

A GENUINELY MULTIDISCIPLINARY JOURNAL

CHEMPLUSCHEM

CENTERING ON CHEMISTRY

Accepted Article

Title: Synthesis and Investigation of 2,3,5,6-Tetra(1H-tetrazol-5-yl)pyrazine based Energetic Materials

Authors: Tomasz Witkowski, Paul Richardson, Bulat Gabidullin, Anguang Hu, and Muralee Murugesu

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemPlusChem 10.1002/cplu.201800414

Link to VoR: http://dx.doi.org/10.1002/cplu.201800414



WILEY-VCH

www.chempluschem.org

FULL PAPER

WILEY-VCH

Synthesis and Investigation of 2,3,5,6-Tetra(1*H*-tetrazol-5yl)pyrazine Based Energetic Materials

Dr. Tomasz G. Witkowski,^[a] Paul Richardson,^[a] Dr. Bulat Gabidullin,^[a] Dr. Anguang Hu,^{*[b]} Prof. Muralee Murugesu^{*[a]}

Abstract: The structures and properties of several energetic compounds based on a high nitrogen content anion, namely 2,3,5,6tetra(1H-tetrazol-5-yl)pyrazine (H4TTP) are reported here for the first time. These energetic salts were synthesized via reacting H₄TTP with various alkali metal hydroxides (sodium, potassium, rubidium, caesium) and N-bases (ammonia, hydrazine, hydroxylamine, guanidine carbonate, aminoguanidine bicarbonate). The resulting materials were comprehensively characterized by multinuclear (¹H, ¹³C) NMR spectroscopy, infrared spectroscopy, elemental analysis, DSC, as well as low temperature single-crystal X-ray diffraction. Heats of formation for the metal-free species as well as detonation parameters were calculated. Presented energetic materials (EMs) show high thermal stability (207 °C $\leq T_{dec} \leq$ 300 °C), while the metalfree ionic derivatives exhibits desirable properties such as detonation velocity (6873 m s⁻¹ \leq V_{C-J} \leq 8364 m s⁻¹), detonation pressure (14.3 GPa $\leq p_{CJ} \leq$ 24.9 GPa), and specific impulse (141.4 $\leq I_{sp} \leq$ 192.5 s).

Introduction

Growing environmental concerns over the last few years have increased the need for cleanly combusting energetic materials, and therefore new replacements for the commonly used toxic compounds (*e.g.*, heavy metal derivatives such as lead and mercury) are highly desired.^[11] It is not only enough to design non-toxic energetic materials themselves, but the decomposition products should be environmentally benign as well. In order to obtain promising compounds, which fulfill the toxicity, sensitivity, stability, and performance requirements, researchers use many different strategies.^[1a, 1e] One of the currently used approaches in the development of new energetic materials (EMs) is the synthesis of high-nitrogen content tetrazole salts, which combine large positive standard enthalpies of formation (caused by significant differences in the bond energies for singly: 160 kJ mol⁻¹, doubly: 418 kJ mol⁻¹, and triply: 954 kJ mol⁻¹ bonded nitrogen atoms), relatively high thermal stability (due to their aromatic ring system), and low volatility (caused by very strong ionic bonds).^{[1a,} ^{1e]} Therefore, the tetrazole motif is widely used in the synthesis of high-performance nitrogen-rich salts, which have tailored properties for different applications. For example, metal-free ionic compounds can be used either as explosives (e.g., 5nitriminotetrazoles,^[2] 5,5'-bistetrazole-1,1'-diolates,[3] 1,1'dinitramino-5,5'-bitetrazolates,^[4]) or in propellant charges (e.g., 5,5'-bistetrazolates^[5]), while metal-containing salts can be used as energetic colorants in modern smokeless pyrotechnical compositions (e.g., 5-aminotetrazolates^[6]) as well as primary explosives (e.g., potassium 1,1'-dinitramino-5,5'-bistetrazolate^[7]). Recently we reported a new nitrogen-rich (N-rich) EM, 2,3,5,6tetra(1H-tetrazol-5-yl)pyrazine (H₄TTP) from readily available starting materials.^[8] Although this compound is characterized by high-nitrogen content (N = 71.58%), high thermal stability (T_{dec} = 260 °C) and sought after detonation parameters ($V_{C-J} = 8655 \text{ m s}^-$ ¹, $p_{C-J} = 28.0 \text{ GPa}$),^[8] it is yet to be explored as a *N*-rich content energetic material. Furthermore, H4TTP possesses four acidic protons that can be removed to form a variety of ionic species. This is advantageous, since energetic materials can often achieve higher thermal stability through the formation of ionic compounds with suitable counter ions. In that regard, H₄TTP is attractive as a precursor for ionic energetic materials applications. For example, H₄TTP is a highly promising precursor in the synthesis of nitrogenrich metal-free derivatives for study as components in either gun or rocket propellant systems, which could help to resolve often encountered barrel erosion problems. The latter issue originates from the formation of iron carbide (via the reaction of iron from the bore with carbon from carbon monoxide) at high temperatures.^[1e] Therefore, decreasing the carbon content of propellant reduces the formation of iron carbide. Furthermore, an enlarged N2:CO ratio in the combustion gases results in the generation of iron nitride in the bore, which has a higher melting point than iron carbide, forming a protective layer on the inside of the bore, which benefits in increasing the lifetime of the equipment by up to a factor of four.^[1e] Nowadays, research on propellant charges is focused on the development of materials that have as large as possible N2:CO ratio (for conventional propellant charges the N₂:CO ratio is ca. 0.5), and burn at the lowest possible temperatures, all while exhibiting enhanced performance.^[1e] It is also noteworthy that metal salts of H4TTP could be useful as colorants in modern smokeless pyrotechnical compositions. These potential applications of TTP⁴⁻ based EMs make it viable avenue to explore. As such, herein, we present a family of ionic derivatives of the TTP4- anion as a part of our ongoing studies of the structures and properties of novel energetic materials.

 [[]a] Department of Chemistry and Biomolecular Sciences, University of Ottawa, 10 Marie Curie, Ottawa, ON, Canada K1N 6N5 E-mail : m.murugesu@uottawa.ca
 Fax: +1 (613) 562 5170; Tel: +1 (613) 562 5800 ext. 2733.

[[]b] Defence Research and Development Canada-Suffield, PO Box 4000, Stn Main, Medicine Hat, AB, T1A 8K6 Canada Supporting information for this article is given *via* a link at the end of the document.

Supporting information for this article is given *via* a link at the end of the document.

FULL PAPER

Results and Discussion

Synthesis

The synthesis of H₄TTP has already been described in our previous report.^[8] In the first step of the process towards H₄TTP, diaminomaleonitrile undergoes a condensation reaction with diiminosuccinonitrile (which was prepared *in situ via* oxidation of diaminomaleonitrile using dicyano-1,4-benzoquinone, DDQ) to give pyrazine-2,3,5,6-tetracarbonitrile as a main product. The second step involves a ring closure reaction in a [2+3] dipolar azide-nitrile cycloaddition reaction between pyrazine-2,3,5,6-tetracarbonitrile as a main product. The reaction of H₄TTP with different bases (alkali metal hydroxides and *N*-bases) resulted in the formation of TTP⁴⁻ salts containing the following cations: sodium (**5**), potassium (**6**), rubidium (**7**), cesium (**8**), ammonium (**9**), hydrazinium (**10**), hydroxylammonium (**11**), guanidinium (**12**), aminoguanidinium (**13**; Scheme 2).



Scheme 1. Synthetic route for the isolation of energetic salts based on 2,3,5,6-tetra(1H-tetrazol-5-yl)pyrazine (H₄TTP).

Single-crystal X-ray analysis

Single crystals were isolated for of K₄[TTP] (**6**), Cs₄[TTP] (**8**), [HA]₄[TTP] (**11**), and [GuH]₄[TTP] (**12**) compounds and the molecular structures were determined using low-temperature single-crystal X-ray diffraction studies.^[9] Attempts to crystalize Xray quality single crystals of **7**, **9**, **10**, **13** were unsuccessful. Therefore, we only report herein the aforementioned compounds **6**, **8**, **11** and **12**. Crystallographic details can be found in the Supporting Information. Compound **6** crystallizes as colourless needles from an ethanol/water mixture in the monoclinic $P_{2_1/c}$ space group. The molecular structure of compound **6** with **5H**₂**O** is shown in Figure 1. Crystal structure collected at 200 K reveals four TTP⁴⁻ molecules in the unit cell along with H₂O molecules of crystallization with an overall density of 1.849 g cm⁻³.



Figure 1. Molecular structure of compound 6 with 5H₂O. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are shown as spheres of arbitrary radii. Color code: K, yellow; O, red; N, blue; C, grey vertices.

Crystallization of the Cs congener (8) from an ethanol/water mixture resulted in X-ray quality yellow prism single crystals. Compound 8 crystallizes in the triclinic *P*-1 space group, with a density of 2.997 g cm⁻³ at 200 K and one molecule in the unit cell. Due to the close-packed arrangement the metal salt, the obtained density is by far the highest density reported of all the congeners. The molecular structure of compound 8 with $2H_2O$ is shown in Figure 2.



Figure 2. Molecular structure of compound 8 with $2H_2O$. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are shown as spheres of arbitrary radii. Colour code: Cs, purple; O, red; N, blue; C, grey vertices.

FULL PAPER

In order to increase the nitrogen density and subsequently use as a green combusting high-energy material (increased N₂:CO ratio upon combustion), we synthesized various TTP^{4-} congeners with organic counter cations (ammonium (9), hydrazinium (10), hydroxylammonium (11), guanidinium (12), aminoguanidinium (13)).

We have successfully isolated X-ray quality colourless plate-like single crystals of the hydroxylammonium salt of TTP⁴⁻ ([HA]₄[TTP], **11**) using ethanol/water mixture. Compound **11** crystallizes in the monoclinic $P2_1/c$ space group, with a density of 1.646 g cm⁻³ at 200 K and two molecules in the unit cell. The molecular structure of compound **11** with **2H₂O** is shown in Figure 3.



Figure 3. Molecular structure of compound 11 with 2H₂O. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are shown as spheres of arbitrary radii. Disordered molecules are presented as partially transparent. Colour code: O, red; N, blue; C, grey vertices.

Using a similar crystallization strategy, the guanidinium salt of TTP⁴⁻ ([GuH]₄[TTP] (**12**)) was crystallized as yellow needles from ethanol/water mixture. Compound **12** crystallizes in the monoclinic *C*2/*c* space group, with a density of 1.497 g cm⁻³ at 200 K and four TTP⁴⁻ molecules in the unit cell. The molecular structure of compound **12** with **2H**₂**O** is shown in Figure 4.



Figure 4. Molecular structure of compound 12 with $2H_2O$. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are shown as spheres of arbitrary radii. Disordered molecules are presented as partially transparent. Colour code: O, red; N, blue; C, grey vertices.

Spectroscopy

All isolated energetic materials were investigated through NMR spectroscopy and infrared spectroscopy. The ¹H NMR spectrum of the ammonium salt (9) revealed one broad proton signal for the NH_4^+ protons at δ = 7.92 ppm in DMSO-*d*₆. A resonance band for the $H_2 NN H_3^+$ (10) protons of the hydrazinium derivative was observed as one broad signal at δ = 7.00 ppm in DMSO- d_6 . For hydroxylammonium salt (11), one broad signal can be found at δ = 9.06 ppm in DMSO-d₆. A resonance band for the C-NH₂ protons of the guanidinium salt (12) can be found at δ = 7.23 ppm. A signal for the C-N H_2 protons in the aminoguanidinium (13) derivative can be found at δ = 7.21 ppm. Furthermore, due to the presence of both NH and NH₂ groups in the aminoguanidinium moiety, additional resonances at $\delta = 9.12$ (NH) and 4.71 ppm $(NHNH_2)$ are observed. All ¹³C{¹H} NMR spectra of the investigated compounds reveal two resonance signals which can be attributed to the TTP4- anion. Signals in the range of δ = 158.5–160.7 can be assigned to the carbon atom of the tetrazole ring while the other signal at a higher field of 141.7-144.3 ppm refers to the pyrazine carbons. The guanidine carbon atom signal can be found at δ = 158.4 and 159.3 ppm for the guanidinium (12) and aminoguanidinium (13) derivatives, respectively. The assignments are in agreement to those previously reported in the literature for known structures such as H₄TTP,^[8] 5,5'-bistetrazolates^[5], 5-(1H-tetrazolyl)-1hydroxytetrazoles,^[10] and TKX-50^[3a]. In the proton NMR spectra of all obtained salts, we do not observe signals connected to the non-deprotonated tetrazole moieties which indicate that we obtained only the tetra-cationic derivatives of H₄TTP.

Thermal stabilities and energetic properties

It is worth mentioning that regardless of the high-nitrogen content of the presented molecules, none of them show decomposition at temperatures below 200 °C (see the Supporting Information). Most of the obtained ionic derivatives of H₄TTP show higher decomposition temperatures than the neutral molecule ($T_{dec} = 260 \,^{\circ}C^{[8]}$). The hydroxylammonium salt of TTP⁴⁻ (**11**) has the lowest decomposition temperature ($T_{dec} = 207 \,^{\circ}C$), the highest thermal stability is shown by the cesium (**8**) ($T_{dec} = 300 \,^{\circ}C$) and the guanidinium (**12**) ($T_{dec} = 297 \,^{\circ}C$) salts (**Table 3**). The metal salts show much lower decomposition temperatures than the previously reported corresponding 5,5'bistetrazolate (BT²⁻) salts;^{(11]} however, in the case of the metalfree nitrogen-rich salts, the values are comparable.^[5]

Theoretical calculations

Although metal-containing energetic materials tend to yield high densities due to their coordination and tight packing, the metalcontaining byproducts of their burning are environmentally undesirable. Since the amount of gaseous products liberated during the decomposition of EMs depends on the composition of the material being initiated, computational studies were carried out to investigate the non-metal energetic salts of H₄TTP for possible green propellant applications. The gas phase absolute enthalpies of anions, using the fully optimized molecular structures without symmetry constraints. These calculations were accomplished by applying the modified complete basis set method (CBS-4M) with the Gaussian 09 (Revision E.01) software.^[12] Gas phase enthalpies of formation ($\Delta t H^{\circ}_{(g)}$) were computed using the atomization energy method (**Table 1**).^[13]

FULL PAPER

Table 1.	CBS-4M	results	and	gas-phase	enthal	oies
Tuble I.		results	ana	guo priuse	Cintinai	pico.

	Formula	<i>−H</i> ²⁹⁸ [a.u.]	Δ _f H _(g) [kJ mol⁻¹]
TTP4-	C ₄ N ₁₆ ⁴⁻	1288.355711	2000.9
A+	NH_4^+	56.796608	635.3
Hy⁺	$N_2H_5^+$	112.030517	773.4
HA+	H₄NO ⁺	131.863249	686.4
GuH⁺	CH ₆ N ₃ ⁺	205.453189	571.2
AGuH⁺	CH ₇ N ₄ +	260.701807	670.7

Condensed phase heats of formation of energetic salts (Table 2) for non-metal nitrogen-rich ionic derivatives of H₄TTP (9-13) were calculated using the gas phase heat of formation and heat of phase transition (lattice energy) according to Hess's law of constant summation (using the Born-Haber energy cycle). The lattice energy (ΔU_L) and lattice enthalpy (ΔH_L) were calculated from the corresponding densities according to the equations provided by Jenkins, Tudela, and Glasser.^[14] With the calculated lattice enthalpy (Table 2), and the gas-phase enthalpy of formation (Table 1) of ions, the standard molar enthalpy of formation $(\Delta_f H^{\circ}_{(s)})$ of energetic salts was calculated (**Table 3**).

Table 2. CBS-4M results and gas-phase enthalpies.

	Ŭ I			
	$\Delta_f H_{(g)}$	∆ <i>U</i> ∟	∆H∟	$\Delta_f H^{\circ}(s)$
	[kJ mol⁻¹]	[kJ mol⁻¹]	[kJ mol⁻¹]	[kJ mol⁻¹]
(A)4TTP (9)	4542.1	4247.3	4222.5	319.6
(Hy)₄TTP (10)	5094.6	4093.6	4105.9	988.7
(HA)₄TTP (11)	4746.7	4146.6	4121.8	624.8
(GuH)₄TTP (12)	4285.6	3787.1	3762.3	523.3
(AGuH)₄TTP (13)	4683.6	3781.9	3757.1	926.4

The Chapman-Jouquet (C-J) characteristics, (i.e. heat of detonation, $\Delta_E U^\circ$; detonation temperature, T_{C-J} ; detonation pressure, p_{C-J} ; detonation velocity V_{C-J}) were computed using the EXPLO5 V6.04 thermochemical computer code.^[15] Calculations for the studied energetic materials assume ideal behavior. Estimation of the detonation parameters is based on the chemical equilibrium steady-state model of detonation. The Becker-Kistiakowsky-Wilson equation of state (BKW EOS) with the following sets of constants: $\alpha = 0.5$, $\beta = 0.38$, $\kappa = 9.32$, and $\Theta =$ 4120 for gaseous detonation products and the Murnaghan equation of state for condensed products (compressible solids and liquids) were applied.

Calculation of the equilibrium composition of the detonation products used the modified White, Johnson and Dantzig's free energy minimization technique. Specific impulse was calculated assuming free expansion of the gases in the atmosphere or space (isobaric combustion at p = 6.0 MPa).

Table 3. Properties of investigated metal-free ionic derivatives of H47	ΓTΡ
---	-----

The densities of the presented metal-free anionic salts of H₄TTP are lower than those reported for H₄TTP (between 1.55 and 1.75 g cm⁻³ versus 1.945 g cm⁻³ for H₄TTP^[8]). Similarly, the enthalpy of formation of these ionic derivatives is considerably lower than the calculated value for H₄TTP (ranging from 760 to 2058 kJ kg⁻¹, versus 3926 kJ kg⁻¹ for H₄TTP^[8]). This gives rise to the moderate values found in the detonation parameters (e.g., p_{C-J} , V_{C-J} , T_{C-J}) of these energetic salts (Table 3). Out of the presented herein energetic materials, the HA congener has the highest potential to act as an ingredient for gun propellants, due to its high specific impulse (193 s) and its good detonation parameters (24.9 GPa, 8360 m s⁻¹).

Conclusions

Deprotonation of a new nitrogen-rich derivative, namely H₄TTP, with different bases led to a variety of alkali metal salts: sodium (5), potassium (6), rubidium (7), and caesium (8); and metal-free salts: ammonium (9), hydrazinium (10), hydroxylammonium (11), guanidinium (12), and aminoguanidinium (13). All nitrogen-rich ionic EMs were obtained in high yields and excell Amongst the presented ionic derivatives of H₄TTP, t decomposition temperature was achieved with the (300 °C) and guanidinium (297 °C) salts; the lo attributed to hydroxylammonium (207 °C). The dece temperature of the metal-free ionic EMs follow the ord $> A_4^+ > AGuH^+ > Hy^+ > HA^+$, which is in good agreeme previously reported trend for the corresponding sal bistetrazolates.^[5] Similarly the most remarkable performance characteristics (e.g. $\Delta_E U^{\circ}$, p_{C-J} , V_{C-J} , I_{sp}), presented EMs, were seen in the hydrazinium, (Hy -3166 kJ kg⁻¹, 24.9 GPa, 8360 m s⁻¹, 192.5 hydroxylammonium, (HA)₄TTP (11; -2450 kJ kg⁻¹, 8364 m s⁻¹, 183.5 s) salts. This tendency correlate corresponding performance values for 5,5'-bistetr These properties, in addition to their straightforward makes the presented novel EMs as promising can environmentally friendly energetic materials application

ely H ₄ TTP, Its: sodium I metal-free onium (11), itrogen-rich lent purity. the highest e caesium owest was omposition der of GuH ⁺ ent with the Its of 5,5'- values of	Manuscri
anong the j₄TTP (10 ; 5 s) and 23.7 GPa, as with the razolates. ^[5] synthesis, didates for ns.	septed N
TP (4) ^[8]	00

Table 3. Properties of investigated metal-free ionic derivatives of H4TTP.						
	(A)4TTP (9)	(Hy)₄TTP (10)	(HA)₄TTP (11)	(GuH)₄TTP (12)	(AGuH)₄TTP (13)	H ₄ TTP (4) ^[8]
Formula	C ₈ H ₁₆ N ₂₂	C ₈ H ₂₀ N ₂₆	C ₈ H ₁₆ N ₂₂ O ₄	C ₁₂ H ₂₄ N ₃₀	C ₁₂ H ₂₈ N ₃₄	C ₈ H ₄ N ₁₈
N ^{a)} (%)	73.31	75.80	63.62	71.40	73.43	71.58
−Ω ^{b)} (%)	91.34	86.58	66.06	97.86	93.73	81.75
T _{dec} ^{c)} (°C)	286	247	207	297	267	260
ρ ^{d)} (g cm⁻³)	1.65	1.66	1.75	1.55	1.70	1.945
∆ _f H ^o (s) ^{e)} (kJ mol ^{−1})	320	989	625	523	926	1383
∆ <i>fH</i> ° _(s) (kJ kg ⁻¹)	760	2058	1290	889	1428	3926
EXPLO5 6.04 ^[15]						
$-\Delta_E U^{\circ f}$ (kJ kg ⁻¹)	1161	2450	3166	1314	1840	3530
<i>Т</i> с-Ј ^{g)} (К)	1278	1910	2350	1376	1600	2692
<i>р</i> с-Ј ^{h)} (GPa)	15.5	23.7	24.9	14.3	22.4	28.0
V _{C-J} ⁱ⁾ (m s ⁻¹)	7229	8364	8360	6873	8248	8655
Gas vol. ^{j)} (dm ³ kg ⁻¹)	830	852	833	829	839	678
Isp ^{k)} (S)	141	184	193	147	167	203
a) Nitrogen content. b) Oxyge	en balance. c) Temperati	ure of decomposition. d) De	ensity at 298 K. e) Standard	molar enthalpy of formation	on. ¹⁾ Heat of detonation. ⁹⁾	Detonation temperature.

h) Detonation pressure. ¹⁾ Detonation velocity. ¹⁾ Volume of detonation gases at standard temperature and pressure conditions. Specific impulse

FULL PAPER

Experimental Section

Materials

All manipulations were performed under aerobic/ambient conditions. All chemicals were purchased from Alrich or Strem Chemicals and used without any further purification.

Physical Characterization

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometry was performed using a Thermo Scientific Nicolet Avatar 6700 FTIR spectrometer equipped with an attenuated total reflectance device. All spectra were recorded at ambient temperature. NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer; all samples were measured at 25 °C. Elemental analysis was carried out internally by the Materials Characterization facility on an Elemental Analyzer vario ISOTOPE cube, by pyrolysis of the sample and subsequent analysis of the formed gases.

Caution! 2,3,5,6-Tetra(1*H*-tetrazol-5-yl)pyrazine (**4**) and its derivatives (**5-13**) are energetic compounds with potential sensitivities to various stimuli. While we encountered no issues in the handling these compounds, proper protective measures are recommended to be used at all times.

 H_4TTP 2,3,5,6-tetra(1*H*-tetrazol-5-yl)pyrazine (4) is obtained *via* a published previously synthesis.^[8]

Na₄**TTP (5):** To a solution of sodium hydroxide (4.0 mmol, 160.0 mg) in ethanol (10.0 mL) H₄TTP (1.0 mmol, 352.2 mg) is added. Subsequently, the reaction mixture is heated under reflux for 3 h. The product is filtered off, washed with ethanol and dried under high vacuum at 100 °C. Yield: 343.0 mg (78%). **DSC** (5 °C min⁻¹, onset): 217 °C (endoth.), 288 °C (exoth.); ¹³C{¹H} NMR (76.0 MHz, DMSO-*d*₆, ppm) δ: 159.1 (*C*N₄⁻), 143.6 (*C*₄N₂); **IR** (ATR, cm⁻¹) $\tilde{\nu}$: 1685.93(w), 1635.61(w), 1517.88(w), 1433.11(w), 1401.19(w), 1380.10(w), 1284.45(w), 1170.94(s), 1133.02(s), 1058.25(m), 1023.64(vs), 763.29(w), 739.08(w), 583.36(s), 556.16(m), 533.58(m); elemental analysis calcd (%) for C₈N₁₈Na₄, 440.17: C 21.83, N 57.28; found: C 22.03, N 57.58.

K₄TTP (6): To a solution of potassium hydroxide (4.0 mmol, 224.4 mg) in ethanol (10.0 mL) H₄TTP (1.0 mmol, 352.2 mg) is added. Subsequently, the reaction mixture is heated under reflux for 3 h. The product was filtered off, washed with ethanol and dried under high vacuum at 100 °C. Yield: 425.0 mg (84%). **DSC** (5 °C min⁻¹, onset): 220 °C (endoth.), 227 °C (exoth.); ¹³C{¹H} NMR (76.0 MHz, DMSO-*d*₆, ppm) δ : 158.9 (*C*N₄⁻), 143.3 (*C*₄N₂); **IR** (ATR, cm⁻¹) $\tilde{\nu}$: 1659(w), 1515(w), 1382(m), 1278(m), 1163(s), 1139(m), 1123(m), 1052(m), 1018(vs), 762(w), 735(m), 694(m), 623(m), 580(s); elemental analysis calcd (%) for C₈K₄N₁₈, 504.60: C 19.04, N 49.96; found: C 19.23, N 50.21

Rb₄TTP (7): To a water solution of rubidium hydroxide (4.0 mmol, 409.9 mg, 50 wt. %, 0.471 mL) in ethanol (10.0 mL) H₄TTP (1.0 mmol, 352.2 mg) is added. Subsequently, the reaction mixture is heated under reflux for 3 h. The product was filtered off, washed with ethanol and dried under high vacuum at 100 °C. Yield: 650.1 mg (94%). **DSC** (5 °C min⁻¹, onset): 256 °C (exoth.); ¹³**C**{¹H} **NMR** (76.0 MHz, DMSO-*d*₆, ppm) $\overline{\delta}$: 159.3 (CN₄⁻¹), 143.6 (C₄N₂); **IR** (ATR, cm⁻¹) $\tilde{\nu}$: 1683(w), 1509(w), 1393(m), 1366(s), 1280(s), 1166(vs), 1144(m), 1129(vs), 1117(w), 1073(w), 1018(vs), 769(w), 733(w), 606(s), 578(vs); elemental analysis calcd (%) for C₈N₁₈Rb₄, 690.08: C 13.92, N 36.54; found: C 14.14, N 37.14.

Cs₄TTP (8): To a water solution of caesium hydroxide (4.0 mmol, 600 mg, 50 wt. %, 0.697 mL) in ethanol (10.0 mL) H₄TTP (1.0 mmol, 352.2 mg) is added. Subsequently, the reaction mixture is heated under reflux for 3 h. The product was filtered off, washed with ethanol and dried under high vacuum at 100 °C. Yield: 845.5 mg (96%). **DSC** (5 °C min⁻¹, onset): 300 °C (exoth.); ¹³C{¹H} **NMR** (76.0 MHz, D₂O, ppm) δ : 159.2 (*C*N₄⁻), 143.6 (*C*₄N₂); **IR** (ATR, cm⁻¹) $\tilde{\nu}$: 1520(w), 1500(w), 1388(m), 1376(m),

 $\begin{array}{l} 1357(w),\,1276(m),\,1271(m),\,1167(s),\,1155(s),\,1125(s),\,1066(w),\,1043(m),\\ 1032(w),\,\,1015(vs),\,\,779(w),\,\,769(w),\,\,761(w),\,\,731(m),\,\,697(w),\,\,635(w),\\ 614(w),\,578(s),\,561(w),\,529(w);\,elemental \,analysis\,calcd\,(\%)\,for\,C_8Cs_4N_{18},\\ 879.83:\,C\,\,10.92,\,N\,\,28.66;\,found:\,C\,\,10.65,\,N\,\,27.73. \end{array}$

(A)₄TTP (9): H₄TTP (1.0 mmol, 352.2 mg) is suspended in ethanol (10.0 mL). Subsequently, gaseous ammonia is bubbled through the reaction mixture. Then, the reaction mixture is heated under reflux for 3 h. The product was filtered off, washed with ethanol and dried under high vacuum at 50 °C. Yield: 395.5 mg (94%). DSC (5 °C min⁻¹, onset): 277 °C (endoth.), 286 °C (exoth.); ¹H NMR (300.00 MHz, DMSO-*d*₆, ppm) δ : 7.46 (s, br, 4 H, NH₄+); ¹³C{¹H} NMR (76.0 MHz, DMSO-*d*₆, ppm) δ : 157.7 (CN₄⁻), 141.2 (C₄N₂); **IR** (ATR, cm⁻¹) \tilde{v} : 3180(m), 3000(m), 2788(m), 1520(w), 1482(s), 1455(m), 1409(vs), 1390(vs), 1167(s), 1139(m), 1124(m), 1066(m), 1058.46(s), 1041.62(m), 1019.18(s), 585.47(m), 543.03(m); elemental analysis calcd (%) for C₈H₁₆N₂₂, 420.36: C 22.86, H 3.84, N 73.31; found: C 23.50, H 3.26, N 71.90.

(Hy)₄TTP (10): H₄TTP (1.0 mmol, 352.2 mg) is suspended in ethanol (10.0 mL). Subsequently, hydrazine monohydrate (4.0 mmol, 200.2 mg) is added. Then, the reaction mixture is heated under reflux for 3 h. The product was filtered off, washed with ethanol and dried under high vacuum at 100 °C. Yield: 447.0 mg (93%). **DSC** ($5 \,^{\circ}$ C min⁻¹, onset): 229 °C (endoth.), 247 °C (exoth.); ¹H **NMR** (300.00 MHz, DMSO-*d*₆, ppm) δ : 6.60 (s, br, 5 H, *H*₂NN*H*₅⁺); ¹³C{¹H} **NMR** (76.0 MHz, DMSO-*d*₆, ppm) δ : 159.6 (CN₄⁻),142.7 (*C*₄N₂); **IR** (ATR, cm⁻¹) \tilde{v} : 3301(w), 3079(m), 2931(m), 2843(m), 2741(s), 2626(s), 2109(w), 1661(w), 1510(s), 1382(s), 1280(w), 1125(vs), 1060(s), 1047(w), 1020(vs), 982(s), 948(vs), 758(w), 732(m), 580(s), 564(m); elemental analysis calcd (%) for C₈H₂₀N₂₆, 480.42: C 20.00, H 4.20, N 75.80; found: C 19.49, H 4.06, N 73.66.

(HA)₄TTP (11): To a water solution of hydroxylamine (4.0 mmol, 132.1 mg, 50 wt. %, 0.245 mL) in ethanol (10.0 mL) H₄TTP (1.0 mmol, 352.2 mg) is added. Subsequently, the reaction mixture is heated under reflux for 3 h. The product was filtered off, washed with ethanol and dried under high vacuum at 100 °C. Yield: 456.0 mg (94%). **DSC** (5 °C min⁻¹, onset): 175 °C (endoth.), 207 °C (exoth.); ¹H **NMR** (300.00 MHz, DMSO-*d*₆, ppm) δ : 9.87 (s, br, 4 H, HON*H*₃+); ¹³C{¹H} **NMR** (76.0 MHz, DMSO-*d*₆, ppm) δ : 158.1 (*C*N₄⁻),141.3 (*C*₄N₂); **IR** (ATR, cm⁻¹) \tilde{v} : 2950(m), 2680(s), 1635(m), 1635(m), 1593(m), 1524(s), 1401(m), 1375(s), 1287(m), 1216(s), 1178(vs), 1139(vs), 1066(m), 1025(vs), 997(m), 879(m), 842(m), 819(m), 790(w), 783(w), 729(s), 587(s); elemental analysis calcd (%) for C₈H₁₆N₂₂O₄, 484.36: C 19.84, H 3.33, N 63.62; found: C 19.49, H 4.06, N 73.66.

(GuH)₄TTP (12): H₄TTP (1.0 mmol, 352.2 mg) is suspended in ethanol (10.0 mL). Subsequently, guanidine carbonate (4.0 mmol, 360.3 mg) is added. Then, the reaction mixture is heated under reflux for 3 h. The product was filtered off, washed with small amount of ethanol and dried under high vacuum at 100 °C. Yield: 535.6 mg (91%). **DSC** (5 °C min⁻¹, onset): 297 °C (exoth.); ¹H NMR (300.00 MHz, DMSO-*d*₆, ppm) δ : 7.23 (s, br, 6 H, *H*₂NC(=N*H*₂*)N*H*₂); ¹³C{¹H} NMR (75.0 MHz, DMSO-*d*₆, ppm) δ : 159.5 (*C*N₄⁻), 157.9 (H₂NC(=NH₂*)NH₂), 143.7 (*C*₄N₂); **IR** (ATR, cm⁻¹) $\tilde{\nu}$: 3450(m), 3360(m), 3139(m), 3050(m), 1644(vs), 1582(w), 1521(w), 1386(m), 1373(m), 1282(w), 1160(m), 1131(m), 1060(m), 1042(m), 1025(m), 1015(m), 731(m), 626(s), 580(s), 553(m); elemental analysis calcd (%) for C₁₂H₂₄N₃₀, 588.52: C 24.49, H 4.11, N 71.40; found: C 23.70, H 4.52, N 69.66.

(AGuH)₄TTP (13): H₄TTP (1.0 mmol, 352.2 mg) is suspended in ethanol (10.0 mL). Subsequently, aminoguanidine bicarbonate (4.0 mmol, 544.4 mg) is added. Then, the reaction mixture is heated under reflux for 3 h. The product was filtered off, washed with small amount of ethanol and dried under high vacuum at 100 °C. Yield: 608.5 mg (94%). **DSC** (5 °C min⁻¹, onset): 260 °C (endoth.), 267 °C (exoth.); ¹H NMR (300.00 MHz, DMSO-*d*₆, ppm) δ : 9.19 (s, br, 1 H, H₂NNHC(=NH₂⁺)NH₂), 7.19 (s, br, 4 H, H₂NNHC(=NH₂⁺)NH₂), 4.75 (s, br, 2 H, H₂NNHC(=NH₂⁺)NH₂); ¹³C{¹H} NMR (76.0 MHz, DMSO-*d*₆, ppm)

FULL PAPER

 $\bar{\textrm{o}}{:}~159.5~(CN_4^-),~158.8~(H_2NNHC(=NH_2^+)NH_2),~143.8~(C_4N_2);~IR~(ATR,~cm^{-1})~\tilde{\textit{v}}{:}~3442(w),~3364(m),~3309(m),~3230(m),~3170(m),~1692(s),~1652(vs),~1586(m),~1539(w),~1510(w),~1436(w),~1393(m),~1374(w),~1283(m),~1204(w),~1164(m),~1138(m),~1056(w),~1020(m),~991(m),~902(m),~817(w),~788(w),~762(w),~733(w),~577(m);~elemental analysis calcd~(\%)~for~C_{12}H_{28}N_{34},~648.58;~C~22.22,~H~4.35,~N~73.43;~found:~C~22.49,~H~4.22,~N~72.97.~(AGH)_4C_8N_{18}{:}~C~22.22,~H~4.35,~N~73.43.$

Acknowledgements

This project was solely funded by Defense Research and Development Canada. We acknowledge collaborations with Dr. Mila Krupka (OZM Research, Czech Republic), in the development of new testing and evaluation methods for energetic materials, and with Professor Dr. Muhamed Sućeska (University of Zagreb, Croatia), in the development of new computational codes for prediction of the detonation and propulsion parameters of energetic materials.

Keywords: energetic materials • nitrogen-rich molecules • X-ray diffraction • tetrazole • pyrazine

- a) H. Gao, J. M. Shreeve, *Chem. Rev.* 2011, *111*, 7377-7436; b) M. A. Ilyushin, I. V. Tselinsky, I. V. Shugalei, *Cent. Eur. J. Energ. Mater.* 2012, 9, 293-327; c) T. M. Klapötke, J. Stierstorfer in *Green Energetic Materials* (Ed.: T. Brinck), Wiley, Chichester, 2014 pp. 133-178; d) Z. Zhao, Z. Du, Z. Han, Y. Zhang, C. He, *J. Energ. Mater.* 2016, *34*, 183-196; e) T. M. Klapötke, *Chemistry of High-Energy Materials*, 4th Edition, De Gruyter, 2017.
- [2] N. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, Z. Anorg. Allg. Chem. 2012, 638, 302-310.

a) N. Fischer, D. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, J. Mater. Chem. 2012, 22, 20418-20422; b) T. Yang, J.-G. Zhang, Z.-B. Zhang, M. Gozin, J. Mol. Struct. 2018, 1156, 544-549; c) Y. Yu, S. Chen, X. Li, S. Jin, L. Li, G. Zhang, X. Ma, Q. Shu, RSC Advances 2017, 7, 18523-18528.

- [4] D. Fischer, T. M. Klapötke, J. Stierstorfer, N. Szimhardt, Chem. -Eur. J. 2016, 22, 4966-4970.
- [5] N. Fischer, D. Izsák, T. M. Klapötke, S. Rappenglück, J. Stierstorfer, *Chem. – Eur. J.* 2012, 18, 4051-4062.
- [6] V. Ernst, T. M. Klapötke, J. Stierstorfer, Z. Anorg. Allg. Chem. 2007, 633, 879-887.
- a) D. Fischer, T. M. Klapötke, J. Stierstorfer, Angew. Chem. Int. Ed. 2014, 53, 8172-8175; b) D. Fischer, T. M. Klapötke, J. Stierstorfer, Angew. Chem. 2014, 126, 8311-8314.
- [8] T. G. Witkowski, E. Sebastiao, B. Gabidullin, A. Hu, F. Zhang, M. Murugesu, ACS Appl. Energy Mater. 2018, 1, 589-593.
- [9] CCDC 1833389, 1585052, 1833391, and 1833392 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
- [10] D. Fischer, T. M. Klapötke, M. Reymann, P. C. Schmid, J. Stierstorfer, M. Sućeska, *Propellants, Explos., Pyrotech.* 2014, 39, 550-557.
- [11] L. H. Finger, F. G. Schröder, J. Sundermeyer, Z. Anorg. Allg. Chem. 2013, 639, 1140-1152.
- [12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. J. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J.

Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B.
Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann,
O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L.
Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J.
Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J.
V. Ortiz, J. Cioslowski, F. D. J., *Gaussian 09, Revision E.01*, Gaussian,
Inc., Wallingford CT, **2009**.

- [13] a) E. F. C. Byrd, B. M. Rice, J. Phys. Chem. A 2006, 110, 1005-1013; b)
 B. M. Rice, S. V. Pai, J. Hare, Combust. Flame 1999, 118, 445-458; c) L.
 A. Curtiss, K. Raghavachari, P. C. Redfern, J. A. Pople, J. Chem. Phys. 1997, 106, 1063-1079.
- [14] H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* 2002, 41, 2364-2367.
- [15] M. Sućeska, EXPLO5, Version 6.04 (OZM Research), Zagreb, Croatia, 2017.

This article is protected by copyright. All rights reserved.

FULL PAPER

Entry for the Table of Contents

FULL PAPER



The synthesis and comprehensive characterization of a series of relevant nitrogenrich ionic derivatives of 2,3,5,6-Tetra(1*H*-tetrazol-5-yl)pyrazine with potential applications in novel propellant systems. In addition to their good thermal and chemical stabilities, the high nitrogen content results in improved N₂:CO ratios when combusted, which aids with erosion problems in gun barrels. Dr. Tomasz G. Witkowski, Paul Richardson, Dr. Bulat Gabidullin, Dr. Anguang Hu,* Prof. Muralee Murugesu*

Page No. – Page No.

Synthesis and Investigation of 2,3,5,6-Tetra(1*H*-tetrazol-5-yl)pyrazine based Energetic Materials