Neutral and Charged Nitrophenyl-N-methylnitramines - A DFT Treatment

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Abstract

In the present density functional study neutral and positively charged (mono and dication forms) nitrophenyl-N-methylnitramines have been considered within the constraints of the theory and the basis set employed. Depending on the closed and open-shell nature of the systems considered, B3LYP/6-31++G(d,p) and UB3LYP/6-31++G(d,p) level of theories have been adopted, respectively. Some quantum chemical properties of those neutral and cationic systems have been obtained and discussed. The neutral and monocation systems are found to have exothermic heat of formation values and favorable Gibbs free energy of formations at the standard state. All the neutral systems and the monocations, except just one case, are electronically stable. In the *ortho* monocation case nitramine group decomposes by releasing the nitro moiety. Whereas, all the dication systems considered undergo similar type decomposition. In all the neutral systems, the nitro group of nitramine moiety possesses some minute negative partial charge, but in the monocation systems it has some positive partial charge (decomposed or not). In contrast, the dication forms, release nitramine NO_2 moiety which carries positive formal charge.

1. Introduction

Nitramines (also known as nitroamines) are compounds of the chemical form $R_1R_2N\text{-}NO_2$. The category of nitramines encompasses a wide range of substances depending on the characteristics of R_1 and R_2. An area of increasing policy interest relative to nitramines regards nitramine explosives. Various aspects of nitramines have been investigated through years [1-18].

Tetryl which is a nitramine type energetic material was frequently used as the primary and secondary charges of blasting caps [16]. Some DFT calculations have revealed that when it is exposed to α-particles, Tetryl decomposes by emanating NO_2 group from the methylnitramine moiety it possesses [17]. Whereas primary cosmic rays (which are mostly protons) causes elimination of hydrogen molecule from methyl group of Tetryl and in the case of protonated form of nitramine amino group, Tetryl expels nitronium ion from the nitramine moiety [18]. In order to investigate the process further, (investigating effect of charging some related molecules) presently an approach has been adopted, namely starting from the simplest case that is no other body present in the vicinity of the molecule of interest. Therefore, o-, m-, and p-mononitrophenylmethylnitramines (which are embedded in Tetryl structure) have been considered in the neutral, mono and dication forms.

2. Method of Calculations

In the DFT study of presently considered nitrophenyl-N-methylnitramines, all the initial geometry optimizations of the mono and dications leading to energy minima have been achieved by using molecular mechanics (MM2) method then the structures were subjected to semi empirical PM3 self consistent fields molecular orbital (SCF MO) method [19,20] at the restricted or unrestricted level [21] depending on the spin state of the cations. Afterwards, the structure optimizations have been managed within the framework of Hartree-Fock (HF) and finally by using density functional theory (DFT) at the level of UB3LYP/6-31++G(d,p) for the monocations (doublet state) and B3LYP/6-31++G(d,p) for the dications (singlet state) [22,23]. 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 [24]. Also note that the correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [25] and Lee, Yang, Parr (LYP) correlation correction functional [26]. In the present treatment, 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 each structure 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 have occurred or not during the geometry optimization process. All these computations were performed by using SPARTAN 06 program [27].

3. Results and Discussion

In the present study, firstly *ortho*, *meta* and *para* nitro-substituted phenyl-N-methylnitramines and then their mono and dication forms are considered. Thus, the study enlightens some facts about electrostatic charging of the molecules under consideration. Note that those positions mentioned above are defined regarding the nitramine moiety as the main substituent. Figure 1 shows optimized structures of neutral forms of the nitramines considered. The figure also shows the direction of the dipole moment vectors. In the figure, *meta* and *meta C* stand for two different conformers which are energetically close to each other.
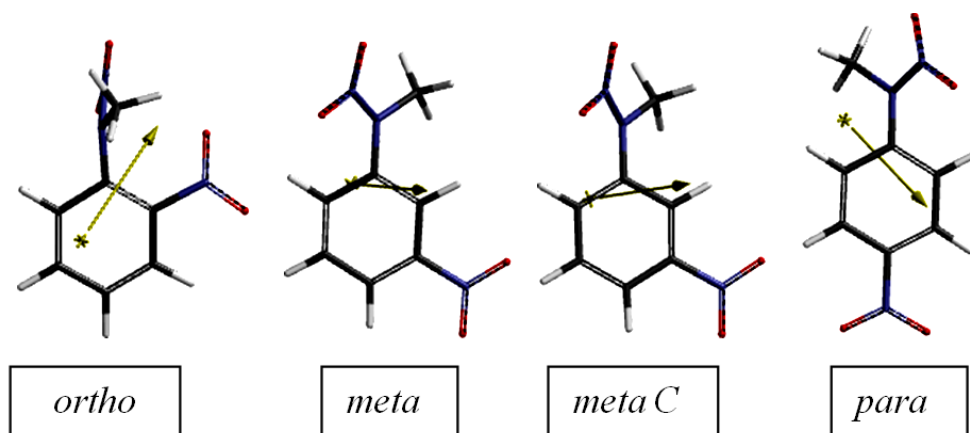

Figure 1. Optimized structures of neutral forms of the nitramines considered.

In the optimized structures, the o,m and p- nitro groups are coplanar or almost coplanar with the phenyl group whereas the nitramine group possesses certain twist angle with the phenyl group therefore conjugative effects vary from structure to structure. Thus, they affect various properties of these structures.

Table 1 shows some thermo chemical properties of the neutral compounds considered. They all have exothermic heat of formation values (H°) and favorable Gibbs free energy of formations (G°) at the standard state. The algebraic orders of H° and G° values are *meta C< para< meta< ortho* and *meta C< meta< para< ortho,* respectively.

Table 1. Some thermo chemical properties of the neutral compounds considered.

Structure	H°	S° (J/mol°)	G°
ortho	-1931763.463	417.06	-1931887.811
meta	-1931783.979	419.83	-1931909.154
meta C	-1931784.352	420.01	-1931909.579
para	-1931784.218	418.50	-1931908.996

Energies in kJ/mol. For structures see Figure 1.

Table 2 shows some energies of the neutral compounds considered. In the table, 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 the neutral structures are electronically stable and following the algebraic order of E_C values of *meta C< para< meta< ortho*. Thus, electronically *meta C* is the most stable whereas *ortho* is the least stable structures in the group. The electronic effects and the steric crowdinning might be the reason for relatively less stable nature of the *ortho* isomer. Note that it possesses the least negative G° value, thus standing for the less favorable isomer in the group (Table 1).

Table 2. Some energies of the neutral compounds considered.

Structure	E	ZPE	E_C
ortho	-1932168.56	393.34	-1931775.22
meta	-1932189.53	393.80	-1931795.73
meta C	-1932189.58	393.47	-1931796.11
para	-1932190.08	394.17	-1931795.91

Energies in kJ/mol. For structures see Figure 1.

The optimized structures of monocations of the nitramines presently considered are depicted in Figure 2. Whereas the optimized structures of dications are shown in Figure 3. In each figure also direction of the dipole moment vectors are displayed. The head of the vector in each case is towards the phenyl nitro group.

In Figure 2, structures having compound-label with "C" stand for different conformers of the nitramine group of *ortho* and *meta* isomers. However, their associated initial structures prior to the optimization had possessed the *ortho* or *meta* NO₂ moiety at the other *ortho* or *meta* position with respect to the nitramine NO₂ group. During the optimization, those initial structures conformationally arranged themselves around the nitramine group turning into the final structures labeled as "*ortho C*" or "*meta C*". It is to be emphasized that during the optimization, the *ortho* isomer decomposed by releasing the nitramine NO₂ moiety which has the total overall charge of 0.435 esu.
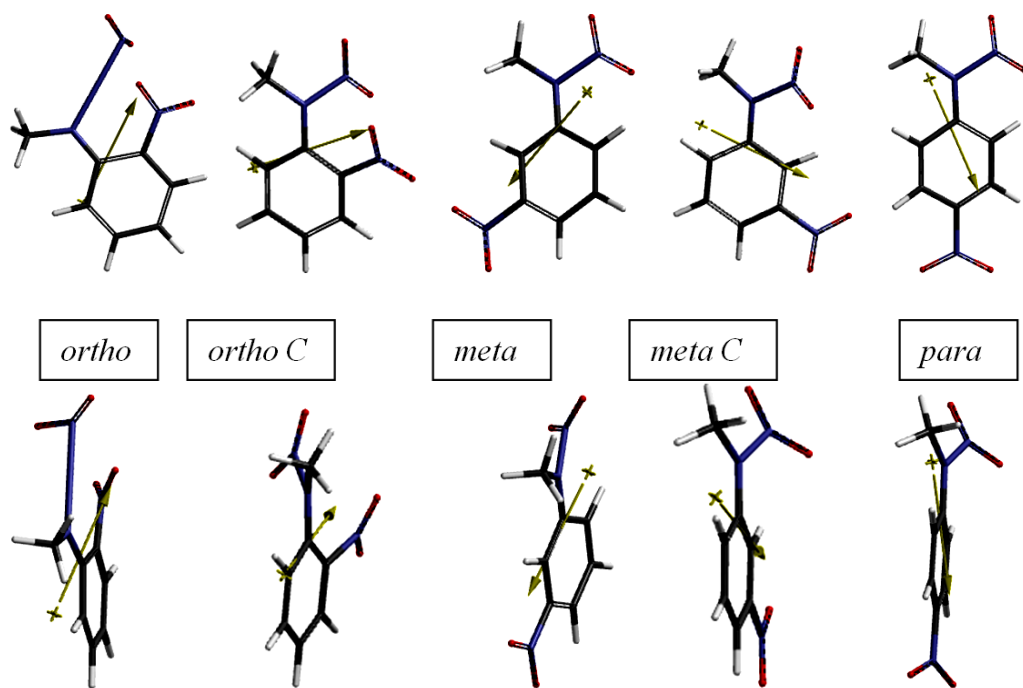

| ortho | ortho C | meta | meta C | para |

Figure 2. Optimized structures (top and side views) of monocations of the nitramines considered.

In the monocation case, optimized structures indicate that the o-, m- and p- nitro groups are coplanar or almost coplanar with the phenyl group whereas the nitramine group possesses certain twist angle with the phenyl group like the case in neutral forms.

Table 3 lists some thermo chemical properties of the monocations considered. The data reveal that H° and G° values of the monocation systems follow the same (algebraic) order of *meta< meta C< para< ortho C< ortho*.

Table 3. Some thermo chemical properties of the monocations considered.

Structure	H°	S° (J/mol°)	G°
ortho	-1930842.599	431.20	-1930971.161
ortho C	-1930905.801	424.30	-1931032.307
meta	-1930926.199	425.46	-1931053.049
meta C	-1930924.87	425.20	-1931051.644
para	-1930922.274	425.62	-1931049.173

Energies in kJ/mol. For structures see Figure 2.

Whereas as seen in Table 4, "*ortho C*" system is electronically more stable than the system entitled "*ortho*". However, note that "*ortho*" stands for a decomposed structure. As for the "*meta*" and "*meta C*", the former one is more stable electronically. The relative order of E_C values of the monocation systems considered follow the same order of G° values.

Table 4. Some energies of the monocations considered.

Structure	E	ZPE	E_C
ortho	-1931239.29	383.01	-1930856.28
ortho C	-1931306.85	388.18	-1930918.67
meta	-1931327.99	389.11	-1930938.88
meta C	-1931326.74	389.16	-1930937.58
para	-1931323.86	388.85	-1930935.01

Energies in kJ/mol. For structures see Figure 2.

Figure 3 shows the optimized structures of dications of the nitramines considered. In the figure, structures labeled "*meta* R1" and "*meta* R2" were initially constructed as different conformers of the nitramine group which during the optimization turned into the final decomposed systems shown in Figure 3. As seen in the figure the nitramines considered are all decomposed in the dication form by expelling a NO_2 moiety. The overall charge of the departing NO_2 moieties are 0.959, 1.001, 1.000, 1.001, respectively. So the tendency of NO_2 moiety is to leave the molecule as a nitronium ion when the

molecule is in the dication form. The adjacent nitrogen atoms possess the electrostatic charges of -0.254, -0.295, -0.319 and -0.315, respectively for the *ortho*, *meta* R1, *meta* R2 and *para* isomers.
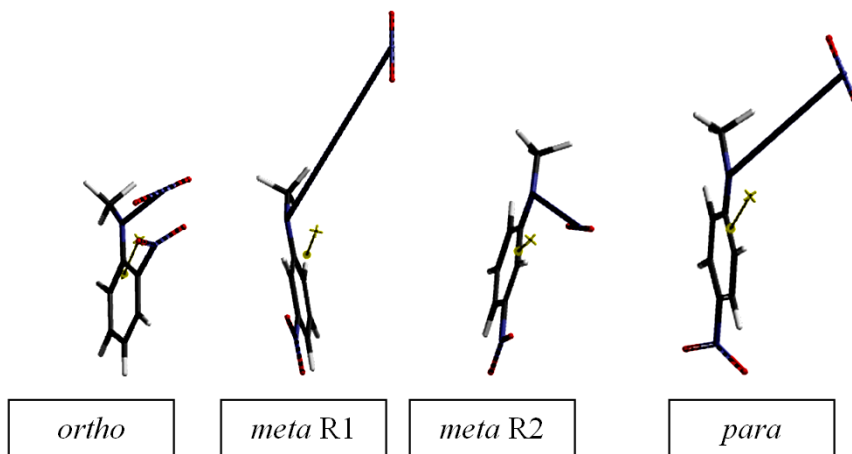

| *ortho* | *meta* R1 | *meta* R2 | *para* |

Figure 3. Optimized structures of dications (side views) of the nitramines considered.

The optimized structures of dications reveal that in the cases of *ortho* and *para* systems ring -NO_2 group has a certain twist angle with the ring but it is coplanar in *meta* R1 and *meta* R2 cases. On the other hand, the nitramine group in these systems is coplanar with the phenyl ring but N-NO_2 bond has a certain twist angle.

Table 5 lists some thermo chemical properties of the dication systems considered. Note that they all stand for decomposed structures. The final systems are characterized with negative H^o and G^o values. Table 6 contains E, ZPE and E_C values of the decomposed dication systems considered which possess the order of E_C values (algebraic) as *meta* R1< *meta* R2< *para*< *ortho*.

Table 5. Some thermo chemical properties of the dications considered.

Structure	H^o	S^o (J/mol^o)	G^o
ortho	-1929745.358	441.33	-1929876.941
meta R1	-1929869.217	469.62	-1930009.236
meta R2	-1929837.664	459.35	-1929974.619
para	-1929831.347	460.76	-1929968.725

Energies in kJ/mol. For structures see Figure 3.

Table 6. Some energies of the decomposed dication systems considered.

Structure	E	ZPE	E_C
ortho	-1930143.51	383.64	-1929759.87
meta R1	-1930266.94	383.57	-1929883.37
meta R2	-1930235.48	383.68	-1929851.80
para	-1930228.82	383.29	-1929845.53

Energies in kJ/mol. For structures see Figure 3.

Miscellaneous properties

Position of nitro group on the phenyl ring affects outcome of many properties of these systems. Table 7 lists the $N\text{-}NO_2$ distances in the systems considered.

Table 7. The $N\text{-}NO_2$ distances (Å).

Structure	Neutral forms	Monocations	Dications
ortho	1.388	3.348	5.811
ortho C		1.599	
meta	1.394	1.558	
meta C	1.394	1.567	
meta R1			37.447
meta R2			18.978
para	1.395	1.561	19.336

The calculated dipole moments of the systems are listed in Table 8. As seen in the table, generally more charge loading on the systems causes increasing values of the dipole moments. However, net dipole moments are vector quantities and dictated by the magnitudes and directions of bond dipoles which are functions of magnitudes of charges on atoms and distances between them.

Table 8. Calculated dipole moments.

Structure	Neutral	Mono cations	Dications
ortho	7.24	1.01	11.80
ortho C		6.22	
meta	3.53	3.51	
meta C	3.64	6.66	
meta R1			124.78
meta R2			64.62
para	4.62	4.78	74.05

In debye units. For structures see Figures 1-3.

Tables 9-11 show the effect of ring-nitro group on the electrostatic charges of the nitramine group (Nitrogen atom and NO_2 group) of the neutral and charged structures considered.

In the neutral case, the algebraic orders of negative charge on the nitrogen atoms and positive charges on the NO_2 moieties are *ortho< meta C< para< meta* and *meta< meta C< para< ortho,* respectively (Table 9).

Table 9. Effect of ring-nitro group on the electrostatic charges (esu) of the nitramine group (NNO_2CH_3) of the neutral structures considered.

Structure	N	NO_2 (group)
ortho	-0.246	-0.006
meta	-0.180	-0.072
meta C	-0.204	-0.065
para	-0.199	-0.063

For structures see Figure 1.

In the monocation case, the algebraic orders of negative charge on the nitrogen atoms and positive charge on the NO_2 moieties are *ortho< meta C< para= meta< ortho C* and *meta<=para< meta C< ortho C< ortho,* respectively (Table 10).

Table 10. Effect of ring-nitro group on the electrostatic charges (esu) of the nitramine group (NNO_2CH_3) of the monocation structures considered.

Structure	N	NO_2 (group)
ortho	-0.404	0.435
ortho C	-0.064	0.224
meta	-0.092	0.201
meta C	-0.113	0.216
para	-0.097	0.201

For structures see Figure 2. *ortho* stands for decomposed structure.

In the dication case, the algebraic orders of negative charge on the nitrogen atoms and positive charge on the NO_2 moieties are *meta* R2< *para* < *meta* R1< *ortho* and *ortho* <*meta* R2 < *para*= *meta* R1, respectively (Table 11).

Table 11. Effect of ring-nitro group on the electrostatic charges (esu) of the nitramine group (NNO_2CH_3) of the dication structures considered.

Structure	N	NO_2 (group)
ortho	-0.254	0.959
meta R1	-0.295	1.001
meta R2	-0.319	1.000
para	-0.315	1.001

For structures see Figure 3. All are decomposed structures.

As seen in the Tables 9-11 in the neutral and charged forms, nitramine nitrogen atom possesses some negative partial charge in spite of the fact that it is linked to an electron withdrawing nitro group. It might be due to the inductive electron donating effect of the methyl group and lack or partially diminished electron donation to the nitro substituted phenyl moiety.

As for the overall charge of the NO_2 moiety of the nitramine group, it is negative in all the neutral cases but positive in the charged forms. Note that NO_2 moiety is lost from the *ortho* structure in mono cation case and in all the dication forms as well.

All the outcome of charges mentioned above should be due to overall charge of the initial structures (neutral or type of the cation initially set) as well as its distribution mainly dictated by the combined affects of phenyl-nitro group (positional effect) and the nitramine group.

Figure 4 shows the distribution of electrostatic charges in the monocation systems considered which are structurally intact except the one labeled *ortho*.
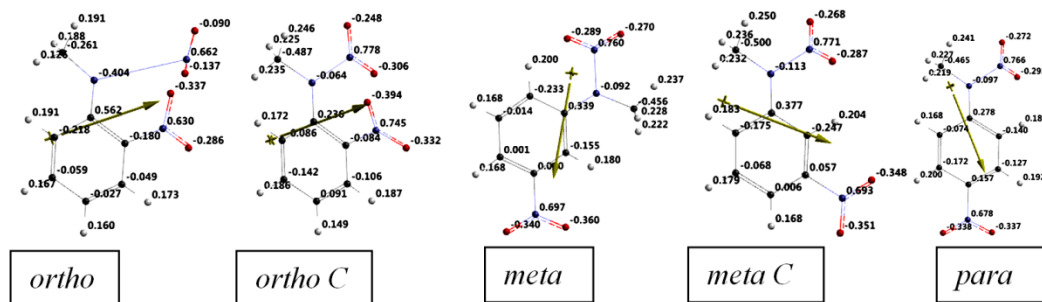

Figure 4. Distribution of electrostatic charges in the monocation systems considered.

Frontier molecular orbital energies

The HOMO, LUMO energies (ε_{HOMO} and ε_{LUMO}, respectively) and interfrontier molecular orbital energy gap $\Delta\varepsilon$ ($\Delta\varepsilon = \varepsilon_{LUMO}-\varepsilon_{HOMO}$) values of the isomeric neutral structures and the monocations are shown in Tables 12 and 13, respectively. The data in Table 12 reveal that the orders of the HOMO and LUMO energies for the neutral structures are *ortho< para< meta C< meta* and *ortho< meta C< meta< para*, respectively. Consequently, Δv values follow the order of *meta< meta C< para< ortho*.

Table 12. The HOMO, LUMO energies and Δv values of the neutral structures considered.

Structure	HOMO	LUMO	Δv
ortho	-765.95	-319.57	446.38
meta	-733.52	-312.97	420.55
meta C	-735.34	-313.10	422.24
para	-738.76	-312.93	425.83

For structures see Figure 1.

Figure 5 shows the LUMO maps of the neutral molecules 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.
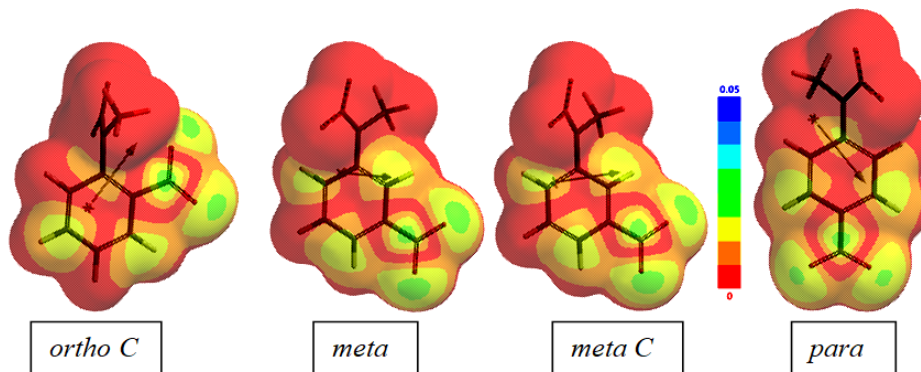

Figure 5. The LUMO maps of the neutral structures considered.

As revealed by Table 13, the HOMO, LUMO energies of the stable monocations considered are *meta< meta C< ortho C< para* and *para< meta< ortho C< meta C*, respectively. Their Δν values follow the order of *para< meta< meta C< ortho C*. Note that in the case of monocations due to unrestricted type of calculations α- and β-type molecular orbitals exist.

As compared to the neutral structures, in the monocation case both of the frontier molecular orbitals are lowered down energetically at different extents, depending on the position of the phenyl-nitro group.

Table 13. The HOMO , LUMO energies and Δν values of the stable monocations considered.

Structure	HOMO	LUMO	Δν
ortho C	-1180.79	-725.50	455.29
meta	-1184.33	-731.81	452.52
meta C	-1181.80	-722.25	459.55
para	-1172.84	-731.97	440.87

Energies in kJ/mol. For structures see Figure 2

It appears that positive charging of the molecules affects the frontier molecular orbitals as if an electron withdrawing group were present on the phenyl ring. Note that it is a well established fact that electron withdrawing groups lower the HOMO and LUMO orbitals but in unequal extents [28].

Spin densities and spin density maps

Monocation species are open-shell systems. Therefore, spin density and spin density maps arise for them. Note that spin density stands for the difference in the number of electrons per unit volume of "up" spin and "down" spin at a point in space. The function is defined over all the space and summed over all space to give the difference in the total number of electrons of "up" and "down" spin [29]. Figure 6 shows the spin densities on atoms of the monocation species considered.

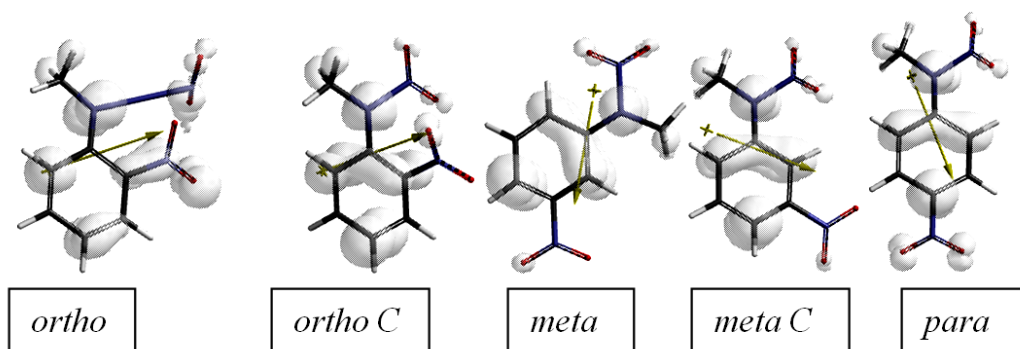| *ortho* | *ortho C* | *meta* | *meta C* | *para* |

Figure 6. Spin densities on atoms of the monocation species considered.

As seen in Figure 6, the spin density has been distributed over quite a number of sites which reflects the tendency of localization of the unpaired electron in the monocation species. Figure 7 shows the spin density maps on atoms of the monocation species considered. Note that a spin density map is a graph that shows the value of the spin density on an electron density isosurface corresponding to a van der Waals surface. By convention, colors blue/bluish indicate high concentration of spin density while colors red/reddish indicate low concentration [29].
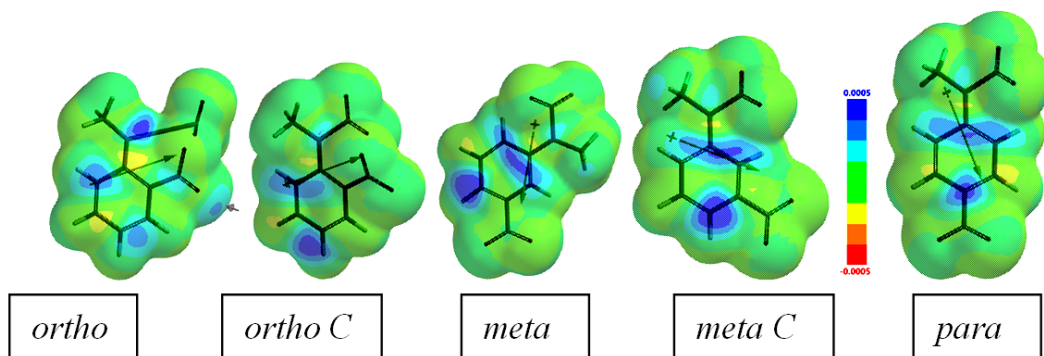
| ortho | ortho C | meta | meta C | para |

Figure 7. Spin density maps of the monocation species considered.

4. Conclusion

Within the limitations of the theory and basis set used, the present DFT treatment has indicated that the neutral and monocation systems considered have exothermic heat of formation values and favorable Gibbs free energy of formations at the standard state. All the neutral systems and the monocations, except *ortho* monocation case, are electronically stable. In the *ortho* monocation case, while optimization passing through a certain conformation state, the structure may undergo decomposition by emanating NO_2 moiety of the nitramine group. All the dications undergo decomposition by emanating NO_2 moiety of the nitramine group.

The calculations reveal that although the nitro group of nitramine moiety in all the neutral systems, have tendency to possess some minute negative partial charge, in the monocation systems it has some positive partial charge (decomposed or not). In contrast, the dication forms, release nitramine NO_2 moiety carrying positive formal charge of unity.

As compared to the neutral forms, positive charging of the molecules lowers the frontier molecular orbital energy levels at unequal extents as if an electron attracting group has been substituted. The effect varies depending on the position of the nitro group on the phenyl ring.

The study indicates that the neutral structures considered resist positive charging up to a certain extent forming the respective monocations but undergo decomposition in the dication form releasing nitramine NO_2 moiety. Thus, the present study also puts some light on to the electrostatic charging of the compounds of interest.

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