

Quantum-chemical Investigation of Substituted s-Tetrazine Derivatives as Energetic Materials

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s-Tetrazine is the essential candidate of many energetic compounds due to its high nitrogen content, enthalpy of formation and thermal stability. The present study explores the design of s-tetrazine derivatives in which different -NO₂, -NH₂ and -N₃ substituted azoles are attached to the tetrazine ring via C-N linkage. The density functional theory (DFT) is used to predict the geometries, heats of formation (HOFs) and other energetic properties. The predicted results show that azide group plays a very important role in increasing HOF values of the s-tetrazine derivatives. The densities for designed molecules were predicted by using the crystal packing calculations. The introduction of -NO₂ group improves the density as compared to -N₃, and -NH₂ groups and hence the detonation performance. Bond dissociation energy analysis and insensitivity correlations revealed that amino derivatives are better candidates considering insensitivity and stability.

Key Words : s-Tetrazine, Density functional theory, Heat of formation, Bond dissociation energy, Density

Introduction

s-Tetrazine chemistry has been known for more than one century^{1,2} and their photophysical,³ electrochemical,⁴ fluorescence spectroscopy,⁵ coordination,⁶ and explosive⁷⁻⁹ properties have been briefly recognized. s-Tetrazine is an *azo* compound with a high nitrogen content (68.27%), making it of interest for the theoretical and synthesis of high energy materials (HEMs). s-Tetrazines have demonstrated powerful synthetic utility through their ability to participate in inverse electron demand Diels-Alder reactions^{10,11} providing access to a wide range of heterocycles based HEMs. Furthermore, s-tetrazines also possess high positive HOFs, crystal densities and essential properties for energetic materials applications.¹²⁻¹⁵

The synthesis and theoretical study on the nitrogen-rich compounds have received considerable interest due to the low percentage of carbon and hydrogen in these compounds, enhances the density and allows a good oxygen balance (O.B.) to be achieved more easily.^{16,17} In contrast to traditional energetic materials, nitrogen-rich materials have a large number of N-N and C-N bonds and therefore possess large positive enthalpy of formation and less from the oxidation of hydrocarbon framework. The need for energetic materials that exhibit a combination of good thermal stability, lower impact sensitivity and higher HOFs continues to expand. Analogy of thermal and physical properties between related carbocyclic and heterocyclic compounds would predict the desired stability of the heterocyclic skeleton of compound.¹⁸ Polyazido organic compounds have high relative HOFs as one azido group adds about 87 kcal/mol of energy to a hydrocarbon compound.^{19,20} However, so far, there is no experimental data available on densities and

HOFs for this new class of energetic compounds. It is well known that evaluation of explosive performances of energetic materials requires knowledge of the HOFs but it is impractical to measure HOF for an energetic compound since there are many intermediates for energetic compounds. In these cases, it is of great importance to use computational methods that can accurately estimate HOFs.

In order to evaluate the s-tetrazine derivatives, this work theoretically investigates several important properties including HOFs, densities, detonation performance, stability and sensitivity by employing DFT methods. DFT methods can provide theoretical proof for judging whether the designed

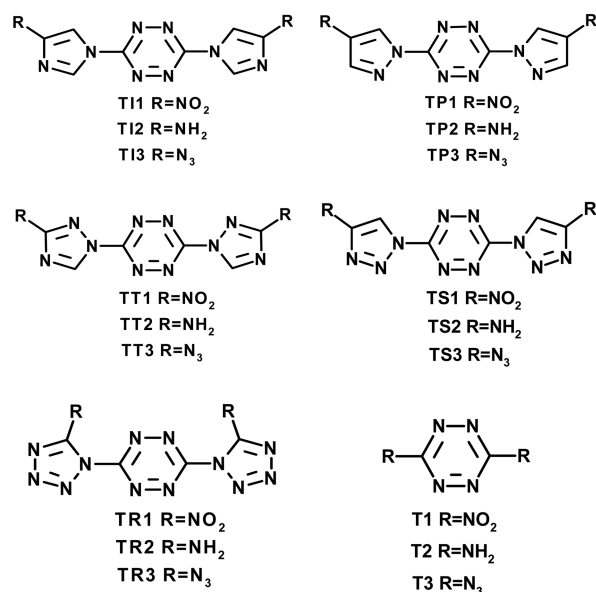


Figure 1. Molecular framework of the s-tetrazine derivatives.

compounds are worth synthesizing. The designed s-tetrazine derivatives have been shown in Figure 1.

Computational Methods

All quantum mechanical calculations were performed with *Gaussian 03* program suite.²¹ The Becke three-parameter hybrid (B3)²² functional was used along with Lee-Yang-Parr (LYP)^{23,24} correlation. For all optimization and harmonic vibrational frequency calculations, 6-31G* basis set has been employed. HOF has been predicted by designing appropriate isodesmic reactions for the designed s-tetrazine derivatives.^{25,26} In an isodesmic reaction, number of each kind of formal bond is conserved according to bond separation reaction (BSR) rules. The target molecule is broken down into a set of heavy atom molecules containing same

Table 1. Total energy (E_0) at the B3LYP/6-31G* level and experimental gas phase HOFs for the reference compounds

Compd.	E_0 (au)	HOF (kJ/mol)
CH ₄	-40.4694	-74.6 ³⁰
NH ₃	-56.5096	-45.9 ³⁰
CH ₃ NH ₂	-95.7845	-22.5 ³¹
CH ₃ NO ₂	-244.9538	-74.7 ³²
CH ₃ N ₃	-204.0373	238.4 ³⁰
Imidazole	-226.1386	129.5 ³³
Pyrazole	-226.1225	179.4 ³³
1,2,4-Triazole	-242.1848	192.7 ³⁴
1,2,3-Triazole	-242.1587	271.7 ³⁴
Tetrazole	-258.2464	326.0 ³⁵
s-Tetrazine	-296.2645	487.2 ³⁰

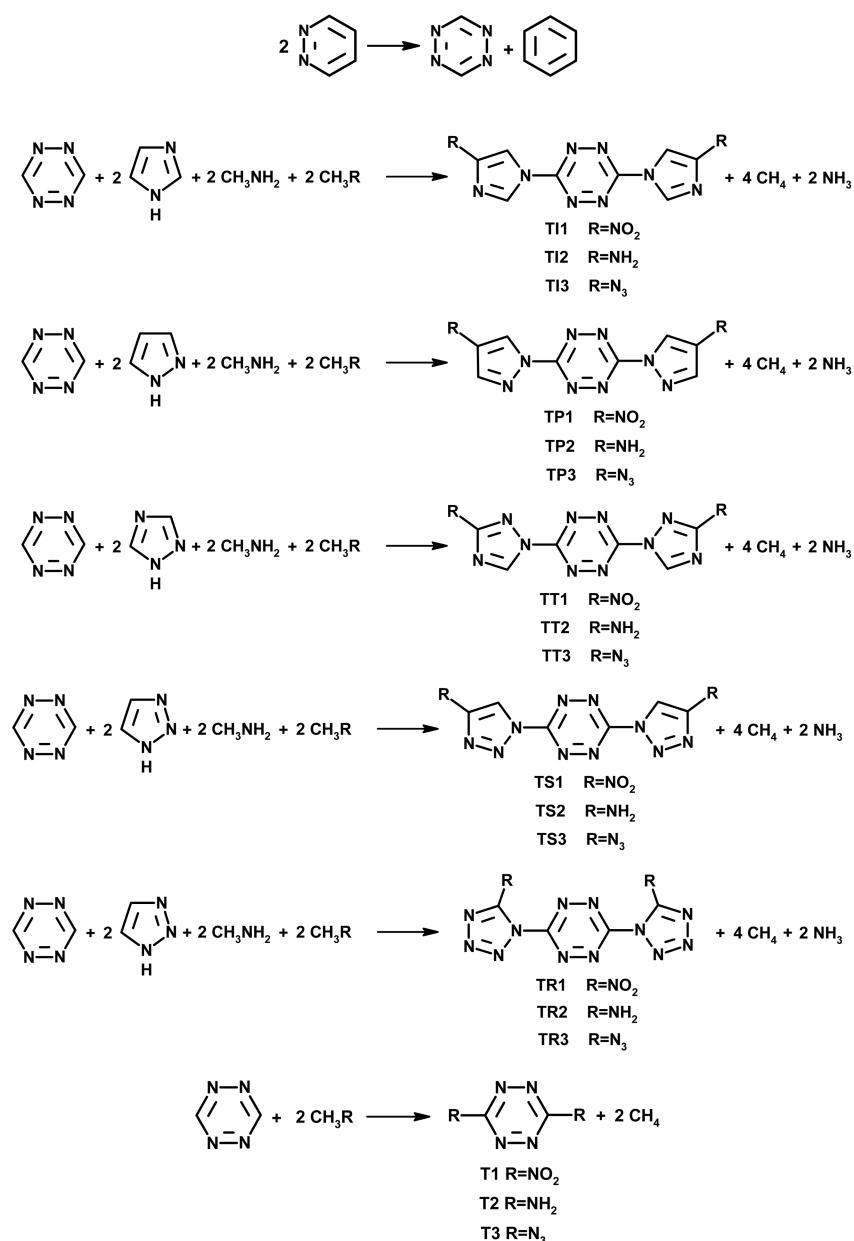


Figure 2. The designed isodesmic reaction schemes for the calculation of HOFs.

component bonds. BSR rules cannot be applied to the molecules with delocalized bonds and cage skeletons because of large calculated errors of HOFs. In view of the above, present study involves the design of isodesmic reactions in which a numbers of all kinds of bonds keep invariable to decrease the calculation errors of HOF. Imidazole, pyrazole, triazole, tetrazole and s-tetrazine rings are kept intact while constructing isodesmic reactions and this approach proved to be reliable.²⁷⁻²⁹ The total energies and experimental gas phase HOFs of the reference compounds³⁰⁻³⁵ used in the isodesmic reactions have been listed in Table 1. There are no experimental HOFs values of s-tetrazine and hence, obtained from the designed isodesmic reaction as shown in Figure 2.

The crystal packing calculation have been adopted to predict the crystal density from molecular structure using the dreiding force field^{36,37} with the most common space groups such as $P2_1/c$, $P2_12_12_1$, $P1$, $P2_1$, $C2/c$, $Pbca$, $Pna2_1$, $Pnma$, $Pbcn$ and Cc are considered.^{38,39} Consequently, highly probable molecular crystal structures can be obtained by determining the most stable structures in few space groups and comparing the results to search for low-lying minima in lattice energy surface.⁴⁰

The empirical Kamlet-Jacobs⁴¹ equations were employed to estimate the values of D and P for the HEMs containing C, H, O and N as following equations:

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho_0) \quad (1)$$

$$P = 1.55\rho_0^2 NM^{1/2}Q^{1/2} \quad (2)$$

Where in above equations D is detonation velocity (km/s), P is detonation pressure (GPa), N is moles of gaseous detonation products per gram of explosives, M is average molecular weights of gaseous products, Q is chemical energy of detonation (kJ/mol) defined as the difference of the HOFs between products and reactants, and ρ_0 is the density of explosive (g/cm^3).

Thermal stability of the s-tetrazine derivatives have been evaluated by calculating bond dissociation energies (BDEs)⁴² of the C-NO₂, C-NH₂ and C-N₃ bonds. BDE is defined as the difference between the zero point energy corrected total energies at 0K of the parent molecules and those of the corresponding radicals in the unimolecular bond dissociation. This has been frequently used as a measure of the thermal stability of the compounds. In the present study, BDE has been calculated using this equation:

$$\begin{aligned} \text{BDE}_{298}(\text{R}_1-\text{R}_2) \\ = [\Delta_f H_{298}(\text{R}_1) + \Delta_f H_{298}(\text{R}_2)] - \Delta_f H_{298}(\text{R}_1-\text{R}_2) \end{aligned} \quad (3)$$

Where, R_1-R_2 is the neutral molecule, and R_1 and R_2 are the corresponding radicals.^{43,44}

The HOMO-LUMO gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) can be correlated with the sensitivity of the molecules.⁴⁵ The HOMO-LUMO gap of s-tetrazine derivatives has been predicted using DFT at B3LYP/6-31G* level.

Results and Discussion

The present study investigates important energetic properties including HOFs, densities, detonation performance, stability and sensitivity by employing density functional theory. A systematic structure-property relationship has been established by varying different substituents on the s-tetrazine backbone. The predicted energetic properties of the designed molecules have been compared with 3,6-dinitro-1,2,4,5-tetrazine (**T1**), 3,6-diamino-1,2,4,5-tetrazine (**T2**), and 3,6-diazo-1,2,4,5-tetrazine (**T3**) to evaluate the performance. These tetrazine derivatives show high explosive performance with better insensitivity.³⁰

Heat of Formation. HOFs of s-tetrazine derivatives have been predicted using B3LYP method in combination with the 6-31G* basis set through appropriate design of isodesmic reactions (Fig. 2). HOFs of the designed compounds are listed in Table 2. All the designed compounds show high positive HOFs and it may be attributed to the large number of energetic N-N and C-N bonds of molecular framework. Previous studies⁴⁶⁻⁴⁸ show that the theoretically predicted values are in good agreement with experiments by choosing the appropriate reference compounds in the isodesmic reaction.

The calculated ΔH_f^0 of the designed molecules have been compared with **T1**, **T2**, and **T3** to evaluate the performance. The predicted gas phase HOFs of **T1**, **T2**, and **T3** using isodesmic reaction approach are 549.8, 330.8, and 1080.5 kJ/mol, respectively. The predicted HOFs of **T2** and **T3** are comparable with the experimental values (**T2**=307; **T3**=1101 kJ/mol).⁴⁹ Among the designed compounds, azido derivatives such as, **TI3**, **TP3**, **TT3**, **TS3**, and **TR3** show very high positive HOFs (> 1300 kJ/mol). Azido group is more energetic than nitro and amino substituents and significantly enhances HOFs of the designed compounds.³⁰ The order of contribution in total HOFs by the substituents can be given as $\text{N}_3 > \text{NO}_2 > \text{NH}_2$. Among the different azoles, energy contribution from tetrazole is very high (326 kJ/mol) and hence **TR1**, **TR2**, and **TR3** shows higher HOFs as com-

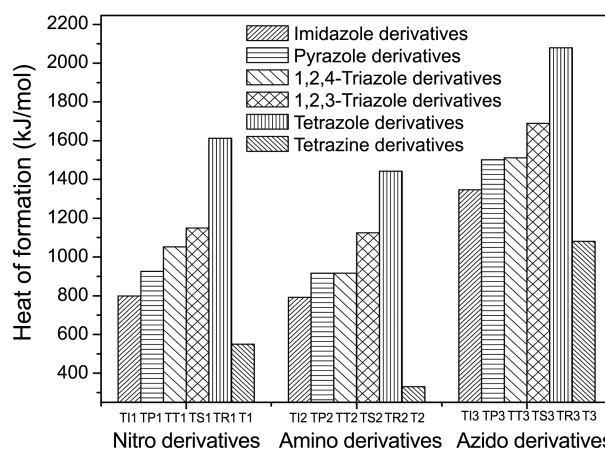


Figure 3. Heat of formation (kJ/mol) profile of the s-tetrazine derivatives.

Table 2. Calculated energetic properties of the *s*-tetrazine derivatives

Compd	E ₀ (au)	O.B. (%)	HOF (kJ/mol)	Q (cal/g)	D (km/s)	P (GPa)	BDE (kJ/mol)	ΔE (eV)
TI1	-1155.1766	-73.7	797.9	1181.4	7.25	22.18	290.5	2.25
TI2	-856.8797	-131.2	791.6	775.4	6.46	17.45	446.9	3.42
TI3	-1073.3728	-97.3	1346.8	1087.5	6.42	16.13	374.1	2.44
TP1	-1155.1333	-73.7	926.3	1282.3	7.70	25.98	302.5	2.82
TP2	-856.8366	-131.2	915.8	897.1	6.81	19.70	438.8	3.61
TP3	-1073.3197	-97.3	1501.4	1212.3	6.77	18.44	366.2	3.04
TT1	-1187.2372	-47.1	1052.4	1269.8	7.78	25.36	268.4	2.86
TT2	-888.9728	-97.5	916.4	890.3	6.79	18.91	471.2	3.64
TT3	-1105.4506	-69.8	1511.5	1212.3	6.99	19.72	376.5	3.08
TS1	-1187.1909	-47.1	1149.3	1345.5	8.22	29.38	284.9	2.84
TS2	-888.9016	-97.5	1124.4	1092.5	7.14	20.94	455.3	3.59
TS3	-1105.3906	-69.8	1689.8	1355.3	7.16	20.59	375.5	2.74
TR1	-1219.2312	-20.8	1613.3	1594.9	9.09	36.01	242.9	3.38
TR2	-920.9972	-64.5	1442.5	1390.2	8.19	28.72	486.3	3.76
TR3	-1137.4588	-42.7	2080.1	1657.2	7.84	25.13	370.7	3.27
T1	-705.2096	0.0	549.8	1857.6	9.43	40.47	229.4	3.66
T2	-406.9103	-85.7	330.8	705.9	6.79	18.63	330.5	3.70
T3	-623.4376	-39.0	1080.5	1574.6	8.20	28.82	309.3	3.63

E₀- total energy, O.B.- oxygen balance, HOF- heat of formation, Q- chemical energy of detonation, *D*- detonation velocity, *P*- detonation pressure, BDE- bond dissociation energy, and ΔE- HOMO-LUMO gap.

pared to other derivatives. HOF of the pyrazole is higher than imidazole, hence **TP1**, **TP2** and **TP3** shows higher HOFs than **TI1**, **TI2**, and **TI3**, respectively. Similarly, energy contribution of the 1,2,3-triazole is higher than the 1,2,4-triazole and hence, **TT1**, **TT2** and **TT3** shows lower HOFs than **TS1**, **TS2** and **TS3**, respectively. The introduction of different azole rings on *s*-tetrazine improves the nitrogen content and HOFs. Figure 3 compares the heat of formation of *s*-tetrazine derivatives. Substitution of azido group increases the nitrogen content and these compounds possess high HOFs. Overall study shows that designed compounds possess high positive HOFs than the **T1**, **T2**, and **T3** due to the significant energy contribution from azole rings.

Density. Crystal packing calculations have been performed for the prediction of densities by using polymorph calculation in Material studio.⁵⁰ The calculated densities and lattice parameters are listed in Table 3. The results reveal that substitution of nitro group play important role in increasing the density as compared to other substituents such as amino and azido. However, the role of amino group cannot be clearly defined since packing pattern is highly dependent on the electronic structure of the molecule.⁵¹ Predicted density of **T2** and **T3** molecules are 1.55 and 1.72 g/cm³, respectively, found close to with earlier reported values by Xiao *et al.* (**T2**=1.52; **T3**=1.70 g/cm³).³⁰ The pyrazole derivatives (**TP1**, **TP2** & **TP3**) show slightly higher densities as compared to imidazole derivatives (**TI1**, **TI2** & **TI3**). The tetrazole compounds *viz.*, **TR1**, **TR2**, and **TR3** are denser in the designed *s*-tetrazine derivatives and their densities are 1.75, 1.70, and 1.58 g/cm³, respectively. The nitro derivative of 1,2,3-triazole (**TS1**) shows higher density than corresponding 1,2,4-triazole derivative (**TT1**). Com-

Table 3. Calculated crystal densities and lattice parameters of the *s*-tetrazine derivatives

Compd.	Density (g/cm ³)	Space group	Lattice parameters					
			Length (Å)			Angle (deg.)		
			a	b	c	α	β	γ
TI1	1.66	<i>P2₁/c</i>	18.54	12.80	13.56	90.0	157.2	90.0
TI2	1.64	<i>C2/c</i>	19.37	9.71	18.49	90.0	145.1	90.0
TI3	1.48	<i>P1</i>	11.94	10.15	8.61	101.1	124.0	112.7
TP1	1.76	<i>P2₁/c</i>	10.85	4.75	22.95	90.0	101.3	90.0
TP2	1.68	<i>Cc</i>	17.13	10.14	8.67	90.0	138.5	90.0
TP3	1.54	<i>P2₁/c</i>	22.19	10.61	11.94	90.0	152.6	90.0
TT1	1.64	<i>PNA2₁</i>	17.92	12.25	5.70	90.0	90.0	90.0
TT2	1.59	<i>P2₁/c</i>	7.97	19.88	7.58	90.0	118.9	90.0
TT3	1.55	<i>P2₁</i>	16.69	10.28	3.80	90.0	81.1	90.0
TS1	1.74	<i>P2₁/c</i>	15.63	17.04	17.62	90.0	165.5	90.0
TS2	1.59	<i>P1</i>	7.30	15.73	5.30	82.5	99.7	118.0
TS3	1.54	<i>P2₁/c</i>	8.50	18.57	9.33	90.0	118.3	90.0
TR1	1.75	<i>P2₁</i>	8.41	12.47	7.30	90.0	130.3	90.0
TR2	1.70	<i>C2/c</i>	27.40	4.01	21.84	90.0	124.6	90.0
TR3	1.58	<i>P2₁/c</i>	33.93	13.25	30.69	90.0	174.6	90.0
T1	1.88	<i>PBCA</i>	9.99	9.81	12.29	90.0	90.0	90.0
T2	1.55	<i>Cc</i>	7.57	10.06	6.83	90.0	108.3	90.0
T3	1.72	<i>C2</i>	19.98	4.28	24.06	90.0	161.9	90.0

parison of **TT2** and **TS2** shows that there is no significant change in density by changing the molecular skeleton. A similar phenomenon is observed in case of **TT3** and **TS3**.

Detonation Performance. Computed values of velocity of detonation (*D*) and detonation pressure (*P*) are summarized in Table 2. The detonation velocity is proportional to

density, while the Chapman-Jouguet detonation pressure is proportional to the square of initial density.^{41,52} The detonation performance is more dependent on density rather than HOFs. The results reveal that though azido derivatives have high HOF but due to the low densities overall performance is less. The performance of nitro derivatives is better due to the higher densities and O.B. which increase the concentration of detonation products like CO, CO₂, and H₂O. The nitro derivatives (**TI1**, **TP1**, **TT1**, **TS1**, and **TR1**) show *D* about 7.5 to 9.09 km/s and *P* of 25.8 to 36 GPa. The tetrazole derivatives (**TR1**, **TR2** and **TR3**) show better performance in the series due to the better densities, O.B. and high nitrogen content. HOFs and densities of pyrazole derivatives are higher than that of imidazole derivatives, therefore **TP1**, **TP2**, and **TP3** shows better performance over corresponding **TI1**, **TI2**, and **TI3**, respectively. Similar phenomena is observed in case of 1,2,3-triazole and 1,2,4-triazole derivatives. All designed molecules show comparable detonation performance to **T1**, **T2**, and **T3**.

Thermal Stability. All the BDEs are calculated by employing the hybrid DFT using B3LYP methods together with the 6-31G* basis set. BDE is often a key factor in investigating the pyrolysis mechanism of the energetic material. Generally, smaller the BDE, weaker is the bond.⁵³⁻⁵⁵ Different studies illustrate that C-NO₂ is the possible trigger bond in the nitro-aromatic compounds^{53,54} and it can be ruptured easily during pyrolysis. The strength of weakest bond of explosive molecule plays an important role in the initiation event. According to the criteria of HEMs, BDE should be higher than 80-120 kJ/mol.⁵⁶ In the present study, BDE of C-NO₂, C-NH₂ and C-N₃ have been calculated to find out the possible trigger bond and thermally unstable compounds. All the predicted values for BDE are shown in Table 2. The BDEs of C-NO₂ bonds are lower in comparison with C-NH₂ and C-N₃. The NH₂ group is electron rich and hence involved in conjugation through donation of lone pair of electrons on nitrogen. Resonance strengthens the C-NH₂ bond and requires high energy for the pyrolysis. It can be deduced that substitution of the -N₃ and -NH₂ are very useful for increasing the thermal stability.³⁰ This shows that the C-NO₂ bond have less bond strength and susceptible for earlier pyrolysis. Predicted BDEs of C-NO₂, C-NH₂, and C-N₃ bonds in **T1**, **T2**, and **T3** are 229.4, 330.5 and 309.3 kJ/mol, respectively. The NO₂ group of **TI1** is found to be susceptible for the pyrolysis as compared to **TP1**. Among the triazole derivatives, **TT1** is found to be unstable than **TS1**. The overall study shows that **TR1** is more unstable than all nitro derivatives. All the nitro compounds show BDEs in between 248 to 302 kJ/mol, while amino and azido derivatives show the BDE higher than 366 kJ/mol. Predicted BDEs reveals that s-tetrazine derivatives are thermally stable due to aromatic and symmetric skeleton. The symmetry in molecular skeleton can delocalize the π -electron density of ring and improves the stability of compounds. All designed molecules show higher BDEs for C-NO₂, C-NH₂, and C-N₃ bonds as compared to **T1**, **T2**, and **T3** may be due to the presences of azole rings.

Sensitivity Correlation. The HOMO-LUMO gap has been correlated with the sensitivity of material.⁵⁷ In general, smaller is the HOMO-LUMO gap, easier the electron transition and larger the sensitivity. The predicted HOMO-LUMO gap of the designed molecules have been compared with different nitrobenzene derivatives such as 2,4,6-trinitrotoluene (TNT), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitroaniline (TNA). The HOMO-LUMO gap of designed molecules and nitrobenzene derivatives has been obtained using B3LYP/6-31G* method. The predicted HOMO-LUMO gap of tetrazine derivatives is listed in Table 2. Introduction of an amino group into aromatic skeleton is well known strategy to increase stability and insensitivity under stimuli of impact and shock due to its electron donating nature.^{58,59} The calculated HOMO-LUMO gap of TNT, TATB, TNB and TNA are 4.32, 4.56, 3.94, and 4.41 eV, respectively. These values reveal that presence of amino group ortho to nitro group in aromatic skeleton (TATB and TNA) improves insensitivity due to the strong inter- and intra-molecular hydrogen bonding. From the HOMO-LUMO gap values of the s-tetrazine derivatives, it can be seen that amino derivatives (**TI2**, **TP2**, **TT2**, **TS2**, and **TR2**) are more insensitive than nitro (**TI1**, **TP1**, **TT1**, **TS1**, and **TR1**) and azido (**TI3**, **TP3**, **TT3**, **TS3**, and **TR3**) derivatives. Predicted HOMO-LUMO gap of **T1**, **T2**, and **T3** are 3.66, 3.70, and 3.63 eV, respectively. Among the designed molecules, imidazole derivatives (**TI1**, **TI2** and **TI3**) reveal lower HOMO-LUMO gap and more sensitive. However, tetrazole derivatives (**TR1**, **TR2** and **TR3**) shows higher HOMO-LUMO gap in the series. The replacement of 1,2,4-triazole in **TT1**, **TT2** and **TT3** with 1,2,3-triazole in **TS1**, **TS2** and **TS3** slightly reduces the HOMO-LUMO gap. The order of sensitivity in imidazole, pyrazole and 1,2,4-triazole derivatives can be given as NO₂ > N₃ > NH₂, while for 1,2,3-triazole and tetrazole derivatives is N₃ > NO₂ > NH₂. Overall sensitivity correlations revealed that the amino derivatives are better candidates in terms of insensitivity, however, more sensitive than the nitrobenzene derivatives.

Conclusions

In summary, by using first-principles calculations at the DFT level, energetic properties of the s-tetrazine derivatives have been studied. Based on designed sets of isodesmic reactions, standard gas-phase HOFs are predicted. The energetic properties of the designed molecules have been compared with 3,6-dinitro-1,2,4,5-tetrazine, 3,6-diamino-1,2,4,5-tetrazine, and 3,6-diazido-1,2,4,5-tetrazine. It has been found that high-nitrogen compounds, with their high-energy content, are a very promising set of potential energetic materials. Among the designed compounds, azido derivatives show very high positive HOF (> 1300 kJ/mol). Introduction of nitro group increases the density (1.66 g/cm³) and hence overall detonation performance of the molecule than amino and azido derivatives. Thermal stability and sensitivity of the designed compounds has been evaluated by

using bond dissociation energies and HOMO-LUMO gap analysis. Designed molecules have better thermal stability and insensitivity as evidenced from BDE and HOMO-LUMO gap index. Overall performance of designed compounds is moderate and may find their applications in gas generators and smoke-free pyrotechnic fuels as they are rich in nitrogen content.

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