1,5-Di(nitramino)tetrazole: High Sensitivity and Superior Explosive Performance**

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Abstract: Highly energetic 1,5-di(nitramino)tetrazole and its salts were synthesized. The neutral compound is very sensitive and one of the most powerful non-nuclear explosives to date. Selected nitrogen-rich and metal salts were prepared. The potassium salt can be used as a sensitizer in place of tetracene. The obtained compounds were characterized by low-temperature X-ray diffraction, IR and Raman spectroscopy, multi-nuclear NMR spectroscopy, elemental analysis, and DSC. Calculated energetic performances using the EXPLO5 code based on calculated (CBS-4M) heats of formation and X-ray densities support the high energetic performances of the 1,5-dinitraminotetrazolates as energetic materials. The sensitivities towards impact, friction, and electrostatic discharge were also explored.

The 1-nitrimotetrazoles are of particular interest in the development of high-energy-density materials (HEDM) since they possess large positive heats of formation and good oxygen balances.[1] The combination of both aspects yields very powerful energetics. The known nitramino tetrazoles without alkyl chains[2] are limited to the examples shown in Scheme 1. While C-nitrimotetrazoles are usually synthesized by common acidic nitration conditions (for example, HNO₃; 100%), N-nitramino tetrazoles are synthesized by nitration of the corresponding N-aminotetrazoles with mild nitration reagents such as NOBF₄ and N₂O₅. Herein we present a new representative of this class of compounds, namely 1,5-di(nitramino)tetrazole (1). The synthesis of this compound has been a long-term goal in energetic materials research because of its outstanding predicted performance. To date, many attempts of direct nitration have failed.[3,4]

The synthesis of 1, shown in Scheme 2, starts with commercially available dimethyldicarbonate, which is treated with hydrazine hydrate to give the methyl carbazate (2). Species 2 is reacted with cyanogen azide to yield N-methoxycarbonyl protected 1,5-diaminotetrazole (3), which is then nitrated in acetonitrile with N₂O₅. The nitramide 4 is decomposed in solution with aqueous KOH to give 5 as a white precipitate from which 1 can be isolated by acidification and extraction into organic solvents.

The ammonium (6), hydrazinium (7), and hydroxylammonium (8) salts are prepared by dissolving 1 in methanol and reacting it with the corresponding base in aqueous solution. In the case of 8, an adduct of 8 with hydroxylamine (8b) was obtained with an excess of hydroxylamine.

Low-temperature X-ray diffraction was used to characterize all of the compounds obtained and to obtain accurate densities for performance calculations. 1,5-Di(nitramino)tetrazole (1) crystallizes in the orthorhombic space group P2₁2₁2₁ and a density of 1.968 g cm⁻³ at 173 K. The molecule, shown in Figure 1, is nearly planar (C₁-N₁-N₅-O₁ = 3.9(6)°) but the N-nitramine is twisted out of the ring plane (C₄-N₂-N₁-N₇-N₈ 72.0°). The proton at N₄ is within the ring plane and the proton located at N₇ forms pyramidal system with N₈ and N₁ (C₄-N₂-N₁-N₇-H₇ = -47.9°). The bond length between N₅ and N₆ (1.356(2) Å) is significantly shorter than the bond length between N₇ and N₈ (1.462(2) Å).

The dipotassium salt of the 1,5-di(nitramino)tetrazole (5) crystallizes anhydrously from water in the monoclinic space group P2₁/c with a density of 2.177 g cm⁻³ (173 K) and four molecules in the unit cell. Figure 2 illustrates the molecular unit of 5. The nitramino moiety attached to the carbon is...
almost planar with the ring (C1-N7-N8-O3 2.73(2)°) and the N-nitramino moiety is twisted out of the ring plane by 99.3°.

The N5–N6 bond (1.331(3) Å) is shorter than in 1 as well as the bond length between N7 and N8 (1.314(3) Å).

The diammonium (6) and dihydrazinium salt of 1,5-di(nitramino)tetrazole crystallize in common space groups (6: monoclinic, P2₁/c; 7: triclinic, P1). The densities at 173 K are observed in the same range of (6: 1.730; 7: 1.709 g cm⁻³). The molecular units are displayed in Figure 3. The bond lengths and angles are similar to those observed for 5.

The dihydroxylammonium salt was obtained with two different stoichiometries. Crystallization from water yields solvent free 8a which crystallizes in the triclinic space group P1 and a density of 1.848 g cm⁻³ at 173 K (Figure 4, left). Additional hydroxylamine leads to a hydroxylamine adduct 8b which crystallizes in the form of an ammonia oxide (Figure 4, right). 8b crystallizes in the monoclinic space group P2₁/c with four molecular units in the unit cell and a density of 1.853 (173 K), which is slightly higher than that of 8a.

Salts 6–8 violently exploded in the DSC sample containers at temperatures of 130°C (8a,b), 150°C (7), and 170°C (6). Ca. 1 mg of 1 even destroyed the PT1000 sensor at a temperature of 110°C. Compound 5 is the most thermally stable salt with a decomposition point of 240°C. None of the compounds melted before decomposition.

Compound 1 and its salts 5–7 and 8a are very sensitive compounds. The measured sensitivity values (according to the German BAM) can be seen in Table 1. The impact sensitivities are in the range of 1 J, which is comparable to the impact.
and its nitrogen-rich salts have highly positive calculated detonation velocities and pressures even close to 10000 m s⁻¹ and 434 kbar, which makes them powerful explosives. For comparison, the corresponding values for CL-20 (hexanitro-2,4,6,8,10,12-hexaazaicosowurtzitane) are listed, which is probably still the benchmark for explosives with respect to performance. Potassium salt 5 shows very promising performance values (Vdet > 10000 m s⁻¹, pDet > 500 kbar). Therefore its use as ingredient in primary explosives was investigated. In the test (Figure 5), about 50 mg of 5 were initiated using a standard pyrotechnical igniter. The shock-wave produced by 5 was easily strong enough to detonate 500 mg of hexogen (RDX).

The test was repeated with 50 mg 5 without RDX. Only a very small dent in the copper plate was observed, which is displayed in the Supporting Information.

It can be concluded that 1,5-di(nitramino)tetrazole (1) is one of the most powerful explosives synthesized to date, however the use will be limited owing to its low decomposition point and high sensitivities. Its potassium salt 5 is stable up to 240°C and shows ideal behavior for use in primary compositions. We recommend using 5 as an environmentally benign and thermally stable sensitizer for example in place of tetracene.[11]

sensitivity of lead azide, and the friction sensitivities are also quite low (<30N). The compounds should therefore be classified as primary explosives. Except for the potassium salt, 1 and its nitrogen-rich salts have highly positive calculated enthalpies of formation (for example, 1: 508.6, 7: 573.5 kJ mol⁻¹). Details on the computations are given in the Supporting Information.

As shown in Table 1, compound 1 and its salts 6–8a have also very high calculated (EXPLO5 6.02) detonation velocities and pressures even close to 10000 m s⁻¹ and 434 kbar, which makes them powerful explosives. For comparison, the corresponding values for CL-20 (hexanitro-2,4,6,8,10,12-hexaazaicosowurtzitane) are listed, which is probably still the benchmark for explosives with respect to performance. Potassium salt 5 shows very promising performance values (Vdet > 10000 m s⁻¹, pDet > 500 kbar). Therefore its use as ingredient in primary explosives was investigated. In the test (Figure 5), about 50 mg of 5 were initiated using a standard pyrotechnical igniter. The shock-wave produced by 5 was easily strong enough to detonate 500 mg of hexogen (RDX).

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Experimental Section

1-Methoxycarbonyl-1,5-diaminotetrazole (3): Methylcarbazate (1.65 g, 18 mmol) in water (10 mL) was added to a freshly prepared solution of cyanogen azide in acetonitrile (20 mmol in 50 mL) at RT. After stirring at RT for one day, the solution was left for crystallization. After most of the acetonitrile was gone, the partially crystalline residue was suspended in 5 mL ice–water and stirred until a white filterable suspension has formed. The suspension was filtered and washed with a little ice–water. The product was dried in air and 1.08 g (37%) of colorless 3 was obtained. IR (ATR): v = 3365 (w),

$$\text{Table 1: Energetic performance parameters of 1, 5–7, and 8a.}$$

<table>
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<th>1</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8a</th>
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<td>Detonation velocity [m s⁻¹]</td>
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Figure 5. Detonation test using 50 mg 5 and 500 mg RDX and a conventional pyrotechnical igniter: A) Picture of the test setup; B) representation of the test setup; C) perforated copper plate as the result of RDX detonation.