

# Quantum chemical study on 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO) and some of its constitutional isomers

Lemi Türker\*, Taner Atalar

Middle East Technical University, Department of Chemistry, 06531 Ankara, Turkey

Received 29 March 2006; received in revised form 4 May 2006; accepted 5 May 2006

Available online 11 May 2006

## Abstract

Presently, certain isomeric compounds of NTO and their tautomers have been investigated by performing density functional theory (DFT) calculations at B3LYP/6-31G(d,p) and ROB3P86/6-311G(d,p) levels and also *ab initio* calculations at RHF/6-311G(d,p) level. The optimized geometries, vibrational frequencies, electronic structures and some thermodynamical values for the presently considered NTO isomers have been obtained in their ground states. Also, detonation performances were evaluated by the Kammler–Jacobs equations, based on the calculated densities and heat of formation values. The homolytic bond dissociation energies (BDEs) (at ROB3P86/6-311G(d,p) level) of N–NO<sub>2</sub> and C–NO<sub>2</sub> for the molecules were calculated. Moreover, aromatic character of NTO and its isomers and tautomers were investigated by performing NICS calculations using the gauge invariant atomic orbital (GIAO) approach at the B3LYP/6-31G(d,p) and B3LYP/cc-pVDZ levels.  
© 2006 Elsevier B.V. All rights reserved.

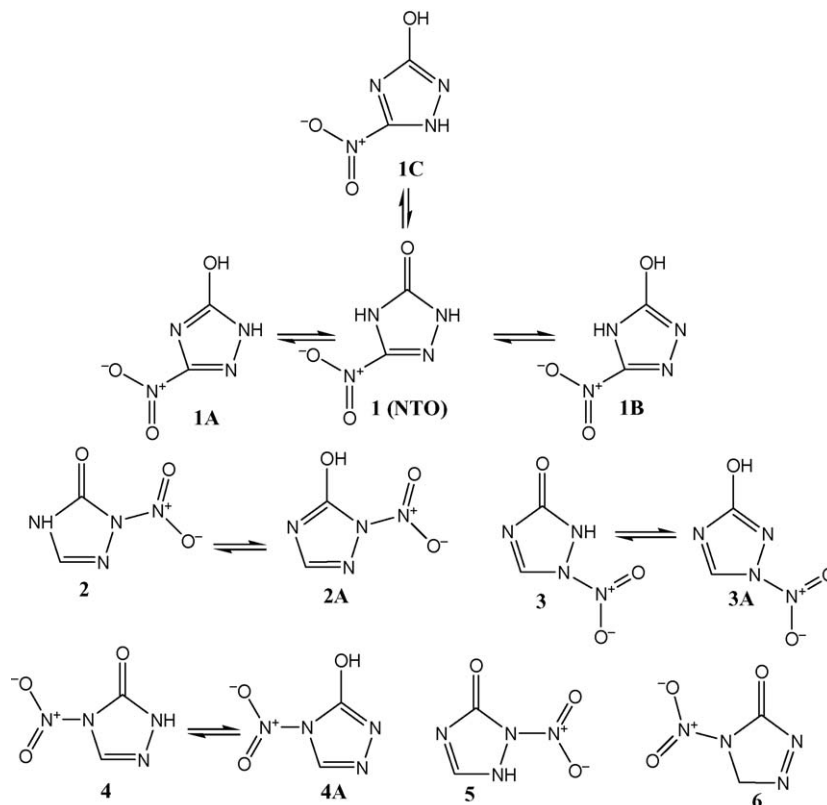
**Keywords:** NTO; Explosives; Nitro compounds; Nitramines; Tautomers; HEDM

## 1. Introduction

For the last couple of decades, there has been an extensive search for new high energy density materials (HEDM) to serve fuels or explosives [1]. Good HEDMs have high density, a fast velocity of detonation (*D*) and are energetically unstable with respect to their reaction products. In the past, common explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4,6-trinitrotoluene (TNT) were considered adequate for all weapon applications [2–4]. Because of many catastrophic explosions resulting from unintentional initiation of munition by either impact or shock, aboard ships, aircraft carriers and munition trains, these explosives have become less attractive [1]. Thus, in modern ordnance, there are strong requirements for explosives having good thermal stability, impact and shock insensitivity and better performance. One of the foremost objectives at the stage of the synthesis of new explosives consists in finding the molecules having a good energy capability of optimal safety. The synthesis of nitrotriazoles as energetic materials and

as intermediates to energetic materials has received a great deal of attention in the past 10 years [5]. 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 [6] and low chemical sensitivity to radiation damage [7] and is relatively insensitive to impact and shock [8]. The molecular structure of a generic NTO and its tautomers and isomers and their numbering are shown in Schemes 1 and 2, respectively. NTO was first reported in 1905 [9] incorrectly as its hydroxy tautomer [10]. Its explosive nature was recognized later. A large number of papers related to NTO and its tautomers **1A** and **1B** have been published [11]. As a result of these properties of NTO, it was first characterized as an insensitive energetic material in 1988 [12]. NTO as an explosive compound was developed at Los Alamos in 1983 as a result of on-going explosives synthesis program [12]. Its explosive performance characteristic is similar to RDX, but it is less sensitive [13]. Some applications of NTO have been reported, such as AFX-644, which is a mixture of TNT:NTO:wax:Al (powder), in the proportion of 30:40:10:20. The baseline AFX-644 meets the United Nations' (UN) criteria for extremely insensitive detonating substances [14]. The presence of NTO in the 25:25:50, RDX:NTO:TNT charges, significantly improves the sensitivity, mechanical properties and structural integrity of the explosive [15]. Shells with NTO, such

\* Corresponding author. Fax: +90 312 2101200.  
E-mail address: lturker@metu.edu.tr (L. Türker).



Scheme 1. NTO and its tautomers (**1A**, **1B** and **1C**), its isomers (**2–6**) and tautomers of its isomers.

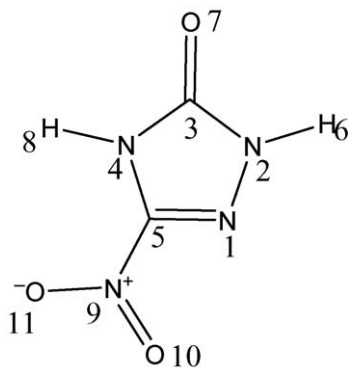
as 40:60 NTO:TNT charges, are relatively insensitive to bullet impact and fuel fire tests [15]. Also, crystals of NTO have been studied and two polymorphic phases are known to exist [16]. The  $\alpha$ -polymorph is the most stable, but an accurate crystal structure has yet to be determined because it undergoes a significant degree of twinning [17]. The  $\beta$ -form of it was reported to be unstable [18] with a monoclinic unit cell (space group  $P2_1/c$ ). A useful summary of the structural aspects, chemical and explosives properties and thermal behavior, has been published [19]. On the other hand, the synthesis and structural characterization of metal salts of NTO, i.e. K, Cu and Pb-NTO were also studied in literature [20]. Although, there have been many studies about NTO in literature [21–29], there has been very rare information about the constitutional isomers or tautomers of NTO

(**2** and **4**, see Fig. 1). In the case of the compound **2**, there is only one paper published concerning the synthesis of it [30] and **4** was mentioned in the literature as an intermediate as a result of decomposition of NTO [31]. Furthermore, to the best of our knowledge, there has been no information about compounds **3**, **5** and **6**, which are the constitutional isomers of NTO. In the literature, there is no theoretical study on the constitutional isomers or tautomers of NTO: **2**, **3**, **4**, **5** and **6**. These structures derived from the NTO have the same main skeleton of the ring. In this study, the position of the  $\text{NO}_2$  changes on the ring for the different isomers of NTO, so derived molecules are mostly nitramine type molecules (see Scheme 1).

Presently, geometric features, electronic structures, thermodynamic properties and detonation performances have been systematically studied for NTO and its isomers and their tautomers using theoretical approaches. In addition, thermal stabilities have been evaluated from the homolytic bond dissociation energies (BDE).

## 2. 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 [32,33] at the restricted level [34]. Then, geometry optimizations were achieved within the framework of density functional theory (DFT, B3LYP) [35,36] at the level of 6-31G(d,p) (restricted closed-shell). The exchange term of B3LYP consists of hybrid Hartree–Fock and local spin



Scheme 2. The numbering scheme and molecular structure of a generic NTO (**1**) molecule.

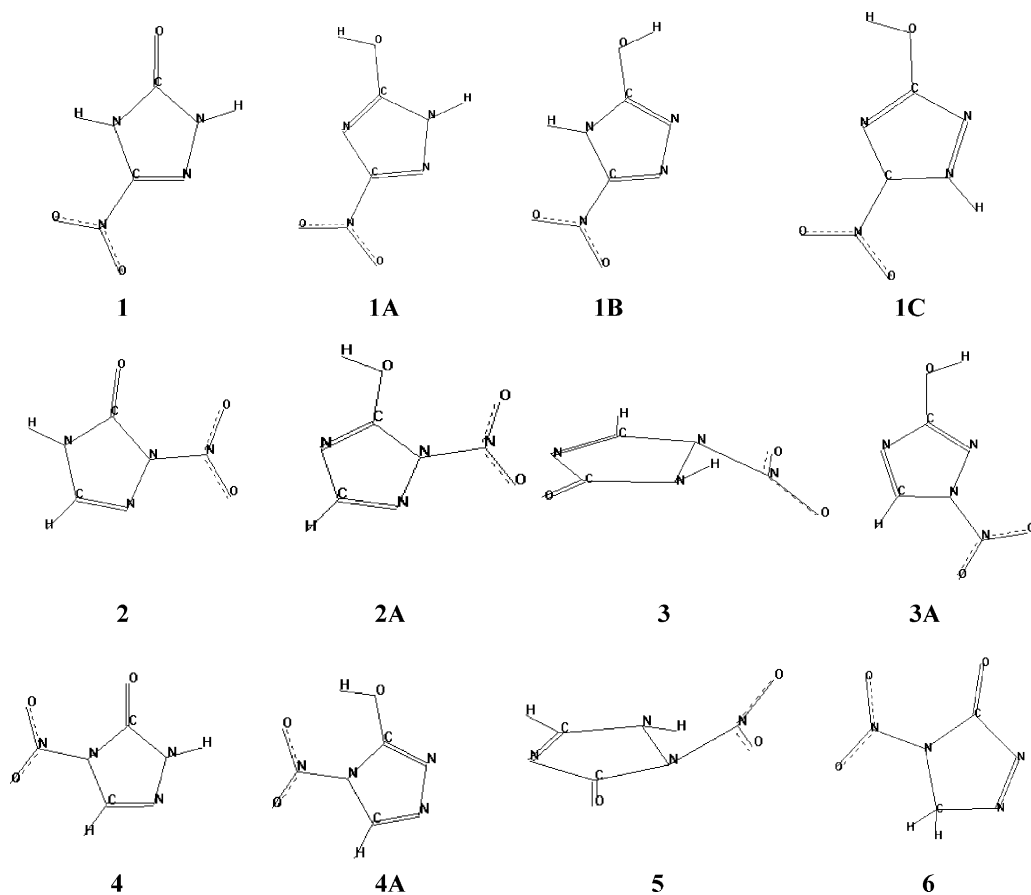


Fig. 1. The geometry optimized (B3LYP/6-31G(d,p)) structures of present concern.

density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [37]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [38] and Lee, Yang, Parr (LYP) correlation correction functional [39]. Also, geometry optimizations for all the structures were achieved within B3P86 [40,41] at the level of 6-311G(d,p) (restricted open-shell).

In addition to the DFT calculations, *ab initio* RHF/6-311G(d,p) calculations [42] were performed. Furthermore, single-point MP2 calculations were carried out (for the *ab initio* RHF calculations) in order to obtain more accurate energy data.

Nucleus independent chemical shift (NICS) calculations at the center of the rings were performed on all the molecules using the gauge invariant atomic orbital (GIAO) approach [43] at the B3LYP/6-31G(d,p) and B3LYP/cc-pVDZ levels. Since cc-pVDZ basis set gives better results in NMR chemical shift values [44,45], it has been adopted for the NICS calculations based on the chemical shift value of the ghost atom. The B3LYP/6-31G(d,p) optimized geometries were used for the NICS calculations.

In this study, in order to compare the C–NO<sub>2</sub> bond strengths in NTO tautomers and N–NO<sub>2</sub> bond strengths in its isomers, homolytic bond dissociation energy (BDE) calculations, for the removal of nitrogen dioxide moiety from the structures, were performed (the geometry optimized structures were calculated at ROB3P86/6-311G(d,p)). The homolytic BDE [46,47] is defined

for the present case as:  $BDE = E(\text{NO}_2) + E(\text{R}) - E(\text{R}-\text{NO}_2)$ , where  $E$  stands for the respective total electronic energy corrected for the zero-point energy for each parent structure and the fragments of the low-energy NO<sub>2</sub> scission reaction. Furthermore, the basis set superposition error (BSSE) analyses were carried out with the counterpoise method, introduced by Boys and Bernardi [48]. 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 [49].

### 3. Results and discussion

The geometry optimized structures of the compounds (see Scheme 1) calculated at the B3LYP/6-31G(d,p) level are presented in Fig. 1. The bond lengths and angles for the geometry

Table 1  
Calculated and experimental bond lengths (Å) and angles (°) for NTO (**1**)

	RHF/6-311G(d,p)	ROB3P86/6-311G(d,p)	B3LYP/6-31G(d,p)	B3LYP/6-311G(d,p) <sup>a</sup>	B3LYP/6-311++G(d,p) <sup>a</sup>	Exp <sup>b</sup> (298 K)	Exp <sup>b</sup> (100 K)
N1–N2	1.353	1.350	1.360	1.359	1.358	1.366	1.370
N2–C3	1.369	1.393	1.399	1.398	1.398	1.369	1.368
C3–N4	1.382	1.398	1.403	1.405	1.403	1.373	1.377
N4–C5	1.359	1.359	1.366	1.365	1.366	1.352	1.352
C5–N1	1.254	1.289	1.297	1.290	1.291	1.290	1.295
N2–H6	0.991	1.007	1.009	1.008	1.009		
C3–O7	1.183	1.201	1.210	1.203	1.205	1.228	1.235
N4–H8	0.994	1.008	1.009	1.008	1.009		
C5–N9	1.446	1.444	1.445	1.451	1.452	1.444	1.444
N9–O10	1.175	1.209	1.222	1.214	1.215	1.226	1.230
N9–O11	1.190	1.223	1.236	1.230	1.230	1.212	1.222
N1–N2–C3	113.713	114.753	114.731	114.570	114.470	113.000	112.900
N2–C3–N4	101.54	100.503	100.592	100.540	100.700	103.500	104.000
C5–N1–N2	103.725	103.173	103.046	103.290	103.380	102.600	102.300
H6–N2–N1	120.380	120.088	120.112	120.090	120.060		
O7–C3–N2	129.362	129.563	129.417	129.630	129.490	127.000	126.900
O7–C3–N4	129.099	129.934	129.990	129.840	129.810	129.000	129.100
H8–N4–C3	125.993	126.199	126.284	126.080	125.930		
N9–C5–N4	121.437	121.730	121.747	121.740	121.880	123.100	123.000
O10–N9–C5	117.922	118.208	118.401	118.270	118.460	117.200	117.100
O11–N9–C5	114.733	114.569	114.668	114.670	114.730	117.100	116.700
O10–N9–O11	127.345	127.223	126.932	127.050	126.800	125.700	126.200

<sup>a</sup> Values are as reported in literature [51].

<sup>b</sup> Reported in literature [50].

optimized NTO at the different theoretical levels are presented in Table 1. The numbering in Table 1 is consistent with the numbering scheme employed in Scheme 2. The corresponding experimental X-ray diffraction values of  $\beta$ -NTO [50] are shown in Table 1 (at both 100 and 273 K). Also, geometric parameters of isolated NTO molecule previously published are presented in Table 1 at the B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) levels [51]. In the present calculations, the RHF/6-311G(d,p) bond lengths differ from the crystal averages with rms deviations of 0.027 Å (298 K) and 0.031 Å (100 K). The rms deviations in ROB3P86/6-311G(d,p) bond lengths are 0.017 Å (298 K) and 0.019 Å (100 K). For the isolated molecule, in the case of B3LYP/6-31G(d,p) results, the rms deviations become 0.019 Å at both 298 and 100 K. The corresponding values for the larger basis set B3LYP/6-311++G(d,p) calculation (taken from the literature) are 0.018 Å (298 K) and 0.019 Å (100 K). Furthermore, the experimental and calculated results indicate that C–O bond length of NTO in the crystal state is longer than that of an isolated molecule in the gas phase because of intermolecular hydrogen bonding. Also, there were changes in bond lengths of hydrogen as well as oxygen atoms. Additionally, some ring deformations in the crystalline phase compared to the structure in the gas phase exist (see Table 1).

The structures **2**, **3**, **4**, **5** and **6** are the nitramine type organic molecules (**2**, **5** and **4**, **6** are related structures) which are potential candidates for explosives and it was found that polynitro aliphatics containing at least one N–NO<sub>2</sub> (nitramine) linkage are more sensitive than nitroaliphatic explosives containing C–NO<sub>2</sub> linkage [52]. In the case of compound **1** (NTO), it is an explosive containing one C–NO<sub>2</sub> linkage shown in Fig. 1. NTO, a planar molecule containing five-membered heterocyclic ring with one

nitro substituent (see Fig. 1), is an extra ordinary stable high energy compound.

Fig. 1 shows the geometry optimized structures (B3LYP/6-31G(d,p) level) of the materials studied. They have C<sub>s</sub> type molecular point groups except **3** and **5** for which the type of molecular point group is C<sub>1</sub> (see Table 2). Table 2 shows some geometrical features of the NTO and its isomeric structures. Comparing the N1–N2 bond lengths of **1A** and **2A**, one finds that **2A** has the longer bond length. This might be due to electron withdrawing effect of NO<sub>2</sub> group attached to N2 atom in **2A**. Structure **3** has the longest N–NO<sub>2</sub> bond length among the nitramine type isomers. The C5–N9 bond in tautomer **1A** stands for the longest bond length among the NTO and its tautomers. The geometry optimizations indicate that **3** and **5** possess puckered structures. Although, **5** and **6** are similar molecules, unlike to **5**, compound **6** has a planar geometry. Furthermore, the N–NO<sub>2</sub> bond length in **5** is longer than the same type of bond in **6**. All the calculations performed in the present study are in accord on these results.

Fig. 2 shows the 3D electrostatic potential field and atomic charges for the species considered (B3LYP/6-31G(d,p)). Some explosive materials are sensitive to electromagnetic and electrostatic fields they are exposed [53–55]. The effect is due to interaction of the external field with electron distribution within the molecule (thus with the electrostatic potential field) such that in some sensitive explosives this interaction causes the rupture of chemical bonds.

Table 3 shows the total energies calculated at different levels of theory for the compounds. Total electronic energies are corrected for zero-point vibration energy (ZPVE). As seen from the table, generally a good agreement of stability order

Table 2

Comparison of selected bond lengths (Å) for NTO, its tautomers and isomers and their symmetry point groups

	RHF			ROB3P86			B3LYP			Symmetry
	N (or C)—NO <sub>2</sub>	N1—N2	C3—N4	N (or C)—NO <sub>2</sub>	N1—N2	C3—N4	N (or C)—NO <sub>2</sub>	N1—N2	C3—N4	
<b>1</b>	1.446	1.353	1.382	1.444	1.35	1.398	1.445	1.360	1.403	C <sub>s</sub>
<b>1A</b>	1.457	1.344	1.292	1.462	1.35	1.311	1.462	1.360	1.317	C <sub>s</sub>
<b>1B</b>	1.440	1.362	1.341	1.438	1.362	1.350	1.439	1.374	1.355	C <sub>s</sub>
<b>1C</b>	1.451	1.343	1.352	1.446	1.343	1.352	1.447	1.353	1.359	C <sub>s</sub>
<b>2</b>	1.426	1.377	1.399	1.426	1.377	1.399	1.426	1.377	1.399	C <sub>s</sub>
<b>2A</b>	1.362	1.363	1.277	1.399	1.357	1.298	1.440	1.369	1.310	C <sub>s</sub>
<b>3</b>	1.393	1.385	1.413	1.458	1.378	1.421	1.468	1.393	1.429	C <sub>1</sub>
<b>3A</b>	1.372	1.356	1.367	1.428	1.349	1.369	1.426	1.363	1.374	C <sub>s</sub>
<b>4</b>	1.369	1.364	1.421	1.409	1.365	1.437	1.414	1.377	1.443	C <sub>s</sub>
<b>4A</b>	1.374	1.381	1.378	1.424	1.389	1.382	1.397	1.406	1.410	C <sub>s</sub>
<b>5</b>	1.386	1.386	1.391	1.438	1.380	1.389	1.451	1.393	1.398	C <sub>1</sub>
<b>6</b>	1.359	1.212	1.391	1.399	1.239	1.401	1.404	1.246	1.406	C <sub>s</sub>

Basis sets are reported in Section 2.

among the calculated total energies of the compounds obtained at different levels has been found. In the limitations of the levels of the theory, the most stable compound in terms of total energy consideration is NTO and the least stable one is isomer **6**. Furthermore, it is obvious that the estimated energy differences between NTO and its tautomers **1A**, **1B** and **1C** and its isomers are sensitive to the theoretical methods employed (see Table 3). Smaller energy differences are obtained with the use of correlated methods. The related hydroxy (iminol)

tautomers **1A**, **1B** and **1C** are less stable than NTO. On the other hand, these tautomers are evidently stabilized as compared to the other isomers of NTO (nitramine type isomers). We may ascribe this stability to the enhanced aromaticity in these structures (also, **2A**, **3A** and **4A** have six  $\pi$ -electrons), whereas structures **3**, **5** and **6** do not conform to the aromatic criteria. Also, in the case of the structure **4A**, it is destabilized because of the repulsion between the neighboring lone pairs on the ring nitrogens N1 and N2. Neglecting **6** (contains N=N bond

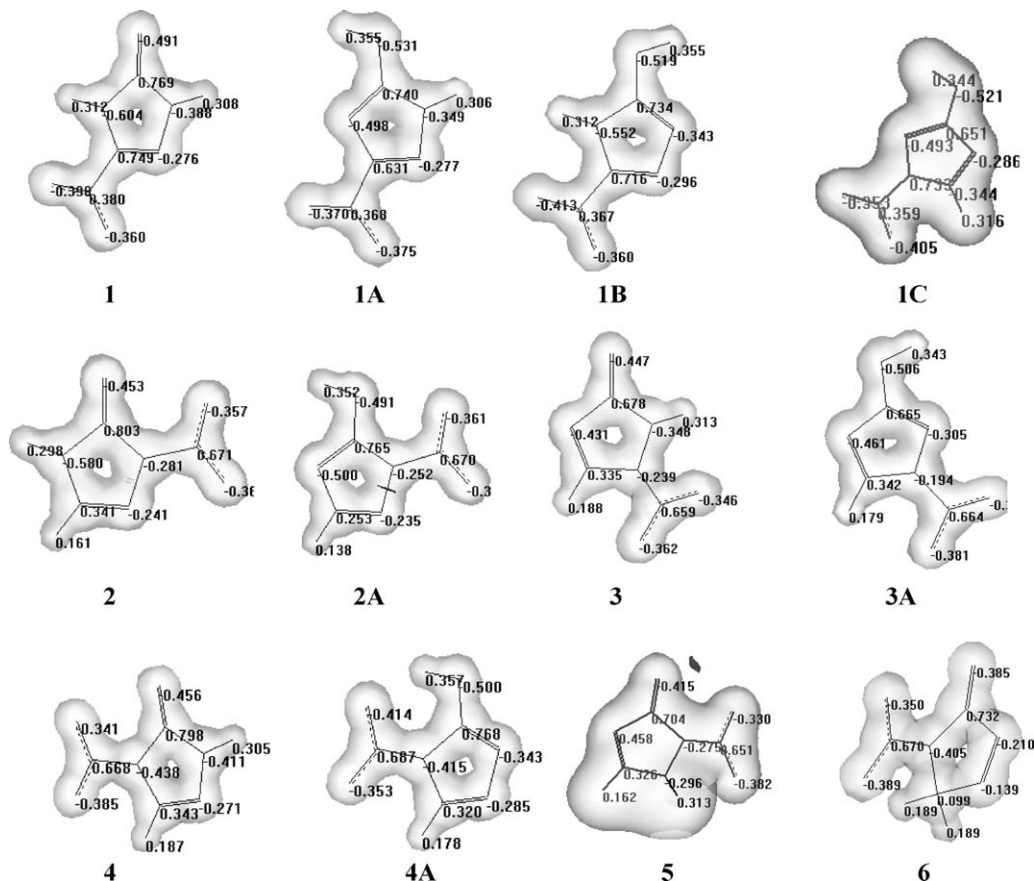


Fig. 2. 3D-electrostatic potential field maps and charges of atoms of NTO and its isomers (B3LYP/6-31G(d,p)). Each molecule is oriented as in Scheme 2.



Table 3

Calculated total energies (in kJ/mol) for NTO(1) its tautomers and isomers at different theoretical levels

	B3LYP/ 6-31G(d,p)	ROB3P86/6- 311G(d,p)	RHF/ 6-311G(d,p)	MP2/ 6-311G(d,p) <sup>a</sup>
<b>1</b>	-1370275	-1373720	-1363143	-1367928
<b>1A</b>	-1370240	-1373683	-1363119	-1367909
<b>1B</b>	-1370218	-1373658	-1363089	-1367877
<b>1C</b>	-1370251	-1373693	-1363116	-1367919
<b>2</b>	-1370194	-1373639	-1363061	-1367871
<b>2A</b>	-1370154	-1373610	-1363031	-1367817
<b>3</b>	-1370154	-1373596	-1363028	-1367799
<b>3A</b>	-1370164	-1373608	-1363033	-1367818
<b>4</b>	-1370193	-1373637	-1363060	-1367838
<b>4A</b>	-1370127	-1373564	-1362991	-1367776
<b>5</b>	-1370144	-1373586	-1363011	-1367786
<b>6</b>	-1370102	-1373533	-1362974	-1367739

The total energies are corrected for ZPVE.

<sup>a</sup> Single-point calculation after RHF/6-311G(d,p) geometry optimization.

which is absent in the others), structure **4A** is found to be the least stable isomer. The stability order in terms of total energy is: **1** > **1C** > **1A** > **1B** > **2** > **4** > **2A** > **3A** > **3** > **5** > **4A** > **6** at the ROB3P86/6-311G(d,p) level. According to the MP2/6-311G(d,p) level, the stability order is: **1** > **1C** > **1A** > **1B** > **2** > **4** > **3A** > **2A** > **3** > **5** > **4A** > **6**. At the B3LYP/6-31G(d,p) level, **6** is 173 kJ/mol less stable than NTO, whereas 187 kJ/mol and 169 kJ/mol with ROB3P86 and RHF/6-311G(d,p), respectively. The heat of formation values are reported in Table 4. The calculated heat of formation values are generally endothermic. The values indicate that **1** is the least endothermic (exothermic based on PM3 geometry optimization) structure. This result is consistent with the *ab initio* and DFT calculations, whereas the most endothermic structure differs from one calculation method to the other.

Another main problem for the explosives is whether they are stable enough to be of practical interest. So, studies on the bond dissociations are important and essential for understanding the decomposition process of the energetic materials, since they are

Table 4

Calculated heat of formation values (in kJ/mol) for the structures in the gas phase

	PM3 <sup>a</sup>	PM3 <sup>b</sup>	PM3 <sup>c</sup>
<b>1</b>	35.30	44.53	-12.37
<b>1A</b>	74.32	85.05	12.47
<b>1B</b>	54.47	63.64	-2.84
<b>1C</b>	72.69	82.94	14.80
<b>2</b>	109.30	382.78	66.19
<b>2A</b>	163.92	186.52	106.34
<b>3</b>	139.58	152.87	90.84
<b>3A</b>	161.99	173.43	107.08
<b>4</b>	106.69	114.79	70.39
<b>4A</b>	159.76	157.38	125.36
<b>5</b>	145.19	157.98	90.34
<b>6</b>	128.93	134.11	97.36

<sup>a</sup> Single-point PM3(RHF) calculations over B3LYP/6-31G(d,p) geometry optimized structures.

<sup>b</sup> Single-point PM3(UHF) calculations over ROB3P86/6-311G(d,p) geometry optimized structures.

<sup>c</sup> PM3(RHF) geometry optimization results.

directly relevant to the sensitivity and stability of the energetic materials [56]. Previous studies [57,58] 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<sub>2</sub> (or N–NO<sub>2</sub>) bond scission in the molecule and its sensitivities. Usually, the larger the BDE value, the lower the sensitivity. However, this is only applied to the molecules in which R–NO<sub>2</sub> (or N–NO<sub>2</sub>) bond is the weakest one. For instance, the C–C bond of nitro cubanes is weaker than the C–NO<sub>2</sub> bonds, and the initial step in the decomposition is rupture of the cube C–C bond [59]. In the literature, there are many studies on the decomposition of NTO [60], and initial step for several proposed decomposition mechanisms of NTO have been studied theoretically, and all these computations suggest that the C–NO<sub>2</sub> bond homolysis is the most probable initial step for unimolecular decomposition of NTO. Furthermore, at high temperatures, ca. above 900 °C, the most important pathway for decomposition of nitro aromatic explosives is by initial cleavage of the C–NO<sub>2</sub> bond [61]. Thus, it is logical to assume that the same mechanism should be operative for the nitramine type isomers of NTO.

On the other hand, for designing and evaluating new energetic materials, it is accordingly important to be able to determine computationally the dissociation energies of these bonds. Shao et al. [62] studied bond dissociation energies for removal of nitrogen dioxide moiety in some nitro aromatic molecules, by using three hybrid density functional theory B3LYP, B3PW91 and B3P86 methods with different basis sets. By comparing the computed energies and experimental results, the B3P86 method was found to give the best agreement with the experimental BDE data, especially with 6-311G(d,p) basis set.

Table 5 summarizes the computed homolytic BDE values of N–NO<sub>2</sub> and C–NO<sub>2</sub> for the presently considered species at B3P86/6-311G(d,p) level of theory. 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: **1A** > **1C** > **1B** > **1** > **3A** > **2A** > **2** > **4** > **4A** > **5** > **3** > **6**. Generally speaking, C–NO<sub>2</sub> bond strength is higher than the N–NO<sub>2</sub> bond strength. The positions of nitramine group also have an important effect on the BDE. For example, although both **2** and **4** have a planar geometry, the BDE of N–NO<sub>2</sub> value of **2** is 24 kJ/mol higher than the BDE of N–NO<sub>2</sub> value of **4**, which can also be judged from their total energies (see Table 5).

According to the suggestion of Chung et al. [63], a molecule should have more than a 20 kcal/mol (83.68 kJ/mol) barrier to dissociate in order to be considered as a viable candidate for HEDM, thus we can conclude that the molecules in Fig. 1 except **3**, **5** and **6** are all viable candidates for HEDMs. As it is already known that NTO is one of the HEDMs, it is worth nothing that bond strength of C–NO<sub>2</sub> in **1A** is much more higher than the corresponding bond strength in NTO. This might be explained partially due to the aromaticity of **1A** (contains six π-electrons) compared to NTO (cyclic conjugation via charge separated resonance structures). Furthermore, density (ρ), detonation velocity

Table 5

The calculated homolytic bond dissociation energies (BDE) of N–NO<sub>2</sub> and C–NO<sub>2</sub> bonds for the species considered at ROB3P86/6-311G(d,p) theoretical level

Molecules	Energy	BDE
<b>1</b>	–1373720	276
<b>1</b> radical	–833837	
<b>1A</b>	–1373683	438
<b>1A</b> radical	–833638	
<b>1B</b>	–1373658	290
<b>1B</b> radical	–833761	
<b>1C</b>	–1373693	389
<b>1C</b> radical	–833697	
<b>2</b>	–1373639	115
<b>2</b> radical	–833914	
<b>2A</b>	–1373610	136
<b>2A</b> radical	–833862	
<b>3</b>	–1373596	52
<b>3</b> radical	–833935	
<b>3A</b>	–1373608	174
<b>3A</b> radical	–833824	
<b>4</b>	–1373637	91
<b>4</b> radical	–833935	
<b>4A</b>	–1373564	89
<b>4A</b> radical	–833864	
<b>5</b>	–1373586	68
<b>5</b> radical	–833908	
<b>6</b>	–1373533	29
<b>6</b> radical	–833893	
NO <sub>2</sub>	–539595	

Energies in kJ/mol; the BDEs include the basis set superposition error (BSSE) and zero-point energy (ZPE) corrections.

(*D*) and detonation pressure (*P*) are the important parameters to evaluate the explosive performances of energetic materials and can be predicted by the empirical Kamlet–Jacob equations [64] as follows:

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 130\rho) \quad (1)$$

Table 6

Predicted densities and detonation properties of the NTO its tautomers and isomers

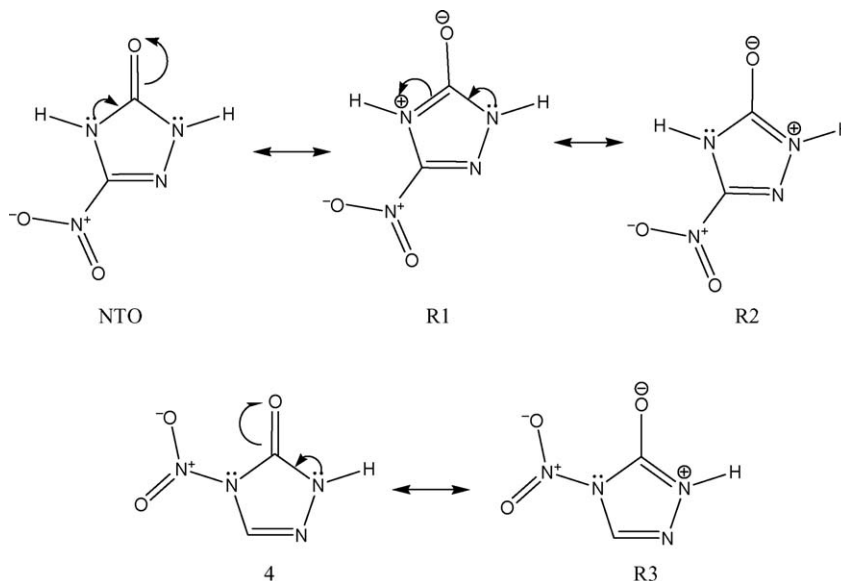
Molecules	$\rho$ (g/cm <sup>3</sup> )	$\Omega$ (%)	HOF <sup>a</sup>	<i>Q</i> (kJ/g)	<i>V</i> <sup>b</sup> (cm <sup>3</sup> /mol)	<i>D</i> (km/s)	<i>P</i> (Gpa)
<b>1</b>	1.73	–24.60	35.3	1232.24	75.21	7.95	27.38
<b>1A</b>	1.79	–24.60	74.32	1303.91	72.58	8.27	30.16
<b>1B</b>	1.76	–24.60	54.47	1267.44	74.07	8.17	28.74
<b>1C</b>	1.77	–24.60	72.69	1300.91	73.69	8.19	29.45
<b>2</b>	1.75	–24.60	109.3	1368.18	74.29	8.24	29.52
<b>2A</b>	1.72	–24.60	163.92	1468.53	75.57	8.29	29.55
<b>3</b>	1.68	–24.60	139.58	1423.81	77.45	8.08	27.76
<b>3A</b>	1.7	–24.60	161.99	1465.55	76.64	8.21	31.46
<b>4</b>	1.75	–24.60	106.69	1363.38	74.34	8.22	29.47
<b>4A</b>	1.77	–24.60	159.76	1460.89	73.45	8.43	31.21
<b>5</b>	1.72	–24.60	145.19	1434.12	75.7	8.23	28.86
<b>6</b>	1.71	–24.60	128.93	1404.25	76.01	8.15	28.56

<sup>a</sup> Heat of formation values obtained from the PM3 single-point calculations over B3LYP/6-31G(d,p) geometry optimized structures.

<sup>b</sup> Average volume from 100 single-point volume calculations at the B3LYP/6-311G(d,p) level. For notations, refer the text.

$$P = 1.558\rho^2NM^{1/2}Q^{1/2} \quad (2)$$

where each term in Eqs. (1) and (2) is defined as: *D*, detonation velocity in km/s; *P*, detonation pressure in GPa;  $\rho$ , density of a compound in g/cm<sup>3</sup>; *N*, moles of gaseous detonation products per gram of explosive (in mol/g); *M*, average molecular weight of gaseous products (in g/mol); *Q*, chemical energy of detonation in kJ/g. Here, the parameters *N*, *M* and *Q* were calculated according to the chemical composition of each explosive [64,65]. On the other hand, the density of each molecule was predicted from the molecular volume, while the molecular volume of each molecule was obtained from the statistical average of 100 single-point calculations for each optimized structures. The molar volume was defined as inside a contour of 0.001 electrons/Bohr<sup>3</sup> density that was evaluated using a Monte Carlo integration implemented in the Gaussian 98 program. This method has been successfully tested on various CHNO molecules and accurately predicts the explosive properties [66–71]. In this study, single-point molecular volume calculations at B3LYP/6-311G(d,p) performed based on the B3LYP/6-31G(d,p) geometry optimized structures. Table 6 collects the predicted densities and detonation properties of the NTO and its isomers. The oxygen balance ( $\Omega$ ) and heats of formation (HOF) values were also calculated and listed in the table. The previously reported studies have proven that HOF values calculated by the PM3 method could replace the experimental data reasonably well. (The parameterization of PM3 method is such that its HOF data are reliable. Moreover, it is a fast method [71–77].) All these data in Table 6, compared to NTO which is well known explosive, gave some clue about the explosive character of the molecules derived from NTO, so far unknown compounds in the literature. The position of nitro group in the five-membered ring skeleton also have an important effect on the explosive properties of energetic materials (see Table 6). For example, in the case of the compound **3**, **5** and **6**, only the position of NO<sub>2</sub> differs and all are nitramine type compounds, but **5** (a tautomer of **2** and **2A**) has the highest detonation velocity and pressure value among them. The isomers of NTO (preserving the main skeleton of the ring), which are the subject of present study have better detonation performances than NTO or close to it.

Scheme 3. Some resonance forms of NTO and its isomeric compound **4**.

Therefore, if these stable isomers of NTO, which are nitramine type molecules, can be synthesized, they will have higher or comparable exploitable values.

On the basis of valence bond theory, NTO (a monocyclic coplanar system with seven  $\pi$ -electron over the ring atoms) in structure **1** cannot have the extra stabilization produced by  $\pi$ -electron delocalization. Whereas in the case of tautomeric forms of NTO (**1A**, **1B** and **1C**)  $\pi$ -skeleton contains six  $\pi$ -electrons and they all planar systems thus conforming to the criteria of the Hückel's aromaticity. On the other hand, NTO may gain some aromatic character if the charge separated resonance structures **R1**, **R2**, etc. (Scheme 3) have some contribution. Note that they are coplanar systems with six  $\pi$ -electrons. An analysis based on absolute magnetic shielding [31] confirms that NTO (**1**) indeed exhibits significant aromatic character. This effect partially accounts for its unusual stability.

Scheleyer and co-workers [78] examined the aromaticity of a comprehensive set of five-membered ring heterocycles and showed that there was excellent agreement between the magnitudes of the NICS (nucleus independent chemical shift) values and the corresponding aromatic stabilization energies for these type compounds. We have investigated the NICS values for NTO and its isomers and their tautomers to examine their aromaticity. Table 7 shows the calculated NICS (ppm) values of them at different levels of theory. Aromaticity order at B3LYP/cc-pVDZ level is: **1A** > **1C** > **2A** > **1** > **3A** > **1B** > **4** > **2** > **4A** > **5** > **3** > **6**. At the B3LYP/6-31G(d,p) level, the aromaticity order is: **1A** > **1C** > **2A** > **3A** > **1B** > **1** > **4** > **2** > **4A** > **3** = **5** > **6**. Also, pyrrole and triazole's NICS values were calculated at the same theoretical levels (see Table 7) for comparison purpose. The keto form of NTO, **2** and **3** are less aromatic than the enol tautomers **1A**, **1B**, **2A** and **3A**. Whereas, it is interesting that the keto tautomer of **4** is more aromatic than the enol tautomer **4A**, which suggests the contribution of some aromatic, charge separated resonance structures in to the resonance hybrid of **4** (Scheme 3).

It is obvious from the NICS values that isomers **3**, **5** and **6** lack of aromatic character. All the NICS values for the presently considered structures should be considered on the relative basis, just to compare relative aromaticities of the isomers and tautomers. Since, no experimental values are available for the aromaticity of these structures, it is not possible to evaluate the precision of the NICS data presently. However, the two calculation methods used for this purpose generally give comparable results for each structure.

Fig. 3 shows the frontier molecular orbitals of presently considered molecules. As seen there, most of these frontier molecular orbitals mainly possess  $\pi$ -type symmetry except **3**, **5** and **6**. Tables 8a and 8b tabulate the HOMO and LUMO energies of the structures considered. In **4A**, contribution of  $\text{NO}_2$  orbitals to HOMO is nil. Whereas, for all other isomers,

Table 7  
Calculated NICS (ppm) values for the considered species

	Symmetry	NICS <sup>a</sup>	NICS <sup>b</sup>	Dipole moment <sup>c</sup>
<b>1</b>	C <sub>s</sub>	-11.4	-11.2	1.5576
<b>1A</b>	C <sub>s</sub>	-13.1	-13.4	6.2676
<b>1B</b>	C <sub>s</sub>	-11.1	-11.3	5.3321
<b>1C</b>	C <sub>s</sub>	-12.5	-12.2	1.4535
<b>2</b>	C <sub>s</sub>	-10.5	-10.3	6.2093
<b>2A</b>	C <sub>s</sub>	-12.0	-12.1	3.2717
<b>3</b>	C <sub>1</sub>	-6.2	-6.2	2.5369
<b>3A</b>	C <sub>s</sub>	-11.3	-11.4	0.8823
<b>4</b>	C <sub>s</sub>	-10.6	-10.6	3.336
<b>4A</b>	C <sub>s</sub>	-10.0	-10.0	3.0646
<b>5</b>	C <sub>1</sub>	-6.4	-6.2	6.0439
<b>6</b>	C <sub>s</sub>	-0.3	-0.2	3.3437
Pyrrole	C <sub>2v</sub>	-14.8	-15.9	1.9019
Triazole	C <sub>2v</sub>	-12.8	-13.1	5.6090

<sup>a</sup> Calculated at B3LYP/cc-pVDZ.

<sup>b</sup> Calculated at B3LYP/6-31G(d,p).

<sup>c</sup> Dipole moments in Debye. For NICS and dipole moment calculations, optimized geometries are obtained from B3LYP/6-31G(d,p) theoretical level.



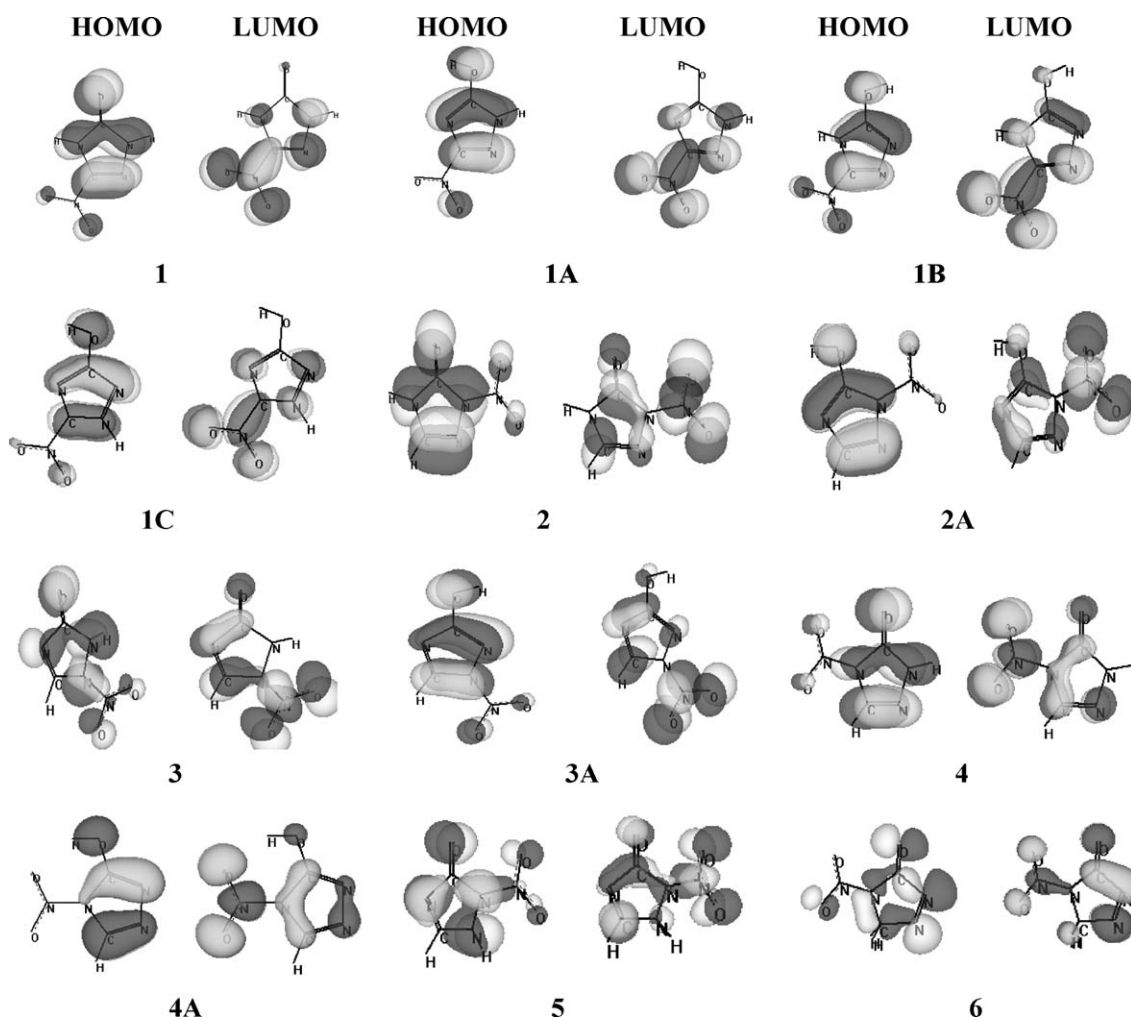


Fig. 3. The frontier molecular orbitals, the HOMO and LUMO, of NTO and its isomers (B3LYP/6-31G(d,p)).

Table 8a

The HOMO and LUMO energies ( $\epsilon$ ) of considered species at B3LYP/6-31G(d,p) level (energies in eV)

	1	1A	1B	1C	2	2A	3	3A	4	4A	5	6
HOMO	-7.28	-7.718	-7.633	-7.484	-7.327	-7.652	-7.835	-7.572	-7.313	-7.584	-7.698	-7.787
LUMO	-3.166	-2.414	-2.896	-3.173	-2.203	-2.591	-2.932	-2.875	-2.67	-3.479	-2.444	-3.42
$\Delta\epsilon$	4.113	5.303	4.737	4.311	5.124	5.062	4.903	4.698	4.644	4.105	5.254	4.368

$$\Delta\epsilon = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$$

contribution of NO<sub>2</sub> orbitals to HOMO occurs (Fig. 3), and there exists an extended conjugation involving nitro group. Note that a NO<sub>2</sub> group, according to Dewar, can be considered as a NO group when in conjugation with another  $\pi$ -system because one of the oxygen atoms present in NO<sub>2</sub> group is crossly conjugated with the rest of  $\pi$ -skeleton of the whole

system [79,80]. In the case of the energy difference between HOMO–LUMO energy levels ( $\Delta\epsilon = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$ ), the order is: **1A > 5 > 2 > 2A > 3 > 1B > 3A > 4 > 6 > 1C > 1 > 4A** at the B3LYP/6-31G(d,p) level. The same property order is obtained at RHF/6-311G(d,p) level is: **5 > 3 > 2 > 6 > 1A > 4 > 2A > 4A > 3A > 1B > 1C > 1**.

Table 8b

The HOMO and LUMO energies ( $\epsilon$ ) of considered species at RHF/6-311G(d,p) level (energies in eV)

	1	1A	1B	1C	2	2A	3	3A	4	4A	5	6
HOMO	-10.631	-11.06	-10.833	-10.8	-10.807	-11.187	-11.783	-11.039	-10.739	-10.861	-11.489	-12.11
LUMO	1.085	1.95	1.404	0.982	2.473	1.489	1.57	1.485	1.971	1.709	1.984	1.087
$\Delta\epsilon$	11.716	13.01	12.238	11.782	13.28	12.676	13.353	12.525	12.71	12.57	13.472	13.197

$$\Delta\epsilon = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$$

Table 9  
Theoretical (RHF/6-311G(d,p)) and available experimental vibrational frequencies

1	Thin film <sup>a</sup>	Ar matrix <sup>a</sup>	1A	1B	1C	2	2A	3	3A	4	4A	5	6
75.3			25.2	81.8	70.0	55	96.5	99.4	97.3	67.3	69	69.9	69.1
156.9			196	183.3	194.4	116.2	128.6	127.3	122.3	130.5	138.1	119	86.4
225.2			230	220.3	221.1	238	298.9	241.9	246.4	216.3	252.8	246.9	190
321.1			395.2	392.4	382.2	266.1	329.6	314.6	366.4	255.9	333.7	309.8	246.8
450.3			443.4	438.6	406.0	457.3	453.7	484.7	402.7	447.7	428.1	455.3	437.5
481.9	480	512	445.4	454.7	441.3	508.4	533.9	539.9	471.3	463.4	480.1	521.4	440
515.5		573	487.6	483.9	495.4	532.4	590.1	568.5	518.1	530.4	509.2	543.9	532
555.4	606	613	597.9	594.7	634.5	682.8	676	669	607.3	679	655.6	644.2	680.9
644.1	693		624.1	628.9	642.6	683.1	688.6	689.5	665.2	690.2	698.1	729.9	800.2
707	728	730	737.9	714.8	720.9	806.3	807.2	849.9	830.1	822.4	793.1	807.9	832.7
827.9	751	738	821	805.2	825.1	841.1	812	894.3	860.5	838	805.4	873.4	882.6
852.6	805	822	843	829.2	852.6	877.6	869.8	919.9	870.4	883.3	878.6	908.6	906.2
881.4	830		908.1	878.9	884.6	971.8	982.8	930.5	958.2	959.1	966.5	957.1	977.1
951.1	1021	991	968.2	954.4	959.4	1000.2	1029.9	1005	1054.5	987.7	966.8	965.5	1052.9
1079.7	1111	1085	1120.6	1122.6	1113.7	1025.2	1073	1054.1	1059.8	987.9	1022.1	1089.4	1131.9
1106.9	1185	1174	1186.4	1145.5	174.3	1182.4	1233.5	1097.8	1137.1	1189.4	1161.5	1162.4	1192.4
1221.7	1282	1257	1269	1241.8	1252.4	1228.7	1330.2	1242.1	1298.6	1294.9	1307.6	1217.9	1306.3
1330.9	1343	1361	1306.4	1287.8	1327.1	1343.2	1354	1316.3	1344.9	1329	1326.2	1290.2	1371.3
1417.4	1477	1338	1468.5	1344.1	1422.3	1408.8	1398.6	1414.3	1447.7	1391.5	1377.5	1392.7	1404.8
1544.9	1550	1463	1501.5	1546.7	1538.6	1456.3	1432	1450.4	1503.7	1480.1	1442.7	1473.5	1511.9
1582.7	1605	1563	1631.3	1623.9	1636.5	1558.9	1533.5	1554.1	1556.5	1557.2	1574.9	1566.5	1565.6
1668.4	1695	1768	1688.6	1701.2	1674.4	1574.5	1586.5	1584	1595.5	1571.2	1643.2	1603.2	1629.5
1862.3	1716	1789	1784.1	1771.6	1722.3	1851.6	1744.6	1836	1677.5	1849.7	1765.5	1799.1	1861.7
1894.7			1813.7	1805.4	1835.5	1876.7	1821.3	1892.8	1861.3	1877.6	1814.3	1877.5	1888.1
2019.6			1874.6	1875.4	1884.9	2059.3	1926.6	2071.8	1901.7	2058.5	1913.4	2100.2	2120.4
3893.8	3200	3489	3896.3	3884.5	3892.0	3424.3	3424.5	3434.1	3453.6	3467.4	3464.1	3385.7	3246.6
3911.9			4129.5	4124.1	4159.5	3896.4	4048.1	3824.2	4155.1	3916.2	4115.5	3809.5	3300.9

<sup>a</sup> Experimental vibrational frequencies for the NTO molecule [26].

Table 9 presents the calculated vibrational frequencies and available experimental data [26] for the NTO and its isomers at RHF/6-311G(d,p) level of theory. Since there are no corresponding experimental values about the isomers/tautomers of NTO, these data would be helpful for further studies on them.

#### 4. Conclusion

In the present study, a high energy density material (HEDM) NTO and its isomers/tautomers have been investigated using quantum chemical calculations. Stability of the compounds were investigated in terms of the total electronic energy, BDE values of N–NO<sub>2</sub> and C–NO<sub>2</sub> and NICS values for aromaticity. The detonation properties have been investigated and found that there might be some candidates of HEDMs among the NTO isomers so far not investigated in the literature from this point of view. The initial step for pyrolysis of NTO is the homolysis of the C–NO<sub>2</sub> bond, and according to this information BDEs of isomers have been calculated. It is concluded that C–NO<sub>2</sub> bond is stronger than the nitramine bond (as it is expected). Consequently, if some isomers of NTO are used as explosive materials they would not be impact insensitive explosives compared to NTO due to their low BDEs of N–NO<sub>2</sub> values. Furthermore, aromatic character of NTO and its isomers were investigated by using NICS calculations. As a result of these calculations, NTO shows some aromatic character but it is not fully aromatic compound. The present study sheds some valuable light on to this subject by exploring their structural energetic properties.

#### References

- [1] A.K. Sikder, N. Sikder, A review of advanced high performance, insensitive and thermally stable energetic materials emerging for military and space, *J. Hazard. Mater.* A112 (2004) 1–15.
- [2] D. Chakraborty, R.P. Muller, S. Dasgupta, W.A. Goddard, The mechanism for unimolecular decomposition of RDX (1,3,5-trinitro-1,3,5-triazine), an *ab initio* study, *J. Phys. Chem. A* 104 (2000) 2261–2272.
- [3] Y.Q. Guo, M. Greenfield, E.R. Bernstein, Decomposition of nitramine energetic materials in excited electronic states: RDX and HMX, *J. Chem. Phys.* 122 (2005) 244310–244315.
- [4] P. Politzer, J.S. Murray, *Energetic Materials Part 2*, Elsevier Publ., New York, 2003.
- [5] O. Yuxiang, C. Boren, L. Jiarong, D. Shuan, L. Jianjuan, J. Huiping, *Heterocycles* 38 (1994) 1651–1664.
- [6] E.F. Rothger, D.E. Audette, R.C. Wedlich, D.A. Csejka, The study of the thermal decomposition of 3-nitro-1,2,4-triazol-5-one (NTO) by DSC, TGA-MS, and accelerating rate calorimetry (ARC), *Thermochim. Acta* 185 (2) (1991) 235–243.
- [7] B.C. Beard, J. Sharma, Early decomposition chemistry of NTO (3-nitro-1,2,4-triazol-5-one), *J. Energ. Mater.* 11 (4–5) (1993) 325–343.
- [8] Y. Xie, R. Hu, X. Wang, X. Fu, C. Zhunhua, Thermal behavior of 3-nitro-1,2,4-triazol-5-one and its salts, *Thermochim. Acta* 189 (1991) 283–296.
- [9] V.W. Manchot, R. Noll, Triazole derivatives, *Justus Liebigs Ann. Chem.* 343 (1905) 1–27.
- [10] C.F. Kroger, R. Mietchen, H. Fank, M. Siemer, S. Pilz, 1,2,4-Triazoles. XVII. Nitration and bromination of 1,2,4-triazolinones, *Chem. Ber.* 102 (1969) 755–766.
- [11] Y.M. Wang, C. Chen, S.T. Lin, Theoretical studies of the NTO unimolecular decomposition, *J. Mol. Struct. (THEOCHEM)* 460 (1999) 79–102.
- [12] K.Y. Lee, M.D. Coburn, 3-Nitro-1,2,4-triazol-5-one, a less sensitive explosive, Report, 1985, 7 pp. (LA-10302-MS; Order No. DE86009787).

- [13] D.C. Sorescu, T.R.L. Sutton, D.L. Thompson, D. Beardallm, C.A. Wight, Theoretical and experimental studies of the structure and vibrational spectra of NTO, *J. Mol. Struct.* 384 (1996) 87–99.
- [14] B.M. Kosowski, R.C. Taylor, New processing aid and emulsifier for energetics, *Int. Annu. Conf. ICT (27th)* (1996) 152.1–152.11.
- [15] F.C. Fouche, V. Schalkwyk, C. Gideon, TNT-based insensitive munitions, *Int. Annu. Conf. ICT (27th)* (1996) 69.1–69.12.
- [16] E.A. Zuhorova, A.A. Pinkerton, Chemical bonding in energetic materials:  $\beta$ -NTO, *Acta Crystallogr., Sect. B: Struct. Sci.* B57 (2001) 359–365.
- [17] N. Bolotina, K. Krischbaum, A.A. Pinkerton, Energetic materials:  $\alpha$ -NTO crystallizes as a four-component triclinic twin, *Acta Crystallogr.* B61 (2005) 577–584.
- [18] K.Y. Lee, R. Gilardi, NTO polymorphs, in: *Materials Research Society Symposium Proceedings*, vol. 296, Structure and Properties of Energetic Materials, 1993, pp. 237–242.
- [19] R.J. Spear, C.N. Louey, M.G. Wolfson, A Preliminary Assessment of NTO as an Insensitive High Explosive, MRL-TR-89-18 Materials Research Laboratory, Vic., Australia, 1989.
- [20] Y. Xie, R.Z. Hu, X.Y. Wang, X.Y. Fu, Thermal behavior of NTO and its salts, in: *Proceedings of the 17th International Pyrotech Seminar (Combined with the Second Beijing International Symposium on Pyrotechnics and Explosives)*, vol. 1, Beijing Institute of Technology Press, Beijing, 1991, p. 509.
- [21] P.B. Kulkarni, T.S. Reddy, J.K. Nair, A.N. Nazare, M.B. Talawar, T. Mukundan, S.N. Asthana, Studies on salts of 3-nitro-1,2,4-triazol-5-one (NTO) and 2,4,6-trinitroanilino benzoic acid (TABA): potential energetic ballistic modifiers, *J. Hazard. Mater.* 123 (1–3) (2005) 54–60.
- [22] K. Mitsuo, W. Jemmy, K. Yoshihito, *Kayagu Gakkaishi* 62 (6) (2001) 283.
- [23] F.J. Owens, Calculation of energy barriers for bond rupture in some energetic molecules, *J. Mol. Struct. (THEOCHEM)* 370 (1) (1996) 11–16.
- [24] K.Y. Lee, L.B. Chapman, M.D. Coburn, 3-Nitro-1,2,4-triazol-5-one, a less sensitive explosive, *J. Energ. Mater.* 5 (1987) 27.
- [25] Y. Kohno, O. Takahashi, K. Saito, *Phys. Chem. Chem. Phys.* 3 (14) (2001) 2742.
- [26] R.I. Hiyoshi, Y. Kohno, J. Nakamura, Vibrational assignment of energetic material 5-nitro-2,4-dihydro-1,2,4-triazol-3-one (NTO) with labeled isomers, *J. Phys. Chem. A* 108 (27) (2004) 5915–5920.
- [27] H.M. Ma, J.R. Song, W. Dong, R.Z. Hu, G.H. Zhai, Z.Y. Wen, Molecular structure, the quantum chemical investigation and the thermal behavior of the dimethylamine salt of 3-nitro-1,2,4-triazol-5-one,  $(\text{CH}_3)_2\text{NH}_2^+\text{C}_2\text{N}_4\text{O}_3\text{H}^-$ , *J. Mol. Struct. (THEOCHEM)* 678 (1–3) (2004) 217–222.
- [28] G. Singh, S.P. Felix, Studies on energetic compounds. Part 32. Crystal structure, thermolysis and applications of NTO and its salts, *J. Mol. Struct.* 649 (1–2) (2003) 71–83.
- [29] J. Vagenknecht, P. Marecek, W.A. Trzcinski, Sensitivity and performance properties of TEX explosives, *J. Energ. Mater.* 20 (3) (2003) 245–253.
- [30] V.L. Zbarskii, V.V. Kuz'min, N.V. Yudin, Synthesis and properties of 1-nitro-4,5-dihydro-1H-1,2,4-triazol-5-one, *Russ. J. Org. Chem.* 40 (7) (2004) 1069–1070.
- [31] C. Meredith, T.P. Russell, R.C. Mowrey, J.R. McDonald, Decomposition of 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO): energetics associated with several proposed initial routes, *J. Phys. Chem. A* 102 (1998) 471–477.
- [32] J.J.P. Stewart, Optimization of parameters for semi empirical methods I, *Method J. Comput. Chem.* 10 (1989) 209–220.
- [33] J.J.P. Stewart, Optimization of parameters for semi empirical methods II, *Appl. Comput. Chem.* 10 (1989) 221–264.
- [34] A.R. Leach, *Molecular Modeling*, Longman, Essex, 1997.
- [35] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* 140 (1965) 1133–1138.
- [36] R.G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, London, 1989.
- [37] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A* 38 (1988) 3098–3100.
- [38] S.H. Vosko, L. Vilk, M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis, *Can. J. Phys.* 58 (1980) 1200–1211.
- [39] C. Lee, W. Yang, R.G. Parr, Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* 37 (1988) 785–789.
- [40] B. Miehlich, A. Savin, H. Stoll, H. Preuss, Results obtained with the correlation energy density functionals of Becke and Lee, Yang and Parr, *Chem. Phys. Lett.* 157 (1989) 200–206.
- [41] J.P. Perdew, Density-functional approximation for the correlation energy of the inhomogeneous electron gas, *Phys. Rev. B* 33 (1986) 8822–8824.
- [42] I.N. Levine, *Quantum Chemistry*, Prentice Hall, New Jersey, 2000.
- [43] P. Pulay, J.F. Hinton, K. Wolinski, in: J.A. Tossel (Ed.), *Nuclear Magnetic Shieldings and Molecular Structure*, NATOASI Series C, vol. 386, Kluwer, The Netherlands, 1993, pp. 243–262.
- [44] C.F. Tormena, G.V.J. da Silva, Chemical shifts calculations on aromatic systems: a comparison of models and basis sets, *Chem. Phys. Lett.* 398 (2004) 466–470.
- [45] S.M. Bachrach, Aromaticity of annulated benzene, pyridine and phosphabenzene, *J. Org. Chem.* 643–644 (2002) 39–46.
- [46] B.M. Rice, S. Sahu, F.J. Owens, Density functional calculation of bond dissociation energies for  $\text{NO}_2$  scission in some nitroaromatic molecules, *J. Mol. Struct. (THEOCHEM)* 583 (2002) 69–72.
- [47] J. Shao, X. Cheng, X. Yang, Density functional calculations of bond dissociation energies for removal of the nitrogen dioxide moiety in some nitroaromatic molecules, *J. Mol. Struct. (THEOCHEM)* 755 (2005) 127–130.
- [48] S.F. Boys, F. Bernardi, The calculation of small molecular interaction by the differences of separate total energies: some procedures with reduced errors, *Mol. Phys.* 19 (1970) 553–566.
- [49] M.F. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheesman, et al., *Gaussian 98, Revision A.6*, Gaussian Inc., Pittsburg, PA, 1998.
- [50] N.B. Bolotina, E.A. Zhurova, A.A. Pinkerton, Energetic materials: variable-temperature crystal structure of  $\beta$ -NTO, *J. Appl. Crystallogr.* 36 (2003) 280–285.
- [51] J.A. Cizek, S.F. Trevino, Theoretical and experimental study of the inelastic neutron scattering spectra of  $\beta$ -5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one, *J. Mol. Struct. (THEOCHEM)* 732 (2005) 211–218.
- [52] A.K. Sikder, G. Maddalla, J.P. Agraval, H. Singh, Important aspects of behavior of organic energetic compounds: a review, *J. Hazard. Mater.* A84 (2001) 1–26.
- [53] H.D. Gruschka, F. Wecken, *Gasdynamic Theory of Detonation*, Gordon and Breach, New York, 1971.
- [54] M.A. Cook, *The Science of High Explosives*, Robert E. Krieger Publ., New York, 1971.
- [55] L. Türker, Quantum chemical studies on EGDN and its monovalent ions, *J. Mol. Struct. (THEOCHEM)* 717 (2005) 9–14.
- [56] S. Ye, K. Tonokura, M. Koshi, Energy transfer rates and impact sensitivities of crystalline explosives, *Combust. Flame* 132 (1–2) (2003) 240–246.
- [57] F.J. Owens, Relationship between impact induced reactivity of trinitroaromatic molecules and their molecular structure, *J. Mol. Struct. (THEOCHEM)* 121 (1985) 213–220.
- [58] H. Dorset, A. White, Aeronautical and Maritime Research Laboratory, Defense Science and Technology Organization (DSTO), DSTO Technical Report DSTO-GD-0253, Australia, 2000.
- [59] F. Owens, Molecular orbital calculation of decomposition pathways of nitrocubanes and nitroazacubanes, *J. Mol. Struct. (THEOCHEM)* 460 (1999) 137–140.
- [60] W. Leung, Y.Z.F. Liu, Application of *ab initio* molecular dynamics for a priori elucidation of the mechanism in unimolecular decomposition: the case of 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO), *J. Am. Chem. Soc.* 123 (2001) 2243–2250.
- [61] T.B. Brill, K.J. James, Kinetics and mechanisms of thermal decomposition of nitroaromatic explosives, *Chem. Rev.* 93 (1993) 2667.
- [62] J. Shao, X. Cheng, X. Yang, Density functional calculations of bond dissociation energies for removal of the nitrogen dioxide moiety in some nitroaromatic molecules, *J. Mol. Struct. (THEOCHEM)* 755 (2005) 127–130.
- [63] G.S. Chung, M.W. Schmidt, M.S. Gordon, An *ab initio* study of potential energy surfaces for  $\text{N}_8$  isomers, *J. Phys. Chem. A* 104 (2000) 5647–5650.

- [64] M.J. Kamlet, S.J. Jacobs, Chemistry of detonations. 1. Simple method for calculating detonation properties of C–H–N–O explosives, *J. Chem. Phys.* 48 (1968) 23–36.
- [65] X.H. Zhang, Z.H. Yun, Explosive Chemistry, National Defense Industry Press, Beijing, 1989.
- [66] L. Qiu, H.M. Xiao, X.H. Ju, X.D. Gong, Theoretical study of the structures and properties of cyclic nitramines: tetranitrotetraazadecalin (TNAD) and its isomers *Int. J. Quantum Chem.* 105 (2005) 48–56.
- [67] J.J. Xiao, J. Zhang, D. Yang, H.M. Xiao, *Acta Chim. Sinica* 60 (2002) 2110.
- [68] L. Qiu, H.M. Xiao, X.H. Ju, X.D. Gong, *Chin. J. Chem. Phys.* 18 (2005) 541.
- [69] L. Qiu, H.M. Xiao, X.H. Ju, X.D. Gong, *Acta Chim. Sinica* 63 (2005) 377.
- [70] X.J. Xu, H.M. Xiao, X.D. Gong, X.H. Ju, Z.X. Chen, Theoretical studies on the vibrational spectra, thermodynamic properties, detonation properties, and pyrolysis mechanisms for polynitroadamantanes, *J. Phys. Chem. A* 109 (2005) 11268–11274.
- [71] L. Qiu, H. Xiao, X. Gong, X. Ju, W. Zhu, Theoretical studies on the structures, thermodynamic properties, detonation properties and pyrolysis mechanisms of spiro nitramines, *J. Phys. Chem. A* 110 (2006) 3797–3807.
- [72] C.I. Williams, M.A. Whitehead, Aromatic nitrogen heterocyclic heats of formation: a comparison of semi empirical and *ab initio* treatments, *J. Mol. Struct. (THEOCHEM)* 393 (1–3) (1997) 9–24.
- [73] H.M. Xiao, J.F. Fan, X.D. Gong, *Propel. Explos. Pyrot.* 22 (1997) 360.
- [74] X. Ma, H.H. Schobert, Estimating heats of formation of hydrocarbon radicals by a combination of semi empirical calculation and family correlation with experimental values, *J. Phys. Chem. A* 104 (5) (2000) 1064–1074.
- [75] H.M. Xiao, J. Fifing, Z.M. Go, H.S. Dong, Theoretical study on paralysis and sensitivity of energetic compounds: (3) Nitro derivatives of aminobenzenes, *Chem. Phys.* 226 (1998) 15–24.
- [76] M.H. Keshavarz, H.R. Pouretedal, Predicting the detonation velocity of CHNO explosives by a simple method, *Propel. Explos. Pyrot.* 30 (2) (2005) 105–108.
- [77] J. Zhang, J. Xiao, H. Xiao, Theoretical studies on heats of formation for cubyl nitrates using density functional theory B3LYP method and semiempirical MO methods, *Int. J. Quantum Chem.* 86 (3) (2002) 305–312.
- [78] G. Subramanian, P.V.R. Scheleyer, F. Jiao, Are the most stable fused heterobicycles the most aromatic, *Angew. Chem. Int. Ed.* 35 (1996) 2638–2641.
- [79] M.J.S. Dewar, R.C. Dougherty, *PMO Theory of Organic Chemistry*, Plenum-Rosetta, New York, 1975.
- [80] M.J.S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York, 1969.