Some dinitramines from tetraaminoethylene and their interactions with magnesium – DFT study

Lemi Türker

Department of Chemistry, Middle East Technical University, Üniversiteler, Eskişehir Yolu No: 1, 06800 Çankaya/Ankara, Turkey
e-mail: lturker@gmail.com; lturker@metu.edu.tr

Abstract

Certain isomeric dinitramines derived from tetraaminoethylene have been designed which possess an embedded push-pull type conjugated system(s) operative in different extents which may attract attention as an insensitive high energy materials. Those structures and their magnesium composites have been investigated within the restrictions of density functional theory at the level of B3LYP/6-311++G(d,p). The results indicate that the dinitramines considered are exothermic and favorable in terms of H° and G° values. However, their magnesium composites are not all stable, (two of them decompose) and Mg atom acquires some positive charge in each case. Various structural, quantum chemical and UV-VIS spectral data are collected and discussed.

1. Introduction

The category of nitramines encompasses a wide range of substances depending on the characteristics of R1 and R2 in their structures having the chemical form of $R_1R_2NNO_2$. Nitramines are also known as nitroamides. There are great demands to develop explosives with higher performance accompanied by reduced sensitivities towards external stimuli, higher thermal stability and improved environmental acceptability. Various aspects of nitramines have been investigated and published through years [1-19]. The nitramines, which have found practical application as explosives are multi-functional nitramines, usually cyclic and include high explosives like RDX, HMX, and bicyclo-HMX (BC-HMX). Complexes of the explosively unstable nitramine ligands *N*-nitromethylamine (HL), N,N′-dinitrodiamino-ethane (H₂L′), and 5-nitraminotetrazole (H₂L″) with ammine derivatives of divalent copper, nickel or palladium explode on heating or under a hammer blow [20]. Dimethylnitramine has been used as a simple model for cyclic nitramines because it is easier to deal with experimentally and theoretically. Nano-nitramine explosives (RDX, HMX, CL-20) are produced on a bi-directional grinding mill [21] and compared with the micron-sized samples; the nano-products show obvious decrease in friction and impact sensitivities. On the other hand, toxicological testing of nitramines and nitrosamines indicate a genotoxic potential of these substances [22].

In the present study, some dinitramines derived from tetraaminoethylene and their interactions with magnesium have been considered within the restrictions of density functional theory (DFT).

2. Method of Calculation

In the presently considered DFT study, all the initial geometry optimizations leading to energy minima have been achieved by using molecular mechanics (MM2) method then the structures were subjected to semi

empirical PM3 self consistent fields molecular orbital (SCF MO) method [23-25] at the restricted level. Afterwards, the structure optimizations have been managed within the framework of Hartree-Fock (HF) and finally by using density functional theory (DFT) at the level of B3LYP/6-311++G(d,p) [26,27]. Note that 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 [28]. Also note that the correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [29] and Lee, Yang, Parr (LYP) correlation correction functional [30]. In the present treatment, the normal mode analysis for each structure yielded no imaginary frequencies for the $3N$–6 vibrational degrees of freedom, where N is the number of atoms in the system. This search has indicated that each structure corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths have been thoroughly searched in order to find out whether any bond cleavages have occurred or not during the geometry optimization process. All these computations were performed by using SPARTAN 06 program [31].

3. Results and Discussion

Nitramines are employed as important oxidizer ingredients for solid propellants. Note that well known explosives, RDX and HMX, are nitramines. Nitramines are highly energetic structures and produce high impetus and specific impulse for gun and rocket propulsion systems. Additionally, they generally produce little smoke, less toxicity and environmental risks.

Figure 1 shows the optimized structures of the nitramines presently considered**.** They are dinitramines of tetraaminoethylene and designed in accord to *trans*, *cis* and *geminal* configurational patterns. One should notice the conformations of the groups in each case. The isomer-C has some resembles to FOX-7 explosive and possesses some degree of push-pull type resonance characteristics. The figure also displays the direction of the dipole moment vectors whose directions and magnitudes are dictated by orientation and conformation of the amino and nitramine groups they possess.
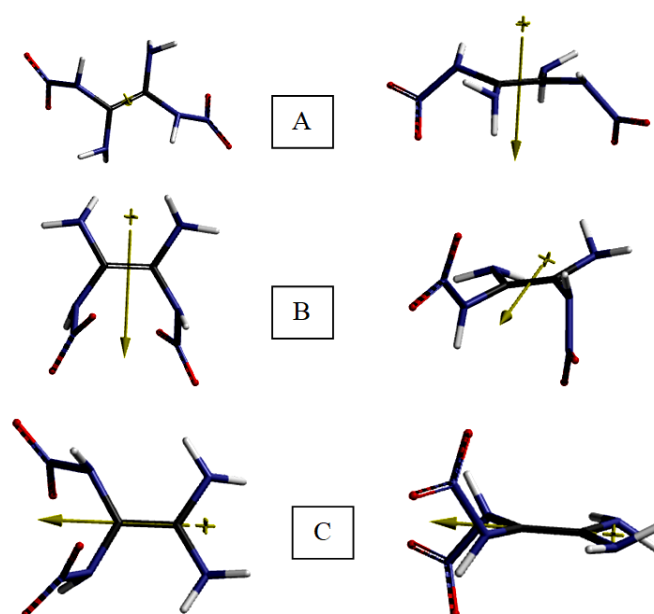
Figure 1. Optimized structures of the dinitramines considered (Top and side views)**.**

Table 1 shows some of the standard thermo chemical formation and constant volume heat capacity (C_v) data of the species considered. The data reveal that the standard heat of formation (Hº) values of all the isomers are

exothermic and they are favored according to their G^o (Gibbs free energy of formation) values. The algebraic order of H^o and G^o values are the same as C<A<B whereas S^o values follow the order of B>A>C. On the other hand, C_v values exhibit the order of B>C>A. Note that isomers C and B are the most and least exothermic structures in terms of H^o values.

Table 1. Some thermo chemical properties of the dinitramine isomers considered.

Isomer	H^o	S^o (J/mol^o)	G^o	C_v (J/mol^o)
A	-1861675.173	416.64	-1861799.392	131.71
B	-1861661.909	417.47	-1861786.380	134.63
C	-1861724.837	408.59	-1861846.659	134.52

Energies in kJ/mol.

Table 2 shows some energies of the species considered where E, ZPE and E_C stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. According to the data, they are all electronically stable structures. The stability order is C>A>B which is the same order of H^o and G^o values. Note that ZPE values exhibit the order of C>A>B.

Table 2. Some energies of the nitramine isomers considered.

Isomer	E	ZPE	E_C
A	-1862016.53	329.09	-1861687.44
B	-1861999.72	324.99	-1861674.73
C	-1862067.04	330.72	-1861736.32

Energies in kJ/mol.

Aqueous and solvation energy values (E_{aq} and E_{solv}, respectively) for the isomers considered are shown in Table 3. The solvation energies were calculated by adopting SM5.4/A model [31]. The algebraic order of aqueous and solvation energy values are C<A<B and C<B<A, respectively. Thus, dinitramine-C is solvated better compared to the other isomers and associated with more negative E_{aq} value.

Table 3. Some energies of the dinitramine isomers considered.

Isomer	E_{aq}	E_{solv}
A	-1862049.63	-33.101
B	-1862039.59	-39.863
C	-1862118.26	-51.221

Energies in kJ/mol. Solvation energy by SM5.4/A model.

Table 4 list some properties of the isomers considered. It is worth mentioning that the polar surface area (PSA) is defined as the amount of molecular surface area arising from polar atoms (N, O) together with their attached hydrogen atoms [31]. Although these compounds are isomeric, their PSA values differ from each other, meaning that the same kind of atoms might be influenced by electronic factors differently at different positions.

Table 4. Some properties of the dinitramine isomers considered.

Isomer	Area (Å²)	Volume (Å³)	PSA (Å²)	Ovality	Log P
A	179.18	135.83	160.459	1.40	-0.68
B	180.13	135.83	161.112	1.41	-0.68
C	178.64	135.44	159.252	1.40	-0.68

Polarizabilities in 10^{-30} m³ units.

As for the log P values, note that a negative value for log P means the compound has a higher affinity for the aqueous phase (it is more hydrophilic).

The dipole moment and polarizability values for them are tabulated in Table 5. The orders of dipole moment and polarizability values are C>B>A and B>A>C, respectively.

Table 5. Dipole moment and polarizability values for the nitramine isomers considered.

| Isomer	Dipole moment	Polarizability
A	2.66	51.42
B	5.31	51.47
C	6.20	51.29

Dipole moments in debye units. Polarizabilities in 10^{-30} m³ units.

Figure 2 shows the electrostatic potential (ESP) charges on the atoms of the dinitramine species considered. Note that the ESP charges are obtained by the program based on a numerical method that generates charges that reproduce the electrostatic potential field from the entire wavefunction [31]. Electrostatic potential maps of the isomers considered are shown in Figure 3, where negative potential regions reside on red/reddish and positive
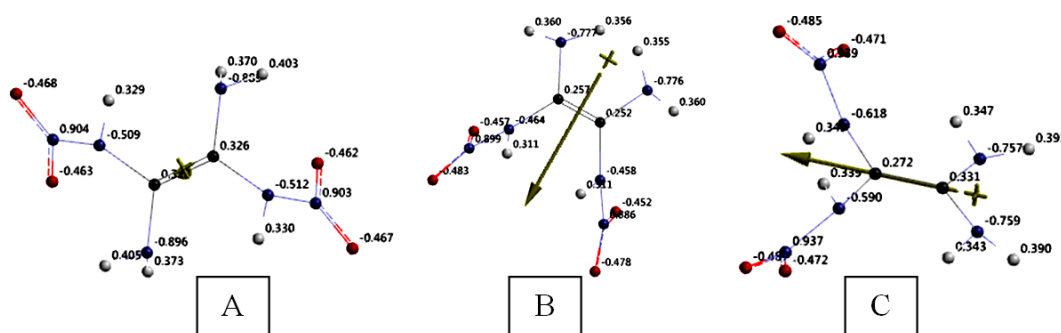
Figure 2. ESP charges on the atoms of the isomeric dinitramine species considered.
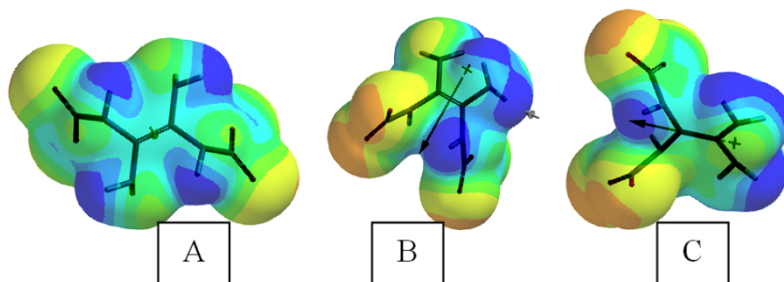
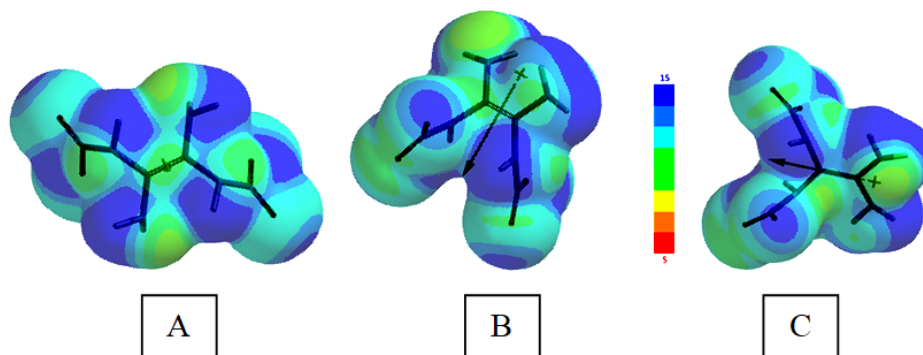**Figure 3.** ESP maps of the isomeric dinitramine species considered.

ones on blue/bluish parts of the maps. Thus, the location and distribution of the colors indicate the extent of push-pull character of the isomers. The best one resides on isomer-C where the direction of the dipole moment vector is a clear indication of that property.

The calculated bond lengths (Å) of the isomeric dinitramine species considered are shown in Figure 4. As seen in the figure, the same types of bond lengths vary from one structure to other. For instance, the C-C double bond is 1.35, 1.34 and 1.37 going from structures A to C. The push-pull type resonance existing in isomer-C somewhat causes elongation of the double bond.
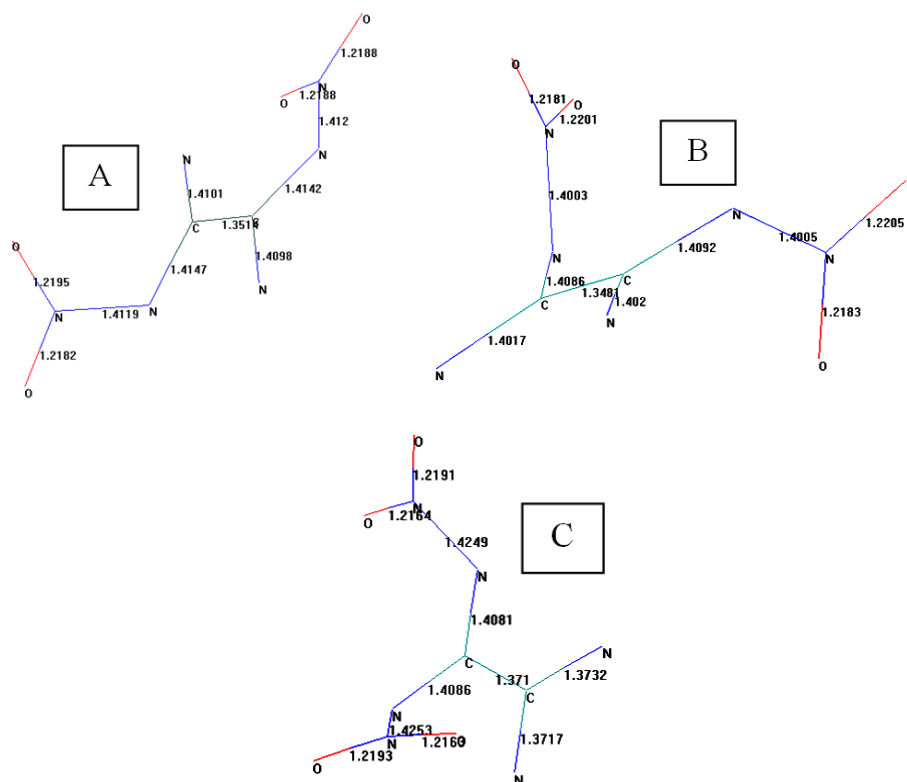

Figure 4. The calculated bond lengths (Å) of the isomeric dinitramine species considered (hydrogens omitted).

Figure 5 displays the local ionization maps of the isomeric nitramine species considered, where conventionally red/reddish regions (if any exists) on the density surface indicate areas from which electron removal is relatively easy, meaning that they are subject to electrophilic attack. It is worth remembering that the local ionization potential map is a graph of the value of the local ionization potential on an isodensity surface corresponding to a van der Waals surface.


Figure 5. The local ionization maps of the isomeric dinitramine species considered.

The LUMO maps of the isomeric dinitramine species considered are shown in Figure 6. Note that a LUMO map displays the absolute value of the LUMO on the electron density surface. The blue color (if any exists) stands for the maximum value of the LUMO and the red colored region, associates with the minimum value. Note that the LUMO and NEXTLUMO are the major orbitals directing the molecule towards of the attack of nucleophiles [31]. Positions where the greatest LUMO coefficient exists is the most vulnerable site in nucleophilic reactions.
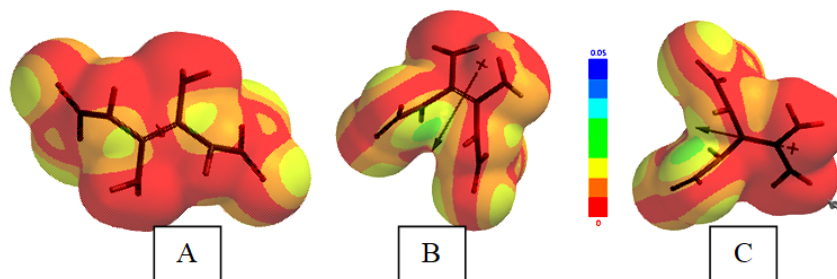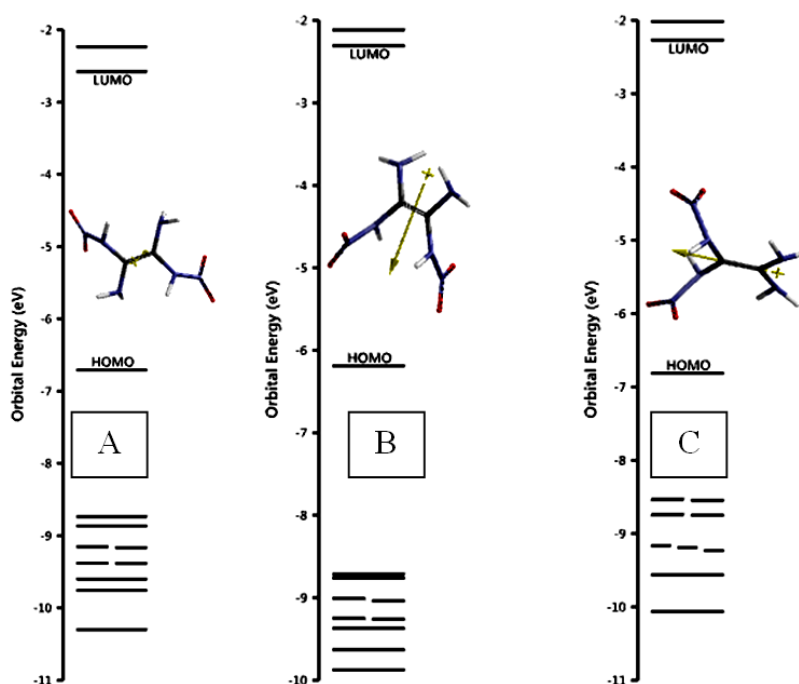

Figure 6. The LUMO maps of the isomeric dinitramine species considered.

Figure 7 displays the bond densities of the isomeric dinitramine species considered.
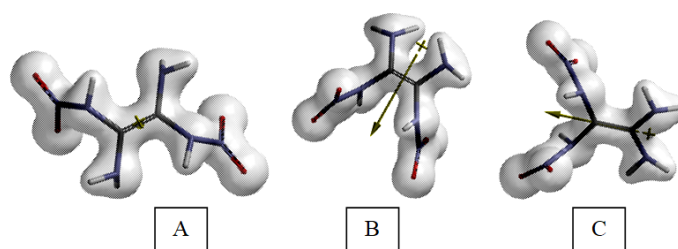
Figure 7. The bond densities of the isomeric dinitramine species considered.

Figure 8 shows some of the orbital energies of the isomeric dinitramine species considered.

Figure 8. Some of the orbital energy levels of the isomeric dinitramine species considered.

The HOMO, LUMO energies and the interfrontier molecular orbital energy gap, $\Delta\varepsilon$, values ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$) of the dinitramine isomers considered are listed in Table 6. The algebraic orders of the HOMO and LUMO energies are C<A<B and A<B<C, respectively. Thus, the interfrontier molecular orbital energy gap values ($\Delta\varepsilon$), possesses the order of C>A>B. The substituents depending on their orientations and conformations exert rather different electron donating and attracting abilities to lower or raise the frontier molecular orbital energy levels. Consequently, $\Delta\varepsilon$ values yield the above mentioned order.

Some ballistic properties of explosives are correlated with the interfrontier molecular orbital gap values, for instance the impact sensitivity of explosives are related to the interfrontier molecular orbital energy gap values e.g., narrower the gap, the explosive becomes more sensitive to an impact stimulus [32, 33].

Table 6. The HOMO, LUMO energies and $\Delta\varepsilon$ values of the nitramine isomers considered.

Isomer	HOMO	LUMO	$\Delta\varepsilon$
A	-647.00	-248.82	398.18
B	-597.31	-222.28	375.03
C	-657.47	-218.94	438.53

Energies in kJ/mol.

Figure 9 displays the calculated UV-VIS spectra (time dependent DFT) of the isomeric dinitramines presently considered. As seen in the figure, all the spectra except for isomer-B are mainly confined into UV region having two absorption peaks. They vary in shape for the isomers, in terms of intensities and positions of the absorptions. The spectra are influenced by the value of the transition moments which are responsible for the excitations of nonbonding or π-orbitals [34, 35].
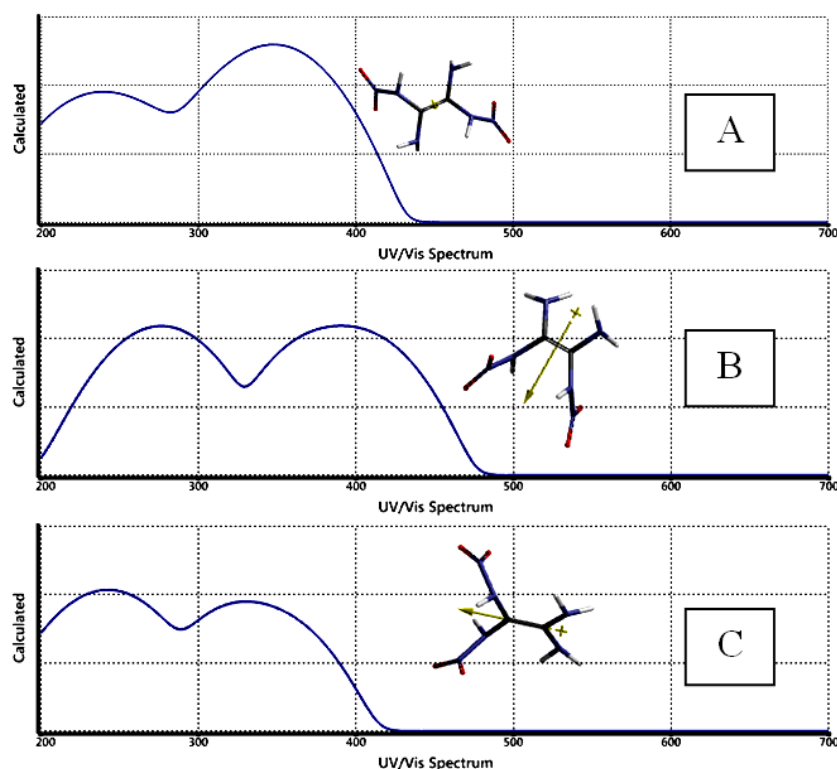

Figure 9. The calculated UV-VIS spectra (TDDFT) of the isomeric dinitramine species considered.

Interaction with magnesium

The presently considered dinitramines interact with magnesium atom such that composites A+Mg and B+Mg undergo rupture of one of HN-NO$_2$ bonds. The distance standing for the broken bonds are 6.036 Å and 3.972 Å, respectively. The composite C+Mg remains intact and HN-NO$_2$ bonds have the lengths of 1.411 Å and 1.407 Å.
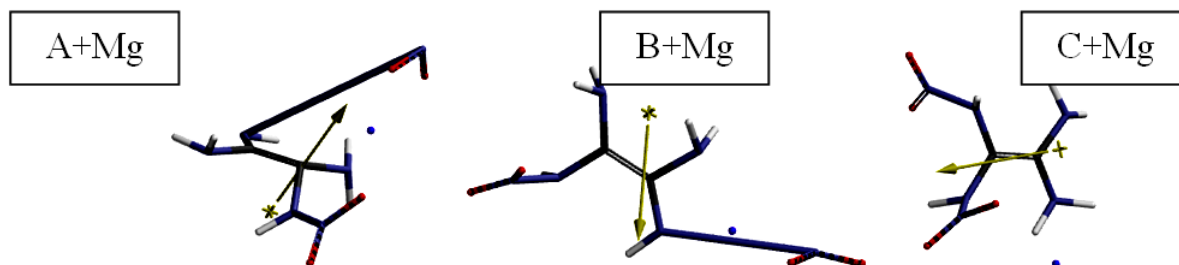
Figure 10. Optimized structures of the magnesium composites of the dinitramine systems considered.

Table 7 contains some thermo chemical properties of the magnesium composites of the dinitramine isomers considered. The values for the decomposed ones are for the resultant systems. As seen in the table, they are more exothermic and have more favorable G° values compared to C+Mg composite. Also note that they possess more favorable entropies of formation.

Table 7. Some thermo chemical properties of the magnesium composites of the dinitramine isomers considered.

Isomer	H°	S° (J/mol°)	G°
A+Mg	-2387395.801	442.37	-2387527.694
B+Mg	-2387382.933	446.65	-2387516.105
C+Mg	-2387075.234	439.42	-2387206.248

Energies in kJ/mol.

Some energies of the magnesium composites of the dinitramine isomers considered are collected into Table 8. As seen there the decomposed system standing for A+Mg is more stable than the respective system of B+Mg.

Table 8. Some energies of the magnesium composites of the nitramine isomers considered.

Isomer	E	ZPE	E$_C$
A+Mg	-2387730.92	323.83	-2387407.09
B+Mg	-2387719.39	325.19	-2387394.20
C+Mg	-2387416.63	330.96	-2387085.67

Energies in kJ/mol.

Figure 11 displays the ESP charges on the atoms of the magnesium composites of dinitramine species considered. As seen in the figure, in all three cases the magnesium atom acquires positive charge, they are respectively 1.437, 1.280 and 0.344 esu for A+Mg through C+Mg composites. Thus, the isomer-A is a much better oxidant compared to the others, thus the magnesium gets more positive charge. It is worth mentioning

that the expelled NO_2 moieties in A+Mg and B+Mg composites have negative partial charge. Note that in isomer-C the nitramine groups have *geminal* configuration (see Figure 1).
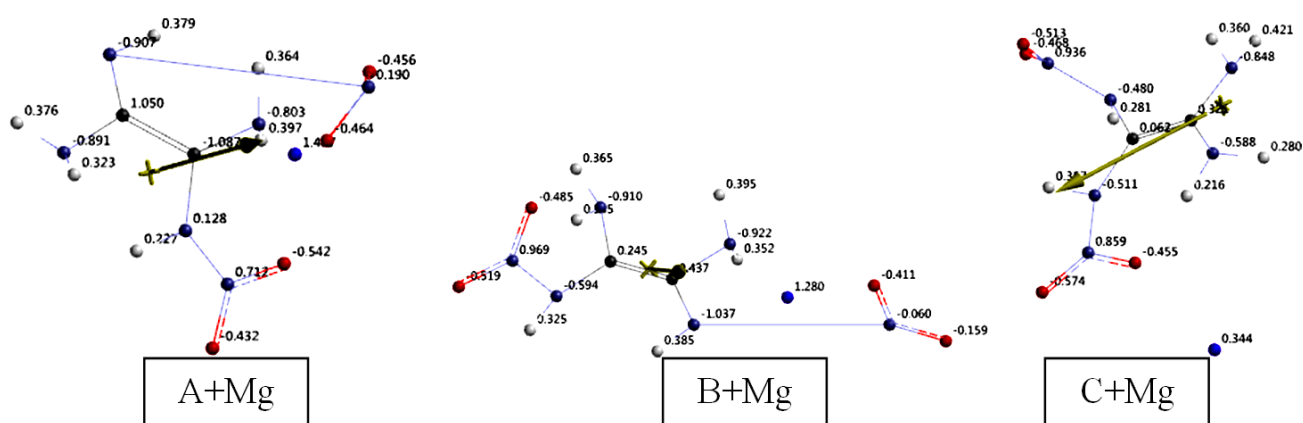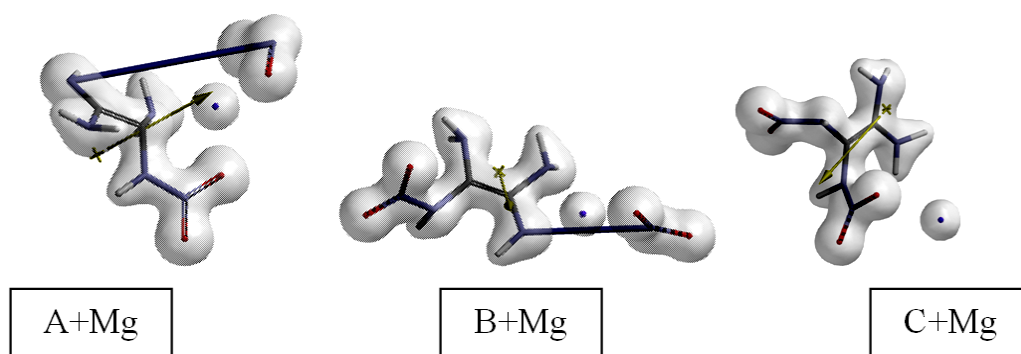

Figure 11. ESP charges on the atoms of the magnesium composites of nitramine systems considered.

Figure 12 displays the ESP maps of magnesium composites of the isomeric dinitramines considered. Note that negative potential regions reside on red/reddish and positive ones on blue/bluish parts of the maps.
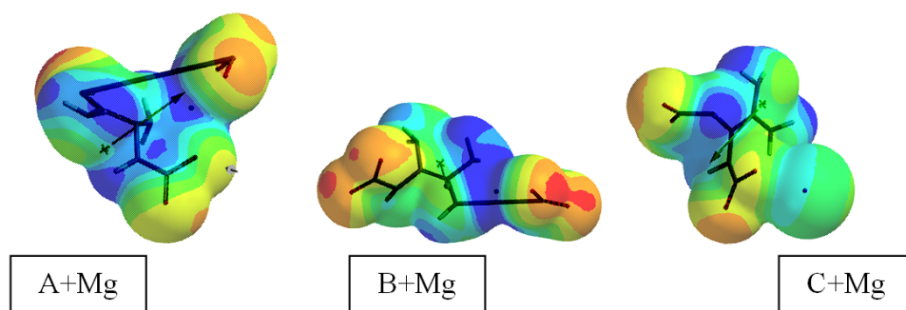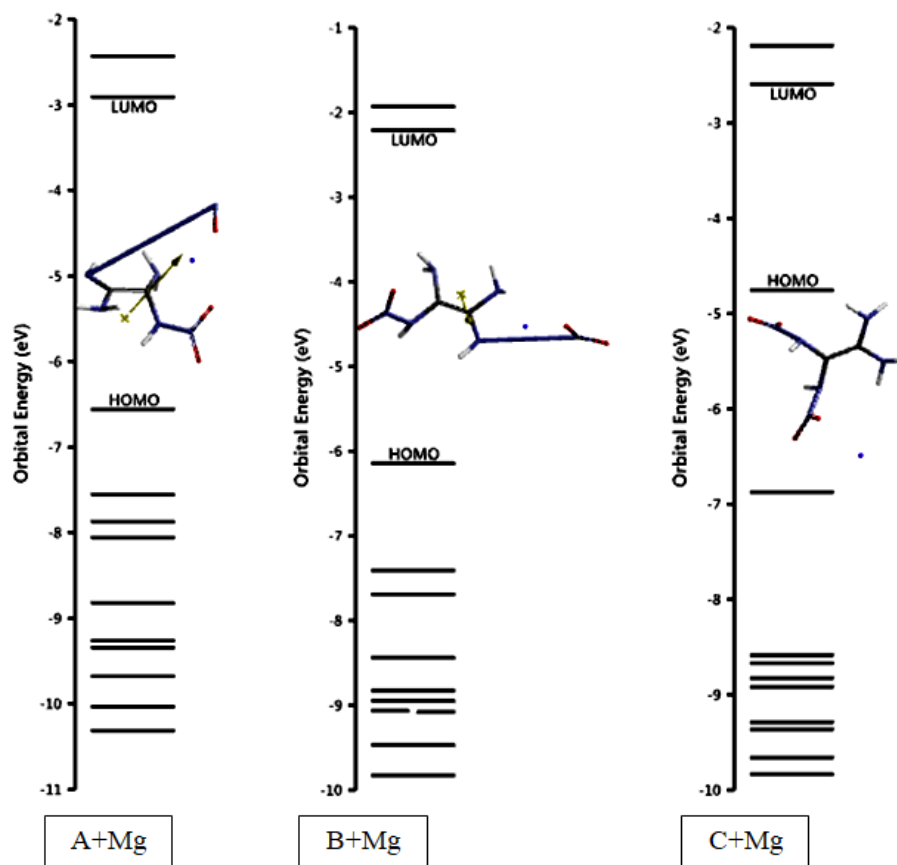

Figure 12. ESP maps of magnesium composites of the isomeric dinitramine systems considered.

Figure 13 shows the bond densities of magnesium composites of the isomeric dinitramine systems considered.

Figure 13. The bond densities of magnesium composites of the isomeric dinitramine systems considered.

Some of the orbital energy levels of the magnesium composites/systems of the dinitramine systems considered are depicted in Figure 14. Note the condensed appearance of the inner molecular orbital energy levels in C+Mg composite (intact composite in the group) is indicative of its thermal stability.

Figure 14. Some of the orbital energy levels of the magnesium composites of the dinitramine systems considered.

The HOMO, LUMO energies and Δε values of the magnesium composite/systems of the nitramine isomers considered are shown in Table 9. The algebraic order of HOMO and LUMO energies are A+Mg< B+Mg< C+Mg and A+Mg< C+Mg< B+Mg, respectively. Consequently the order of Δε values turn out to be B+Mg< A+Mg< C+Mg.

Table 9. The HOMO, LUMO energies and Δε values of the magnesium composite/systems of the nitramine isomers considered.

Isomer	HOMO	LUMO	Δε
A+Mg	-632.95	-280.59	352.36
B+Mg	-592.74	-213.21	379.53
C+Mg	-458.43	-250.15	208.28

Energies in kJ/mol.

Figure 15 displays the calculated UV-VIS spectra (TDDFT) of the magnesium composites of isomeric dinitramine systems considered. As seen in the figure, all the spectra except C+Mg are mainly confined into UV region having two absorption peaks in A+Mg, three overlapped peaks in B+Mg which vary in shape, resulting from the intensities and positions. The spectrum of C+Mg is completely different from the others which covers both the UV and visible region. It has the narrowest Δε value among the others. Thus, possesses a very high λ_{max} value in the visible region.
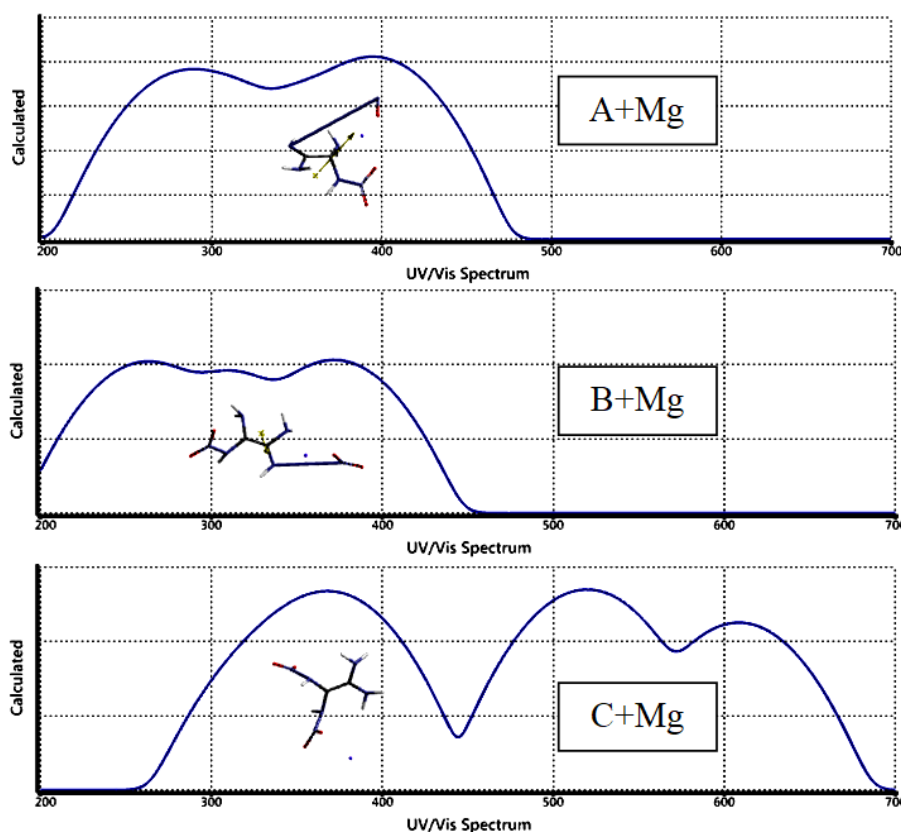
Figure 15. The calculated UV-VIS spectra (TDDFT) of the magnesium composites of isomeric nitramine systems considered.

4. Conclusion

The present study, performed on the some newly designed nitramines and their interactions with magnesium within the restrictions of density functional theory has revealed that the nitramines are thermally and electronically stable at the vacuum conditions. However, magnesium somewhat perturbs the parent structures by transferring some electron population to the organic component, acquiring some positive charge itself. The extent of transfer is such that some of the parent dinitramines decompose by the cleavage of one of two $N-NO_2$ bonds. In the intact dinitramine structure, the presence of magnesium atom narrows the interfrontier frontier molecular orbital energy gap making it at least more susceptible to impulse stimulus compared to the parent structure. Note that magnesium or some other metals contribute the thermal effect of energetic materials affirmatively. The some other ballistic properties or others of those dinitramines (if they are dictated by the interfrontier frontier molecular orbital energy gap values) are expected to be affected by the influence of magnesium (or similar metallic components).

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