



## Hydrazinium 5-Aminotetrazolate: an Insensitive Energetic Material Containing 83.72% Nitrogen

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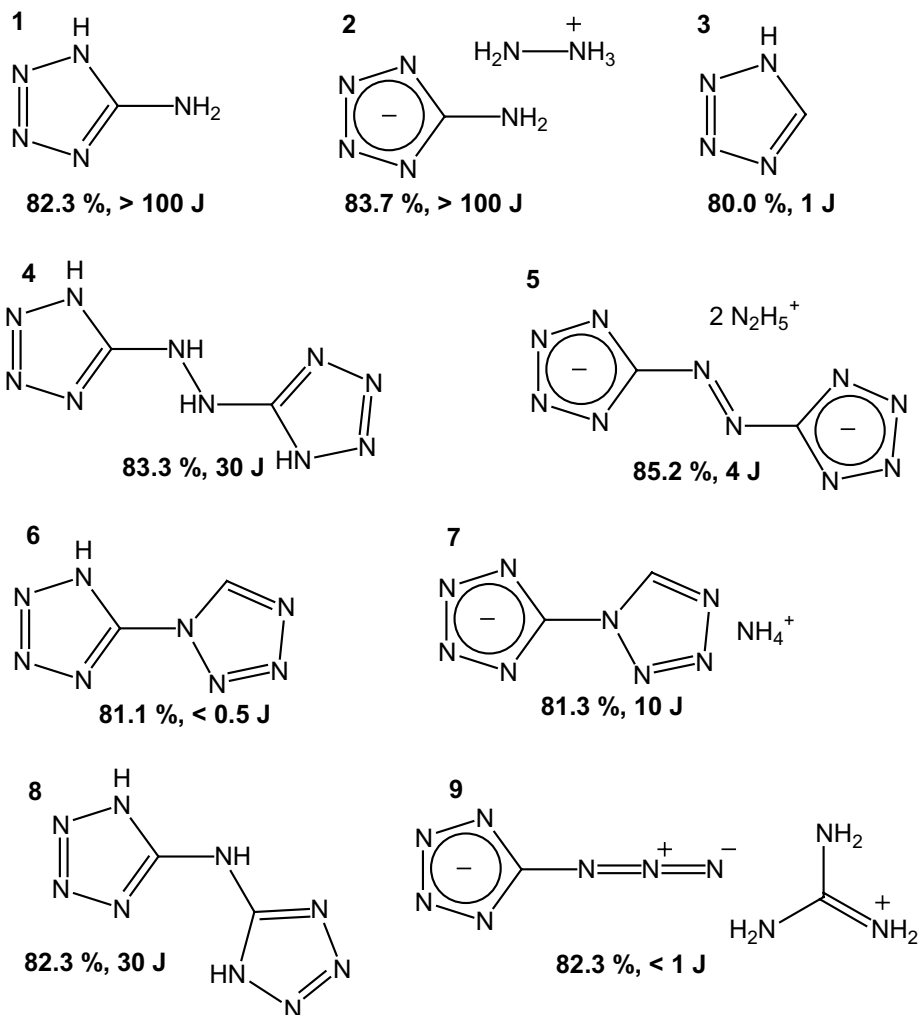
**Abstract:** Hydrazinium 5-aminotetrazolate (**2**) was synthesized via two facile routes. Both the reaction of 5-amino-1H-tetrazole (**1**) with hydrazine hydrate in aqueous solution and the reaction of **1** with diluted hydrazine solution in THF yield **2** in excellent purities and yields. **2** was characterized comprehensively by X-ray diffraction, IR, Raman and multinuclear NMR spectroscopy, mass spectrometry, elemental analysis and differential scanning calorimetry. The heat of formation was calculated (CMS-4M) using the atomization method to be 373 kJ mol<sup>-1</sup>. With this value and the X-ray density several detonation parameter (heats of explosion, detonation pressure, detonation velocity, explosion temperature) were calculated with the EXPLO5 computer software. An incredible high value (9516 m s<sup>-1</sup>) was obtained for the detonation velocity. Therefore experimentally tests to determine the velocity of detonation were performed. In addition the use of **2** in solid propellant compositions was calculated and tested in combination with oxidizers, e.g. ammonium dinitramide. Lastly the sensitivities towards impact, friction and electrostatic discharge were determined with the BAM drophammer, friction tester and an ESD machine.

**Keywords:** hydrazines, tetrazoles, crystal structure, energetic materials, sensitivities

## Introduction

The investigation of energetic, non-nuclear materials for military and space application has been a long term goal in our research group [1]. One approach is the synthesis of high-nitrogen salts which combine a positive heat of formation

( $\Delta_f H > 0$ ) and therefore high explosive and propulsive power with relatively high thermal stability and low volatility and therefore low inhalation toxicity [2, 3]. Future energetic materials should be insensitive, e.g. towards impact, friction and electrical discharge. Usually salts with a nitrogen content above 80% show definite sensitivities. However, these values strongly depend on the constitution of the atoms and cannot be correlated to the nitrogen content. Figure 1 gives an overview about selected CHN compounds based on tetrazoles with their N-content and the determined impact sensitivities. As a matter of principle electron-rich tetrazoles and tetrazolates show lower sensitivities than those, which are bonded to electron withdrawing groups. This is the reason that **1** as well as **2** are insensitive towards impact [4]. In contrast 1*H*-tetrazole and hydrazinium 5,5'-azotetrazolate show increased impact sensitivities of 1 J and 4 J, respectively [5, 6]. The bistetrazoles HBT (**4**) and H<sub>2</sub>bta (**8**) are characterized by moderate impact sensitivities of 30 J [7, 8]. However, 1,5-bistetrazole (**6**) is extremely sensitive towards impact and friction, which can be lowered by deprotonation, e.g. forming ammonium 1,5-bistetrazolate (**7**) [9]. Extremely sensitive are salts of 5-azidotetrazolate, e.g. guanidinium 5-azidotetrazolate (**9**) [10].



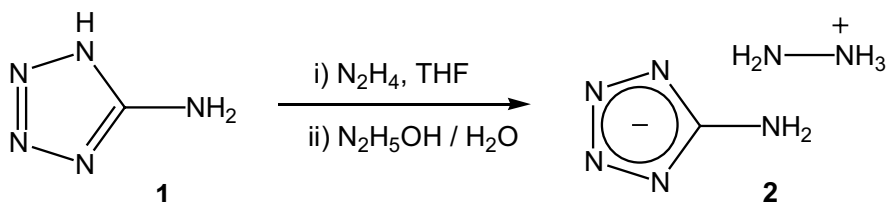
**Figure 1.** Tetrazole derivatives with a nitrogen content above 80%. **1:** 5-amino-1*H*-tetrazole, **2:** hydrazinium 5-aminotetrazolate, **3:** 1*H*-tetrazole, **4:** BTH, bis(1*H*-tetrazolyl)hydrazine, **5:** hydrazinium azotetrazolate, **6:** 1,5-bistetrazole, **7:** ammonium 1,5-bistetrazolate, **8:** H<sub>2</sub>bta, 5,5'-bis(1*H*-tetrazolyl)amine, **9:** guanidinium 5-azidotetrazolate.

The motivation of this study is the insensitivity of **2** in combination with an extraordinarily high calculated detonation pressure and velocity, even succeeding those of HMX. Here we report on an easy one-step synthesis of hydrazinium

aminotetrazolate (**2**), a full characterization as well as its detonation and propulsion parameters.

### Synthesis

Hydrazinium 5-aminotetrazolate can be synthesized via two facile routes. (i) The synthesis under exclusion of water by the reaction of 5-amino-1*H*-tetrazole (**1**) with hydrazine in THF yields **2** in high purity and yield. **2** is recrystallized from hot ethanol yielding colorless needle shaped crystals which can be washed with diethyl ether. (ii) Also possible is the reaction of **1** or its monohydrate with hydrazine hydrate in water or in alcoholic (MeOH, EtOH) solutions.



**Scheme 1.** Two synthetic protocols of the formation of hydrazinium 5-aminotetrazolate (**2**).

### Structure

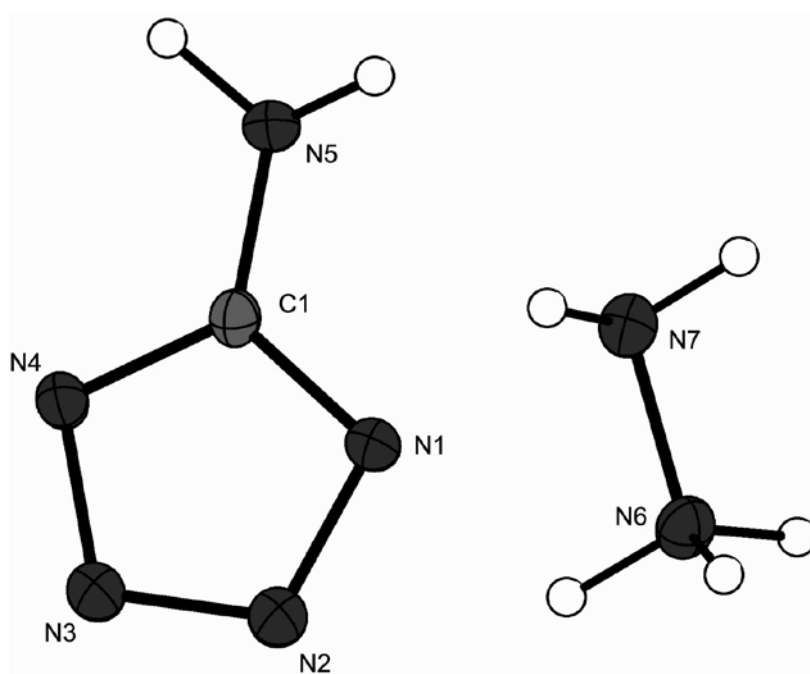
A suitable single crystal was picked from the crystallization mixture, mounted in Kel-F oil and transferred to the N<sub>2</sub> stream of an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection was performed using the CrysAlis CCD software [11], the data reduction with the CrysAlis RED software [12]. The structure was solved with SIR-92, refined with SHELXL-97 [13] and finally checked using the PLATON software [14]. All programs are implemented in the WinGX suite [15]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorption was corrected by a SCALE3 ABSPACK multi-scan method [16]. All relevant data and parameters of the X-ray measurements and refinements are given in Table 1. Further information on the crystal-structure determinations have been deposited as cif file [17] with the Cambridge Crystallographic Data Centre [18] as supplementary publication No. 697710.

**Table 1.** X-ray data and parameter for **2**

	<b>2</b>
Formula	CH <sub>7</sub> N <sub>7</sub>
Form. weight [g mol <sup>-1</sup> ]	117.14
Crystal system	orthorhombic
Space Group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 (No. 18)
Color / Habit	colorless needles
Size, mm	0.04 x 0.09 x 0.09
<i>a</i> [Å]	9.7179(6)
<i>b</i> [Å]	13.5958(8)
<i>c</i> [Å]	3.8056(3)
<i>V</i> [Å <sup>3</sup> ]	502.81(6)
<i>Z</i>	4
ρ <sub>calc.</sub> [g cm <sup>-3</sup> ]	1.547
μ [mm <sup>-1</sup> ]	0.122
<i>F</i> (000)	248
λ <sub>MoKα</sub> [Å]	0.71073
<i>T</i> [K]	200
Theta Min-Max [°]	3.7, 31.5
Dataset	-9:14; -19:19; -5:5
Reflection collected	3815
Independent reflection	1013
<i>R</i> <sub>int</sub>	0.065
Observed reflection	522
No. parameters	101
<i>R</i> <sub>1</sub> (obs)	0.0398
w <i>R</i> <sub>2</sub> (all data)	0.0778
GooF	0.85
Min/Max Resd. [e/ Å <sup>3</sup> ]	-0.26, 0.20
Device type	Oxford Xcalibur CCD
Solution	SIR-92
Refinement	SHELXL-97
Absorption correction	multi-scan
CCDC No.	697710

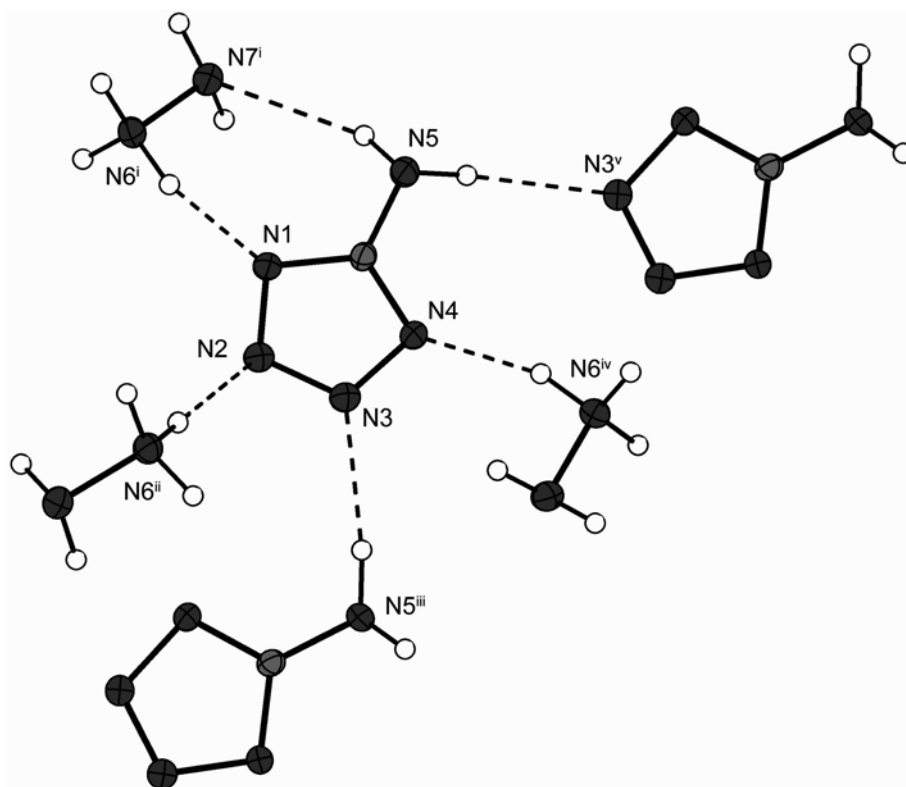
Hydrazinium 5-aminotetrazolate (**2**) crystallizes as correctly published in 1958 [19] in the chiral orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2 with four molecules in the unit cell. However, in the previously solved structure no hydrogen atoms

have been located. Therefore a short reinvestigation is given in this work. The density of **2** was calculated to be  $1.547 \text{ g cm}^{-3}$ . The planar tetrazolate ring system, which can be seen in Figure 2 is comparable to other 5-aminotetrazolates e.g. triaminoguanidinium 5-aminotetrazolate or alkali 5-aminotetrazolate salts in the literature [20, 21]. The bond lengths and angles are also in the range of those found in neutral 5-aminotetrazole monohydrate [4]. The  $\text{NH}_2$  protons of the anion do not follow the planarity of the ring system and are angulated showing torsion angles of  $\text{N1-C1-N5-H5a} = 31.32(16)^\circ$  and  $\text{N4-C1-N5-H5b} = 24.07(15)^\circ$ . The hydrazine bond with a distance of  $1.455(3) \text{ \AA}$  fits exactly to value observed for other tetrazole hydrazinium structures in literature, e.g. dihydrazinium bis(tetrazolato)hydrazine [23] and dihydrazinium azotetrazolate [24].



**Figure 2.** Formula unit of **2** with its labelling scheme. Hydrogen atoms shown as spheres of arbitrary radius and thermal displacements set at 50% probability.

**2** forms an extensive hydrogen bond network, which could be the reason for the stability and low sensitivities. All nitrogen atoms of the anions (depicted in Figure 3) as well of the hydrazinium cations participate in hydrogen bonds.



**Figure 3.** View of the hydrogen bonds of one 5-aminotetrazolate anion. i:  $x, y, 1+z$ ; ii:  $1-x, -y, z$ ; iii:  $-0.5+x, 0.5-y, 1-z$ ; iv:  $1.5-x, 0.5+y, -z$ ; v:  $0.5+x, 0.5-y, 1-z$ .

## Detonation experiments

### *Theoretical calculations*

The enthalpies and free energies of formation were calculated using the CBS-4M method [25, 26] implemented in G03W [27] combined with the atomization energy procedure [28-30]. The lattice energies were estimated according to Jenkins et al. [31-33]. For compound **2** the following energies and enthalpies of formation were calculated:

$$\Delta_f H^\circ(\mathbf{2}, s) = +373.2 \text{ kJ mol}^{-1},$$

$$\Delta_f U(\mathbf{2}, s) = +3333.6 \text{ kJ kg}^{-1}.$$

The detonation parameters were calculated using the EXPLO5 computer program [34]. The program is based on the chemical equilibrium, steady-state

model of detonation. It uses the Becker-Kistiakowsky-Wilson's equation of state (BKW EOS) for gaseous detonation products and Cowan-Fickett's equation of state for solid carbon [35-39]. The calculation of the equilibrium composition of the detonation products is done by applying modified White, Johnson and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point. The BKW equation in the following form was used with the BKWN set of parameters ( $\alpha$ ,  $\beta$ ,  $\kappa$ ,  $\theta$ ) as stated below the equations and  $X_i$  being the mol fraction of  $i$ -th gaseous product,  $k_i$  is the molar covolume of the  $i$ -th gaseous product [35-39]:

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

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

The detonation parameters calculated with the EXPLO5 program using the experimentally determined density (X-ray) are summarized in Table 2.

**Table 2.** Calculated detonation parameters for compound **2**

	[N <sub>2</sub> H <sub>5</sub> ] <sup>+</sup> [CH <sub>2</sub> N <sub>5</sub> ] <sup>-</sup> ( <b>2</b> )
$\rho / \text{g cm}^{-3}$	1.547
$\Omega / \%$	-75.1
$Q_v / \text{kJ kg}^{-1}$	-4295
$T_{\text{ex}} / \text{K}$	2759
$P / \text{kbar}$	296
$D / \text{m s}^{-1}$	9516
$V_0 / \text{L kg}^{-1}$	959

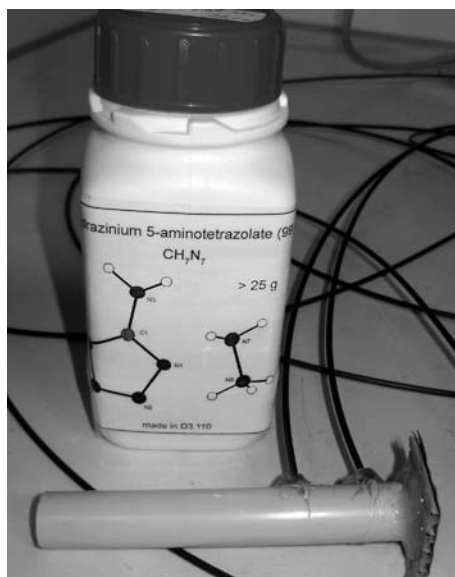
$\rho$  = density,  $\Omega$  = oxygen balance,  $Q_v$  = heat of detonation,  $T_{\text{ex}}$  = detonation temperature,  $P$  = detonation pressure,  $D$  = detonation velocity,  $V_0$  = Volume of detonation gases bar.

### **Experimental study**

In order to evaluate the detonation velocity and the initiation properties of compound **2** experimentally, it was prepared on a 100 g scale. The detonation velocity tests were performed in an OZM laboratory detonation chamber (model KV-250). The measurement of the detonation velocity was performed using the OZM detonating velocity measuring system EXPLOMET-FO-2000. The use of the fiber optic technique insures excellent electrical noise immunity (Figure 4). The system used had five independent timers measuring the time intervals (in  $\mu\text{s}$ ) between the illumination of two adjacent optical probes and calculated the velocity of detonation ( $\text{m s}^{-1}$ ). The WinExplomet software package was used to transfer the results to a PC via a serial interface. For the detonation velocity



measurement a 14 mm PE tube was equipped with two optical fibers in a distance of 2 cm. The amount of compound **2** used for the test was 15 g. The compound was loaded into the PE tube and manually compressed with ca. 50 N. As a booster charge 2 g of nitropenta (PETN) were added on top and carefully compressed manually using ca. 20 N force. Initiation was achieved with an electrically ignited (40 V, 5 A) PETN-SAcN detonator (1 g PETN, 0.2 g silver acetylide nitrate).



**Figure 4.** Setup for the determination of the velocity of detonation showing a plastic tube filled with **2**.

Although initiation of the detonator and the booster charge were achieved without any problems, compound **2** could not be initiated using this set up. This clearly shows the insensitivity of compound **2** towards initiation even when a PETN booster charge was used. Although one could try to initiate with a RDX booster charge, for practical applications the use of a detonator that has already been filled is always preferred.

### Specific impulse

Energetic materials are most commonly used in either high explosives (HE) or propellant formulations. Whereas the performance of HEs can be related to heat of explosion (Q), detonation pressure (P) and detonation velocity (D), the performance of rocket/missile propellants is best characterized by their specific

impulse ( $I_{sp}$ ) [2b]. Moreover, for gun propellants, erosivity is an additional concern and lower reaction temperatures and a high  $N_2/CO$  ratio of the reaction gases are desirable [40]. Equally important, an increase of the  $I_{sp}$  of only 20 s would be expected to increase the payload or range by ca. 100%. Moreover, smokeless combustion, which is an inherent feature of high-nitrogen compounds, is not only of environmental but particularly of strategic interest since location of the gun, missile or rocket is much more difficult.

In order to evaluate the properties of compound **2** as a potential energetic component in gun or missile propellants we calculated the specific impulses and combustion temperatures under isobaric conditions at 45 and 70 bar, representative for rocket and gun propellants, using the EXPLO5 code [35-39].

Table 3 summarizes the computed isobaric combustion temperatures ( $T_c$ , the lower the better for gun-propellants), the specific impulses ( $I_{sp}$ ) and the molar  $N_2/CO$  ratios for mixtures of **2** with ADN and three typical conventional gun-propellants (single-, double-, triple-base) at 70 bar.

**Table 3.** Computed propulsion parameters for formulations of **2** with ADN and for single-, double- and triple-base propellants for comparison

O	F	$\rho / \text{g cm}^{-3}$	$\Omega / \%$	$T_c / \text{K}$	$I_{sp} / \text{s}$	$N_2/CO$
ADN <sup>a</sup>	Hy-At					
10	90	1.573	-65.0	1863	227	9.6
20	80	1.599	-55.0	1922	229	9.2
30	70	1.625	-44.9	2110	236	4.6
40	60	1.651	-34.8	2377	246	5.2
50	50	1.678	-24.7	2653	254	6.3
60	40	1.704	-14.6	2916	260	8.7
70	30	1.730	-4.5	3091	261	17.7
80	20	1.756	+5.6	2954	250	88.8
90	10	1.782	+15.7	2570	229	1440.0
NC <sup>b</sup>		1.66	-30.2	2750	232	0.3
NC <sup>b</sup> /NG (50:50)		1.63	-13.3	3287	248	0.7
NC <sup>b</sup> /NG <sup>c</sup> /NQ <sup>d</sup> (25:25:50)		1.70	-22.0	2663	235	1.4

<sup>a</sup> ADN, ammonium dinitramide; <sup>b</sup> NC-13.3 (N content 13.3%); <sup>c</sup> NG, nitroglycerine; <sup>d</sup> NQ, nitroguanidine.

Whereas single-base propellants are used in all guns from pistols to artillery weapons, the more powerful (see  $I_{sp}$ ) double-base propellants are commonly used in pistols and mortars [41]. The disadvantage of double-base propellants is the excessive erosion of the gun barrel (see  $N_2/CO$  ratio) by the much higher

flame temperatures, and the presence of a muzzle flash (fuel-air explosion of the combustion products). In order to reduce erosion and muzzle flash, triple-base propellants with up to 50% nitroguanidine are used in tank guns, large calibre guns and naval guns. However, the performance of triple-base propellants is lower than that of double-base propellants. A formulation of **2** with ADN (**2**:ADN = 40:60) shows a relatively low combustion temperature (comparable to single- and triple-base propellants), with excellent molar N<sub>2</sub>/CO ratios (which are usually 0.5 for conventional propellants). The computed specific impulse for such a mixture make a possible application of **2** as promising energetic component in erosion-reduced gun propellants very interesting.

Table 4 summarized the propulsion parameters for formulations of **2** with ADN at 45 bar pressure and for a stoichiometric formulation of AP/Al which is presently used in large booster motors (e.g. ARIANE5, Space Shuttle).

**Table 4.** Computed propulsion parameters for formulations of **2** with ADN and for an AP/Al formulation for comparison

O	F	$\rho / \text{g cm}^{-3}$	$\Omega / \%$	$T_c / \text{K}$	$I_{sp} / \text{s}$
ADN <sup>a</sup>	Hy-At				
10	90	1.573	-65.0	1857	220
20	80	1.599	-55.0	1909	221
30	70	1.625	-44.9	2106	229
40	60	1.651	-34.8	2375	238
50	50	1.678	-24.7	2648	245
60	40	1.704	-14.6	2903	251
70	30	1.730	-4.5	3063	251
80	20	1.756	+5.6	2932	240
90	10	1.782	+15.7	2563	221
AP <sup>b</sup>	Al <sup>c</sup>				
70	30	2.178	-2.9	4199	232

<sup>a</sup> ADN, ammonium dinitramide; <sup>b</sup> ammonium perchlorate, <sup>c</sup> aluminum.

A 60:40 mixture of **2** with ADN possesses a calculated specific impulse of 251 s which is ca. 20 s higher than that of a mixture of AP/Al commonly used in solid state boosters.

In conclusion, compound **2** is a new high nitrogen salt which may be suitable as a very powerful, low-erosion, smokeless (no signature) and environmentally benign high-nitrogen ingredient for gun-propellants and solid boosters.

## Experimental part

*CAUTION! Although hydrazinium 5-aminotetrazolate is an insensitive compound and we never had problems in synthesis proper protective measures such as plastic spatulas, leather jacket, helmet, Kevlar® gloves and earthened shoes should be used when working on larger scales.*

5-Aminotetrazole (97%) was received from Aldrich,  $\text{N}_2\text{H}_4$  (1M) in THF from Fluka and hydrazinium hydrate from Merck. Melting points were measured with a Linseis PT10 DSC [41] and checked with a Büchi Melting Point B-450 apparatus (uncorrected). DSC measurements were performed at a heating rate of  $5\text{ }^\circ\text{C min}^{-1}$  in closed aluminum sample pans with a  $1\text{ }\mu\text{m}$  hole in the top for gas release under a nitrogen flow of  $20\text{ mL min}^{-1}$  with an empty identical aluminum sample pan as a reference. NMR spectra were recorded with a Jeol Eclipse 270, Jeol EX 400 or a Jeol Eclipse 400 instrument. All chemical shifts are quoted in ppm relative to TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and  $\text{MeNO}_2$  ( $^{14}\text{N}$ ,  $^{15}\text{N}$ ). Infrared (IR) spectra were recorded using a Perkin-Elmer Spektrum One FT-IR instrument [42]. Transmittance values are qualitatively described as “very strong” (vs), “strong” (s), “medium” (m) and “weak” (w). Raman spectra were measured using a Perkin-Elmer Spektrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). The intensities are reported as percentages of the most intense peak and are given in parentheses. Elemental analyses were performed with a Netsch Simultaneous Thermal Analyzer STA 429.

**Method 1:** 5-Aminotetrazole (42.54 g, 0.5 mol) was suspended in 300 mL of THF (dry, over mol. sieves) and the suspension was heated to  $50\text{ }^\circ\text{C}$ . Hydrazine (1M in THF, 500 mL, 0.5 mol) was added in small portions under vigorous stirring. Insoluble hydrazinium 5-aminotetrazolate formed instantaneously as a white, flocculent precipitate in quantitative yields. After being stirred for further 5 minutes, the solid was filtered off and dried. The crude product was recrystallized from hot ethanol.

**Method 2:** 5-Aminotetrazole (42.54 g, 0.5 mol) was suspended in 100 mL water and heated to  $50\text{ }^\circ\text{C}$ . Hydrazinium hydrate 25.03 g, 0.5 mol) was added dropwise to the suspension until the 5-aminotetrazole was completely deprotonated and the solution was clear. The water was removed under reduced pressure and the crude product was recrystallized from ethanol.

DSC ( $5\text{ }^\circ\text{C min}^{-1}$ ,  $^\circ\text{C}$ ): 118 -  $122\text{ }^\circ\text{C}$  (m.p.),  $186\text{ }^\circ\text{C}$  (dec.); IR (KBr,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3405$  (vs), 3351 (vs), 3290 (vs), 3195 (s), 2964 (s), 2721 (s), 2160 (m), 1630 (s), 1522 (s), 1442 (m), 1232 (m), 1106 (s), 1083 (s), 961 (m), 939 (m), 756 (w), 658 (w), 558 (w); Raman (1064 nm, 400 mW,  $25\text{ }^\circ\text{C}$ ,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3286$  (17), 3181 (21), 1630 (14), 1523 (56), 1452 (17), 1235 (55), 1116 (32), 1085

(30), 1064 (100), 1009 (17), 962 (22), 941 (30), 758 (29), 427 (25), 229 (30);  $^1\text{H}$  NMR ( $[\text{d}_6]$ -DMSO, 25 °C, ppm)  $\delta$ : 7.43 (s);  $^{13}\text{C}$  NMR ( $[\text{d}_6]$ -DMSO, 25 °C, ppm)  $\delta$ : 161.5(CN<sub>4</sub>);  $^{15}\text{N}$  NMR ( $[\text{d}_6]$ -DMSO, 25 °C)  $\delta$  = -8.0 (N1), -116.4 (N2), -332.0 (H<sub>2</sub>N-NH<sub>3</sub><sup>+</sup>), -342.4 (N5); m/z (FAB<sup>+</sup>): 33 (100); m/z (FAB<sup>-</sup>): 84 (100); EA (CH<sub>7</sub>N<sub>7</sub>, 117.11): calcd.: C 10.26, H 6.02, N 83.72; found: C 10.65, H 5.72, N 83.85; BAM drophammer: 100 J; friction tester: >360 N, ESD: 3.0 J, Flame test: low flammable.

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