

Effect of zinc on some dinitronaphthalenes – A DFT treatment

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Abstract

A mixture of 1,3-, 1,5-, and 1,8-dinitronaphthalenes is called Dinal and is used in explosive compositions such as Schneiderites. Presently, those isomers and their interaction with metallic zinc atoms are investigated within the constraints of density functional theory (DFT) at the level of B3LYP/6-31++G(d,p). Zinc and some similar metals are used to increase the heat effect of explosives in ammunitions. Various data have been collected including heats of formation and Gibbs free energy of formation values. Also, some structural and quantum chemical data have been collected and discussed, including bond densities and time dependent density functional UV-VIS spectra.

1. Introduction

Of various isomers of dinitronaphthalene, a mixture of 1,3-, 1,5-, and 1,8-dinitronaphthalenes is called Dinal or DN [1], which is used in explosive compositions especially in French explosive mixtures (Schneiderites) as fuel mixture with ammonium nitrate [2]. Dinal is a grey yellow powder.

Figure 1 shows the planar structures of the dinitronaphthalene (DNN) isomers of consideration which are employed for the perturbation molecular orbital discussion.

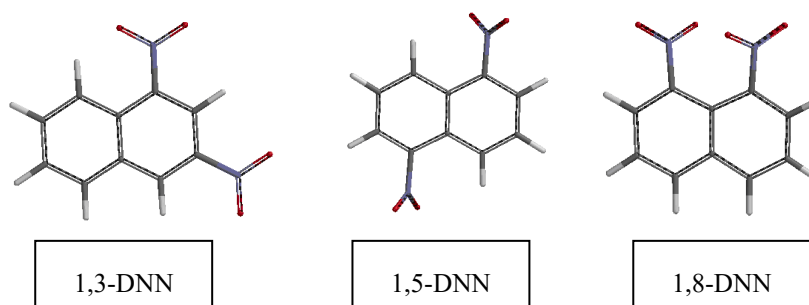


Figure 1. Structures of the DNN isomers of consideration.

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 [9-11]. 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/6-31++G(d,p) [12,13]. 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 [14]. The correlation

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term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [15] and Lee, Yang, Parr (LYP) correlation correction functional [16]. 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 cleavages occurred or not during the geometry optimization process. All these computations were performed by using SPARTAN 06 program [17].

3. Results and Discussion

Figure 2 shows isoconjugate alternant hydrocarbon [18,19] systems of the DNN species considered. They are even alternant systems of which 1,3- and 1,8-substituted ones for which $n^*-n^0 \geq 2$ are classified as non-Kekulé structures [18-20] inherently having some instability. The even alternant hydrocarbons have molecular orbital energy levels symmetrically distributed about the zero energy level [18,19]. The heteroatom substitution, depending on the position, lowers both the occupied and unoccupied energy levels at unequal extents. In real systems instability is removed, up to a certain extent by some bond distortions or removing the co-planarity (see Figure 3).

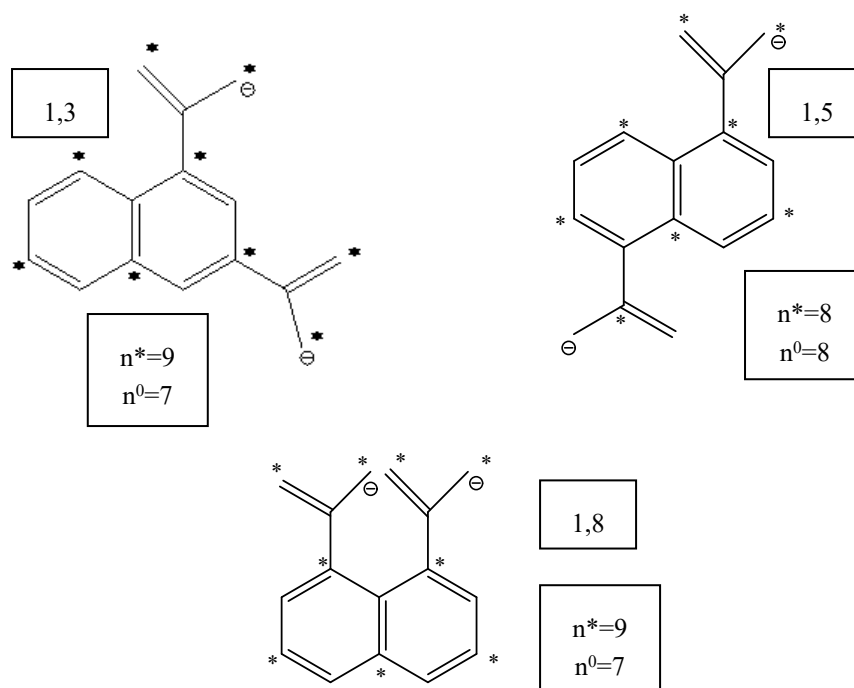
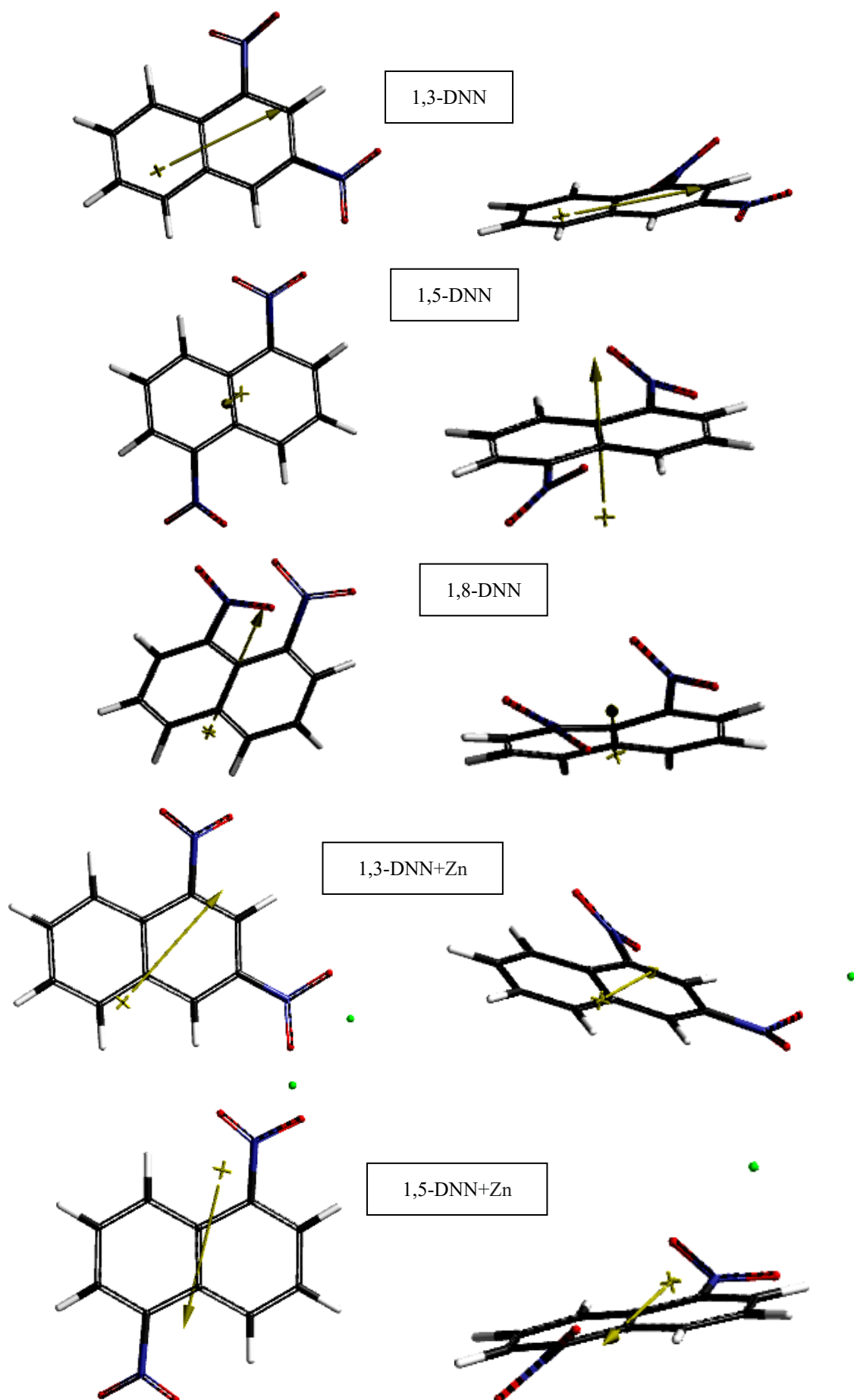


Figure 2. Isoconjugate alternant hydrocarbon systems of the DNN isomers considered.

Figure 3 shows the optimized structures, as well as the direction of the dipole moment vectors of the species of consideration. The arrows stand for the direction of calculated dipole moment vectors. Note that a resultant dipole moment vector of a molecule is the vectorial sum of the individual bond dipoles, thus location of the heteroatoms greatly affects both the magnitudes and the directions. Note the variation of the direction of the dipole moment vector depending on the location of the substituents and the zinc atom.



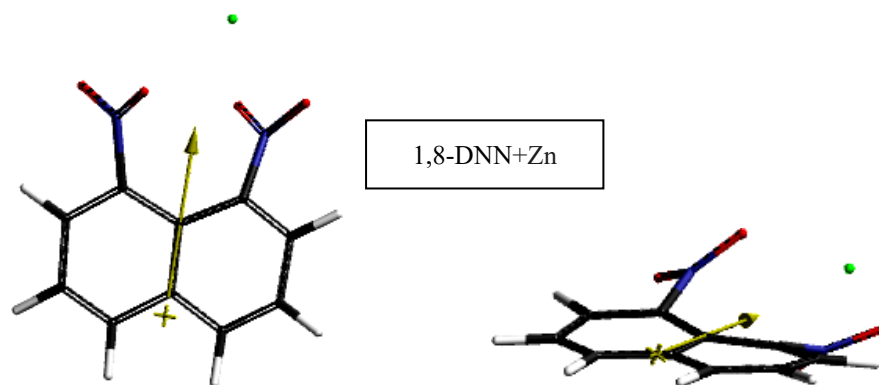


Figure 3. Optimized structures of the DNN and DNN+Zn species of consideration (two different views).

Table 1 shows some standard thermo chemical properties of the structures considered. The absolute value of orders of H° and G° values are $1,8\text{-DNN+Zn} < 1,5\text{-DNN+Zn} < 1,3\text{-DNN+Zn}$. They are all isomeric structures thus the variation observed should be due to overall topological factors (gross and fine) operating on the systems of consideration.

Table 1. Some thermo chemical properties of the structures considered.

Species	H°	S° (J/mol $^\circ$)	G°
1,3-DNN	-2086648.15	0.463	-2086786.35
1,5-DNN	-2086656.34	423.72	-2086782.67
1,8-DNN	-2086613.23	0.453	-2086748.24
1,3-DNN+Zn	-6757780.165	457.73	-6757916.640
1,5-DNN+Zn	-6757770.188	456.07	-6757906.164
1,8-DNN+Zn	-6757760.159	453.82	-6757895.452

Energies in kJ/mol.

Some energies of the structures considered are included in Table 2, 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 data, all the structures are electronically stable. The order of stabilities are $1,3\text{-DNN+Zn} > 1,5\text{-DNN+Zn} > 1,8\text{-DNN+Zn}$.

Table 2. Some energies of the structures considered.

Species	E	ZPE	E_c
1,3-DNN	-2087081.48	399.18	-2086682.30
1,5-DNN	-2087066.65	399.55	-2086667.10
1,8-DNN	-2087045.99	398.99	-2086646.99
1,3-DNN+Zn	-6758150.40	398.83	-6757751.57
1,5-DNN+Zn	-6758141.17	399.64	-6757741.53
1,8-DNN+Zn	-6758129.58	397.91	-6757731.67

Energies in kJ/mol.

Table 3 lists the calculated heat of formation values. T1 has been developed to closely reproduce heats of formation calculated from G3(MP2) [17]. It replaces the large basis set MP2 calculation by a dual basis set RI-MP2 calculation and replace QCIS(T) calculation and the vibrational frequency calculation by an empirical correction based on atom and bond counts. T1 is limited to closed shell uncharged molecules comprised of common atoms only [17].

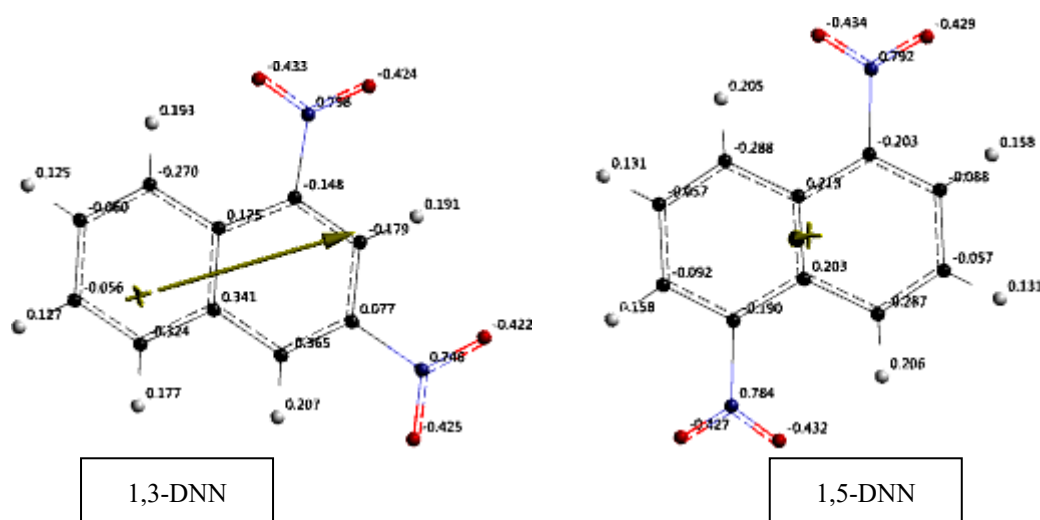
Table 3. Calculated heat of formation values.

Species	Enthalpy of formation [2]	T1	PM3//B3LYP/6-31++G(d,p)
1,3-DNN	-	128.04	148.485
1,5-DNN	140.0 (3031)	136.04	164.524
1,8-DNN	172.6 (3064)	145.72	185.259
1,3-DNN+Zn	-	-	289.656
1,5-DNN+Zn	-	-	314.756
1,8-DNN+Zn	-	-	356.431

Energies in kJ/mol. T1 calculations failed for Zn containing species. Enthalpy of formations in kJ/kg. Energy of explosions are in parenthesis and kJ/Kg.

The order is 1,8-DNN+Zn>1,5-DNN+Zn>1,3-DNN+Zn. Experimental values follow the order of 1,8-DNN>1,5-DNN for energy of formation, enthalpy of formation and energy of explosion (all positive).

Figure 4 displays the ESP charges on the atoms of the structures considered. 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 [17,21]. Figure 4 shows that in each case, the zinc atom acquires some positive partial charge, q , which is less than 0.6 esu [17].



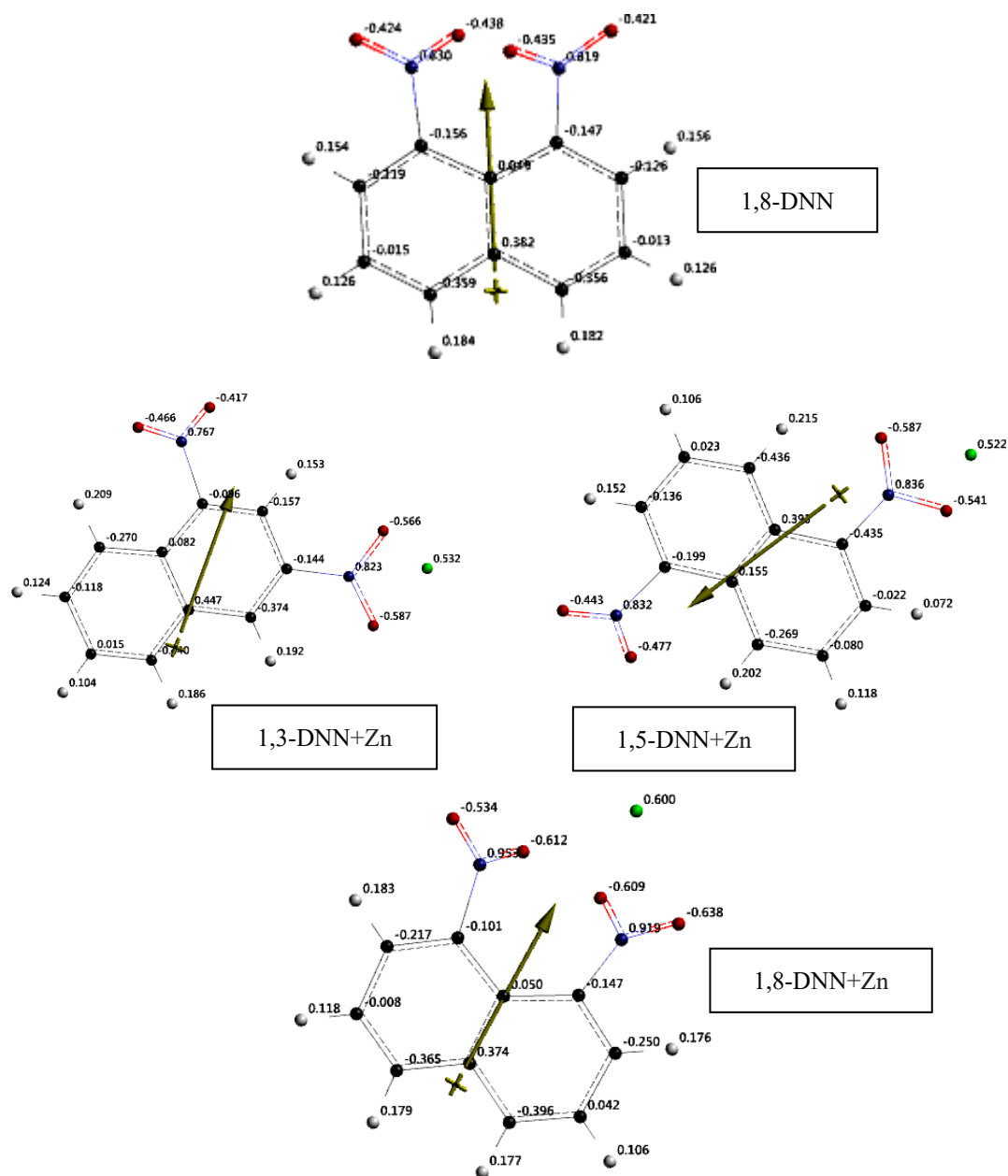
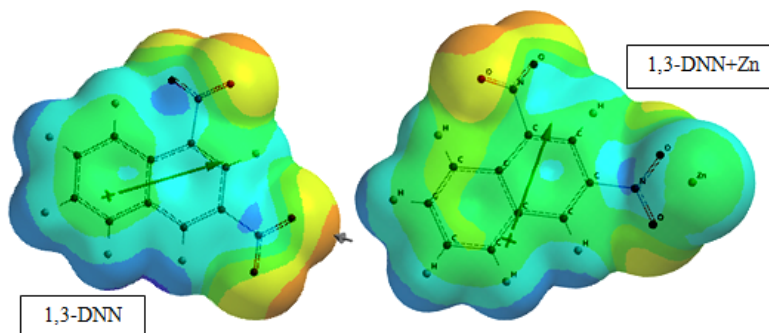


Figure 4. ESP charges on atoms of DNN and DNN+Zn species of consideration.

Figure 5 displays the electrostatic potential maps of the species presently considered. Note that electro static potential is the energy of interaction of a positive charge with the nuclei and fixed electron distribution of a molecule [17,21]. In an electrostatic potential map negative potential regions reside on red/reddish and positive ones on blue/bluish parts of the maps.



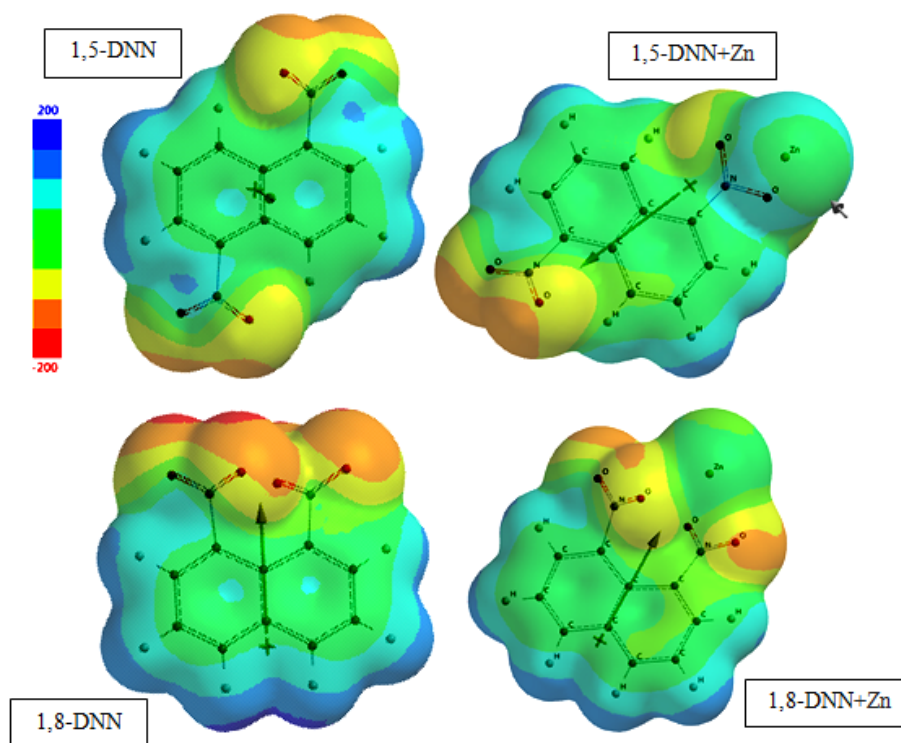
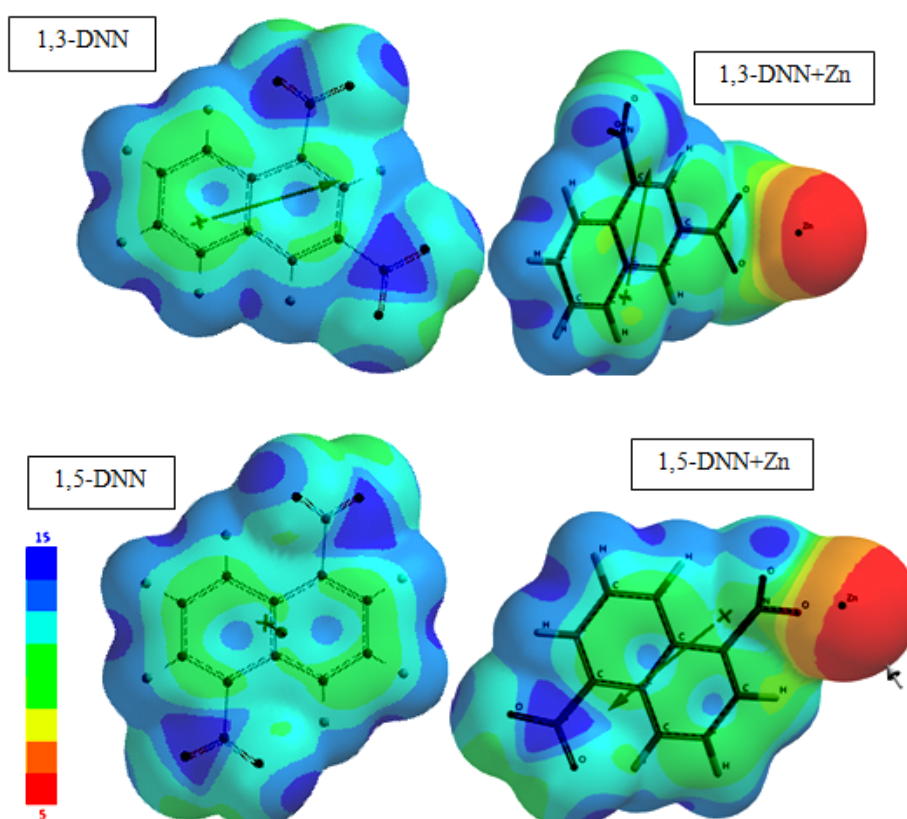


Figure 5. Electrostatic potential maps of DNN and DNN+Zn species of consideration.

The local ionization potential maps of the species presently considered are shown in Figure 6. The local ionization potential is a measure of the relative ease of electron removal (ionization) as a function of



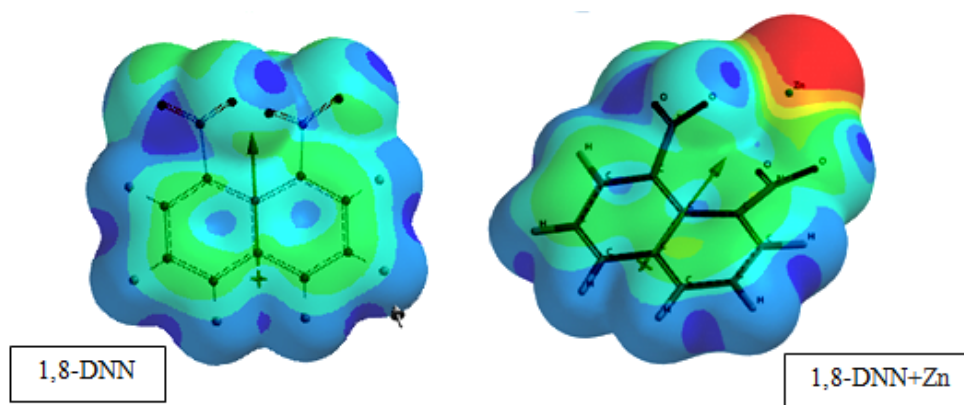
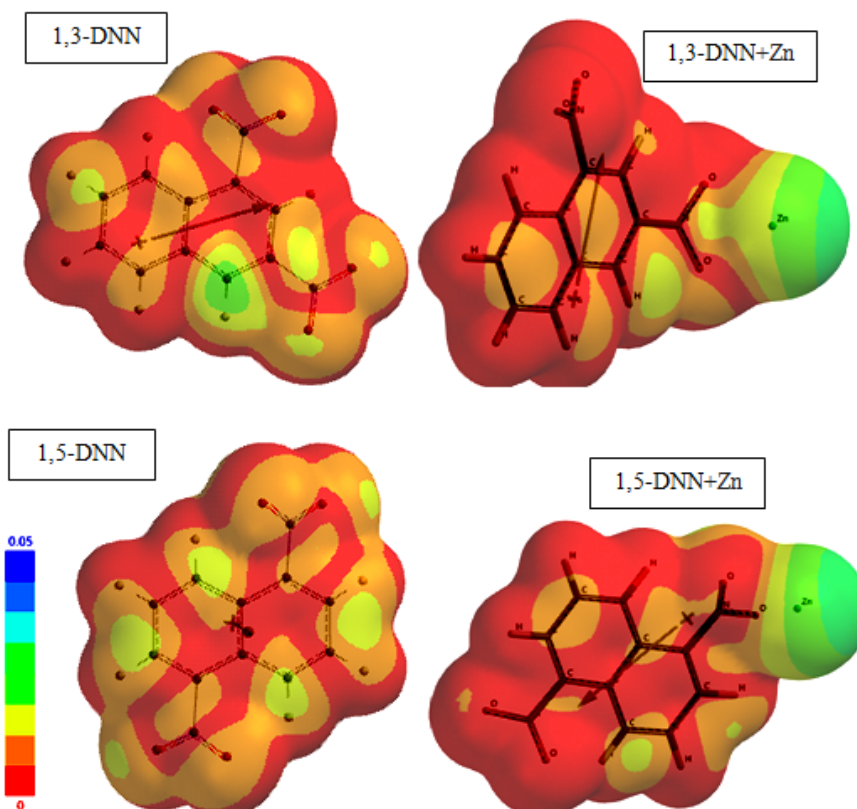


Figure 6. Local ionization potential maps of DNN and DNN+Zn species of consideration.

localization [17,21]. The local ionization potential shows the local ionization potential maps of the species 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. Note that the local ionization potential map is a graph of the value of the local ionization potential on an isodensity surface corresponding to a van der Waals surface [17,21].

Figure 7 stands for the LUMO maps of the DNN+Zn species of consideration. Note that LUMO maps display 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 whereas the red colored region, the minimum value. It is to be noted that the LUMO and NEXTLUMO (LUMO+1) are the major orbitals directing the molecule towards the attack of nucleophiles [17,21]. Positions where the greatest LUMO coefficient exists is the most vulnerable site in nucleophilic reactions.



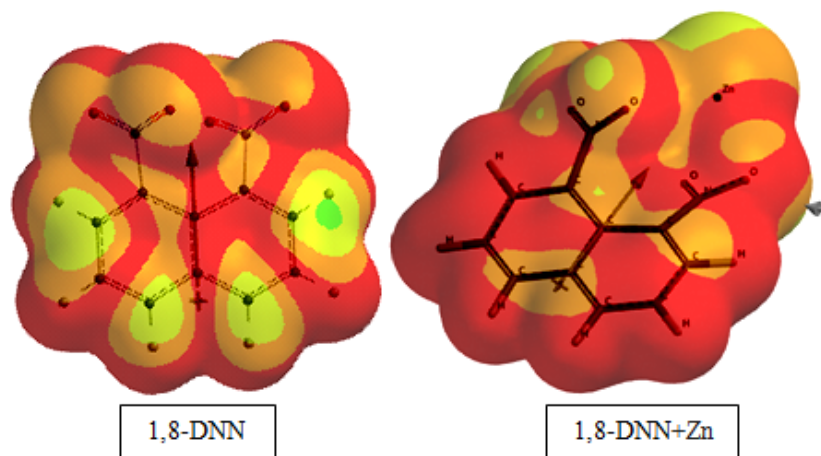


Figure 7. The LUMO maps of DNN and DNN+Zn species of consideration.

Figure 8 stands for the bond density maps of the species considered. The bond density contains fewer electrons in total and demarks atomic connectivity. The figure reveals that the bond density between the zinc and DNN moiety is nil within the restrictions of the presently adopted level of calculations.

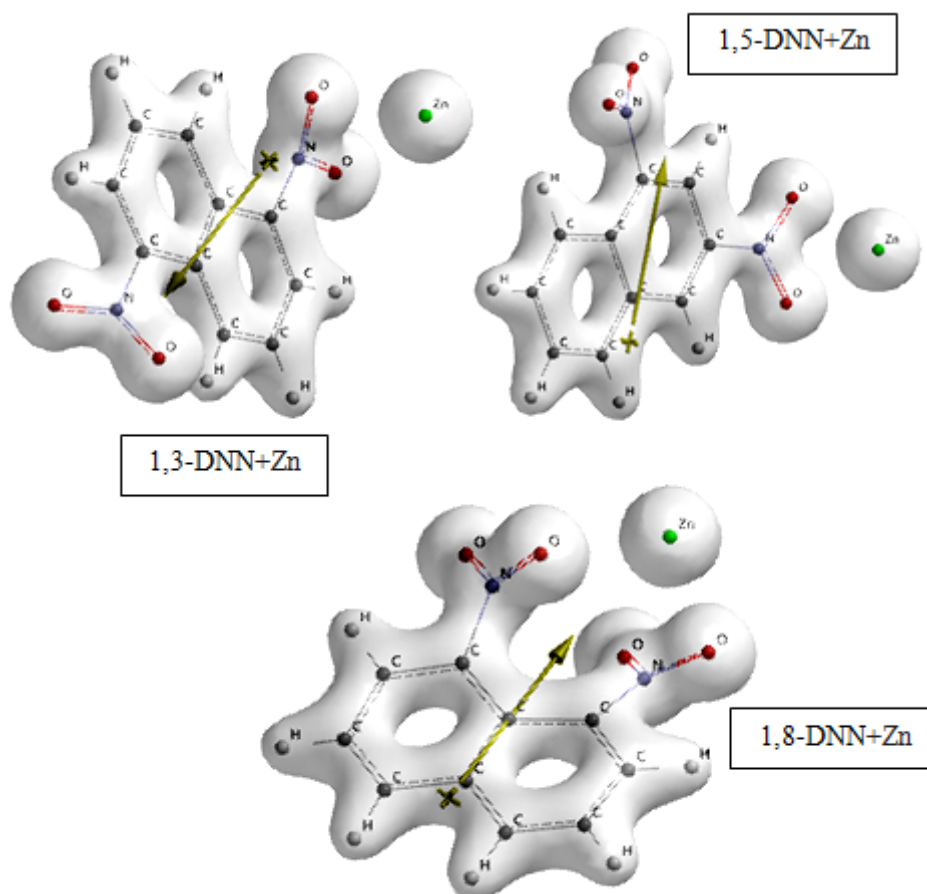


Figure 8. Bond density maps of the DNN+Zn species of consideration.

Figure 9 shows some of the molecular orbital energy levels of the DNN+Zn species of consideration and Table 4 lists the HOMO,LUMO energies and $\Delta\epsilon$ values where $\Delta\epsilon$ values are the frontier molecular orbital energy gap ($\Delta\epsilon = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$) values of the DNN+Zn species of consideration.

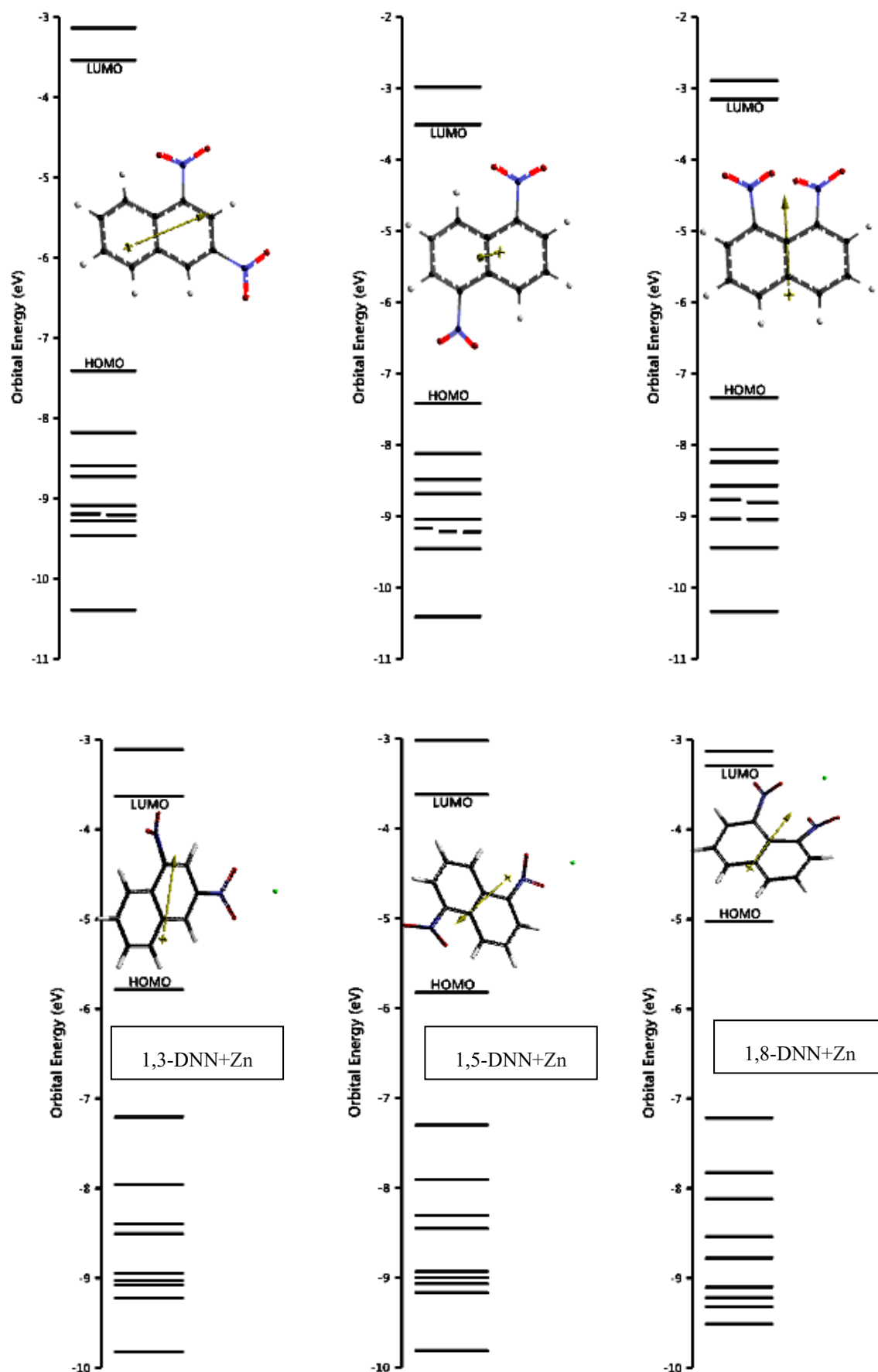


Figure 9. Some of the molecular orbital energy levels of DNN and DNN+Zn species of consideration.

Table 4. The HOMO,LUMO energies and $\Delta\epsilon$ values of the DNN+Zn species of considered.

Species	HOMO	LUMO	$\Delta\epsilon$
1,3-DNN	-715.18	-341.83	373.35
1,5-DNN	-715.63	-338.93	376.7
1,8-DNN	-708.12	-304.36	403.76
1,3-DNN+Zn	-558.12	-350.28	207.84
1,5-DNN+Zn	-561.95	-349.38	212.57
1,8-DNN+Zn	-484.86	-317.57	167.29

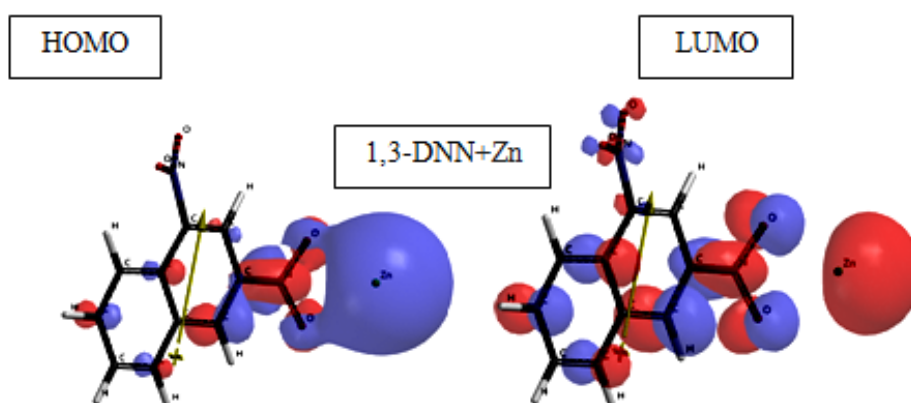
Energies in kJ/mol.

The algebraic order of the HOMO energies for DNN and zinc containing species are the same namely, 1,8-DNN+Zn>1,3-DNN+Zn>1,5-DNN+Zn. As for the LUMO energies, for DNN and zinc containing species are the same and the order becomes, 1,8-DNN+Zn>1,5-DNN+Zn>1,3-DNN+Zn. Consequently, the order for $\Delta\epsilon$ values turns out to be 1,8-DNN>1,5-DNN>1,3-DNN and 1,5-DNN+Zn>1,3-DNN+Zn>1,8-DNN+Zn.

On the other hand, any ballistic property which correlates with the narrowness of the interfrontier energy gap ($\Delta\epsilon$ value) should have the highest of that property value among the isomers considered. An example is the impact sensitivity, that is narrower the gap, the explosive becomes more sensitive to an impact stimulus [22-26].

DNN isomers have some explosive potential [2]. The energy of explosion values of 1.5- and 1.8-DNN are 3031 kJ/kg and 3064 kJ/kg, respectively [2]. Note that 1.8-DNN possesses a non-Kekulé isoconjugate in contrast to its isomer 1,5-DNN. The $\Delta\epsilon$ order for DNN isomers consider is 1,8-DNN>1,5-DNN>1,3-DNN. As a conjecture 1,3-DNN should have the least explosion energy. Zinc and some other metals are usually common additives to ammunitions to increase their energy output. In that respect, 1,8-DNN+Zn is expected to be the most and 1,3-DNN+Zn the least energetic isomeric explosives, Note that the order of $\Delta\epsilon$ values for them fallow the order of 1,5-DNN+Zn>1,3-DNN+Zn>1,8-DNN+Zn and reverse order is followed for explosive character. but comparatively less to the LUMO.

Figure 10 shows the HOMO and LUMO patterns of DNN+Zn species considered. They generally possess π -symmetry. In each case, zinc atom contributes to the HOMO.



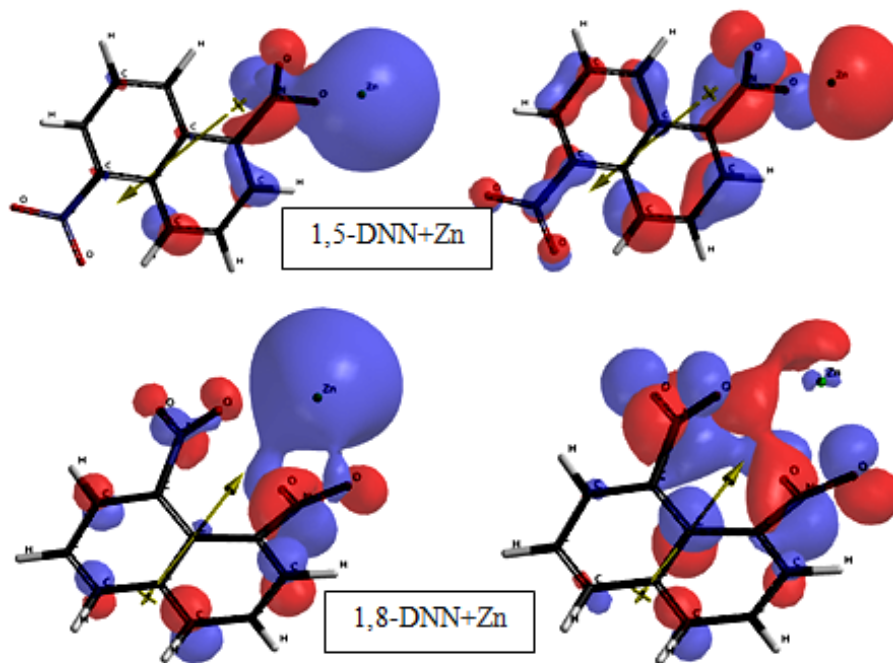
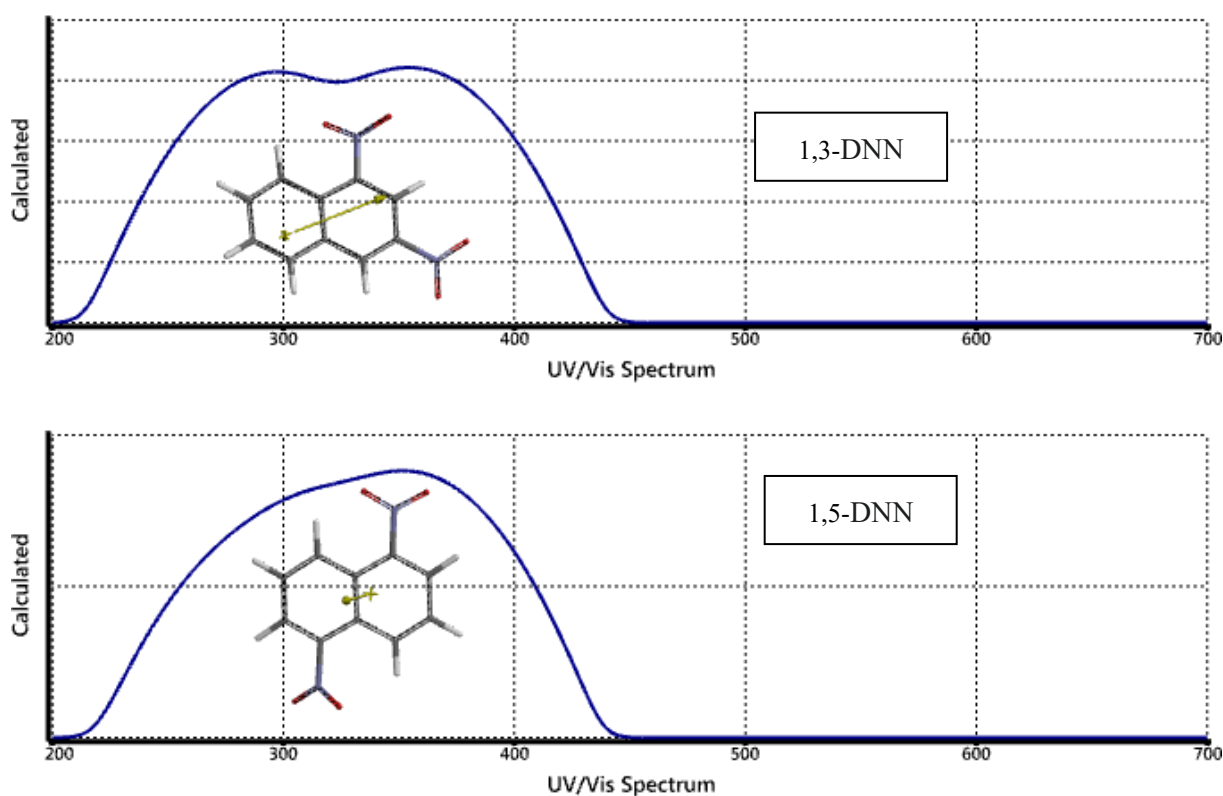


Figure 10. The HOMO and LUMO patterns of the species of considerations.

Figure 11 shows the UV-VIS (time dependent density functional, TDDFT) spectrums of the species considered. The spectrums cover large part of the ultraviolet and visible regions of the spectrum.



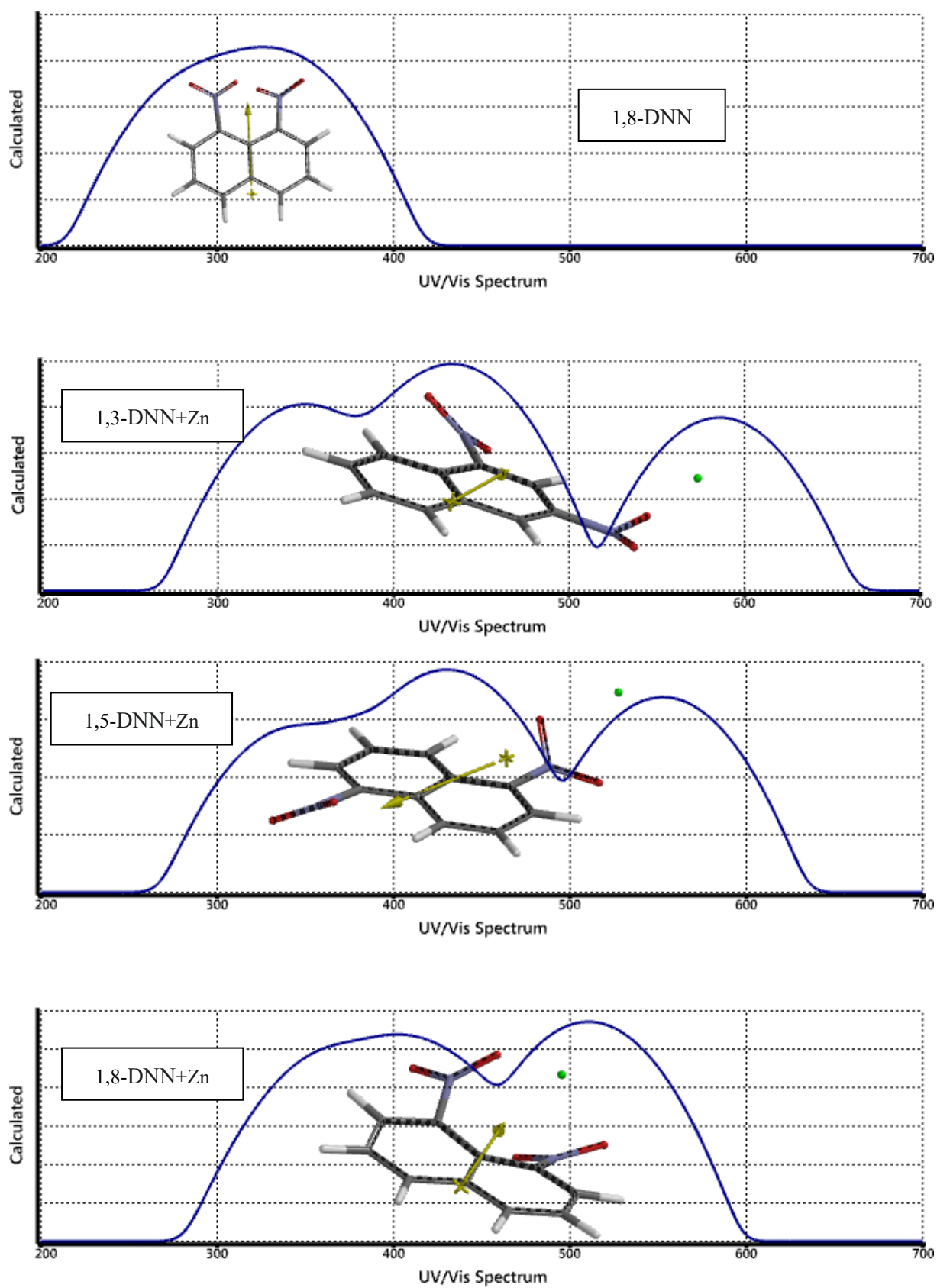


Figure 11. TDDFT spectra of DNN and DNN+Zn species of consideration.

Table 5 lists the $\lambda_{\max}$ values and intensities of peaks of the spectrums of species of interest. The calculated intensities of the peaks are related to magnitudes of the transition moments between the orbitals involved which vary from one isomeric structure to the other [4,38].

Table 5. The $\lambda_{\max}$ values and intensities of the peaks of the spectrums of species of interest.

Species	$\lambda_{\max}$ (nm)
1,3-DNN	297.19 (0.007), 341.72 (0.029), 358.17 (0.091)
1,5-DNN	325.35 (0.045), 354.28 (0.179)
1,8-DNN	315.12 (0.056), 332.42 (0.084)
1,3-DNN+Zn	357.30 (0.001), 395.70 (0.025), 433.33 (0.827), 585.86 (0.033)
1,5-DNN+Zn	0.362.70 (0.001), 384.90 (0.033), 430.46 (0.623), 552.74 (0.120)
1,8-DNN+Zn	369.63 (0.105), 402.48 (0.202), 423.46 (0.050)

Intensities are in parenthesis.

Table 6 lists some properties of the structures considered. 1,8-DNN and 1,8-DNN+Zn have the highest dipole moment within the groups, whereas the lowest ones are associated with 1,5-DNN and 1,5-DNN+Zn. The dipole moment is dependent of gross and fine topology of the structure. Note that 1,5-DNN structure is isoconjugate with a Kekule whereas the others are non-Kekulé structures.

Table 6. Some properties of the structures considered.

Species	Dipole (debye)	E _{aq} (kJ/mol)	Log P	Polarizability	C _v (J/mol ^o)
1,3-DNN	6.27	-2087094.01	3.10	56.16	149.65
1,5-DNN	0.26	-2087079.21	3.10	56.13	149.61
1,8-DNN	8.66	-2087086.82	3.10	56.10	149.89
1,3-DNN+Zn	4.76	-	-	57.17	163.63
1,5-DNN+Zn	2.42	-	-	57.13	163.39
1,8-DNN+Zn	6.09	-	-	57.27	164.44

Polarizabilities in 10⁻³⁰ m³ units.

4. Conclusion

Three of the isomers of DNN and their interaction with metallic zinc (1:1 mol ratio) have been subjected to DFT treatment at the level of B3LYP/6-31++G(d,p). Heats of formation and Gibbs energy of formation values have been calculated performing various methods. Optimized structures indicate that in all the species considered, nitro group are not coplanar with the aromatic kernel of them. The direction of dipole moments are dictated by the topology of nitro groups in DNN species whereas in DNN+Zn species also localization of the zinc atom is effective which acquires some positive partial charge. Most of the properties of these species, including molecular orbital energy values and UV-Vis spectra are overall topology dependent.

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