^2$	$R^2 = 0.9988$	$V = 108.90 + 15.84n + 0.41n^2$	$R^2 = 0.9991$
$\rho = 1.49 + 0.15n - 0.01n^2$	$R^2 = 0.9928$	$\rho = 1.48 + 0.16n - 0.01n^2$	$R^2 = 0.9940$
$D = 4.09 + 1.86n - 0.16n^2$	$R^2 = 0.9979$	$D = 3.99 + 1.95n - 0.17n^2$	$R^2 = 0.9972$
$P = 3.44 + 11.09n - 0.71n^2$	$R^2 = 0.9989$	$P = 2.83 + 11.68n - 0.78n^2$	$R^2 = 0.9992$

$V$ : molecular volume ( $\text{cm}^3 \text{mol}^{-1}$ );  $\rho$ : theoretical molecular density ( $\text{g cm}^{-3}$ );  $D$ : detonation velocity ( $\text{km s}^{-1}$ );  $P$ : detonation pressure (GPa);  $R^2$ : correlation coefficient.

could be adjusted. Therefore, the above prediction indicates that polynitroimidazopyridines appear to be promising candidates comparable to nitramine explosives RDX and HMX.

#### Thermal stability

The relationship between the impact sensitivity and electronic structures of polynitroimidazopyridines can be established by the charge analysis of the nitro group.<sup>47</sup> Nitro compounds are very strong electron acceptors and have a strong ability to attract electrons. Such ability can be represented by the net charges of the nitro group. The lower the negative charge on the nitro group, the lower the electron attraction ability, and therefore, the more stable the nitro compound. In the present study, the charge on the nitro group ( $-Q_{\text{NO}_2}$ ) is considered for its correlation to impact sensitivity:

$$Q_{\text{NO}_2} = Q_{\text{N}} + Q_{\text{O}_1} + Q_{\text{O}_2} \quad (6)$$

The charge on the nitro group ( $-Q_{\text{NO}_2}$ ) is calculated by the sum of atomic charges on the nitrogen ( $Q_{\text{N}}$ ) and oxygen ( $Q_{\text{O}_1}$  and  $Q_{\text{O}_2}$ ) atoms of the nitro group.  $-Q_{\text{NO}_2}$  can be regarded as the criterion for estimating the impact sensitivities. Based on the highest  $-Q_{\text{NO}_2}$  value, the probable decreasing order is as follows: molecule **L** (0.245) > molecule **F** (0.234) > molecule **E** (0.136) > molecule **K** (0.118). This shows that molecule **L** is more sensitive than the other molecules.

Studies of BDE provide useful information for understanding the stability of polynitroimidazopyridines.

The stability of compounds is affected by bond dissociation energies, so the weakest bonds (N–N bonds that are out of ring) were selected as the breaking bond based on the bond overlap populations to calculate BDE at B3LYP/6-31+G(d) level. The values of bond dissociation energies are listed in Table 5. The calculated  $\text{BDE}_{\text{ZPE}}$  values indicate the relative stability of energetic materials. Variations of  $\text{BDE}_{\text{ZPE}}$  for N–NO<sub>2</sub> are in the range of 4.31–132.73 kJ mol<sup>-1</sup>. The initial step should be via N–NO<sub>2</sub> cleavage in thermal decomposition. The  $\text{BDE}_{\text{ZPE}}$  value of molecule **B** (132.73 kJ mol<sup>-1</sup>) is the largest while molecule **L** is the smallest (4.31 kJ mol<sup>-1</sup>) indicating that the former is more stable than the latter. Compared with  $\text{BDE}_{\text{ZPE}}$  values of RDX (141.22 kJ mol<sup>-1</sup>) and HMX (146.61 kJ mol<sup>-1</sup>) computed at the B3LYP/6-31+G(d) level, polynitroimidazopyridines are less stable than RDX and HMX.

By analyzing the structures of these compounds, it is easy to find that nitramine compounds have symmetric structures. Therefore, molecules **B**, **D**, **H** and **J** have higher  $\text{BDE}_{\text{ZPE}}$  than molecules **A**, **C**, **G** and **I**, respectively. This indicates that a symmetric structure is very useful for improving thermal stability. The symmetry can delocalize the  $\pi$  electron cloud density of system, but the five-membered rings of these compounds have larger tension, leading to the  $\text{BDE}_{\text{ZPE}}$  decrease of polynitroimidazopyridines. Repulsion is an important role in the stability of the title compounds. Take molecule **L** as an example, the repulsion between the neighboring nitro group rotates the oxygen atoms from the molecular plane and makes the value of  $\text{BDE}_{\text{ZPE}}$  decrease. This shows that structures of these compounds have a great influence on the thermal stability.

**Table 5.** Bond dissociation energies (BDE) of the weakest bonds for polynitroimidazopyridines computed at the B3LYP/6-31+G(d) level

Compound	A	B	C	D	E	F
Bond	N8–NO <sub>2</sub>	N8–NO <sub>2</sub>	N9–NO <sub>2</sub>	N8–NO <sub>2</sub>	N9–NO <sub>2</sub>	N9–NO <sub>2</sub>
$\text{BDE}_{\text{ZPE}} / (\text{kJ mol}^{-1})$	125.22	132.73	86.27	90.19	76.05	16.22
Compound	G	H	I	J	K	L
Bond	N8–NO <sub>2</sub>	N8–NO <sub>2</sub>	N10–NO <sub>2</sub>	N10–NO <sub>2</sub>	N10–NO <sub>2</sub>	N10–NO <sub>2</sub>
$\text{BDE}_{\text{ZPE}} / (\text{kJ mol}^{-1})$	119.80	125.12	88.80	95.26	98.04	4.31

The calculations on bond dissociation energies suggest that the N–N bond is the trigger bond during the pyrolysis initiation process of polynitroimidazopyridines. Taking detonation properties and relative stability into account, molecules **E** and **K** were finally confirmed to be the best HEDCs for polynitroimidazopyridines. The above investigations provide important theoretic information for the molecular design of novel high energetic density polynitroimidazopyridines.

## Conclusions

The full geometrical optimizations of polynitroimidazopyridines were performed using density functional theory at the B3LYP/6-31+G(d) level, without any symmetry restriction. The detailed structure-property studies were performed on these molecules to achieve energetic performance for the first time. Stability correlations are established for the title compounds by analyzing bond dissociation energies. For the polynitroimidazopyridines, with the increase in the number of nitro groups, the volume, density, detonation velocity and detonation pressure increase. Calculation results of detonation velocity and detonation pressure for the compounds indicate that molecules **D**, **J**, **E**, **K**, **F** and **L** outperform RDX, and molecules **D** and **J** perform similarly to HMX. According to the calculated BDE, the N–NO<sub>2</sub> bond is the trigger bond during the thermolysis initiation process. Molecules **E** and **K** essentially satisfy the quantitative criteria of energetics and stability as HEDCs. These results provide theoretical support for the molecular design of novel high energetic density compounds and experimental synthesis.

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