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Molecular design of aminopolynitroazole-based high-energy materials

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Abstract The density functional theory (DFT) was employed to calculate the energetic properties of several aminopolynitroazoles. The calculations were performed to study the effect of amino and nitro substituents on the heats of formation, densities, detonation performances, thermal stabilities, and sensitivity characteristics of azoles. DFT-B3LYP, DFT-B3PW91, and MP2 methods utilizing the basis sets 6-31 G* and 6-311 G (2df, 3p) were adopted to predict HOFs via designed isodesmic reactions. All of the designed aminopolynitroazoles had heats of formation of >220 kJ mol^{-1}. The crystal densities of the aminopolynitroazoles were predicted with the cvff force field. All of the energetic azoles had densities of >1.83 g/cm^3. The detonation velocities and pressures were evaluated using the Kamlet–Jacobs equations, utilizing the predicted densities and heats of formation. It was found that aminopolynitroazoles have a detonation velocity of about 9.1 km/s and detonation pressure of 36 GPa. The bond dissociation energies for the C–NO$_2$ and N–NO$_2$ bonds were analyzed to investigate the stabilities of the designed molecules. The charge on the nitro group was used to assess impact sensitivity in the present study. The results obtained imply that the designed molecules are stable and are expected to be candidates for high-energy materials (HEMs).

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Introduction

High material performance has been of prime importance in the development and study of new energetic materials for various applications. However, an emerging trend in the field of energetic materials has been the development of high-performance compounds with a combination of properties, including stability, reliability, safety, and low toxicity [1–6]. Five-member heterocyclic rings such as imidazole, pyrazole, and triazole possess high nitrogen contents, making them of interest for the synthesis of HEMs [7, 8]. The relative energy characteristics of such HEMs are dependent on their nitrogen contents and ring structures. Heterocycles that contain large amounts of nitrogen are relatively dense, while smaller amounts of hydrogen and carbon contribute to a better oxygen balance (OB). Additionally, they possess higher heats of formation (HOF) due to higher percentages of decomposition products (usually dinitrogen) and the presence of inherently energetic N–N and C–N bonds [9, 10].

The performance of a nitrogen-rich heterocycle can be optimized and improved by replacing hydrogen atoms with various energetic functional groups. Among these groups, the nitro group is a vital constituent of energetic materials. The performance of a polynitro compound is enhanced by achieving a good oxygen balance; this results in higher exothermicity during the combustion and detonation processes [11, 12]. The introduction of an amino group is one of the simplest routes to enhancing the thermal stability of an energetic material [13]. The study of the relationship between the molecular structures of energetic materials and their thermal stabilities and sensitivities has been an

ongoing area of research. The bond dissociation energy of the weakest bond of an energetic molecule is expected to play an important role in the initiation of detonation [14, 15]. Thermal stability has been evaluated by calculating the bond dissociation energy (BDE) of the weakest C–NO$_2$ or N–NO$_2$ bond in the designed polynitro compound. Sensitivity is another important issue in the safe handling of energetic materials [16, 17]. Zhang et al. demonstrated that the relationship between the impact sensitivities and the electronic structures of some nitro compounds can be obtained through a charge analysis of the nitro group [18, 19].

In the present study, we considered azole-based molecules with high energies and densities as a step toward the design of novel HEMs. Theoretical studies make it possible to screen for appropriate compounds, avoiding hazardous and expensive experimental studies. They can also provide an understanding of the relationships between molecular structure and molecular properties, which aid in designing better and more efficient laboratory tests. The molecules were designed using different combinations of amino and nitro groups on the azole rings; the structures of the molecules studied are shown in Fig. 1.

Fig. 1 Chemical structures of the aminopolynitroazole derivatives studied, as well as that of 1-methyl-2,4,5-trinitroimidazole (MTNI)

2,4,5-Trinitro-1*H*-imidazol-1-amine (A1)

1,4,5-Trinitro-1*H*-imidazol-2-amine (A2)

1,2,5-Trinitro-1*H*-imidazol-4-amine (A3)

1,2,4-Trinitro-1*H*-imidazol-5-amine (A4)

3,4,5-Trinitro-1*H*-pyrazol-1-amine (B1)

1,4,5-Trinitro-1*H*-pyrazol-3-amine (B2)

1,3,5-Trinitro-1*H*-pyrazol-4-amine (B3)

1,3,4-Trinitro-1*H*-pyrazol-5-amine (B4)

3,5-Dinitro-1*H*-1,2,4-triazol-1-amine (C1)

1,5-Dinitro-1*H*-1,2,4-triazol-3-amine (C2)

1,3-Dinitro-1*H*-1,2,4-triazol-5-amine (C3)

3,5-Dinitro-4*H*-1,2,4-triazol-4-amine (C4)

4,5-Dinitro-4*H*-1,2,4-triazol-3-amine (C5)

4,5-Dinitro-1*H*-1,2,3-triazol-1-amine (D1)

1,5-Dinitro-1*H*-1,2,3-triazol-4-amine (D2)

1,4-Dinitro-1*H*-1,2,3-triazol-5-amine (D3)

1-Methyl-2,4,5-trinitroimidazole (MTNI)

Calculation methodology

All quantum mechanical calculations were performed with the Gaussian 03 software suite [20]. The heats of formation of the designed compounds were calculated at the B3LYP, MP2, and B3PW91 levels of theory, in combination with the basis sets 6-31 G* and 6-311 G (2df, 3p), via designed isodesmic reactions. The zero point energies (ZPEs) and the corresponding thermal corrections (H_T) to the enthalpy at 298.15 K were obtained from frequency calculations and were subsequently added to the electronic energies (Table 1). In an isodesmic reaction, the number of each type of formal bond is conserved according to bond separation reaction (BSR) rules [21, 22]. The target molecule is broken down into a set of heavy atom molecules containing the same component bonds. BSR rules cannot be applied to molecules with delocalized bonds and cage skeletons because of large calculated errors in the HOF. In view of this, the present study involved designing isodesmic reactions in which the numbers of all types of bonds are kept constant, in order to decrease the HOF calculation errors. Imidazole, pyrazole, and triazole rings were kept intact while constructing the isodesmic reactions, and this approach proved to be reliable [23–25].

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

$$\Delta H_{298K} = \Delta H_{f,p} - \Delta H_{f,R}, \tag{1}$$

where $\Delta H_{f,R}$ and $\Delta H_{f,p}$ are the heats of formation of the reactants and products at 298 K, respectively. The ΔH^0_f values of the designed molecules can be evaluated when the heat of reaction ΔH_{298K} is known. Therefore, the main

quantity to compute is ΔH_{298K}, which can be calculated using the following expression:

$$\Delta H_{298K} = \Delta E_{298K} + \Delta(PV)$$
$$= \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT, \tag{2}$$

where 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 energies (ZPE) of the products and the reactants, and ΔH_T is the thermal correction from 0 to 298 K. $\Delta(PV)$ is equal to ΔnRT for the reactions of an ideal gas. Table 1 lists the calculated total energies at 298 K (including the zero-point energy and thermal corrections in the calculations) and the experimental gas-phase HOFs for the reference compounds in isodesmic reactions, where calculations were performed at the B3LYP/6-31 G*, B3LYP/6-311 G (2df, 3p), MP2/6-31 G*, and B3PW91/6-31 G* levels of theory.

The oxygen balance is the percentage of the oxygen chemically bound in a molecule that is needed to oxidize it completely. Available oxygen (in the molecule) is needed to convert explosives into their gaseous reaction products, such as CO_2, CO, H_2O, and NO_x. The oxygen balance (O.B., %) is calculated for an explosive of general formula $C_aH_bN_cO_d$ with molecular mass M as follows:

$$O.B.(\%) = \frac{[d - (2a) - (b/2)] \times 1600}{M}. \tag{3}$$

The density of the crystal structure of each compound was predicted by performing molecular packing calculations using the polymorph module of Material Studio [26]. The approach was based on the generation of possible packing arrangements in all reasonable space groups ($P2_1/c$, P-1, $P2_12_12_1$, $P2_1$, $C2/c$, $Pbca$, $Pna2_1$, $Pbcn$, Cc, and $C2$) [27,

Table 1 Total energies (E_0) calculated via the B3LYP/6-31 G*, B3LYP/6-311 G (2df, 3p), MP2/6-31 G*, and B3PW91/6-31 G* methods (with zero-point energy and thermal corrections included in the calculations) as well as experimental gas-phase HOFs for the reference compounds

Compound	E_0 (au)				HOF (kJ/mol)
	B3LYP		MP2/6-31 G*	B3PW91/6-31 G*	
	6-31 G*	6-311 G (2df, 3p)			
CH₄	−40.4694	−40.5366	−40.3325	−40.5034	−74.6
NH₃	−56.5096	−56.5826	−56.3542	−56.5277	−45.9
CH₃NH₂	−95.7844	−95.8962	−95.5065	−95.8185	−22.5
CH₃NO₂	−244.9539	−245.0975	−244.3313	−244.9182	−74.7
NH₂NH₂	−111.7962	−111.9065	−111.4955	−111.8131	95.2
NH₂NO₂	−260.9873	−261.1211	−260.3337	−260.9255	8.0
Imidazole	−226.1386	−226.2926	−225.5191	−226.1307	129.5
Pyrazole	−226.1225	−226.2760	−225.5033	−226.1151	179.4
1,2,4-Triazole	−242.1848	−242.3297	−241.5434	−242.1591	192.7
1,2,3-Triazole	−242.1587	−242.3027	−241.5174	−242.1324	271.7

28] to search for the low-lying minima on the lattice energy surface.

The empirical Kamlet–Jacobs [29, 30] equations were employed to estimate the values of D and P for the energetic materials containing C, H, O, and N:

$$D = 1.01\left(NM^{0.5}Q^{0.5}\right)^{0.5}(1 + 1.30\rho_o) \qquad (4)$$

$$P = 1.55\rho_o{}^2 NM^{0.5}Q^{0.5}, \qquad (5)$$

where D is the detonation velocity (km/s), P is the detonation pressure (GPa), N is the number of moles of gaseous detonation products per gram of explosives, M is the average molecular weight of the gaseous products, Q is the chemical energy of detonation (kJ mol^{-1}), defined as the difference in the HOFs of the products and reactants, and ρ_o is the density of the explosive (g/cm^3).

Thermal stability can be evaluated based on the bond dissociation energy (BDE), which is defined as the difference between the ZPE-corrected total energies at 0 K of the parent molecules and those of the corresponding radicals in unimolecular bond dissociation [31, 32]. In an energetic molecule, either C–NO$_2$ or N–NO$_2$ is generally the trigger bond that undergoes fission due to the application of heat or mechanical impact, so we have presented the BDE values of these bonds [33]. In the present study, the BDE was calculated using the following equation:

$$\begin{aligned}
BDE_{298}(R_1 - R_2) = & \left[\Delta_f H_{298}(R_1) + \Delta_f H_{298}(R_2)\right] \\
& - \Delta_f H_{298}(R_1 - R_2), \qquad (6)
\end{aligned}$$

where R_1–R_2 is the neutral molecule, R_1 and R_2 are the corresponding radicals, and $\Delta_f H_{298}(R_1), \Delta_f H_{298}(R_2)$, and $\Delta_f H_{298}(R_1 - R_2)$ are the heats of formation at 298 K of R_1, R_2, and R_1–R_2, respectively.

Atomic charges were computed for the optimized geometries of the designed molecules by natural bond orbital (NBO) analysis at the B3LYP/6-31 G* level. In this study, the charge on the nitro group ($-Q_{NO2}$) was considered due to its correlation with impact sensitivity. The charge on the nitro group ($-Q_{NO2}$) was calculated as the sum of the net charge on the nitrogen atom (Q_N) and oxygen atoms (Q_{O1} and Q_{O2}) in the nitro group.

Results and discussion

The designed aminopolynitroazoles had nitrogen contents of >38% and oxygen balances of −7 to −10%. Systematic structure–property relationships were studied in order to analyze the performances of the designed molecules. The predicted energetic properties of the designed molecules were compared with that of 1-methyl-2,4,5-trinitroimidazole (MTNI) to evaluate their performance (Fig. 1). MTNI is an insensitive melt-cast high explosive with an explosive performance that is comparable to RDX, and its sensitivity is intermediate between those of RDX and TNT [34, 35].

Heat of formation

The heat of formation is indicative of the energy content of the energetic material, and is of great importance as it strongly influences detonation performance. The HOFs of the designed compounds were calculated at the B3LYP, MP2, and B3PW91 levels of theory in combination with the basis sets 6-31 G* and 6-311 G (2df, 3p) via designed isodesmic reactions. The calculated HOFs of the designed molecules were compared with that of MTNI to evaluate their performance. The HOF calculated for MTNI using the isodesmic reaction approach at the B3LYP/6-31 G*, B3LYP/6-311 G (2df, 3p), MP2/6-31 G* and B3PW91/6-31 G* levels of theory are 170.4, 175.1, 164.9, and 175.5 kJ mol^{-1}, respectively. These values are comparable with those reported earlier by Su et al. (173.4 and 176.2 kJ mol^{-1}) [36, 37]. From Table 1, the HOFs of the different azoles are highly positive, clearly indicating their influence on the total energies. The HOFs predicted for MTNI using the B3LYP, MP2, and B3PW91 theories in conjunction with the basis sets 6-31 G* and 6-311 G (2df, 3p) reveal that the predicted HOF values are comparable to the reported ones. Hence, the basis set 6-31 G* was chosen for further studies. Previous studies have shown that B3LYP/6-31 G* methods produce more reliable enthalpies of formation [38–41].

The predicted HOFs for the designed compounds are highly positive in the range of 220 to 410 kJ mol^{-1}. These high HOFs can be attributed to the presence of large numbers of N–N and C–N bonds and energetic nitro groups. Table 2 summarizes the calculated HOFs of the aminonitroazole derivatives. The isodesmic reactions for the aminopolynitroazole derivatives with N–NH$_2$ and N–NO$_2$ functionalities are shown in Fig. 2a and b. Among the designed molecules, N–NH$_2$ derivatives (A1, B1, C1, C4, and D1) show slightly higher HOFs than their N–NO$_2$ isomers. This can be clearly seen for the imidazole derivatives: A1 possesses a higher HOF than A2, A3, and A4. Similar trends are also observed for the pyrazole and triazole derivatives. In general, the energy contribution from the pyrazole is higher than that from the imidazole, so B1, B2, B3, and B4 show higher HOFs than A1, A2, A3, and A4. Similarly, 1,2,3-triazole contributes more energy than 1,2,4-triazole, so D1, D2, and D3 show higher HOFs than C1, C2, and C3. Among the 1,2,4-triazole derivatives, C4 and C5 show slightly higher HOFs than the corresponding

Table 2 Calculated heats of formation for the aminopolynitroazole derivatives

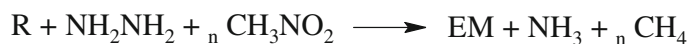| Compound	HOF$_{gas}$ (kJ/mol)			
	B3LYP		MP2/6-31 G*	B3PW91/6-31 G*
	6-31 G*	6-311 G (2df, 3p)		
A1	263.1	279.2	262.4	273.2
A2	244.7	242.8	233.2	236.1
A3	244.4	244.1	233.6	238.0
A4	224.9	226.0	224.9	217.2
B1	326.5	342.6	311.1	331.2
B2	302.1	296.8	287.7	291.9
B3	281.1	279.6	275.5	264.1
B4	265.0	257.2	257.3	251.6
C1	325.6	335.0	322.9	330.5
C2	321.6	321.2	313.3	311.3
C3	279.3	269.7	278.7	266.9
C4	359.1	368.8	364.9	371.9
C5	344.9	332.7	340.6	370.5
D1	411.5	416.6	402.6	413.2
D2	389.4	381.1	378.1	369.3
D3	351.2	341.7	353.7	336.7
MTNI	170.4 (173.4)	175.1	164.9	175.5

Values in parentheses are theoretically predicted from [36, 37]

isomers **C1**, **C2**, and **C3**, which can be attributed to the adjacent arrangement of the chemical groups on the ring and the molecular framework of the triazole. **D1** shows the highest HOF among the aminopolynitroazole derivatives, which may be due to the presence of adjacent nitro groups and the 1,2,3-triazole ring in the molecular structure. The adjacent nitro groups result in high repulsive energy and steric hindrance for the molecule. The overall study shows that all of the designed compounds possess higher HOFs than MTNI.

Density

Density has been referred to as the physical parameter that has the greatest effect on detonation performance, because the detonation velocity and pressure of the explosive are proportional to the packing density and square of it, respectively [29, 30]. Densities predicted using the cvff force field (Table 3) were used to calculate detonation characteristics, as they lead to marginally better results for nitro compounds

Fig. 2a–b Isodesmic reaction schemes for the designed molecules. **a** Scheme for N–NH$_2$ molecules, **b** scheme for N–NO$_2$ molecules

$$R + NH_2NH_2 + {}_n CH_3NO_2 \longrightarrow EM + NH_3 + {}_n CH_4$$

R = Azole Ring

EM = Energetic Molecule

(a)

$$R + NH_2NO_2 + CH_3NH_2 + {}_n CH_3NO_2 \longrightarrow EM + NH_3 + {}_{n+1} CH_4$$

R = Azole Ring

EM = Energetic Molecule

(b)

Table 3 Predicted explosive characteristics for the aminopolynitroazole derivatives

Compound	O.B. (%)	Density (g/cm³)	Q (J/g)	D (km/s)	P (GPa)
A1	−7.34	1.96	6437.21	9.46	41.63
A2	−7.34	1.95	6353.05	9.43	41.35
A3	−7.34	1.95	6351.79	9.43	41.35
A4	−7.34	1.95	6262.19	9.39	41.06
B1	−7.34	1.95	6728.61	9.56	42.56
B2	−7.34	1.93	6616.82	9.46	41.34
B3	−7.34	1.92	6520.10	9.39	40.61
B4	−7.34	1.91	6445.99	9.33	39.96
C1	−9.20	1.82	6138.69	9.06	36.70
C2	−9.20	1.84	6161.71	9.14	37.58
C3	−9.20	1.84	5895.85	9.04	36.76
C4	−9.20	1.83	6354.31	9.18	37.75
C5	−9.20	1.84	6273.08	9.18	37.91
D1	−9.20	1.86	6655.34	9.39	39.91
D2	−9.20	1.84	6528.48	9.27	38.68
D3	−9.20	1.83	6309.09	9.16	37.61
MTNI	−25.81	1.82 (1.79)	5149.34	8.82 (8.80)	34.75 (34.66)

O.B. oxygen balance, *Q* chemical energy of detonation, *D* velocity of detonation, *P* detonation pressure. The experimental *values in parentheses* are reported in [42]

[40, 41]. The predicted density of the MTNI molecule (1.82 g/cm³) using the cvff force field was to be found close to the experimental value (1.79 g/cm³) [42]. The densities of the designed molecules were found to be slightly high, and varied from 1.82 to 1.96 g/cm³. The presence of NH_2 and NO_2 groups in the molecular structure increases the chances of inter- and intramolecular hydrogen bonding and improves the crystal packing. The imidazole and pyrazole derivatives show higher densities than the triazole derivatives, which is due to the additional nitro group present in the molecular structures of the imidazole and pyrazole derivatives. Among the designed compounds, the imidazole derivatives possess the highest densities (1.95 g/cm³). There is no significant change in the densities of the imidazole derivatives (**A1**, **A2**, **A3** and **A4**) when the positions of NH_2 and NO_2 on the molecular framework are changed. A comparison of the N–NH_2 and N–NO_2 derivatives of pyrazole shows that **B1** possesses a slightly higher density than **B2**, **B3**, and **B4**. A similar trend is also observed for the 1,2,3-triazole derivatives (**D1**, **D2**, and **D3**). Replacing the 1,2,4-triazole with the 1,2,3-triazole does not lead to a significant change in the density.

Detonation properties

Detonation velocity and detonation pressure are two important performance parameters for an energetic material. Table 3 presents the detonation properties of the aminopolynitroazoles. For comparison, the experimental detonation performance of a known explosive, MTNI, is also listed in Table 3. The predicted detonation velocity (8.82 km/s) and

pressure (34.75 GPa) of MTNI obtained using the Kamlet–Jacobs empirical equations were found to be similar to the experimental values (D=8.80 km/s; P=34.66 GPa) [42]. Detonation performance depends mainly on crystal density and less on the HOF of the compound [43]. As the number of nitro substituents increases, the density, the D, and the P values of the substituted aminopolynitroazoles increase. Hence, imidazole and pyrazole derivatives show better performance than triazole derivatives. Moreover, their D and P values are very high—close to 9.5 km/s and 42 GPa, respectively. It was also found that the pyrazole derivative with an N–NH_2 group (**B1**) has the largest D and P values among these derivatives. 1,2,3-Triazole derivatives (**D1**–**D3**) give better performance than the 1,2,4-triazole derivatives (**C1**–**C3**) due to their better HOFs and densities. All of the designed molecules show better detonation performance than MTNI, which may be due to their better oxygen balances, higher densities, and HOFs.

Thermal stability

The thermal stability of an energetic material determines its applicability for practical purposes. The present study explored the stabilities of the designed compounds by analyzing the bond dissociation energy (BDE) of the weakest bond. All of the BDEs were calculated via hybrid DFT using the B3LYP method together with the 6-31 G* basis set. The BDE for each possible trigger bond is often a key factor when investigating the pyrolysis mechanism for an energetic compound [24]. The smaller the BDE, the weaker the bond. Various studies have illustrated that N–NO_2 and C–NO_2 are

the most probable trigger bonds in nitroaromatic compounds [17, 44], and they can easily be ruptured during pyrolysis. All of the predicted BDEs are listed in Table 4. The calculated BDE for C–NO$_2$ in MTNI (251 kJ mol^{-1}) was found to be similar to the results predicted previously (255.6 kJ mol^{-1}) by Su et al. [36]. The BDEs for the C–NO$_2$ bonds of the amino-polynitroazole derivatives were found to be >236 kJ mol^{-1}, while those for N–NO$_2$ bonds were found to be >31 kJ mol^{-1}. The BDEs for cleaving N–NO$_2$ bonds were found to be much lower than those for the C–NO$_2$ bonds. The presence of an amino group in the molecular structure strengthens the C–NO$_2$ bond due to its electron-donating nature. The imidazole derivatives show lower BDEs for the cleavage of the N–NO$_2$ bond than the pyrazole and triazole derivatives. This may be due to the adjacent nitro groups present in the imidazole derivatives. The presence of a nitro and an amino group in the same molecule increases the chances of inter- and intra-molecular hydrogen bonding, and may be responsible for improving the stability of aminopolynitroazoles. All of the designed molecules possessed C–NO$_2$ BDEs that were comparable to that of MTNI.

Sensitivity correlations

The relationship between the impact sensitivities and the electronic structures of some nitro compounds can be established via charge analysis of the nitro group [18, 19]. In this work, the longest C–NO$_2$ bond was selected as the weakest bond. The charges on the corresponding atoms were calculated using NBO analysis. It was found that increasing the number of substituted nitro groups decreased $-Q_{NO2}$ and increased the C–NO$_2$ bond length and oxygen balance. Table 4 lists the computed $-Q_{NO2}$ values from NBO analysis and the bond length of the weakest C–NO$_2$ bond in each compound calculated at the B3LYP/6-31 G* level. The higher the value of $-Q_{NO2}$, the greater the compound's impact insensitivity, so $-Q_{NO2}$ can be regarded as an indicator of the impact sensitivity. $-Q_{NO2}$ values calculated for the aminopolynitroazole derivatives ranged from 0.102 to 0.299 e. The presence of adjacent nitro groups leads to steric hindrance and repulsive energy, which reduces the charge on the nitro groups. Among the designed compounds, **B1** and **B2** show $-Q_{NO2}$ values that are far lower than that of MTNI. The three adjacent nitro groups in these two designed compounds increase their impact sensitivity. Overall, $-Q_{NO2}$ analysis reveals that aminopolynitroazole derivatives are less impact sensitive than MTNI.

Conclusions

In this work, we calculated the heats of formation for a series of aminopolynitroazole derivatives using the B3LYP/6-31 G*, B3LYP/6-311 G (2df, 3p), MP2/6-31 G*, and B3PW91/6-31 G* methods by designing appropriate isodesmic reactions. The results reveal that the designed compounds possess highly positive HOFs due to the energy contribution from the azole ring. Crystal density was predicted using molecular packing calculations, and the calculated densities varied from 1.83 to 1.96 g/cm^3. The designed

Table 4 Calculated bond lengths, bond dissociation energies, and charges on the nitro groups for the aminopoly-nitroazole derivatives

Compound	Bond length (Å)		BDE (kJ/mol)		$-Q_{NO2}$ (e)
	C–NO$_2$	N–NO$_2$	C–NO$_2$	N–NO$_2$	
A1	1.4603		249.72		0.176
A2	1.4649	1.4468	250.26	43.51	0.240
A3	1.4547	1.5648	236.75	31.52	0.207
A4	1.4501	1.4484	245.07	51.05	0.217
B1	1.4634		254.25		0.112
B2	1.4692	1.4520	237.56	64.13	0.102
B3	1.4423	1.5116	261.40	54.20	0.237
B4	1.4680	1.4298	247.28	101.25	0.171
C1	1.4626		273.19		0.197
C2	1.4662	1.4481	239.26	56.49	0.177
C3	1.4702	1.4239	269.07	100.36	0.194
C4	1.4437		270.95		0.217
C5	1.4479	1.4395	249.67	54.15	0.214
D1	1.4532		259.39		0.185
D2	1.4112	1.4910	261.43	59.09	0.299
D3	1.4210	1.4226	318.78	97.23	0.288
MTNI	1.4573 (1.455)		251.34 (255.6)		0.170

BDE bond dissociation energy, $-Q_{NO2}$ charge on the nitro group. The *values in parentheses* are experimental or theoretical, and are reported in [36, 45]

molecules possess detonation velocities of >9.1 km/s and pressures of >36 GPa, as computed via the Kamlet–Jacobs empirical equations. Analysis of the BDEs for the C–NO$_2$ and N–NO$_2$ bonds revealed that the aminopolynitroazole derivatives should be stable. The energetic properties of the designed molecules were compared with those of 1-methyl-2,4,5-trinitroimidazole (MTNI), and it was found that these molecules exhibit better energetic performance than MTNI.

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