A DFT study on nitrotriazines

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ABSTRACT

In this study, all possible mono-, di- and tri-nitro-substituted triazine compounds have been considered as potential candidates for high-energy density materials (HEDMs) by using quantum chemical treatment. Geometric and electronic structures, thermodynamic properties and detonation performances of these nitro-substituted triazines have been systematically studied using 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 basis sets. Moreover, thermal stabilities have been evaluated from the homolytic bond dissociation energies (BDEs). Detailed molecular orbital (MO) investigation has been performed on these potential HEDMs. According to the results of the calculations, mono-, di- and tri-nitro-substituted derivatives of symmetric 1,3,5-triazine have been found to be more stable than their 1,2,3 and 1,2,4 counterparts.

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1. Introduction

The six-membered heterocycle consisting of three nitrogen atoms and three carbon atoms have three isomers. Of these, the nitrogens alternately located in the ring is known as the symmetrical triazine ring system (**1**) [1]. This heterocycle is ordinarily abbreviated as s-triazine (or sym-triazine). The other two isomeric triazines are asymmetrical triazine (**2**) [1], designated as-triazine (asymm-triazine) and vicinal triazine (**3**) [1], designated v-triazine (vic-triazine) (see Fig. 1).

s-Triazine exhibits a high degree of thermal stability; it can be purified without appreciable loss by repeated distillation over metallic sodium. Some 1,2,4-triazines are known to be dyes for wool but it is doubtful whether they are actually used for this purpose. U.S. patents issued to Wolf and Pfister [2,3] state that certain 1,2,4-benzotriazine derivatives show promise in the treatment of malaria. Although the first synthesis of a 1,2,3-triazine was reported in 1874, still little is known about this group of compounds.

The search for new potential high-energy density materials (HEDMs) is on going [4–7]. Good high-energy materials possess high-density, have a fast velocity of detonation, and are energetically unstable with respect to their reaction products. We have been interested in compounds having high nitrogen content because of the relative stability of dinitrogen as a reaction product. This strengthens our interest in triazine rings. When nitro-group(s) are attached to the 1,3,5-triazine (**1**), 1,2,4-triazine (**2**) and 1,2,3-triazine (**3**) rings, all together 15 different nitrotriazine structures have been obtained. Presently, geometric features, electronic structures, ther-

modynamic properties and detonation performances have been systematically studied for these 15 nitrotriazine compounds. Additionally, thermal stabilities have been evaluated from the homolytic bond dissociation energies (BDEs).

2. Method of calculation

The Gaussian 03 package [8] was used as the calculation tool. Full optimization of all bond lengths, bond angles and torsional angles was initially achieved by using the framework of density functional theory (DFT, B3LYP) [9,10] with 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p), cc-PVDZ basis sets (restricted closed-shell). The exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [11]. The term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [12] and Lee, Yang, Parr (LYP) correlation correction functional [13,14].

Moreover, in order to compare the bond strengths, homolytic BDE calculations were performed at the level of UB3LYP/6-311G(d,p). The homolytic BDE [15,16] is defined for the present case as: BDE = E(X) + E(R) − E(R–X), where E stands for the respective total energy corrected for the zero-point energy for each parent structure and the fragments (R and X) of the low-energy R–X bond scission reaction.

Nucleus independent chemical shift calculations at the center of rings (NICS(0)) were performed on all the molecules using the gauge invariant atomic orbital (GIAO) approach [17] at the B3LYP/6-31G(d,p) level. The B3LYP/6-31G(d,p) optimized geometries were used for the NICS calculations.

For each set of calculations, vibrational analyses were done (using the same basis set employed in the corresponding geometry optimizations). The normal mode analysis for each structure

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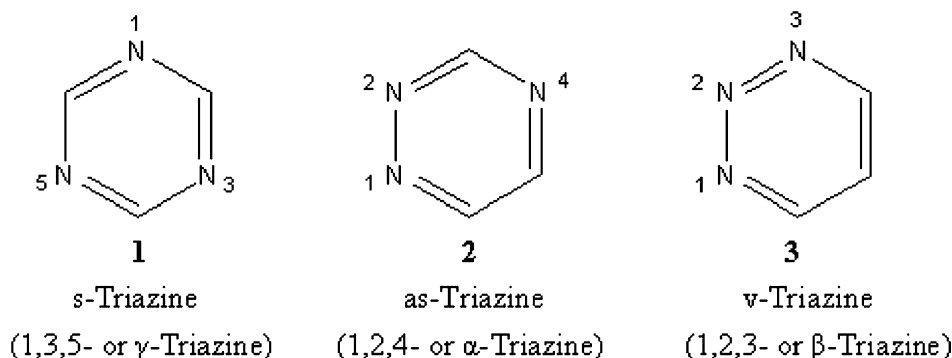*E-mail address:* lturker@metu.edu.tr (L. Türker).

Fig. 1. Nomenclatures and structures of triazines.

yielded no imaginary frequencies for the $3N - 6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface.

3. Results and discussion

Some structural data of the present systems have been given in Tables 1–3. Fig. 2 shows the geometric structures and atomic numbering of the nitrotriazine derivatives and the three-dimensional electrostatic potential maps of the nitrotriazines are shown in Fig. 3. The dark loops indicate negative charge development for a particular system. As can be seen from the figures the negative charge is located on the nitro-groups as expected due to the electron withdrawing character of the nitro-groups. However, charge development on nitro substituents decreases with increasing number of nitro-groups in the structure.

3.1. Bond lengths

There are five types of bonds in the present structures, namely: C–N, C–C, C–NO$_2$, N–N and C–H bonds. The bond lengths are tabulated in Tables 1–3.

Table 1
Optimized structural parameters of some nitro-1,3,5-triazines calculated at B3LYP/cc-pVDZ level.

Bond	1A	IB	1C
N1–C2	1.3219	1.3253	1.3237
C2–N3	1.3219	1.3221	1.3237
N3–C4	1.3412	1.3400	1.3237
C4–N5	1.3373	1.3400	1.3237
N5–C6	1.3373	1.3221	1.3237
C6–N1	1.3412	1.3253	1.3237
C2–N7	1.5061	1.5033	1.5230
C6–N8	–	1.5033	1.5229
C4–N9	–	–	1.5229
N7–O10	1.2179	1.2170	1.2144
N7–O11	1.2179	1.2164	1.2144
N8–O12	–	1.2164	1.2145
N3–O13	–	1.2170	1.2145
N9–O14	–	–	1.2145
N9–O15	–	–	1.2145
N1–C2–N3	128.8884	128.3755	127.6633
C2–N3–C4	112.6038	113.1695	112.3357
N3–C4–N5	125.7550	125.3223	127.6663
C4–N5–C6	114.3482	113.1696	112.3327
N5–C6–N1	125.7550	128.3754	127.6663
C6–N1–C2	112.6038	111.4354	112.3357
N3–C2–N7–O11	141.4608	−139.5164	180.0000
N5–C6–N8–O12	–	139.5059	180.0000
N5–C4–N9–O14	–	–	−180.0000

The unit of bond length is Å, bond angles and dihedral angles are °.

The results of the calculations showed that, the longest C–N bond among all the triazine systems corresponds to C3–N4 bond of molecule **2F**, which is 1.3448 Å, and the shortest one is 1.309 Å and stands for C5–N4 bond of the same molecule. Consequently, all these C–N bonds in triazine rings are much shorter than the normal C–N single bond that is referred to 1.49 Å [18]. The same trends are obtained for bond lengths of the N–N and C–C bonds in the triazine rings which lie in the range of 1.3228–1.3337 Å and 1.3846–1.4030 Å, respectively and are also shorter than that of the normal N–N (1.45 Å) and C–C single bonds (1.54 Å).

All the C–NO$_2$ bond lengths are in the range of 1.4796–1.5230 Å and they are around the normal C–N single bond length which is known as 1.49 Å.

3.2. Bond angles and dihedral angles

In mono-, di- and tri-nitro-1,3,5-triazine molecules (**1A**, **1B**, **1C**), N–C(NO$_2$)–N bond angles are greater than C(NO$_2$)–N–C(NO$_2$) bond angles. This behavior can be explained as follows: all angles in benzene ring are 120°, indicating a perfect hexagon. However, in the case of nitro-1,3,5-triazines the hexagon is distorted by the insertion of three nitrogen atoms. Since nitrogen is more electronegative than carbon, the distribution of the π-electrons in triazines ring is not uniform leading to a less effective delocalization of π-electrons. Thus, the π-electrons of the system are more located around three nitrogens, resulting an increase in the N–C(NO$_2$)–N bond angles. In the present case, nitro substitution(s) at position 3 in **1A**, at positions 1 and 3 in **1B**, at positions 1, 3 and 5 in **1C** increase(s) the N–C–N bond angle up to 125–128°. This is quite reasonable, since nitro-group pulls the lone pair electrons of the nitrogens toward itself increasing π-electron density around N–C(NO$_2$)–N angle (but decreasing on the other side), which results an increase in the N–C(NO$_2$)–N angle. Generally, the N–C(NO$_2$)–N bond angles are decreasing with the increasing number of nitro-groups. Structure **1C** has dihedral angles (ONCN) of 180°, so it is in the same plane with the main ring resulting a better π-conjugation.

In nitro-1,2,4-triazine molecules (**2A**, **2B**, **2C**, **2D**, **2E**, **2F**, **2G**), N–C–N bond angles are larger than N–N–C, N–C–C and C–N–C bond angles. The **2A** has the largest bond angle (N2–C3–N4) of 129.7117°, while **2E** has the smallest bond angle (C3–N4–C5) of 112.5966°.

In nitro-1,2,3-triazine molecules (**3A**, **3B**, **3C**, **3D**, **3E**), **3B** has the smallest bond angle (N3–C4–C5) of 120.4928°, whereas 3D has the smallest C4–C5–C6 bond angle of 111.5354°.

3.3. NICS

Aromaticity continues to be an actively investigated area of chemistry. The simplest criteria for aromatic compounds are that they possess cyclic conjugated π-systems containing the proper number of π-electrons (i.e., the Hückel rule). While these criteria
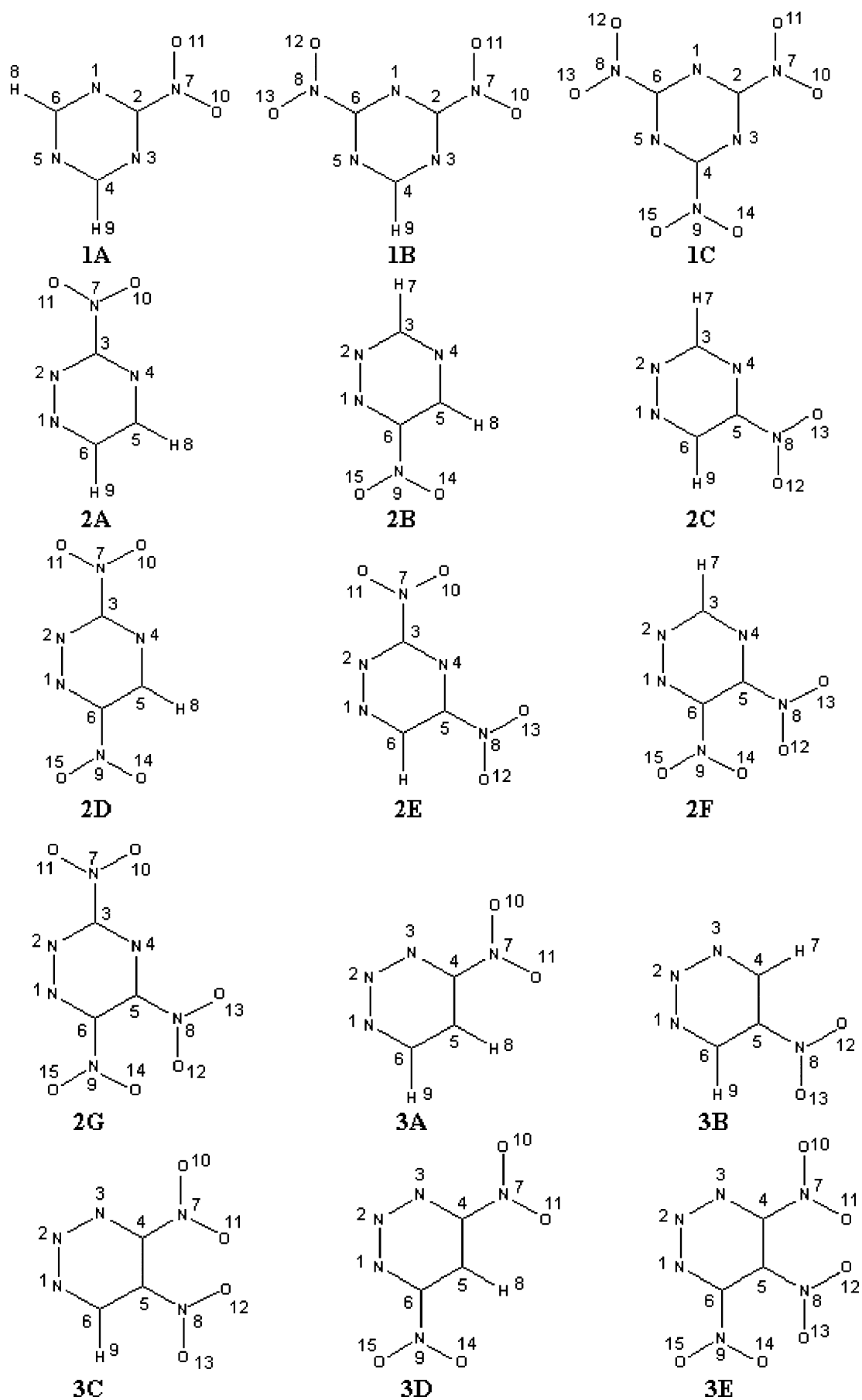
Fig. 2. Geometric structures and numbering of nitrotriazine derivatives.

Table 2
Optimized structural parameters of some nitro-1,2,4-triazines calculated at B3LYP/cc-pVDZ level.

Bond	2A	2B	2C	2D	2E	2F	2G
N1–N2	1.3337	1.3313	1.3311	1.3305	1.3313	1.3307	1.3306
N2–C3	1.3246	1.3394	1.3376	1.3277	1.3256	1.3361	1.3249
C3–N4	1.3276	1.3428	1.3435	1.3284	1.3288	1.3448	1.3307
N4–C5	1.3313	1.3300	1.3115	1.3302	1.3126	1.3111	1.3123
C5–C6	1.4022	1.3990	1.3961	1.4011	1.3982	1.4005	1.4030
C6–N1	1.3355	1.3196	1.3375	1.3205	1.3377	1.3197	1.3205
C3–N7	1.4399	–	–	1.4955	1.4986	–	1.4967
C5–N8	–	–	1.5056	–	1.5047	1.4928	1.4918
C6–N9	–	1.4964	–	1.4964	–	1.4873	1.4872
N7–O10	1.2190	–	–	1.2179	1.2176	–	1.2170
N7–O11	1.2177	–	–	1.2167	1.2165	–	1.2156
N8–O12	–	–	1.2250	–	1.2241	1.2206	1.2197
N8–O13	–	–	1.2133	–	1.2118	1.2125	1.2113
N9–O14	–	1.2267	–	1.2257	–	1.2234	1.2224
N9–O15	–	1.2131	–	1.2119	–	1.2125	1.2113
N1–N2–C3	116.8183	117.6180	118.4377	116.4212	117.2397	117.7005	116.5732
N2–C3–N4	129.7117	127.3835	126.5874	129.6657	128.9150	126.5159	128.8124
C3–N4–C5	113.0830	114.7304	113.5674	113.7431	112.5966	114.8408	113.8124
N4–C5–C6	120.3873	118.7924	123.0344	118.6114	122.7189	120.6081	120.4002
C5–C6–N1	121.8175	123.7793	119.6691	123.7604	119.8320	121.4514	121.5757
C6–N1–N2	118.1391	117.6964	118.7040	117.7462	118.6532	118.8710	118.8006
O11–N7–C3–N4	–141.8602	–	–	–135.7623	141.2376	–	139.2362
O13–N8–C5–C6	–	–	–179.9997	–	176.1170	131.7941	131.5668
O14–N9–C6–N1	–	–179.9999	–	–178.4437	–	136.9385	134.7617

The unit of bond length is Å, bond angles and dihedral angles are °.

are robust enough to predict the aromaticity of a host of neutral and charged ring systems, it is not always a clear indicator of aromaticity for more complex systems (as in our case).

Aromaticity is expressed by a combination of properties in cyclic delocalized systems. In general, aromaticity is discussed in terms of energetic, structural and magnetic criteria [19–24]. In 1996, Schleyer has introduced a simple and efficient probe for aromaticity: NICS [25], which is the computed value of the negative magnetic shielding at some selected point in space, generally, at a ring or cage center. Negative NICS values denote aromaticity (e.g., –11.5 for benzene, –11.4 for naphthalene) and positive NICS values denote antiaromaticity (28.8 for cyclobutadiene) while small NICS values indicate non-aromaticity (e.g., –2.1 for cyclohexane, –1.1 for adamantane). NICS may be a useful indicator of aromaticity that usually correlates well with the other energetic, structural and magnetic criteria for aromaticity [26–29]. Resonance energies and magnetic susceptibilities are measures of the overall aromaticity of a polycycle, but do not provide information about the individual rings. However, NICS is an effective probe for local aromaticity of individual rings of polycyclic systems.

In the present case, NICS values of the various nitrotriazine derivatives have been calculated by the application of density functional theory using the standard 6-31G(d,p) basis set (Table 4). All the molecules have been found to be aromatic. This was somewhat expected although for all the cases, the electrons are expected mainly to be located on the nitrogen atoms (due to its comparably high electronegativity than carbon atom) of the unsubstituted six-membered ring now have been pulled towards the

Table 3
Optimized structural parameters of some nitro-1,2,3-triazines calculated at B3LYP/cc-pVDZ level.

Bond	3A	3B	3C	3D	3E
N1–N2	1.3227	1.3258	1.3223	1.3266	1.3228
N2–N3	1.3302	1.3258	1.3243	1.3266	1.3228
N3–C4	1.3223	1.3419	1.3305	1.3240	1.3255
C4–C5	1.3846	1.3852	1.3871	1.3859	1.3889
C5–C6	1.3905	1.3852	1.3870	1.3859	1.3889
C6–N1	1.3431	1.3419	1.3417	1.3240	1.3255
C4–N7	1.5063	–	1.4860	1.5069	1.4948
C5–N8	–	1.4796	1.4807	–	1.4835
C6–N9	–	–	–	1.5069	1.4948
N7–O10	1.2123	–	1.2150	1.2114	1.2106
N7–O11	1.2255	–	1.2150	1.2238	1.2217
N8–O12	–	1.2218	1.2199	–	1.2145
N8–O13	–	1.2218	1.2201	–	1.2145
N9–O14	–	–	–	1.2238	1.2217
N9–O15	–	–	–	1.2114	1.2106
N1–N2–N3	121.1475	122.0008	121.5912	120.7256	120.5925
N2–N3–C4	118.9137	119.9491	119.9684	119.3234	120.0286
N3–C4––C5	124.4968	120.4928	121.9583	124.5461	123.2997
C4–C5–C6	113.0354	117.1154	115.0539	111.5354	112.7509
C5–C6–N1	122.3086	120.4928	121.6910	124.5461	123.2997
C6–N1–N2	120.0980	119.9490	119.7371	119.3234	120.0286
O11–N7–C4–N3	–179.9975	–	88.6163	–179.9997	137.6366
O13–N8–C5–C4	–	180.0000	–179.9705	–	119.4027
O15–N9–C6–C5	–	–	–	–179.9998	137.6372

The unit of bond length is Å, bond angles and dihedral angles are °.
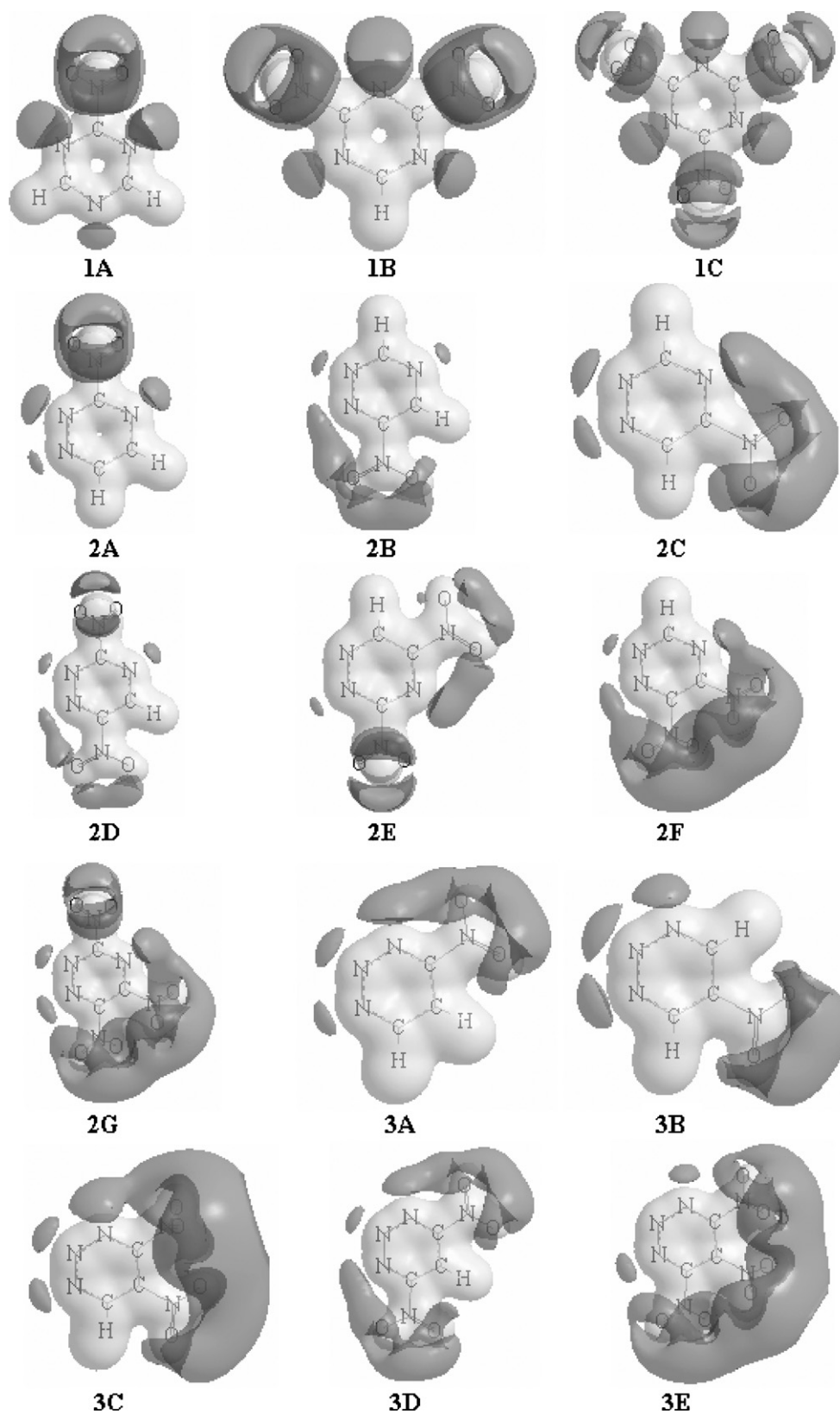
Fig. 3. 3D-electrostatic potential maps of the nitrotriazine.

carbon atom(s) by the attachment of very strongly electron with-drawing nitro-group(s), which decrease the tendency of electrons to be localized thus enhancing cyclic conjugation. For all the series (1, 2 and 3) as the number of nitro-groups increases the average NICS values increase in absolute value. According to the NICS data the most aromatic, thus the most stable compound among the series is **1C** (has the most negative NICS value), which can be explained by the symmetry in this structure. The nitrogens of the triazine system and the three-nitro-groups are arranged symmetrically in this structure so that, as explained above, the pulling of electrons

Table 4
NICS values (ppm) for the nitrotriazine derivatives (calculated at B3LYP/6-31G(d,p) level).

Structures	NICS
1A	−6.368
1B	−7.593
1C	−10.677
2A	−5.542
2B	−5.863
2C	−6.305
2D	−6.671
2E	−7.255
2F	−7.396
2G	−8.129
3A	−6.197
3B	−5.941
3C	−7.214
3D	−7.821
3E	−7.960

towards the carbon atoms (consequently better cyclic conjugation) by the electron withdrawing nitro-groups is the most effective in this case. Therefore, the ring current has been quite strongly increased; leading to a NICS of the most negative value. The sta-

bility order in three nitrotriazine derivatives is: **1C > 2G > 3E** in very good agreement with the total energies calculated (see Table 5 for the total energies). The same argument can hold for the other series.

3.4. Energetics

The number and position of nitro substituents in the structure of triazines presently considered to change their electronic characters as well as its chemistry. Theoretically nitro-group can be either coplanar or nonplanar with the aromatic nucleus. In the case of coplanar nitro-group, shift of electrons from the aromatic ring to the nitro-group occurs through resonance. This effect produces a flat geometry for the NO_2 group with an sp^2 hybridized nitrogen atom and a relatively short C–N bond of "partially double" character. The exact balance of these processes is subtle and depends on the statistical weight of the contributing canonical structures. Table 5 shows the calculated total energies of the compounds at spin-restricted B3LYP hybrid function with 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p), cc-PVDZ basis sets, respectively. Total energies are corrected for zero-point vibrational energy (ZPVE). As seen from Table 5, generally among the calculated total energies of the nitrotriazine compounds there exists a good

Table 5
Calculated total energies (in a.u.) for nitrotriazine derivatives at different theoretical levels.

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
1A	−484.785890	−484.807821	−484.907635	−484.921985	−484.820520
1B	−689.263187	−689.280433	−689.442952	−689.464297	−689.319813
1C	−893.734860	−893.773046	−893.971442	−893.997914	−893.813743
2A	−484.743161	−484.764867	−484.863821	−484.878055	−484.778446
2B	−484.746039	−484.766869	−484.866168	−484.879557	−484.781190
2C	−484.747221	−484.768113	−484.867501	−484.880939	−484.782453
2D	−689.222241	−689.252929	−689.400193	−689.406503	−689.279158
2E	−689.223176	−689.253622	−689.401150	−689.421646	−689.280140
2F	−689.217477	−689.248311	−689.395502	−689.416382	−689.274099
2G	−893.689908	−893.730105	−893.925697	−893.953378	−893.768520
3A	−484.721427	−484.742139	−484.840926	−484.854209	−484.757156
3B	−484.721882	−484.742451	−484.841074	−484.854076	−484.757422
3C	−689.191306	−689.221866	−689.368145	−689.388470	−689.248637
3D	−689.200595	−689.229933	−689.377265	−689.396972	−689.258014
3E	−893.659274	−893.698712	−893.893558	−893.920872	−893.738181

The total energies are corrected for ZPVE.

Table 6
Calculated total energies (B3LYP/6-311G(d,p), including zero-point vibrational energies) of nitrotriazine molecules, fragments and NO_2 at the equilibrium geometries and resulting bond dissociation energies (BDE).

	Formula	Parent (hartrees)	Fragment (hartrees)	NO_2 (hartrees)	BDE (kcal/mol)
1A	$C_3H_2N_4O_2$	−484.90764	−279.69924	−205.06338	91.0
1B	$C_3H_1N_5O_4$	−689.44295	−484.23677	−205.06338	89.6
1C	$C_3N_6O_6$	−893.97144	−688.76806	−205.06338	87.9
2A	$C_3H_2N_4O_2$	−484.86382	−279.65346	−205.06338	92.2
2B	$C_3H_2N_4O_2$	−484.86618	−279.65575	−205.06338	92.3
2C	$C_3H_2N_4O_2$	−484.86750	−279.66233	−205.06338	89.0
2D(3)	$C_3H_1N_5O_4$	−689.40019	−484.19132	−205.06338	91.3
2D(6)	$C_3H_1N_5O_4$	−689.40019	−484.19132	−205.06338	91.3
2E(3)	$C_3H_1N_5O_4$	−689.40115	−484.19312	−205.06338	90.8
2E(5)	$C_3H_1N_5O_4$	−689.40115	−484.19730	−205.06338	88.1
2F(5)	$C_3H_1N_5O_4$	−689.39552	−484.19956	−205.06338	83.2
2F(6)	$C_3H_1N_5O_4$	−689.39552	−484.19473	−205.06338	86.2
2G(3)	$C_3N_6O_6$	−893.92570	−688.71877	−205.06338	90.1
2G(5)	$C_3N_6O_6$	−893.92570	−688.72981	−205.06338	83.2
2G(6)	$C_3N_6O_6$	−893.92570	−688.72534	−205.06338	86.0
3A	$C_3H_2N_4O_2$	−484.84093	−279.63348	−205.06338	90.4
3B	$C_3H_2N_4O_2$	−484.84107	−279.62743	−205.06338	94.3
3C(4)	$C_3H_2N_4O_2$	−689.36815	−484.17089	−205.06338	84.0
3C(5)	$C_3H_2N_4O_2$	−689.36815	−484.16392	−205.06338	88.4
3D	$C_3H1N_5O_4$	−689.37727	−484.17142	−205.06338	89.4
3E(4)	$C_3N_6O_6$	−893.89356	−688.69583	−205.06338	84.3
3E(5)	$C_3N_6O_6$	−893.89356	−688.69590	−205.06338	84.3

Key to the notation: aB(L) stands for the radical obtained from aB nitrotriazine by removing the NO_2 group at position L; a is the compound numbers.

agreement of stability order among the different levels of calculations. In terms of the energy considerations, the stability order is **1A > 2C > 2B > 2A > 3B > 3A** for mono-nitro-substituted triazines, whereas for dinitrated triazines order of **1B > 2E > 2D > 2F > 3D > 3C**, and for the three-nitro-substituted triazines **1C > 2G > 3E** order have been obtained at the theoretical levels performed (see Table 5).

3.5. BDE

Another main concern for the explosives is whether they are kinetically stable enough to be of practical interest. So, studies on the bond dissociations are important and essential for understanding the decomposition process of the energetic materials, since they are directly relevant to the sensitivity and stability of the energetic materials [30]. Previous studies [31,32] on the BDE for the nitro compounds such as nitro aromatic and nitramine molecules have shown that there is a parallel relationship between BDE for the weakest R–NO$_2$ (or N–NO$_2$) bond scission in the molecule and its sensitivity. Usually, the larger the BDE value, the lower the sensitivity is. However, this is only applied to the molecules in which R–NO$_2$ (or N–NO$_2$) bond is the weakest one. The C–C bond of nitrocubanes is weaker than the C–NO$_2$ bonds, and initial step in the decomposition is rupture of the cube C–C bond [33]. On the other hand, for designing and evaluating new energetic materials, it is accordingly important to be able to determine computationally the dissociation energies of these bonds. This is complicated, however, by the well-known difficulties involved in describing the electronic structure of nitro molecules. By comparing the computed energies and experimental results, the B3LYP method is able to give the best agreement with experimental BDE data [30].

However, in the present study, the BDE is defined as the difference between the zero-point energy corrected total energies at 0 K of the parent nitrotriazines and those of their corresponding radicals in the unimolecular bond dissociations. This has been successfully and frequently used to measure and determine the bond strength and relative stability of the compounds and corresponding radicals [32–39]. Therefore, the BDEs were computed at 0 K according to the energy changes of the bond dissociation process at the UB3LYP/6-311G(d,p) level, defined as BDE(A–B) = ΔE = [E(A*) + E(B*)] − E(A–B). The thermal decomposition mechanism can also be determined from the calculated BDE.

Table 6 shows calculated total energies (including zero-point vibrational energies) of nitrotriazine molecules, fragments and NO$_2$ at the equilibrium geometries and resulting BDE at UB3LYP/6-311G(d,p) level of theory. On the basis of the BDE for the initial steps in their thermal decompositions, it can be deduced that the relative stability order of these molecules may be in the order of **3B > 2B > 2A > 2D(3) = 2D(6) > 1A > 2E(3) > 3A > 2G(3) > 1B > 3D > 2C > 3C(5) > 2F(5) > 1C > 2F(6) > 2G(6) > 3E(4) = 3E(5)** (see Table 6). As seen in the table, BDEs for these compounds are highly position dependent and it is hard to generalize certain trends. According to suggestion of Chung et al. [40], more than a 20 kcal/mol (83.68 kJ/mol) barrier to dissociation should exists for a molecule to be considered as a viable candidate of HEDM. Therefore, we can conclude that the molecules in Fig. 2 are all viable candidates of HEDMs.

3.6. The frontier molecular orbital energies

Tables 7 and 8 show the HOMO and LUMO energies (ε) and dipole moments of the nitrotriazines calculated at B3LYP/6-311+G(d,p) and B3LYP/cc-pVDZ levels, respectively. The energies of the frontier orbitals decrease by increasing the number of nitro substituent on the triazine ring in all the cases. This is a general trend of electron withdrawing substituents which lower the LUMO and HOMO energy levels. As for the fron-

Table 7
The HOMO and LUMO energies (ε) (B3LYP76-311+G(d,p), in hartrees) and dipole moments (in Debye) of nitrotriazine derivatives.

Structures	Dipole moment	HOMO	LUMO	$\Delta\varepsilon$
1A	3.8791	−0.31860	−0.11790	0.20070
1B	3.6061	−0.34200	−0.14132	0.20068
1C	0.0004	−0.35161	−0.18635	0.16526
2A	5.8439	−0.29299	−0.12721	0.16578
2B	3.6053	−0.29178	−0.13948	0.15230
2C	1.3869	−0.28975	−0.14971	0.14004
2D	2.5167	−0.31617	−0.15649	0.15968
2E	2.9995	−0.32071	−0.17406	0.14665
2F	4.0533	−0.31715	−0.15855	0.15860
2G	0.3415	−0.34453	−0.18236	0.16217
3A	4.7420	−0.30160	−0.14494	0.15666
3B	1.0982	−0.30107	−0.15651	0.14456
3C	2.9590	−0.32585	−0.17418	0.15167
3D	1.3783	−0.33010	−0.17288	0.15722
3E	0.8999	−0.34869	−0.18476	0.16393

tier molecular orbital energy gap values, that is the difference between the LUMO and HOMO energy levels, the order is **1A > 1B > 2A > 1C > 3E > 2G > 2D > 2F > 3D > 3A > 2B > 3C > 2E > 3B > 2C** at the B3LYP/6-311+G(d,p) level.

3.7. Predicted densities and detonation of the nitrotriazine derivatives

As mentioned above Chung et al. suggested that a molecule should have more than a 20 kcal/mol (83.68 kJ/mol) barrier to dissociate in order to be considered as a viable candidate for HEDM [40]. Thus, we can conclude that the molecules in Fig. 2 are all viable candidates for insensitive HEDMs. This stability of the concerned compounds might be explained partially due to the aromaticity and some ballistic properties of them might be interesting.

Furthermore, density (ρ) detonation velocity (D), and detonation pressure (P) are the important parameters to evaluate the explosive performances of energetic materials and can be predicted by the empirical Kamlet–Jacobs equations [41] as follows:

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 130\rho) \tag{1}$$

$$P = 1.558\rho^2 NM^{1/2}Q^{1/2} \tag{2}$$

where each term in Eqs. (1) and (2) is defined as 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. Here, the parameters N, M and Q were calculated according

Table 8
The HOMO and LUMO energies (ε) (B3LYP/cc-pVDZ, in hartrees) and dipole moments (in Debye) of nitrotriazine derivatives.

Structures	Dipole moment	HOMO	LUMO	$\Delta\varepsilon$
1A	3.6284	−0.30347	−0.11248	0.19099
1B	3.3733	−0.32441	−0.13931	0.18510
1C	0.0003	−0.33319	−0.16937	0.16382
2A	5.3694	−0.27722	−0.11271	0.16451
2B	3.2590	−0.27762	−0.12352	0.15410
2C	1.2008	−0.27579	−0.13316	0.14263
2D	2.4174	−0.30683	−0.15078	0.15605
2E	2.8121	−0.30378	−0.15734	0.14644
2F	3.6577	−0.30153	−0.14206	0.15947
2G	0.2049	−0.32562	−0.16553	0.16009
3A	4.3096	−0.28750	−0.12859	0.15818
3B	1.0767	−0.28677	−0.13929	0.14748
3C	2.6554	−0.31019	−0.15946	0.15073
3D	1.4013	−0.31468	−0.15638	0.15830
3E	0.7775	−0.33110	−0.16548	0.16562

Table 9
Methods for calculating the N, M, and Q parameters of the $C_aH_bO_cN_d$ explosive[a,b].

Parameters	Stoichiometric ratio		
	$c \geq 2a + b/2$	$2a + b/2 > c \geq b/2$	$(b/2) > c$
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	$(28.9b+94.05a+0.23\Delta Hf^\circ)/MW$	$[28.9b+94.05(c/2-b/4)+0.239\Delta Hf^\circ]/MW$	$57.8c+0.239\Delta Hf^\circ)/MW$

[a] $C_aH_bO_cN_d$ denotes the compound composed of the C, H, O, and N elements; a, b, c, and d stand for the number of C, H, O, and N atoms in the compound.

[b] N is moles of gaseous detonation products per gram of explosive (in mol/g); M is the average molecular weight of the gaseous products (in g/mol); Q is the chemical energy of detonation (in kJ/g); MW in the formula is the molecular weight of the title compounds (in g/mol); ΔHf° is the standard heat of formation of the studied compound (in kJ/mol).

Table 10
Predicted densities and detonation properties of the nitrotriazine derivatives.

Structures	OB_{100}	HOF[a] (kJ/mol)	Q (kJ/g)	V^b (cm^3/mol)	P (g/cm^3)	D (km/s)	P (GPa)
1A	−63.43	176.12	1165.14	74.34	1.70	7.20	22.24
1B	−23.39	173.03	1372.77	95.19	1.80	8.18	29.67
1C	0.00	502.21	1861.59	115.44	1.87	9.30	39.23
2A	−63.49	360.43	1514.72	78.70	1.60	7.41	22.62
2B	−63.49	345.59	1486.59	78.03	1.62	7.41	22.80
2C	−63.49	352.03	1498.80	77.11	1.63	7.49	23.44
2D	−23.39	431.52	1733.89	95.84	1.78	8.63	32.89
2E	−23.39	43S.51	1743.66	94.90	1.80	8.70	33.64
2F	−23.39	430.52	1732.49	93.54	1.83	8.78	34.51
2G	0.00	528.51	1890.69	113.81	1.90	9.43	40.68
3A	−63.49	401.77	1593.10	78.80	1.60	7.49	23.14
3B	−63.49	3S0.5S	1552.92	77.75	1.62	7.51	23.47
3C	−23.39	341.29	1607.83	94.57	1.81	8.55	32.53
3D	−23.39	479.07	1800.32	96.62	1.77	8.67	32.98
3E	0.00	365.76	1710.64	112.06	1.93	9.30	39.91

Q: heat of explosion; V: molar volume; D: velocity of detonation; P: pressure of explosion.

[a] Heat of formation obtained from the calculation at the PM3 level.

[b] Average value from 100 single-point volume calculations at the B3LYP/6-31 lG(d,p) level.
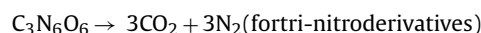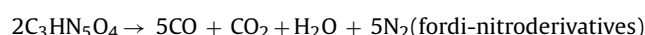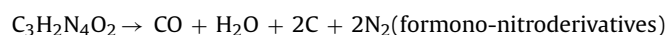
to the chemical composition of each explosive [42,43] as listed in Table 9. On the other hand, the density of each molecule was predicted from the molecular volume, while the molecular volume of each molecule was obtained from the statistical average of 100 single-point calculations for each optimized structures. The molar volume was defined as inside a contour of 0.001 e/Bohr^3 density that was evaluated using a Monte Carlo integration implemented in the Gaussian 03 package. This method has been successfully tested on various CHNO molecules and accurately predicts the explosive properties [43–48]. In the present study, single-point molecular volume calculations at B3LYP/6-311G(d,p) performed based on the B3LYP/6-311G(d,p) geometry optimized structures. Table 10 collects the predicted densities and detonation properties of the nitrotriazine derivatives. The heats of formation (HOF) values were also calculated and listed in the table. The previously reported studies have proven that the HOF calculated by the PM3 method is reliable [49–52]. All these data in Table 10, gave some clue about the explosive character of the molecules derived from triazine molecules.

Table 11
Comparison of D (km/s) and P (GPa) values of RDX and HMX with certain presently considered compounds. Experimental values are in parenthesis.

	V	P
RDX	8.83 (8.75)	34.11 (34.70)
HMX	8.99 (9.10)	35.92 (39.00)
1C	9.30	39.23
2D	8.63	32.89
2E	8.70	33.64
2F	8.78	34.51
2G	9.43	40.68
3C	8.55	32.53
3D	8.67	32.98
3E	9.30	39.91

It was clear that from mono-substituted to tri-substituted nitrotriazines, density (ρ), velocity of detonation (D) and detonation pressure (P) all increase with the increasing number of the nitrogroups. This might show good group additivity on the detonation properties and also supports the claim that introducing more nitro substituents into a molecule usually helps to increase its detonation performance. For RDX and HMX, experimental value of D and P are 8.75, 9.10 km/s and 34.70, 39.00 GPa, respectively (see Table 11). Furthermore, at the same theoretical level, the calculated performance parameters D and P of RDX and HMX were found to be 8.83, 8.998 km/s and 34.11, 35.92 GPa, respectively. Comparing these values with tri-substituted nitrotriazine compounds, **1C** (has velocity of detonation value of 9.30 km/s and detonation pressure value of 39.23 GPa), **2G** (has velocity of detonation value of 9.43 km/s and detonation pressure value of 40.68 GPa), **3E** (has velocity of detonation value of 9.30 km/s and detonation pressure value of 39.91 GPa), one finds them to be more powerful explosives than the famous explosives HMX and RDX. Furthermore, the relative positions of the nitro substituents in the triazine compounds affect the detonation properties (see Table 10). Especially di- and tri-nitro-substituted triazines will be novel potential candidates for HEDMs when they are successfully synthesized.

The possible detonation products of the presently considered structures, based on Kistiakowsky–Wilson and modified Kistiakowsky–Wilson rules [53] are as follows:

$$C_3H_2N_4O_2 \rightarrow CO + H_2O + 2C + 2N_2 \text{(formono-nitroderivatives)}$$

$$2C_3HN_5O_4 \rightarrow 5CO + CO_2 + H_2O + 5N_2 \text{(fordi-nitroderivatives)}$$

$$C_3N_6O_6 \rightarrow 3CO_2 + 3N_2 \text{(fortri-nitroderivatives)}$$

As seen in the case of di-nitro derivatives, two molecules of the di-nitro compounds are needed for the complete mass balance

which indicated that detonation of these compounds requires intra- as well as inter-molecular redox processes [54].

4. Conclusion

In the present study, all possible mono-, di- and tri-nitro-substituted triazine compounds have been investigated by using quantum chemical calculations in order to find some novel potential candidates of HEDMs. Stability of these compounds was investigated in terms of the total energy, BDE values of C–NO$_2$, and NICS values for aromaticity. The detonation properties have been investigated and found that there might be some candidates of HEDMs among the investigated triazine structures so far not reported in the literature from this point of view. The present study sheds some valuable light on this subject by exploring their structural energetic properties.

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