

# Theoretical investigations on the structure, density, thermodynamic and performance properties of amino-, methyl-, nitroso- and nitrotriazolones

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Received: 23 May 2012 / Accepted: 20 June 2012 / Published online: 10 July 2012  
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**Abstract** We have studied herein the effect of position and the number of -NO, -NO<sub>2</sub>, -NH<sub>2</sub> and -CH<sub>3</sub> groups on the structure, stability, impact sensitivity, density, thermodynamic and detonation properties of triazolones by performing density functional theory calculations at the B3LYP/aug-cc-pVDZ level. The optimized structures, vibrational frequencies and thermodynamic values for triazolones have been obtained in their ground state. Kamlet-Jacob equations were used to calculate the detonation velocity and detonation pressure of model compounds. The detonation properties of NNTO (*D* 8.75 to 9.10 km/s, *P* 34.0 to 37.57 GPa), DNTO (*D* 8.80 to 9.05 km/s, *P* 35.55 to 38.27 GPa), ADNTO (*D* 9.01 to 9.42 km/s and *P* 37.81 to 41.10 GPa) and ANNTO (*D* 8.58 to 9.0 km/s, *P* 30.81 to 36.25 GPa) are compared with those of 1,3,5-trinitro-1,3,5-triazine (RDX) (*D* 8.75 km/s, *P* 34.70 GPa) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (*D* 8.96 km/s, *P* 35.96 GPa). The designed compounds satisfy the criteria of high energy materials.

**Keywords** Density · Detonation pressure · Detonation velocity · DFT method · Stability · Triazolones

## Introduction

Nitrotriazoles have recently drawn renewed attention from explosives chemists due to their high performance, high thermal stability and remarkably low detonation sensitivity

to impact, friction and spark [1]. One of these identified candidates is 3-nitro-1,2,4-triazol-5-one (NTO), a well known insensitive thermally stable explosive [2–5]. The unique insensitivity of NTO is attributed to the high degree of hydrogen bonding carbonyl and nitro 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) [6], however, the first report on the explosive nature of NTO was published by Lee and Coburn in 1985 [7]. In the past few decades, researchers have been evaluating NTO based explosive formulations to replace highly sensitive explosives such as 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) [8]. Several amine and metal salts of NTO have been synthesized for use in gun propellants or as primary explosives [9–17]. There have been computational studies on the constitutional isomers or tautomers of NTO [18–25]. Türker et al. [24, 25] studied the structure and explosive properties of isomers of NTO and its picryl derivatives.

The heat of explosion, detonation velocity, detonation pressure, explosion temperature and volume of released gases are the important criteria for explosives. To calculate the detonation velocity and detonation pressure we require thermodynamic values such as the heat of explosion, from which detonation temperature can be obtained. It is true that the performance of explosives is increased by increasing the density, oxygen balance and/or heat of formation of the material. It is known that introduction of amino (-NH<sub>2</sub>) groups into nitroarene molecules decreases the sensitivity of the product relative to the unaminated starting materials [1]. Nitroso (-NO) and nitro (-NO<sub>2</sub>) groups increases the heat of formation and density of azoles. Also, substituting one of the N-H hydrogen atoms of azoles for a methyl (-CH<sub>3</sub>) group decreases melting point and heat of formation, however, increases the stability and lowers the density [1]. To our knowledge, there were no such reports on how these

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substituent groups affect the geometric and electronic structures, stability/or sensitivity, thermodynamic and detonation properties of triazolones (TO). Accordingly, one of our objectives was to determine whether they can be expected to exist. It would be useful to be able to predict their detonation energies, densities, detonation performances and stabilities/or sensitivities. In the present study, density functional theory (DFT) calculations at the B3LYP/aug-cc-pVDZ level have been performed to study the geometric features, electronic structures, thermodynamic properties and detonation performances of different isomers of substituted triazolones for explosives applications. In addition, our objective is to address relative roles of the number of moles gaseous detonation products, average molecular mass of detonation products, heat release, density and detonation velocity and detonation pressure of triazolones.

### Methods and computational detail

All the calculations were performed on the desktop Pentium computer using the Gaussian 03 package [26]. The geometry optimizations of all the structures leading to energy minima were achieved within the framework of density functional theory (DFT, B3LYP) [27, 28] at the aug-cc-pVDZ level. The exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density exchange with Beck's gradient correlation to local spin density exchange [29]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [30] and Lee, Yang, Parr (LYP) correlation functional [31]. 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 3 N-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 the correction terms were estimated by the following set of equations [32].

$$[H(T) - H(0)]_{trans} = \frac{5}{2}RT \quad (1)$$

$$[H(T) - H(0)]_{rot} = \frac{3}{2}RT \quad (2)$$

$$[H(T) - H(0)]_{vib} = RT \sum_{i=1}^f \left( \frac{hv_i}{KT} \right) \frac{\exp^{-\frac{hv_i}{KT}}}{(1 - \exp^{-\frac{hv_i}{KT}})} \quad (3)$$

The heats of explosion ( $Q$ ) have been 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.

$$Q = \Delta E_{298.15K} + \Delta(PV) \\ = \Delta E_0 + \Delta ZPE + \Delta_T H + \Delta nRT, \quad (4)$$

where  $\Delta E_0$  is the change in total energy between the products and reactants at 0 K;  $\Delta ZPE$  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 to  $\Delta nRT$ .  $\Delta n=0$  for an ideal gases.

The optimized structures were used to determine the densities of nitrotriazolones using Materials Studio 4.1 package with CVFF force field and Ewald summation method [33]. Kamlet and Jacob semi-empirical equations [34] were used to determine the detonation performance:

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

$$P = 15.58 NM^{1/2} Q^{1/2} \rho^2, \quad (6)$$

where D is the detonation velocity in km/s, P is the detonation pressure in GPa, N is the number of 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 kcal/g of explosive and  $\rho$  is the density in g/cm<sup>3</sup>.

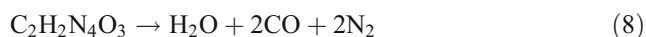
Oxygen balance can be defined as the amount of oxygen liberated as a result of the complete conversion of the explosive with the general formula  $C_a H_b N_c O_d$  to carbon monoxide, carbon dioxide, water and so on. In other words, oxygen balance (OB%) represents the lack or excess of oxygen required to produce H<sub>2</sub>O, CO and CO<sub>2</sub>.

$$OB\% = \frac{[d - 2a - \frac{b}{2}] \times 1600}{Mw}, \quad (7)$$

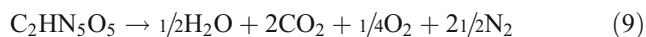
where Mw is the molecular weight of explosive. It is related to Q, D and P and sensitivity. Generally, Q value reaches maximum for pyrazoles containing three NO<sub>2</sub> groups corresponds to the oxidation of carbon to more CO<sub>2</sub> and less CO and hydrogen to H<sub>2</sub>O. Based on the composition of explosive, the main components of gaseous products may include CO, CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O with lesser quantities of other molecules and radicals such as H<sub>2</sub>, NO, H, O, CHO and N<sub>2</sub>O. The

possible detonation products of designed compounds have been written based on the modified Kistiakowsky-Wilson rules [35].

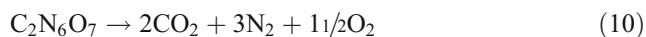
Nitrotriazolones (NTO):



Dinitrotriazolones (DNTO):



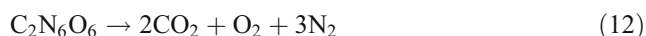
Trinitrotriazolones (TNTO):



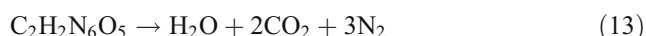
Nitrosonitrotriazolones (NNTO):



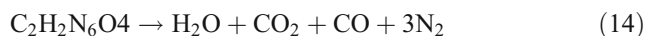
Nitrosodinitrotriazolones (NDNTO):



Aminodinitrotriazolones (ADNTO):



Aminonitrosonitrotriazolones (ANNTO):



Methyldinitrotriazolones (MDNTO):



We also have approximated the impact sensitivities (h50%) of the model compounds from the electronic structures using a Mulliken atomic charge analysis of the nitro (NO<sub>2</sub>) groups [36–40]. The stability has been determined from the frontier molecular orbital energies and their gaps [41, 42].

## Results and discussion

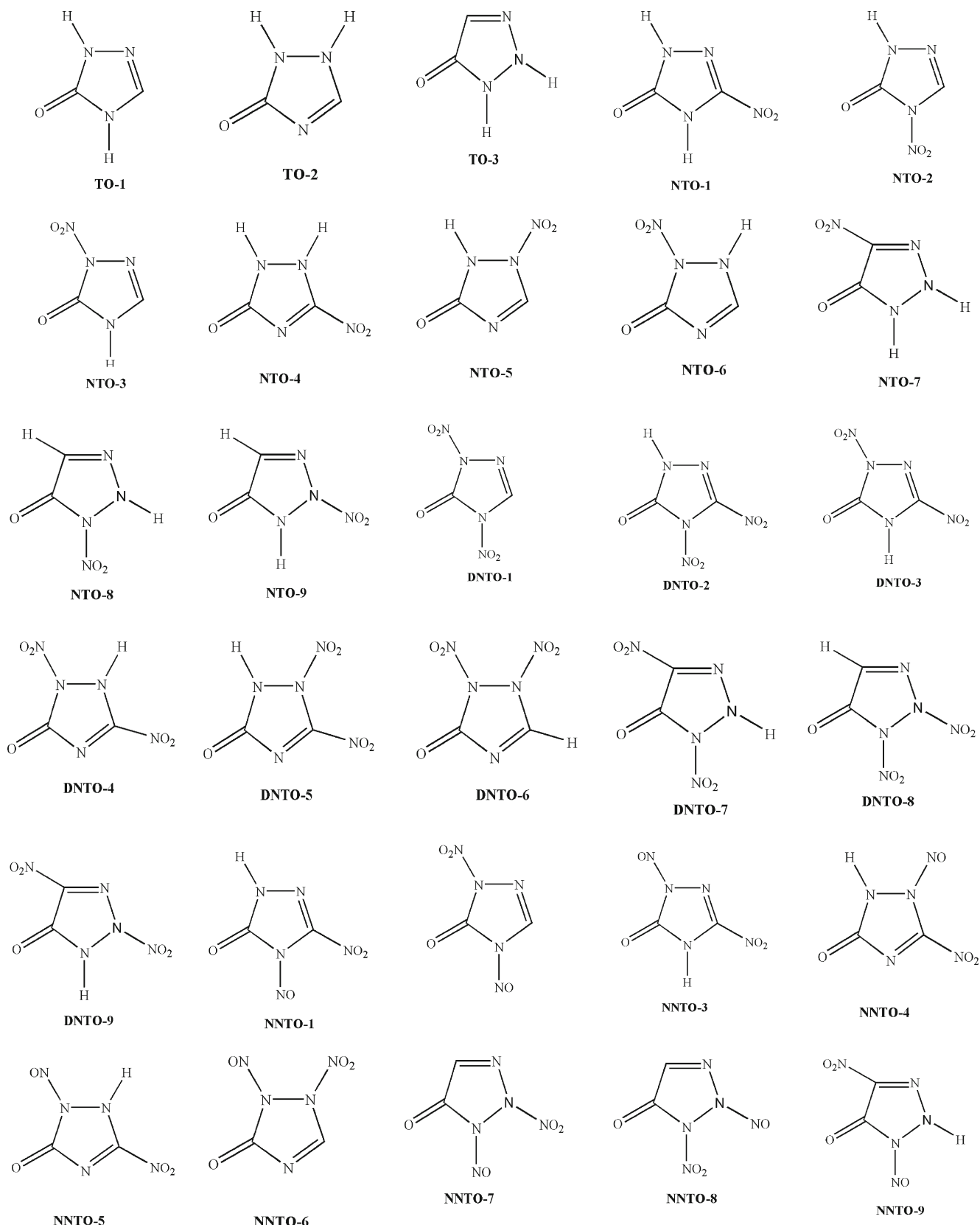
### Optimized structures

The molecular frameworks of model compounds computed from the B3LYP/aug-cc-pVDZ level are presented in Fig. 1. No imaginary vibration frequencies were found confirming that these structures correspond to true energy minima. All the model compounds belong to C<sub>1</sub> point group. The non-planarity or co-planarity of a molecule is due to the repulsion between the neighboring nitro/or nitroso groups, which rotate the oxygen atoms away from the molecular plane. Two nitro (or nitroso) groups and one of the hydrogen atoms of methyl or amino group form the molecular plane and the oxygen atoms of other nitro 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 triazolones are summarized in Table 1. The lowest frequencies varying from 24.18 to 84.50 cm<sup>-1</sup> are for the torsions of NO<sub>2</sub> groups [43, 44]. The bond lengths, bond angles, total energies and frontier molecular orbital energies vary with the relative positions and the nature of substituent groups. The C-NO<sub>2</sub> lengths of the optimized structures of C-nitrotriazolones (NTO) indicate that C-NO<sub>2</sub> bond is longer in NTO-4 (1.482 Å), NTO-7 (1.452 Å) and NTO-1 (1.447 Å). In all N-NO<sub>2</sub> containing compounds, N-NO<sub>2</sub> lengths vary from 1.413 to 1.674 Å. The N-NO<sub>2</sub> length is longer in NTO-9 (1.495 Å), however, N-NO<sub>2</sub> length is shorter in NTO-2 (1.413 Å), NTO-3 (1.424 Å) and NTO-8 (1.428 Å) among all N-nitrotriazolones. DNTO-5, DNTO-7, TNTO-1, TNTO-2, TNTO-3, NNTO-7, NDNTO-4, NDNTO-6, ADNTO-7, ANNTO-11, MDNTO-7 and MDNTO-9 have N-NO<sub>2</sub> distances 1.572, 1.557, 1.476, 1.545, 1.586, 1.543, 1.673, 1.644, 1.561, 1.552, 1.572 and 1.537 Å respectively. The C3-NO<sub>2</sub> length is longer in DNTO-2 (1.461 Å) and DNTO-3 (1.457 Å). Methyl-, amino- and nitrotriazolones have C...O (2.760 to 3.031 Å), N-H...O (2.720 to 2.990 Å) and N...O (2.686 to 2.953 Å) interactions respectively that are shorter than sum of the vander Waals radii [45–47]. The discrepancies in the total and zero-point energies, thermal correction to enthalpy, frontier molecular orbital energies, trigger lengths and C5-O lengths are presumably due to the relative positions of -NO, -NO<sub>2</sub>, -NH<sub>2</sub> and -CH<sub>3</sub> groups in the triazole ring.

### Theoretical density

Density ( $\rho$ ) continues to be one of the top priorities in the development of new energetic materials. Several researchers have attempted to predict the densities with satisfactory accuracy [48–50]. We have taken the optimized structures computed from the B3LYP/aug-cc-pVDZ level to predict the densities using Materials Studio 4.1 with CVFF force field and 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<sub>1</sub>, P2<sub>1</sub>/c, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, P-1, Pbc<sub>a</sub>, Pbc<sub>n</sub>, Pna2<sub>1</sub>, C<sub>c</sub> and/or C<sub>2</sub> space groups [51, 52]. The crystal characteristics of model compounds are summarized in Table 2. NNTO, ANNTO and MDNTO have densities varying from 1.802 to 1.878 g/cm<sup>3</sup> comparable with RDX. Similarly, the densities of DNTO and ADNTO have densities varying from 1.900 to 1.964 g/cm<sup>3</sup> comparable with HMX and CL-20. TNTO, NDNTO-1, NDNTO-3, NDNTO-4 and NDNTO-6 have higher densities (2.054 to 2.301 g/cm<sup>3</sup>). The substitution of amino hydrogen of triazolones by -CH<sub>3</sub> group substantially decreases the density



**Fig. 1** Molecular frame works of triazolones

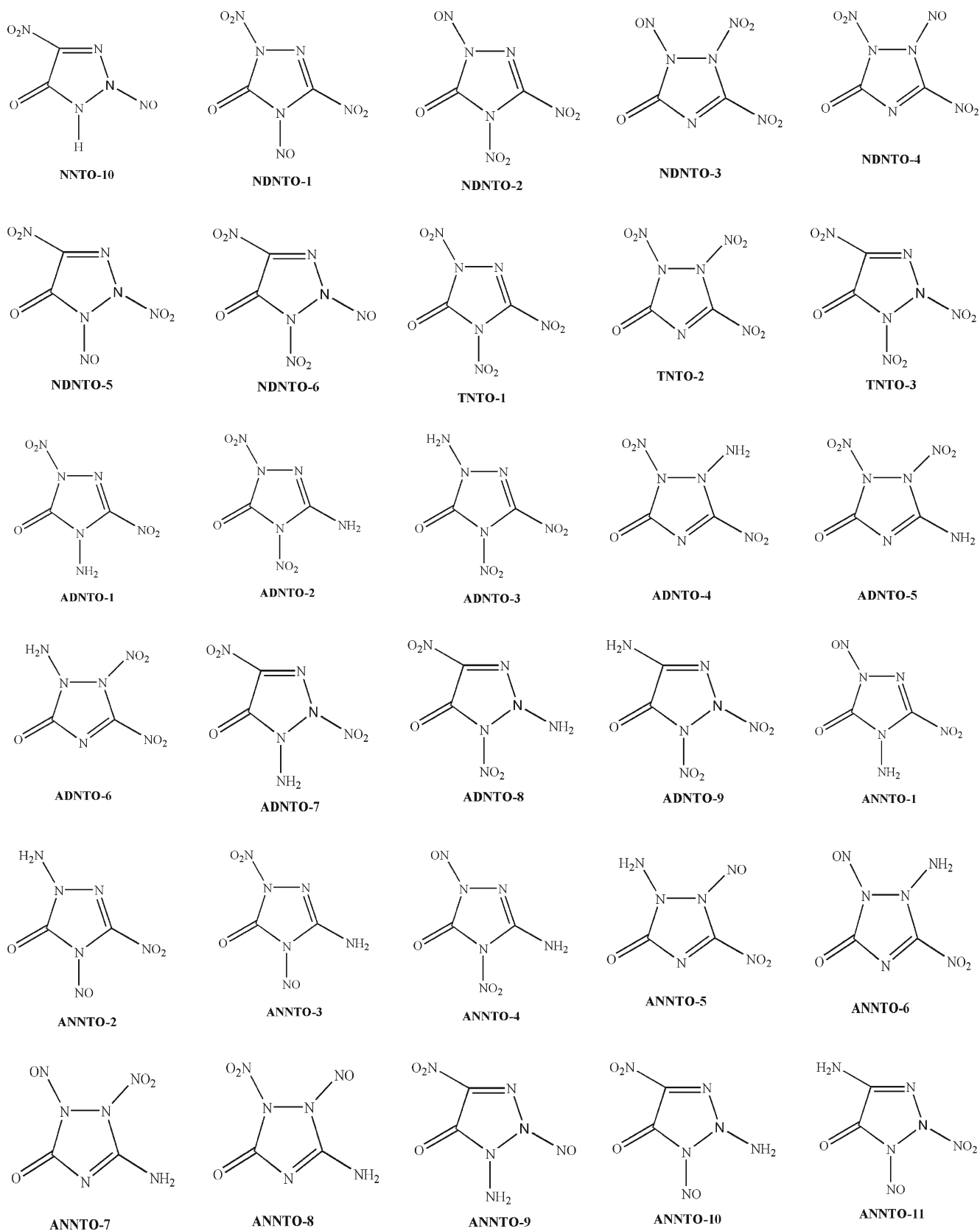
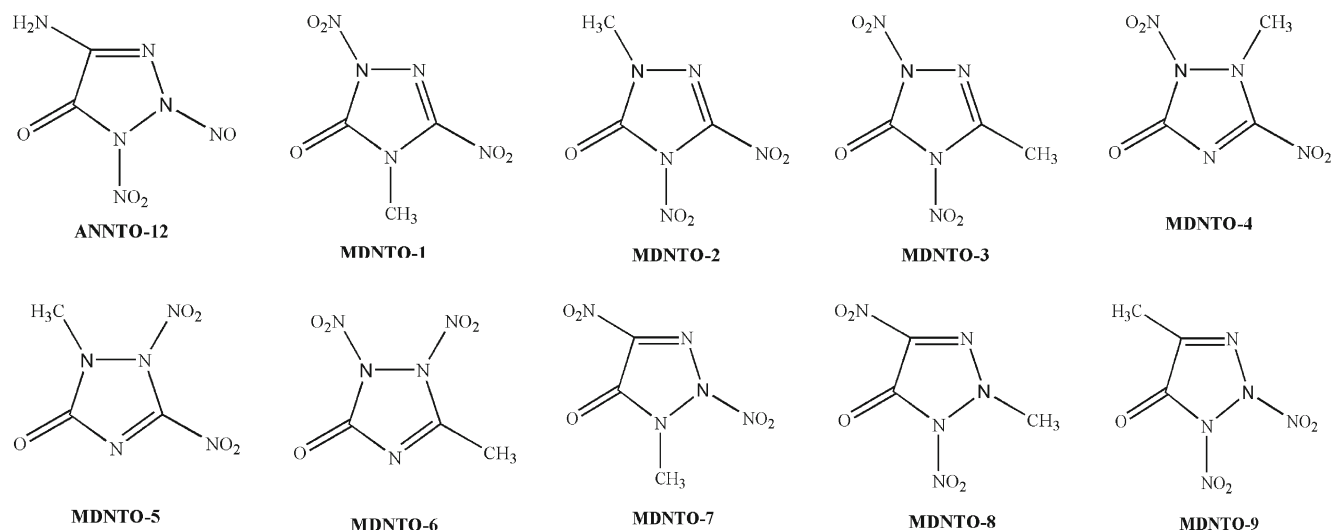


Fig. 1 (continued)



**Fig. 1** (continued)

values in the case of MDNTO. The higher densities are due to the intramolecular hydrogen bonds, layered structures in the crystal lattice and also as per the atom/or group additivity. The absolute error in the predicted densities are believed to be less than  $0.03 \text{ g/cm}^3$  and thus known to be fairly good to calculate the performance properties of designed compounds [48].

#### 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 released is ultimately lost to surroundings. The determination of composition of the products of a detonation or explosion process has been known to be a key issue. The modified Kistiakowsky-Wilson rules [35] give an approximate for the products of decomposition, which is independent of the temperature of explosion. Also, the composition of detonation products may vary considerably depending upon the loading density of the explosive compound. We have calculated the heats of explosion ( $Q$ ) of triazolones assuming the explosive reactions go to total completion [34, 35, 45]. Table 3 presents the calculated oxygen balance, heats of explosion and performances of triazolones computed from 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. NTO have higher  $Q$  values varying from 0.64 to 1.04 kcal/g and the discrepancies are due to the relative position of the N-atom in the azole ring and position of the nitro group. NTO-1 has lower  $Q$  value of 0.641 kcal/g and NTO-8 has higher  $Q$  value of 1.04 kcal/g. DNTO have higher  $Q$  values (1.234 to 1.456 kcal/g) compared with those

of TNTO. DNTO-3 has lower  $Q$  value of 1.120 kcal/g and DNTO-8 has higher  $Q$  value of 1.456 kcal/g. The exceptionally lower  $Q$  values of trinitrotriazolones are due to the surplus oxygen (i.e., higher OB% +21.82). It is seen from Table 3 that substituting one of the hydrogen atoms of NTO by nitroso (-NO) group markedly increased the  $Q$  values. The amino (-NH<sub>2</sub>) group has been found to increase the  $Q$  values markedly compared with the nitro (-NO<sub>2</sub>) group (ADNTO vs TNTO). ANNTO-9 and ANNTO-10 have exceptionally higher  $Q$  values 1.392 and 1.420 kcal/g respectively among other ANNTO. ADNTO have higher  $Q$  values (1.355 to 1.571 kcal/g) compared with those of NDNTO. MDNTO have  $Q$  values varying from 1.030 to 1.165 kcal/g. Particularly striking is the effect of the nitroso (-NO) group in increasing the  $Q$  values compared to the nitro analogues and it is notable in the case of NNTO and NDNTO. The heats of explosion reaches maximum for an oxygen balance of zero, since this corresponds to the stoichiometric oxidation of carbon to carbon dioxide 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 triazole, number and the relative positions of substituent groups and the strength of C=O bond. The detonation energies obtained are for the gas phase compounds and in reality they should be for the solid phase which would diminish the magnitude of  $Q$  values [44, 53, 54].

#### Detonation velocity and detonation pressure

Two key measures of detonation performance are the detonation velocity and the detonation pressure which refers to the stable velocity of the shock front that characterizes



**Table 1** Lowest frequency ( $\omega_L$ ), total energy ( $E_0$ ), zero-point energy (ZPE), thermal correction to enthalpy (ET), and frontier molecular orbital energies (HOMO and LUMO) of triazolones computed from the B3LYP/aug-cc-pVDZ level

HEM	$\omega_L$ ( $\text{cm}^{-1}$ )	$E_0$ (a.u.)	ZPVE (a.u.)	$H_T$ (a.u.)	HOMO (a.u.)	LUMO (a.u.)	$\epsilon_{(\text{LUMO-HOMO})}$ (a.u.)
T-1	573.33	-242.28781	37.457	0.064	-0.284	-0.019	0.265
T-2	559.87	-242.27765	36.956	0.063	-0.271	-0.029	0.242
T-3	592.30	-242.26163	36.948	0.0634	-0.277	-0.023	0.254
T-4	558.81	-242.26831	37.381	0.064	-0.286	-0.026	0.260
TO-1	232.34	-317.54195	40.209	0.069	-0.245	-0.022	0.223
TO-2	248.81	-317.45360	40.063	0.069	-0.264	-0.053	0.211
TO-3	259.41	-317.48912	39.778	0.063	-0.258	-0.067	0.191
NTO-1	84.49	-522.06731	41.672	0.074	-0.281	-0.133	0.187
NTO-2	59.07	-522.03281	41.126	0.073	-0.281	-0.112	0.169
NTO-3	65.88	-522.01494	40.615	0.073	-0.295	-0.105	0.190
NTO-4	61.94	-522.03888	41.311	0.074	-0.289	-0.148	0.141
NTO-5	85.944	-522.01951	40.875	0.065	-0.300	-0.124	0.176
NTO-6	65.98	-522.01494	40.615	0.073	-0.294	-0.105	0.189
NTO-7	35.65	-522.009055	41.095	0.073	-0.286	-0.123	0.163
NTO-8	65.87	-521.98327	40.543	0.073	-0.289	-0.120	0.169
NTO-9	76.64	-521.99022	40.319	0.072	-0.290	-0.120	0.170
DNTO-1	42.46	-726.51955	41.773	0.077	-0.310	-0.133	0.177
DNTO-2	44.11	-726.54052	42.248	0.078	-0.308	-0.145	0.163
DNTO-3	44.30	-726.55267	42.256	0.078	-0.310	-0.156	0.154
DNTO-4	47.40	-726.53173	41.755	0.077	-0.320	-0.168	0.152
DNTO-5	40.44	-726.52617	41.755	0.077	-0.320	-0.151	0.169
DNTO-6	56.50	-726.50952	41.426	0.076	-0.328	-0.138	0.190
DNTO-7	29.14	-726.49939	41.659	0.077	-0.313	-0.151	0.162
DNTO-8	43.51	-726.47678	40.899	0.076	-0.316	-0.140	0.176
DNTO-9	34.90	-726.50437	41.479	0.077	-0.311	-0.153	0.158
TNTO-1	37.31	-931.02324	42.698	0.081	-0.331	-0.163	0.168
TNTO-2	36.03	-931.03716	42.281	0.081	-0.345	-0.164	0.181
TNTO-3	31.17	-930.98815	41.964	0.080	-0.332	-0.171	0.161
NNTO-1	55.62	-651.34329	38.510	0.071	-0.300	-0.151	0.149
NNTO-2	46.01	-651.32303	38.256	0.071	-0.308	-0.149	0.159
NNTO-3	61.30	-651.35875	38.746	0.071	-0.302	-0.159	0.143
NNTO-4	24.56	-651.33194	38.315	0.071	-0.311	-0.156	0.155
NNTO-5	24.17	-651.33884	38.118	0.071	-0.309	-0.170	0.139
NNTO-6	77.28	-651.31283	37.959	0.070	-0.305	-0.136	0.169
NNTO-7	52.04	-651.28088	37.386	0.070	-0.385	-0.144	0.241
NNTO-8	54.79	-651.27656	37.171	0.069	-0.294	-0.146	0.148
NNTO-9	29.18	-651.30580	38.146	0.071	-0.309	-0.163	0.135
NNTO-10	25.81	-651.30523	37.753	0.071	-0.298	-0.166	0.132
NDNTO-1	39.04	-855.8292	38.701	0.075	-0.309	-0.175	0.134
NDNTO-2	38.97	-855.85914	38.699	0.075	-0.309	-0.175	0.134
NDNTO-3	37.77	-855.81608	38.508	0.074	-0.314	-0.158	0.156
NDNTO-4	39.10	-855.81983	38.564	0.074	-0.312	-0.185	0.127
NDNTO-5	33.52	-855.79157	38.171	0.074	-0.312	-0.165	0.147
NDNTO-6	26.91	-855.79153	38.194	0.074	-0.303	-0.186	0.117
ADNTO-1	43.53	-781.87566	52.599	0.096	-0.293	-0.147	0.146
ADNTO-2	32.24	-781.89754	52.249	0.095	-0.275	-0.130	0.145
ADNTO-3	42.03	-781.81138	52.451	0.096	-0.302	-0.142	0.160
ADNTO-4	29.94	-781.85505	52.054	0.095	-0.313	-0.163	0.150

**Table 1** (continued)

HEM	$\omega_L$ (cm <sup>-1</sup> )	$E_0$ (a.u.)	ZPVE (a.u.)	$H_T$ (a.u.)	HOMO (a.u.)	LUMO (a.u.)	$\varepsilon_{(LUMO-HOMO)}$ (a.u.)
ADNTO-5	53.56	-781.90444	53.565	0.095	-0.315	-0.125	0.190
ADNTO-6	42.09	-781.85850	52.220	0.095	-0.310	-0.143	0.167
ADNTO-7	33.95	-781.83743	51.952	0.095	-0.303	-0.150	0.153
ADNTO-8	34.13	-781.83170	51.892	0.095	-0.301	-0.149	0.152
ADNTO-9	32.36	-781.86175	51.236	0.095	-0.290	-0.142	0.148
ANNTO-1	40.934	-706.68158	49.083	0.088	-0.291	-0.150	0.141
ANNTO-2	52.86	-706.67489	48.715	0.089	-0.294	-0.150	0.144
ANNTO-3	32.83	-706.70175	48.618	0.089	-0.271	-0.141	0.130
ANNTO-4	42.75	-706.70628	48.866	0.089	-0.271	-0.128	0.143
ANNTO-5	42.50	-706.65769	48.619	0.089	-0.300	-0.151	0.149
ANNTO-6	37.18	-706.65971	48.597	0.089	-0.292	-0.133	0.159
ANNTO-7	62.07	-706.70297	48.482	0.088	-0.278	-0.122	0.156
ANNTO-8	59.68	-706.70348	48.747	0.088	-0.305	-0.136	0.169
ANNTO-9	28.77	-706.63797	48.129	0.088	-0.288	-0.162	0.126
ANNTO-10	31.33	-706.63223	48.230	0.885	-0.295	-0.148	0.147
ANNTO-11	30.42	-706.66267	47.734	0.088	-0.276	-0.132	0.144
ANNTO-12	32.25	-706.66016	47.735	0.087	-0.262	-0.122	0.140
MDNTO-1	28.64	-765.86468	59.818	0.107	-0.297	-0.148	0.149
MDNTO-2	42.78	-765.85806	59.564	0.107	-0.295	-0.141	0.154
MDNTO-3	37.62	-765.84650	59.088	0.106	-0.299	-0.127	0.172
MDNTO-4	32.15	-765.84194	59.226	0.107	-0.307	-0.145	0.162
MDNTO-5	39.72	-765.84134	59.010	0.107	-0.304	-0.144	0.160
MDNTO-6	50.68	-765.83915	58.643	0.106	-0.320	-0.127	0.193
MDNTO-7	34.31	-765.82044	58.871	0.106	-0.300	-0.145	0.155
MDNTO-8	34.85	-765.81604	59.046	0.106	-0.301	-0.143	0.158
MDNTO-9	40.0441	-765.80752	58.117	0.105	-0.306	-0.130	0.176

detonation and the stable pressure that is developed behind the front respectively [35, 44]. Detonation velocity and the detonation pressure can be as high as is compatible avoiding 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 detonation velocity and detonation pressure. It appears to a higher power in each equation 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  $\rho$  for most explosives while detonation pressure ( $P$ ) increases with the square of  $\rho$ , when  $\rho$  is greater than one. Detonation energy, oxygen balance, detonation velocity and detonation pressure of triazolones are summarized in Table 3. The detonation properties of NNTO ( $D$  8.75 to 9.10 km/s,  $P$  34.0 to 37.57 GPa), DNTO ( $D$  8.80 to 9.05 km/s,  $P$  35.55 to 38.27 GPa) and ANNTO ( $D$  8.58 to 9.0 km/s,  $P$  30.81 to 36.25 GPa) are compared with those of RDX ( $D$  8.75 km/s,  $P$  34.70 GPa) and HMX ( $D$  8.96 km/s,  $P$  35.96 GPa). ADNTO have higher performance properties ( $D$  9.01 to

9.42 km/s and  $P$  37.81 to 41.10 GPa) compared with HMX. NDNTO ( $D$  ~8.50 km/s and  $P$  ~34.10 GPa) and MDNTO ( $D$  8.31 to 8.73 km/s and  $P$  30.48 to 33.88 GPa) have shown comparable detonation properties with RDX. The higher performance properties of ADNTO-8 and NDNTO-6 are presumably due to their higher densities (1.935 and 2.3301 g/cm<sup>3</sup> respectively). Overall, the performance properties are related to the number and the relative positions of substituent groups and the strength of trigger bonds.

#### Impact sensitivity correlations

The impact sensitivity is usually measured by the height, from where a given weight falling upon the explosive gives 50 % probability of initiating detonation. Depluech and Cherville [55, 56] related the shock and thermal sensitivities to the molecular structure and the properties of bond length and strength of C-NO<sub>2</sub>, N-NO<sub>2</sub> and O-NO<sub>2</sub> bonds. Xiao [57] suggested that the stronger these trigger bonds, the more stable the molecule. Kamlet and Adolph [58] found the



**Table 2** Crystal characteristics of triazolones

HEM	$\text{\AA}^3$	$E_L$ (kJ mol $^{-1}$ )	Point group	Crystal system	a, b, c $\alpha$ , $\beta$ , $\gamma$ (degree)	$\rho$ (g cm $^{-3}$ )
T-1	258.3953	36.17831	P2 $_1$	monoclinic	a=6.47, b=8.87, c=4.51 $\alpha=\gamma=90$ , $\beta=85.6$	0.888
T-2	369.9938	21.46158	P2 $_1$ 2 $_1$ 2 $_1$	rhombic	a=6.46, b=8.85, c=4.48 $\alpha=\gamma=\beta=90$	1.240
T-3	350.3796	-0.60443	P2 $_{1/C}$	monoclinic	a=10.06, b=10.07, c=9.27 $\alpha=\gamma=90$ , $\beta=158$	1.310
T-4	369.1680	3.33703	P2 $_{1/C}$	monoclinic	a=6.09, b=8.94, c=6.77 $\alpha=\gamma=90$ , $\beta=157.4$	1.312
TO-1	365.8623	0.65763	P2 $_{1/C}$	monoclinic	a=9.96, b=9.91, c=10.43 $\alpha=\gamma=90$ , $\beta=159.2$	1.544
TO-2	364.2390	-17.82303	P2 $_1$ 2 $_1$ 2 $_1$	rhombic	a=3.65, b=10.88, c=9.17 $\alpha=\gamma=\beta=90$	1.551
TO-3	182.4634	1.41547	P $_{-1}$	triclinic	a=11.93, b=3.69, c=5.36 $\alpha=69.8$ , $\beta=63.3$ , $\gamma=62.2$	1.548
NTO-1	239.0883	-253.39362	P2 $_1$	monoclinic	a=4.85, b=5.68, c=8.67 $\alpha=\gamma=90$ , $\beta=89.23$	1.806
NTO-2	484.2640	-60.92738	P2 $_1$ 2 $_1$ 2 $_1$	rhombic	a=5.80, b=15.98, c=5.23 $\alpha=\gamma=\beta=90$	1.784
NTO-3	490.2546	-17.82316	P2 $_1$ 2 $_1$ 2 $_1$	rhombic	a=5.28, b=6.18, c=15.0 $\alpha=\gamma=\beta=90$	1.762
NTO-4	543.6965	-17.58808	P2 $_1$ 2 $_1$ 2 $_1$	rhombic	a=5.48, b=18.62, c=5.32 $\alpha=\gamma=\beta=90$	1.772
NTO-5	542.9867	-17.59810	P2 $_1$ 2 $_1$ 2 $_1$	rhombic	a=5.53, b=18.63, c=5.42 $\alpha=\gamma=\beta=90$	1.773
NTO-6	490.2264	-17.82210	P2 $_1$ 2 $_1$ 2 $_1$	rhombic	a=14.96, b=5.30, c=6.18 $\alpha=\gamma=\beta=90$	1.762
NTO-7	491.3264	-17.72209	P2 $_1$ 2 $_1$ 2 $_1$	rhombic	a=14.97, b=5.31, c=6.18 $\alpha=\gamma=\beta=90$	1.763
NTO-8	466.8325	-17.38430	P2 $_1$ 2 $_1$ 2 $_1$	rhombic	a=9.53, b=5.44, c=9.42 $\alpha=\gamma=\beta=90$	1.774
NTO-9	1030.026	5.85447	Pbcn	rhombic	a=6.16, b=15.02, c=11.08 $\alpha=\gamma=\beta=90$	1.677
DNTO-1	591.9104	-95.66010	P2 $_{1/C}$	monoclinic	a=6.31, b=9.42, c=12.65 $\alpha=\gamma=90$ , $\beta=52$	1.964
DNTO-2	592.9545	-76.85353	P2 $_1$ 2 $_1$ 2 $_1$	rhombic	a=13.71, b=6.57, c=6.58 $\alpha=\gamma=\beta=90$	1.961
DNTO-3	589.6748	-38.17715	P2 $_1$ 2 $_1$ 2 $_1$	rhombic	a=9.62, b=6.35, c=9.66 $\alpha=\gamma=\beta=90$	1.972
DNTO-4	602.5892	-16.99304	P2 $_{1/C}$	monoclinic	a=12.37, b=6.16, c=10.38 $\alpha=\gamma=90$ , $\beta=130.4$	1.930
DNTO-5	608.1558	-32.47674	Pna2 $_1$	rhombic	a=9.76, b=6.77, c=9.19 $\alpha=\gamma=\beta=90$	1.912
DNTO-6	590.6229	-67.58937	P2 $_{1/C}$	monoclinic	a=7.05, b=9.31, c=11.3 $\alpha=\gamma=90$ , $\beta=127.2$	1.968
DNTO-7	597.72658	-43.64879	P2 $_{1/C}$	monoclinic	a=10.40, b=9.28, c=13.1 $\alpha=\gamma=90$ , $\beta=151.8$	1.945
DNTO-8	609.0914	-42.87418	P2 $_{1/C}$	monoclinic	a=12.25, b=12.11, c=10.35 $\alpha=\gamma=90$ , $\beta=162.5$	1.910
DNTO-9	307.7556	-20.65559	P2 $_1$	monoclinic	a=5.25, b=9.618, c=6.17 $\alpha=\gamma=90$ , $\beta=99.3$	1.890
TNTO-1	711.4137	-96.96124	P2 $_1$ 2 $_1$ 2 $_1$	rhombic	a=13.10, b=8.40, c=6.45 $\alpha=\gamma=\beta=90$	2.054
TNTO-2	711.4137	-96.96124	P2 $_1$ 2 $_1$ 2 $_1$	rhombic	a=13.11, b=8.4, c=6.46 $\alpha=\gamma=\beta=90$	2.054

**Table 2** (continued)

HEM	$\text{\AA}^3$	$E_L$ (kJ mol <sup>-1</sup> )	Point group	Crystal system	a, b, c $\alpha$ , $\beta$ , $\gamma$ (degree)	$\rho$ (g cm <sup>-3</sup> )
TNTO-3	711.9895	-84.56703	P212121	rhombohedral	a=10.48, b=6.14, c=11.07 $\alpha=\gamma=\beta=90$	2.053
NNTO-1	564.4250	-10.65442	P212121	rhombohedral	a=5.18, b=11.02, c=9.88 $\alpha=\gamma=\beta=90$	1.872
NNTO-2	1341.982	-54.71917	C2/C	monoclinic	a=27.58, b=6.53, c=22.3 $\alpha=\gamma=90$ , $\beta=160.4$	1.882
NNTO-3	562.4723	-7.4904433	P21/C	monoclinic	a=10.64, b=6.31, c=8.57 $\alpha=\gamma=90$ , $\beta=101.97$	1.878
NNTO-4	567.0940	-9.01080	P21/C	monoclinic	a=6.68, b=15.32, c=5.81 $\alpha=\gamma=90$ , $\beta=108.0$	1.863
NNTO-5	1380.273	-41.28213	Pbca	rhombohedral	a=9.79, b=17.23, c=8.18 $\alpha=\gamma=\beta=90$	1.964
NNTO-6	565.3219	-28.43234	P212121	rhombohedral	a=23.35, b=4.61, c=5.24 $\alpha=\gamma=\beta=90$	1.868
NNTO-7	482.1295	5.68078	P21/C	monoclinic	a=16.38, b=7.21, c=7.42 $\alpha=\gamma=90$ , $\beta=126.6$	1.791
NNTO-8	1136.111	-40.70326	Pbca	rhombohedral	a=8.90, b=12.73, c=10.02 $\alpha=\gamma=\beta=90$	1.860
NNTO-9	566.6333	-18.75016	P21/C	monoclinic	a=11.42, b=6.88, c=18.96 $\alpha=\gamma=90$ , $\beta=162.5$	1.864
NNTO-10	1219.870	-31.09841	Pbca	rhombohedral	a=7.08, b=18.40, c=8.62 $\alpha=\gamma=\beta=90$	1.883
NDNTO-1	1341.943	-54.72092	C2/C	monoclinic	a=27.58, b=6.53, c=22.2 $\alpha=\gamma=90$ , $\beta=160.38$	2.020
NDNTO-2	653.2943	-20.14243	P212121	rhombohedral	a=5.94, b=6.11, c=17.87 $\alpha=\gamma=\beta=90$	1.912
NDNTO-3	1355.113	-53.464085	Pbca	rhombohedral	a=11.22, b=13.07, c=9.28 $\alpha=\gamma=\beta=90$	2.002
NDNTO-4	1355.008	-53.46408	Pbca	rhombohedral	a=11.23, b=13.07, c=9.27 $\alpha=\gamma=\beta=90$	2.001
NDNTO-5	1380.474	-41.28144	Pbca	rhombohedral	a=8.180, b=9.8, c=17.25 $\alpha=\gamma=\beta=90$	1.964
NDNTO-6	548.5844	-236.17351	P212121	rhombohedral	a=5.80, b=8.36, c=11.32 $\alpha=\gamma=\beta=90$	2.301
ADNTO-1	1304.810	-14.50863	Pbcn	rhombohedral	a=19.36, b=7.73, c=8.83 $\alpha=\gamma=\beta=90$	1.935
ADNTO-2	655.3125	-115.54261	P21/C	monoclinic	a=5.75, b=8.70, c=16.0 $\alpha=\gamma=90$ , $\beta=125$	1.926
ADNTO-3	1299.526	-71.28377	Pbca	rhombohedral	a=7.02, b=21.07, c=8.8 $\alpha=\gamma=\beta=90$	1.943
ADNTO-4	660.1206	-18.72874	P21/C	monoclinic	a=8.82, b=10.33, c=11.85 $\alpha=\gamma=90$ , $\beta=142.33$	1.912
ADNTO-5	655.9094	-87.49592	P212121	rhombohedral	a=6.34, b=11.36, c=9.01 $\alpha=\gamma=\beta=90$	1.925
ADNTO-6	662.2513	-26.01264	P212121	rhombohedral	a=7.05, b=7.14, c=13.17 $\alpha=\gamma=\beta=90$	1.906
ADNTO-7	1317.933	-15.73062	Pbcn	rhombohedral	a=19.17, b=7.84, c=8.76 $\alpha=\gamma=\beta=90$	1.916
ADNTO-8	652.2741	-66.73367	P21/C	monoclinic	a=9.33, b=6.52, c=11.28 $\alpha=\gamma=90$ , $\beta=107.86$	1.935
ADNTO-9	1318.555	-33.33759	Pbca	rhombohedral	a=8.88, b=6.96, c=21.33 $\alpha=\gamma=\beta=90$	1.914
ANNTO-1	646.3895	-22.95609	C2	monoclinic	a=28.48, b=5.44, c=4.9 $\alpha=\gamma=90$ , $\beta=58.3$	1.788

**Table 2** (continued)

HEM	$\text{\AA}^3$	$E_L$ (kJ mol <sup>-1</sup> )	Point group	Crystal system	a, b, c $\alpha$ , $\beta$ , $\gamma$ (degree)	$\rho$ (g cm <sup>-3</sup> )
ANNTO-2	1237.325	-5.01048	Pbca	rhombic	a=17.23, b=10.43, c=6.88 $\alpha=\gamma=\beta=90$	1.870
ANNTO-3	314.2762	-58.62991	P-1	triclinic	a=5.83, b=6.38, c=10.7 $\alpha=127.88, \beta=89.92, \gamma=90$	1.840
ANNTO-4	1237.820	-82.03007	Pbca	rhombic	a=12.70, b=10.52, c=9.3 $\alpha=\gamma=\beta=90$	1.865
ANNTO-5	632.7598	3.48999	P212121	rhombic	a=7.47, b=14.15, c=5.98 $\alpha=\gamma=\beta=90$	1.827
ANNTO-6	312.8602	9.48432	P21/C	monoclinic	a=7.23, b=6.13, c=7.1 $\alpha=\gamma=90, \beta=96.23$	1.848
ANNTO-7	623.8683	-47.11021	P21/C	monoclinic	a=7.99, b=5.422, c=14.4 $\alpha=\gamma=90, \beta=90.8$	1.853
ANNTO-8	641.4651	-57.37356	P212121	rhombic	a=11.68, b=6.31, c=8.7 $\alpha=\gamma=\beta=90$	m
ANNTO-9	631.0772	-19.30248	P21/C	monoclinic	a=9.38, b=5.75, c=12.07 $\alpha=\gamma=90, \beta=75.7$	1.832
ANNTO-10	637.1487	-37.33804	P21/C	monoclinic	a=10.26, b=5.72, c=11.65 $\alpha=\gamma=90, \beta=68.5$	1.815
ANNTO-11	629.6456	6.23110	P21/C	monoclinic	a=8.05, b=12.12, c=11.23 $\alpha=\gamma=90, \beta=144.7$	1.836
ANNTO-12	628.6790	-28.49713	P212121	rhombic	a=13.85, b=8.07, c=5.62 $\alpha=\gamma=\beta=90$	1.840
MDNTO-1	1394.533	-21.07763	Pbca	rhombic	a=14.18, b=10.51, c=9.37 $\alpha=\gamma=\beta=90$	1.801
MDNTO-2	705.8131	-69.29748	P21/C	monoclinic	a=9.98, b=10.34, c=7.02 $\alpha=\gamma=90, \beta=77.0$	1.780
MDNTO-3	686.4133	-93.73290	P21/C	monoclinic	a=20.45, b=6.01, c=13.38 $\alpha=\gamma=90, \beta=155.3$	1.830
MDNTO-4	694.9778	-9.27434	P21/C	monoclinic	a=14.7, b=9.17, c=6.18 $\alpha=\gamma=90, \beta=56.5$	1.807
MDNTO-5	696.2120	-23.07666	P212121	rhombic	a=7.35, b=7.27, c=13.04 $\alpha=\gamma=\beta=90$	1.804
MDNTO-6	686.2365	-64.78744	P21/C	monoclinic	a=7.10, b=19.55, c=12.96 $\alpha=\gamma=90, \beta=157.6$	1.830
MDNTO-7	352.2511	-10.87991	P21	monoclinic	a=9.72, b=6.25, c=6.22 $\alpha=\gamma=90, \beta=68.9$	1.783
MDNTO-8	713.7998	-46.05897	P212121	rhombic	a=6.01, b=6.18, c=19.20 $\alpha=\gamma=\beta=90$	1.760
MDNTO-9	693.5574	-37.77901	P21/C	smonoclinic	a=14.0, b=6.14, c=18.8 $\alpha=\gamma=90, \beta=154.8$	1.810

linear relationship between the impact sensitivity and the oxygen balance. Mullay [59] gave a statistically significant relationship between impact sensitivity and molecular electronegativity of nitro compounds. Politzer and coworkers [60, 61] related the bond energies, electrostatic potential maxima and impact sensitivity. They also have related impact sensitivity to the degree of positive charge buildup over the covalent bonds within the molecular frame work [62–65]. Pospíšil [66] gave the relationship between the crystal volume and impact sensitivity. Zeman [67, 68] related the detonation and thermal decomposition, <sup>13</sup>C NMR and <sup>15</sup>N

NMR chemical shifts to impact sensitivity. Zhang et al. [36–39] correlated the electronic structure to impact sensitivity by the nitro group charge analysis. As for the nitro (-NO<sub>2</sub>) groups in nitro compounds, they are electron-withdrawing. The higher negative charge the nitro group possesses the lower the electron withdrawing ability and thus the stability of a molecule increases. In explosives, R-NO<sub>2</sub> bonds (R=C, N, O) are usually weakest and their breaking is often the initial step in the detonation of explosive.

The trigger length, nitro group charge ( $-Q_{NO_2}$ ) and mid-point electrostatic potential ( $V_{mid}$ ) and frontier molecular

**Table 3** Explosive properties of triazolones

HEM	Formula	Mw (g mol <sup>-1</sup> )	OB%	Q (kcal g <sup>-1</sup> )	$\rho$ (g cm <sup>-3</sup> )	D (km s <sup>-1</sup> )	P (GPa)
NTO-1	C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>	130	-24.61	0.641	1.806	7.54	25.25
NTO-2	C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>	130	-24.61	0.804	1.784	7.91	27.58
NTO-3	C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>	130	-24.61	0.840	1.817	8.10	29.25
NTO-4	C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>	130	-24.61	0.866	1.772	8.03	28.27
NTO-5	C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>	130	-24.61	0.866	1.773	8.02	28.27
NTO-6	C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>	130	-24.61	0.887	1.762	8.03	28.26
NTO-7	C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>	130	-24.61	0.920	1.763	8.11	28.80
NTO-8	C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>	130	-24.61	1.040	1.774	8.40	31.00
NTO-9	C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>	130	-24.61	1.004	1.677	8.01	27.23
DNTO-1	C <sub>2</sub> HN <sub>5</sub> O <sub>5</sub>	175	-13.71	1.307	1.964	8.98	37.64
DNTO-2	C <sub>2</sub> HN <sub>5</sub> O <sub>5</sub>	175	-13.71	1.234	1.961	8.84	36.47
DNTO-3	C <sub>2</sub> HN <sub>5</sub> O <sub>5</sub>	175	-13.71	1.120	1.972	8.80	36.22
DNTO-4	C <sub>2</sub> HN <sub>5</sub> O <sub>5</sub>	175	-13.71	1.264	1.930	8.80	35.74
DNTO-5	C <sub>2</sub> HN <sub>5</sub> O <sub>5</sub>	175	-13.71	1.291	1.912	8.81	35.55
DNTO-6	C <sub>2</sub> HN <sub>5</sub> O <sub>5</sub>	175	-13.71	1.341	1.968	9.05	38.27
DNTO-7	C <sub>2</sub> HN <sub>5</sub> O <sub>5</sub>	175	-13.71	1.380	1.945	9.04	37.92
DNTO-8	C <sub>2</sub> HN <sub>5</sub> O <sub>5</sub>	175	-13.71	1.456	1.910	9.04	37.56
DNTO-9	C <sub>2</sub> HN <sub>5</sub> O <sub>5</sub>	175	-13.71	1.361	1.890	8.86	35.94
TNTO-1	C <sub>2</sub> N <sub>6</sub> O <sub>7</sub>	220	21.82	0.772	2.054	8.11	31.47
TNTO-2	C <sub>2</sub> N <sub>6</sub> O <sub>7</sub>	220	21.82	0.801	2.054	8.18	31.98
TNTO-3	C <sub>2</sub> N <sub>6</sub> O <sub>7</sub>	220	21.82	0.872	2.053	8.35	33.44
NNTO-1	C <sub>2</sub> HN <sub>5</sub> O <sub>4</sub>	159	-5.03	1.290	1.872	8.75	34.76
NNTO-2	C <sub>2</sub> HN <sub>5</sub> O <sub>4</sub>	159	-5.03	1.367	2.020	8.91	36.18
NNTO-3	C <sub>2</sub> HN <sub>5</sub> O <sub>4</sub>	159	-5.03	1.221	1.878	8.64	33.94
NNTO-4	C <sub>2</sub> HN <sub>5</sub> O <sub>4</sub>	159	-5.03	1.333	1.863	8.80	35.01
NNTO-5	C <sub>2</sub> HN <sub>5</sub> O <sub>4</sub>	159	-5.03	1.305	1.964	8.63	33.28
NNTO-6	C <sub>2</sub> HN <sub>5</sub> O <sub>4</sub>	159	-5.03	1.405	1.868	8.93	36.14
NNTO-7	C <sub>2</sub> H <sub>2</sub> N <sub>5</sub> O <sub>4</sub>	159	-5.03	1.528	1.791	8.85	34.65
NNTO-8	C <sub>2</sub> H <sub>2</sub> N <sub>5</sub> O <sub>4</sub>	159	-5.03	1.544	1.860	9.11	37.57
NNTO-9	C <sub>2</sub> H <sub>2</sub> N <sub>5</sub> O <sub>4</sub>	159	-5.03	1.435	1.864	8.96	36.37
NNTO-10	C <sub>2</sub> H <sub>2</sub> N <sub>5</sub> O <sub>4</sub>	159	-5.03	1.436	1.883	9.03	37.12
NDNTO-1	C <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	204	15.86	0.982	2.020	8.50	34.18
NDNTO-2	C <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	204	15.86	0.982	1.912	8.50	34.18
NDNTO-3	C <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	204	15.86	1.021	2.002	8.51	34.16
NDNTO-4	C <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	204	15.86	1.011	2.001	8.50	34.02
NDNTO-5	C <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	204	15.86	1.102	1.964	8.55	34.12
NDNTO-6	C <sub>2</sub> N <sub>6</sub> O <sub>6</sub>	204	15.86	1.101	2.301	9.61	46.85
ADNTO-1	C <sub>2</sub> H <sub>2</sub> N <sub>6</sub> O <sub>5</sub>	190	-16.84	1.430	1.935	9.20	39.20
ADNTO-2	C <sub>2</sub> H <sub>2</sub> N <sub>6</sub> O <sub>5</sub>	190	-16.84	1.355	1.926	9.06	37.81
ADNTO-3	C <sub>2</sub> H <sub>2</sub> N <sub>6</sub> O <sub>5</sub>	190	-16.84	1.446	1.943	9.26	39.75
ADNTO-4	C <sub>2</sub> H <sub>2</sub> N <sub>6</sub> O <sub>5</sub>	190	-16.84	1.495	1.912	9.23	39.14
ADNTO-5	C <sub>2</sub> H <sub>2</sub> N <sub>6</sub> O <sub>5</sub>	190	-16.84	1.332	1.925	9.01	37.46
ADNTO-6	C <sub>2</sub> H <sub>2</sub> N <sub>6</sub> O <sub>5</sub>	190	-16.84	1.484	1.906	9.20	38.75
ADNTO-7	C <sub>2</sub> H <sub>2</sub> N <sub>6</sub> O <sub>5</sub>	190	-16.84	1.554	1.916	9.34	40.07
ADNTO-8	C <sub>2</sub> H <sub>2</sub> N <sub>6</sub> O <sub>5</sub>	190	-16.84	1.571	1.935	9.42	41.10
ADNTO-9	C <sub>2</sub> H <sub>2</sub> N <sub>6</sub> O <sub>5</sub>	190	-16.84	1.470	1.914	9.20	38.88
ANNTO-1	C <sub>2</sub> H <sub>2</sub> N <sub>6</sub> O <sub>4</sub>	174	-9.19	1.240	1.788	8.58	32.57
ANNTO-2	C <sub>2</sub> H <sub>2</sub> N <sub>6</sub> O <sub>4</sub>	174	-9.19	1.265	1.868	8.90	35.92
ANNTO-3	C <sub>2</sub> H <sub>2</sub> N <sub>6</sub> O <sub>4</sub>	174	-9.19	1.164	1.840	8.62	33.43

**Table 3** (continued)

HEM	Formula	Mw (g mol <sup>-1</sup> )	OB%	Q (kcal g <sup>-1</sup> )	ρ (g cm <sup>-3</sup> )	D (km s <sup>-1</sup> )	P (GPa)
ANNT0-4	C2H2N6O4	174	-9.19	1.148	1.865	8.68	35.10
ANNT0-5	C2H2N6O4	174	-9.19	1.323	1.827	8.86	35.13
ANNT0-6	C2H2N6O4	174	-9.19	1.316	1.848	8.92	35.84
ANNT0-7	C2H2N6O4	174	-9.19	1.158	1.853	8.65	30.81
ANNT0-8	C2H2N6O4	174	-9.19	1.157	1.802	8.48	31.96
ANNT0-9	C2H2N6O4	174	-9.19	1.393	1.832	9.00	36.25
ANNT0-10	C2H2N6O4	174	-9.19	1.420	1.815	8.97	35.90
ANNT0-11	C2H2N6O4	174	-9.19	1.288	1.836	8.83	35.00
ANNT0-12	C2H2N6O4	174	-9.19	1.310	1.840	8.88	35.45
MDNT0-1	C3H3N5O5	189	-4.23	1.007	1.801	8.34	30.88
MDNT0-2	C3H3N5O5	189	-4.23	1.030	1.780	8.31	30.48
MDNT0-3	C3H3N5O5	189	-4.23	1.064	1.830	8.55	32.76
MDNT0-4	C3H3N5O5	189	-4.23	1.080	1.807	8.51	32.20
MDNT0-5	C3H3N5O5	189	-4.23	1.096	1.804	8.53	32.32
MDNT0-6	C3H3N5O5	189	-4.23	1.086	1.830	8.60	33.10
MDNT0-7	C3H3N5O5	189	-4.23	1.150	1.783	8.56	32.34
MDNT0-8	C3H3N5O5	189	-4.23	1.165	1.760	8.51	31.71
MDNT0-9	C3H3N5O5	189	-4.23	1.190	1.810	8.73	33.88

orbital energy gap of triazolones are presented in Table 4. The nitro group charge is calculated by the sum of the net Mulliken atomic charges on the nitrogen and oxygen atoms and of the nitro group:

$$-Q_{NO_2} = Q_N + Q_{O1} + Q_{O2} \quad (25)$$

$$V_{mid} = \frac{Q_C}{0.5R} + \frac{Q_N}{0.5R}, \quad (26)$$

where R is trigger length,  $Q_C$ ,  $Q_N$  and  $Q_{O1}$ ,  $Q_{O2}$  and are the Mulliken charges on carbon, nitrogen and oxygen atoms respectively.

As the number of NO<sub>2</sub> groups on the triazolone framework increases, competition for the available charge increases and thus the molecule becomes unstable. In other words, when there is one nitro group on triazolone (NTO), it will have a larger negative charge than if there are two or more nitro groups (DNTO, TNTO). Therefore, more sensitive compounds will have smaller charges on their nitro groups. As per that predicted by Zhang et al., the approximated  $-Q_{NO_2}$  values of several triazolones are superior with respect to RDX (0.105 e), HMX (0.112 e), TNAZ (0.114 e), ONC (0.146 e), TNT (0.249 e), TATB (0.416 e), FOX-7 (0.365 e), LLM-105 (0.264 e) and NTO (0.264 e) and thus appear to be more insensitive. However, DNTO-1 (0.09 e), ANNT0- 8 (0.085 e), ANNT0- 11 (0.075 e) and MDNT0-7 (0.070 e) have similar sensitivity like CL-20 (0.081 e). The Higher the  $-Q_{NO_2}$  value the higher the impact insensitivity of the compound. The presence of -NO<sub>2</sub> and -NO group

noticeably decreases the  $-Q_{NO_2}$  values of model molecules. The N-NO<sub>2</sub> or N-NO bond is the site of impact/or shock initiation. The similar trend has also been observed for the midpoint electrostatic potentials ( $V_{mid}$ ) of model molecules. The substitution of secondary amino hydrogen of triazolones by -NH<sub>2</sub> or -CH<sub>3</sub> group shows better impact sensitivity. The impact sensitivity can also be used to show the stability of model compounds and the stability here is attributed to the presence of  $\pi$ -excessive aromatic heterocyclic ring, delocalization of  $\pi$ -electrons and presence of intramolecular N-H $\cdots$ O, C $\cdots$ O and N $\cdots$ O interactions [45, 46, 53].

#### Stability correlations

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies play a crucial role in governing the chemical reactions. In several studies it is revealed that the band gap between the frontier molecular orbital energies is an important stability index of the molecules [40–42, 69–78]. 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. In other words, the smaller the band gap between HOMO and LUMO the easier the electron transition and it thus lowers the stability. In the molecule with large band gap, that is if  $\varepsilon_{HOMO} - \varepsilon_{LUMO} \gg 0$ , then very little electron transfer occurs. If the respective orbital energies are quite similar, that is if  $\varepsilon_{HOMO} - \varepsilon_{LUMO} \approx 0$ , strong electron transfer

**Table 4** Trigger bond length, the Mulliken charges of nitro group ( $-Q_{\text{NO}_2}$ ), mid-point electrostatic potential ( $V_{\text{mid}}$ ) and bond gap ( $\varepsilon$  (LUMO-HOMO)) of triazolones

HEM	Trigger bond	Length (Å)	$-Q_{\text{NO}_2}$ (e)	$V_{\text{mid}}$	$\varepsilon$ (LUMO-HOMO) (a.u.)
NTO-1	C2-NO <sub>2</sub>	1.447	0.48	1.99	0.187
NTO-2	N4-NO <sub>2</sub>	1.413	0.15	1.75	0.169
NTO-3	N1-NO <sub>2</sub>	1.424	0.31	1.52	0.190
NTO-4	C3-NO <sub>2</sub>	1.482	0.48	1.71	0.141
NTO-5	N1-NO <sub>2</sub>	1.466	0.24	0.55	0.176
NTO-6	N1-NO <sub>2</sub>	1.446	0.21	0.35	0.189
NTO-7	C4-NO <sub>2</sub>	1.452	0.57	1.65	0.163
NTO-8	N1-NO <sub>2</sub>	1.428	0.11	1.34	0.169
NTO-9	N2-NO <sub>2</sub>	1.495	0.15	1.28	0.170
DNTO-1	N1-NO <sub>2</sub>	1.441	0.09	1.90	0.177
DNTO-2	C3-NO <sub>2</sub>	1.461	0.18	1.30	0.163
DNTO-3	C3-NO <sub>2</sub>	1.457	0.29	1.87	0.154
DNTO-4	N1-NO <sub>2</sub>	1.466	0.22	1.70	0.152
DNTO-5	N2-NO <sub>2</sub>	1.572	0.15	0.38	0.169
DNTO-6	N1-NO <sub>2</sub>	1.497	0.13	0.87	0.190
DNTO-7	N1-NO <sub>2</sub>	1.577	0.23	1.18	0.162
DNTO-8	N1-NO <sub>2</sub>	1.480	0.11	1.31	0.176
DNTO-9	N2-NO <sub>2</sub>	1.531	0.14	1.29	0.158
TNTO-1	N1-NO <sub>2</sub>	1.476	0.16	0.59	0.168
TNTO-2	N2-NO <sub>2</sub>	1.545	0.14	0.33	0.181
TNTO-3	N2-NO <sub>2</sub>	1.586	0.05	1.37	0.161
NNTO-1	C3-NO <sub>2</sub>	1.462	0.49	1.85	0.149
NNTO-2	N1-NO <sub>2</sub>	1.436	0.23	1.52	0.159
NNTO-3	C3-NO <sub>2</sub>	1.461	0.48	1.93	0.143
NNTO-4	C3-NO <sub>2</sub>	1.478	0.23	1.65	0.155
NNTO-5	C3-NO <sub>2</sub>	1.484	0.44	1.87	0.139
NNTO-6	N2-NO <sub>2</sub>	1.494	0.19	0.57	0.169
NNTO-7	N2-NO <sub>2</sub>	1.543	0.15	0.36	0.241
NNTO-8	N1-NO <sub>2</sub>	1.483	0.22	0.38	0.148
NNTO-9	C4-NO <sub>2</sub>	1.453	0.44	1.72	0.135
NNTO-10	C4-NO <sub>2</sub>	1.458	0.56	1.58	0.132
NDNTO-1	N4-NO	1.668	0.51	1.76	0.134
NDNTO-2	N1-NO	1.668	0.22	2.00	0.134
NDNTO-3	N1-NO	1.554	0.50	2.15	0.156
NDNTO-4	N2-NO	1.773	0.11	1.16	0.127
NDNTO-5	N1-NO	1.604	0.16	1.39	0.147
NDNTO-6	N2-NO	1.744	0.55	1.32	0.117
ADNTO-1	N1-NO <sub>2</sub>	1.447	0.31	1.81	0.146
ADNTO-2	N4-NO <sub>2</sub>	1.419	0.19	1.59	0.145
ADNTO-3	N4-NO <sub>2</sub>	1.463	0.18	1.29	0.160
ADNTO-4	N1-NO <sub>2</sub>	1.482	0.14	0.24	0.150
ADNTO-5	N1-NO <sub>2</sub>	1.489	0.17	0.24	0.190
ADNTO-6	N2-NO <sub>2</sub>	1.532	0.17	0.19	0.167
ADNTO-7	N2-NO <sub>2</sub>	1.561	0.15	0.55	0.153
ADNTO-8	N1-NO <sub>2</sub>	1.459	0.25	1.13	0.152
ADNTO-9	N2-NO <sub>2</sub>	1.548	0.13	1.04	0.148
ANNTO-1	C3-NO <sub>2</sub>	1.463	0.52	1.79	0.141
ANNTO-2	N4-NO	1.514	0.52	1.77	0.144
ANNTO-3	N1-NO <sub>2</sub>	1.420	0.41	1.67	0.130



**Table 4** (continued)

HEM	Trigger bond	Length (Å)	-Q <sub>NO2</sub> (e)	V <sub>mid</sub>	ε (LUMO-HOMO) (a.u.)
ANNT0-4	C4-NO2	1.416	0.17	1.61	0.143
ANNT0-5	C3-NO2	1.479	0.51	1.99	0.149
ANNT0-6	C3-NO2	1.477	0.56	1.91	0.159
ANNT0-7	N2-NO2	1.481	0.22	1.67	0.156
ANNT0-8	N1-NO2	1.514	0.08	2.30	0.169
ANNT0-9	N2-NO	1.534	0.54	1.57	0.126
ANNT0-10	C4-NO2	1.453	0.55	1.65	0.147
ANNT0-11	N2-NO2	1.552	0.07	1.87	0.144
ANNT0-12	N1-NO2	1.495	0.19	1.40	0.140
MDNT0-1	N1-NO2	1.446	0.40	1.68	0.149
MDNT0-2	C4-NO2	1.458	0.21	1.25	0.154
MDNT0-3	N1-NO2	1.435	0.19	1.34	0.172
MDNT0-4	N1-NO2	1.482	0.17	0.16	0.162
MDNT0-5	N2-NO2	1.572	0.14	1.75	0.160
MDNT0-7	N2-NO2	1.577	0.07	1.56	0.193
MDNT0-8	N1-NO2	1.464	0.28	0.36	0.155
MDNT0-9	N2-NO2	1.537	0.15	1.33	0.158

occurs. The frontier molecular orbital energies have been decreased by increasing the -NO<sub>2</sub>/or -NO group (s) from one to three in the triazolone ring. However, the frontier orbital energies are increased by -NH<sub>2</sub> and -CH<sub>3</sub> groups in the triazolone ring. The electron withdrawing groups lowers the LUMO and HOMO energy levels while electron donating groups increase the LUMO and HOMO energy levels. It is also clear that if one -NO<sub>2</sub> group of DNNT0 or TNT0 is replaced by -NO group, stability values are significantly diminished (Table 1). In general, R-NO<sub>n</sub> (where *n*=1 or 2) bonds are the trigger sites and resonance in the triazolone moiety strengthens these bonds thereby the molecules become stabilized. The larger the trigger length of 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 [41, 70, 73, 74]. This correlation indicates that thermodynamically stable compounds are also kinetically stable. Thus, for a molecule to be isolated, it must be not only thermodynamically but also kinetically stable.

## 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 amino-, nitroso, nitro-

, methyl substituted triazolones. Our computational results indicate that triazolones (NTO, DNTO, TNT0, NNTO, ADNT0, NDNT0, ANNT0 and MDNT0) do correspond to energy minima and accordingly should be able to exist. Detonation properties were evaluated by the Kamlet-Jacob equations based on the calculated density and heat of chemical energy. The partial replacement of nitro groups by nitroso group appears to be a particularly promising area for investigation since it may lead to the two desirable consequences of higher heat of explosion and diminished sensitivities. NNTO, DNTO, ANNT0, ADNT0 have higher performance properties compared with those of 1,3,5-trinitro-1,3,5-triazine (RDX) (*D* 8.75 km/s, *P* 34.70 Gpa) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (*D* 8.96 km/s, *P* 35.96 GPa). MDNT0-1, MDNT0-2, MDNT0-4, MDNT0-5, MDNT0-7 and MDNT0-7 may replace 1-methyl-2,4,5-trinitroimidazole (MTNI), 3,4-dinitropyrazole (3,4-DNP) and 1-methyl-3,4,5-trinitropyrazole (MTNP) in near future for melt cast explosive applications.

**Acknowledgments** We are grateful to the referees for enlightening comments and useful suggestions. We thank Defense Research Development Organization, India for the financial assistance through Advanced Centre of Research in High Energy Materials.

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