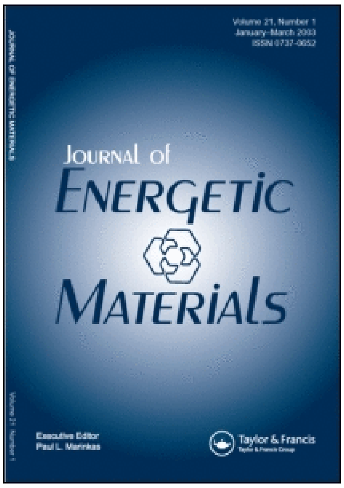

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A Theoretical Study on Nitrourea and its Tautomers

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In the present study, nitrourea and its possible tautomers have been subjected to theoretical analysis by performing Hartree-Fock and also density functional theory (DFT) calculations. The optimized geometries, vibrational frequencies, and some thermodynamical values for the presently considered species have been obtained in their ground states.

Keywords: DFT, explosive, Hartree-Fock, nitrourea, tautomers

Introduction

Nitrourea (see Fig. 1) is a cool but powerful explosive, and it tends to decompose spontaneously in the presence of moisture. The mechanism of its reactions is the same as that of the reactions of nitroguanidine, which differs from nitrourea by containing an >NH group instead of a carbonyl group, but the reactions of nitrourea are very much more rapid. The nitro group promotes the urea rearrangement, so that nitrourea when

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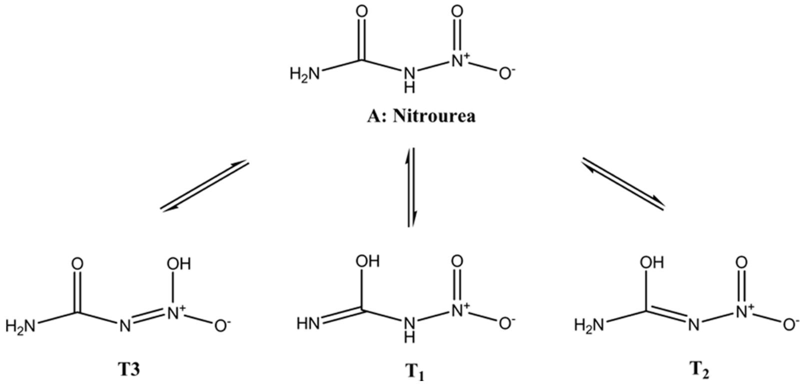


Figure 1. Various tautomers of nitrourea.

dissolved in water or when warmed breaks down into cyanic acid and nitroamide much more readily than urea breaks down under like conditions into cyanic acid and ammonia. Whereas the imido group in the structure of guanadine in place of the carbonyl of nitrourea hinders it, thus guanidine rearranges less readily than urea [1].

Nitrourea is prepared by adding dry urea nitrate in small portions to concentrated sulfuric acid with gentle stirring while the temperature of the mixture is kept below 0°C.

In water and in hydrophilic solvents, nitrourea dearranges rapidly into cyanic acid and nitroamide. Alkalis promote the reaction. If an aqueous solution of nitrourea is warmed, bubbles of nitrous oxide begin to come off at about 60°C. It reacts with alcohols to form carbamic esters (urethanes) and with primary and secondary amines to form mono- and unsym-di-substituted ureas [1].

In the literature, apart from being an explosive material, nitrourea has found use in some synthetic applications [2–4]. Almog and coworkers used nitrourea to convert deactivated aromatic compounds to the corresponding nitrated derivatives with a high yield and a high regioselectivity under very mild conditions [2]. Moreover, Klasek and coworkers studied the reaction of 3-aminoquinoline-2,4-diones with nitrourea [3].

The synthesis, characterization, and thermal studies of 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane, which is an explosive nitrourea derivative (contains an embedded nitrourea), has been performed by Sikder's group [4].

In the present study, the molecular orbital properties of nitrourea (a powerful explosive) and its possible tautomers have been investigated by the application of Hartree-Fock, MP2, and DFT calculations with various basis sets.

Method

Determination of the most stable configurational form of the tautomers and the initial geometry optimizations of all the structures leading to energy minima were achieved by using a molecular mechanics (MM2) method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [5,6] at the restricted level [7] followed by STO type calculations. Then, geometry optimizations were achieved within the framework of density functional theory (DFT, B3LYP) [8,9] at the levels of 6-311G(d,p), and 6-311++G(d,p; both restricted and unrestricted). 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 [10]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [11] and Lee, Yang, Parr (LYP) correlation correction functional [12].

In addition to the DFT calculations, Hartree-Fock 6-311G(d,p) and 6-311++G(d,p) calculations [13] were performed at both restricted and unrestricted levels. Furthermore, single-point MP2 calculations were carried out (for the ab initioRHF calculations) in order to obtain more accurate energy data.

In this study, in order to study N-NO_2 bond strengths in nitrourea tautomers, homolytic bond dissociation energy (BDE) calculations (DFT calculations by using 6-311G(d,p) basis set) for the removal of nitrogen dioxide moiety from the structures were performed. The homolytic BDE [14,15] is defined for the present case as: $\mathrm{BDE} = E(\mathrm{NO_2}) + E(\mathrm{R}) - E(\mathrm{R} - \mathrm{NO_2})$, where E stands for the respective total energy corrected for the zero-point energy for each parent structure and the fragments of the low-energy NO_2 scission reaction. Furthermore, the basis set superposition error (BSSE) analyses were carried out with the counterpoise method, introduced by Boys and Bernardi [16]. The corresponding BSSE analyses were performed at the same theoretical level.

For each set of calculations, vibrational analyses were done (using the same basis set employed in the corresponding geometry optimizations). 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 the Gaussian 98 package program [17].

Results and Discussion

One of the important processes effective on explosives is tautomerism, which influences the composition as well as interferes with mechanisms occurring during detonation of high-energetic nitro compounds, by the involvement of the transfer of a hydrogen atom either by an unimolecular 1,3- or 1,5-shift or by a bimolecular process where the transfer occurs intermolecularly [18–26]. This hydrogen (proton) shift leads to the establishment of *aci*-nitro equilibrium in which most of the cases the *aci* form dissociates by release of energy to give small fragments. Of course, tautomerism is competitive to many other reactions that occur during the detonation. Hydrogen transfer reactions involving a 1,3-H shift are very common in organic and biological systems. More prevalent tautomeric processes are keto-enol, imine-enamine, nitroso-oxime, thiol-thione, amide-iminol, nitro-*aci*, hydrazo-azo, phenol-keto, etc. Keto-enol tautomerism is the most commonly observed and most widely studied process and is very important in many chemical, biochemical and medicinal chemistry applications. Nitro-*aci* tautomerism occupies a special role as it has been speculated to occur under conditions where high-energy explosive detonates. It has been proposed as one of the important initial steps responsible for the cascade of reactions leading to the high energy release during detonation [18]. In this study, the discussion deals with nitrourea and its tautomers by using quantum chemical investigation. Nitrourea (A) and its tautomers (T1, T2, and T3) are shown in Fig. 1, whereas Fig. 2 shows the numbering of the atoms used in this study. The geometry optimized structures of the compounds at the RHF/6-311++G (d,p) level are presented in Fig. 3. Furthermore, we found very good agreement between the calculated geometries of the molecules among the different theoretical levels performed in this study. Unfortunately, we did not reach any X-ray diffraction study about concerned molecules, so they were not compared with any experimental data.

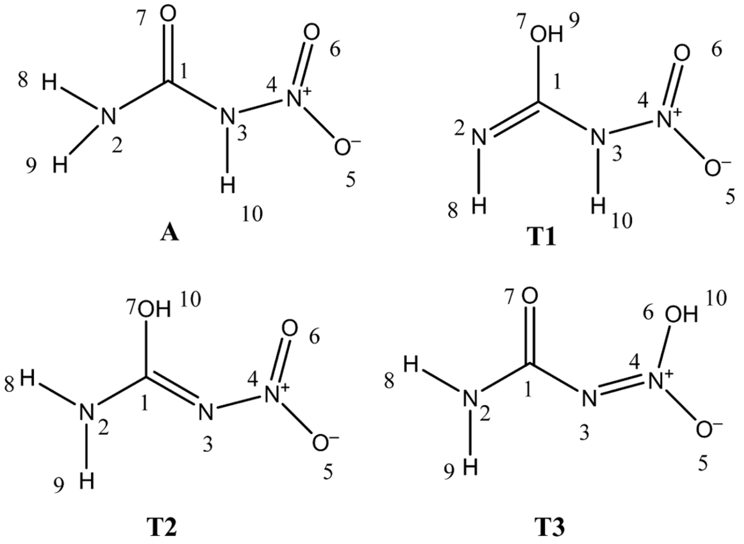
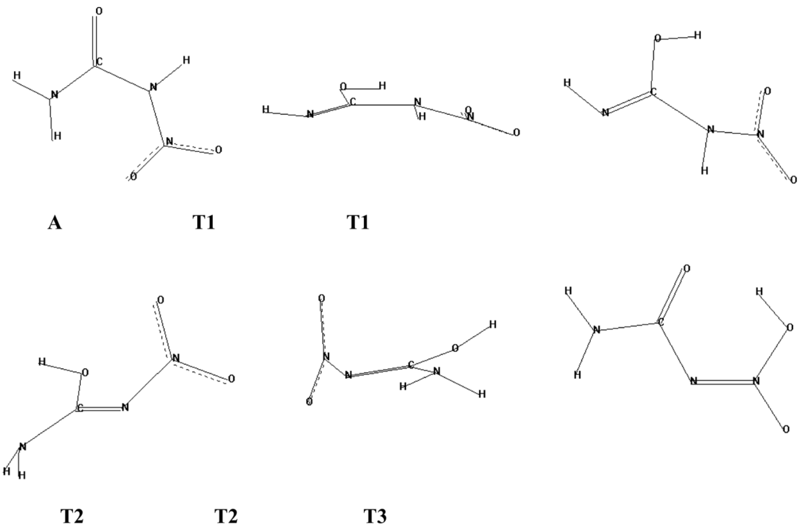


Figure 2. Numbering of atoms.



A T1 T1

T2 T2 T3

Figure 3. RHF/6-311++G (d,p) optimized structures.

Nitrourea is the nitramine-type organic explosive and it was found that polynitro aliphatics containing at least one N-NO_2 (nitramine) linkage are more sensitive than nitroaliphatic explosives containing C-NO_2 linkage [27]. As shown in Fig. 3, nitrourea and its tautomer T3 are planar molecules; however, other tautomers possess nonplanar structures. Furthermore, the position of nitro group in tautomer T2 is vertical to the molecular plane, unlike to the other tautomers (see Fig. 3). As mentioned before, nitrourea is a planar molecule, which might be due to the involvement of full conjugation of lone pairs of nitrogen atoms in the molecule.

The numbering in Table 1 is consistent with the numbering scheme employed in Fig. 2. The calculated geometric parameters of the molecules presently considered at different theoretical levels are shown in Table 1. Average bond length of C-N in amines is 1.473 Å [28]. In the nitrourea and its tautomers, the corresponding bond is found to be significantly smaller than this value at all theoretical levels performed here (see Table 1). Thus, some extent of conjugation between

Table 1
Calculated structural parameters (bond lengths in Å and dihedral angles in degrees) of concerned species

RHF/6-311G (d,p)						RHF/6-311++G(d,p)				
	C1-N2	C1-O7	C1-N3	N3-N4	O6-N4-N3-C1	C1-N2	C1-O7	C1-N3	N3-N4	O6-N4-N3-C1
A	1.3345	1.1875	1.4165	1.3465	179.9	1.3345	1.1885	1.4155	1.3475	180.0
T1	1.2395	1.3135	1.4195	1.3485	21.6	1.2415	1.3135	1.4205	1.3505	23.7
T2	1.3615	1.3195	1.2615	1.3915	109.2	1.3605	1.3185	1.2635	1.3905	112.0
T3	1.3265	1.2935	1.3868	1.2729	180.0	1.3335	1.2155	1.3875	1.2735	180.0
B3LYP/6-311G (d,p)						B3LYP/6-311++G(d,p)				
	C1-N2	C1-O7	C1-N3	N3-N4	O6-N4-N3-C1	C1-N2	C1-O7	C1-N3	N3-N4	O6-N4-N3-C1
A	1.3465	1.2095	1.4365	1.3875	12.9	1.3465	1.2115	1.4365	1.3875	−165.5
T1	1.2605	1.3315	1.4305	1.3755	−17.1	1.2615	1.3325	1.4305	1.3765	19.5
T2	1.3475	1.3445	1.3075	1.3965	170.7	1.3465	1.3445	1.3075	1.3935	167.3
T3	1.3465	1.2435	1.3965	1.3025	180.0	1.3465	1.2435	1.3985	1.2995	180.0

nitrogen's lone pairs and the carbonyl group should exist. The longest N3-N4 bond length is found to be in the tautomer T2, due to the absence of any π-interaction between nitro and attached nitrogen atom, because the nitro group is vertical to the plane of the molecule. Except for T2, C1-N2 bond length is significantly shorter than C1-N3 bond. This is due to an electron withdrawing effect of the nitro substituent. As for the N-NO_2 bond length, this bond in T2 is longer than the bonds in other isomers. It is well known that for the same type bond, the shorter the bond length is, the stronger the bond is, and vice versa. Keeping in mind that for the nitramine type of explosives, one of the possible initiation steps for the decomposition reactions is the N-NO_2 bond cleavage [29]. So this tautomer (T2) might have a relatively important role in the inititation step compared to other tautomers according to the calculated bond lengths. The N-NO_2 bond lengths from the DFT methods of calculation suggest that the order of N-NO_2 bond strengths in this tautomer is in the following order: T2 $>$ A $>$ T1 $>$ T3, on the other hand, in the Hartree-Fock method the order is T2 $>$ T1 $>$ A $>$ T3.

Note that the hydrogen bonding in T2 and T3 are destabilizing and stabilizing, respectively, because in T2, to form hydrogen bonding, the nitro oxygen atom linked to hydrogen by donation of its lone pair acquires a partial positive charge, which is, of course, next to the positively charged nitrogen thus a destabilizing effect arises, whereas in T3, the hydrogen bonding results in an elongated O-H bond; hence, the bonding electron of oxygen atom is confined to oxygen more effectively, which should be a favorable situation next to the positive nitrogen atom. Indeed, the geometry optimized structure for T3 is favorable for the hydrogen bonding but not for T2 (see Fig. 3).

Table 2 shows the calculated total energies of concerned species (zero-point energies are taken into account). In terms of energy considerations, stability order is A $>$ T3 $>$ T1 $>$ T2 at all theoretical levels (except UHF/6-311G (d,p) level); see Table 2. This result is also consistent with the geometrical parameters. T2 has the longest bond length of N-NO_2.

Table 2

Calculated total energies (in au) of concerned species at different theoretical levels

	A	T1	T2	T3
RHF/6-311G(d,p)	−427.4752940	−427.4435820	−427.4418930	−427.4639740
	(−428.9592389)	(−428.9322415)	(−428.9291534)	(−428.9467871)
RHF/6-311++G(d,p)	−427.4860960	−427.4540640	−427.4536780	−427.4684150
	(−428.9805185)	(−428.9540158)	(−428.9533560)	(−428.9688311)
UHF/6-311G(d,p)	−427.4752940	−427.4435820	−427.4449230	−427.4581760
B3LYP/6-311G(d,p)	−429.8040370	−429.7752410	−429.7734460	−429.7941330
UB3LYP/6-311G(d,p)	−429.8040370	−429.7752410	−429.7734460	−429.7941340
B3LYP/6-311++G(d,p)	−429.8193600	−429.7901300	−429.7896950	−429.8090150

The total energies are corrected for ZPVE. The values in parentheses are MP2 single-point calculations on corresponding RHF geometry optimizations.

Studies on the bond dissociations are important and essential for understanding of the decomposition process of the energetic materials, since they are directly relevant to the sensitivity and stability of the energetic materials [30–34]. Previous studies [35,36] on BDE for the nitro compounds such as nitro aromatic and nitramine molecules have shown that there is a parallel relationship between the BDE for the weakest R-NO_2 or N-NO_2 bond scission in the molecule and its sensitivity. Usually, the larger the BDE value, the lower the sensitivity. However, this is only applied to the molecules in which R-NO_2 (or N-NO_2) bond is the weakest one. Table 3 summarizes the computed homolytic BDE values of N-NO_2 for the presently considered species. The BDEs include the BSSE and ZPVE corrections. For the initial stages in their thermal decompositions, it can be deduced on the basis of the BDE that the relative stability order of these molecules may be in the following sequence: $A > T2 > T1$ by the DFT method. Since T3 contains $N{=}NO_2H$ group (*aci* form) in which NN double bond is less likely to undergo any cleavage, T3 has been excluded in the BDE calculations.

Due to the likely delocalization of lone-pair of amide nitrogen toward the nitro group in A and T1, the NN bond has some double bond character. Thus, the expected NN bond lengths should follow the order of $T2 > A > T1$ and indeed it is the calculated sequence in DFT calculations (see Table 1). So, the expected BDE values based on bond distances should normally be $T2 < A < T1$ because, as the distance increases, the bond should be less stable. However, for polar bonds, the homolytic BDE is to be affected by the charge distribution and the magnitudes of the partial charges on the atoms involved in the particular bond considered. Thus, the presently calculated hemolytic BDE order ($T1 < T2 < A$) is probably dictated not only by the bond lengths but also the charges accumulated. Moreover, the stabilities of the fragments are to be considered as well.

The chemical reactivity is affected by HOMO of the nucleophile and LUMO of the electrophile interaction. By studying the HOMO and LUMO it is foreseen whether or not the reaction is feasible. The calculated frontier molecular orbital energy

Table 3

The calculated homolytic bond dissociation energies (BDE) of N-NO_2 bonds for the species considered at different theoretical levels (UB3LYP/6-311G (d,p))

	A	A fragment	T1	T1 fragment	T2	T2 fragment	NO_2
Total energy	−429.80404	−224.60988	−429.77524	−224.59477	−429.77345	−224.58537	−205.12390
BDE	168.6		131.5		154.1		

Total energies are in au, BDEs are in kJ/mol, the BDEs include the basis set superposition error (BSSE) and zero-point energy (ZPE) corrections.

Table 4
The HOMO and LUMO energies (ε) of considered species at B3LYP/6-311++G(d,p) level (energies in eV)

	A	T1	T2	T3
HOMO	−8.559	−8.221	−7.932	−8.479
LUMO	−2.739	−2.984	−2.413	−2.817
$\Delta\varepsilon$	5.821	5.237	5.520	5.663

$\Delta\varepsilon = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$.

Table 5
The HOMO and LUMO energies (ε) of considered species at MP2/6-311++G(d,p) single-point calculations over corresponding RHF geometry optimizations (energies in eV)

	A	T1	T2	T3
HOMO	−12.329	−11.647	−11.615	−11.732
LUMO	1.027	1.201	0.475	0.917
$\Delta\varepsilon$	13.356	12.848	12.09	12.649

$\Delta\varepsilon = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$.

gap of the molecules obtained at various levels is displayed in Tables 4 and 5. According to the results, the largest energy gap belongs to nitrourea and the smallest energy gap belongs to the tautomer T1. Generally, the higher value of energy gap resulting from higher energy of LUMO and lower energy of HOMO indicate that neither losing nor capturing electron would happen on the compound easily, so it is more stable.

Conclusion

The present calculations revealed that nitrourea is closely followed by T3 (the *aci* form) in terms of stability. On the other hand, based on homolytic BDE calculations, the N-N bond in T1 is more susceptible to undergo cleavage than either nitrourea or T2. However, one should note that our calculations are for isolated molecules at vacuum conditions. In the bulk and crystalline form, the behavior of all the species presently considered might be different than the ones obtained by calculations.

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