Electronic Supplementary Material (ESI) for Materials Advances.

Combining the Most Suitable Energetic Tetrazole and Triazole Moieties: Synthesis and Characterization of 5-(1-Hydroxy-3-Nitro-1,2,4-Triazol-5-yl)-1-Hydroxy-Tetrazole and its Nitrogen-Rich Ionic Derivatives

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Content

1. Experimental and General Part

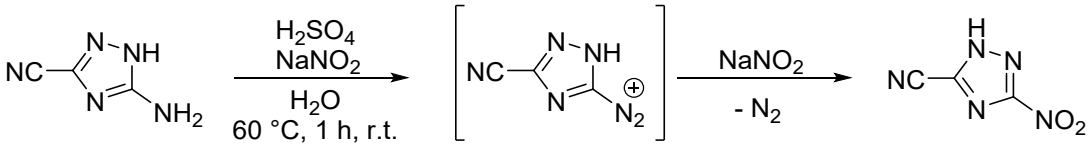
^{1}H, ^{13}C, ^{14}N and ^{15}N NMR spectra were recorded on *BRUKER AMX 400* instruments. Chemical shifts are referenced with respect to tetramethylsilane ($^{1}H/^{13}C$) and nitromethane ($^{14}N/^{15}N$). Infrared spectra (IR) were recorded in the region 4000-400 cm^{-1} on a *PERKIN ELMER Spectrum BX-59343* instrument with a *SMITHS DETECTION DuraSamplIR II Diamond ATR* sensor. Raman spectra were recorded with a Bruker MultiRAM. The absorption bands are reported in wavenumbers (cm^{-1}). Decomposition temperatures were measured via differential thermal analysis (DTA) with an *OZM Research DTA 552-Ex* instrument at a heating rate of 5 °C/min and in a range of room temperature to 400 °C. Sensitivities toward impact (IS) and friction (FS) were determined according to the UN Recommendations on the Transport of Dangerous Goods (ST/SG/AC.10/11/Rev.7) using a BAM drop hammer and a BAM friction apparatus by applying the 1 of 6 method.[S1] All energetic compounds were tested for sensitivity towards electrical discharge using an *Electric Spark Tester ESD 2010 EN* from OZM. Energetic properties have been calculated with the EXPLO5 6.02 computer [S2] code using the RT converted X-ray density and calculated solid state heats of formation.

CAUTION! *All investigated compounds are potentially explosive materials. Safety precautions and equipment (such as wearing leather coat, face shield, Kevlar sleeves, Kevlar gloves, earthed equipment and ear plugs) must be used during all manipulations.*

A different synthesis procedure was developed for the synthesis of 3-nitro-1,2,4-triazole-5-carbonitrile because of an incident in which a crystallizing shell was destroyed by the detonation of a side compound during the evaporation of the solvent. It was suspected that the highly sensitive intermediate was 3-diazo-1,2,4-triazole-5-carbonitrile. By modifying the reaction procedure, it was possible to prevent the formation of 3-diazo-1,2,4-triazole-5-carbonitrile or to destroy already formed diazonium compound by the appropriate conditions.

Experimental Procedures

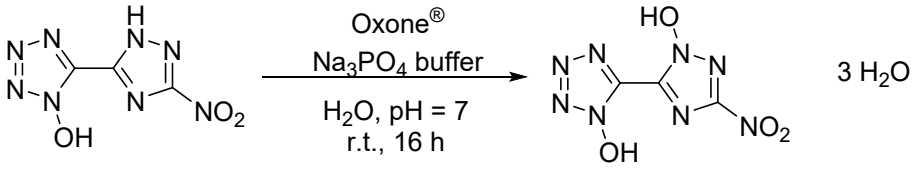
Improved synthesis of 3-nitro-1,2,4-triazole-5-carbonitrile.



3-Amino-1,2,4-triazole-5-carbonitrile (2.00 g, 18.3 mmol, 1.0 eq.) and sodium nitrite (19.0 g, 275 mmol, 15 eq.) were dissolved in water (40 mL). Sulfuric acid (1 M, 40 mL) was added dropwise to the yellow suspension resulting in a gas evolution (nitrous gases) and clarification to a yellow solution. The solution was heated at 60 °C for one hour, leading to an orange solution. After cooling down to room temperature sulfuric acid (20 %) was added leading to a color change of the solution from orange to yellow to green and the formation of nitrous gases. Just enough sulfuric acid was added until no more visible evolution of nitrous gases could be observed. The aqueous solution was extracted with ethyl acetate (3 x 200 mL) and the organic phase was dried over sodium sulfate. Removing of the solvent led to the formation of orange 3-nitro-1,2,4-triazole-5-carbonitrile (2.16 g, 15.5 mmol, 85%).

All analytic data correspond with the literature values.[S3, S4]

5-(1-Hydroxy-3-nitro-1,2,4-triazol-5-yl)-1-hydroxy-tetrazole trihydrate (**1**)

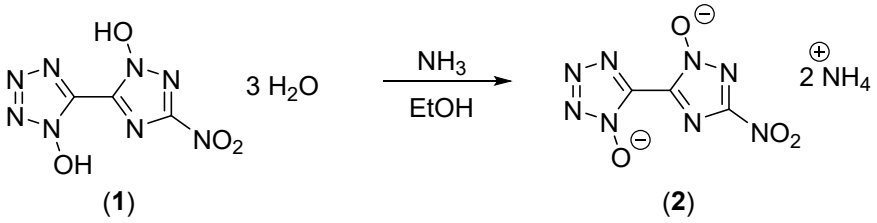


(**1**)

5-(3-Nitro-1,2,4-triazol-5-yl)-1-hydroxy-tetrazole (1.30 g, 6.56 mmol, 1.0 eq)[S4] was dissolved in water (52 mL). The pH value of the solution was adjusted to pH = 7 by adding solid sodium triphosphate. When the desired pH value was reached, Oxone® (24.7 g, 80.4 mmol, 12 eq) and sodium triphosphate dodecahydrate were added equally in that way keeping the pH value at around 7. After complete addition of Oxone®, the yellow suspension was stirred at room temperature for 16 hours. For work up, the suspension was cooled with ice, the formed solid was filtered and washed with small amounts of cold water. The yellow precipitate was dissolved in water (200 mL) and concentrated hydrochloric acid (37%, 65 mL). The mixture was extracted with ethyl acetate (3 x 200 mL). The aqueous phase was further acidified with concentrated hydrochloric acid (25 mL) and extracted with ethyl acetate (2 x 100 mL). This process was repeated two more times. The combined organic phases were dried over sodium sulfate. Removing of the solvent led to the formation of yellow **1** (1.23 g, 4.59 mmol, 70%).

DTA (5 °C min^{-1}): 103 °C (endo, H_2O), 169 °C (exo, dec.); **BAM: drop hammer:** >40 J (100–500 µm); **friction tester:** >360 N (100–500 µm); **ESD:** 0.50 J (100–500 µm); **IR** (rel. int.): ν = 3550(s), 3536(s), 3530(s), 3478(s), 3471(s), 3450(s), 3434(s), 3419(s), 3412(s), 3396(s), 3388(s), 3370(s), 3335(s), 3309(s), 3301(s), 3293(s), 3274(s), 1543(vs), 1450(vs), 1361(s), 1315(s), 1267(s), 1144(s), 1144(s), 771(s), 761(s), 725(s), 696(s), 667(s), 625(s), 498(vs), 490(vs), 470(vs), 455(vs), 442(s), 438(s), 410(s) cm^{-1}; **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 7.80 (br s, 8H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 155.3, 137.0, 133.3; **^{15}N NMR** (DMSO-D_6, 41 MHz, ppm) δ = −0.8, −19.5, −28.0, −51.9 −89.4, −108.0, −119.4, −139.9; **Elem. Anal.** ($C_3H_8N_8O_7$, 268.15 g mol^{-1}) calcd.: C 13.44, H 3.01, N 41.79 %. Found: C 13.78, H 2.87, N 41.94 %; **HRMS** (ESI, 70 eV): *m/z*: $[M - H]^-$ Calcd for $C_3HO_4N_8$ 213.0126; Found: 213.0126.

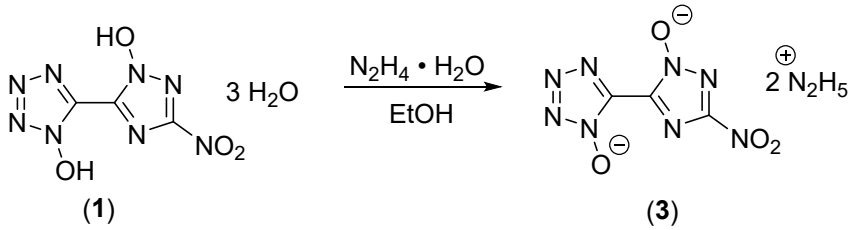
Bis-ammonium 5-(3-nitro-1,2,4-triazol-1-olate-5-yl)-tetrazol-1-olate (**2**)



5-(1-Hydroxy-3-nitro-1,2,4-triazol-5-yl)-1-hydroxy-tetrazole trihydrate (**1**) (0.52 g, 1.94 mmol, 1.0 eq) was dissolved in ethanol (20 mL). Gaseous ammonia was bubbled through the yellow solution for one minute, resulting in the immediate precipitation of a solid, which was filtered and washed with little amounts of cold ethanol to yield the respective bis-ammonium salt **2** as a yellow-orange solid. (0.41 g, 2.18 mmol, 85%).

DTA (5 °C min^{-1}): 265 °C (exo, dec.); **BAM: drop hammer:** >40 J (100–500 µm); **friction tester:** >360 N (100–500 µm); **ESD:** 0.37 J (100–500 µm); **IR** (rel. int.): ν = 3235(m), 3216(m), 3163(m), 3115(m), 2989(m), 2801(m), 1538(m), 1458(s), 1441(s), 1419(s), 1372(vs), 1353(s), 1305(vs), 1264(w), 1231(m), 1179(m), 1116(m), 1043(s), 1034(s), 998(m), 852(w), 782(m), 756(w), 756(w), 741(s), 706(w), 681(w), 674(w), 648(m), 563(w), 512(m), 490(w), 478(w), 464(w) cm^{-1}; **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 7.25 (s, 8H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 151.3, 135.0, 132.0; **^{15}N NMR** (DMSO-D_6, 41 MHz, ppm) δ = −12.6, −17.5, −25.7, −54.1, −78.2, −84.9, −85.8, −138.1, −358.7; **Elem. Anal.** ($C_3H_8N_{10}O_4$, 248.16 g mol^{-1}) calcd.: C 14.52, H 3.52, N 56.44 %. Found: C 14.15, H 3.15, N 55.98 %.

Bis-hydrazinium 5-(3-nitro-1,2,4-triazol-1-olate-5-yl)-tetrazol-1-olate (**3**)

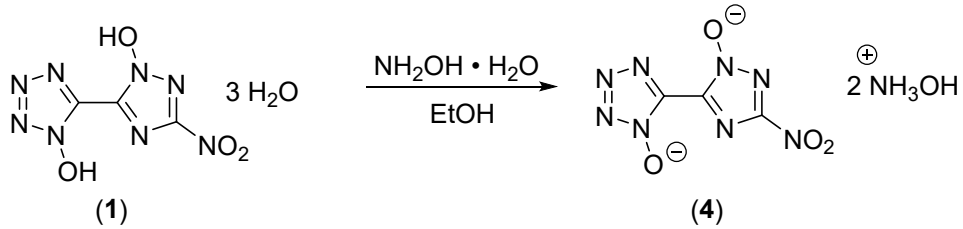


(**1**) (**3**)

5-(1-Hydroxy-3-nitro-1,2,4-triazol-5-yl)-1-hydroxy-tetrazole trihydrate (**1**) (0.50 g, 1.86 mmol, 1.0 eq) was dissolved in ethanol (30 mL). The yellow solution was heated to 50 °C followed by the addition of hydrazine hydrate (0.18 mL, 3.72 mmol, 2.0 eq). The solution was cooled to room temperature and the formed precipitate was filtered off and washed with cold ethanol. The solid was recrystallized from hot methanol, ethanol and acetone to yield the bis-hydrazinium salt **3** as an orange solid (0.47 g, 1.68 mmol, 90%).

DTA (5 °C min^{-1}): 206 °C (exo, dec.); **BAM: drop hammer:** 10 J (100–500 µm); **friction tester:** 216 N (100–500 µm); **ESD:** 0.10 J (100–500 µm); **IR** (rel. int.): ν = 3351(m), 3324(m), 3291(w), 3257(w), 3244(w), 3072(m), 2971(m), 2939(m), 2804(m), 2725(m), 2633(s), 2362(w), 2343(w), 1644(w), 1619(m), 1591(m), 1516(s), 1467(s), 1371(vs), 1348(s), 1306(vs), 1270(m), 1219(s), 1219(s), 1194(w), 1176(s), 1116(s), 1096(vs), 1045(s), 1033(s), 997(s), 966(s), 852(m), 841(m), 786(s), 746(s), 701(w), 681(w), 674(w), 645(m), 565(w), 511(m) cm^{-1}; **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 7.13 (br s, 10H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 151.5, 136.0, 133.0; **^{14}N NMR** (DMSO-D_6, 29 MHz, ppm) δ = −25, −363; **Elem. Anal.** ($C_3H_{10}N_{12}O_4$, 278.19 g mol^{-1}) calcd.: C 12.95, H 3.62, N 60.42 %. Found: C 13.21, H 3.68, N 59.58 %.

Bis-hydroxylammonium 5-(3-Nitro-1,2,4-triazol-1-olate-5-yl)-tetrazol-1-olate (**4**)

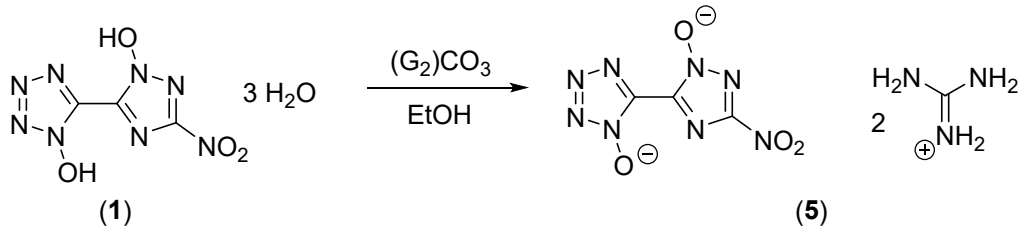


(**1**) (**4**)

5-(1-Hydroxy-3-nitro-1,2,4-triazol-5-yl)-1-hydroxy-tetrazole trihydrate (**1**) (0.20 g, 0.75 mmol, 1.0 eq) was dissolved in ethanol (10 mL). The yellow solution was heated to 50 °C followed by the addition of an aqueous solution of hydroxylamine (50% w/w in H_2O, 0.10 mL, 1.51 mmol, 2.0 eq). The solution was cooled to room temperature and the formed precipitate was filtered off and washed with little cold ethanol to yield the bis-hydroxylammonium salt **4** as a yellow solid (0.17 g, 0.62 mmol, 83%).

DTA (5 °C min^{-1}): 205 °C (exo, dec.); **BAM: drop hammer:** 20 J (100–500 µm); **friction tester:** 324 N (100–500 µm); **ESD:** 0.20 J (100–500 µm); **IR** (rel. int.): ν = 3222(m), 3202(m), 3188(m), 3151(m), 3137(m), 3116(m), 3090(m), 3056(m), 3049(m), 3034(m), 3020(m), 3008(m), 2962(m), 2928(m), 2841(m), 2678(m), 2514(m), 1530(m), 1523(m), 1513(m), 1465(m), 1450(m), 1376(vs), 1376(vs), 1308(vs), 1233(m), 1224(m), 1183(s), 1147(m), 1119(s), 1046(s), 1033(s), 1008(s), 999(s), 852(m), 781(m), 740(s), 667(m), 646(s), 623(m), 561(m), 505(s) cm^{-1}; **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 9.66 (br s, 8H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 153.2, 136.5, 133.0; **^{14}N NMR** (DMSO-D_6, 29 MHz, ppm) δ = −28, −360; **Elem. Anal.** ($C_3H_8N_{10}O_6$, 280.16 g mol^{-1}) calcd.: C 12.86, H 2.88, N 50.00 %. Found: C 12.55, H 2.90, N 49.50 %.

Bis-guanidinium 5-(3-Nitro-1,2,4-triazol-1-olate-5-yl)-tetrazol-1-olate (**5**)

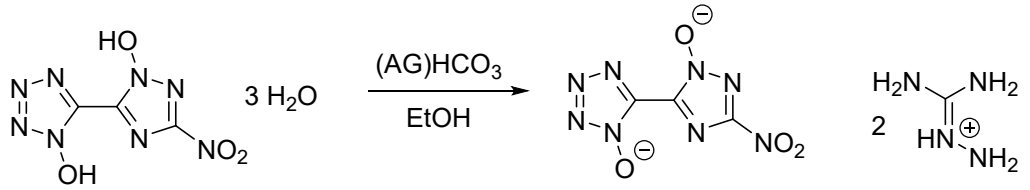


(**1**) (**5**)

5-(1-Hydroxy-3-nitro-1,2,4-triazol-5-yl)-1-hydroxy-tetrazole trihydrate (**1**) (0.64 g, 2.39 mmol, 1.0 eq) was dissolved in ethanol (50 mL). The yellow solution was heated to 50 °C followed by the addition guanidinium carbonate (0.43 g, 2.39 mmol, 1.0 eq). The solution was stirred for 30 min at this temperature and cooled to room temperature. The formed precipitate was filtered off and washed with little cold ethanol to yield the bis-guanidinium salt **5** as a reddish solid (0.71 g, 2.13 mmol, 89%).

DTA (5 °C min^{-1}): 200 °C (endo, melt.), 270 °C (exo, dec.); **BAM: drop hammer:** >40 J (100–500 µm); **friction tester:** >360 N (100–500 µm); **ESD:** 0.25 J (100–500 µm); **IR** (rel. int.): ν = 3468(m), 3426(m), 3411(m), 3346(m), 3331(m), 3315(m), 3269(m), 3262(m), 3235(m), 3227(m), 3159(s), 3137(s), 2803(w), 1659(s), 1645(s), 1640(s), 1582(m), 1505(m), 1456(s), 1377(vs), 1309(s), 1269(m), 1231(m), 1231(m), 1171(s), 1092(s), 1060(s), 1031(s), 1013(m), 999(s), 850(m), 789(m), 753(s), 671(m), 648(s), 618(s), 546(s), 529(s), 515(s), 505(s), 472(vs), 463(vs), 442(vs), 435(vs) cm^{-1}; **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 7.13 (s, 12H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 158.1, 151.2, 134.9, 132.1; **^{14}N NMR** (DMSO-D_6, 29 MHz, ppm) δ = −28; **Elem. Anal.** ($C_5H_{12}N_{14}O_4$, 332.24 g mol^{-1}) calcd.: C 18.08, H 3.64, N 59.02 %. Found: C 17.91 H 3.55, N 58.42 %.

Bis-aminoguanidinium 5-(3-Nitro-1,2,4-triazol-1-olate-5-yl)-tetrazol-1-olate (**6**)

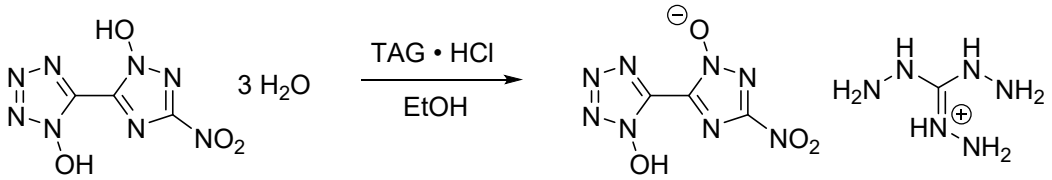


(**1**) (**6**)

5-(1-Hydroxy-3-nitro-1,2,4-triazol-5-yl)-1-hydroxy-tetrazole trihydrate (**1**) (0.78 g, 2.91 mmol, 1.0 eq) was dissolved in a mixture of ethanol (20 mL) and water (10 mL) and heated to 70 °C. Amoniguanidine hydrogen carbonate (0.79 g, 5.82 mmol, 2.0 eq). The solution was stirred for 10 min at this temperature and cooled to room temperature. The solution was reduced under nitrogen stream and the formed precipitate was filtered off and washed with little cold ethanol to yield the bis-aminoguanidinium salt **6** as an orange solid (0.80 g, 2.21 mmol, 76%).

DTA (5 °C min^{-1}): 217 °C (endo, melt.), 219 °C (exo, dec.); **BAM: drop hammer:** 40 J (100–500 µm); **friction tester:** >360 N (100–500 µm); **ESD:** 0.25 J (100–500 µm); **IR** (rel. int.): ν = 3469(w), 3334(m), 3304(m), 3220(m), 3160(m), 3135(m), 2875(m), 2755(w), 1660(s), 1652(s), 1646(s), 1529(s), 1471(s), 1454(m), 1377(s), 1306(s), 1259(m), 1226(m), 1177(s), 1117(s), 1100(m), 1041(s), 1036(s), 1036(s), 996(s), 966(m), 850(m), 839(m), 785(m), 750(s), 702(m), 681(m), 647(s), 615(s), 547(s), 536(s), 499(vs), 483(vs), 465(vs), 458(vs), 447(vs), 437(vs), 428(s), 420(s) cm^{-1}; **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 8.93 (br s, 2H), 7.21 (br s, 8H), 4.65 (s, 4H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 159.0, 151.4, 135.0, 132.2; **^{14}N NMR** (DMSO-D_6, 29 MHz, ppm) δ = −32; **Elem. Anal.** ($C_5H_{14}N_{16}O_4$, 362.28 g mol^{-1}) calcd.: C 16.58, H 3.90, N 61.86 %. Found: C 16.58 H 4.12, N 60.72 %.

Triaminoguanidinium 5-(3-Nitro-1,2,4-triazol-1-olate-5-yl)-1-hydroxy-tetrazole (**7**)



(**1**) (**7**)

5-(1-Hydroxy-3-nitro-1,2,4-triazol-5-yl)-1-hydroxy-tetrazole trihydrate (**1**) (0.58 g, 2.16 mmol, 1.0 eq) was dissolved in a mixture of ethanol (20 mL) and water (10 mL) and heated to 70 °C. Triaminoguanidinium hydrochloride (0.61 g, 4.32 mmol, 2.0 eq). The solution was stirred for 10 min at this temperature and cooled to room temperature. The solution was reduced under nitrogen stream and the formed precipitate was filtered off and washed with little cold ethanol to yield the triaminoguanidinium salt **7** as a yellow/orange solid (0.63 g, 1.98 mmol, 92%).

DTA (5 °C min^{-1}): 165 °C (endo, melt), 204 °C (exo, dec.); **BAM: drop hammer:** 7 J (100–500 µm); **friction tester:** 192 N (100–500 µm); **ESD:** 0.10 J (100–500 µm); **IR** (rel. int.): ν = 3363(m), 3322(m), 3197(s), 1683(s), 1667(s), 1661(s), 1622(m), 1531(s), 1460(s), 1374(vs), 1348(vs), 1309(vs), 1229(m), 1175(s), 1130(s), 1040(s), 1031(s), 1002(s), 961(vs), 851(m), 782(s), 740(s), 702(m), 702(m), 679(s), 667(m), 646(s), 637(s), 612(vs), 533(s), 517(s), 458(s), 436(vs), 412(s) cm^{-1}; **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 8.61 (br s, 3H), 5.68 (br s, 6H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 159.0, 154.9, 136.7, 132.7; **^{14}N NMR** (DMSO-D_6, 29 MHz, ppm) δ = −27; **Elem. Anal.** ($C_4H_{10}N_{14}O_4$, 318.21 g mol^{-1}) calcd.: C 15.10, H 3.17, N 61.62 %. Found: C 14.66 H 3.55, N 60.70 %.

2. X-ray Diffraction

Crystal structure data were obtained from an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD area for data collection using Mo-*Kα* radiation (*λ* = 0.71073 Å) or a Bruker D8 Venture TXS diffractometer equipped with a multilayer monochromator, a Photon 2 detector and a rotation-anode generator (Mo-K_α radiation). The data collection was performed using the CRYSTALIS RED software.[S5] The solution of the structure was performed by direct methods and refined by full-matrix least-squares on F2 (SHELXT)[S6] implemented in the OLEX2[S7] software suite. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorption correction was carried out by a SCALE3 ABSPACK multiscan method.[S8] The DIAMOND2 plots shown with thermal ellipsoids at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. The SADABS program embedded in the Bruker APEX3 software was used for multi-scan absorption corrections in all structures.[S9]

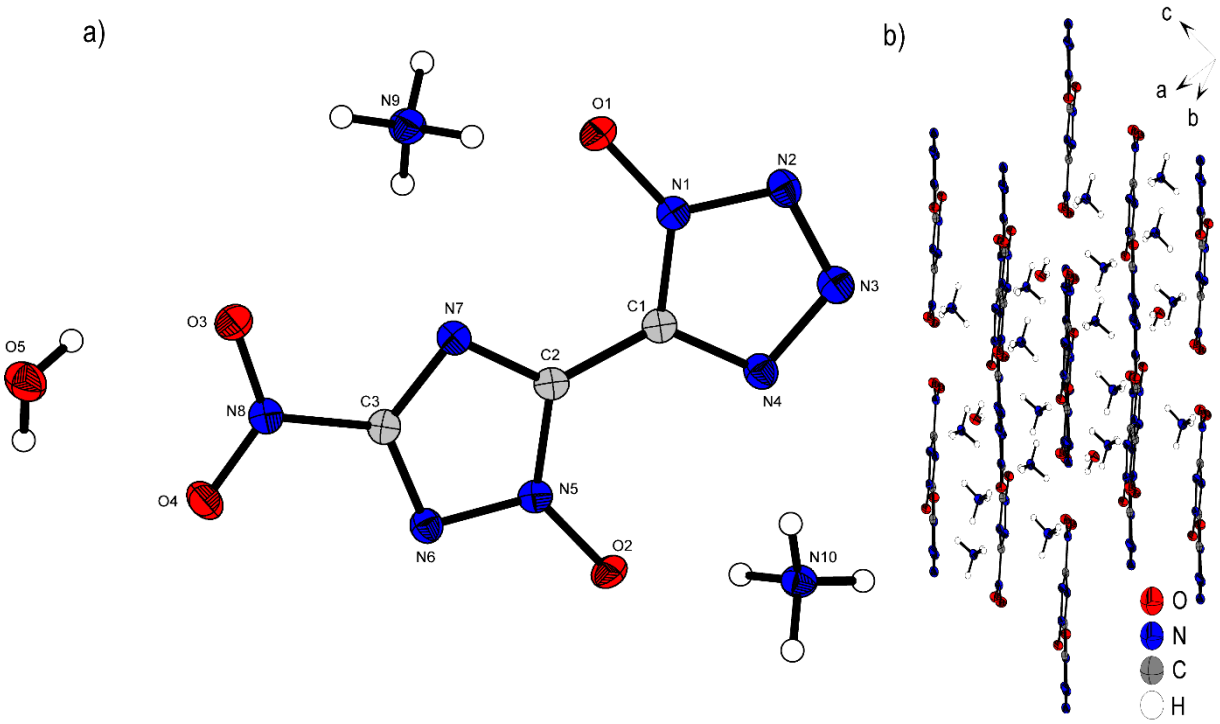


Figure S1. Representation of the molecular unit of bis-ammonium 5-(3-Nitro-1,2,4-triazol-1-olate-5-yl)-tetrazol-1-olate hydrate (**2** • H_2O), showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. a) Molecular unit of **2** • H_2O, b) packing of **2** • H_2O in the specified direction of view.

2 • H_2O crystallizes in the triclinic space group *P*−1 with a density of 1.784 g cm^{-3} at 103 K and a cell volume of 495.52(6) Å^3 and two molecular units per cell. Hydrogen bonds are formed

from all hydrogen atoms to respective oxygen and nitrogen atoms of the anion. Anions are forming layers.

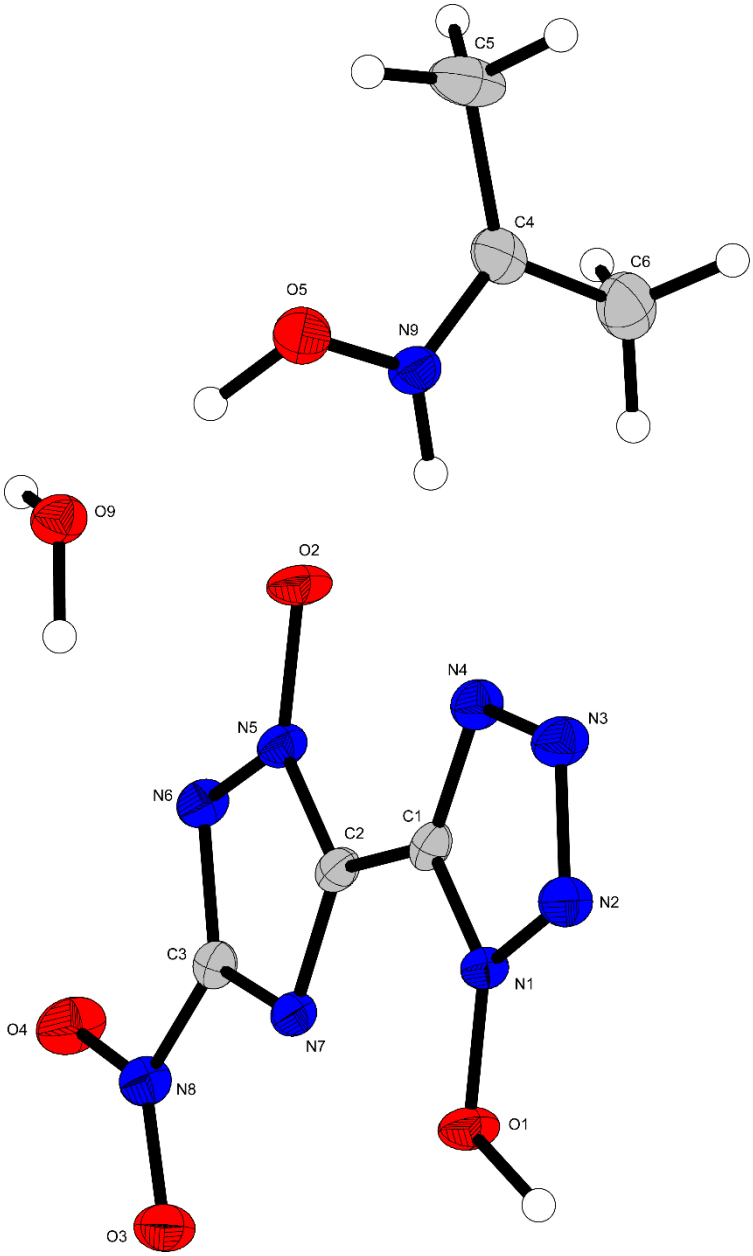


Figure S2. Representation of the molecular unit **4a**, showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

Compound **4a** was obtained by recrystallizing **4** from acetone. It can be interpreted as the acetone condensed product of the mono hydroxylammonium salt of **1**. **4a** crystallizes in the triclinic space group *P*−1, with a cell volume of 608.07(9) Å^3 with 2 molecular units per cell. The density is 1.667 g cm^{-3} at 123 K. The proton H1 is bond between O1 and O2^i of the nearby molecular unit (O1–H1, 1.29(2) Å; O2^i···H1, 1.19(1) Å), which is much significantly longer than for the neutral compound **1** (O1–H1; O2–H2, 0.86(4) Å)

Table S1. Crystallographic data of **1**–**3**.

	1	**2**	**3**
Formula	$C_3H_2N_8O_4 \bullet 3\ H_2O$	$C_3N_8O_4\ (NH_4)_2$	$C_3N_8O_4\ (N_2H_5)_2$
FW [g mol^{-1}]	268.17	248.19	278.23
Crystal system	orthorhombic	monoclinic	triclinic
Space group	*Cmca* (No. 64)	$P2_1/n$ (No. 14)	*P*-1 (No. 2)
Color / Habit	colorless rod	colorless rod	yellow rod
Size [mm]	0.02 x 0.02 x 0.05	0.02 x 0.03 x 0.11	0.02 x 0.03 x 0.08
a [Å]	6.2387(12)	4.3259(1)	3.6755(4)
b [Å]	7.8415(16)	26.9849(8)	8.0751(9)
c [Å]	40.259(8)	7.9243(2)	17.8693(18)
α [°]	90	90	87.041(4)
β [°]	90	98.770(1)	88.105(4)
γ [°]	90	90	85.965(4)
V [Å^3]	1969.5(7)	914.22(4)	528.11(10)
Z	8	4	2
$\rho_{calc.}$ [g cm^{-3}]	1.809	1.803	1.750
μ [mm^{-1}]	0.172	0.160	0.154
F(000)	1104	512	288
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	293	106	173
θ Min-Max [°]	3.0, 25.3	2.7, 26.4	3.3, 25.4
Dataset	-7: 7 ; -9: 9 ; -47: 48	-5: 5 ; -33: 33 ; -9: 9	-4: 4 ; -9: 9 ; -20: 21
Reflections collected	10605	15707	5647
Independent refl.	980	1872	1893
R_{int}	0.035	0.036	0.040
Observed reflections	911	1664	1449
Parameters	133	186	212
R_1 (obs)[a]	0.0468	0.0320	0.0495
wR_2 (all data)[b]	0.1085	0.0781	0.1107
S [c]	1.19	1.15	1.10
Resd. dens [e Å^{-3}]	-0.26, 0.27	-0.25, 0.25	-0.25, 0.24
Device type	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture
Solution	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-2013	SHELXL-2013	SHELXL-2013
Absorption correction	multi-scan	multi-scan	multi-scan
CCDC	2144427	2144428	2144432

[a]$R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; [b]$wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0)^2]]^{1/2}$; $w = [\sigma c^2(F_0^2)+(xP)^2+yP]^{-1}$ and $P=(F_0^2+2F_c^2)/3$; [c]$S = (\Sigma[w(F_o^2-F_c^2)^2]/(n-p))^{1/2}$ (n = number of reflections; p = total number of parameters).

Table S2. Crystallographic data of **4** • H_2O and **6**–**7**.

	4 • H_2O	**6**	**7**
Formula	$C_3N_8O_4(NH_3OH)_2 \bullet H_2O$	$C_3N_8O_4(CN_4H_7)_2$	$C_3HN_8O_4(CH_9N_6)$
FW [g mol^{-1}]	298.21	362.32	318.26
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$I2/a$ (No. 15)	P-1 (No. 2)
Color / Habit	colorless rod	yellow platelet	yellow block
Size [mm]	0.02 x 0.02 x 0.10	0.01 x 0.03 x 0.04	0.25 x 0.40 x 0.98
a [Å]	7.3751(11)	11.245(2)	7.5556(8)
b [Å]	15.0961(19)	6.7268(15)	8.1499(8)
c [Å]	10.4402(14)	37.486(8)	11.4798(12)
α [°]	90	90	102.425(8)
β [°]	108.817(5)	91.125(9)	100.781(9)
γ [°]	90	90	112.073(9)
V [Å^3]	1100.2(3)	2835.0(10)	611.07(13)
Z	4	8	2
$\rho_{calc.}$ [g cm^{-3}]	1.800	1.698	1.730
μ [mm^{-1}]	0.169	0.144	0.149
F(000)	616	1504	328
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	298	100	102
θ Min-Max [°]	3.2, 25.1	3.1, 26.3	1.9, 26.4
Dataset	-8: 8 ; -17: 17 ; -12: 12	-13: 13 ; -8: 8 ; -46: 46	-8: 9 ; -10: 10 ; -14: 13
Reflections collected	17438	21495	4703
Independent refl.	1938	2869	2499
R_{int}	0.039	0.095	0.020
Observed reflections	1634	2110	2121
Parameters	221	282	239
R_1 (obs)[a]	0.0372	0.0723	0.0348
wR_2 (all data)[b]	0.0953	0.1628	0.0937
S [c]	1.12	1.12	1.04
Resd. dens [e Å^{-3}]	-0.26, 0.30	-0.34, 0.39	-0.25, 0.24
Device type	Bruker D8 Venture	Bruker D8 Venture	Xcalibur Sapphire3
Solution	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-2013	SHELXL-2013	SHELXL-2013
Absorption correction	multi-scan	multi-scan	multi-scan
CCDC	2144430	2144425	2144429

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; [b] $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0)^2]]^{1/2}$; $w = [\sigma c^2(F_0^2)+(xP)^2+yP]^{-1}$ and $P=(F_0^2+2F_c^2)/3$; [c] $S = (\Sigma[w(F_o^2-F_c^2)^2]/(n-p))^{1/2}$ (n = number of reflections; p = total number of parameters).

Table S3. Crystallographic data of **2** • H_2O and **8**.

	2 • H_2O	**4a**
Formula	$C_3N_8O_4\ (NH_4)_2$ • H_2O	$C_3HN_8O_4$, (C_3H_8NO) • H_2O
FW [g mol^{-1}]	266.21	305.24
Crystal system	triclinic	triclinic
Space group	*P*-1 (No. 2)	*P*-1 (No. 2)
Color / Habit	yellow block	colorless platelet
Size [mm]	0.24 x 0.38 x 0.77	0.04 x 0.10 x 0.30
a [Å]	8.0995(5)	6.7012(5)
b [Å]	8.1851(5)	7.5041(6)
c [Å]	8.7285(4)	13.0554(9)
α [°]	87.370(4)	104.374(7)
β [°]	80.330(5)	102.328(6)
γ [°]	60.399(6)	98.117(7)
V [Å^3]	495.52(6)	608.07(9)
Z	2	2
$\rho_{calc.}$ [g cm^{-3}]	1.784	1.667
μ [mm^{-1}]	0.161	0.147
F(000)	276	316
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073
T [K]	103	123
θ Min-Max [°]	2.4, 26.7	2.9, 26.4
Dataset	-7: 10 ; -10: 10 ; -11: 11	-8: 8 ; -9: 9 ; -16: 16
Reflections collected	4782	9231
Independent refl.	2101	2497
R_{int}	0.020	0.042
Observed reflections	1864	1902
Parameters	203	208
R_1 (obs)[a]	0.0356	0.0639
wR_2 (all data)[b]	0.0948	0.1986
S [c]	1.06	1.07
Resd. dens [e Å^{-3}]	-0.20, 1.31	-0.26, 0.62
Device type	Xcalibur Sapphire3	Xcalibur Sapphire3
Solution	SIR-92	SIR-92
Refinement	SHELXL-2013	SHELXL-2013
Absorption correction	multi-scan	multi-scan
CCDC	2144424	2144426

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; [b] $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0)^2]]^{1/2}$; $w = [\sigma c^2(F_0^2)+(xP)^2+yP]^{-1}$ and $P=(F_0^2+2F_c^2)/3$; [c] $S = (\Sigma[w(F_o^2-F_c^2)^2]/(n-p))^{1/2}$ (n = number of reflections; p = total number of parameters).

3. Thermal Analysis

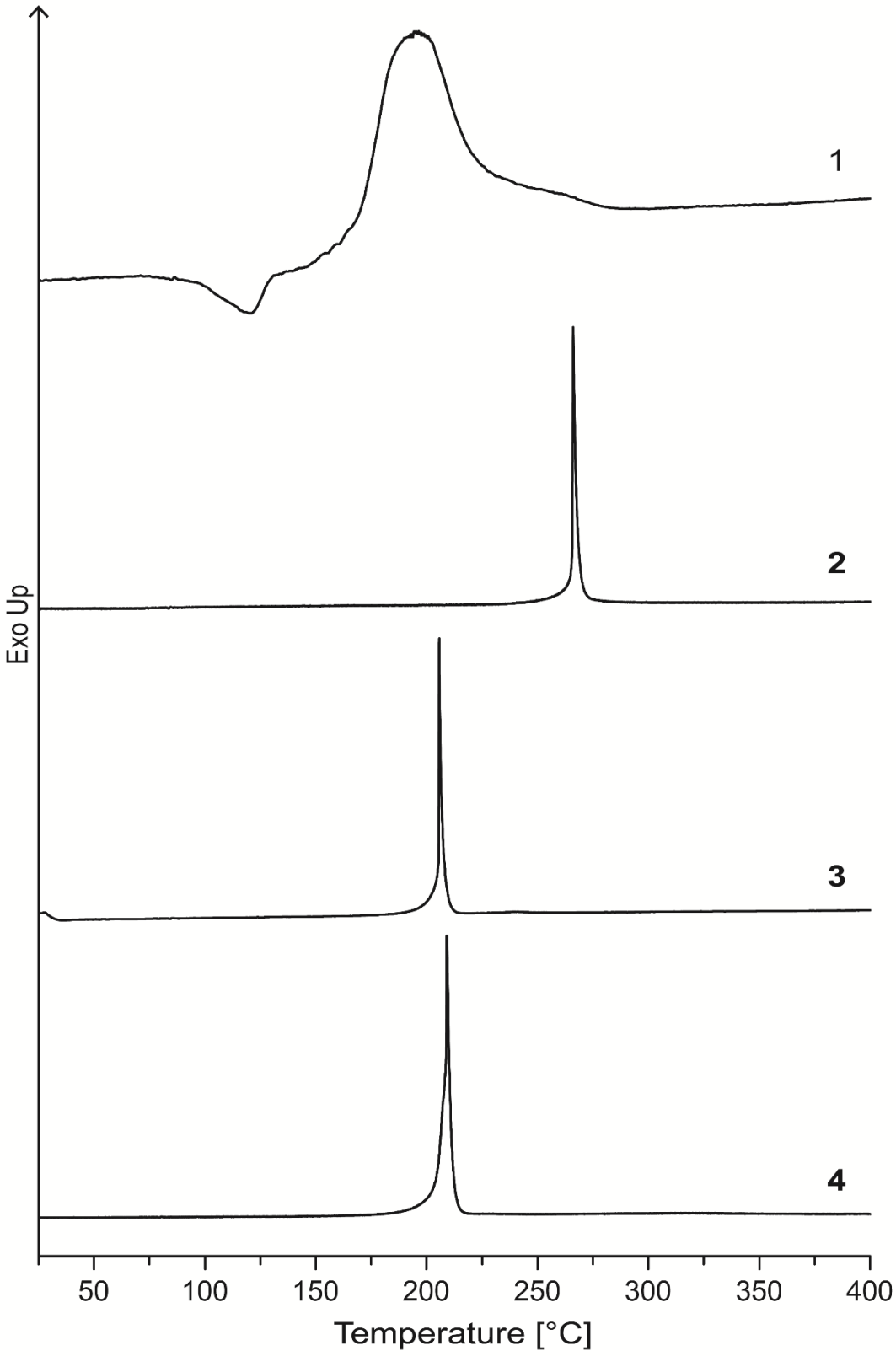


Figure S3. DTA plots of neutral compound **1** and nitrogen-rich derivatives **2**-**4**.

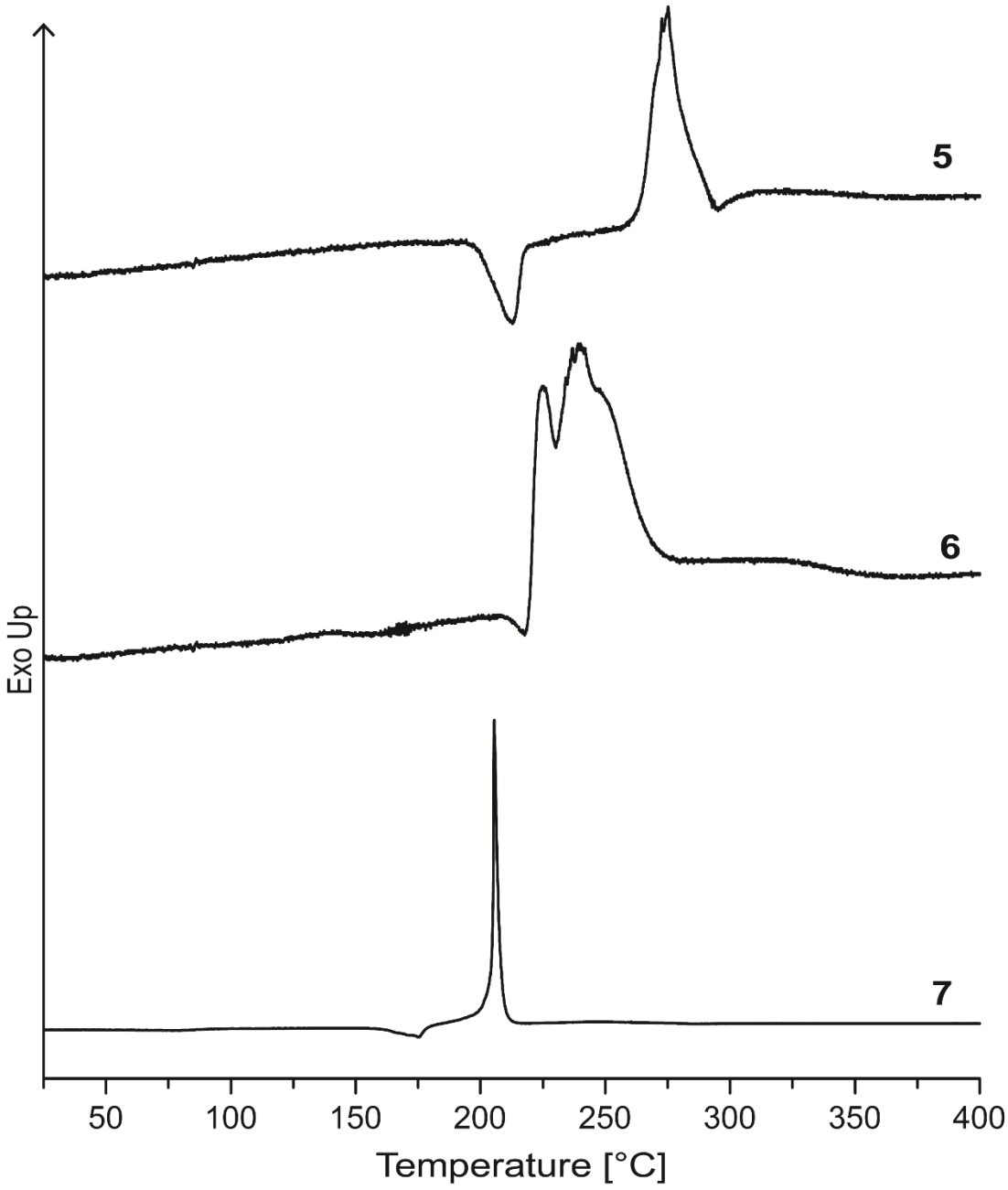


Figure S4. DTA plots of guanidinium derivatives **5**-7.

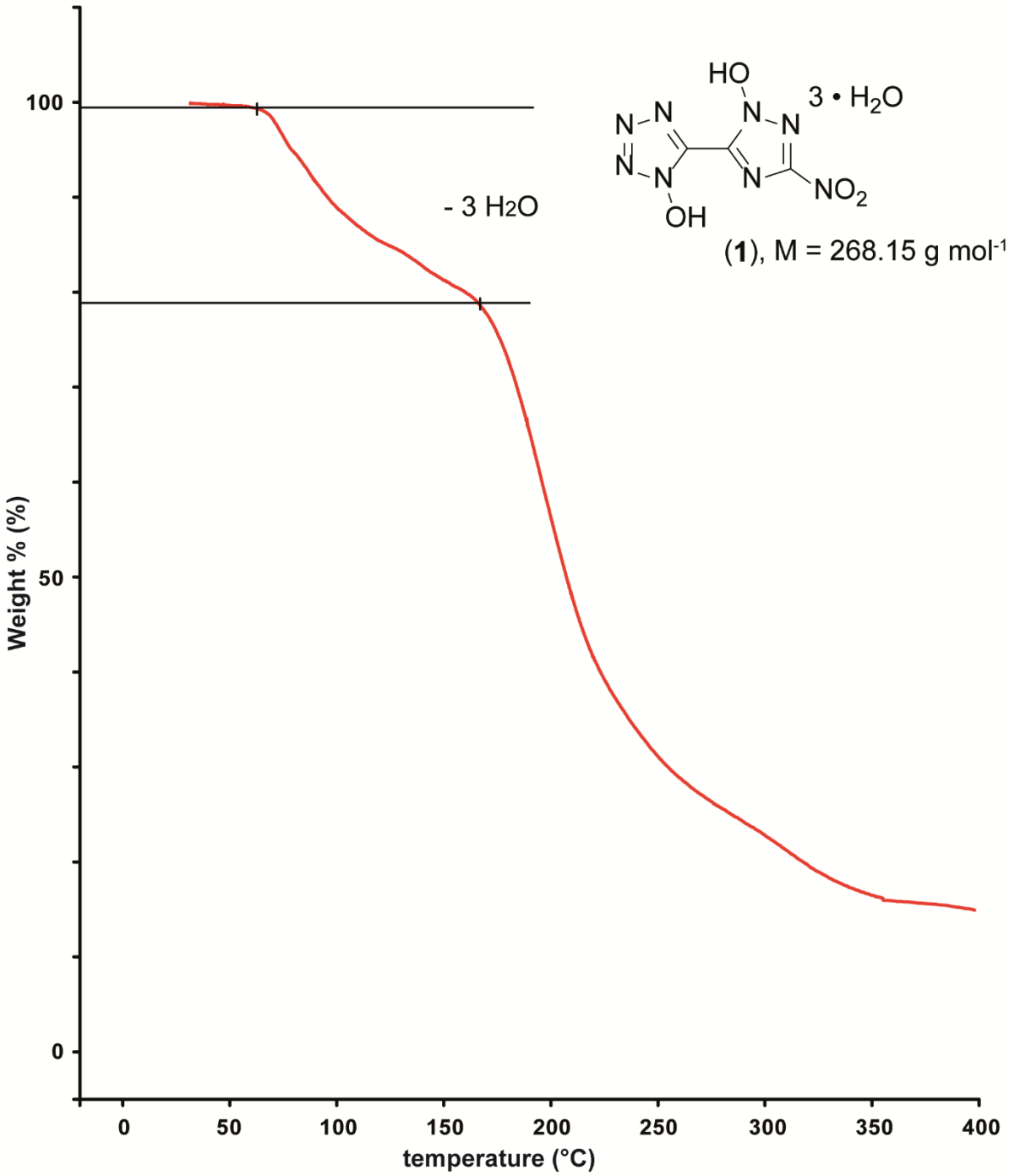


Figure S5. TGA plot of **1** with a heating rate of 5 °C min^{-1}.

4. Computation

Heat of Formation Computation

All quantum chemical calculations were carried out using the Gaussian G09 program package.[S10] The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and co-workers in order to obtain very accurate energies. The CBS models are using the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated CBS limit. CBS-4 starts with an HF/3-21G(d) geometry optimization; the zero-point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and an MP2/6- 31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+ (d,p) calculation is used to approximate higher order contributions. In this study, we applied the modified CBS-4M.

Heats of formation of the synthesized ionic compounds were calculated using the atomization method (equation E1) using room temperature CBS-4M enthalpies, which are summarized in Table S4.[S11, S12]

$$\Delta_f H^\circ_{(g,\,M,\,298)} = H_{(Molecule,\,298)} - \sum H^\circ_{(Atoms,\,298)} + \sum \Delta_f H^\circ_{(Atoms,\,298)} \qquad (E1)$$

Table S4. CBS-4M electronic enthalpies for atoms C, H, N and O and their literature values for atomic $\Delta H^\circ_f{}^{298}$ / kJ mol^{-1}

	$-H^{298}$ [a.u.]	NIST[S13]
H	0.500991	218.2
C	37.786156	717.2
N	54.522462	473.1
O	74.991202	249.5

For neutral compounds the sublimation enthalpy, which is needed to convert the gas phase enthalpy of formation to the solid state one, was calculated by the *Trouton* rule.[S14] For ionic compounds, the lattice energy (U_L) and lattice enthalpy (ΔH_L) were calculated from the corresponding X-ray molecular volumes according to the equations provided by *Jenkins* and *Glasser*.[S15] With the calculated lattice enthalpy the gas-phase enthalpy of formation was

converted into the solid state (standard conditions) enthalpy of formation. These molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to equation E2.

$$\Delta U_m = \Delta H_m - \Delta n\, RT \qquad \text{(E2)}$$

(Δn being the change of moles of gaseous components)

The calculation results are summarized in Table S5.

Table S5. Calculation results.

	$-H^{298}$ [a] [a.u.]	$\Delta_f H°$(g,M) [kJ mol^{-1}] [b]	V_M [Å^3] [c]	ΔU_L; ΔH_L [d] [kJ mol^{-1}]	$\Delta_f H°$(s) [e] [kJ mol^{-1}]	Δn [f]	$\Delta_f U$(s) [g] [kJ kg^{-1}]
A^-	852.651081	196.2					
A^{2-}	852.001852	367.4					
NH_4^+	56.796608	635.3					
$N_2H_5^+$	112.030523	773.4					
NH_3OH^+	131.863229	686.5					
G^+	205.453192	571.2					
AG^+	260.701802	670.7					
TAG^+	371.197775	873.1					
2	-	1638.0	235	1430.0; 1437.5	200.6	11.0	918.0
3	-	1914.2	269	1359.5; 1366.9	547.3	13.0	2083.4
4	-	1740.4	240	1416.5; 1423.9	316.4	12.0	1235.6
5	-	1509.8	343	1240.5; 1247.9	261.9	15.0	900.1
6	-	1708.8	365	1210.8; 1218.3	490.6	17.0	1470.5
7	-	1069.3	315	448.8; 453.7	615.5	14.0	2043.3

[a] CBS-4M electronic enthalpy; [b] gas phase enthalpy of formation; [c] molecular volumes taken from X-ray structures and corrected to room temperature; [d] lattice energy and enthalpy (calculated using Jenkins and Glasser equations); [e] standard solid state enthalpy of formation; [f] Δn being the change of moles of gaseous components when formed; [g] solid state energy of formation.

5. References

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