IranJOC

Iranian Journal of Organic Chemistry

Effect of nitro and amino substituents on structural and energetically properties of 1,2,4,5- tetrazine: DFT and ab-initio study

Mehdi Nabati* and Mehrdad Mahkam

Chemistry Department, Faculty of Science, Azarbaijan Shahid Madani University, Tabriz, Iran.

Abstract: In the present work, a series of nitrogen-rich compounds based on sym-tetrazine was designed and optimized to obtain molecular geometries and electronic structures at ab initio and density functional theory (DFT, B3LYP) at the levels of 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p) and cc-pvDZ. Some important properties such as bond dissociation enthalpy, density, frontier orbital energy, thermodynamic parameters, and heat of formation (HOF) and detonation parameters were then calculated. The volumes of the structures computed to get the densities of the molecules. The HOFs were estimated via isodesmic reactions. It deduced that the introduction of nitro group can improve the detonation properties of the structures. The simulation results revealed that these compounds exhibit excellent performance; and the all structures are viable candidate of high energy density materials (HEDMs). Comparing the detonation properties of molecules with standards (RDX and HMX) shows 3-nitro-1,2,4,5-tetrazine can be an explosive. It has low aromaticity and is unstable.

Keywords: S-tetrazine, Nitrogen-rich compounds, Bond dissociation energy, Heat of formation, Detonation properties.

Introduction

An explosive is a material, either a pure single substance or a mixture of substances, which is capable of producing an explosion by its own energy. High-nitrogen energetic materials offer distinct advantages to conventional carbon-based energetic materials. These materials have a large number of N-N and C-N bonds and therefore possess large positive heats of formation [1]. The low percentage of carbon and hydrogen in these compounds has a double positive effect: it enhances the density and allows a good oxygen balance to be achieved more easily [2,3]. Pletz proposed the theory of "explosophores" and "auxoploses" in a way analogous to Witt's suggestion of chromophores and auxochromes in the dyes [4]. An explosophore has been defined as a group of atoms such as azo, azide, nitroso, peroxide, ozonide and perchlorate which is

capable of forming an explosive compound on introduction into a hydrocarbon. Groups such as hydroxyl, carboxyl, chlorine, sulfur, ether, oxygen and amine which do not produce explosive properties, but may influence them, are called auxoplosives [5]. The six-membered heterocycle consisting of four nitrogen atoms and two carbon atoms are known as the tetrazine ring system. The symmetrical tetrazine ring system is ordinarily abbreviated as s-tetrazine (or sym-tetrazine), although the designation 1,2,4,5-tetrazine is also common, particularly in the British literature. Aromatic 1,2,4,5-tetrazines are typically formed by oxidation of the corresponding dihydro derivatives by such oxidizing agents as hydrogen peroxide, isoamyl nitrite, Cl_2, Br_2, oxygen, NBS, DDQ, $FeCl_3$, $NaNO_2/H^+$, etc [6-8]. 3,6- Diamino- 1,2,4,5-tetrazine was synthesized unequivocally for the first time by Lin, Lieber and Horwitz [9], but other nitro and amino derivatives of s-tetrazine weren't synthesized nowadays. Computational

*Corresponding author. Tel: (+98) 4134327501, Fax: (+98) 4134327501, E-mail: mnabati@ymail.com

chemistry is used in different ways [10]. A particularly important method is to model a molecular system prior to synthesizing that molecule in the laboratory. This method is so useful because of synthesizing a compound could need months of labor and raw materials, and generates toxic waste [11]. A second use of computational chemistry is in understanding a problem more completely [12]. There are some properties of a molecule that can be obtained theoretically more easily than by experimental means [13]. Density functional theory (DFT) has become very popular in recent years. This is justified based on the pragmatic observation that it is less computationally intensive than other methods with similar accuracy. This theory has been developed more recently than other ab-initio methods [14,15]. In this paper, stabilities of six structures as potential candidates for high energy density materials (HEDMs) have been investigated theoretically by using quantum chemical treatment. Geometric features, electronic structures of these sym-tetrazine derivatives have been systematically studied using ab initio and density functional theory (DFT, B3LYP) at the level of 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p) and cc-pvDZ. Moreover, the properties of these molecules were investigated at B3LYP/6-311G(d,p) level of theory.

Results and discussion

The geometries of interested molecules:

The studied six molecules are s-tetrazine (A), 3-amino s-tetrazine (B), 3, 6-diamino s-tetrazine (C), 3-nitro s-tetrazine (D), 3, 6- dinitro s-tetrazine (E) and 3-amino- 6- nitro s-tetrazine (F). The molecular frameworks of six title compounds were displayed in Figure **1**. The chemical structures and atomic numbering of the compounds are showed in Figure **2**. The geometric structures of the molecules with electron charge of the elements of each compound are shown in Figure **3**. The dipole moments of the molecules were listed in Table **1**. As seen from the table, the μ order is F > D > B > A = C = E for the structures at B3LYP/6-311G(d,p) level of theory.
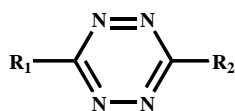
Figure 1: Molecular frameworks of studied compounds.
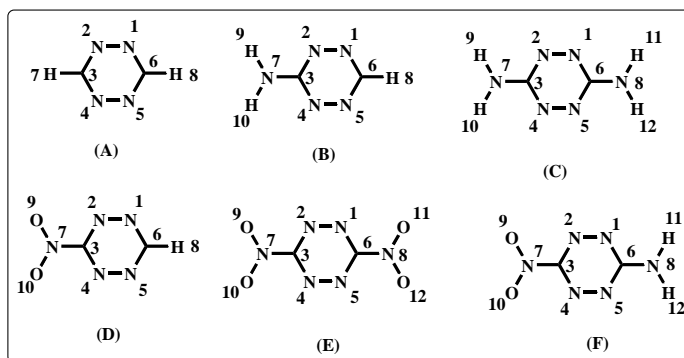
Figure 2: The chemical structures and their atomic numbering.

The bond angles data of the molecules was given in Tables *Energies of structures:*

Tables **5** and **6** shown the total energies calculated from the structures at spin-restricted Hartree-Fock (RHF) level and density functional theory (DFT, B3LYP) at the 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p) and cc-pvDZ basis sets, respectively. Total energies are corrected for zero-point vibrational energy (ZPVE). As seen from the Tables, the stability order is E > F > D > C > B > A for the structures at these performed theoretical levels. The stability values of the molecules show more stability for nitro derivatives. The aromaticity of 1,2,4,5-tetrazine structure is low as expected due to the electron withdrawing character of nitrogen atoms of ring. The nito groups with electron withdrawiong property increase the ring current and aromaticity. For this reason, the nitro derivatives of tetrazine ring are stable.
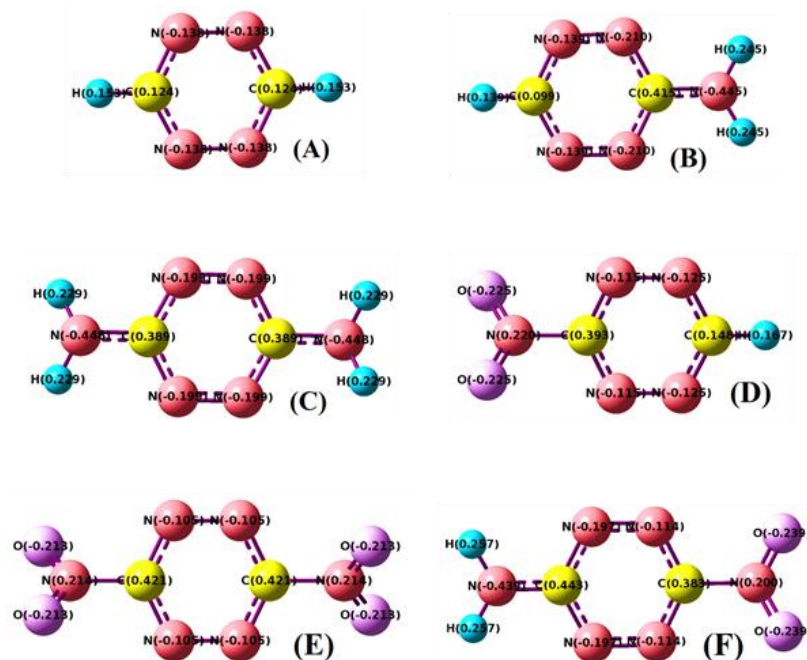
and 4. It is observed that the amino groups increase the N-N-C angles and decrease the N-C-N angles in the tetrazine rings. The same analyses have been carried out for nitro group effect on the tetrazine rings. According to the data of the tables, nitro group increases N-C-N angles and decreases N-N-C angles in the rings. In all molecules, the C has the greater bond angle (N-N-C) of 117.658° and has the lower bond angle (N-C-N) of 125.655°. Also, it is obtained that the nitro group increases H-N-H angle in the F structure. The same analysis shows us that the amino group decreases O-N-O angle in the F molecule. The dihedral angles of structures show us that planar structure is compound A only.

Energies of structures:

Tables **5** and **6** shown the total energies calculated from the structures at spin-restricted Hartree-Fock (RHF) level and density functional theory (DFT, B3LYP) at the 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p),

6-311+G(d,p) and cc-pvDZ basis sets, respectively. Total energies are corrected for zero-point vibrational energy (ZPVE). As seen from the Tables, the stability order is E > F > D > C > B > A for the structures at these performed theoretical levels. The stability values of the molecules show more stability for nitro derivatives. The aromaticity of 1,2,4,5-tetrazine structure is low as expected due to the electron withdrawing character of nitrogen atoms of ring. The nito groups with electron withdrawiong property increase the ring current and aromaticity. For this reason, the nitro derivatives of tetrazine ring are stable.

Figure 3: The geometric structures of the molecules.

Table 1: Dipole moments of the structures.

Structures	μ_X (Debye)	μ_Y (Debye)	μ_Z (Debye)	μ_{Tot} (Debye)
A	0.0000	0.0000	0.0000	0.0000
B	2.5075	0.0000	0.1478	2.5118
C	0.0000	0.0000	0.0000	0.0000
D	3.5250	0.0003	-0.0003	3.5250
E	0.0000	0.0001	0.0000	0.0001
F	-6.8286	0.0011	-0.0050	6.8286

Table 2: Bond lengths of structures calculated at B3LYP/6-311G(d,p) level.

Bonds (A°)	A	B	C	D	E	F
N1-N2	1.322	1.312	1.311	1.321	1.320	1.307
N2-C3	1.335	1.354	1.347	1.324	1.326	1.326
C3-N4	1.335	1.354	1.346	1.324	1.326	1.326
N4-N5	1.322	1.313	1.311	1.321	1.320	1.308
N5-C6	1.335	1.337	1.347	1.337	1.326	1.358
C6-N1	1.335	1.336	1.346	1.338	1.326	1.358
C3-H7	1.084	-	-	-	-	-
C6-H8	1.084	1.081	-	1.083	-	-
C3-N7	-	1.347	1.366	1.493	1.491	1.488
C6-N8	-	-	1.366	-	1.491	1.339
N7-H9	-	1.005	1.007	-	-	-
N7-H10	-	1.005	1.008	-	-	-
N8-H11	-	-	1.008	-	-	1.007

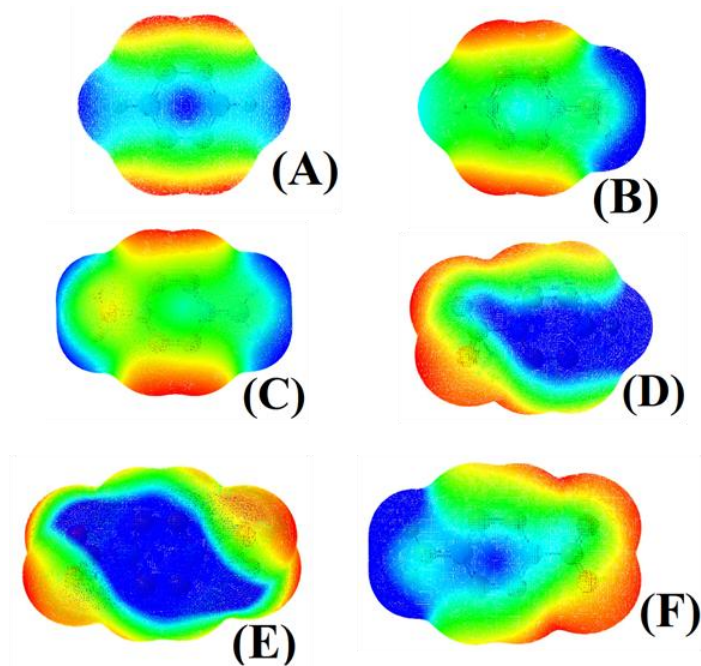|						
N8-H12	-	-	1.007	-	-	1.006
N7-O9	-	-	-	1.214	1.214	1.218
N7-O10	-	-	-	1.215	1.214	1.217
N8-O11	-	-	-	-	1.213	-
N8-O12	-	-	-	-	1.214	-

Figure 4: The 3-D electrostatic potential maps of the structures.

Table 3: Bond angles of the structures calculated at B3LYP/6-311G(d,p) level.

Bond angles (degree)	A	B	C	D	E	F
N1-N2-C3	116.795	116.800	117.658	115.673	115.685	116.971
N2-C3-N4	126.409	125.208	124.655	128.640	128.453	127.496
C3-N4-N5	116.795	116.783	117.687	115.665	115.725	116.885
N4-N5-C6	116.795	117.821	117.658	116.831	115.682	116.826
N5-C6-N1	126.409	125.536	124.655	126.293	128.452	125.014
C6-N1-N2	116.795	117.839	117.687	116.830	115.730	116.775
N2-C3-H7	116.795	-	-	-	-	-
N2-C3-N7	-	117.415	117.625	115.703	115.799	116.280
N4-C3-H7	116.795	-	-	-	-	-
N4-C3-N7	-	117.377	117.687	115.657	115.749	116.224
N5-C6-H8	116.795	117.227	-	116.838	-	-
N5-C6-N8	-	-	117.625	-	115.797	117.465
N1-C6-H8	116.795	117.236	-	116.869	-	-
N1-C6-N8	-	-	117.687	-	115.751	117.521
C3-N7-H9	-	119.274	116.399	-	-	-
C3-N7-H10	-	119.252	116.334	-	-	-
H9-N7-H10	-	120.771	117.345	-	-	-
C3-N7-O9	-	-	-	115.949	115.714	116.392
C3-N7-O10	-	-	-	115.971	115.659	116.426
O9-N7-O10	-	-	-	128.080	128.627	127.182
C6-N8-O11	-	-	-	-	115.719	-
C6-N8-O12	-	-	-	-	115.648	-
O11-N8-O12	-	-	-	-	128.633	-
C6-N8-H11	-	-	116.334	-	-	119.529
C6-N8-H12	-	-	116.399	-	-	119.607
H11-N8-H12	-	-	117.345	-	-	120.860

Table 4: Dihedral angles of the structures calculated at B3LYP/6-311G(d,p) level.

Dihedral angles (degree)	A	B	C	D	E	F
N2-C3-N7-H9	-	-4.820	18.546	-	-	-
N2-C3-N7-H10	-	-175.284	163.420	-	-	-
N4-C3-N7-H9	-	175.298	-163.436	-	-	-
N4-C3-N7-H10	-	4.834	-18.562	-	-	-
N5-C6-N8-H11	-	-	-163.420	-	-	179.621
N5-C6-N8-H12	-	-	-18.546	-	-	0.298
N1-C6-N8-H11	-	-	18.562	-	-	-0.431
N1-C6-N8-H12	-	-	163.436	-	-	-179.755
N2-C3-N7-O9	-	-	-	47.517	50.055	-31.639
N2-C3-N7-O10	-	-	-	-132.349	-129.866	148.301
N4-C3-N7-O9	-	-	-	-132.436	-129.885	148.401
N4-C3-N7-O10	-	-	-	47.698	50.194	-31.659
N5-C6-N8-O11	-	-	-	-	-129.859	-
N5-C6-N8-O12	-	-	-	-	50.151	-
N1-C6-N8-O11	-	-	-	-	50.082	-
N1-C6-N8-O12	-	-	-	-	-129.908	-
N1-N2-C3-N7	-	-178.682	177.585	178.779	177.595	-179.179
N2-N1-C6-N8	-	-	177.584	-	177.592	-178.946
N5-N4-C3-N7	-	178.700	-177.584	178.766	177.476	-179.072
N4-N5-C6-N8	-	-	-177.585	-	177.479	-179.330
N1-N2-C3-N4	0.000	1.191	-0.280	-1.275	-2.474	0.775
N2-C3-N4-N5	0.000	-1.172	0.280	-1.180	-2.455	0.973
C3-N4-N5-C6	0.000	0.179	-0.260	2.274	4.586	-1.612
N4-N5-C6-N1	0.000	0.763	0.280	-1.190	-2.452	0.727
N5-C6-N1-N2	0.000	-0.745	-0.280	-1.290	-2.477	0.997
C6-N1-N2-C3	0.000	-0.214	0.260	2.360	4.605	-1.649

Table 5: Calculated total energies (in a.u.) for the structures at spin-restricted Hartree-Fock (RHF) method with different basis sets.

Structures	HF/6-31G(d,p)	HF/6-31+G(d,p)	HF/6-311G(d,p)	HF/6-311+G(d,p)	HF/cc-pvDZ
A	-294.539910	-294.547492	-294.601418	-294.606738	-294.563519
B	-349.573124	-349.583381	-349.647334	-349.654705	-349.598468
C	-404.598025	-404.610915	-404.685402	-404.695002	-404.626022
D	-497.979400	-497.994373	-498.095319	-498.106532	-498.024118
E	-701.412195	-701.435762	-701.585480	-701.601237	-701.481849
F	-553.019543	-553.035363	-553.147618	-553.159848	-553.065892

The total energies are corrected for ZPVE.

Table 6: Calculated total energies (in a.u.) for the structures at B3LYP method with different basis sets.

Structures	B3LYP/6-31G(d,p)	B3LYP/6-31+G(d,p)	B3LYP/6-311G(d,p)	B3LYP/6-311+G(d,p)	B3LYP/cc-pvDZ
A	-296.272423	-296.284474	-296.339689	-296.347174	-296.290938
B	-351.633799	-351.650587	-351.716876	-351.727115	-351.653528
C	-406.986120	-407.007442	-407.084632	-407.097928	-407.007504
D	-500.748554	-500.770376	-500.873504	-500.888249	-500.788696
E	-705.220082	-705.251433	-705.402763	-705.424401	-705.282162
F	-556.114240	-556.139698	-556.254299	-556.271225	-556.155635

The total energies are corrected for ZPVE.

Bond dissociation energies (BDE):

Bond dissociations investigation is an essential and basic property for understanding the decomposition process of the High energy materials, since they are directly relevant to the stability and sensitivity of the high energy materials [18]. The energy required for bond hemolysis at 298 K temperature and 1 atmosphere pressure corresponds to the energy of reaction A-B → A**º** + B**º**, which is the bond dissociation energy of the compound A-B by definition. Therefore, the bond dissociation energy can be given in terms of follow equation:

$BDE_{(A-B)} = E_{(A^{o})} + E_{(B^{o})} - E_{(A-B)}$

Where A-B corresponds for the structures, A**º** and B**º** stand for the corresponding product radicals after the

bond dissociation, $BDE_{(A-B)}$ is the bond dissociation energy of bond A-B. The bond dissociation energy with ZPE correction can be calculated by follow equation:

$$BDE_{(A-B)ZPE} = BDE_{(A-B)} + \Delta ZPE$$

The bond dissociation energies were calculated at the B3LYP/6-311G(d,p) level. Table **7** shows calculated total energies of s-tetrazine derivatives, fragments, NO_2 and NH_2 at the equilibrium geometries and resulting BDEs at mentioned level of theory. As seen from the Table, the relative stability order of these structures may be in the order: F(6)>B>C(3)=C(6)>F(3)>D>E(3)=E(6). It can be deduced that the BDEs for these molecules are highly substitution dependent. According to suggestion of Chung [19], the bond dissociation energy more than 20 kcal/mol corresponds for a compound to be considered as a viable candidate of high energy density material (HEDM). Therefore, we can conclude that the all molecules are viable candidate of HEDMs.

The frontier molecular orbital energies:

Table **8** shown the HOMO and LUMO energies (ε) of the molecules computed at the B3LYP/6-311G(d,p) level of theory. The frontier orbitals energies increase by increasing amino substituent and decrease by increasing the number of nitro substituent on the sym-tetrazine ring. These are general trends of electron withdrawing substituents which lower the frontier orbitals energy levels and electron donating substituents which higher the frontier orbitals energy levels. The order of energy gap values, that is the difference between the LUMO and HOMO energy levels, is E>F>D>B>C>A at the B3LYP/6-311G(d,p) level of theory. Figures **5** and **6** provide the frontier orbitals map.

Table 7: Calculated total energies of the structures, fragments, NH_2 and NO_2 at the equilibrium geometries and resulting bond dissociation energies (BDE).

Structures	Formula	Parent energy (hartrees)	Fragment energy (hartrees)	NO_2 energy (hartrees)	NH_2 energy (hartrees)	BDE (kcal/mol)
B	$C_2H_3N_5$	-351.71688	-295.66502	-205.12390	-55.87623	110.210
C(3)	$C_2H_4N_6$	-407.08463	-351.03939	-205.12390	-55.87623	106.055
C(6)	$C_2H_4N_6$	-407.08463	-351.03939	-205.12390	-55.87623	106.055
D	$C_2HN_5O_2$	-500.87350	-295.66502	-205.12390	-55.87623	53.075
E(3)	$C_2N_6O_4$	-705.40276	-500.19492	-205.12390	-55.87623	52.673
E(6)	$C_2N_6O_4$	-705.40276	-500.19492	-205.12390	-55.87623	52.673
F(3)	$C_2H_2N_6O_2$	-556.25430	-351.03939	-205.12390	-55.87623	57.110
F(6)	$C_2H_2N_6O_2$	-556.25430	-500.19492	-205.12390	-55.87623	114.928

Key to the notation: B(L) stands for the radical obtained from B structure by removing the functional group at position L.

Table 8: The HOMO and LUMO energies of the structures calculated at B3LYP/6-311G(d,p) level.

Structures	MOs number	HOMO orbital	HOMO (a.u.)	LUMO orbital	LUMO (a.u.)	$\Delta\varepsilon$ (a.u.)
A	120	21 (B3G)	-0.25552	22 (AU)	-0.12199	0.13353
B	144	25 (A)	-0.23703	26 (A)	-0.10212	0.13491
C	168	29 (A)	-0.22829	30 (A)	-0.09442	0.13387
D	168	32 (A)	-0.28954	33 (A)	-0.15402	0.13552
E	216	43 (A)	-0.32011	44 (A)	-0.18219	0.13792
F	192	36 (A)	-0.26908	37 (A)	-0.13305	0.13603

*Heats of formation, predicted densities and detonation of the structures:*

The heats of formation (HOF) values were calculated at B3LYP/6-311G(d,p) level and are listed in the Table **9**. In this study, the isodesmic reaction method is employed. In an isodesmic reaction, the numbers of bonds and bond types are preserved on both sides of the reaction [20]. The accuracy of HOF obtained computationally was conditioned by the reliability of HOF of the reference compounds. The isodesmic reactions for HOF calculation are shown in Scheme 1.

$$Ar\text{-}NO_2 + CH_4 \longrightarrow Ar\text{-}H + CH_3NO_2$$

$$Ar\text{-}NH_2 + CH_4 \longrightarrow Ar\text{-}H + CH_3NH_2$$
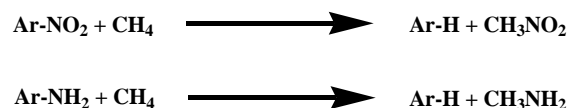
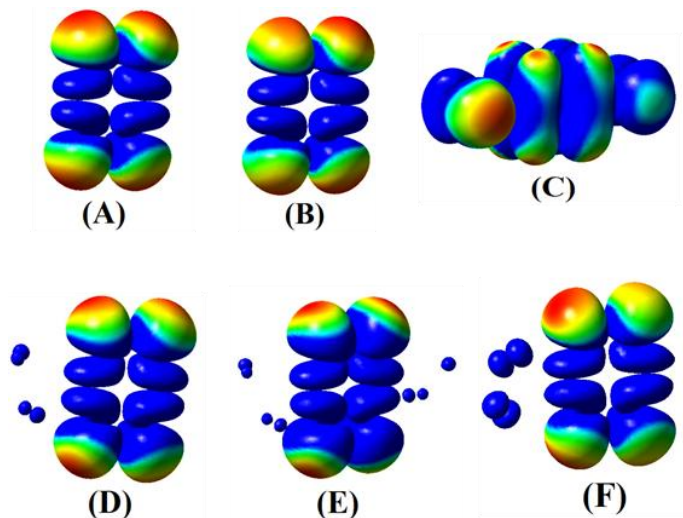**Scheme 1:** The isodesmic reactions for HOF calculations.
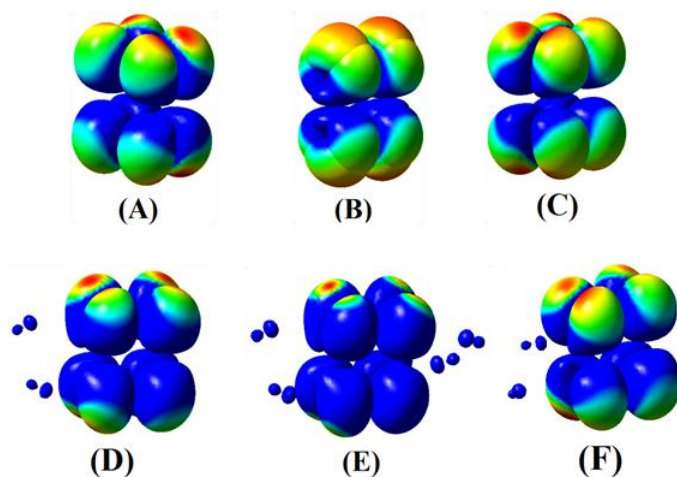
Figure 5: HOMO orbital maps of structures.

Figure 6: LUMO orbital maps of structures.

For the isodesmic reactions, heat of reaction ΔH at 298 K can be calculated from the following equations:

$\Delta H_{298} = \Sigma \Delta H_{f,P} - \Sigma \Delta H_{f,R}$

$\Delta H_{298.15K} = \Delta E_{298.15K} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT = \Sigma \Delta H_{f,P} - \Sigma \Delta H_{f,R}$

Where $\Delta H_{f,P}$ and $\Delta H_{f,R}$ are the heats of formation of products and reactants at 298 K, respectively. ΔE_0 and ΔZPE correspond to the total energy difference and the zero point energy difference between products and reactants at 0 K, respectively. ΔH_T is the changes in thermal correction to enthalpies between products and reactants. $\Delta(PV)$ equals ΔnRT for reaction in gas phase. For isodesmic reactions, Δn=0. As seen from the Table, the HOF order is E>D>A>F>B>C for the structures at B3LYP/6-311G(d,p) level of theory.

	Stoichiometric ratio		
parameters	$c \geq 2a+b/2$	$2a+b/2 > c \geq b/2$	$b/2 > c$
N	(b+2c+2d)/4MW	(b+2c+2d)/4MW	(b+d)/2MW
M	4MW/(b+2c+2d)	(56d+88c-8b)/(b+2c+2d)	(2b+28d+32c)/(b+d)
Q	(28.9b+94.05a+0.239ΔH$_f^o$)/MW	[28.9b+94.05(c/2-b/4)+0.239ΔH$_f^o$]/MW	(57.8c+0.239ΔH$_f^o$)/MW

Furthermore, density (ρ), detonation velocity (D), and detonation pressure (P) are the important parameters to evaluate the explosive performance of high energy materials and can be predicted by the following empirical Kamlet-Jacob equations [21]:

D=1.01(NM$^{1/2}$Q$^{1/2}$)$^{1/2}$(1+1.3ρ)   Eq. 1

P=1.558ρ^2NM$^{1/2}$Q$^{1/2}$ Eq. 2

Where D: detonation velocity in km/s, P: detonation pressure in GPa, ρ: density of a compound in g/cm^3, N: moles of gaseous detonation products per gram of explosive (in mol/g), M: average molecular weight of gaseous products (in g/mol), Q: chemical energy of detonation in kJ/g. Table **9** collects the predicted V, ρ,

Q, D and P values of the structures. As seen from the table, the D and P order is D>E>F>A>C>B for the structures at B3LYP/6-311G(d,p) level of theory. It is noted that the D and P values gradually increase when the number of –NO2 group increases. In a word, it shows that the introduction of nitro group can improve the detonation properties of the structures. For RDX and HMX, experimental value of D and P are 8.75 km/s, 9.10 km/s and 34.70 GPa, 39.00 GPa, respectively [22]. The RDX and HMX are the current standards for detonation behavior. Comparing these values with data of Table **10** shows molecule D can be an explosive.

Table 9: HOFs, predicted densities and detonation properties of the molecules.

Structures	OB$_{100}$	HOF (kJ/mol)	Q (kJ/g)	V* (cm^3/mol)	ρ (g/cm^3)	D (km/s)	P (GPa)
A	-97.53	487.2	1419.526	52.303	1.568	7.553	23.20
B	-90.69	421.353	1037.763	65.417	1.483	7.043	19.437
C	-85.68	380.19	810.938	70.080	1.599	7.179	21.235
D	-31.49	499.265	1722.354	72.228	1.759	8.590	32.277
E	0.00	523.13	1820.532	105.403	1.632	8.504	30.188
F	-33.80	424.893	1453.096	86.831	1.636	7.952	26.437

*Average valu from 100 single-point volume calculations at the B3LYP/6-311G(d,p) level.

Q: Heat of explosion, V: Volume of explosion, D: Velocity of detonation, P: Pressure of explosion.

Conclusion

In this study, stabilities of six structures as potential candidates for high energy density materials (HEDMs) were investigated computationally by using quantum chemical treatment. Full geometrical optimizations of nitrogen-rich structures were performed using ab initio and density functional theory (DFT, B3LYP) at the levels of 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p), cc-pvDZ. Introduction of nitro and amino groups into sym-tetrazine compound slightly affects the BDE and HOF. The detonation performance data are calculated according to the HOFs calculated by B3LYP/6-311G(d,p) level of theory and the values of D and P increase when the number of –NO2 group increases. Also, it concluded that the all structures are viable candidate of high energy density materials (HEDMs).

Computational methods

Computations were performed with the Gaussian 03 package [23] using the spin-restricted Hartree-Fock (RHF) and the B3LYP methods with 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p) and cc-pvDZ basis sets. All calculations and geometry optimization for each molecule were obtained by mentioned theories (RHF and B3LYP). The designation of B3LYP

consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [24] and the Lee, Yang, Parr (LYP) correlation correction functional [25,26]. For comparing of the bond strengths, homolytic bond dissociation energy (BDE) calculations were performed by B3LYP/6-311G(d,p) level of theory. The mentioned level was used to predict the HOFs (heat of formation) of all molecules via isodesmic reactions. Theoretical calculations have been performed in the gas phase [27, 28]. The restricted method was used for the systems. An efficient and convenient statistics average method was worked out to predict the crystalline densities of all derivatives. To calculate the densities of structures, the molecular volume data was required. The molecular volume V was defined as inside a contour of 0.001 electrons/bohr^3 density. The computational molecular density ρ (ρ=M/V, where M = molecular weight) was also calculated. Oxygen balance (OB$_{100}$) is an expression that is used to indicate the degree to which an explosive can be oxidized. OB$_{100}$ was calculated as follows:

$$OB\% = \frac{-1600}{Mol.\,wt} \times \left(2a + \frac{b}{2} - c\right)$$

Where: a = number of atoms of carbon, b = number of atoms of hydrogen, c = number of atoms of oxygen.

References

[1]   Mahkam, M.; Nabati, M.; Latifpour, A.; Aboudi, J. *Des. Monomers Polym.* **2014,** *17,* 453.

[2]   Mahkam, M.; Namazifar, Z.; Nabati, M.; Aboudi, J. *Iran. J. Org. Chem.* **2014,** *6,* 1217.

[3]   Nabati, M.; Mahkam, M. *Iran. Chem. Commun.* **2014,** *2,* 164.

[4]   Jursic, B. S. *J. Mol. Struct.* **2000,** *499,* 137.

[5]   Lothrop, W. C.; Handrick, G. R. *Chem. Revs.* **1949,** *44,* 419.

[6]   Babler, J. H.; Sarussi, S. J. *J. Org. Chem.* **1983,** *48,* 4416.

[7]   Pinner, A. *Liebigs Ann. Chem.* **1897,** *297,* 221.

[8]   Matyushecheva, G. I.; Mikhailov, V. S.; Yagupol'skii, L. M. *Zh. Org. Khim.* **1974,** *10,* 124.

[9]   Derrick Clive, L. J.; Angoh, A. G.; Bennett S. M. *J. Org. Chem.* **1987,** *52,* 1339.

[10]   Türker, L. *J. Mol. Struct. (Theochem)* **2004,** *681,* 15.

[11]   Tompa, A. S. *Thermochim. Acta.* **1984,** *80,* 367.

[12]   Whelan, D. J.; Spear, R. J.; Read, R. W. *Thermochim. Acta.* **1984,** *80,* 149.

[13]   He, Y.; Liu, X.; Lin, M. C. *Int. J. Chem. Kinet.* **1991,** *23,* 1129.

[14]   Wong, M. W. *Chem. Phys. Lett.* **1996,** *256,* 391.

[15]   Nabati, M.; Mahkam, M.; Heidari, H. *Iran. Chem. Commun.*, **2014,** *2,* 236.

[16]   Mahkam, M.; Nabati, M.; Kafshboran, H. R. *Iran. Chem. Commun.,* **2014,** *2,* 34.

[17]   Nabati, M.; Mahkam, M. *Iran. J. Org. Chem.*, **2013,** *5,* 1157.

[18]   Nabati, M.; Mahkam, M. *Iran. Chem. Commun.,* **2014,** *2,* 129.

[19]   Chung, G. S.; Schimidt, M. W.; Gordon, M. S. *J. Phys. Chem. A* **2000,** *104,* 5647.

[20]   Mahkam, M.; Kafshboran, H. R.; Nabati, M. *Des. Monomers Polym.*, **2014,** *17,* 784.

[21]   Kamlet, M. J.; Jacobs, S. J. *J. Chem. Phys.* **1968,** *48,* 23.

[22]   Teymori, A.; Amiri, S.; Massoumi, B.; Mahkam, M.; Nabati, M. *Iran. J. Org. Chem.* **2014,** *6,* 1287.

[23]   Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03. Revision B.01.* Gaussian Inc. Wallingford. CT. **2004**.

[24]   Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980,** *58,* 1200.

[25]   Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988,** *37,* 785.

[26]   Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989,** *157,* 200.

[27]   Nabati, M.; Mahkam, M. *Silicon* **2015,** *7,* in press.

[28]   Nabati, M.; Mahkam, M. *Iran. J. Org. Chem.* **2014,** *6,* 1331.