Highly Energetic Salts of 3,6-Bishydrazino-1,2,4,5-tetrazine

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Abstract: 3,6-Bishydrazino-1,2,4,5-tetrazine was synthesized as described by hydrazinolysis of 3,6-bis-(3,5-dimethylpyrazolyl)-1,2,4,5-tetrazine. Doubly protonated 1:1 and 1:2 salts of the highly energetic anions were synthesized. These are bishydrazinium-tetrazine dichloride dihydrate (1:2) (BHT-2HCl·2H$_2$O) (**2**), bishydrazinium-tetrazine (5,5´-azotetrazolate) dihydrate (1:1) (BHT-ATz·2H$_2$O) (**3**), bishydrazinium-tetrazine bis (3,5-dinitrotriazolate) dihydrate (1:2) (BHT-(DNT)$_2$·2H$_2$O) (**4**), bishydrazinium-tetrazine bis (5-nitrotetrazolate) (1:2) (BHT-(NT)$_2$) (**5**), bishydrazinium-tetrazine (5,5´-bistetrazolate) dihydrate (1:1) (BHT-BT·2H$_2$O) (**6**), bishydrazinium-tetrazine bistetrazolylamine (1:1) (BHT-BTA) (**7**), bishydrazinium-tetrazine bis (3-amino-5-nitrotriazolate) (1:2) (BHT-(ANTA)$_2$) (**8**) and bishydrazinium-tetrazine 4,4´,5,5´-tetranitro-2,2´-bisimidazolate (1:1) (**9**). Compounds **2-6** could be characterized by low temperature X-ray diffraction. All of the compounds were sufficiently analyzed by *^{1}H* and *{^{1}H}^{13}C* and *^{14}N* NMR spectroscopy, elemental analysis (CHN), mass spectroscopy (FAB)) and vibrational spectroscopy (IR and Raman). The detonation parameters of the most promising candidates **5** and **9** in terms of energetic applications were calculated using the EXPLO5 V5.05 computer code. The energies of formation were calculated using CBS-4M electronic enthalpies and the atomization method. Furthermore, since all of the compounds are energetic materials, sensitivity tests towards impact (IS), friction (FS) and electrostatical discharge (ESD) were carried out. In addition their thermal stabilities were determined using a differential scanning calorimeter with a heating rate of 5 °C min^{-1}.

Keywords: 1,2,4,5-tetrazine, energetic materials, explosives, sensitivities, crystal structures

Introduction

Most commercial secondary explosives like RDX (hexogen) and HNS (hexanitrostilbene) are very toxic for human and animal organisms [1]. In terms of performance, secondary explosives are characterized by parameters like the detonation velocity ($V_{det.}$), detonation pressure (P_{C-J}), heat of detonation ($\Delta_{Ex}U°$) and the volume of detonation gases (V_0) which is created during their detonation [2]. It is a recent project to forge energetic materials and compositions [3] with higher thermal stability, lower sensitivity (towards impact (*IS*), friction (*FS*), electrostatic discharge (*ESD*)) and lower toxicity than the currently used ones. One approach is the use of azoles in combination with energetic substituents like nitro or azide groups at the carbon atom(s) [4].

High positive heats of formation, which are strongly desired, are also found in 1,2,4,5-tetrazines [5]. 3,6-Bishydrazino-1,2,4,5-tetrazine (**BHT**, **1**) is a highly energetic molecule with a highly positive enthalpy of formation (577.0 kJ·mol⁻¹) [6], due to the N–N single bonds of the hydrazine moiety and the aromatic N–N bonds of the 1,2,4,5 tetrazine. It can serve as a doubly charged cation to create 1:2 or 1:1 salts. This was already investigated by Hiskey *et al.* in the 1990's with respect to propellant ingredients [7]. They synthesized 1:1 and 1:2 salts by direct protonation of BHT using nitric acid, perchloric acid, ammonium dinitramide and 4,4′,5,5′-tetranitro-2,2′-bisimidazole (TNBI) as acids and characterized their sensitivity towards impact as well as their thermal stability. Additionally the 1:1 5,5′-bistetrazolate and the bis-tetrazolyl amine salts were investigated with respect to low smoke producing pyrotechnic compositions. However their structures were not yet determined [8]. Herein we report on the syntheses and potential use as ionic explosives of various energetic BHT 1:1 and 1:2 salts. The compounds were synthesized by salt metathesis or direct acid/base reaction in good yields and purity.

Results and Discussion

Synthesis

3,6-Bishydrazino-1,2,4,5-tetrazine (**1**) was synthesized as described in the literature [9-12] in four steps *via* triaminoguanidinium chloride and acetyl acetone, followed by oxidation with liquid NO₂ in NMP or NaNO₂ in CH₂Cl₂/glacial acid and substitution with hydrazine. An overall synthetic protocol is displayed in Scheme 1. 3,6-Bishydrazino-1,2,4,5-tetrazine (**1**) and the corresponding 4,4′,5,5′-tetranitro-2,2′-bisimidazolate (**9**) were also

synthesized as described in the literature [7, 9]. The reaction of gaseous HCl with **1** suspended in methanol at 0 °C yielded the 3,6-bishydrazinium-tetrazine dichloride dihydrate (BHT-2HCl·2H$_2$O, **2**) in high yield after recrystallization from i-PrOH/H$_2$O. By metathesis reactions with alkaline metal salts of highly energetic anions, 1:1 and 1:2 salts of **BHT** were synthesized. These are bishydrazinium-tetrazine (5,5´-azotetrazolate) dihydrate (1:1) (BHT-ATz·2H$_2$O) (**3**), bishydrazinium-tetrazine bis (3,5-dinitrotriazolate) dihydrate (1:2) (BHT-(DNT)$_2$·2H$_2$O) (**4**), bishydrazinium-tetrazine bis (5-nitrotetrazolate) (1:2) (BHT-(NT)$_2$) (**5**), bishydrazinium-tetrazine (5,5'-bistetrazolate) dihydrate (1:1) (BHT-BT·2H$_2$O) (**6**), bishydrazinium-tetrazine bistetrazolylamine (1:1) (BHT-BTA) (**7**) and bishydrazinium-tetrazine bis (3-amino-5-nitrotriazolate) (1:2) (BHT-(ANTA)$_2$) (**8**). All of these specified anions were synthesized as described in the literature [13-18]. Furthermore we tried to use N-oxides as potentially energetic anions, namely 5-nitrotetrazole 1- oxide and 5,5'- azotetrazole 1,1'-dioxide. Unfortunately BHT seems to be incompatible with these N-oxide species and decomposition due to oxidation reactions of the hydrazine moiety occurs.
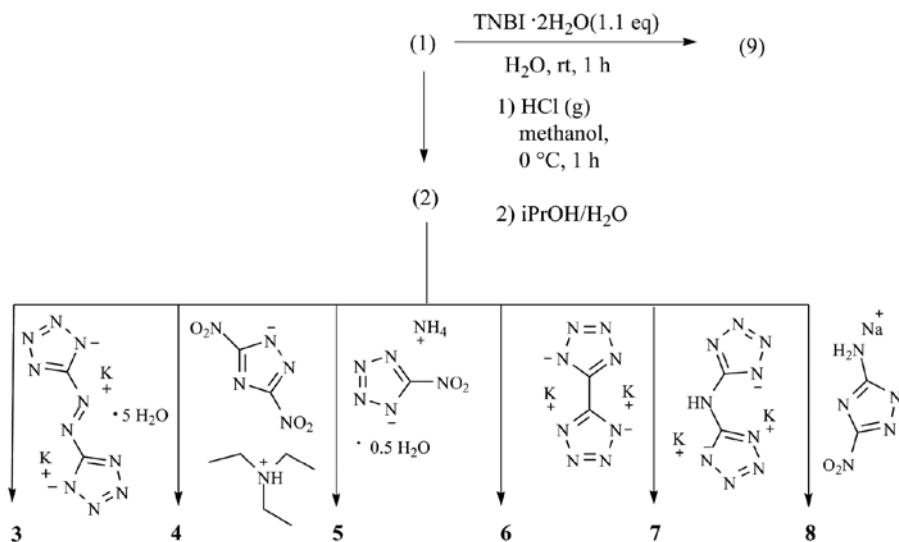
Scheme 1. Overall synthetic scheme for compounds **2-9**; reaction conditions: ambient temperature 2 h for each compound (**3–9**), 1:1 or 1:2 stoichiometry.

Crystal Structures

The single crystal X-ray diffraction data were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current

40 mA) and a KappaCCD detector. The data collections were undertaken using the CRYSALIS CCD software [19] and the data reductions were performed with the CRYSALIS RED software [20]. The structures were solved with SIR-92 [21], refined with SHELXL-97 [22] and finally checked using PLATON [23]. In all of the structures the hydrogen atoms were located and refined. The absorptions of the structures were corrected using the SCALE3 ABSPACK multi-scan method [24]. Selected data and parameters from the X-ray data collection and refinements are given in Table 1. Further information regarding the crystal-structure determinations have been deposited with the Cambridge Crystallographic Data Centre [25] as supplementary publication Nos. 926094 (**2**), 926097 (**3**), 926095 (**4**), 926096 (**5**) and 926098 (**6**).

Table 1.   XRD data and parameters

Compound	BHT · 2 HCl · 2 H$_2$O (**2**)	BHT(ATZ) · 2 H$_2$O (**3**)	BHT(DNT)$_2$ · 2 H$_2$O (**4**)	BHT(NT)$_2$ (**5**)	BHT(BT) · 2 H$_2$O (**6**)
Formula	C$_2$H$_{12}$Cl$_2$N$_8$O$_2$	C$_4$H$_{10}$N$_{18}$O$_2$	C$_6$H$_{12}$N$_{18}$O$_{10}$	C$_4$H$_8$N$_{18}$O$_4$	C$_4$H$_{12}$N$_{16}$O$_2$
FW [g mol^{-1}]	251.08	342.25	496.27	372.22	316.13
Crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	*P–1*	*P 2$_1$/c*	*P 2$_1$/n*	*P–1*	*P–1*
Habitus	orange needle	red needle	orange needle	yellow needle	orange needle
Crystal Size [mm]	0.18 x 0.21 x 0.28	0.11 x 0.13 x 0.24	0.20 x 0.29 x 0.34	0.20 x 0.22 x 0.29	0.13 x 0.18 x 0.24
a [Å] b [Å] c [Å] α [°] β [°] γ [°]	6.3094(6) 6.9132(6) 7.4141(7) 114.060(9) 97.162(7) 112.699(9)	4.3434(7) 12.0583(16) 12.9592(17) 90.00 91.900(14) 90.00	10.7777(18) 6.1512(15) 13.668(3) 90.00 93.110(18) 90.00	6.4465(6) 7.1755(7) 8.0547(7) 99.369(8) 103.574(8) 96.879(8)	7.7949(8) 9.2606(10) 9.9301(12) 117.382(12) 90.858(9) 97.500(9)
V [Å^3]	256.70(4)	678.35(17)	904.8(3)	352.47(6)	628.76(12)
Z	2	2	4	1	2
ρ$_{calc.}$ [g cm^{-3}]	1.624	1.686	1.822	1.754	1.671
μ [mm^{-1}]	0.627	0.139	0.167	0.151	0.137
F(000)	130	356	508	190	328
λ$_{MoKα}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173	173
θ Min–Max [°]	4.54, 25.98	4.62, 26.25	4.13, 26.48	4.32, 26.00	4.13, 25.00
Dataset	-7:7; -8:8; -9:9	-5:5; -14:14; -15:16	-13:13; -5:7; -16:17	-7:7; -8:8; -9:9	-9:8; -10:10; -11:11

Reflections collected	2597	3485	4666	3546	2647
Independent refl.	997	1362	1870	1373	2103
R_{int}	0.025	0.048	0.027	0.028	0.020
Observed reflections	879	737	1357	1004	1750
Parameters	88	133	192	134	247
R_1 (obs)	0.0209	0.0361	0.0320	0.0321	0.0394
wR_2 (all data)	0.0590	0.0542	0.0737	0.0782	0.0998
S^c	1.015	0.752	0.970	0.924	1.081
Resd. Dens. [e Å^{-3}]	-0.204, 0.206	-0.281, 0.246	-0.177, 0.186	-0.222, 0.195	-0.187, 0.503
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SiR-92	SiR-92	SiR-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
CCDC No.	926094	926097	926095	926096	926098

2 crystallizes in the triclinic space group *P-1* with 2 formula units per unit cell and a density of 1.624 g·cm^{-3} at 173 K. The generally planar structure of the dication (trans arrangement of the hydrazinium moieties) is in agreement with a previously published tetrazolate derivative [26].
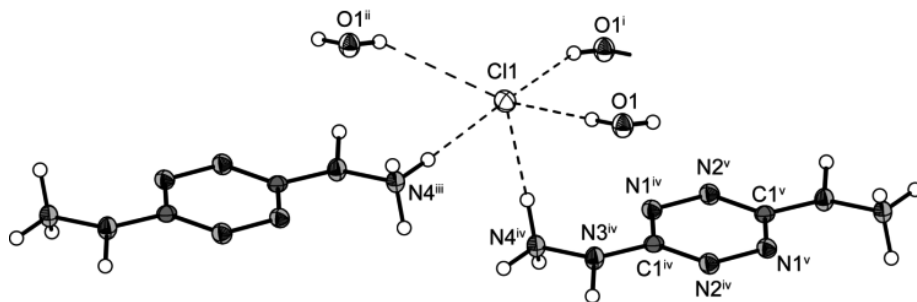

Figure 1. View of the coordination sphere of one chloride anion in the crystal structure of **2** showing the labelling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. Selected bond lengths [Å]: N1^{iv}–C1^{iv} 1.341(2), N2^{iv}–N1^v 1.323(2), N2^{iv}–C1^{iv} 1.338(2), N3^{iv}–C1^{iv} 1.376(2), N3^{iv}–

N4^{iv} 1.427(2); Cl1–O1 3.142(5); selected bond angles [°]: N2^{iv}–N1^{iv}–C1^{iv} 117.4(1), C1^{iv}–N3^{iv}–N4^{iv} 115.4(1), N2^{iv}–C1^{iv} –N1^{iv} 126.1(1), N1^{iv} –C1^{iv} –N3^{iv} 118.1(1); selected torsion angles [°]: N4^{iv}–N3^{iv}–C1^{iv}–N2^{iv} 171.1(1), N4^{iv}–N3^{iv}–C1^{iv}–N1^{iv} -11.2(2), N3^{iv}–C1^{iv}–N2^{iv}–N1^{iv} 177.9(1); illustrated hydrogen bonds: N4^{iv}–H2B^{iv}···Cl1, D–H 0.94(2) Å, H···A 2.28(2) Å, D···A 3.158(1) Å, <D–H···A 155.0 (2)°; N4^{iii}–H2B^{iii}···Cl1, 0.90(2) Å, 2.18(2) Å, 3.078(1) Å, 176.7(17)°; symmetry codes: (i) -x, 2-y, 2-z; (ii) 1+x, y, z; (iii) x, y, -1+z; (iv) -x, 1-y, 2-z; (v) -1+x, y, z; selected crystal data: a = 6.3094(6) Å, b = 6.9132(6) Å, c = 7.4141(7) Å, α = 114.060(9)°, β = 97.162(7)°, γ = 112.699(9)°. V = 256.70(4) Å^3.

Single crystals of compound **5** could be obtained in the anhydrous form. **5** crystallizes in the triclinic space group *P-1* with one formula unit per unit cell and a density of 1.754 g·cm^{-3} at 173 K. The nitrotetrazolate anions also follow the planar structure described previously for *e.g.* ammonium 5-nitrotetrazolate [27].
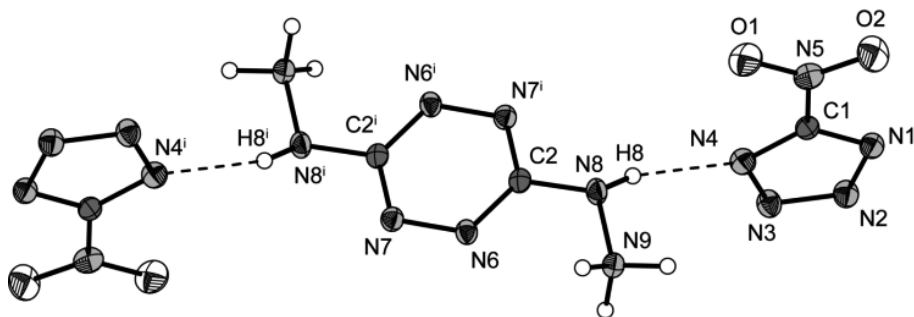

Figure 2.   View of the coordination sphere of one BHT cation in compound **5** showing the labelling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. Selected bond lengths [Å]: C2–N7 1.334(2), O1–N5 1.225(2), N6–N7 1.325(2), N6–C2 1.340(2), N7–C2 1.334(2), N8–C2 1.377(2), N8–N9 1.428(2); selected bond angles [°]: O1–N5–O2 125.7(1), O1–N5–C1 116.7(1), O2–N5–C1 117.4(1), N6–N7–C2 116.2(1), C2–N8–N9 115.6(1), C2–N8–H8 116.4(12), N9–N8–H8 114.3(12) N7–C2–N8 116.5(1), N6–C2–N8 117.5(1), C1–N1–N2 103.2(1), N3–N2–N1 109.5(1), N2–N3–N4 109.7(1); selected torsion angles [°]: O1–N5–C1–N1 176.1(1), O2–N5–C1–N4 173.9(1), N9–N8–C2–N6 11.7(2), N2–N1–C1–N5 179.2(1); illustrated hydrogen bonds: N8–H8···N4, D–H 0.88(2) Å, H···A 2.16(2) Å, D···A 3.008(2) Å,

<D–H···A 162.5(16)°; symmetry codes: (i) –x, 2–y, –z; selected crystal data: a = 6.4465(6) Å, b = 7.1755(7) Å, c = 8.0547(7) Å, α = 99.369(8)°, β = 103.574(8)°, γ = 96.879(8)°, V = 352.47(6) Å^3.

BHT-(ATZ) · 2H$_2$O crystallizes in the monoclinic space group $P\,2_1/c$ with 2 formula units per unit cell. The unit cell has the dimensions of a = 4.3434(7) Å, b = 12.0583(16) Å, c = 12.9592(17) Å, β = 91.900(14) °. It crystallizes with a cell volume of 678.35(17) Å^3 and a density of 1.686 g·cm^{-3} at 173 K.
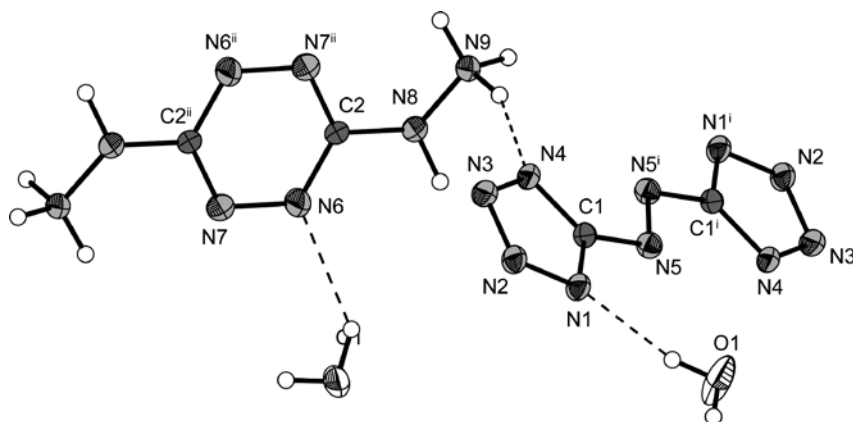

Figure 3. Molecular unit of **3**; the non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. Selected bond lengths [Å]: C1–N1 1.329(2), C1–N4 1.335(2), C1–N5 1.414(2), O1–H1A 0.83(2), O1–H1B 0.87(3), N4–N3 1.342(2), N8–C2 1.377(2), N8–N9 1.436(2), N8–H8 0.93(2), N3–N2 1.331(2),N1–N2 1.345(2); selected bond angles [°]:N1–C1–N4 112.8(2), N1–C1–N5 119.2(2), N4–C1–N5 128.0(2), C1–N4–N3 104.0(2), C2–N8–N9 117.5(2), N9–N8–H8 110.7(1), N2–N3–N4 109.9(1),C1–N1–N2 104.7(2), N3–N2–N1 108.7(2), N8–N9–H9A 106.8(2), N8–N9–H9B 112.5(2); selected torsion angles [°]: N7–N6–C2–N8 -175.9(2), N1–C1–N5–N5' 179.9(2), N6–C2–N8–N9 -162.0(2).

BHT-(DNT)$_2$ · 2 H$_2$O crystallizes in the monoclinic space group $P\,2_1/n$ with 4 formula units per unit cell. The unit cell has the dimensions of a = 10.7777(18) Å, b = 6.1512(15) Å, c = 13.668(3) Å, β = 93.110(18) °. It crystallizes with a cell volume of 904.8(3) Å^3 and a density of 1.822 g·cm^{-3} at 173 K.
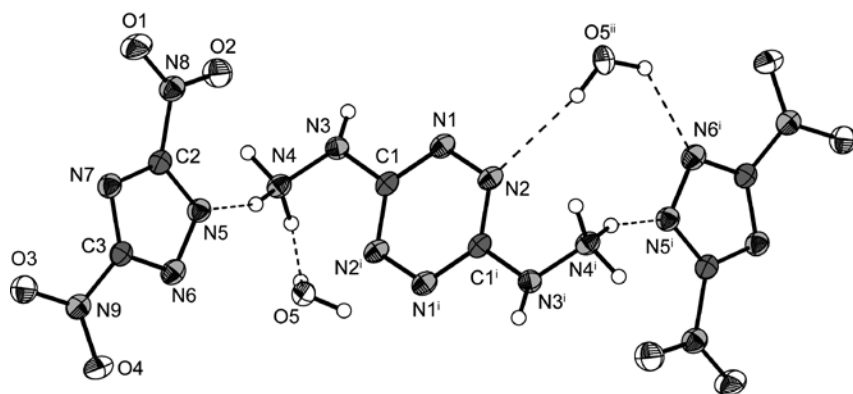
Figure 4.   Molecular unit of **4**; the non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. Selected bond lengths [nm]: O1–N8 0.1224(2), O2–N8 0.1224(2), O3–N9 0.1227(2), O4–N9 0.1230(2), N5–C2 0.1335(2), N5–N6 0.1352(2), N6–C3 0.1336(2), N7–C2 0.1326(2); selected bond angles [°]: C2–N5–N6 104.4(1), C3–N6–N5 103.8(1), O1–N8–O2 124.9(1), O1–N8–C2 117.7(1), O2–N8–C2 117.4(1), O3–N9–O4 124.0(1), O4–N9–C3 116.9(1), N7–C2–N5 116.9(1), N5–C2–N8 120.2(1); selected torsion angles [°]: C2–N5–N6–C3 0.5(1), C3–N7–C2–N5 0.7(2), C3–N7–C2–N8 179.2(1), N6–N5–C2–N7 -0.8(2), N6–N5–C2–N8 179.4(1), O1–N8–C2–N7 3.4(2), O2–N8–C2–N7 -175.7(1); symmetry codes: (i) 1–x, –y, –z ; (ii) 0.5+x, 0.5–y, –0.5+z.

BHT-(BT) ·2 H_2O crystallizes in the triclinic space group *P-1* with 2 formula units per unit cell. The unit cell has the dimensions of $a = 7.7949(8)$ Å, $b = 9.2606(10)$ Å, $c = 9.9301(12)$ Å, $\alpha = 117.382(12)$ °, $\beta = 90.858(9)$ °, $\gamma = 97.500(9)$ °. It crystallizes with a cell volume of 628.76(12) Å^3 and a density of 1.671 g·cm^{-3} at 173 K. In contrast to all of the other structures mentioned here, the hydrazinium moieties have a cis-configuration whereas structure 2, 3, 4 and 5 show a trans arrangement.
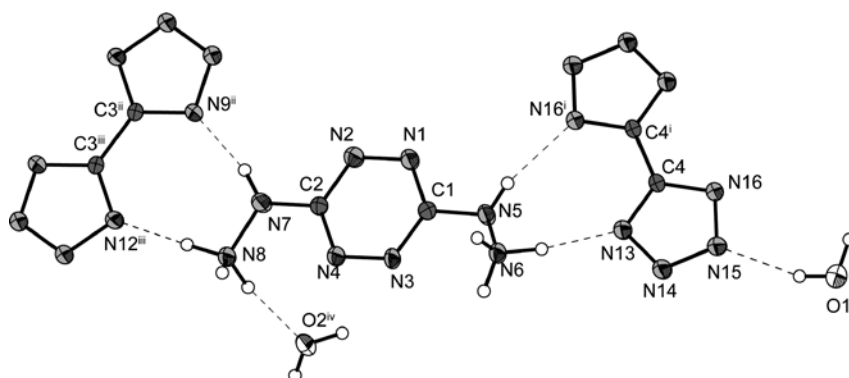
Figure 5. Molecular unit of **6**; the non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. Selected bond lengths [nm]: N1–N2 0.1328(2), N1–C1 0.1350(3), N2–C2 0.1348(3), N4–N3 0.1324(2), N4–C2 0.1343(3), N3–C1 0.1338(3), N5–C1 0.1369(3), N5–N6 0.1438(3); selected bond angles [°]: N2–N1–C1 117.6(12), N1–N2–C2 116.6(2), N3–N4–C2 117.4(2), N4–N3–C1 117.4(2), C1–N5–N6 114.6(2), N6–N5–H5 109.1(2), N5–N6–H6C 102.4(2), N5–N6–H6B 110.7(2), H6C–N6–H6B 116.3(2), N5–N6–H6A 108.7(2); selected torsion angles [°]: C1–N1–N2–C2 0.8(3), C2–N4–N3–C1 0.3(3), N4–N3–C1–N1 1.1(3), N2–N1–C1–N5 174.3(2), N6–N5–C1–N3 -31.0(3), N6–N5–C1–N1 152.7(2), N3–N4–C2–N2 -1.0(3), N1–N2–C2–N4 0.5(3), N8–N7–C2–N4 -13.8(3), N8–N7–C2–N2 167.8(2); selected hydrogen bonds: O1–H12···N15 (0.084(5), 0.210(4), 0.2902(3) nm, 159.0(4)°); N5–H5···N16^i (0.085(3), 0.205(3), 0.2874(3) nm, 165.0(3)°; N6–H6C···N13 (0.099(3), 0.186(3), 0.2836(4) nm, 172.0(3)°; symmetry codes: (i) 1-x, 1-y, 1-z; (ii) x, 1+y, z; (iii) 1-x, 2-y, -z; (iv) 1-x, 1-y, -z.

Thermodynamic and energetic properties

Differential scanning calorimetric measurements to determine the decomposition temperatures ($T_{dec.}$) of **1-9** were performed in sealed Al-containers, with a hole (0.1 mm) for gas release, with a nitrogen flow of 20 ml·min^{-1} on a Linseis PT-10 DSC calibrated with standard pure indium and zinc at a heating rate of 5 K·min^{-1}.

Compounds **1-9** were also tested for their sensitivities towards impact (IS), friction (FS) and electrostatical discharge (ESD). The sensitivity data of compounds **1-9** and their thermal stabilities are shown in Table 2.

Table 2.   Sensitivity data and thermal stability of compounds **1-9**

	IS [J] [a]	FS [N] [b]	ESD [J] [c]	$T_{dec.}$ [°C] [d]
1	30	>360	>1.0	140
2	35	>360	0.80	170
3	4	120	0.10	104
4	10	96	0.10	165
5	2	24	0.10	176
6	15	360	0.40	126
7	10	260	0.40	145
8	20	>360	0.50	150
9	8	252	0.15	217
RDX [21]	7.5	160	0.1	210

[a] impact sensitivity (BAM drophammer, 1 of 6); [b] friction sensitivity (BAM friction tester 1 of 6); [c] electrostatic discharge device, [d] decomposition temperature [°C]

The thermal stabilities of compounds **2-9** strongly depend on the acidity of the corresponding acid. When strong acids are used the thermal stabilities are enhanced (**2**, **4**, **5**, **9**). Interestingly compounds **3**, **6** and **7** suffers low thermal stability. **5** is the most sensitive compound towards external stimuli (IS 2 J, FS 24 N). Due to their crystallization without crystal water, only the detonation parameters of **5** and **9** were calculated using the EXPLO5 V.5.05 code and the measured low temperature X-ray densities. The energies of formation, which are needed for the EXPLO5 input, were calculated to be 2058 kJ·kg^{-1} (**5**) and 582 kJ·kg^{-1} (**9**). Table 3 shows the CBS-4M calculation results and the molecular volumes, and Table 4 shows the detonation parameters of **5** and **9** in comparison to RDX. Although **5** has a quite high enthalpy of formation ($\Delta_f H_m°$), the detonation pressure of **5** is ~20% lower than that of RDX. Its detonation velocity is only 5% lower. Nevertheless **5** is too sensitive and its thermal stability is not high enough for it to be considered as a potential RDX replacement. **9**, which is the most stable BHT salt mentioned here, has the highest density. Unfortunately its detonation parameters are lower in comparison to RDX, due to its low heat of formation.

Heats of formation

Solid state heats of formation ($\Delta_f H°$(s,M)) were calculated with the atomization method (Equation 1) using CBS-4M enthalpies (computed by Gaussian09W.A.02 [28]) and summarized in Table 2 [29]. The gas phase enthalpies of formation ΔH_m(g) were converted into the solid state enthalpies of formation (ΔH_m(s)) either by using Jenkins' equations for $X^{2+}Y^{2-}$ and $X^{2+}Y^{2-}$ salts [30] (for ionic derivatives) or Trouton's rule [31] (Equation 1).

$$\Delta_f H°_{(g, M, 298)} = H_{(M, 298)} - \sum H°_{(Atoms, 298)} + \sum \Delta_f H°_{(Atoms, 298)} \tag{1}$$

Table 3. CBS-4M calculation results and molecular volumes

M	$-H^{298}$ / a.u.	$\Delta_f H°(g,M)$ / kJ mol^{-1}	V_M / Å^3	$\Delta_f H°(s,M)$ / kJ mol^{-1}
BHT	516.99351	654.7		577.0
BHTI^{2+}	517.532665	101.6		
NT$^-$	461.705513	2307.0		
TNBI^{2-}	1266.677508	−33.9		
5		2268.7	352	762.3
9		2031.5	454*	353.0

* recalculated from K$_2$TNBI and BHT·2HCl·2H$_2$O (V_m(Cl$^-$)= 28 Å^3, V_m(H$_2$O)= 24 Å^3, V_m(K$^+$)=10 Å^3) [30a].

Lastly, the molar standard enthalpies of formation (ΔH_m) were used to calculate the molar, solid state energies of formation (ΔU_m) according to Equation (2) (Table 2).

$$\Delta U_m = \Delta H_m - \Delta n\, RT \qquad (2)$$
(Δn being the change in moles of gaseous components)

Table 4. Energetic properties of compounds **5** and **9** in comparison to RDX

	5	**9**	**RDX**
Formula	C$_4$H$_8$N$_{18}$O$_4$	C$_8$H$_8$N$_{16}$O$_8$	C$_3$H$_6$N$_6$O$_6$
FW / g mol^{-1}	372.10	456.07	222.12
IS / J ^{a}	2	8	7.5
FS / N ^{b}	24	252	120
ESD / J ^{c}	0.10	0.15	0.1-0.2
N / % ^{d}	67.73	49.12	37.8
Ω / % ^{e}	-34.38	-42.08	-21.6
$T_{Dec.}$ / °C ^{f}	176	217	210
ρ / g cm^{-3} ^{g}	1.754 (X-ray), 1.722 ^{o}	1.84 (pyc., RT)	1.80 (RT) [32]
$\Delta_f H_m°$ / kJ·mol^{-1} ^{h}	762.3	353.0	70.0 [32]
$\Delta_f U°$ / kJ·kg^{-1} ^{i}	2057.9	860.6	410.0
EXPLO5.05 values:			
$-\Delta_{Ex} U°$ / kJ kg^{-1} ^{j}	4601, 4599 ^{p}	4594	6125
T_{det} / K ^{k}	3519, 3540 ^{p}	3515	4236
P_{CJ} / kbar ^{l}	290, 279 ^{p}	295	349
$V_{Det.}$ / m s^{-1} ^{m}	8409, 8300 ^{p}	8257	8748
V_o / l kg^{-1} ^{n}	779, 779 ^{p}	685	739

^{a} impact sensitivity (BAM drophammer, 1 of 6); ^{b} friction sensitivity (BAM friction tester 1 of 6); ^{c} electrostatic discharge device; ^{d} nitrogen content; ^{e} oxygen balance; ^{f} decomposition temperature from DSC (β = 5°C/min); ^{g} from X-ray diffraction; ^{h} calculated heat of formation; ^{i} energy of formation; ^{j} energy of explosion; ^{k} explosion temperature; ^{l} detonation pressure; ^{m} detonation velocity; ^{n} assuming only gaseous products; ^{o} extrapolated to RT by the formula $d_{298K} = \dfrac{d_T}{1 + \alpha_v (298 - T_0)}$, $\alpha_v = 1.50 \cdot 10^{-4}$ K^{-1}.[33]; ^{p} RT values.

Experimental

Raman spectra were recorded with a Bruker MultiRAM FT-Raman fitted with a liquid nitrogen cooled, germanium detector and a Nd:YAG laser (λ = 1064 nm), and infrared spectra were measured with a Perkin-Elmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSampl*IR* II ATR device. All spectra were recorded at ambient temperature, the samples being in the solid state. ^{1}H decoupled ({^{1}H}) NMR spectra were recorded at 25 °C with a JEOL Eclipse 400 ECX instrument, and chemical shifts were determined with respect to external Me$_4$Si (^{1}H, 400.2 MHz; ^{13}C, 100.6 MHz), MeNO$_2$ (^{14}N, 29.0 MHz). Mass spectrometric data were obtained with a JEOL MStation JMS 700 spectrometer (FAB+/FAB-) using glycerol as the matrix. Elemental analyses (C/H/N) were performed with an Elementar Vario EL analyzer. Melting points were determined in capillaries with a Büchi Melting Point B-540 instrument and are uncorrected. Decomposition points were determined by Differential Scanning Calorimetry (DSC) measurements with a Linseis DSC-PT10, using a heating rate of 5 °C·min^{-1}. Pycnometric measurements were carried out with a Quantachrome helium gas pycnometer. Quantum chemical calculations were performed with the Gaussian09 software. Sensitivity data (impact and friction) were performed using a drophammer and friction tester analogous to BAM (Bundesanstalt für Materialforschung und Prüfung). Electrostatic sensitivities were measured with an OZM small scale electrostatic discharge tester [34-42].

CAUTION! All high nitrogen and oxygen containing compounds are potentially explosive energetic materials, although no hazards were observed during preparation and handling of these compounds. Nevertheless, this necessitates additional, meticulous safety precautions (earthed equipment, Kevlar® gloves, Kevlar® sleeves, face shield, leather coat, and ear plugs).

Synthesis of 3,6-bishydrazino-1,2,4,5-tetrazinium dichloride dihydrate (BHT-2HCl·2H$_2$O) (2)

1 (14.2 g 100 mmol) was suspended in methanol (150 ml) and hydrogen chloride gas was bubbled through the suspension at 0 °C until a solution was obtained. An additional 10 min of HCl injection resulted in the precipitation of anhydrous **2**. Subsequently, the mixture was stirred for 1 h at 0 °C. The precipitate was filtered off and washed with methanol. Afterwards **2** was recrystallized from 2-propanol/water under reflux. The solution was then left to stand overnight at 4 °C in the fridge and single crystals of **2** could be isolated.

DSC (5 °C·min^{-1}): $T_{dec.}$ = 170 °C; **EA** (C$_2$H$_{12}$N$_8$Cl$_2$O$_2$ M = 251.1 g·mol^{-1})

found (calc): C 9.52 (9.57), H 4.56 (4.82), N 44.90 (44.63); **^{1}H NMR** (d_6-DMSO, 25 °C, ppm), δ = 6.75 (s, br, 6H, NH$_3$), 10.75 (s, 2H, NH); **{^{1}H}^{13}C NMR** (d_6-DMSO, 25 °C, ppm): δ = 162.8 (2C, C$_q$ tetrazine), **Sensitivities: IS**: > 35.00 J; **FS**: > 360 N; **ESD**: 0.80 J.

Synthesis of 3,6-bishydrazino-1,2,4,5-tetrazinium 5,5'-azotetrazolate dihydrate (BHT-(ATZ)·2H$_2$O) (3)

Bis-potassium 5,5'-azotetrazolate pentahydrate (1.32 g, 3.98 mmol) was dissolved in water (20.0 ml). This solution was added to a stirred solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride dihydrate (1.00 g, 3.98 mmol) in water (20.0 ml). The mixture was stirred at ambient temperature and then stored at 5 °C overnight. Afterwards the crystals were filtered off and dried, yielding 1.17 g (3.58 mmol; 90%) of light red needles of **(3)**.

DSC (5 °C·min^{-1}): T$_{dec.}$ = 104 °C; **EA** (C$_4$H$_{12}$N$_{18}$O$_2$ M = 344.3 g·mol^{-1}) found (calc): C 13.62 (13.96), H 3.46 (3.51), N 72.93 (73.24); **^{1}H NMR** (d_6-DMSO, 25 °C, ppm): δ = 6.71 (s, br, 6H, NH$_3$), 10.70 (s, 2H, NH); **{^{1}H}^{13}C NMR** (d_6-DMSO, 25 °C, ppm): δ = 162.8 (2C, C$_q$ tetrazine), 171.0 (2C, C$_q$ azotetrazolate); **Raman [cm^{-1}]:** $\tilde{v}$ = 1491 (49), 1423 (9), 1393 (100), 1100 (36), 1078 (6), 917 (5); **IR (ATR, cm^{-1}):** $\tilde{v}$ = 3554 (m), 3166 (br, m), 1644 (s), 1567 (s), 1526 (s), 1430 (s), 1400 (vs), 1314 (s), 1254 (m), 1210 (s), 1180 (s), 1166 (w), 1087 (s), 1042 (vs), 926 (vs), 875 (s), 776 (s), 740 (vs), 682 (vs); **Mass spec.:** (FAB (-) m/z): 165.2 (12) [C$_2$HN$_{10}$$^-$], 257.4 (10) [(Gly)$_1$ + C$_2$H$_2$N$_{10}$], 349.5 (5) [(Gly)$_3$ + C$_2$N$_{10}$$^{2-}$]; **Sensitivities: IS**: > 4.00 J; **FS**: > 120 N; **ESD**: 0.10 J.

Synthesis of 3,6-bishydrazino-1,2,4,5-tetrazinium bis-(3,5-dinitro-triazolate) dihydrate (BHT-(DNT)$_2$·2 H$_2$O) (4)

Triethylammonium 3,5-dinitro-1,2,4-triazolate (2.07 g, 7.98 mmol) was dissolved in water (20.0 ml). This solution was added to a stirred solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride dihydrate (1.00 g, 3.98 mmol) in water (20.0 ml). The mixture was stirred at ambient temperature and then stored at 5 °C overnight. Afterwards the crystals were filtered off and dried, yielding 1.78 g (3.58 mmol; 90%) of dark orange needles of **4**.

DSC (5 °C·min^{-1}): T$_{dec}$ = 165 °C; **EA** (C$_6$H$_{12}$N$_{18}$O$_{10}$ M = 496.3 g·mol^{-1}) found (calc): C 14.76 (14.52), H 2.39 (2.44), N 50.19 (50.80); **^{1}H NMR** (d_6-DMSO, 25 °C, ppm): δ = 6.65 (s, br, 6H, NH$_3$), 10.68 (s, 2H, NH); **{^{1}H}^{13}C NMR** (d_6-DMSO, 25 °C, ppm): δ =161.7 (2C, C-NO$_2$), 163.3 (. 2C, C$_q$ tetrazine); **^{14}N NMR** (d_6-DMSO, 25 °C, ppm): δ = - 22 (2N, -NO$_2$); **Raman [cm^{-1}]:** $\tilde{v}$ = 1544 (4), 1493 (3), 1405 (100), 1354 (14), 1312 (2), 1303 (2), 1139 (63), 1022 (5), 872 (7), 833 (7), 770 (3), 685 (2), 299 (3); **IR (ATR, cm^{-1}):** $\tilde{v}$ = 3467 (m), 3246 (w),

1675 (w), 1604 (br, s), 1554 (s), 1528 (s), 1492 (vs), 1428 (s), 1385 (vs), 1350 (s), 1311 (m), 1301 (s), 1257 (m), 1142 (s), 1056 (s), 945 (s), 848 (vs), 832 (s), 756 (m); **Mass spec.:** (FAB (-) m/z): 142.0 (10) $[C_2N_5O_3^-]$, 158.0 (86) $[C_2N_5O_4^-]$, 250.0 (14) $[(Gly)_1 + C_2HN_5O_4]$, 311.0 (15) $[(Gly)_{1.7} + C_2N_5O_4^-]$, 342.0 (3) $[(Gly)_2 + C_2HN_5O_4]$, 463.0 (3) $[(Gly)_{3.3} + C_2N_5O_4^-]$; **Sensitivities: IS:** > 10.0 J; **FS:** > 96.0 N; **ESD:** 0.10 J. 2C, C_q tetrazine.

Synthesis of 3,6 Bishydrazino 1,2,4,5-tetrazinium bis-(5-nitrotetrazolate) (BHT-(NT)₂) (5)

Ammonium 5-nitrotetrazolate 0.5 H_2O (1.12 g, 7.97 mmol) was dissolved in water (20.0 ml). This solution was added to a stirred solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride dihydrate (1.00 g, 3.98 mmol) in water (20.0 ml). The mixture was stirred at ambient temperature and then stored at 5 °C overnight. Afterwards the crystals were filtered off and dried, yielding 1.26 g (3.38 mmol; 85%) of yellow needles of **5**.

DSC (5 °C·min⁻¹): T_{dec} = 176 °C; **EA** ($C_4H_8N_{18}O_4$ M = 372.2 g·mol⁻¹) found (calc): C 13.26 (12.91), H 2.19 (2.17), N 66.79 (67.73); **¹H NMR** (d_6-DMSO, 25 °C, ppm): δ = 6.76 (s, br, 6H, NH₃), 10.73 (s, 2H, NH); **{¹H}¹³C NMR** (d_6-DMSO, 25 °C, ppm): δ =162.7 (2C, C_q tetrazine), 169.2 (2C, C-NO₂); **Raman [cm⁻¹]:** $\tilde{v}$ = 1914 (7), 1772 (7), 1627 (7), 1559 (9), 1495 (9), 1464 (5), 1422 (95), 1327 (8), 1072 (63), 876 (24), 835 (12), 774 (10), 459 (11), 314 (8); **IR (ATR, cm⁻¹):** $\tilde{v}$ = 3194 (w), 3140 (w), 1566 (s), 1546 (vs), 1506 (w), 1452 (s), 1422 (vs), 1340 (m), 1318 (vs), 1238 (w), 1211 (m), 1189 (m), 1176 (m), 1107 (m), 1060 (s), 945 (s), 835 (vs), 774 (w), 731 (w), 664 (s); **Mass spec.:** (FAB (-) m/z): 114.2 (26) $[CN_5O_2^-]$, 206.4 (12) $[(Gly)_1 + CHN_5O_2]$; **Sensitivities: IS:** > 2.00 J; **FS:** > 24 N; **ESD:** 0.10 J.

Synthesis of 3,6-bishydrazino-1,2,4,5-tetrazinium 5,5'-bistetrazolate dihydrate (BHT-(BT)·2 H₂O) (6)

Bis-potassium 5,5'-bistetrazolate (0.96 g, 3.98 mmol) was dissolved in water (20.0 ml). This solution was added to a stirred solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride dihydrate (1.00 g, 3.98 mmol) in water (20.0 ml). The mixture was stirred at ambient temperature and was then stored at 5 °C overnight. Afterwards the crystals were filtered off and dried, yielding 1.01 g (3.18 mmol; 80%) of dark red needles of 3,6-bishydrazinium-1,2,4,5-tetrazine 5,5'-bistetrazolate dihydrate (**6**).

DSC (5 °C·min⁻¹): T_{dec} = 126 °C; **EA** ($C_4H_{12}N_{16}O_2$ M = 316.1 g·mol⁻¹) found (calc): C 15.65 (15.29), H 3.71 (3.82), N 70.14 (70.87); **¹H NMR** (d_6-DMSO, 25 °C, ppm): δ = 6.93 (br, s, 6H, NH₃), 10.59 (s, 2H, NH); **{¹H}¹³C NMR** (d_6-

DMSO, 25 °C, ppm): δ = 150.6 (2C, C_q tetrazolate), 162.6 (2C, C_q tetrazine) ; **Raman [cm^{-1}]:** $\tilde{v}$ = 1587 (99), 1490 (20), 1221 (12), 1120 (25), 1095 (14), 865 (30), 417 (8); **IR (ATR, cm^{-1}):** $\tilde{v}$ = 3544 (m), 3313 (br, m), 3150 (br, m), 1542 (s), 1471 (s), 1408 (s), 1327 (s), 1306 (s), 1269 (m), 1202 (m), 1188 (m), 1142 (m), 1112 (w), 1086 (vw), 1051 (s), 1027 (s), 950 (vs), 853 (br, m), 804 (w), 732 (s), 665 (vs); **Mass spec.:** (FAB (+) m/z): 143 (5) [$C_2H_7N_8^+$]; (FAB (-) m/z): 137.2 (68) [$C_2HN_8^-$], 275.4 (16) [(2 $C_2H_2N_8$]; **Sensitivities: IS:** > 15 J; **FS**: > 360 N; **ESD**: 0.40 J.

Synthesis of 3,6-bishydrazino-1,2,4,5-tetrazinium 5,5'bis-tetrazolyl-amine (BHT-BTA) (7)

Bis-potassium 5,5'-bistetrazolyl-amine (0.91 g, 3.98 mmol) was dissolved in water (20.0 ml). This solution was added to a stirred solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride dihydrate (1.00 g, 3.98 mmol) in water (20.0 ml). Stirring of the mixture at ambient temperature (13 °C) already precipitated a pale-orange powder. The powder was filtered off, washed with cold water and dried, yielding 0.96 g (3.26 mmol; 82%) of light orange needles of 3,6-bishydrazinium-1,2,4,5-tetrazine 5,5'bis-tetrazolyl-amine (**7**).

DSC (5 °C·min^{-1}): T_{dec} = 145 °C; **EA** ($C_4H_9N_{17}$ M = 295.2 g·mol^{-1}) found (calc): C 16.15 (16.27), H 3.32 (3.07), N 78.55 (80.55); **^{1}H NMR** (d_6-DMSO, 25 °C, ppm): δ = 6.84 (br, s, 6H, NH$_3$), 10.64 (s, 2H, NH); **{^{1}H}^{13}C NMR** (d_6-DMSO, 25 °C, ppm): δ =154.9 (2C, C_q tetrazole), 163.7 (2C, C_q tetrazine); **Raman [cm^{-1}]:** $\tilde{v}$ = 3197 (25), 1574 (15), 1512 (91), 1331 (22), 1122 (14), 1075 (33), 862 (73), 803 (13), 673 (22), 633 (13), 458 (51), 411 (22), 308 (18); **IR (ATR, cm^{-1}):** $\tilde{v}$ = 3376 (br, m), 3312 (w), 1626 (s), 1561 (m), 1501 (vs), 1418 (s), 1344 (m), 1324 (m), 1278 (w), 1260 (w), 1167 (w), 1138 (m), 1103 (w), 1051 (s), 947 (s), 875 (m), 792 (m), 730 (m), 683 (m); **Mass spec.:** (FAB (-) m/z): 152.2 (18) [$C_2H_2N_9^-$], 244.4 (9) [(Gly)$_1$ + $C_2H_3N_9$], 336.5 (4) [(Gly)$_2$ + $C_2H_3N_9$], 428.7 (3) [(Gly)$_3$ + $C_2H_3N_9$]; **Sensitivities: IS**: > 10.0 J; **FS**: > 260 N; **ESD**: 0.40 J.

Synthesis of 3,6-bishydrazino-1,2,4,5-tetrazinium bis-(3-amino-5-nitro-1,2,4-triazolate) BHT-(ANTA)$_2$ (8)

Sodium 3-amino-5-nitro-triazolate (1.20 g, 7.97 mmol) was dissolved in water (20.0 ml). This solution was added to a stirred solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride dihydrate (1.00 g, 3.98 mmol) in water (20.0 ml). Stirring of the mixture at ambient temperature caused **8** to precipitate as a red solid. The solid was filtered off, washed with cold water and dried, yielding 1.39 g (3.46 mmol; 87%) of a red powder of **8**.

DSC (5 °C·min^{-1}): T_{dec} = 150 °C; **EA** ($C_6H_{12}N_{18}O_4$ M = 400.3 g·mol^{-1}) found

(calc): C 18.27 (18.00), H 3.01 (3.02), N 63.06 (62.99); **¹H NMR** (d_6-DMSO, 25 °C, ppm): δ = 4.60 (s, br, 2H, NH$_2$), 6.76 (s, 6H, NH$_3$), 10.53 (s, 2H, NH); **{¹H}¹³C NMR** (d_6-DMSO, 25 °C, ppm): δ = 157.9 (2C, C-NH$_2$) , 161.4 (2C, C-NO$_2$), 163.9 (2C, C$_q$ tetrazine); **Raman [cm⁻¹]:** $\tilde{v}$ = 3235 (5), 3218 (16), 1653 (14), 1553 (12), 1518 (27), 1426 (15), 1381 (100), 1305 (17), 1136 (23), 1019 (18), 870 (37), 449 (10); **IR (ATR, cm⁻¹):** $\tilde{v}$ = 3396 (s), 3346 (s), 3316 (s), 3259 (w), 3230 (m), 3209 (m), 1590 (s), 1558 (s), 1536 (w), 1518 (vs), 1464 (w), 1422 (s), 1379 (s), 1305 (vs), 1281 (m), 1160 (s), 1133 (s), 1089 (m), 1064 (m), 1025 (w), 1003 (s), 946 (vs), 850 (m), 837 (s), 758 (w), 751 (s), 724 (vs); **Mass spec.:** (FAB (-) m/z): 128.0 (9) [C$_2$H$_2$N$_5$O$_2$⁻], 220.3 (7) [(Gly)$_1$ + C$_2$H$_3$N$_5$O$_2$], 282.0 (5) [(Gly)$_{1.7}$ + C$_2$H$_3$N$_5$O$_2$] 312.6 (4) [(Gly)$_2$ + C$_2$H$_3$N$_5$O$_2$]; **Sensitivities: IS:** > 20.0 J; **FS**: > 360 N; **ESD**: 0.50 J.

Synthesis of 3,6-bishydrazino-1,2,4,5-tetrazinium 4,4',5,5'-tetranitro-2,2'-bisimidazolate BHT-TNBI (**9**)

4,4',5,5'-Tetranitro-2,2'-bisimidazole dihydrate (1.39 g, 3.98 mmol) was dissolved in water (20.0 ml). This solution was added to a stirred solution of 3,6-bishydrazino-1,2,4,5-tetrazine (0.57 g, 3.98 mmol) in water (20.0 ml). Stirring of the mixture at ambient temperature caused **9** to precipitate as an orange powder. The solid was filtered off, washed with cold water and dried, yielding 1.69 g (3.70 mmol; 93%) of an orange powder of 3,6-bishydrazinium-1,2,4,5-tetrazine 4,4',5,5'-tetranitro-2,2'-bisimidazolate (**9**).

DSC (5 °C·min⁻¹): T$_{dec}$ = 217 °C; **EA** (C$_8$H$_8$N$_{16}$O$_8$ M = 456.1 g·mol⁻¹) found (calc): C 21.24 (21.06), H 1.54 (1.77), N 48.04 (49.12); **¹H NMR** (d_6-DMSO, 25 °C, ppm): δ = 6.89 (s, br, 6H, NH$_3$), 10.50 (s, br, 2H, NH); **{¹H}¹³C NMR** (d_6-DMSO, 25 °C, ppm): δ = 139.9 (2C, C$_q$ TNBI), 142.3 (4C, C-NO$_2$), 162.9 (2C, C$_q$ tetrazine); **IR (ATR, cm⁻¹)**: $\tilde{v}$ = 3204 (m), 3128 (w), 1593 (m), 1544 (s), 1494 (s) 1464 (s), 1392 (vs), 1362 (br, s), 1311 (vs), 1273 (s), 1226 (br, vs), 1117 (s) 1092 (m), 1050 (s), 942 (s), 854 (s), 839 (w), 810 (vs), 754 (s), 700 (s); **Sensitivities: IS**: > 8.00 J; **FS**: > 252 N; **ESD**: 0.15 J.

Conclusions

From this experimental study the following conclusions can be drawn:
- Highly energetic salts using BHT as a doubly charged cation can be synthesized in high yields.
- Crystal structures of compounds **2**, **3**, **4**, **5**, **6** could be determined by low temperature X-ray diffraction.

- All of the compounds mentioned here were fully characterized towards thermal stability and sensitivities towards impact, friction and electrostatic discharge.
- BHT bis-(5-nitrotetrazolate) (**5**) shows the best calculated detonation parameters (*e.g.* $V_{det} = 8409$ m·s^{-1}) but is too sensitive and already decomposes at 176 °C.
- BHT tetranitrobisimidazolate (**9**) has the highest thermal stability (217 °C) but shows much lower calculated detonation parameters ($V_{det} = 8257$ m·s^{-1}) in comparison to RDX.
- The BHT cation is incompatible with aromatic N-oxides like 5-nitro-tetrazole 1-oxide and 5,5'-azotetrazole1,1'-dioxide.

Supporting Information

Crystallographic data for the structures **2**, **3**, **4**, **5** and **6** reported in this article have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Copies of the data can be obtained free of charge by quoting the numbers Nos. 926094 (**2**), 926097 (**3**), 926095 (**4**), 926096 (**5**) and 926098 (**6**) from CCDC (12 Union Road, Cambridge, CB2 1EZ, UK [fax (internat.) +44(0)1223 /336033; e-mail: deposit@ccdc.cam.ac.uk]).

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