

A DFT study of tautomers of 3-amino-1-nitroso-4-nitrotriazol-5-one-2-oxide

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Abstract We report herein the structure and explosive properties of the possible isomers of 3-amino-1-nitroso-4-nitrotriazol-5-one-2-oxide computed from the B3LYP/aug-cc-pVDZ level. The optimized structures, vibrational frequencies and thermodynamic values for triazol-5-one-N-oxides were obtained in the ground state. Several designed compounds have densities varying from 2.103 to 2.177 g/cm³. The detonation properties were evaluated by the Kamlet-Jacob equations based on the predicted density and the calculated heat of explosion. The detonation properties of triazol-5-one-N-oxides (D 9.87 to 10.11 km s⁻¹ and P 48.95 to 50.61 GPa) appear to be promising compared with those of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (D 9.20 km s⁻¹, P 42.0 GPa) and octanitrocubane (D 9.90 km s⁻¹, P 48.45 GPa). The substitution of secondary amino hydrogen of the triazole ring by amino group shows better impact sensitivity/or stability however the model compounds seem to be highly sensitive.

Keywords Density · Detonation pressure · Detonation velocity · Heat of explosion · Triazol-5-one-N-oxides

Introduction

Triazol-3(5)-one based explosives have attracted renewed attention by explosives 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]. The unique insensitivity of NTO is due to the high degree of hydrogen bonding carbonyl (-C=O) and nitro (-NO₂) groups along with the molecular symmetry which allows the molecule to form the layered crystal structure. Researchers have been evaluating NTO based formulations to replace sensitive explosives such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). Several metal and amine salts of NTO have been synthesized and evaluated for use in gun propellants or as primary explosives [2]. Computational studies on the structure and explosive properties of NTO isomers have been reported elsewhere [3–8].

Two key measures of explosive performance are the detonation velocity (D) and the detonation pressure (P). These refer to the stable velocity of the shock front that characterizes detonation and the stable pressure that is developed behind the front [1]. It is desired that the detonation velocity and pressure be as high as is compatible with avoiding excessive sensitivity of the compound to unintended stimuli to impact, shock, friction and so on. The detonation velocity and pressure can be increased by increasing the density, oxygen balance and/or heat of formation of the compound. The nitroso (-NO), nitro (-NO₂) and N-oxide (-N → O) groups increases the heat of formation, density and thus detonation velocity and pressure. On the other hand, the amino (-NH₂) and carbonyl (-C=O) groups decreases the sensitivity of the product relative to the unaminated compounds [1]. To our knowledge there were no such studies on the structure, stability/or sensitivity, thermodynamic properties and detonation properties of triazol-5-one-N-oxides. Herein the density functional theory calculations at the B3LYP/aug-cc-pVDZ level were performed to explore such properties of isomers of 3-amino-1-nitroso-4-nitrotriazol-5-one-2-oxide. We have addressed how the relative positions of -NH₂, -NO and -NO₂

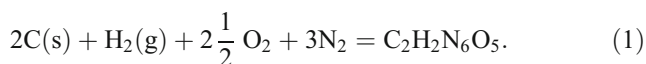
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groups affect the structure, stability, heat release, density, detonation velocity and detonation pressure of triazol-5-one-N-oxides (TONO).

Methods and computational detail

All the calculations were performed using the Gaussian 03 package [9]. The structure optimizations of model compounds leading to the energy minima were achieved at the B3LYP/aug-cc-pVDZ level. The basis set and the method has been known to provide adequate results for several nitroazoles [10–14]. Vibrational analyses were carried out using the same basis set employed in the corresponding structure 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. All the bond lengths were thoroughly searched in order to find out whether any bond cleavage occurred or not during the geometry optimization process.

The heat of explosion (Q) was calculated from the difference between sum of the energies for the formation of explosive components and sum of the energies for the formation explosive products. The gas phase heat of formation was calculated by the following equation:



The condensed phase heat of formation ($\Delta_f H_{\text{cond}}^0$) was determined from the gas phase heat of formation ($\Delta_f H_{\text{gas}}^0$) and the heat of sublimation ($\Delta_f H_{\text{sub}}^0$) according to Hess law [15]:

$$\Delta_f H_{\text{cond}}^0 = \Delta_f H_{\text{gas}}^0 - \Delta_f H_{\text{sub}}^0. \quad (2)$$

Poltizer et al. [16, 17] related ΔH_{sub} to the molecular electrostatic potential by the following expression:

$$\Delta_f H_{\text{sub}}^0 = \beta_1 A^2 + \beta_2 (\nu \sigma_{\text{tot}}^2)^{0.5} + \beta_3, \quad (3)$$

where A is the area of the isosurface of 0.01 electrons/bohr³, ν is the degree of balance between positive and negative potential on the molecular surface; σ_{tot}^2 is a measure of variability of the electrostatic potential and β_1 , β_2 and β_3 are the correlation coefficients.

The optimized structures were used to determine the densities of triazol-5-one-N-oxides using Materials Studio 4.1 suite with CVFF force field and Ewald summation method

[18]. The Poltizer et al. [19] approach also was followed to estimate the crystal density by the following expression:

$$\rho = \alpha \left[\frac{M}{V(0.001)} \right] + \beta (\nu \sigma_{\text{tot}}^2) + \gamma, \quad (4)$$

where M is the molecular mass (g/molecule) and V(0.001) is the volume (cm³/molecule) defined as the space inside as contour of electron density of 0.001 electron/Bohr³. α , β and γ are regression coefficients. ν is the degree of balance between the positive and negative charges on the isosurface. σ_{tot}^2 is a measure of variability of the electrostatic potential on the surface.

Kamlet and Jacob equations [20] were used to estimate the performance of model compounds:

$$D = 1.01 \left(NM^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30\rho) \quad (5)$$

$$P = 1.558 NM^{1/2} Q^{1/2} \rho^2, \quad (6)$$

where D is the detonation velocity in km s⁻¹, P is the detonation pressure in GPa, N is the number moles of gaseous detonation products per gram of explosive, M is the average molecular weight of gaseous products, Q is the energy of explosion in cal g⁻¹ of explosive and ρ is the density in g/cm³.

The strength of bonding can be evaluated by the bond dissociation energy. The energy required for homolytic bond cleavage at 298.15 K and 1 atm corresponds to the enthalpy of reaction ($\Delta_f H_{298.15K}$), i.e., the bond dissociation enthalpy ($DH_{298.15K}$) of the molecule (A-B)



It is the reaction enthalpy of the bond homolysis ($\Delta_f H_{298.15K}$) and thus depends on the enthalpies formation of reactants and products.

$$\begin{aligned} \Delta_f H_{298.15K} &= \Delta_f H_{298.15K}(A\cdot) + \Delta_f H_{298.15K}(B\cdot) - \Delta_f H_{298.15K}(A - B), \\ &= DH_{298.15K}(A - B), \end{aligned} \quad (8)$$

where $\Delta_f H_{298.15K}(A\cdot)$ and $\Delta_f H_{298.15K}(B\cdot)$ are the enthalpies of formation of radicals and $\Delta_f H_{298.15K}(A - B)$ is the enthalpy of formation of the molecule.

However at 0 K the homolytic bond dissociation energy can be given as:

$$BDE_0(A - B) = E_0(A\cdot) + E_0(B\cdot) - E_0(A - B). \quad (9)$$

The bond dissociation energy with ZPE correction may be written as:

$$BDE(A - B)_{\text{ZPE}} = BDE_0(A - B) + \Delta ZPE, \quad (10)$$

where ZPE is the difference between the zero point energy of the products and reactants.

Furthermore, we also have approximated the stabilities of triazol-5-one-N-oxides from the frontier molecular orbitals [21]. The impact sensitivities of model compounds were predicted by the nitro group charge analysis [22].

Results and discussion

Optimized structures

We have optimized the structures of triazol-5-one-N-oxides at the DFT-B3LYP/aug-cc-pVDZ level and the molecular frameworks are presented in Fig. 1. All triazol-5-one-N-oxides belong to C_1 point group. The non-planarity or coplanarity of a molecule is due to the repulsion between the

neighboring nitro and nitroso groups, which rotate the oxygen atoms away from the molecular plane. Nitro or nitroso group form the molecular plane and the hydrogen atoms of amino group are either perpendicular or coplanar to the ring. The lowest frequency, total energy, zero-point energy, thermal correction to enthalpy and frontier molecular orbital energies and their gaps of triazol-5-one-N-oxides are summarized in Table 1. The lowest frequencies varying from 30 to 62 cm^{-1} are for the torsion angles of NO_2 groups [10–14]. The bond lengths and angles, total energies and frontier molecular orbital energies vary with the relative positions and the nature of substituent groups. The selected bond lengths and angles of the computed structures are shown in Table 2. Triazol-5-one-N-oxides have N-H...O interactions (2.324 to 2.875 Å) that are shorter than the sum of the van der Waals radii [23]. The discrepancies in the total and zero-point energies, thermal correction to enthalpy, frontier

Fig. 1 Molecular frameworks with the atomic numbering of triazol-5-one-N-oxides; with R- NO_2 linkages encircled; the list of values besides each structure shows the trigger length (in Å), nitro group charge (in e) and midpoint electrostatic potential

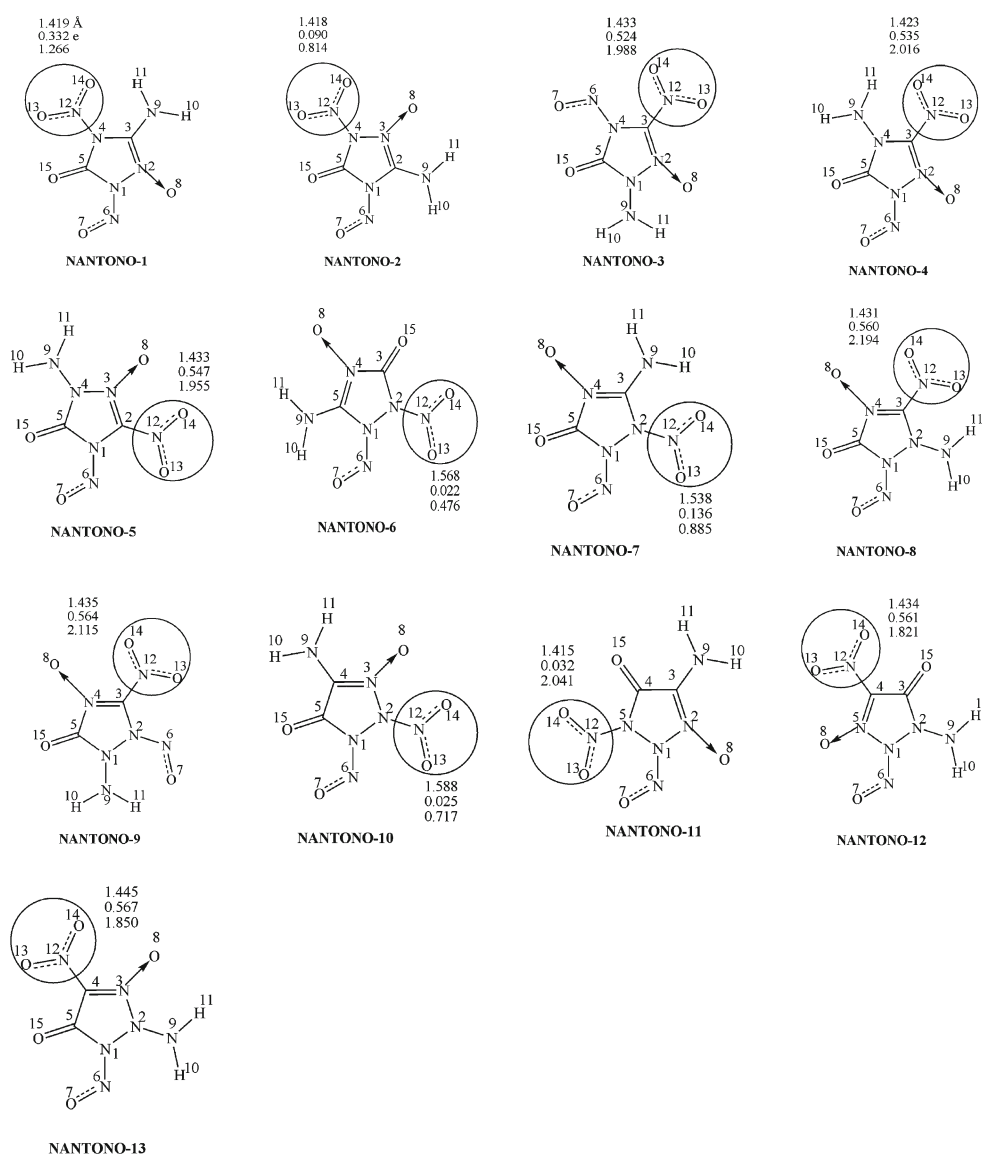


Table 1 Lowest frequencies (ω_L), electronic energies (E_0), zero-point vibrational energies (ZPVE), thermal correction to enthalpy (H_T) and frontier molecular orbital energies of triazol-5-one-N-oxides computed at the DFT-B3LYP/aug-cc-pVDZ level

HEM	ω_L (cm ⁻¹)	E_0 (a.u.)	ZPVE (kJ mol ⁻¹)	H_T (a.u.)	HOMO (a.u.)	LUMO (a.u.)	$\epsilon_{(LUMO-HOMO)}$ (a.u.)
NANTONO-1	32.8821	-781.849209	50.23836	0.092973	-0.22916	-0.15559	0.07357
NANTONO-2	45.8497	-781.854274	50.50903	0.092216	-0.24232	-0.14261	0.09971
NANTONO-3	61.7342	-781.8358986	50.65008	0.093768	-0.26818	-0.15379	0.11439
NANTONO-4	37.6447	-781.825952	50.65253	0.093792	-0.26127	-0.16561	0.09566
NANTONO-5	19.8821	-781.8361454	50.75996	0.092912	-0.28273	-0.14536	0.13737
NANTONO-6	53.7503	-781.854321	50.77684	0.093350	-0.24623	-0.14175	0.10448
NANTONO-7	54.0317	-781.8554016	50.294412	0.092912	-0.24036	-0.13674	0.10362
NANTONO-8	55.6424	-781.8149224	51.30227	0.094053	-0.28181	-0.17144	0.11037
NANTONO-9	39.4202	-781.8210174	50.61846	0.093798	-0.25578	-0.16962	0.08916
NANTONO-10	29.9878	-781.8323005	49.64561	0.092394	-0.25657	-0.13436	0.12221
NANTONO-11	24.3177	-781.8282916	49.88104	0.092783	-0.24884	-0.15842	0.09042
NANTONO-12	42.7656	-781.8079001	50.72616	0.093793	-0.28955	-0.17270	0.11685
NANTONO-13	47.9163	-781.810329	50.69365	0.093350	-0.29946	-0.15066	0.14880

molecular orbital energies, trigger (i.e., C-NO₂, N-NO₂ and N-NO), C-NH₂, N-NH₂, C=O and N→O lengths are presumably due to the relative positions of -NO, -NO₂ and -NH₂ groups in the triazole ring.

Theoretical crystal density

According to Kamlet-Jacob equations (Eqs. 5 and 6) density is considered to be one of the top priorities in the development of new explosives. Several research groups have attempted to predict the densities of explosive compounds with satisfactory accuracy [19, 24, 25]. We have taken the optimized structures computed from the B3LYP/aug-cc-pVDZ level to predict the crystal density using Materials Studio 4.1 with CVFF force field and Ewald summation method. The approach is based on the generation of possible packing arrangements in all reasonable space groups to search for the low lying minima in the lattice energy surface. Many organic compounds are known to pack in C2/c, P2₁, P2₁/c, P2₁2₁2₁, P₋₁, Pbc_a, Pbc_n, Pna2₁, C_C and/or C₂ space groups [26]. The high density polymorph is sorted out from the large number of potential crystal structures and the lattice parameters of model compounds are presented in Table 3. In addition, we carefully compared the densities predicted from CFFF force field and from the volume inside an electron density contour of 0.001 e/Bohr³. The densities of triazol-5-one-N-oxides using Eq. (4) are lower varying from 2.103 to 2.177 g/cm³. The calculated values are higher compared with those of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) (2.040 g/cm³) [27] and octanitrocubane (ONC) (1.979 g/cm³) [28]. NANTONO-2, NANTONO-3, NANTONO-4 and NANTONO-9 have higher ρ values of 2.175, 2.177 and 2.171 g/cm³ respectively. However, NANTONO-1, NANTONO-10, NANTONO-11,

NANTONO-12 and NANTONO-13 have lower ρ values of 2.103, 2.143, 2.144 and 2.142 g/cm³ respectively. Nevertheless, the absolute error in the calculated crystal densities according to ref. [19] are expected to be reliable to estimate the detonation properties.

Heat of explosion

The determination of the products of explosion is a key issue. Higher is the value of heat of explosion for an explosive compound, more is the heat generated when an explosion occurs. Kim et al. [25] reported that a difference of 10 kcal mol⁻¹ in the heat of formation had little influence on the performance. For assessment of the potential performance of the energetic materials of interest, the condensed phase heat of formation is the desired quantity. The condensed phase heat of formation was determined from the gas phase heat of formation and the heat of sublimation according to Hess's law. The calculated heats of explosion and detonation velocity and pressure of triazol-5-one-N-oxides are summarized in Table 4. The Q values of NANTONO (1.442 to 1.553 kcal g⁻¹) are higher compared with those of CL-20 (1.342 kcal g⁻¹) and ONC (1.337 kcal g⁻¹). NANTONO-11, NANTONO-12 and NANTONO-13 have Q values of 1.553, 1.535 and 1.524 kcal g⁻¹ respectively. The amino (-NH₂) group increases the heats of explosion markedly compared with the nitro (-NO₂) group however, striking is the effect of the nitroso (-NO) group in increasing the Q values. It is to note that 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 [29]. Also, the total amount of energy liberated depends

Table 2 Predicted crystal characteristics of triazol-5-one-N-oxides

NANTONO-1	NANTONO-2	NANTONO-3	NANTONO-4	NANTONO-5	NANTONO-6	NANTONO-7
N1-N2	1.406	1.399	1.388	1.426	1.397	1.391
N2-C3	1.324	1.322	1.341	N2-C3	N2-C3	N2-C3
C3-N4	1.401	1.435	1.448	C3-N4	C3-N4	C3-N4
N4-C5	1.403	1.440	1.388	N4-C5	N4-C5	N4-C5
C5-N1	1.405	1.425	1.418	C5-N1	C5-N1	C5-N1
N1-N6	1.645	1.386	1.497	N1-N6	N1-N6	N1-N6
N6-O7	1.142	1.211	1.176	N6-O7	N6-O7	N6-O7
N2-O8	1.280	1.270	1.220	N2-O8	N2-O8	N2-O8
C3-N9	1.351	1.347	1.357	N4-N9	N4-N9	C3-N9
N9-H10	1.016	1.009	1.017	N9-H10	N9-H10	N9-H10
N9-H11	1.012	1.013	1.015	N9-H11	N9-H11	N9-H11
N4-N12	1.419	1.418	1.433	C3-N12	C2-N12	N2-N12
N12-O13	1.228	1.198	1.231	N12-O13	N12-O13	N12-O13
N12-O14	1.208	1.202	1.226	N12-O14	N12-O14	N12-O14
C5-O15	1.197	1.193	1.205	C5-O15	C5-O15	C5-O15
N1-N2-C3	111.3	108.9	110.2	N1-N2-C3	110.2	105.6
N2-C3-N4	108.0	109.7	105.8	N2-C3-N4	105.8	105.2
C3-N4-C5	108.1	106.7	110.0	C3-N4-C5	109.0	109.8
N4-C5-N1	104.6	104.4	104.2	N4-C5-N1	104.2	109.5
C5-N1-N2	107.7	109.5	109.3	C5-N1-N2	109.3	109.7
H10-N9-H11	118.1	120.2	112.0	H10-N9-H11	112.0	123.6
O13-N12-O14	128.0	131.7	126.7	O13-N12-O14	126.4	131.5
						105.7
						111.0
						109.3
						104.2
						109.3
						121.5
						130.0

NANTONO-8	NANTONO-9	NANTONO-10	NANTONO-11	NANTONO-12	NANTONO-13
N1-N2	1.410	1.371	1.392	N1-N2	N1-N2
N2-C3	1.406	1.385	1444	N2-C3	N2-C3
C3-N4	1.335	1.345	1.323	C3-N4	C3-C4
N4-C5	1.508	1.490	1.459	N4-C5	C4-C5
C5-N1	1.390	1.398	1.439	C5-N1	N5-N1
N1-N6	1.403	1.566	1.477	N1-N6	N1-N6
N6-O7	1.196	1.138	1.178	N6-O7	N6-O7
N4-O8	1.239	1.247	1.225	N2-O8	N5-O8
N2-N9	1.472	1.391	1.347	C3-N9	N2-N9
N9-H10	1.022	1.020	1.009	N9-H10	N9-H10
N9-H11	1.024	1.018	1.012	N9-H11	N9-H11
C3-N12	1.431	1.435	1.588	C5-N12	C4-N12
N12-O13	1.239	1.233	1.192	N12-O13	N12-O13
N12-O14	1.221	1.225	1.200	N12-O14	N12-O14
C5-O15	1.186	1.199	1.207	C4-O15	C3-O15
N1-N2-C3	102.8	103.3	104.4	N1-N2-C3	111.5
N2-C3-N4	113.7	113.5	111.4	N2-C3-N4	102.8
C3-N4-C5	107.0	105.5	109.4	C3-N4-C5	109.2
N4-C5-N1	102.5	102.7	103.5	N4-C5-N1	110.0
C5-N1-N2	113.9	114.3	111.1	C5-N1-N2	105.6
H10-N9-H11	104.5	108.5	119.3	H10-N9-H11	107.9
O13-N12-O14	126.2	126.6	132.3	O13-N12-O14	126.4
					103.6
					111.4
					111.5
					127.0

Table 3 Explosive properties, bond dissociation energies, nitro group charges and mid-point electrostatic potentials of triazol-5-one-N-oxides computed from the B3LYP/aug-cc-pVDZ level

HEM	E_L (kJ mol ⁻¹)	Point group	Crystal system	a, b, c (Å) α, β, γ (degree)	ρ (g cm ⁻³)	^a ρ (g cm ⁻³)
NANTONO-1	-327.8224195	P2 ₁ 2 ₁ 2 ₁	rhombic	$a=9.530, b=5.441, c=9.422$ $\alpha=\gamma=\beta=90$	2.194	2.103
NANTONO-2	-478.5605897	P2 ₁ /C	monoclinic	$a=5.55, b=10.22, c=11.27$ $\alpha=\gamma=90, \beta=51.96$	2.233	2.175
NANTONO-3	-478.5615997	P2 ₁ /C	monoclinic	$a=6.31, b=9.42, c=12.68$ $\alpha=\gamma=90, \beta=52.9$	2.230	2.177
NANTONO-4	-495.1998005	P2 ₁ 2 ₁ 2 ₁	rhombic	$a=8.84, b=5.72, c=11.17$ $\alpha=\gamma=\beta=90$	2.233	2.172
NANTONO-5	-494.9929044	Pbca	rhombic	$a=10.62, b=11.10, c=9.62$ $\alpha=\gamma=\beta=90$	2.231	2.168
NANTONO-6	-455.9748262	Pna2 ₁	rhombic	$a=10.22, b=9.24, c=6.06$ $\alpha=\gamma=\beta=90$	2.204	2.162
NANTONO-7	-404.4732616	Pbca	rhombic	$a=17.08, b=6.57, c=10.23$ $\alpha=\gamma=\beta=90$	2.221	2.175
NANTONO-8	-503.5340558	P2 ₁ /C	monoclinic	$a=10.98, b=5.93, c=9.76$ $\alpha=\gamma=90, \beta=127.18$	2.251	2.163
NANTONO-9	-503.544667	P2 ₁ /C	monoclinic	$a=10.97, b=9.87, c=13.16$ $\alpha=\gamma=90, \beta=152.82$	2.252	2.171
NANTONO-10	-425.0858785	P2 ₁ 2 ₁ 2 ₁	rhombic	$a=6.30, b=9.77, c=9.35$ $\alpha=\gamma=\beta=90$	2.198	2.143
NANTONO-11	-425.1748764	P2 ₁ 2 ₁ 2 ₁	rhombic	$a=6.32, b=9.75, c=9.33$ $\alpha=\gamma=\beta=90$	2.197	2.144
NANTONO-12	-202.1934453	P2 ₁ /C	monoclinic	$a=12.32, b=5.42, c=11.32$ $\alpha=\gamma=90, \beta=131$	2.188	2.142
NANTONO-13	-202.1926325	P2 ₁ /C	monoclinic	$a=12.13, b=5.54, c=11.27$ $\alpha=\gamma=90, \beta=130.5$	2.187	2.146

^a Values were obtained using Eq. (4)

upon the relative proportions of the reactants to the products. The Q values are related to the nature of triazol-5-one-N-oxides and the relative positions of substituent groups and the strength of trigger linkages.

Table 4 Calculated heats of explosion and detonation velocity and pressure of triazol-5-one-N-oxides

HEM	Q (kcal g ⁻¹)	ρ (g cm ⁻³)	D (km s ⁻¹)	P (GPa)	R-NO ₂ (kcal mol ⁻¹)	N-NO (kcal mol ⁻¹)	-Q _{NO₂} (e)	V _{mid}
NANTONO-1	1.442	2.103	9.87	48.95	6.445	12.053	0.322	1.266
NANTONO-2	1.438	2.175	10.11	50.31	8.751	2.231	0.090	0.814
NANTONO-3	1.442	2.177	10.02	50.25	2.933	42.607	0.524	1.988
NANTONO-4	1.446	2.172	10.08	50.00	2.223	36.661	0.535	2.016
NANTONO-5	1.441	2.168	10.10	50.26	34.581	42.386	0.547	1.955
NANTONO-6	1.445	2.162	10.11	50.91	5.134	7.118	0.022	0.476
NANTONO-7	1.443	2.175	10.07	50.61	9.506	6.026	0.136	0.885
NANTONO-8	1.512	2.163	10.06	50.53	5.042	34.371	0.560	2.194
NANTONO-9	1.502	2.171	10.05	50.22	8.708	42.101	0.564	2.115
NANTONO-10	1.551	2.143	10.14	50.05	5.925	0.331	0.025	0.717
NANTONO-11	1.553	2.144	10.13	50.05	9.751	2.253	0.322	2.041
NANTONO-12	1.535	2.142	10.02	50.77	0.618	14.971	0.561	1.821
NANTONO-13	1.524	2.146	10.0	50.57	5.328	13.514	0.567	1.850

^a Values obtained from Eq. (4) were used for the estimation of performance

Detonation velocity and detonation pressure

Two key measures of performance are the detonation velocity and the detonation pressure refers to the stable velocity of the shock front that characterizes detonation and the stable pressure that is developed behind the front respectively [1]. Kamlet and Jacob indicated the importance of the density as a determinant of detonation velocity and detonation pressure. It appears to a higher power in each equation (Eqs. 5 and 6) than do any of the other quantities. However one or more of the other factors do sometimes override the effects of the density. Detonation velocity (D) linearly increases with ρ for most of explosives while detonation pressure (P) increases with the square of ρ , when ρ is greater than one. The detonation properties of NANTONO (D 9.87 to 10.11 km s⁻¹, P 48.95 to 50.91 GPa) are higher compared with those of CL-20 (D 9.20 km s⁻¹, P 42.0 GPa) [27] and ONC (D 9.90 km s⁻¹, P 48.45 GPa) [28]. Detonation energy and detonation velocity and pressure of triazol-5-one-N-oxides are summarized in Table 4. The higher performance properties of triazol-5-one-N-oxides are presumably due to their higher densities. Also, the detonation properties are related to the number, the relative positions of substituent groups and the strength of trigger bonds.

Frontier molecular orbital energies

The highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) play a key role in governing the chemical reactions. The band gap between the frontier molecular orbital energies is an important stability index of the molecules [21, 30–33]. A large band gap implies high stability and small band gap implies low stability in turn high stability indicates low chemical reactivity and low stability indicates high reactivity. The molecule with large band gap that is if $\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}} \gg 0$, then very little electron transfer occurs. If the respective orbital energies are quite similar that is if $\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}} \approx 0$, strong electron transfer occurs. The electron withdrawing groups lowers the LUMO and HOMO energy levels while electron donating groups increases the LUMO and HOMO energy levels. The band gap of NANTONO-15 is the largest (0.1488 a.u.) and NANTONO-1 is the smallest (0.07357 a.u.). NANTONO-1, NANTONO-2, NANTONO-4, NANTONO-9, NANTONO-11 have lower band gap values of 0.07357, 0.09971, 0.09566, 0.08916 and 0.09042 a.u. respectively (i.e., highly unstable compounds). In general, R-NO_x (where R=C or N, x=1 or 2) bonds are the trigger sites and resonance in the triazol-5-one-N-oxides moiety strengthens these bonds thereby the molecules become stabilized. The larger the trigger length of the molecule, the easier the dissociation or breakdown and thus the molecule become less stable. Furthermore, the band gap is highly correlative with the Hess-Schaad resonance energy per

π -electron, a measure of thermodynamic stability due to the cyclic conjugation [30]. This correlation indicates that thermodynamically stable compounds are also kinetically stable and hence for a molecule to be isolated, it must be not only thermodynamically but also kinetically stable. Nevertheless, the $\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}}$ gap to predict the stability of compounds is very speculative and unreliable.

Bond dissociation energies

Studies of bond dissociation energies (BDE) provide useful information for understanding the stability of triazolones. The stability/or sensitivity of compound depends on temperature, nature of materials and explosives in the molecular structure. A systematic study of this quantity should be useful in understanding initiation events. The initial stages in the decompositions of energetic materials can be assumed on the basis of the BDEs. In general, the larger the BDE value of the R-NO_x (where, R=C, N, or O and x=1 or 2) bond breaking, the higher the stability will be. Thus, the calculated BDE for removal of the NO₂ or NO group can be used to index the relative strength of the compounds. Conversely this is only applied to the molecules in which the R-NO_x bond is the weakest. The nitro/or nitroso group often represents the primary cause of initiation reactivity of nitroarenes. Therefore, we have computed these R-NO_x bonds at the UB3LYP/aug-cc-pVDZ level. Compared with the BDE values of TNT (60 kcal mol⁻¹), RDX (39.2 kcal mol⁻¹) and TATB (73.05 kcal mol⁻¹) all of the designed compounds have lower BDE values (0.688 to 34.581 kcal mol⁻¹ for C-NO₂, 2.933 to 9.751 kcal mol⁻¹ for C-NO, and 0.331 to 42.607 kcal mol⁻¹ for N-NO) [34]. The calculated BDE values reveal that the position of amino, nitro and nitroso groups in the structure has strong influences on the BDE value. It is worthy of note that the adjacent groups or closer the distance between R-NO_x groups, BDE is less for the pyrolysis (i.e., changing theazole ring has shown significant variation in the BDEs). The compound could be considered as a practical energetic material if it has BDEs more than ~20.07 kcal mol⁻¹ [1]. However, this is only marginally sufficient to make the compound metastable and it would have preferable stability if BDE > 30.11 kcal mol⁻¹. Also, it can be deduced that the designed compounds have no sufficient energy barrier against the removal of NO_x group and thus are not stable enough for practical use.

Nitro group charge analysis

The impact sensitivity is usually measured by the height from where a given weight falling upon the explosive gives 50 % probability of initiating detonation. We have predicted the impact sensitivity of triazol-5-one-N-oxides from the electronic structures by the Mulliken atomic charge analysis of nitro group. In explosives, R-NO₂ bonds (R=C or N) are

usually weakest and their breaking is often the initial step in the decomposition or detonation of explosive molecule. The nitro group charge ($-Q_{\text{NO}_2}$) is calculated by the sum of the net Mulliken atomic charges on the nitrogen and oxygen atoms and of the nitro group:

$$-Q_{\text{NO}_2} = Q_{\text{N}} + Q_{\text{O}_1} + Q_{\text{O}_2} \quad (11)$$

$$V_{\text{mid}} = \frac{Q_{\text{C}}}{0.5R} + \frac{Q_{\text{N}}}{0.5R}, \quad (12)$$

where R is trigger length, Q_{C} , Q_{N} and Q_{O_1} , Q_{O_2} and are the Mulliken charges on carbon, nitrogen and oxygen atoms respectively.

The molecular structures of triazol-5-one-N-oxides with the $R\text{-NO}_2$ bond encircled; the list of the values beside each structure shows the $R\text{-NO}_2$ lengths, nitro group charges and midpoint electrostatic potentials are presented in Fig. 1. The computed nitro group charge ($-Q_{\text{NO}_2}$), midpoint electrostatic potential (V_{mid}) along with their explosive properties of triazol-5-one-N-oxides are presented in Table 4. The higher $-Q_{\text{NO}_2}$, the higher the impact insensitivity. The calculated $-Q_{\text{NO}_2}$ values of triazol-5-one-N-oxides vary from 0.025 to 0.567 e. As per the predicted by Zhang et al. [22], the calculated $-Q_{\text{NO}_2}$ values of several triazol-5-one-N-oxides are found to be higher with respect to ONC (0.146 e) and thus appear to be more insensitive. However the calculated $-Q_{\text{NO}_2}$ values of NANTONO-2 (0.090 e), NANTONO-6 (0.022 e), NANTONO-7 (0.136 e) and NANTONO-10 (0.025 e) are lower compared with those of RDX (0.105 e), HMX (0.112 e) and TNAZ (0.114 e), ONC (0.146 e) and CL-20 (0.081 e). The $-Q_{\text{NO}_2}$ values of NANTONO-3 (0.524 e), NANTONO-4 (0.535 e), NANTONO-5 (0.547 e), NANTONO-8 (0.560 e), NANTONO-9 (0.564 e), NANTONO-12 (0.561 e) and NANTONO-13 (0.567 e) are superior to TNT (0.249 e), TATB (0.416 e), FOX-7 (0.365 e), LLM-105 (0.264 e) and NTO (0.264 e). However, NANTONO-2 (0.090 e), NANTONO-6 (0.022 e), NANTONO-7 (0.136 e) and NANTONO-10 (0.025 e) are less insensitive than the other isomers. The similar trend has also been observed for the midpoint electrostatic potentials (V_{mid}) of model molecules. The V_{mid} values of NANTONO-3 (1.988), NANTONO-4 (2.016), NANTONO-5 (1.955), NANTONO-8 (2.194), NANTONO-9 (2.115), NANTONO-12 (1.821) and NANTONO-13 (1.85) are superior with those of TNT (0.251), TATB (0.416), FOX-7 (0.365), LLM-105 (0.264) and NTO (0.264). The substitution of secondary amino hydrogen of triazol-5-one-N-oxides by the amino ($-\text{NH}_2$) group shows better impact sensitivity. The impact sensitivity can also be used to show the stability of model compounds and here the stability is attributed to the presence of π -

excessive aromatic heterocyclic ring, delocalization of π -electrons and presence of intramolecular $\text{N-H}\cdots\text{O}$ interactions.

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 triazol-5-one-N-oxides. Our computational results indicate that NANTONO corresponds to energy minima and accordingly should be able to exist. Detonation properties were evaluated by the Kamlet-Jacob equations based on the predicted density and the calculated heat of chemical energy. All model compounds have higher Q values varying from 1.438 to 1.553 kcal g^{-1} and the discrepancy is due to the relative position of the N-atom in the triazol-5-one-N-oxides ring and position of the nitro or nitroso group. Several triazol-5-one-N-oxides have densities varying from 2.134 to 2.252 g/cm^3 which are higher compared with CL-20 (2.040 g/cm^3) and ONC (1.979 g/cm^3). The detonation properties of NANTONO (D 9.87 to 10.11 km s^{-1} , P 48.95 to 50.61 GPa) are higher compared with those of CL-20 (D 9.20 km s^{-1} , P 42.0 GPa) and ONC (D 9.90 km s^{-1} , P 48.45 GPa). NANTONO-3, NANTONO-4, NANTONO-5, NANTONO-8, NANTONO-9, NANTONO-12 and NANTONO-13 are insensitive compared with those of TNT, TATB, FOX-7, LLM-105 and NTO. The substitution of secondary amino hydrogen of triazol-5-one-N-oxides by amino group shows better impact sensitivity. The HOMO-LUMO gaps and the Mulliken atomic charges to predict sensitivity are very speculative and unreliable and thus several of the designed compounds seem to be highly sensitive.

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