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Effect of magnesium on isomers of 1,2-diamino-1,2-dinitroethylenes – A DFT treatment

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Abstract

The *cis* and *trans* isomers of 1,2-diamino-1,2-dinitroethylene which might be extracted from FOX-7 structure are considered and have been investigated thoroughly within the constraints of density functional theory at the level of B3LYP/6-311++G(d,p). Then their interactions with magnesium atom at the same level of theory have been considered. The collected data revealed that all the optimized structures considered have exothermic heats of formation and favorable Gibbs free energy of formation values. They are thermally favored and electronically stable at the standard states. In all the cases the magnesium atom acquires positive charge indicating that some electron population has been conveyed to the organic partner. Various structural and quantum chemical data have been collected and discussed, including UV-VIS spectra.

1. Introduction

Diaminodinitroethylenes could be in *cis*, *trans* or *geminal* isomeric forms. The *cis* and *trans*-isomers are two structures which could be engendered from structure of FOX-7 by certain structural modifications whereas the *geminal* one, 1,1-diamino-2,2-dinitroethylene, is a famous explosive known as FOX-7 which is a novel insensitive high-energy material exhibiting good thermal stability and low sensitivity. Moreover, it possesses excellent application performance among the solid propellants and insensitive ammunitions. In spite of the fact that it has a simple molecular composition and structure, it exhibits abundant chemical reactivity such as coordination reactions, nucleophilic substitutions, acetylate reactions, oxidation and reduction reactions, electrophilic addition reactions etc., [1,2]. FOX-7 is much less sensitive than RDX (in terms of impact, friction, and electrostatic discharge sensitivities).

On the other hand, push-pull alkenes are substituted alkenes (like FOX-7) with one or two electron-donating substituents (D) on one end of C=C double bond and with one or two electron-accepting substituents (A) at the other end [3,4]. This push-pull effect is of decisive influence on both the dynamic behavior and the chemical reactivity of this class of compounds [3,5].

Different aspects of push-pull effect have been investigated by various scientists [6-13]. Isomeric aminonitroethylenes presently considered combine the effects of resonance-donating NH_2 and the inductively and mesomerically electron-withdrawing NO_2 groups in a molecular framework containing polarizable electronic charge. Note that FOX-7 explosive contains *cis* and *trans* forms of aminonitroethylenes in embedded form.

No one explosive molecule has all of the properties desired from the perspective of both performance characteristics and sensitivity properties. Some immense effort has been devoted to ameliorate or reach to

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desirable qualities such as insensitivity to handling (impact, spark and friction) stimuli and shock as well as high thermal stability [14]. Certain metals are added to formulation of explosives to ameliorate their thermal output [15].

Some metallized FOX-7 compositions were reported [2,17-19]. Also some molecular orbital calculations were reported on aluminized FOX-7 [17-21].

2. Method of Calculations

In the present study, all the initial optimizations of the structures leading to energy minima have been achieved first by using MM2 method which is then followed by semi empirical PM3 self consistent fields molecular orbital method [22-24]. Afterwards, the structure optimizations have been achieved within the framework of Hartree-Fock and finally by using density functional theory (DFT) at the level of B3LYP/6-311++G(d,p) [25,26]. 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 [27]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [28] and Lee, Yang, Parr (LYP) correlation correction functional [29]. In the present study, 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 the structure of each molecule considered 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 cleavage occurred or not during the geometry optimization process. All these computations were performed by using SPARTAN 06 program [30].

3. Results and Discussion

Figure 1 stands for the optimized structures of the *cis* and *trans* isomers and their magnesium composites

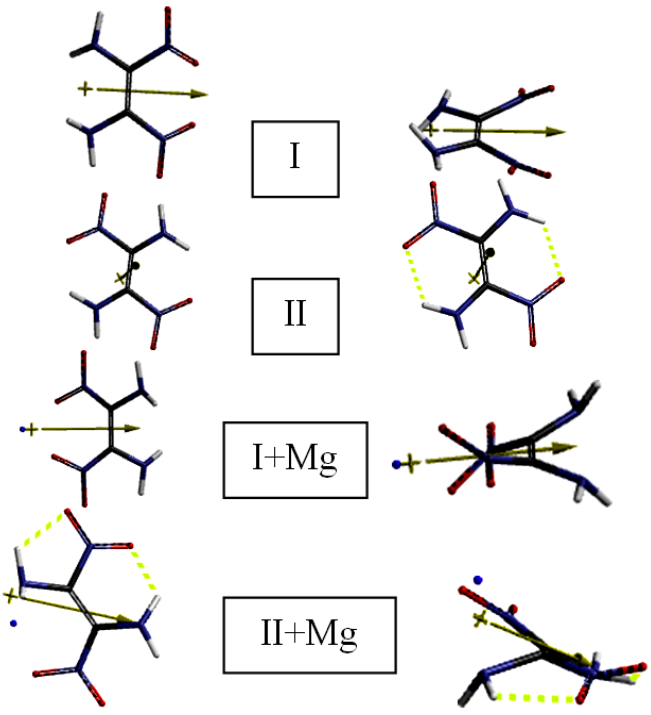


Figure 1. Optimized structures of the *cis* and *trans* isomers and their magnesium composites considered.

considered. In the case of the *cis* isomer, in contrast to the *trans* one, the substituents are not coplanar. Some repulsive interactions cause *cis* isomer to prefer the twisted form. Both of the magnesium composites are also in the twisted form. Note that there exist hydrogen bonds between the amino and nitro groups in the *trans* isomer, in the absence or presence of the magnesium atom.

The magnesium atom is nearby one of the nitro groups in the *cis* isomer, whereas the preference is nearby the amino group in the *trans* case.

Bond lengths (Å) of the species considered are shown in Figure 2. As seen in the figure the presence of magnesium atom causes variations of the bond lengths, note the elongation of carbon-carbon bond in each case.

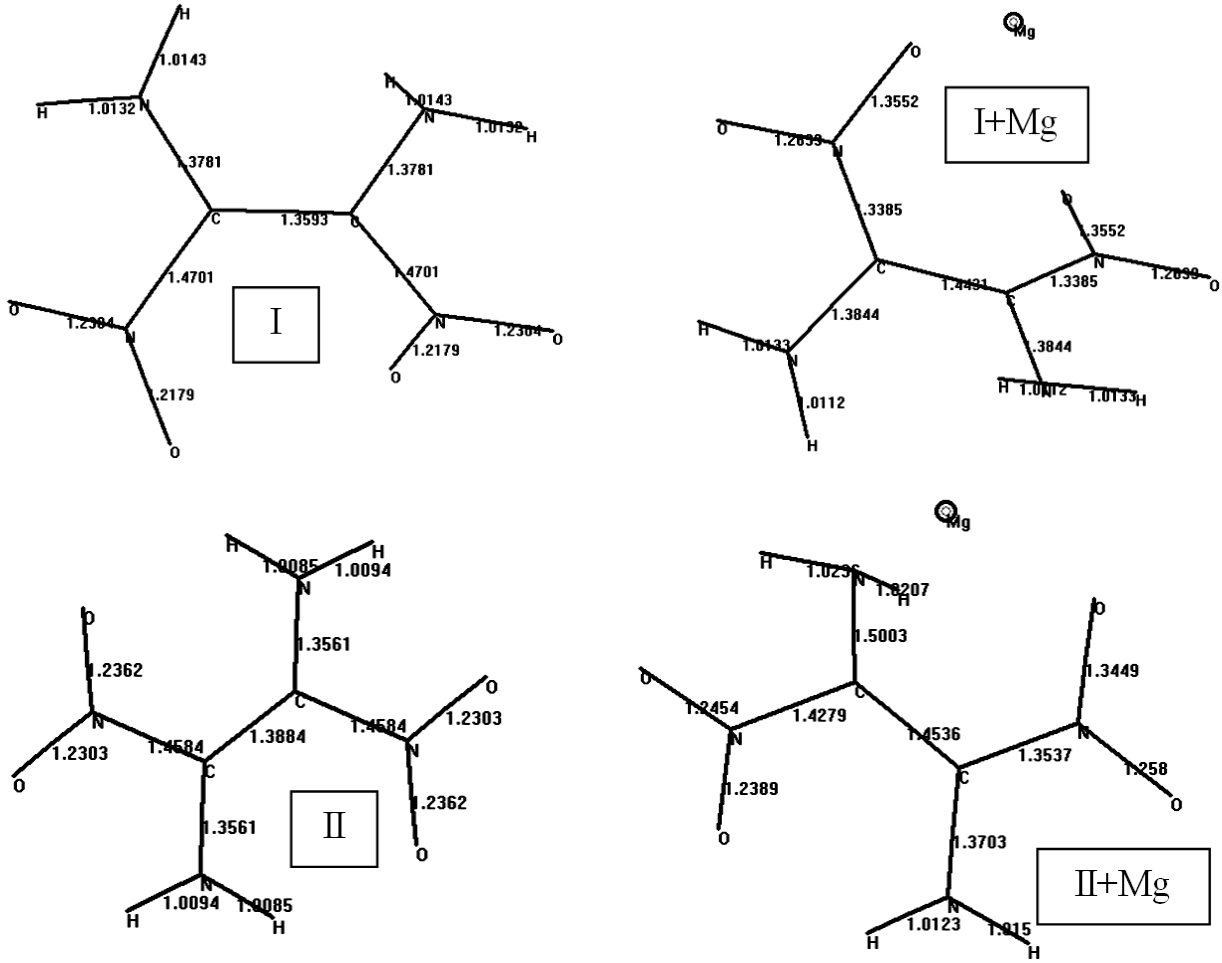


Figure 2. Bond lengths (Å) of the species considered**.**

Some thermo chemical properties of the species considered are listed in Table 1. The data in Table 1 reveal that the standard heats of formation (H^o) values of 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 II< I and I+Mg< II+Mg, namely II is more exothermic and favored than I. Whereas in the case of composites the respective orders become I+Mg< II+Mg. It is the effect of Mg atom on the push-pull behavior of the isomers dependent on the stereochemistry.

Table 1. Some thermo chemical properties of the species considered.

Species	H^o	S^o (J/mol^o)	G^o
I	-1571065.553	373.58	-1571176.936
II	-1571114.787	367.40	-1571224.329
I+Mg	-2096594.451	392.58	-2096711.501
II+Mg	-2096514.454	393.51	-2096631.778

Energies in kJ/mol.

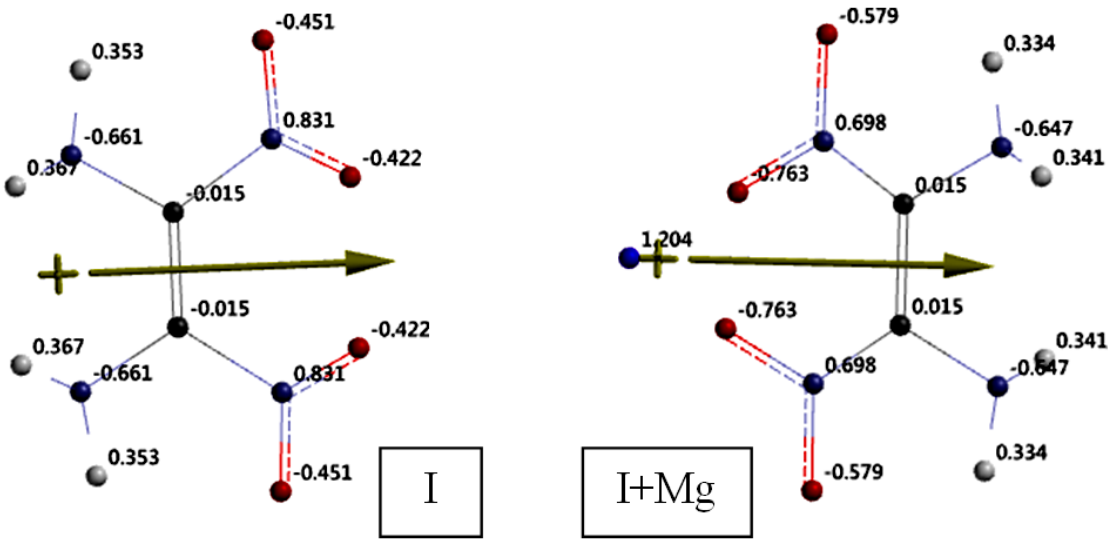
Table 2 includes some energies of species considered. The data in the table reveal that they are all electronically stable structures. The stability order is II > I and I+Mg > II+Mg.

Table 2. Some energies of the species considered.

Species	E	ZPE	E_C
I	-1571315.41	239.43	-1571075.98
II	-1571363.68	238.79	-1571124.89
I+Mg	-2096842.96	240.27	-2096602.69
II+Mg	-2096764.32	242.19	-2096522.13

Energies in kJ/mol.

Figure 3 shows the ESP charges on atoms of the species considered. Note that the ESP charges are obtained by the program which uses a numerical method that generates charges thus reproducing the electrostatic potential field from the entire wavefunction [30].



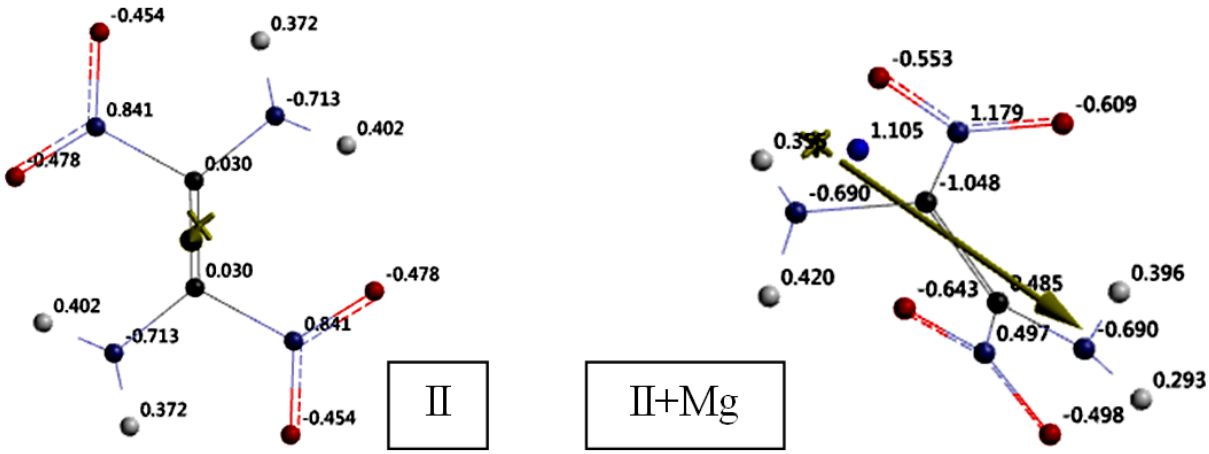


Figure 3. The ESP charges on atoms of the species considered.

As seen in Figure 3, the magnesium atoms in the composites possess some positive charges such that the one in I+Mg has more positive value than the magnesium atom in II+Mg. Although in the parent structures, the partial charge distribution in pairs of the amino or nitro groups are the same, which is no longer the case in the composites considered.

Figure 4 shows the electrostatic potential maps of the species considered. As seen in the figure, due to the twist form of the *cis* isomer, electron donating effects of the amino groups are not equally balanced. In the composites the magnesium atom greatly electron donates beside the amino group (dark blue regions in the maps).

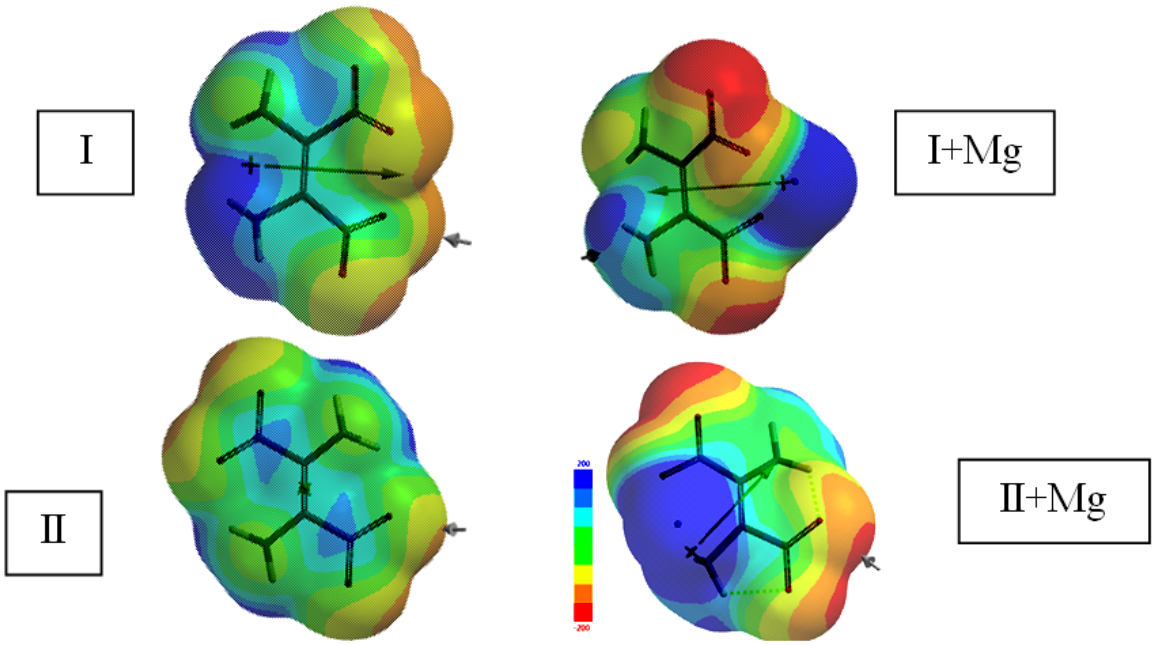


Figure 4. Electrostatic potential maps of the species considered.

Figure 5 shows the Mulliken charges on atoms of the species considered. This time, the magnesium atom in the composites still has positive charge but in contrast to ESP charge distribution, II+Mg composite has more positive charge on Mg atom as compared to the I+Mg case. In general, charge distributions between the same type substituents of the parent structures are highly symmetrical which is disturbed by the presence of Mg atom.

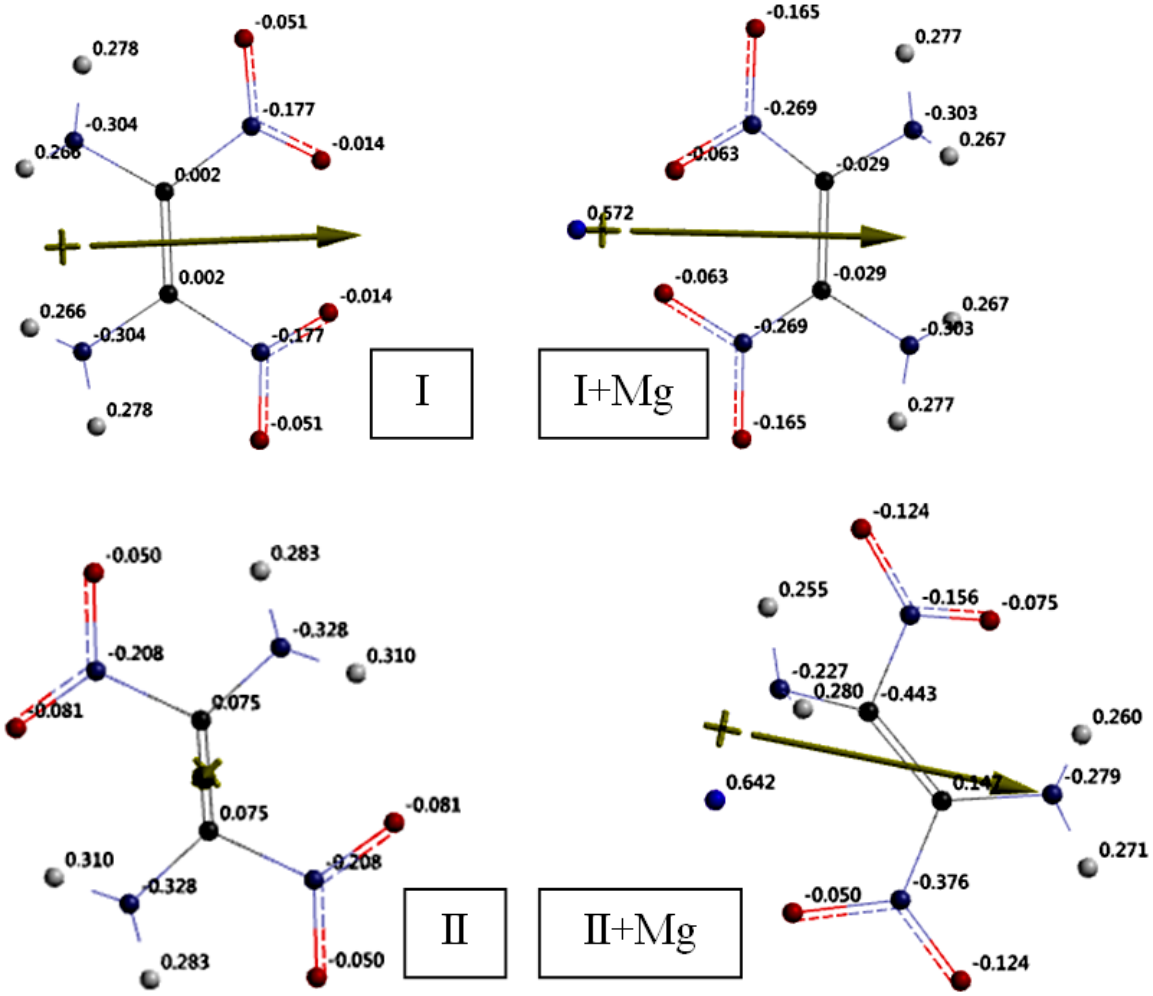


Figure 5. The Mulliken charges on atoms of the species considered.

Mulliken and electrostatic-fit schemes lead to different atomic charges. Within each scheme charges also depend on the underlying molecular orbital method and even change with basis set employed for *ab initio* methods. In the latter regard, Mulliken charges generally show larger variations with basis set than electrostatic-fit charges. Clearly electrostatic-fit charges more closely reproduce the calculated dipole moment at each level of theory [31].

Figure 6 displays the local ionization potential maps of the species considered. In those maps 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. In the composites red regions are nearby the magnesium partner and also note that its presence has decreased the blue regions compared to the parent structures.

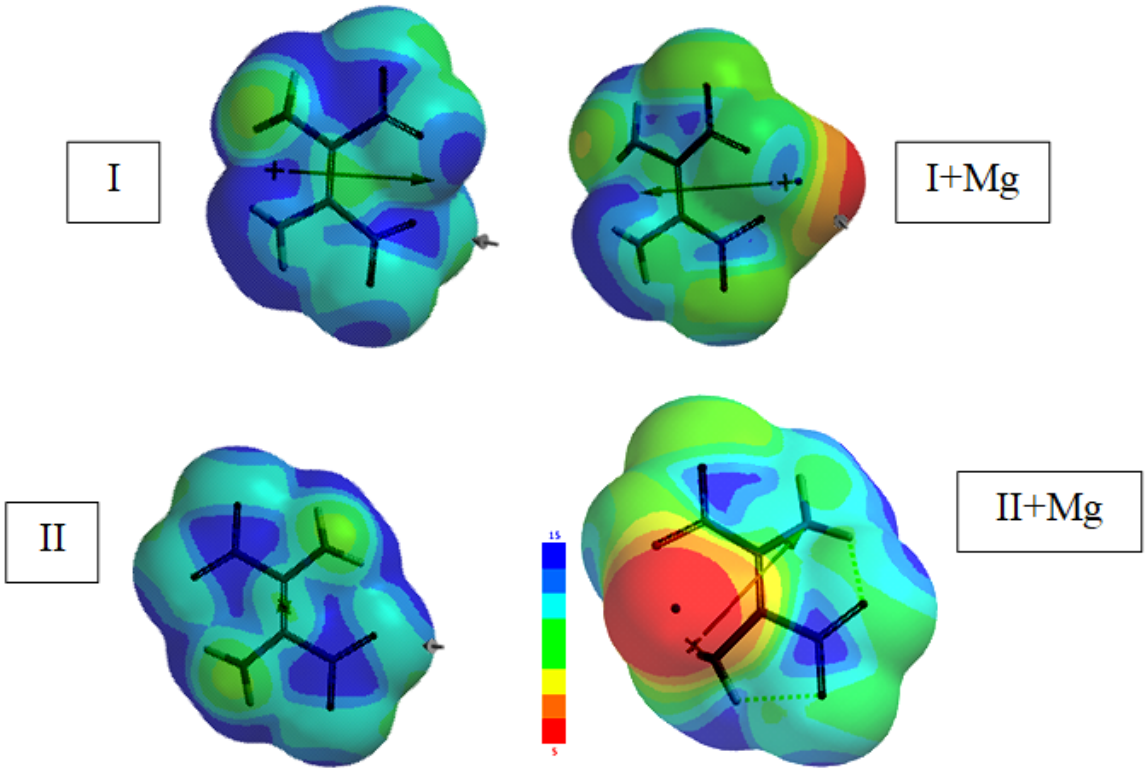


Figure 6. Local ionization potential maps of the species considered.

Figure 7 shows the LUMO maps of the species considered. 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.

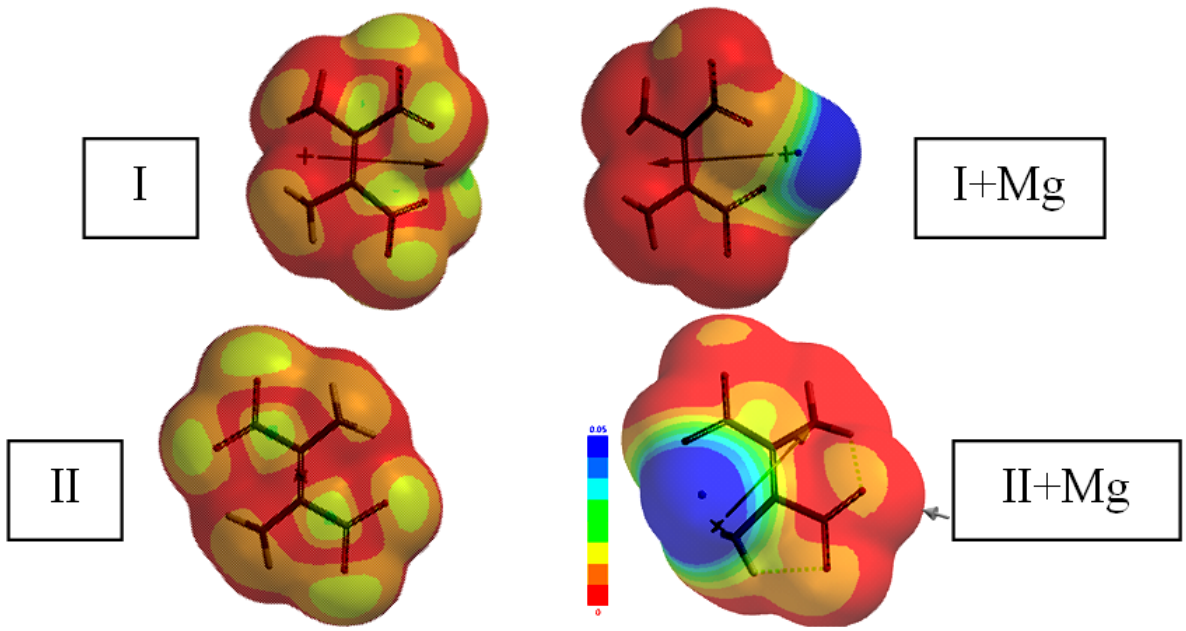


Figure 7. The LUMO maps of the species considered.

Figure 8 shows the exposed areas of atoms of the species considered. The exposed area of the same atoms have been highly affected by the *cis* or *trans* nature of the species.

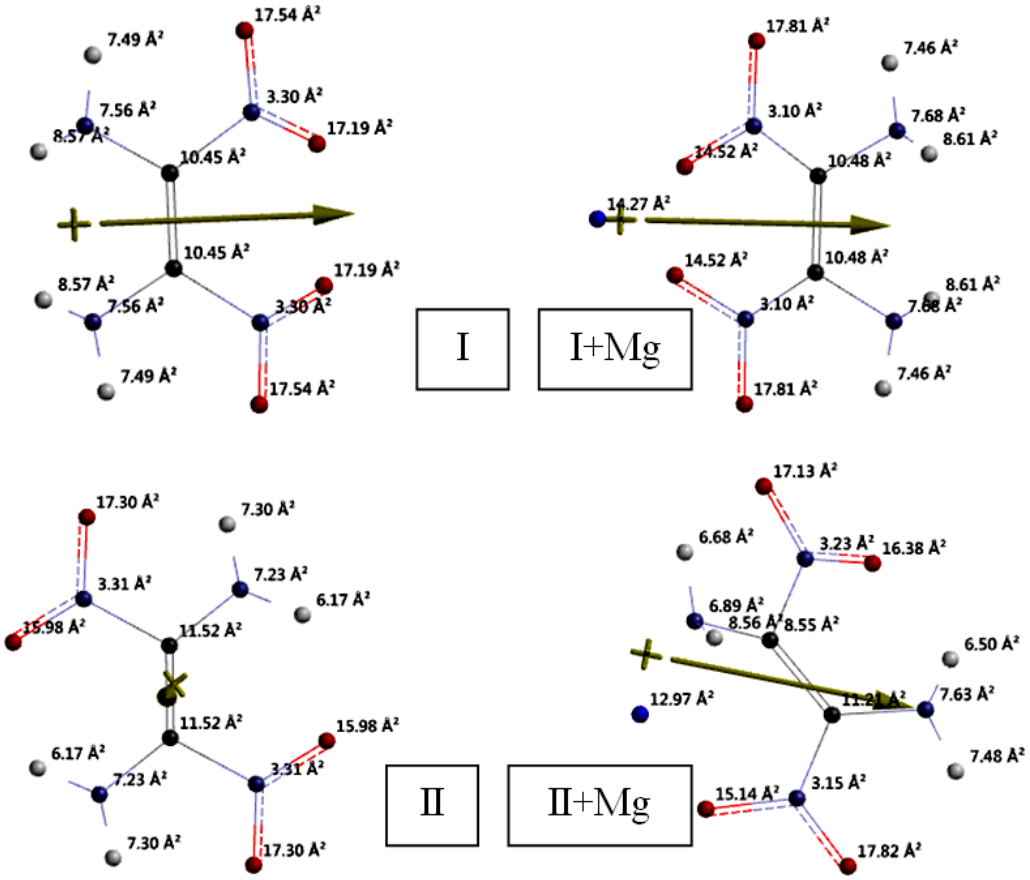


Figure 8. The exposed areas of atoms of the species considered.

Figure 9 displays the bond densities of the species considered. As seen in the figure bond densities in the composites do not spread over the magnesium atoms.

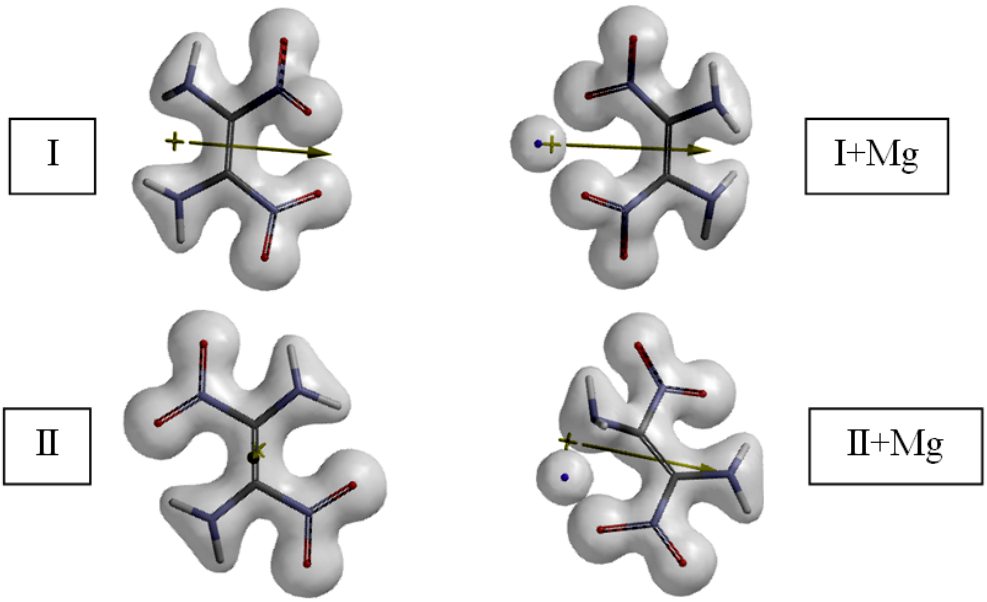


Figure 9. The bond densities of the species considered.

Figure 10 shows some of the molecular orbital energy levels of the species considered. The effect of cis/trans isomerism is seen on distribution of the molecular orbital energy levels. The effect arises from the fact that some of the substituent orbitals may not be coplanar with the π-backbone, for instance the *cis* isomer has a twisted form whereas the *trans* one has more extended conjugation. Thus, the *trans* isomer possesses higher HOMO but lower LUMO energy levels compared to the *cis* isomer (see Table 3).

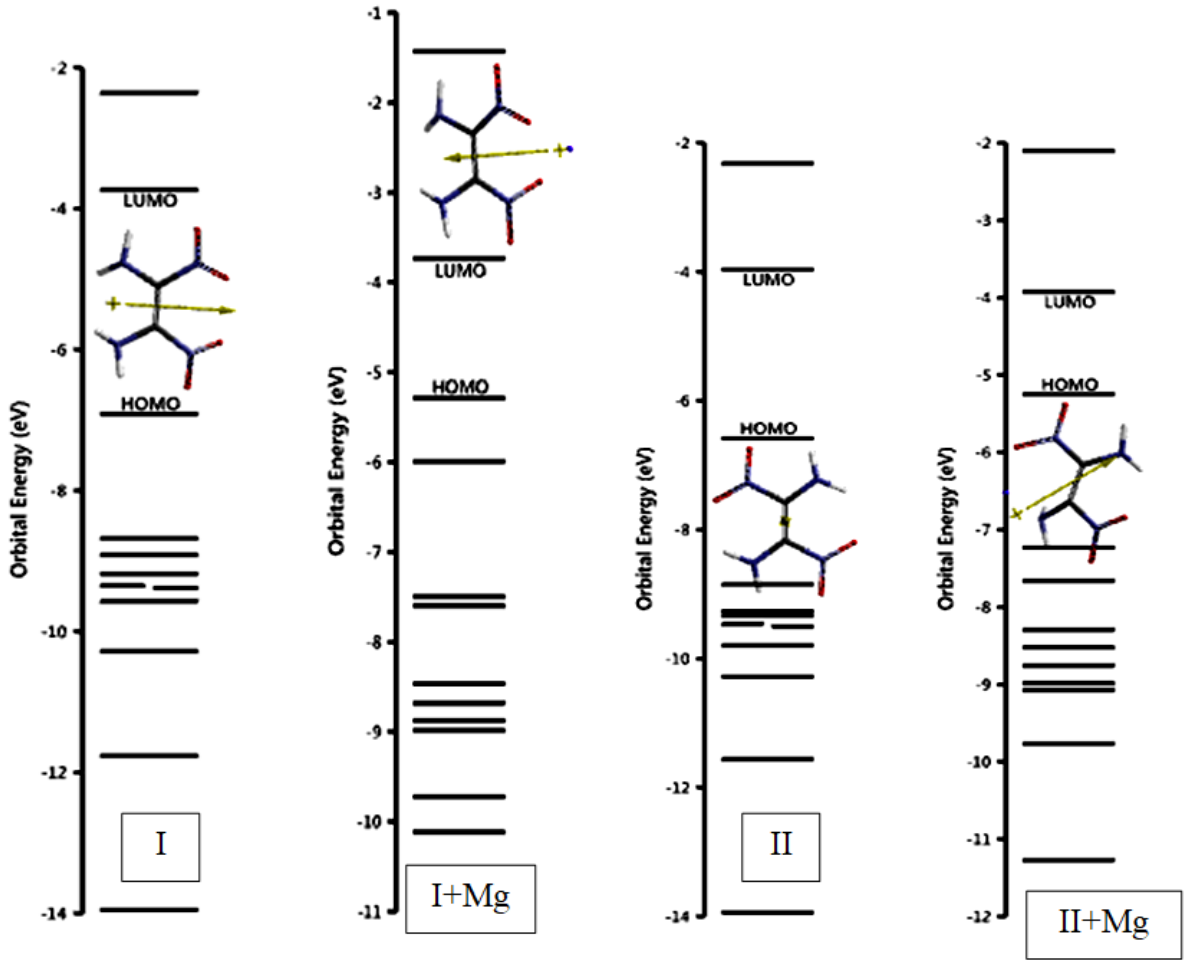


Figure 10. Some of the molecular orbital energy levels of the species considered.

The HOMO, LUMO energies and interfrontier molecular orbital energy gap ($\Delta\varepsilon = \varepsilon_{LUMO}-\varepsilon_{HOMO}$) values of the species considered are listed in Table 3. As for the composites, Mg atom in II+Mg raises the HOMO energy level but lowers the LUMO as compared to I+Mg composite. The effect of Mg is parallel when the respective energies compared with the respective parent structures, thus indicating the electron donor character of Mg atom in the composite system. Consequently, it possesses positive charge development. The overall order of Δε values is I> II> I+Mg> II+Mg. Namely, the magnesium component effectively narrows the interfrontier molecular orbital energy gap in the *trans* case. Thus, certain explosive properties which are dictated by decrease of Δε could be improved/modified, such as the impact sensitivity. Note that narrower the gap, the explosive becomes more sensitive to an impact stimulus [32,33].

Table 3. The HOMO, LUMO energies and Δε values of the species considered.

Species	HOMO	LUMO	Δε
I	-667.18	-359.59	307.59
II	-634.90	-382.49	252.41
I+Mg	-510.06	-360.51	149.55
II+Mg	-506.16	-378.83	127.33

Energies in kJ/mol.

The effect of magnesium atom on the HOMO and LUMO patterns of the species considered is shown in Figure 11.

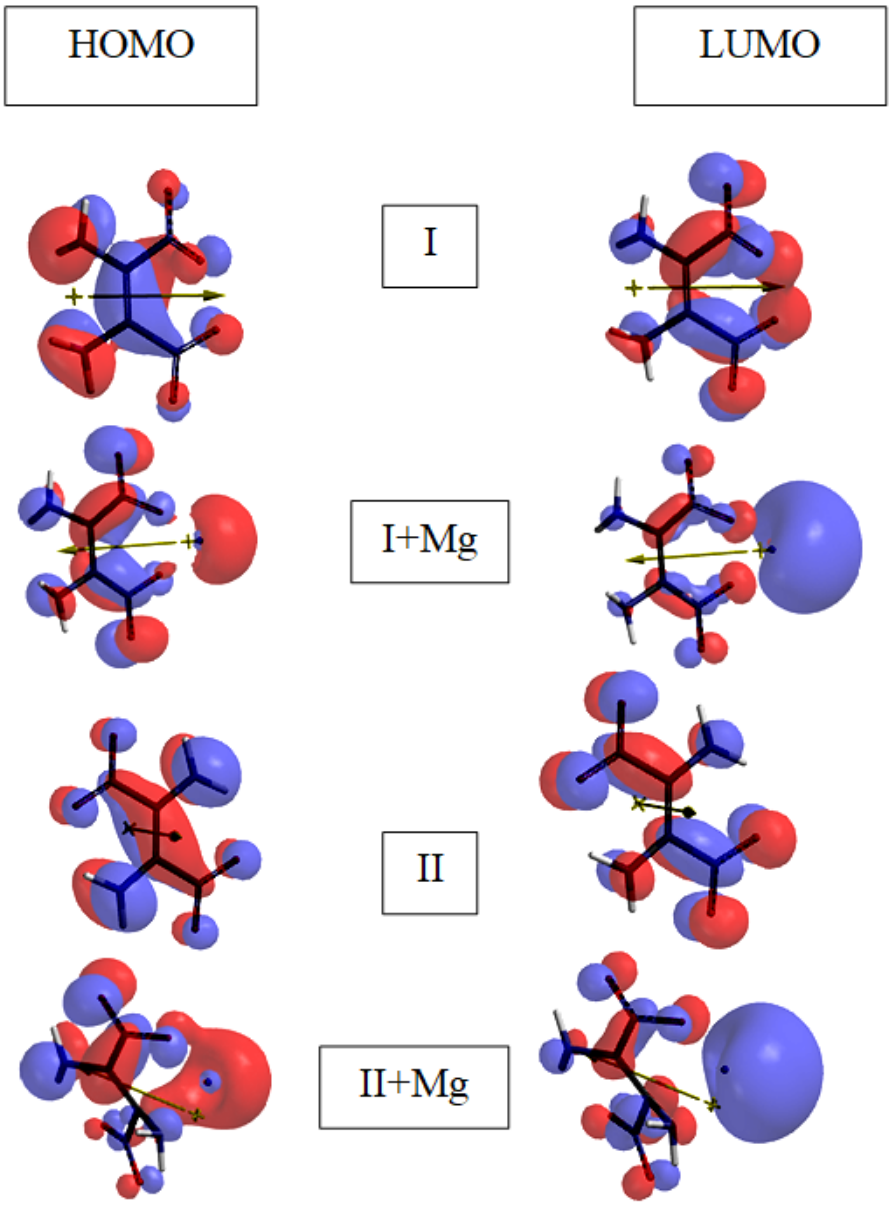


Figure 11. The effect of magnesium atom on the HOMO and LUMO patterns of the species considered.

The UV-VIS (Time dependent density functional, TDDFT) spectra of the species considered are shown in Figure 12. Both of the isomers absorb in the UV-VIS region namely the *cis* and *trans* isomers have peaks at 310.37 nm, 405.62 nm and 297.91 nm, 413.07 nm, respectively. However spectrum of the *trans* isomer is characterized with the presence of relatively huge absorption peak in the visible side. As for the composites, their spectrums exhibit strong bathochromic effect. The peaks of I+Mg are at 344.58, 400.75, 659.36 nm, whereas II+Mg absorbs at 352.11, 409.82, 443.35, 685.51 nm. Actually, the extended conjugation and kind of atoms involved in the extension dictates the emergence of the peaks, their positions and shape(s). The calculated intensities of the peaks are related to magnitudes of the transition moments of the orbitals involved and varies from one (isomeric) structure to the other [4,34].

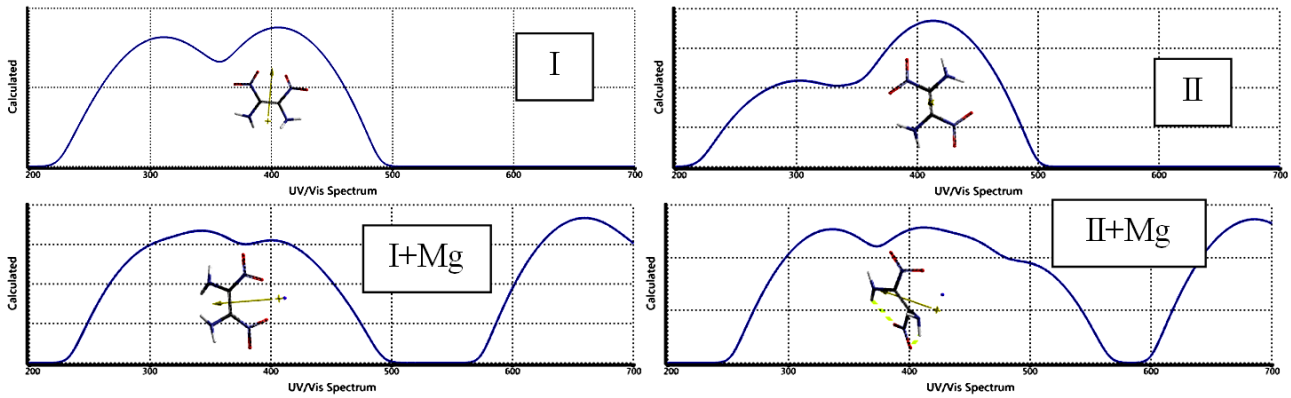


Figure 12. The calculated UV-VIS spectra of the species considered.

4. Conclusion

The present computational study firstly considers *cis* and *trans* isomers of diaminodinitroethylene and then their interactions with magnesium atom. The present results have indicated that all the optimized structures considered have exothermic heats of formation and favorable Gibbs free energy of formation values. They are thermally favored and electronically stable at the standard states. The *trans* isomer is more stable than the *cis* as normally expected. However, its magnesium composite seems to be less stable than the *cis* counterpart. In all the *trans* forms, hydrogen bondings exist between the amino and nitro groups.

The magnesium atom in each of the composites transfers some electron population to the organic component and acquires some positive charge, however there is no bond density between them, thus implying mainly ionic interactions.

Mg atom in the case of *trans* composite raises the HOMO energy but lowers the LUMO as compared to the *cis* composite. Some of the data presented herewith might be helpful in designing some other energetic materials.

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