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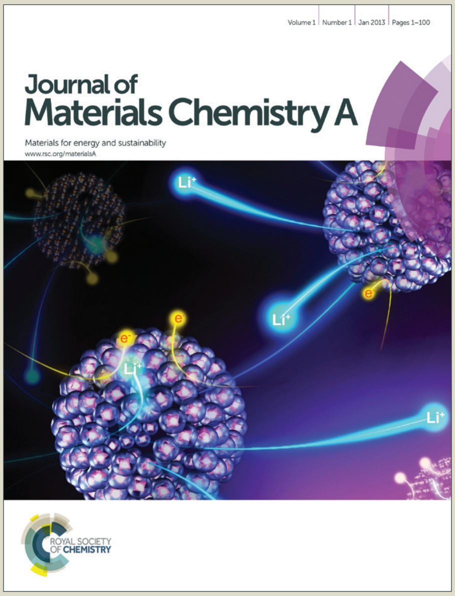

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ARTICLE TYPE

3-Nitro-1-(2*H*-tetrazol-5-yl)-1*H*-1,2,4-triazol-5-amine (HANTT) and its energetic salts: highly thermally stable energetic materials with low sensitivity

Chengming Bian,[a] Man Zhang,[a] Chuan Li[a] and Zhiming Zhou*[a,b]

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Abstract: A new family of nitrogen-rich energetic salts based on 3-nitro-1-(2*H*-tetrazol-5-yl)-1*H*-1,2,4-triazol-5-amine(HANTT) were synthesized and characterized by ^{1}H and ^{13}C nuclear magnetic resonance, infrared spectroscopy and elemental analysis. The crystal structure of neutral HANTT (**2**), its guanidinium salt (**3**), and 1,5-diamino-tetrazolium salt (**9**) were determined by single-crystal X-ray diffraction. All energetic salts exhibit excellent thermal stabilities with decomposition temperatures ranging within 264–321 ℃ and are insensitive to impact, friction and electrostatic discharge. The densities of salts **3**–**10** ranged from 1.65 g cm^{-3} to 1.81 g cm^{-3}. Theoretical performance calculations (Gaussian 03 and EXPLO5) provided detonation pressures and velocities for the energetic salts within the ranges of 22.6–32.6 GPa and 7742–8779 m s^{-1}, respectively, making them competitive energetic materials.

Introduction

Recently, nitrogen-rich heterocyclic energetic compounds have been the focus of several research groups worldwide,[1] as they proved to be promising high-energy-density materials (HEDMs) with high thermal and mechanical stabilities in suitable designs. For examples, dihydroxylammonium 3,3’-dibitroamino-4,4’-azoxyfurazanate[2] which contains the azoxy [–N=N(O)–] moiety has high density (1.9 g cm^{-3}), acceptable impact sensitivity (IS = 19 J, 120 N), excellent detonation pressure (P = 42.2 GPa) and velocity (v_D = 9511 m s^{-1}); dihydroxylammonium 3,3’-dinitro-5,5’bis-1,2,4-triazole-1,1’-diol[3] bearing *N*-oxide moieties is thermally stable (T_d = 217 ℃), exceedingly powerful (P = 39 GPa, v_D = 9087 m s^{-1}) and safe to handle (IS > 40 J).

Among these nitrogen-rich heterocycles, 1,2,4-triazole shows a perfect balance between thermal stability and high positive heat of formation, and has drawn much attention as backbone molecule for HEDMs. Moreover, 5-amino-3-nitro-1*H*-1,2,4-triazole (ANTA) is a typical thermally stable (T_d = 238 ℃)[4] and insensitive explosive based on 1,2,4-triazole.[5] Researchers have reported several derivatives of ANTA in the past years, which were synthesized either by modifying the original amino group to generate new energetic compounds, such as 3-nitro-5-nitramino-1*H*-1,2,4-triazole[6] and 5-azido-3-nitro-1*H*-1,2,4-triazole;[7] using a diazo bridge, such as 5,5’-dinitro-3,3’-azo-1,2,4-triazole (DNAT);[8] or with a direct C-N/N-N connection of energetic group/compounds to triazole, such as 1,5-diamino-3-nitro-1,2,4-triazole (BANT),[9] 4,6-bis-(3-amino-5-nitro-1*H*-1,2,4-triazole-1-yl)-5-nitropyrimidine (DANTNP),[10,11] and 1-nitroguanyl-3-nitro-5-amino-1,2,4-triazole (ANTA-NQ).[12] However, these derivatives more or less have some drawbacks. Decomposition temperatures of 3-nitro-5-nitramino-1*H*-1,2,4-triazole, 5-azido-3-nitro-1*H*-1,2,4-triazole and ANTA-NQ are 135 ℃, 174 ℃ and 200 ℃, respectively, which are much lower than that of ANTA; whereas DNAT and DANTNP are less energetic than ANTA due to the moderate charge density of DNAT powder (d = 1.67 g cm^{-3})[8] and the poor oxygen balance (-52.74%) and the lower energy of exothermic decomposition (reduced by approximately 324 J g^{-1}) of DANTNP.[10]

The tetrazole ring is an excellent building block of HEDMs owing to its high-nitrogen content, ready availability and high positive heat of formation, especially the good thermal stability derived from its aromaticity. The C—N combination of tetrazole (ΔH_f^o = 273 kJ mol^{-1})[13] with ANTA (ΔH_f^o = 88 kJ mol^{-1})[14] will greatly improve heat of formation, which is associated with increased detonation performance;[15] Introduction of tetrazole would also lead to improved stability and density due to intermolecular hydrogen bonds, represented as plane, pseudo-fused heterocycles from the close proximity between hydrogen atom in the amino group and the nitrogen atom in the tetrazole ring, which is especially obvious when tetrazole deprotonated to obtain tetrazolate anion.

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[a] C. Bian, M. Zhang, C. Li and Prof. Dr. Z. Zhou
School of Chemical Engineering and the Environment
Beijing Institute of Technology
Beijing, 100081(P.R. China)
E-mail: zzm@bit.edu.cn
[b] Prof. Dr. Z. Zhou
State Key Laboratory of Explosion Science and Technology
Beijing Institute of Technology
Beijing, 100081(P.R. China)

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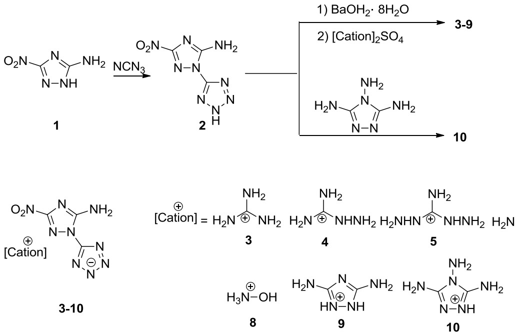
Based on the considerations above, we report on the synthesis, characterization and calculation of the detonation properties of 3-nitro-1-(2*H*-tetrazol-5-yl)-1*H*-1,2,4-triazol-5-amine (HANTT) and its energetic salts.

Results and Discussion

The synthetic pathway to HANTT (**2**) and its energetic salts are depicted in Scheme 1. An initial attempt to synthesize HANTT (**2**) by selective diazotization of 3,5-diamino-1-(1*H*-tetrazol-5-yl)-1*H*-1,2,4-triazole with sodium nitrite in dilute sulfuric acid followed by denitrification and nitration proved unsuccessful and gave rise to 3,5-dinitro-1*H*-1,2,4-triazole as main product. Neverless, the desired product **2** was finally prepared from ANTA with the reaction of cyanogen azide according to the method reported by Joo and Shreeve.[16]

Energetic salts **3** to **9** were readily synthesized through the metathesis reactions of $Ba(ANTT)_2$, which was formed in situ with one equivalent of the corresponding sulphate salt. HANTT (**2**) reacted directly with 3,4,5-triamino-1,2,4-triazole to form salt **10**. Colorless crystals of **2**, **3** and **9** suitable for single-crystal X-ray analysis by slowly evaporating solvent at room temperature and their crystallographic and structural refinement data are listed in Table 2.



Scheme 1 Synthesis of HANTT and its salts.

All of the energetic salts are soluble in hot water or methanol, stable in air and could be stored for extended periods of time. Their structures were confirmed by IR spectroscopy, ^1H, ^{13}C NMR spectroscopy and elemental analysis. The data are listed in the Experimental Section.

The signal at $\delta \approx 7.71$ ppm in ^1H NMR spectra of the energetic salts is assigned to the amino group in ANTT anion, while the rest signals are assigned to the cations. In this study, the ^{13}C NMR shifts related to cations are consistent with previously recorded shifts for such cations.[17, 18] The ^{13}C NMR resonances observed for the triazole carbon bonded to the nitro group and the other bonded to the amino group in all salts are approximately at δ = 157.9 and 155.7 ppm, respectively. These resonances are downfielded compared with those of precursor **2** (δ = 156.8 and154.6 ppm). The signal at δ = 160.7 is attributed to the tetrazole carbon, which is upfielded from that of **2** (δ = 161.8 ppm).

HANTT and its salts had been heated at 60 ℃ for 2 h before their thermal stabilities were measured by differential scanning calorimetry (Table 1) at a heating rate of 10 ℃ min^{-1}. Salt formation is usually an efficient method of improving thermal stability. Decomposition temperatures of new energetic salts ranging from 264 ℃ (**8**) to 321 ℃ (**3**) are higher than that of HANTT at 246 ℃. Thus, the energetic salts of HANTT exhibit excellent thermal stabilities which are superior to that of 1,3,5-trinitro-1,3,5-triazinane (RDX) (T_d = 230 ℃).It is noteworthy that the increase of amino substituent in analogous guanidine cations give rise to a decrease in thermal stability, as salts **4**, **5** and **6** melts at 246, 239 and 231 ℃, respectively.

Density is one of the most important properties contributing to the performance of an explosive. As shown in Table 1, HANTT possesses a density of 1.77 g cm^{-3}, while the densities of new salts range from 1.65 g cm^{-3} (**3**) to 1.81 g cm^{-3} (**8**; RDX = 1.82 g cm^{-3}), as measured using a gas pycnometer.

Table 1 Physiochemical properties and detonation parameters of HANTT and its energetic salts.

Compd	T_m[a]	T_d[b]	d[c]	$\Delta_f H_L$[d]	$\Delta_f H_{sal}$[e]	$\Delta_{Ex} U^o_{sal}$[f]	P_{cj}[g]	v_D[h]	IS[i]	FS[j]	ESD[k]	OB[l]	N%[m]
2	-	246	1.77	-	487.2	2559.9	28.8	8316	> 40	>360	7.04	-44.6	64.0
3	-	321	1.65	477.5	392.2	1637.2	22.6	7742	> 40	>360	>44	-62.4	65.6
4	246	269	1.72	475.2	486.0	1901.8	25.9	8149	> 40	>360	>44	-61.9	67.1
5	239	-[n]	1.69	467.3	595.5	2193.3	26.4	8249	> 40	>360	>44	-61.5	68.5
6	231	-[n]	1.69	461.0	707.9	2465.2	27.5	8390	> 40	>360	>44	-61.1	69.7
7	-	281	1.79	511.1	409.1	2014.5	29.6	8507	> 40	>360	>44	-52.3	65.4
8	217	264	1.81	502.5	460.8	2104.6	32.6	8779	> 40	>360	>44	-41.7	60.8
9	-	277	1.68	462.3	595.5	2110.7	23.6	7840	> 40	>360	>44	-64.8	66.2
10	-	301	1.74	460.2	711.2	2388.6	26.7	8217	> 40	>360	>44	-64.2	67.5
TATB	350	~360	1.93	-	-154.2	-511	31.2	8114	50	>360	-	–55.8	32.5
RDX	-	230	1.82	-	92.6	617.3	34.8[o]	8748[o]	7	120	0.2	-21.6	37.8

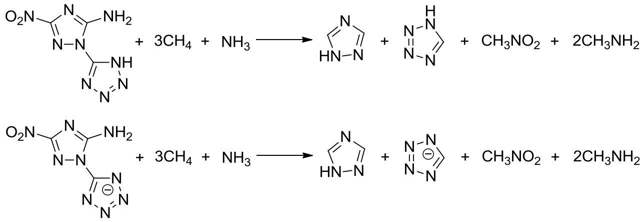
[a] Melting point [℃]. [b] Thermal degradation [℃]. [c] Measured density (gas pynometer) [g cm^{-3}]. [d] Calculated molar lattice energy [kJ mol^{-1}]. [e] Calculated molar enthalpy of formation of salts [kJ mol^{-1}]. [f] Energy of formation [kJ kg^{-1}]. [g] Detonation pressure [GPa]. [h] Detonation velocity [m s^{-1}]. [i] Impact sensitivity. [j] Friction sensitivity (BAM friction apparatus) [N]. [k] Electrostatic discharge device [J]. [l] Oxygen balance (OB) is an index of the deficiency or excess of oxygen in a compound required to convert all C into CO_2 and all H into H_2O, for the compound with the molecular formula of $C_aH_bN_cO_d$ (without crystal water), OB(%) = 1600[(d-2a-b/2)/Mw] [%]. [m]nitrogen content. [n] No sharp decomposition point. [o] From Ref. 20.

Oxygen balance (OB) is an expression which indicates the degree to which an explosive can be oxidized.[21, 22] All salts have negative OB which range from -64.8%(**9**) to -41.7%(**8**) and display high nitrogen contents ranging from 60.8%(**8**) to

69.7%(**6**).

Impact sensitivity (IS) was determined using the BAM fall hammer BFH-10 apparatus test with approximately 20 mg samples (5.0 kg drop hammer).[23] The IS values of HANTT and its salts are higher than 40 J, and their FS values are higher than 360 N, placing them in the insensitive class. This result may be attributed to intramolecular hydrogen bonds and extensive hydrogen-bonding interactions between the cation and the anion in salt formation. It is interesting that all salts are insensitive to electrostatic discharge with the ESD values above 44 J while the neutral compound **2** is relatively insensitive (ESD = 7.04 J).

Heat of formation is fundamentally important in evaluating compounds for their possible value as explosives. More positive values lead to potentially better detonation properties. The ΔH_f of HANTT and its anion salt are 487.2 kJ mol^{-1} and 293.8 kJ mol^{-1}, respectively, as calculated using Gaussian 03 (Revision E.01) suite of programs based on isodesmic reactions (Scheme 2). The cation values are provided in the literature.[19] The positive ΔH_f values of salts **3** to **10** are much higher than that of ANTA (ΔH_f^o = 88 kJ mol^{-1}), and range from 392.2 kJ mol^{-1} (**3**) to 711.2 (**10**) kJ mol^{-1} as computed using the Born—Haber energy cycle (Figure 1).



Scheme 2 Isodesmic reactions for HANTT and ANTT anion.

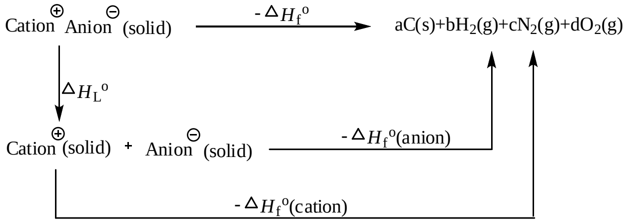


Figure 1 Born-Haber cycle for the formation for energetic salts.

The detonation pressures (*P*) and velocities (v_D) of the new energetic salts were determined using **EXPLO5** program (Version 5.05) according to the measured density and the calculated ΔH_f.[24] The calculated detonation pressures range between 22.6 GPa to 32.6 GPa, and the calculated detonation velocities fall between 7742 m s^{-1} to 8779 m s^{-1}. Salt **7** (v_D = 8507 m s^{-1}, P = 29.6 GPa) has an excellent detonation performance due to its high density and moderate oxygen balance. Salt **8** possesses the highest density and the best oxygen balance, thus confirming its excellent detonation performance (v_D = 8779 m s^{-1}, P = 32.6 GPa) which is comparable to RDX (v_D = 8748 m s^{-1}, P = 34.8 GPa).

X-ray Crystallography

Suitable colourless crystals of HANTT (**2**) were obtained for single-crystal X-ray analysis by slowly evaporating ethyl alcohol/water at room temperature. Compound **2** crystallizes in the monoclinic space group *P2(1)/c* with a calculated density of 1.710 g·cm^{-3}. Figure 2 shows that the unit consists of one HANTT molecule and one H_2O molecule. Table 2 lists the crystallographic and structural refinement data.

All atoms of **2** are roughly coplanar, and the largest torsion angle is 169.55(12) °. This angle is located among N2–N1–C3–N6. The length of C3–N1 bond which combines the triazole to tetrazole is 1.3939(15) Å. The dihedral angle between triazole (C1–N1–N2–C2–N3) and tetrazole (C3–N6–N7–N8–N9) is 9.46 °. The 1.3013(16) Å C2–N2 bond length is the shortest while the 1.3746(16) Å C1–N1 bond length is the longest in the two heterocyclic rings. This may be caused by the electron-donating amino group and the strong electron-withdrawing inductive effects of the nitro group. As expected, an intramolecular hydrogen bond is represented in the form of a six-membered ring by the close proximity of N4–H4B···N6 (2.298 Å). The amino (H4A–N4–H4B) and nitro (O1–N5–O2) groups are approximately coplanar with the triazole ring. The dihedral angles between the triazole and the amino and nitro groups are 1.79 ° and 2.35 °, respectively, which are samller than those in 3-nitro-1*H*-1,2,4-triazol-5-amine,[25] at 21.83 ° and 10.32 °, respectively. This result suggests that the introduction of the tetrazole ring lead to a strong conjugation of the charge throughout the whole HANTT molecule. The packing structure of **2** was built up and linked to a 2D double layer by various hydrogen bonds, as depicted along the *b* axis in Figure 2b.

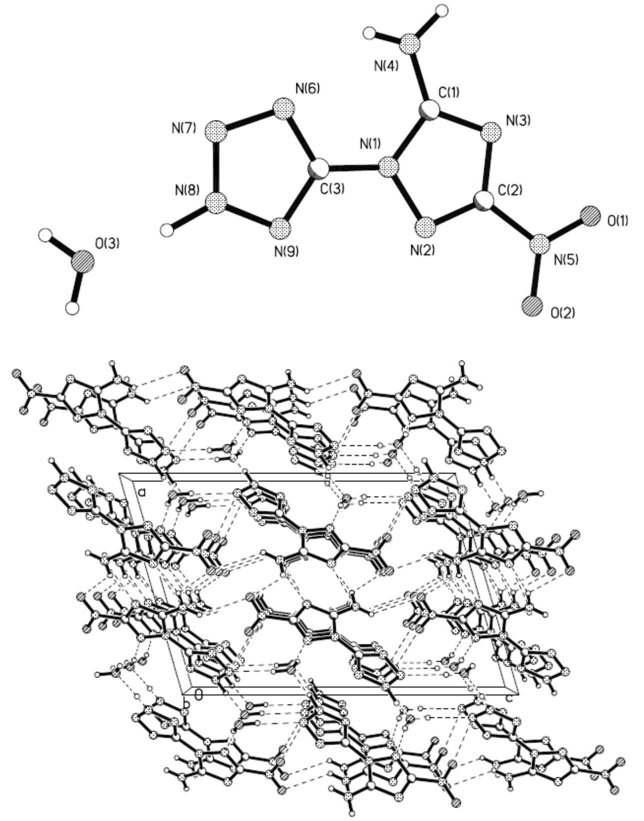


Figure 2 a) Displacement ellipsoid plot (50%) of **2**. The hydrogen atoms are included but unlabeled for clarity. b) Ball and stick packing diagram of **2** viewed down the b axis. The dashed lines indicate hydrogen bonding.

A crystal of **3** suitable for X-ray deiffraction analysis was obtained by slow evaporation of water from water at room temperature. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with a calculated density of 1.641 g cm^{-3}. Its crystallographic data are summarized in Table 2.

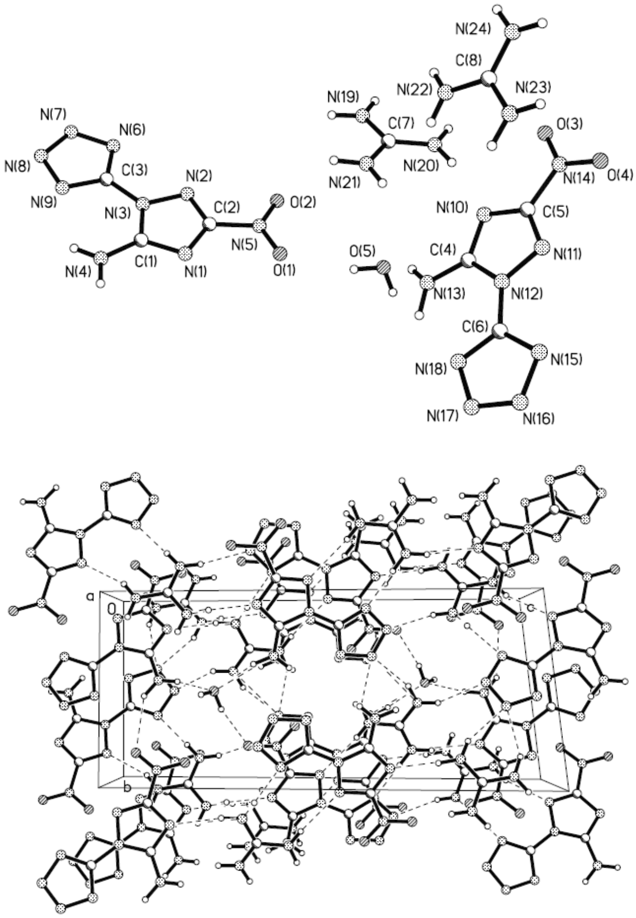


Figure 3 a) Displacement ellipsoid plot (50%) of **3**. The hydrogen atoms are included but unlabeled for clarity. b) Ball and stick packing diagram of **3** viewed down the a axis. The dashed lines indicate hydrogen bonding.

Figure 3a shows the presence of one H_2O molecule and two asymmetric units. Each unit contains one ANTT anion and one guanidinium cation, in which proton transfers from the tetrazole of HANTT to guanidine is confirmed. All atoms of ANTT anion are roughly coplanar with the largest torsion angle of 171.96(10) ° between N11–N12–C6–N18. Intramolecular hydrogen bonds between N13 of the amino group and N18 of the tetrazole [N13–H13A ⋯ N18 (2.212 Å)], N4–H4B and N9[N4–H4B ⋯ N9 (2.246Å)] are the strongest in the three confirmed crystals of **2**, **3** and **9**, which greatly improve the thermal stability of **3** at the highest decomposition temperature (T_d = 321 ℃). The dihedral angles between triazole and tetrazole are 2.98 ° and 7.40 °, respectively, which are smaller than that of HANTT. From a structural point of view, the whole ANTT anion looks like a plane pseudo-fused aza-cyclic compound by the connection of intramolecular hydrogen bonds. In an asymmetric unit, the cation and triazole ring in ANTT tend to be coplanar with a dihedral angle between them of 4.28 °. The N–N bond lengths in the tetrazolate ring of the ANTT anion vary from 1.3094(14) Å to 1.3551(13) Å and thus lie between those of N-N single bonds (1.454 Å) and N=N double bonds (1.245 Å).[26] This result indicates delocalization of the negative charge throughout the aromatic rings, as observed in other tetrazolate salts.[27, 28] Viewed along the *a* axis, the packing structure of **3** shows a variety of hydrogen bonds in the salt structure.

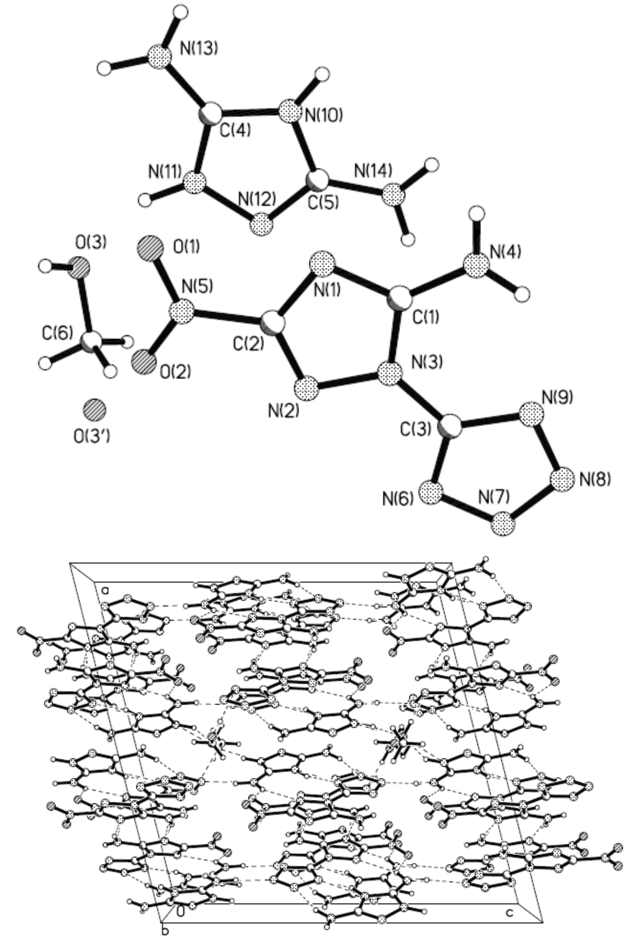


Figure 4 a) Displacement ellipsoid plot (50%) of **9**. The hydrogen atoms are included but unlabeled for clarity, while the disordered MeOH were partly deleted for clarity. b) Ball and stick packing diagram of **9** viewed down the b axis. The dashed lines indicate hydrogen bonding.

Suitable colourless crystals of **9** were obtained for single-crystal X-ray analysis by slowly evaporating methanol/water at room temperature. Compound **9** crystallizes in the monoclinic space group *PC2/c* with a calculated density of 1.657 g cm^{-3}.

As shown in Figure 4a, the salt is formed through transfer of proton from the N7/N8 position in ANTT anion to the resulting cation. Disorder of CH_3OH and H_2O molecules was observed in the crystal. The ratio of solvent molecules and salts is 0.5:1, while the former consist of 0.461:0.039 CH_3OH and H_2O ratio. Intramolecular hydrogen bond is shorter than that of the neutral compound **2**, as represented by the close proximity of N4–H4A⋯ N9 (2.259 Å), which lead to high thermal stability (T_d = 277 ℃). The dihedral angle between triazole and tetrazole in ANTT anion is 1.40 ° and all atoms of ANTT anion are nearly in one plane with the largest torsion angle of 175.59 ° (O2–N5–C2–N9). 3,5-Diamino-1,2,4-triazolium cation and ANTT anion tend to be coplanar with a dihedral angle of 4.23 ° between the two triazole rings. Similar to the situation in **3**, the N-N bond lengths in the tetrazolate ring of the ANTT anion vary from 1.3095(16) to

1.3612(17) Å and thus lie between those of N–N single bonds (1.454 Å) and N=N double bonds (1.245 Å). This result indicates the conjugation of the negative charge throughout the aromatic rings. As shown in Figure 4b, the discrete ANTT anions and 3,5-diamino-1,2,4-triazolium cations are linked into a 3D network by extensive hydrogen bonds.

Table 2 Crystallographic data and structure refinement parameters for **2**, **3** and **9**.

	2	**3**	**9**
Formula	$C_3H_5N_9O_3$	$C_4H_9N_{12}O_{2.50}$	$C_{5.46}H_{9.92}N_{14}O_{2.50}$
Mw	215.16	265.23	311.73
Crystal system	monoclinic	triclinic	monoclinic
Space group	*P2(1)*/c	$P\bar{1}$	*PC2/c*
a[Å]	10.830(4)	7.0181(17)	17.869(6)
b[Å]	5.0641(18)	8.833(2)	7.864(2)
c[Å]	15.865(6)	18.795(6)	18.347(6)
V[Å^3]	835.9(5)	1073.5(5)	2499.2(14)
Z	4	4	8
T[K]	153(2)	163(2)	163(2)
λ[Å]	0.71073	0.71073	0.71073
ρ_{calcd}[mg m^{-3}]	1.710	1.641	1.657
μ[mm^{-1}]	0.15	0.14	0.14
F(000)	440	548	1286
Crystal size[mm^{-3}]	0.59 × 0.13 × 0.05	0.50 × 0.25 × 0.13	0.52 × 0.37 × 0.07
θ range[°]	2.7-29.1	2.2-31.5	2.4-31.0
index ranges	$-14\leq h\leq 14$ $-6\leq k\leq 6$ $-21\leq l\leq 21$	$-9\leq h\leq 10$ $-12\leq k\leq 12$ $-27\leq l\leq 27$	$-24\leq h\leq 25$ $-11\leq k\leq 11$ $-26\leq l\leq 25$
reflns collected	8820	16124	14198
Independent reflns (R_{int})	2245[0.026]	7031	3929
data/retraints/parameters	2245/0/156	7031/0/406	3929/1/245
GOF on F^2	1.003	1.002	1.002
$R[F^2 > 2\sigma(F^2)]$	0.041	0.039	0.050
$wR(F^2)$	0.112[a]	0.089[b]	0.137[c]

[a] $w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 0.106P]$, where $P = (F_o^2 + 2F_c^2)/3$; [b] $w = 1/[\sigma^2(F_o^2) + (0.0391P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$; [c] $w = 1/[\sigma^2(F_o^2) + (0.0786P)^2 + 1.260\,P]$, where $P = (F_o^2 + 2F_c^2)/3$

Conclusions

In this study, HANTT (**2**) and its salts **3** to **10** were synthesized and fully characterized. The structures of neutral compound **2**, salt **3** and **9** have been analyzed by single-crystal X-ray diffraction analysis. The densities of all nitrogen-rich salts lie in the range between 1.65 g cm^{-3} (**3**) and 1.81 g cm^{-3} (**8**). Intramolecular hydrogen bond represented in the form of plane pseudo-fused heterocycles by the close proximity between hydrogen atom in the amino group and the nitrogen atom in the tetrazole ring, greatly improves thermal stability and IS, especially obvious when tetrazole deprotonated to obtain tetrazolate anion as we expected. It is notable that all energetic salts exhibit excellent thermal stabilities with decomposition temperatures ranging within 264–321 ℃ and are insensitive to impact, friction and electrostatic discharge. Their detonation velocities and detonation pressures were calculated to be 7742 m s^{-1} to 8779 m s^{-1} and 22.6 GPa to 32.6 GPa, respectively. Salt **7** (v_D = 8507 m s^{-1}, P = 29.6 GPa) has an excellent detonation performance due to its high density and moderate oxygen balance. Salt **8** possesses the highest density and the best oxygen balance, thus confirming its excellent detonation performance (v_D = 8779 m s^{-1}, P = 32.6 GPa). Finally, in view of thermal and mechanical stabilities, salt **8** is superior to RDX.

Experimental Section

Caution! Although we experienced no difficulties in handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly encouraged!

General methods: ^{1}H, ^{13}C NMR spectra were recorded on a 500 MHz nuclear magnetic resonance spectrometer operating at 400 and 100 MHz, respectively. Chemical shifts are reported relative to TMS for ^{1}H and ^{13}C NMR spectra. The solvent was [D$_6$] dimethyl sulfoxide ([D$_6$]DMSO) unless otherwise specified. The melting and decomposition points were recorded on a differential scanning calorimetry (DSC) at a scan rate of 10 ℃ min^{-1} in a dynamic nitrogen atmosphere (flow rate=50 mL min^{-1}). Infrared spectra were recorded using a Bruker Alpha with a ATR-Ge device. Densities were measured at 25 ℃ using a Micromeritics Accupyc Ⅱ 1340 gas pycnometer. Elemental analyses were obtained on an Elementar Vario MICRO CUBE (Germany) elemental analyzer.

X-ray crystallography

Crystals of **2**, **3** and **9** was removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was then selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream. Data for **2** was collected at 153(2) K while for **3** and **9** were collected at 163(2) K, using a Rigaku Saturn724 CCD (AFC10/Saturn724+ for 7) diffractometer equipped with a graphite-monochromatized MoKα radiation (λ = 0.71073 Å) using omega scans. Data collection and reduction were performed and the unit cell was initially refined by using CrystalClear -SM Expert 2.0 r2 software.[29] The reflection data were also corrected for Lp factors. The structure was solved by direct methods and refined by the least squares method on F^2 using the SHELXTL-97 system of programs.[30] Structure were solved in the space group *P*2(1)*/c* for **2**, $P\bar{1}$ for **3**, *PC2/c* for **9**, by analysis of systematic absences. In this all-light-atom structure the value of the Flack parameter did not allow the direction of polar axis to be determined and Friedel reflections were then merged for the final refinement. Details of the data collection and refinement are given in Table 2.

CCDC-1017630 (**2**), CCDC-1017631 (**3**) and CCDC-1017632 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./data_request/cif.

3-Nitro-1-(2H-tetrazol-5-yl)-1H-1,2,4-triazol-5-amine (HANTT, 2)

At 0 ℃, 10 mmol cyanogen bromide was dissolved in 50 mL dry acetonitrile to which was added 40 mmol sodium azide. The reaction mixture was stirred at 0-5 ℃ for 4h. The inorganic salt was filtered off. The cyanogens azide solution is added to a solution containing 5 mmol ANTA which has been neutralized in 20 mL water at 0 ℃. After stirring over 4h at ambient temperature, the solvent was removed in air. The product was purified by washing with water and acetonitrile. Yield 78%, yellow solid, m.p. 246 ℃. ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 ℃, TMS): δ= 7.96 (s, 1H), 6.31 (brs, 2H) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ=161.8, 156.8, 154.6 ppm. IR (neat): 3568, 3417, 3167, 1639, 1582, 1554, 1518, 1404, 1307, 1218, 1155, 1020, 990, 846, 766, 722, 612, 478 cm^{-1}.MS (ESI): 196 (M-H)$^-$. Anal. calcd. for $C_3H_3N_9O_2$: C 18.28, H 1.53, N

63.95%; found C 18.28, H 1.54, N 63.93%。

General Procedures for the Preparation of Energetic salts 3-9: $Ba(OH)_2 \cdot 8H_2O$ (158 mg, 0.5 mmol) was added to a solution of HANTT (197 mg, 1.0 mmol) in H_2O (10 mL) and the resulting mixture was stirred at 60 ℃ until all of the solids had dissolved, and the sulfate salt (0.5 mmol) was added and the mixture was stirred at 60 ℃ for an additional 2 h. After removal of $BaSO_4$, the solvent was evaporated in vacuo and the residue was recrystallized from H_2O to give the target product.

Guanidinium ANTT (3)

Yellow solid (228 mg, 89%). ^1H NMR ([D$_6$]DMSO, 400 MHz, 25 ℃, TMS): δ= 7.72 (s, 2H), 7.02 (s, 6H) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ= 160.7, 158.4, 157.9, 155.7 ppm. IR (neat): 3449, 3056, 1636, 1541, 1515, 1434, 1403, 1308, 1152, 1132, 1037, 847, 766, 445 cm^{-1}. Anal. calcd. for $C_4H_8N_{12}O_2$: C 18.75, H 3.15, N 65.61%; found C 18.74, H 3.18, N 65.63%。

Aminoguanidinium ANTT (4)

Yellow solid (238 mg, 88%). ^1H NMR ([D$_6$]DMSO, 400 MHz, 25 ℃, TMS): δ=8.60 (s, 1H), 7.71(s, 2H), 4.70 (s, 2H) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ= 160.7, 159.2, 158.0, 155.7 ppm. IR (neat): 3460, 3405, 3342, 3063, 1694, 1653, 1545, 1524, 1406, 1311, 1207, 1154, 1099, 959, 846, 767, 726, 618, 458 cm^{-1}. Anal. calcd. for $C_4H_9N_{13}O_2$: C 17.71, H 3.34, N 67.14%; found C 17.69, H 3.35, N 67.15%。

Diaminoguanidinium ANTT (5)

Yellow solid (269 mg, 94%). ^1H NMR ([D$_6$]DMSO, 400 MHz, 25 ℃, TMS): δ= 8.58 (s, 2H), 7.71 (s, 2H), 7.17 (s, 2H), 4.45 (brs, 4H) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ= 160.7, 160.2, 157.9, 155.7 ppm. IR (neat): 3407, 3370, 3339, 3147, 1650, 1505, 1433, 1402, 1310, 1172, 1144, 924, 848, 724, 565 cm^{-1}. Anal. calcd. for $C_4H_{10}N_{14}O_2$: C 16.79, H 3.52, N 68.51%; found C 16.77, H 3.52, N 68.50%。

Triaminoguanidinium ANTT (6)

Yellow solid (271 mg, 90%). ^1H NMR ([D$_6$]DMSO, 400 MHz, 25 ℃, TMS): δ= 8.61 (s, 3H), 7.70 (s, 2H), 4.50 (s, 6H) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ= 160.7, 159.5, 158.0, 155.7 ppm. IR (neat): 3413, 3371, 3196, 1678, 1651, 1533, 1505, 1404, 1310, 1131, 927, 848, 766, 723, 617, 522 cm^{-1}.Anal. calcd. for $C_4H_{11}N_{15}O_2$: C 15.95, H 3.68, N 69.75%; found C 15.97, H 3.67, N 69.74%。

Ammonium ANTT (7)

Yellow solid (160mg, 75%). ^1H NMR ([D$_6$]DMSO, 400 MHz, 25 ℃, TMS): δ= 7.71 (s, 2H), 7.20 (s, 4H). ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ= 160.7, 157.9, 155.7 ppm. IR (neat): 3381, 3160, 3034, 2857, 1654, 1521, 1432, 1407, 1308, 1077, 1034, 851, 609 cm^{-1}. Anal. calcd. for $C_3H_6N_{10}O_2$: C 16.83, H 2.82, N 65.41%; found C 16.81, H 2.83, N 65.42%。

Hydroxylammonium ANTT (8)

Yellow solid (184mg, 80%). ^1H NMR ([D$_6$]DMSO, 400 MHz, 25 ℃, TMS): δ=10.12(s, 4H), 7.71(s, 2H) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ=160.7, 157.9, 155.7 ppm. IR (neat): 3386, 3204, 3151, 3103, 2706, 1643, 1540, 1509, 1437, 1411, 1308, 1151, 1118, 1013, 852, 770, 615, 504 cm^{-1}. Anal. calcd. for $C_3H_6N_{10}O_3$: C 15.66, H 2.63, N 60.86%; found C 15.67, H 2.66, N 60.85%。

1,5-Diamino-tetrazolium ANTT (9)

Yellow solid (266mg, 90%). ^1H NMR ([D$_6$]DMSO, 400 MHz, 25 ℃, TMS): δ=7.71 (s), 6.32 (brs). ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ= 160.8, 157.8, 155.8, 151.9 ppm. IR (neat): 3463, 3379, 3333, 3007, 1704, 1661, 1515, 1398, 1313, 1158, 1139, 1029, 851, 768, 724, 613, 445 cm^{-1}. Anal. calcd. for $C_5H_8N_{14}O_2$: C 20.27, H 2.72, N 66.20%; found C 20.28, H 2.73, N 66.18%。

3,4,5-Triamino-1,2,4-triazolium ANTT (10)

3,4,5-Triamino-1,2,4-triazole (1.0 mmol) was added to a solution of HANTT (197 mg, 1.0 mmol) in 10 mL water. After stirring at 80℃ for 2 h, the solvent was evaporated in vacuo and the residue was crystallized from water. Yellow solid (264mg, 85%). ^1H NMR ([D$_6$]DMSO, 400 MHz, 25 ℃, TMS): δ= 7.70 (s, 2H), 7.11 (s, 4H), 5.62 (s, 2H). ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ= 160.7, 158.0, 155.7, 150.4 ppm. IR (neat): 3424, 3338, 3248, 2964, 1708, 1635, 1541, 1514, 1437, 1405, 1310, 1151, 1024, 930, 848, 762, 618, 425 cm^{-1}. Anal. calcd. for $C_5H_9N_{15}O_2$: C 19.30, H 2.91, N 67.51%; found C 19.31, H 2.93, N 67.50%。

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