Earthline Journal of Chemical Sciences
E-ISSN: 2581-9003; CODEN: EJCSB4
Volume 11, Number 1, 2024, Pages 121-140
https://doi.org/10.34198/ejcs.11124.121140

Tautomers of 2,4-dihydro-3H-1,2,4-triazol-3-one and their Composites with NTO - A DFT Treatment

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Abstract

In the present density functional study, some tautomers of 2,4-dihydro-3H-1,2,4-triazol-3-one (1,2-dihydro-1,2,4-triazol-3-one) and their composites formed with NTO have been considered within the constraints of the density functional theory and the basis set employed (B3LYP/6-311++G(d,p)). The triazolone considered is the precursor of NTO in various methods. It may exhibit 1,3-proton tautomerism. Various energies, QASR, quantum chemical and spectral properties have been harvested and discussed. All the considered species have exothermic heat of formation and favorable Gibbs free energy of formation values at the standard states and they are stable electronically. Although most of the composites considered exhibit a directed interaction between their partners, one of them possesses perpendicular (T-type) orientation. Certain hydrogen bondings between the tautomers and NTO occur at different extents, depending on the particular tautomer involved in the composite. Both of the components have hydrogen bond donor and acceptor properties except composite NTO+T2, in which the tautomer is the hydrogen bond donor and NTO is the acceptor. The tautomers absorb in the UV region of the spectrum like NTO, whereas in all the composites appreciable changes in the appearance of the spectra happen and certain degree of bathochromic effect occurs as compared to the respective spectra of the partners.

1. Introduction

5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one [1] (in the literature it is alternatively named as 3-Nitro-1,2,4-triazol-5-one [2]), also known as NTO, is the most extensively

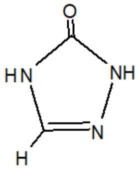
Received: November 3, 2023; Accepted: December 5, 2023; Published: December 10, 2023

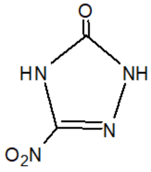
Keywords and phrases: 5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one; 3-Nitro-1,2,4-triazol-5-one; NTO; tautomers; density functional.

studied nitrotriazole explosives [3-5]. It is relatively easy to synthesize. In research of energetic materials, NTO has captured a major role because it possesses good thermal stability [3], low chemical sensitivity to radiation damage [4] and is relatively insensitive to impact and shock [5]. Various articles on NTO and its tautomers have been published through the years [6-18].

Chipen et al. correctly identified the chemical structure of NTO [19], and its detonation properties were investigated by Cobura *et al*. [20]. Most of the methods reported for the synthesis of NTO are based on a two-step process. In the first step 2,4-dihydro-3H-1,2,4-triazol-3-one (TO) (1,2-dihydro-1,2,4-triazol-3-one) is synthesized and in the second step it is nitrated to give NTO. 2,4-Dihydro-3H-1,2,4-triazol-3-one (1,2-dihydro-1,2,4-triazol-3-one) TO can be prepared by several methods [19-23]. The originally reported method for the synthesis of TO is the reaction of semicarbazide with formic acid [20].

TO





NTO

NTO can be pressed without a binder into desired morphology having a high density [24]. Several authors have tailored particle size and morphology of NTO in order to meet the requirement of energetic materials formulations. Spherical morphology has been found to be appropriate for better processability and has great impact on scale to alter the performance and insensitivity towards a sudden mechanical stimuli compared to non-spherical crystals [25,26].

Since tautomers having different structures possess dual reactivity, it is anticipated that 2,4-dihydro-3H-1,2,4-triazol-3-one may exhibit 1,3-proton tautomerism and should display variable biological properties (beside others) depending on its tautomer content (allelotropic mixture [27,28]). Note that substances which are isomeric under certain conditions are tautomeric under more drastic conditions [27,28]. In the present treatment, interactions of 2,4-dihydro-3H-1,2,4-triazol-3-one tautomers with NTO to form certain composites have been considered within the constraints of density functional theory and the basis set employed.

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 [29-31]. 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) [32,33]. 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 [34]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [35] and Lee, Yang, Parr (LYP) correlation correction functional [36]. 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 [37].

3. Results and Discussion

Many organic reactions involve intermediates and produce various side product(s) which may interact with each others even though not all of those interactions yield chemically isolable product(s). Tautomers in that sense exist in certain concentrations together with each others, as well as with other intermediates and products in the reaction medium.

2,4-dihydro-3H-1,2,4-triazol-3-one (1,2-dihydro-1,2,4-triazol-3-one) is the precursor of NTO synthesis in several methods [19-23]. It may exhibit 1,3-proton tautomerism. Figure 1 shows optimized structures of the tautomers, as well as the direction of the dipole moment vectors of them. The Boltzman distribution values are in the order of T4>T3>T2>T1. The structure T4 represents the chemical known as 2,4-dihydro-3H-1,2,4-triazol-3-one alone (TO).

Figure 1. Optimized structures of the tautomers of the triazolone (4) considered.

The structure of the ring in T2 is different from the others because N-H bonds at the α- and β-positions to the carbonyl group are not coplanar with the ring. That tautomer is the only one among the group in which three of the hydrogens are side by side (the lone pairs of two adjacent nitrogen atoms should exert an α-effect [28,38]) therefore the hydrogens are not in plane of the ring.

Table 1 shows some thermo chemical values of the tautomers considered. The data in the table reveal that all the tautomers have exothermic heat of formation values and they are favored in terms of Gibbs free energy of formation at the standard states. The most exothermic and favorable tautomer is T4 followed by T3. The least favored tautomer is T2 among the group.

Table 1. Some thermo chemical values of the tautomers considered.

Composites	H°	S° (J/mol°)	G°
T1	-833585.8194	294.14	-833673.5172
T2	-833586.4311	291.97	-833673.4831
T3	-833615.7871	293.05	-833703.1620
T4	-833652.2951	294.48	-833740.0953

Energies in kJ/mol.

Table 2 shows some energies of the tautomers 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 present calculations all the tautomers are electronically stable and the stability order is T4>T3>T2>T1.

Table 2. Some energies of the tautomers considered.

Composites	E	ZPE	E_C
T1	-833759.37	166.48	-833592.89
T2	-833761.01	168.06	-833592.95
T3	-833791.35	168.70	-833622.65
T4	-833827.28	168.12	-833659.16

Energies in kJ/mol.

Figure 2 shows the optimized structures of the composites formed as a result of association of the tautomers (see Figure 1) with NTO. The figure also shows the direction of the dipole moment vectors which are generally originate from somewhere around the particular tautomer and directs to NTO molecule (directed interaction). The composite, NTO+T2, is exceptional in which the components are almost perpendicular to each other. In the figure, the possible hydrogen bonds are shown by dashed lines. Note that in all the composites, except NTO+T2 case, both of the components have hydrogen bond donor and acceptor properties in different extents, whereas in NTO+T2, the tautomer is the donor and NTO is the acceptor.

The components of the composites considered should have certain intermolecular forces arising from partial charges (charge-charge or/and charge-dipole types), dipole-dipole and also dipole-induced dipole type forces because each component has a permanent dipole [39]. All those interactions cause certain perturbations on the components of the composites.

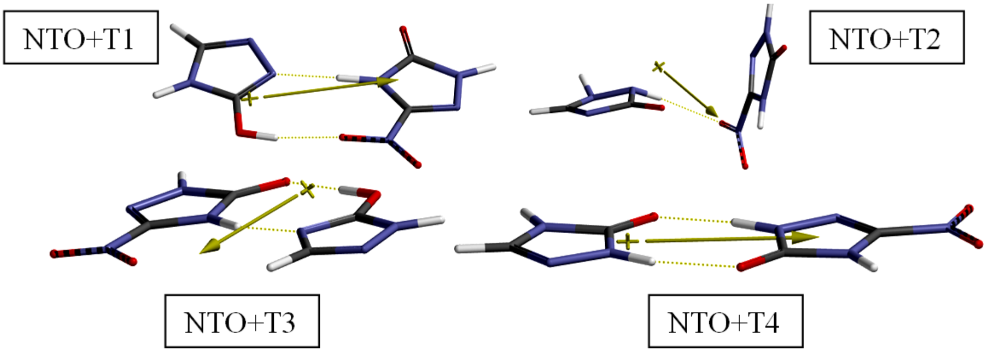


Figure 2. Optimized structures of the composites considered.

On the other hand, the hydrogen bondings between the tautomers and NTO occur at different extents depending on the particular tautomer involved in the composite. Note that dipole-dipole forces play a dominant role in the hydrogen bond, however they are not the sole effective contributing factor [39,40].

Table 3 includes some thermo chemical values of the composites considered. The data indicate that they all have exothermic heat of formation (H^o) values at the standard state and favorable Gibbs free energy (G^o) of formations. The algebraic order of H^o and G^o values are the same, being NTO+T4<NTO+T3<NTO+T1<NTO+T2.

Table 3. Some thermo chemical values of the composites considered.

Composites	H^o	S^o (J/mol°)	G^o
NTO+T1	-2204338.203	431.42	-2204466.832
NTO+T2	-2204308.301	433.41	-2204437.524
NTO+T3	-2204386.163	427.50	-2204513.622
NTO+T4	-2204406.585	430.21	-2204534.852

Energies in kJ/mol.

Some energies of the composites considered are shown in Table 4. The data reveal that the composites are electronically stable and the order is NTO+T4 < NTO+T3 < NTO+T1 < NTO+T2. Thus, NTO+T4 is the most and NTO+T2 is the least stable electronically. The results also show aqueous energies of the composites NTO+T1 to NTO+T4 which are -2204955.47, -2204774.30, -2205037.23 and -2204901.75 kJ/mol., respectively. Thus, composite NTO+T3 is aquated better than NTO+T4. The outcome could be due to structures of both the tautomeric partner and the whole composite.

Table 4. Some energies of the composites considered.

Composites	E	ZPE	E_C
NTO+T1	-2204692.42	343.92	-2204348.50
NTO+T2	-2204663.65	344.53	-2204319.12
NTO+T3	-2204742.30	346.51	-2204395.79
NTO+T4	-2204763.62	346.97	-2204416.65

Energies in kJ/mol.

The interaction energy (E_{A----B}) between two molecules A and B is defined as,

$$E_{A----B} = E_{AB} - (E_A + E_B)$$

where in the present case, E_{AB}, E_A and E_B are the corrected total energies of the composites, tautomers and NTO, respectively. Just to give an idea about the order of magnitudes of interactions, Table 5 sequentially shows the E_C values of the composites, tautomers, NTO and the crude interaction energy E_{A----B} (without basis set superposition error correction (BSSE)).

Table 5. The E_C values of the composites, tautomers, NTO and the relative interaction energy E_{A----B}.

Composites	Tautomers	NTO	Relative E_{A----B}
-2204348.50	-833592.89	-1370698.58	-29.44
-2204319.12	-833592.95	-1370698.58	0
-2204395.79	-833622.65	-1370698.58	-46.97
-2204416.65	-833659.16	-1370698.58	-31.32

Energies in kJ/mol. E_{A---B} of NTO+T2 is -27.59

In the table, although interaction energies do not contain BSSE correction, the basis set used (6-311++G(d,p)) should have minimized the error. Table reveals that interaction energy of NTO+T3 is greater than NTO+T4. It should be not only due to favorable hydrogen bondings in NTO+T3 (which has CO---HON and NH---N types whereas NTO+T4 has two CO---HN type hydrogen bondings) but some other factors as well. Note that minimal relative interaction energy for NTO+T2 could also have some contributions from the T-shaped geometry of the components. Also note that it has only NH----ON type hydrogen bonding.

Table 6 lists the aqueous and solvation energies of the composites considered. The solvation energy calculations are based on SM5.4/A model. The orders of aqueous and solvation energies of the composites are the same that is NTO+T3< NTO+T1< NTO+T4< NTO+T2.

Table 6. Aqueous and solvation energies of the composites considered.

Composites	Eaq (kJ/mol)	Solvation Energy (SM5.4/A)
NTO+T1	-2204955.47	-263.044
NTO+T2	-2204774.30	-110.650
NTO+T3	-2205037.23	-294.932
NTO+T4	-2204901.75	-138.130

Energies in kJ/mol.

In Figure 3, IR spectra of NTO, and the composites considered are depicted. NTO spectrum exhibits N-H stretching at 3650 cm^{-1} whereas the amide (lactam) carbonyl stretches at 1847 cm^{-1}. The asymmetric and symmetric N-O stretchings occur at 1599 cm^{-1} and 1362 cm^{-1}, respectively.

In composite, NTO+T1, the N-H and lactim O-H stretchings of the tautomer moiety occur at 3648 cm^{-1}. The peak at 2898 cm^{-1} belongs to hydrogen bonded N-H of NTO moiety which is located in the structure between the carbonyl and the nitro groups. The C=O stretching of NTO component occurs at 1840 cm^{-1}.

The N-H stretchings appeared at 3652 cm^{-1} and 3656 cm^{-1} belong to NTO component whereas the ones at 3513 cm^{-1} and 3656 cm^{-1} stand for the respective stretchings of tautomer-T2 in the composite NTO+T2. The carbonyl stretchings occurring at 1844 cm^{-1} and 1788 cm^{-1} belong to NTO and the tautomer, respectively.

In the case of NTO+T3, the N-H stretchings at 3658 cm^{-1}, and 3260 cm^{-1} are due to the tautomer, whereas 3646 cm^{-1} and 2806 cm^{-1} belong to NTO component. The O-H stretching of the tautomer appears at 3192 cm^{-1}. Note that it is hydrogen bonded to NTO carbonyl oxygen atom.

In the spectrum of NTO+T4, N-H stretching frequencies of the tautomer occur at 3663 cm^{-1} and 3425 cm^{-1} whereas N-H frequencies of NTO component take place at 3651 cm^{-1} and 3181 cm^{-1}. The carbonyl of NTO vibrates at 1799 cm^{-1} whereas the carbonyl of T4 component stretches at 1766 cm^{-1}.

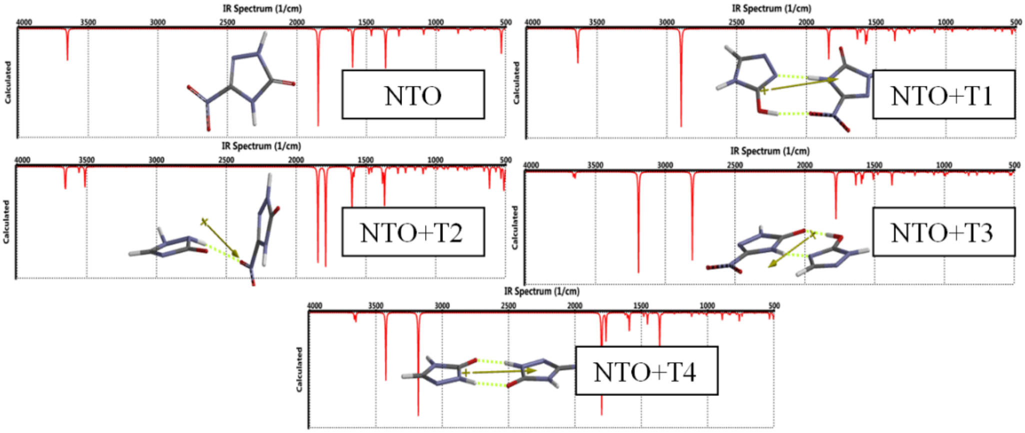


Figure 3. IR spectra of NTO, and the composites considered.

Table 7 lists some calculated properties of the species considered. The data reveal that the tautomers and the composites have the orders of dipole moments of T3<T4<T1<T2 and NTO+T3< NTO+T1< NTO+T4< NTO+T2, respectively. Namely, dipole moments of the composites are dictated by the tautomers involved in the composites. As for the polarizability orders of the tautomers and the composites, one finds T3<T1<T4<T2 and NTO+T3< NTO+T4< NTO+T1< NTO+T2, respectively.

Table 7. Some calculated properties of the species considered.

Structure	Dipole moment	Log P	Polarizability
T1	4.42	0.21	45.84
T2	6.47	-1.12	46.00
T3	2.03	0.21	45.75
T4	3.05	-0.96	45.90
NTO+T1	4.04	0.23	54.00
NTO+T2	6.18	-1.10	54.09
NTO+T3	3.38	0.23	53.87
NTO+T4	5.58	-0.94	53.99

Dipole moments in debye units. Polarizabilities in 10^{-30} m^3 units.

The log P values for T2 and T4 are negative so for their respective composites are. Note that polarizability of a molecule is its tendency to acquire a dipole moment when subjected to an electric field. If the electric field is weak, the induced dipole moment varies linearly with the strength of the applied field. As the field strength increases, higher order terms need to be included to determine the dipole moment. The total dipole moment is the sum of the permanent and induced dipole moments [41].

Figure 4 shows the electrostatic potential maps of the composites considered where negative potential regions coincides with red/reddish and positive ones with blue/bluish parts of the maps. As seen in the maps, the distribution of positive and negative potential regions arise from mutual perturbations dictated by the components upon each other.

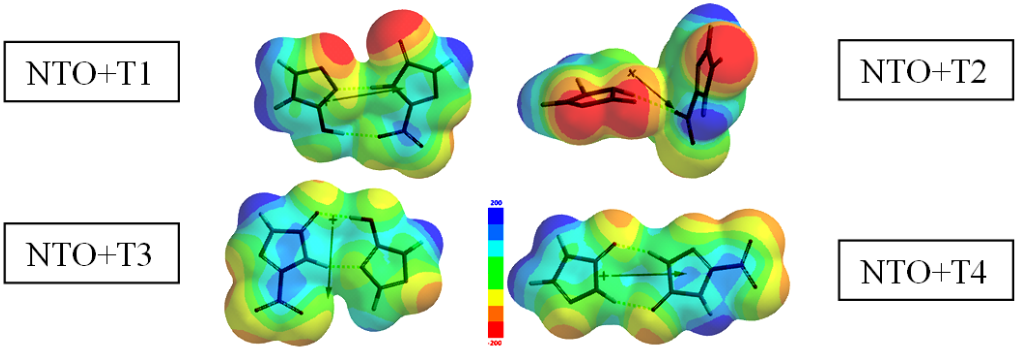


Figure 4. The electrostatic potential maps of the composites considered.

Figure 5 displays some molecular orbital energy levels of NTO and the composites considered. As seen in the figure, the tautomers mainly affect the HOMO energy level of NTO rather than its LUMO energy level. In all the cases the HOMO energy level of the composites are raised up somewhat as compared to NTO. In that sense the tautomers acting as if they were electron donating.

Table 8 shows the HOMO, LUMO energies and the interfrontier molecular orbital energy gap ($\Delta\varepsilon=\varepsilon_{LUMO}-\varepsilon_{HOMO}$) values of the species considered. The orders of HOMO energy levels of the tautomers and the composites are T2<T3<T1<T4 and NTO+T3< NTO+T2< NTO+T1< NTO+T4, respectively. The LUMO energy levels have the orders of T2< T1< T3< T4 and NTO+T1< NTO+T3< NTO+T2< NTO+T4. Consequently, Δε values exhibit the order of T2<T4<T1<T3 for the tautomers and NTO+T1< NTO+T4< NTO+T2< NTO+T3 for the composites.

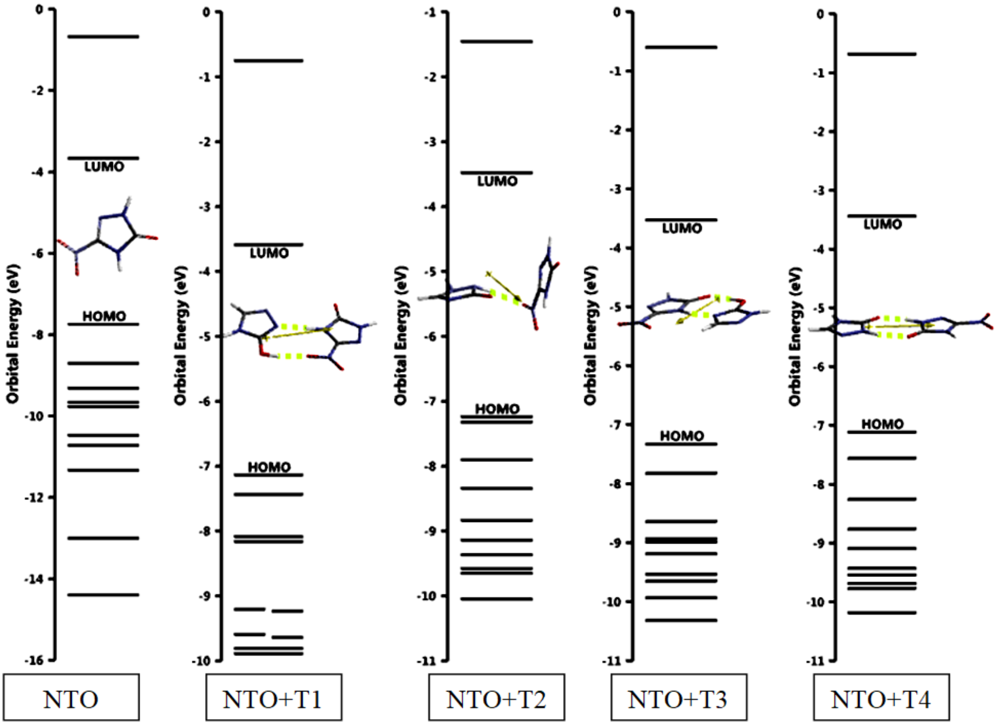


Figure 5. Some molecular orbital energy levels of NTO and the composites considered.

Table 8. The HOMO, LUMO energies and Δε values of the species considered.

Tautomer	HOMO	LUMO	Δε
T1	-680.68	-65.52	615.16
T2	-696.87	-138.70	558.17
T3	-694.18	-53.01	641.17
T4	-649.99	-52.95	597.04
Composite			
NTO+T1	-688.76	-346.20	342.56
NTO+T2	-698.70	-335.71	362.99
NTO+T3	-706.79	-340.33	366.46
NTO+T4	-686.01	-331.45	354.56

Energies in kJ/mol.

Figure 6 shows the HOMO and LUMO orbitals of NTO and the composites considered.

As seen in the figure, T1 does not contribute either to the HOMO and LUMO of the respective composite. In the case of NTO+T2, the tautomer almost contributes nothing to the LUMO of the composite. Whereas in NTO+T3, NTO contributes almost nothing to the HOMO and T3 nothing to the LUMO of the composite. A similar situation occurs for NTO+T4 case.

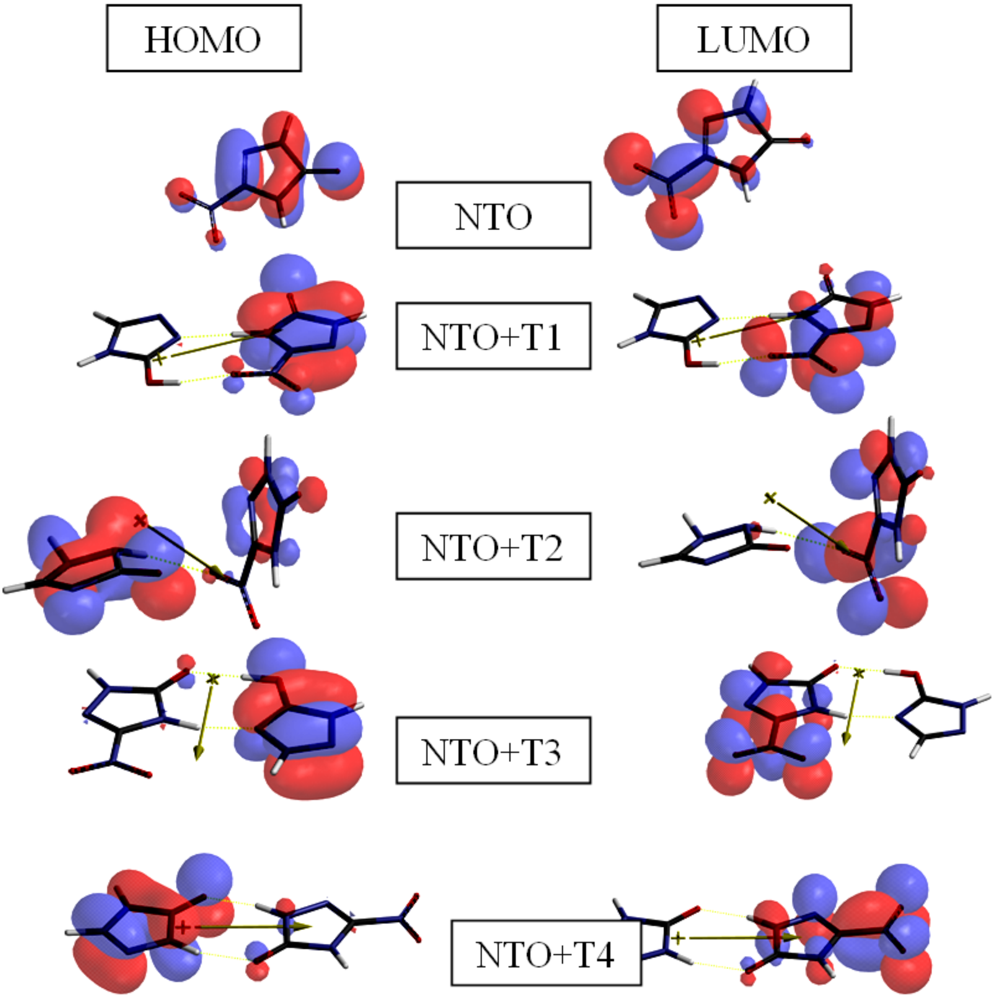
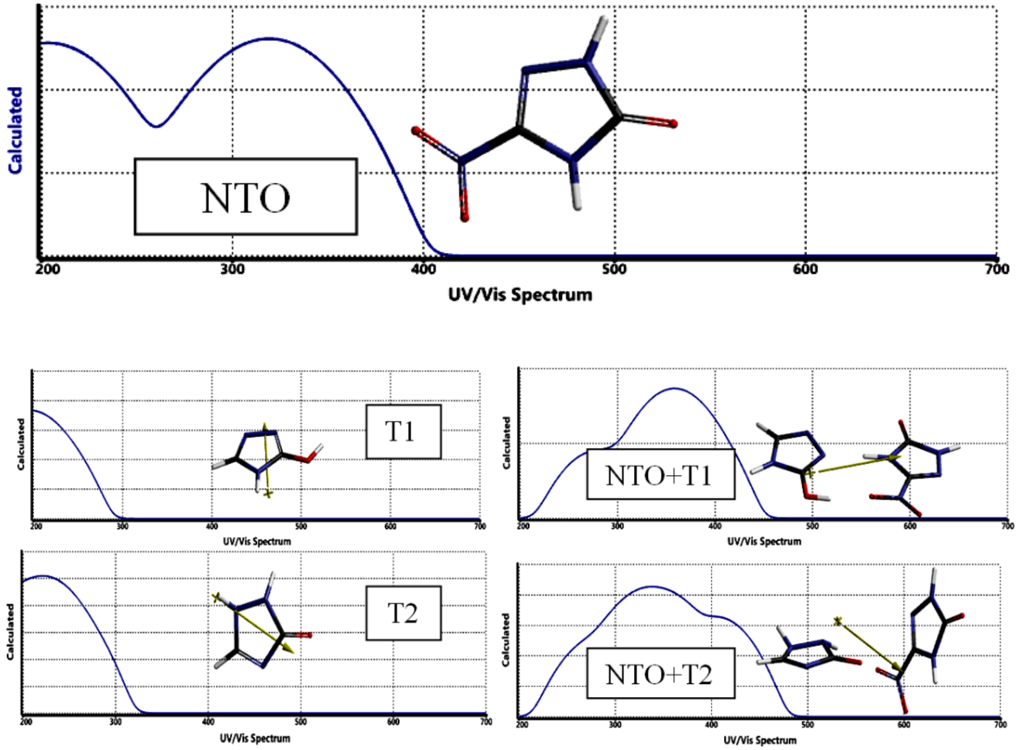


Figure 6. The HOMO and LUMO orbitals of NTO and the composites considered.

Figure 7 displays the calculated (Time dependent density functional) UV-VIS spectra of NTO, the tautomers and composites considered. As seen in the figure, the tautomers absorb in the UV region of the spectrum like NTO. Whereas in all the composites appreciable changes in the appearance of the spectra happen and certain degree of bathochromic effect occurs and absobtion shifts to above 400 nm.

Table 9 lists the λ_{max} values (nm) of the composites considered. The reason for the bathochromic shift should be due to mutual perturbations have taken place between the components which should be as a result of partial charges, hydrogen bondings and the accompanying dipole-dipole and dipole-induced dipole interactions. As a collective effect of those perturbations, the interfrontier molecular orbital energy gap in each composite changes compared to respective gaps of both NTO and the tautomers. The intensities of absorptions also vary compared to the components which should be the results of accompanied transition moment values.



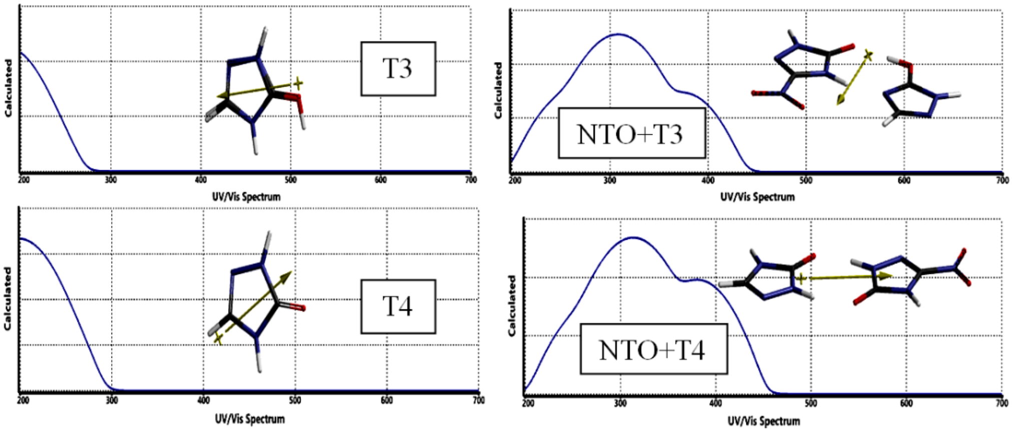


Figure 7. The calculated UV-VIS spectra of NTO, the tautomers and composites considered.

Table 9. λ_{max} values (nm) of the composites considered.

NTO+T1	NTO+T2	NTO+T3	NTO+T4
275.88, 358.18	277.91, 332.77, 406.49	259.70, 308.39, 375.44	264.81, 313.30, 380.96

λ_{max} (NTO) : 203.39, 319.12 nm. λ_{max}(T1-T4) :200-350 nm.

Figure 8 shows the local ionization potential maps of the tautomer T4 (the most abounded tautomer) and NTO 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.

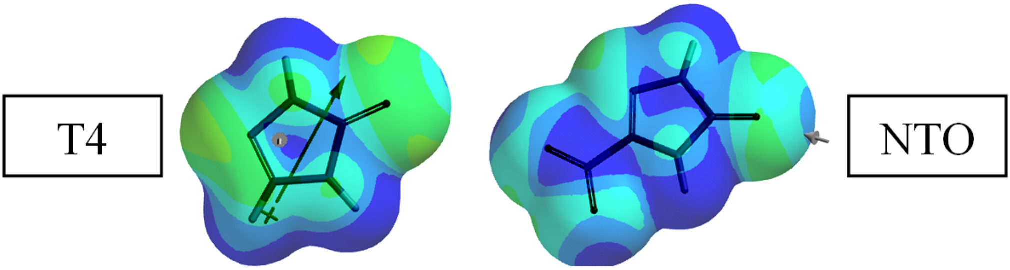


Figure 8. The local ionization potential maps of T4 and NTO.

Similar maps of the composites considered are shown in Figure 9. Figures 8 and 9 illustrate how greatly the components affect each other.

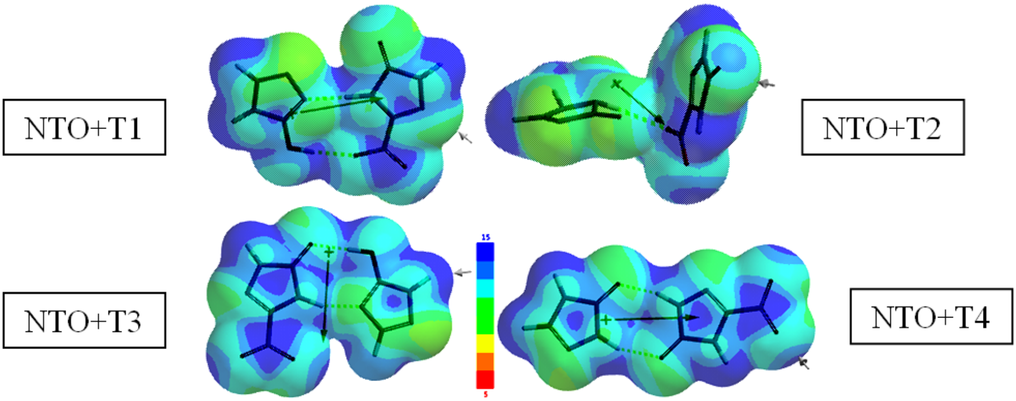


Figure 9. The local ionization potential maps of the composites considered.

Figure 10 displays the LUMO maps of tautomer T4 and NTO. 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 11 shows the LUMO maps of the composites considered. Also note that in all the cases the tautomer component coincides with the minimum value of the LUMO. Thus, the presence of NTO in the vicinity of the tautomers highly changes their character.

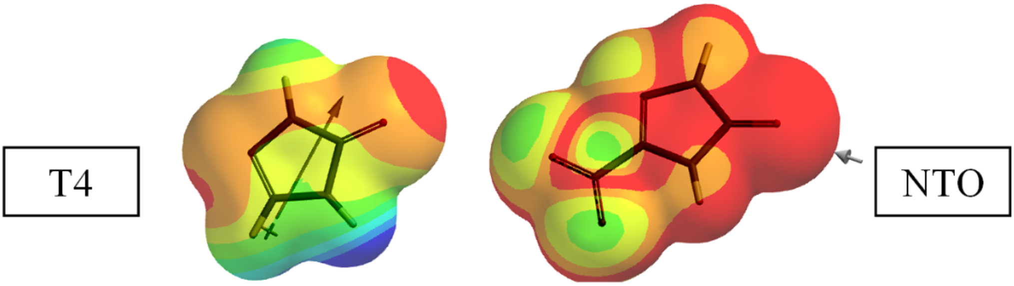


Figure 10. The LUMO maps of tautomer T4 and NTO.

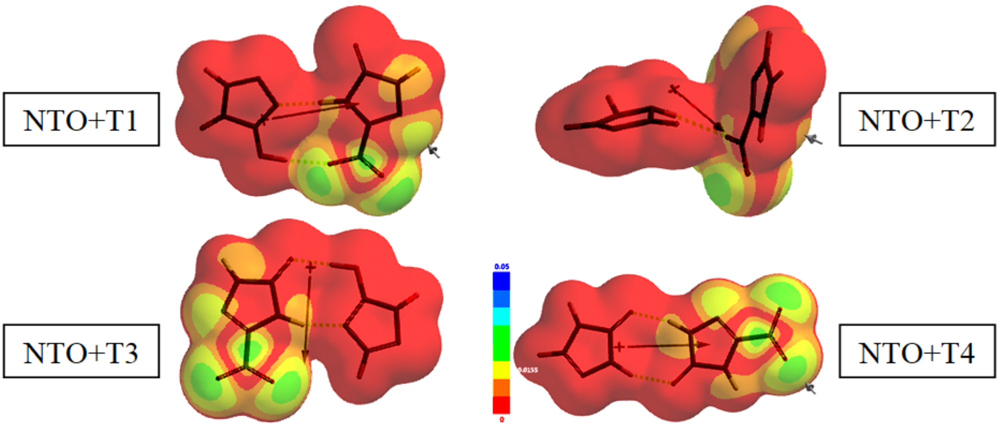


Figure 11. The LUMO maps of the composites considered.

As revealed by Figures 10 and 11 the components highly affect their electrophilic and nucleophilic characteristics.

4. Conclusion

The present density functional treatise has revealed that among the various 1,3 (or 1,5-) tautomers originated from 2,4-dihydro-3H-1,2,4-triazol-3-one structure, tautomer-T4 in vacuum conditions is thermally more favorable than the others at the standard state and electronically more stable. Their composites formed with NTO have exothermic heat of formation and favorable Gibbs free energy of formation values at the standard states and they are stable electronically too. The hydrogen bonding between the tautomers and NTO occurs at different extents depending on the particular tautomer involved in the composite. Both of the components have hydrogen bond donor and acceptor properties except composite NTO+T2, in which the tautomer is the hydrogen bond donor and NTO is the acceptor. The partners of the composites highly perturb characteristics of each others in many respects, such as the molecular orbital energies. The tautomers mainly affect the HOMO energy level of NTO rather than its LUMO energy level. In all the cases the HOMO energy level of the composites are raised up somewhat as compared to NTO. Consequently, although the tautomers absorb in the UV region of the spectrum (like NTO), in all the composites shapes of the spectra change and certain degree of bathochromic effect occurs as compared to the respective spectra of the partners.

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