DOI: 10.1002/ejic.200800261

# The New Energetic Compounds 1,5-Diaminotetrazolium and 5-Amino-1-methyltetrazolium Dinitramide – Synthesis, Characterization and Testing

Thomas M. Klapötke*[a] and Jörg Stierstorfer[a]

**Keywords:** Energetic materials / Tetrazoles / Amides / Structure elucidation / Detonation parameters

The new energetic compounds 1,5-diamino-1*H*-tetrazol-4-ium dinitramide (**1**) and 5-amino-1-methyl-1*H*-tetrazol-4-ium dinitramide (**2**) were synthesized by the reaction of potassium dinitramide with 1,5-diamino-1*H*-tetrazolium perchlorate and 5-amino-1-methyl-1*H*-tetrazolium perchlorate, respectively. Both compounds were fully characterized by single-crystal X-ray diffraction, IR and Raman spectroscopy, multinuclear ($^1$H, $^{13}$C, $^{14}$N, $^{15}$N) NMR spectroscopy, differential scanning calorimetry, and mass spectrometry. In addition, their sensitivities towards impact, friction, and electrical discharge were investigated. The heats of formation were calculated (CBS-4M) in an extensive computational study. The detonation parameters of **1** and **2** were calculated by using the EXPLO5 software. The calculations yielded auspicious values for potential application as highly explosive compounds.

## Introduction

The development of tetrazole compounds and other high-nitrogen derivatives as new energetic materials[1] for civil and military applications is of great interest in many research programs worldwide. Tetrazoles have the outstanding property of often combining a high nitrogen content with good thermal and kinetic stabilities, which is due to their aromatic ring system. "High-nitrogen" compounds form a unique class of energetic materials whose energy is derived from their very high heats of formation rather than from the overall heat of combustion. The high heat of formation is directly attributable to the large number of energetic N–N, N–C, and N–O bonds.[2] Especially energetic ionic salts of tetrazoles have been utilized in energetic roles because of their higher heats of formation, density, and oxygen balance relative to those of their carbocyclic analogues. Tetrazolium cations paired with nitrate, perchlorate, dinitramide, or picrate anions form highly energetic salts. With the exception of the perchlorate salts, the tetrazolium salts and their decomposition products are often environmentally benign. Probably most suitable as highly explosive compounds, gas generators, or components in propellants or propellant charges[3–6] are tetrazolium salts containing the dinitramide anion, $N(NO_2)_2^-$ (DN).[7] They often show excellent oxygen balances by combining both the fuel (tetrazole heterocycle) and the oxidizer (dinitramide). Many N-rich dinitramides like guanidinium dinitramide,[8] aminoguanidinium dinitramide,[9] biguanidinium dinitramide,[10] and triaminoguanidinium dinitramide[4,5] were synthesized and characterized as energetic materials. In addition, tetrazolium salts, e.g. 5-aminotetrazolium dinitramide,[11] 5-amino-1,4-dimethyltetrazolium dinitramide,[12] 1,5-diamino-4-methyltetrazolium dinitramide,[13] are described as energetic materials in the literature.[14] However, there are many gaps in the literature of dinitramide chemistry. There is still misbelief in the strength of dinitramine as an acid, which indeed is a very strong acid ($pK_s = -5.6$).[15]

The following work describes the syntheses and characterization of two new highly explosive compounds: 1,4-diamino-1*H*-tetrazolium dinitramide (HDAT_DN, **1**) and 5-amino-1-methyl-1*H*-tetrazolium dinitramide (1MeHAT_DN, **2**). Both compounds show a suitable oxygen balance,[16] which is desirable for HEDM (high energetic density materials). 1,5-Diaminotetrazole (DAT)[17] and its ionic derivatives[18] are frequently described in the literature because of their high nitrogen contents, and there have been many attempts to produce 1,5-diaminotetrazole on a larger scale. 5-amino-1-methyltetrazole (1MeAT)[19,20] as the starting material for **2** can already be synthesized on a larger scale by methylation of commercially available 5-aminotetrazole (5-AT).[21,22]

## Results and Discussion

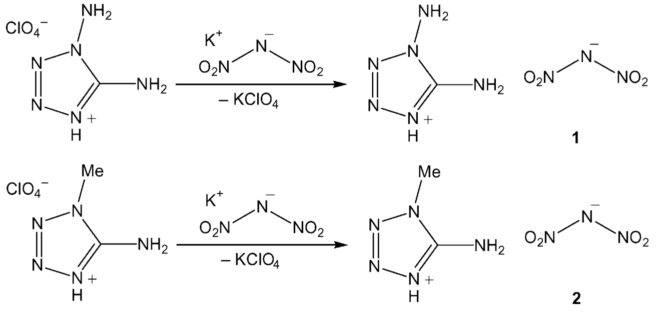
### Synthesis

1,5-Diamino-1*H*-tetrazol-4-ium dinitramide (**1**) as well as 5-amino-1-methyl-1*H*-tetrazol-4-ium dinitramide (**2**) were prepared according to the syntheses presented in Scheme 1. The impetus of the reaction of 1,5-diamino-1*H*-tetrazolium perchlorate ($HDAT\_ClO_4$) and 5-amino-1-methyl-1*H*-

---

[a] Chair of Inorganic Chemistry, Energetic Materials Research, Ludwig-Maximilian University of Munich,
Butenandtstr. 5–13, 81377 Munich, Germany
Fax: +49-89-2180-77492
E-mail: tmk@cup.uni-muenchen.de

tetrazolium perchlorate (1MeHAT_ClO$_4$) with potassium dinitramide (KDN) is the precipitation of the less soluble KClO$_4$, which can be separated by filtration. HDAT_ClO$_4$ and 1MeHAT_ClO$_4$ were prepared according to a recently developed synthesis method.[18a,23]



Scheme 1. Synthesis of 1,5-diamino-1*H*-tetrazol-4-ium dinitramide (**1**) and 5-amino-1-methyl-1*H*-tetrazol-4-ium dinitramide (**2**).

The separated KClO$_4$ byproduct can be converted back into the free acid and reused in the synthetic cycle to make more HDAT_ClO$_4$ and 1MeHAT_ClO$_4$ starting material. Thus, the new syntheses not only afford the desired products **1** and **2** in high yields but also fulfil the sustainability criterion of the preparation cycle.

### Molecular Structures

To determine the molecular structures of **1** and **2** in the crystalline state, an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector were used. Both structures were solved by using SIR-92,[24] the refinement was performed with SHELXL-97[25] implemented in the WinGX software package,[26] and the structures were finally checked with the PLATON software.[27] In both crystal structures the hydrogen atoms were located and refined. Selected data and parameters of the X-ray determinations are given in Table 10.

1,5-Diamino-1*H*-tetrazol-4-ium dinitramide (**1**) crystallizes in the monoclinic space group $P2_1/c$ with eight molecules in the unit cell and has a calculated density of 1.771 g cm$^{-3}$. The geometry of the 1,5-diaminotetrazolium moiety (Figure 1) is consistent with that found for diaminotetrazolium nitrate in the literature.[13b] The bond lengths between the tetrazolate ring atoms N1, N2, N3, and N4 vary from 1.26 to 1.37 Å and fit in the range between N–N single bonds (1.45 Å) and N=N double bonds (1.25 Å).[28] Also the distances between C1–N1 [1.327(2) Å] and C1–N4 [1.327(2) Å] are equal and lie within the values for C–N single and C=N double bonds. However, the bond N1–N6 [1.381(2) Å] to the external amino group is significantly shorter than a N–N single bond. The geometry in the dinitramide anion is comparable to that of 1,5-diamino-4-methyltetrazolium dinitramide,[13a] in which also two different N–N bond lengths [N7–N8 1.355(2), N8–N9 1.377(2) Å] are found.

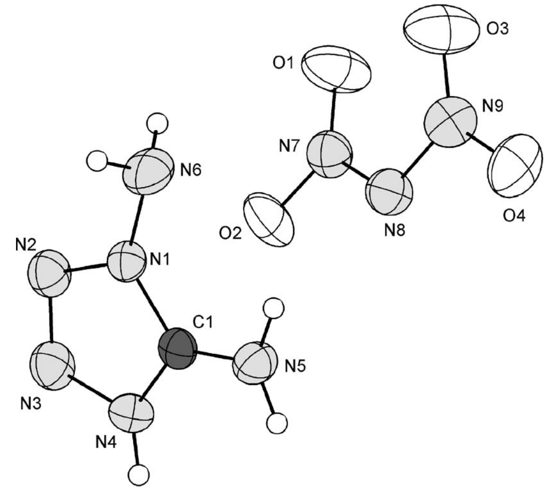


Figure 1. Molecular unit of **1**. Thermal ellipsoids represent the 50% probability level. Selected distances [Å]: N1–C1 1.327(2), N1–N2 1.365(2), N1–N6 1.381(2), N2–N3 1.264(2), N3–N4 1.358(2), N4–C1 1.327(2), N5–C1 1.311(3), N7–N8 1.355(2), N8–N9 1.377(2), O1–N7 1.214(2), O2–N7 1.245(2), O3–N9 1.213(3), O4–N9 1.239(2); selected angles [°]: N2–N1–C1 110.6(2), N2–N1–N6 124.9(2), N6–N1–C1 124.4(2), N1–N2–N3 107.1(2), N2–N3–N4 108.1(2), N3–N4–C1 110.5(2), N4–C1–N5 130.4(2), N1–C1–N5 126.0(2), N1–C1–N4 103.7(2), O2–N7–N8 112.0(2), O1–N7–O2 122.0(2), O1–N7–N8 125.9(2), N7–N8–N9 116.0(2), O3–N9–N8 125.8(2), O3–N9–O4 123.04(2), O4–N9–N8 111.1(2); selected torsion angles [°]:C1–N1–N2–N3 –0.7(2), N2–N1–C1–N4 1.3(2), N6–N1–N2–N3 –179.2(2), N6–N1–C1–N5 –0.6(3), O1–N7–N8–N9 11.2(3), O2–N7–N8–N9 –172.9(2), N7–N8–N9–O3 16.0(3), N7–N8–N9–O4 –167.6(2).

The packing of the structure is dominated by an 2D network in which single plains are connected by several strong hydrogen bonds. A view on the hydrogen bonds of one plane and the unit cell along the *b* axis is shown in Figure 2.

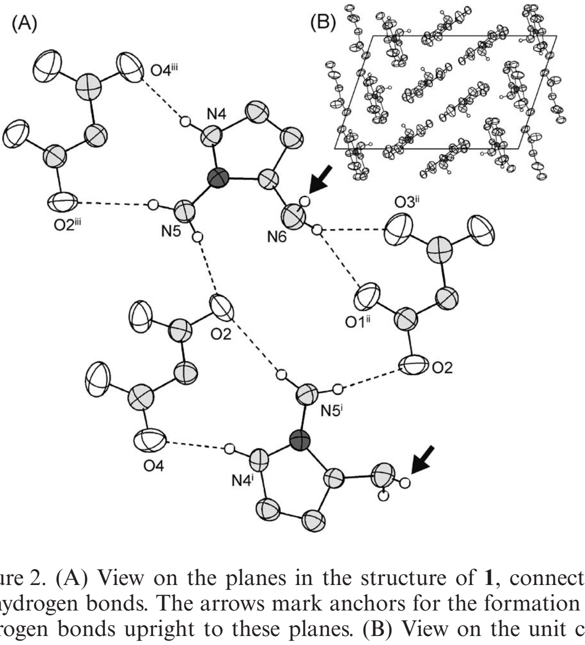


Figure 2. (A) View on the planes in the structure of **1**, connected by hydrogen bonds. The arrows mark anchors for the formation of hydrogen bonds upright to these planes. (B) View on the unit cell of **1** along the *b* axis.

5-Amino-1-methyl-1*H*-tetrazol-4-ium dinitramide (**2**) crystallizes in the monoclinic space group $P2_1/m$ with two molecules in the unit cell and has a density of 1.646 g cm$^{-3}$. The geometry of the 5-amino-1-methyltetrazolium moiety is similar to these found for other 5-amino-1-methyltetrazolium salts, e.g. the nitrate salt in literature.[13] The molecular moiety is shown in Figure 3. Because the mirror plane appears in $P2_1/m$, the dinitramide anions are completely planar. However, again there are two different N–N bond lengths found in the anions [N6–N7 1.353(3), N7–N8 1.393(3) Å] forming the N6–N7–N8 angle of 115.4(2)°. The occurrence of a planar dinitramide is very rare. To the best of our knowledge, there is no other crystal structure containing planar dinitramide anions.

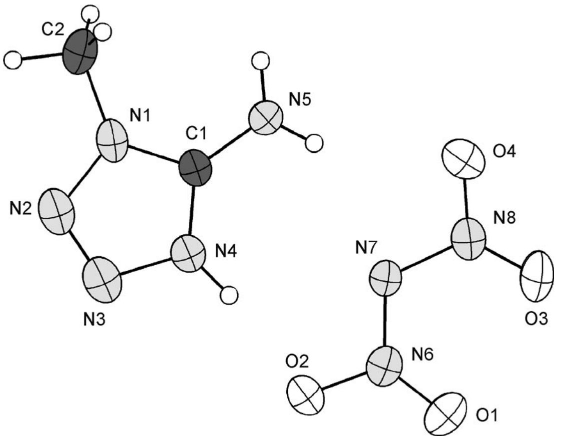


Figure 3. Molecular unit of **2**. Thermal ellipsoids represent the 50% probability level. Selected distances [Å]: N1–N2 1.372(4), N1–C1 1.344(4), N2–N3 1.273(4), N3–N4 1.367(4), N4–C1 1.323(4), N1–C2 1.464(5), N5–C1 1.315(4), N6–N7 1.353(3), N7–N8 1.393(3), O1–N6 1.202(3), O2–N6 1.277(3), O3–N8 1.204(3), O4–N8 1.233(4); selected angles [°]: N2–N1–C1 109.1(3), N2–N1–C2 122.0(2), C1–N1–C2 128.9(3), N1–N2–N3 108.4(2), N2–N3–N4 107.3(3), N3–N4–C1 110.7(2), N1–C1–N5 125.9(3), N4–C1–N5 129.5(3), N1–C1–N4 104.7(2), O2–N6–N7 110.1(2), O1–N6 –O2 121.7(2), O1–N6–N7 128.2(2), N6–N7–N8 115.4(2), O3–N8–N7 125.7(3), O4–N8–N7 111.0(2) O3–N8–O4 123.4(2); selected torsion angles [°]: C1–N1–N2–N3 0.00(1), O1–N6–N7–N8 0.00(1).

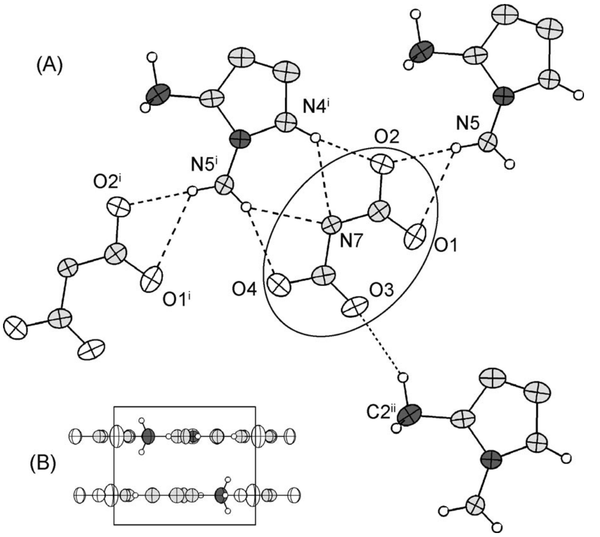


Figure 4. (A) Coordination of one dinitramide anion. Selected hydrogen bonds: N4$^i$–H4···O2 0.91(3) Å, 1.95(3) Å, 2.855(3) Å, 173(3)°; N4$^i$–H4···N7 0.91(3) Å, 2.40(4) Å, 3.052(3) Å, 128(3)°; N5–H5A···O2 0.88(3) Å, 2.05(3) Å, 2.934(4) Å, 178(3)°; N5–H5A···O1 0.88(3) Å, 2.65(3) Å, 3.24(4) Å, 125.4(2)°; C2$^{ii}$–H2B···O3 1.03(4) Å, 2.33(4) Å, 3.294(4) Å, 155(3)°; N5$^i$–H5B···N7 0.85(3) Å, 2.37(4) Å, 3.109(4) Å, 147(3)°; N5$^i$–H5B···O4 0.85(3) Å, 2.30(3) Å, 3.101(4) Å, 158(3)°; i: –1 + *x*, *y*, *z*; ii: *x*, *y*, –1 + *z*. (B) View on the unit cell of **2** along the *c* axis.

The packing of **2** is characterized by the formation of a layer structure containing the anions and cations. All oxygen atoms of the dinitramide (marked in Figure 4) anion participate in several strong hydrogen bonds. Also a strong nonclassical hydrogen bond [C2$^{ii}$–H2B···O3 1.03(4), 2.33(4), 3.294(4) Å, 155(3)°] is found in the structure.

## Spectroscopy

Vibrational spectroscopy such as IR and Raman spectroscopy was useful in the qualitative analysis of **1** and **2**, especially in evaluating the formation of the hydrogen-bond network. In both spectra, the bands of $N(NO_2)_2^-$ were obvious, and as these bands usually have characteristic fingerprints in both the infrared and Raman spectra, they could be identified easily. The dinitramide anion, $N(NO_2)_2^-$, shows strong stretching vibrations in the infrared spectrum at around 1530, 1445, 1345, 1183, and 1025 cm$^{-1}$ and strong bands in the Raman spectrum at 1335 and 830 cm$^{-1}$.[7] The IR and Raman spectra of compounds **1** and **2** contain a set of characteristic absorption bands for the cations: 3400–3100 cm$^{-1}$ [ν(N–H)], 3000–2850 [ν(C–H), 2], ca. 1715 [ν(C1–N5)], 1680–1550 [δ(N–H$_2$),], 1550–1350 [ν(tetrazole), $\delta_{as}(CH_3)$, δ(N–H)], ca. 1380 [$\delta(CH_3)$, 2], 1350–700 [ν(N1–C1–N4), *ν*(N–N), δ(N–NH$_2$) 1, γ(CN), δ(tetrazole) ring], <700 [$\delta_{oop}$(N–H), δ(N–H$_2$)]. Because of the formation of intermolecular hydrogen bonds in the crystalline network, a red shift of the stretching modes establishes that the heteromolecular hydrogen-bond interaction between the N–H (donor) groups of the tetrazole moieties and the anion (acceptor) are strong.

Compounds **1** and **2** were also investigated by using $^1$H, $^{13}$C, $^{14}$N, and $^{15}$N NMR (proton coupled) spectroscopy, and the chemical shifts are given with respect to TMS ($^1$H, $^{13}$C) as well as $MeNO_2$ ($^{14}$N, $^{15}$N) as external standards. In both cases [D$_4$]MeOH was used as the solvent. In the $^1$H NMR spectra, for the resonance of the N–H-bound protons, only one signal was observed for **1** and **2**. Relative to the starting materials DAT and 1-MeAT, this signal is shifted upfield due to fast proton exchange. In the $^{13}$C spectra for both compounds, the tetrazole carbon can be assigned to one signal at $\delta$ = 150.5 (**1**) and 149.6 (**2**) ppm. The methyl group in **2** is found at $\delta$ = 32.7 ppm. Since only the NO$_2$ group is detectable in the $^{14}$N spectra of **1** and **2**, the proton-coupled $^{15}$N spectra were recorded and are shown in Figure 5. The assignments of the signals are based on the analysis of the observed $^{15}$N–$^1$H coupling constants and comparison with the literature.[12,18,29] The $^{15}$N peaks of the amino substituents are well separated (315–330 ppm) from those of the tetrazole ring. The $^1J_{NH}$ coupling cannot

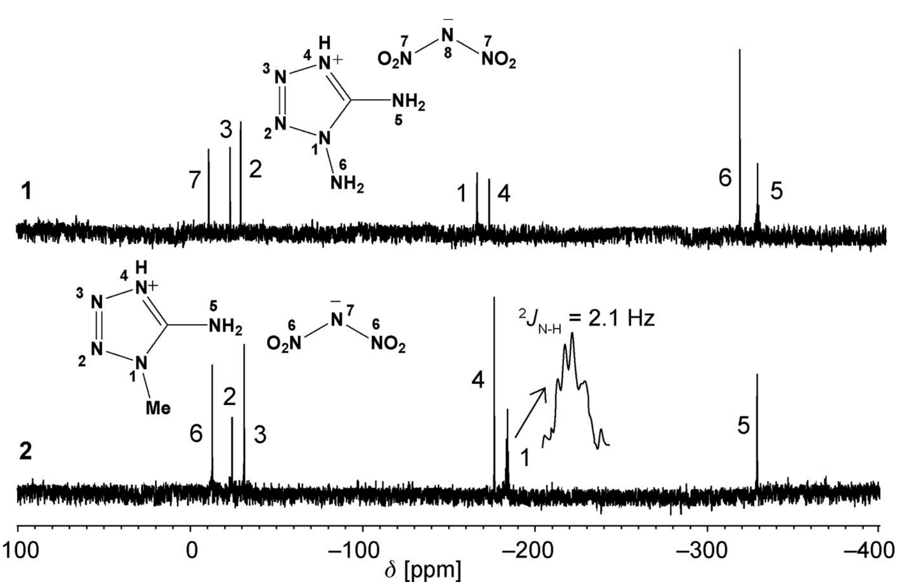


Figure 5. $^{15}$N NMR spectra of HDAT_DN (**1**) and 1MeHAT_DN (**2**) in [D$_4$]MeOH. **1**: $\delta$ = –12.8 [N($N$O$_2$)$_2$], –21.5 (N3), –34.7 (N2), –165.8 (N1), –172.5 (N4), –318.6 (N6) –330.7 (N5) ppm; **2**: $\delta$ = –12.8 [N($N$O$_2$)$_2$], –24.3 (N2, q, $^3J_{\text{NH}}$ = 1.9 Hz), –31.3 (N3), –176.3 (N4), –183.4 (N1, q, $^2J_{\text{NH}}$ = 2.1 Hz), –328.7 (N5) ppm.

be detected in [D$_4$]MeOH as the solvent. Also not visible in the $^{15}$N spectra is the resonance of the centered dinitramide nitrogen atom.

## Energetic Properties

### *DSC (Differential Scanning Calorimetry)*

In order to determine the decomposition temperatures, a Linseis DSC PT 10[30] instrument with a heating rate ($\beta$) of 5 K min$^{-1}$ and a nitrogen flow of 5 L h$^{-1}$ was used. The measurements with ca. 1.5 mg of **1** and **2** were performed in a pressed aluminum container, containing a hole (0.1 mm) for gas release. The DSC plots in Figure 6 show the thermal behavior of **1** and **2** in the 50–360 °C temperature range. Temperatures are given as "onset temperatures". Compound **1** decomposes violently above 135 °C, while **2** melts at 75 °C and decomposes above 145 °C.

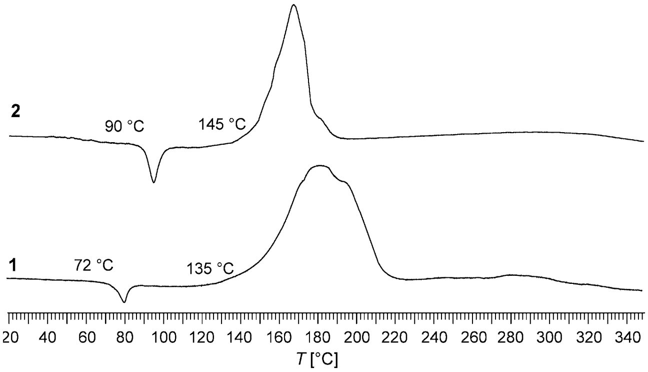


Figure 6. Thermograms (DSC plots, 5 deg min$^{-1}$) of HDAT_DN (**1**) and 1MeHAT_DN (**2**).

## Computational Study

Due to the highly energetic character of **1** and **2**, bomb calorimetric measurements could only performed with small amounts, consequently doubtful combustion energies were obtained. Therefore, an extensive computational study was accomplished which is presented in the following discussion. All calculations were carried out by using the Gaussian G03W (revision B.03) program package.[31] The enthalpies ($H$) and free energies ($G$) were calculated by using the complete basis set (CBS) method of Petersson and co-workers in order to obtain very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4 begins with a 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 a MP2/6-31+G calculation with a CBS extrapolation for a second-order correction in the energy. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher-order contributions. In this study we applied the modified CBS-4M method (M referring to the use of minimal population localization), which is a re-parametrized version of the original CBS-4 method and also includes some additional empirical corrections.[32,33] The enthalpies of the gas-phase species M were computed according to the atomization energy method (Table 1, Table 2, and Table 3).[34,35]

Table 1. CBS-4M results.

| | Point group | $-H_{298}$ [a.u.] | $-G_{298}$ [a.u.] | NIMAG |
|---|---|---|---|---|
| HDAT$^+$ | $C_1$ | 368.793548 | 368.829752 | 0 |
| DN$^-$ | $C_2$ | 464.499549 | 464.536783 | 0 |
| 1-MeHAT$^+$ | $C_1$ | 352.779155 | 352.816869 | 0 |
| H | | 0.500991 | 0.514005 | 0 |
| C | | 37.786156 | 37.803062 | 0 |
| N | | 54.522462 | 54.539858 | 0 |
| O | | 74.991202 | 75.008515 | 0 |

Table 2. Literature values for atomic $\Delta H^\circ{}_f{}^{298}$/kcal mol$^{-1}$.

| | Ref.[36] | NIST[37] |
|---|---|---|
| H | 52.6 | 52.1 |
| C | 170.2 | 171.3 |
| N | 113.5 | 113.0 |
| O | 60.0 | 59.6 |

Table 3. Enthalpies of the gas-phase species M.

| M | M | $\Delta_f H^\circ$(g,M) [kcal mol$^{-1}$] |
|---|---|---|
| HDAT$^+$ | $CH_5N_6^+$ | +252.2 |
| DN$^-$ | $N(NO_2)_2^-$, $N_3O_4^-$ | –29.6 |
| 1MeHAT$^+$ | $C_2H_6N_5^+$ | +224.0 |

$$\Delta_f H^\circ{}_{(g,M,298)} = H_{(Molecule,298)} - \Sigma H^\circ{}_{(Atoms,298)} + \Sigma \Delta_f H^\circ{}_{(Atoms,298)}$$

The lattice energies ($U_L$) and lattice enthalpies ($\Delta H_L$) were calculated from the corresponding molecular volumes (Table 4) according to the equations provided by Jenkins et al.[38] and are summarized in Table 5.

Table 4. Molecular volumes.

| | $V_M$ [Å$^3$] | $V_M$ [nm$^3$] |
|---|---|---|
| DN$^-$ | 89[a] | 0.089 |
| [HDAT]$^+$ | 93[b] | 0.093 |
| [1MeHAT]$^+$ | 99[c] | 0.099 |
| [HDAT][DN] | 182[d] | 0.182 |
| [1MeHAT][DN] | 208[e] | 0.208 |

[a] This work, back-calculated from V(ADN) by using the molecular volume for $NH_4^+$ from the literature. [b] The molecular volume of [HDAT]$^+$ was calculated from the molecular volumes of [HDAT][$NO_3$] and [HDAT][$ClO_4$]. [c] From single-crystal X-ray data. [d] The molecular volume of [HDAT][DN] was taken to be equal to V([HDAT]$^+$) + V([DN]$^-$). [e] From X-ray data, $V$ = 416 Å$^3$, $Z$ = 2.

Table 5. Lattice energies and lattice enthalpies.

| | $V_M$ [nm$^3$] | $U_L$ [kJ mol$^{-1}$] | $\Delta H_L$ [kJ mol$^{-1}$] | $\Delta H_L$ [kcal mol$^{-1}$] |
|---|---|---|---|---|
| **1** | 0.182 | 517.8 | 522.8 | 124.9 |
| **2** | 0.208 | 499.7 | 504.7 | 120.6 |

With the calculated lattice enthalpies (Table 5) the gas-phase enthalpies of formation (Table 3) were converted into the solid-state (standard conditions) enthalpies of formation (Table 6). These molar standard enthalpies of formation ($\Delta H_m$) were used to calculate the molar solid-state energies of formation ($\Delta U_m$) (Table 7) according to the equation $\Delta U_m = \Delta H_m - \Delta nRT$ ($\Delta n$ being the change in mol of gaseous components).

Table 6. Enthalpies of formation of the solid species M.

| | $\Delta_f H^\circ$(s,M) [kcal mol$^{-1}$] |
|---|---|
| **1** | +97.7 |
| **2** | +73.8 |

Table 7. Solid-state energies of formation ($\Delta_f U^\circ$).

| | $\Delta_f H^\circ$(s)/ [kcal mol$^{-1}$] | $\Delta n$ | $\Delta_f U^\circ$(s) [kcal mol$^{-1}$] | $M$ | $\Delta_f U^\circ$(s) [kJ kg$^{-1}$] |
|---|---|---|---|---|---|
| **1** | +97.7 | –9 | 103.0 | 207.1 | +2080.8 |
| **2** | +73.8 | –9 | +79.1 | 206.1 | +1605.8 |

## Detonation Parameters

The calculation of the detonation parameters was performed with the program package EXPLO5 (version 5.02).[39] The program is based on the chemical equilibrium, steady-state model of detonation. It uses Becker–Kistiakowsky–Wilson's equation of state (BKW EOS) for gaseous detonation products and Cowan–Fickett's equation of state for solid carbon.[40,41] The calculation of the equilibrium composition of the detonation products is done by applying the modified White, Johnson, and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the Chapman–Jouguet (CJ) point. The BKW equation in the following form was used with the BKWN set of parameters ($\alpha$, $\beta$, $\kappa$, $\theta$) as stated in the equations below, where $x_i$ is the mol fraction of the $i$th gaseous product and $k_i$ is the molar covolume of the $i$th gaseous product.[39,40]

$$pV/RT = 1 + xe^{\beta x} x = (\kappa \Sigma X_i k_i)/[V(T + \theta)]^\alpha$$

$$\alpha = 0.5,\ \beta = 0.176,\ \kappa = 14.71,\ \theta = 6620.$$

Especially the detonation parameters for compound **1** consist of very promising values exceeding these of TNT and RDX, and in part even these of HMX. The most important criteria of highly explosive compounds are the detonation velocity $v_{Det.}$ = (**1**: 9306, TNT: 7000, RDX: 8796, HMX: 9100 m s$^{-1}$), detonation pressure ($p_{Det.}$ = **1**: 360, RDX: 299 kbar), and the energy of explosion ($\Delta_E U_m^\circ$ = **1**: –6192, RDX: –5902 kJ kg$^{-1}$), Table 8.

Table 8. Detonation parameters.

| | | 1 | 2 | RDX |
|---|---|---|---|---|
| Density [g cm$^{-3}$] | $\rho$ | 1.77 | 1.646 | 1.82 |
| Oxygen balance [%] | $\Omega$ | –3.9 | –23.3 | –21.6 |
| Energy of formation [kJ kg$^{-1}$] | $\Delta_f U$ | 2081 | 1606 | 67 |
| Heat of detonation [kJ kg$^{-1}$] | $Q_V$ | –6192 | –5842 | –5902 |
| Detonation temperature [K] | $T$ | 4632 | 4280 | 3986 |
| Detonation pressure [kbar] | $p$ | 360 | 287 | 299 |
| Detonation velocity [m s$^{-1}$] | $v$ | 9306 | 8481 | 8796 |
| Volume of det. gases [L kg$^{-1}$] | $V_0$ | 865 | 844 | 932 |

### Sensitivities

For initial safety testing, the impact and friction sensitivities as well as the electrostatic sensitivity were determined.[42] The impact sensitivity tests were carried out according to STANAG 4489,[43] which was modified with the instructions[44] for using a BAM (Bundesanstalt für Materialforschung)[45] drop hammer.[46] The friction sensitivity tests were carried out according to STANAG 4487,[47] which was modified with the instructions[48] for using the BAM friction tester. Compound **1** is very sensitive towards impact (2 J) and extremely friction-sensitive ($< 5$ N). **2** is also sensitive towards impact (4 J) but has a lower sensitivity towards friction (112 N). According to the "UN Recommendations on the transport of dangerous goods",[49] **1** is classified as "very sensitive" in both categories. However, **2** is "only" classified as "sensitive".

The electrostatic sensitivity tests were carried out by using an electric spark tester ESD 2010EN (OZM Research) operating with the "Winspark 1.15 software package".[50] The electrical spark sensitivities on crystalline material were determined to be 670 mJ (**1**) and 980 mJ (**2**).

## Conclusions

From this combined experimental and theoretical study the following conclusions can be drawn:

(i) 1,4-Diamino-1*H*-tetrazolium dinitramide (HDAT_DN, **1**) and 5-amino-1-methyl-1*H*-tetrazolium dinitramide (1MeHAT_DN, **2**) were prepared in high yields from the reaction of potassium dinitramide with 1,4-diamino-1*H*-tetrazolium perchlorate and 5-amino-1-methyl-1*H*-tetrazolium perchlorate, respectively.

(ii) The solid-state structure of **1** and **2** were determined by single-crystal X-ray diffraction.

The explosion and detonation parameters of **1** and **2** were obtained from a combined experimental and computational study, and they are summarized in Table 9. By comparison with the literature values reported for RDX, it can be concluded that both compounds may also be valuable ingredients in highly explosive compositions.

Table 9. Explosion and detonation parameters for 1,4-diamino-1*H*-tetrazolium dinitramide (HDAT_DN, **1**), 5-amino-1-methyl-1*H*-tetrazolium dinitramide (TAG-DN, **2**), and RDX.

| | 1 | 2 | RDX |
|---|---|---|---|
| Molecular mass [$g\,mol^{-1}$] | 207.11 | 206.12 | 222.1[51] |
| Impact sensitivity [J] | 2 | 4 | 7[51] |
| Friction sensitivity [N] | 5 | 112 | 120[51] |
| Electrical discharge [J] | 0.67 | 0.98 | 0.15–0.2[52] |
| Nitrogen content [%] | 60.87 | 54.36 | 37.8[51] |
| Oxygen balance [%] | –3.9 | –23.3 | –21.6[51] |
| $T_{dec.}$ [°C] | 135 | 145 | 213[51] |
| Density [$g\,cm^{-3}$] | 1.771 | 1.646 | 1.82[51] |
| $\Delta_f H_m°$ [$kJ\,mol^{-1}$] | 431 | 331 | 66.5[51] |
| $\Delta_f U°$ [$kJ\,kg^{-1}$] | 2081 | 1606 | 1310 |
| Values calculated by EXPLO5 | | | |
| $\Delta_E U_m°$ [$kJ\,kg^{-1}$] | –6192 | –5842 | –5902 |
| Explosion temp. ($T_E$) [K] | 4632 | 4280 | 3986 |
| Det. pressure ($p$) [kbar] | 360 | 287 | 299 |
| Det. velocity ($v$) [$m\,s^{-1}$] | 9306 | 8481 | 8796 |
| Gas vol. [$L\,kg^{-1}$] | 865 | 844 | 932 |

## Experimental Section

*CAUTION! **1**, **2**, and their perchlorate derivatives are energetic compounds with increased sensitivities towards heat, impact, and friction. Although we had no problems in synthesis, proper protective measures (safety glasses, face shield, leather coat, grounded equipment and shoes, Kevlar® gloves, and ear plugs) should be used during work on **1–2**, especially when preparing them in larger amounts.*

All reagents and solvents were used as received (Sigma–Aldrich, Fluka, Acros Organics) unless stated otherwise. Melting points were measured with a Linseis PT10 DSC by using heating rates of 5 °C$\,min^{-1}$ and were checked by a Büchi Melting Point B-450 apparatus. The m.p. values are not corrected. All NMR spectra were recorded with a Jeol Eclipse 270, Jeol EX 400, or a Jeol Eclipse 400 instrument. The chemical shifts are quoted in ppm relative to TMS ($^1H$, $^{13}C$) and $MeNO_2$ ($^{14}N$, $^{15}N$). Infrared (IR) spectra were recorded with a Perkin–Elmer Spektrum One FT-IR instrument. Raman spectra were measured with a Perkin–Elmer Spektrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). Elemental analyses were performed with a Netsch STA 429 Simultaneous Thermal Analyzer. Bomb calorimetry was undertaken by using a Parr 1356 Bomb calorimeter with a Parr 1108CL oxygen bomb. The sensitivity data were determined by using a BAM drop hammer, a BAM friction tester, and an OZM electrical discharge testing device.

**1,5-Diamino-1*H*-tetrazol-4-ium Dinitramide (1):** A solution of 1,5-diamino-1*H*-tetrazolium perchlorate (4.00 g, 20 mmol) in water (10 mL) was combined with a solution of potassium dinitramide (2.90 g, 20 mmol) in water (10 mL). EtOH (10 mL) was added, and the mixture was stirred for 30 min. The potassium perchlorate precipitate was filtered off, and the solution was concentrated to dryness by using high vacuum. The residue was dissolved in EtOH (15 mL), and the remaining $KClO_4$ was again removed by filtration. After evaporation of EtOH, the product was obtained as a colorless crystalline residue. (3.94 g, 85%). Single crystals suitable for X-ray diffraction were obtained by recrystallization from ethanol. M.p. 72 °C, 135 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3318 (s), 3251 (s), 3153 (s), 3093 (s), 1781 (vs), 1616 (w), 1535 (s), 1429 (m), 1343 (m), 1290 (m), 1202 (s), 1177 (s), 1143 (m), 1119 (m), 1022 (s), 951 (w), 827 (w), 813 (w), 761 (m), 749 (w), 731 (m), 703 (w), 689 (w), 653 (w), 626 (m), 567 (m) $cm^{-1}$. Raman (1064 nm): $\tilde{\nu}$ = 3367 (12), 3305 (22), 3251 (11), 1717 (10), 1624 (9), 1581 (13), 1512 (19), 1447 (26), 1350 (26), 1313 (100), 1186 (11), 1130 (11), 1002 (26), 962 (25), 932 (15), 821 (63), 783 (80), 691 (26), 487 (45), 315 (46), 302 (47), 239 (24) $cm^{-1}$. $^1H$ NMR ([D$_4$]MeOH): $\delta$ = 5.14 (s, NH, N$H_2$) ppm. $^{13}C$ NMR ([D$_4$]MeOH): $\delta$ = 150.5 ($CN_4$) ppm. $^{14}N$ NMR ([D$_4$]MeOH): $\delta$ = –11 [N($NO_2$)] ppm. $^{15}N$ NMR ([D$_4$]MeOH): $\delta$ = –12.8 [N($NO_2$)$_2$], –21.5 (N3), –34.7 (N2), –165.8 (N1), –172.5 (N4), –318.6 (N6) –330.7 (N5) ppm. MS (FAB$^+$): $m/z$ = 101; MS (FAB$^-$): $m/z$ = 106. $CH_5N_9O_4$ (207.11): calcd. C 5.80, H 2.43, N 60.87; found (not determinable). BAM drop hammer: 2 J, BAM friction test: $< 5$ N. ESD: 670 mJ.

**5-Amino-1-methyl-1*H*-tetrazol-4-ium Dinitramide (2):** A solution of 5-amino-1-methyl-1*H*-tetrazolium perchlorate (1.99 g, 10 mmol) in water (10 mL) was combined with a solution of potassium dinitramide (1.45 g, 10 mmol) in water (10 mL). EtOH (10 mL) was added, and the mixture was stirred for 20 min. The potassium perchlorate precipitate was filtered off, and the solution was concentrated to dryness by using high vacuum (1.96 g, 95%). Single crystals suitable for X-ray diffraction were obtained by recrystallization from ethanol. M.p. 90 °C, 145 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3352 (s), 3258 (s), 3179 (s), 3105 (s), 2860 (m), 2739 (m), 2677 (m), 1692 (vs), 1542 (s), 1462 (m), 1417 (m), 1352 (m), 1200 (s), 1066 (w), 1030 (s), 972 (w), 953 (w), 804 (m), 777 (m), 745 (m), 714 (m), 665 (w), 627 (w), 485 (m), 448 (w) $cm^{-1}$. Raman (1064 nm): $\tilde{\nu}$ = 3262 (5), 3052 (10), 3013 (8), 2962 (22), 1715 (8), 1610 (6), 1535 (18), 1511 (8), 1464 (27), 1452 (29), 1419 (13), 1356 (17), 1302 (62), 1272 (27), 1235 (8), 1150 (8), 1064 (8), 1043 (14), 1013 (20), 975 (14), 810 (36), 777 (100), 672 (19), 487 (31), 464 (21), 450 (15), 301 (57), 229 (21) $cm^{-1}$. $^{1}H$ NMR ([$D_6$]DMSO): $\delta$ = 8.48 (s, 2 *H*), 3.68 (3 *H*, $CH_3$) ppm. $^{13}C$ NMR ($D_6$ DMSO): $\delta$ = 153.7 ($CN_4$), 32.7 ($CH_3$) ppm. $^{14}N$ NMR ([$D_6$]DMSO): $\delta$ = –11 [$N(NO_2)$] ppm. $^{15}N$ NMR ([$D_4$]-MeOH): $\delta$ = –12.8 [$N(NO_2)_2$], –24.3 (q, $^{3}J_{NH}$ = 1.9 Hz, N2), –31.3 (N3), –176.3 (N4), –183.4 (q, $^{2}J_{NH}$ = 2.1 Hz, N1), –328.7 (N5) ppm. MS ($FAB^+$): *m/z* = 100; MS ($FAB^-$): *m/z* = 106. $C_2H_6N_8O_4$ (206.12): calcd. C 11.65, H 2.93, N 54.36; found C 12.00, H 3.04, N 54.06. BAM drop hammer: 4 J, BAM friction test: 112 N. ESD: 980 mJ.

### X-ray Crystallography

Table 10 contains the parameters and data obtained from the single-crystal X-ray diffraction determinations.

Table 10. Crystallographic data.

| | HDAT_DN (**1**) | 1MeHAT_DN (**2**) |
|---|---|---|
| Formula | $CH_5N_6$, $N_3O_4$ | $C_2H_6N_5$, $N_3O_4$ |
| Form. weight [$g\,mol^{-1}$] | 207.14 | 206.15 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/c$ (No. 14) | $P2_1/m$ (No. 11) |
| Color/habit | colorless blocks | colorless rods |
| Size [mm] | 0.07 × 0.10 × 0.12 | 0.06 × 0.08 × 0.09 |
| *a* [Å] | 15.7942(8) | 7.2601(7) |
| *b* [Å] | 10.1115(4) | 5.9178(5) |
| *c* [Å] | 10.2757(5) | 9.8713(7) |
| $\beta$ [°] | 108.817(6) | 101.185(8) |
| *V* [$Å^3$] | 1553.35(14) | 416.05(6) |
| *Z* | 8 | 2 |
| $\rho_{calcd.}$ [$g\,cm^{-3}$] | 1.771 | 1.646 |
| $\mu$ [$mm^{-1}$] | 0.165 | 0.151 |
| *F*(000) | 848 | 212 |
| $\lambda$(Mo-$K_\alpha$) [Å] | 0.71073 | 0.71073 |
| *T* [K] | 200 | 200 |
| Theta min, max [°] | 4.0, 26.0 | 3.9, 27.5 |
| Data set | –19:19; –11:12; –12: 12 | –7:9; –7:7; –12:12 |
| Reflections collected | 9875 | 2315 |
| Independent reflections | 3048 | 1024 |
| $R_{int}$ | 0.033 | 0.038 |
| Observed reflections | 1628 | 508 |
| No. parameters | 293 | 101 |
| $R_1$ (obs) | 0.0328 | 0.0371 |
| $wR_2$ (all data) | 0.0702 | 0.1016 |
| *S* | 0.84 | 0.91 |
| Resd. Dens. [$e\,Å^{-3}$] | –0.23, 0.17 | –0.25, 0.18 |
| Device type | Oxford Xcalibur3 CCD | Oxford Xcalibur3 CCD |
| Solution | SIR-92 | SIR-92 |
| Refinement | SHELXL–97 | SHELXL–97 |
| Absorption correction | multiscan | multiscan |

CCDC-680292 (for **1**) and CCDC-680291 (for **2**) 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.

## Acknowledgments

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the Fonds der Chemischen Industrie (FCI), the European Research Office (ERO) of the U.S. Army Research Laboratory (ARL) under contract nos. N-62558–05-C-0027, 9939-AN-01 and W911NF-07–1-0569 and the Bundeswehr Research Institute for Materials, Explosives, Fuels and Lubricants (WIWEB) under contract nos. E/E210/4D004/X5143 and E/E210/7D002/4F088 is gratefully acknowledged. The authors are indebted to and thank apl.-Prof. Dr. K. Karaghiosoff as well as Dr. Betsy Rice for many helpful discussions. The authors also acknowledge collaborations with Dr. M. Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr. M. Sućesca (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation parameters of high-nitrogen explosives.

---

[1] a) T. M. Klapötke in *Moderne Anorganische Chemie* (Ed.: E. Riedel), vol. 3, Walter de Gruyter, Berlin, New York, **2007**, 99–104; b) R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2006**, *45*, 3584; c) T. M. Klapötke in *High Energy Density Materials* (Ed.: T. M. Klapötke), Springer, Berlin, Heidelberg, **2007**, 85–122; d) R. D. Chapman in *High Energy Density Materials* (Ed.: T. M. Klapötke), Springer, Berlin, Heidelberg, **2007**, 123–152.

[2] M. A. Hiskey, D. E. Chavez, D. L. Naud, S. F. Son, H. L. Berghout, C. A. Bolme, *Proc. Int. Pyrotech. Semin.* **2000**, *27*, 3–14.

[3] Y. N. Matyushin, T. S. Kon'kova, A. B. Vorob'ev, Y. A. Lebedev, *36th International Annual Conference of ICT* **2005**, 92/1–92/9.

[4] a) T. M. Klapötke, J. Stierstorfer, *ChemSusChem* **2008**, submitted; b) T. M. Klapötke, J. Stierstorfer, *New Trends in Research of Energetic Materials*, Proceedings of the 11th Seminar, Pardubice, Czech Republic, **2008**, *2*, 810–831.

[5] N. Wingborg, N. V. Latypov, *Propellants Explos. Pyrotech.* **2003**, *28*, 314–318.

[6] H. R. Blomquist, U. S. **1999**, 9 pp. US patent 6004410, A 19991221.

[7] a) K. O. Christe, W. W. Wilson, M. A. Petrie, H. H. Michels, J. C. Bottaro, R. Gilardi, *Inorg. Chem.* **1996**, *35*, 5068–5071; b) V. A. Shlyapochnikov, M. A. Tafipolsky, I. V. Tokmakov, E. S. Baskir, O. V. Anikin, Yu. A. Strelenko, O. A. Luk'yanov, V. A. Tartakovsky, *J. Mol. Struct.* **2001**, *559*, 147–166; c) J. C. Bottaro, P. E. Penwell, R. J. Schmitt, *Synth. Commun.* **1991**, *21*, 945; d) O. A. Luk'yanov, V. P. Gorelik, V. A. Tartakovskii, *Russ. Chem. Bull.* **1994**, *43*, 89.

[8] R. Gilardi, R. J. Butcher, *J. Chem. Crystallogr.* **2002**, *32*, 477–484.

[9] M. E. Sitzmann, R. Gilardi, R. J. Butcher, W. M. Koppes, A. G. Stern, J. S. Trasher, N. J. Trivedi, Z.-Y. Yang, *Inorg. Chem.* **2000**, *39*, 843–850.

[10] N. B. Bolotina, M. J. Hardie, A. A. Pinkerton, *J. Appl. Crystallogr.* **2003**, *36*, 1334–1341.

[11] a) V. P. Sinditskii, A. I. Levshenkov,V. Y. Egorshev, V. V. Serushkin, *New Trends in Research of Energetic Materials*, Proceedings of the 7th Seminar, Pardubice, Czech Republic, **2004**, *2*, 649–658; b) C. J. Hinshaw, R. B. Wardle,T. K. Highsmith, U. S. patent **1998**, US 5741998, A 19980421.

[12] K. Karaghiosoff, T. M. Klapötke, P. Mayer, C. M. Sabate, A. Penger, J. M. Welch, *Inorg. Chem.* **2008**, *47*, 1007–1019.

[13] a) T. M. Klapötke, P. Mayer, A. Schulz, J. J. Weigand, *J. Am. Chem. Soc.* **2005**, *127*, 2032–2033; b) G. Fischer, G. Holl, T. M. Klapötke, P. Mayer, J. J. Weigand, *New Trends in Research of Energetic Materials*, Proceedings of the 8th Seminar, Pardubice, Czech Republic, **2005**, *1*, 190–199.

[14] J. J. Weigand, Dissertation, Ludwig Maximilian University Munich, **2005**.

[15] T. Brinck, J. S. Murray, P. Politzer, *J. Org. Chem.* **1991**, *56*, 5012–5015.

[16] a) Calculation of the oxygen balance [$\Omega = (x\mathrm{O} - 2y\mathrm{C} - z\mathrm{H}/2)\ 1600/M$]; b) J. Köhler, R. Meyer, *Explosivstoffe*, 9th ed., Wiley-VCH, Weinheim, **1998**, pp. 251–252.

[17] a) P. N. Gaponik, P. P. Karavai, *Khim. Geterotsikl. Soedin.* **1984**, 1388–1391; b) A. S. Lyakhov, P. N. Gaponik, S. V. Voitekhovich, *Acta Crystallogr., Sect. C* **2001**, *57*, 185–186; c) H. A. Hiskey, *Chem. & Eng. News* **2005**, *83*, 5.

[18] a) J. C. Galvez-Ruiz, G. Holl, K. Karaghiosoff, T. M. Klapoetke, K. Löhnwitz, P. Mayer, H. Noeth, K. Polborn, C. J. Rohbogner, M. Suter, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 4237–4253; b) H. Xue, H. Gao, B. Twamley, J. M. Shreeve, *Chem. Mat.* **2007**, *19*, 1731–1739; c) J. Geith, T. M. Klapötke, J. J. Weigand, G. Holl, *Propellants Explos. Pyrotech.* **2004**, *29*, 3–8; d) G. Fischer, G. Holl, T. M. Klapötke, J. J. Weigand, *Thermochim. Acta* **2005**, *437*,168–178.

[19] R. A. Henry, W. G. Finnegan, *J. Am. Chem. Soc.* **1954**, *76*, 923.

[20] R. M. Herbst, C. W. Roberts, E. J. Harvill, *J. Org. Chem.* **1951**, *16*, 139.

[21] J. Thiele, J. T. Marais, *Liebigs Ann. Chem.* **1893**, *273*, 144–160.

[22] a) J. Thiele, *Liebigs Ann. Chem.* **1892**, *270*, 1; b) R. Stollé, *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 1118.

[23] G. W. Drake, T. W. Hawkins, J. Boatz, L. Hall, A. Vij, *Propellants Explos. Pyrotech.* **2005**, *30*, 156–164.

[24] *SIR-92, A Program for Crystal Structure Solution*: A. Altomare,G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343.

[25] G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[26] *WinGX Suite for Small Molecule Single-Crystal Crystallography*: L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

[27] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **1999**.

[28] N–N values and N=N values from: *International Tables for X-ray Crystallography*, Kluwer Academic Publishers, Dordrecht, The Netherlands, **1992**, vol. C.

[29] K. Karaghiosoff, T. M. Klapötke, P. Meyer, H. Piotrowski, K. Polborn, R. L. Willer, J. J. Weigand, *J. Org. Chem.* **2006**, *71*, 1295–1305.

[30] http://www.linseis.com.

[31] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03*, Revision C.02, Gaussian, Inc., Wallingford CT, **2004**.

[32] J. W. Ochterski, G. A. Petersson, J. A. Montgomery Jr, *J. Chem. Phys.* **1996**, *104*, 2598.

[33] J. A. Montgomery Jr, M. J. Frisch, J. W. Ochterski, G. A. Petersson, *J. Chem. Phys.* **2000**, *112*, 6532.

[34] L. A. Curtiss, K. Raghavachari, P. C. Redfern, J. A. Pople, *J. Chem. Phys.* **1997**, *106*, 1063.

[35] a) E. F. Byrd, B. M. Rice, *J. Phys. Chem. A* **2006**, *110*, 1005–1013; b) B. M. Rice, S. V. Pai, J. Hare, *Combust. Flame* **1999**, *118*, 445–458.

[36] L. A. Curtiss, K. Raghavachari, P. C. Redfern, J. A. Pople, *J. Chem. Phys.* **1997**, *106*, 1063.

[37] P. J. Linstrom, W. G. Mallard, *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, June **2005**, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov.

[38] a) H. D. B. Jenkins, H. K. Roobottom, J. Passmore, L. Glasser, *Inorg. Chem.* **1999**, *38*, 3609–3620; b) H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* **2002**, *41*, 2364–2367.

[39] M. Sućeska, *EXPLO5 Program*, Zagreb, Croatia, **2005**.

[40] a) *Calculation of Detonation Parameters by EXPLO5 Computer Program*, M. Sućeska, *Mater. Science Forum* **2004**, *465–466*, 325–330; b) M. Sućeska, *Propellants Explos. Pyrotech.* **1991**, *16*, 197–202; c) M. Sućeska, *Propellants Explos. Pyrotech.* **1999**, *24*, 280–285.

[41] M. L. Hobbs, M. R. Baer, *Calibration of the BKW-EOS with a Large Product Species Data Base and Measured CJ Properties*, Proceedings of the 10th International Symposium on Detonation, ONR 33395–12, Boston, MA, July 12–16, **1993**, p. 409.

[42] M. Sućeska, *Test Methods for Explosives*, Springer, New York **1995**, p. 21 (impact), p. 27 (friction).

[43] *NATO Standardization Agreement (STANAG) on Explosives, Impact Sensitivity Tests*, No. 4489, 1st ed., Sept. 17, **1999**.

[44] *WIWEB-Standardarbeitsanweisung 4–5.1.02, Ermittlung der Explosionsgefährlichkeit, hier der Schlagempfindlichkeit mit dem Fallhammer*, Nov. 8, **2002**.

[45] http://www.bam.de.

[46] http://www.reichel-partner.de.

[47] *NATO Standardization Agreement (STANAG) on Explosives, Friction Sensitivity Tests*, No. 4487, 1st ed., Aug. 22, **2002**.

[48] *WIWEB-Standardarbeitsanweisung 4–5.1.03*, *Ermittlung der Explosionsgefährlichkeit oder der Reibeempfindlichkeit mit dem Reibeapparat*, Nov. 8, **2002**.

[49] Impact: Insensitive $>$ 40 J, less sensitive $\geq$ 35 J, sensitive $\geq$ 4, very sensitive $\leq$ 3 J. Friction: Insensitive $>$ 360 N, less sensitive = 360 N, sensitive $<$360 N and $>$80 N, very sensitive $\leq$ 80 N, extremely sensitive $\leq$10 N. According to the *UN Recommendations on the Transport of Dangerous Goods.*

[50] http://www.ozm.cz/testing-instruments/small-scale-electro-static-discharge-tester.htm.

[51] J. Köhler, R. Meyer, *Explosivstoffe*, 9th ed., Wiley-VCH, Weinheim, **1998**, pp. 166–168.

[52] V. Pelikán, OZM research, Czech Republic, private communication.

Received: March 12, 2008