

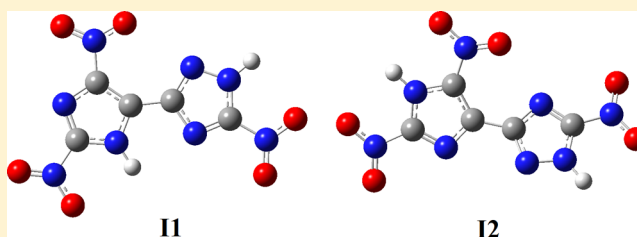
# Computational Studies on Energetic Properties of Trinitro-Substituted Imidazole–Triazole and Pyrazole–Triazole Derivatives

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**S** Supporting Information

**ABSTRACT:** Heats of formation (HOFs) for 24 designed compounds were obtained by using the density functional theory (DFT). Molecular structures were investigated at the B3PW91/6-31G(d,p) level, and isodesmic reactions were designed for calculating the gas phase heats of formation. The solid state heats of formation for designed compounds were calculated by the Politzer approach using heats of sublimation. All the designed compounds possess solid state heats of formation above 140 kJ/mol. The distance between nitro groups influences the steric and repulsive interactions. Detonation performances were evaluated by the Kamlet–Jacobs equations based on the predicted densities and solid state heats of formation, and susceptibility of decomposition was studied by the computations of bond dissociation energy (BDE). Further, the present study might provide useful information for the structure–property relationship, the laboratory synthesis of imidazole–triazole and pyrazole–triazole based nitro derivatives and the development of novel high energy materials (HEMs).



## 1. INTRODUCTION

Most explosives in military use today were developed before or during the first half of the 20th century<sup>1</sup> and huge research continue to develop the material composed of heterocycles<sup>2–7</sup> and strained rings<sup>8–11</sup> to meet the continuing need for improved energetic materials in military and civil applications. The present research is also directed toward the development of novel materials, which exhibit high safety, performance, density, and stability. Five-membered nitrogen containing heterocycles are traditional sources of energetic materials and preferred over hydrocarbon analogs due to their nitrogen content, better oxygen balance, positive heats of formation, and stability.<sup>4</sup> Imidazole, pyrazole, and triazole have the outstanding property of often combining high nitrogen content with good thermal stability due to their aromatic ring system. Literature review<sup>12–15</sup> reveals that energetic materials containing triazole ring are of multipurpose interests because the triazole system confers a high density, thermal stability, high nitrogen content, high volume of detonation products, and reduced sensitivity to impact. The performance of a nitrogen-rich heterocycle can be optimized and improved by replacing hydrogen atoms with nitro groups. Nitro compounds are an important class of HEMs and have attracted attention of researchers due to their ability to endure the high temperatures and low pressures encountered in space.<sup>16</sup> Hence, in the present work, the H atoms in azoles were systematically replaced with nitro groups. In addition, the performance of the polynitro compounds is enhanced by excellent oxygen balance, which results in a higher exothermicity of the combustion, better density, and high detonation process.

The experimental synthesis of novel materials is hazardous to humans and the environment. On the other hand, computational modeling provides an effective way to screen the promising candidate without laborious synthesis, so it has been used to design various energetic materials. Consequently, it has become an important tool to deal with the complex and large systems. The key properties of energetic materials in relation to its electronic structure are heat of formation (HOF), density ( $\rho_0$ ), detonation velocity ( $D$ ), detonation pressure ( $P$ ), and thermal stability. The performance of an energetic compound is a function of its density, oxygen balance, and HOF. Density is one of the primary factors because the detonation pressure is dependent on the square of the density and the detonation velocity is proportional to the density based on an empirical equation proposed by Kamlet and Jacobs.<sup>17,18</sup> In the present work, the detonation velocities and pressures have been calculated for a series of designed compounds using the Kamlet–Jacobs equations.<sup>17,18</sup> Densities and heats of formation necessary for computing detonation parameters are all derived from the density functional theory B3PW91 level. Bond dissociation energies are calculated for the rupture of weakest C–NO<sub>2</sub> bond in designed molecules and used to examine the initiation event and indication for the molecular stability.

The objective of the present study is to model imidazole/pyrazole–triazole based nitrogen-rich compounds that are capable of storing a large amount of energy and have better density and high detonation performance while being

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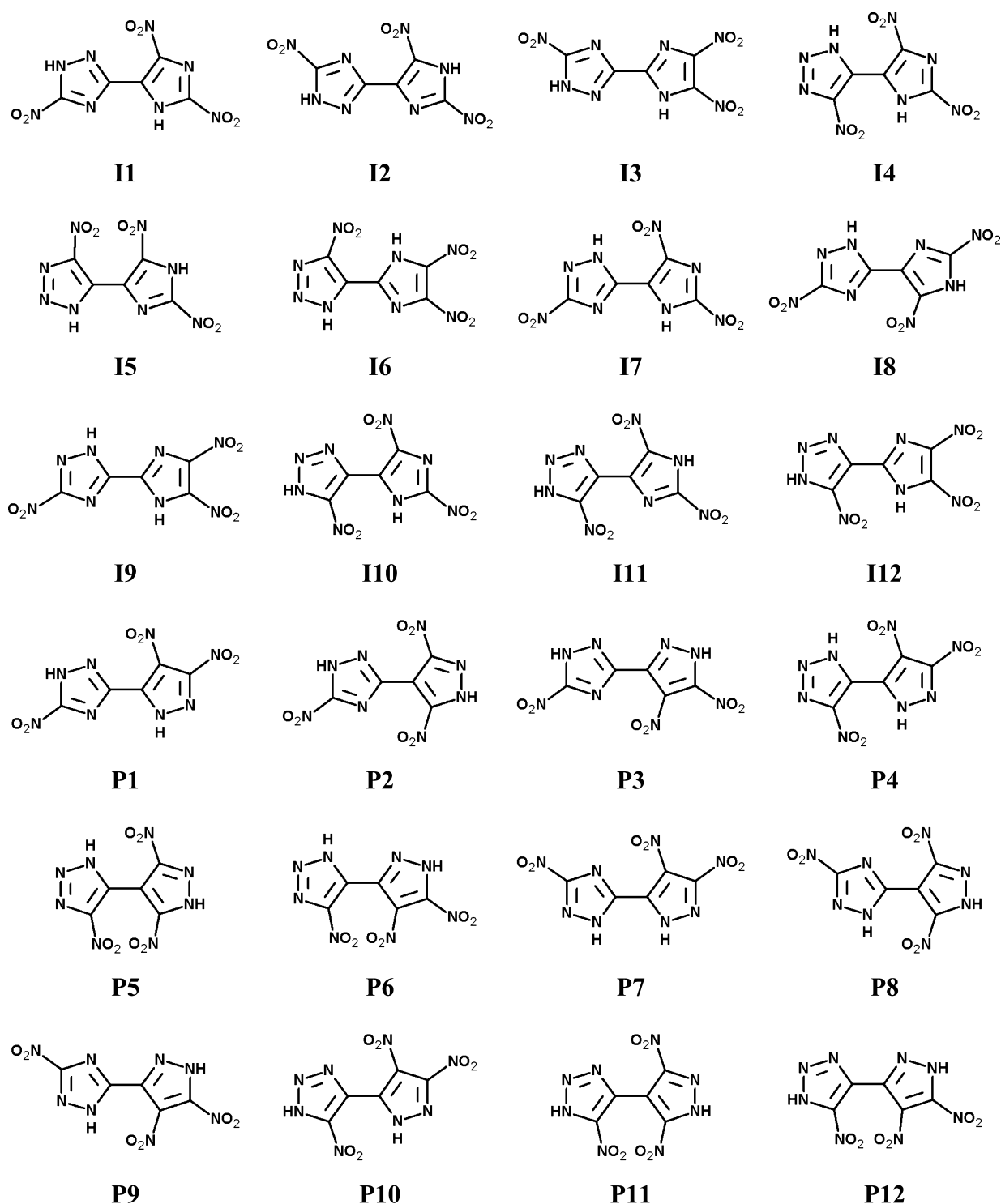


Figure 1. Molecular structure of designed imidazole/pyrazole-triazole derivatives.

sufficiently stable for potential application as HEMs. The designed compounds are presented in Figure 1. The remainder of this article is organized as follows. A brief description of computational method is given in the Computational Details followed by the Results and Discussion and a summary in the last section.

## 2. COMPUTATIONAL DETAILS

The geometries of the designed compounds were fully optimized without any symmetry restriction using density

functional theory (DFT) at the B3PW91 functional with the 6-31G(d,p) basis set in the Gaussian 03 software package.<sup>19</sup> All of the optimized structures were characterized to true local energy minima on the potential-energy surface without imaginary frequencies. HOFs of the designed compounds are needed to calculate their detonation energies. In previous studies, isodesmic reactions have been successfully employed to estimate the HOFs from the total energies obtained from ab initio calculations.<sup>20–23</sup> Therefore, isodesmic reactions are designed in which the basic structural units, imidazole, pyrazole,

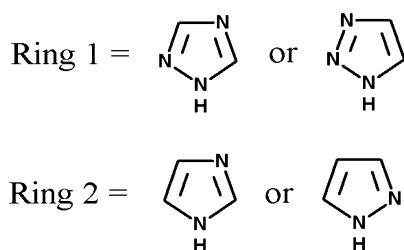
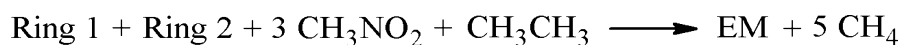


Figure 2. Designed isodesmic reaction for the prediction of gas phase HOF of designed compounds.

and triazole were retained to minimize errors. The isodesmic reaction used for the prediction of gas phase HOF ( $\text{HOF}_{\text{gas}}$ ) of designed compounds is shown in Figure 2. Table 1 lists the

Table 1. Total Energy ( $E_0$ ), Zero Point Energy (ZPE), and Thermal Correction ( $\Delta H_T$ ) at the B3PW91/6-31G(d,p) Level and Experimental  $\Delta_f H_{\text{gas}}^{\circ}$  for the Reference Compounds

compd	$E_0$ (au)	ZPE (au)	$\Delta H_T$ (au)	$\Delta_f H_{\text{gas}}^{\circ}$ (kJ/mol)
$\text{CH}_4$	-40.45976	0.0451	0.0038	-74.6 <sup>36</sup>
$\text{CH}_3\text{NO}_2$	-244.86654	0.0503	0.0052	-74.7 <sup>37</sup>
$\text{CH}_3\text{CH}_3$	-79.73010	0.0750	0.0044	-84.0 <sup>38</sup>
Imidazole	-226.06264	0.0716	0.0047	129.5 <sup>39</sup>
Pyrazole	-226.04685	0.0718	0.0047	179.4 <sup>40</sup>
1H-1,2,3-triazole	-242.07495	0.0596	0.0045	271.7 <sup>a</sup>
1H-1,2,4-triazole	-242.10068	0.0604	0.0045	192.7 <sup>40</sup>

<sup>a</sup>Values calculated using G3 calculations.

total energy ( $E_0$ ), zero point energy (ZPE), and thermal corrections ( $\Delta H_T$ ) for reference compounds used in the isodesmic reactions. For estimation of the potential performance of the energetic material, it is also significant to calculate their solid phase HOF ( $\text{HOF}_{\text{solid}}$ ) because it is related directly with the detonation characteristics. According to Hess' law, solid phase HOF can be obtained by

$$\text{HOF}_{\text{solid}} = \text{HOF}_{\text{gas}} - \text{HOF}_{\text{sub}}$$

where  $\text{HOF}_{\text{sub}}$  is the heat of sublimation and can be evaluated by the Byrd and Rice method<sup>24</sup> in the framework of the Politzer approach,<sup>25,26</sup> using the following empirical relation,

$$\text{HOF}_{\text{sub}} = \beta_1 A^2 + \beta_2 (\nu \sigma_{\text{tot}}^2)^{0.5} + \beta_3$$

where  $A$  is the area of the isosurface of 0.001 electrons/bohr<sup>3</sup> electronic density,  $\nu$  indicates the degree of balance between the positive and negative surface potentials,  $\sigma_{\text{tot}}^2$  is a measure of variability of the electrostatic potential, and  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  are determined through a least-squares with the experimental  $\text{HOF}_{\text{solid}}$  of a selected set of known materials.<sup>24</sup> Surface area, degree of balance between the positive and negative surface potentials and variability of the electrostatic potential are calculated using WFA program.<sup>27</sup> Oxygen balance (OB) is used to indicate the degree to which an explosive can be oxidized and oxygen is needed in a molecule to oxidize it completely into their gaseous reaction products. The molecule is said to have a positive (negative) oxygen balance if it contains more (less) oxygen than is needed for complete combustion. Explosophoric nitro groups are responsible for appropriate oxygen balance in explosives. OB (%) for an explosive

containing the general formula  $\text{C}_a\text{H}_b\text{N}_c\text{O}_d$  with molecular mass  $M$  can be calculated as

$$\text{OB} (\%) = \frac{(d - 2a - b/2) \times 1600}{M}$$

Knowing the geometry of a molecule, several methods can be used to predict its crystal density. Packing optimization methods are the most sophisticated ones, which build packing arrangements in various space groups. The crystal densities of all designed molecules are predicted by the molecular packing calculations using polymorph module of Material Studio Suite. The empirical Kamlet–Jacobs<sup>17,18</sup> equations were employed to estimate the values of  $D$  and  $P$  for the high energy materials containing C, H, O, and N as the following equations:

$$\begin{aligned} D &= 1.01(\text{NM}^{0.5}\text{Q}^{0.5})^{0.5}(1 + 1.30\rho_0)\text{and}P \\ &= 1.55\rho_0^2\text{NM}^{0.5}\text{Q}^{0.5} \end{aligned}$$

where  $D$  is the detonation velocity (km/s),  $P$  is the detonation pressure (GPa),  $N$  is the 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 (cal/g) defined as the difference of the HOFs between products and reactants, and  $\rho_0$  is the density of explosive (g/cm<sup>3</sup>). The C–NO<sub>2</sub> bond strength in the designed compounds is obtained by calculating the BDE, defined here as the difference between the total energy of the parent molecule and the energies of the products of the unimolecular dissociation in which an NO<sub>2</sub> group is removed.<sup>28–30</sup>

### 3. RESULTS AND DISCUSSION

Imidazole/pyrazole rings and triazoles are connected via C–C linkage and all the possible derivatives are designed. The H atoms on the imidazole/pyrazole–triazole framework are substituted with nitro groups. The predicted energetic properties of designed compounds are compared with the benchmark explosives like RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), TNT (2,4,6-trinitrotoluene), TATB (2,4,6-trinitro-1,3,5-triaminobenzene), and MTNI (1-methyl-2,4,5-trinitroimidazole).

**3.1. Heat of Formation.** The HOF is the most important parameter for experimental researchers to determine the energetic properties and energy content of a chemical system. However, it is impractical to determine the HOFs of novel energetic materials because of their unstable intermediates and unknown combustion mechanism. Unfortunately, no experimental HOFs are available for the designed compounds in the literature. The solid phase HOFs of the designed compounds have been obtained through application of the Politzer

**Table 2.** Calculated Total Energy ( $E_0$ ), Zero Point Energy (ZPE), and Thermal Correction ( $\Delta H_T$ ) at the B3PW91/6-31G(d,p) Level and Molecular Surface Properties of Designed Compounds, RDX, TNT, TATB, and MTNI

compd	$E_0$ (au)	ZPE (au)	$\Delta H_T$ (au)	HOF <sub>gas</sub> (kJ/mol)	A ( $\text{\AA}^2$ )	$\sigma_{\text{tot}}^2$ (kJ/mol)	$\nu$	HOF <sub>sub</sub> (kJ/mol)
I1	−1080.23276	0.1201	0.0158	265.57	240.59	1188.34	0.182	126.73
I2	−1080.21260	0.1199	0.0158	318.50	242.29	1029.98	0.142	118.85
I3	−1080.21078	0.1200	0.0159	323.28	243.52	1264.15	0.157	126.21
I4	−1080.20415	0.1194	0.0154	352.15	233.22	771.45	0.153	109.88
I5	−1080.19022	0.1198	0.0157	388.73	234.66	1402.27	0.154	123.57
I6	−1080.19541	0.1197	0.0157	375.09	237.18	939.02	0.127	112.17
I7	−1080.22719	0.1204	0.0156	280.20	239.39	929.56	0.147	115.91
I8	−1080.21580	0.1200	0.0158	310.11	241.23	1315.32	0.203	132.65
I9	−1080.21540	0.1202	0.0159	311.15	243.56	1155.75	0.117	118.00
I10	−1080.18920	0.1195	0.0157	391.39	236.35	1278.17	0.168	124.36
I11	−1080.18839	0.1196	0.0157	393.53	235.43	1110.10	0.141	116.61
I12	−1080.18683	0.1195	0.0157	397.63	237.69	1279.43	0.173	125.74
P1	−1080.18889	0.1204	0.0159	387.24	239.83	1319.72	0.153	124.69
P2	−1080.19019	0.1202	0.0158	383.80	240.31	1156.46	0.129	118.18
P3	−1080.18519	0.1200	0.0159	396.92	240.60	1126.21	0.126	117.39
P4	−1080.17381	0.1198	0.0154	438.25	231.28	788.64	0.141	107.82
P5	−1080.16838	0.1202	0.0156	452.52	228.64	1340.85	0.163	120.75
P6	−1080.16093	0.1199	0.0157	472.08	233.96	1272.61	0.173	123.68
P7	−1080.19695	0.1206	0.0157	366.06	237.26	980.02	0.131	113.53
P8	−1080.19100	0.1203	0.0157	381.67	236.71	1399.72	0.181	128.83
P9	−1080.18564	0.1201	0.0161	395.74	241.55	1444.74	0.162	129.26
P10	−1080.16325	0.1197	0.0158	465.99	234.65	1338.75	0.154	122.38
P11	−1080.16614	0.1199	0.0157	458.40	232.45	1188.09	0.124	113.74
P12	−1080.15783	0.1196	0.0159	480.23	236.93	1157.75	0.127	116.20
RDX	−896.93186	0.1440	0.0134	179.95 (191.62) <sup>31</sup>	197.84	756.26	0.1763	95.14
TNT	−884.89498	0.1365	0.0144	27.19 (24.06) <sup>41</sup>	216.52	393.67	0.2177	95.10 (104.60) <sup>42</sup>
TATB	−1011.30595	0.1601	0.0156	−108.45	219.80	464.09	0.2494	102.67 (168.07) <sup>43,44</sup>
MTNI	−878.53971	0.1076	0.0138	161.97 (173.4) <sup>45</sup>	199.58	809.52	0.1814	97.86

approach as outlined in Computational Details. Table 2 summarizes the total energies, the zero-point energies, and the values of the thermal correction for the designed compounds. The calculated HOF<sub>solid</sub> of the designed compounds are listed in Table 3. According to the data in Table 3, the HOFs are all found to be positive values, which is one of the necessary characteristics of energetic materials and can be considered as endothermic materials. In general, the higher the HOF, the greater the energy content of the molecule. From Table 1, it can be seen that the energy contribution from the 1,2,3-triazole is more than the 1,2,4-triazole; therefore, among the imidazole–triazole (I1–I12) isomers, I4, I5, I6, I10, I11, and I12 shows higher HOF than I1, I2, I3, I7, I8, and I9. A similar trend is observed in pyrazole–triazole (P1–P12) isomers. In the imidazole–triazole derivatives, I11 has the largest HOF value (276.9 kJ/mol); however, P12 possesses the highest HOF (364.0 kJ/mol) among the pyrazole–triazole derivatives. It is also notable that the HOFs of designed isomers with the same number of nitro groups are affected by the positions of C–C linkage in imidazole/pyrazole and triazole rings. From Table 1, it can also be noticed that energy contribution from pyrazole is higher than that of imidazole and hence all the pyrazole–triazole derivatives possess higher HOFs than corresponding imidazole–triazole derivatives. In pyrazole–triazole derivatives, the isomers in which pyrazole ring connected to 1,2,4-triazole at C3 position (P1–P3) have slightly higher HOFs than the pyrazole ring connected to 1,2,4-triazole via the C5 position (P7–P9). Similarly, the isomers in which the pyrazole ring connected to 1,2,3-triazole at the C4 position (P10–P12) have slightly

higher HOFs compared to isomers with the pyrazole ring connected to 1,2,3-triazole at the C5 position (P4–P6). As is evident in Table 3, the calculated HOFs of the RDX, TNT, TATB, and MTNI are comparable with the available experimental values. The overall study reveals that, compared to the HOFs of RDX, TNT, TATB, and MTNI, the presence of nitrogen-rich azole rings in designed compounds dramatically increases the HOF.

**3.2. Density.** Density is the crucial factor for the prediction of the performance and high density also desirable in terms of the amount of material who can be packed into volume-limited warhead or propulsion configurations. The CVFF force field has been used to predict the densities. Table 3 lists the calculated densities for the designed compounds. The densities for designed compounds have been found to be in the range of 1.79–1.88 g/cm<sup>3</sup>. Among the designed compounds, the molecules I5 and P3 show the lowest density (1.79 g/cm<sup>3</sup>) whereas P12 shows the highest density of about 1.88 g/cm<sup>3</sup>. The presence of nitro groups and N–H in the molecular framework increases the opportunity for hydrogen bonding and may responsible for the better densities in the designed compounds. The repulsion associated in the adjacent and close vicinity nitro groups affects the molecular orientation in space, and hence, molecules I5 and P3 exhibit lower densities. However, though P12 possesses adjacent nitro groups in the molecular framework, their orientation perpendicular to each other reduces the repulsion and the presence of a neighboring N–H proton enhances intramolecular hydrogen bonding. Replacement of 1,2,4-triazole with 1,2,3-triazole or imidazole with pyrazole does not show a great effect on the density. The

Table 3. Calculated Energetic Properties of Designed Compounds, RDX, TNT, TATB, and MTNI

compd	OB (%)	HOF <sub>solid</sub> (kJ/mol)	$\rho_0$ (g/cm <sup>3</sup> )	D (km/s)	P (GPa)	Q (cal/g)	R–NO <sub>2</sub> (Å)	BDE (kJ/mol)
I1	−29.6	138.84	1.85	8.09	29.50	826.15	1.4495	312.54
I2	−29.6	199.65	1.84	8.19	30.11	879.98	1.4480	278.93
I3	−29.6	197.07	1.80	8.05	28.78	877.70	1.4566	259.11
I4	−29.6	242.27	1.81	8.18	29.76	917.71	1.4501	275.72
I5	−29.6	265.16	1.79	8.16	29.42	937.97	1.4486	276.64
I6	−29.6	262.92	1.87	8.41	32.08	935.99	1.4564	258.52
I7	−29.6	164.29	1.85	8.14	29.90	848.68	1.4598	278.01
I8	−29.6	177.46	1.83	8.11	29.45	860.34	1.4600	279.81
I9	−29.6	193.15	1.80	8.05	28.72	874.23	1.4601	277.67
I10	−29.6	267.03	1.81	8.23	30.11	939.63	1.4564	259.72
I11	−29.6	276.92	1.83	8.31	30.92	948.38	1.4491	277.97
I12	−29.6	271.89	1.86	8.39	31.87	943.93	1.4574	257.78
P1	−29.6	262.55	1.86	8.38	31.73	935.66	1.4513	264.23
P2	−29.6	265.63	1.85	8.35	31.44	938.39	1.4542	273.98
P3	−29.6	279.53	1.79	8.19	29.62	950.69	1.4544	263.78
P4	−29.6	330.43	1.87	8.54	33.09	995.75	1.4593	253.89
P5	−29.6	331.77	1.85	8.48	32.40	996.94	1.4501	281.23
P6	−29.6	348.40	1.85	8.51	32.64	1011.66	1.4473	276.61
P7	−29.6	252.53	1.87	8.39	31.92	926.79	1.4599	243.64
P8	−29.6	252.84	1.80	8.17	29.58	927.07	1.4616	253.51
P9	−29.6	266.48	1.81	8.22	30.10	939.14	1.4599	279.32
P10	−29.6	343.61	1.87	8.56	33.28	1007.42	1.4585	263.43
P11	−29.6	344.66	1.82	8.40	31.54	1008.35	1.4525	279.18
P12	−29.6	364.03	1.88	8.64	33.94	1025.49	1.4494	264.92
RDX	−21.6	93.17 (79.08) <sup>46</sup>	1.80 (1.82) <sup>46</sup>	8.79 (8.60) <sup>46</sup>	34.29 (33.92) <sup>46</sup>	1138.50	1.4109	164.13 (141.25) <sup>49</sup>
TNT	−74.0	−68.82 (−67.36) <sup>47</sup>	1.65	7.21 (6.94) <sup>48</sup>	22.49 (22.0) <sup>48</sup>	1043.79 (1010.02) <sup>48</sup>	1.4752	252.38 (246.44) <sup>50</sup>
TATB	−56.0	−211.12 (−154.39) <sup>47</sup>	1.89	8.13 (8.11) <sup>46</sup>	30.17 (31.10) <sup>46</sup>	972.22	1.4267	305.59 (290.37) <sup>50</sup>
MTNI	−25.7	64.11	1.82 (1.78) <sup>46</sup>	8.60 (8.80) <sup>46</sup>	33.06 (34.66) <sup>46</sup>	1112.89	1.4526	254.82

arrangement of nitro groups in the molecular skeleton allows other molecules to pack closely in the cell and increases the chances for inter and intra molecular hydrogen bonding. Overall, the presence of nitrogen-rich azole rings and nitro groups are essential to improve the density.

**3.3. Detonation Performance.** Two key measures of explosive performance are the detonation velocity ( $D$ ) and the detonation pressure ( $P$ ). These refer to the stable velocity of the shock front that characterizes detonation and the stable pressure that is developed behind the front, respectively.<sup>17,18</sup> Kamlet–Jacobs equations clearly indicate the importance of the density as a determinant of detonation parameters; it appears to a higher power in each equation than do any of the other quantities. Table 3 reports the chemical energy of detonation, that is, the energy released in the process of detonation. The chemical energies of detonations for designed compounds composed of three nitro groups are above 972 kJ/mol indicate that the energetic densities of these derivatives are large. Among the designed compounds, **P4–P6** and **P10–P12** have chemical energy of detonation over 1100 kJ/mol. The chemical energy of detonation of 1,2,3-triazole derivatives are found to be larger than the corresponding 1,2,4-triazole derivatives. Predicted detonation properties for RDX, TNT, TATB, and MTNI are in good agreement with experimental results. The performance of nitro derivatives is better due to the higher densities and oxygen balance (OB), which increases the concentration of detonation products like CO, CO<sub>2</sub>, and H<sub>2</sub>O. In the present study, the designed compounds composed only of the atoms C, H, N, and O and hence, N<sub>2</sub>(g), H<sub>2</sub>O(g), CO<sub>2</sub>(g), and C(s) are assumed as important detonation products, explained by Kamlet et al.<sup>17,18</sup> and Politzer and

Murray.<sup>31</sup> Furthermore, assuming the detonation product composition to be N<sub>2</sub>(g)/H<sub>2</sub>O(g)/CO<sub>2</sub>(g)/C(s) gives overall quite satisfactory results for CHNO-based energetic compounds using an H<sub>2</sub>O–CO<sub>2</sub> arbitrary decomposition scheme. In addition, all the designed compounds possess oxygen balance (OB) −29.6%, where OB is the percentage of oxygen chemically bound in a molecule to oxidize it completely. Oxygen is needed for the conversion of explosives into their gaseous reaction products, such as CO<sub>2</sub>, CO, H<sub>2</sub>O, etc. available within the molecule. Compounds **I6**, **P4–P6**, **P10**, and **P12** show detonation velocity higher than 8.4 km/s and pressure over 32 GPa. **P12** ( $D$  = 8.64 km/s,  $P$  = 33.94 GPa) possess a detonation performance comparable to that of RDX ( $D$  = 8.60 km/s,  $P$  = 33.92 GPa) and MTNI ( $D$  = 8.60 km/s,  $P$  = 33.06 GPa). As observed, designed compounds exhibit better detonation performance than the TNT ( $D$  = 7.21 km/s and  $P$  = 22.49 GPa) whereas most of the designed compounds show higher performance than TATB ( $D$  = 8.13 km/s and  $P$  = 30.17 GPa). The predicted detonation velocities and pressures for most of the designed compounds are much larger than that of TATB and found comparable to those of RDX and MTNI, indicating that selective designed compounds could also be used as energetic compounds.

**3.4. Bond Dissociation Energy.** The strength of a chemical bond is expressed in terms of bond dissociation energy (BDE) and is one of the most important thermochemical properties of explosive molecules, useful for the indication of molecular stability and decomposition mechanism. Further, stability or sensitivity of energetic material depends on temperature, nature of materials, and explosives in the molecular structure.<sup>32</sup> A systematic study of this quantity



should be useful in understanding initiation events. The initial stages in thermal decompositions of energetic materials can be assumed on the basis of the BDEs. In general, the larger the BDE value of the C–NO<sub>2</sub> bond breaking is, the higher the stability will be. Thus, the calculated BDE for removal of the NO<sub>2</sub> group can be used to index the relative strength of the compounds composed of nitro substituents. However, this is only applied to the molecules in which the R–NO<sub>2</sub> (R = C, N, or O) bond is the weakest. Compared with the BDE of the commonly used explosive RDX (~164 kJ/mol), all of the designed compounds have higher BDE values (>250 kJ/mol). In addition, TATB is found to be more stable (305.59 kJ/mol) due to presence of three amino groups which strengthens the C–NO<sub>2</sub> bonds via electron donating effect and strong hydrogen bonding. The designed compounds show comparable BDEs of C–NO<sub>2</sub> bond comparable to TNT (252.38 kJ/mol) and MTNI (254.82 kJ/mol). This implies that they have good C–NO<sub>2</sub> bond strength and may be attributed to the aromatic skeleton and the intramolecular hydrogen bonding. The results also reveal that the position of nitro groups in the structure has strong influences on the BDE. It is worthy of note that the adjacent nitro groups or closer the distance between C–NO<sub>2</sub> groups, BDE is less for the pyrolysis. Changing theazole rings in the backbone does not show significant variation in the BDEs. Previous studies<sup>33–35</sup> have reported that a compound could be considered as a practical energetic material if it has BDEs more than ~84 kJ/mol. However, this is only marginally sufficient to make the compound metastable; and it would have preferable stability if BDE > ~126 kJ/mol. According to this, it can be deduced that the designed compounds have sufficient energy barrier against the removal of –NO<sub>2</sub> group and are stable enough for use.

#### 4. CONCLUSIONS

Electronic structures of the designed compounds have been studied using the density functional theory at the B3PW91/6-31G(d,p) level. The gas phase HOF of designed compounds have been computed by designing appropriate isodesmic reactions and the solid phase HOF predicted from the heat of sublimation in the framework of the Politzer approach. Results revealed that all the designed compounds possess high positive HOFs due to the presence of five memberedazole rings. The detonation velocity and pressure have been calculated using Kamlet–Jacobs method from the predicted densities and solid phase HOFs. It is found that designed compounds show detonation velocity about 8.0 km/s, and detonation pressure of 30 GPa. The designed compounds are expected to be stable for C–NO<sub>2</sub> bond rupture as judged by the BDE values larger than that of RDX and comparable to those of TNT and MTNI. These compounds present good performance and are worthy of synthesis and further investigation. The predicted results for 24 derivatives also expected to provide some useful information for the molecular design of novel HEMs.

#### ■ ASSOCIATED CONTENT

##### ■ Supporting Information

Tables S1–S24 contains the structural parameters of the designed molecules. Table S25 lists the thermodynamic properties of designed molecules. Table S26 contains total energies of designed compounds and their corresponding radicals used in the calculation of bond dissociation energies. The details of electrostatic potential theory are summarized in

the last section. Full ref 19. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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##### Notes

The authors declare no competing financial interest.

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