



## Theoretical Studies of High-nitrogen-containing Energetic Compounds Based on the *s*-Tetrazine Unit

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**Abstract:** In order to develop new high-energy-density materials (HEDMs), we have investigated 12 substituted *s*-tetrazine (TZ) compounds, where *s*-tetrazine was substituted by amino, amido and related groups. Density functional theory (DFT) was used to predict the optimized geometries, electronic structures, total energy, heats of formation (HOFs) and densities. In addition the detonation properties were evaluated by using the VLW equation of state (EOS). The standard enthalpy of formation, the Gibbs free energy, entropy and equilibrium constants were used to estimate the success of the synthetic substitution reactions, which provided theoretical support for practical work. The bond dissociation energy (BDE) of bond C-R was calculated at each stage of the substitution reaction. The calculated results showed that substitution of amino, amido and their derivatives in the TZ ring enhances the HOF values and is favorable for increasing the thermal stability. The calculated detonation properties indicated that incorporating the above groups into the TZ ring is beneficial for improving the explosive performance. Considering the detonation properties and thermal stability, the 12 derivatives may be regarded as promising candidates as high-energy-density materials (HEDMs).

**Keywords:** high-energy-density materials (HEDMs), substituted *s*-tetrazine compounds, electronic properties, thermodynamic properties, detonation properties

### Introduction

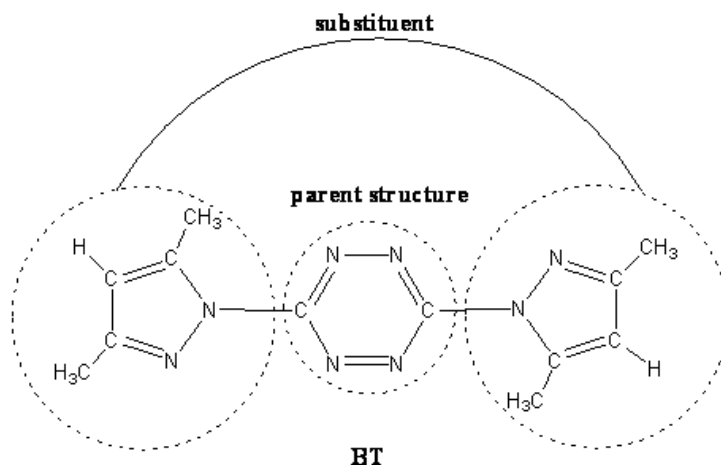
With a high enthalpy of formation, excellent thermal stability and low friction and impact sensitivity, high-nitrogen heterocyclic compounds play an

increasingly important role in the field of energetic materials [1, 2]. In addition, these heterocyclic compounds have a high density, are readily oxygen balanced, and their decomposition products are generally environmentally-friendly [3, 4]. Therefore, as green energetic materials, these compounds have been more and more widely used in the fields of propellants, gas agents and primary explosives. The study of nitrogen-rich energetic compounds has gradually become one of the forefronts and hot areas of energy materials' research [5]. For their high nitrogen content, high density, and readily achieved oxygen balance, as well as their structural advantages, *s*-tetrazine compounds have gradually come into peoples' sight as an excellent parent-structure to be investigated in designing more useful materials in the field of energetic compounds [6, 7].

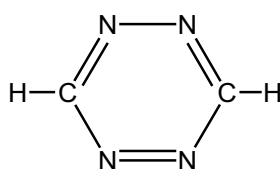
For their high nitrogen content, high energy and simple reaction conditions for their formation, amino derivatives and their analogues have attracted a lot of attention as substituents of *s*-tetrazine [8-10], and there have been numerous reports on *s*-tetrazines substituted by amino and hydrazino groups [11-15]. Generally speaking, *s*-tetrazine compounds are synthesized from 3,6-bis(3,5-dimethylpyrazole-1-yl)-*s*-tetrazine (BT) as the precursor, and BT has been synthesized by many researchers [3, 14]. In this paper, we have designed amino, amido and related systems, where one or both of the 3,6-hydrogen atoms of *s*-tetrazine have been replaced. The selected objects are mainly amino, hydrazino, carbamido, semi-carbazido, and carbohydrazido, as mono- or bi-substituted *s*-tetrazines. We discuss the relations between structure and properties, by the study of the electrostatic potential energy, the natural bond orbital, the second-order stabilization energy, and analyze the position of coordination compounds. The bond dissociation energy of every compound was calculated in order to refine the thermal stabilities of the compounds, and each compound's potential application in the field of energetic materials was predicted through the estimation of the detonation velocity and pressure, in order to provide more theoretical support for new primary explosives.

Generally speaking, analogs of *s*-tetrazine (TZ) are mainly synthesized by a route based on the BT molecular unit. There are two fragments in a BT unit, the TZ ring and the substituent groups connected to the C atoms of the ring (Figure 1). In this study, 12 types of compounds are discussed based on the structural principle of BT, taking the TZ ring as the parent structure and the amino groups (amino, hydrazino, carbamido, semicarbazido, 2-semicarbazido, carbohydrazido are included) (Figure 2) as substituents, including 6 kinds of mono-substituted TZs and 6 kinds of bi-substituted TZs. The compounds have been formed by substitution of one or both H atoms of the TZ ring by the listed substituents. The optimized geometries were calculated by using the framework

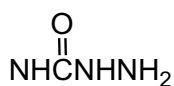
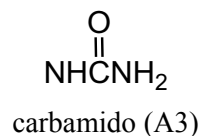
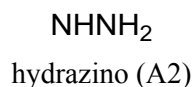
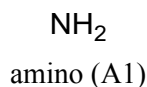
of density functional theory (DFT) [13] at the level of 6-311G (d) basis set. The results show that all of the structures are points of energy minimum on the potential energy surface without imaginary frequency. Therefore, based on the optimized structures of these compounds, the other properties of all of these molecules, such as frontier orbital energies, electronic structures and natural bond orbitals, electrostatic potential, Wiberg energy level and bond dissociation energies (BDEs), heats of formation (HOFs), densities, detonation velocities and pressures, were calculated and are discussed below.



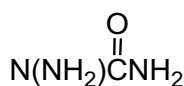
**Figure 1.** The structural characteristics of the BT molecule.



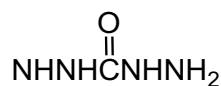
*s*-tetrazine (TZ)



semicarbazido(A4)



2-semicarbazido (A5)



carbohydrazido (A6)

**Figure 2.** Structures of all nitrogenous groups and *s*-tetrazine.

## Methods and Computational Details

### Natural bond orbital (NBO) analysis

Electronic structures, charge distribution, Wiberg orbital level and frontier orbital energies were obtained by way of natural bond orbital analysis. Natural atomic electrons ( $q$ ) are the total sum of the Mulliken population ( $q_i$ ), shown as Eq. 1:

$$q = \sum_i q_i. \quad (1)$$

The Wiberg Bond Index (WBI) stands for the stability of the bonds, the higher the WBI value is, the more stable the bond will be [17]. WBI means the quadratic sum of the density matrix ( $p_{jk}$ ), and additionally it also equals the d-value between the double orbital atom charge density ( $p_{jj}$ ) and the squared  $p_{jj}$ , shown as Eq. 2:

$$WBI = \sum_k p_{jk}^2 = 2p_{jj} - p_{jj}^2. \quad (2)$$

The force of inter-molecule and intra-molecule is obtained by NBO analysis on the donor-acceptor electrons. The molecule orbital stabilization energy ( $E_{ij}$ ) of each donor electron NBO ( $i$ ) and each acceptor electron NBO ( $j$ ) is defined by Eq. 3;  $q_i$  is the population of the donor orbital,  $\varepsilon_i$  and  $\varepsilon_j$  are the orbital energies, and  $F(i, j)$  is the NBO orbital energy:

$$E_{ij} = q_i \frac{F(i, j)^2}{\varepsilon_j - \varepsilon_i}. \quad (3)$$

### Density calculations

A convenient method was used to predict the densities of the energetic materials [19, 20]. The density ( $\rho$ , g/cm<sup>3</sup>) was obtained from the molecular volume divided by the mass, whilst the volume was derived from the calculation of the single-point molar volume of optimized geometries by the Gaussian03 program package [21]. The molecular volume was defined as the space within a contour of 0.001 e/Bohr<sup>3</sup> density that was evaluated by using Monte Carlo integration.

### Heats of formation (HOFs) calculations

The theoretical heats of formation were calculated by using Eq. 4 and Eq. 5:

$$\Delta_f H^0(M, 0K) = \sum_{atoms} x \Delta_f H^0(X, 0K) - \left[ \sum_{atoms} x \varepsilon_0(X) - \varepsilon_0(M) - \varepsilon_{ZPE}(M) \right] \quad (4)$$

$$\begin{aligned} \Delta_f H^0(M, 298.15K) &= \Delta_f H^0(M, 0K) + (H_M^0(298.15K) - H_M^0(0K)) \\ &- \sum_{atoms} x (H_X^0(298.15K) - H_X^0(0K)) \end{aligned} \quad (5)$$

where  $M$  denotes the molecule,  $X$  represents each element making up  $M$ ,  $x$  is the number of atoms of  $X$  in  $M$ ,  $\varepsilon_0(M)$  is the total energy of the molecule, and  $\varepsilon_{ZPE}(M)$  is its zero-point energy;  $(H_M^0(298.15K) - H_M^0(0K))$  and  $(H_X^0(298.15K) - H_X^0(0K))$  are enthalpy corrections for the molecular and atomic elements, respectively. The latter one can be obtained from both calculated and experimental data.

### Thermodynamic functions ( $\Delta_r H_m^\theta$ ) of the reactivity calculations

The thermodynamic properties of the substitution reaction were calculated, including  $\Delta_r H_m^\theta$ ,  $\Delta_r G_m^\theta$ , and  $\Delta_r S_m^\theta$ .

$$\Delta_r H^\theta = \sum (\varepsilon_0 + H_{corr})_{products} - \sum (\varepsilon_0 + H_{corr})_{reactants} \quad (6)$$

### Detonation property calculations

All detonation properties were calculated by the VLW equation of state (EOS) [22], law of energy conservation. The detonation velocity ( $D$ , km/s), and detonation pressure ( $p$ , GPa) can be predicted using the modified nitrogen equivalent (MNE) as follows:

$$D = (690 + 1160\rho_0) \sum N^w \quad (7)$$

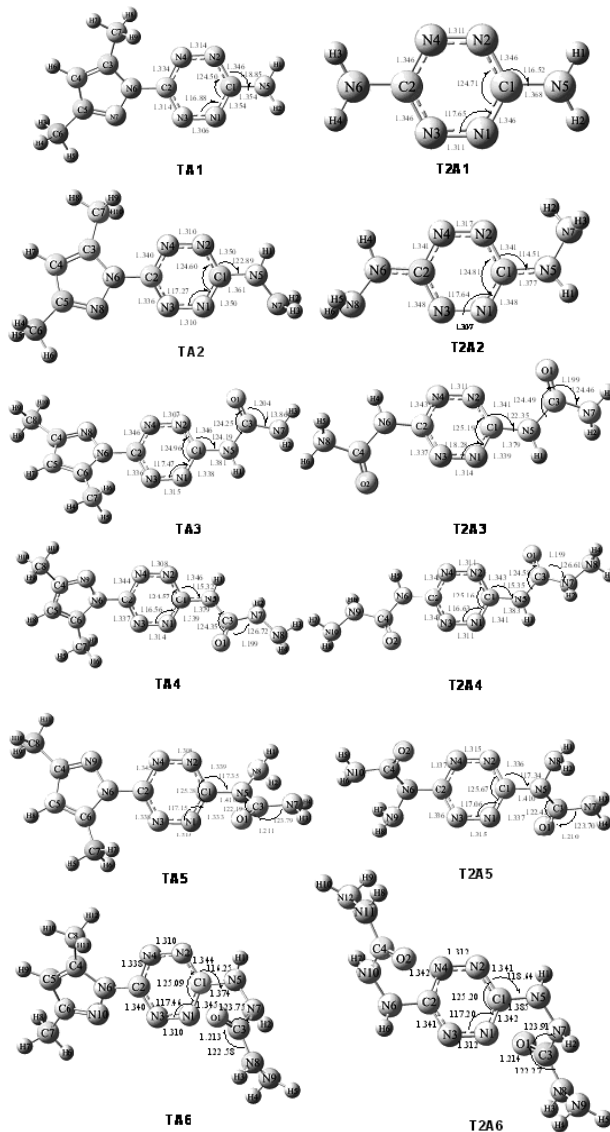
$$p = 11.06(\rho_0 \sum N^w)^2 - 8.40 \quad (8)$$

$$\sum N^w = \frac{100}{m} (\sum P_i N_{P_i} + \sum B_k N_{B_k} + \sum G_j N_{G_j}) \quad (9)$$

where  $\sum N^w$  is the corrected nitrogen equivalent of the explosive,  $P_i$  is the molar number of gaseous detonation products per gram of explosive,  $N_{P_i}$ ,  $N_{B_k}$  and  $N_{G_j}$  are the coefficients of the corrected nitrogen equivalent for products, bonds and groups, respectively. The data are from the literature.  $B_k$  and  $G_j$  are the numbers of each kind of bond and group in the molecule.

## Results and Discussion

### Geometric structures



**Figure 3.** Optimized geometries of all substituted *s*-tetrazine compounds (TA1-TA6 are mono-substituted compounds, and T2A1-T2A6 are bi-substituted compounds, respectively) calculated at the level of 6-311G(d) basis set.

Figure 3 shows all of the bond lengths, bond angles and dihedral angles of the fully optimized geometries. It can be inferred by comparing the structures, that the introduction of amino (A1) and hydrazino (A2) groups destroyed the original conjugated system in the TZ ring. However, compared to the single-substituted TZ ring (TA1, TA2) and BT, the bond lengths of C1-N1, N2-C1, N5-C1 tended to be average, fluctuating around 1.345 Å and close to the standard C=N of 1.30 Å in bi-substituted systems, which means that there existed a p- $\pi$  hyper-conjugation effect caused by the groups on both sides, general benefit of lowering the energy of the system. Moreover, the same applies to the bond angles, on account of the hybridization between the C1, C2 atoms and their substituents; the bond angle N1-C1-N2 and N2-C1-N5 were around 120°. Considering the symmetry, (T2A1) and (T2A2) were symmetrical along the axis through the mid-points of bonds N1-N3 and N2-N4. The N5, N6 atoms were almost coplanar with the TZ ring, the deviation being only 0.3811°, whilst the distant NH<sub>2</sub> group of the hydrazino groups was off the plane by 22.1157°.

It can also be observed from Figure 3 that with the introduction of a carbonyl group, the substituent's destructive effect to the TZ ring decreased, because the C=O in the carbamido (A3), semicarbazido (A4), 2-semicarbazido (A5) and carbohydrazido (A6) groups were strongly electrophilic, the p- $\pi$  hyper-conjugation effect of the amino and hydrazino was no longer strong, the C-N bond between the TZ ring and the substituent became stretched, to about 1.39 Å, falling between the 1.47 Å of C-N and 1.30 Å of C=N. In the isomers incorporating a semicarbazido group, (T2A5) was less stable than (T2A4), as the electron-withdrawing effect of the C=O and the inductive effect of the NH<sub>2</sub> weakened the N's nucleophilic substituent effect, as could be seen from their C1-N5 bonds, which were 1.383 Å and 1.410 Å, respectively. All atoms of the TZ ring formed a new conjugated system, and C-N and N-N were 1.341 Å and 1.311 Å, respectively. The C atom of the C=O group was hybridized in the *sp*<sup>2</sup> mode, which could be concluded from the bond angle of 120°. Among the TZs substituted by carbamido (A3) and semicarbazido (A4), the NH<sub>2</sub> distorted the plane within the C=O group, the dihedral angle N1-C1-N5-C3 in the molecules (T2A3), (T2A4), (T2A5), (T2A6) being 36.41°, 41.72°, 54.87° and 109.46°, respectively.

Bi-substituted TZ compounds were more coplanar than mono-substituted structures when comparing the N(3)-C(2)-N(4)-N(2) unit, especially after carbonyl groups were attached. This is because of the existence of two  $\pi$  conjugated systems formed by the pyrazole rings and the TZ ring in the BT molecule. However, both  $\pi$  systems were perturbed by the step by step substitution process, and were finally replaced by the p- $\pi$  hyper-conjugation between the TZ ring and the new groups.

### Electronic structure and natural bond orbital analysis

Table 1 lists the natural atomic charge of the whole ring and each atom in the TZ ring by natural bond orbital (NBO) analysis of the 12 derivatives, as well as the electronic occupation and the Wiberg (WBI) bond order of the C2-N6 bond. As can be seen from Table 1, the positive charge of the C atoms increased sharply, where, most obviously in the mono-substitution case, part of the electron density was transferred from the ring to the substituent, especially in the presence of  $-\text{NH}_2$ ,  $-\text{NHNH}_2$ ,  $-\text{NHCONH}_2$  and  $-\text{NHCONHNH}_2$ , which showed a strong electrophilic affect connected with the TZ, especially the  $-\text{NHCONH}_2$ .  $-\text{NH}_2$  group exhibited an electron-donating inductive effect, but it showed a conjugated electron-withdrawing effect. Because the  $\text{C}=\text{O}$  group was strongly electron withdrawing in  $-\text{NHCONH}_2$ , the TZ ring became more positive. In  $-\text{NHNH}_2\text{CONHNH}_2$ , the  $\text{C}=\text{O}$  is connected with two  $-\text{NHNH}_2$  groups, and since  $-\text{NH}_2$  is electron-donating, the TZ ring was negative. In terms of bond lengths, mono-substitution caused a longer length of the C-N bond, which was close to  $1.47\text{\AA}$ . It could be deduced from an analysis of the bond orders in the 12 derivatives, in which all values of the C-N bond order were close to each other, and were more stable than the C-H of TZ, except for (T2A5), in which the C-N bond order was less than 1, caused by the electron-withdrawing effect of  $-\text{NH}_2$ . It can be learned from an analysis of electron occupation, that values which were close to 2, indicating the C-N bond shared a pair of electrons, with no electron shift, meaning the bonds were covalently stable. It can also be seen from Table 1 that (T2A5) and (T2A6) had relatively poor stability, the products' bond order in the mono-substitution cases were lower than in bi-substitution, and that the synthetic intermediates could hardly exist.

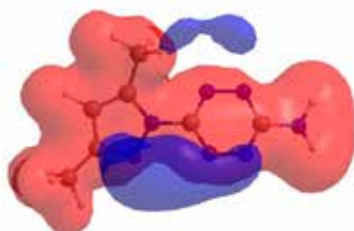
Frontier orbital theory provides information about a molecule by calculating the difference in energy levels to balance the stability of the molecular structure. Comparing the frontier orbital energy gap ( $\Delta E_{H-L}$ ) in Table 1, we could see that the orbital energy gap of bi-substituted compounds was higher than that of mono-substituted compounds. Thus it could be inferred that the former had better stability, electrons were more difficult to activate, and also that they were difficult to decompose. Comparing the stability of doubly substituted TZs, it could be concluded that: (T2A6) > (T2A4) > (T2A1) > (T2A3) > (T2A5) > (T2A2).



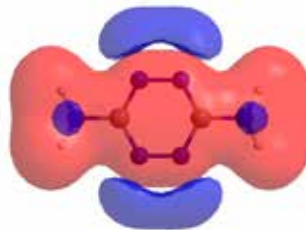
**Table 1.** Charge distribution of atoms in TZ and the TZ ring,  $e_{occ}$  of the bond C2-N6, bond length, energy difference ( $\Delta E_{H-L}$ ) of frontier orbitals and bond order WBI

Cpd.	C1	C2	N1	N2	N3	N4	TZ-ring	$e_{occ}$	b	$\Delta E_{H-L}$	WBI
TZ	0.014	0.014	-0.133	-0.133	-0.133	-0.133	-0.504	1.977	1.086	364.65	0.792
TA1	0.521	0.433	-0.200	-0.205	-0.128	-0.184	0.237	1.981	1.4	343.73	1.01
T2A1	0.483	0.483	-0.200	-0.200	-0.200	-0.200	0.006	1.988	1.368	350.45	1.161
TA2	0.531	0.426	-0.168	-0.218	-0.129	-0.183	0.259	1.981	1.401	341.77	1.006
T2A2	0.489	0.489	-0.166	-0.216	-0.166	-0.216	0.214	1.985	1.377	345.74	1.126
TA3	0.486	0.46	-0.142	-0.198	-0.133	-0.192	0.281	1.982	1.396	344.21	1.032
T2A3	0.522	0.523	-0.201	-0.240	-0.201	-0.240	0.276	1.983	1.384	349.19	1.081
TA4	0.489	0.467	-0.147	-0.197	-0.198	-0.136	0.278	1.981	1.396	349.79	1.033
T2A4	0.482	0.482	-0.152	-0.198	-0.152	-0.198	0.264	1.983	1.383	350.69	1.083
TA5	0.438	0.479	-0.127	-0.135	-0.201	-0.141	0.313	1.990	1.393	341.41	1.043
T2A5	0.453	0.453	-0.138	-0.145	-0.145	-0.138	0.34	1.979	1.410	347.55	0.989
TA6	0.499	0.442	-0.194	-0.201	-0.134	-0.183	0.229	1.981	1.400	342.39	1.015
T2A6	0.484	0.484	-0.194	-0.205	-0.205	-0.194	-0.170	1.984	1.385	354.03	1.104

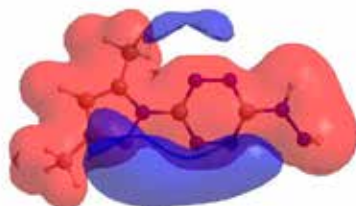
Note:  $e_{occ}$ , b, and WBI means TZ's occupied value of C-H, bond length and bond order, units of  $e_{occ}$ , b,  $\Delta E$  and WBI are eV, Å, Hartree, and kJ/mol, respectively.



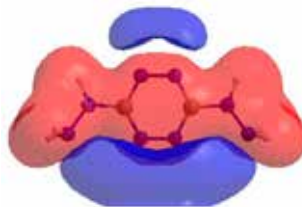
**Figure 4.1.** Electrostatic potential surface of (TA1).



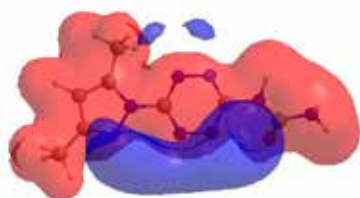
**Figure 4.2.** Electrostatic potential surface of (T2A1).



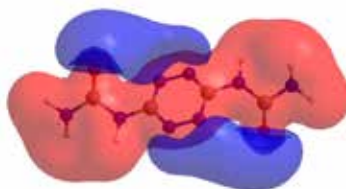
**Figure 4.3.** Electrostatic potential surface of (TA2).



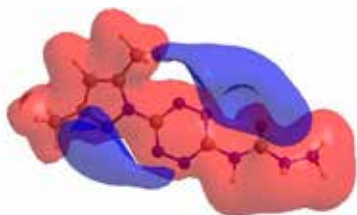
**Figure 4.4.** Electrostatic potential surface of (T2A2).



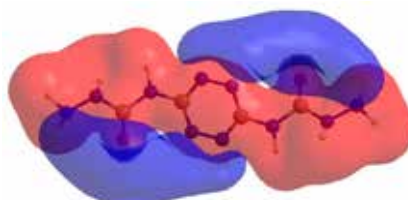
**Figure 4.5.** Electrostatic potential surface of (TA3).



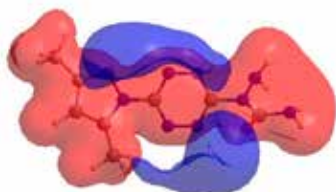
**Figure 4.6.** Electrostatic potential surface of (T2A3).



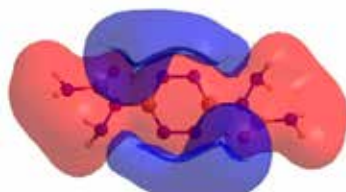
**Figure 4.7.** Electrostatic potential surface of (TA4).



**Figure 4.8.** Electrostatic potential surface of (T2A4).



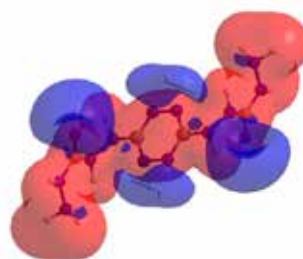
**Figure 4.9.** Electrostatic potential surface of (TA5).



**Figure 4.10.** Electrostatic potential surface of (T2A5).



**Figure 4.11.** Electrostatic potential surface of (TA6).



**Figure 4.12.** Electrostatic potential surface of (T2A6).

**Figures 4.1- 4.12.** Electrostatic potential surfaces of the 12 derivatives.

The electrostatic potential surface of the 12 derivatives are shown in Figures 4.1-4.12. Overall, the positive charges were mainly inside, whilst the negative electrostatic potential was concentrated on the N atoms of the TZ ring and the peripheral N atoms of the substituents without H atoms. It can be observed from the Figures, because of strong electron-withdrawing effects, electrons are mainly distributed on N atoms, N1, N2, N3, N6 are in a large negative electric field in the mono-substituted systems (TA1), (TA2), this position being advantageous for metal atom attack to form poly-coordination. In (T2A1) and (T2A2), the negative charges were symmetrical, whilst the TZ ring and the substituents were positive, electron density was reduced as a result of the withdrawing effect of  $-NH_2$ . Introduction of a carbonyl group added electron density to the TZ ring, thus making TA3 exhibit aromatic properties. There exists an electron nodal surface in the mono-substituted systems TA4 and TA5, resulting in a decrease in the N2, N4 charges, which were -0.136 and -0.141 respectively. Electrons flowed from the pyrazole and the TZ ring to the substituted group. This was actually an unstable state and tended to form a ring. Negative charges were relatively balanced if the substitution process proceeded completely, as TA4 showed an even charge distribution, and had better stability. This agreed with the conclusion from structural analysis. Due to the strong steric-hindrance in (T2A4) and (T2A5), as well as the conjugative or inductive effect of  $-NH_2$  showed differently, the electrons accumulated mainly near the N atoms of TZ and the O atom of the carbonyl group.

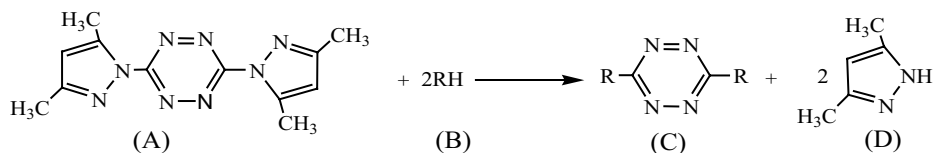
It can be concluded from Table 2 that the WBI values of C(1)-N(5) in mono-substituted systems were larger than that in bi-substituted systems. Besides, the values of C-N decreased, but the N-N's increased in the TZ ring, thus bonds' length of the ring became averaged. As mentioned before, the interaction of C(2)-N(6) in the mono-substituted systems was weak. The bond order of C-R in (T2A2) was only 1.161, much lower than that of the TZ ring, such as 1.327 of C-N, 1.462 of N-N, C(1)-N(5) in T2A2 1.126, and C-N was close to N-N in the TZ ring. However, for  $p-\pi$  conjugated effects, N(5)-N(7) in the hydrazino group was the weakest and easiest to break, especially in the mono-substituted system; the value was only 0.076. In short, the interactions of C-NH<sub>2</sub> and C-NHNH<sub>2</sub> were weak. Generally, bonds C(3)-N(5) were the weakest in molecules with carbonyl groups, for two possible reasons. Firstly, due to the  $p-\pi$  conjugation between the C and N of TZ, secondly, the strong electron-withdrawing effect of the O atom decreased the degree of overlap between C-N and N-N, weakening the interaction of C(3)-N(5). Therefore, these derivatives were the least stable towards decomposition; the order of thermodynamic stability was: C(3)-N(5) < C(1)-N(5).

**Table 2.** WBI bond level of molecules at B3LYP/6-311G(d) level

Compound	Bond	Bond level	Bond	Bond level	Bond	Bond level
TA1	C(1)-N(5)	1.204	C(2)-N(6)	1.011	C(1)-N(2)	1.323
	N(1)-N(3)	1.497				
T2A1	C(1)-N(5)	1.161	C(2)-N(6)	1.161	C(1)-N(2)	1.327
	N(1)-N(3)	1.462				
TA2	C(1)-N(5)	1.176	C(2)-N(6)	1.006	C(1)-N(2)	1.311
	N(1)-N(3)	1.484	N(5)-N(7)	0.076		
T2A2	C(1)-N(5)	1.126	C(2)-N(6)	1.126	C(1)-N(2)	1.32
	N(1)-N(3)	1.454	N(5)-N(7)	1.041		
TA3	C(1)-N(5)	1.088	C(2)-N(6)	1.032	C(1)-N(2)	1.368
	N(1)-N(3)	1.5	C(3)-N(5)	0.993	C(3)-N(7)	1.132
T2A3	C(1)-N(5)	1.081	C(2)-N(6)	1.081	C(1)-N(2)	1.35
	N(1)-N(3)	1.463	C(3)-N(5)	1	C(3)-N(7)	1.129
TA4	C(1)-N(5)	1.095	C(2)-N(6)	1.033	C(1)-N(2)	1.332
	N(1)-N(3)	1.451	C(3)-N(5)	0.975	C(3)-N(7)	1.097
	N(7)-N(8)	1.042				
T2A4	C(1)-N(5)	1.083	C(2)-N(6)	1.083	C(1)-N(2)	1.349
	N(1)-N(3)	1.463	C(3)-N(5)	0.978	C(3)-N(7)	1.095
	N(7)-N(8)	1.042				
TA5	C(1)-N(5)	0.986	C(2)-N(6)	1.043	C(1)-N(2)	1.361
	N(1)-N(3)	1.442	C(3)-N(5)	1.011	C(3)-N(7)	1.135
	N(5)-N(8)	1.024				
T2A5	C(1)-N(5)	0.99	C(2)-N(6)	0.99	C(1)-N(2)	1.381
	N(1)-N(3)	1.454	C(3)-N(5)	1.01	C(3)-N(7)	1.13
	N(5)-N(8)	1.024				
TA6	C(1)-N(5)	1.137	C(2)-N(6)	1.015	C(1)-N(2)	1.327
	N(1)-N(3)	1.473	N(5)-N(7)	1.039	C(3)-N(7)	1.064
	C(3)-N(8)	1.102	N(8)-N(9)	1.034		
T2A6	C(1)-N(5)	1.104	C(2)-N(6)	1.104	C(1)-N(2)	1.341
	N(1)-N(3)	1.459	N(5)-N(7)	1.039	C(3)-N(7)	1.076
	C(3)-N(8)	1.096	N(8)-N(9)	1.034		

Note: C.B. means chemical bond, B.O. means bond order. The units of WBI level is Hartree.

The reactivity and bond dissociation energy (BDE) of the molecules



R = NH<sub>2</sub> (A1), NHNH<sub>2</sub> (A2), NHCONH<sub>2</sub> (A3), NHCONHNH<sub>2</sub> (A4),  
 NHNHCONH<sub>2</sub> (A5), NHNHCONHNH<sub>2</sub> (A6)

As the precursor of most s-tetrazine compounds, BT possesses relatively high reactivity, and it may be easily substituted. R replaces dimethylpyrazole stepwise in the substitution process. Thus, in order to study the feasibility of the reaction, the thermodynamic functions such as  $\Delta_r G_m^\theta$  and  $\Delta_r G_m^\theta$  (kJ/mol) at 298K were listed in Table 3. All the data were computed by Gaussian03 under the level of B3LYP/6-311G(d) basis set. It could be concluded that all of the processes were exothermic, the Standard Moore Reaction Gibbs Free Energy ( $\Delta_r G_m^\theta$ ) decreased whilst the entropy increased, suggesting that the reactions are theoretically feasible. The equilibrium constant for the reaction was calculated, and it indicated that the substitution process could go to completion. However, with the introduction of an amido group, the value of  $\Delta_r G_m^\theta$  increased, whilst the equilibrium constant was reduced. Although it was concluded by the Frontier orbital theory that semicarbazido-, and 2-carbamido-TZ had higher stability than amino- and hydrazino-TZ, the introduction of the amido blocked the reaction according to the reaction dynamics. This may be connected with the structure of the molecule, the smaller the substituent group, the more stable the product would be.

**Table 3.** Molar Gibbs free energy of reactants and the 6 reactions

R	$\Delta_r H_m^\theta$	$\Delta_r G_m^\theta$	$\Delta_r S_m^\theta$
(A1)	-587.917	-572.417	52.002
(A2)	-605.512	-596.963	28.694
(A3)	-526.231	-519.151	23.741
(A4)	-471.607	-466.247	17.977
(A5)	-470.694	-467.558	10.520
(A6)	-624.386	-623.306	3.627

Note: Units kcal/mol.

In order to discuss the level of difficulty for the substitution reaction sufficiently, the BDE of characteristic chemical bonds were calculated. The BDEs provided us with information about the stability of the compounds.

The substitution mainly started at C1-N5 or C2-N6, and the BDEs of C1-N5 and C2-N6 were mainly calculated at B3LYP/6-311G(d) basis set. T was TZ, R1 was 3,5-dimethylpyrazole, T-R1 was the molecule which had lost its 3-dimethylpyrazole, X-T-R1 (X was A1, A2, A3, A4, A5, A6 group) were mono-substituted derivatives, X-T was a mono-substituted derivative which had lost its 3-dimethylpyrazole, X-T-X were bi-substituted systems.

$$\begin{aligned} \text{BDE}_1 &= E_{(\text{T-R1})} + E_{(\text{R1})} - E_{(\text{R1-T-R1})}, \text{BDE}_2 = E_{(\text{T-R1})} + E_{(\text{R1})} - E_{(\text{X-T-R1})}, \text{BDE}_3 = E_{(\text{X-T})} + E_{(\text{R1})} - \\ &E_{(\text{X-T-R1})}, \text{BDE}_4 = E_{(\text{X-T})} + E_{(\text{X})} - E_{(\text{X-T-X})} \\ \text{R}_1\text{-T-R}_1 &\xrightarrow{-\text{R1}} \text{T-R}_1 \xrightarrow{+\text{X}} \text{X-T-R}_1 \xrightarrow{-\text{R1}} \text{X-T} \xrightarrow{+\text{X}} \text{X-T-X} \end{aligned}$$

**Table 4.** Bond dissociation energies (BDE) of characteristic chemical bonds

R	BDE <sub>1</sub>	BDE <sub>2</sub>	BDE <sub>3</sub>	BDE <sub>4</sub>
(A1)	99.088	273.768	4.146	316.524
(A2)	99.088	228.684	5.861	271.330
(A3)	99.088	30.972	-24.964	56.088
(A4)	99.088	-16.995	-19.722	8.593
(A5)	99.088	116.489	21.957	183.211
(A6)	99.088	141.782	-16.557	166.686

Note: Units of Bond dissociation energy is kcal/mol.

It can be inferred from Table 4 that removal of 3,6-dimethylpyrazole from BT was endothermic. It could also be shown that the intermediate from (A4) had the worst stability of the 6 molecules, whilst (A1) and (A2) were more stable. For lower bond dissociation energy, it is difficult to synthesize (A4) and (A3). From the data for BDE<sub>3</sub>, we could also conclude that the stability of the mono-substituted systems, the intermediate of (A3), (A4), and (A6) tended to lose the second R1 easily during reaction, thus substitution at both sites were expected. The value of the bond dissociation energy could reflect the stability of the molecule, the higher the value is, the lower the combined energy, therefore, the easier of the reaction will be. Thus BDE<sub>4</sub> showed orders of stability of the molecule under ideal conditions, (A1)>(A2)>(A5)>(A6)>(A3)>(A4).

### Molecular total energy, standard heat of formation, density, detonation velocity and pressure

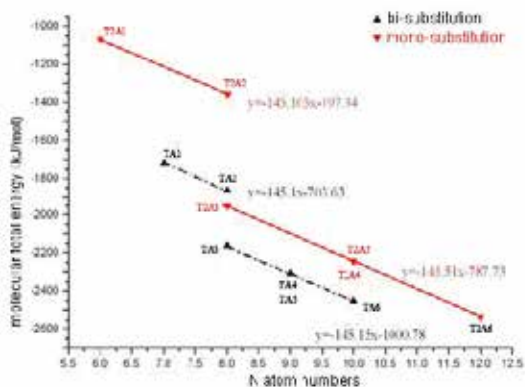
Table 5 lists the molecular total energy, density, detonation properties and nitrogen content, in order to explore the relations between mono-substitution and bi-substitution at 298 K. It can be concluded that the introduction of energetic groups improved the standard heat of formation of bi-substituted systems by

different degrees, compared to the theoretical heat of formation of a single TZ unit 450.1 kJ/mol, estimated by atomization proposal.

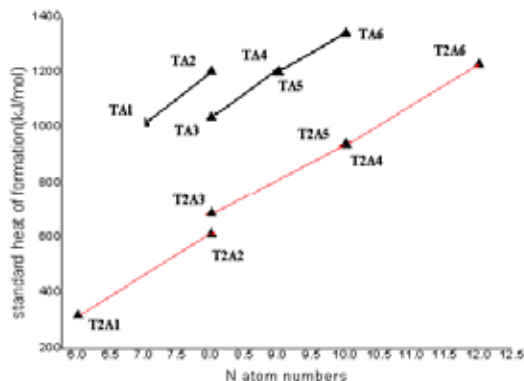
**Table 5.** Nitrogen atoms numbers, nitrogen content (%), electron total energy, standard heat of formation and density, detonation velocity and pressure, of the series of TZ derivatives

Cpd.	N Quantity number	N%, %	$E_{TOTAL}$ , kJ/mol	$\Delta_f H^0_{298K}$ , kJ/mol	$\rho$ , g/cm <sup>3</sup>	$D_{CJ}$ , km/s	$P_{CJ}$ , GPa
(TA1)	7	51.28	-1719.33	1018.03	1.45	6.81	17.88
(T2A1)	6	74.97	-1067.97	319.29	1.26	5.89	12.08
(TA2)	8	54.34	-1864.43	1202.24	1.29	6.62	15.55
(T2A2)	8	78.84	-1358.18	425.56	1.64	7.36	22.67
(TA3)	8	47.84	-2161.94	1034.82	1.34	7.63	21.25
(T2A3)	8	56.55	-1951.77	611.85	1.58	7.52	23.12
(TA4)	9	50.57	-2307.05	1196.24	1.82	8.21	30.08
(T2A4)	10	61.38	-2243.41	936.72	1.45	7.60	22.29
(TA5)	9	50.57	-2307.04	1200.75	1.23	6.34	13.76
(T2A5)	10	61.38	-2243.41	941.54	1.55	7.95	25.51
(TA6)	10	53.00	-2452.23	1339.98	1.31	6.16	13.62
(T2A6)	12	65.09	-2533.79	1226.12	1.61	8.50	29.90

All of the listed compounds fell into 4 groups: mono-substituted and bi-substituted without a carbonyl group, and mono-substituted and bi-substituted with a carbonyl group, respectively. It can be seen in Figure 5 (molecular total energy vs. nitrogen atom numbers) that all lines had a similar trend, which means that whatever the situation is, an increase in nitrogen atoms, decreases the total molecular energy. Hence, one extra N atom, reduces the energy by 145.10 kJ/mol on average for the series. It can also be seen in Figure 6 (standard heat of formation vs. nitrogen atoms numbers), that addition of N atoms, causes an increase in the HOF of the target compound. The above relations imply that N atoms have a big influence on the molecular total energy and the HOF in this series of TZ compounds. It could also be deduced from Figure 6 that introduction of a single substituent group and a carbonyl group both improved the HOF of the compounds.



**Figure 5.** Relation between molecular total energy and nitrogen atom numbers.



**Figure 6.** Relation between standard heat of formation and nitrogen atom numbers.

We used the K-J equation, with the density calculated earlier and the standard heat of formation of the product gases, to estimate the detonation velocity and pressure for the 12 compounds. Comparing the results in Table 5, we found that nitrogen content and density determined the detonation properties. Table 5 showed that the more N atoms, the higher the value of the detonation velocity and pressure. Additionally, it could also be found from Table 5 that the density of the bis-hydrazino derivative of s-TZ was  $1.64 \text{ g/cm}^3$ , and that the detonation velocity and pressure could reach  $9.27 \text{ km/s}$  and  $36.02 \text{ GPa}$ , respectively. Its detonation properties were close to those of the traditional high explosive HMX ( $\rho = 1.85 \text{ g/cm}^3$ ,  $D_{CJ} = 8.92 \text{ km/s}$ ). The mono-semicarbazido-s-TZ also possessed excellent explosive properties, the nitrogen content was as high as



50.57%, ( $\rho = 1.82 \text{ g/cm}^3$ ,  $D_{CJ} = 8.21 \text{ km/s}$ ), the bis-carbohydrazido-*s*-TZ had a detonation velocity and pressure of 8.50 km/s and 29.90 GPa respectively, the detonation velocity also being close to that of HMX. This illustrated that the introduction of hydrazino and carbohydrazido groups had a significant effect on improving the detonation velocity of high-nitrogen compounds. Therefore, hydrazino and carbonyl derivatives have good prospects in the field of applied energetic materials.

## Conclusions

In this paper, 12 substituted *s*-tetrazine compounds were designed, and their optimized geometries, electronic structure, thermal stability, molecular total energy, standard heat of formation, density and explosive performance were investigated by theoretical methods. The results were as follows:

- i) The  $p$ - $\pi$  conjugative effect between the N atom of the substituent and the TZ ring resulting from the introduction of amino and hydrazino groups, lowered the total energy of the whole system, whilst introduction of a carbonyl containing group had little effect on the TZ ring. Additionally, the difference between the energy levels of the named compounds was obtained by frontier orbital theory calculation, and the order of thermal stability was compared: (T2A6) > (T2A4) > (T2A1) > (T2A3) > (T2A5) > (T2A2).
- ii) Compared with the *s*-tetrazine molecule, substitution reduced the total electric charge of the TZ ring, which means the degree of electronic delocalization improved with substitution.
- iii) The positive charge is centered mainly inside the molecule, whilst the negative electrostatic charge is distributed on the N atoms of the TZ ring and the peripheral N atoms of substituents without H atoms.
- iv) BDE analysis implied that the C1-N5 bond was easiest to break in the amino and hydrazino bi-substituted *s*-tetrazine derivatives, and under ideal circumstances, the ranking for ease of synthesis was (T2A1) > (T2A2) > (T2A5) > (T2A6) > (T2A3) > (T2A4).
- v) A high nitrogen content is helpful for enhancing the molecular stability and improving the HOFs. However, the introduction of carbonyl and amido groups raised the total energy, which worked against the stability. The detonation properties were affected by both density and nitrogen content, and the introduction of hydrazino and carbohydrazido groups greatly improved the explosive performance, *s*-tetrazines substituted by hydrazino, semicarbazido and their relatives displayed favorable explosive performance,

indicating that this series of compounds has the potential to become novel energetic compounds, and it would be valuable to synthesize them.

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