

Comparative theoretical studies of energetic pyrazole-pyridine derivatives

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Abstract The pyrazole-pyridine derivatives were optimized to obtain their molecular geometries and electronic structures at the DFT-B3LYP/6-31G(d,p) and DFT-B3P86/6-31G(d,p) levels. Molecular mechanics (MM) calculations were performed for the title compounds. Heats of formation (HOFs) were predicted through designed isodesmic reactions. Detonation performance was evaluated by using the Kamlet-Jacobs equations based on the calculated densities and heats of formation. The thermal stability of the title compounds was investigated *via* the bond dissociation energies (BDEs). The simulation results reveal that the compound with one pyrazole ring that is fully nitro-substituted performs similarly to the famous explosive HMX, and the compound with two pyrazole rings that are fully nitro-substituted outperforms HMX. According to the quantitative standard of energetics and stability as high energy density materials (HEDMs), the compound with two pyrazole rings that are fully nitro-substituted essentially satisfies this requirement.

Keywords Bond dissociation energy · Density functional theory · Detonation properties · Heat of formation · Pyrazole-pyridine derivatives

Introduction

There is an ongoing need for powerful but insensitive high energy density materials [1–4]. For HEDMs, besides high detonation performance, sensitivity is a prerequisite requirement [5–7]. They should be safe, stable, and reliable enough to detonate under specific conditions. Among various types

of HEDMs, pyridine derivatives constitute a unique class of energetic materials and have received a substantial amount of interests due to their favorable insensitivity, good explosive performance, and environmental acceptability during the past two decades [8–10].

Pyridine is a six-membered heterocyclic compound. The derivatives of pyridine have higher nitrogen contents than the carbocyclic analogues, enabling these compounds to release more nitrogen gases and in turn higher energy in explosion. On the other hand, since a N atom contributes more to the density than a C atom, the presence of pyridine in molecule is supposed to improve its density and correspondingly increase the detonation velocity and pressure [11]. Therefore, energetic pyridine derivatives are promising candidates for HEDMs and have become a hot research area owing to their novel properties including high density, high positive heat of formation and high thermal stability [12–14].

As a pyridine based compound, 2,6-diamino-3,5-dinitropyridine-1-oxide (DADNPO), originally reported in 1993 [15] and investigated subsequently in the US [16], was synthesized in the late 1990s and found to have high insensitivity. 3,5-Dinitro-2,6-bis(picrylamino) pyridine (PYX) [17] was reported as an attractive thermally stable explosive with decomposition temperature 460 °C, which can offer higher velocity of detonation (7.50 km/s) and detonation pressure (30.8 GPa). Li *et al.* [18, 19] reported 3,5-diamino-2,4,6-trinitropyridine and its *N*-oxide were most possibly low-sensitive or insensitive explosives. The energies for 3,5-diamino-2,4,6-trinitropyridine and its *N*-oxide were about 15 % and 25 % larger than that of TATB, respectively. Therefore, efforts in the area are focussed on the target pyridine derivatives, which would have higher explosive power.

The insensitive property of explosives containing pyridine is combined with the high nitrogen contents of pyrazole, and the concept of new explosives containing pyrazole and pyridine is proposed, into which nitro group with C-N bonds are

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introduced as much as possible. Properties are often manipulated by making structural modifications. The optimization of molecules with high energy and density is the primary step for searching and synthesizing HEDMs. Owing to the difficulties in the synthesis of the molecules under consideration, computer tests become an effective way to design high energy density materials theoretically [20–23]. Theoretical studies not only make it possible to screen candidate compounds, but also provide understanding in terms of the relationships between molecular structure and property. Therefore, they can help to design better and more efficient laboratory tests.

In this work, the crystal structures of pyrazole-pyridine derivatives were obtained using molecular packing calculations. A systematic study on the HOFs, detonation properties, and thermal stability of pyrazole-pyridine derivatives by using the DFT method was reported. First, the HOFs of seven pyrazole-pyridine derivatives were calculated using different methods *via* designed isodesmic reactions, and the reliability of methods was compared. Then, the detonation velocities and pressures were predicted using the calculations of HOFs and molecular densities. Finally, the thermal stabilities were evaluated based on the bond dissociation energies. The seven pyrazole-pyridine derivatives are 2,3,5-trinitro-6-(1H-pyrazol-1-yl)pyridine (**A**), 2,3,5-trinitro-6-(4-nitro-1H-pyrazol-1-yl)pyridine (**B**), 2-(3,4-dinitro-1H-pyrazol-1-yl)-3,5,6-trinitropyridine (**C**), 2,3,5-trinitro-6-(3,4,5-trinitro-1H-pyrazol-1-yl)pyridine (**D**), 3,5-dinitro-2,6-bis(4-nitro-1H-pyrazol-1-yl)pyridine (**E**), 2,6-bis(3,4-dinitro-1H-pyrazol-1-yl)-3,5-dinitropyridine (**F**), 3,5-dinitro-2,6-bis(3,4,5-trinitro-

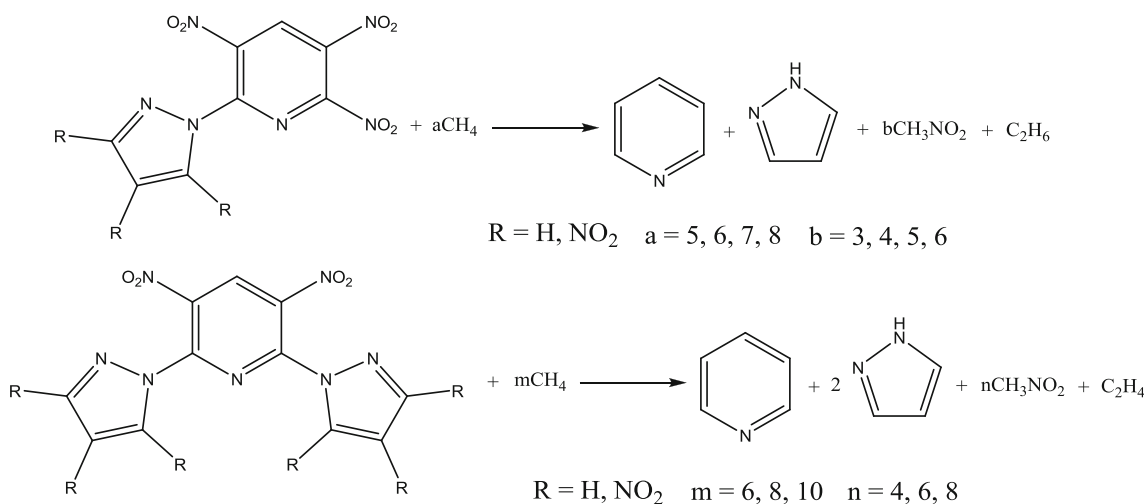
1H-pyrazol-1-yl)pyridine (**G**). The structures of seven title compounds are listed in Fig. 1.

Computational methods

Geometry optimization of the molecular structures was carried out with the Gaussian 03 package [24]. It is known that the DFT has emerged as a very reliable theoretical method [25, 26] and the DFT functional with appropriate basis set is able to reproduce experimental molecular geometry, electronic structure and heat of formation [27, 28]. The hybrid density functional used in this study are semi-empirical exchange-correlation functionals B3LYP [12, 29] and B3P86 [30–32] with the 6-31G(d,p) [33] basis set.

The optimized structures were characterized to the relative energy minimum of the potential surface by frequency calculation. Thermal corrections to the enthalpy at 298.15 K were also obtained from frequency calculation. The molecules that possess internal rotation and a thermodynamic degree of freedom have been treated in the default level as it is implemented in Gaussian 03 package.

The hybrid DFT-B3LYP and DFT-B3P86 methods with the 6-31G(d,p) basis set were adopted for the prediction of HOFs *via* designing isodesmic reactions. The method of isodesmic reactions has been employed very successfully to calculate HOF from total energies obtained from ab initio calculations [34–36]. The isodesmic reactions used to obtain the HOFs of pyrazole-pyridine derivatives at 298 K are as follows:



For the isodesmic reaction, the heat of reaction (ΔH_{298}) at 298 K can be calculated from the following equation:

$$\begin{aligned} \Delta H_{298} &= \sum \Delta H_{f,p} - \sum \Delta H_{f,r} \\ &= \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \end{aligned}$$

where $\Delta H_{f,p}$ and $\Delta H_{f,r}$ are the heats of formation of the reactants and the products at 298 K, respectively. ΔE_0 is the change in total energy between the products and the reactants at 0 K, ΔZPE is the difference between the zero-point energy (ZPE) of the products and the reactants, and ΔH_T is

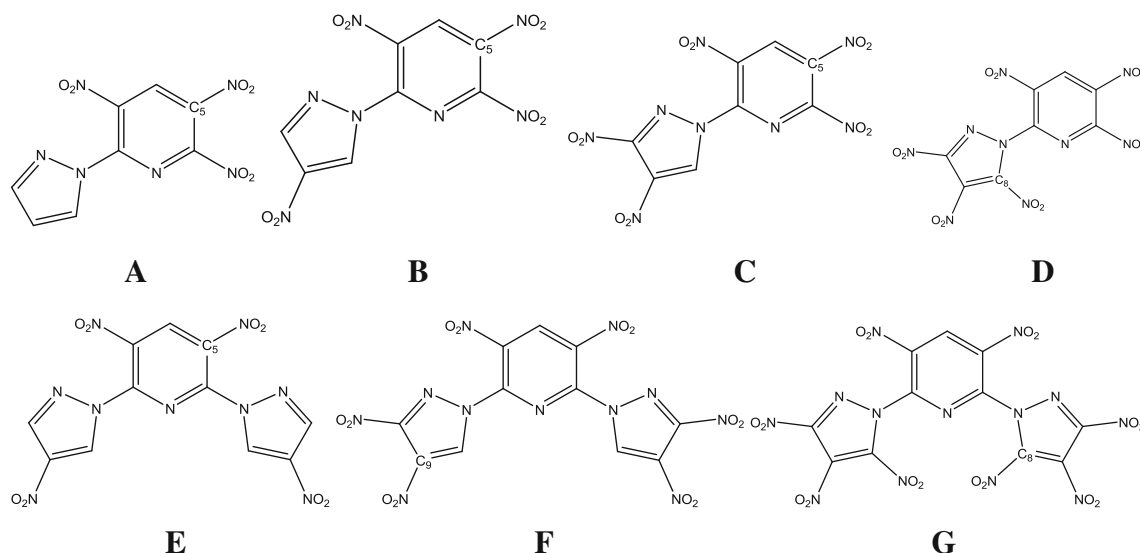


Fig. 1 Structures and atom numbering of pyrazole-pyridine derivatives

the thermal correction from 0 to 298 K. ΔnRT is the work term, which equals zero here.

Detonation velocity (D) and pressure (P), two important parameters reflecting the explosive performance of energetic materials, were estimated by empirical Kamlet-Jacobs formulas [37] as follows:

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

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

where P is detonation pressure in GPa, D is detonation velocity in $\text{km}\cdot\text{s}^{-1}$, N is the number 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 $\text{J}\cdot\text{g}^{-1}$ of explosive and ρ is the crystal density in $\text{g}\cdot\text{cm}^{-3}$. N , M and Q are determined according to the largest exothermic principle [38], *i.e.*, for the explosives with

CHNO elements, all the N atom converts into N_2 , the O atom forms H_2O with H atom first and the remainder forms 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 O_2 if O atom is superfluous.

The strength of bonding, which can be evaluated by the bond dissociation energy, is fundamental to understanding chemical processes [39]. BDE is the required energy in homolysis of a bond and is commonly denoted by difference between total energies of product and reactant after zero-point energy correction. The expressions for the homolysis of A—B bond (3) and for calculating its BDE (4) are shown as follows [40]:



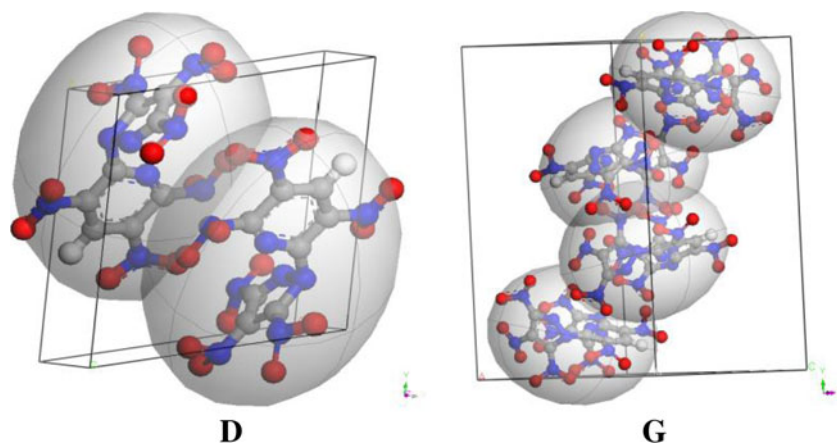
$$\text{BDE(A—B)}_{\text{ZPE}} = E(\text{A}\cdot)_{\text{ZPE}} + E(\text{B}\cdot)_{\text{ZPE}} - E(\text{A—B})_{\text{ZPE}} \quad (4)$$

where A—B stands for neutral molecules and $\text{A}\cdot$ and $\text{B}\cdot$ for the corresponding product radicals after bond dissociation;

Table 1 Molecular packings for pyrazole-pyridine derivatives obtained with the Compass force field

Compound	Z	space groups	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
A	8	<i>Pbca</i>	7.202	17.567	16.784	90.00	90.00	90.00
B	4	<i>P2₁2₁2₁</i>	27.008	4.683	9.126	90.00	90.00	90.00
C	4	<i>P2₁/C</i>	9.451	24.576	7.212	90.00	129.49	90.00
D	2	<i>P-1</i>	9.559	9.193	8.551	89.94	113.03	77.89
E	4	<i>P2₁/C</i>	4.724	26.778	11.910	90.00	108.23	90.00
F	2	<i>P2₁</i>	8.510	6.611	16.180	90.00	113.43	90.00
G	4	<i>P2₁/C</i>	19.642	20.470	10.517	90.00	153.22	90.00

Fig. 2 Crystal structures of molecules **D** and **G**



$BDE(A-B)$ is the BDE of bond $A-B$; $E(A-B)_{ZPE}$, $E(A\bullet)_{ZPE}$ and $E(B\bullet)_{ZPE}$ are zero-point energy corrected total energies of parent compound and corresponding radicals, respectively.

Because high energy density materials are usually in condensed phases, especially solid forms, we predicted the possible polymorphs and crystal structures of pyrazole-pyridine derivatives by rigorous molecular packing calculations using polymorph module of Materials Studio [41]. The Compass force field capable of predicting the condensed phase properties by searching the possible molecular packing among the most probable space groups.

Results and discussion

Crystal structure

In this study, the crystal structure has been predicted from the crystal packing calculations based on the molecular mechanics (MM) method. Compass force field [42] has been employed, which is based on the generation of possible packing arrangements in all reasonable space groups to search for the low-lying minima in the lattice energy surface. Since more than 80 % organic compounds crystallize in seven space groups ($P2_1/c$, $P-1$, $P2_12_12_1$, $Pbca$, $C2/c$,

$P2_1$ and $Pna2_1$) on the basis of statistical data [43, 44], the search of the possible crystal structure has been confined to these most typical groups only. The B3LYP/6-31G(d,p) optimized structures were taken as the input geometry for the polymorph search.

The lattice parameters of the pyrazole-pyridine derivatives are presented in Table 1. Some of the representative crystal structures are shown in Fig. 2. The results reveal that all the molecules fall under five space groups, viz., $P2_1$, $P-1$, $P2_1/C$, $Pbca$ and $P2_12_12_1$. Molecule **A** offers a crystal density of 1.75 g/cm^3 , and further the packing efficiency in the condensed phase increased by the introduction of $-\text{NO}_2$ to the basic skeleton. Molecules **D** and **G** have the crystal densities of 2.05 g/cm^3 and 1.99 g/cm^3 respectively, which may exhibit good detonation performance because density is the key factor affecting the detonation properties of high energetic density materials. We carefully compared the density of CL-20 predicted from the Compass force field ($2.173 \text{ g}\cdot\text{cm}^{-3}$) and from the volume inside an electron density contour of $0.001 \text{ e}\cdot\text{Bohr}^{-3}$ using Monte Carlo method ($2.040 \text{ g}\cdot\text{cm}^{-3}$) with the experimental value ($2.035 \text{ g}\cdot\text{cm}^{-3}$). For CL-20, the value predicted from the molecular structure is closer to the experimental one. Therefore, we believe the Monte Carlo method from the volume inside an electron density contour of $0.001 \text{ e}\cdot\text{Bohr}^{-3}$ for pyrazole-pyridine derivatives is more reliable.

Table 2 Calculated electronic energies (E_0), zero-point energies (ZPE) and experimental heats of formation (HOFs) of the reference compounds at the B3LYP and B3P86 levels with 6-31G(d,p) basis set

Compound		CH ₄	C ₂ H ₄	C ₂ H ₆	CH ₃ NO ₂	C ₃ H ₄ N ₂	C ₅ H ₅ N
B3LYP	E_0 (a.u.)	-40.47899	-78.54268	-79.76381	-244.96333	-226.13562	-248.20372
	ZPE (a.u.)	0.04503	0.05112	0.07492	0.05005	0.07140	0.08889
B3P86	E_0 (a.u.)	-40.66025	-78.82838	-80.09135	-245.53323	-226.78403	-248.95645
	ZPE (a.u.)	0.04513	0.05125	0.07512	0.05037	0.07191	0.08923
HOF (kJ mol ⁻¹) [40]		-74.78	52.25	-84.60	-74.65	118.29	140.49

Table 3 Calculated electronic energies (E_0), zero-point energies (ZPE), and heats of formation (HOFs) of the pyrazole-pyridine derivatives at the B3LYP/6-31G(d,p) and B3P86/6-31G(d,p) levels

Compound	B3LYP/6-31G(d,p)			B3P86/6-31G(d,p)		
	E_0 (a.u.)	ZPE (a.u.)	HOF (kJ mol ⁻¹)	E_0 (a.u.)	ZPE (a.u.)	HOF (kJ mol ⁻¹)
A	-1086.609025	0.146355	295.63	-1089.142142	0.147826	293.00
B	-1291.094924	0.148788	291.45	-1294.016598	0.150472	289.07
C	-1495.563734	0.150680	332.54	-1498.874121	0.152626	329.99
D	-1700.027511	0.152288	386.64	-1703.726498	0.154494	384.23
E	-1516.059997	0.200501	413.99	-1519.594520	0.202598	395.10
F	-1924.998104	0.204343	494.49	-1929.310029	0.206910	475.33
G	-2333.929104	0.207574	586.63	-2339.018542	0.210705	566.91

Heats of formation

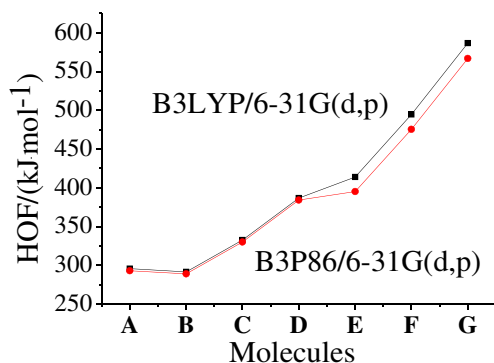
Heat of formation is usually taken as the indicator of the “energy content” of the HEDM. Therefore, it is very important to predict the heat of formation accurately. We design isodesmic reactions in which the numbers of all kinds of bonds remain invariable to decrease the calculation errors of HOF. Because the electronic circumstances of reactants and products are very similar in isodesmic reactions, the errors of electronic correction energies can be counteracted, and then the errors of the calculated HOF can be greatly reduced. In the designed reactions, the basic structural unit of the pyridine and pyrazole ring skeleton keeps invariable, and the big molecules are also changed into small ones.

The experimental heats of formation (HOFs) of the reference molecules CH₄, C₂H₄, C₂H₆, CH₃NO₂, C₃H₄N₂, C₅H₅N used in the isodesmic approach and the electronic energies (E_0), zero point energies (ZPE) calculated at the B3LYP and B3P86 levels with 6-31G(d,p) basis set are listed in Table 2. It is noted from Table 3 that the HOFs calculated by B3LYP/6-31G(d,p) and B3P86/6-31G(d,p) methods are similar and the HOFs calculated by B3P86/6-31G(d,p) method are slightly smaller than those by B3LYP/6-31G(d,p) method (Fig. 3). Table 3 also shows that the calculated heats of formation for pyrazole-pyridine derivatives are all endothermic which is desirable for high

energy density materials. In addition, from Table 3, the studied compounds can be divided into two categories, one is called monocyclopyrazole pyridine derivatives (molecules **A**, **B**, **C** and **D**) and the other is bicyclopiazole pyridine derivatives (molecules **E**, **F** and **G**).

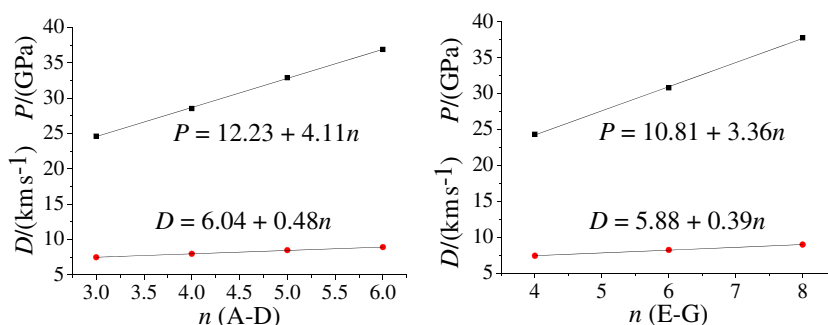
It is evident from the data listed in Table 3 that all HOFs of pyrazole-pyridine derivatives are quite large positive values, which shows that the introduction of nitro groups is the main energy origin of this series. For the monocyclopyrazole pyridine derivatives, molecule **C** has five nitro groups and its HOF is 332.54 kJ mol⁻¹ at B3LYP/6-31G(d,p) level. When another NO₂ group is attached to the molecule **C**, the HOF of molecule **D** increases and is equal to 386.64 kJ mol⁻¹. If the NO₂ group of molecule **D** at 6-position is replaced by trinitropyrazole, the HOF of molecule **G** dramatically increases and its value is 586.63 kJ mol⁻¹. From above analysis, we can conclude that the value of HOF relates to the number of the nitro groups and pyrazole groups, and increases with the augment of the number of the NO₂ group for the pyrazole-pyridine derivatives.

The HOFs of molecules **E**, **F** and **G** are 413.99, 494.49 and 586.63 kJ mol⁻¹ at B3LYP/6-31G(d,p) level, respectively. This shows that the value of HOF relates to the number of nitro groups and increases with the augment of the number of the NO₂ group for the substituted bicyclopiazole pyridine derivatives. That is because the pyrazole ring shows the strong positive inductive effect, which makes the density of electric

**Fig. 3** Influence of various methods on heats of formation**Table 4** Detonation properties of pyrazole-pyridine derivatives

Molecule	V (cm ³ mol ⁻¹)	ρ (g/cm ³)	Q (J/g)	D (km/s)	P (Gpa)
A	157.18	1.78	1336.98	7.47	24.64
B	177.37	1.83	1421.60	7.98	28.53
C	195.15	1.90	1514.87	8.48	32.89
D	212.60	1.95	1595.41	8.91	36.90
E	218.86	1.79	1284.10	7.42	24.32
F	256.61	1.87	1452.49	8.23	30.81
G	287.73	1.98	1572.67	8.97	37.75

Fig. 4 Correlations between D , P and the number of nitro group (n) for pyrazole-pyridine derivatives



cloud increase greatly and has effect on the properties of the substituted bicyclopiazole pyridine derivatives. Comparing the calculated HOFs by B3LYP/6-31G(d,p) and B3P86/6-31G(d,p) methods, one can obtain that the discrepancy of the two levels is very small, with deviations ranging from 2.38 to 19.72 kJ mol⁻¹. Further, the effects of the number and position of nitro groups on HOFs for the two levels are consistent with each other.

Detonation performance

Detonation velocity (D) and pressure (P) are the most important targets of scaling the detonation characteristics of energetic materials. Table 4 presents the calculated ρ , Q , D and P . For known explosives, the Q and ρ can be measured experimentally; thus the D and P can be calculated according to Eqs. (1) and (2). However, for some compounds, their Q and ρ can not be evaluated from experimental measures. Therefore, to estimate the D and P , we first need to calculate the Q and ρ .

For the pyrazole-pyridine derivatives, Q was evaluated by the HOF difference between products and explosives according to the principle of exothermic reactions. In the Kamlet-Jacobs equations, the products are supposed to be only CO₂, H₂O, and N₂, so released energy in the decomposition reaction reaches its maximum. The theoretical density was obtained from the molecular weight divided by the average molecular volume. The molecular volume V was defined as inside a contour of 0.001 electrons/bohr³ density that was evaluated using Monte-Carlo integration. The molecular volumes thus obtained were random digits with normal distribution. We therefore performed 100 single-point calculations

from optimized structure to get an average volume. The theoretical density of the molecule is slightly greater than practical loaded density. Therefore, according to the Kamlet-Jacobs equations, the D and P values can be regarded as their upper limits. The theoretical density and HOFs calculated by B3LYP/6-31G(d,p) level are used.

It can be found from Table 4 that all pyrazole-pyridine derivatives have good detonation properties ($Q=1284.10$ – 1595.41 J·g⁻¹, $D=7.42$ – 8.97 km·s⁻¹, $P=24.32$ – 37.75 GPa). Meanwhile, with the number of nitro groups increasing, D and P of the corresponding compounds increase. Molecule **G** is calculated to have the highest D and P values among pyrazole-pyridine derivatives. As a whole, D and P linearly increase with the increasing number of -NO₂ groups. Figure 4 presents the relationships between D , P and the number of nitro group (n), which all exist in linear relationships. 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 [38, 45]. The correlation equations are as following:

$$\begin{aligned} D(\text{A-D}) &= 6.04 + 0.48n & R^2 &= 0.9977 \\ P(\text{A-D}) &= 12.23 + 4.11n & R^2 &= 0.9993 \\ D(\text{E-G}) &= 5.88 + 0.39n & R^2 &= 0.9986 \\ P(\text{E-G}) &= 10.81 + 3.36n & R^2 &= 0.9993 \end{aligned}$$

Compared with the famous nitramine explosive RDX (1,3,5-trinitro-1,3,5-triazinane) ($\rho=1.82$ g/cm³, $D=8.75$ km/s, $P=34.70$ GPa) [46, 47], they have better detonation performance when the number of nitro groups is not less than 6, which indicates that they are potential energetic materials. Calculation results of detonation velocity and detonation

Table 5 Bond dissociation energies (BDEs, kJ mol⁻¹) for pyrazole-pyridine derivatives at B3LYP/6-31G(d,p) and B3P86/6-31G(d,p) levels

Compound	A	B	C	D	E	F	G
Bond	C5-NO ₂	C5-NO ₂	C5-NO ₂	C8-NO ₂	C5-NO ₂	C9-NO ₂	C8-NO ₂
B3LYP/6-31G(d,p) BDE _{ZPE} (kJ·mol ⁻¹)	241.36	235.90	232.61	246.74	228.78	267.71	241.34
B3P86/6-31G(d,p) BDE _{ZPE} (kJ·mol ⁻¹)	257.93	252.55	249.28	263.44	245.42	283.20	256.46

pressure for pyrazole-pyridine derivatives indicate that molecule **D** performs similarly to HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) ($\rho=1.92\text{ g/cm}^3$, $D=8.96\text{ km/s}$, $P=35.96\text{ GPa}$) [46, 47], molecule **G** outperforms HMX. Therefore, in the design of molecule, we could adjust detonation properties by changing the substituted group. The above prediction indicates that pyrazole-pyridine derivatives appear to be promising candidates comparable to the nitramine explosive RDX and HMX.

Thermal stability

As a high energetic explosive, the thermal stability of the title compounds should be emphasized. The bond dissociation energy could evaluate the strength of bonding that is fundamental to understanding chemical processes [48], and provide useful information for understanding the stability of the substituted pyrazole-pyridine derivatives. Studies on BDEs are important and essential to understand the stability and decomposition process of energetic materials. At present, people have reached a consensus that nitro groups often represent the primary cause of initiation reactivity of organic polynitro compounds [49, 50]. Therefore, we select the weakest bonds (C-NO₂ bonds) as the breaking bond based on the bond overlap populations to calculate BDE at the B3LYP and B3P86 levels with 6-31G(d,p) basis set.

The BDE calculated by B3P86 functional is about 16.26 kJ mol^{-1} larger than the result calculated by B3LYP functional. Considering the practical requirements and based on the results of these studies, a quantitative criteria associated stability (BDE of the trigger bond) requirements, *i.e.*, $\text{BDE}\approx 80\text{--}120\text{ kJ mol}^{-1}$ [51], is proposed and employed to filtrate and recommend potential HEDMs. The calculated BDE_{ZPE} values indicate relative stability of energetic materials. The initial step should be *via* C-NO₂ cleavage in thermal decomposition. The BDE_{ZPE} value of molecule **F** ($267.71\text{ kJ mol}^{-1}$) at the B3LYP/6-31G(d,p) level is the largest while the molecule **E** is the smallest ($228.78\text{ kJ mol}^{-1}$) at the B3LYP/6-31G(d,p) level which is less stable than the former (Table 5).

By analyzing the structures of the compounds, it is easy to find that molecules **E**, **F** and **G** have symmetric structures. The symmetry can delocalize π electron cloud density of system, which makes BDE_{ZPE} of molecules **E**, **F** and **G** increase. However, repulsion is also an important role in stability of the title compounds. Take molecule **G** as an example, the repulsion between neighboring nitro group rotate oxygen atoms from molecular plane and make the value of BDE_{ZPE} decrease. This shows that the structures of these compounds have a great influence on their thermal stability. The above investigations provide important theoretic information for molecular design of novel high energy density materials.

Conclusions

Based on the density function theory and molecular mechanics computations for the pyrazole-pyridine derivatives, the following conclusions can be drawn:

- (1) The crystal structures of pyrazole-pyridine derivatives fall under five space groups, *viz.*, $P2_1$, $P-1$, $P2_1/C$, $Pbca$ and $P2_12_12_1$ using molecular packing calculations.
- (2) All the title compounds possess large heats of formation. The HOFs relates to the number of nitro groups and increases with the augment of the number of -NO₂ group for the pyrazole-pyridine derivatives.
- (3) The detonation performance are calculated according to the HOFs calculated by B3LYP/6-31G(d,p) level and the values of D and P gradually increase when the number of -NO₂ group increases. Considering the detonation performance and thermal stability, molecules **D** and **G** are very promising candidates of HEDMs with lower sensitivity and higher performance.
- (4) An analysis of bond dissociation energies for several relatively weak bonds suggests that C-NO₂ bond is the weakest one and can happen in thermal decomposition. These results provide theoretical support for molecular design and experimental synthesis of HEDMs.

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References

1. Bushuyev OS, Brown P, Maiti A, Gee RH, Peterson GR, Weeks BL, Hope-Weeks LJ (2012) *J Am Chem Soc* 134:1422–1425
2. Gutsev GL, Weatherford CA, Johnson LE, Jena P (2012) *J Comput Chem* 33:416–424
3. Windler GK, Zhang MX, Zitterbart R, Pagoria PF, Vollhardt KPC (2012) *Chem Eur J* 18:6588–6603
4. Zhao GZ, Lu M (2012) *J Mol Model* 18:2443–2451
5. Liu H, Wang F, Wang GX, Gong XD (2012) *J Comput Chem* 33:1790–1796
6. Elbeih A, Jungova M, Zeman S, Vavra P, Akstein Z (2012) *Propellants Explos Pyrotech* 37:329–334
7. Bravo E, Martinez-Pinedo G (2012) *Phys Rev C* 85:055805
8. Liu H, Du HC, Wang GX, Liu Y, Gong XD (2012) *J Mol Model* 18:1325–1331
9. Li XH, Fu ZM, Zhang XZ (2012) *Struct Chem* 23:515–524
10. Scott AM, Petrova T, Odbadrakh K, Nicholson DM, Fuentes-Cabrera M, Lewis JP, Hill FC, Leszczynski J (2012) *J Mol Model* 18:3363–3378
11. Turker L, Atalar T (2006) *J Hazard Mater* 137:1333–1344
12. Rice BM, Pal SV, Hare J (1999) *Combust Flame* 118:445–458
13. Zeman S, Trzcinski WA, Matyas R (2008) *J Hazard Mater* 154:192–198
14. Chavez DE, Hiskey MA, Gilardi RD (2000) *Angew Chem Int* 39:1791–1793

15. Licht HH, Ritter H (1993) Neue explosivstoffe: Dinitropyridine. 24th Int. Annual Conference of ICT, Karlsruhe, Germany
16. Hollins RA, Merwen LH, Nissan RA, Wilson WS (1996) *J Heterocycl Chem* 33:895–904
17. Jadhav HS, Talwar MB, Dhavale DD, Asthana SN, Krishnamurthy VN (2006) *Ind J Heterocycl Chem* 15:383–386
18. Li JS, Huang YG, Dong HS, Yang GC (2003) *J Energ Mater* 11:177–181
19. Li JS, Huang YG, Dong HS (2004) *Chin J Energ Mater* 12:576–579
20. Zhao GZ, Lu M (2012) *Int J Quantum Chem* 112:2794–2800
21. Politzer P, Murray JS (2011) *Cent Eur J Energ Mater* 8:209–220
22. Politzer P, Martinez J, Murray JS, Concha MC, Toro-Labbe A (2009) *Mol Phys* 107:2095–2101
23. Sharia O, Kuklja MM (2011) *J Phys Chem C* 115:12677–12686
24. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA, Vreven T Jr, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, 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 JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PM, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2003) *Gaussian 03*. Gaussian Inc, Pittsburgh
25. Wei T, Zhu WH, Zhang J, Xiao HM (2010) *J Hazard Mater* 179:581–590
26. Fan XW, Ju XH, Xiao HM (2008) *J Hazard Mater* 156:342–347
27. Wei T, Zhu WH, Zhang XW, Li YF, Xiao HM (2009) *J Phys Chem A* 113:9404–9412
28. Wang GX, Gong XD, Liu Y, Xiao HM (2010) *Int J Quantum Chem* 110:1691–1701
29. Zhang GH, Zhao YF, Hao FY, Zhang PX, Song XD (2009) *Int J Quantum Chem* 109:226–235
30. Becke AD (1993) *J Chem Phys* 98:5648–5652
31. Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785–789
32. Perdew JP, Wang Y (1992) *Phys Rev B* 45:13244–13249
33. Becke AD (1992) *J Chem Phys* 97:9173–9177
34. Xiao HM, Chen ZX (2000) *The modern theory for tetrazole chemistry*. Science Press, Beijing
35. Hehre WJ, Radom L, Schleyer PVR, Pople JA (1986) *Ab initio molecular orbital theory*. Wiley, New York
36. Zhang XW, Zhu WH, Xiao HM (2010) *J Phys Chem A* 114:603–612
37. Kamlet MJ, Jacobs ST (1968) *J Chem Phys* 48:23–35
38. Zhang XH, Yun ZH (1989) *Explosive chemistry*. National Defence Industry Press, Beijing
39. Politzer P, Murray JS (1996) *J Mol Struct* 376:419–424
40. Lide DR (ed) (2002) *CRC Handbook of chemistry and physics*. CRC, Boca Raton
41. *Materials Studio 4.4*. (2008) Accelrys
42. Sun H (1998) *J Phys Chem B* 102:7338–7364
43. Wilson AJC (1988) *Acta Crystallogr A Found Crystallogr* 44:715–724
44. Mighell AD, Himes VL, Rodgers J (1983) *Acta Crystallogr A Found Crystallogr* 39:737–740
45. Klapotke TM, Piercey DG, Stierstorfer J (2011) *Chem Eur J* 17:13068–13077
46. Agrawal JP, Hodgson RD (2007) *Organic chemistry of explosives*. John , New York
47. Pagoria PF, Lee JS, Mitchell AR, Schmidt RD (2002) *Thermochim Acta* 384:187–204
48. Benson SW (1976) *Thermochemical kinetics*. Wiley, New York
49. Murray JS, Politzer P (1990) *Chemistry and physics of energetic materials*. Kluwer, Dordrecht
50. Murray JS, Concha MC, Politzer P (2009) *Mol Phys* 107:89–97
51. Chung G, Schmidt MW, Gordon MS (2000) *J Phys Chem A* 104:5647–5650