Trinitroanisole isomers - A DFT treatment

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Abstract

Trinitroanisole isomers have been investigated within the constraints of density functional theory at the level of B3LYP/6-311++G(d,p). All the isomers are electronically stable, thermodynamically exothermic and have favorable Gibbs' free energy of formation values at the standard states. Various quantum chemical properties, including UV-VIS spectra have been obtained and discussed. Some of the isomers considered are associated with non-Kekule alternant isoconjugate systems, therefore they might have some potential explosive character. 2,4,6-Trinitrophenylanisole is one of them and indeed it was extensively and exclusively used by Japanese as an explosive in the II world war.

1. Introduction

2,4,6-Trinitroanisole (methyl picrate, 2,4,6-trinitrophenyl methyl ether, methoxy-2,4,6-trinitrobenene) is white to yellow crystals ($C_7H_5N_3O_7$). Maxim and DuPont were the first to suggest the application of 2,4,6-trinitroanisole as an explosive material [1-3]. It was obtained by Cahourus [4] by the direct nitration of anisole. The compound was used by the Germans in mixtures with TNT and sometimes also with ammonium nitrate for filling bombs. Dry 2,4,6-trinitroanisole is very stable, however the methoxy group is rather reactive and may be substituted by certain nucleophiles [5,6]. It is poisonous [7-9] and considered as environmentally hazardous material [9]. It forms complexes with certain compounds [10]. 2,4,6-Trinitroanisole (TNA) explodes by heat or shock [11]. During I WW TNa was manufactured in Germany under the names of Nitrolit, Trinol and An. It was used alone or in admixture with ammonium nitrate, hexyl or

hexanitrodiphenyl sulfide [12]. In France TNA was used of only on the semi-commercial scale in mixtures with picric acid or ammonium or sodium nitrate for filling bombs. During II WW it was manufactured in Japan for filling armour piercing shells [12]. Historically, 2,4,6-trinitroanisole was used as a military explosive (e.g., Japanese Type 91) [13-15], however, due to its tendency to form picric acid and dangerous picrate salts, its use has largely been abandoned. Also the Japanese have used it in their suicide planes [15]. Although, it has many isomers they are scarcely mentioned in the literature [16].

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 [17-19]. 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) [20,21]. 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 [22]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [23] and Lee, Yang, Parr (LYP) correlation correction functional [24]. 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 [25].

3. Results and Discussion

Figure 1 shows the structures of 2,4,6-trinitroanisole and its isoconjugate alternant hydrocarbon (AH) [26,27]. Note that although aliphatic or aromatic nitro compounds, aliphatic nitro esters, nitrogen halides, etc., all have topological assembly of various atoms, their explosophore groups (e.g., nitro group) have a common isoconjugate system, methylenepropenyl dianion. It is an odd alternant hydrocarbon anion [28,29]. The nitro group in the structure of explosives links to adjacent atom via an unstarred position when

its isoconjugate propenyl anion is considered. The explosives in the completely coplanar form may display odd, even or non-Kekule type alternant hydrocarbon characteristics depending on the overall structure of them [30]. Note that a non-Kekule AH is much less stable than any isomeric Kekule-type AH [26,27] and the characteristic feature of non-Kekule systems is that the difference (Δ=n*-n) between the number of starred and unstarred positions is either equal to two or far exceeds it [26,27]. However, one should keep in mind that any compound which is a non-Kekule type may get rid of that form if structurally certain rotations or twisting is possible. Thus, an explosive molecule isoconjugate with a non-Kekule AH system may remain in metastable form at room temperature. See Figure 1 where some isomers which are by definition non-Kekule structures, (in the coplanar form) possess nitro groups having large dihedral angle at the point of attachment and in reality turn into Kekule type structures. Explosive character of ammunitions arises not only from molecular structure of the explosive used but also depends on some other factors, such as loading density, etc., [31].
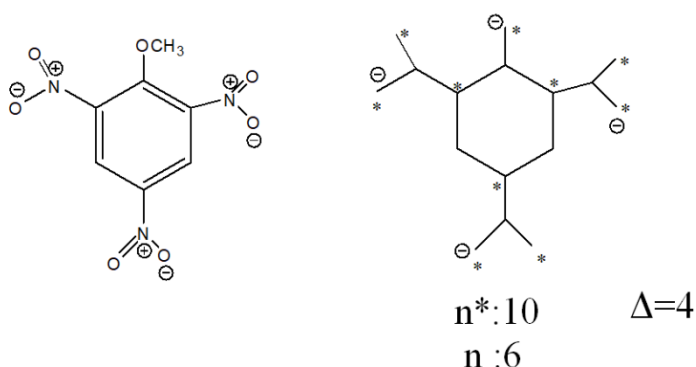

Figure 1. The structure of 2,4,6-trinitroanisole and its isoconjugate alternant hydrocarbon.

Figure 2 shows the optimized structures of the isomers considered. Note that in the structures not all of the nitro groups are coplanar with the ring. The figure also shows the direction of the dipole moment vectors. Generally the vectors originate from somewhere nearby the methoxide group and tips to one of the nitro groups present.

Table 1 shows some structural properties of the isomeric molecules considered where HBD and HBA stand for hydrogen bond donors and acceptors, respectively. On the other hand, 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.
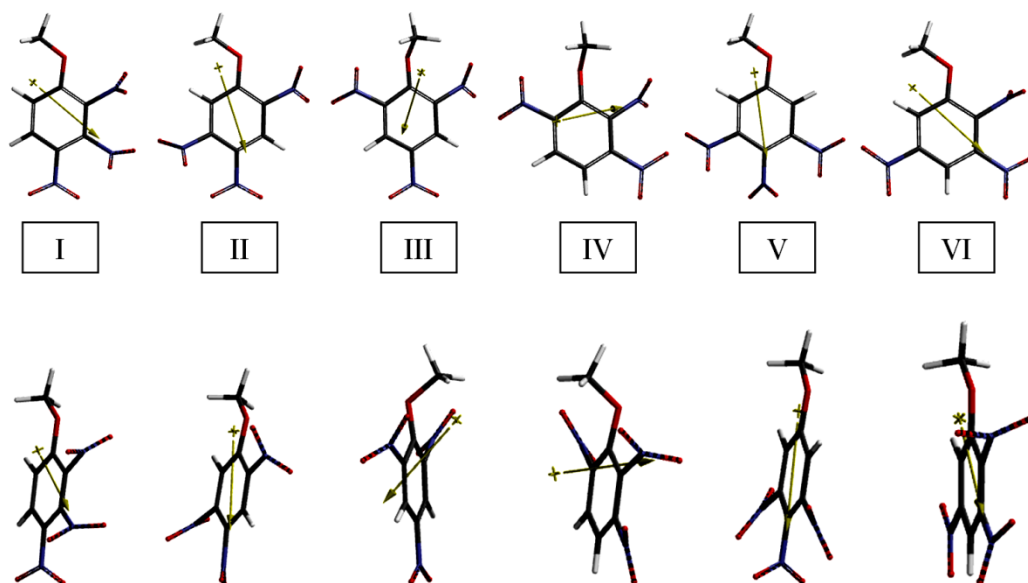
Figure 2. Optimized structures of the isomers considered.

Table 1. Some structural properties of the isomeric molecules considered.

Molecule	Area (Å²)	Volume (Å³)	PSA (Å²)	Ovality
I	223.00	191.53	122.459	1.39
II	222.58	191.32	122.702	1.39
III	218.68	191.27	120.482	1.36
IV	219.35	191.57	120.242	1.36
V	222.06	191.35	121.965	1.38
VI	222.42	191.14	122.632	1.39

They have HBD and HBA counts of 0 and 10, respectively.

Figure 3 shows the electrostatic potential maps of the isomers considered where negative potential regions coincides with red/reddish and positive ones with blue/bluish parts of the maps.
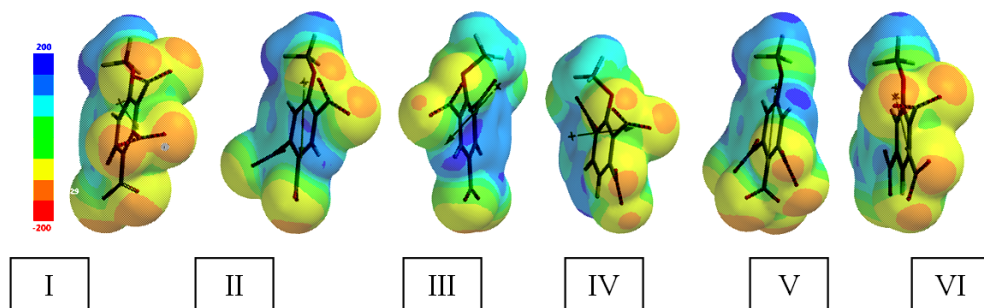
Figure 3. The electrostatic potential maps of the isomers considered.

Table 2 shows some thermo chemical values of the molecules considered. It also indicates the type of the molecules considered and their Δ values. Note that explosive molecules have non-Kekule isoconjugates that it is a necessary but not a sufficient condition for having explosive character [28,29]. For all the other factors being the same, among the structures listed in the table, compound-III (2,4,6-trinitroanisole) is expected to have the highest explosive character due to the highest Δ value it possesses.

Table 2. Some thermo chemical values of the molecules considered.

Molecule and its type	Δ	H°	S° (J/mol°)	G°
I nK	2	-2521449.442	461.74	-2521587.109
II nK	2	-2521470.921	462.19	-2521608.725
III nK	4	-2521476.608	462.98	-2521614.648
IV nK	2	-2521448.586	463.13	-2521586.668
V K	0	-2521461.315	462.26	-2521599.139
VI K	0	-2521479.890	462.42	-2521617.764

Energies in kJ/mol.

All the structures considered are exothermic and the order of H° values is VI< III< II< V< I< IV, whereas G° values follow the order of VI< III< II< V< I< IV and all have favorable Gibbs' free energy of formations at the standard states.

Table 3 lists some energies of the molecules considered where E, ZPE and EC stand for the total electronic energy, zero point vibrational energy and the corrected total

electronic energy, respectively. As the data reveal, all of the structures are electronically stable. The algebraic order of E_C values is VI< III< II< V< I< IV. Namely, isomer-VI is electronically the most stable isomer which is followed by III. Note that in isomer-VI, one of the nitro groups (ortho nitro group) is almost perpendicular to plane of the ring whereas in isomer-III (2,4,6-trinitroanisole) all the nitro groups are crossly conjugated with each other. All these affect some properties of the isomers.

Table 3. Some energies of the molecules considered.

Molecule	E	ZPE	E_C
I	-2521826.12	364.76	-2521461.36
II	-2521847.29	364.58	-2521482.71
III	-2521852.40	363.90	-2521488.50
IV	-2521824.56	363.94	-2521460.62
V	-2521837.82	364.61	-2521473.21
VI	-2521855.90	364.14	-2521491.76

Energies in kJ/mol.

Table 4 shows some calculated properties of the isomeric molecules considered.

Table 4. Some properties of the isomeric molecules considered.

Molecule	Dipole moment	E_{aq}	Solvation Energy	Hardness	ZPE	Polarizability
I	9.68	-2521849.03	-22.91	220.68	364.76	55.83
II	6.09	-2521853.73	-6.44	211.46	364.58	55.86
III	2.44	-2521852.58	-0.18	235.07	363.90	55.74
IV	3.55	-2521836.53	-11.97	215.67	363.94	55.86
V	8.79	-2521852.30	-14.48	207.62	364.61	55.88
VI	5.64	-2521866.28	-10.38	201.46	364.14	55.89

Point group of all is C1. Energies in kJ/mol. Dipole moments in debye units. Polarizabilities in 10^{-30} m^3 units. All have Log P value of -1.50.

Where hardness is defined as [25],

$$\text{Hardness} = -(\varepsilon_{HOMO} - \varepsilon_{LUMO})/2$$

where ε_{HOMO} and ε_{LUMO} are the molecular orbital energies of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbital energies (Frontier molecular orbital energies), respectively. Whereas, the polarizability is defined according to the multivariable formula [25].

$$\text{Polarizability} = 0.08*V - 13.0353*h + 0.979920*h^2 + 41.3791$$

where V and h are the Van der Waals volume and hardness, respectively.

As seen in Table 4, dipole moments highly structure dependent, both magnitude and direction wise (see Figure 2), because dipole moment is a vectorial sum of bond dipoles, thus highly structure dependent property. The order of dipole moments is I>V>II>VI>IV>III. The order of solvation energies is I<V<IV<VI<II<III. So, isomer-I is solvated better than the others. Note that some physicochemical properties are implicit functions of many others.

The ZPE values are also variable from isomer to isomer, because the topology of the site of the perturbation caused by changing position of the nitro groups, in each case should be governed by a different potential energy surface than the reference structure owed.

Figure 4 shows some of the molecular orbital energy levels of the isomers considered. As seen in the figure, the isomers presently considered exhibit distribution of molecular orbital energy levels highly dependent on the position of the nitro groups on the aromatic ring. However, in structure of most of the isomers not all of the nitro groups are coplanar with the ring, thus the extent of conjugation differs from structure to structure which affects the energy levels. The energy spacings between the HOMO and NEXTHOMO or LUMO and NEXTLUMO exhibit varieties. For instance, in isomer III both the HOMO and NEXTHOMO and LUMO and NEXTLUMO energy levels are close to each other but in isomer V the LUMO and NEXTLUMO energy levels are close to each other but the NEXTHOMO and LUMO levels are not. Note that although nitro groups are electron withdrawing mesomerically and inductively, the methoxide group is mesomerically electron donating but inductively electron attracting. In addition to these electronic effects of the substituents present, some of them are crossly conjugated with each other depending on their positions of attachment. Therefore in some isomers their effects are stronger or weaker. It is worth mentioning that isomer-VI is characterized
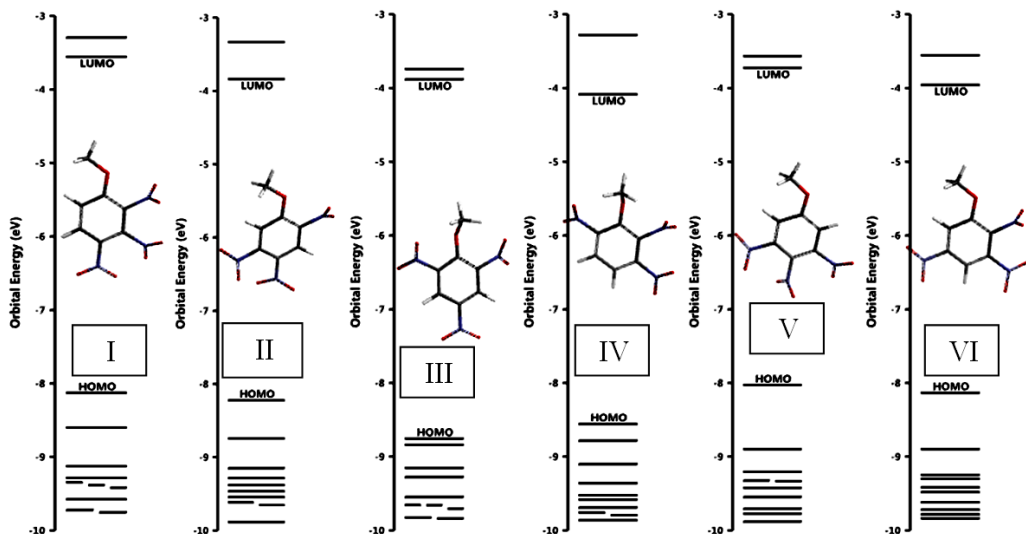
Figure 4. Some of the molecular orbital energy levels of the isomers considered.

with having highly dense inner-lying occupied molecular orbital energy level distribution indicative of its thermal stability.

Table 5 lists the HOMO, LUMO energies and the interfrontier molecular orbital energy gap ($\Delta\varepsilon=\varepsilon_{LUMO}-\varepsilon_{HOMO}$) values of the molecules considered. The data reveal that the orders of HOMO and LUMO energies are III< IV< II< VI< I< V and IV< VI< III< II< V< I, respectively. Whereas, $\Delta\varepsilon$ values follow the order of VI< V< II< IV< I< III. Note that the impact sensitivity of explosives are related to the interfrontier molecular

Table 5. The HOMO, LUMO energies and $\Delta\varepsilon$ values of the molecules considered.

Molecule	ε_{HOMO}	ε_{LUMO}	$\Delta\varepsilon$
I	-784.33	-342.96	441.37
II	-793.26	-370.34	422.92
III	-844.84	-374.69	470.15
IV	-825.53	-394.19	431.34
V	-774.73	-359.49	415.24
VI	-784.77	-381.84	402.93

Energies in kJ/mol.

orbital energy gap values. That is narrower the gap, the explosive becomes more sensitive to an impact stimulus [32,33]. Thus, isomer-III should be the least and VI most sensitive to impact stimulus. This outcome should have arisen from the electronic perturbations resulting from orientation of the nitro groups present.

Figure 5 displays the top views of the HOMO and LUMO patterns of the isomers considered. In each case, the HOMO spreads over the ring atoms and partly over the nitro groups but contributions coming from the nitro groups in some cases are very little. Not all the nitro groups contribute into the LUMOs either, for instance isomer-I. Contribution of the methoxide atomic orbitals to the LUMO is also structure dependent. For instance, in the case of isomers IV-VI, it does not contribute at all. In general the HOMO and LUMO patters of the isomers exhibit certain type of π-symmetry in a great extent. Since the frontier molecular orbitals greatly dictate the chemical behavior of a molecule patterns of the HOMO and LUMO are worth scrutinizing.
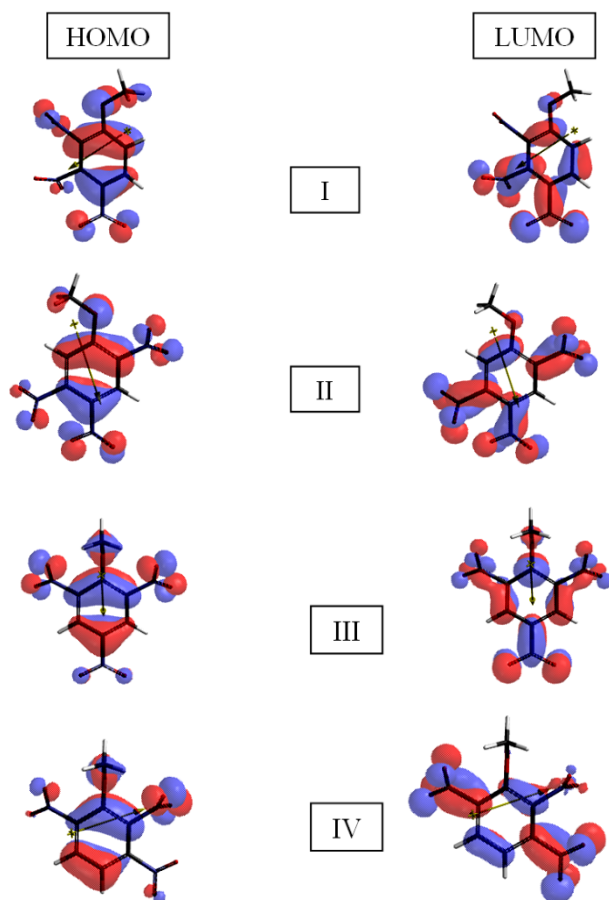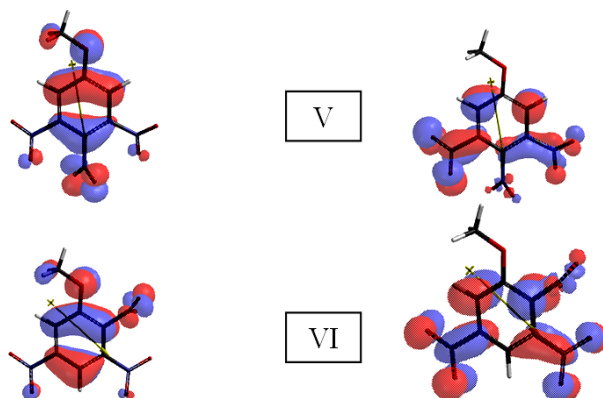
Figure 5. The HOMO and LUMO patterns of the isomers considered.

Figure 6 shows the local ionization maps of the isomers 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.
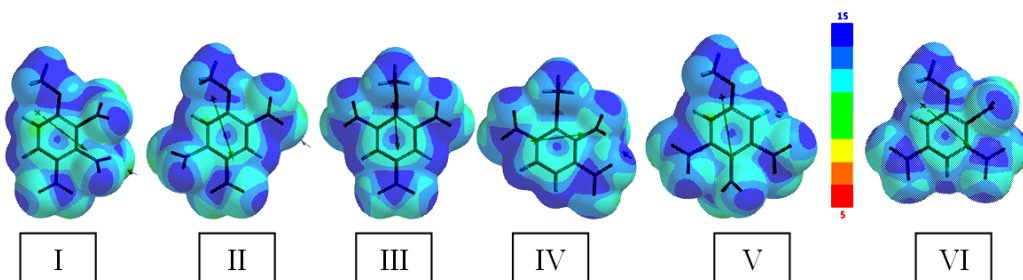

Figure 6. The local ionization maps of the isomers considered.

Figure 7 displays the LUMO maps of the isomers 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. Note that the LUMO and NEXTLUMO are the major orbitals directing the molecule towards of the attack of nucleophiles. Positions where the greatest LUMO coefficient exists is the most vulnerable site in nucleophilic reactions.
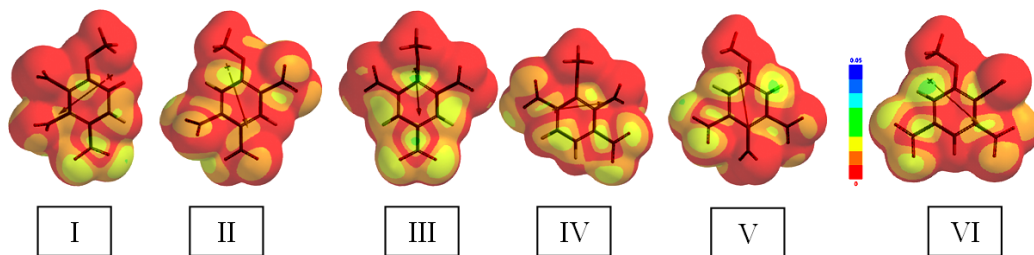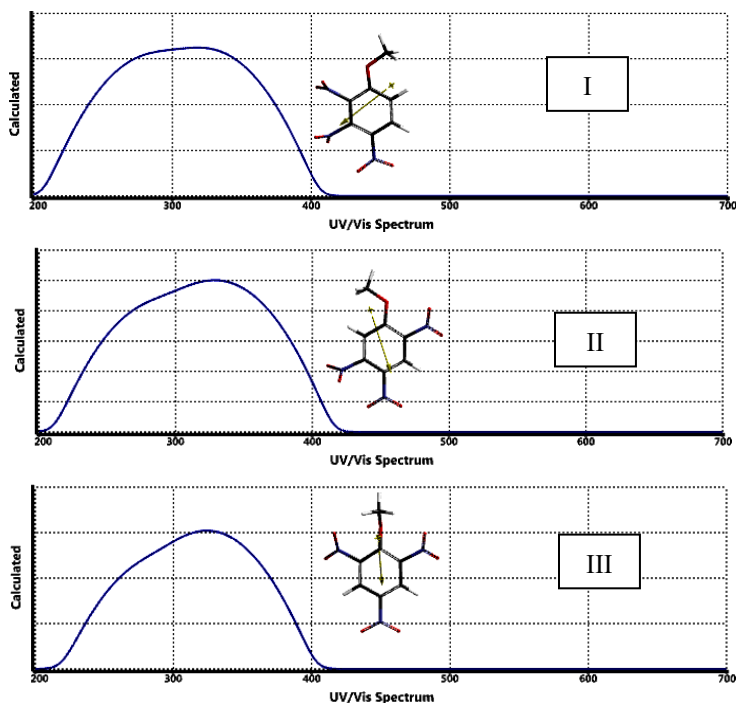
Figure 7. The LUMO maps of the isomers considered.

Figure 8 shows the calculated (time dependent DFT) UV-VIS spectra of the isomers considered. As seen in the figure, they all absorb mainly in the UV region having a negligible absorbance in the visible part.

As seen in the figure, variation of positions of the nitro groups has some influence on the spectra. Isomer-IV exhibits quite a symmetrical spectrum whereas the others have a feebly emerged shoulder at the lower wavelength-side of the spectra. Since the spectra are mainly absorb in the UV region, albeit the fact that many auxochromic groups exist in the isomers, indicate that the conjugation is not an extended type sufficiently in order to decrease the interfrontier molecular orbital energy gap to cause any bathochromic effect.
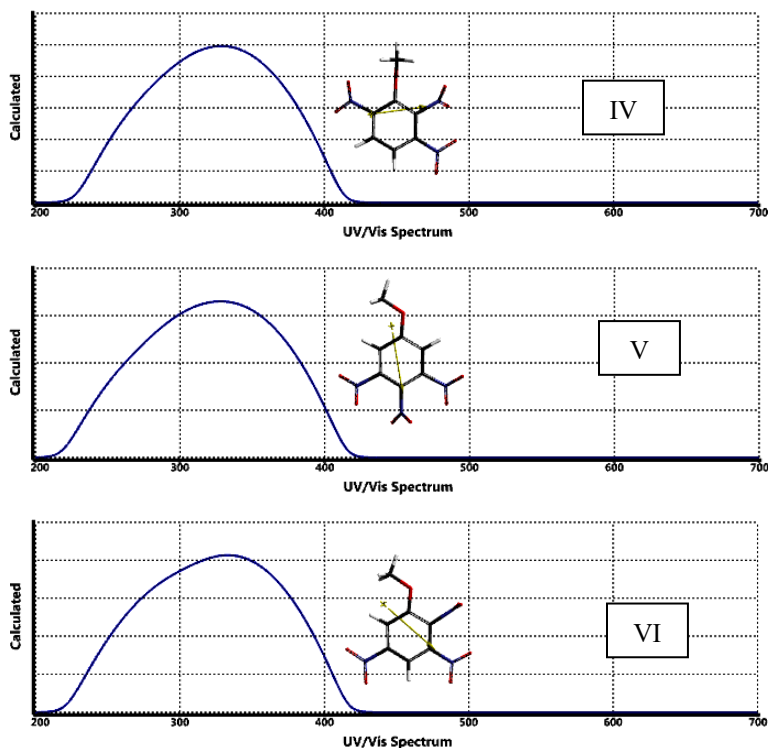
Figure 8. Calculated UV-VIS spectra of the isomers considered.

4. Conclusion

The present study within the restrictions of density functional theory and the level of basis set employed has revealed that all the trinitroanisole isomers considered are exothermic, electronically stable and have favorable Gibbs' free energy of formations at the standard states. Perturbational molecular orbital treatment reveals that some of them are isoconjugate with non-Kekule type alternant hydrocarbons and thus are expected to be potentially explosive compounds. The positions and conformations of the substituents on the ring play an important role on dictating various properties of the isomers. Extending or shortening of the conjugation path involving the ring electrons dictates electronically related different properties involving some ballistic ones such as impact sensitivity. 2,4,6-Trinitroenisole is one of them which was extensively and exclusively used (in the II-world war) but being unaware of the theoretical grounds behind.

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