Computational Study on Substituted *s*-Triazine Derivatives as Energetic Materials

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Received 4 August 2011; Accepted 19 October 2011

Abstract: *s*-Triazine is the essential candidate of many energetic compounds due to its high nitrogen content, enthalpy of formation and thermal stability. The present study explores *s*-triazine derivatives in which different -NO₂, -NH₂ and -N₃ substituted azoles are attached to the triazine ring via C-N linkage. The density functional theory is used to predict geometries, heats of formation and other energetic properties. Among the designed compounds, -N₃ derivatives show very high heats of formation. The densities for designed compounds were predicted by using the crystal packing calculations. Introduction of -NO₂ group improves density as compared to -NH₂ and -N₃, their order of increasing density can be given as NO₂>N₃>NH₂. Analysis of the bond dissociation energies for C-NO₂, C-NH₂ and C-N₃ bonds indicates that substitutions of the -N₃ and -NH₂ group are favorable for enhancing the thermal stability of *s*-triazine derivatives. The nitro and azido derivatives of triazine are found to be promising candidates for the synthetic studies.

Keywords: *s*-Triazine, HEMs, Density functional theory, HOF, Bond dissociation energy, Density.

Introduction

s-Triazine is an intriguing heterocycle for high energy materials (HEMs) and exhibits a high degree of thermal stability^{1,2}. Triazine rings have been studied for use in a number of applications such as herbicides, chemicals, synthesis, dyes, and polymers³⁻⁷. Energetic materials combined with triazines show the desirable properties of high nitrogen content and astonishing kinetic and thermal stabilities. The enthalpies of energetic chemical systems are governed by their molecular structure. Nitrogen-rich compounds derive their energy from the large number of energetic N-N and C-N bonds in these compounds⁸. With interesting properties including high density, large positive heat of formation (HOF) and thermal stability, nitrogen-rich compounds have potential applications as explosives, smoke free pyrotechnics, gas generators, solid fuels in micropropulsion and precursors for nano materials⁹⁻¹⁴.

Imidazole, pyrazole, triazole, and tetrazole are natural frameworks for energetic materials, as they have inherently high nitrogen contents. Adding these functionalities to the ring typically alters the HOF, making them more positive, which is a desired characteristic for most energetic

materials¹⁵. The key properties of energetic materials in relation to their electronic structure are HOF, density, detonation characteristics, thermal stability, and sensitivity. HOF is frequently taken as indicative of the energy content of HEMs, but it is impractical to measure HOF experimentally since there are many intermediates for energetic compounds. Isodesmic reaction approach has been employed for the calculation of HOFs of the designed compounds¹⁶⁻¹⁸. Density is being predicted by crystal structure packing calculations as it is superior to the group additive approaches¹⁹⁻²¹. Crystal structure prediction tools automatically take into account molecular structure, conformation and crystal packing efficiency. The explosive performance characteristics, viz., detonation velocity (D) and pressure (P), were evaluated by Kamlet-Jacobs empirical relations from their theoretical densities and calculated HOFs. Thermal stability of energetic material determines its applicability in the field of HEMs. Thermal stability has been evaluated by calculating the bond dissociation energy (BDE) and predicted the relative stability of designed compounds. In addition, sensitivity is another important issue for safe handling of the energetic materials. The sensitivity of designed compounds have been predicted on the basis of band gap between highest occupied molecular orbital and lowest unoccupied molecular orbital.

In the present study, different combinations of azoles on the triazine skeleton as model energetic compound have been selected. To evaluate the effect of different substituents on the performance of energetic material $-\text{NO}_2$ group has been replaced by $-\text{NH}_2$ and $-\text{N}_3$. These groups are the essential functional groups usually contained in propellants and explosives. Additionally, this study tries to shed some light on the theoretical design of energetic materials so as to improve the synthesis efficiency. The designed triazine derivatives are shown in Figure 1.

Figure 1. Chemical structures of the *s*-triazine derivatives studied.

Experimental

Density functional theory (DFT)²² has been applied to optimize all structures at the B3LYP/6-31G* level by using Gaussian 03 package²³. The appropriate isodesmic reactions have been designed for the prediction of HOFs, in which numbers of electron pairs and chemical bond types are conserved. The calculated and experimental gas phase HOFs of the reference compounds imidazole, pyrazole, triazoles, *s*-triazine, CH₄, NH₃, CH₃NO₂, CH₃NH₂, and CH₃N₃ are listed in Table 1. The designed isodesmic reactions for the prediction of gas phase HOF are shown in Figure 2.

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

Compd.	E_0 (au)	HOF, kJ/mol
CH ₄	-40.4694	-74.6
NH ₃	-56.5096	-45.9
CH ₃ NH ₂	-95.7845	-22.5
CH ₃ NO ₂	-244.9538	-74.7
CH ₃ N ₃	-204.0373	238.4
Imidazole	-226.1386	129.5
Pyrazole	-226.1225	179.4
1,2,4-Triazole	-242.1848	192.7
1,2,3-Triazole	-242.1587	271.7
<i>s</i> -Triazine	-280.2942	225.8

Figure 2. Isodesmic reaction schemes for *s*-triazine derivatives.

The crystal packing calculation have been adopted to predict crystal density from molecular structure using the dreiding force field^{24,25}. 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. The empirical Kamlet-Jacobs²⁶ equations were employed to estimate the values of *D* and *P* for the high energy materials 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/cm³).

Thermal stability of the *s*-triazine derivatives have been evaluated by calculating bond dissociation energies (BDEs)²⁷ of the C-NO₂, C-NH₂ and C-N₃ bonds. The 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 thermal stability of the compounds. In the present study, BDE has been calculated using this equation:

$$BDE_{298}(R_1-R_2) = [\Delta_f H_{298}(R_1) + \Delta_f H_{298}(R_2)] - \Delta_f H_{298}(R_1-R_2), \quad (3)$$

where, R_1 - R_2 is the neutral molecule, and R_1 and R_2 are the corresponding radicals^{28,29}. The band gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) can be correlated with sensitivity of the molecules³⁰. The band gap of *s*-triazine derivatives has been predicted using DFT at B3LYP/6-31G* level.

Results and Discussion

The present study brings out the structure-property relationships of triazine derivatives by comparing their characteristics like gas phase HOF, density (ρ_0), detonation characteristics (D and P), thermal stability and insensitivity. Different substituents such as $-\text{NO}_2$, $-\text{NH}_2$ and $-\text{N}_3$ have attached to the triazine ring via C-N linkage of azoles to understand the role of substituents and nitrogen-rich molecular skeleton.

Heat of Formation

In the present study, HOFs have been calculated for triazine derivatives using DFT-B3LYP method with 6-31G* basis sets via designed isodesmic reactions (Figure 2). Previous studies³¹⁻³⁴ show that the theoretically predicted values are in good agreement with experiments by choosing the appropriate reference compounds in the isodesmic reaction. The different five member heterocycles such as imidazole, pyrazole, 1,2,4-triazole and 1,2,3-triazole have been substituted on the *s*-triazine to study the changes in HOF systematically. Table 2 lists the calculated energetic properties of triazine derivatives.

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

Compd.	E_0 (au)	O. B. %	HOF, (kJ/mol)	Q (cal/g)	D (km/s)	P (GPa)	BDE (kJ/mol)	ΔE (eV)
V1	-1568.6809	-81.2	640.92	980.2	6.60	17.82	289.06	3.64
V2	-1121.2348	-148.2	635.82	469.0	5.16	10.32	445.93	4.47
V3	-1445.9752	-107.5	1466.64	871.9	5.97	13.95	374.36	3.71
P1	-1568.6141	-81.2	840.50	1095.4	7.19	22.33	300.93	4.12
P2	-1121.1804	-148.2	802.29	591.8	5.47	11.59	436.78	4.90
P3	-1445.8964	-107.5	1696.35	1008.6	6.21	15.20	366.15	4.16
R1	-1616.7721	-51.8	956.82	1041.4	7.36	22.70	266.23	4.16
R2	-1169.3759	-110.1	819.30	598.8	5.91	13.99	469.52	4.50
R3	-1494.0929	-77.1	1710.94	1009.7	6.62	17.76	375.94	4.20
Q1	-1616.7017	-51.8	1173.23	1165.4	7.51	23.43	283.10	3.71
Q2	-1169.2675	-110.1	1135.23	829.7	6.22	15.00	453.63	4.58
Q3	-1494.0021	-77.1	1980.81	1168.9	6.65	17.43	375.73	3.79

E_0 - 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 - band gap.

Among the designed compounds, azido derivatives (**V3**, **P3**, **R3**, and **Q3**) exhibit very high positive HOF. The contribution of substituents in the total HOF can be given as $\text{N}_3 > \text{NO}_2 > \text{NH}_2$. HOF of the pyrazole (179.4 kJ/mol) is higher than the imidazole (129.5 kJ/mol), hence **P1**, **P2**, and **P3** shows higher HOF than **V1**, **V2**, and **V3**. Similarly, energy contribution of the 1,2,3-triazole (271.7 kJ/mol) is higher than the 1,2,4-triazole (192.7 kJ/mol) and hence **Q1**, **Q2**, and **Q3** shows higher HOF than **R1**, **R2**, and **R3**. The

introduction of different azoles on *s*-triazine improves the nitrogen content and HOF. Increase in nitrogen content enhances HOF. Substitution of azido group increases the nitrogen content and these compounds possess very high HOF. Figure 3 compares the heat of formation of triazine derivatives. *s*-Triazine compounds form a unique class of energetic materials whose energy is derived from their very high HOF directly attributable to the large number of inherently energetic N-N and C-N bonds rather than from overall heats of combustion.

Figure 3. Heat of formation (kJ/mol) profile of the triazine derivatives.

Density

Density is one of the most important factors that determine the performance of an explosive, since the detonation pressure (P) is dependent on square of the density and the detonation velocity (D) is proportional to the density according to an empirical equation proposed by Kamlet and Jacobs²⁶. The densities of designed compounds have been predicted by using the crystal packing calculations in Material studio³⁵. The calculated densities and lattice parameters of the *s*-triazine derivatives are listed in Table 3. The substitution of $-\text{NO}_2$ group play important role in increasing the density as compared to other substituents like $-\text{NH}_2$ and $-\text{N}_3$. The increasing order of density can be given as, $\text{NO}_2 > \text{NH}_2 > \text{N}_3$. All the triazine derivatives follow same order. The nitro substituted derivatives like **V1**, **P1**, **R1**, and **Q1** possess higher densities and their densities are 1.58, 1.72, 1.64 and 1.62 g/cm^3 , respectively. The nitro derivative of pyrazole (**P1**) exhibit higher density than corresponding nitro imidazole derivative (**V1**), while amino and azido derivatives reveals comparable densities. The 1,2,4-triazole derivatives (**R1**, **R2**, and **R3**) are found to be denser than corresponding 1,2,3-triazole derivatives (**Q1**, **Q2**, and **Q3**).

Detonation Performance

Computed values of velocity of detonation (D) and detonation pressure (P) are summarized in Table 2. 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 high densities and oxygen balance which increase the concentration of detonation products like CO , CO_2 and H_2O . The nitro derivatives **V1**, **P1**, **R1**, and **Q1** show D about 6.6 to 7.5 km/s and P of 17.8 to 23.4 GPa. The triazole derivatives show better performance in the series due to the higher HOF and densities. The order of the performance can be given as, $\text{NO}_2 > \text{N}_3 > \text{NH}_2$. The poor performance of amino compounds (**V2**, **P2**, **R2**, and **Q2**) is attributed to lower densities and HOF. Figure 4 compares the detonation velocities of the triazine derivatives.

Table 3. The calculated densities and lattice parameters of the triazine derivatives.

Compd.	Density (g/cm ³)	Space group	Lattice parameters					
			Length (Å)			Angle (°)		
			a	b	c	α	β	γ
V1	1.58	<i>PI</i>	11.5	8.5	13.4	89.8	128.6	113.9
V2	1.46	<i>C2</i>	34.2	4.3	18.2	90.0	145.1	90.0
V3	1.48	<i>PI</i>	13.3	1.5	19.5	77.7	69.3	66.4
P1	1.72	<i>P2₁/c</i>	4.4	34.3	11.8	90.0	116.2	90.0
P2	1.46	<i>P2₁2₁2₁</i>	17.3	22.1	3.9	90.0	90.0	90.0
P3	1.49	<i>PI</i>	25.7	3.9	21.9	66.9	145.4	130.8
R1	1.64	<i>Pbca</i>	17.2	18.4	10.8	90.0	90.0	90.0
R2	1.53	<i>P2₁/c</i>	19.1	19.7	20.3	90.0	169.0	90.0
R3	1.56	<i>PI</i>	12.7	8.1	11.4	74.2	57.2	61.9
Q1	1.62	<i>PI</i>	12.1	7.9	12.9	116.6	106.8	112.4
Q2	1.46	<i>PI</i>	15.8	5.7	9.5	99.9	100.4	111.5
Q3	1.49	<i>PI</i>	6.2	13.9	13.6	54.5	105.6	100.8

Figure 4. The profile of velocity of detonation (km/s) of the triazine derivatives.

Thermal Stability

According to the criteria of HEMs, compounds should be stable enough for the practical use and safe handling. The stability of triazine derivatives has been analyzed using bond dissociation energies of C-NO₂, C-NH₂, and C-N₃ bonds. 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. In general, smaller the BDE for breaking a bond is, the compound become more unstable. Different studies illustrate that C-NO₂ is the possible trigger bond in nitroaromatic compounds³⁶⁻³⁸ and it can be ruptured easily during pyrolysis. The strength of weakest bond of explosive molecule plays an important role in the initiation event. All the predicted values for BDE are shown in Table 2. The BDE of the C-NO₂ bond is 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 of nitrogen. Resonance strengthens the C-NH₂ bond and requires high energy for the pyrolysis. It can be deduced that the substitution of the -N₃ and -NH₂ are very useful for increasing the thermal stability³⁹. This shows that the C-NO₂ bond have less bond strength and susceptible for earlier pyrolysis. The NO₂ group of **R1** is found

to be more susceptible for the pyrolysis and its BDE is 266 kJ/mol. Among the nitro derivatives of imidazole (**V1**) and pyrazole (**P1**), nitroimidazole derivatives are found to be more unstable. Similarly, nitro derivative of 1,2,4-triazole (**R1**) is more unstable than the 1,2,3-triazole derivative (**Q1**). The order of unstability of triazine derivatives can be given as, $\text{NO}_2 > \text{N}_3 > \text{NH}_2$. The amino and azido derivatives show the BDE higher than 366 kJ/mol. The results reveal that the triazine derivatives are thermally stable due to the aromatic, planar and symmetric skeleton. This symmetry can delocalize the π -electron cloud density of the ring and makes the molecule more stable.

Sensitivity Correlations

The band gaps of predicted triazine derivatives are summarized in Table 2. Xiao et al. research group suggested a principle of easiest transition (PET) to predict the sensitivity of ionic metal azides⁴⁰. The principle states that, smaller the band gap (ΔE) between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), easier the electron transition and larger the sensitivity will be. Many experimental results have been illustrated by the principle⁴¹⁻⁴⁴. Comparison of triazine derivatives reveal that nitro compounds are more sensitive than amino and azido compounds. A similar trend is observed in all the triazine derivatives. Amino derivatives (**V2**, **P2**, **R2**, and **Q2**) found to be more insensitive due to its electron donating effect, which strengthens the bonds in molecular structure. Replacement of imidazole (**V1**, **V2**, and **V3**) with the pyrazole (**P1**, **P2**, and **P3**) slightly increases the band gap, similar phenomena is observed in case of 1,2,3-triazole and 1,2,4-triazole derivatives. Analysis of the band gap of triazine derivatives shows that amino derivatives are more insensitive candidates.

Conclusion

In the present study, energetic properties of the designed s-triazine derivatives have been studied by using the density functional theory. Based on appropriate designed sets of isodesmic reactions, standard gas-phase HOFs are predicted. All the triazine derivatives show HOF higher than 630 kJ/mol. The nitro derivatives show highest densities as compared to amino and azido derivatives hence, the better detonation performance. The nitro derivatives possess density above 1.58 g/cm³, detonation velocity and pressure over 6.6 km/s and 17.8 GPa, respectively. Thermal stability and sensitivity of the designed compounds has been evaluated by using bond dissociation energies and band gap analysis. Designed molecules have better thermal stability and insensitivity as evidenced from BDE and band gap index. Overall performance of triazine derivatives is moderate and may find their applications in solid fuels in micropropulsion systems, carbon nitride nanomaterials and smoke-free pyrotechnic fuels as they are rich in nitrogen content.

Acknowledgment

We thank Prof. M. Durga Prasad, School of chemistry, University of Hyderabad, Hyderabad and Mr. R. S. Patil, High Energy Materials Research Laboratory, Pune for their support. The author V. D. Ghule thanks ACRHEM, University of Hyderabad for financial support.

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