



Effect of Nitro-Iodyl Group Replacement on TNT - A DFT Treatment

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Abstract

The present density functional treatment (B3LYP/6-311++G(d,p)) within the restrictions of the theory and the basis set employed, considers perturbational effects at the molecular level by the replacement of one of the nitro groups of 2,4,6-trinitro toluene (TNT) with iodyl moiety. The process yield two iodyl isomers which are stable electronically and structurally. Various quantum chemical, IR and UV-VIS spectral properties are investigated and compared with the respective values of TNT. The nitro-iodyl group replacement causes narrowing of the interfrontier molecular orbital gap and increases the impact sensitivity of the systems considered.

1. Introduction

An almost explosive growth in the field of organic hypervalent iodine chemistry has been observed over the last few decades. Iodine is a very special element (having the ground state electronic configuration of $[\text{Kr}]4d^{10}5s^25p^5$) and it is the largest, the least electronegative and the most polarizable of the halogens. It formally belongs to the main group, p-block elements; however, because of the large atom size, the bonding description in iodine compounds differs from the light main group elements [1].

A variety of tri- and penta-valent iodine compounds have received increasing attention over the past few decades as useful reagents in organic synthesis [2-6]. Polyvalent iodine derivatives have been utilized for halogenation, arylation and various oxidative transformations [2-12].

In compounds containing one or two formal double bond, such as iodosylbenzene or iodylbenzene (formerly iodobenzene and iodoxybenzene, respectively) hypervalent

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bonding is different. The bonding is highly polarized so that zwitterionic rather than double-bond notations are nearer a correct assignment [13]. In iodyl benzene for instance, iodine uses three p- and two d-orbitals to form bonds collectively with the phenyl moiety and two of the oxygen atoms of which π_{dp} type bonding is assigned to iodine-oxygen linkages [14].

In the present study, in order to investigate some effects of the perturbations caused by nitro-iodyl group replacement on TNT molecule, some molecular orbital calculations have been performed within the limitations of the density functional theory (DFT).

2. Method of Calculations

The initial geometry 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 [15,16] at the restricted level [17,18]. Subsequent optimizations were achieved at Hartree-Fock level employing various basis sets. Then, geometry optimizations were managed within the framework of density functional theory [19,20] at the level of B3LYP/6-311++G(d,p) [17,21]. 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 [20,22]. 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]. Also, vibrational analyses have been done on the optimized structures. 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 stands for the number of atoms in the system. This has indicated that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. All these calculations have been done by using the Spartan 06 package program [25].

3. Results and Discussion

In the present DFT treatment, one of the nitro groups located either at 2- or 4-positions of TNT molecule is replaced by iodyl group to engender dinitromonoiodyl toluene isomers. Note that most of the iodyl derivatives of arenes generally have low stability and different degrees of explosive character, such as iodylbenzene [11,12]. They explode upon heating or mechanical impact. The nitro group is isoconjugate with propenyl anion which is an odd alternant hydrocarbon system. When a nitro group is

linked to a conjugated structure, depending on the point of attachment a non-Kekule structure may arise [26] and this occurrence yields some instability. This is a necessary but not a sufficient condition for being an explosive compound [26,27]. TNT molecule is isoconjugate with a nonKekule hydrocarbon system. The replacement of one of the nitro groups with an iodyl moiety also produces a structure isoconjugate with a nonKekule hydrocarbon system. However, due to the different characters of those groups some perturbations are expected which might arise from the differences between the group electronegativities, types of hybridizations, conformations of the groups etc. The present calculations reveal that not all three nitro groups of TNT are coplanar with aromatic ring. In the case of 2-iodyl derivative only one of the NO_2 groups is coplanar with the ring but the other groups are not. Whereas, in 4-iodyl derivative all the groups have some angle of rotation with the aromatic ring. Moreover, due to the size mismatch between the atomic orbitals of carbon and iodine atoms, the iodyl moiety cannot be as much effective as the nitro group is as regard to electron delocalization but inductive effects are operative.

Figure 1 shows optimized structures and the direction of the dipole moment vectors

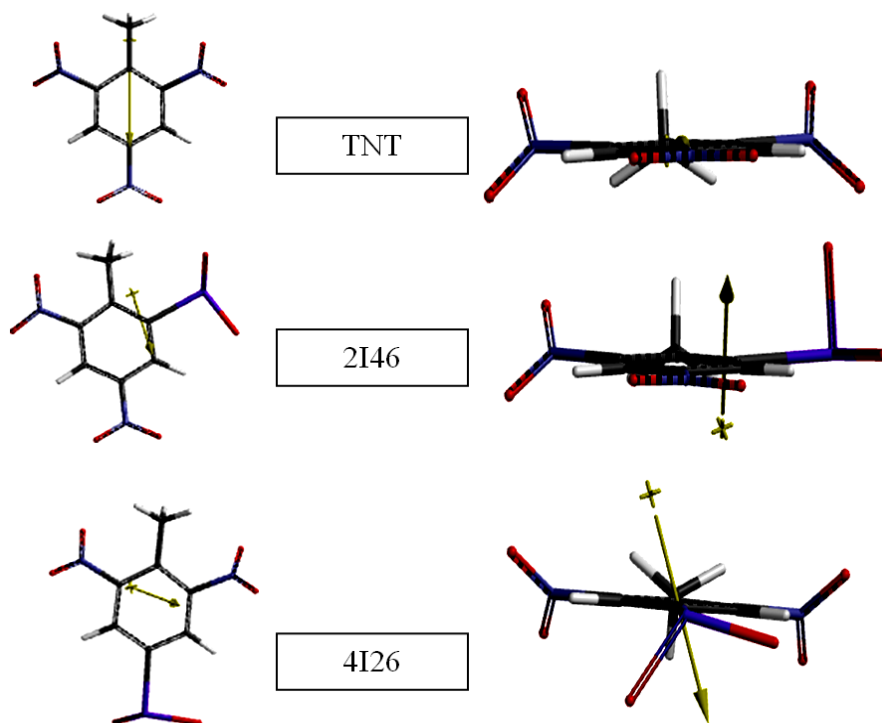


Figure 1. Optimized structures of the species considered (Top and side views).

of the species considered. The dipole moments are 1.67, 4.99 and 3.93 debye, respectively for TNT, 2I46 and 4I26 (See Table 1). It seems replacement of the nitro group at the 2-position to produce isomer 2I46 is more effective to raise the dipole moment than the replacement at the 4-position. In each case the iodyl group highly increases the dipole moment as compared to TNT case. The polarizability values are 54.93, 56.66 and 56.66, respectively for those species.

Table 1. The dipole moment components and the resultant dipole moments of the species considered.

Structure	X	Y	Z	Dipole
TNT	-0.063806	-0.000289	-1.673556	1.674772
2I46	1.380473	-3.160958	3.613929	4.995782
4I26	1.626414	0.202331	-3.574521	3.932348

In debye units.

Figure 2 shows the calculated bond lengths of the species considered. The data reveal

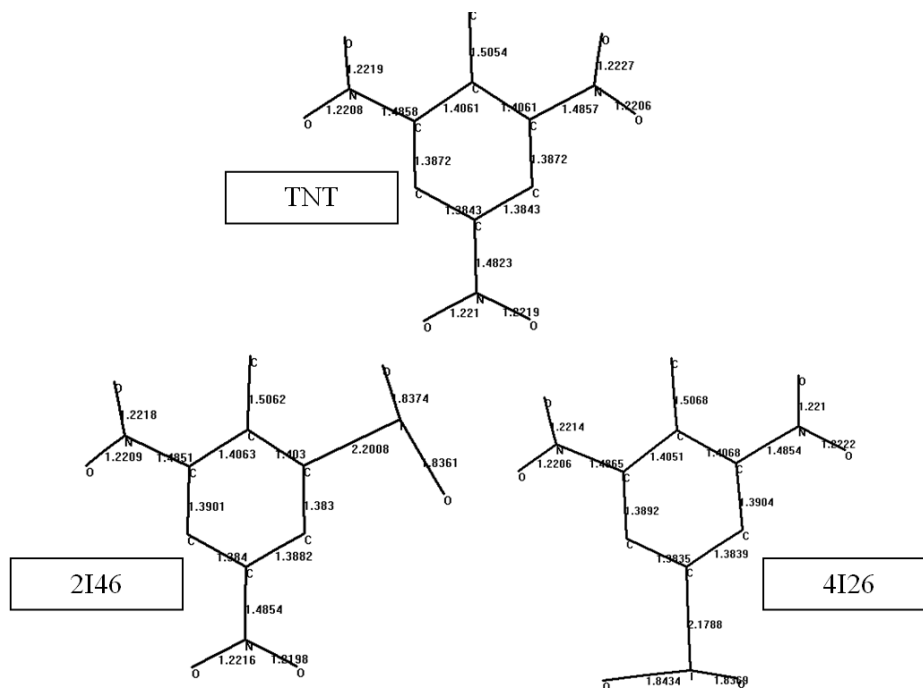


Figure 2. Bond lengths of the species considered (Hydrogens depleted).

that C-C bond lengths in TNT and the iodyl derivatives considered are very comparable. The C-NO₂ bond lengths in iodyl isomers considered are about 1.48 Å. As for the C-IO₂ bonds, they are 2.20 and 2.17 Å for 2I46 and 4I26, respectively. On the other hand, the O-I-O bond angles are 112.42 and 114.11 degrees for those isomers. Note that the O-N-O bond angles in TNT are about 125°.

Table 2 displays some energies of the isomeric iodyl structures considered where E, ZPE and E_C stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. The data in the table reveal that isomer 2I46 is electronically more stable one.

Table 2. Some energies of the isomeric iodyl structures considered.

Structure	E	ZPE	E _C
2I46	-20347517.18	331.65	-20347185.53
4I26	-20347505.62	332.44	-20347173.18

Energies in kJ/mol.

Table 3 lists some thermodynamic energies of the species considered where H°, S° and G° are the standard enthalpy, entropy and Gibbs free energy, respectively. Of the two iodyl isomers considered, 2I46 is the enthalpy and free energy favored isomer, but entropically less favored.

Table 3. Some thermodynamic energies of the species considered.

Structures	H°	S° (J/mol°)	G°
TNT	-2324000.54	444.63	-2324133.106
2I46	-20347337.40	477.48	-20347479.76
4I26	-20347325.01	478.03	-20347467.55

Energies in kJ/mol.

Figure 3 shows the IR spectra of TNT and two isomers obtained by replacing one of the nitro groups of TNT by iodyl moiety. In the case of TNT the band at 1651 cm⁻¹ stands for skeletal breathing of the aromatic ring whereas the peak at 1587 cm⁻¹ is due to asymmetric N-O stretchings (more pronounced for the 4-nitro group). The peak at 1378 cm⁻¹ stands for symmetric N-O stretchings of nitro substituents at 2- and 6- positions of

TNT molecule. In the case of isomer 2I46, the peak at 1636 cm^{-1} is the asymmetric N-O stretching of the nitro group occupying 4-position of the isomer. The skeletal vibrations of the ring coupled with asymmetric N-O stretching of the other nitro group occur at 1597 cm^{-1} . Whereas the symmetric stretchings of N-O bonds happen at 1379 cm^{-1} . The I-O stretchings occur at $762\text{--}720\text{ cm}^{-1}$, coupled with some other vibrations. In the case of isomer 4I26, the ring vibrations occur at 1635 cm^{-1} , the peak at 1593 cm^{-1} stands for asymmetric N-O stretchings and C-H bendings whereas at 1376 cm^{-1} symmetrical N-O stretchings occur.

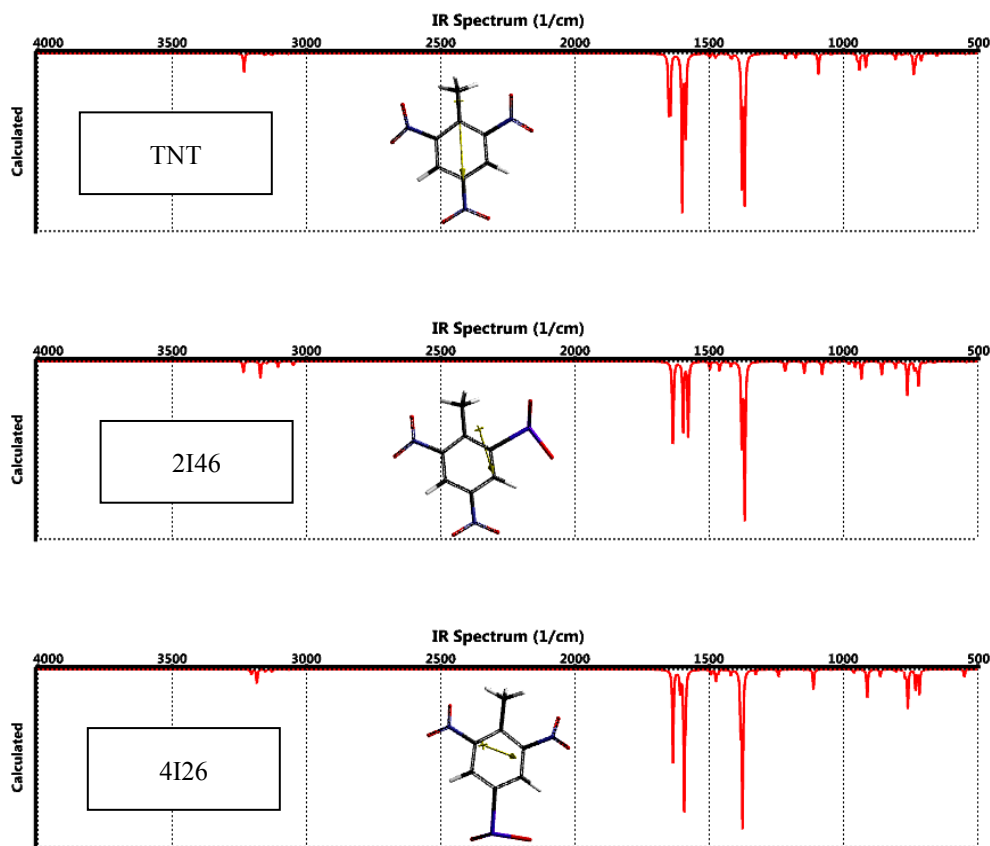


Figure 3. The calculated IR spectra the molecules considered.

Figure 4 shows the electrostatic potential (ESP) charges on the atoms of the isomers considered. 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 [25]. When both iodyl isomers are considered, the positive charge on the iodine atom of 2I46 is more positive and the adjacent carbon atom is more negative

compared to the respective values of the other isomer. The direction of dipole moment vectors are quite different for those isomers. In TNT, due to some symmetry of the system, tail of the dipole moment vector originates somewhere around the methyl group and points to *para* position of the ring. In the case of the iodyl isomers, due to some prevailing inductive and mesomeric effects the charge distribution as well as the direction and magnitudes of the dipole moment vectors are quite different.

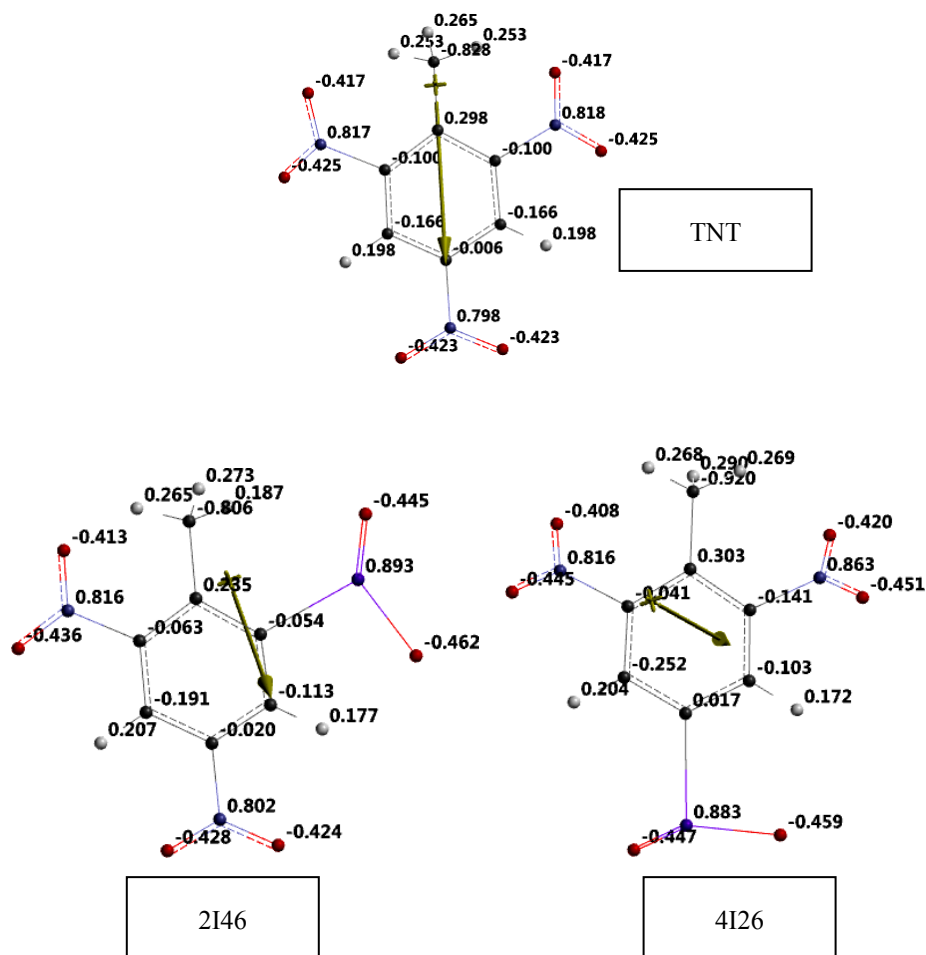


Figure 4. The ESP charges on atoms of the molecules considered.

Figure 5 shows the electrostatic potential maps of the isomers where the blue regions relatively stand for the most positive potential field and red ones, if exists any, the most negative ones. The iodyl group at 2- or 4-positions has negative partial charge on oxygens, somewhat balanced by partial positive charge on the iodine atom. On the other

hand, most of the ring carbons possess partial negative charges. Thus, the iodyl isomers are apt to internal (maybe also external) redox reactions which might be in the form of explosion if a suitable initiating stimulus happens.

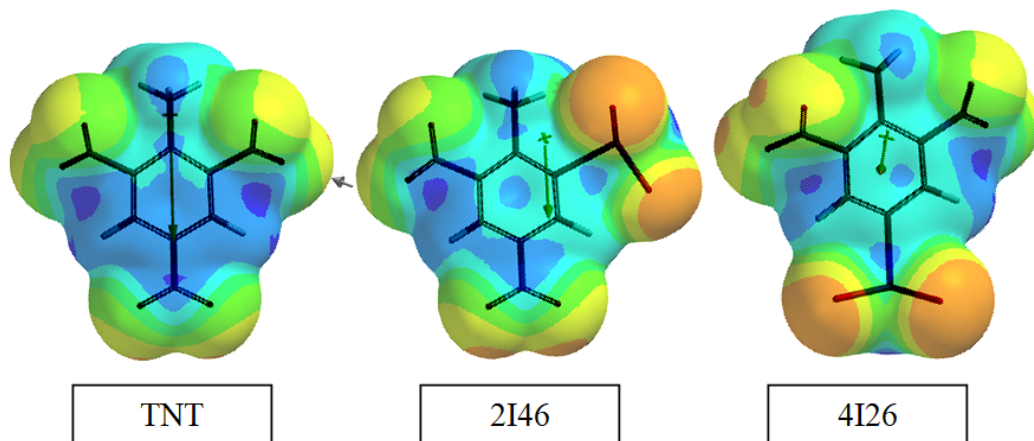


Figure 5. Electrostatic potential maps of the species considered.

Figure 6 shows the local ionization potential maps of TNT and the iodyl isomers presently 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.

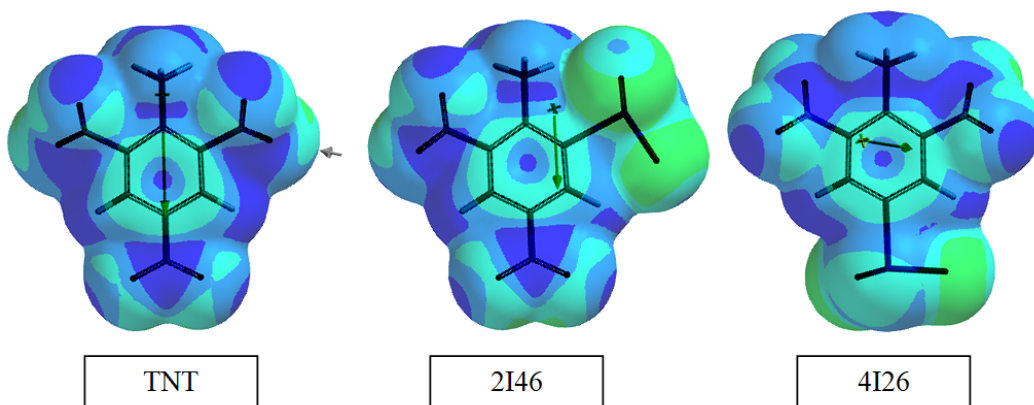


Figure 6. Local ionization potential maps of the species considered.

Figure 7 shows the LUMO maps of TNT and the iodyl isomers 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.

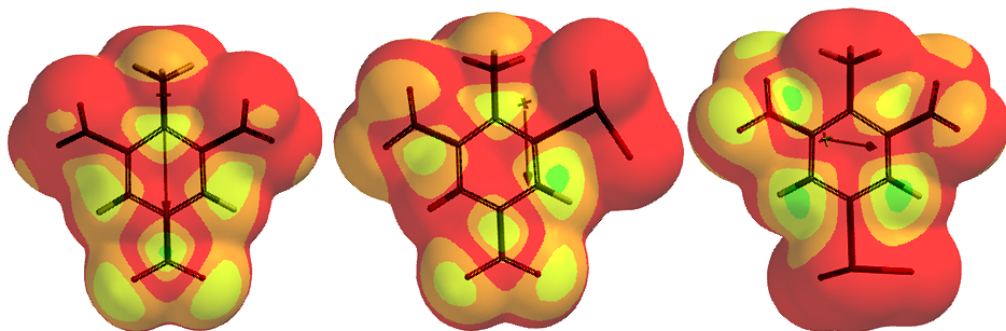


Figure 7. LUMO maps of the species considered.

Figure 8 shows some of the molecular orbital energy levels of the molecules considered. As seen in the figure, replacement of one nitro group of TNT by an iodanyl group lowers both the HOMO and LUMO energies (See also Table 4). Table 4 lists the HOMO, LUMO energies and $\Delta\epsilon$ ($\Delta\epsilon = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$) values of the structures presently considered.

Both of the HOMO and LUMO energies follow the order of TNT < 2I46 < 4I26. As seen in Figure 8, there exist a large energy gap between the HOMO and NextHOMO energies in the iodanyl isomers compared to TNT. Note that electron attracting groups lower both the HOMO and LUMO whereas conjugative groups raise the HOMO but lowers the LUMO energy levels [28]. Nitro groups have conjugative as well as electron attracting properties mesomerically and inductively. Also note that iodine atom is much bigger atom than carbon atom. Consequently, the conjugation of the atomic orbitals of iodine of the iodanyl group with the aromatic ring has to be much poorer compared to the nitro group. Also it is worthy to note that not only the size mismatch between the adjacent orbitals of atoms but also the twist angle between the aromatic ring and the substituent orbitals is important for conjugative effects to be influential. As seen in Figure 1 some of the substituents in the present structures are not completely coplanar with the ring, hence some resonance effects and inductive effect should be operating mutually (at different extents) to dictate the orbital energies of the structures considered. The nitro-iodanyl group replacement raises both the frontier molecular orbitals (the HOMO and LUMO orbitals) as if the iodanyl groups had been electron donating substituents but actually the effect arises because of abolition of the electron withdrawing effect of the nitro group by the replacement process. Thus, instead of narrowing of interfrontier molecular orbital energy gap, the nitro-iodanyl group replacement cannot decrease $\Delta\epsilon$ value by raising the HOMO and lowering the LUMO energy levels simply by conjugative

effects. As seen in Table 4, the data reveal that raising of both the frontier molecular orbitals at unequal extents as compared to TNT occurs. On the other hand, the interfrontier molecular orbital energy gap, $\Delta\varepsilon$, values follow the order of $2I46 < 4I26 < \text{TNT}$. Thus, 2I46 isomer should be more susceptible to impact stimulus than 4I26 and TNT, because there exists a reverse correlation between the impact sensitivity and $\Delta\varepsilon$ values [29,30].

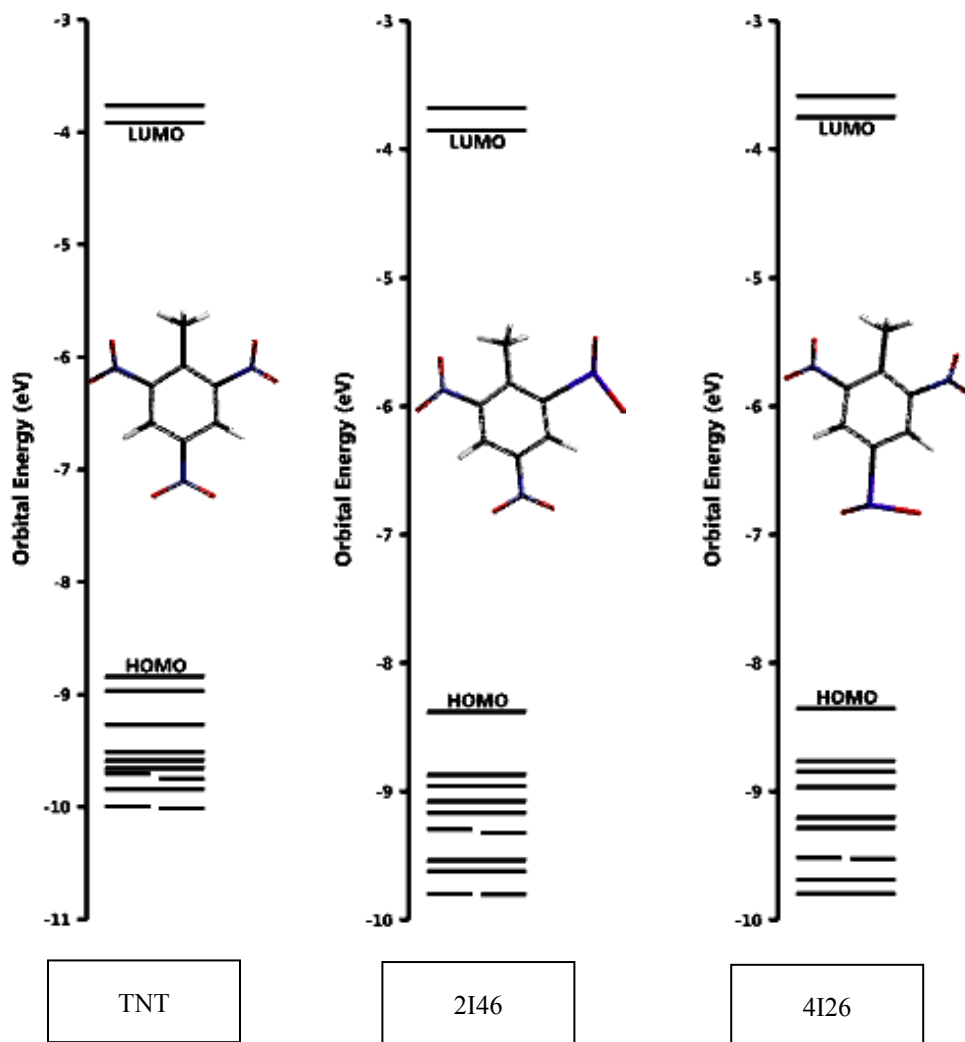


Figure 8. Some of the molecular orbital energy levels of the molecules considered.

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

Structure	HOMO	LUMO	$\Delta\varepsilon$
TNT	-853.17	-377.93	475.24
2I46	-808.32	-371.76	436.56
4I26	-805.87	-361.63	444.24

Energies in kJ/mol.

Figure 9 shows the calculated (time-dependent DFT, TDDFT) UV-VIS spectra of the molecules considered. All the three structures absorb in the UV region of the spectrum and exhibit very comparable absorption features.

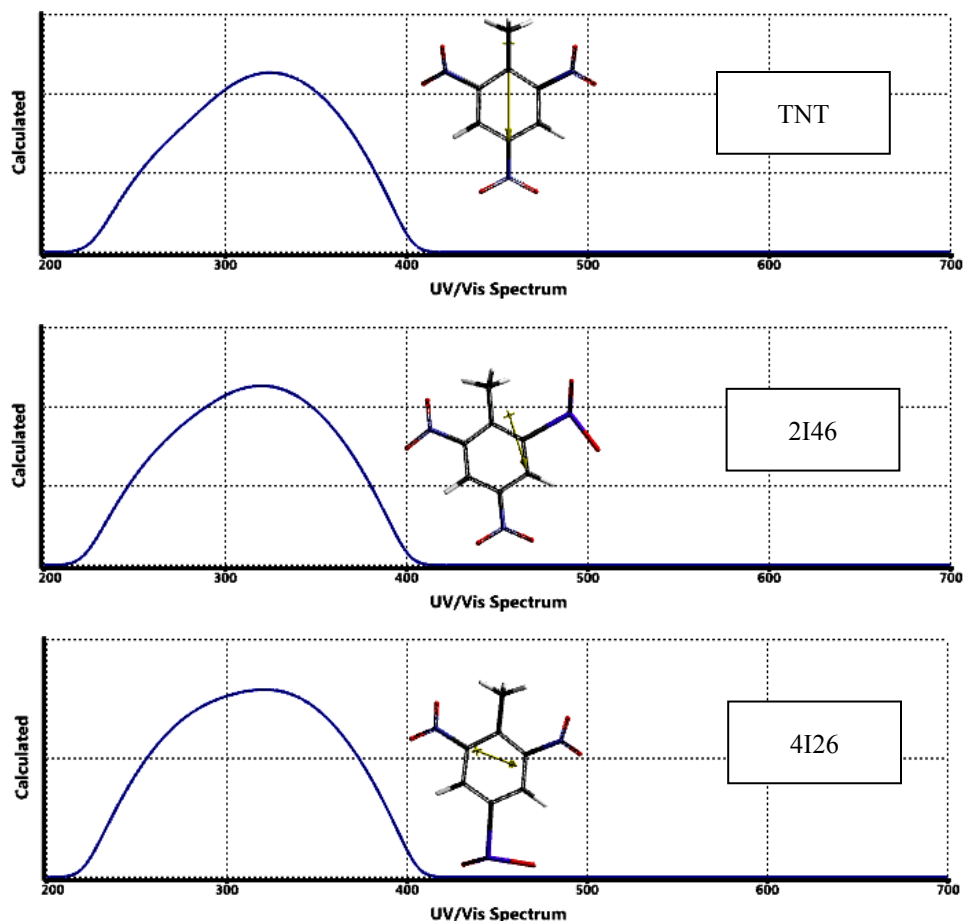
**Figure 9.** The calculated UV-VIS spectra of the molecules considered.

Figure 10 depicts the HOMO and LUMO patterns of the species considered. The HOMO of TNT shows that very little contribution comes from the nitro group occupying

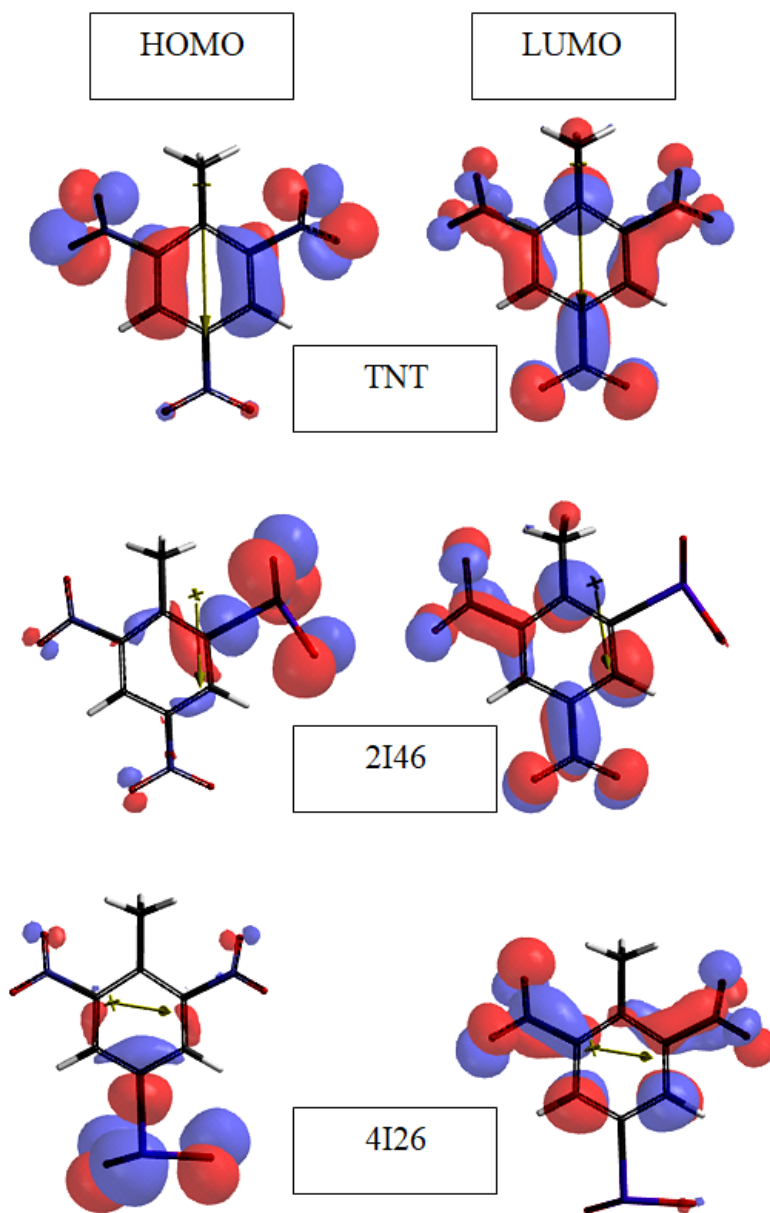


Figure 10 . The HOMO and LUMO patterns of the species considered.

4-position. This is also the case for 2I46 isomer but iodyl group contributes greatly in to the HOMO in both of the isomers. As seen in the figure iodyl group in both of the isomers possesses an anti-bonding interaction with the carbon atomic p-orbital. Also note that no contribution comes from the methyl group. As for the LUMO the nitro groups are in conjugation with the ring system in all the cases whereas the iodyl groups contributes almost nil to the LUMO in each iodyl isomer.

4. Conclusion

The present density functional treatment has indicated that the replacement of one of the nitro groups of TNT by an iodyl moiety should yield electronically and thermally stable iodyl isomers having higher dipole moments than TNT. The presence of iodyl substituent raises both of the frontier molecular orbital energies of the systems with respect to parent TNT molecule, while the interfrontier molecular orbital energy gap narrows which implies the iodyl isomers are to be more susceptible to impact stimulus than the TNT is.

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