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## Theoretical Investigation of *N*-Aminopolynitrodiazoles

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**Abstract:** The density functional theory (DFT) calculation method was used to investigate electronic structures, energy gaps and sensitivities of *N*-aminopolynitrodiazoles at B3LYP/aug-cc-pVDZ level. The heat of formation (HOF) in the solid phase and the density were predicted by the Politzer model. Thermal stabilities were predicted by bond dissociation energies (BDEs), and all the compounds were with high BDEs in the range of 238.94 kJ · mol<sup>-1</sup> to 283.95 kJ · mol<sup>-1</sup>. Kamlet-Jacob equations were employed to predict the detonation performance of the title compounds. Results show that 1-amino-3,4,5-trinitropyrazole (8.99 km · s<sup>-1</sup>, 36.12 GPa) and 1-amino-2,4,5-trinitroimidazole (8.92 km · s<sup>-1</sup>, 35.56 GPa) exhibit comparable detonation performance to those of cyclotrimethylenetrinitramine (RDX, 8.75 km · s<sup>-1</sup>, 34.7 GPa) and cyclotetramethylenetetranitramine (HMX, 9.1 km · s<sup>-1</sup>, 39.00 GPa). Considering thermal stability and detonation performance, 1-amino-3,4,5-trinitropyrazole and 1-amino-2,4,5-trinitroimidazole can be used as potential high energy density materials.

**Key words:** *N*-aminopolynitrodiazoles; heat of formation (HOF); sensitivities; bond dissociation energy (BDE); detonation performance

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### 1 Introduction

Over the past decades, more and more researchers have interested the development of the smart energetic materials with high detonation properties, low sensitivities and good thermal stabilities<sup>[1-3]</sup>. However, these properties are often contradictory to each other<sup>[4]</sup>, making the development of novel energetic materials becomes a difficult and challenging task. Diazole (imidazole and pyrazole) based compounds have attracted a great deal of attention because of their high heats of formation (HOFs) and good thermal stabilities<sup>[5-8]</sup>. For example, 2,4-dinitroimidazole<sup>[9-10]</sup>, 2,4,5-trinitroimidazole<sup>[11-12]</sup> and 3,4,5-trinitropyrazole<sup>[13-15]</sup> have been synthesized and investigated to be favorable explosives. It is known that the hydrogen attached to N1 atom is quite acidic and labile in nitrodiazole based compounds. When the nitro (—NO<sub>2</sub>) or azido (—N<sub>3</sub>) group is attached to N1 atom of nitrodiazole based compounds, the HOFs and densities increase, whereas they exhibit poor thermal stabilities and safety characteristics. In contrast, the presence of NH<sub>2</sub> group will enhance the stabilities, HOFs, densities and detonation performance<sup>[16]</sup>. Moreover, the amino group can undergo further functionalization, such as nitration<sup>[17-18]</sup>, diazotization<sup>[19]</sup> to provide versatile energetic materials.

As is well known, the dissociation energy of the weakest bond plays an important role in the initiation of detonation. Moreover, the stabilities of energetic materials have frequently been related to energy of the weakest bond<sup>[20]</sup>. Besides, the HOF is one of the most crucial thermodynamic quantities and

it is usually taken as indicator of the “energy content” of an energetic compound<sup>[21-22]</sup>. However, to the best of our knowledge, for *N*-aminopolynitrodiazoles, no data are available for the HOFs in solid state as well as bond dissociation energies (BDEs).

Thus, this work theoretically investigated the HOFs in condensed phase, densities, detonation properties, frontier energy gaps ( $\Delta E$ ), BDEs, stabilities and sensitivities of the six *N*-aminopolynitrodiazoles by density functional theory (DFT) method at B3LYP/aug-cc-pVDZ level. Meanwhile, two known explosives 2,4-dinitroimidazole (2,4-DNI) and 3,4-dinitropyrazole (3,4-DNP) were computed using the same method, which were used to prove the results.

### 2 Methods and computational details

The six *N*-aminopolynitrodiazoles were optimized at B3LYP/aug-cc-pVDZ level using the Gaussian 09 quantum chemical package<sup>[23]</sup>. The optimized structures were positively identified to be true local minima of the potential energy surfaces with no imaginary frequencies by frequency calculations.

Detonation velocity and pressure were evaluated by the widely used empirical Kamlet-Jacobs equations<sup>[24]</sup>:

$$D = 1.01 (N \bar{M}^{1/2} Q^{1/2})^{1/2} (1 + 1.3\rho) \quad (1)$$

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

Where  $D$  is the detonation velocity, km · s<sup>-1</sup>;  $p$  is the detonation pressure, GPa;  $N$  is the number of moles of gaseous detonation products per gram of explosive, mol · g<sup>-1</sup>;  $\bar{M}$  is the average molecular weight of the gaseous products, g · mol<sup>-1</sup>;  $\rho$  is the initial density of the explosive, g · cm<sup>-3</sup>; and  $Q$  is the chemical energy of the detonation reaction, J · g<sup>-1</sup>.

In this study, the densities of the title compounds were calculated using the following equation suggested by Politzer et al.<sup>[25]</sup>.

$$\rho = \alpha' \left( \frac{M_{\text{mol}}}{V_{\text{m}}} \right) + \beta' (v\sigma_{\text{tot}}^2) + \gamma' \quad (3)$$

Where  $M_{\text{mol}}$  is the molecular mass, g · mol<sup>-1</sup>;  $V_{\text{m}}$  is the vol-

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ume defined as the space inside a counter of electron density of  $0.001 \text{ e}/\text{Bohr}^3$ ,  $\text{\AA}^3 \cdot \text{mol}^{-1}$ ;  $\alpha'$ ,  $\beta'$  and  $\gamma'$  are regression coefficients and their values are taken from reference [25].

The  $Q$  can be evaluated from the HOFs of the products and reactants. The standard gas phase HOFs ( $\Delta H_f(\text{g}, 298 \text{ K})$ ) were calculated using atomization approach as following [26–28]:

$$\Delta H_f(M, 0\text{K}) = \sum_{\text{atom}} x \Delta H_f(X, 0\text{K}) - \left[ \sum_{\text{atom}} x \varepsilon_0(X) - \varepsilon_0(M) - \varepsilon_{\text{ZPE}}(M) \right] \quad (4)$$

$$\Delta H_f(\text{g}, 298 \text{ K}) = \Delta H_f(M, 0\text{K}) + \sum_{\text{atom}} x (H_x(0\text{K}) - H_x(298 \text{ K})) + (H_M(298 \text{ K}) - H_M(0\text{K})) \quad (5)$$

Where  $M$  denotes the molecule,  $x$  is the number of the atom  $X$  in  $M$ ,  $\varepsilon_0(M)$  is the total energy of the molecule,  $\varepsilon_{\text{ZPE}}(M)$  is its zero-point energy, and  $(H_x(0\text{K}) - H_x(298 \text{ K}))$  stands for enthalpy corrections for atomic elements, which can be found from reference [29].

However, in the case of energetic compounds, the HOFs in solid state of the designed compounds are needed. They can be estimated using Eq. (6) and (7) developed by Politzer et al. [30–31].

$$\Delta H_f(\text{solid}, 298 \text{ K}) = \Delta H_f(\text{gas}, 298 \text{ K}) - \Delta H_{\text{sub}}(298 \text{ K}) \quad (6)$$

$$\Delta H_{\text{sub}}(298 \text{ K}) = \alpha (A_s)^2 + \beta \nu \sigma_{\text{tot}}^{0.5} + \gamma \quad (7)$$

Where  $\Delta H_{\text{sub}}$  is the sublimation enthalpy,  $\text{kJ} \cdot \text{mol}^{-1}$ . The values of coefficients  $\alpha$ ,  $\beta$  and  $\gamma$  are taken from reference [30].  $A_s$  is the molecular surface area,  $\text{\AA}^2$ ;  $\nu$  is a measure of the degree of balance between positive and negative potential on the molecular surface, and  $\sigma_{\text{tot}}^2$  is the total variance of the surface potential,  $(\text{kJ} \cdot \text{mol}^{-1})^2$ .

The strength of the bond and relative stability can be evaluated by the BDE, which means the difference between the energy of a molecule and those of the radicals produced when a bond of this molecule is broken. The energy required for homolytic bond cleavage at 298 K and 1 atm corresponds to the enthalpy of reaction. This has been frequently used as a measure of the thermal stability of the compounds. The BDE of the trigger bond can be given in terms of Eq. (8) [32].

$$\text{BDE}(\text{R-X}) = E(\text{R}) + E(\text{X}) - E(\text{R-X}) \quad (8)$$

Where  $E$  is the total energy,  $\text{kJ} \cdot \text{mol}^{-1}$ ;  $\text{R-X}$  is the designed molecule.  $\text{R}$  and  $\text{X}$  are the radicals produced by dissociation of  $\text{R-X}$ .

The BDE with zero-point energy (ZPE) correction can be calculated by Eq. (9) [33].

$$\text{BDE}_{\text{ZPE}}(\text{R-X}) = \text{BDE}(\text{R-X}) + \Delta \text{ZPE} \quad (9)$$

Where  $\Delta \text{ZPE}$  is the difference between the ZPE of the products and reactants,  $\text{kJ} \cdot \text{mol}^{-1}$ .

The impact sensitivities can be measured by the characteristic drop height ( $H_{50}$ ). Here, the  $H_{50}$  of the title compounds can be calculated from the following equation [34]:

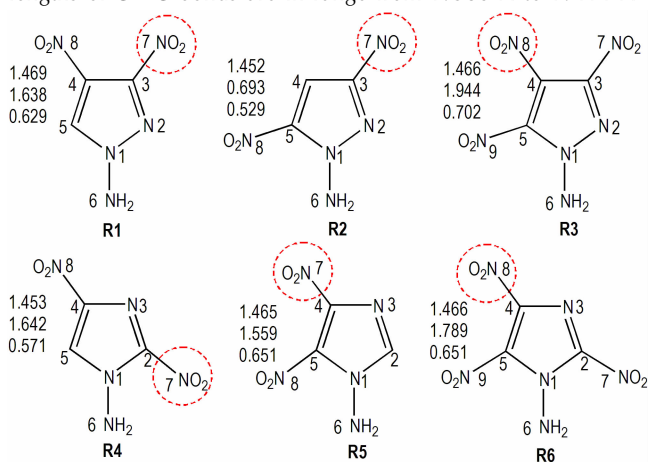
$$\log H_{50} = (46.2923a + 35.6305b - 7.7005c + 7.9425d + 44.4167n_{(-\text{CNC-})} + 102.2749n_{(-\text{CNNC-})}) / M_w \quad (10)$$

Where  $a$ ,  $b$ ,  $c$  and  $d$  present the number of carbon atoms, hydrogen atoms, nitrogen atoms and oxygen atoms, respectively.  $n_{(-\text{CNC-})}$  and  $n_{(-\text{CNNC-})}$  are the number of  $-\text{CNC}-$  and  $-\text{CNNC}-$  moieties in the aromatic ring.  $M_w$  means the average molecular mass,  $\text{g} \cdot \text{mol}^{-1}$ .

### 3 Results and discussion

#### 3.1 Optimized structures

The structures of the title compounds are optimized at the DFT-B3LYP/ aug-cc-pVDZ level and the basic structures and the atom numbering schemes are presented in Fig. 1. Optimized bond lengths of the title compounds are listed in Table 1 and corresponding dihedral angles are listed in Table 2. For these compounds, the lengths of C—N (1.313 ~ 1.469 Å) are much smaller than normal C—N single bond (1.49 Å) [35]. Bond lengths of C—C bonds are in range from 1.386 Å to 1.414 Å



**Fig. 1** Molecular frameworks and the atomic numbering of the title compounds, with trigger linkages (C—NO<sub>2</sub>) encircled in red; the list of values besides each structure shows the trigger bond length (in Å), nitro group charge (in e) and midpoint electrostatic potential from top to bottom, respectively.

**Table 1** Selected bond lengths (Å) of the title compounds computed at B3LYP/ aug-cc-pVDZ level

bond	bond length (R1) / Å	bond length (R2) / Å	bond length (R3) / Å	bond	bond length (R4) / Å	bond length (R5) / Å	bond length (R6) / Å
N1—N2	1.353	1.315	1.314	N1—N6	1.408	1.404	1.391
N1—N6	1.393	1.391	1.389	C4—C5	1.388	1.386	1.398
C3—C4	1.414	1.395	1.394	C2—N1	1.386	1.356	1.369
C4—C5	1.387	1.393	1.396	C2—N3	1.313	1.327	1.326
C3—N2	1.319	1.348	1.345	C4—N3	1.349	1.348	1.332
C3—N7	1.469	1.452	1.452	C5—N1	1.359	1.390	1.374
C5—N1	1.370	1.375	1.372	C2—N7	1.466		1.446
C4—N8	1.437		1.466	C4—N8	1.453		1.466
C5—N8		1.432		C4—N7		1.465	
C5—N9			1.433	C5—N8		1.429	
				C5—N9			1.437

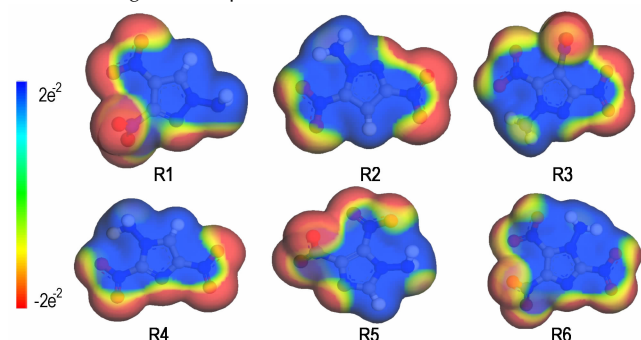
**Table 2** Dihedral angles of the title compounds computed at B3LYP/ aug-cc-pVDZ level

dihedral angle/(°)	R1	R2	R3	dihedral angle/(°)	R4	R5	R6
N1—N2—C3—C4	-0.229	0.654	0.648	N1—C2—N3—C4	0.605	-0.278	0.285
N2—C3—C4—C5	0.348	-0.373	-0.409	C2—N3—C4—C5	-0.832	0.388	0.068
C3—C4—C5—N1	-0.311	-0.052	-0.011	N3—C4—C5—N1	-0.742	-0.350	-0.380
C4—C5—N1—N2	0.196	0.471	0.401	C4—C5—N1—C2	-0.334	0.169	0.515
C5—N1—N2—C3	0.018	-0.677	-0.643	C5—N1—C2—N3	-0.170	0.064	-0.520

and are also shorter than that of normal C—C single bond (1.54 Å)<sup>[36]</sup>, which can be attributed to the presence of hyperconjugation in the whole molecule. From Table 2, it can be found that the dihedral angles in diazole rings are almost zero ( $<\pm 1^\circ$ ) and five atoms in the rings can be considered as nearly coplanar in the title molecules.

### 3.2 Electrostatic potentials and Frontier molecular orbital energies

The optimized structures computed at the B3LYP/aug-cc-pVDZ level were employed to calculate the molecular electrostatic potential surface (MESP) using Materials Studio 6.0 package<sup>[37]</sup>. The MESP of title molecules are given in Fig. 2. Overall, the positive charges are mainly inside, which are stronger and larger in area than that of the negative spatial domains. This is consistent with the views of Klapötke et al.<sup>[38]</sup> for the energetic compounds.



**Fig. 2** Molecular electrostatic potential surface of six compounds (Red and blue surfaces represent negative and positive regions, respectively, with colors representing values between  $-2e^{-2}$  and  $2e^{-2}$  Hartree)

The molecular frontier orbital energies and energy gaps are listed in Table 3. The frontier energy gap ( $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ ) between the Highest Occupied molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) can be used to determine the chemical stability of a molecule due to intramolecular charge transfer<sup>[39-40]</sup>. In general, the smaller the  $\Delta E$  is, the easier the electron transfer and the lower the molecular chemical stability is. From the  $\Delta E$  values of the listed compounds, it is noted that the  $\Delta E$  value of R1 is the largest, and that of R3 is the smallest, which indicates that the former is more stable than the latter. It can be seen that the values decrease with the introduction of  $-\text{NO}_2$  groups from two to three in the diazole ring. The decreasing order of stability of the compounds is as follows: R1>R2>R4>R5>R6>R3.

### 3.3 Impact sensitivities

As is evident in Table 4, the  $H_{50}$  of compounds with molecules R1, R2, R4 and R5 are higher than that of RDX (26 cm<sup>[2]</sup>), implying that these compounds are less insensitive than RDX. In addition,  $H_{50}$  of compounds with R1, R2, R4 and R5 are higher than those of R3 and R6, which indicates that the  $H_{50}$  decreases with the increasing of number of

nitro groups, that is to say, the dinitro compounds are less insensitive than the trinitro compounds.

**Table 3** The values of  $E_{\text{LUMO}}$ ,  $E_{\text{HOMO}}$  and  $\Delta E$  of title molecules computed at the B3LYP/aug-cc-pVDZ level

compound	$E_{\text{LUMO}}/\text{kJ} \cdot \text{mol}^{-1}$	$E_{\text{HOMO}}/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta E/\text{kJ} \cdot \text{mol}^{-1}$
R1	-316.24	-781.31	465.07
R2	-315.89	-770.09	454.20
R3	-405.88	-806.05	400.17
R4	-363.76	-809.18	445.42
R5	-363.26	-790.33	427.07
R6	-430.63	-821.99	391.36

The impact sensitivities of model compounds can also be predicted by the Mulliken atomic charge analysis of nitro group<sup>[41]</sup>. In explosives, C—NO<sub>2</sub> and N—NO<sub>2</sub> bonds are the weakest and their breaking is often the initial step in the detonation of explosive. The nitro group charge ( $-Q_{\text{NO}_2}$ ) is calculated by the sum of net Mulliken atomic charges on the nitrogen and oxygen atoms of the nitro group:

$$-Q_{\text{NO}_2} = Q_{\text{N}} + Q_{\text{O}(1)} + Q_{\text{O}(2)}$$

$$V_{\text{mid}} = \frac{2(Q_{\text{C}} + Q_{\text{N}})}{R_{(\text{C}-\text{N})}}$$

Where  $V_{\text{mid}}$  is the midpoint electrostatic potential,  $R_{(\text{C}-\text{N})}$  is trigger length, Å;  $Q_{\text{C}}$ ,  $Q_{\text{N}}$ ,  $Q_{\text{O}(1)}$  and  $Q_{\text{O}(2)}$  are the Mulliken charges on carbon, nitrogen and oxygen atoms, e, respectively.

The computed trigger bond, Wiberg bond order,  $V_{\text{mid}}$  and  $-Q_{\text{NO}_2}$  values of the title compounds are presented in Table 4. Generally, higher negative charge the nitro group possesses, lower the electron-attraction ability is, therefore, the nitro compound is more stable. Variations of the calculated  $-Q_{\text{NO}_2}$  values range from 0.529 e to 0.702 e. Compared with the  $-Q_{\text{NO}_2}$  values of TNT (0.249 e), FOX-7 (0.365 e), RDX (0.134 e), HMX (0.112 e), TNAZ (0.114 e), LLM-105 (0.292 e) and NTO (0.264 e)<sup>[41-42]</sup>, the title compounds appear to be insensitive. According to the  $V_{\text{mid}}$  values in Table 4, all molecules may exhibit lower sensitivities than (TNT) (0.25) and (TATB) (0.42)<sup>[42]</sup>. The strength of trigger bond can be characterized by Wiberg bond order. The smaller the Wiberg bond order is, the weaker the bond will be and thus the molecule is less stable. These impact sensitivities may attribute to the presence of  $\pi$ -excessive aromatic heterocyclic ring, delocalization of  $\pi$ -electrons and the existence of intra or intermolecular hydrogen bonds.

### 3.4 BDE

It is known that the BDE of the trigger bond can provide information about the stability of a compound. As a whole, the smaller the BDE is, the less the molecular stability will be. The BDEs have been predicted for the title compounds by breaking the weakest bonds (R—NO<sub>2</sub>), shown in Table 4. As

can be seen from Table 4, the BDEs of all the compounds are in the range of 238.94 kJ · mol<sup>-1</sup> to 278.53 kJ · mol<sup>-1</sup>, and BDEs of the title molecules are higher than those of RDX (152.09 kJ · mol<sup>-1</sup>) and HMX (166.48 kJ · mol<sup>-1</sup>)<sup>[43]</sup>,

which implies that they have better thermal stabilities. It could also be noted that the BDEs decrease as the number of nitro group increases.

**Table 4** Trigger bond, Wiberg bond order,  $V_{\text{mid}}$ , Mulliken charges on nitro group ( $-Q_{\text{NO}_2}$ ), BDE and  $H_{50}$  of title compounds

compound	bond	Wiberg bond order	$V_{\text{mid}}$	$-Q_{\text{NO}_2}/e$	BDE/kJ · mol <sup>-1</sup>	$H_{50}/\text{cm}$
R1	C(3)—NO <sub>2</sub>	0.883	1.638	0.629	248.28	80.04
R2	C(3)—NO <sub>2</sub>	0.936	0.693	0.529	278.53	80.04
R3	C(4)—NO <sub>2</sub>	0.896	1.944	0.702	245.63	24.25
R4	C(4)—NO <sub>2</sub>	0.931	1.642	0.571	276.04	66.93
R5	C(4)—NO <sub>2</sub>	0.896	1.559	0.651	244.95	66.93
R6	C(4)—NO <sub>2</sub>	0.899	1.789	0.651	238.94	21.04

### 3.5 HOF and Densities

Table 5 summarizes the  $\Delta H_f(\text{g})$ ,  $\Delta H_f(\text{s})$  and the related data of  $A_S$ ,  $\nu\sigma_{\text{tot}}^2$  and  $\Delta H_{\text{sub}}$ . It is noted from Table 5, all the title compounds show very high positive HOFs ( $\Delta H_f(\text{g})$ , 322.62 kJ · mol<sup>-1</sup> to 432.39 kJ · mol<sup>-1</sup>,  $\Delta H_f(\text{s})$ , 208.52 kJ · mol<sup>-1</sup> to 314.68 kJ · mol<sup>-1</sup>), and are far higher than those of RDX ( $\Delta H_f(\text{s})$ , 191.63 kJ · mol<sup>-1</sup>) and HMX( $\Delta H_f(\text{g})$ , 258.15 kJ · mol<sup>-1</sup>). With the increase in the number of the nitro groups, the HOFs always increase. Table 5 also shows that the HOFs are slightly affected by the relative position of the nitro groups. The title compounds possess higher HOFs due to the contributions of N-N bonds as compared with that of the corresponding compounds 2,4-DNI and 3,4-DNP.

A convenient method was used to predict the densities of

the title compounds proposed by Politzer et al.<sup>[25]</sup>. The densities are listed in Table 6. The predicted densities of 2,4-DNI and 3,4-DNP agree well with experimental values (1.77 g · cm<sup>-3</sup> and 1.81 g · cm<sup>-3</sup>), which indicates this method is reliable. From Table 6, the values have been found to be in range from 1.71 g · cm<sup>-3</sup> to 1.82 g · cm<sup>-3</sup>. The compounds R3 and R6 have equal density 1.82 g · cm<sup>-3</sup>, which is comparable to the experimental density of RDX.

### 3.6 Detonation performance

Several empirical or semi-empirical methods have been applied to estimate these parameters<sup>[24, 45-46]</sup>. Kamlet-Jacobs equations have been proved to be reliable<sup>[47-48]</sup>. Table 6 shows calculated detonation velocity ( $D$ ) and detonation pressure ( $p$ ) of the title compounds along with experimental

**Table 5** Heats of formation (HOFs) and the related parameters of  $A_S$ ,  $\nu\sigma_{\text{tot}}^2$  and  $\Delta H_{\text{sub}}$  of the title compounds and some referred compounds

compound	$A_S/\text{\AA}^2$	$\nu\sigma_{\text{tot}}^2/(\text{kJ} \cdot \text{mol}^{-1})^2$	$\Delta H_{\text{sub}}/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta H_f(\text{g})/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta H_f(\text{s})/\text{kJ} \cdot \text{mol}^{-1}$
R1	178.63	177.88	111.82	389.54	277.72
R2	176.63	141.13	104.09	362.38	258.29
R3	200.13	120.19	117.71	432.39	314.68
R4	175.85	204.86	114.10	322.62	208.52
R5	174.19	173.69	108.03	342.94	234.91
R6	199.00	112.04	115.21	381.95	266.74
2,4-DNI	162.58	198.19	104.15	174.45	70.30
3,4-DNP	162.17	174.00	100.04	247.96	147.92
RDX <sup>[44]</sup>				191.63	
HMX <sup>[44]</sup>			258.15		

**Table 6** Predicted densities, molar volume ( $V_{\text{mol}}$ ) and detonation performance of the title compounds along with these of experimental values of 2,4-DNI, 3,4-DNP, RDX and HMX

compound	$V_{\text{mol}}/\text{cm}^3 \cdot \text{mol}^{-1}$	$\rho/\text{g} \cdot \text{cm}^{-3}$	$Q/\text{J} \cdot \text{g}^{-1}$	$D/\text{km} \cdot \text{s}^{-1}$	$p/\text{GPa}$
R1	100.53	1.74	1564.20	8.38	30.60
R2	101.03	1.71	1537.36	8.24	29.16
R3	118.29	1.82	1688.69	8.99	36.12
R4	100.07	1.77	1468.61	8.34	30.54
R5	101.83	1.72	1505.06	8.23	29.20
R6	117.85	1.82	1636.13	8.92	35.56
2,4-DNI	90.81	1.78 (1.77) <sup>[17]</sup>	1465.70 <sup>[17]</sup>	8.23 (8.13) <sup>[17]</sup>	29.83 (28.10) <sup>[17]</sup>
3,4-DNP	91.44	1.73 (1.81) <sup>[17]</sup>	1258.70 <sup>[17]</sup>	7.85 (8.24) <sup>[17]</sup>	26.83 (28.80) <sup>[17]</sup>
RDX <sup>[2]</sup>		1.82		8.75	34.70
HMX <sup>[2]</sup>		1.90		9.1	39.00

and calculated values of 2,4-DNI and 3,4-DNP. The calculated  $D$  and  $\rho$  of R1–R6 are 8.23–8.99 km · s<sup>-1</sup> and 29.16–36.12 GPa, respectively. It is observed that R3 (8.99 km · s<sup>-1</sup>, 36.12 GPa) and R6 (8.92 km · s<sup>-1</sup>, 35.56 GPa) show better properties in the series due to the better densities and higher HOFs. Calculation results indicate that the values of R3 (8.99 km · s<sup>-1</sup>, 36.12 GPa) and R6 (8.92 km · s<sup>-1</sup>, 35.56 GPa) appear to be superior to that of RDX (8.75 km · s<sup>-1</sup>, 34.70 GPa) and comparable to that of HMX (9.1 km · s<sup>-1</sup>, 39.00 GPa). Additionally, the detonation performance of compounds with molecules R1, R2, R4 and R5 is similarly to that of RDX. In a word, compounds with R1–R6 have comparable detonation performances to RDX and HMX.

## 4 Conclusion

In this paper, density functional theory was employed to study the electronic structures, thermal stabilities, heats of formation, densities and explosive properties of *N*-aminopolynitrodiazoles. Results are as follows:

(1) The  $\Delta E$  of the title molecules decrease as the number of nitro groups increases. Based on atomization approach, standard gas phase HOFs of the title compounds were predicted. The solid state HOFs were estimated in the framework of the Politzer model. Results show that all title molecules possess high positive HOFs ( $\Delta H_f(g)$ , 322.62 kJ · mol<sup>-1</sup> to 432.39 kJ · mol<sup>-1</sup>,  $\Delta H_f(s)$ , 208.52 kJ · mol<sup>-1</sup> to 314.68 kJ · mol<sup>-1</sup>). The HOFs are slightly affected by the relative position of the nitro groups.

(2) The analysis of the bond dissociation energy of the weakest bond (238.94 kJ · mol<sup>-1</sup> to 278.53 kJ · mol<sup>-1</sup>) suggests that the title molecules are with good thermal stabilities. The other analysis of the nitro group charge and  $H_{50}$  shows all the compounds have low impact sensitivities.

(3) The  $D$ ,  $\rho$  and  $\rho$  also increase as the number of nitro groups increases. R3 (8.99 km · s<sup>-1</sup>, 36.12 GPa) and R6 (8.92 km · s<sup>-1</sup>, 35.56 GPa) show better detonation properties in the series due to the better densities and higher HOFs. All title molecules show comparable detonation performances (8.23–8.99 km · s<sup>-1</sup> and 29.16–36.12 GPa) to RDX (8.75 km · s<sup>-1</sup>, 34.70 GPa) and HMX (9.1 km · s<sup>-1</sup>, 39.00 GPa).

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## 氮-氨基多硝基二唑的理论研究

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**摘要:** 采用密度泛函理论 B3LYP 方法, 在 aug-cc-pVDZ 的水平上, 对 6 种 N-氨基多硝基二唑化合物的电子结构、能隙及感度进行了理论研究。运用 Politzer 的方法得到了 6 种化合物的固相生成热和密度; 采用键离解能预估了化合物的热稳定性, 其离解能为  $238.94 \sim 283.95 \text{ kJ} \cdot \text{mol}^{-1}$ ; 运用 Kamlet-Jacob 方程对其爆轰性能进行了预测。结果表明: 1-氨基-3,4,5-三硝基吡唑 ( $8.99 \text{ km} \cdot \text{s}^{-1}$ ,  $36.12 \text{ GPa}$ ) 和 1-氨基-2,4,5-三硝基咪唑 ( $8.92 \text{ km} \cdot \text{s}^{-1}$ ,  $35.56 \text{ GPa}$ ) 的爆轰性能与环三亚甲基三硝胺 (RDX,  $8.75 \text{ km} \cdot \text{s}^{-1}$ ,  $34.7 \text{ GPa}$ ) 及环四亚甲基四硝胺 (HMX,  $9.1 \text{ km} \cdot \text{s}^{-1}$ ,  $39.00 \text{ GPa}$ ) 相当。综合热稳定性和爆轰性能, 认为 1-氨基-3,4,5-三硝基吡唑和 1-氨基-2,4,5-三硝基咪唑是潜在的高能量密度材料。

**关键词:** 氮-氨基多硝基二唑; 生成热; 感度; 键离解能; 爆轰性能

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