Novel High-Nitrogen Content Energetic Compounds with High Detonation and Combustion Performance for use in Plastic Bonded Explosives (PBXs) and Composite Solid Propellants

**Mohammad Hossein Keshavarz,[1,*] Yasin Hayat Abadi,[1]
Karim Esmaeilpour,[1] Sajjad Damiri,[1] Mohsen Oftadeh[2]**

[1] *Malek-ashtar University of Technology,
83145/115 Shahin-shahr, Islamic Republic of Iran*

[2] *Chemistry Department, Payame Noor University,
19395-4697 Tehran, Islamic Republic of Iran*

E-mail: keshavarz7@gmail.com

Abstract: Five novel high-nitrogen content (N>50%) derivatives of tetrazole are introduced in the study reported here. The assessment of various properties of these compounds were performed, which include physicothermal properties (crystal density, condensed phase heat of formation, melting point, enthalpy of fusion and entropy of fusion), detonation performance (velocity and pressure of detonation, detonation temperature and power), sensitivity with respect to external stimuli (impact, shock, friction and electric spark) and combustion performance (specific impulse). The predicted results of these compounds are compared with dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50) and octanitro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) as a high performance ionic salt and a neutral explosive, respectively. The novel energetic compounds were found to have higher detonation and combustion performance than either TKX-50 or HMX. The new explosives are therefore good candidates to obtain high detonation and combustion performance in plastic bonded explosives (PBXs) and composite solid propellants, respectively.

1   Introduction

Nitrogen-rich energetic compounds are important for the explosives industries and users in recent years because they have suitable safety [1], detonation and combustion performances [2], oxygen balances [3], thermochemical properties [4] and high nitrogen content [5]. But the synthesis of these compounds is very costly and time-consuming [6, 7]. Thus, it is important to introduce new candidates and perform assessments of various important properties before their synthesis. Tetrazole energetic derivatives are one of the important categories of nitrogen-rich compounds because they have high detonation/combustion performance [4, 8, 9], are high-energy density compounds (HEDMs) and have high positive heats of formation (HOFs) [10-12]. The properties of some tetrazoles and tetrazolate ions have been predicted using suitable methods recently [13, 14]. The properties of some tetrazole compounds with two identical tetrazole rings have also been studied using the EXPLO5 code [15, 16]. Tetrazole salts such as hydroxyl ammonium 2-dinitromethyl-5-nitrotetrazolate (HADNMNT) and dihydroxyl ammonium 5,5'-bistetrazole-1,1'-diolate (HATO) can be used as energetic ingredients for rocket propulsion [17]. Dihydroxyl ammonium 5,5'-bistetrazolate-1,1'-diolate (TKX-50) is one of the famous bistetrazolate ions that can be synthesized using glyoxime [18], 5,5'-bistetrazole-1,1'-diole isolated, oxidation of 5,5'-bistetrazole and *via* cyclization of diazidoglyoxime [19].

The purpose of this study was to introduce several neutral tetrazole HEDMs with high detonation/combustion performance, *i.e.* the compounds **1** to **5** shown in Figure 1. New and reliable methods are used to predict their detonation and combustion performance as well as their thermodynamic and other physical properties. The sensitivities of these compounds with respect to different types of stimulus were also evaluated, *i.e.* impact, shock, friction and spark sensitivity. The crystalline densities of compounds **1** to **5** were computed quantum mechanically. To confirm the reliability of the methods used, a comparison of the predicted properties was made with TKX-50 and octanitro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), a high performance ionic salt and a neutral energetic compound, respectively.
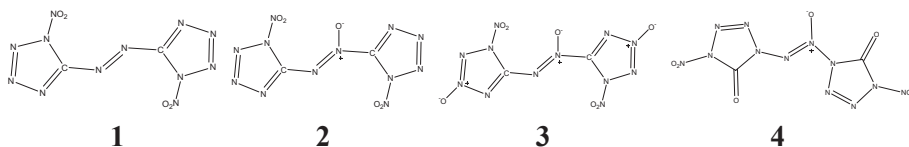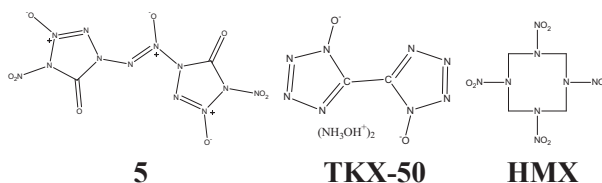
Figure 1.   Molecular structures of new tetrazole derivatives as well as TKX-50 and HMX

2   Results and Discussion

2.1 Crystal density

Crystal density is an important parameter for the assessment of the detonation performance of a desired energetic compound. For the computation of the crystalline densities of compounds **1** to **5**, the quantum mechanical method of Rice and co-workers [20] (whose basis is the B3LYP/6-31G(d,p) level of theory implemented using Gaussian-09 software package [20, 21]) was used:

$$\rho = \alpha_1(M/V_M) + \beta_1(v\sigma^2_{tot}) + \gamma_1 \tag{1}$$

where: ρ, M, V_M, v and σ^2_{tot} are the crystal density of the energetic compound in g/cm^3, the molecular mass in g/molecule, the molecular volume in cm^3/molecule, the electrostatic balance parameter and the total variance of the electrostatic potential on the 0.001 a.u. molecular surface, respectively. The parameters α_1, β_1, and γ_1 are coefficients (details of their computations are given elsewhere [20]). As may be seen in Table 5, replacement of the ($\underset{\text{N}}{\overset{\text{O}}{=}}$) group by (—N$=$N—) between two cycles as well as its introduction into the tetrazole cycle can increase the crystal density of energetic compounds.

2.2 Condensed phase heat of formation

The condensed phase heat of formation (HOF) is a measure of the heat releasing capacity of an energetic compound, and can be predicted on the basis of the following correlation for high-N materials with the empirical formula of C$_a$H$_b$N$_c$O$_d$ using:

$$\Delta_f H^\theta(c) = 39.24a - 40.01b + 83.63c - 49.61d + 115.5(\Sigma IF) - 177.4(\Sigma DF) \tag{2}$$

where $\Delta_f H^\theta(c)$ is the condensed phase HOF in kJ/mol; DF and IF are decreasing and increasing structural parameters, respectively [22]. The value of $\Delta_f H^\theta(c)$ for

compound **1** is larger than the values of the other compounds because it has the least contribution of negative coefficients.

2.3 Melting point

A suitable correlation for the prediction of the melting points of nitramines is given as follows:

$$T_m = 220.47 + 30.220c + 24.780d - 68.691C_{SFG} - 25.891n_{N\text{-}NO2} \tag{3}$$

where T_m is the melting point in K; C_{SFG} is the contribution of specific functional groups, $n_{N\text{–}NO2}$ the number of nitramine groups in the energetic compound [23]. Compound **5** has the highest melting point, which may be due to its high oxygen content.

2.4 Enthalpy of fusion

The enthalpy of fusion can be calculated for any energetic compounds with general formula $C_aH_bN_c(O \text{ or } S)_d(\text{halogen})_e$ using:

$$\Delta H_{fus} = 0.542a + 1.490b + 2.044c + 1.252d + 1.839e + 9.848\Delta H_{Inc,fus} - 675\Delta H_{Dec,fus} \tag{4}$$

where ΔH_{fus} is the enthalpy of fusion in kJ/mol; the values of $\Delta H_{Inc,fus}$ and $\Delta H_{Dec,fus}$ are two correcting parameters [24]. As for the melting point, compound **5** has the highest value of ΔH_{fus} compared to the other new compounds.

2.5 Entropy of fusion

The entropy of fusion is an important property for the prediction of the solubility and melting points of organic compounds [25]. It can be estimated using:

$$\Delta_{fus}S = 39.99 + 5.88c + 1.22d - 23.86\Delta_{fus}S_{non\text{-}add} \tag{5}$$

where $\Delta_{fus}S$ is the entropy of fusion in J/K·mol and $\Delta_{fus}S_{non\text{-}add}$ is a non-additive correcting function [26]. The predicted entropies of fusion for compounds **1** to **5** are given in Table 1, which are consistent with the predicted results for T_m and ΔH_{fus}.

Table 1. Comparison of various properties of the tetrazole derivatives 1 to 5 with corresponding calculated and experimental values of TKX-50 and HMX

Property	1	2	3	4	5	TKX-50[a]	HMX[a]
Molecular formula	$C_2N_{12}O_4$	$C_2N_{12}O_5$	$C_2N_{12}O_7$	$C_2N_{12}O_7$	$C_2N_{12}O_9$	$C_2H_8N_{10}O_4$	$C_4H_8N_8O_8$
Molecular weight	256.1	272.1	304.1	304.1	336.1	236.15	296.155
Oxygen Balance	0	5.88	15.78	15.78	23.80	-27.10	-21.61
Nitrogen percent	65.65	61.79	55.28	55.28	50.02	59.3	18.51
Crystal density [g/cm^3]	1.897	1.930	2.000	1.970	2.002	-1.877[19]	1.95 (1.89 [39])
Condensed phase heat of formation [kJ/mol]	1114.6	1065.0	965.8	540.01	440.79	396.26 (439 [40])	79.1 [41]
Melting point [K]	630.4	655.2	704.8	704.8	754.3	~500 [40]	556.91 (548 [41])
Enthalpy of fusion [kJ/mol]	30.62	31.87	34.38	34.38	36.88	38.45 (38.5 [40])	28.78 (32.1 [42])
Entropy of fusion [kJ/mol]	115.43	116.65	119.09	119.09	121.53	-	61 (58.3 [41])
Velocity detonation [km/s]	9.86	10.11	10.64	9.67	10.03	9.65 (9.19 [40], 9.698 [19])	9.16 (9.1 [43])
Detonation pressure [kbar]	435.95	458.60	508.23	441.95	471.35	418.95 (424 [19])	393.6 (390 [44])
Detonation temperature [K]	5808	5724	5554	5554	5385	3724 (3954 [19])	4406 (4300 [44])
$EP_{BM(\%TNT)}$	151	154	161	161	169	-	144 (150 [45])
$EP_{Trauzl(\%TNT)}$	180	187	200	169	182	140	129 (153 [46])
Impact sensitivity [cm]	6.39	5.30	3.86	3.86	2.98	-81.57 [19]	21.72 (29 [47])
Shock sensitivity 98% [kbar]	16.87	14.65	10.23	10.23	5.81	-	21.29 (17.49 [48])
Friction sensitivity [N]	89.42	80.92	66.61	66.61	55.02	-120 [19]	156.09 (154.4 [35])
Spark sensitivity [J]	6.71	6.06	5.32	5.32	4.90	-	2.65 (2.89 [49])
Specific impulse [N·s/g]	2.860	2.900	2.980	2.69	2.77	-2.56 [19]	-2.614 [50]

[a] Experimental values and corresponding references of different properties of TKX-50 and HMX are given in parentheses.

2.6 Specific impulse

The specific impulse can be used for the assessment of the combustion performance of the new compounds as monopropellants added to composite propellants to attain higher combustion performance, which can be predicted [27] by:

$$I_{sp} = 2.425 - 0.074a - 0.0036b + 0.0237c + 0.04d - 0.1001n_{NHx} - 0.1466(n_{Ar}-1) \tag{6}$$

where I_{sp} is in N·s·g^{-1}; n_{NHx} and n_{Ar} are the number of $-NH_2$ or $-NH$ groups and aromatic rings respectively [27]. A low value of a and the absence of hydrogen atoms and $-NH_x$ groups can increase I_{sp}. Among these compounds, compounds **1**, **2** and **3** are desirable due to high values of I_{sp}.

2.7 Detonation velocity and pressure

Detonation velocity and pressure are two important detonation performance parameters which can be predicted [28, 29] using:

$$D = 1.453\, I_{sp}\, \rho_0 + 1.98 \tag{7}$$
$$P = 44.4\, I_{sp}\, \rho_0{}^2 - 21 \tag{8}$$

where D is the detonation velocity in km/s; P is the detonation pressure in kbar and ρ_0 is the loading density in g·cm^{-1}. All of the new compounds have higher detonation performance than TKX-50 and HMX.

2.8 Detonation temperature

A suitable correlation has recently been introduced to estimate the detonation temperature of different classes of high explosives as follows:

$$T_{det} = 5136 - 190.1a - 56.4b + 115.9c + 148.4d - 466.0(d/a) - \\ 700.8(b/d) - 282.9n_{NHx} \tag{9}$$

where T_{det} is detonation temperature in K [30]. The values of T_{det} for the new compounds are higher than TKX-50 and HMX because there is no hydrogen to form water and also a good oxygen balance.

2.9 Assessment of power by ballistic mortar and Trauzl lead block

Two correlations were used to assess the power of the energetic compounds relative to 2,4,6-trinitrotoluene (TNT) using the ballistic mortar and Trauzl lead

block tests as follows:

$$EP_{BM(\%TNT)} = 113 - 5.16CEC - 46.18OCF \tag{10}$$
$$EP_{Trauzl(\%TNT)} = 373.2 - 6525(a/Mw) - 5059(c/Mw) + 21.74(\Delta_f H^0(c)/Mw) \tag{11}$$

where $EP_{BM(\%TNT)}$ and $EP_{Trauzl(\%TNT)}$ are the explosive powers measured using the ballistic mortar and Trauzl lead block tests, respectively; Mw is the molecular weight of the desired energetic compound; OCF is the correcting function and CEC is equal $a - 0.54c - 0.70d$ [31, 32]. The predicted powers for all the new compounds are higher than for TKX-50 and HMX.

2.10   Impact sensitivity

A new correlation has been developed for the prediction of the impact sensitivity of a wide range of different classes of energetic compounds as follows:

$$\log H_{50} = -0.584 + 61.62a/Mw + 21.53b/Mw + 27.96c/Mw +$$
$$84.47F^+/Mw - 147.1F^-/Mw \tag{12}$$

where H_{50} is the impact sensitivity in cm for a drop weight of 2.5 kg, and F^- and F^+ are two correcting parameters [33]. The predicted results show a high sensitivity for the new compounds. Thus, coating these compounds with appropriate polymers (*e.g.* by hydroxyl-terminated polybutadiene (HTPB) in plastic bonded explosives (PBXs) and composite solid propellants) provides a suitable pathway for decreasing the sensitivity of these compounds with respect to impact stimulus.

2.11   Shock sensitivity 98%

It is possible to calculate the shock sensitivity of the new compounds using a standard small-scale gap test as follows:

$$P_{98\%TMD} = 25.449 + 2.2106(a+b/2-d) - 4.1620E^0_{NNO2} +$$
$$46.392(1.93n_{NH2} - n_{NO2})_{pure} \tag{13}$$

where $P_{98\%TMD}$ is the pressure in kbar that is required to initiate material pressed to 98% of the theoretical maximum density (TMD); n_{NH2} and n_{NO2} are the number of amino and nitro groups, respectively; E^0_{NNO2} equals 1.0 for nitramine or α-C-H linkage in nitroaromatic compounds [34]. Since the shock sensitivities of the new compounds are less than HMX, the coating of these compounds by suitable polymers can improve the safety of these compounds.

2.12   Friction sensitivity

Due to the presence of nitramine groups in these compounds, the assessment of the friction sensitivity of these compounds should be considered using the following relation:

$$FS = 600.8 - 2428.6(b/Mw) - 6481.4(c/Mw) - 9560.9(d/Mw) + 54.5P_{FS}^+ - 77.8P_{FS}^- \tag{14}$$

where FS is the friction sensitivity in N; P_{FS}^+ and P_{FS}^- are two correcting functions for the friction sensitivity [35]. The same as impact and shock sensitivities, friction sensitivities of the new compounds are less than both HMX and TKX-50. Thus, the coating of these compounds by suitable polymers such as HTPB can increase safety of these compounds.

2.13   Spark sensitivity

For the prediction of the spark sensitivity of compounds **1** to **5** with respect to electric spark stimuli, the following correlation can be used:

$$E_{ES} = 3.460 + 6.504(a/d) - 4.059 C_{CH2NNO2>3,C(=O)(O\ or\ NH)} \tag{15}$$

where E_{ES} is the spark sensitivity in J; $C_{CH2NNO2>3,C(=O)(O\ or\ NH)}$ indicates the existence of methylene nitramine groups (the number being greater than or equal to 3) in cyclic nitramines or the presence of COO or CONH functional groups [36]. Fortunately, the predicted E_{ES} of the new compounds are greater than HMX. Thus, the electric spark sensitivity of these compounds is lower than HMX.

3   Conclusion

The properties of several new tetrazole derivatives were evaluated and compared with TKX-50 (a high performance ionic salt) and HMX (a neutral energetic compound). Since these tetrazole compounds have high densities and condensed phase heats of formation, their detonation performance is higher than TKX-50 and HMX. Moreover, high positive values for the condensed phase heats of formation as well as good oxygen balance give the tetrazoles higher values of specific impulse than TKX-50 and HMX. Therefore, these compounds are good candidates for use as oxidizers in composite solid propellant formulations. The calculated values of the impact, shock and friction sensitivities of the tetrazoles investigated are lower than the corresponding values for HMX. Thus, they are

more sensitive with respect to the external mechanical stimuli impact, shock and friction. For their applications as high explosives and oxidizers in composite propellants, higher safety is required. Coating of these compounds with polymers such as is done for HMX in PBX-9501 and PBX-9011 [37] should reduce their sensitivities because PBXs were originally developed to reduce the sensitivity of newly-synthesized explosive crystals by embedding them in a rubber-like polymeric matrix [38]. Thus, coating of these explosives with suitable polymers such as HTPB should improve the safety of these compounds in composite solid propellants or PBXs.

Acknowledgements

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