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Effect of Isotopic Nitrogen Exchange on NTO Molecule-A DFT Approach

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Abstract

5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO), is an insensitive energetic material. It is one of the most studied nitrotriazole type explosives. In the present study, a set of NTO molecules subjected to ^{15}N exchange one at a time have been investigated in terms of energies within the realm of density functional theory at the level of B3LYP/6-311++G(d,p). The effect of isotopic exchanged type perturbation on the infra red frequencies and intensities have been searched. Also, the lactam/lactim tautomerism involving NTO and its ^{15}N exchanged derivatives are studied and discussed.

1. Introduction

The synthesis of nitrotriazoles as energetic materials and as intermediates to energetic materials has received a great deal of attention in the past decades [1]. The most studied nitrotriazole explosives is 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO), because it exhibits good thermal stability [2] and low chemical sensitivity to radiation damage [3] and is relatively insensitive to impact and shock [4]. NTO was first reported in 1905 [5] incorrectly as its hydroxy tautomer [6]. Its explosive nature was recognized later. It was first characterized as an insensitive energetic material in 1988 [7]. In recent years, NTO and some tautomers of it have been published [8,9] in addition to various articles appeared in the literature investigating NTO from different scientific points of interests [10-14].

On the other hand, substituting one isotope for another or an atom at which bonds are breaking or rehybridizing, typically leads to a change in the rate of the reaction. It is known that when the bonds broken or formed involve those to hydrogen, the effect of

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replacing hydrogen with deuterium often is relatively large and can be measured. Isotope effect with other atoms have also been studied but the effects are typically small and sometimes difficult to quantified [15]. To a good approximation the potential energy of the system does not change with substitution of one isotope for another. In other words, the relative energies of the minima and maxima or the energy surface do not change with isotopic substitution [15]. However, the shapes of the potential wells or the energy surface are composites of the various vibrational states of the molecule. When considering a reaction, it is sufficient to consider the shapes of these wells as being dominated by the vibrational modes that are undergoing the most change during the reaction [15].

2. Method of Calculation

In the present study, the initial geometry optimizations of all the structures leading to energy minima were achieved by using MM2 method then followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [16,17] at the restricted level [18]. 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 B3LYP/6-311++G(d,p) [19,20]. 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 [21]. Also note that the correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [22] and Lee, Yang, Parr (LYP) correlation correction functional [23]. Presently, a rather high level of basis set has been employed [18,24]. 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 indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths were thoroughly searched in order to find out whether any bond cleavage occurred or not during the geometry optimization process. All these computations were performed by using SPARTAN 06 [25].

3. Results and Discussion

^{15}N exchanged NTO

NTO molecule can be considered as a five membered lactam having two of them. In the present study, firstly four nitrogen (^{14}N) atoms present in the structure of NTO skeleton have been exchanged with ^{15}N isotope one by one (perturbed NTO, perturbed lactam). Then, the perturbed systems engendered as well as 1,3-proton tautomers of NTO have been investigated computationally. Figure 1 shows the tautomers of present interest.

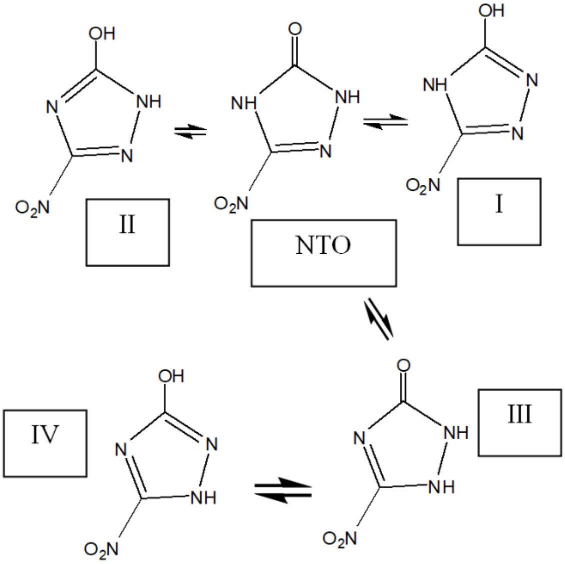

Figure 1. Structures of the tautomers considered.

In general isotopic exchange process is a kind of centric perturbation [26] involving atomic nucleus while the connectivity of atoms remains as it has been previously. Thus, an isotopic exchange affects only limited number of properties of molecules. One of those properties is some of infrared frequencies of the molecules considered. The exchange affects IR spectrum because the accompanying changes in the bond constant(s) and the reduced mass values [27,28]. Note that those factors are also dependent on the environmental factors within the molecule.

Figure 2 shows the sites of exchanged nitrogen atom of NTO molecule. Note that one atom of nitrogen has been exchanged at a time (perturbed NTO). The corresponding NTO molecules are named accordingly as A, B, etc.

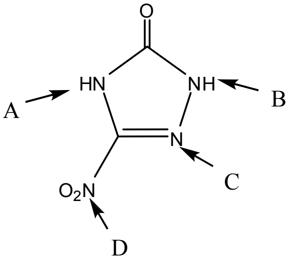

Figure 2. The nitrogen sites where the nitrogen exchange happens.

Table 1 lists the N-H and C=O stretching frequencies of the structures considered. Where, structures A-D possess one nitrogen exchanged with ^{15}N each time. As seen in the table, effect is manly on the intensities, the frequencies are affected very little. All these structures have the calculated dipole moment of 1.66 debye and the polarizability value of 48.15 10^{-30} m^3.

Table 1. The N-H and C=O stretching frequencies of the structures considered.

Structure	ν (N-H)	ν (C=O) cm^{-1}
NTO	3650, 3648	1846
	100.84, 181.40	862.41
A	3650, 3640	1845
	136.77, 143.81	857.07
B	3649, 3641	1845
	137.74, 143.57	858.19
C	3650, 3648	1846
	100.81, 181.44	863.35
D	3650, 3648	1846
	100.95, 181.31	865.12

Frequencies in cm^{-1} units. Second entry in each row stands for intensities.

Table 2 lists the zero point vibrational energies (ZPE), their differences (ΔZPE, with respect to NTO) and the corrected total electronic energies (E_C values) of NTO and the perturbed lactams considered. The order of ZPE values is D<A<B<C<NTO. The order is dictated not only by the isotopic exchange process but also by the topology of the site of the perturbation because in each case the overall effect should be governed by a different potential energy surface that the structure owed. The E_C values follow the order of D<A<B<C<NTO. Thus, electronically the most stable and the least stable structures are D and NTO, respectively. Note that structure-D has the smallest ZPE value, consequently it has the most negative E_C value. However, the variations between the E_C values are small. Because, the isotope effect with heavier atoms rather than deuterium is typically small and sometimes difficult to measure [15]. Also note that nitrogen atom at position-D is a part of the nitro group and different from the other nitrogen atoms in NTO molecule. The nitrogen at position-A is also different (different centers in the π-electron topology) from nitrogens at position-B and especially at position-C. Because, nitrogens at positions

A and B can be in conjugation with the lactam keto group at different extents. Thus, the corresponding potential surfaces and the ZPE values for all the isotopically perturbed NTOs are different.

Table 2. ZPE, ΔZPE and E_C values of NTO and the perturbed lactams considered.

Structure	ZPE	ΔZPE	E_C
NTO	173.96	0	-1370698.550
A	173.515498	-0.4445	-1370698.995
B	173.524965	-0.43503	-1370698.985
C	173.540823	-0.41918	-1370698.969
D	173.417763	-0.54224	-1370699.092

E:-1370872.51kJ/mol.

Table 3 lists some standard state thermo chemical properties of the structures considered. Note that entropy has contributions from translation, rotation, vibration and electronic terms. Since, electronic energy and ZPE as well as some other factors are the contributors of enthalpy and Gibbs free energy they are affected by isotope exchange process [15,29]. The table indicates that all the structures have exothermic heat of formation values and favored Gibbs free energy of formations. The H° and G° values follow the algebraic order of D<A<B<C<NTO and D<B<A<C<NTO, respectively. Structures A ad B exchange their positions in the orders of H° and G° mentioned above because of their entropy values.

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

Structure	H° (kJ/mol)	S° (J/mol°)	G° (kJ/mol)
NTO	-1370691.731	341.38	-1370793.515
A	-1370692.143	341.67	-1370794.014
B	-1370692.125	341.80	-1370794.035
C	-1370692.112	341.76	-1370794.008
D	-1370692.238	341.71	-1370794.119

1,3-Prototropic forms

NTO molecule possesses lactam moieties in a five membered ring which may exhibit lactam/ lactim tautomerism [26]. Due to the fact that tautomers having different structures possess dual reactivity, it is anticipated that an energetic material potent to exhibit tautomerism should display variable ballistic properties (beside others) depending on its tautomer content (allelotropic mixture [30]). Note that substances which are isomeric under certain conditions are tautomeric under more drastic conditions [30]. NTO is such an explosive material which can have different tautomers [9], and intra or inter-molecularly hydrogen bonded species.

In the present study, NTO and the isotopically perturbed tautomers of it have been considered in terms of cationotropic tautomeric transformations, namely prototropic tautomeric conversions of intramolecular type (lactam/lactim tautomers only, the nitro/*aci* tautomerism is not considered.) [30].

Figure 3 shows the optimized forms of lactim species engendered from NTO (NTO and perturbed NTOs). Note that lactim-I and lactim-II are constructed from the lactam by transferring proton at site-B and site-A, respectively.

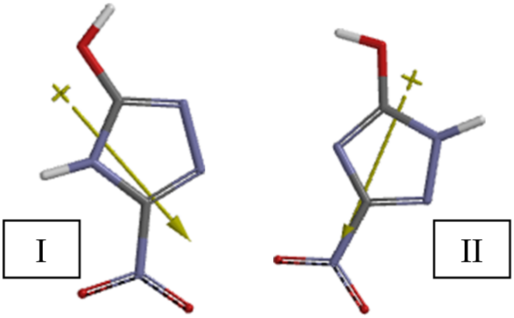

Figure 3. The optimized forms of lactim species considered.

Table 4 shows the ZPE and E_C values of type-I lactims considered. Note that the lactims considered are isotopically perturbed ones. They possess ^{15}N atom at the indicated sites. Structures I and II, in Tables 4 and 5, are the lactims of type-I and type-II, respectively which are obtained from NTO having all nitrogens of ^{14}N. Note that the notation used in the tables is such that number in front of the letter indicates the type of the lactim considered and letter stands for the position of ^{15}N atom. The numbers I and II are two different lactim forms of unperturbed NTO (see Figure 3). The orders of ZPE and E_C values are ID<IA<IB=IC<I and ID <IA<IB=IC<I, respectively.

Table 4. ZPE and E_C values of type-I lactims considered.

Structure	ZPE	E_C
I	172.74	-1370638.50
IA	172.27	-1370638.97
IB	172.33	-1370638.91
IC	172.33	-1370638.91
ID	172.19	-1370639.05

E:-1370811.24 kJ/mol.

Table 5 shows the ZPE and E_C values of type-II lactims considered. The orders or ZPE and E_C are IID<IIB<IIA<IIC<II and IID<IIB<IIA<IIC<II, respectively.

Table 5. ZPE and E_C values of type-II lactims considered.

Structure	ZPE	E_C
II	174.55	-1370661.74
IIA	174.12	-1370662.17
IIB	174.09	-1370662.20
IIC	174.13	-1370662.16
IID	174.00	-1370662.29

E :-1370836.29 kJ/mol.

Tables 6 and 7 show the energy variations in the lactam/lactim tautomerism involving lactims I and II types considered. As seen in the tables, in all the cases lactam forms are preferred in the tautomeric equilibrium. Note that the values listed there implicitly include the combined effects of isotopic exchange (except NTO*) as well as the topology of the π-system involved. In Table 6 the order of values is A<D<NTO*<C<B whereas in Table 7 it is B<D<C<NTO*<A. Since NTO* is isotopically unperturbed structure, comparing the relevant values for NTO* in Tables 6

and 7 it is obvious that the tautomeric equilibrium for lactim-II is relatively more favorable over lactim-I equilibrium for unperturbed NTO and each exchanged case. In all the cases the increased nucleophilicity of nitrogen atom at site-B over the one at site-A might be due to the α-effect [31] exerted by the nitrogen atom at site-C.

Table 6. Energy variation in the tautomerism considered (Lactims of type-I).

Parent lactam Structure	E_C(lactim)-E_C(lactam)
NTO*	60.050
A	60.025
B	60.075
C	60.059
D	60.042

Energies in kJ/mol. * Unperturbed lactam case.

Table 7. Energy variation in the tautomerism considered (Lactims of type-II).

Parent lactam Structure	E_C(lactim)-E_C(lactam)
NTO*	36.810
A	36.825
B	36.785
C	36.809
D	36.802

Energies in kJ/mol. * Unperturbed lactam case.

Table 8 shows the calculated ^{1}H and ^{13}C relative shift values of the tautomers considered (see Figures 1-3 for the structures and labeling of the positions). As seen in the table, isotopic exchange shifts one of the NH protons to down field while the other to high field with respect to NTO lactam form. As for the ^{13}C values they are all shifted to down field as compared to NTO lactam form but at different extents.

Table 8. Calculated ^{1}H and ^{13}C relative shift values of the tautomers considered.

Tautomer	^{1}H	^{13}C
NTO	7.77, 7.57	153.54, 152.54
I	8.72, 5.67	161.65, 159.56
II	8.83, 5.64	168.67, 163.09
II	7.30, 6.31	171.35, 167.11
IV	10.11, 5.13	172.91, 158.20

NMR shifts (ppm). Structures I-IV are lactims.

4. Conclusion

The present DFT treatment of NTO subjected to ^{15}N exchange (within the constraints of the theory and basis set employed) has revealed isotopic exchange of nitrogen decreases the ZPE value with respect to NTO and its more effective on the nitro group whereas the least effective on position-C. Consequently, the electronic stabilities vary in such a way that the exchange produces perturbed NTO structures which are more stable than NTO itself, the most stable one happens when the exchange occurs on the nitro group. On the other hand, the tautomeric equilibrium for lactim-II is relatively more favorable over lactim-I equilibrium for unperturbed NTO and each exchanged case.

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