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Crystal structure and Improved synthesis of 1-(2*H*-tetrazol-5-yl)guanidium nitrate

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Abstract:

Energetic derivatives of tetrazoles are one of the key areas of research focus in pursuit of novel high energy materials, useful as propellants and explosives. The present work reports the crystal structure and an improved synthetic procedure of 1-(2*H*-tetrazol-5-yl)guanidine (**1**) and its nitrate salt (**2**). The synthesized compounds were structurally characterized by spectroscopic {FT-IR, NMR (¹H & ¹³C)} and elemental analysis. The molecular structure of tetrazolyl guanidium nitrate (**2**) was solved using low temperature single crystal X-ray diffraction. **2** crystallized as its hemihydrate in the orthorhombic space group Fdd2, with a crystal density of 1.69 g cm⁻³. Thermal behavior and decomposition of the molecules were studied using differential scanning calorimetry (DSC). Molar enthalpy of formation ($\Delta^f H_m$) of (**2**) was back calculated from heat of combustion ($\Delta_c H^0$) value obtained experimentally using bomb calorimetric measurements. Lattice enthalpy of 1-(2*H*-tetrazol-5-yl)guanidium nitrate was directly calculated from measured crystal density using Jenkins equation. Preliminary ballistic parameters of the compound was predicted and compared with reported high nitrogen tetrazole derivatives.

Keywords: Tetrazolyl guanidium nitrate, Molecular structure, Lattice enthalpy, EXPLO5

1. Introduction

Over the past decade or so the field of ‘High-Energy Materials’, comprising of nitrogen rich molecules have developed as one of the interesting yet challenging topic for scientific community[1-4]. The present status of energetic materials has been achieved through rigorous experimentation and testing for novel materials with enhanced performance. The need for an environmentally benign energetic material has paved the way to look into nitrogen rich compounds as potential candidates, as the combustion of these materials liberates nitrogen as the major component. Five membered azoles, viz., triazoles, tetrazoles, and six membered azines, viz., tetrazines, triazines are the nitrogen rich molecules that have been the center of attraction for the targeted high energy materials [5-7]. In the context of better compromise between high energy output and stability, azoles, especially tetrazoles and the derivatives thereof have been the most explored group of molecules. Interest in high nitrogen energetic salts of azoles continues to

grow in pursuit of novel high energy density materials capable of delivering high impetus, specific impulse and detonation properties. Highly energetic ionic salts of these azoles have shown a lot of promise as futuristic energetic materials [8-10]. These salts having high lattice enthalpy can give rise to highly stable compounds without much dilution to its energy-density. In addition to the extra stability, these salts can offer highly symmetric crystal packing, highly valuable for the design of novel high performing materials. Especially ionic salts with planar oxidizing moieties like nitrate anions have shown to improve the crystal density as well as the oxygen balance, making them attractive monopropellant candidates [11-13]. Tetrazolyl guanidine and its nitrate salt have been explored as an effective propellant ingredient to prepare green energetic materials. The neutral molecule as well as the nitrate salt is thermo-chemically a coolant since both have negative OB. Although the molecule is known, no detailed synthetic methodology and structural characterization were reported [14-15].

The present study explains in detail the synthesis and characterization of, 1-(2*H*-tetrazol-5-yl)guanidine (**1**) and 1-(2*H*-tetrazol-5-yl)guanidium nitrate (**2**). In this work we report the synthesis, complete structural characterization and thermochemical analysis of the molecule. Structural characterization of the prepared compounds was done using spectroscopic methods and elemental analysis. The molecular structure and crystal density was determined from low temperature XRD data. The reported molecules showed good thermal stability, high N% and comparable densities, making them suitable candidates as green energetic materials.

2. Experimental

2.1 Materials and Methods

Cyanoguanidine (TCI, Tokyo) and sodium azide (Alfa Aesar) were used as received. All the solvents used were distilled prior usage. FT-IR spectra were recorded using pressed KBr pellets on a Shimadzu IR Prestige-21 spectrometer. Elemental analysis (C, H, N) were carried out on a EUROEA elemental analyzer. ¹H & ¹³C NMR spectra were recorded on a 300 MHz Bruker Avance Nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz respectively, using d₆-DMSO as the solvent and TMS as the internal standard. The chemical shifts in ppm are reported relative to TMS. Differential Scanning Calorimetry measurements were performed using a Labsys Setaram calorimeter equipped with a Huber circulating water cooler. The calorimeter was calibrated using low temperature and high temperature standards

(melting of pure metals) under nitrogen purging environment. DSC data was obtained by subjecting the sample and reference to a temperature scanning program from 50-500 °C at 10 °C min⁻¹. Bomb calorimetric measurements were performed on a Parr 6200 bomb calorimeter in 1108P oxygen bomb. The samples were burned inside the oxygen bomb pressurized to 3.2 MPa with extra pure oxygen. The constant volume energies thus determined were used to calculate standard molar enthalpies of formation ($\Delta^f H_m$). The calorimeter was calibrated by combustion of extra pure benzoic acid (supplied as standard) prior to usage. Single crystal XRD measurements were obtained from Bruker Kappa CCD diffractometer at low temperature.

2.2 Synthesis

1-(2H-tetrazol-5-yl)guanidine nitrate (2)

1.68 g (0.02mol) of cyanoguanidine was stirred well with 1.5 g (0.023 mol) [slight excess] of NaN₃ in 20 ml (3:1) ethanol:water solution at RT for 30 min. To this solution, 15ml of 2N HCl was added drop wise with stirring over 2 h at 60 °C. After the addition is complete the solution is refluxed for further 3 h. Overnight cooling of the clear solution yields off-white precipitate of 1-(2H-tetrazol-5-yl)guanidine, **1** with 67 % yield. mp: (DSC, 10 °C min⁻¹) 335 °C (endothermic peak dec. temp.). FTIR: (KBr) 3458 (m), 3423(w), 3296(w), 3122(w), 1716(m), 1685(vs), 1647(s), 1623(m), 1517(s), 1506(m), 1384(vs), 1340(s), 1188(m) cm⁻¹. ¹H NMR [D₆]-DMSO, ppm) δ = 7.83 (4H); ¹³C NMR (D₆-DMSO, ppm) δ = 159.91. Mol. Formula. C₂H₅N₇ (127.108 gmol⁻¹) Calc.% C 18.89, H 3.96, N 77.13; Expt. % C 18.5, H 3.7, N 77.0.

1-(2H-tetrazol-5-yl)guanidine, **1** prepared from the first step was treated with slight excess to equimolar quantity of 70 % nitric acid in methanol. The nitrate salt precipitated from the solution by stirring at 0 °C for 15 min. The solution was kept in fridge overnight to complete the precipitation. The nitrate salt was recrystallized from hot aqueous solution as colourless shiny flakes, suitable for XRD analysis. The yield was almost quantitative (~95 %) with respect to the first step. mp: (DSC, 10 °C min⁻¹) 191 °C (dec.). FTIR: (KBr) 3458 (m), 3423(w), 3296(w), 3122(w), 1716(m), 1685(vs), 1647(s), 1623(m), 1517(s), 1506(m), 1384(vs), 1340(s), 1188(m) cm⁻¹. ¹H NMR ([D₆]-DMSO, ppm) δ = 9.70 (2H, br), 8.01, 7.71(4H, br); ¹³C NMR ([D₆]-DMSO, ppm) δ = 155.66, 154.83. Mol. Formula. C₂H₇N₈O_{3.5} (199.16 gmol⁻¹) Calc.% C 12.63, H 3.18, N 58.94; Expt. % C 12.5, H 3.1, N 58.8.

3. Results and Discussion

3.1 Structural aspects

Tetrazolyl guanidine was reported to be prepared by two methods, viz, by the reaction of cyanamide and 5-amino tetrazole [16] and by cycloaddition of hydrazoic acid on dicyanamide. The former method results in the addition product, 1-(1*H*-tetrazol-5-yl)guanidine, whereas the latter leads to 2*H* derivative. The compound under investigation for the present study, **1** was first reported in Stolle's work on tetrazole compounds. The molecule was also mentioned in the Picatinny Arsenal project report on development of superior propellants, showing the importance of the compound as propellant ingredients (refer ref. 14, 15). Herein we report the crystal structure and improved synthetic procedure for the synthesis of 1-(2*H*-tetrazol-5-yl)guanidine (**1**) and 1-(2*H*-tetrazol-5-yl)guanidium nitrate (**2**) as shown in scheme 1. In this work the construction of tetrazole ring on dicyanamide was accomplished by 1,3- dipolar cycloaddition of HN₃ (*insitu* generated from NaN₃ in HCl solution) in alcoholic medium. Utilizing the concept of 'Click Chemistry' to synthesize energetic tetrazole derivatives have been one of the key areas of our research group [17]. 1-(2*H*-tetrazol-5-yl)guanidium nitrate (**2**) was prepared by protonating **1** using 70% nitric acid in methanol medium at 0 °C. The synthesized compounds were characterized for their structure using spectroscopic (FTIR, multinuclear NMR) and elemental analysis (C, H, N%). The ¹H & ¹³C NMR spectra were measured in [D₆] DMSO solvent with TMS as the internal standard. **1** showed only one single broad resonance peak at δ 7.83 ppm corresponding to the hydrogen atoms of the guanyl side chain, probably due to fast proton exchange in DMSO. But in the case of **2**, quaternation of the imino nitrogen on the guanyl side chain resulted in different resonance peaks for the hydrogen atoms at δ 9.70, δ 8.01 & δ 7.71 ppm respectively, probably due to the different chemical environment created by the presence of localized charge. ¹³C NMR showed resonance at δ 155.66 and δ 154.83 ppm corresponding to the tetrazolyl and guanyl carbon atoms.

< schr1>

3.2 Molecular Structure

Molecular structure of 5-guanyl tetrazole nitrate was determined from low temperature single crystal XRD analysis. Crystallographic and refinement data of **2** is listed in table 1. Complete list of bond angles, bond lengths, atomic co-ordinates and thermal displacement parameters can be obtained from ESI. X-ray quality crystals of 1-(2*H*-tetrazol-5-yl)guanidium nitrate, **2** was prepared from warm water via slow evaporation as its hemihydrate abbreviated as **2**. 0.5H₂O. The molecule crystallized in the orthorhombic space group Fdd2, with unit cell consisting of 16 molecules (including discrete units of cation, anion and water molecule) and cell volume of 3.131 nm³. **2**.0.5H₂O forms layered structure with highly symmetric crystal packing as evident from the figure 2. The planarity of tetrazolyl guanidium cation has resulted in the effective charge distribution among the amino groups of guanyl side chain, evidently supported by the similar N-C bond lengths (C1-N1 0.131 nm and C1-N2 0.132 nm).

< figr1>

The delocalized charges on the amino nitrogen are stabilized by H-bonding with the nitrate anion: N1-H1....O2, D-H = 0.086 nm, H...A = 0.208 nm, D-A = 0.294 nm, D-H-A = 176.5⁰; N2-H3....O3, D-H = 0.085 nm, H...A = 0.201 nm, D-A = 0.286 nm, D-H-A = 174.3⁰. The asymmetric unit of the compound showed comparatively strong hydrogen bonding with the water molecule: O1-H7....O2, D-H = 0.081 nm, H...A = 0.207 nm, D-A = 0.287 nm, D-H-A = 165.2⁰.

< figr2>

< tabr1>

3.3 Thermo-Chemical Studies

The thermal decomposition behaviour and energy of decomposition of **(1)** and **(2)** were assessed using Differential Scanning Calorimetric (DSC) measurements. Approximately 1mg of the respective compounds were subjected to a temperature scanning programme, heating the sample and reference from 50-500 °C, under dynamic nitrogen purging environment with a flow rate of 50 ml min⁻¹ in aluminium crucibles. The experiment was done at 10 °min⁻¹ heating rate with empty aluminium crucible as the reference. Both the compounds showed entirely different decomposition pattern, with the former decomposing endothermically whereas the latter showed sharp exothermic decomposition. **1** showed excellent thermal stability with endothermic decomposition happening only at 335 °C. **2** showed no melting on DSC and showed exothermic decomposition with a peak temperature of 191 °C corresponding to the deflagration temperature.

< figr3>

Constant volume combustion energy of **2** was experimentally calculated using a Parr bomb calorimeter. The total energy on combustion, $\Delta_c U$ inside an oxygen bomb was recorded to be - $1515 \pm 7 \text{ kJ mol}^{-1}$. The enthalpy of combustion was calculated from the relation, $\Delta_c H = \Delta_c U + \Delta nRT$, where ΔnRT is the correction factor for gas volume increase. The standard energies of formation ($\Delta_f H^0$) was back calculated from $\Delta_c H$, on the basis of the combustion relation eqn. (1), Hess's law eqn. (2) and the known standard heats of formation for H₂O_(l) and CO_{2(g)}. The calculated heat of formation value of **2** was -281.7 kJ mol⁻¹. Heat of combustion for 1*H* isomer of **1** was reported in literature [18].

$$\Delta_f H^0 (\text{TzGuNit, s}) = 2 \Delta_f H^0 (\text{CO}_2, \text{g}) + 3.5 \Delta_f H^0 (\text{H}_2\text{O, l}) - \Delta_c H^0 (\text{TzGuNit, s}) \quad (2)$$

The lattice enthalpy of Tetrazolyl guanidium nitrate was calculated directly from experimental density measurements using Jenkin's method [19, 20]. The lattice potential energy (U_{POT}) was calculated using equation (Eq. 3), where γ (1981.2 kJ mol⁻¹ cm) and δ (103.8 kJ mol⁻¹) are the coefficients appropriately fitted for salts with different stoichiometry, ρ_M (g cc⁻¹) is the density of the salt and M_m (g mol⁻¹) is the molecular mass of the ionic salt.

$$U_{\text{POT}} = \gamma(\rho_M/M_m)^{1/3} + \delta \quad (3)$$

Using the relation, the lattice energy of **2** was estimated to be +507 kJ mol⁻¹.

The corresponding lattice enthalpy, ΔH_L for the salt is derived from U_{POT} using the equation (Eq. 4), where n_M and n_X depends on the nature of the ions (n_M & n_X is equal to 6 for non-linear polyatomic atoms) and q & p represents the magnitude of charge on the positive and negative ion respectively.

$$\Delta H_L = U_{\text{POT}} + [p((n_M/2) - 2)) + q((n_X/2) - 2)]RT \quad (4)$$

Finally, the lattice enthalpy (ΔH_L) of **2** (1-(2*H*-tetrazol-5-yl)guanidium nitrate) was estimated as +512 kJ mol⁻¹.

The efficiency of **2** as a gas generator/propellant ingredient was predicted using EXPLO5 code [21] and compared with the values of reported high nitrogen tetrazole derivatives like Guanidium azotetrazolate (GZT) and triaminoguanidium azotetrazolate (TaGZT). In general, high nitrogen tetrazole derivatives can be used as effective cool gas generators, owing to the low adiabatic flame temperature during isobaric combustion. The higher percentage of nitrogen gas among the combustion products greatly reduces the flame temperature.

<tabr2>

In the case of the targeted molecule 1-(2*H*-tetrazol-5-yl)guanidium nitrate, the combustion temperature (T_f) predicted at 7.0 MPa is 1340 K which is considerably lower when compared to TaGZT and comparable with that of GZT. The better oxygen balance of **2** increased the gas yield (V_g) and less condensibles during combustion. The table 2, compares the combustion parameters simulated for **2**, GZT and TaGZT.

4. Conclusions

The present study discusses in detail the crystal structure and modified synthetic procedure of 1-(2*H*-tetrazol-5-yl)guanidium nitrate, a promising candidate as monopropellant ingredient for cool gas generators. The investigated compound, 1-(2*H*-tetrazol-5-yl)guanidium nitrate (GuTzNit) was synthesized in good yield and purity via, 1,3-dipolar cycloaddition of cyanoguanidine. The structure of the molecule was unequivocally established using low temperature X-ray diffraction measurements. The prepared molecules were fully characterized using spectroscopic (IR, Raman, NMR) as well as analytical methods (elemental analysis). The thermogram of 1-(2*H*-tetrazol-5-yl)guanidium nitrate showed single stage exothermic decomposition with peak temperature of 191⁰C, showing relatively good thermal stability. The enthalpy of formation the molecule was determined using both theoretical and experimental methods. The molar enthalpy of formation (-281.7 kJ mol⁻¹) of the molecule was experimentally determined from combustion energy obtained from bomb calorimetric measurements. Preliminary understanding of the molecule as propellant ingredient/ gas generator was predicted using EXPLO5 code. The traits like better oxygen balance, low flame temperature and high gas yield makes 1-(2*H*-tetrazol-5-yl)guanidium nitrate worthy of further consideration as ‘Cool Gas’ generator or as propellant ingredient for space, military and civilian applications.

Supporting Information Available: Spectroscopic and Crystallographic data results. An X-ray crystallographic file (CIF, CCDC 1010920)

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Table: 1 Crystal data and refinement of 1-(2*H*-tetrazol-5-yl)guanidium nitrate hemihydrate

Crystal data	2.0.5 H ₂ O
Empirical Formula	C ₂ H ₇ N ₈ O _{3.50}
Formula weight	199.16
T, K	113(2)
λ , Mo K α , nm	0.071073
Crystal system	Orthorhombic
Space group	Fdd2
a, nm	10.6318(7)
b, nm	41.095(2)
c, nm	7.1680(4)
V, nm ³	3.1318(3)
Z	16
ρ , g cm ⁻³	1.690
μ , mm ⁻¹	0.152
F(000)	1648
Crystal size, mm ³	0.40 x 0.40 x 0.06
Theta range for data collection, °	1.98 to 28.28
Reflections collected	11783
Independent reflections	1048 [R(int) = 0.0350]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9909 and 0.9416
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1048 / 16 / 151
Goodness-of-fit on F2	1.124
Final R indices [σ]	R1 = 0.0257, wR2 = 0.0641
R indices (all data)	R1 = 0.0270, wR2 = 0.0720

Table: 2 Comparison of predicted combustion parameters of $2.0.5\text{H}_2\text{O}$ with high nitrogen tetrazole derivatives

Properties	$2.0.5\text{H}_2\text{O}$	GZT	TaGZT
Mol. Formula	$\text{C}_2\text{H}_7\text{N}_8\text{O}_{3.5}$	$\text{C}_4\text{H}_{12}\text{N}_{16}$	$\text{C}_4\text{H}_{18}\text{N}_{22}$
OB ^a , [%]	-32.1	-78.8	-72.6
ΔH_f ^b [kJ mol ⁻¹]	-281	+410	+1075
T _f ^c [K]	1340	1261	1807
V _{Tf} ^d [L kg ⁻¹]	1176.1	1145.8	1313.7
V _g ^e [L kg ⁻¹]	1055.8	1030.2	1229.7
Av. M _m ^f [g]	21.3	17.81	15.85
M _{cond.} ^g [g]	28.2	77.1	83.7
Isp, ^h [s]	183.7	173.6	216.8

- a) Oxygen balance (CO_2)
- b) Molar enthalpy of formation
- c) Isobaric combustion temperature
- d) Volume of gaseous products at combustion temperature
- e) Volume of gaseous products at nozzle throat
- f) Mean average molecular mass of combustion products
- g) Mass of condensible products at 0.1 MPa
- h) Specific impulse at atmospheric pressure (equilibrium expansion)

Figure Captions

Figure 1. Asymmetric unit of 1-(2*H*-tetrazol-5-yl)guanidium nitrate hemihydrate (Thermal ellipsoid at 50% probability) showing H-bonding.

Figure 2. Unit cell lattice of GuTz.HNO₃.½ H₂O along the b-axis showing the symmetric packing of discrete ions of the salt.

Figure 3. Differential scanning calorimetric thermograms of **1** & **2** subjected to a heating profile of 50-500 °C at 10 °C min⁻¹

Scheme 1. Synthesis of 1-(2*H*-tetrazol-5-yl)guanidine and its nitrate salt

Figure 1

Figure 2

Figure 3

Scheme 1