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Some Isomers of DNNC and Radicals from Them - A DFT Treatment

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Abstract

In the present density functional study, some isomers of 1,3,5,5-tetranitrohexahydropyrimidine (DNNC) have been considered within the constraints of the theory and the basis set employed (UB3LYP/6-31++G(d,p)). Various geometrical, QASR and quantum chemical properties are harvested and discussed. All the considered isomers of DNNC have exothermic heat of formation and favorable Gibbs free energy of formation values at the standard states and they are stable electronically. Based on the interfrontier molecular orbital energy gap values DNNC is found to be more sensitive to impulse stimulus than the others. Also radicals obtained from DNNC isomers considered (by the homolytic rapture of C-NO_2 or N-NO_2 bonds) have been focus of present interest. The radicals obtained by the cleavage of *geminal* C-NO_2 bonds have exothermic H^o and favorable G^o values at the standard states and electronically stable as their respective parent compounds. Although, some of the radicals generated by the homolytic cleavage of N-NO_2 bonds are thermo chemically exothermic and stable, like the radicals mentioned above, the radicals from the isomer having all the nitro groups in *vicinal* configuration decomposes by eliminating one of the *geminal* nitro groups.

1. Introduction

DNNC (1,3,5,5-Tetranitrohexahydropyrimidine, French abbreviation is DNNC it is also named as TNDA [1]) is an explosive as well as an oxidant for propellants and pyrotechnics. It possesses C-NO_2 and N-NO_2 bonds. It is relatively novel explosive which may also find some applications as an oxidant for propellants and pyrotechnics [2]. DNNC exhibited great promise as a green oxidant in solid propellant formulations to replace ammonium perchlorate (AP) [3].

It can also find some applications as filling materials for warheads, shell and bombs.

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It was synthesized in 1982. DNNC has the mp. 151-154°C [4-6], density: 1.82 g/cm^3, VOD: 8730 m/s, PCJ: 34 Pa, OB: 6%. It has very low impact sensitivity [7]. The hybrid molecular structure (it possesses C-NO_2 and N-NO_2 bonds) of DNNC produces an energetic material having impact sensitivity much lower than RDX and more like that of TNT. It is a thermally stable and insensitive high-energy oxidizer that could have a potential candidate for replacement of RDX in explosive and propeller formulations [8]. Crystal structure of DNNC was studied by Oyumi et al. [9]. Thermo chemical decomposition studies of DNNC have been published by Shackelford and Goldman [10-12]. The heat of fusion for DNNC and its DNNC-d_6 analogue compound have been determined using differential scanning calorimetry analysis. No significant difference in the DNNC and DNNC-d_6 heat of fusion values was detected at the 95 and 99 percent student t-confidence levels. Melting points were also determined for the subject compounds using this analysis technique. These melting points are compared to literature values obtained by conventional methods [8].

Pyrolysis of 5-substituted 1,3,5-trinitrohexahydropyrimidines was studied also by Roos and Brill [13]. The thermal stability of 1,3,5,5-tetranitrohexahydropyrimidine (DNNC, TNDA) in liquid phase under isothermal conditions was studied by Sinditskii et al. [5]. The surface temperature and combustion mechanism of DNNC (TNDA) were established with the help of thermocouple studies.

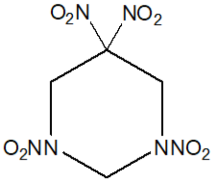
In the present study some isomers of DNNC have been considered within the framework of density functional theory (DFT) within the constraints of UB3LYP/6-31++G(d,p) approach. Then radicals obtained from DNNC isomers considered for the homolytic rapture of C-NO_2 or N-NO_2 bonds.

2. Method of Calculations

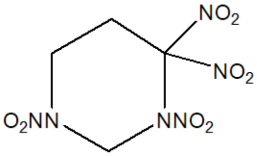
In the present study, all the initial structure optimizations of the closed-shell structures leading to energy minima have been achieved by using MM2 method then followed by semi empirical PM3 self-consistent fields molecular orbital (SCF MO) method [14,15] at the restricted level [16]. Afterwards, the 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) [17,18]. For the radicals considered unrestricted protocol has been applied (UB3LYP/6-31++G(d,p)) at the doublet state. It is worth mentioning 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 [19]. Also note that the correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [20] and Lee, Yang, Parr (LYP) correlation correction functional [21]. 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 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 [22].

3. Results and Discussion

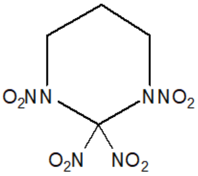
In the present study the following isomers of DNNC (D1) have been considered within the framework of density functional theory.



D1



D2



D3

Structurally DNNC molecule has two *geminally* located C-NO_2 bonds and two nitramine type bonds. As seen in the above structures, isomerization among D1-D3 arises from varying location of the *geminal* nitro groups. Since the hexahydropyrimidine ring involved in the isomers considered does not contain any cyclic π-conjugation, the perturbational effects happening by changing the position of the *geminal* nitro groups can be transmitted through σ-skeleton or through the space or both of them operating simultaneously. Extent of the field effects should be operative depending on the conformations of the six-membered ring as well as the nitro groups. The extent of the conjugation occurring (which depends on the conformation of the nitro groups) within the nitramine groups should be an important dictating factor on the over all perturbational effect as well.

Figure 1 shows the optimized structures as well as the directions of the dipole moment vectors of DNNC isomers considered. Keep in mind that only the position of *geminal* nitro groups is changed in the isomers considered. The six-membered ring in all the cases possesses chair or somewhat distorted chair conformation having *equatorial* and *axial* substituents. The direction of head of the dipole moments is towards somewhere nearby the *geminal* nitro groups.

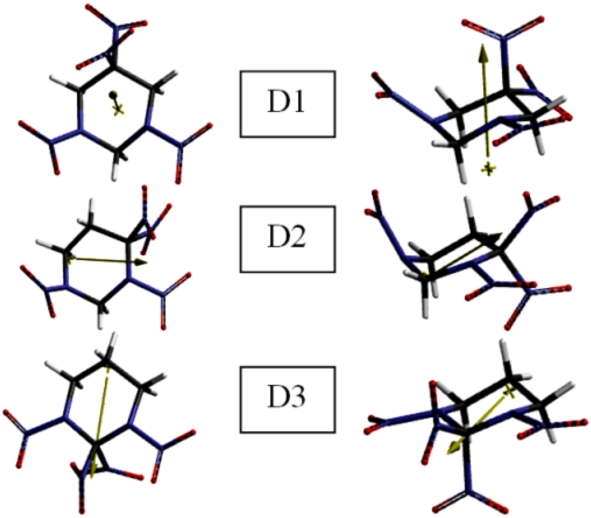


Figure 1. Optimized structures of the isomers (top and side views).

Figure 2 shows the electrostatic potential (ESP) charges on the atoms of the isomers considered. It is worth noting 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 [22].

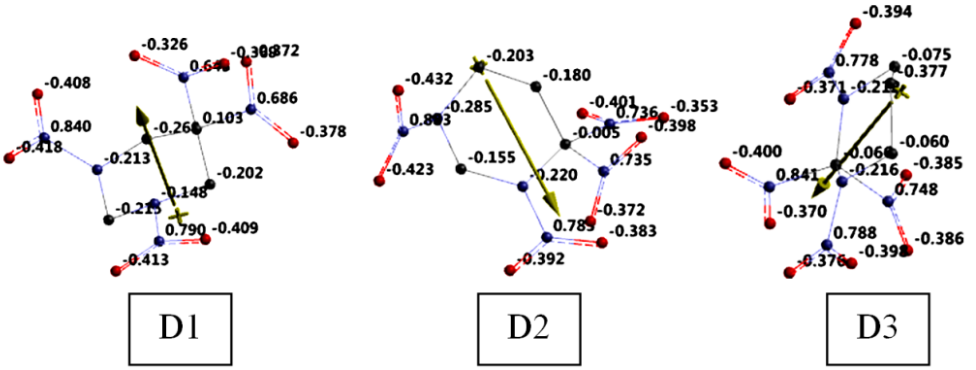
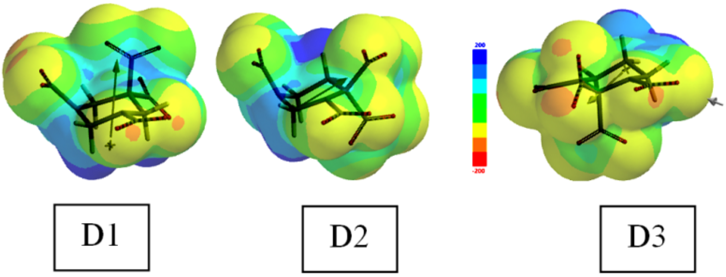


Figure 2. The ESP charges on the atoms of the isomers considered (Hydrogens not shown).

Since the isomers have C1 symmetry, the charges on supposedly symmetric positions possess unequal magnitudes. Generally the ring nitrogens of the nitramine groups have negative partial charges but much less than (algebraically) 0.3 esu. The carbon atom having the *geminal* nitro groups possesses a positive partial charge in D1, in contrast to the respective carbon atom in the other isomers which has very minute negative charge.

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



D1 D2 D3

Figure 3. The electrostatic potential maps of the isomers considered.

Some properties of the isomers considered are tabulated in Table 1. The polarizability is defined according to the multivariable formula [22].

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

where V and h are the Van der Waals volume and hardness, respectively. Hardness is defined as,

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

where $\varepsilon_{\text{HOMO}}$ and $\varepsilon_{\text{LUMO}}$ are the molecular orbital energies of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbital energies, respectively. Note that the dipole moment values are highly position dependent on the *geminal* nitro group and the order is D2< D1< D3. On the other hand, the order of Log P values is D1< D2< D3. The log P values, are all positive quantities. Note that hydrophilic compounds (having low octanol/water partition coefficients) are found primarily in aqueous regions. 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. The order is D3< D2< D1 which is the reverse order of Log P values.

Table 1. Some properties of the isomers considered.

Isomers	Area ($Å^2$)	Volume ($Å^3$)	PSA ($Å^2$)	Ovality	Log P	Polarizability	Dipole moment
D1	224.04	189.25	161.789	1.41	2.73	55.52	5.03
D2	222.16	189.69	158.218	1.39	3.35	55.48	4.96
D3	221.87	189.85	154.777	1.39	3.75	55.52	7.58

Polarizabilities in 10^{-30} m^3 units. Dipole moments in debye units. PSA: Polar surface area.

Table 2 lists some thermo chemical values for the isomers considered. As seen in the table they are all characterized with exothermic heat of formation values at the standard states and favorable G^o values. The orders of H^o, S^o and G^o values (algebraically) are D1< D2< D3, D2< D1< D3 and D1< D2< D3, respectively. All these orders should have been dictated by the implicitly related geometrical and electronic factors specific for each isomer.

Table 2. Some thermo chemical values for the isomers considered.

Isomers	H^o	S^o (J/mol^o)	G^o
D1	-2850682.528	468.54	-2850822.232
D2	-2850670.713	466.38	-2850809.761
D3	-2850625.501	472.06	-2850766.256

Energies in kJ/mol.

Table 3 tabulates some energies of the isomers 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 order of E_C values is D1< D2< D3, thus D1 and D3 are the most and least stable isomers, respectively. Note that D3 possesses the least favorable G^o value due to its least exothermic character (H^o) and its most positive S^o value among the group. The structure of D3 has a highly crowded orientation of the nitro groups, hence should create unfavorable steric contribution which may cause more pronounced through space repulsive interactions. Therefore, D1 and D3 represent the most stable and least stable isomers among the all.

Table 3. Some energies of the isomers considered.

Isomers	E	ZPE	E_C
D1	-2851101.26	408.71	-2850692.55
D2	-2851089.91	409.20	-2850680.71
D3	-2851041.66	405.11	-2850636.55

Energies in kJ/mol.

Table 4 lists the aqueous and solvation energies the isomers considered. In terms of aqueous energies of the isomers, D1 and D3 possess the most and relatively least negative energy values, thus a positive solvation energy associated with D3 isomer. Note that in D3 all the nitro groups are substituted *vicinally*.

Table 4. Aqueous and solvation energies the isomers considered.

Isomers	E_{aq}	Solvation E
D1	-2851114.11	-12.85
D2	-2851091.44	-1.53
D3	-2851041.08	0.57

Energies in kJ/mol.

Figure 4 shows some of the molecular orbital energy levels of the isomers considered.

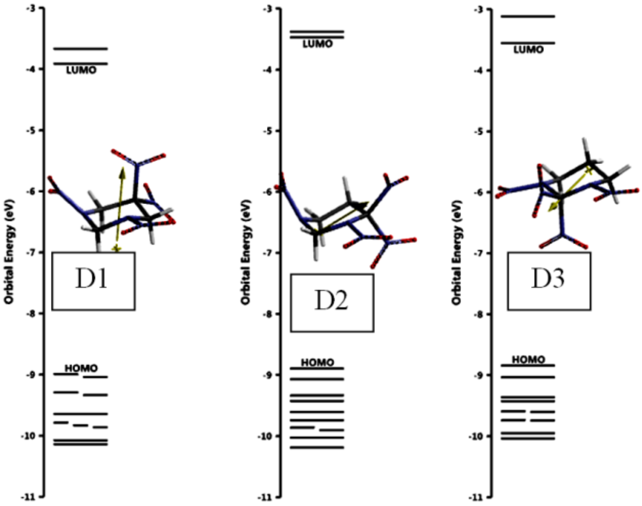


Figure 4. Some of the molecular orbital energy levels of the isomers considered.

As seen in the figure, location of the *geminal* nitro groups mainly affects the inner lying occupied molecular orbital energy levels. However, in D3 the energy spacing between the LUMO and NEXTLUMO is noticeable. The energy gap between those orbitals decreases from D1 to D2 and increases the largest one in isomer D3.

Table 5 tabulates the HOMO, LUMO energies and the interfrontier molecular orbital energy gap ($\Delta\varepsilon=\varepsilon_{LUMO}-\varepsilon_{HOMO}$) values of the isomers considered. The HOMO and LUMO energy orders (algebraically) are D1< D2< D3 and D1< D3< D2, respectively. Consequently, Δε values exhibit the order of D1< D3< D2. Since usually electron withdrawing substituents lower both the HOMO and LUMO energy levels, the *geminal* nitro groups acting as if they were less electron attracting as going from D1 to D3. The effect of the *geminal* nitro groups observed on the HOMO energy order is somewhat disturbed in the case of the LUMO energy order, that is D3 precedes D2. Note that the impact sensitivity of an explosive is related to Δε value such that decrease of it increases the sensitivity [23,24]. Hence, DNNC (D1) is expected to be more sensitive to impulse stimulus than the other isomers considered.

Table 5. The HOMO, LUMO energies and Δε values of the isomers considered.

Isomers	HOMO	LUMO	Δε
D1	-867.80	-377.52	490.28
D2	-858.03	-335.03	523.00
D3	-853.14	-343.11	510.03

Energies in kJ/mol.

Figure 5 displays the local ionization potential 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.

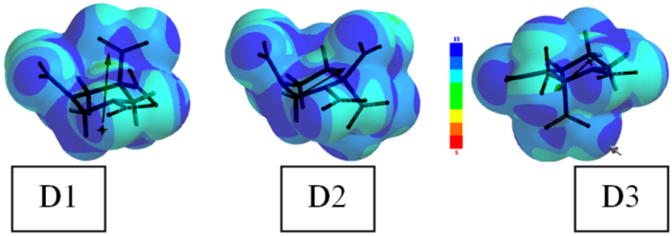


Figure 5. The local ionization potential maps of the isomers considered.

Figure 6 shows the LUMO maps of DNNC 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.

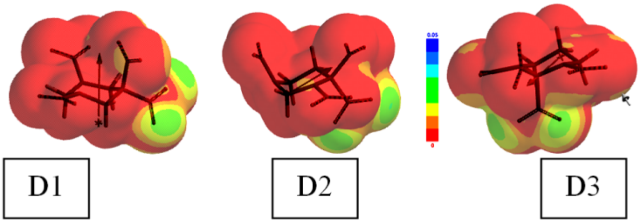


Figure 6. The LUMO maps of the isomers considered.

Radicals

Many researchers believe that C–NO_2, N–NO_2, or O–NO_2 bonds are trigger spots in nitro-contained explosives. So, seeking the relationship between the molecular structure of energetic materials, and their sensitivities to external stimuli, have been of interest for many years [25-31].

By Rice et al., it has been shown that density functional calculations of the bond dissociation energy (BDE) for removal of the NO_2 group can be used to index the relative sensitivity of nitro aromatic molecules. This only applies to molecules in which the R–NO_2 bond is the weakest bond. In nitrocubanes it has been shown that the C–C bond of the cube is weaker than the C–NO_2 bonds and that the initial step in decomposition is an opening of the cube C–C bond [29].

In the work of Song et al., [26] the geometries of nine CHNO nitro-contained explosive molecules were fully optimized employing the B3LYP method of density functional theory with the 6-31G(d) basis set. The bond dissociation energy (BDE) for removal of the NO_2 group in nitroamine molecules with nitro alkyl, and benzoate with nitro alkyl were calculated at the same level. The calculation results of B3LYP/6-31G(d) and B3P86/6-311G(d) levels showed that the strength of C–NO_2 is weaker than that of N–NO_2 bond in nitroamine molecules with nitro alkyl group. The weakest bond is the C–NO_2 in these computed molecules.

In the work of Tan et al., the cage strain energies of polynitroadamantanes, polynitrocubanes, hexanitrohexaazaisowurtzitane (HNIW or Cl-20) and polynitrogen compounds were theoretically calculated in terms of DFT/BOP/TNP method and homodesmotic reactions. They found that with the increase in number of the nitro groups, the skeletons of carbon cages were gradually deformed for polynitrocubanes, and their cage strain energies also increased drastically [30].

Although in some caged/strained polynitro molecules the homolytic cleavage of C-C or N-NO_2 bonds occurs [29]. In the present DNNC isomers the rapture of C-NO_2 bond is more likely to happen as discussed in the work of Song et al., [26,31]. Therefore, in the present treatment, instead of homolytic bond dissociation energies (BDE), interest has been concentrated on the stabilities of the radicals produced via homolytic cleavage of C-NO_2 and N-NO_2 bonds in the DNNC isomers presently considered. The radicals produced from the rupture of one of the *geminal* C-NO_2 bonds are labeled as D1A, D1B, D2A, D2B, etc., where the numbers indicate the position of the *geminal* nitro groups and the *geminal* C-NO_2 bonds are differentiated as A and B. Whereas the radicals generated from the cleavage of one of the N-NO_2 bonds of isomers D1-D3 are labeled as D1X, D1Y, D2X, D2Y, etc., respectively. Note that there exist two N-NO_2 bonds in each isomer and indicated by letters X and Y.

The radicals from the cleavage of *geminal* C-NO_2 bonds

Figure 7 displays the optimized structures and the direction of the dipole moment vectors of the radicals obtained by the homolytic cleavage of one of the C-NO_2 bonds in the isomers considered.

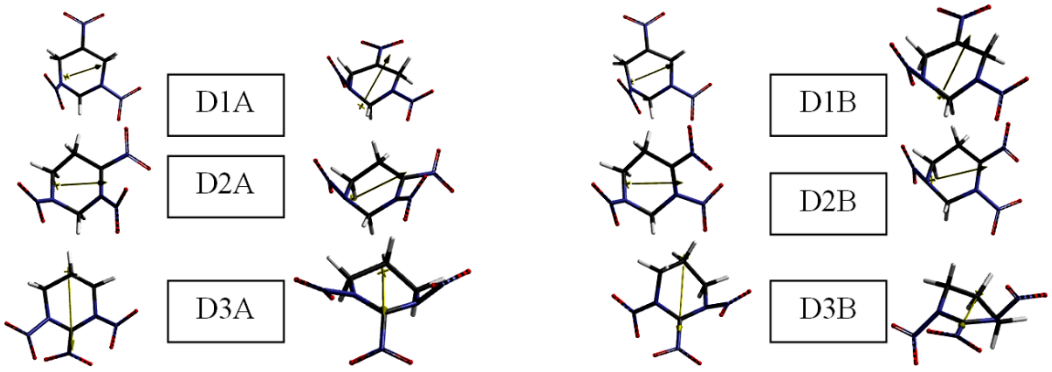


Figure 7. Optimized structures of the radicals obtained by the homolytic cleavage of one of the C-NO_2 bonds in the isomers considered (two different views).

As seen in the figure all the radicals considered have reasonable bond lengths. All the structures have planar or nearly so at the radical carbon atom but the rest of the ring has been distorted.

Table 6 shows some thermo chemical values for the radicals obtained by the homolytic cleavage of one of the *geminal* C-NO_2 bonds in the isomers considered. As seen in the table they all have exothermic heat of formation and favorable G° values at the standard state. The orders for H° and G° values are the same which is D2A< D2B< D1A< D1B< D3B< D3A. The entropy values, S°, follow the order of D1A> D1B> D3A> D3B> D2B> D2A. As seen in the table D1A and D2A, are more exothermic and more favorable than their respective B-type radicals but reverse holds in the case of radicals from isomer D3.

Table 6. Some thermo chemical values for the radicals obtained by the homolytic cleavage of one of the *geminal* C-NO_2 bonds in the isomers considered.

Radicals	H°	S° (J/mol°)	G°
D1A	-2312131.416	433.09	-2312260.545
D1B	-2312131.175	433.07	-2312260.296
D2A	-2312139.004	428.66	-2312266.812
D2B	-2312134.984	430.59	-2312263.367
D3A	-2312111.893	432.65	-2312240.888
D3B	-2312119.922	431.26	-2312248.502

Energies in kJ/mol.

Table 7 shows some energies of the radicals obtained by the homolytic cleavage of one of the *geminal* C-NO_2 bonds in the isomers considered. The data of E_C values indicate

Table 7. Some energies of the radicals obtained by the homolytic cleavage of one of the *geminal* C-NO_2 bonds in the isomers considered.

Radicals	E	ZPE	E_C
D1A	-2312508.32	367.03	-2312141.29
D1B	-2312508.23	367.19	-2312141.04
D2A	-2312517.24	368.63	-2312148.61
D2B	-2312513.66	368.91	-2312144.75
D3A	-2312489.03	367.02	-2312122.01
D3B	-2312497.68	367.84	-2312129.84

Energies in kJ/mol.

that all these radicals are electronically stable and the order of E_C values is D2A< D2B< D1A< D1B< D3B< D3A which is the same with the orders of H° and G° values.

Figure 8 shows the spin densities of the radicals obtained by the homolytic cleavage of one of the C-NO_2 bonds in the isomers considered.

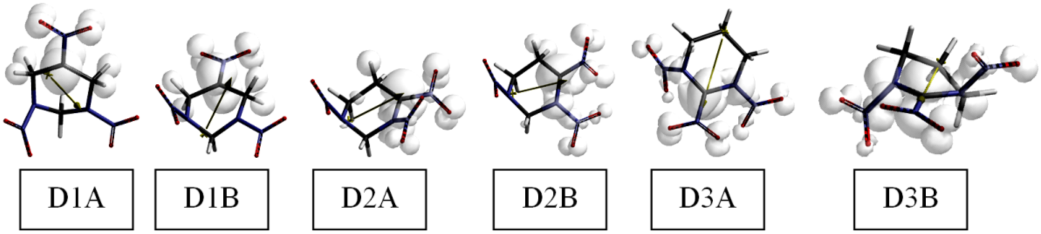


Figure 8. Spin densities of the radicals obtained by the homolytic cleavage of one of the C-NO_2 bonds in the isomers considered.

As seen in the figure the spin density concentrates on the radical center and atoms around it. The rest of the structures cannot bear any appreciable unpaired electron population.

Figure 9 shows the spin density maps of the radicals obtained by the homolytic cleavage of one of the C-NO_2 bonds in the isomers considered. In the figure the blue or bluish green regions represents the highest and high spin density onto an electron density surface, respectively.

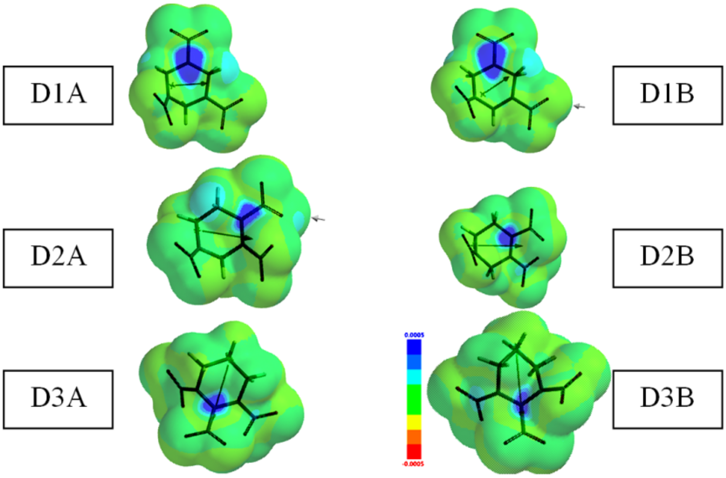


Figure 9. Spin density maps of the radicals obtained by the homolytic cleavage of one of the C-NO_2 bonds in the isomers considered.

The radicals from cleavage of the N-NO_2 bonds

The isomers D1-D3 possess two nitramine moieties addition to two *geminal* C-NO_2 bonds. At first sight the homolytic cleavage of N-NO_2 bonds (one by one) of any isomeric structure considered, should result in two different radicals. However, the picture is not so simple and radicals from D3 undergo further reaction.

Figure 10 displays the optimized structures and the direction of the dipole moment vectors of the radicals obtained by the homolytic cleavage one of N-NO_2 bonds in the isomers considered.

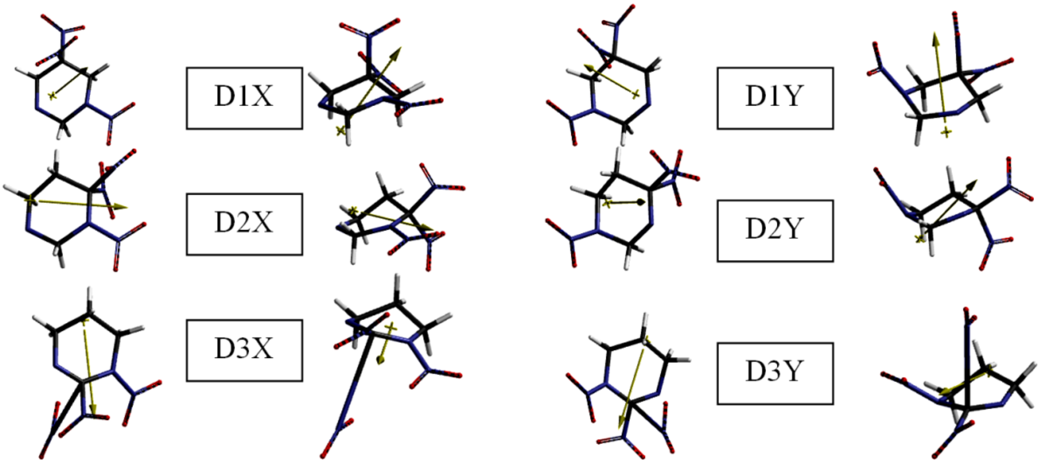


Figure 10. Optimized structures of the radicals obtained by the homolytic cleavage of one of N-NO_2 bonds in the isomers considered (two different views).

All the radical structures in this category, except D3X and D3Y are structurally stable but after generation, those radicals from D3 undergo bond elongation in one of the *geminal* C-NO_2 bonds undergoing decomposition and eventually produce D3X and D3Y. In all the cases, the ring system possesses either a chair or distorted chair conformation. Moreover, the radical site is not planar around the nitrogen atom from where a homolytic cleavage of N-NO_2 bond has happened.

Table 8 shows some thermo chemical values for the radicals obtained by the homolytic cleavage of one of N-NO_2 bonds in the isomers considered. As seen in the table all the radicals of these sort are exothermic and have favorable G^o values. However, note that the values in the table for D3X and D3Y stand for the decomposed radicals. The departing NO_2 moieties have minute ESP charges of 0.054 esu and 0.06 esu, respectively.

Table 8. Some thermo chemical values for the radicals obtained by the homolytic cleavage of one of N-NO$_2$ bonds in the isomers considered.

Radicals	H^o	S^o (J/mol^o)	G^o
D1X	-2312120.933	435.91	-2312250.899
D1Y	-2312117.84	432.14	-2312246.682
D2X	-2312108.251	435.15	-2312237.992
D2Y	-2312128.594	433.46	-2312257.833
D3X	-2312206.026	452.47	-2312340.931
D3Y	-2312208.076	450.81	-2312342.488

Energies in kJ/mol.

Table 9 shows some energies of the radicals obtained by the homolytic cleavage of one of N-NO$_2$ bonds in the isomers considered. Again note that the values in Table 9 for D3X and D3Y stand for the decomposed radicals.

Table 9. Some energies of the radicals obtained for the radicals obtained by the homolytic cleavage of one of N-NO$_2$ bonds in the isomers considered.

Radicals	E	ZPE	E$_C$
D1X	-2312495.99	364.57	-2312131.42
D1Y	-2312493.72	365.68	-2312128.04
D2X	-2312482.81	363.87	-2312118.94
D2Y	-2312503.73	364.70	-2312139.03
D3X	-2312578.25	359.95	-2312218.3
D3Y	-2312580.12	359.93	-2312220.19

Energies in kJ/mol.

Figure 11 shows the spin densities of the radicals obtained by the homolytic cleavage of one of the N-NO$_2$ bonds in the isomers considered. The spin density has been distributed over a few number of sites which reflects the tendency of localization of the unpaired electron in the radical produced.

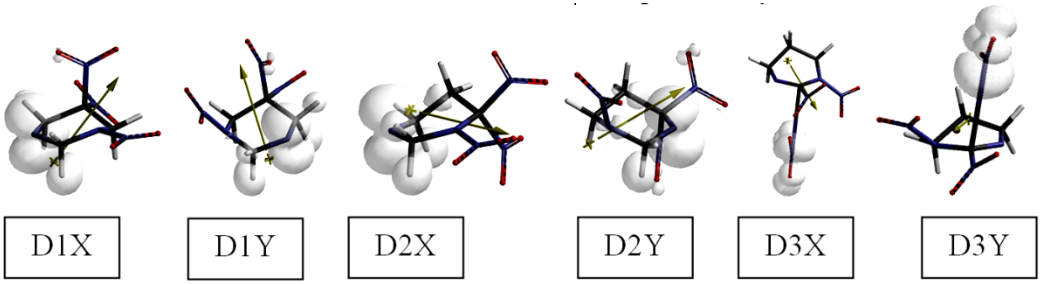


Figure 11. Spin densities of the radicals obtained by the homolytic cleavage of one of the $N\text{-}NO_2$ bonds in the isomers considered.

Figure 12 shows the spin density maps of the radicals obtained by the homolytic cleavage of one of the $N\text{-}NO_2$ bonds in the isomers considered. In the figure the blue or bluish green regions stands for the relative spin density onto an electron density surface.

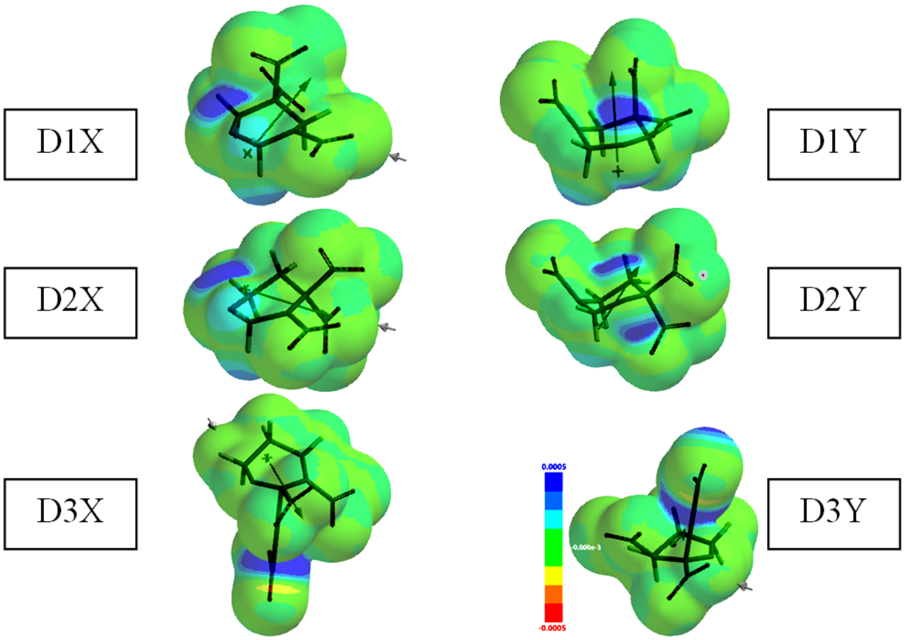


Figure 12. Spin density maps of the radicals obtained by the homolytic cleavage of one of the $N\text{-}NO_2$ bonds in the isomers considered.

4. Conclusion

The present DFT study at the level of B3LYP/6-31++G(d,p) indicates that in vacuum conditions the DNNC isomers considered have exothermic heat of formation values and favorable Gibbs free energy of formation values. They have negative aqueous energies and negative solvation energies except isomer D3. In the isomers, as the nitro groups create more and more steric crowding stability of the structures decrease from D1 to D3. The interfrontier molecular orbital energy gap values indicate that DNNC (D1) is expected to be more sensitive to impulse stimulus than the other isomers considered.

The radicals produced by the homolytic cleavage of C-NO_2 bonds have exothermic H^o and favorable G^o values and are structurally stable. On the other hand, the radicals from the rapture of N-NO_2 bonds , with the exceptions of D3X and D3Y, are structurally stable and have exothermic H^o and favorable G^o values too. The present treatment at the molecular level reveals some similarities and differences not only between the parent DNNC isomers considered but also between the radicals produced by the homolytic cleavages of C-NO_2 and N-NO_2 bonds.

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