

# 1-(2*H*-Tetrazolyl)-1,2,4-triazole-5-amine (TzTA) – A Thermally Stable Nitrogen Rich Energetic Material: Synthesis, Characterization and Thermo-Chemical Analysis

Sasidharan Nimesh<sup>\*[a]</sup> and How-Ghee Ang<sup>[a]</sup>

**Abstract:** The targeted high nitrogen energetic material 1-(2*H*-tetrazol-5-yl)-1,2,4-triazol-5-amine (TzTA) was synthesized from 3-amino-1,2,4-triazole via a two-step procedure using cyanogen bromide and sodium azide. TzTA was prepared in good yields and characterized using analytical (elemental) and spectroscopic (IR, Raman, NMR) techniques. The crystal structure of sulfate salt of the molecule was solved by means of low temperature X-ray crystallography, which showed the co-planarity of the two rings. The sulfate salt of the molecule crystallized in monoclinic system *P*21/*n*, with a crystal density of 1.856 g cm<sup>-3</sup>. The thermal stability of the molecule was assessed by DSC. The molecule

showed excellent thermal stability better than many known nitrogen rich energetic molecules and showed comparable thermal stability with HMX. Non-isothermal kinetics was performed on the molecule to derive the activation energy. Constant volume combustion energy was determined using oxygen bomb calorimeter and back calculated the heat of formation. Preliminary insight on the gas generating capability of the molecule was tested by measuring the dynamic pressure generated inside a closed bomb. Dynamic pressure of an oxygen balanced system (TzTA and ADN) was also measured using the Parr dynamic pressure measurement system.


**Keywords:** High nitrogen content • P–t analysis • Non-isothermal kinetics • Explo5

## 1 Introduction

Syntheses of nitrogen containing heterocycles as energetic molecules [1–5] have received considerable attention over the last decade. The recent approach of opting for the nitrogen rich heterocycles, when compared to their carbon analogues, is owing to the inherent high energy-density as well as due to the environmentally benign decomposition products. These nitrogen-rich heterocyclic compounds derive most of their energy from the higher positive heat of formation rather than from the oxidation of carbon backbone. Energetic tetrazoles, tetrazolates and tetrazolium salts are of primary interest in the development of new stable and less sensitive energetic materials. Literature presents with many references of energetic derivatives of triazoles and tetrazoles [6–9] and a few of them have been studied for their application as gas generators, propellant additives and as double base gun propellants. Attributes such as thermal stability and density are key factors in determining the suitability of these molecules as replacements for the existing carbon rich energetic molecules. Among the reported high nitrogen compounds, like salts of azotetrazolates, e.g. GZT, TAGZT [10,11], not many has good thermal stability and better density, to make them potential replacements for existing traditional energetic materials. The two novel triazolyl tetrazoles reported recently, viz, ATT [12] and TATT [13] showed better thermal stability, but the density seems to be lower. The targeted

compound, 1-(2*H*-tetrazolyl)-1,2,4-triazolyl-5-amine (TzTA) was prepared and characterized for the first time, employing a convenient, safer synthetic protocol. The concept of click chemistry was used to create the tetrazole ring on to the amino triazole moiety. Various methods are reported for the efficient synthesis of tetrazole ring, mainly through addition of azide ion on nitriles, under a variety of environments. The reported methods to affect this transformation fall into three main categories; those that make use of heavy metal or silicon azides, those that use strong Lewis acids and those that run in acidic media [14–17]. Here in we report the cycloaddition of nitrile with azide to tetrazole rings [18,19], by using NaN<sub>3</sub> in acidic solution. This process is advantageous in avoiding the usage of heavy metal azides, toxic and explosive HN<sub>3</sub> and metal catalysts.

[a] S. Nimesh, H.-G. Ang  
Energetics Research Institute  
Nanyang Technological University  
N1-B4a, 50 Nanyang Avenue  
Singapore 639798, Singapore  
\*e-mail: nsasidharan@ntu.edu.sg

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## 2 Experimental

**Caution:** Although we have not experienced any safety issues in handling or during synthesis of the reported compounds, tetrazoles are energetic materials capable of decomposing/deflagrating under external stimuli. Hence appropriate safety precautions should be taken at all times while manipulating these compounds.

### 2.1 General Methods

The reagents, 3-amino-1,2,4-triazole,  $\text{NaN}_3$  (Alfa Aesar) and CNBr (Sigma Aldrich), and solvents were pure analytical grade materials and were used without further purification. FT-IR spectra were recorded using pressed KBr pellets on a Shimadzu IR Prestige-21 spectrometer. FT-Raman spectra were recorded using a Renishaw Invia-Raman with integrated microscope enabling high resolution confocal measurements, with a laser diode (785 nm). Elemental analysis (C, H, N) were carried out on a EUROEA elemental analyzer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a 300 MHz Bruker Avance Nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz respectively, using  $\text{DMSO}-d_6$  as the solvent and TMS as the internal standard. The chemical shifts in ppm are reported relative to TMS. Density was measured using a Micrometrics Accupyc 1330 V2.04N gas pycnometer at  $27^\circ\text{C}$ . Differential Scanning Calorimetric 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  $50$ – $500^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$ . Bomb calorimetry measurements were performed on a Parr 6200 bomb calorimeter using a 1108P oxygen bomb. The samples were burned inside the oxygen bomb pressurized to  $3.2\text{ MPa}$  with pure oxygen. Theoretical predictions were performed using the Gaussian 09 quantum chemistry package and explosive parameters were computed using EXPLO5 thermodynamic code. Kinetic analysis of the compounds was done by the method of Kissinger and Ozawa, using differential heating rate method, as per the ASTM standard [20]. Energy of activation was calculated from the peak values of exothermic decomposition peaks from DSC thermogram. Experiments were carried out from  $50$ – $400^\circ\text{C}$  at different heating rates of  $\beta = 2, 4, 6, 8$ , and  $10^\circ\text{C}$ . The rate constant for the solid state decomposition was assumed to follow the Arrhenius rate law, and the first stage exothermic decomposition reaction is used to calculate the kinetic parameters, considering it as a single step. In the present study activation energies were computed using the logarithmic relations coined by Kissinger [21] and Ozawa [22]. The calculated activation energy from Ozawa relation was refined as per the ASTM procedure. The simplified form of Ozawa (refined form) and Kissinger relations used for acti-

vation energy calculation are given in Equation (1) and (2).

$$E_a = -2.303 \frac{R}{D} [d \log_{10} \beta / d(1/T)] \quad (1)$$

$$E_a = -R [d \ln(\beta / T p^2) / d(1/T)] \quad (2)$$

### 2.2 Synthesis of TzTA

#### 2.2.1 1-(2H-tetrazol-5-yl)-1H-1,2,4-triazol-5-amine (TzTA)

CNBr (2.12 g, 0.02 mol) was pulverized and added in parts to a ethanol solution (3 : 1 ethanol : water) of 3-amino-1,2,4-triazole (1.68 g, 0.02 mol) at  $10^\circ\text{C}$ . The slurry was stirred to dissolve the reagents and slowly heated to  $40^\circ\text{C}$ . The clear solution yields white precipitate on stirring at  $40^\circ\text{C}$  for 45 min. The slurry was stirred for another 1 h to complete the precipitation. The white compound was filtered and washed with water and dried. The filtrate was kept overnight at room temperature to collect the second crop of precipitate. Yield: white solid, 1.60 g (73%). The cyano derivative (2.18 g, 0.02 mol) and  $\text{NaN}_3$  (1.3 g 0.02 mol) were taken up in an ethanol solution (10 mL, 3 : 1) at room temp. and slowly heated to  $60^\circ\text{C}$ . To the well stirred solution, 2 N HCl (15 mL) was added drop wise over a period of 1 h and the temperature was slowly increased to reflux temperature. The clear solution was heated to reflux for another 3 h and cooled overnight. The off-white precipitate of TzTA separated from the solution. The precipitate was filtered off and washed with hot water. Recrystallization from acidic solution yielded colorless microcrystals. Yield: off-white solid, 1.70 g (56%).  $\text{C}_3\text{H}_4\text{N}_8$  calcd: C 23.69, H 2.65, N 73.68; found: C 23.98, H 2.80, N 73.62. FTIR (KBr),  $\tilde{\nu} = 3380, 3284, 3137, 3097, 1866, 1683, 1569, 1490, 1458, 1419, 1380, 1186, 1112, 1047, 908, 732, 632, 567, 532, 435\text{ cm}^{-1}$ . Raman (785 nm,  $27^\circ\text{C}$ ): 1579, 1453, 1235, 1058,  $761\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , ppm):  $\delta = 7.87$  (s, 1 H), 7.49 (br., 2 H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ , ppm):  $\delta = 155.45, 152.88, 151.96$ .  $\Delta_{\text{comb}} U$ :  $-2116 \pm 5\text{ kJ mol}^{-1}$ .

**Supporting Information** (see footnote on the first page of this article): Crystallographic data, Spectroscopic data and ab initio calculation results. An X-ray crystallographic file (CIF, CCDC-1010919)

## 3 Results and Discussion

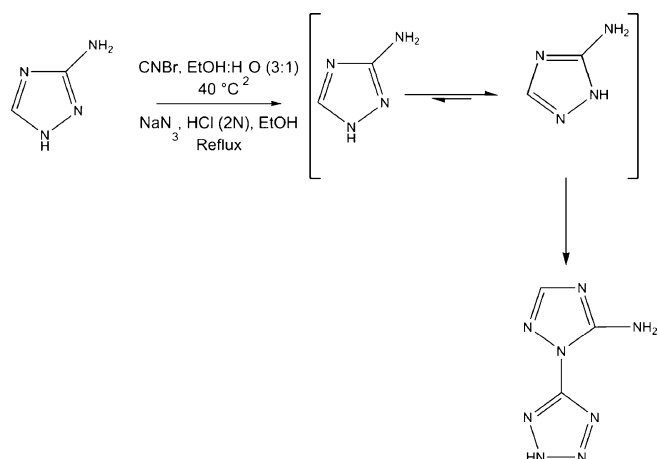
### 3.1 Synthesis and Characterization

A two-step process involves the synthesis of TzTA from 3-amino-1,2,4-triazole. Pulverized CNBr was slowly added to an ethanol solution of 3-amino-1,2,4-triazole at room temperature and slowly heated to  $40^\circ\text{C}$  resulting in the precipitation of the possible cyano derivative of triazole. The obtained precipitate was filtered off dried and used as such for the next step to convert to the tetrazole derivative. TzTA was obtained in high purity and good yields and was characterized for its structure by spectroscopic (IR, Raman,

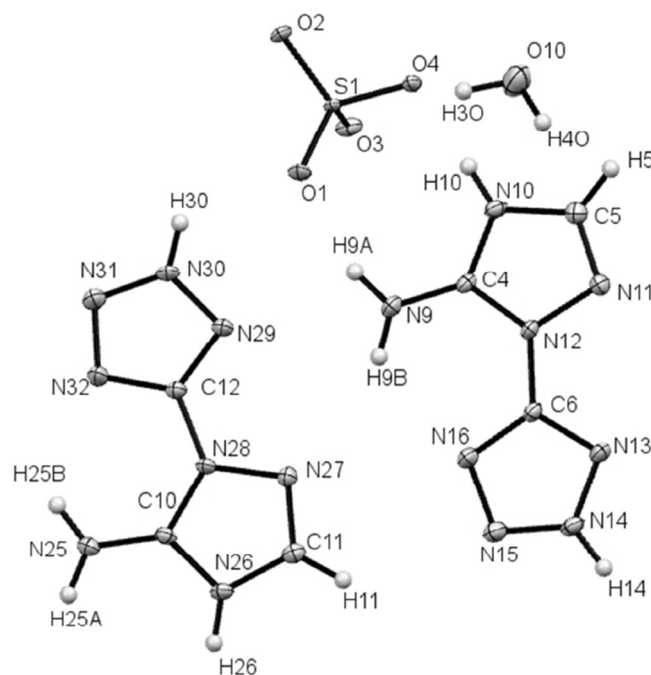
NMR) and elemental analysis. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured in  $\text{DMSO-}d_6$  solvent. The broad resonance peak at  $\delta = 7.49$  ppm in  $^1\text{H}$  spectrum corresponds to the amino group in the triazole ring. The de-shielding of the resonance peak may be due to the electronic effects of the tetrazole ring. The three chemically different carbon atoms in the molecule showed resonance at  $\delta = 155.45$ , 152.88, and 151.96 ppm, respectively. The carbon atom on the tetrazole ring is the most de-shielded and resonated at  $\delta = 155.45$  ppm downfield from TMS. As expected the carbon atoms on the triazole ring were less de-shielded and resonated at  $\delta = 152.88$  and 151.96 ppm, respectively. Vibrational spectroscopy, like IR and Raman spectral analysis, proved an essential tool in the qualitative analysis of the molecule, especially the tetrazole formation. FT-IR spectrum revealed absorption peaks at  $3097\text{ cm}^{-1}$  of the C–H group stretching (triazole ring) and  $3380$  and  $3280\text{ cm}^{-1}$  of N–H stretching modes of the primary amino group. Raman spectrum showed vibrational modes characteristic of tetrazole ring. TzTA showed stretching bands at  $1579\text{ cm}^{-1}$  ( $\text{C}_{\text{tet}}\text{--N--C}_{\text{triaz}}$ ),  $1453\text{ cm}^{-1}$  ( $\text{N}=\text{N}$ ),  $1235\text{ cm}^{-1}$  ( $\text{N--N}$ ),  $1058\text{ cm}^{-1}$  ( $\text{C--N--N}_{\text{ring str}}$ ) and  $761\text{ cm}^{-1}$  ( $\text{N--N}$  wagging)  $\text{cm}^{-1}$ .

### 3.2 Molecular Structure

The molecular structure of the molecule was ascertained from the single crystal XRD data of its sulfate salt (see Scheme 1 and Figure 1). Crystallographic data for the molecule is tabulated in Table 1. The complete list of bond lengths, bond angles, atom coordinates and thermal displacement parameters can be obtained from ESI. TzTA showed solubility only in polar organic solvents like DMF and DMSO, but suitable crystals for XRD could not be obtained from either of these solvents. TzTA was found soluble and could be recovered from strong acid solutions. Slow evaporation of 20% sulfuric acid solution yielded microcrystals of TzTA as its sulfate salt, suitable for diffraction measurement.



**Scheme 1.** Synthetic route towards 1-(2H-tetrazolyl)-1,2,4-triazol-5-amine.



**Figure 1.** Thermal ellipsoid plot of asymmetric unit of TzTA·H<sub>2</sub>SO<sub>4</sub> hydrate. Hydrogen atoms are shown as spheres with arbitrary radii.

**Table 1.** Crystal data and refinement for TzTA·H<sub>2</sub>SO<sub>4</sub> monohydrate.

Crystal data	TzTA·H <sub>2</sub> SO <sub>4</sub> hydrate
Empirical Formula	C <sub>3</sub> H <sub>6</sub> N <sub>8</sub> O <sub>2.50</sub> S <sub>0.50</sub>
Formula weight	210.19
<i>T</i> [K]	103(2)
$\lambda$ , Mo-K $\alpha$ [nm]	0.071073
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> [nm]	1.16796(11)
<i>b</i> [nm]	2.09000(14)
<i>c</i> [nm]	1.23291(10)
<i>V</i> [nm <sup>3</sup> ]	3.0093(4)
<i>Z</i>	16
$\rho$ [g cm <sup>−3</sup> ]	1.856
$\mu$ [mm <sup>−1</sup> ]	0.288
<i>F</i> (000)	1728
Crystal size [mm <sup>3</sup> ]	0.40 × 0.30 × 0.30
Theta range for data collection [°]	1.92 to 32.88
Reflections collected	41460
Independent reflections	10913 [ <i>R</i> (int) = 0.0365]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9185 and 0.8934
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	10913/0/505
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.068
Final <i>R</i> indices [ $\sigma$ ]	<i>R</i> 1 = 0.0490, <i>wR</i> 2 = 0.1329
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0675, <i>wR</i> 2 = 0.1475

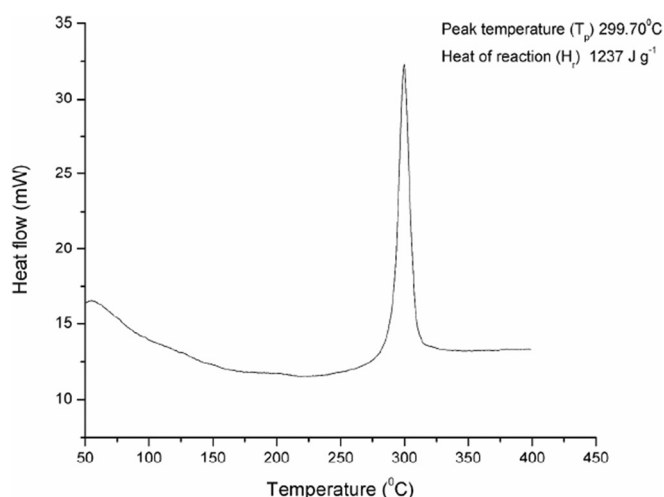
From the crystal structure it was clear that the N–C bond formation has happened at the N2 carbon, possibly due to the 1,2-tautomerism. TzTA·H<sub>2</sub>SO<sub>4</sub> crystallizes in monoclinic

space group  $P21/n$ . The unit cell consisted of 16 TzTA cations, eight sulfate anions and eight water molecules, with a cell volume of  $3.009 \text{ nm}^3$ . The crystal structure revealed an almost planar molecular structure (torsion angle  $170.18^\circ$ ) of TzTA, with co planarity between the triazole and tetrazole rings. Co planarity of the five membered rings might have induced the delocalization of the charge with in the molecule. The shorter bond length of the amine nitrogen (C–N  $0.131 \text{ nm}$ ) is indicative of a possible lone pair delocalization into the molecule, evidently supported by the shorter N–N and C–N bonds with in the rings (C–N, N–N  $0.133$ ,  $0.133 \text{ nm}$ ) and co planarity of the amino hydrogen atoms. Charge delocalization in the whole molecule is stabilized by the extensive hydrogen bonding. TzTA·H<sub>2</sub>SO<sub>4</sub> hydrate forms a highly layered structure with intra as well as intermolecular hydrogen bonding. The oxygen atom of sulfate ion shows strong hydrogen bonding with –NH<sub>2</sub> (N9–H9A···O1, D–H =  $0.088 \text{ nm}$ , H–A =  $0.202(4) \text{ nm}$ , D–A =  $0.287(6) \text{ nm}$ , D–H–A =  $162.5(3)^\circ$ ) as well as the –NH (N10–H10···O4, D–H =  $0.088(1) \text{ nm}$ , H–A =  $0.186(1) \text{ nm}$ ; D–A =  $0.273 \text{ nm}$ , D–H–A =  $168^\circ$ ) group of triazole ring. The water molecule was found to have a weak hydrogen bonding with oxygen atom of the sulfate ion (O3–H30···O10, D–H =  $0.093(4) \text{ nm}$ , H–A =  $0.208 \text{ nm}$ , D–A =  $0.302 \text{ nm}$ , D–H–A =  $173.5(4)^\circ$ ).

### 3.3 Thermo-Chemical Properties

Differential scanning calorimetry (DSC) was used to assess the thermal stability and decomposition behavior of the molecule. TzTA (less than  $1 \text{ mg}$ ) in an aluminium crucible was subjected to a temperature scanning programme, heating the sample and reference from  $50$ – $500^\circ\text{C}$ , under dynamic nitrogen purging environment with a flow rate of  $50 \text{ mL min}^{-1}$ . The experiment was done at  $10^\circ\text{C min}^{-1}$  heating rate with empty aluminium crucible as the reference. TzTA showed no melting on DSC and showed exothermic decomposition with a peak temperature of  $299^\circ\text{C}$  corresponding to the deflagration temperature. The decomposition peak temperature of TzTA is higher than that of many reported high nitrogen energetic materials, e.g. GZT, HBT, DAAT, BTATz and comparable to TNT and HMX (see Figure 2).

The peak temperature from the DSC thermograms were utilised for non-isothermal kinetic analysis. Peak values ( $T_p$ ),



**Figure 2.** DSC plot of 1-(2H-tetrazol-5-yl)-1,2,4-triazol-5-amine (heating rate of  $10^\circ\text{C min}^{-1}$ ).

from thermograms run at five different heating rates were used to generate the kinetic parameters with Kissinger and Ozawa methods. As observed for many energetic materials, the decomposition temperature of both the compounds increased with increase in temperature. In order to have good correlation, the  $E_a$  value obtained by Ozawa method is refined as per the ASTM E-698 standard. A correction factor, D, was introduced into the simplified Ozawa relation, which depends up on the  $E_a/RT$  value, obtained from the unrefined relation. The activation energy values obtained from Kissinger and Ozawa method, with a correlation factor of  $>0.99(-r)$ , showed good agreement ( $176.54 \text{ kJ mol}^{-1}$  Ozawa and  $176.46 \text{ kJ mol}^{-1}$  Kissinger) for TzTA. The higher thermal stability of the molecule is reflected in the higher activation energy of the molecule. Using these two methods, the kinetic parameters like  $E_a$ , Frequency factor (A), and  $\text{Ln}A$  were derived (Table 2).

### 3.4 Constant Volume Calorimetry

Constant volume combustion energy of TzTA was experimentally calculated using a Parr bomb calorimeter. The total energy on combustion,  $\Delta_c U$  inside an oxygen bomb was recorded to be  $-2116 \pm 5 \text{ kJ mol}^{-1}$ . The enthalpy of combustion was calculated from the relation,  $\Delta_c H = \Delta_c U +$

**Table 2.** Non-isothermal kinetic analysis data using Kissinger and Flynn/Wall/Ozawa methods.

$\beta^a$ [ $^\circ\text{C min}^{-1}$ ]	$T_p^b$ [ $^\circ\text{C}$ ]	Frequency factor ( $\text{Ln}A$ ) [ $\text{min}^{-1}$ ]	$E_a$ Kissinger <sup>c</sup> [ $\text{kJ mol}^{-1}$ ]	$E_a$ Ozawa <sup>d</sup> [ $\text{kJ mol}^{-1}$ ]
2	276.9	36.6	176.46	176.54
4	286.7			
6	292.5			
8	296.2			
10	299.7			

a) Heating rate. b) Peak temperature of decomposition from DSC thermograms; c) Activation energy calculated from Kissinger equation; d) Activation energy calculated from Ozawa method.



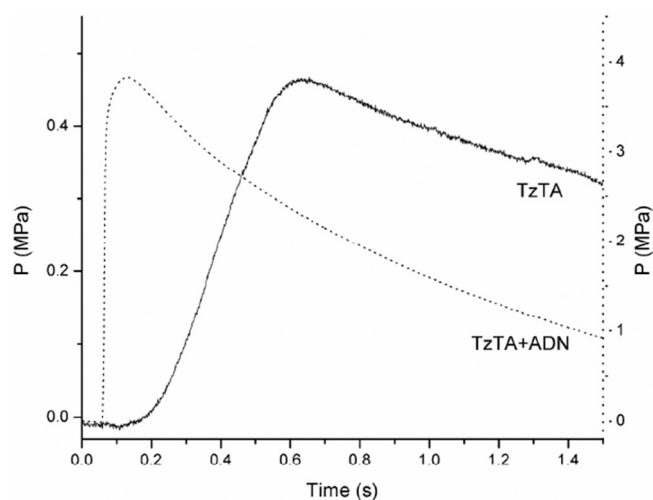
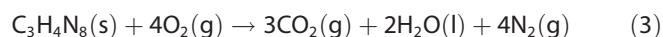


Figure 3.  $P$ - $t$  traces of TzTA and TzTA:ADN mixture.

$\Delta nRT$ , where  $\Delta nRT$  is the correction factor for gas volume increase. The standard energies of formation ( $\Delta_f H^\circ$ ) was back calculated from  $\Delta_c H$ , on the basis of the combustion relation Equation (3), Hess's law Equation (4) and the known standard heats of formation for  $H_2O(l)$  and  $CO_2(g)$ . The calculated heat of formation value was  $+356.6 \text{ kJ mol}^{-1}$ .



$$\Delta_f H^\circ (\text{TzTA}, s) = 3 \Delta_f H^\circ (CO_2, g) + 2 \Delta_f H^\circ (H_2O, l) - \Delta_c H^\circ (\text{TzTA}, s) \quad (4)$$

### 3.5 Pressure-Time Data Analysis

Dynamic pressure generated during nichrome wire ignition of the molecule was measured using a Parr dynamic pressure measurement system. The study was aimed to get an insight into the gas generating capability of the molecule. Pressure-time measurement technique is widely used in the study of high energy materials. The maximum pressure developed by combustion of a given mass of the material serves as a measure of its capacity to do work, although the character of the work is determined by the rate at which this pressure is built up [23]. From the  $P$ - $t$  trace maximum pressure rise ( $P_{\max}$ ) upon ignition and time to achieve maximum pressure ( $t_{\max}$ ) were determined. The rate of pressurization  $dP/dt$ , is of great importance in considering the capability of compounds as propellant ingredients or gas generators, which can be determined from the slope of pressure rise. In the present study TzTA was charged inside 240 mL high strength combustion vessel (Parr 1104) equipped with a pressure-transducer capable of recording a maximum pressure of 34 MPa (5000 Psi). The transducer was connected to a high speed ( $100 \text{ kS s}^{-1}$ ) data acquisition board, recording the output of the transducer (in V) as

a function of time. The system was equipped with a firing line which can be discharged manually. The combustion vessel was filled with argon at 2.75 MPa (400 Psi) prior to firing. The  $P$ - $t$  traces of pure TzTA and the mixture is shown in Figure 3. The initial pressure was useful to get a considerably detectable  $P_{\max}$  owing to the small amount of sample.

The  $P$ - $t$  trace of TzTA showed  $P_{\max}$  of 0.46 MPa, with a time to maximum pressure  $t_{\max}$  of 0.67 s at a charging density of  $0.001 \text{ g cm}^{-3}$ . Slope of the pressure rise with respect to time, i.e.  $dP/dt$  was measured to be  $1.17 \text{ MPa s}^{-1}$ . Although TzTA showed lower  $dP/dt$  when compared with powerful gas generators, the molecule exhibited possible capability of the molecule to be used as propellant ingredients or gas generator ingredients. Because of the high negative oxygen balance ( $-84\%$ ), it will be suitable to study the energetic parameters of mixture of TzTA with oxidizers. The combustion behaviour of TzTA was tested with ADN, the high energy-density oxidiser. Reactivity and pressure release of TzTA:ADN mixture was tested by firing a stoichiometric mixture (23.5:76.5 wt.-%) inside the combustion vessel with an initial filling pressure of 2.75 MPa of argon gas. The mixture charged with a loading density of  $0.002 \text{ g cm}^{-3}$  showed  $P_{\max}$  of 3.83 MPa, with a time to maximum pressure  $t_{\max}$  of 0.13 s. Notably, the time delay for initial pressure rise was very short compared to that of the fuel alone (0.19 s for TzTA and 0.059 s for mixture).  $dP/dt$  was calculated to be  $37.95 \text{ MPa s}^{-1}$ , showing a large increase in pressurization rate of the mixture when compared with TzTA. The increase in  $P_{\max}$  and  $dP/dt$  is clearly indicating the high burn rate of the mixture. The result from the  $P$ - $t$  analysis assimilates the capability of the material to be used as gas generator or propellant additive, in conjunction with a proper oxidizer.

### 3.6 Theoretical Study

Computational methods were utilized to calculate the heat of formation, charge density and possible spatial orientation of the molecule. Gaussian G09 A.02 [24] suite of programs was used for the computations. Hybrid basis set was utilized for the prediction and atomization energies of individual atoms were used for calculation. Optimization of the structure and the frequency calculations were performed using DFT level of theory, using the B3LYP 6-311g++ (3d,3p) basis set. The optimized structures were used to find the single point energy using MP2 6-311g++ basis set. The predicted heat of formation of the molecule in gas phase was  $+442.2 \text{ kJ mol}^{-1}$ . Condensed phase heat of formation can be predicted from electrostatic potential of the molecule using the quantum mechanical calculations explained by Rice [25] et al. and Politzer [26] et al. By taking into consideration, the heat of sublimation value of the solid, condensed phase heat of formation can be computed [ $\Delta H_{\text{(solid)}} = \Delta H_{\text{(gas)}} - \Delta H_{\text{(sublimation)}}$ ]. The difference observed between experimentally determined condensed phase heat of formation and theoretically predicted gas phase heat of for-

**Table 3.** Comparison of physiochemical and explosive properties of TzTA with some known energetic materials.

Properties	TzTA	AZT	GZT	TAGZT	DAAT	BTATz
Molecular Formula	C <sub>3</sub> H <sub>4</sub> N <sub>8</sub>	C <sub>2</sub> H <sub>8</sub> N <sub>12</sub>	C <sub>4</sub> H <sub>12</sub> N <sub>16</sub>	C <sub>4</sub> H <sub>18</sub> N <sub>22</sub>	C <sub>4</sub> H <sub>4</sub> N <sub>12</sub>	C <sub>4</sub> H <sub>4</sub> N <sub>14</sub>
Molecular mass [g mol <sup>-1</sup> ]	152.12	200.18	284.26	374.33	220.15	248.16
N <sup>a)</sup> [%]	73.68	83.97	78.84	82.32	76.35	79.02
OB <sup>b)</sup> [%]	-84	-63.93	-78.80	-72.66	-72.67	-64.4
T <sub>dec</sub> <sup>c)</sup> [°C]	293	190	261	212	251	264
D <sup>d)</sup> [g cm <sup>-3</sup> ]	1.73	1.53	1.54	1.60	1.78	1.76
Δ <sub>f</sub> H <sub>m</sub> <sup>e)</sup> [kJ mol <sup>-1</sup> ]	+356	+444	+410	+1075	+862	+883
T <sub>ex</sub> <sup>f)</sup> [K]	2172	2189	1783	2392	—	2888
D <sup>g)</sup> [m s <sup>-1</sup> ]	7821	7533	7071	8415	7400	8300
P <sub>c-j</sub> <sup>h)</sup> [GPa]	20.30	18.39	15.52	23.8	24.1	25.46
Ref. [28]						

a) Nitrogen content. b) Oxygen balance. c) Decomposition temperature. d) Density gas pycnometer 25 °C. e) Heat of formation. f) Detonation temperature. g) Velocity of detonation. h) Detonation pressure.

mation can be well explained by the aforesaid reasons. On comparison with few reported high nitrogen molecules, TzTA showed good performance parameters as simulated theoretically using EXPLO5 [27] thermodynamic code. The distribution of detonation products were predicted using the BKWG-S library. The experimental values of true density and heat of formation were used in the calculation. The results are summarized in the Table 3. The molecule showed a VOD 7680 m s<sup>-1</sup> at a P<sub>c-j</sub> pressure of 20.3 GPa. At c-j point the adiabatic flame temperature of detonation was calculated to be 2184 K.

## 4 Conclusions

The investigated compound, 1-(2H-tetrazol-5-yl)-1H-1,2,4-triazol-5-amine (TzTA) is an interesting and useful high energy, high nitrogen molecule capable of finding application as gas generator or propellant additive. TzTA was synthesized in good yield and purity from 3-aminotriazole, cyanogen bromide and sodium azide in ethanol solution under acidic environment. The structure of the molecule, investigated using X-ray diffraction, showed monoclinic crystal system with almost planar arrangement of the N–C bonded bicyclic system. The investigated compound was fully characterized using spectroscopic (IR, Raman, NMR) as well as analytical methods (elemental analysis). The thermal behaviour and non-isothermal kinetics performed on the molecule revealed good thermal stability and high activation energy for decomposition. The high positive molar enthalpy of formation (+356 kJ mol<sup>-1</sup>) showed by the molecule was determined from combustion energy obtained from bomb calorimetric measurements. Preliminary investigation on the gas generating capability of the molecule with an oxidizer, tested inside a high strength oxygen bomb, showed promising results.

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