



Detonation Performance of Oxygen-rich Trinitromethyl-substituted Pyrazoles: an *in-silico* Investigation

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Abstract: A new class of high energy molecules was designed and their detonation properties were evaluated using thermo-chemical parameters obtained from quantum chemical calculations at B3LYP/6-31G(d,p) level. The designed molecules exhibited high density, positive oxygen balance and excellent detonation properties. The impact sensitivity of these molecules, in terms of H_{50} values, was also evaluated from structural correlations. Among these, 3,4,5-tris(trinitromethyl)-1H-pyrazol-1-amine (N13) showed the highest detonation pressure (40.67 GPa) and highest detonation velocity (9.17 km/s), though it exhibited high impact sensitive ($H_{50} = 15$ cm). Interestingly, 4,5-dinitro-3-(trinitromethyl)-1H-pyrazol-1-amine (N01) (detonation pressure 39.69 GPa; detonation velocity 9.23 km/s) was found to be an ideal high energy molecule with a near zero oxygen balance. The H_{50} value of N01 was predicted to be 64 cm, which is higher in magnitude, indicating a lower sensitivity than that of the conventionally used RDX ($H_{50} = 26$ cm).

Keywords: nitropyrazoles, aminonitropyrazoles, detonation velocity, detonation pressure, density functional theory, high energy molecules

Supporting Information (SI) available at: <http://www.wydawnictwa.ipo.waw.pl/CEJEM/contents/2018/vol-15-no-4.html>

1 Introduction

Eco-friendly materials with thermal stability, impact insensitivity and enhanced detonation performance are needed for future high energy materials (HEMs)

and continuous efforts are being made by researchers to meet these civil and military requirements [1-4]. Even though numerous high energy materials like 1,3,5-trinitrotriazacyclohexane (RDX), 1,3,5,7-tetranitrotetraazacyclooctane (HMX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclododecane (CL-20) and 1,1-diamino-2,2-dinitroethene (FOX-7), *etc.* are known, the quest is still on to develop high energy molecules with superior detonation performance [5, 6]. Studies on nitrogen rich ionic compounds and bridged structures showed interesting results [7-9]. Nitro derivatives of pyrazole attracted attention due to its high heat of formation, high density and thermal stability, in spite of its critical oxygen balance [10, 11]. Dinitromethyl- and fluorodinitromethyl-substituted polynitroaliphatic compounds were reported in the late 1960s, which showed promising detonation properties and oxygen balance [12, 13]. Trinitromethyl-derivatives of nitro heteroarenes were difficult to synthesise, however these substituents help to improve the heat of formation of HEMs. Gobel *et al.* reported the synthesis of a new class of HEMs with the trinitroethyl group substituted in tetrazoles [2, 14]. In addition, Venugopal *et al.* synthesized trinitromethyl-substituted triazoles with excellent energetic properties [15].

The major concern associated with the development of new HEMs is safety and environmental hazards. Substitution of the trinitromethyl group in HEMs increases the oxygen and nitrogen contents, thereby providing increased thermal stability and release of high energy, which in turn improves the detonation performance. Screening of hypothetical energetic molecules through computational chemistry helps to select suitable candidates without any laborious experimental work, avoiding wastage of resources and preventing hazards as well as environmental degradation. Various computational methods have been developed [16-18] for performance evaluation of energetic materials and this is complemented by the availability of high performance computers. With the aim of enhancing the detonation performance of HEMs, trinitromethyl-substituted nitropyrazoles and aminonitropyrazoles were designed and studied. The electronic structures, detonation properties as well as the impact sensitivity of these molecules were evaluated *in-silico* using quantum chemical methods.

2 Computational Methods

2.1 Quantum Chemical Calculations

Geometry optimization and energy calculations for all molecules were performed using the Gaussian 09 software suite [19], and GaussView 5.0 [20] was used for

visualization. Initially, the geometry was optimized using the RHF method to shortlist the various possible configurations. The B3LYP method with 6-31G(d,p) basis set was used for further geometry optimization and frequency calculation to evaluate detonation properties. Previous studies showed that the 6-31G(d,p) basis set is a good choice for molecular structure and energy prediction [21].

2.2 Heat of Formation

The atom equivalent method by Rice *et al.* [16] was employed to calculate the gas phase heats of formation (HOF):

$$\Delta H_{f(g)}^o = E - \sum n_j \varepsilon_j \quad (1)$$

where E is the quantum mechanically determined electronic energy of a molecule, n_j is the number of atom type j contained in the molecule and ε_j is the atom equivalent energy. The geometries of all molecules were optimized at B3LYP level using 6-31G(d) basis set and the minimized energy was used to obtain gas phase HOFs. According to Hess's law of constant heat summation, the solid-phase HOF was calculated by subtracting the heat of sublimation (ΔH_{sub}) from the gas phase HOF. Politzer *et al.* [22, 23] established a correlation between electrostatic potential (ESP) mapped onto the isodensity surface of isolated molecules and their heat of sublimation as:

$$\Delta H_{\text{Sub}} = a(SA)^2 + b\sqrt{(\sigma_{\text{tot}}^2 \nu)} + c \quad (2)$$

where SA is the surface area of the 0.001 electron/bohr³ isosurface of the electron density of the molecule, σ_{tot}^2 is a measure of the variability of the electronic potential on the surface, and ν is the degree of balance between the positive and negative charges on the isosurface. These descriptors were calculated using Multiwfn, a multifunctional wave function analyzer developed by Lu *et al.* [24]. a , b and c were constants having values 0.00042343, 2.5793785 and -6.7335407, respectively.

Condensed phase heats of formation were also evaluated using the empirical method reported by Jafari *et al.* [25] for high nitrogen content materials (Equation 3):

$$(\Delta_f H_c^o)_{\text{B3LYP}} = -57.28 + 0.9350(\Delta_f H_g^o)_{\text{B3LYP}} + 27.86 \quad (3)$$

where $(\Delta_f H_c^o)_{\text{B3LYP}}$ is the condensed phase heat of formation and $(\Delta_f H_g^o)_{\text{B3LYP}}$ is the heat of formation in the gaseous state calculated by B3LYP/6-31G*.

IF and DF are the contributions from the groups having an increasing (IF) and decreasing (DF) effect on the heat of formation.

2.3 Detonation Properties

Detonation velocity (D) and pressure (P) were evaluated using the Kamlet-Jacob (K-J) equations [18] given as:

$$P = 15.58\rho^2\varphi \quad (4)$$

$$D = 1.01\varphi^{0.5}(1 + 1.30\rho) \quad (5)$$

$$\varphi = NM^{0.5}Q^{0.5} \quad (6)$$

where P is detonation pressure in GPa, D is detonation velocity in km/s, N is the number of moles of gaseous detonation products per gram of explosive, M is the average molecular weight of the gaseous products, Q is the chemical energy of detonation in cal per gram of explosive and ρ is the density in g/cm³. Theoretical density was obtained by dividing the molecular weight M with the average molecular volume (V_m). V_m was estimated from inside the contour of 0.001 electron/bohr³ density by Monte Carlo integration. Subsequently, the crystal density was calculated using the equation by Politzer *et al.* [26], which includes the interaction index $v\sigma_{tot}^2$:

$$\rho = \alpha \left(\frac{M}{V_m} \right) + \beta(v\sigma^2) + \gamma \quad (7)$$

Chemical energy of detonation was calculated by a detonation reaction based on the Kistiakowsky-Wilson rule [27] using the equation:

$$\Delta H_{298} = -Q = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (8)$$

where ΔE_0 is the change in total energy between reactant and product at 0 K, ΔZPE is the difference between the zero-point energy of the products and that of the reactant, ΔH_T is the thermal correction from 0 K to 298 K and Δn is the difference in number of moles of reactants and products. R is the gas constant and T the absolute temperature.

Oxygen balance (OB), which provides information about the chemical composition of a compound and does not yield any information about its structure, is an important parameter for the evaluation of detonation performance and was calculated using the method reported by Kamlet and Adolph [28].

Recently, Jafari and Keshavarz [29, 30] reported an improved and simple method to calculate the detonation pressure and detonation velocity using the

empirical relationship given below:

$$D = 5.468N^{0.5}(MQ)^{0.25}\rho_0 + 2.045 \quad (9)$$

$$P = 24.436N(MQ)^{0.25}\rho_0^2 - 0.874 \quad (10)$$

where P is detonation pressure in GPa, D is detonation velocity in km/s, N is the number of moles of gaseous detonation products per gram of explosive, M is the average molecular weight of the gaseous products, Q is the chemical energy of detonation in cal per gram of explosive and ρ is the density in g/cm³. Chemical energy of detonation (Q) was calculated using the following equation:

$$Q = \frac{-[\sum_i \Delta_f H^0(\text{Products})_i - \Delta_f H^0(C)]}{\text{formula weight of explosive}} \quad (11)$$

where $\Delta_f H^0(\text{Products})_i$ and are the standard enthalpies of formation of the i^{th} -product and the condensed phase standard enthalpy of formation of the explosive, respectively.

2.4 Thermodynamic Properties

Gibbs free energy of formation [31], enthalpy of fusion [32], entropy of fusion [33], enthalpy of sublimation [34], melting point [35] and deflagration temperature [36] of the molecules under investigation in this study, were calculated using the empirical relationship reported by Keshavarz *et al.* [31-36].

2.5 Stability and Sensitivity

Even though impact sensitivity measurements are crude qualitative estimates, they are extremely important for understanding the factors that govern sensitivity [37]. Several methods have been reported to predict the impact sensitivity of nitro compounds [17, 38-39]. Zhang [40] reported a nitro group charge method (NGCM) to predict the molecular stability and impact sensitivity of nitro compounds. The nitro group charge (\bar{Q}_{nitro}) is the algebraic sum of Mulliken charges of all three atoms of a nitro group and the average value for \bar{Q}_{nitro} can be calculated by using the following equations:

$$Q_{\text{nitro}} = Q_N + Q_{O1} + Q_{O2} \quad (12)$$

$$\bar{Q}_{\text{nitro}} = \frac{1}{n} \sum_{i=1}^n Q_{\text{nitro},i} \quad (13)$$

Drop-weight impact sensitivity (H_{50} , cm) is the parameter used to define the sensitivity of high energy compounds, which can be predicted from the molecular structure correlation. Keshavarz [41] has given a general correlation for predicting

impact sensitivity of energetic compounds containing nitropyrazoles and can be calculated using the equations:

$$(\log H_{50})_{core} = -0.584 + 61.62a + 21.53b + 27.96c \quad (14)$$

$$\log H_{50} = (\log H_{50})_{core} + 84.47 \frac{F^+}{MW} - 147.1 \frac{F^-}{MW} \quad (15)$$

where a , b and c are the number of carbon, hydrogen and nitrogen atoms divided by the molecular mass of the energetic compound. F^+ and F^- are factors for specific molecular moieties responsible for increasing or decreasing the value of $(\log H_{50})_{core}$. F^+ and F^- values for the nitropyrazoles were reported by Keshavarz [41] and the same were used to predict the impact sensitivity of the present designed molecules.

3 Results and Discussion

3.1 Electronic Structure

Fourteen different molecules, obtained by substituting one, two or three nitro groups attached to carbon atoms in (a) 1,3,4,5-tetranitropyrazole and (b) 1-amino-3,4,5-trinitropyrazole (Figure 1) with trinitromethyl groups, were selected for this study. All configurations were optimized using RHF/6-31G(d,p) basis set and are listed in Table S1, Supporting Information. There are three possible structures for single substitution of a trinitromethyl group in (a) as well as in (b). Similarly three possibilities exist for di-substitution. From the set of the three possible structures in each case, the one with minimum energy was selected for further investigation (Table S1). For tri-substitution, only one structure is possible in each of (a) and (b). In total six structures were selected for further evaluation of their detonation properties. The optimized structures of these molecules at B3LYP/6-31G(d,p) level are shown in Figure 2. Frequency calculations were performed to calculate their thermo-chemical properties and to ensure the absence of negative frequencies, indicating the stability of the molecules. Significant bond lengths for these molecules are given in Supporting Information (Table S2). The N-N bond lengths for N01, N04, N07, N10, N13 and N14 were 1.3895 Å, 1.4979 Å, 1.3909 Å, 1.5340 Å, 1.3880 Å and 1.5705 Å, respectively. In the cases of N01, N07 and N13, the N-N bond lengths correspond to the N-NH₂ group whereas in N04, N10 and N14 it corresponds to the N-NO₂ group. The higher bond length in the case of N-NO₂ shows that it is a weaker bond, and the increasing bond length with trinitromethyl substitution indicates increasing impact sensitivity in the molecule on substitution.

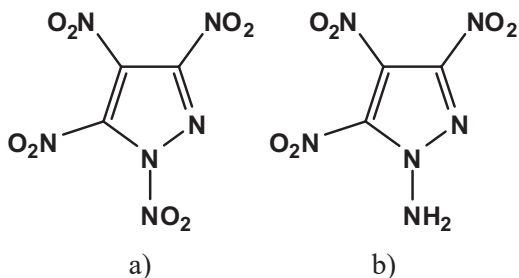
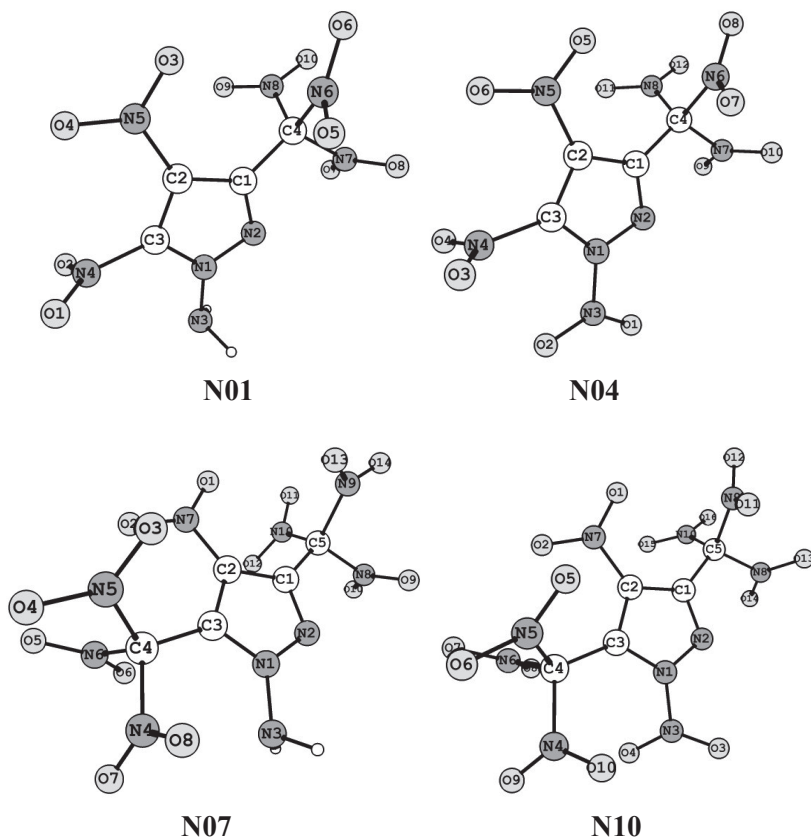


Figure 1. Structures of (a) 1,3,4,5-tetranitropyrazole and (b) 1-amino-3,4,5-trinitropyrazole



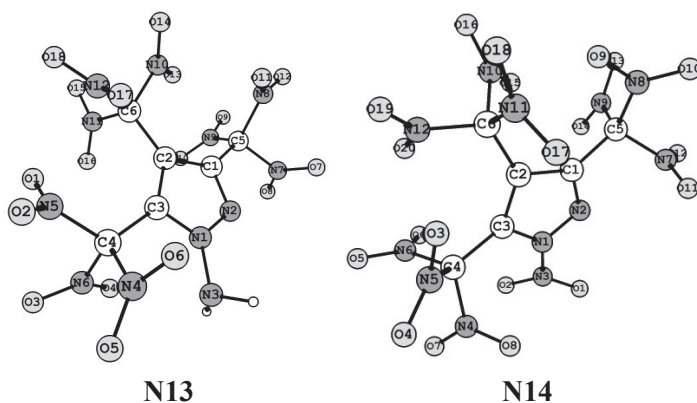


Figure 2. Optimized geometries of the molecules at B3LYP/6-31G(d,p) level

3.2 Heat of formation (HOF)

The solid phase heat of formation $\Delta H_f(s)$, is an important parameter for assessing the detonation performance of energetic materials, and was evaluated by subtracting the heat of sublimation from the gas phase HOF (method 1) [16]. Electrostatic potential (ESP) parameters, solid phase HOFs ($\Delta H_f(s)$) and gas phase heats of formation ($\Delta H_f(g)$) were used for calculating the heats of sublimation, and the latter are listed in Table 1.

All of the molecules under study were found to have high positive HOFs, attributed to the presence of the trinitromethyl group(s). It may be seen from Table 1 that gas phase HOFs increase with an increase in number of trinitromethyl group substitutions. Also, the heat of formation of molecules containing the N-NO₂ bond (N04, N10 and N14) were comparatively higher than those for molecules containing the N-NH₂ bond because of the higher energetics associated with the N-NO₂ bond. The gas phase HOFs of N13 and N14 were very high compared to the other molecules, probably due to the high degree of steric hindrance from the three trinitromethyl groups.

Additionally the HOFs were also determined using the method reported by Jafari *et al.* [25] (method 2) and these results are also listed in Table 1. It was observed that the gaseous HOFs obtained using both methods were comparable, however the condensed phase HOFs estimated by method 2 were higher than those obtained by method 1

In order to validate the methods used for calculating HOFs, $\Delta H_f(s)$ of RDX and 1H-tetrazole were calculated by both methods and compared with their experimental values. It was noted that the HOFs for both the molecules obtained by method 1 were comparable to the experimental values, whereas the values

Table 1. Calculated energy at B3LYP/6-31G(d) level, surface parameters (S_A , v and $(\sigma_{ot})^2$) obtained from electrostatic potential, density (ρ), gas phase heat of formation, $\Delta H_f(g)$ and solid phase heat of formation, $\Delta H_f(s)$

S. No.	Energy (Hartree)	S_A [Å ²]	N	$(\sigma_{ot})^2$ [kcal/mol]	P [g/cm ³]	$\Delta H_f(g)^s$ [kcal/mol]	$\Delta H_f(s)^s$ [kcal/mol]	$\Delta H_f(g)^{\#}$ [kcal/mol]	$\Delta H_f(s)^{\#}$ [kcal/mol]
N01	-43.239655	254.62	0.07653	288.28	1.896	92.35	59.52	102.86	68.09
N04	-92.362172	270.19	0.06532	174.78	2.031	92.28	59.39	107.26	86.58
N07	-91.508494	311.87	0.05264	308.47	2.028	101.10	56.26	117.01	81.32
N10	-0.625333	322.29	0.07653	114.11	1.901	104.60	59.73	124.82	103.00
N13	-9.749334	350.94	0.05055	242.37	2.094	127.42	72.99	148.42	110.69
N14	-88.86123	361.55	0.07711	96.87	2.023	134.02	78.35	159.22	135.16
RDX	-7323575	197.78	0.17775	181.03	1.820	45.32	20.86 (18.9)*	47.05	30.29
1H-tetrazole	-3169241	122.75	0.206	225.65	-	80.06	59.58 (56.46)*	80.18	54.08

^sas per Ref. [16], [#]as per Ref. [25], *experimental value [20, 25]

obtained using method 2 estimated a higher HOF for RDX. It was observed that though method 2 is reliable for the high nitrogen content materials for the majority of molecules, for a few molecules it tends to overestimate the HOF. The relative deviation in the HOF reported for the molecules 1,3,5-triazine-2,4,6-triamine, 3-(5-amino-1H-tetrazol-1-yl)propanenitrile, 4,4'-hydrazobis-(1,2,5-oxadiazol-3-amine) and 1H-tetrazol-1-amine, using method 2 were 84.9%, 36.3%, 54.2% and 41.9%, respectively.

3.3 Detonation properties

Detonation properties of the designed molecules were calculated using the Kamlet-Jacob method [18] as well as the improved method reported by Jafari and Keshavarz [29, 30]. The thermo-chemical properties obtained from the quantum chemical calculations for the molecules under study are listed in Supporting Information (Table S3). The detonation properties, for example oxygen balance, chemical energy of detonation, density, detonation pressure and detonation velocity are listed in Table 2.

Table 2. Oxygen balance (OB), chemical energy of detonation (Q), detonation pressure (P) and detonation velocity (D) of the designed molecules

Molecule	OB [%]	Q [cal/g]	P ^a [GPa]	P ^b [GPa]	D ^a [km/s]	D ^c [km/s]
N01	4.97	1505.49	37.33	37.662	9.034	8.912
N04	18.18	1107.3	36.05	38.969	8.707	9.027
N07	11.26	1297.02	39.53	41.239	9.122	9.223
N10	21.05	1011.82	30.24	33.318	8.125	8.513
N13	17.54	1211.94	40.67	43.194	9.173	9.388
N14	22.86	988.23	33.88	37.765	8.451	8.921
RDX	-21.6	1162.91	34.23	36.75	8.864	8.830

^a as per Ref. [18], ^b as per Ref. [29], ^c as per Ref. [30]

Oxygen balance is the parameter that determines the degree to which an explosive can be oxidized. Although a positive oxygen balance is better for the performance of an explosive, an excess of oxygen is not favourable as additional oxygen in the molecule will produce oxygen that takes away a significant amount of energy during the explosion. Hence, ideally, the oxygen balance should be near zero. In the present study, the oxygen balance of all molecules was found to be positive. Molecule N01 showed the lowest oxygen balance, 4.97%, and N14 showed the highest, 22.86%.

Two important parameters that determine the detonation performance

of energetic materials are detonation velocity and detonation pressure. The Kamlet-Jacob equation is a reliable method for predicting the detonation velocity and detonation pressure of energetic molecules and has been proven by several studies [42-44]. Density, an important parameter in the Kamlet-Jacob equation, is critical in the evaluation of the detonation performance of HEMs. Politzer *et al.* [25] reported an error of 0.050 g/cm^3 in the estimation of density for many compounds, as the method does not account for intermolecular interactions within the crystal. Hence, an improved equation was used for predicting the density, by including the interaction index $v(\sigma_{\text{tot}})^2$. From the values shown in Table 5, it was observed that the detonation performance of the molecules with an N-NH₂ bond increases with the increase in trinitromethyl substitution. N13 had the highest detonation pressure and detonation velocity. This trend was not followed in the case of molecules containing an N-NO₂ group, where the detonation performance decreased on di-substitution and then increased on further substitution, probably due to the density which followed a similar trend. According to the Kamlet-Jacob equation, detonation properties are directly dependent on density. The density of the molecules containing an N-NH₂ group increased with increasing substitution, as each substitution increased the molecular weight by 104 and the volume increased correspondingly, resulting in the increased density, whereas in the case of the molecules containing an N-NO₂ group, the second substitution was near to the N-NO₂ group and, due to steric hindrance, the increase in volume was greater than the increase in molecular weight, resulting in a lower density. The detonation properties are dependent on many factors, such as oxygen balance, density, strain in the molecule, substitution of energetic groups, *etc.* and it is not possible to correlate the properties based on one parameter alone. It was reported that detonation properties for N-NO₂ containing molecules are better than N-NH₂ containing molecules [45]. In the present study, the values of detonation pressure and detonation velocity are marginally higher for N-NO₂ containing compounds than for N-NH₂ containing compounds. In order to validate our calculations, the properties of RDX were calculated and compared with experimental values. The calculated detonation pressure and detonation velocity of RDX were 34.23 GPa and 8.86 km/s, respectively, which was in close agreement with the experimental values of 34.00 GPa and 8.75 km/s reported by Talawar *et al.* [3]. The detonation properties of molecules N01, N07, N13, and N14 were comparable or better than RDX.

The detonation pressure and detonation velocity obtained by the improved method are also reported in Table 2. It was evident from these results that the detonation properties calculated using the new method were comparable with those obtained by the Kamlet-Jacob method.

3.4 Thermodynamic properties

The Gibbs free energy of formation, enthalpy of fusion, entropy of fusion, enthalpy of sublimation, melting point and deflagration temperature were evaluated and are listed in Table 3.

Table 3. Gibbs free energy of formation ($\Delta G_{\text{formation}}$), enthalpy of fusion (ΔH_{fusion}), entropy of fusion (ΔS_{fusion}), enthalpy of sublimation (ΔH_{sub}), melting point and deflagration temperature of the designed molecules

Molecule	$\Delta G_{\text{formation}}$ [kJ/mol]	ΔH_{fusion} [kJ/mol]	ΔS_{fusion} [J/K mol]	ΔH_{sub} [kJ/mol]	Melting point [K]	Deflagration temperature [K]
N01	794.6	40.7	56.9	112.5	540.2	466.8
N04	853.2	33.5	54.7	153.6	440.4	454.4
N07	1007.9	50.3	59.6	181.3	566.5	455.1
N10	1066.5	43.2	57.4	140.3	466.6	442.6
N13	1221.2	59.9	62.3	209.0	592.7	443.3
N14	1279.8	52.8	60.0	168.0	492.8	430.9

As expected, the Gibbs free energy, enthalpy and entropy were found to be increased by increasing trinitromethyl substitution. The melting points are on the higher side for the molecules with an N-NH₂ group, indicating their stability relative to the molecules with an N-NO₂ group. All the molecules had deflagration temperatures in a similar range and below their melting points, except for N04.

3.5 Stability and sensitivity

The stability of HEMs is mainly described by their total energy, bond lengths, bond dissociation energy, frontier orbital energy, band gaps as well as charge on the nitro group. Of all these parameters, band gap and charge on the nitro group are prominent and easy to calculate from the Mullikan charge. In the present study too, the stability of the molecules was investigated by means of band gap and nitro group charges (\bar{Q}_{nitro}), and the results are listed in Table 4. A more negative value of the nitro group charge indicates a more stable molecule. Band gap for all of the molecules was high in comparison to RDX (0.105). Of the six molecules, N01 had the highest nitro charge whereas N14 had the lowest charge, which was comparable to that of RDX. N14 had three trinitromethyl groups, which were responsible for the weak N-NO₂ bond, resulting reduced stability.

The impact sensitivity itself is a sensitive term in the area of explosives. A high level of detonation with a low degree of sensitivity may not always be ideal, as pointed out by Licht [46], but it was observed that high performance

was generally accompanied by high sensitivity. Politzer *et al.* [47] addressed the issue in detail. Sensitivity is dependent on many parameters, such as heat release during detonation, free space per molecule in the crystal lattice *etc.*, but correlation parameters such as H_{50} (cm) values will give trends in similar types of molecule. H_{50} (cm) refers to the height from which a hammer of standard weight falling upon the explosive will lead to a 50% probability of detonation. The impact sensitivity of all of the molecules in this study were calculated in terms of H_{50} (cm) using the correlation given by Keshavarz [41], and the results are listed in Table 4. N01 was predicted to be more impact insensitive among all the designed molecules, having an H_{50} value of 64 cm. N10 and N14 had H_{50} values of 5 cm and 4 cm, respectively, suggesting the high impact sensitivity of these molecules.

Table 4. HOMO LUMO energies, band gap, average nitro group charge (Q_{Nitro}) in atomic units, and H_{50} values for impact sensitivity

	E_{HOMO}	E_{LUMO}	$E_{\text{LUMO}} - E_{\text{HOMO}}$	-	H_{50} [cm]
N01	-0.32519	-0.13575	0.18944	0.2279	64
N04	-0.34207	-0.16122	0.18085	0.1565	8
N07	-0.3308	-0.14533	0.18547	0.1669	21
N10	-0.34315	-0.17037	0.17278	0.1230	5
N13	-0.3282	-0.15928	0.16892	0.1296	15
N14	-0.34019	-0.16509	0.1751	0.0973	4

4 Conclusions

The electronic structure, detonation properties, stability and impact sensitivity of a new class of HEMs were studied computationally. The designed HEMs exhibited high detonation pressure and detonation velocity with positive oxygen balance. Due to the high positive oxygen balance in some of the new compounds, it should be expected that they show high sensitivity to some external stimuli, *e.g.* impact. As expected, N04, N10 and N14 displayed low H_{50} values indicating high impact sensitivity due to weak N-NO₂ bonds and could be unstable molecules. Interestingly, N01 was found to be a promising HEM with near zero oxygen balance, with a detonation pressure of 37.33 GPa, a detonation velocity of 9.034 km/s and an H_{50} value of 64 cm, whereas N13 displayed an oxygen balance of 17.54% with the highest detonation pressure and velocity of 40.67 GPa and 9.173 km/s, respectively, which make N13 a suitable candidate as an eco-friendly

energetic oxidizer. The predicted detonation properties of these molecules were found to be better than those of RDX, making them a better choice for future applications as environmentally friendly and high-performance HEMs.

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Reference

- [1] Chi, W. J.; Guo, Y. Y.; Li, Q.S.; Li, Z. S. Substituent Effects on the Properties Related to Detonation Performance and Stability for Pentaprismane Derivatives. *Theor. Chem. Acc.* **2016**, *135*: 145-155.
- [2] Gobel, M.; Klapotke, T. M. Development and Testing of Energetic Materials: the Concept of High Densities Based on the Trinitroethyl Functionality. *Adv. Funct. Mater.* **2009**, *19*: 347-365.
- [3] Talawar, M. B.; Sivabalan, R.; Mukundan, T.; Muthurajan, H.; Sikder, A. K.; Gandhe, B. R.; Rao, A. S. Environmentally Compatible Next Generation Green Energetic Materials (GEMs). *J. Hazard. Mater.* **2009**, *161*: 589-607.
- [4] Wei, T.; Zhu, W.; Zhang, X.; Li, Y.F.; Xiao, H. Molecular Design of 1,2,4,5-Tetrazine Based High Energy Density Materials. *J. Phys. Chem. A.* **2009**, *113*: 9404-9412.
- [5] Anniappan, M.; Talwar, G. M.; Venugopalan, S.; Gandhe, B. R. Synthesis, Characterization and Thermolysis of 1,1-Diamino-2,2-dinitroethylene (FOX-7) and its Salts. *J. Hazard. Mater.* **2006**, *137*: 812-819.
- [6] Garg, S.; Gao, H.; Joo, Y-H.; Parrish, D.A.; Shreeve, J. M. J. Taming of the Silver FOX. *J. Am. Chem. Soc.* **2010**, *132*: 8888-8890.
- [7] Zhu, W.; Zhang, C.; Wei, T.; Xiao, H. Computational Study of Energetic Nitrogen-rich Derivatives of 1,1'- and 5,5'-Bridged Ditetrazoles. *J. Comput. Chem.* **2011**, *32*: 2298-2312.
- [8] Zhu, W.; Yan, Q.; Li, J.; Cheng, B.; Shao, Y.; Xia, X.; Xiao, H. Prediction of the Properties and Thermodynamics of Formation for Energetic Nitrogen-rich Salts Composed of Triaminoguanidinium Cation and 5-Nitroiminotetrazolate-Based Anions. *J. Comput. Chem.* **2012**, *33*: 1781-1789.
- [9] Liu, H.; Wang, F.; Wang, G.-X.; Gong, X.-D. Theoretical Investigations on Structure, Density, Detonation Properties, and Sensitivity of the Derivatives of PYX. *J. Comput. Chem.* **2012**, *33*: 1790-1796.
- [10] Zaitsev, A. A.; Dalinger, I. L.; Shevelev, S. A. Dinitropyrazoles. *Russ. Chem. Bull.* **2009**, *78*: 589-627.
- [11] Herve, G.; Roussel, C.; Graindorg, H. Selective Preparation of 3,4,5-Trinitro-1H-pyrazole: A Stable All-carbon-nitrated Arene. *Angew. Chem. Int. Ed.* **2010**, *49*: 3177-3181.

- [12] Kamlet, M. J.; Adolph, H. G. Fluoronitroaliphatics. II. Fluorodinitromethyl Compounds. Synthetic Approaches and General Properties. *J. Org. Chem.* **1968**, *33*: 3073-3080.
- [13] Grakauskas, V.; Baum, K. Michael Reactions of 2-Fluoro-2,2-dinitroethanol and 2,2-Dinitropropanol with Olefinic and Acetylenic Acceptors. *J. Org. Chem.* **1969**, *34*: 3927-3930.
- [14] Gobel, M.; Tchitchanov, B. H.; Murray, J. S.; Politzer, P.; Klapotke, T. M. Chlorotrinitromethane and its Exceptionally Short Carbon-chlorine Bond. *Nat. Chem.* **2009**, *1*: 229-235.
- [15] Venugopal, T.; Gao, H.; Shreeve, J.M. Trinitromethyl-substituted 5-Nitro- or 3-Azo-1,2,4-triazoles: Synthesis, Characterization, and Energetic Properties. *J. Am. Chem. Soc.* **2011**, *133*: 6464-6471.
- [16] Rice, B. M.; Pai, S. V.; Hare, J. Predicting Heats of Formation of Energetic Materials Using Quantum Mechanical Calculations. *Combust. Flame* **1999**, *118*: 445-458.
- [17] Rice, B. M.; Hare, J. J. A Quantum Mechanical Investigation of the Relation between Impact Sensitivity and the Charge Distribution in Energetic Molecules. *J. Phys. Chem. A* **2002**, *106*: 1770-1783.
- [18] Kamlet, M. J.; Jacob, S. J. Chemistry of Detonation. I. A Simple Method for Calculating Detonation Properties of C, H, N, O Explosives. *J. Chem. Phys.* **1968**, *48*: 23-35.
- [19] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr. T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, 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 E.01. Gaussian, Inc., Wallingford CT, **2004**.
- [20] Dennington, R.; Keith, T.; Millam, J. GaussView, Version 5. Semichem Inc., Shawnee Mission KS, **2009**.
- [21] Tirado-Rives, J.; Jorgensen, W. L. Performance of B3LYP Density Functional Methods for a Large Set of Organic Molecules. *J. Chem. Theo Comput.* **2008**, *4*: 297-306.
- [22] Politzer, P.; Lane, P.; Murry, J. S. Computational Characterization of a Potential Energetic Compound: 1,3,5,7-Tetranitro-2,4,6,8-tetraazacubane. *Cent. Eur. J. Energ. Mater.* **2011**, *8*(1): 39-52.

- [23] Politzer, P.; Murry, J. S. Some Perspective on Estimating Detonation Properties of C, H, N, O Compounds. *Cent. Eur. J. Energ. Mater.* **2011**, 8(3): 209-220.
- [24] Lu, T.; Chen, F. Multiwfn: A Multifunctional Wave Function Analyzer. *J. Comput. Chem.* **2012**, 33: 580-592.
- [25] Jafari, M.; Keshavarz, M. H.; Noorbala, M. R.; Kamalvand, M. A Reliable Method for Prediction of the Condensed Phase Enthalpy of Formation of High Nitrogen Content Materials through their Gas Phase Information. *Chem. Sel.* **2016**, 1: 5286-5296.
- [26] Politzer, P.; Martinez, J.; Murray, J. S.; Concha, M. C.; Toro-Labbe, A. An Electrostatic Interaction Correction for Improved Crystal Density Prediction. *Mol. Phys.* **2009**, 107: 2095-2101.
- [27] Akhavan, J. *The Chemistry of Explosives*. 2nd Eds., Royal Society of Chemistry, Cambridge, **2004**; ISBN 0854046402.
- [28] Kamlet, M. J.; Adolph, H. G. The Relationship of Impact Sensitivity with Structure of Organic High Explosives II. Polynitro Aromatic Explosives. *Propellants Explos. Pyrotech.* **1979**, 4: 30-34.
- [29] Jafari, M.; Keshavarz, M. H. A Simple Method for Calculating the Detonation Pressure of Ideal and Non-ideal Explosives Containing Aluminium and Ammonium Nitrate. *Cent. Eur. J. Energ. Mater.* **2017**, 14(4): 966-983.
- [30] Keshavarz, M. H.; Kamalvand, M.; Jafari, M.; Zamani, A. An Improved Simple Method for the Calculation of the Detonation Performance of CHNOFCl, Aluminized and Ammonium Nitrate Explosives. *Cent. Eur. J. Energ. Mater.* **2016**, 13(2): 381-396.
- [31] Keshavarz, M. H.; Pouretedal, H. R.; Ghaedsharafi, A. R.; Taghizadeh, S. E. Simple Method for Prediction of the Standard Gibbs Free Energy of Formation of Energetic Compounds. *Propellants Explos. Pyrotech.* **2014**, 39: 815-818.
- [32] Oskoei, Y. M.; Keshavarz, M. H. Improved Method for Reliable Predicting Enthalpy of Fusion of Energetic Compounds. *Fluid Phase Equilibria.* **2012**, 326: 1-14.
- [33] Keshavarz, M. H.; Pouretedal, H. R. A New Simple Approach to Predict Entropy of Fusion of Nitroaromatic Compounds. *Fluid Phase Equilibria.* **2010**, 298: 24-32.
- [34] Keshavarz, M. H. Improved Prediction of Heats of Sublimation of Energetic Compounds Using their Molecular Structure. *J. Hazard. Mater.* **2010**, 177: 648-659.
- [35] Keshavarz, M. H.; Gharagheizi, F.; Pouretedal, H. R. Improved Reliable Approach to Predict Melting Points of Energetic Compounds. *Fluid Phase Equilibria.* **2011**, 308: 114-128.
- [36] Keshavarz, M. H.; Moradi, S.; Saatluo, B. E.; Rahimi, H.; Madram, A. R. A Simple Accurate Model for Prediction of Deflagration Temperature of Energetic Compounds. *J. Therm. Anal. Calorim.* **2013**, 112: 1453-1463.
- [37] Politzer, P.; Murray, J. S. Impact Sensitivity and Crystal Lattice Compressibility/Free Space. *J. Mol. Model.* **2014**, 20: 2223-2227.
- [38] Cao, C.; Gao, S. Two Dominant Factors Influencing the Impact Sensitivities of Nitrobenzene and Saturated Nitro Compounds. *J. Phys. Chem. B.* **2007**, 111: 12399-12402.

- [39] Srinivasan, P.; Maheshwari, K.; Jothi, M.; Kumaradhas, P. Charge Density Distribution and Sensitivity of the Highly Energetic Molecule 2,4,6-Trinitro-1,3,4-triazine: a Theoretical Study. *Cent. Eur. J. Energ. Mater.* **2012**, *9*(1): 59-76.
- [40] Zhang, C. Review of the Establishment of Nitro Group Charge Method and its Applications. *J. Hazard. Mater.* **2009**, *161*: 21-28.
- [41] Keshavarz, M. H. A New General Correlation for Predicting Impact Sensitivity of Energetic Compounds. *Propellants Explos. Pyrotech.* **2013**, *38*: 754-760.
- [42] Li, J.; Huang, Y.; Dong, H. Theoretical Calculation and Molecular Design for High Explosives: Theoretical Study on Polynitropyrazines and their N-Oxides. *Propellants Explos. Pyrotech.* **2004**, *29*: 231-235.
- [43] Yang, K.; Park, Y. H.; Cho, S. G.; Lee, H. W.; Kim, C. K.; Koo, H. J. Theoretical Studies on the Formation Mechanism and Explosive Performance of Nitro-substituted 1,3,5-Triazines. *J. Comput. Chem.* **2010**, *31*: 2483-2492.
- [44] Wang, R.; Xu, H.; Guo, Y.; Sa, R.; Shreeve, J.M.J. Bis[3-(5-nitroimino-1,2,4-triazolate)]-based Energetic Salts: Synthesis and Promising Properties of a New Family of High-density Insensitive Materials. *J. Am. Chem. Soc.* **2010**, *132*: 11904-11905.
- [45] Wang, G.; Xiao, H.; Ju, X.; Gong, X. Calculation of Detonation Velocity, Pressure, and Electric Sensitivity of Nitro Arenes Based on Quantum Chemistry. *Propellants Explos. Pyrotech.* **2006**, *31*: 361-368.
- [46] Licht, H.-H. Performance and Sensitivity of Explosives. *Propellants Explos. Pyrotech.* **2000**, *25*: 126-132.
- [47] Politzer, P.; Murray, J. S. High Performance, Low Sensitivity: Conflicting or Compatible? *Propellants Explos. Pyrotech.* **2016**, *41*: 414-425.

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