


# The coplanar family of bis(nitrotriazoles) tetrazine and oxides based as energetic compounds

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## Abstract

Searching for energetic materials that balance detonation performance with sensitivity is an enduring ambition in the evolution of high-energy density materials (HEDMs). The coplanar molecular structures of energetic compounds have a powerful impact on performance. Novel compounds of bis(nitrotriazoles) tetrazine (BNTT) were designed and investigated by density functional theory methods. The coplanar BNTT's oxides were a highlight in molecules with superior performance and acceptable sensitivities. Results showed that all these designed compounds possess high densities, positive heats of formation, remarkable detonation performance, and acceptable impact sensitivity. In particular, B1-3 possessed higher density ( $\rho = 1.97 \text{ g cm}^{-3}$ ) and exhibited good balance between detonation performance ( $Q = 1779.83 \text{ cal g}^{-1}$ ,  $D = 9.48 \text{ km s}^{-1}$ ,  $P = 42.01 \text{ GPa}$ ) and sensitivity ( $h_{50\%} = 28 \text{ cm}$ ) than trinitroperhydro-1,3,5-triazine (RDX). The theoretical study demonstrated that all designed compounds possess acceptable sensitivity. They were seen as the potential candidates of HEDMs.

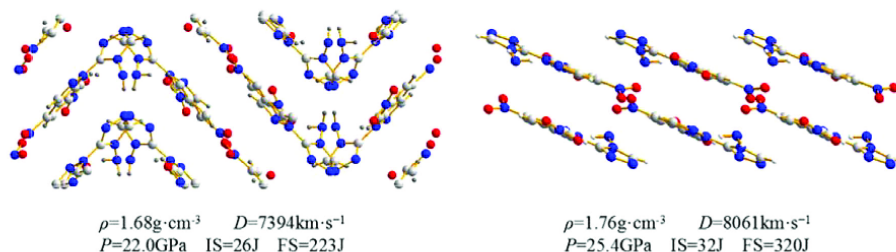
## KEYWORDS

bis(nitrotriazoles) tetrazine, coplanar structure, detonation properties, molecular design

## 1 | INTRODUCTION

In the process of designing and synthesizing high-energy density materials (HEDMs), it was found that compounds with a planar structure can reduce sensitivity.<sup>[1,2]</sup> The compounds had high density, good detonation performance, and low sensitivity<sup>[3]</sup> due to the planar structure. Polycyclic nitrogen-rich heterocycles<sup>[4]</sup> (such as tetrazole,<sup>[5]</sup> triazole,<sup>[6]</sup> tetrazin<sup>[7]</sup>) were often the subject of research and demonstrated good detonation performances. Safety was the most critical area of attention of energetic materials. Research<sup>[8-11]</sup> found that planar molecules improved detonation performance while ensuring sensitivity, which is equivalent to reducing sensitivity. Jie tang<sup>[12]</sup> believed that the coplanar structure that exhibits face-to-face stacking obviously improved in density, heat of formation, detonation performance, and sensitivity.  $\beta$ -3 showed the coplanar

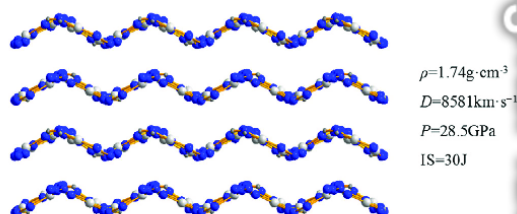
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**FIGURE 1** Single-crystal structures of  $\alpha$ -3(left) and  $\beta$ -3(right)



**FIGURE 2** The structures of Fanion (A) and Tanion (B) and FTanion (C)



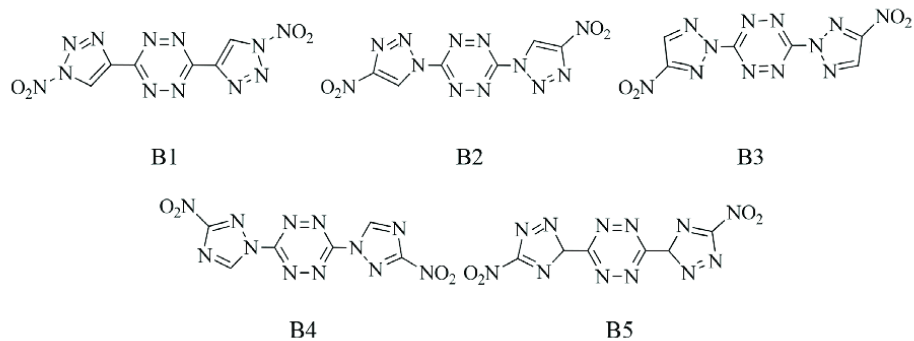
**FIGURE 3** The parallel crystal stacking

structure in Figure 1, which possessed better detonation properties and sensitivities. Previous studies showed that the planar structure reduces "hotspots" caused by sliding arising from an external mechanical force.

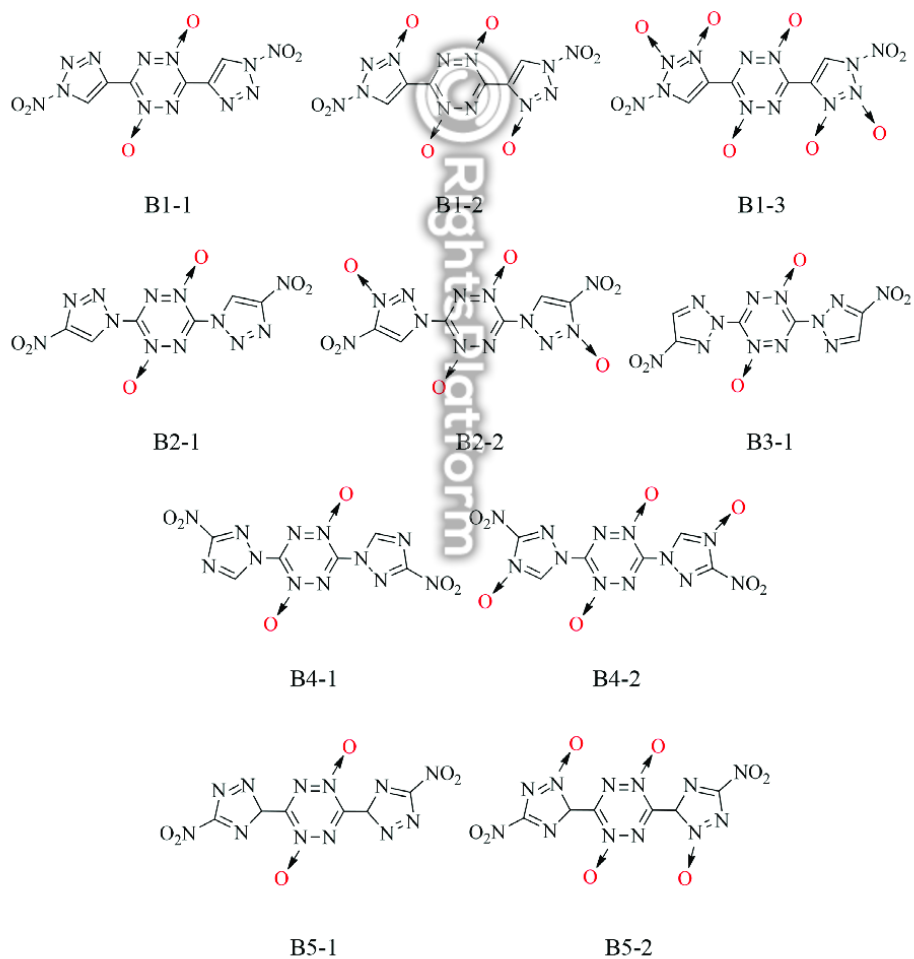
Tang,<sup>[13]</sup> found that dinitromethyl group of the Fanion structure (a, 3-nitramino-4-dinitromethyl-furazanate) and Tanion structure (b, 3-nitramino-5-dinitromethyl-1,2,4-triazolate) were twisted out of the plane of the central ring which were shown in Figure 2. However, when the triazole and furazan rings combined in the same molecule (c, 3-(dinitromethanide)-1H-[1,2,4-triazol-5-yl]-4-nitraminofurazanate), the dinitromethyl group substituents were nearly coplanar with the rings (FTanion, a planar anion). Results showed that the highly distorted structures of Fanion and Tanion, the planar molecules or anions (FTanion), lead to lower sensitivities. The energetic salts based on the coplanar FTanion were less impact-sensitive (at 20–32 J) than those based on the Fanion or Tanion. The friction sensitivities of FTanion were also greater than 360 N.

Due to the  $\pi$ - $\pi$  interaction<sup>[14,15]</sup> and hydrogen bonding,<sup>[16,17]</sup> the orderly stacked derivative compounds had a significant improvement in face-to-face accumulation, density, formation heat, detonation performance, and sensitivity. Jie Tang<sup>[18]</sup> believed that the intramolecular cyclization reaction of pyridohydrazole optimized the molecular structure to a certain extent and improved the detonation preference and stability of corresponding high-energy materials. Peter Politzer<sup>[19]</sup> also thought that compounds with planar molecular structure were helpful for the exploration of new HEDM. Ping Yin<sup>[20]</sup> reported that polynitro-functionalized dipyrazolo-1,3,5 triazines with nearly planar backbones enhanced the density and thermal stability. These contributions confirmed the potential energetic backbone of planar structure and provided a new thinking on the chemistry of polycyclic heterocycles.

Recently, the Shreeve group<sup>[21]</sup> observed that energetic materials with parallel face-to-face crystal stacking (Figure 3) showed higher densities and relative low sensitivities because of  $\pi$ -stacked interaction and free interlayer sliding. From a molecular design perspective, the planar structure, which increased the density and thermal stability, became a promising strategy to generate new insensitive energetic materials.



**SCHEME 1** Newly designed series of bis(nitrotriazoles) tetrazine



**SCHEME 2** The series of bis(nitrotriazoles) tetrazine oxide

Based on the statements above, we aimed to design high-performance insensitive materials that have the following structure characteristics: (a) polycyclic nitrogen-rich heterocycles with good detonation performances; (b) the near-coplanar molecular structure with face-to-face stacking to achieve a high density; and (c) the high contents of nitrogen and oxygen that lead to high heat of formation and good oxygen balance. Thus, this work attempted to design a series of bis(nitrotriazoles) tetrazine (BNTT). The five novel compounds are reported in Scheme 1.

Related oxides based on BNTT were also designed, which added two, four, and six N–O bonds to them, named BNTT's oxides (Scheme 2). The molecules ensured coplanar structures and increased the oxygen balance. We achieved density functional theory (DFT) and volume-based thermodynamics calculations to select energetic compounds of low sensitivity.

## 2 | COMPUTATIONAL DETAILS

To verify the basis set we used, the geometries optimization of the single-crystal structure (3,3'-dinitro-5,5'-bitriazole) was calculated using B3LYP/6-311++G\*, 6-311G\*, 6-311+G\* and MPW1b95/6-31+G\*. The results are listed in Supporting Information. B3LYP/6-311+G\* was believed to be the best method for the theoretical study of bitriazole compounds. The structure optimizations of BNTT compounds used the hybrid DFT-B3LYP method with the 6-311+G\* basis set. All the calculations involved in this work were carried out using the Gaussian 09 suite of programs.<sup>[22]</sup>

All optimized structures were determined to be the local energy minima on the potential energy surface without imaginary frequencies. The HOMO-LUMO orbitals, electronic density and electrostatic potential (ESP), and thermodynamic parameters were calculated at the same level of theory based on the optimized gas-phase structures. Heat of formation is the most important parameter for energetic compounds. Atom-equivalent schemes converted quantum mechanical energies to heats of formation of molecules in terms of Equation (1).<sup>[23,24]</sup> Based on the ESP of molecule through quantum mechanical prediction, the enthalpy of sublimation or vaporization can be represented as<sup>[25,26]</sup>

$$\text{HOF}(g) = E(g) - \sum_i n_i x_i \quad (1)$$

The density, as another important parameter of energetic material, was obtained using an improved equation proposed by Politzer considering intermolecular interactions within the crystal,<sup>[27]</sup> where  $V(0.001)$  is the volume in  $\text{cm}^3/\text{molecule}$  and is encompassed by the 0.001 au contour of the electronic density;  $M$  is the molecular mass in  $\text{g}/\text{molecule}$ ;  $\nu\sigma_{\text{tot}}^2$  is derived from the molecular ESP calculation; and  $\alpha$ ,  $\beta$ , and  $\gamma$  are coefficients assigned through fitting Equation (2) to the experimental densities of the series BMNT compounds.

$$\rho = \alpha \left( \frac{M}{V(0.001)} \right) + \beta (\nu\sigma_{\text{tot}}^2) + \gamma \quad (2)$$

The critical detonation parameters of energetic compounds, including the detonation velocity and pressure, were estimated by Empirical Kamlet-Jacob equations as Equations (3) and (4).<sup>[28]</sup> Due to the sensitivities of explosives, Rice and Hare<sup>[29]</sup> used the statistical parameters of surface potentials and the property structure relation method to predict  $h_{50\%}$  of explosives using Equation (5). Impact sensitivity was noted to closely correlate with the explosives properties.<sup>[30,31]</sup>

$$V = 1.01 \left( N \bar{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30 \rho_0) \quad (3)$$

$$P = 1.558 \rho_0^2 N \bar{M}^{1/2} Q^{1/2} \quad (4)$$

$$h_{50\%} = 27.8 + 0.1135 \times \exp[-(2.6479 \text{ g/kJ} \times [Q_d - 6.9496 \text{ kJ/g}])] \quad (5)$$

where  $V$  is detonation velocity ( $\text{km s}^{-1}$ ), and  $P$  is detonation pressure (GPa);  $N$  is moles of detonation gases per gram explosive, and  $\bar{M}$  is the average molecular weight of these gases;  $Q$  is heat of detonation ( $\text{cal g}^{-1}$ );  $\rho$  is replaced by the theoretical density ( $\text{g cm}^{-3}$ ); and  $Q_d$  is heat of detonation.

## 3 | RESULTS AND DISCUSSION

The calculation results of BNTT and BNTT's oxides were discussed, including molecular structure, electronic structure, bond-dissociation energy (BDE), and physicochemical and energetic properties. Comparing these properties of BNTT and their oxides could find the potential candidates of HEDMs.

### 3.1 | Molecular structure

In Schemes 1 and 2, the BNTT and its oxides' molecular structures were designed. BNTT compounds were formed by different forms of bis(nitrotriazoles) with bridged tetrazine, while BNTT's oxides were composed of N—O bonds and ensure coplanar structures. The optimized geometry structures of BNTT and BNTT's oxides were shown in Supporting Information. All molecular structures were coplanar and possessed a symmetric structure.

The lengths of C—N and C=N bonds of the 1,2,3-triazole ring skeleton in B1 to B3 ranged from 1.35 to 1.38 Å, and the lengths of N—N bonds ranged from 1.30 to 1.37 Å. Although both were triazoles, the structures were slightly different. The lengths of C—N and C=N bonds of the 1,2,4-triazole ring skeleton in B4 and B5 ranged from 1.30 to 1.37 Å, and the lengths of N—N bonds were about 1.35 Å. The lengths of N—N bonds of the tetrazine ring were about 1.31 Å, and the lengths of C—N and C=N bonds of the tetrazine ring were about 1.34 Å. At the same time, tetrazine structure had excellent symmetry. The nitro groups were attached to the triazole ring with a bond length of 1.45 to 1.47 Å. The lengths of N—O bonds were always maintained at 1.21 Å.

When adding oxygen atom to the rings, the bond lengths had some changes. The bond lengths of the nitrogen atom, which added the oxygen atom, with the adjacent atom became longer. If N—O bonds were added to the tetrazine ring, it had no effect on the bond length of the triazole ring. While N—O bond added to the triazole ring, it did not have much effect on the bond length of the tetrazine ring and had a slight effect on the adjacent nitro group. Comparing the N—O bonds length of the single-crystal structure compounds<sup>[32–34]</sup> (CCDC: 971681; CCDC: 1822383; CCDC: 1439832) with the designed BNTT's oxides structures, changes were found to be consistent with the theory of heterocyclic structure. The data of N—O length were listed in Supporting Information.

The bond angles (C1—N1—C2 and N2—N3—C2) of the triazole ring skeleton varied between 101° and 109°, and the bond angles (C3—N4—N5 and N5—C4—N6) of the tetrazine ring skeleton varied between 117° and 124°, which fitted the range of the ring bond. While adding an oxygen atom did not have much effect on the bond angles of molecular structures, the addition of nitro group gained the explosive property of BNTT. Undoubtedly, the coplanar structure increased the density, improved the molecular stability, and boosted the detonation performance.

### 3.2 | Electronic structure

The HOMO-LUMO orbitals and ESP were explored, which aimed at analyzing substantial electronic structures and properties of these compounds. However, it was believed that HOMO-LUMO gap values suggested a reactivity approximation. The HOMO-LUMO orbitals of BNTT and BNTT's oxides, including the energy gap, were represented in Figure 4, in which the positive phase is red and the negative phase is green. The following situations were found by analyzing the data:

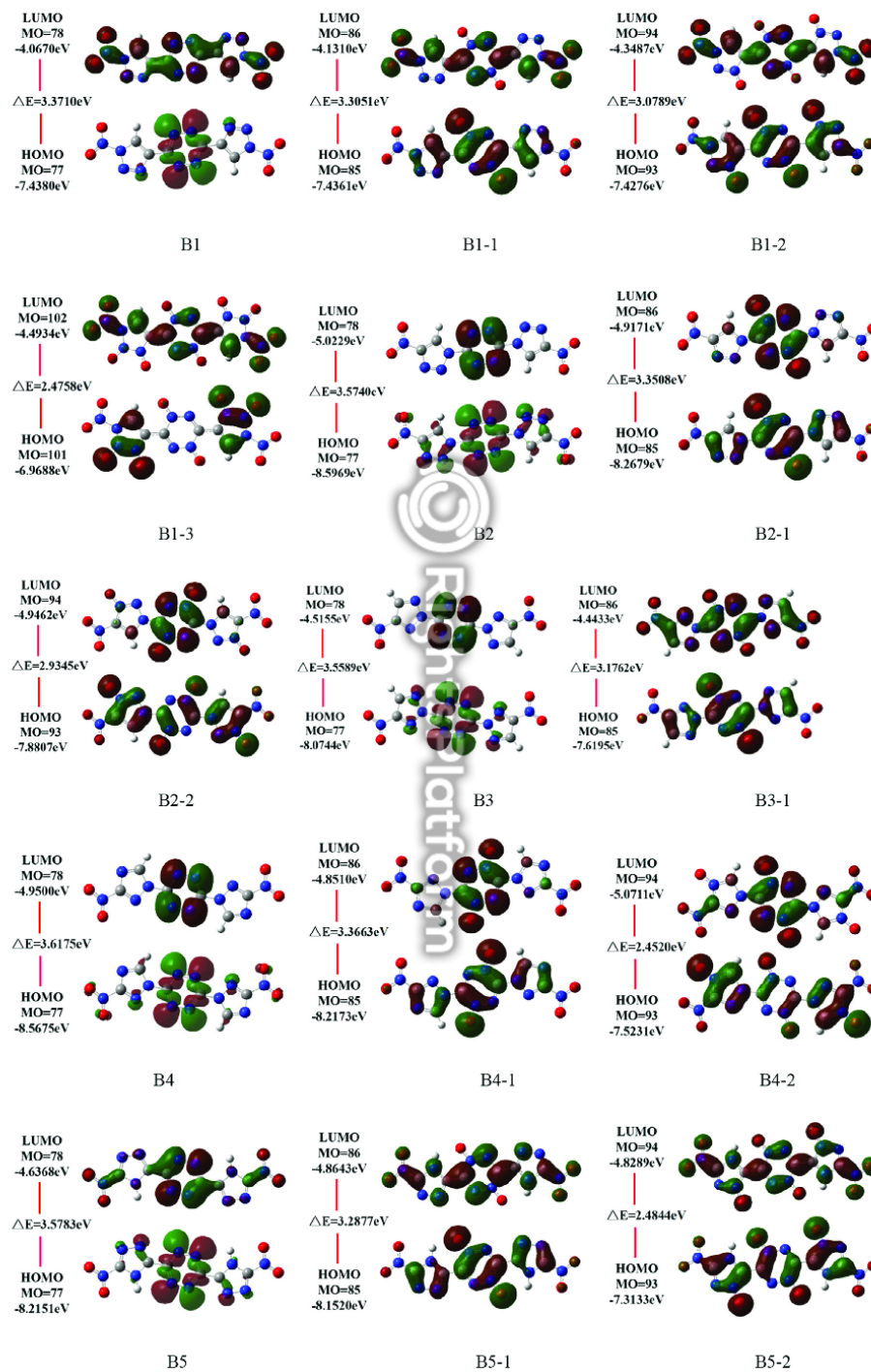
1. When the N—O bond was not added to BNTT, the LUMOs of B2, B3, and B4 merely occupied the tetrazine ring, but the HOMOs mainly occupied the tetrazine ring and part of the bistriazole rings. While the LUMOs of B1 and B5 were scattered almost over the entire molecular plane, the HOMOs of B1 and B5 were relatively scattered over a smaller area and mainly focused on the tetrazine ring.
2. When N—O bonds were added to BNTT, the LUMOs of BNTT's oxides contributed more to the corresponding oxygen positions and did not change much compared with BNTT. This indicated that the parent rings interact mainly with the HOMO orbital. The HOMOs gradually expanded to bistriazole rings and the nitro group, and the electron density also gradually increased. This showed that the N—O bonds interacted predominately with the LUMO orbital.
3. The values of energy separation between the HOMO and LUMO of BNTT ranged from 3.37 to 3.61 eV, which was relative to a comparably stable range. As the oxygen content gradually increased, the value of energy separation between the HOMO and LUMO gradually decreased.

The quantitative molecular surface analysis was performed using the Multiwfn program.<sup>[35]</sup> These ESP maps on the molecular surface easily perceived a visual representation of the intermolecular interaction and chemical reactivity sites.<sup>[30]</sup> The positive and negative potentials were delocalized inside and outside the rings, which the blue and red colors represent, respectively, in Figure 5.

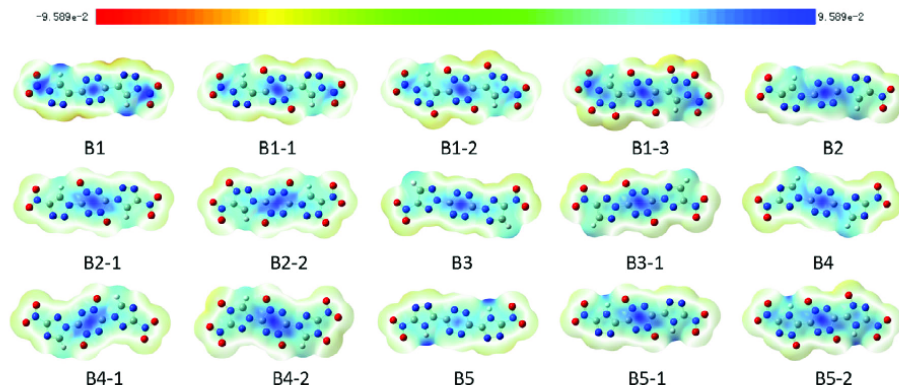
The deeper the blue, the more positive the potentials, which were between  $-0.09589$  and  $0.09589$  au. They mostly distributed close to tetrazine ring. According to the evidence, these positions demonstrated positive potential, which indicated that the ESP was dominated by nuclear charge and may react with a nucleophile. Among them, the ESP near the tetrazine ring was higher than the bistriazole ring. Hence, the nucleophiles could easily attack the tetrazine ring of BNTT and oxides and part of the nitro group of B1 and B1-2. As can be seen, the negative potential areas appear to be fewer, which may indicate that BNTT and BNTT's oxides are more likely to have nucleophilic reactions.

The quantitative molecular surface analysis is given in Figure 6, performed using the Multiwfn program.<sup>[35]</sup> It can be seen that there are more positive ESP areas than negative areas, which meant a nucleophilic reaction. The ESP histograms displayed an approximate inverted "U" type. The





**FIGURE 4** The HOMO-LUMO orbitals of bis(nitrotriazoles) tetrazine (BNTT) and BNTT's oxides



**FIGURE 5** Molecular electrostatic potential of bis(nitrotriazoles) tetrazine (BNTT) and BNTT's oxides

biggest negative areas were about  $-20$  to  $-10$  kcal/mol, which could be due to the weak influence of electron-withdrawing groups ( $-\text{NO}_2$ ). At the same time, the biggest positive areas were around  $20$  to  $30$  kcal/mol.

### 3.3 | Bond-dissociation energy

BDE is a powerful physical quantity for predicting the thermal stability of compounds, especially nitrogen-rich energetic compounds. Dissociation of bond with the lowest BDE value was presumed to be the first step in the molecule decomposition; thus, this BDE value provided the stability of this compound. The smaller the value, the weaker the bond and the more unstable the compound. This meant that the compound which had relatively better thermal stability can be experimentally synthesized. Therefore, in order to predict the experimental viability of the related BNTT and BNTT's oxides, the BDEs of the corresponding C—NO<sub>2</sub> and N—NO<sub>2</sub> bonds were studied.

The BDEs of BNTT and BNTT's oxides were presented in Table 1. Most compounds had a higher BDE than CL-20, except B1-1, B1-2, and B1-3. The structures of B1 and B1's oxides may not have been stable, especially for B1-3 (BDE = 0.0 kJ/mol), which could not be synthesized. The remaining compounds had more stable structures than CL-20. The more N—O bonds, the lower the BDE values of compounds. Although several compounds had four N—O bonds, their BDE values were much higher than CL-20, indicating that they were still stable enough to be synthesized. Therefore, B2 was thought to be the most stable in the BNTT series, and B2-1 was determined to be the most stable in BNTT's oxides series.

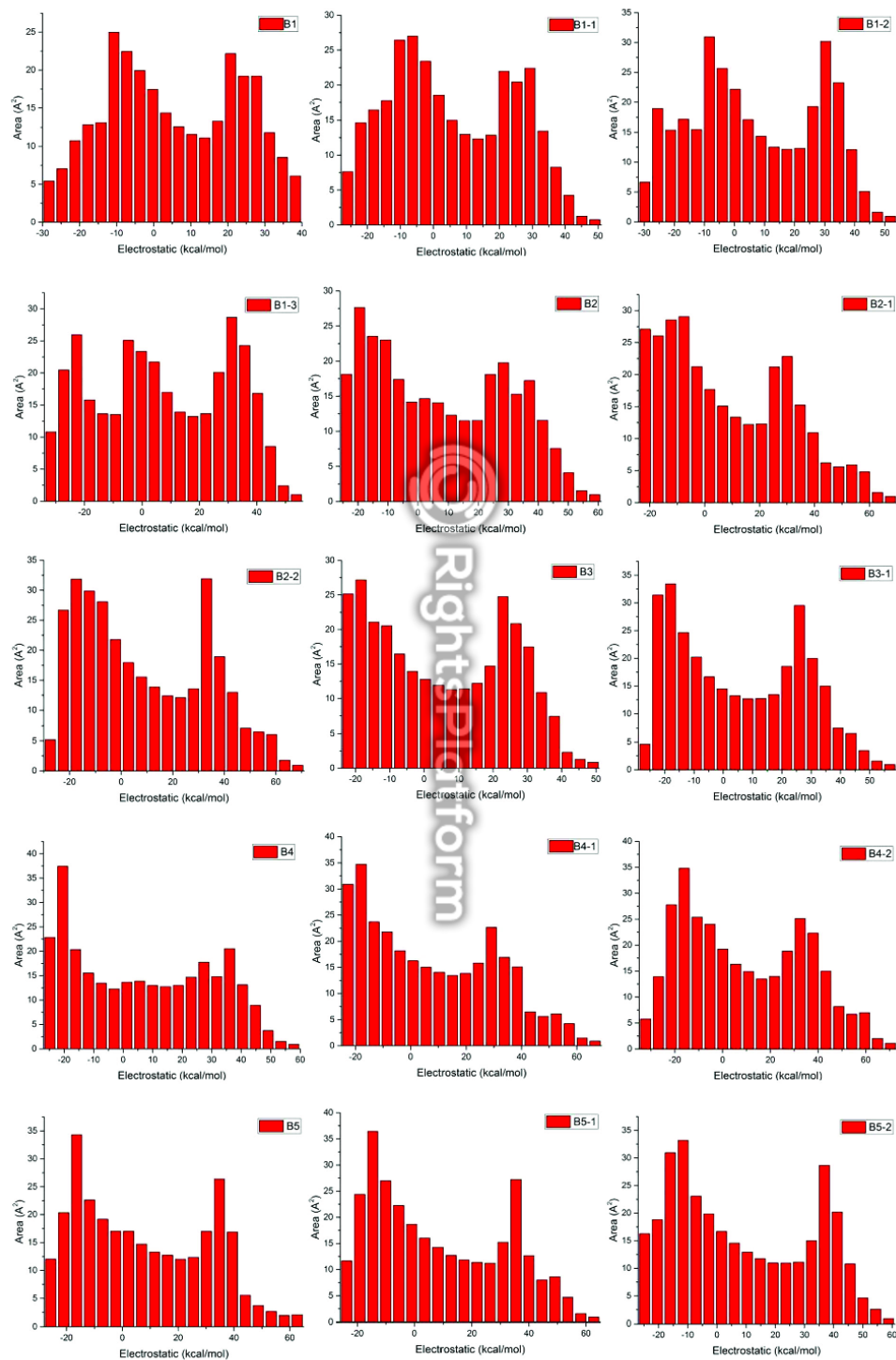
### 3.4 | Physicochemical and energetic properties

Table 2 showed the total calculated physicochemical and energetic properties of title energetic compounds and three common explosives 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and cyclotetramethylenete-tranitramine (HMX) for comparison. The energetic properties, including density ( $\rho$ ), heats of formation (HOF), heat of detonation (Q), detonation velocity (D), detonation pressure (P), oxygen balance (OB), and impact sensitivity ( $h_{50\%}$ ), were predicted in detail. The calculation parameters of BNTT and their oxides are given in Supporting Information.

It can be seen from Table 2 that the introduction of N—O bonds for BNTT-N oxides afforded higher densities in comparison with the parent compound BNTT. The greater the number of N—O bonds, the higher the density. When four N—O bonds were added to molecular structures, such as B1-2, B2-2, B4-2, and B5-2, their densities were close to the high-energy explosive HMX ( $\rho = 1.90 \text{ g cm}^{-3}$ ). The B1-3 compound was discovered to have the highest density ( $\rho = 1.97 \text{ g cm}^{-3}$ ), which had six N—O bonds. The greater the number of oxygen atom, the larger the molecular surface level. It may pile up into a closer layer-by-layer structure, which can improve density.

In Table 2, the HOFs of title compounds were all positive and did not exceed  $1000 \text{ kJ mol}^{-1}$ . The B1-3 compound had the highest HOF value (HOF =  $982.20 \text{ kJ mol}^{-1}$ ), which had the effect of four N—O bonds on bistriazole ring. However, the HOF value of the majority of molecules to which N—O bonds were added are lower than those to which N—O bonds were not added. The BNTT's oxides, which had four N—O bonds, such as B1-2, B2-2, B4-2, and B5-2, were observed to gain more HOF value than the BNTT's oxides that had two N—O bonds, such as B1-1, B2-1, B4-1, and B5-1. The results showed that oxidation of the triazole ring afforded higher HOF values.

The Q of these compounds were approximately equal to that of common energetic compounds, and compound B1-3 had the highest value of  $1779.83 \text{ cal g}^{-1}$ , indicating that the N—O bonds of BNTT's oxides effectively increased the Q. The Q of BNTT and their oxides improved with



**FIGURE 6** The area percentage in each electrostatic potential range of bis(nitrotriazoles) tetrazine (BNTT) and BNTT' oxides



**TABLE 1** Bond-dissociation energies of bis(nitrotriazoles) tetrazine (BNTT) and BNTT's oxides (kJ/mol)

Bond-dissociation energy	B1	B1-1	B1-2	B1-3	B2	B2-1	B2-2	B3	B3-1	B4	B4-1	B4-2	B5	B5-1	B5-2	CL-20
N–NO <sub>2</sub>	181.8	132.8	29.6	0.0	–	–	–	–	–	–	–	–	–	–	–	146.0
C–NO <sub>2</sub>	–	–	–	–	282.5	281.8	274.2	276.3	258.7	266.4	263.5	251.3	273.5	272.3	255.9	–

**TABLE 2** Detonation parameters for bis(nitrotriazoles) tetrazine (BNTT) and BNTT's oxides

Compounds	$\rho^a$	HOF <sup>b</sup>	Q <sup>c</sup>	D <sup>d</sup>	P <sup>e</sup>	OB <sup>f</sup>	$h_{50\%}^g$
B1	1.77	944.31	1386.73	7.91	27.50	–47	30
B1-1	1.80	849.99	1466.98	8.26	30.25	–33	29
B1-2	1.92	850.51	1594.58	8.98	37.21	–22	28
B1-3	1.97	982.20	1779.83	9.48	42.01	–12	28
B2	1.76	843.82	1308.29	7.77	26.43	–47	33
B2-1	1.77	804.09	1434.54	8.13	29.02	–33	29
B2-2	1.89	830.24	1581.49	8.84	35.65	–22	28
B3	1.75	832.23	1299.24	7.73	26.05	–47	34
B3-1	1.86	814.73	1442.06	8.42	32.06	–33	29
B4	1.79	715.27	1207.94	7.69	26.13	–47	44
B4-1	1.85	673.74	1342.41	8.23	30.49	–33	31
B4-2	1.94	792.84	1557.35	8.98	37.34	–22	28
B5	1.78	700.39	1196.33	7.64	25.72	–47	46
B5-1	1.84	614.11	1300.27	8.16	29.99	–33	34
B5-2	1.89	593.30	1428.51	8.62	33.89	–22	29
TNT <sup>31</sup>	1.64	–63.12	1295	6.95	19.00	–74	98
RDX <sup>36</sup>	1.80	79.00	1591	8.75	34.00	–22	28
HMX <sup>36</sup>	1.90	102.41	1498	9.10	39.30	–22	32

<sup>a</sup>Density,  $\rho$ /(g cm<sup>–3</sup>).<sup>b</sup>Heat of formation, HOF/(kJ mol<sup>–1</sup>).<sup>c</sup>Heat of detonation, Q/(cal g<sup>–1</sup>).<sup>d</sup>Detonation velocity, D/(km s<sup>–1</sup>).<sup>e</sup>Detonation pressure, P/(GPa).<sup>f</sup>Oxygen balance for C<sub>a</sub>H<sub>b</sub>O<sub>c</sub>, OB/% [1600(c-2a-b/2)/MW, (MW = molecular weight)]<sup>37</sup>.<sup>g</sup>Impact sensitivity,  $h_{50\%}$ /(cm)<sup>29</sup>.

increasing N–O bonds. Overall, the B1 compound and their oxides possessed higher Q than TNT, especially the B1-3 compound, which had the highest Q (Q = 1779.83 cal g<sup>–1</sup>).

The D and P of these compounds improved with increasing N–O bonds. The D of BNTT's oxides were all more than 8.00 km s<sup>–1</sup>. The P of the BNTT's oxides, which have four N–O bonds, such as B1-2, B2-2, B4-2, and B5-2, were all about 34GPa and above RDX. The best detonation performance compound was B1-3 (D = 9.48 km s<sup>–1</sup>, P = 42.01 GPa), which was higher than the common explosives, such as TNT, RDX, and HMX.

The impact sensitivity  $h_{50\%}$  of these title compounds was nearly above 28 cm, and most of them were comparable with that of common explosives, RDX (28 cm) and HMX (32 cm). The sensitivity increased with the number of oxygen atoms in BNTT oxides. The phenomenon may result from oxides that had a strong power to attract electrons, which reduced their impact sensitivity to some extent. However, because of the complexity of assessing impact sensitivity, these judgments could become insightful rather than conclusive. B4 (44 cm) and B5 (46 cm) have the relatively highest  $h_{50\%}$  values.

To find the potential HEDM candidates among the designed compounds, we intuitively compared their detonation parameters with those of TNT, RDX, and HMX in Figure 7. Most of these compounds possessed better excellent detonation performance than those of common explosives. It clearly illustrated the better detonation properties ( $\rho$ , Q, D, P) of BNTT' oxides than that of BNTT compounds. Although the performance of five BNTT compounds (B1-B5) is roughly the same, the performance of the B1 compound was better than the remaining four compounds. Moreover, the B1-3 compound, which had 10 N–O bonds, has excellent performance, high density ( $\rho$  = 1.97 g cm<sup>–3</sup>), heat of detonation (Q = 1779.83 cal g<sup>–1</sup>), detonation velocity (D = 9.48 km s<sup>–1</sup>), detonation pressure (P = 42.01 GPa).

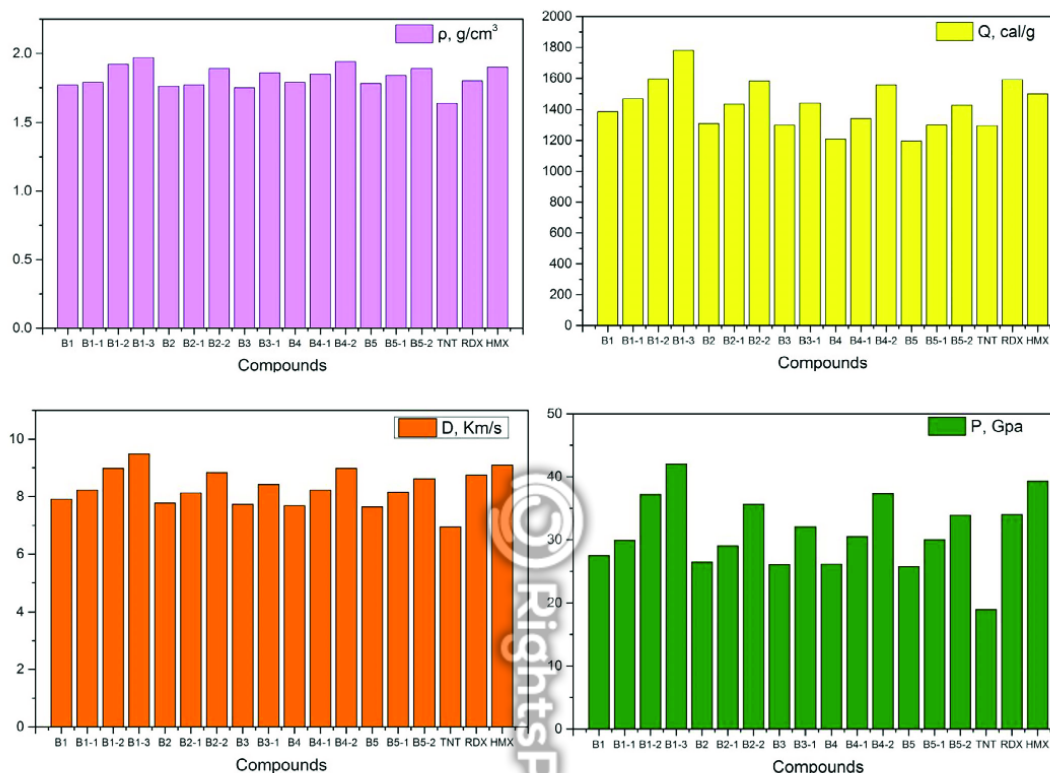


FIGURE 7  $\rho$ ,  $Q$ ,  $D$ , and  $P$  of designed compounds compared to common explosives

## 4 | CONCLUSION

In this study, we explored the structure property relationship of five BNTT compounds and 10 BNTT's oxides compounds by using DFT calculations. The molecular structure, HOMO-LUMO orbitals, ESP, physicochemical properties, BDEs, detonation performance, and impact sensitivities of these designed compounds were investigated in this work by using the DFT-B3LYP method with the 6-311+G\* basis set. The results showed that the introduction of N—O bonds in the coplanar compounds was useful for improving density and detonation performance. At the same time, the coplanar structure piled up into a layer-by-layer structure, which can increase their density to improve detonation performance.

The findings revealed that the density always increased with the number of oxygen atoms in BNTT's oxides. All these novel designed compounds illustrated high positive  $HOF$ , ranging from 593.30 to 982 kJ mol<sup>-1</sup>. This may have been due to the coplanar structure, which can generate higher  $HOF$  compared to TNT, RDX, and HMX. These compounds possessed high heat of detonations ( $Q = 1196.33$ - $1779.83$  cal g<sup>-1</sup>), excellent detonation velocities ( $D = 7.64$ - $9.48$  km s<sup>-1</sup>), and outstanding detonation pressures ( $P = 25.72$ - $42.01$  GPa). In particular, B1-3 possessed high density ( $\rho = 1.97$  g cm<sup>-3</sup>) and exhibited good balance between detonation performance ( $Q = 1779.83$  cal g<sup>-1</sup>,  $D = 9.48$  km s<sup>-1</sup>,  $P = 42.01$  GPa) and sensitivity ( $h_{50\%} = 28$  cm). These novel coplanar compounds with superior performance and acceptable sensitivities can be promising candidates for HEDMs. More relative experimental and theoretical work in the future is needed based on the coplanar compounds.

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