

## Effect of magnesium on FOX-7+TNAZ composite - A DFT treatise

Lemi Türker

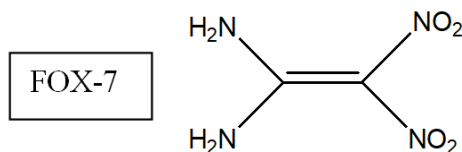
Department of Chemistry, Middle East Technical University, Üniversiteler, Eskişehir Yolu No: 1, 06800 Çankaya/Ankara, Turkey; e-mail: lturker@gmail.com; lturker@metu.edu.tr

### Abstract

In the present computational study, the 1:1 binary composite of FOX-7 and TNAZ system and the effect of magnesium on it have been investigated within the constraints of density functional theory at the level of B3LYP/6-31++G(d,p). The composites with and without magnesium are found to be electronically stable. Thermo chemically they have exothermic heat of formation and favorable free energy of formation values. The data reveal the striking effect of Mg such that narrowing of the frontier molecular orbitals occurs which should cause the increased sensitivity to impact stimulus. Some geometrical, quantum chemical and spectral data also have been harvested and discussed.

### 1. Introduction

FOX-7 is an insensitive high explosive also known as DADE or DADNE [1-3]. Its chemical name is 1,1-diamino-2,2-dinitroethylene. Its explosive potential has been investigated thoroughly [4-18].



The nitration of 4,6-dihydroxy-2-methylpyrimidine and then hydrolysis is one of the ways to synthesis of FOX-7 [18]. FOX-7 is a push-pull type molecule having donor and acceptor groups in its structure, namely amino and nitro groups, respectively. In spite of the fact that it is a small molecule, it exhibits abundant chemical reactivity. Of those, coordination reactions, nucleophilic substitutions, acetylate reactions, oxidation and

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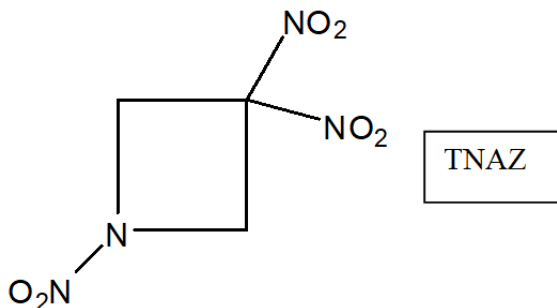
Keywords and phrases: FOX-7; DADNE; TNAZ; explosives; magnesium; DFT.

reduction reactions, electrophilic addition reactions etc., are to be mentioned [19,20]. Compared to RDX, FOX-7 is much less sensitive in terms of impact, friction, and electrostatic discharge sensitivities [21]. Previous couple of decades have evidenced several FOX-7 based propellant formulations which have been developed in order to obtain propellant composites possessing reduced smoke production [22].

On the other hand, TNAZ is an energetic small-ring compound (1,3,3-trinitroazetidine). It is a four-membered nitrogen heterocyclic ring, highly nitrated, having C-NO<sub>2</sub> and N-NO<sub>2</sub> groups. In recent years, it is almost the most widely studied explosive [23,24]. In comparison to conventional melt castable explosive 2,4,6-trinitrotoluene (TNT), it exhibits improved performance such that its performance is approximately 30% greater than TNT. The presence of strained ring system is assumed to be responsible factor contributing some additional energy in to TNAZ [25-30]. The literature, has numerous reported methods for the synthesis of 1,3,3-trinitroazetidine [31].

TNAZ, has been proposed as potential replacement for TNT because of its high performance and being melt castable explosive [32]. TNAZ having low melting point (101 °C) enables the processing of formulations on modified production lines. It shows remarkable thermal stability (>180 °C) [33]. Also it has many additional advantages over the known explosives. Some of them to be mentioned are highly energetic material, more powerful than RDX and is less vulnerable than most other nitramines [34,35]. TNAZ unlike HMX, is soluble in molten TNT moreover it is compatible with certain materials such as aluminum, steel, brass and glass [36-38].

The compatibility of TNAZ with some energetic components and inert materials of solid propellants was studied by using the pressure DSC method [39]. On the other hand, desensitization of TNAZ via molecular structure modification has been investigated theoretically [40].



On the other hand, certain metals usually are added into explosive compositions to improve their performances. Aluminum and magnesium are the most widely used materials for this purpose. Titanium, zirconium and tungsten are also used [41].

In the present study, effect of magnesium on the FOX-7+TNAZ composite has been investigated quantum chemically within the realm of density functional theory (DFT).

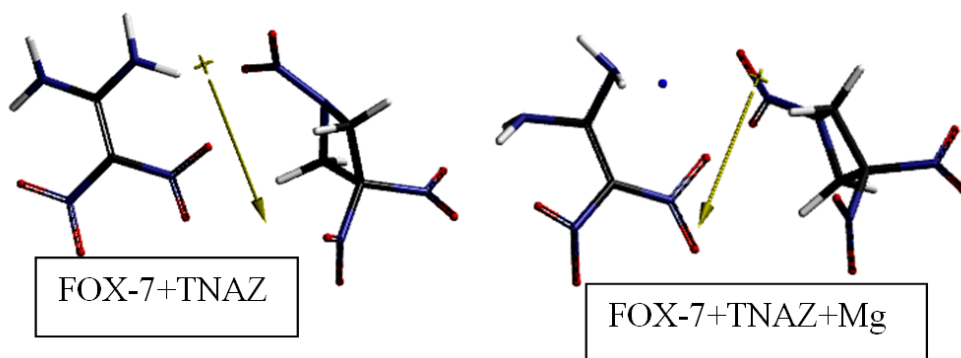
## 2. Method of Calculation

In the present study, the initial structural optimizations of all the structures leading to energy minima have been achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [42,43] at the restricted level [44,45]. Subsequent optimizations were achieved at Hartree-Fock level using various basis sets. Then, the structural optimizations were managed within the framework of density functional theory (DFT) [46,47] at the level of B3LYP/6-31++G(d,p) [45,48]. 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 [47,49]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [50] and Lee, Yang, Parr (LYP) correlation correction functional [51]. Also, the vibrational analyses have been done. The total electronic energies are corrected for the zero point vibrational energy (ZPE). 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 indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. All these calculations were done by using the Spartan 06 package program [52].

## 3. Results and Discussion

The present research has shown that FOX-7 forms a stable 1:1 composite with TNAZ. Figure 1 shows the optimized structures of it where the amino hydrogens of FOX-7 are next to the nitramine NO<sub>2</sub> group of TNAZ molecule. The figure also shows the optimized structure of the ternary composite, FOX-7+ TNAZ+ Mg. It is also a stable composite. However, the presence of Mg atom causes some conformational changes of the groups. Figure 1 shows the direction of the dipole moment vectors as well. Note that the tip point of the dipole moment vector aims to the geminal nitro groups of TNAZ in

FOX-7+TNAZ composite whereas in the presence of Mg it is directed to the nitro group of the FOX-7 in the ternary composite.



**Figure 1.** Optimized structures of the composites considered.

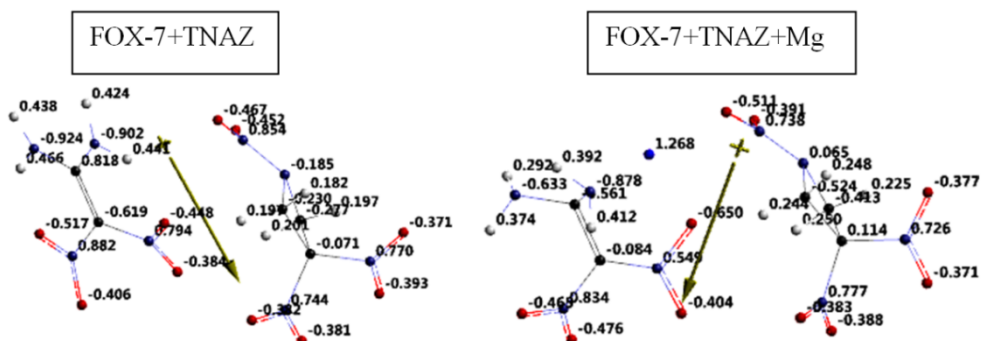
Table 1 displays some calculated properties of these composite structures. Note that the ternary composite has an appreciably high dipole moment compared to the binary one. Probably, the presence of Mg atom causes some changes in the bond dipoles by influencing the bond lengths and distribution of the charges.

**Table 1.** Some properties of the composites considered.

Composite	Dipole moment (Debye)	Polarizability	Ovality	Area (Å <sup>2</sup> )	Volume (Å <sup>3</sup> )
FOX-7+TNAZ	8.64	60.59	1.59	305.23	249.50
FOX-7+TNAZ+Mg	10.89	61.97	1.59	311.56	258.30

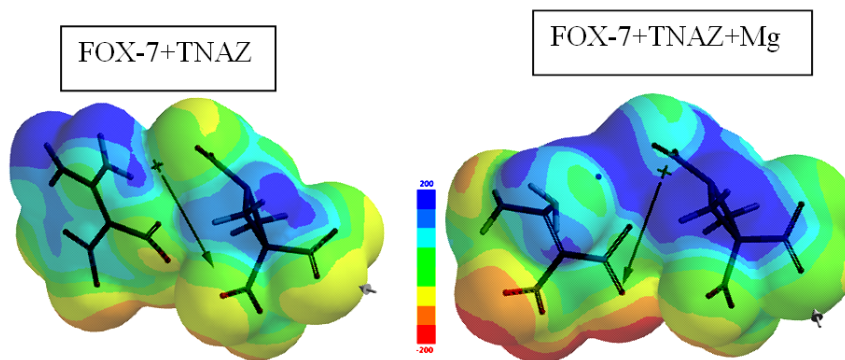
Polarizabilities in  $10^{-30}$  m<sup>3</sup> units.

Figure 2 shows the electrostatic potential charges (ESP) on the atoms of the composites. 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 [52]. As seen in the figure Mg atom acquires some positive charge in the composite.



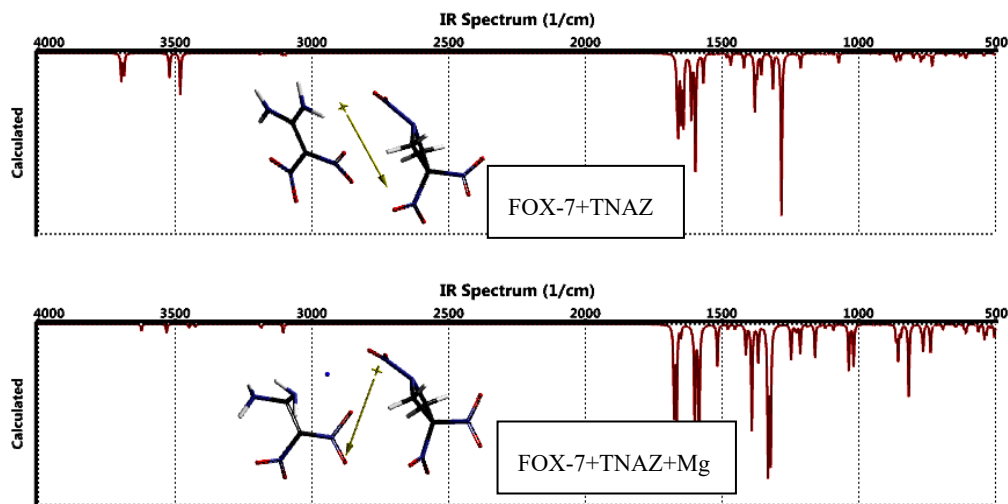
**Figure 2.** Electrostatic charges on the atoms of the composites.

Figure 3 shows the electrostatic potential maps of the composites considered. Variation of colors between the maps may give some idea about how the transferred electron population from Mg is shared between the organic components of the second composite. Note that red/reddish and blue/ green regions stand for negative and positive potential fields, respectively. As seen in the figure the Mg atom donates some electron population mostly into FOX-7 component and red region extends its boundary at the expense of the blue region.



**Figure 3.** Electrostatic potential maps of the composites.

Figure 4 stands for the calculated IR spectra of the composites. The FOX-7+TNAZ spectrum shows symmetrical and asymmetrical N-H stretchings (FOX-7) in the region of 3698-3480  $\text{cm}^{-1}$ . They appear at 3624-3426  $\text{cm}^{-1}$  in the spectrum of the Mg having composite. The symmetrical and asymmetrical C-H stretchings of TNAZ component occur at 3099-3189  $\text{cm}^{-1}$  and 3100-3188  $\text{cm}^{-1}$  in the binary and ternary composites, respectively. The  $\text{NO}_2$  and C=C stretchings occur around 1600  $\text{cm}^{-1}$  in both of the composites.



**Figure 4.** Calculated IR spectra of the composites.

Table 2 shows some of the thermo chemical data of the composites considered. The data reveal that formations of the composites are exothermic and favored.

**Table 2.** Some thermo chemical properties of the composites.

Composite	H°	S° (J/mol°)	G°
FOX-7+TNAZ	-3636092.881	555.95	-3636258.631
FOX7+TNAZ+Mg	-4161452.173	573.49	-4161623.174

Energies in kJ/mol.

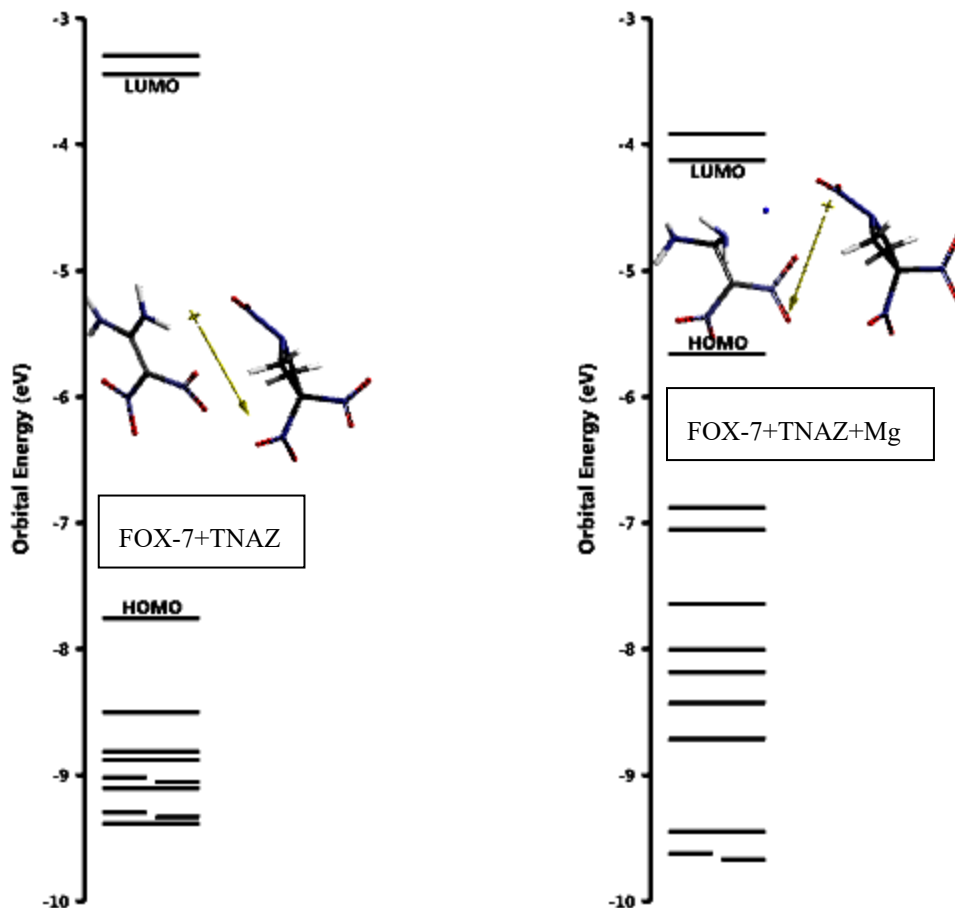
Table 3 shows some energies of the composites considered where E, ZPE and E<sub>C</sub> stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. As the data reveal, both of the structures are electronically stable.

**Table 3.** Some energies of the composites.

Composite	E	ZPE	E <sub>C</sub>
FOX-7+TNAZ	-3636632.72	524.33	-3636108.39
FOX7+TNAZ+Mg	-4161990.24	524.43	-4161465.81

Energies in kJ/mol.

Figure 5 shows some of the molecular orbital energy levels of the composites. In the figure the energy scales are very comparable and the striking effect of Mg is evident. The HOMO and NEXTHOMO levels of FOX-7+TNAZ composite have been highly raised up while the LUMO and NEXTLUMO levels are somewhat lowered down by the effect of Mg.



**Figure 5.** Some of the molecular orbital energy levels of the composites.

It is usually the case that electron donor groups raise both the HOMO and LUMO levels of the parent system while electron attractors lower both of them. The increased conjugation causes the narrowing of the frontier molecular orbital energy gap. Thus in the present system, the presence of Mg atom donates some electron population and raises up the HOMO level but some sort of back donation should occur to lower the LUMO level.

This effect somehow means increased conjugation between the Mg atom and the organic components. This observation brings in mind that the Mg atom undergoes some complex formation with  $\text{NH}_2$  or  $\text{NO}_2$  group or both of the components. Mg atom has the ground state electronic configuration of  $1s^2 2s^2 2p^6 3s^2$ . It is known that magnesium can form various chelate and/or non-chelate complexes with various substances [53].

Table 4 shows the HOMO, LUMO energies and the interfrontier molecular orbital energy gaps ( $\Delta\varepsilon$ ) of the composites considered. The data reveal that the Mg atom causes appreciable degree of frontier molecular orbital (FMO) energy gap narrowing.

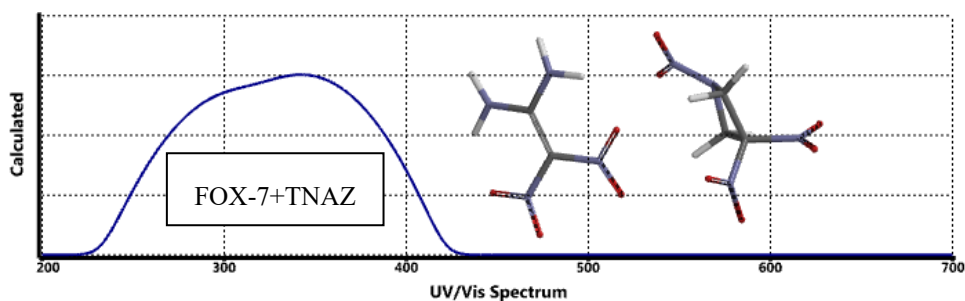
**Table 4.** The HOMO, LUMO energies and  $\Delta\varepsilon$  values of the composites.

Structure	HOMO	LUMO	$\Delta\varepsilon$
FOX-7+TNAZ	-748.30	-332.40	415.9
FOX-7+TNAZ+Mg	-545.87	-397.91	147.96

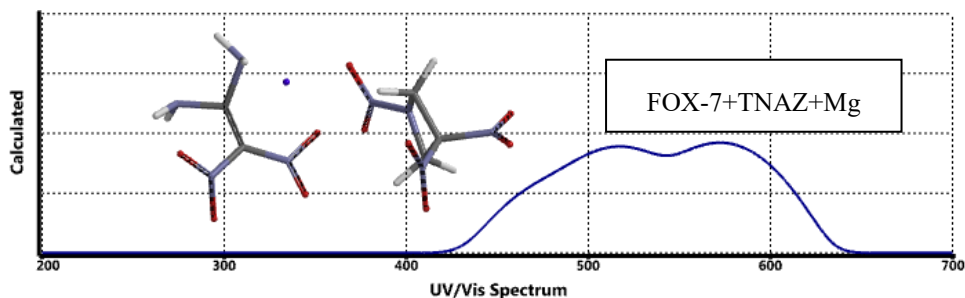
Energies in kJ/mol.

It is assumed that narrowing of FMO energy gap causes increased sensitivity to impact stimulus [54,55]. Hence, FOX-7+ TNAZ+ Mg ternary composite should be more sensitive than FOX-7+TNAZ binary composite. Usually metals are incorporated with energetic materials to increase their energy output. However, in some case, like the present one they might change the ballistic properties in undesirable directions. However, variation of molar ratio of the components might overcome emergence of undesirable properties.

Figure 6 stands for the time-dependent density functional UV-VIS spectra of the composites. The highly striking bathochromic effect into the visible part of the spectrum of the Mg containing composite is to be mentioned.

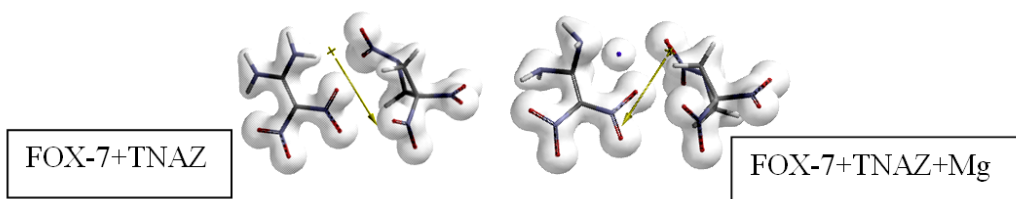






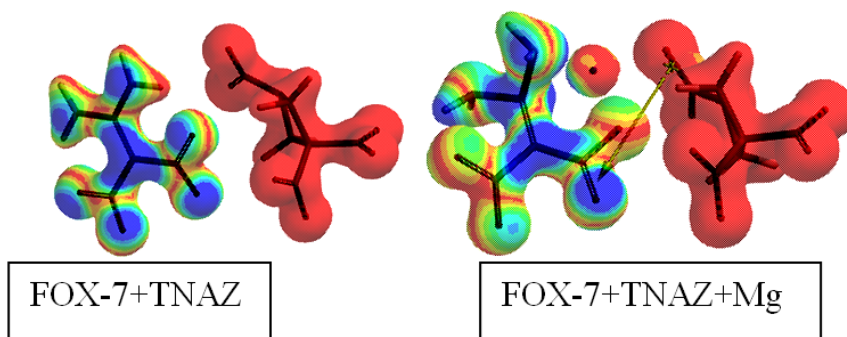
**Figure 6.** Calculated UV-VIS spectra of the composites considered.

Figure 7 shows the bond densities in the composites. Note that bond density contains fewer electrons in total and demarks atomic connectivity of a molecule.



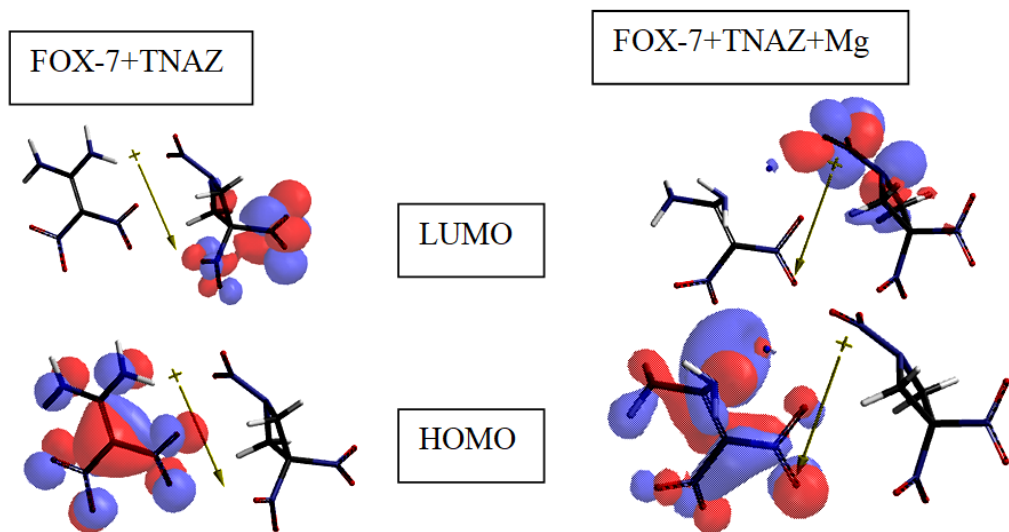
**Figure 7.** Bond densities in the composites.

Figure 8. shows the bond densities on the HOMOs of the composites.



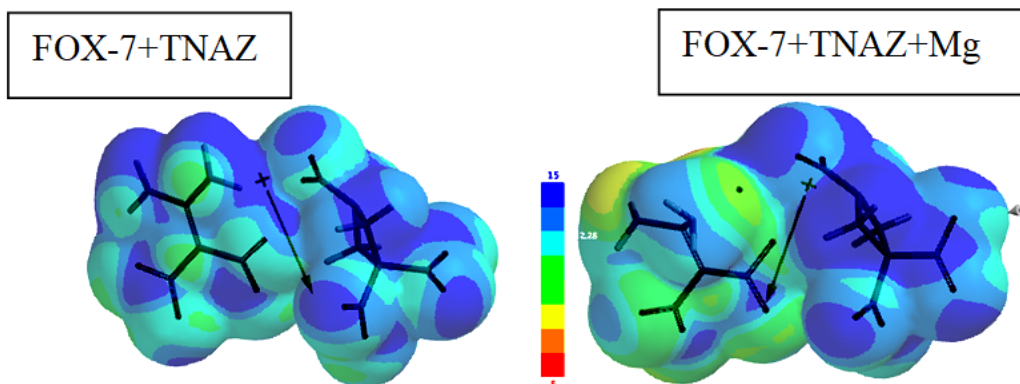
**Figure 8.** Bond densities on the HOMOs of the composites.

Figure 9 shows the HOMO and LUMO patterns of the composites considered. As seen in the figure the HOMO of FOX-7+TNAZ composite exhibits some  $\pi$ -symmetry whereas it is highly perturbed in the Mg containing composite. TNAZ molecule does not contribute in to the HOMO of both composites. As for the LUMOs, this time FOX-7 component does not have any contribution in both of the composites.



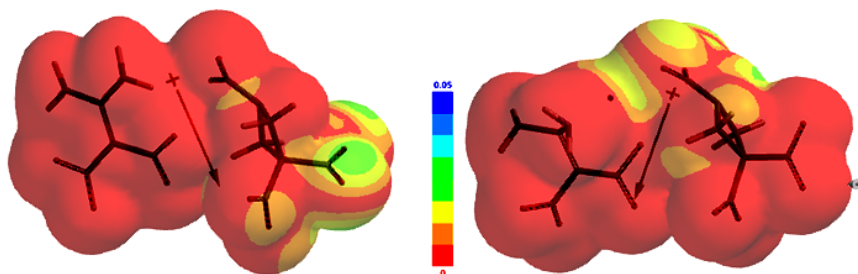
**Figure 9.** The HOMO and LUMO patterns of the composites considered.

Figure 10 shows the local ionization map of the composites. In a local ionization potential map conventionally red regions on the density surface indicate areas from which electron removal is relatively easy, meaning that they are subject to electrophilic attack.



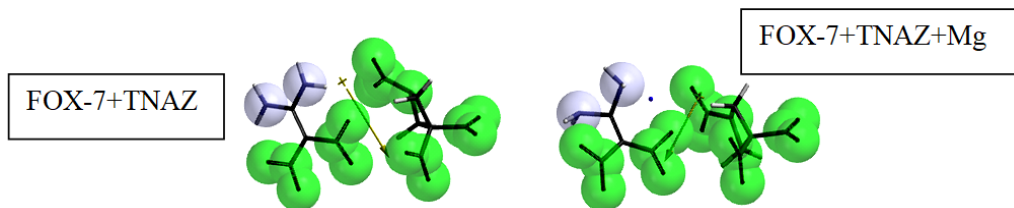
**Figure 10.** Local ionization map of the composites.

Figure 11 shows the LUMO maps of the composites. A LUMO map displays the absolute value of the LUMO on the electron density surface. Conventionally, the blue/bluish color stands for the maximum value of the LUMO and the color red/reddish, the minimum value.



**Figure 11.** The LUMO maps of the composites.

The chemical function descriptors (CFD) of the composites are shown in Figure 12 where HBA and HBD stand for hydrogen bond acceptor and donor, respectively. As seen in the figure the magnesium (in its cation-like form) does not have any substantial change on the binary composite in terms of CFD character of the amino and nitro groups of the components. However, it does not mean that all the amino groups or the nitro groups possess the same chemical avidity in both of the composites and even in the same partner of the particular composite.



**Figure 12.** The chemical function descriptors (CFD) of the composites (Green: HBA; Purplish: HBA, HBD).

#### 4. Conclusion

Presently, FOX-7+TNAZ and FOX-7+TNAZ+Mg composites are considered within the limitations of the density functional theory at the applied level of calculation. The effect of Mg on 1:1 binary composite is found to be striking, causing the narrowing of the frontier molecular orbital energy gap which should result in increased sensitivity to impact. The Mg atom donates some electron population, mostly into FOX-7 component and itself acquiring some partial positive charge. The positively charged magnesium atom lowers the LUMO energy level either by complexation or through space effect. This influence manifests itself in the UV-VIS spectrum as great bathochromic effect.

However, one has to be aware of the fact that varying the molar ratios of the components, a completely different situation might arise.

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