

UDC 548.737:541.6

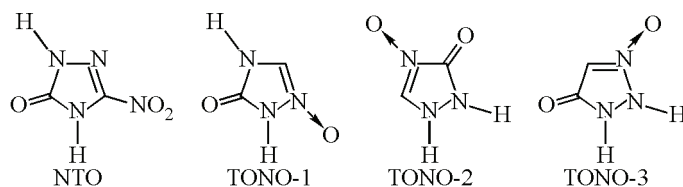
**STRUCTURES AND ENERGIES OF THE TAUTOMERS OF
1-NITROSO-1,2,4-TRIAZOL-5-ONE-2-OXIDE: NEW TRIAZOL-5-ONE-N-OXIDES****P. Ravi, S.P. Tewari***Advanced Centre of Research in High Energy Materials, University of Hyderabad, Hyderabad, India*
E-mail: rpiitb@hotmail.com*Received February, 24, 2012*

Molecular orbital calculations at the DFT-B3LYP/aug-cc-pVDZ level are performed for the possible tautomers of 1-nitroso-1,2,4-triazol-5-one-2-oxide. We have examined the substitution effects of carbonyl, N-oxide, and nitroso groups by comparing the calculated geometries, relative energies, and electrostatic potentials of model molecules. The optimized structures, vibrational frequencies, and thermodynamic values for triazolone-N-oxides are obtained in the ground state. The results show that 1H, 4H tautomers are most stable. Detonation velocity and detonation pressure are evaluated by the Kamlet—Jacob equations based on the predicted density and the calculated heat of explosion. The explosive properties of the designed compounds seem to be promising compared with those of 1,3,5-trinitroperhydro-1,3,5-triazine (D 8.75 km/s, P 34.70 GPa), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (D 9.10 km/s, P 39.3 GPa), and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (D 9.20 km/s, P 42.0 GPa).

Keywords: triazol-5-one-N-oxides, density, heat of explosion, detonation velocity, detonation pressure.

INTRODUCTION

Synthesis and development of triazolone based explosives is of current interest to chemists due to their high performance, high thermal stability, and remarkably low detonation sensitivity to impact, friction, and spark [1]. 3-Nitro-1,2,4-triazol-5-one (NTO) is an insensitive thermally stable explosive [2, 3]. The unique insensitivity/or stability of NTO is attributed to a high degree of hydrogen bonding of carbonyl (—C=O) and nitro (—NO₂) groups along with the molecular symmetry which allows the molecule to form the layered crystal structure. It was first synthesized in 1905 by nitration of 1,2,4-triazole-5-one (TO) [4], however, the first report on the explosive nature of NTO was published by Lee and Coburn in 1985 [2]. Several amine and metal salts of NTO have been synthesized for the use in gun propellants or as primary explosives. In the past few decades, researchers have been evaluating the NTO based explosive formulations to replace 1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX).



Computational studies on the constitutional isomers of NTO have been reported elsewhere [5—7]. Türker *et al.* [8, 9] studied the structure and explosive properties of NTO isomers and their picryl

derivatives. Detonation velocity and detonation pressure can be increased by increasing the density, oxygen balance, and/or heat of the formation of explosives. It is known that the introduction of nitroso ($-\text{NO}$), N-oxide ($-\text{N} \rightarrow \text{O}$), and carbonyl ($-\text{C}=\text{O}$) groups increases the heat of formation, density and thus, the detonation velocity and detonation pressure of azoles. To our knowledge there were no such reports on the geometric and electronic structures, stability/or sensitivity, thermodynamic and detonation properties of nitrosotriazolone-N-oxides. Accordingly, one of our objectives was to determine whether they can be expected to exist. We have performed the density functional theory (DFT) calculations at the B3LYP/aug-cc-pVDZ level to explore the geometric features, electronic structures, thermodynamic and detonation properties of the possible tautomers of 1-nitroso-1,2,4-triazol-5-one-2-oxide. In addition, we have examined the substitution effects of the carbonyl, N-oxide, and nitroso groups by comparing the heat release, density, detonation velocity and detonation pressure of triazolone-N-oxides (TONO).

METHODS AND COMPUTATIONAL DETAIL

All the calculations were performed on the desktop Pentium computer using the Gaussian 03 package [10]. Optimizations of all the structures leading to energy minima were achieved within the framework of density functional theory (DFT, B3LYP) [11, 12] at the aug-cc-pVDZ level. The exchange term of B3LYP consists of hybrid Hartee-Fock and local spin density exchange with Beck's gradient correlation to the local spin density exchange [13]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [14] and the Lee, Yang, Parr (LYP) correlation functional [15]. Vibrational analyses were carried out 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.

The heats of explosion (Q) have been calculated from the difference between the sum of energies for the formation of explosive components and the sum of energies for the formation explosive products.

$$Q = \Delta E_{298.15\text{ K}} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta_T H + \Delta nRT, \quad (1)$$

where ΔE_0 is a change in the total energy between the products and reactants at 0 K; ΔZPE is the difference between the zero point energies of the products and reactants; $\Delta_T H$ is the difference between the thermal correction from 0 to 298.15 K of the products and reactants; $\Delta(PV)$ equals ΔnRT .

The optimized structures were used to determine the densities of triazolone-N-oxides using Materials Studio 4.1 with the CVFF force field and the Ewald summation method [16].

Kamlet and Jacob equations [17] were used to estimate the detonation velocity and detonation pressure

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho), \quad (2)$$

$$P = 1.558NM^{1/2}Q^{1/2}\rho^2, \quad (3)$$

where D is the detonation velocity in km/s, P is the detonation pressure in GPa, N is the number moles of gaseous detonation products per gram of the explosive, M is the average molecular weight of gaseous products, Q is the energy of explosion in cal/g of the explosive, and ρ is the density in g/cm^3 .

Oxygen balance can be defined as the amount of oxygen liberated as a result of the complete conversion of the explosive with the general formula $\text{C}_a\text{H}_b\text{N}_c\text{O}_d$ to carbon monoxide, carbon dioxide, water and so on. In other words, oxygen balance (OB%) represents the lack or excess of oxygen required to produce H_2O , CO , and CO_2 . Generally, the Q value reaches maximum for triazolone-N-oxides containing two NO_2 groups corresponds to the oxidation of carbon to more CO_2 and less CO and hydrogen to H_2O . Based on the composition of the explosive, the main components of gaseous products may include CO , CO_2 , N_2 , H_2O with lesser quantities of other molecules and radicals such as H_2 , NO , H , O , CHO , and N_2O . The possible detonation products of the model triazolone-N-oxides have been written

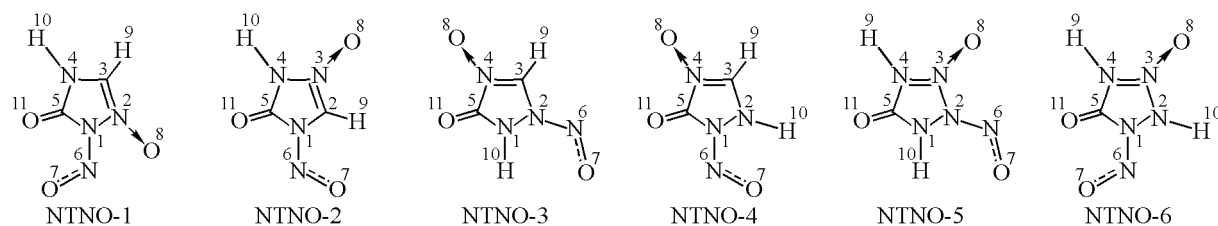


Fig. 1. Molecular frameworks of nitrosotriazolone-N-oxides

based on the modified Kistiakowsky—Wilson rules [18]



The highest occupied molecular orbitals and the lowest unoccupied molecular orbitals play an important role in governing the stability or sensitivity of compounds. We have determined the stability of triazolone-N-oxides from the frontier molecular orbital energies and their gaps and the total energies [19—21].

RESULTS AND DISCUSSION

Optimized structures. At the outset we have optimized the structures at the DFT-B3LYP/aug-cc-pVDZ level, and the molecular frameworks of triazolone-N-oxides are presented in Fig. 1. No imaginary vibrational frequencies were found, confirming that these structures correspond to true energy minima. All triazolone-N-oxides belong to the C_1 point group. The non-planarity or co-planarity of a molecule is due to the repulsion between the neighboring nitroso ($-\text{NO}$), N-oxide ($-\text{N} \rightarrow \text{O}$), and carbonyl ($-\text{C}=\text{O}$) groups, which rotate the oxygen atom(s) away from the molecular plane. The lowest frequency, total energy, zero-point energy, thermal correction to enthalpy and frontier molecular orbital energies and their gaps of triazolone-N-oxides are summarized in Table 1. The lowest frequencies varying from 22.8379 cm^{-1} to 84.8999 cm^{-1} are for the wagging modes of the NO group [22]. The selected structural parameters at the B3LYP/aug-cc-pVDZ level are listed in Table 2. The N—NO lengths have been found to be longer in NTNO-1 (1.435 \AA) and NTNO-6 (1.437 \AA). The N1—N2, N2—N3/or N3—N4, and N1—C5 lengths are longer in the triazole ring. The $\text{N} \rightarrow \text{O}$ length is longer in NTNO-4 (1.265 \AA) and is shorter in NTNO-6 (1.234 \AA). The $\text{C}=\text{O}$ lengths of NTNO-1, NTNO-2, NTNO-3, NTNO-4, NTNO-5, and NTNO-6 are 1.207 \AA , 1.204 \AA , 1.195 \AA , 1.191 \AA , 1.212 \AA , and 1.205 \AA respectively. The $\text{C}=\text{O}$ length is longer in NTNO-1 (1.207 \AA) and is shorter in NTNO-4 (1.191 \AA). Furthermore, NTNO-2, NTNO-3, NTNO-4, NTNO-5 and NTNO-6 have $\text{N} \cdots \text{O} \cdots \text{H}$ interactions (2.602 \AA , 2.315 \AA , 2.367 \AA , 2.234 \AA , and 2.351 \AA respectively) that are shorter than sum of the van der Waals radii [23]. The discrepancies in the total and zero point energies, thermal correction to enthalpy, frontier molecular orbital energies, C—C, C—N, N—N, N—NO, C=O and $\text{N} \rightarrow \text{O}$ lengths are presumably due to the relative positions of N atoms in the triazole ring.

Table 1

Lowest frequencies (ω_L), total energies (E_0), zero-point vibrational energies (ZPVE), thermal correction to enthalpy (H_T) and frontier molecular orbital energies of nitrosotriazolone-N-oxides computed at the B3LYP/aug-cc-pVDZ level

HEM	ω_L, cm^{-1}	$E_0, \text{a.u.}$	ZPVE, $\text{kJ} \cdot \text{mol}^{-1}$	$H_T, \text{a.u.}$	HOMO, eV	LUMO, eV	$\epsilon_{(\text{LUMO}-\text{HOMO})}, \text{eV}$
NTNO-1	61	-521.9866684	38.94300	0.070900	-6.61	-3.31	3.30
NTNO-2	22	-521.9999988	39.47755	0.071596	-7.15	-3.48	3.67
NTNO-3	53	-521.9868824	39.53674	0.071542	-7.05	-3.58	3.47
NTNO-4	63	-521.9751982	39.72165	0.071567	-6.81	-3.81	3.00
NTNO-5	84	-521.9627541	39.29895	0.070905	-7.93	-3.71	4.22
NTNO-6	65	-521.9580648	39.31148	0.071054	-7.77	-3.48	4.29

Table 2

Selected structural parameters^a of nitrosotriazolone-N-oxides computed from the B3LYP/aug-cc-pVDZ level

NTNO-1		NTNO-2		NTNO-3		NTNO-4		NTNO-5		NTNO-6	
Parameter	Value	Parameter	Value	Parameter	Value	Parameter	Value	Parameter	Value	Parameter	Value
N1–N2	1.445	N1–C2	1.394	N1–N2	1.373	N1–N2	1.393	N1–N2	1.391	N1–N2	1.408
N2–C3	1.315	C2–N3	1.319	N2–C3	1.381	N2–C3	1.393	N2–N3	1.456	N2–N3	1.429
C3–N4	1.388	N3–N4	1.406	C3–N4	1.326	C3–N4	1.323	N3–C4	1.325	N3–C4	1.328
N4–C5	1.384	N4–C5	1.383	N4–C5	1.505	N4–C5	1.478	C4–C5	1.457	C4–C5	1.447
C5–N1	1.434	C5–N1	1.431	C5–N1	1.374	C5–N1	1.411	C5–N1	1.418	C5–N1	1.469
N1–N6	1.435	N1–N6	1.383	N2–N6	1.348	N1–N6	1.368	N2–N6	1.396	N1–N6	1.437
N6–O7	1.188	N6–O7	1.209	N6–O7	1.225	N6–O7	1.210	N6–O7	1.207	N6–O7	1.189
N2–O8	1.251	N3–O8	1.251	N4–O8	1.255	N4–O8	1.265	N3–O8	1.226	N3–O8	1.234
C3–H9	1.081	C2–H9	1.078	C3–H9	1.081	C3–H9	1.082	C4–H9	1.082	C4–H9	1.082
N4–H10	1.009	N4–H10	1.012	N1–H10	1.014	N2–H10	1.021	N1–H10	1.019	N2–H10	1.025
C5–O11	1.207	C5–O11	1.204	C5–O11	1.195	C5–O11	1.191	C5–O11	1.212	C5–O11	1.205
N1–N2–C3	106.5	N1–C2–N3	108.0	N1–N2–C3	108.7	N1–N2–C3	104.5	N1–N2–N3	107.2	N1–N2–N3	106.0
N2–C3–N4	109.9	C2–N3–N4	107.8	N2–C3–N4	109.1	N2–C3–N4	112.3	N2–N3–C4	108.1	N2–N3–C4	110.2
C3–N4–C5	111.6	N3–N4–C5	111.8	C3–N4–C5	108.5	C3–N4–C5	108.4	N3–C4–C5	110.4	C3–C4–C5	110.3
N4–C5–N1	102.6	N4–C5–N1	101.5	N4–C5–N1	102.9	N4–C5–N1	102.4	N4–C5–N1	104.8	C4–C5–N1	103.8
C5–N1–N2	109.2	C5–N1–C2	110.7	C5–N1–N2	110.6	C5–N1–N2	111.8	C5–N1–N2	108.9	C5–N1–N2	108.3
N1–N6–O7	113.2	N1–N6–O7	112.6	N2–N6–O7	112.9	N2–N6–O7	112.6	N2–N6–O7	112.1	N1–N6–O7	114.4

^a Bond lengths in Å and angles in degree.

Frontier molecular orbitals. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies play a prominent role in governing the chemical reactions of the compounds. It has been revealed in several studies that the band gap $\Delta E_{(LUMO-HOMO)}$ between the LUMO and HOMO is an important stability index of the molecules [24–29]. A large band gap implies high stability and a small band gap implies low stability; in turn, high stability indicates low chemical reactivity and low stability indicates high reactivity, i.e., the smaller the band gap between HOMO and LUMO, the easier the electron transition is and thus lesser the stability is. The compound having large differences in frontier orbital energies, that is if $\epsilon_{HOMO} - \epsilon_{LUMO} \gg 0$, then very little electron transfer occurs. If the respective orbital energies are quite similar, that is if $\epsilon_{HOMO} - \epsilon_{LUMO} \approx 0$, strong electron transfer occurs. The frontier molecular orbital energies and their gaps are shown in Table 1. The band gap values of triazolone-N-oxides vary from 3.30 eV to 4.30 eV. NTNO-5 (4.22 eV) and NTNO-6 (4.30 eV) are more stable while NTNO-4 (3.0 eV) and NTNO-1 (3.30 eV) are lesser stable. The high frontier orbital gap is also associated with a low chemical reactivity and high kinetic stability [24]. Thus NTNO-5 and NTNO-6 seem to be kinetically more stable and chemically less active than the other triazolone-N-oxides. The discrepancies in the band gap values among the isomers are caused by the relative positions of NO, N → O, and C=O groups in the triazole ring. The larger the length of C=N, C–N and N–N bonds of molecule is, the easier the dissociation or breakdown, thus the molecule becomes lesser stable. The N–NO bonds are the trigger sites in these molecules, and resonance in the triazole moiety strengthens these bonds, thereby the molecules get stabilized. Also, the higher the total energy of the molecule, the lesser the stability is.

Assignment of IR spectra. The optimized structures of nitrosotriazolone-N-oxides belong to the C1 point group as it does not display any special symmetry. As a result of this all the 27 fundamental vibrational modes of the molecules are IR active and are spread over the functional and fingerprint regions. The calculated IR spectra of model compounds are shown in Fig. 2. The calculated wave

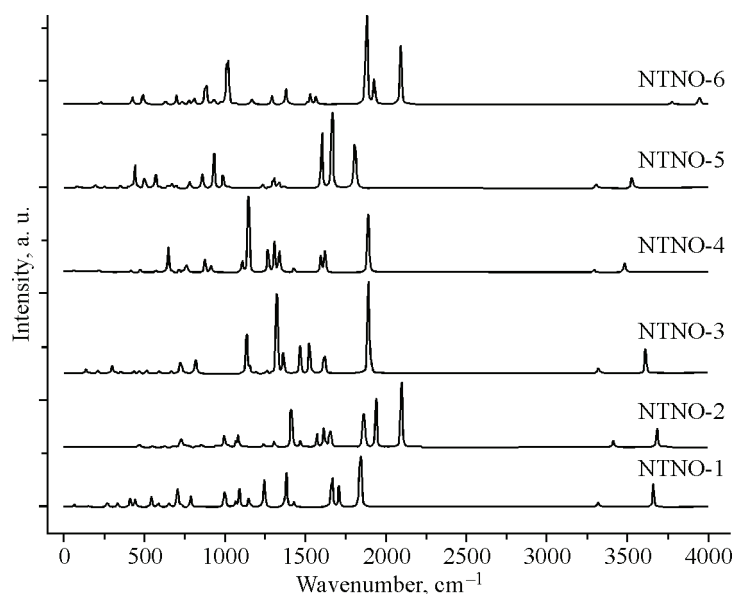


Fig. 2. Calculated IR spectra of nitrosotriazolone-N-oxides

numers are expected to be higher compared with the corresponding experimental quantities because of the combination of electron correlation effects and basis set deficiencies. Also, these discrepancies are taken into account either by computing anharmonic corrections explicitly or by introducing a scalar field or even by a direct scaling of the calculated wave numbers with a proper scaling factor. The vibrational assignments have been made based on the relative intensities, line shape and the animation option of Gaussview 3.0. The appearance of a strong band in the IR spectra around 1522–1895 cm^{-1} in azoles shows the presence of the carbonyl group. The wave number of the stretching is due to that the carbonyl group (—C=O) mainly depends on the bond strength, which in turn depends upon the inductive, conjugative, field, and steric effects. The identification of C—N stretching is not an easy task due to the possible mixing of other vibrations. The strong band from 3290 cm^{-1} to 3336 cm^{-1} is for C—H stretching vibrations. Vibrations involving C—H in-plane bending are found throughout the region from 1100 cm^{-1} to 1500 cm^{-1} . The C—H wagging mode starts appearing at 960 cm^{-1} and has contributions up to 738 cm^{-1} and is assigned well in the spectra. The wave numbers from 3445 cm^{-1} to 3656 cm^{-1} are for N—H stretching vibrations.

Theoretical density. The density appears to a higher power in the Kamlet—Jacob expressions [17] than does any of the other variables; it is considered to be one of the top priorities in the development of new explosives. Several researchers have attempted to predict the densities with satisfactory accuracy [30–32]. We have taken the optimized structures computed at the B3LYP/aug-cc-pVDZ level to predict the densities using Materials Studio 4.1 with the CVFF force field and the Ewald summation method. This approach is based on the generation of possible packing arrangements in all reasonable space groups. Many organic compounds are known to pack in $C2/c$, $P2_1$, $P2_1/c$, $P2_12_12_1$, $P-1$, $Pbca$, $Pbcn$, $Pna2_1$, C_C and/or C_2 space groups [33, 34]. The crystal characteristics of triazolone-N-oxides are summarized in Table 3. The model compounds have densities varying from 2.194 g/cm^3 to 2.217 g/cm^3 , which are higher compared with octanitrocubane (ONC) (1.979 g/cm^3) [35] and hexanitrohexaazaisowurtzitane (CL-20) (2.040 g/cm^3) [36]. The higher densities are due to the intramolecular hydrogen bonds ($\text{N—O}\cdots\text{H}$), layered structures in the crystal lattice as well as per atom/or group additivity. The absolute error in the calculated densities is believed to be less than 0.03 g/cm^3 and thus is known to be fairly good to calculate the performance properties of the designed compounds [1].

Chemical energy of explosion. The heat of explosion provides information about the work capacity of the explosive. The liberation of heat under adiabatic conditions is called the heat of explosion. It is an irreversible process and whatever the amount of heat is released, it is ultimately lost to

Table 3

Predicted crystal characteristics of nitrosotriazolone-N-oxides

HEM	Cell volume, Å ³	Total energy, kJ·mol ⁻¹	Point group	Crystal system	<i>a</i> , <i>b</i> , <i>c</i> , Å; <i>α</i> , <i>β</i> , <i>γ</i> , deg.	<i>ρ</i> , g·cm ⁻³
NTNO-1	408.5	-395.7	<i>P</i> 2 ₁ 2 ₁ 2 ₁	Rhombic	<i>a</i> = 5.11, <i>b</i> = 16.13, <i>c</i> = 4.97; <i>α</i> = <i>γ</i> = <i>β</i> = 90	2.147
NTNO-2	395.6	-389.1	<i>P</i> 2 ₁ / <i>c</i>	Monoclinic	<i>a</i> = 11.0, <i>b</i> = 9.41, <i>c</i> = 9.44; <i>α</i> = <i>γ</i> = 90, <i>β</i> = 156.1	2.217
NTNO-3	799.5	-369.2	<i>P</i> <i>bca</i>	Rhombic	<i>a</i> = 7.46, <i>b</i> = 17.43, <i>c</i> = 6.15; <i>α</i> = <i>γ</i> = <i>β</i> = 90	2.194
NTNO-4	400.6	-374.8	<i>P</i> <i>na</i> 2 ₁	Rhombic	<i>a</i> = 9.40, <i>b</i> = 8.52, <i>c</i> = 5.0; <i>α</i> = <i>γ</i> = <i>β</i> = 90	2.190
NTNO-5	458.1	-122.7	<i>P</i> 2 ₁ / <i>c</i>	Monoclinic	<i>a</i> = 12.62, <i>b</i> = 11.41, <i>c</i> = 9.28; <i>α</i> = <i>γ</i> = 90, <i>β</i> = 160	2.140
NTNO-6	447.4	-123.2	<i>P</i> 2 ₁ 2 ₁ 2 ₁	Rhombic	<i>a</i> = 6.46, <i>b</i> = 6.82, <i>c</i> = 10.15; <i>α</i> = <i>γ</i> = <i>β</i> = 90	2.142

Table 4

Calculated explosive properties of nitrosotriazolone-N-oxides

HEM	Formula	Mw, g·mol ⁻¹	OB, %	<i>Q</i> , kcal·g ⁻¹	<i>ρ</i> , g·cm ⁻³	<i>D</i> , km·s ⁻¹	<i>P</i> , GPa
NTNO-1	C ₂ H ₂ N ₄ O ₃	130	-24.61	1.015	2.147	9.57	44.86
NTNO-2	C ₂ H ₂ N ₄ O ₃	130	-24.61	0.953	2.217	9.65	46.37
NTNO-3	C ₂ H ₂ N ₄ O ₃	130	-24.61	1.016	2.194	9.73	46.90
NTNO-4	C ₂ H ₂ N ₄ O ₃	130	-24.61	1.073	2.190	9.85	48.04
NTNO-5	C ₂ H ₂ N ₄ O ₃	130	-24.61	1.130	1.915	9.81	47.04
NTNO-6	C ₂ H ₂ N ₄ O ₃	130	-24.61	1.153	1.961	9.87	47.61
RDX ^a	C ₃ H ₆ N ₆ O ₆	222	-21.62	1.27	1.82	8.75	34.70
HMX ^a	C ₄ H ₈ N ₈ O ₈	296	-21.62	1.27	1.92	8.96	35.96
NTO ^b	C ₂ H ₂ N ₄ O ₃	130	-24.60	1.03	1.918	8.56	31.12
CL-20 ^c	C ₃ H ₆ N ₁₂ O ₁₂	438	-11.00	1.342	2.042	9.20	42.00
ONC ^d	C ₈ N ₈ O ₁₆	464	0	1.337	1.979	10.10	48.45

^a Experimental values of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are taken from ref. [37].

^b Experimental values of 3-nitro-1,2,4-triazol-5-one (NTO) are taken from ref. [11].

^c Experimental values of 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) are taken from ref. [36].

^d Experimental values of octanitrocubane (ONC) are taken from ref. [35].

surroundings. The higher the value of heat of explosion is, the more the heat generated when an explosion occurs. The determination of the composition of the products of a detonation or explosion process has been known to be a key issue. Kim *et al.* [32] reported that a difference of 10 kcal/mol in the heat of formation had little influence on the explosive performance. For the accurate prediction of the detonation performance the heat of formation should be provided within an error of 5 kcal/mol. If the explosive compound is composed of C, H, N, and O atoms, the products can conceivably be expected to be CO₂, CO, N₂, H₂O, H₂, O₂, NH₃, CH₄, and NO gases as well as soot or free carbon. The modified Kistiakowsky—Wilson rules [18] give an approximate for the decomposition products, which is independent of the temperature of explosion. We have calculated the heats of explosion (*Q*) of triazolone-N-oxide assuming the explosive reactions to achieve a total completion. Table 4 presents the

calculated oxygen balance, heats of explosion and performances of triazolone-N-oxide computed at the B3LYP/aug-cc-pVDZ level. Usually a good oxygen balance results in a greater heat of explosion and therefore leads to a better performance of the explosive. NTNO-1 has a lower Q value of 1.015 kcal/g and NTNO-6 has a higher Q value of 1.153 kcal/g (OB% -24.61, stoichiometric oxidation of carbon to carbon monoxide and hydrogen to water). Nevertheless, the calculated Q values do not exactly agree with those obtained experimentally because the conditions of loading density, temperature, pressure and so on are not taken into consideration. The total amount of energy liberated depends upon the relative proportions of the reactants to the products. The Q values are related to the nature of triazolone-N-oxide and the strength of C=O and N \rightarrow O bonds. The detonation energies obtained are for the gas phase compounds and in the reality they should be for the solid phase, which would diminish the magnitude of Q values [1].

Detonation velocity and detonation pressure. Two key measures of the detonation performance are the detonation velocity and the detonation pressure, referring to the stable velocity of the shock front that characterizes detonation and the stable pressure developed behind the front respectively [1, 17, 18]. The detonation velocity and the detonation pressure are desired to be as high as it is compatible avoiding the excessive sensitivity of the compound to unintended stimuli (i.e., like impact, shock, friction, and electric spark). Kamlet and Jacob indicated the importance of the density as a determinant of the detonation velocity and the detonation pressure. However, one or more of the other factors do sometimes override the effects of the density. The detonation velocity (D) linearly increases with ρ for most of explosives while the detonation pressure (P) increases with the square of ρ , when ρ is greater than one. Detonation energy, oxygen balance, detonation velocity and detonation pressure of triazolone-N-oxides are summarized in Table 4. The detonation properties of NTNO-1 (D 9.57 km/s, P 44.86 GPa), NTNO-2 (D 9.65 km/s, P 46.37 GPa), NTNO-3 (D 9.73 km/s, P 46.90 GPa), NTNO-4 (D 9.85 km/s, P 48.04 GPa), NTNO-5 (D 9.81 km/s, P 47.04 GPa), and NTNO-6 (D 9.87 km/s, P 47.61 GPa) are higher compared with those of RDX (D 8.75 km/s, P 34.70 GPa), HMX (D 8.96 km/s, P 35.96 GPa), NTO (D 8.56 km/s, P 31.12 GPa), and CL-20 (D 9.20 km/s, P 42.0 GPa [1, 36]. The higher performance properties of triazolone-N-oxides are presumably due to their higher densities. Overall, the performance properties are related to the number, the relative positions of substituent groups, and the strength of trigger bonds.

CONCLUSIONS

The density functional theory calculations at the B3LYP/aug-cc-pVDZ level have been carried out to explore the structure and explosive properties of nitrosotriazolone-N-oxides. Our computational results indicate that the designed molecules do correspond to the energy minima and accordingly should be able to exist. All triazolone-N-oxides belong to the C_1 point group. Detonation properties were evaluated by the Kamlet—Jacob equations based on the calculated density and the chemical energy heat. The partial replacement of hydrogen by nitroso group appears to be a particularly promising area for the investigation since it may lead to two desirable consequences of the higher explosion heat and diminished sensitivities. All model compounds have Q values varying from 0.953 kcal/g to 1.153 kcal/g and the discrepancies are due to the relative position of the N atom in the triazolone-N-oxide ring and the position of nitroso ($-\text{NO}$), N-oxide ($-\text{N} \rightarrow \text{O}$), and carbonyl ($-\text{C}=\text{O}$) groups. Triazole-N-oxides have densities varying from 2.140 g/cm³ to 2.217 g/cm³, which are higher compared with those of CL-20 (2.040 g/cm³) and ONC (1.979 g/cm³). The detonation properties of NTNO-1, NTNO-2, NTNO-3, NTNO-4, NTNO-5, and NTNO-6 are higher compared with those of RDX (D 8.75 km/s, P 34.70 GPa), HMX (D 8.96 km/s, P 35.96 GPa), NTO (D 8.56 km/s, P 31.12 GPa), and CL-20 (D 9.20 km/s, P 42.0 GPa). The designed compounds satisfy the criteria of high energy materials. Furthermore, these triazolone-N-oxides may hold promise as detergents, fluorescent agents, and biologically active compounds (i.e., insecticides, fungicides, bactericides, nematocides, acaricides, and blood ocular compounds) in the near future.

We thank the Defense Research Development Organization, India for the financial assistance through the Advanced Centre of Research in High Energy Materials.

REFERENCES

1. *Klapotke T.M.* High energy density materials, Springer, Berlin, 2007.
2. *Lee K.Y., Coburn M.D.* 3-Nitro-1,2,4-triazol-5-one, a less sensitive explosive (LA10302-MS), Los Alamos National Laboratory, Los Alamos, NM, 1985.
3. *Smith M.W., Cliff M.D.* NTO based explosive formulations: A technology review (DSTO-TR-0796), MRL Technical Report, AR-1-873, Material Research Laboratory, Maribyrnong, Australia, 1999.
4. *Manchot V.W., Noll R.* // *Liebigs, Ann der Chem.* – 1905. – **343**. – P. 1 – 27.
5. *Hiyoshi R.I., Kohno Y., Nakamura J.* // *J. Phys. Chem. A.* – 2004. – **108**. – P. 5915 – 5920.
6. *Ma H.M., Song J.R., Dong W., Hu R.Z., Zhai G.H., Wen Z.Y.* // *J. Mol. Struct (THEOCHEM).* – 2004. – **678**. – P. 217 – 222.
7. *Harris N.J., Lamnestsma K.* // *J. Amer. Chem. Soc.* – 1996. – **118**. – P. 8048 – 8055.
8. *Turker L., Atalar T.* // *J. Hazard. Mater. A.* – 2006. – **137**. – P. 1333 – 1334.
9. *Turker L., Bayer C.* // *J. Energ. Mater.* – 2012. – **30**. – P. 72 – 96.
10. *Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Montgomery J.A., Vreven T., Kudin K.N., Burant J.C., Millam J.M., Iyengar S.S., Tomasi J., Barone V., Mennucci B., Cosi M., Scalmani G., Rega N., Petersson G.A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J.E., Hratchian H.P., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Ayala P.Y., Morokuma K., Voth G.A., Salvador P., Dannenberg J.J., Zakrzewski V.G., Dapprich S., Daniels A.D., Strain M.C., Farkas O., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Ortiz J.V., Cui Q., Baboul A.G., Clifford S., Cioslowski J., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R.L., Fox D.J., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.W., Gonzalez C., Pople J.A.* Gaussian 03, revision B.04. Gaussian Inc, Pittsburgh, 2003.
11. *Kohn W., Sham L.J.* // *Phys. Rev.* – 1965. – **140**. – P. A1133 – A1138.
12. *Parr R.G., Yang W.* Density Functional Theory of Atoms, Molecules. – L.: Oxford University Press, 1989.
13. *Becke D.* // *Phys. Rev. A.* – 1988. – **38**. – P. 3098 – 3100.
14. *Vosko S.H., Vilk L., Nusair M.* // *Canad. J. Phys.* – 1980. – **58**. – P. 1200 – 1211.
15. *Lee C., Yang W., Parr R.G.* // *Phys. Rev. B.* – 1988. – **37**. – P. 785 – 789.
16. Materials Studio 4.1, Accelrys Inc., San Diego, CA, 2004.
17. *Kamlet M.J., Jacobs S.J.* // *J. Chem. Phys.* – 1968. – **48**. – P. 23 – 35.
18. *Akhavan J.* Chemistry of Explosives, The Royal Society of Chemistry, Cambridge, 1998.
19. *Fukui F., Yonezawa T., Shingu H.* // *J. Chem. Phys.* – 1952. – **20**. – P. 722 – 725.
20. *Zhou Z., Parr R.G.* // *J. Amer. Chem. Soc.* – 1990. – **112**. – P. 5720 – 5724.
21. *Pearson R.G.* // *J. Org. Chem.* – 1989. – **54**. – P. 1423 – 1430.
22. *Ravi P., Tewari S.P.* // *Struct. Chem.* – 2012. – doi 10.1007/s11224.012-0028-9.
23. *Desiraju G.R., Steiner T.* The Weak Hydrogen Bond. – New York: Oxford University Press, 1999.
24. *Hess B.A. Jr, Schaad L.J.* // *J. Amer. Chem. Soc.* – 1971. – **93**. – P. 2413 – 2416.
25. *Haddon R.C., Fukunaga T.* // *Tetrahedron Lett.* – 1980. – **21**. – P. 1191 – 1972.
26. *Schmalz T.G., Seitz W.A., Klein D.J., Hite G.E.* // *J. Amer. Chem. Soc.* – 1988. – **110**. – P. 1113 – 1127.
27. *Zhou Z., Parr R.G., Garst J.F.* // *Tetrahedron Lett.* – 1988. – **29**. – P. 4843 – 4846.
28. *Zhou Z., Parr R.G.* // *J. Amer. Chem. Soc.* – 1989. – **11**. – P. 7371 – 7379.
29. *Murray J.S., Sen K.D.* Molecular Electrostatic Potentials: Concepts, Applications. – Amstardam, Netherlands: Elsevier, 1996.
30. *Cho S.G., Goh E.M., Kim J.K.* // *Bull. Korean Chem.Soc.* – 2001. – **22**. – P. 775 – 778.
31. *Politzer P., Martinez J., Murray J.S., Concha M.C., Toro-Labbe A.* // *Mol. Phys.* – 2009. – **107**. – P. 2095 – 2101.
32. *Kim C.K., Cho S.G., Kim C.K., Park H.Y., Zhang H., Lee H.W.* // *J. Comput. Chem.* – 2008. – **29**. – P. 1818 – 1824.
33. *Belsky V.K., Zorkii P.M.* // *Acta Cryst. A.* – 1977. – **13**. – P. 1004 – 1006.
34. *Manolopoulos D.E., May J.C., Down S.E.* // *Chem. Phys. Lett.* – 1991. – **181**. – P. 105 – 111.
35. *Eaton P.E., Gilardi R., Zhang M.-X.* // *Adv. Mat.* – 2000. – **12**. – P. 1143 – 1148.
36. *Hoffman D.M.* // *Prop., Explos., Pyrotech.* – 2003. – **28**. – P. 194 – 200.
37. *Mathieu J., Stucki H.* // *Chimia.* – 2004. – **58**. – P. 383 – 389.