



A Composite of NTO and TNAZ-A DFT Treatment

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Abstract

NTO and TNAZ are two important explosive materials. In the present study, 1:1 molar composite of them are investigated within the constraints of density functional theory at the level of B3LYP/6-31++G(d,p). Certain quantum chemical, physicochemical and spectral properties of the composite have been harvested and compared with the respective values of its components. The formation of composite is exothermic and favorable. The components in the composite undergo certain type of interaction to affect properties of each other.

1. Introduction

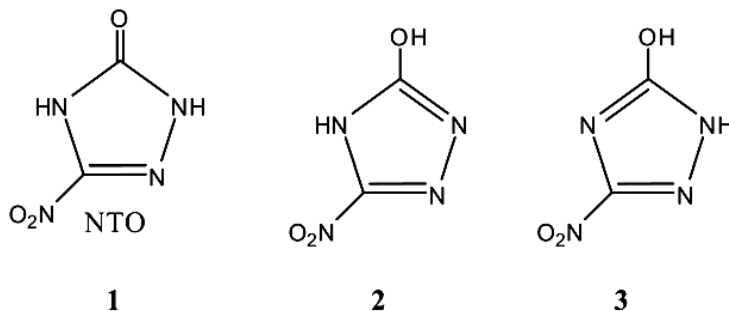
Nitrotriazoles as intermediates to energetic materials and/or as energetic materials have received a great deal of attention in the last decades [1]. 5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO, **1**) is the most extensively studied nitrotriazole explosives. It possesses good thermal stability [2], low chemical sensitivity to radiation damage [3] and is relatively insensitive to impact and shock [4]. The first report on NTO appeared in early 1905 [5] however it was erroneously reported as its hydroxy tautomer [6]. The recognition of its explosive nature occurred later. Various articles on NTO and its tautomers (**2** and **3**) have been published [7-13]. Characterization of NTO as an insensitive energetic material happened in 1988 [12]. NTO was developed as an explosive compound in 1983 at Los Alamos center [12]. Although, its explosive performance characteristics are similar to RDX, it has been observed that NTO is less sensitive [13]. Also, crystallographic studies have been performed which revealed that NTO has two polymorphic phases [14]; the most stable α -polymorph (for which an

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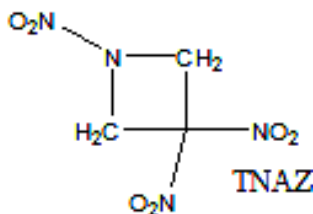
Keywords and phrases: NTO, TNAZ, explosive, composite, DFT.

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accurate crystal structure has yet to be determined because it undergoes a significant degree of twinning [15]) and the β -form which was reported to be unstable [16].



On the other hand, 1,3,3-trinitroazetidine (known as TNAZ) is the most widely studied explosive in the recent decades [17, 18]. Structurally, it is a highly nitrated four membered nitrogen heterocyclic ring having both C-NO₂ and N-NO₂ groups. As compared to conventional melt castable explosive trinitrotoluene (TNT), it possesses improved performance. It is attributed that the presence of strained ring system contributes additional energy [19-24]. There exist various methods reported for the synthesis of 1,3,3-trinitroazetidine [25]. TNAZ, being a melt castable high performance explosive has been proposed as potential replacement for TNT [26]. The low melting point of TNAZ (101°C) enables the processing of formulations on modified production lines. It has been reported that its performance is approximately 30% greater than TNT. It shows excellent thermal stability (>180°C) [27]. Over the known explosives TNAZ has many added advantages. It is a highly energetic material, more powerful than RDX and is less vulnerable than most other nitramines [28, 29]. Moreover, unlike HMX, TNAZ is soluble in molten TNT, and is compatible with aluminum, steel, brass and glass [30-32].



In the present study, 1:1 composite of NTO and TNAZ is considered within the restrictions of density functional theory (DFT).

2. Method of Calculation

The initial geometry optimizations of all the structures leading to energy minima were achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [33, 34] at the restricted level [35]. Then, the structure optimizations have been achieved within the framework of Hartree-Fock (HF) and finally by using density functional theory (DFT) at the level of B3LYP/6-31++G(d,p) (restricted closed-shell) [36, 37]. 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 [38]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [39] and Lee, Yang, Parr (LYP) correlation correction functional [40]. 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. Furthermore, all the bond lengths were 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 [41].

3. Results and Discussion

Both of NTO and TNAZ are insensitive high energy explosive materials which have been focus of interest in recent decades. Figure 1 shows the optimized structures of NTO, TNAZ and their 1:1 composite labeled as NTO+TNAZ in the present study. The figure also shows the direction of the dipole moment vectors. Note that in the composite, the direction is from TNAZ to NTO molecule.

Figure 2 shows the electrostatic potential charges (ESP) on the atoms of the components and the composite system of the present consideration. 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 [41].

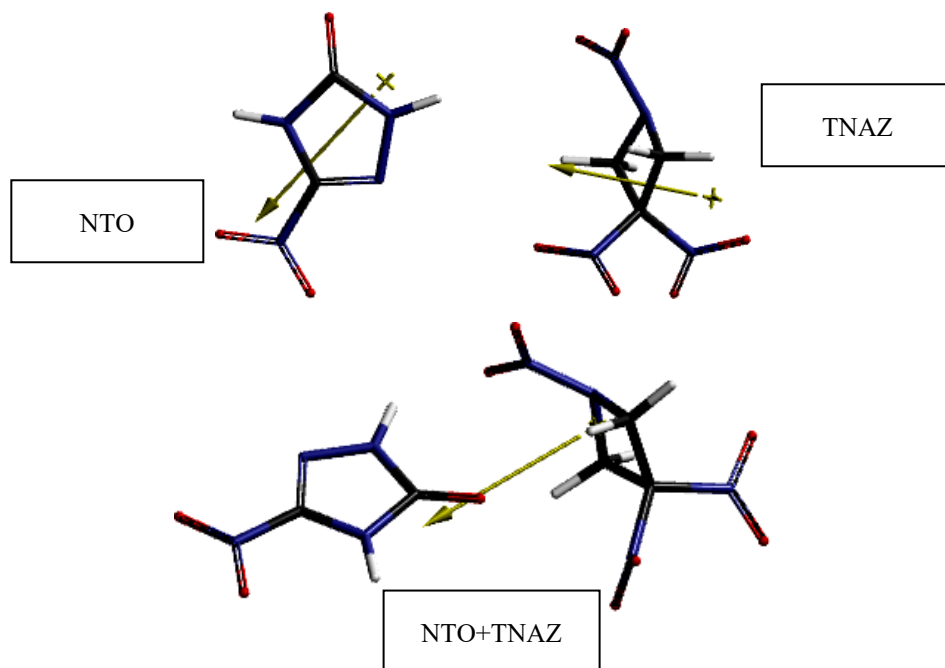


Figure 1. Optimized structures of the systems of present consideration.

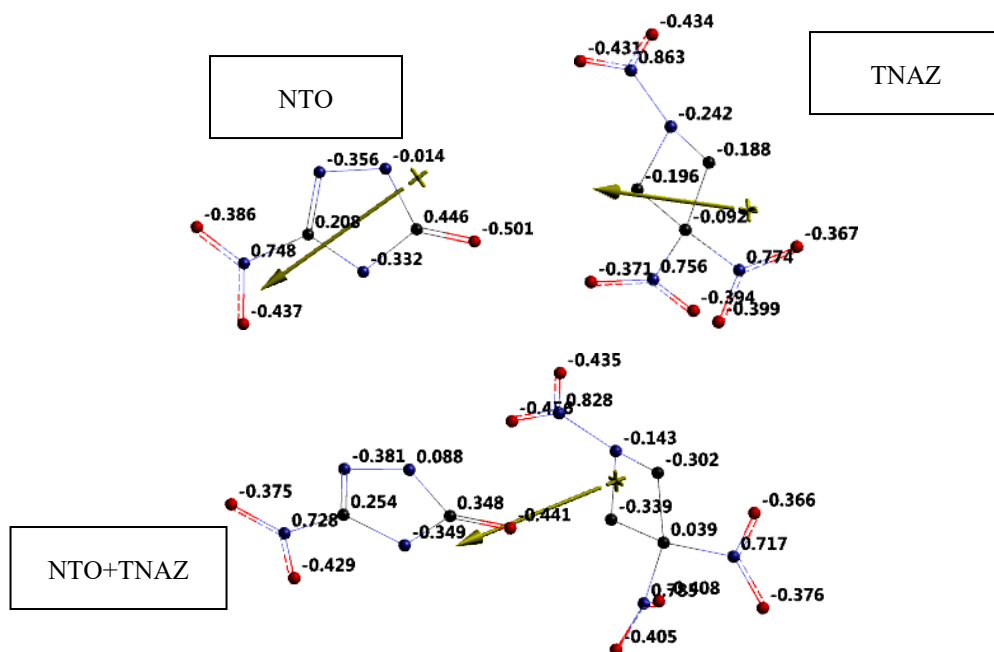


Figure 2. ESP charges on atoms of the systems of consideration.

As a result of charge-charge, charge-dipole and dipole-dipole interactions present in the composite the charges in the composite differ considerably from the charges on the components on the respective atoms. Figure 3 displays the electrostatic potential maps of the components and the composite considered. In the figure red/reddish and blue/ green regions stand for negative and positive potential fields, respectively. As seen in the figure the components in the composite are in mutual interaction with each other.

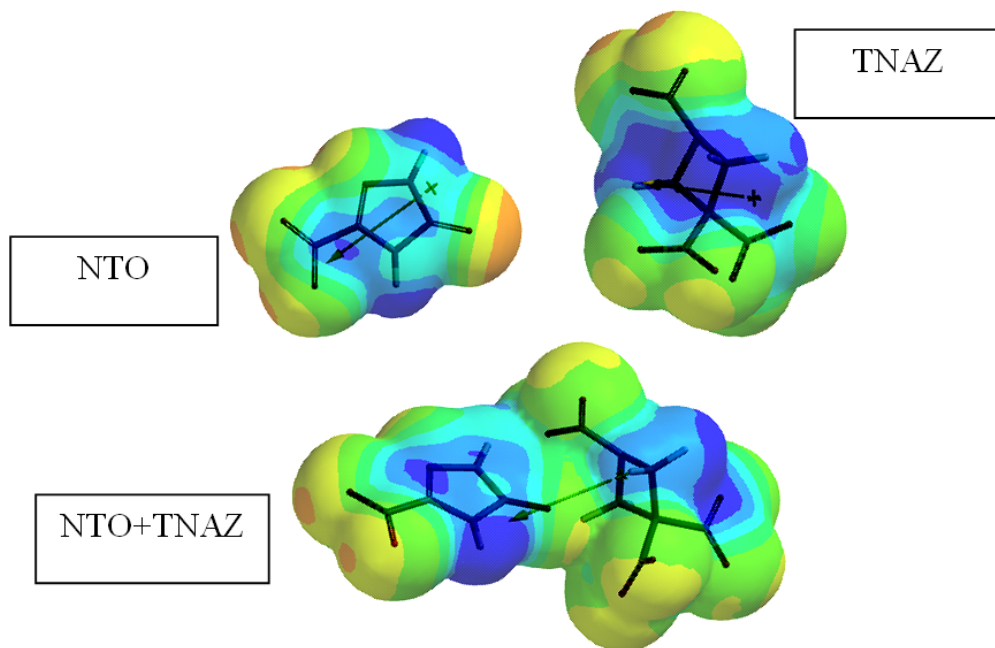


Figure 3. Electrostatic potential maps of the systems of consideration.

Figure 4 shows the IR spectra of the systems of consideration. Note that in the spectrum of NTO a single N-H stretching is observed at 3666 cm^{-1} whereas in the composite two N-H stretchings belonging to NTO happen at 3658 and 3547 cm^{-1} . Also the asymmetric NO_2 stretching of TNAZ are highly perturbed in the composite spectrum. The carbonyl stretching of NTO occurring at 1848 cm^{-1} shifts to 1812 cm^{-1} in the composite. Note that in the composite one of N-H moiety of NTO hydrogen bonds with nitramine NO_2 group of TNAZ.

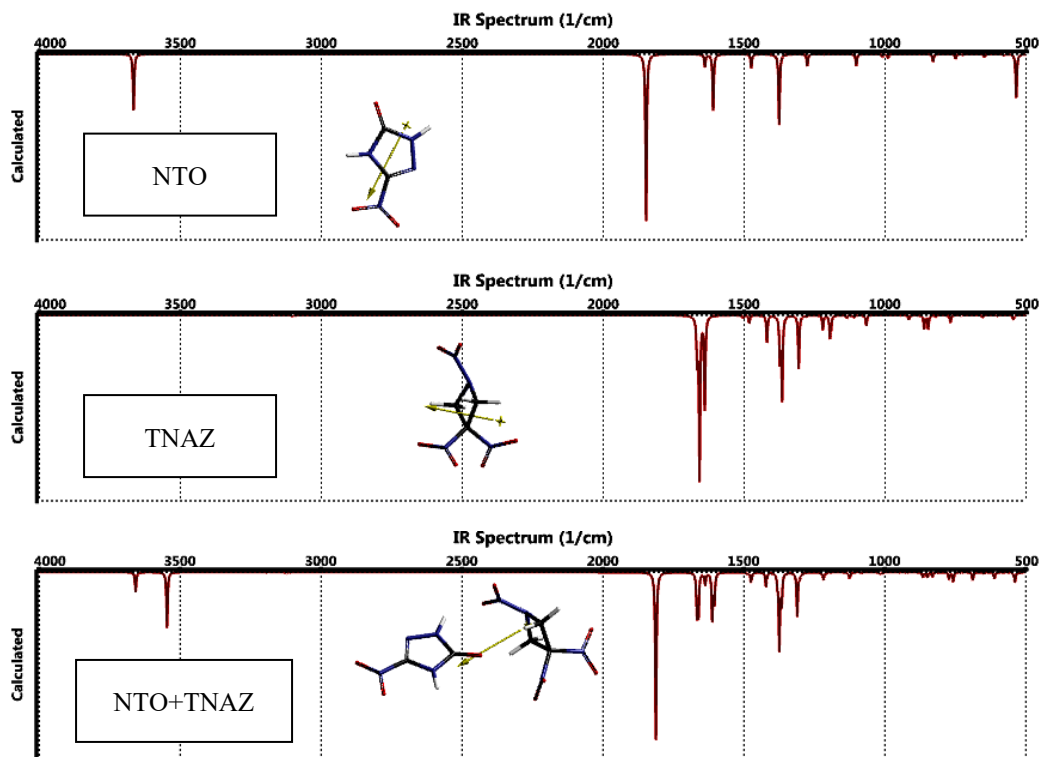


Figure 4. IR spectra of the systems considered.

Table 1 lists some properties of the composite. The log P and polarizability values of NTO and TNAZ are 0.02, 1.72 and 48.18, 51.49, respectively. Therefore, the composite is characterized with higher log P and polarizability values than the respective values of the components. This accentuation effect is due to mutual interaction of the components.

Table 1. Some properties of the composite.

Dipole moment	Area (Å ²)	Volume (Å ³)	PSA (Å ²)	Ovality	Log P	Polarizability
1.64	284.63	234.17	205.633	1.55	1.74	59.38

The composite has -3435715.407 kJ/mol and -3435872.676 kJ/mol of H° and G° formation values. Its formation is accompanied with 527.51 J/mol of entropy of formation. Thus, its formation is exothermic and favorable but entropically characterized with a positive value.

Figure 5 shows some of the molecular orbital energy levels of the systems of present concern. Whereas, Table 2 lists the HOMO, LUMO energies and the interfrontier molecular orbital energy gap values ($\Delta\varepsilon$) of them. The data reveal that the HOMO order

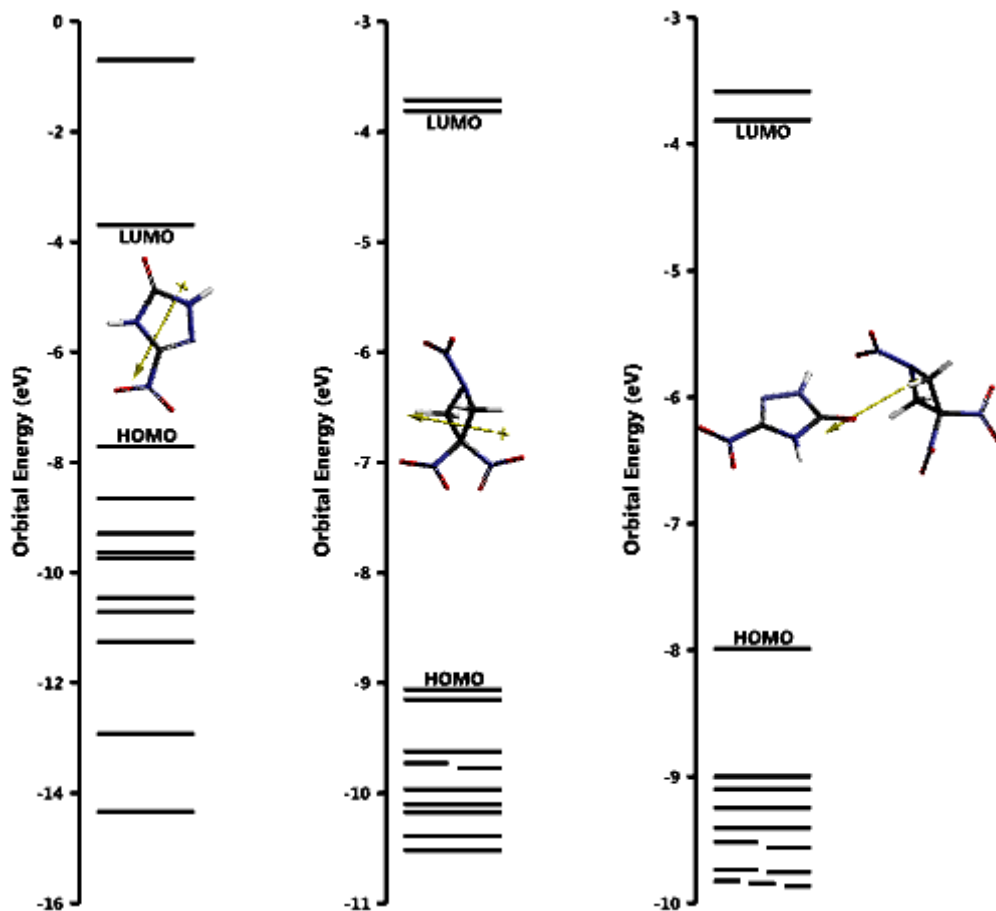


Figure 5. Some molecular orbital energy levels of the systems presently considered.

Table 2. The HOMO, LUMO energies and $\Delta\varepsilon$ values of the systems considered.

Structure	HOMO	LUMO	$\Delta\varepsilon$
NTO	-743.61	-356.87	386.74
TNAZ	-874.18	-368.15	506.03
NTO+TNAZ	-770.45	-367.87	402.58

Energies in kJ/mol.

is TNAZ<NTO+TNAZ<NTO. The LUMO order is the same. Therefore, the $\Delta\varepsilon$ values follow the order of TNAZ>NTO+TNAZ>NTO. The order indicates that the presence of TNAZ lowers the HOMO and LUMO of NTO. Contrarily, the presence of NTO raises up the HOMO and LUMO of TNAZ. However the effect is much less pronounced on the LUMO energy level. As for the $\Delta\varepsilon$ values, the composite has a $\Delta\varepsilon$ value greater than the respective value of NTO but less than the value of TNAZ. In that sense, as a conjecture, these components in different proportions can be used to modify certain ballistic properties of each other. For example, the impact sensitivity of an explosive is related to $\Delta\varepsilon$ value such that decrease of it increases the sensitivity [42, 43]. Thus the composite should be less sensitive to impact stimulus than NTO but more sensitive than TNAZ.

Figure 6 shows the HOMO, LUMO and HOMO-1, LUMO+1 patterns of the present composite. It is to be emphasized that TNAZ component in the composite does not contribute either to the HOMO or LUMO. In the LUMO+1 the contribution of NTO is nil.

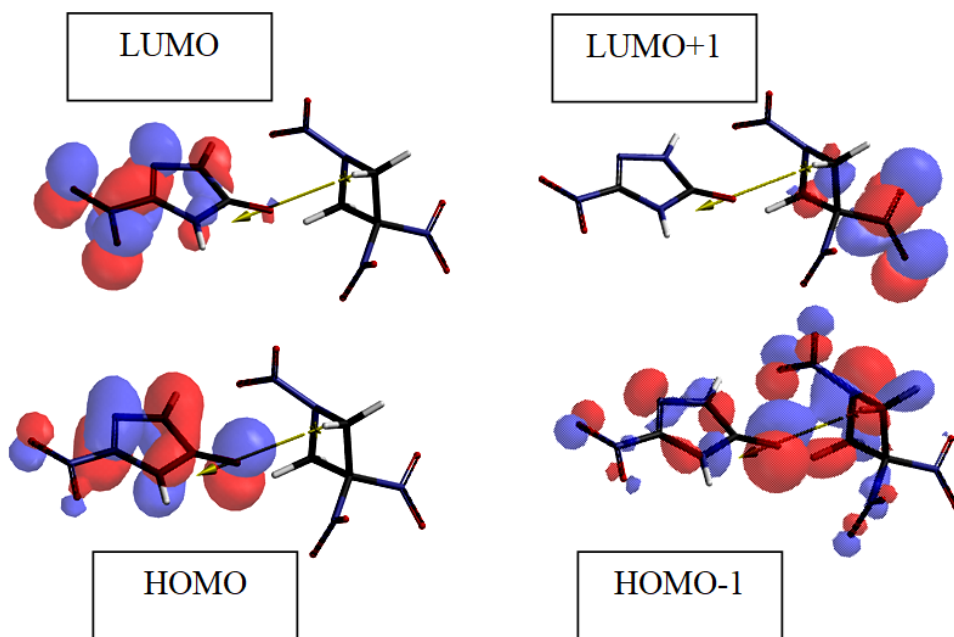


Figure 6. The HOMO, LUMO and HOMO-1, LUMO+1 patterns of the composite considered.

Figure 7 depicts the time-dependent UV-VIS spectra of the systems considered. The calculated spectra indicate that all of the systems absorb in the UV region and in the

composite the spectrum resembles the spectrum of TNAZ but not to NTO. The λ_{\max} values are 204.9, 323.2; 282.6 and 310.8 nm, respectively for NTO, TNAZ and NTO+TNAZ systems.

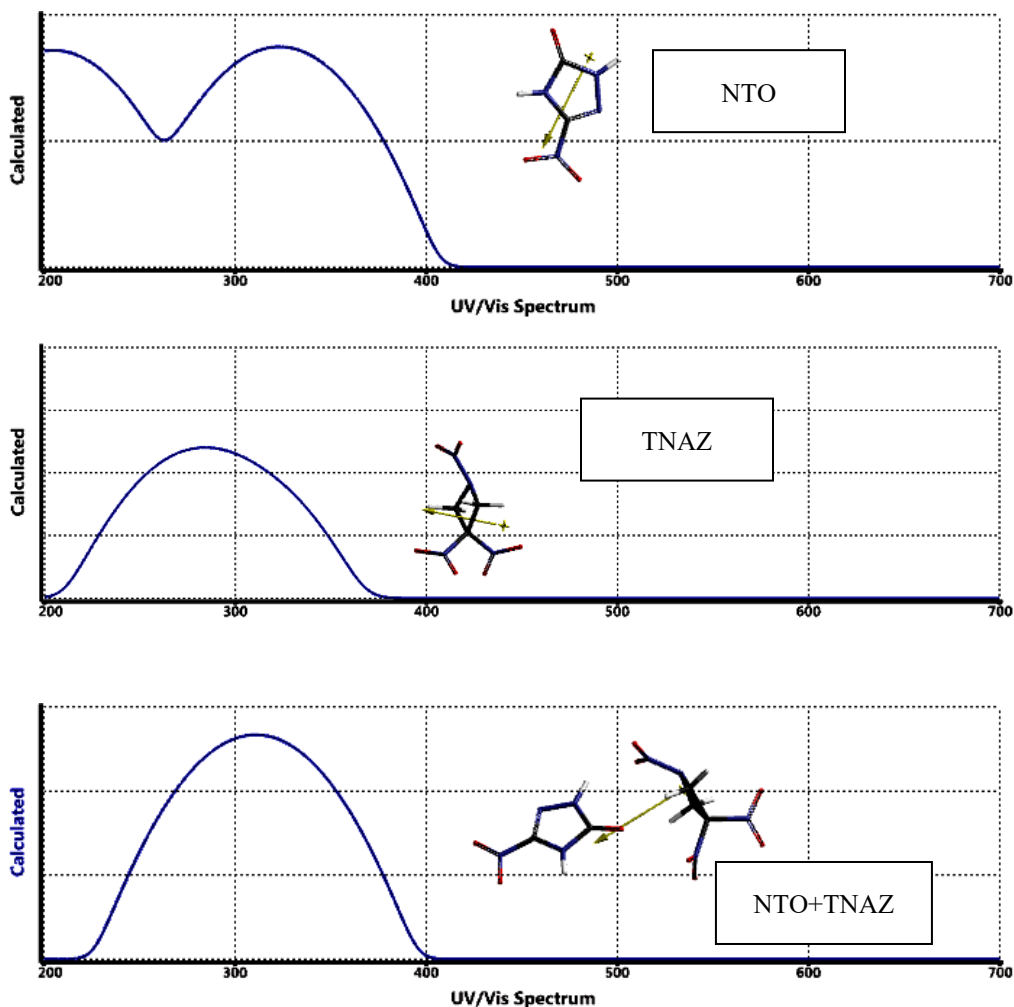


Figure 7. UV-VIS spectra of the systems considered.

Figure 8 displays the local ionization potential maps of the systems considered. In the 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. On the other hand, regions having blue color represent areas where ionization is relatively difficult.

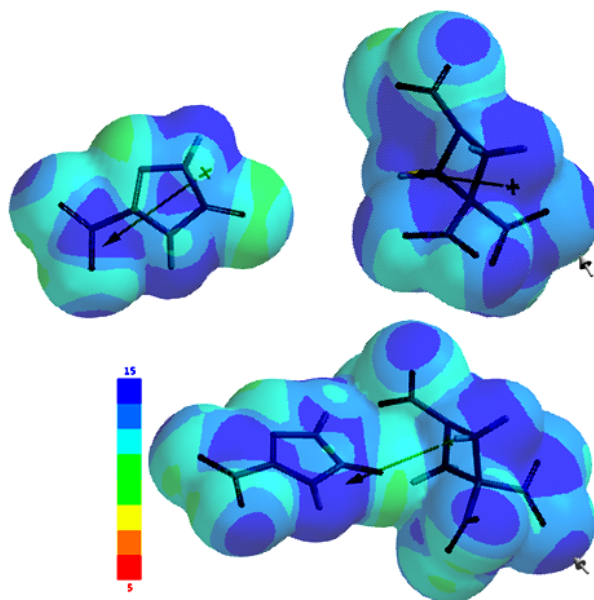


Figure 8. Local ionization potential maps of the systems of consideration.

Figure 9 stands for the LUMO maps of the structures considered. A LUMO map displays the absolute value of the LUMO on the electron density surface. The blue color stands for the maximum value of the LUMO and the color red, the minimum value.

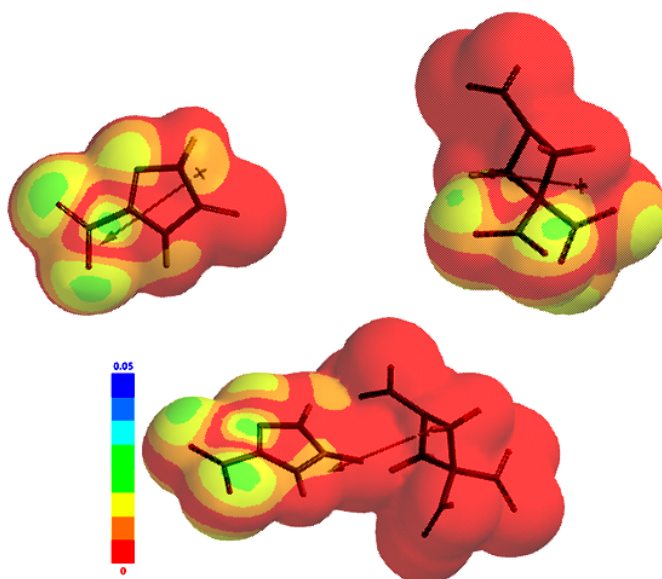


Figure 9. The LUMO maps of the systems of consideration.

Hence, a nucleophile attacks on the atom having the blue/bluish color. Figure indicates that TNAZ component in the composite is relatively more susceptible to nucleophilic attack.

4. Conclusion

The 1:1 composite formed between NTO and TNAZ, within the constraints of DFT theory and the applied basis set is electronically stable and components undergo some interaction evidenced by certain quantum chemical, physicochemical and spectral properties calculated. Formation of the composite is exothermic and favorable. The composite should be less sensitive to impact stimulus than NTO but more sensitive than TNAZ. As a conjecture, these components in different proportions can be used to modify certain ballistic properties of each other.

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