

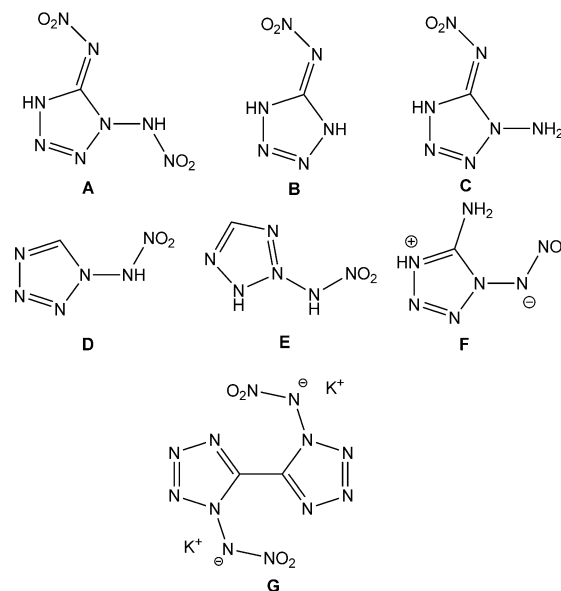
1,5-Di(nitramino)tetrazole: High Sensitivity and Superior Explosive Performance**

Dennis Fischer, Thomas M. Klapötke,* and Jörg Stierstorfer

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-nitraminotetrazoles 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-nitraminotetrazoles 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 NO₂BF₄ 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 dimethylcarbonate, 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



Scheme 1. A) 1,5-di(nitramino)tetrazole (**1**) and known nitraminotetrazoles B) 5-nitraminotetrazole,^[5] C) 5-nitramino-1-aminotetrazole,^[6] D) 1-nitraminotetrazole,^[7] E) 2-nitraminotetrazole,^[7] F) 1-nitramino-5-aminotetrazole,^[3] G) dipotassium 1,1'-di(nitramino)-5,5'-bitetrazolate.^[8]

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.

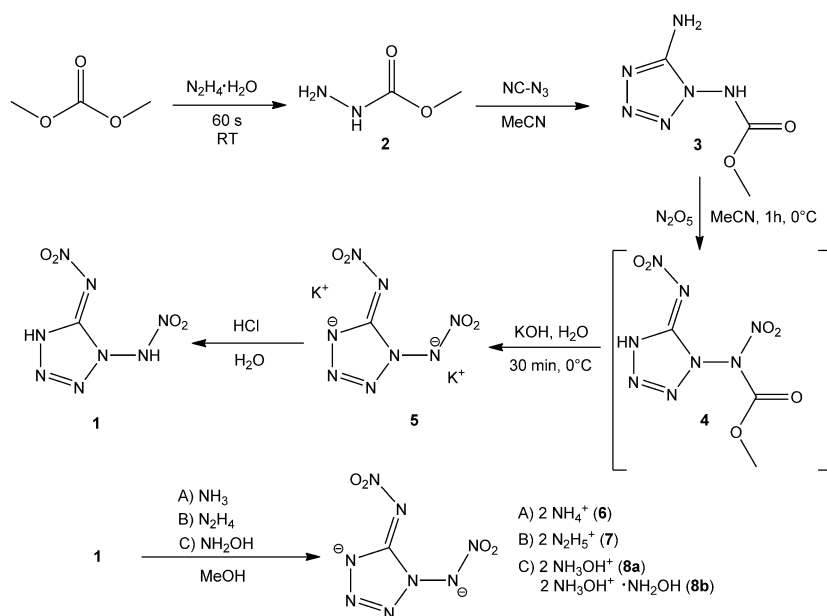
Low-temperature X-ray diffraction was used to characterize all of the compounds obtained and to obtain accurate densities for performance calculations. 1,5-Di(nitramino)tetrazole (**1**) crystallizes in the orthorhombic space group *P*2₁2₁2₁ and a density of 1.968 g cm⁻³ at 173 K. The molecule, shown in Figure 1, is nearly planar ($\angle$ C1-N6-N5-O1 $-3.9(6)^\circ$) but the N-nitramine is twisted out of the ring plane ($\angle$ 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 ($\angle$ 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 *P*2₁/*n* 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

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Scheme 2. Synthesis of 1,5-di(nitramino)tetrazole as well as its potassium and selected nitrogen-rich salts.

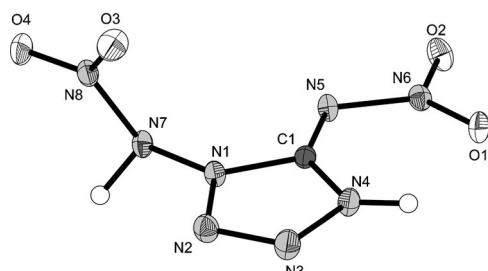


Figure 1. Molecular structure of **1**, showing the atom-labeling. Ellipsoids are set at 50% probability.

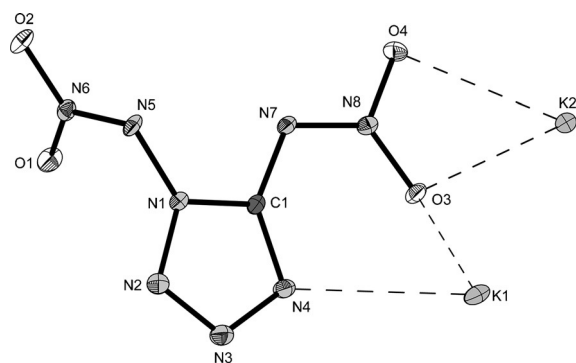


Figure 2. Representation of the molecular unit of **5**. Ellipsoids are set at 50% probability.

almost planar with the ring ($\angle \text{C1-N7-N8-O3 } 2.73(2)^\circ$) and the *N*-nitramino moiety is twisted out of the ring plane by 99.3° . The N5–N6 bond ($1.331(3) \text{ \AA}$) is shorter than in **1** as well as the bond length between N7 and N8 ($1.314(3) \text{ \AA}$).

The diammonium (**6**) and dihydrazinium salt of 1,5-di(nitramino)tetrazole crystallize in common space groups (**6**: monoclinic, $P2_1/c$; **7**: triclinic, $P\bar{1}$). 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 $P\bar{1}$ 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 $P2_1/c$ 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

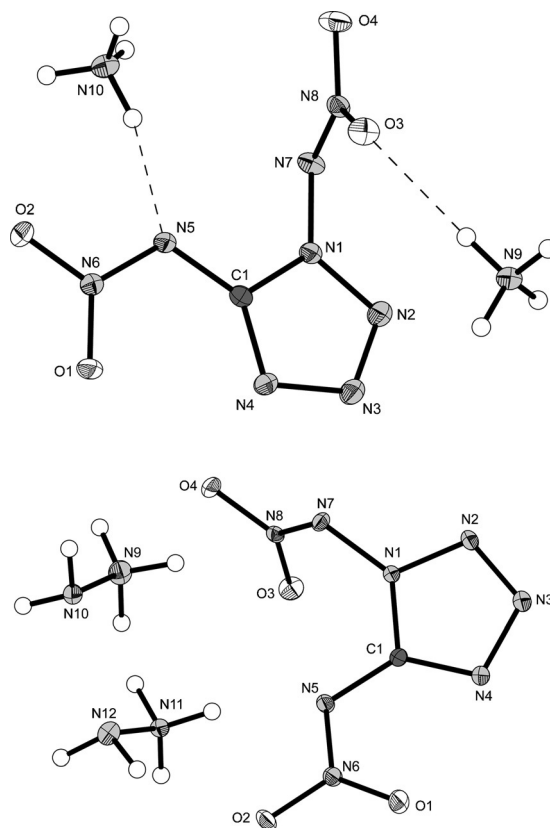


Figure 3. Molecular structures of salts **6** (top) and **7** (bottom). Ellipsoids are set at 50% probability.

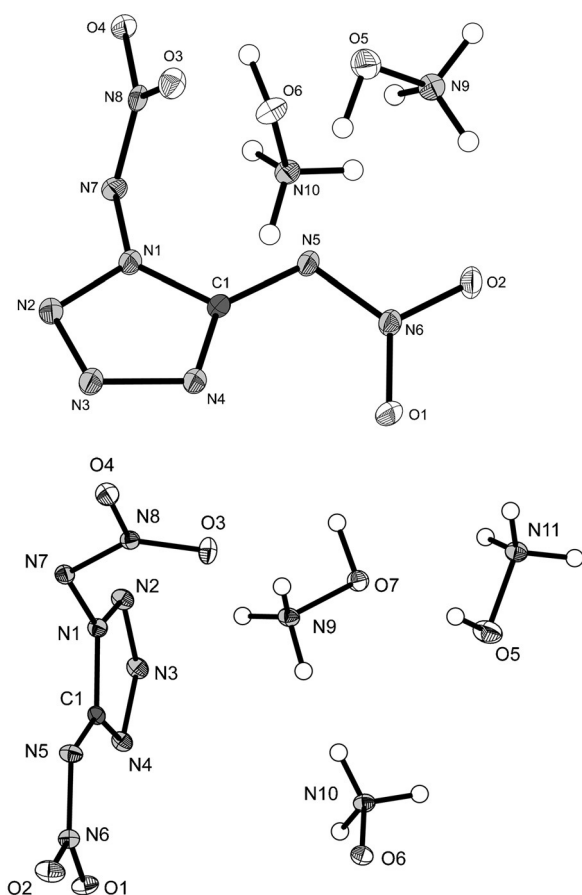


Figure 4. Molecular structures of hydroxylammonium salts **8a** (top) and **8b** (bottom). Ellipsoids are set at 50% probability.

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)^[9] detonation velocities and pressures even close to 10000 ms⁻¹ and 434 kbar, which makes them powerful explosives. For comparison, the corresponding values for CL-20 (hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) are listed, which is probably still the benchmark for explosives with respect to performance.^[10] Potassium salt **5** shows very promising performance values ($V_{\text{det}} > 10000 \text{ ms}^{-1}$, $p_{\text{CJ}} > 500 \text{ kbar}$). 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]

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): $\tilde{\nu} = 3365 \text{ (w)}$,

Table 1: Energetic performance parameters of **1**, **5–7**, and **8a**.

	1	5	6	7	8a	CL-20
Formula	CH ₂ N ₈ O ₄	CK ₂ N ₈ O ₄	CH ₈ N ₁₀ O ₄	CH ₁₀ N ₁₂ O ₄	CH ₈ N ₁₀ O ₆	C ₆ H ₆ N ₁₂ O ₁₂
IS ^[a] [J]	1	1	1.5	1	1.5	4 ^[10]
FS ^[b] [N]	< 5	< 5	30	6	10	48 ^[10]
N + O ^[c] [%]	92.62	66.12	91.04	91.31	92.16	82.18
Ω_{CO} ; Ω_{CO_2} ^[d] [%]	16.84; 8.42	−6.02; −12.03	−7.14; −14.27	−12.59; −18.88	6.25; 0	10.95; −10.95
T_{dec} ^[e] [°C]	110	240	170	150	130	221
ρ ^[f] [g cm ⁻³]	1.968 (173 K) 1.93 (298 K)	2.177 (173 K) 2.137 (298 K)	1.730 (173 K) 1.698 (298 K)	1.779 (173 K) 1.746 (298 K)	1.847 (173 K) 1.813 (298 K)	2.083 (100 K) ^[12] 2.04 (298 K) ^[10]
$\Delta_f H^{\circ}_{\text{gas}}$ [kJ mol ⁻¹]	486.3	−112.4	212.0	541.3	351.5	365.4
$\Delta_f U^{\circ}_{\text{gas}}$ [kJ kg ⁻¹]	2649.6	−366.8	1067.4	2256.5	1488.3	918.7
EXPLO6.02 values:						
$-\Delta_{\text{ex}} U^{\circ}_{\text{gas}}$ [kJ kg ⁻¹]	5921	3938	5240	6082	6619	6168
P_{CJ} ^[j] [kbar]	434	522	315	376	399	444
V_{det} ^[k] [m s ⁻¹]	9967	10011	9078	9872	9807	9730
V_0 ^[l] [L kg ⁻¹]	836	413	978	1003	951	715

[a] Impact sensitivity, BAM drophammer (method 1 of 6). [b] Friction sensitivity, BAM friction tester (method 1 of 6). [c] Summated nitrogen and oxygen content. [d] Oxygen balance. [e] < temperature of decomposition according to DSC (onset temperatures at heating rates of 5 deg min⁻¹); [f] X-ray densities at 173 K and the corresponding RT values calculated using the equation ($\rho_{298\text{K}} = \rho_T / (1 + \alpha_V(298 - T_0))$; $\alpha_V = 1.5 \times 10^{-4} \text{ K}^{-1}$). [g] Heat of formation. [h] Energy of formation. [i] Heat of detonation. [j] Detonation pressure. [k] Detonation velocity. [l] Volume of gases after detonation.

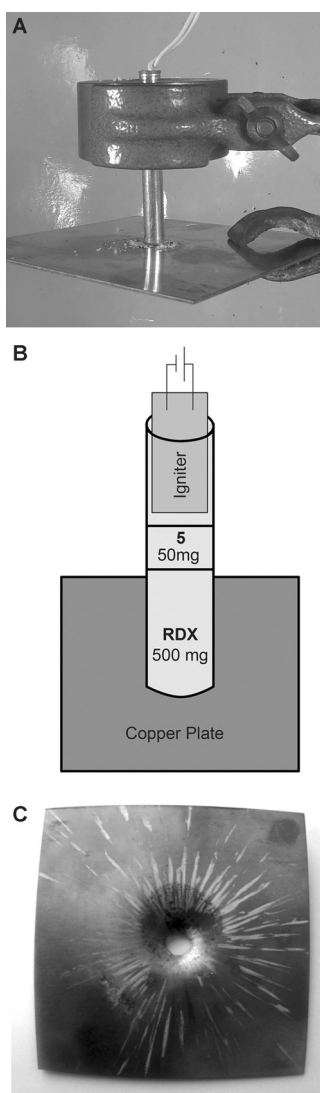


Figure 5. Detonation test using 50 mg **5** and 500 mg RDX and a conventional pyrotechnical igniter. A) Picture of the test setup; B) representation of the test setup; C) perforated copper plate as the result of RDX detonation.

3310 (w), 3258 (w), 3197 (w), 3095 (w), 2863 (w), 1740 (s), 1650 (vs), 1579 (w), 1483 (w), 1448 (m), 1322 (s), 1197 (w), 1117 (m), 1065 (s), 986 (m), 924 (w), 828 (m), 756 (m), 742 (m), 720 (w), 686 (w), 667 cm^{-1} (w); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3257 (9), 3195 (18), 2964 (48), 2864 (15), 1747 (17), 1654 (30), 1580 (21), 1510 (8), 1485 (35), 1460 (9), 1338 (85), 1199 (9), 1119 (51), 1071 (16), 988 (43), 926 (41), 832 (100), 773 (43), 757 (53), 668 (9), 521 (26), 450 (33), 372 (29), 318 cm^{-1} (11); ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): δ = 11.21, 7.06, 3.72 ppm; ^{13}C NMR $\{^1\text{H}\}$ (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C) δ = 155.2, 155.1, 53.7 ppm; EA calcd for $\text{C}_3\text{H}_6\text{N}_6\text{O}_2$ (158.06 g mol^{-1}): C 22.79, H 3.82, N 53.15%; found: C 23.26, H 3.91, N 51.38%.

1,5-Di(nitramino)tetrazole (**1**): **3** (1.58 g, 10 mmol) was suspended in dry acetonitrile (30 mL) at 0 °C. N_2O_5 (3.24 g, 30 mmol) in acetonitrile (30 mL) was added in one portion and the mixture was stirred at 0 °C for one hour. The reaction was vigorously stirred and

quenched by adding KOH (3.36 g, 60 mmol) dissolved in water (30 mL). The aqueous phase was separated and the water was evaporated under high vacuum. The residue was stirred in methanol (50 mL) for a few hours. The white precipitate consisting of pure KNO_3 and K_2DNAT was filtered, washed with a little methanol, and dried. The solid was dissolved in HCl (30 mL, 2 M) and extracted with four portions of ethylacetate (4×20 mL). The solvent was removed from the organic phase in vacuo at RT and the colorless crystalline product was dried in high vacuum to give 950 mg (50 %) of colorless **1**. DSC (5 °C min^{-1} , °C): 110 °C (dec.); IR (ATR): $\tilde{\nu}$ = 2967 (w), 2757 (w), 1636 (w), 1591 (vs), 1502 (s), 1304 (s), 1222 (s), 1136 (m), 1022 (m), 1006 (m), 964 (m), 886 (w), 836 (m), 773 (m), 695 cm^{-1} (m); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3101 (7), 1614 (17), 1596 (43), 1425 (45), 1320 (36), 1260 (100), 1139 (8), 1025 (11), 1011 (26), 979 (68), 891 (16), 841 (26), 781 (16), 762 (26), 632 (9), 492 (45), 418 (43), 315 (29), 284 (49), 217 cm^{-1} (10); ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): δ = 11.91 ppm; ^{13}C NMR $\{^1\text{H}\}$ (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C) δ = 147.6 ppm; EA calcd for $\text{CH}_2\text{N}_8\text{O}_4$ (190.02 g mol^{-1}): C 6.32, H 1.06, N 58.95%; found: C 7.29, H 1.39, N 57.14%; BAM drophammer: 1 J (< 100–500 μm); friction tester: < 5 N (< 100–500 μm); ESD: 0.3 J.

The synthesis of salts **5–8** as well as the general methods are described in the Supporting Information.

Keywords: energetic materials · nitramines · sensitivity · structure elucidation · tetrazoles

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- [1] J. A. Agrawal, *High Energy Materials*, Wiley-VCH, Weinheim, **2010**.
- [2] R. L. Willer, R. A. Henry, *J. Org. Chem.* **1988**, *53*, 5371–5374.
- [3] T. M. Klapötke, F. A. Martin, J. Stierstorfer, *Chem. Eur. J.* **2012**, *18*, 1487–1501.
- [4] L. Liu, C. He, C. Li, Z. Li, *J. Chem. Crystallogr.* **2012**, *42*, 816–823.
- [5] a) T. E. O'Connor, G. Fleming, J. Reilly, *J. Soc. Chem.* **1949**, 68, 309–310; b) T. M. Klapötke, J. Stierstorfer, *Helv. Chim. Acta* **2007**, *90*, 2132–2150; c) Y.-H. Joo, J. M. Shreeve, *J. Am. Chem. Soc.* **2010**, *132*, 15081–15090.
- [6] D. Fischer, T. M. Klapötke, J. Stierstorfer, New Trends in Research of Energetic Materials, Proceedings of the Seminar, 15th, Pardubice, Czech Republic, Apr. 18–20, **2012**, *1*, 117–129.
- [7] M. A. Ilyushin, A. N. Terpigorev, I. V. Tselinskii, *Russ. J. Gen. Chem.* **1999**, *69*, 1645–1657.
- [8] D. Fischer, T. M. Klapötke, J. Stierstorfer, *Angew. Chem. Int. Ed.* **2014**, *53*, 8172–8175; *Angew. Chem.* **2014**, *126*, 8311–8314.
- [9] M. Sućeska, EXPLO5 V6.02 program, Brodarski Institute, Zagreb, Croatia, **2014**.
- [10] R. Mayer, J. Köhler, A. Homburg, *Explosives 5th edn.*, Wiley VCH, Weinheim, **2002**, p. 164.
- [11] a) J. W. Fronabarger, M. D. Williams, PCT Int. Appl. WO 2012003031, **2012**; b) Q.-L. Yan, S. Zeman, J.-G. Zhang, P. He, T. Musil, M. Bartošková, *Phys. Chem. Chem. Phys.* **2014**, *16*, 24282–24291.
- [12] N. B. Bolotina, M. J. Hardie, R. L. Speer, Jr., A. A. Pinkerton, *J. Appl. Crystallogr.* **2004**, *37*, 808–814.

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