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N-Rich Salts of 2-Methyl-5-nitraminotetrazole: Secondary Explosives with Low Sensitivities[†]

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2-Methyl-5-nitraminotetrazole (**1**) was formed by nitration of 2-methyl-5-aminotetrazole. 2-Methyl-5-aminotetrazole was obtained by an improved synthesis starting from sodium 5-aminotetrazolate, which is methylated with dimethyl sulfate in dimethyl formamide giving 2-methyl-5-aminotetrazole in 29% yield. Nitrogen-rich salts such as guanidinium (**2**), 1-aminoguanidinium (**3**), 1,3-diamino-guanidinium (**4**), 1,3,5-triamino-guanidinium (**5**), azidoformamidinium (**6**), hydrazinium (**7**), diaminouronium 2-methyl-5-nitraminotetrazolate (**8**), as well as an urea adduct (**9**), were prepared by facile deprotonation or metathesis reactions. Diaminourea was synthesized by hydrazinolysis of dimethyl carbonate with hydrazine hydrate. All compounds were fully characterized by vibrational spectroscopy (IR and Raman), multinuclear NMR spectroscopy, elemental analysis, and differential scanning calorimetry (DSC) measurements. The crystal structures of **2**−**6**, **8**, and **9** could be determined using single crystal X-ray diffraction. The heats of formation of **2**−**9** were calculated using the atomization method based on CBS-4M enthalpies. With these values and the experimental (X-ray) densities several detonation parameters such as the detonation pressure, velocity, energy, and temperature were computed using the EXPLO5 code. In addition, the sensitivities toward impact, friction, and electrical discharge were tested using the BAM drop hammer, BAM friction tester, as well as a small scale electrical discharge device.

Introduction

The development of new high-energy-density materials (HEDMs)[1] with improved performance and decreased sensitivity is one of the main goals in our research group.[2] Generally, the class of HEDMs is divided into two main groups, according to their different applications in military and civil sectors. These main groups are explosives and propellants. Because of their qualification profile the materials have to meet specific characteristics. Important criteria for the group of explosives are the detonation velocity V_{det} and the detonation pressure p_{CJ}. Thereby the focus lies on the synthesis of compounds which feature values as high as possible for both magnitudes to reach maximum performance. Another critical parameter is the density ρ of the explosive, because the detonation pressure is directly proportional to the squared density ρ^2. In contrast the detonation velocity depends on the molar quantity N of formed gaseous products and also on the density. Also high, endothermic heats of formation ($\Delta_f H°$) are required for effective energetic materials.[3] Unfortunately, performance and sensitivity are often mutually exclusive parameters. Moreover, the new explosive should be cheap to synthesize, stable toward temperature, storable for long periods, and of course safe to handle. One way of counteracting the mutual exclusivity between sensitivity and performance is the use of systems with great possibility to form hydrogen bonds, which stabilize the material. In this regard, nitrogen-rich compounds will have many electronegative atoms available for hydrogen bonding and azole- (in particular tetrazole)-based energetic materials have attracted considerable attention since they tend to show a good compromise between high energy content, high chemical/thermal stability, and low sensitivity. Also increasing environmental concerns over the past few years raised the requirements of HEDMs, and new replacements for the commonly used toxic RDX are wanted.[4] Therefore explosives containing high nitrogen contents are in the focus because of the

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[†] Dedicated to Prof. Dr. Hansgeorg Schnöckel on the Occasion of His 70th Birthday

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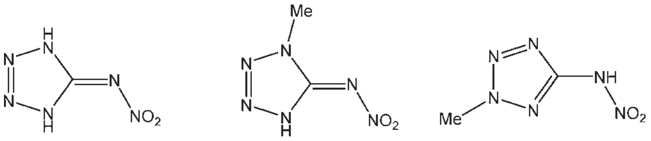

Figure 1. 5-Nitriminotetrazole, 1-methyl-5-nitriminotetrazole, and 2-methyl-5-nitraminotetrazole.

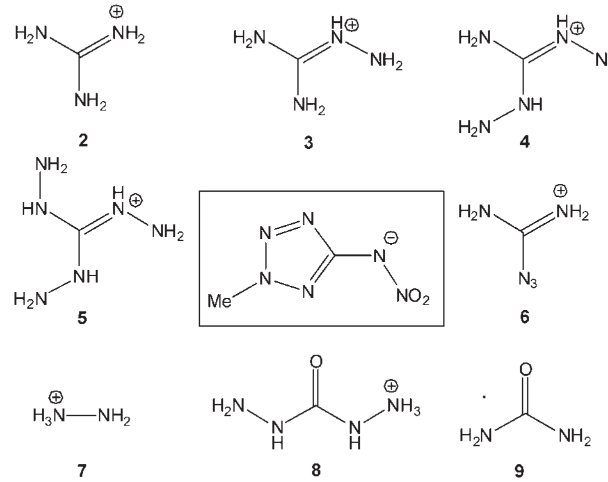

Figure 2. Target molecules presented in this work: guanidinium 2-methyl-5-nitraminotetrazolate (**2**), 1-aminoguanidinium 2-methyl-5-nitraminotetrazolate (**3**), 1,3-diaminoguanidinium 2-methyl-5-nitraminotetrazolate (**4**), 1,3,5-triaminoguanidinium 2-methyl-5-nitraminotetrazolate (**5**), azidoformamidinium 2-methyl-5-nitraminotetrazolate (**6**), hydrazinium 2-methyl-5-nitraminotetrazolate (**7**), diaminouronium 2-methyl-5-nitramino-tetrazolate (**8**), and urea 2-methyl-5-nitraminotetrazole (**9**).

environmentally benign dinitrogen N_2 molecule as the main reaction product.[5] To prepare new energetic materials often tetrazoles,[6] tetrazolates,[7] and tetrazolium[8,9] salts are used since they are mostly endothermic compounds with a high nitrogen content. In addition, these compounds are considered mostly less toxic, easy to handle because of their high kinetic and thermal stability, and easy to prepare. A disadvantage of tetrazolates and tetrazolium compounds is the possible contamination of groundwater since these ionic structures feature a high solubility. On the other side, they show mostly high densities and stabilities based on their lattice energy. Therefore, formation of ionic structures is a popular approach for the synthesis of new energetic materials. It is hard to fulfill all requirements for new energetic materials. However, the compounds described in this work are N-rich salts of 2-methyl-5-nitraminotetrazole (**1**). In accordance to its 1-substituted sister compound, it serves, if deprotonated, as a valuable energetic anion, because of the combination of the nitrogen-rich backbone as a fuel and the nitramine group as an oxidizer. Nitramine moieties are often used in the synthesis of new energetic materials since they increase the oxygen balance of the molecule and therefore lead to a better performance.[10−14] The methyl group attached to the tetrazole ring system lowers the sensitivity in comparison to non-methylated 5-nitriminotetrazole (Figure 1).

Furthermore, deprotonation of **1** affords more suitable compounds with higher decomposition temperatures compared to protonated **1**. For this reason 2-methyl-5-nitraminotetrazolate anions are convenient components for new ionic energetic materials. According to the performance in energetic salts the same requirements have to be applied for the cations of the energetic material. Besides the ammonium salt of 2-methyl-5-nitraminotetrazole[15] and the 2-methyl-5-*N*-(2-nitro-2-azapropyl)-nitraminotetrazole,[10] to also mention a covalent derivative of 2-methyl-5-nitraminotetrazole, only very little about the chemistry of 2-methyl-5-nitraminotetrazole is known in the literature so far. In 2008, we reported on the synthesis and full characterization of nitrogen-rich salts of 1-methyl-5-nitriminotetrazole.[16] Following this approach different nitrogen-rich salts of 2-methyl-5-nitraminotetrazole were synthesized and are presented in this work (Figure 2).

Experimental Section

Caution! *2-Methyl-5-nitriminotetrazole and its salts are energetic materials with increased sensitivities toward shock and friction. Therefore, proper security precautions (safety glass, face shield, earthened equipment and shoes, Kevlar gloves, and ear plugs) have to be applied while synthesizing and handling the described compounds. Specifically, compounds described having the azido group are extremely sensitive and have to be handled very carefully.*

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros). ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded using a JEOL Eclipse 270, JEOL EX 400 or a JEOL Eclipse 400 instrument. The chemical shifts quoted in parts per million (ppm) in the text refer to typical standards such as tetramethylsilane (^{1}H, ^{13}C) and nitromethane (^{15}N). To determine the melting points of the described compounds a Linseis PT 10 DSC (heating rate 5 °C min^{-1}) was used. Infrared spectra were measured using a Perkin-Elmer Spectrum One FT-IR spectrometer as KBr pellets. Raman spectra were recorded on a Bruker MultiRAM Raman Sample Compartment D418 equipped with a Nd:YAG-Laser (1064 nm) and a LN-Ge diode as detector. Mass spectra of the described compounds were measured at a JEOL MStation JMS 700 using either DEI or FAB technique. To measure elemental analyses a Netsch STA 429 simultaneous thermal analyzer was employed.

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Diaminourea, 2-methyl-5-nitraminotetrazole as well as its potassium salt were prepared according to literature.[17–19] Azidoformamidinium chloride was prepared by the reaction of aminoguanidinium chloride with 1 equiv of $NaNO_2$ and HCl, followed by a recrystallization from water/ethanol. Aminoguanidinium chloride was synthesized by neutralization of commercially available aminoguanidinium bicarbonate with 2 N hydrochloric acid followed by recrystallization from water/ethanol. 5-Aminotetrazole, guanidinium carbonate, aminoguanidinium bicarbonate, as well as diaminoguanidinium chloride, were used as commercially available.

2-Methyl-5-aminotetrazole. 5-Aminotetrazole (15.3 g, 180 mmol) is dissolved in a solution containing sodium hydroxide (7.20 g, 180 mmol) in approximately 200 mL of water. The solvent is removed in vacuum, and the residue is suspended in 200 mL of dimethyl formamide. The mixture is heated to reflux and dimethyl sulfate (11.4 g, 90 mmol) is added dropwise to the refluxing suspension by means of a dropping funnel within 15 min. The mixture is then refluxed for 4 h, and then 100 mL of water is added. After being further refluxed for 1 h, the solvent is removed in vacuum, and the residue is extracted with a mixture of ethanol and acetone (1:1 v/v). The combined filtrates are evaporated, and 2-methyl-5-aminotetrazole is extracted from the mixture of isomers with boiling benzene. The benzene is removed from the filtrates in vacuum, and the crude material can be recrystallized from the same solvent to give 2-methyl-5-aminotetrazole in 29% (5.20 g, 52 mmol) yield.

^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 5.92 (s, 2H, NH_2), 4.06 (CH_3); ^{13}C NMR (DMSO-d_6, 25 °C, ppm) δ: 167.7 (CN_4), 39.4 (CH_3).

Guanidinium-2-methyl-5-nitraminotetrazolate (2). 2-Methyl-5-nitraminotetrazole (1.44 g, 10 mmol) is suspended in a few milliliters of water, and a suspension of guanidinium carbonate (0.90 g, 5 mmol) in water is added slowly. The mixture is heated to 40 °C and then filtrated. The solvent is removed in vacuum, and the residue recrystallized from ethanol. Yield: 1.73 g (8.52 mmol, 85%).

DSC (5 °C min^{-1}, °C): 176 °C (m.p.), 212 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3423 (s), 3342 (s), 3276 (s, br), 3173 (s), 2790 (m), 1927 (w), 1694 (vs), 1662 (s), 1488 (s), 1422 (s), 1355 (s), 1217 (m), 1099 (m), 1037 (m), 990 (w), 893 (w), 766 (w), 632 (m, br), 528 (m); Raman (1064 nm, 500 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3202 (2), 2963 (9), 1490 (100), 1404 (6), 1375 (4), 1339 (3), 1224 (4), 1101 (2), 1039 (36), 1015 (45), 896 (2), 743 (5), 705 (8), 539 (4), 450 (9), 398 (4), 349 (3) 207 (5), 145 (3), 129 (15), 91 (31); ^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 7.03 (s, 6H, NH_2), 4.20 (CH_3); ^{13}C NMR (DMSO-d_6, 25 °C, ppm) δ: 168.4 (CN_4), 158.6 ($C(NH_2)_3$), 39.7 (CH_3); *m*/*z* (FAB^+): 60.1 [$C(NH_2)_3^+$]; *m*/*z* (FAB^-): 143.0 [2-$MeATNO_2^-$]; EA ($C_3H_9N_9O_2$, 203.16): calcd: C 17.74, H 4.47, N 62.05%; found: C 17.86, H 4.84, N 61.39%; BAM drophammer: 30 J; friction tester: 192 N; ESD: 0.2 J.

Aminoguanidinium-2-methyl-5-nitraminotetrazolate (3). 2-Methyl-5-nitraminotetrazole (4.32 g, 30 mmol) is suspended in a few milliliters of water, and then a suspension of aminoguanidinium bicarbonate (4.08 g, 30 mmol) in water is added slowly. The mixture is heated to 40 °C and then filtrated. The solvent is removed in vacuum, and the residue then recrystallized from an ethanol/water mixture to yield 5.24 g (24.0 mmol, 80%).

DSC (5 °C min^{-1}, °C): 146 °C (m.p.), 210 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3463 (s), 3336 (s, br), 3238 (s, br), 3113 (s, br), 2831 (m), 2426 (m), 2237 (m), 1950 (w), 1927 (w), 1840 (w), 1776 (w), 1693 (s), 1639 (s), 1598 (m), 1548 (m), 1488 (s), 1401 (vs), 1374 (s), 1358 (s), 1337 (s), 1278 (s), 1221 (s), 1184 (m), 1099 (s), 1061 (s), 1037 (s), 893 (m), 760 (m), 706 (m), 557 (s); Raman (1064 nm, 500 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2963 (3), 1491 (100), 1404 (5), 1372 (2), 1346 (2), 1221 (3), 1039 (15), 1011 (26), 962 (5), 895 (3), 740 (4), 703 (6), 529 (3), 446 (4), 405 (3), 345 (3), 200 (5), 141 (3), 113 (22), 83 (13); ^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 7.34 (s, 5H, $\mathrm{C-N}H_2$, $\mathrm{N}H\mathrm{-NH_2}$), 4.70 (s, 2H, $\mathrm{N}H_2\mathrm{NH}$), 4.20 (CH_3); ^{13}C NMR (DMSO-d_6, 25 °C, ppm) δ: 168.4 (CN_4), 159.4 ($C(NHNH_2)(NH_2)_2$), 39.7 (CH_3); *m*/*z* (FAB^+): 75.1 [$C(NHNH_2)(NH_2)_2^+$]; *m*/*z* (FAB^-): 143.0 [2-$MeATNO_2^-$]; EA ($C_3H_{10}N_{10}O_2$, 218.18): calcd: C 16.52, H 4.62, N 64.20%; found: C 16.73, H 5.01, N 63.88%; BAM drophammer: 6 J; friction tester: 120 N; ESD: 0.2 J.

Diaminoguanidinium-2-methyl-5-nitraminoetrazolate (4). 2-Methyl-5-nitraminotetrazole (1.98 g, 13.74 mmol) is dissolved in a solution of potassium hydroxide in 20 mL of water and an aqueous solution of silver nitrate (13.74 mmol, 2.33 g) is added. The colorless and fluffy precipitate is filtered off and directly given to a solution of diaminoguanidinium chloride (1.73 g, 13.78 mmol) in 50 mL of water. The suspension is stirred under exclusion of light for 20 min, filtered off, and the solvent of the clear solution is removed in vacuo. The residue is recrystallized from ethanol. Yield: 1.98 g (8.49 mmol, 62%).

DSC (5 °C min^{-1}, °C): 138 °C (m.p.), 203 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3457 (s), 3353 (s), 3310 (vs), 3098 (s), 2376 (w), 2284 (w), 2105 (w), 1990 (w), 1957 (w), 1679 (vs, br), 1639 (s), 1567 (m), 1545 (m), 1489 (s), 1385 (s), 1324 (s, br), 1276 (s), 1213 (s), 1182 (s), 1099 (s), 1037 (s), 976 (s), 890 (m), 773 (m), 756 (m), 744 (w), 706 (m), 673 (m), 562 (m), 468 (m); Raman (1064 nm, 500 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2956 (3), 1590 (100), 1443 (3), 1376 (4), 1216 (3), 1101 (4), 1038 (9), 1012 (39), 932 (3), 893 (4), 746 (9), 718 (6), 547 (3), 447 (5), 402 (3), 341 (6), 188 (7), 126 (4), 107 (5), 81 (42); ^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 8.62 (s, 2H, $\mathrm{N}H\mathrm{NH_2}$), 7.17 (s, 2H, $\mathrm{C-N}H_2$), 4.58 (s, 4H, $\mathrm{N}H_2\mathrm{NH}$), 4.16 (CH_3) ; ^{13}C NMR (DMSO-d_6, 25 °C, ppm) δ: 168.4 (CN_4), 160.3 ($C(NHNH_2)_2(NH_2)$), 39.6 (CH_3) ; *m*/*z* (FAB^+): 90.1 [$C(NHNH_2)_2(NH_2)^+$]; *m*/*z* (FAB^-): 143.0 [2-$MeATNO_2^-$]; EA ($C_3H_9N_9O_2$, 203.16): calcd: C 15.45, H 4.75, N 66.07%; found: C 15.71, H 4.83, N 65.79%; BAM drophammer: 10 J; friction tester: 160 N; ESD: 0.16 J.

Triaminoguanidinium-2-methyl-5-nitraminotetrazolate (5). Aminoguanidinium 2-methyl-5-nitraminotetrazolate (1.89 g, 8.7 mmol) is suspended in 20 mL of 1,4-dioxane and hydrazine hydrate (0.96 g, 19.1 mmol) is added dropwise. The solution is heated to 90 °C for 5 h in a constant nitrogen flow. As soon as ammonia is no longer evolved from the reaction mixture, the solution is cooled down, and the solvent is removed in vacuum. The residue is recrystallized from ethanol to give 1.71 g (6.89 mmol, 88%).

DSC (5 °C min^{-1}, °C): 143 °C (m.p.), 188 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3484 (s), 3336 (s, br), 3155 (s, br), 2950 (s), 2801 (s), 2670 (s), 2456 (s), 2379 (m), 2158 (m), 1667 (vs, br), 1595 (s, br), 1521 (m), 1484 (s), 1454 (s), 1321 (s), 1298 (s), 1235 (m), 1158 (s), 1120 (s), 1090 (s), 995 (s), 970 (s), 916 (m, br), 789 (s), 755 (m), 742 (s), 679 (s), 622 (s), 544 (s, br); Raman (1064 nm, 500 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3318 (6), 3218 (3), 2962 (3), 1545 (2), 1481 (100), 1449 (4), 1389 (9), 1360 (3), 1213 (3), 1131 (2), 1096 (3), 1061 (4), 1017 (50), 886 (7), 767 (6), 706 (8), 678 (2), 456 (4), 396 (8), 344 (2), 259 (3), 172 (4), 143 (13); ^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 8.59 (s, 3H, $\mathrm{N}H\mathrm{NH_2}$), 4.50 (s, 6H, $\mathrm{NHN}H_2$), 4.18 (CH_3); ^{13}C NMR (DMSO-d_6, 25 °C, ppm) δ: 168.8 (CN_4), 159.6 ($C(NHNH_2)_3$), 39.6 (CH_3); *m*/*z* (FAB^+): 105.1 [$C(NHNH_2)_3^+$]; *m*/*z* (FAB^-): 142.9 [2-$MeATNO_2^-$]; EA ($C_3H_{12}N_{12}O_2$, 248.21): calcd: C 14.52, H 4.87, N 67.72%; found: C 14.85, H 4.94, N 67.38%; BAM drophammer: 6 J; friction tester: 120 N; ESD: 0.18 J.

Azidoformamidinium-2-methyl-5-nitraminoetrazolate (6). Potassium 2-methyl-5-nitraminotetrazolate (1.82 g, 10 mmol) was prepared by dissolving 2-methyl-5-nitraminotetrazole (1.44 g, 10 mmol) in a solution of potassium hydroxide (85%, 0.66 g, 10 mmol) in 20 mL of water. The resulting solution was added to a solution of silver nitrate (1.70 g, 10 mmol) in 10 mL of water, while the reaction vessel was kept in darkness. Silver

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2-methyl-5-nitraminotetrazolate precipitated instantaneously, the suspension was centrifuged, and the aqueous layer pipetted off. It was washed with three portions of water (50 mL each) and suspended in 25 mL of water afterward. Azidoformamidinium chloride (1.15 g, 9.5 mmol) was dissolved in 10 mL of water and added to the suspension. Silver chloride started to precipitate, and the suspension was stirred in darkness for further 30 min at 30 °C. The precipitate was filtered off, the water was removed in vacuo, and the remaining solid recrystallized from an ethanol/water mixture to yield 1.28 g (5.58 mmol, 56%) of azidoformamidinium 2-methyl-5-nitraminotetrazolate as colorless crystals.

DSC (5 °C min^{-1}, °C): 115 °C (m.p.), 148 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3264 (m), 3029 (m), 2783 (w), 2446 (w), 2185 (vs), 2121 (w), 1931 (w), 1698 (s), 1476 (vs), 1401 (vs), 1366 (vs), 1337 (s), 1287 (m), 1232 (m), 1180 (w), 1120 (m), 1098 (m), 1035 (w), 909 (w), 880 (w), 841 (w), 773 (w), 764 (w), 748 (w), 704 (m), 690 (m), 677 (m), 536 (w), 509 (m), 481 (w); Raman (1064 nm, 500 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3034 (2), 2970 (14), 2185 (14), 2123 (3), 1473 (100), 1418 (10), 1360 (5), 1232 (3), 1183 (7), 1143 (5), 1123 (2), 1098 (2), 1026 (78), 911 (8), 883 (4), 765 (5), 708 (7), 510 (5), 484 (3), 464 (8), 395 (5), 321 (10), 214 (4); ^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 6.40 (s, 4H, NH_2), 4.36 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 25 °C, ppm) δ: 168.4 (CN_4), 158.7 ($C(N_3)_2(NH_2)_2$), 40.4 (CH_3) ; *m*/*z* (FAB^+): 86.1 [$C(N_3)(NH_2)_2^+$]; *m*/*z* (FAB^-): 143.0 [2-MeATNO$_2^-$]; EA ($C_3H_7N_{11}O_2$, 229.16): calcd: C 15.72, H 3.08, N 67.23%; found: C 15.72, H 3.10, N 67.03%; BAM drophammer: 3 J; friction tester: 72 N ; ESD: 0.20 J.

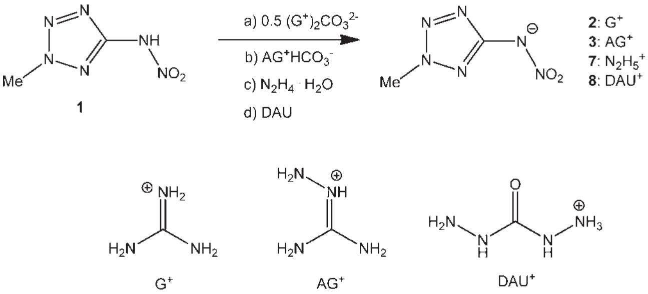
Hydrazinium 2-methyl-5-nitraminotetrazolate (7). 2-Methyl-5-nitraminotetrazole (1.44 g, 10 mmol) is suspended in a few milliliters of water, and hydrazine hydrate (0.50 g, 10 mmol) is added. The mixture is heated to 40 °C, the solvent of the clear solution is removed in vacuum, and the residue then recrystallized from an ethanol/water mixture. Yield: 1.62 g (9.20 mmol, 92%).

DSC (5 °C min^{-1}, °C): 73 °C (m.p.), 208 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3407 (m), 3338 (m), 3063 (m), 2764 (w), 2646 (w), 1618 (w), 1532 (w), 1479 (vs), 1419 (m), 1393 (s), 1369 (m), 1355 (s), 1325 (s), 1274 (m), 1208 (m), 1130 (w), 1091 (m), 1044 (m), 1020 (w), 938 (m), 884 (m), 771 (w), 757 (w), 749 (w), 704 (m), 673 (w), 473 (w); Raman (1064 nm, 130 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3280 (3), 3040 (7), 3018 (4), 2962 (15), 2826 (2), 2694 (2), 2329 (3), 1981 (2), 1929 (2), 1628 (5), 1538 (2), 1480 (100), 1463 (11), 1392 (16), 1358 (5), 1217 (8), 1098 (3), 1079 (3), 1053 (6), 1031 (5), 1014 (87), 971 (7), 880 (3), 751 (16), 702 (14), 452 (13), 407 (7); ^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 7.10 (s, 5H, NH_2, NH_3), 4.19 (CH_3); ^{13}C NMR (DMSO-d_6, 25 °C, ppm) δ: 168.5 (CN_4), 39.7 (CH_3); *m*/*z* (FAB^+): 33.1 [$N_2H_5^+$]; *m*/*z* (FAB^-): 143.0 [2-MeATNO$_2^-$]; EA ($C_2H_8N_8O_2$, 176.14): calcd: C 13.64, H 4.58, N 63.62%; found: C 13.75, H 4.61, N 63.23%; BAM drophammer: 7 J; friction tester: 120 N; ESD: 0.1 J.

Diaminouronium 2-Methyl-5-nitriminotetrazolate (8). 2-Methyl-5-nitraminotetrazole (2.88 g, 20 mmol) is suspended in a few milliliters of water, and a solution of diaminourea (1.80 g, 20 mmol) in water is added. The solvent of the clear solution is removed in vacuum, and the residue then recrystallized from an ethanol/water mixture. Yield: 4.40 g (18.8 mmol, 94%).

DSC (5 °C min^{-1}, °C): 131 °C (m.p.), 195 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3421 (m), 3324 (s), 3283 (s), 3043 (m), 2659 (w), 1708 (m), 1633 (s), 1465 (s), 1572 (m), 1552 (m), 1493 (vs), 1462 (m), 1430 (s), 1415 (s), 1384 (m), 1327 (s), 1311 (s), 1267 (m), 1209 (m), 1164 (m), 1096 (m), 1059 (m), 1035 (m), 979 (w), 887 (w), 767 (w), 756 (w), 741 (m), 704 (w), 678 (w), 637 (w), 560 (w), 516 (w); Raman (1064 nm, 130 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3325 (3), 3282 (9), 3224 (3), 3044 (9), 3022 (3), 2962 (18), 2839 (3), 1718 (2), 1634 (2), 1494 (100), 1463 (5), 1420 (4), 1368 (8), 1272 (2), 1211 (4), 1098 (2), 1059 (3), 1043 (6), 1014 (32), 889 (2), 758 (3), 742 (2), 702 (4), 455 (4), 407 (2), 223 (3); ^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 7.60 (s, br, 7H, NH, NH_2, NH_3^+), 4.19 (CH_3); ^{13}C NMR (DMSO-d_6, 25 °C, ppm) δ: 167.8 (CN_4), 159.8 ($C(O)(NH_2)_2$), 39.8 (CH_3); *m*/*z* (FAB^+): 90.1 [$C(O)(NH)_2(NH_2)_2^+$]; *m*/*z* (FAB^-): 143.0 [2-MeATNO$_2^-$]; EA ($C_3H_{10}N_{10}O_3$, 223.18): calcd: C 15.39, H 4.30, N 59.81%; found: C 15.41, H 4.16, N 59.51%; BAM drophammer: 5 J; friction tester: 168 N; ESD: 0.5 J.

Scheme 1. Syntheses of Compounds **2**, **3**, **7**, and **8** via Brønstedt Acid-Base Reactions



Urea 2-methyl-5-nitraminotetrazole (9). 2-Methyl-5-nitraminotetrazole (1.44 g, 10 mmol) is suspended in a few milliliters of water, and a solution of urea (0.60 g, 10 mmol) in water is added. The solvent of the clear solution is removed in vacuum, and the residue then recrystallized from an ethanol/water mixture. Yield: 1.95 g (9.55 mmol, 96%).

DSC (5 °C min^{-1}, °C): 158 °C (dec 1), 190 °C (dec 2); IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3437 (s, br), 3346 (s, br), 2804 (w), 2642 (w), 2184 (w), 1670 (vs, br), 1465 (s), 1384 (m), 1330 (m), 1279 (m), 1209 (m), 1153 (m), 1050 (m), 1016 (m), 863 (w), 787 (w), 736 (m), 618 (w), 573 (m), 558 (m); Raman (1064 nm, 130 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3437 (2), 3329 (8), 3239 (4), 3124 (2), 2967 (6), 2330 (3), 2130 (1), 1650 (6), 1626 (2), 1538 (11), 1363 (3), 1281 (3), 1176 (5), 1047 (2), 1011 (100), 698 (4), 548 (17), 432 (2), 370 (2), 329 (1), 132 (17), 102 (74), 84 (5); ^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 6.99 (s, 1H, NH), 5.78 (s, 4H, NH_2), 4.30 (CH_3); ^{13}C NMR (DMSO-d_6, 25 °C, ppm) δ: 160.7 ($C(O)(NH_2)_2$), 158.6 (CN_4), 40.6 (CH_3); *m*/*z* (FAB^+): 60.1 [$C(O)(NH_2)_2^+$]; *m*/*z* (FAB^-): 143.0 [2-MeATNO$_2^-$]; EA ($C_3H_8N_8O_3$, 204.15): calcd: C 17.65, H 3.95, N 54.89%; found: C 17.96, H 4.25, N 54.44%; BAM drophammer: 10 J; friction tester: 288 N; ESD: 0.2 J.

Results and Discussion

Synthesis. The synthesis of 2-methyl-5-aminotetrazole has always been a limiting step in the chemistry dealing with 2-methyl-5-aminotetrazole and 2-methyl-5-nitraminotetrazole because of the very low yield of the methylation reaction of 5-aminotetrazole. Henry et al. reported on a synthesis in 1954 doing the methylation with dimethyl sulfate in aqueous medium.[20] This reaction affords 2-methyl-5-aminotetrazole in only 5% yield as a byproduct beside 1-methyl-5-aminotetrazole being the main product. Switching the solvent of the reaction to higher boiling dimethyl formamide allows higher reaction temperatures and therefore the reaction is driven toward the thermodynamic product 2-methyl-5-aminotetrazole, which then can be isolated in up to 29% yield. This makes compounds based on 2-methyl-5-aminotetrazole and especially 2-methyl-5-nitraminotetrazole much more interesting for applications not only as energetic materials but also in coordination chemistry.

Scheme 1 shows the synthesis of the guanidinium (**2**), 1-aminoguanidinium (**3**), hydrazinium (**7**), and diaminouronium salt (**8**) of 2-methyl-5-nitraminotetrazole (**1**). All synthetic routes shown are based on simple Brønstedt acid−base reactions. **2** and **3** were formed by reacting the

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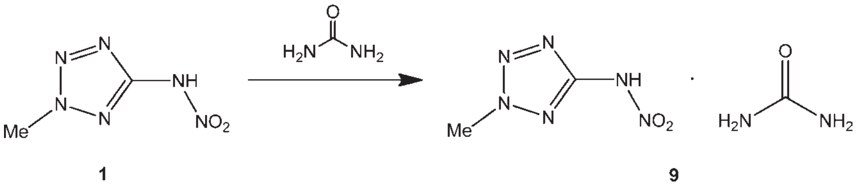
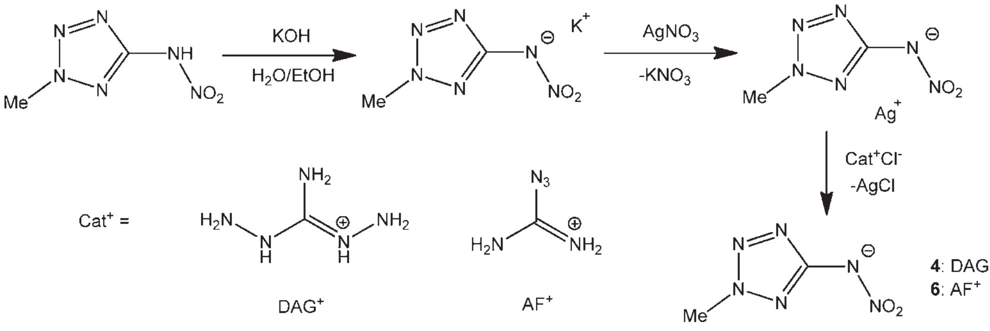
[20] Henry, R. A.; Finnegan, W. G. *J. Am. Chem. Soc.* **1954**, *76*, 923–926.

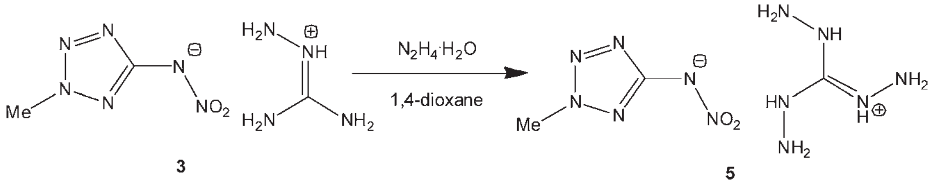
Scheme 2. Formation of the Urea Adduct **9**



Scheme 3. Synthetic Routes to **4** and **6** via Silver 2-Methyl-5-nitraminotetrazolate



Scheme 4. Synthesis of **5** via Hydrazinolysis of **3**



free acid **1** with guanidinium carbonate and aminoguanidinium bicarbonate, respectively, whereas the formation of gaseous CO_2, which can be expelled from the reaction mixture by moderate warming of the solutions, is utilized. The hydrazinium salt (**7**) and the diaminouronium salt (**8**) are synthesized by the reaction of **1** with the free bases hydrazine and diaminourea (DAU) respectively in aqueous solution.

The basicity of urea is not high enough to deprotonate **1** in aqueous solution; hence, the urea adduct **9** is a cocrystallization product, which was obtained by the reaction of **1** with an aqueous solution of urea. (Scheme 2)

The reaction products 1,3-diaminoguanidinium 2-methyl-5-nitraminotetrazolate (**4**) and azidoformamidinium 2-methyl-5-nitraminotetrazolate (**6**) were obtained by metathesis reactions using silver 2-methyl-5-nitraminotetrazolate as an intermediate. It was prepared from potassium 2-methyl-5-nitraminotetrazolate and silver nitrate in aqueous solution and after being separated from the reaction mixture as poorly soluble white salt, it was further reacted with diaminoguanidinium chloride and azidoformamidinium chloride respectively, which was prepared by the reaction of aminoguanidinium chloride with 1 equiv of $NaNO_2$ and HCl, followed by a recrystallization from water/ethanol to yield the above-described salts **4** and **6**. The synthetic routes to **4** and **6** are depicted in Scheme 3.

For the synthesis of the triaminoguanidinium 2-methyl-5-nitraminotetrazolate (**5**), the hydrazinolysis reaction of the aminoguanidinium salt **3** was employed. Therefore **3** was heated with hydrazine hydrate in 1,4-dioxane under the release of ammonia. The reaction procedure is shown in Scheme 4.

Beside from the synthetic routes to the compounds **2**–**6**, that are shown above, a different way via the potassium salt of **1** and the corresponding guanidinium perchlorates and azidoformamidinium perchlorate, respectively, can be considered, where the reaction is driven by the low solubility of potassium perchlorate. Although this route seems to be more practicable than the syntheses that involve intermediates like silver salts, that have to be isolated first, appropriate safety measures have to be applied because of the high sensitivity of the guanidinium and azidoformamidinium perchlorates used as starting material.

Molecular Structures. To determine the molecular structures of **2**–**6**, **8**, and **9** in the crystalline state an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector were used. The data collection was performed using the CrysAlis CCD software,[21] and the data reductions were performed with the CrysAlis RED software.[22] The solution of all structures were performed using SIR-92,[23] SHELXS-97[24] and SHELXL-97[25] implemented in the WinGX software

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(21) *CrysAlis CCD*, Version 1.171.27p5 beta; Oxford Diffraction Ltd.: Abingdon, U.K.

(22) *CrysAlis RED*, Version 1.171.27p5 beta; Oxford Diffraction Ltd.: Abingdon, U.K.

(23) *SIR*-92; Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; *J. Appl. Crystallogr.* **1993**, *26*, 343.

(24) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. X-ray Data and Parameters

	2	**3**	**4**	**5**	**6**	**8**	**9**
formula	$C_3H_9N_9O_2$	$C_3H_{10}N_{10}O_2$	$C_3H_{11}N_{11}O_2$	$C_3H_{12}N_{12}O_2$	$C_3H_7N_{11}O_2$	$C_3H_{10}N_{10}O_3$	$C_3H_8N_8O_3$
fw [g mol^{-1}]	203.16	218.21	234.24	248.25	229.20	234.21	204.17
space group	$P2_1$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a [Å]	3.6562(3)	3.7828(4)	17.4021(14)	6.9170(4)	7.6150(10)	4.1035(3)	7.5867(5)
b [Å]	8.1552(8)	8.5095(8)	8.3403(7)	7.5831(5)	13.7932(14)	27.597(3)	7.3684(7)
c [Å]	13.9458(11)	14.1651(14)	14.7111(13)	11.0147(7)	9.5095(10)	8.1745(5)	15.3282(9)
α [deg]	90	91.281(8)	90	97.315(5)	90	90	90
β [deg]	95.919 (8)	95.299(8)	111.581(9)	106.030(5)	103.988(14)	103.105(7)	95.764(6)
γ [deg]	90	96.743(8)	90	104.979(5)	90	90	90
V [Å^3]	413.61(6)	450.63(8)	1985.5(3)	523.99(6)	969.2(2)	901.61(13)	852.54(11)
Z	2	2	8	2	4	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.632	1.608	1.567	1.573	1.571	1.725	1.591
μ [mm^{-1}]	0.136	0.134	0.065	0.131	0.132	0.148	0.138
F(000)	212	228	488	260	472	488	424
$\lambda_{MoK\alpha}$ [Å]	0.7107(3)	0.7107(3)	0.7107(3)	0.7107(3)	0.7107(3)	0.7107(3)	0.7107(3)
T [K]	200(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
θ min-max [deg]	4.41, 28.29	4.34, 32.36	4.24, 33.41	4.20, 32.35	4.26, 28.78	4.5, 27.0	4.17, 28.76
data set	−4:3; −4:10; −17:16	−4:4; −10:8; −16:17	−19:21; −7:10; −15:18	−8:8; −9: 9 ; −13: 13	−9:5; −15:16; −10:11	−5:4; −13:34; −8:10	−9:6; −9:5; −15:18
refl. coll./ unique	1703/988	3303/1768	5007/1948	5352/2062	3581/1797	3466/1926	3063/1611
R_{int}	0.028	0.024	0.025	0.018	0.027	0.017	0.029
parameters	151	176	189	202	173	185	159
R_1 (obs)	0.0371	0.0320	0.0328	0.0289	0.0352	0.0539	0.0375
wR_2 (all data)	0.0767	0.0710	0.0759	0.0773	0.0700	0.1419	0.0856
GoF	0.92	0.83	0.90	1.04	0.82	1.11	0.88
resd. dens. [e/ Å^3]	−0.24, 0.26	−0.22, 0.15	−0.12, 0.08	−0.23, 0.17	−0.21, 0.18	−0.84, 1.03	−0.22, 0.21
CCDC	783134	783137	783138	783135	783139	783140	783136

package,[26] and finally checked with the PLATON software.[27] In all crystal structures the hydrogen atoms were located and refined. The absorptions were corrected with the SCALE3 ABSPACK multiscan method.[28] Selected data and parameter of the X-ray determinations are given in Table 1.

2-Methyl-5-nitraminotetrazole and its crystal structure was recently investigated and published by our research group.[17] Its structure is different compared to the molecular structures of the anions in the investigated 2-methyl-5-nitraminotetrazolate salts. The position of the nitramine group relative to the tetrazole ring plane differs significantly since there are various hydrogen bonds influencing this building block.

Compounds **2**−**6**, **8**, and **9** ((Figures 3−10) crystallize in the monoclinic and triclinic space groups $P2_1$ (**2**), $P\bar{1}$ (**3** and **5**), $P2_1/c$ (**4** and **8**), and $P2_1/n$ (**6** and **9**) with densities lying in a range from 1.567 g cm^{-3} (**4**) to 1.632 g cm^{-3} (**2**). The bond distances between N1, N2, N3, and N4 vary from 1.30 to 1.33 Å, which fits between the bond lengths of a N−N single bond (1.45 Å) and an N=N double bond (1.25 Å).[29] The torsion angles C1−N2−N3−N4 are close to 0° (0.3(3)° for **2** to −0.24(14)° for **5**) implying a π-aromatic system. Also, the bond lengths C1−N1 and C1−N4 are located between the bond lengths of a C−N single (1.47 Å) and a C=N double bond (1.22 Å),[30] whereas the distance between N2 and the exocyclic carbon atom C2 is in the range of a C−N single bond (1.452(2) (**3**) to 1.462(4) (**2**)). The nitro group of the nitramine unit is more or less strongly twisted out of the tetrazole ring plane indicated by a N1−C1−N5−N6 torsion angle between −1.2(5)° for **2** and up to 30.3(2)° for the triaminoguanidinium salt **5**. The distances between

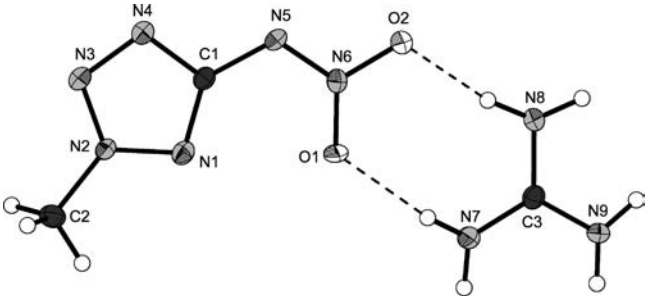

Figure 3. Molecular structure of guanidinium 2-methyl-5-nitraminotetrazolate (**2**). Thermal ellipsoids represent the 50% probability level.

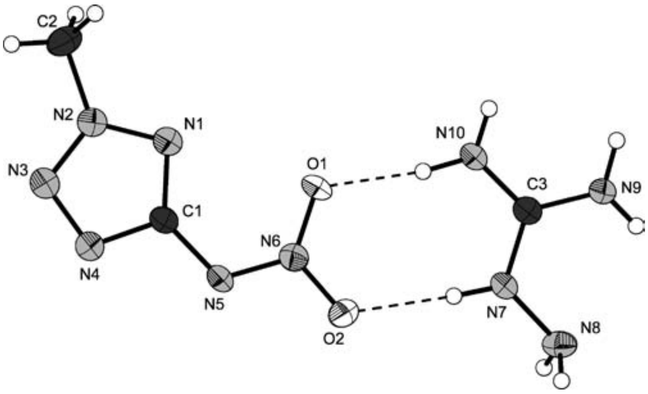

Figure 4. Molecular structure of aminoguanidinium 2-methyl-5-nitraminotetrazolate (**3**). Thermal ellipsoids represent the 50% probability level.

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(25) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1994.

(26) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

(27) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 1999.

(28) *SCALE3 ABSPACK−An Oxford Diffraction program*; Oxford Diffraction Ltd.: Abingdon, U.K., 2005

(29) N−N values and N=N values from: International tables for X-ray crystallography; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1992; Vol. *C*.

(30) Wiberg, N. In *Lehrbuch der Anorganischen Chemie/Holleman-Wiberg*, 101st ed.; Walter de Gruyter: Berlin, Germany, 1995; p 1842.

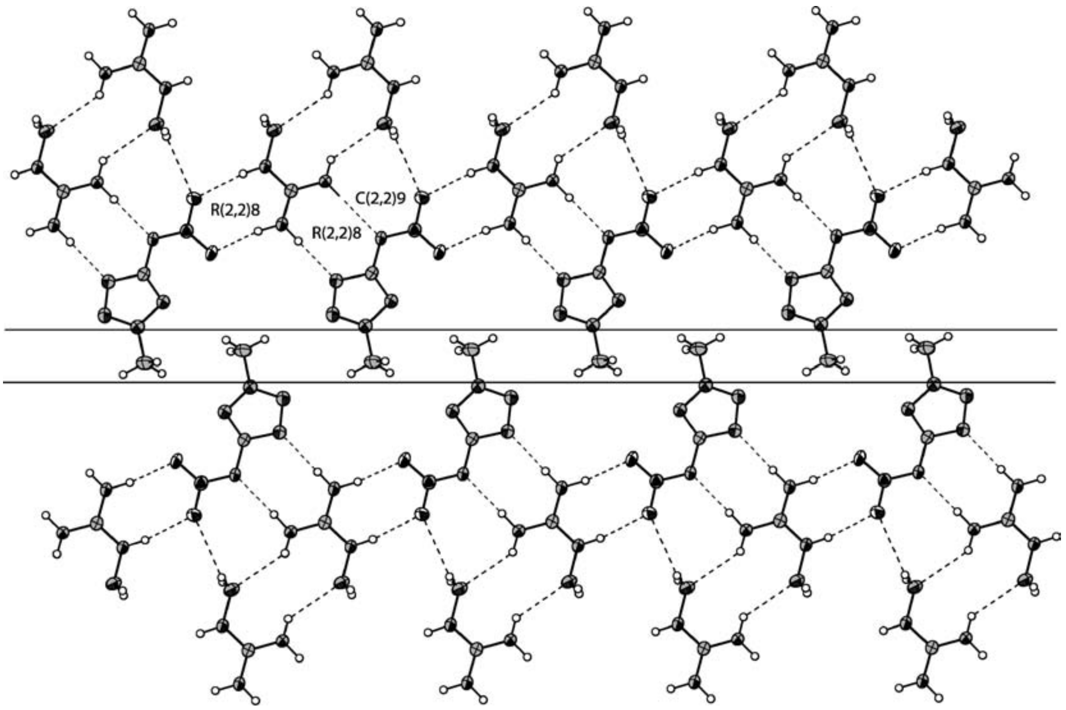

Figure 5. View on the layers in the structure of **3**. A hydrophobic zipper is formed between the lines.

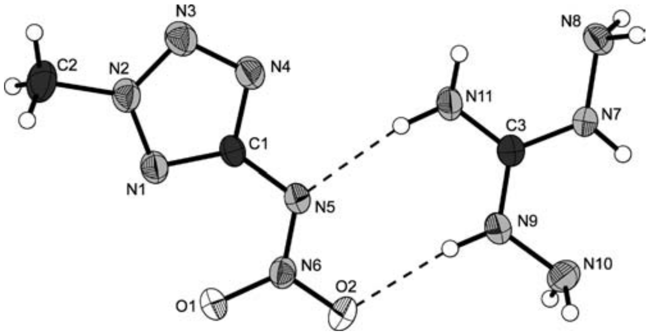

Figure 6. Molecular structure of diaminoguanidinium 2-methyl-5-nitraminotetrazolate (**4**). Thermal ellipsoids represent the 50% probability level.

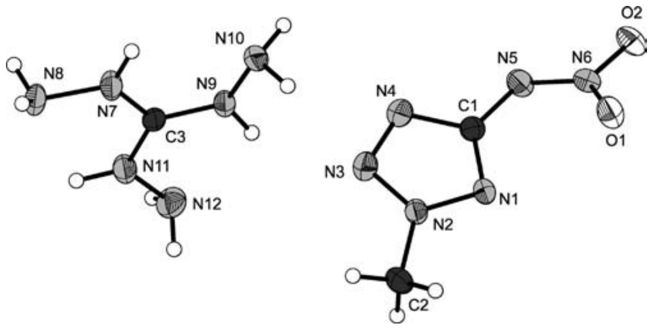

Figure 7. Molecular structure of triaminoguanidinium 2-methyl-5-nitraminotetrazolate (**5**). Thermal ellipsoids represent the 50% probability level.

C1 and N5 are closer to a C−N single bond than to a C=N double bond (1.377(2) Å for **4** to 1.388(2) Å for **3**), which justifies the nomenclature nitraminotetrazolate rather than nitriminotetrazolate. The C−N distances in the cations match the typical values found in literature for guanidinium nitrate[31] and guanidinium chloride,[32] exhibiting a bond order between a single and a double bond. The N−N bond orders of the aminoguanidinium, diaminoguanidinium, and triaminoguanidinium cation are close to a N−N single bond with distances between 1.406(2) Å (**2**) and 1.4191 (17) Å for N9−N10 in **5**. The azidoformamidinium cation is not planar (torsion angle N8−N7−C3−N11 = 16.1(3)°) and angulated (angle N8−N7−C3 = 114.49(15)°), and the bond distances are very similar to those found in azidoformamidinium chloride.[33] The urea moiety in **9** reveals the geometry of urea itself, as it is not protonated but only an adduct, whereas the C−O bond distance is slightly larger (1.225(2) Å) than a classic C=O double bond (1.19 Å)[34] because of a very strong H-bond formed between H5 and O3 (1.57(2) Å).

NMR Spectroscopy. All compounds described were investigated using ^{1}H and ^{13}C NMR. In case of **8**, a ^{15}N NMR (proton coupled) spectrum was recorded additionally. For better comparison, all spectra were measured using d_6-DMSO as solvent, and all chemical shifts are given with respect to TMS (^{1}H, ^{13}C) and $MeNO_2$ (^{15}N), respectively. For the guanidine derivatives **2**−**6**, the cation proton shifts can be found in a range from 4.50 ppm to 8.62 ppm. The proton signals of the hydrazinium and the diaminouronium salt are shifted to 7.10 ppm and 7.60 ppm, respectively, whereas the proton signal of unprotonated urea in **9** is slightly shifted upfield to 5.78 ppm. Additionally, the proton signals of the methyl group in the methylated nitraminotetrazole are observed in a range from 4.16 ppm to 4.36 ppm for all compounds. For the tetrazole moiety, two signals can be observed in the ^{13}C

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(31) Akella, A.; Keszler, D. A. *Acta Crystallogr.* **1994**, *C50*, 1974–1976.

(32) Bryden, J. H. *Acta Crystallogr.* **1957**, *10*, 677–680.

(33) Henke, H.; Barnighausen, H. *Acta Crystallogr.* **1972**, *B28*, 1100.

(34) Wiberg, N. In *Lehrbuch der Anorganischen Chemie/Holleman-Wiberg*, 102nd ed.; Walter de Gruyter: Berlin, Germany, 2007, 2006.

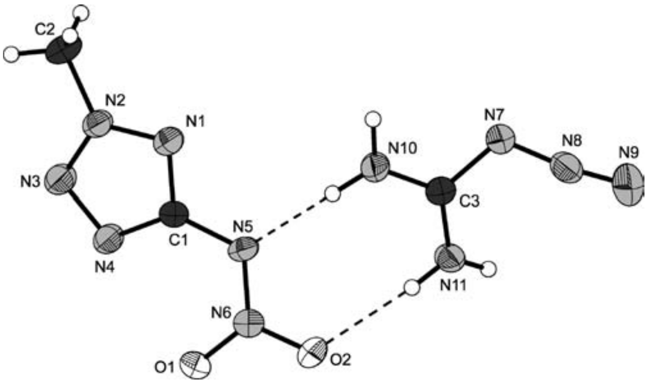

Figure 8. Molecular structure of azidoformamidinium 2-methyl-5-nitramino-tetrazolate (**6**). Thermal ellipsoids represent the 50% probability level.

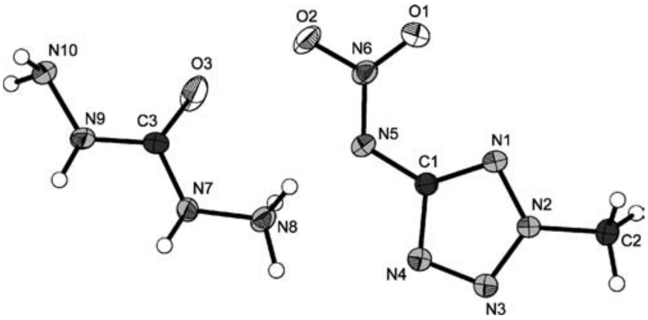

Figure 9. Molecular structure of diaminouronium 2-methyl-5-nitraminotetrazolate (**8**). Thermal ellipsoids represent the 50% probability level.

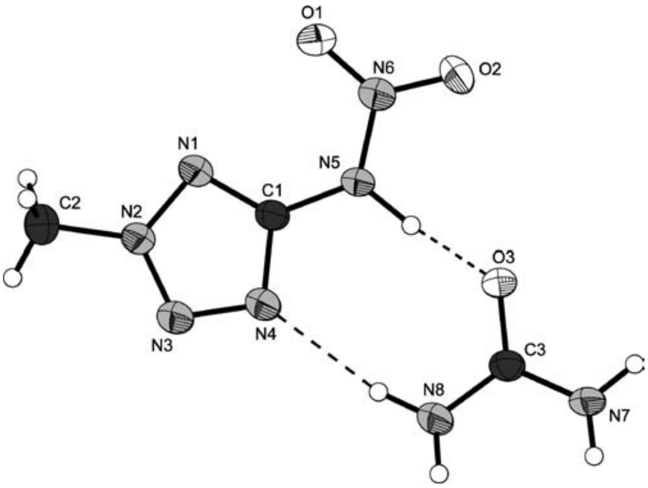

Figure 10. Molecular structure of compound **9**. Thermal ellipsoids represent the 50% probability level.

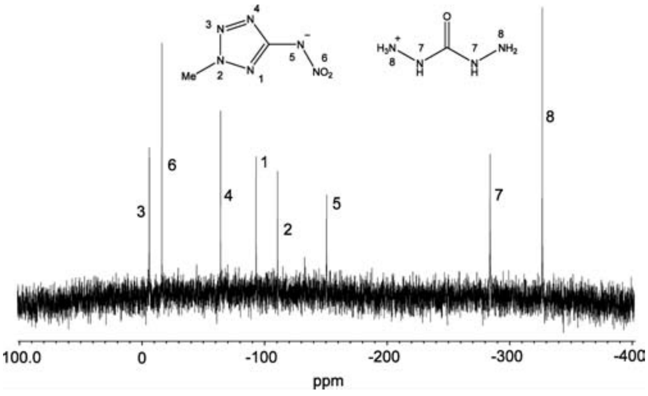

Figure 11. ^{15}N NMR spectrum of **8**: $\delta = -5.8$ (N3, q, $^3J_{NH} = 1.7$ Hz), -16.2 (N6), -64.1 (N4), -93.0 (N1, q, $^3J_{NH} = 1.9$ Hz), -110.5 (N2, q, $^2J_{NH} = 2.2$ Hz), -150.5 (N5), -283.7 (N7), -326.6 (N8).

NMR spectrum whereof the downfield shifted signal of the tetrazole ring carbon atom can reliably be found at 167.8 ppm to 168.8 ppm in the deprotonated species **2**−**8**. For the still protonated 2-methyl-5-nitraminotetrazole in **9**, the signal is found at 160.7 ppm. Deprotonation of the tetrazole ring does not play such an important role for the NMR shift of the methyl group attached to the ring. It can be observed for all species in a range from 39.6 ppm to 40.6 ppm. The comparison of the observed signals in **2**−**9** with the proton and carbon atom signals in 1-methyl-5-nitriminotetrazole and its nitrogen-rich salts allows the conclusion, that alkylation at N2, compared to N1, of the tetrazole moiety in nitrated aminotetrazoles causes a significant downfield shift of about 10 ppm for the ring carbon atom and about 7 ppm for the methyl group attached to it. The same applies to the signals of the methyl protons, which are shifted by about 0.5 ppm to lower field. In the ^{15}N NMR spectrum of **8**, shown in Figure 11, all signals were assigned by analysis of the ^{15}N-^{1}H coupling constants and by comparison with literature.[17,35]

Vibrational Spectroscopy. Also IR and Raman spectroscopy are suitable for the identification of the described nitraminotetrazolate salts. IR and Raman spectra of all compounds were measured, and the absorptions were assigned according to commonly observed values found in literature.[16,36−38] All vibrational spectra are mainly determined by C−H-stretching vibrations of the methyl group attached to the tetrazole ring, N−H-stretching vibrations of the cations, stretching vibrations of the nitro group and characteristic stretching and deformation vibrations of the tetrazole ring. The symmetric and asymmetric N−H-stretching vibrations of the amino groups of the cations are assigned to signals observed in the range from 3238 cm^{-1} up to 3484 cm^{-1}. All of the recorded Raman spectra show a significant, however weak, signal of the symmetric C−H-stretching vibration of the methyl group at 2956 cm^{-1} to 2970 cm^{-1}. For the azidoformamidinium salt **6**, the asymmetric and symmetric stretching vibration of the covalent bonded azido group can be observed at 2185 cm^{-1} and 2121 cm^{-1} additionally. The tetrazole ring system itself exhibits stretching and deformation vibrations that can be detected as a set of signals lying in the range from 1011 cm^{-1} to 1026 cm^{-1}, 1031 cm^{-1} to 1043 cm^{-1}, and 1633 cm^{-1} to 1698 cm^{-1}, the latter being a -C=N-stretching vibration. Another typical vibration observed is the symmetric stretching vibration of the nitro group, which is found to be in the range of 1473 cm^{-1} to 1494 cm^{-1} for the ionic species **2**−**8** and slightly shifted to higher energy (1538 cm^{-1}) for the protonated 2-methyl-5-nitraminotetrazole in **9**.

Differential Scanning Calorimetry (DSC). DSC measurements to determine the melt- and decomposition

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(35) Karaghiosoff, K.; Klapötke, T. M.; Meyer, P.; Piotrowski, H.; Polborn, K.; Weigand, J. J.; Willer, R. L. *J. Org. Chem.* **2006**, *71*, 1295–1305.

(36) Tremblay, M. *Can. J. Chem.* **1965**, *43*, 1154–1157.

(37) Svetlik, J.; Martvon, A.; Lesko *J. Chem. Papers* **1979**, *33*, 521.

(38) Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der Organischen Chemie*, 7th ed., Thieme: Stuttgart, Germany, 2005.

temperatures of **2**−**9** (about 1.5 mg of each energetic material) were performed in covered Al-containers containing a hole (0.1 mm) in the lid for gas release and a nitrogen flow of 20 mL per minute on a Linseis PT 10 DSC[39] calibrated by standard pure indium and zinc at a heating rate of 5 °C min^{-1}. The thermal behavior of all energetic materials investigated herein are displayed as DSC plots in a temperature range from 20 to 400 °C in Figure 12. All temperatures are given as onset temperatures. Since all compounds crystallize without crystal water, the first endothermic step in the recorded DSC curves is not due to dehydration but can be assigned to a melting point. Foremost, the melting point depends on ionic and nonionic attractive forces in the solid state and therefore strongly depends on the number and strength of the hydrogen bonds found in the crystal structures. The lowest melting compounds, which are also characterized by X-ray measurements, are the diaminoguanidinium and the azidoformamidinium salts **6** and **4** (114 °C, 138 °C) with only 7 hydrogen bonds (1 non-classical in **6**) followed by the triaminoguanidinium and the aminoguanidinium salts **5** and **3** (143 °C, 146 °C) having 10 or more hydrogen bonds per unit cell (1 non-classical in **3**). Also the hydrogen bond distances play an important role, which can be seen at the guanidinium salt **2** (176 °C) and the urea adduct **9**, which decomposes at 158 °C before melting. Both exhibit only 8 and 6 hydrogen bonds respectively, 1 non-classical in each compound. In contrast to the compounds discussed above, there are two hydrogen bonds with distances below 2 Å in **2** and one very strong hydrogen bond with a distance of only 1.57 Å in **9**. The diaminouronium salt **8** melts at 131 °C despite having a remarkably high number of hydrogen bonds (13, 1 being non-classical). All hydrogen bonds discussed above and the corresponding bond lengths are summarized in Table 2.

The hydrazinium salt **7** stands out with a very high liquidity range of 135 °C between melting and decomposition point, making it suitable for a possible application as melt-castable explosive. Except from the triaminoguanidinium and the azidoformamidinium salt, which decompose at 188 and 148 °C, respectively, because of the high nitrogen content of the cation and the relative thermal instability of covalent bonded azide groups, all other ionic compounds decompose at temperatures close to or even above 200 °C (188 °C−212 °C). The decomposition of the nonionic urea-adduct **9** takes place in two separate processes, which can be observed at 158 and 190 °C belonging to the decomposition of 2-methyl-5-nitraminotetrazole and urea. Compared to the nitrogen-rich 1-methyl-5-nitriminotetrazolate salts, the melting and especially the decomposition temperatures of the 2-methyl-derivatives are lowered by approximately 10 °C.[16]

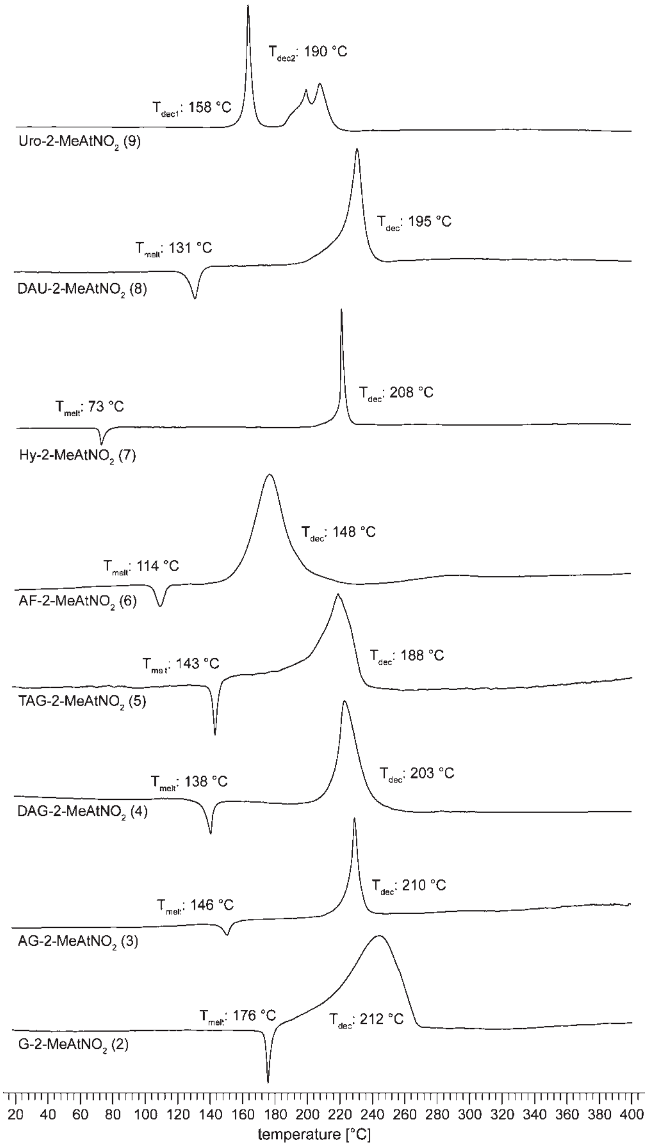

Figure 12. DSC plots (endo down) of compounds **2**−**9** (5 °C min^{-1}). Melting points, T_{onset}: **2**, 176 °C; **3**, 146 °C; **4**, 138 °C; **5**, 143 °C; **6**, 114 °C; **7**, 73 °C; **8**, 131 °C; decomposition temperatures, T_{onset}: **2**, 212 °C; **3**, 210 °C; **4**, 203 °C; **5**, 188 °C; **6**, 148 °C; **7**, 208 °C; **8**, 195 °C; **9**, 158 °C, 190 °C.

Sensitivities. The impact sensitivity tests were carried out according to the STANAG 4489[40] modified instruction[41] using a BAM (Bundesanstalt für Materialforschung) drophammer.[42] The friction sensitivity tests were carried out according to STANAG 4487[43] modified instruction[44] using the BAM friction tester. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods".[45] Additionally all compounds were tested upon the sensitivity toward electrical discharge using the Electric Spark Tester ESD 2010 EN.[46] Beside from the impact sensitivity of **6** (3 J), which has to be classified as very sensitive, the sensitivities of all other compounds **1**−**5** and **7**−**9** are in

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

[40] NATO standardization agreement (STANAG) on explosives, *impact sensitivity tests*, no. 4489, 1st ed., Sept. 17, **1999**.

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

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

[43] NATO standardization agreement (STANAG) on explosive, *friction sensitivity tests*, no. 4487, 1st ed., Aug. 22, **2002**.

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

[45] Impact: Insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J; friction: Insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N a. > 80 N, very sensitive ≤ 80 N, extreme sensitive ≤ 10 N; According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates: not safe for transport.

[46] http://www.ozm.cz.

Table 2. Hydrogen Bonds and Respective Distances

compound	D−H···A	d(H−A) (Å)
2	N7−H7A···N4	2.04(4)
	N7−H7B···O1	2.06(4)
	N8−H8A···O2	1.93(3)
	N8−H8B···O2	1.99(3)
	N9−H9A···O2	2.30(3)
	N9−H9A···N8	2.58(4)
	N9−H9B···N5	2.21(4)
	C2−H2B···O1	2.57(4)
3	N7−H7···O2	2.116(16)
	N8−H8A···N7	2.58(2)
	N8−H8A···O2	2.576(19)
	N8−H8B···O2	2.289(19)
	N9−H9A···N8	2.385(17)
	N9−H9A···N8	2.414(17)
	N9−H9B···N5	2.077(18)
	N10−H10A···O1	1.940(17)
	N10−H10B···N4	2.056(18)
	C2−H2C···O1	2.546(18)
4	N7−H7···N10	2.296(17)
	N8−H8A···O1	2.328(16)
	N8−H8B···N4	2.166(19)
	N9−H9···O2	2.091(17)
	N10−H10B···O1	2.143(17)
	N11−H11A···N8	2.337(18)
	N11−H11B···N5	2.110(19)
5	N7−H7···N10	2.318(15)
	N7−H7···N10	2.45(2)
	N8−H8A···N4	2.290(18)
	N8−H8B···O2	2.16(2)
	N9−H9···N12	2.284(15)
	N9−H9···N3	2.220(16)
	N10−H10A···O2	2.159(15)
	N10−H10B···O1	2.347(15)
5	N10−H10B···N1	2.305(17)
	N11−H11···N8	2.31(2)
	N11−H11···O1	2.195(17)
	N11−H11···O2	2.53(2)
	N12−H12B···O2	2.41(2)
6	N10−H10A···O1	2.092(19)
	N10−H10A···O2	2.48(2)
	N10−H10A···N6	2.623(19)
	N10−H10B···N5	1.92(2)
	N11−H11A···N4	1.92(2)
	N11−H11B···O2	2.12(2)
	C2−H2A···O2	2.59(2)
8	N7−H7···O2	2.24(4)
	N7−H7···O3	2.27(4)
	N8−H8A···O3	2.52(4)
	N8−H8A···N10	1.92(4)
	N8−H8B···O2	1.85(6)
	N8−H8B···N5	2.54(5)
	N8−H8B···N6	2.60(5)
	N8−H8C···N5	2.26(5)
	N9−H9···O2	1.96(4)
	N10−H10A···O1	2.47(4)
	N10−H10B···N4	2.36(3)
	C2−H2A···N1	2.51(3)
	C2−H2B···N3	2.57(3)
	C2−H2C···O1	2.51(4)
9	N5−H5···O3	1.57(2)
	N7−H7A···N3	2.36(2)
	N7−H7B···O3	2.02(2)
	N8−H8A···O1	2.29(2)
	N8−H8B···N4	2.17(2)
	C2−H2C···O1	2.59(2)

the range of 5 to 30 J and therefore have to be classified as sensitive toward impact. The guanidinium salt **2** stands out with a relatively low sensitivity of 30 J. The same classification applies to the friction sensitivities. Again, the azidoformamidinium salt **6** has to be classified as very sensitive with a value of 72 N, whereas the remaining compounds **1**−**5** and **7**−**9** are classified as sensitive having values in a range from 120 to 288 N. Concerning the sensitivities toward electrical discharge, the values for all tested materials **1**−**9** are in the range of 0.1 J−0.5 J, whereas the compounds could not be detonated but started to decompose upon treatment with the specified electrical energy. The explicit sensitivity data can be seen in Tables 3 and 4.

Detonation Parameters. The detonation parameters were calculated using the program EXPLO5 V5.03, as well as with the new version EXPLO5 V5.04.[47] The program is based on the steady-state model of equilibrium detonation and uses Becker−Kistiakowsky−Wilson equation of state (BKW E.O.S) for gaseous detonation products and Cowan−Fickett EOS for solid carbon.[48] 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:[49]

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

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

The calculations were performed using the maximum densities according to the crystal structures. The most promising compound concerning the detonation velocity and pressure discussed here is the diaminouronium salt **8** with values of $V_{\text{det}} = 8864\ \text{ms}^{-1}$ for the detonation velocity and a detonation pressure of $p_{\text{CJ}} = 307$ kbar since the values are in the range of those of commonly used RDX (royal demolition explosive; $p_{\text{CJ}} = 340$ kbar, $V_{\text{det}} = 8882\ \text{m s}^{-1}$). The detonation velocities and pressures of **1**−**6**, **8**, and **9** are slightly lower than those of RDX ranging from $V_{\text{det}} = 7806\ \text{m s}^{-1}$ (**9**) to $V_{\text{det}} = 8864\ \text{m s}^{-1}$ (**8**). Because of their lower nitrogen content and molar amount of gaseous reaction products, compounds **2**−**4**, **6**, and **9** do not reach the levels of **5** and **8** in terms of detonation pressure and velocity. However, the molar amount of gaseous reaction products is subject to only small variations (**2**: 844, **3**: 861, **4**: 876, **5**: 888, **6**: 806, **8**: 853, **9**: 822 L kg^{-1}) which are found in the different detonation temperatures

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(47) (a) Suceska, M. *EXPLO5.V2, Computer program for calculation of detonation parameters*; *Proceedings of 32nd International Annual Conference of ICT*, July 3−6, Karlsruhe, Germany, 2001; pp 110–111. (b) Suceska, M., *Proceedings of 30th International Annual Conference of ICT*, June 29−July 2, Karlsruhe, Germany, 1999; 50/1.

(48) Suceska, M. *Propellants, Explos., Pyrotech.* **1991**, *16*(4), 197–202.

(49) (a) Sućeska, M. *Mater. Sci. Forum* **2004**, *465*−*466*, 325–330. (b) Sućeska, M. *Propellants, Explos., Pyrotech.* **1999**, *24*, 280–285. (c) Hobbs, M. L.; Baer, M. R. *Proceedings of the 10th Symposium* (*International*) *on Detonation*, ONR 33395-12, Boston, MA, July 12−16, 1993; p 409.

Table 3. Explosive and Detonation Parameters of **2**−**5**

	G_2MNAT(**2**)	AG_2MNAT(**3**)	DAG_2MNAT(**4**)	TAG_2MNAT(**5**)
formula	$C_3H_9N_9O_2$	$C_3H_{10}N_{10}O_2$	$C_3H_{11}N_{11}O_2$	$C_3H_{12}N_{12}O_2$
FW/g mol^{-1}	203.17	218.23	233.11	248.27
IS/J	30	6	10	6
FS/N	192	120	160	120
ESD/J	0.2	0.2	0.16	0.18
N/%	62.1	64.2	66.1	67.72
Ω/%	−66.9	−66.0	−65.2	−64.5
$T_{\mathrm{Dec.}}$/°C	212	210	203	188
ρ/g cm^{-3}	1.632	1.608	1.567	1.573
$\Delta_f H_m°$/kJ mol^{-1}	255	366	479	587
$\Delta_f U°$/kJ kg^{-1}	1378	1801	2182	2496
EXPLO5 values: V5.03 (V5.04)				
$-\Delta_{Ex}U°$/kJ kg^{-1}	4148 (4069)	4454 (4367)	4733 (4640)	4959 (4856)
T_{det}/K	2907 (2799)	3039 (2910)	3170 (3014)	3249 (3120)
p_{CJ}/kbar	250 (244)	260 (249)	262 (247)	277 (259)
V_{det}/m s^{-1}	8300 (8059)	8495 (8169)	8603 (8184)	8827 (8354)
V_o/L kg^{-1}	844 (812)	861 (825)	876 (837)	888 (847)

Table 4. Explosive and Detonation Parameters of **6**, **8**, and **9** Compared to RDX

	AF_2MNAT(**6**)	DAU_2MNAT(**8**)	Uro_2MNAT(**9**)	**RDX**
formula	$C_3H_7N_{11}O_2$	$C_3H_{10}N_{10}O_3$	$C_3H_8N_8O_3$	$C_3H_6N_6O_7$
FW/g mol^{-1}	229.16	234.18	204.19	222.12
IS/J	3	5	10	7.5
FS/N	72	168	288	120
ESD/J	0.2	0.50	0.2	0.1−0.2
N/%	67.23	59.81	54.89	37.8
Ω/%	−52.36	−54.7	−54.9	−21.6
$T_{\mathrm{Dec.}}$/°C	148	195	158	210
ρ/g cm^{-3}	1.571	1.73	1.591	1.80
$\Delta_f H_m°$/kJ mol^{-1}	687	345	120	70
$\Delta_f U°$/kJ kg^{-1}	3105	1596	701	417
EXPLO5 values: V5.03 (V5.04)				
$-\Delta_{Ex}U°$/kJ kg^{-1}	5381 (5355)	4948 (4892)	4370 (4353)	6038 (6125)
T_{det}/K	3887 (3700)	3332 (3199)	3179 (3050)	4368 (4236)
p_{CJ}/kbar	258 (252)	307 (305)	224 (227)	341 (349)
V_{det}/m s^{-1}	8290 (8150)	8864 (8730)	7806 (7800)	8906 (8748)
V_o/L kg^{-1}	806 (785)	853 (831)	822 (806)	793 (739)

(**2**: 2907, **3**: 3039, **4**: 3170, **5**: 3249, **6**: 3887, **8**: 3332, **9**: 3179 K).

Compared to the nitrogen-rich salts of the 1-methyl-5-nitriminotetrazole, which recently were synthesized in our research group,[16] the detonation velocities and pressures of the 2-methyl-derivatives are slightly higher with larger differences for the guanidinium and aminoguanidinium salts and smaller differences for the diaminoguanidinium and triaminoguanidinium salts. Also the heats of explosion and the explosion temperatures are higher than those of the 1-methyl-derivatives. The molar amount of gaseous products, however, is nearly in the same range because of the same molecular weights.

Conclusions

From the experimental study of N-rich 2-methyl-5-nitraminotetrazolate salts the following conclusions can be drawn:

2-Methyl-5-nitraminotetrazole can be easily deprotonated in aqueous solution using alkali hydroxides forming the corresponding alkali salts in nearly quantitative yields. These form the silver salt by the reaction with $AgNO_3$ in aqueous solutions.

The nitrogen-rich 2-methyl-5-nitraminotetrazolate salts **2**−**9** can easily be obtained via Brønstedt acid−base reactions using the guanidinium carbonates or metathesis reactions using silver 2-methyl-5-nitraminotetrazolate and the guanidinium chlorides in aqueous solution with high yields and good purity. The triaminoguanidinium salt **5** was synthesized via the hydrazinolysis of the aminoguanidinium salt **3**. The products can be recrystallized from water/ethanol mixtures resulting in colorless crystals.

The crystal structures of **2**−**6**, **8**, and **9** were determined using low temperature single crystal diffraction.

A comprehensive characterization of the physicochemical properties and sensitivities of **2**−**9** is given. Although the salts are energetic materials with high nitrogen contents, they show good stabilities toward friction and impact and a good thermal stability.

Promising detonation parameters were calculated for **2**−**9** compared to common explosives like TNT and RDX. The performance (calculated values: $p_{\mathrm{CJ}} = 307$ kbar; $V_{\mathrm{det}} = 8864$ m s^{-1}) of diaminouronium 2-methyl-5-nitraminotetrazolate (**8**) qualifies it for further investigations concerning military applications.

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Program (SERDP), and the Office of Naval Research (ONR Global, title: “Synthesis and Characterization of New High Energy Dense Oxidizers (HEDO) - NICOP Effort ”) under contract nos. W911NF-09-2-0018 (ARL), W911NF-09-1-0120 (ARDEC), W011NF-09-1-0056 (ARDEC), and 10 WPSEED01-002/WP-1765 (SERDP) is gratefully acknowledged. The authors acknowledge collaborations with Dr. Mila Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr. Muhamed Sucesca (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation and propulsion parameters of novel explosives. We are indebted to and thank Drs. Betsy M. Rice and Brad Forch (ARL, Aberdeen, Proving Ground, MD) and Mr. Gary Chen (ARDEC, Picatinny Arsenal, NJ) for many helpful and inspired discussions and support of our work.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.