Nitrogen-Rich Compounds

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Energetic Nitrogen-Rich Derivatives of 1,5-Diaminotetrazole**

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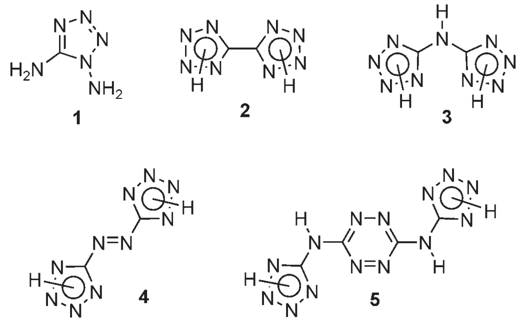
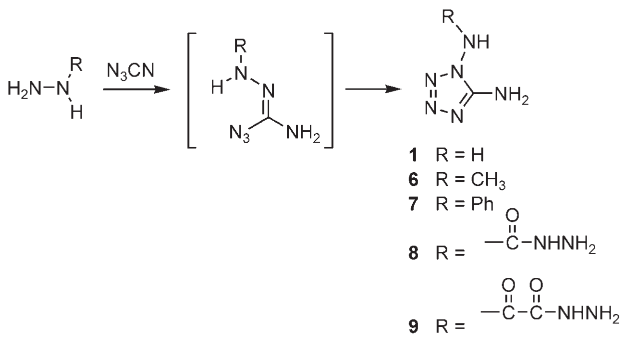
In recent years 1,5-diamino-1*H*-tetrazole (**1**), ditetrazoles **2–5** (Scheme 1), and salt derivatives thereof have been prepared and characterized in order to determine the properties of these high-energy-density materials (HEDM).[1] Surprisingly, substitution of the heterocyclic tetrazole ring with amino groups is one of the simplest methods to enhance thermal stability,[2] even though **1** contains 84.0% nitrogen.



Scheme 1. Examples of reported tetrazoles.

Nearly 80 years ago **1** was prepared by treatment of thiosemicarbazide with lead(II) oxide and sodium azide.[3] In 1984, further investigation into its synthesis and properties gave **1** in 59% yield.[4] Later, **1** was synthesized by using aminoguanidinium chloride and HNO_2.[5] The reaction mixture was carefully brought to pH 8 with sodium carbonate in order to deprotonate the amino-substituted azido guanyl chloride intermediate, which cyclized to form **1** in 58% yield. However, a further report[6] that appeared in the same year recommended special caution in the synthesis of **1**. This stated that **1** was pure following ethanol extraction; however, during extraction by ethanol a very shock sensitive alkali metal salt of tetrazolyl azide[7] often was observed as a byproduct, produced by double diazotization of diaminoguanidine with HNO_2.

In our continuing interest in the development of energetic materials, we have now synthesized derivatives of 1,5-diaminotetrazole in situ by reaction of cyanogen azide[7,8] with monosubstituted hydrazine derivatives (Scheme 2).



Scheme 2. Synthesis of monosubstituted diamino tetrazoles.

The commercially available hydrazine derivatives were treated with 2 equiv of cyanogen azide dissolved in acetonitrile/water (4/1) for 2–24 h to initially give the azidohydrazones as intermediate, cyclization of which led to substituted 1,5-diaminotetrazoles **1** and **6–9** in good yields (**1**: 79, **6**: 70, **7**: 67, **8**: 74, **9**: 56%). We emphasize that the synthesis of cyanogen azide from cyanogen bromide and sodium azide in dry acetonitrile must be carried out with extreme care (see Safety Precautions).[7]

Cyanogen azide, a colorless oil, was first isolated from the reaction of sodium azide and cyanogen chloride.[8a] In 1972, the synthesis of cyanogen azide from sodium azide and cyanogen bromide, as well as its reactivity, characterization, and handling, were reported.[8b] During the reaction, traces of moisture led to the byproducts sodium 5-azidotetrazolate[5,7] and diazidomethylenecyanamide,[9] which were subsequently isolated as highly explosive and shock-sensitive solids.

It is noteworthy that the current method can be efficiently applied to bis(1,5-diaminotetrazole) derivatives (Scheme 3). Reactions of dihydrazines with 5–6 equiv of cyanogen bromide and an excess of sodium azide led to good yields of diaminotetrazoles **10–13** (**10**: 79, **11**: 64, **12**: 74, **13**: 65%).[10] Removal of the acetonitrile/water solvent (which must be accomplished by air drying only) from the reaction mixture was followed by additional washing with small amounts of acetonitrile and water. The structures of all diamino tetrazole derivatives are supported by IR and ^1H, ^{13}C, and ^{15}N NMR spectroscopic data as well as elemental analysis (Table 1).

Diamino tetrazoles **8** and **13** were characterized by the usual spectroscopic methods and by single-crystal X-ray diffraction analyses.[11] Molecular structures of **8** and **13** are

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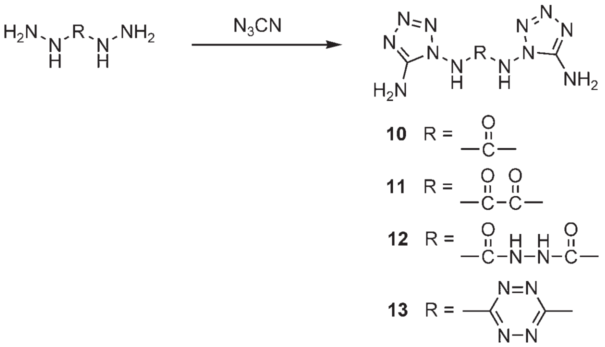

Scheme 3. Synthesis of bis(1,5-diaminotetrazole) derivatives.

Table 1: Selected physical data of diamino tetrazole derivatives.[a]

10: colorless crystal; IR (KBr): $\tilde{\nu}=3331$, 3146, 1707, 1659 cm^{-1}; ^1H NMR ([D$_6$]DMSO): $\delta=7.01$ (s, 4H; NH_2), 11.09 ppm (brs, 2H; NH); ^{13}C NMR ([D$_6$]DMSO): $\delta=152.5$ (s), 154.8 ppm (s); ^{15}N NMR ([D$_6$]DMSO): $\delta=-331.9$ (t, $^1J_{NH}=89.3$ Hz; NH_2), -269.3 (brs; NH), -172.8 (N1), -94.6 (N4), -19.4 (N3), 4.2 ppm (N2); elemental analysis (%): calcd for $C_3H_6N_{12}O$ (226.16): C 15.93, H 2.67, N 74.32; found C 16.27, H 2.77, N 72.71.
11: white solid; IR (KBr): $\tilde{\nu}=3402$, 3339, 3283, 3223, 3183, 1738, 1661, 1452, 1115, 1075, 672 cm^{-1}; ^1H NMR ([D$_6$]DMSO): $\delta=7.13$ (s, 4H; NH_2), 12.71 ppm (s, 2H; NH); ^{13}C NMR ([D$_6$]DMSO): $\delta=154.3$ (s), 156.9 ppm (s); elemental analysis (%): calcd for $C_4H_6N_{12}O_2$ (254.17): C 18.90, H 2.38, N 66.13; found C 19.21, H 2.36, N 65.65.
12: white solid; IR (KBr): $\tilde{\nu}=3412$, 3327, 3291, 3213, 3000, 1717, 1649, 1584, 1518, 1331, 1254, 598 cm^{-1}; ^1H NMR ([D$_6$]DMSO): $\delta=6.80$ (s, 4H; NH_2), 9.13 (s, 2H; NH), 10.75 ppm (brs, 2H; NH); ^{13}C NMR ([D$_6$]DMSO): $\delta=154.9$ (s), 155.4 ppm (s); ^{15}N NMR ([D$_6$]DMSO): $\delta=-332.9$ (t, $^1J_{NH}=89.1$ Hz, NH_2), -276.0 (d, $^1J_{NH}=91.3$ Hz, NH), -270.4 (brs, NH), -172.1 (N1), -96.2 (N4), -18.2 (N3), 1.7 ppm (N2); elemental analysis (%): calcd for $C_4H_8N_{14}O_2$ (284.20): C 16.90, H 2.84, N 69.00; found C 16.88, H 2.95, N 67.21.
13: orange solid; IR (KBr): $\tilde{\nu}=3385$, 3298, 3256, 3192, 3026, 2936, 2843, 1655, 1558, 1483, 1431, 1332, 1112, 1061, 953, 560 cm^{-1}; ^1H NMR ([D$_6$]DMSO): $\delta=7.06$ (s, 4H; NH_2), 11.98 ppm (brs, 2H; NH); ^{13}C NMR ([D$_6$]DMSO): $\delta=154.9$ (s), 161.1 ppm (s); ^{15}N NMR ([D$_6$]DMSO): $\delta=-332.24$ (t, $^1J_{NH}=85.5$ Hz; NH_2), -279.6 (brs; NH), -171.7 (N1), -93.0 (N4), -30.0 (N-tetrazine), -19.7 (N3), 6.2 ppm (N2); elemental analysis (%): calcd for $C_4H_6N_{16}$ (278.20): C 17.27, H 2.17, N 80.56; found: not determinable (explodes).

[a] ^1H, ^{13}C and ^{15}N NMR (CH_3NO_2 as external standard) spectra were recorded at 300.1 MHz, 75.5 MHz and 50.7 MHz, respectively. The data for **6**, **7**, **8**, **9**, **11**·2 H_2O and **12**·4 H_2O are summarized in the Supporting Information.

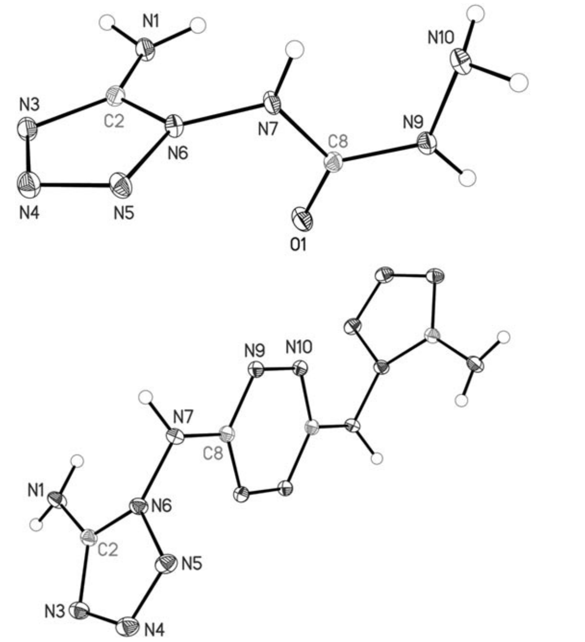

Figure 1. Molecular structures (hydrogen atoms shown as spheres of arbitrary radius and thermal displacement set at 30% probability) of **8** (top) and **13** (bottom). Solvent molecules in **13** have been omitted for clarity and only symmetry unique atoms are labeled. Selected bond lengths [Å] and angles [°]: **8**: C2–N3 1.332(2), N3–N4 1.384(2), N4–N5 1.284(2), N5–N6 1.369(2), N6–N7 1.3654(19), N7–C8 1.394(2), C8–N9 1.337(2), N9–N10 1.409(2); N6-N7-C8 117.51(14), C8-N9-N10 119.21(15); **13**: C2–N3 1.3250(16), N3–N4 1.3739(16), N4–N5 1.2835(16), N5–N6 1.3681(14), N6–N7 1.3807(14), N7–C8 1.3843(16), C8–N9 1.3403(16), N9–N10 1.3225(15); N6-N7-C8 115.13(10).

shown in Figure 1. Structural details are given in the Supporting Information.

The extended structure of compound **8** is a complex 3D network formed by H-bonding (N9···N3_#1 2.968(2), N10···O1_#2 2.993(2) Å; symmetry transformation #1 $x+1/2$, $-y+1/2$, $z+1/2$; #2 $=x+1/2$, $y+1/2$, z). Compound **13** forms a hydrogen-bonded chain involving amino H atoms and the cocrystallized DMSO solvent molecule (N1···O2_#3 2.969(1), N7···O1_#4 2.700(1); symmetry transformation #3 $=x+1$, $-y+1$, $-z+1$; #4 $=-x+1$, $-y+1$, $-z$). Addition of DMSO was necessary to produce a crystal of **13** for structural analysis.

In the ^{15}N NMR spectrum of **13** seven signals were observed (Figure 2). A broad signal assigned to NH appeared at $\delta=-279.6$ ppm, due to the positive nuclear Overhauser effect resulting from the directly bonded protons in the H-decoupled ^{15}N NMR spectrum. By using heteronuclear single quantum correlation (HSQC), the coupling constant of NH_2 ($^1J(^{15}N,^1H)=85.5$ Hz) was determined; however, because the

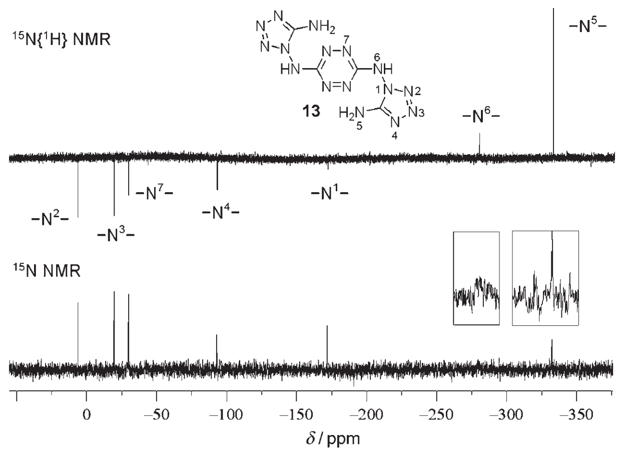

Figure 2. ^{15}N NMR spectra of **13**. Top: decoupled (delay of 10 s between pulses). Bottom: coupled (delay of 60 s between pulses).

NH proton signal is very broad, the value of its $^{15}N,^{1}H$ coupling constant was not determined. The assignments are based on the ^{15}N NMR data and comparison with phenyldiaminotetrazole **7**.[5,12]

Density is one of the most important physical properties of energetic materials. The densities of most of the new diamino tetrazoles range between 1.44 and 1.65 $g\,cm^{-3}$ (Table 2). The decomposition temperatures lie in the range 193–232 °C, and compounds **10**, **11**, and **13** explode at their decomposition temperatures (differential scanning calorimetry, DSC). The heats of formation of **6**–**13** were calculated with Gaussian 03[13] (Table 2) by using the method of isodesmic reactions (Supporting Information). The enthalpy of an isodesmic reaction (ΔH_{r298}) is obtained by combining the MP2/6-311++G** energy difference for the reaction, the scaled zero-point energies, and other thermal factors.

Table 2: Physical properties of diamino tetrazole derivatives.

Compd	T_d[a] [°C]	Density[b] [$g\,cm^{-3}$]	$\Delta_f H^\circ_{298}$[c] [$kJ\,mol^{-1}$]	$\Delta_f H^\circ_{298}$ [$kJ\,g^{-1}$]	P[d,e] [GPa]	vD[e,f] [$m\,s^{-1}$]	IS[g] [J]
6	195	1.44	374.2	3.28	19.00	7600	>60
7	193	1.44	497.7	2.82	14.17	6739	>60
8	209	1.65	283.1	1.79	23.86	8364	>60
9	214	1.58	134.7	0.72	18.19[h]	7285[h]	>60
10	223	1.65	639.1	2.83	24.06	8255	25
11	232	1.65	498.6	1.96	21.15	7767	25
12	215	1.63	523.4	1.84	21.49	7886	25
13	209	1.62	1289.1	4.63	24.98	8331	1.5

[a] Thermal decomposition temperature under nitrogen gas (DSC, 10 °C min^{-1}). [b] Gas pycnometer (25 °C). [c] Heat of formation (calculated with Gaussian 03). [d] Detonation pressure. [e] Using 83.68 $kJ\,mol^{-1}$ for the enthalpy of sublimation for each compound. [f] Detonation velocity. [g] Impact sensitivity (BAM Fallhammer). [h] Using CHEETAH 4.0.

All of the diamino tetrazole derivatives have positive heats of formation, and that of **13** is the highest (1289 $kJ\,mol^{-1}$). By using the calculated heats of formation and the experimental densities of new substituted diamino tetrazoles **6**–**13**, the detonation pressures P and detonation velocities D were calculated by means of traditional Chapman–Jouget thermodynamic detonation theory by using Cheetah 5.0.[14] Impact sensitivities of the diamino tetrazoles, tested with a BAM Fallhammer (Table 2), range from insensitive (**6**–**9**: >60 J) through sensitive (**10**–**12**: 25 J) to very sensitive (**13**: 1.5 J).[15]

Safety Precautions

Pure cyanogen azide is extremely dangerous.[7] Therefore, when utilizing the substance as a reactant, it must always be dissolved in a solvent to give a dilute solution. Manipulations must be carried out in a hood behind a safety shield. Leather gloves must be worn. While we have experienced no difficulties with the shock instability of the 1,5-diaminotetrazole derivatives, they should be synthesized only in amounts of 1–2 mmol, and extreme care is necessary, particularly for compound **13**.

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[10] Preparation of cyanogen azide was based on a modified literature method.[7,8a] At 0 °C, cyanogen bromide (1.30 g, 12.3 mmol) was dissolved in dry acetonitrile (20 mL) and sodium azide (3.82 g, 58.8 mmol) was added. The reaction mixture was stirred at 0–15 °C for 4 h. The inorganic salt was filtered off (**Caution!** After filtering, the salt must be quickly dissolved in cold water). The solution was added to a suspension containing 3,6-dihydrazinyl-1,2,4,5-tetrazine[10b] (100 mg (0.704 mmol) in water (10 mL) at 0 °C. After 4 d[10c] of stirring at ambient temperature, the suspension was filtered to leave an orange filter cake, which was dried in air. Compound **13** was obtained (127 mg, 0.457 mmol, 65 %). a) The unknown salt which is formed is likely the azidotetrazolate salt.[7] b) Synthesis of 3,6-dihydrazinyl-1,2,4,5-tetrazine: D. E. Chavez, M. A. Hiskey, *J. Heterocycl. Chem.* **1998**, *35*, 1329–1332. c) Each compound required a different reaction time (**1**: 4 h, **6**: 2 h, **7**: 2 h, **8**: 24 h, **9**: 3 d, **10**: 2 d, **11**: 4 d, **12**: 24 h, **13**: 4 d).

[11] Crystallographic data: **8**: ($C_2H_6N_8O$): $M_r = 158.15$; crystal size $0.28 \times 0.25 \times 0.13$ mm; monoclinic, space group Cc, $a = 11.2323(7)$, $b = 4.6153(3)$, $c = 11.9898(7)$ Å, $\beta = 91.413(1)°$, $V = 621.37(7)$ Å^3, $Z = 4$, $2\theta_{max} = 58°$, 829 independent reflections, $R_1 = 0.0281$ for 814 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0766$, 100 parameters. **13**: ($C_{12}H_{30}N_{16}O_4S_4$): $M_r = 590.76$; crystal size $0.44 \times 0.23 \times 0.14$ mm; triclinic, space group $P\bar{1}$, $a = 8.6351(5)$, $b = 9.0007(5)$, $c = 9.5097(6)$ Å, $\alpha = 92.8441(8)$, $\beta = 111.4645(7)$, $\gamma = 103.7774(8)°$, $V = 660.37(7)$ Å^3, $Z = 1$, $2\theta_{max} = 52°$, 2606 independent reflections, $R_1 = 0.0258$ for 2482 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0747$, 179 parameters. CCDC-684330 and CCDC-684331 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.

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[15] Classification of impact sensitivities from reference [5] (insensitive: >40 J; less sensitive: ≥ 35 J; sensitive: ≥ 4 J; very sensitive: ≤ 3 J).

