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Dinitro Derivatives of 3,6,7,8-tetraazatricyclo[$1^{1,5}$. $1^{1,5}$.$1^{2,4}$. $1^{2,4}$]octa-1,4-diene – A DFT Treatment

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Abstract

Nitramines constitute an important class of explosive materials. In the present study three isomeric dinitro derivatives (nitramines) of the title structure have been investigated quantum chemically within the constraints of density functional theory at the level of B3LYP/6-311++G(d,p). Certain energies, quantum chemical and spectral properties of these three isomeric dinitro derivatives of the parent tetraazatricyclo structure have been obtained and discussed.

Introduction

The nitramines are the most recently introduced class of organic nitrate explosives [1-4]. They have been subject of various experimental and theoretical studies [5-11]. The most prominent and widely used members of nitramines are RDX (research department explosive; hexahydro-1,3,5-trinitro-1,3,5 triazine, which is also known as cyclonite) and HMX (high melting explosive; octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine). Nitroguanidine, and Tetryl are also significant nitramines. Quite recently caged nitramines, TEX [12-14] and Cl-20 [15-17], have attracted attention in the literature. While there have been other new ingredients over the years, none of them have been successfully scaled up to mass production levels. Some success has been achieved for mass production of CL-20. It offers great potential to meet the performance, insensitive munitions and environmental requirements for future weapons systems. CL-20-based shaped charges have been already being used in the oil well industry.

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On the other hand, sensitivity of explosives has the prime importance. The micron-sized explosives are very sensitive, which seriously threaten the safety of the ammunitions. Thus, the reduction in sensitivity has become a research focus. The studies have shown that the sensitivities of nitramine explosives are affected obviously by the structure, sizes and size distributions of the explosive particles, etc. [18-20].

Method of Calculation

The initial geometry optimizations of all the structures leading to energy minima were achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [21, 22] at the restricted level [23, 24]. Subsequent optimizations were achieved at Hartree-Fock level using various basis sets. Then, geometry optimizations were managed within the framework of density functional theory (DFT, B3LYP) [25, 26] finally at the level of restricted 6-311++G(d,p) [23, 27]. 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 [26, 28]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [29] and Lee, Yang, Parr (LYP) correlation correction functional [30]. The vibrational analyses were also done. 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 is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. All these calculations were done by using the Spartan 06 package program [31].

Results and Discussion

The parent structure (3,6,7,8-tetraazatricyclo[$1^{1,5}$. $1^{1,5}$.$1^{2,4}$. $1^{2,4}$]octa-1,4-diene) and its dinitro (dinitramine structures) derivatives are labeled as F0 and F1-F3, respectively (see Figure 1). F0 is isoconjugate with anion (multiple anion) of an even alternant hydrocarbon (AH) having equal starred and unstarred positions ($N^*=N^0=4$). Whereas, nitro group is isoconjugate with an odd AH system. Attachment of a nitro group to F0 produces an odd alternant system but it does not have any structural isomer. Whereas, the dinitro derivative becomes an even alternant system as F0 and has three isomers. Note that in even AHs occupied and unoccupied molecular orbital energies are symmetrically located about zero energy level [32, 33]. On the other hand, structure F1 having $N^*=8$ and $N^0=6$ is a non-Kekule' system and expected to be unstable. Existence of a non-Kekule' structure is an essential but not a sufficient condition for a molecule being an explosive material [34]. Whereas F2 and F3 are Kekule' systems with $N^*=N^0=7$.

Heteroatom replacement of a carbon atom (centric perturbation) of isoconjugate system lowers the molecular orbital energy levels of an even AH in equal extents but the magnitude of lowering depends on position of the centric perturbation(s) [32, 33]. However, the nonplanar nature of these systems does not allow an easy prediction of certain properties of them simply based on structural theory.

Figure 1 shows numbering of the parent structure F0, optimized structures of it and its isomeric dinitramine ($C_4H_2N_6O_4$) derivatives considered. It also displays the direction of dipole moment vectors. The dipole moment vector of F0 directs from 4-membered bottom ring (having axial hydrogens) to the other one. In F1 the vector is from 1,4-diazetidine ring to the ring having the nitramine groups. In the case of F2 the dipole moment vector is from one nitramine moiety to the other one. In F3 the direction of dipole moment vector is from the site of NH groups to the nitramine moieties. Also note

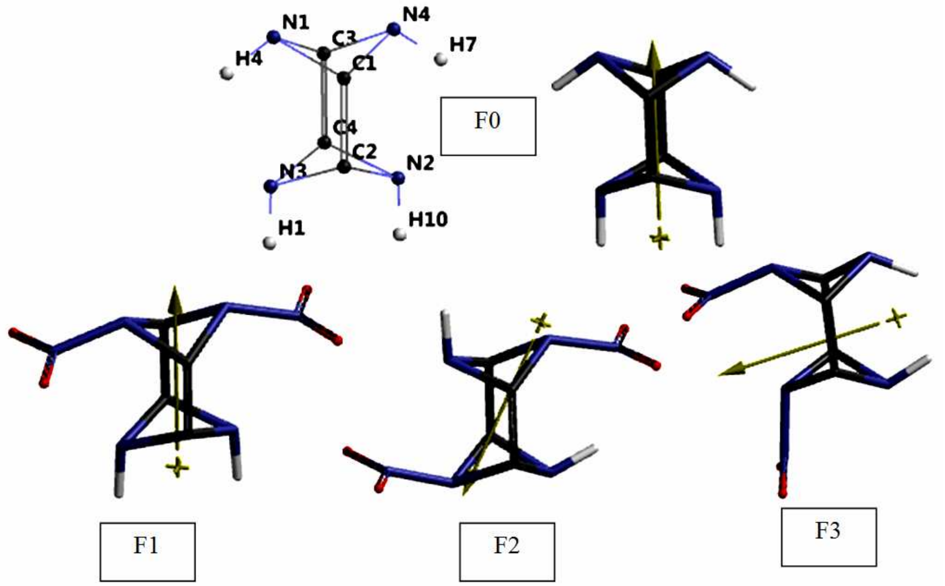

Figure 1. Numbering of F0 and optimized structures of F0 and the dinitramine isomers considered.

the conformation of N-H hydrogens. In F2 one of them is located inwardly the other outwardly. In F1 the hydrogens are nearly parallel but outward. Whereas, in F3 both of the hydrogens oriented head to each other. In terms of conformation, NO_2 groups of F1 are inward. It is also true for F2 nitro groups. Whereas in the case of F3 one of the NO_2 groups prefers inward, but the other outward position. Note that presently the inward and outward terms are defined based on the embedded cyclohexa-1,4-diene like ring system. Also note that in F0 nitrogen inversions might cause 4-membered rings turn into one another.

The structures of present concern are subtle systems allowing the conjugation of lone-pair of nitrogens to undergo conjugation with adjacent π-systems (up to a certain extent) three dimensionally. They have some pull-push type character through resonance, for instance F1 might have the following canonical structures (Figure 2). As seen in Figure 2, the nitro group (thus the nitramine moiety inductively) acts as an electron attractor mesomerically while the N-H group donates electrons. That is why the direction of the dipole moment vectors in F1 and F3 are as shown in Figure 1. The direction of the dipole moment vector in F2 which seems to be from one nitramine group to the other nitramine group arises from the geometry of the system and delicate charge distribution.

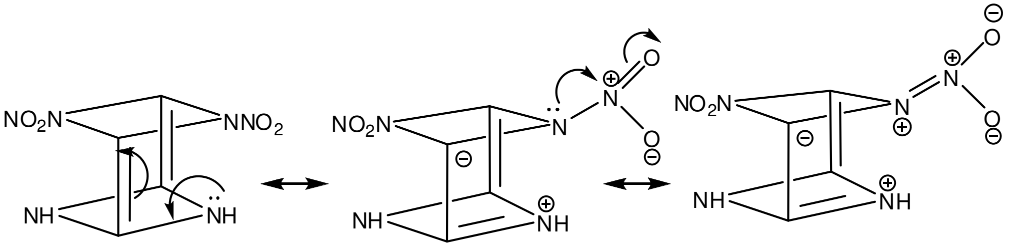

Figure 2. Some resonance structures of F1.

In those resonance structures, charge-charge, lone-pair lone-pair and lone-pair-charge interactions of attractive or repulsive types arise which should dictate the over all stability of the canonical structures.

Structures F1-F3 are isoconjugate with non-Kekule' (F1) and Kekule' (F2,F3) hydrocarbon anions. However, free rotations of nitro groups about N-N bonds and the cage-like nature of the structures do not allow to make simple stability predictions by simple application of perturbation molecular orbital (PMO) [32, 33] theory using their isoconjugate hydrocarbon models. Note that non-Kekule' structures are unstable [32, 33]. Nitro group itself or nitramine group, vital for explosives, is related to a non-Kekule' isoconjugate hydrocarbon system [34].

Table 1 shows some properties of the structures considered. Note that the isomers considered possess a positive oxygen balance which is an important parameter for explosives. They are all endothermic structures (Table 1) having the order of F2>F1>F3.

As a result of the dipole moment orientation, the order of dipole moments is F3>F1>F2 (See Table 2). The direction of the dipole moment vector in F1 indicates that the nitrogens of bottom ring (see Figure 1) donate electrons to the adjacent conjugated system. The ease of conjugation dictates the magnitude of the dipole moment vectors in these isomeric structures. Table 2 shows the dipole moment vector components.

Table 1. Some properties of the structures considered.

	F1	**F2**	**F3**
Area (Å^2)	173.92	120.56	173.67
Volume (Å^3)	146.14	146.40	146.40
Ovality	1.30	1.29	1.29
Log P	2.18	2.18	2.18
Polarizability	52.19	52.27	52.18
Dipole moment (debye)	4.44	2.31	5.82
Heat of formation* (kJ/mol)	1572.42	1592.94	1561.07

Oxygen balance of $C_4H_2N_6O_4$: +8.08. Dipole moment of F0 is 4.65 debye.
* Based on PM3//B3LYP/6-311++G(d,p) level of calculations.

Table 2. Dipole moment components.

Structure	X	Y	Z
F1	0.271485	0.121841	-4.426316
F2	1.676430	-1.593482	-0.001989
F3	-2.223260	-2.223260	0.813988

In Debye unit.

Figure 3 shows the IR spectrums of the unsubstituted structure (F0) and its isomeric dinitramine derivatives (F1-F3) considered. In the parent structure F0, the N-H bonds have symmetrical and antisymmetrical stretchings with respect to each other. They are at

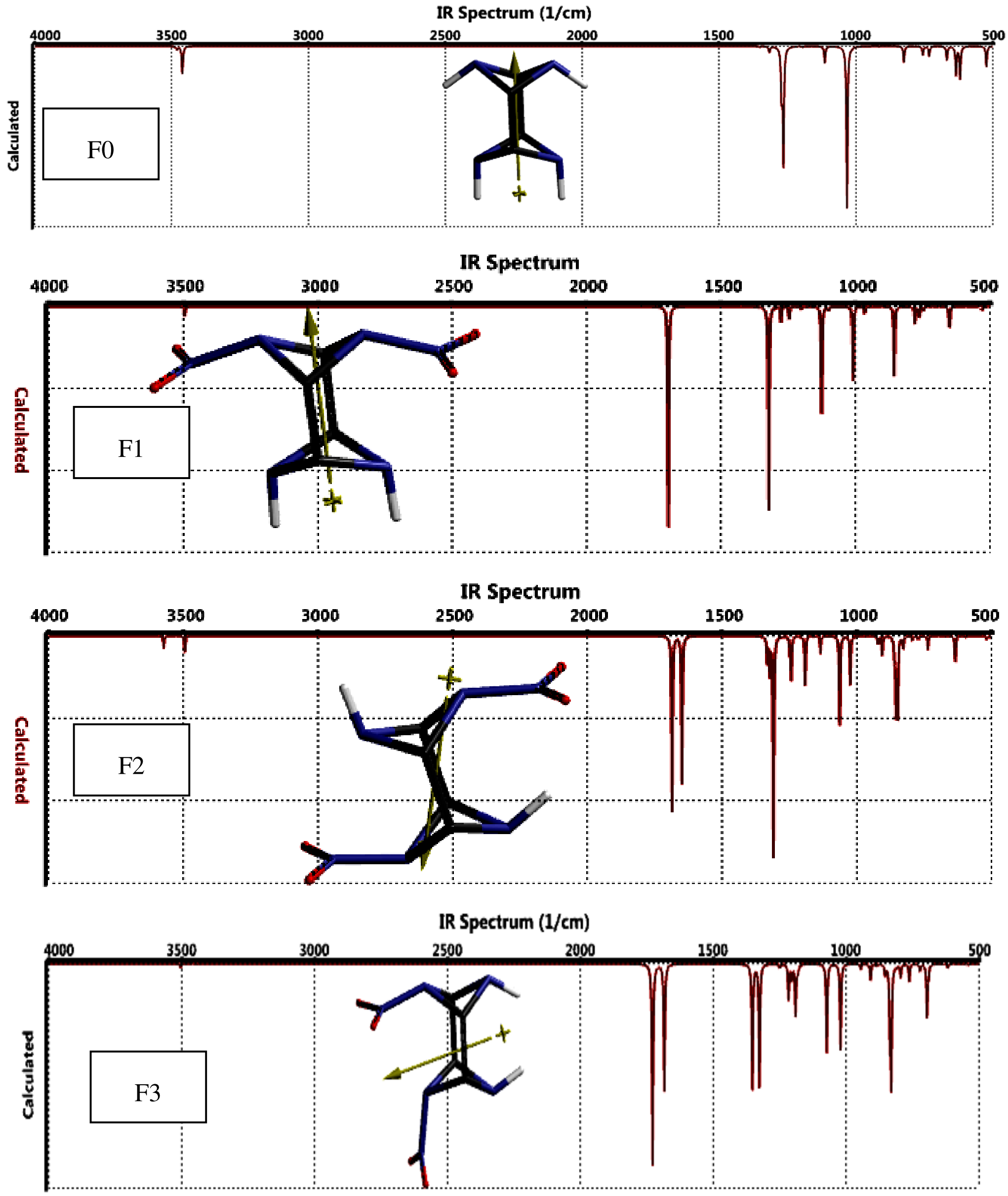

Figure 3. IR spectra of F0 and the dinitramine isomers considered.

3480 cm^{-1} and 3487 cm^{-1}, respectively. The next peak at 1265 cm^{-1} stands for N-H bending vibrations. In isomer F1, N-H stretchings have asymmetric and symmetric occurrence with respect to each other at 3501 cm^{-1} and 3495 cm^{-1}, respectively. The asymmetric and symmetric stretchings of N=O bonds happen at 1696 cm^{-1} and 1323 cm^{-1}, respectively. N-H stretchings of F2 are at 3573 cm^{-1} and 3495 cm^{-1}. They stand for different N-H linkages. The N=O stretchings of F2 are at 1685 (asm) and 1308 (sym). As for F3 isomer, the peaks at 3504 and 3447 cm^{-1} belong to N-H stretchings. With respect to each other the asymmetric stretching of N=O bonds occur at 1684 cm^{-1} and 1728 cm^{-1} and the symmetric ones are at 1353 cm^{-1} and 1326 cm^{-1}.

Table 3 shows 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. Based on E_c values, the stability order of these isomeric structures is F3>F1>F2. Note that this order is the same as the order of dipole moments that is F3>F1>F2. Of course, this outcome is the intricate combination of various interactions prevailing in these systems originating from charge-charge, charge-lone pair and lone pair-lone pair types.

Table 3. Some energies of the isomers considered.

	E	**ZPE**	**E_c**
F1	-2054822.89	225.55	-2054597.34
F2	-2054808.96	222.02	-2054586.94
F3	-2054822.19	221.83	-2054600.36

Energies in kJ/mol.

Figure 4 shows the ESP charges on atoms of the isomers of present concern. Note that ESP charges are obtained by the program based on a numerical method that generates charges that reproduce the electrostatic potential field from the entire wave function [31]. The parent structure, F0 is characterized with 4-membered rings having different polarities such that the dipole moment vector has positive tail on the one having axial N-H bonds and its head points to the other 4-membered ring. Nitramine groups in F1 have almost equal negative charge on the nitrogen atoms whereas in F2 and F3 this not the case. So, the lone pair of those atoms undergo conjugation with the adjacent C=C and nitro groups at different extends in each isomer as a result of some structural requirements. Consequently, the nitramine N-NO_2 bonds should have different strengths in F2 and F3.

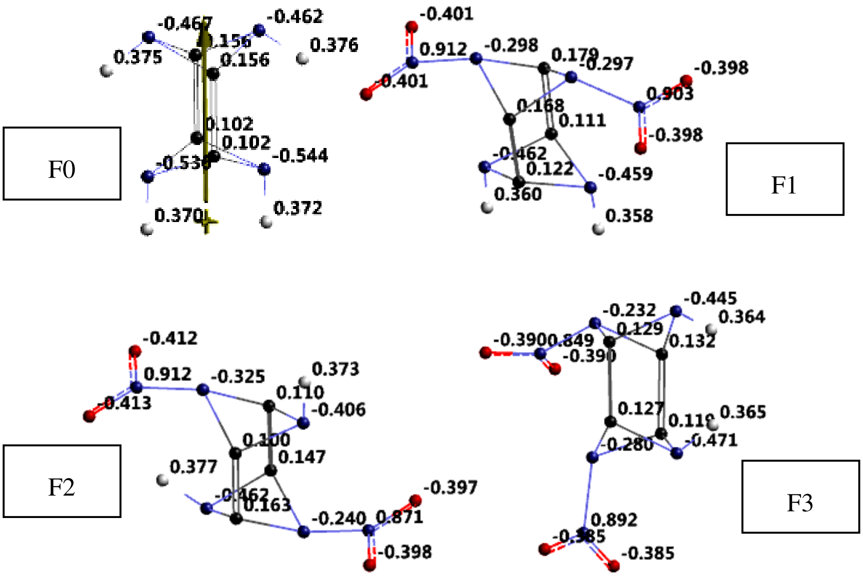

Figure 4. ESP charges on atoms of F0 and of the dinitramine isomers considered.

Figure 5 shows some of the molecular orbital energy levels of F0 and the isomers considered. The HOMO and LUMO energies in kJ/mol are tabulated in Table 4 which also contains the interfrontier molecular orbital energy gaps (Δε). The HOMO and LUMO energy orders are the same and F2<F1<F3<F0. These isomers have embedded enamine as well as nitramine groups. Note that electron donating groups (like NH_2 groups) raise up both the HOMO and LUMO energy levels but electron attractors lower as compared to ethylene [35].

Note that the HOMO and LUMO energy levels of the isomers considered are lower than the respective energies of F0. Comparing the frontier molecular orbital energy levels of F1 and F2, the later one has lower HOMO and LUMO energies. Whereas the comparison between F1 and F3 indicates that F3 has slightly higher HOMO and LUMO energies. The cause of it might be due to intricate charge-charge, lone-pair charge and lone-pair lone-pair type interactions occurring in these structures. In the optimized structures positions of lone pairs are discernable (Figure 1) reflecting the above mentioned interactions.

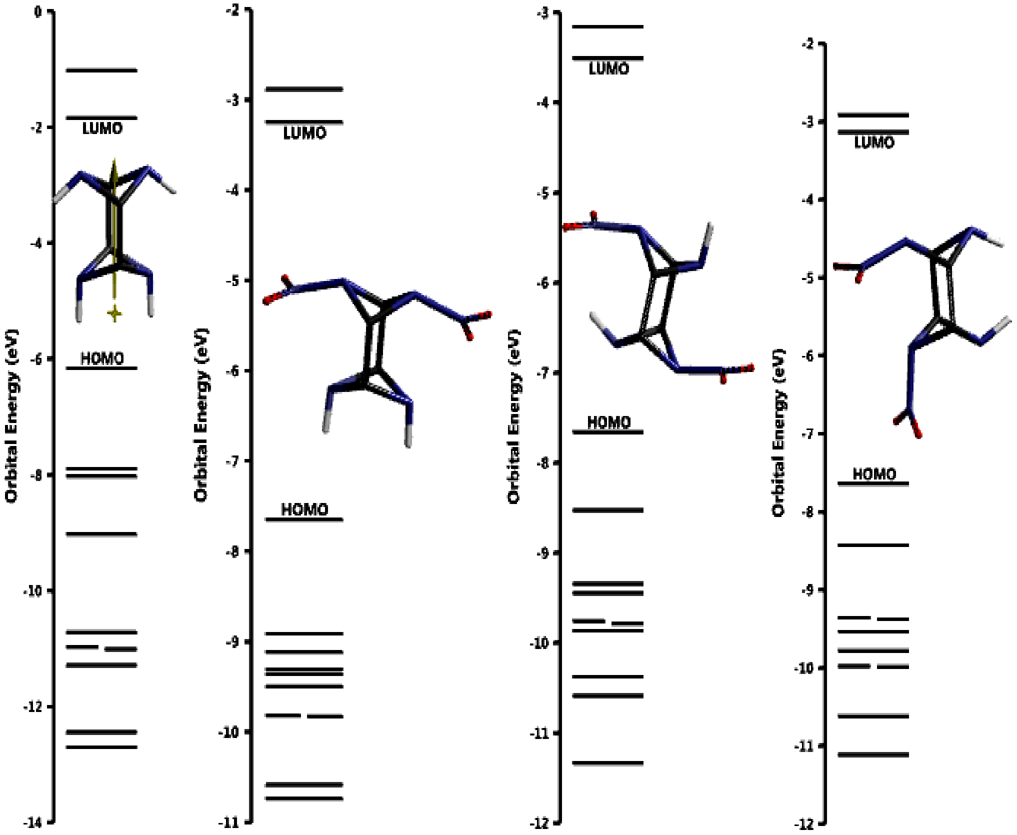

Figure 5. Some of the molecular orbital energy levels of F0 and the dinitramine isomers considered.

Table 4. HOMO, LUMO energies and the interfrontier molecular orbital energy gaps.

	HOMO	LUMO	Δε
F0	-594.37	-177.35	417.02
F1	-737.87	-313.60	424.27
F2	-738.87	-338.38	400.49
F3	-737.23	-302.74	434.49

Energies in kJ/mol.

The order of Δε values is F2<F0<F1<F3, consequently F2 has some sort of bathochromic effect towards the visible region (Figure 6). Note that the spectrums of F1

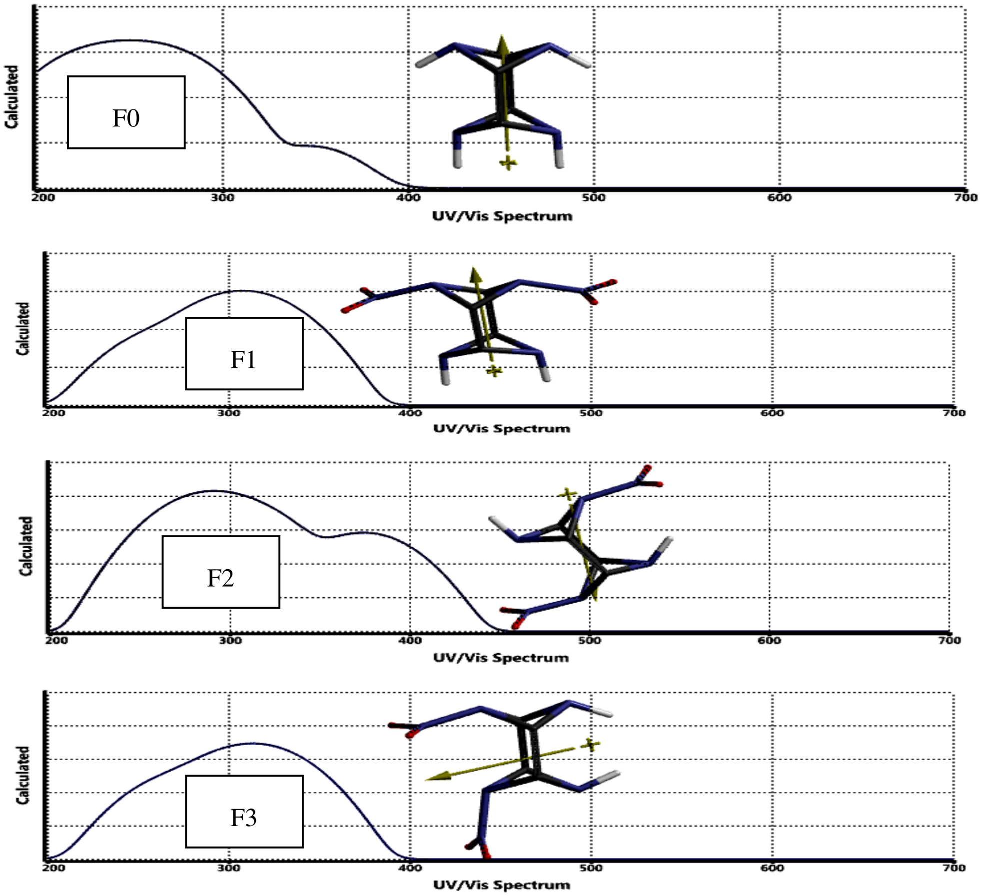

Figure 6. UV-VIS spectra of F0 and the dinitramine isomers considered.

and F3 are quite comparable (time dependent DFT spectra). In those structures, the donor (and acceptor) groups are located at certain site of the molecules. There might be certain parallelism in operation of these groups either in F1 or F3.

On the other hand, the impact sensitivity of explosives has been interrelated with their HOMO-LUMO energy difference (interfrontier molecular orbital energy gap, $\Delta\varepsilon$) [36]. Thus, isomer F2 should be the most sensitive (which is the least stable isomer of all) and F3 be the least sensitive ones.

Figure 7 shows the HOMO and LUMO patters of F1-F3. As seen in the figure, the nitramine NO_2 groups contribute into the HOMO and LUMO either nothing or very little but in each case large contributions come from the ring structure (backbone C_4N_4).

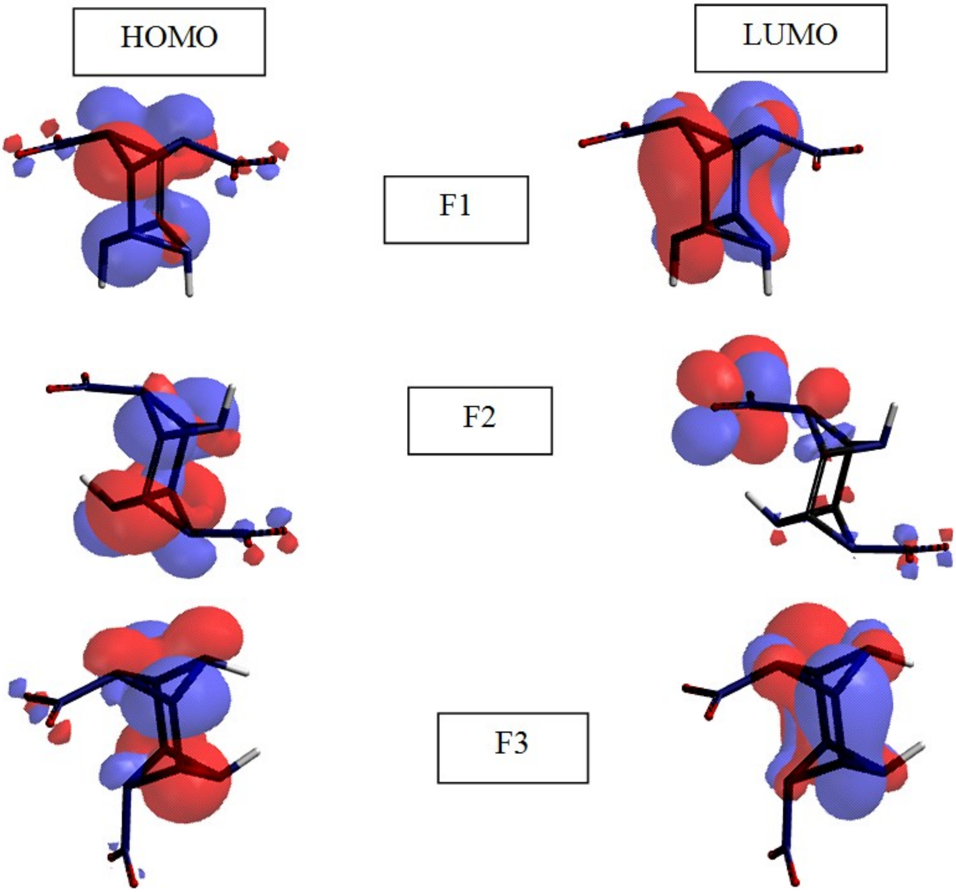

Figure 7. HOMO and LUMO patterns of the isomers considered.

Figure 8 displays the electrostatic potential maps of the isomers considered. In the

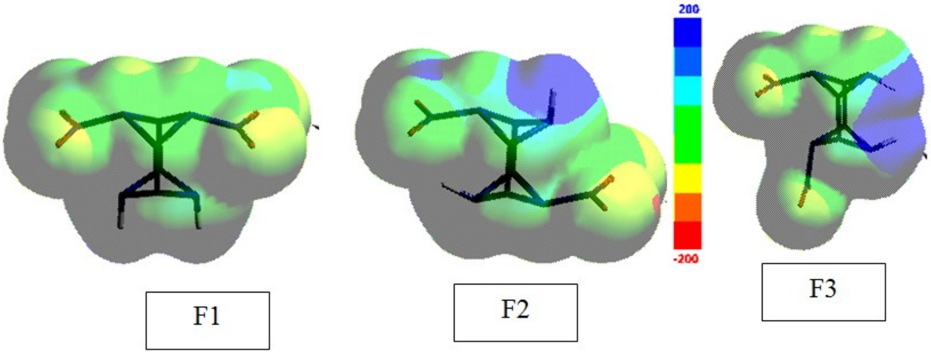

Figure 8. Electrostatic potential maps of the isomers considered.

figure the negative electrostatic potential regions (red ones) are over N-H moieties. Note that impact insensitive organic molecules have smaller areas of negative potentials but significantly stronger than the positive ones. Whereas, impact sensitive compounds possess regions of positive potentials still larger but as strong as or stronger than the negative regions [37].

Figure 9 shows the LUMO maps of the isomers considered. The LUMO map encodes the absolute value of the lowest unoccupied molecular orbital (LUMO) onto an electron density surface [37]. This reveals where an electron pair (a nucleophile) is likely to attack.

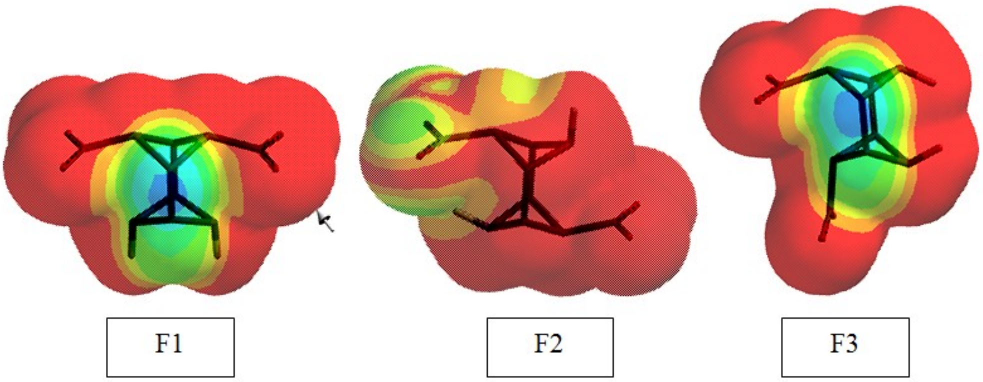

Figure 9. LUMO maps of the isomers considered.

Conclusion

The present treatise has indicated that the isomers of dinitro derivatives of the title structure are highly endothermic but electronically stable. The presence of 1,4-diazetidine decks are somewhat in interaction with each other through resonance over carbon-carbon double bonds. The various charge and lone-pair interactions dictate the conformations of the nitro groups. Positional variations of the nitro groups do not influence the HOMO energies much but have much greater effects on the LUMO energy levels. Consequently, the interfrontier molecular energy gaps happen in such a way that isomer F2 which is the least stable of all has the narrowest gap. Thus it is supposed to be more sensitive to impact stimuli than the others as explosive.

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