

Dihydrazinium Nitrates Derived from Malonic and Iminodiacetic Acid

 Thomas M. Klapötke,^{*,[a]} Burkhard Krumm,^[a] and Thomas Reith^[a]

Abstract: Several hydrazinium nitrates were synthesized on the basis of malonic acid and iminodiacetic acid. The reaction of the corresponding ethyl esters with hydrazine hydrate yielded the dihydrazides in good-to-high yields and high purity. Subsequent protonation with diluted nitric acid or hydrochloric acid resulted in the corresponding nitrate and chloride salts. The neutral compounds and their salts

were fully characterized, including multinuclear NMR spectroscopy, vibrational analysis, X-ray diffraction, differential thermal analysis and elemental analysis. The energies of formation were calculated with the GAUSSIAN program package and the detonation parameters were predicted using the EXPLO5 computer code.

Keywords: Nitrates • Hydrazides • Explosives • Crystal structures • Chlorides

1 Introduction

The ongoing research for safe and environmentally benign energetic materials provides numerous approaches to find replacements for currently used explosives [1]. The development of various energetic salts has shown great potential in all fields of energetic materials, such as primary explosives (K₂DNABT) [2], secondary explosives (TKX-50) [3] and high energy dense oxidizers (ADN) [4] (Figure 1).

The recent synthesis and characterization of the nitrate and dinitrate salts of diaminourea [5] and oxalyl dihydrazide [6] (Figure 2) prompted us for further studies on organic hydrazinium nitrates, also because of their scalable and cost-efficient synthesis in combination with good performance and toxicity values.

The mononitrates of diaminourea and oxalyl dihydrazide are much more stable in terms of thermal decomposition and external stimuli like impact and friction in comparison to the corresponding dinitrates. Therefore, the mononitrates are competitors in the field of insensitive munitions, whereas the positive oxygen balance of the dinitrates distinguishes them as possible high energy dense oxidizers (HEDOs) to replace ammonium perchlorate [5–6].

In order to synthesize thermally stable dinitrates, spacers were introduced to separate the hydrazide groups. An introduction of oxygen would lead to acid anhydride type compounds, which are highly sensitive to hydrolysis [7]. Furthermore, the incorporation of nitrogen as spacer results in iminodicarbonyl dihydrazide and hydrazinedicarbonyl dihydrazide [8]. The hydrazides of both molecules are known, but undergo a fast acid-catalyzed cyclization to urazole and urazine, respectively, which prevents the formation of nitrate salts [8b]. As a consequence, carbon based spacers are introduced between the hydrazide units leading to malonic acid derivatives. Additionally, 2-azapropylene units as a

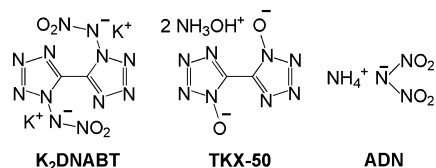


Figure 1. Potassium 1,1'-dinitramino-5,5'-bistetrazole (K₂DNABT), dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50) and ammonium dinitramide (ADN).

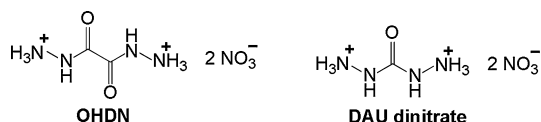


Figure 2. Oxalyl dihydrazinium dinitrate (OHDN) and diaminourea (DAU) dinitrate.

combination of the latter forming iminodiacetic acid derivatives, were investigated.

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2 Experimental Section

General: Solvents were dried and purified with standard methods. Diethylmalonate and iminodiacetic (i.e. aminodiacetic) acid are commercially available and used without further purification. Raman spectra were recorded in glass tubes with a Bruker MultiRAM FT-Raman spectrometer with a Klaastech DENICAFC LC-3/40 laser (Nd:YAG, 1064 nm, up to 1000 mW) in the range of 4000–400 cm^{-1} . Relative intensity is given in percent. IR spectra were recorded with a Perkin-Elmer Spectrum BX-FTIR spectrometer coupled with a Smiths ATR DuraSample IRII device. Measurements were recorded in the range of 4000–650 cm^{-1} . All Raman and IR spectra were measured at ambient temperature. NMR spectra were recorded with JEOL Eclipse and Bruker TR 400 MHz spectrometers at 25 °C. Chemical shifts were determined in relation to external standards Me_4Si (^1H , 399.8 MHz); (^{13}C , 100.5 MHz); MeNO_2 (^{14}N , 28.9 MHz). Elemental analyses (CHN) were obtained with a Vario EL Elemental Analyzer.

The sensitivity data were acquired by measurements with a BAM drophammer and a BAM friction tester [1]. Melting and decomposition points were determined by differential thermal calorimetry (DTA) using a OZM Research DTA 552-Ex instrument at a heating rate of 5 °C min^{-1} . Measurements were performed in open glass vessels against a reference material up to 400 °C.

The crystal structure data were obtained using an Oxford Xcalibur CCD Diffractometer with a KappaCCD detector at low temperature (143 K). Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) was delivered by a Spellman generator (voltage 50 kV, current 40 mA). Data collection and reduction were performed using the CRYSLIS CCD [9] and CRYSLIS RED [10] software, respectively. The structures were solved by SIR92/SIR97 [11] (direct methods) and refined using the SHELX-97 [12] software, both implemented in the program package WinGX22 [13]. Finally, all structures were checked using the PLATON software [14]. Structures displayed with ORTEP plots are drawn with thermal ellipsoids at 50% probability level.

The theoretical calculations were achieved by using the Gaussian 09 program package [15] and were visualized by using GaussView 5.08 [16]. Optimizations and frequency analyses were performed at the B3LYP level of theory (Becke's B3 three parameter hybrid functional by using the LYP correlation functional) with a cc-pVDZ basis set. After correcting the optimized structures with zero-point vibrational energies, the enthalpies and free energies were calculated on the CBS-4M (complete basis set) level of theory [17]. The detonation parameters were obtained by using the EXPLO5 (V6.03) program package [18].

CAUTION! The nitrate salts **2a**, **4a** and **6a**, and the nitramines **5** and **6** are energetic materials and show sensitivities in the range of primary and secondary explosives! They should be handled with caution during synthesis or manipulation and additional protective equipment (leather jacket,

face shield, ear protection, Kevlar gloves) is strongly recommended.

Malonyl dihydrazide (2): The dihydrazide was synthesized according to literature [19]: Diethylmalonate (**1**, 24.0 g, 150 mmol) was dissolved in ethanol (220 mL) and hydrazine monohydrate (18.0 mL, 371 mmol) was added. The solution was refluxed at 90 °C for 4 h. On cooling a white crystalline solid precipitated. After filtration and washings with ethanol malonyl dihydrazide (13.6 g, 69%) was obtained as pure product.

^1H NMR ($\text{DMSO-}D_6$): $\delta = 9.1$ (br, 2H, NH), 4.2 (br, 4H, NH_2), 2.89 (s, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO-}D_6$): $\delta = 166.0$ (CO), 40.1 (CH_2).

Malonyl dihydrazinium dinitrate (2a): 2 M nitric acid (10 mL, 20.0 mmol) was added to a suspension of malonyl dihydrazide (**2**, 1.3 g, 10.0 mmol) in water (5 mL) at room temperature. After 10 minutes the remaining solvent was removed at reduced pressure and the resulting colorless product was dried under high vacuum. Malonyl dihydrazinium dinitrate (**2a**, 1.3 g, 99%) was obtained quantitatively in high purity.

^1H NMR ($\text{DMSO-}D_6$): $\delta = 11.2$ (br, 2H, NH), 9.7 (br, 6H, NH_3), 3.35 (s, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO-}D_6$): $\delta = 165.0$ (CO), 39.1 (CH_2); ^{14}N NMR ($\text{DMSO-}D_6$): $\delta = -4$ (NO_3^-). Raman (800 mW): 3005 (8), 2964 (11), 1858 (2), 1693 (15), 1592 (8), 1445 (5), 1317 (8), 1194 (8), 1104 (10), 1048 (100), 958 (16), 910 (6), 848 (3), 719 (9), 582 (7), 448 (4), 390 (6) cm^{-1} . IR: 3178 (m), 2999.0 (m), 2686 (m), 1684 (m), 1582 (s), 1532 (m), 1296 (vs), 1185 (s), 1040 (m), 958 (m), 848 (w), 821 (m), 664 (w), 616 (w), 569 (m), 481 (w), 449 (w) cm^{-1} . $\text{C}_3\text{H}_{10}\text{N}_6\text{O}_8$ (258.15 g mol^{-1}): C 13.96, H 3.90, N 32.56; found C 13.68, H 4.17, N 31.08. Dec. point: 266 °C. Sensitivities (BAM): impact 20 J; friction 324 N; ESD > 1.5 J (grain size < 100 μm).

Malonyl dihydrazinium dichloride (2b): Malonyl dihydrazide (**2**, 3.0 g, 22.7 mmol) was dissolved in ethanol (5 mL) and heated to the reflux point. Water was added until the starting material dissolved. Concentrated hydrochloric acid was added dropwise to the hot solution in excess and the dichloride **2b** (4.6 g, 99%) was obtained as a colorless crystalline solid in quantitative yield and high purity after filtration.

^1H NMR ($\text{DMSO-}D_6$): $\delta = 11.4$ (br, 2H, NH), 10.6 (br, 6H, NH_3), 3.42 (s, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO-}D_6$): $\delta = 164.8$ (CO), 39.0 (CH_2); Raman (800 mW): 3010 (3), 3088 (5), 3065 (3), 3047 (6), 3008 (4), 2978 (35), 2922 (100), 2895 (3), 2882 (3), 2852 (3), 2846 (15), 2830 (3), 2766 (3), 2673 (28), 2609 (2), 2599 (2), 2569 (4), 2569 (3), 1959 (8), 1695 (81), 1670 (6), 1589 (3), 1573 (8), 1523 (16), 1494 (12), 1286 (8), 1228 (48), 1152 (58), 1088 (28), 1076 (8), 953 (92), 927 (7), 694 (34), 586 (10), 492 (3), 481 (3), 462 (3), 447 (2), 415 (21), 386 (13), 333 (2), 292 (6), 275 (13), 230 (25) cm^{-1} . IR: 3265 (w), 2843 (s), 2660 (vs), 1954 (w), 1566 (m), 1696 (vs), 1666 (m), 1582 (m), 1519 (vs), 1491 (s), 1425 (w), 1376 (s), 1284 (w), 1219 (m), 1148 (m), 1074 (m), 953 (w), 925 (w), 803 (w) cm^{-1} . $\text{C}_3\text{H}_{10}\text{Cl}_2\text{N}_4\text{O}_2$ (205.04 g mol^{-1}): C 17.57, H 4.92, N 27.32; found C 17.5, H 4.76, N 27.34. T_{melt} : 182 °C, Dec. point: 195 °C

Aminodiacetic acid diethylester (3): The ester was synthesized according to literature [20]: Concentrated sulfuric acid (20 mL) was added dropwise to a solution of iminodiacetic acid (aminodiacetic acid, 26.6 g, 200 mmol) in dry ethanol (300 mL). The solution was refluxed at 90 °C for 24 h. After cooling, ethanol was removed under reduced pressure and the remaining aqueous phase was diluted with water (100 mL) and neutralized with sodium bicarbonate. The solution was extracted three times with diethyl ether (50 mL) and the combined organic phases were washed with water (100 mL) and a saturated sodium chloride solution (100 mL). The organic solvent was removed under reduced pressure and aminodiacetic acid diethylester (6.7 g, 18%) was obtained as a colorless oil.

^1H NMR (Acetone- D_6): $\delta = 4.13$ (q, 4H, $^3J(\text{H}, \text{H}) = 7.2$ Hz, CH_2CH_3), 3.41 (s, 4H, CH_2), 1.22 (t, 6H, $^3J(\text{H}, \text{H}) = 7.2$ Hz, CH_3); $^{13}\text{C}\{\text{H}\}$ NMR (Acetone- D_6): $\delta = 172.4$ (CO), 60.9 (CH_2), 50.4 (CH_3), 14.5 (CH_3).

Aminodiacetyl dihydrazide (4) [21]: Hydrazine monohydrate (3.0 g, 60 mmol) was dissolved in a solvent mixture of methanol (7 mL) and diethyl ether (7 mL). Aminodiacetic acid diethylester (3, 3.74 g, 19.8 mmol) was added dropwise at -10°C . The reaction mixture was stirred at -10°C for 2 h and a colorless crystalline precipitate was formed. After filtration the product was washed with diethyl ether and aminodiacetyl dihydrazide (2.0 g, 63%) was obtained as a pure compound.

^1H NMR (DMSO- D_6): $\delta = 9.06$ (s, 2H, NH), 4.2 (br, 4H, NH_2), 3.06 (s, 4H, CH_2); $^{13}\text{C}\{\text{H}\}$ NMR (DMSO- D_6): $\delta = 168.9$ (CO), 51.0 (CH_2). Raman (800 mW): 3341 (10), 3310 (18), 3277 (17), 3264 (15), 3230 (13), 3121 (24), 2947 (23), 2919 (36), 2893 (35), 2867 (16), 2839 (25), 1670 (16), 1634 (33), 1438 (22), 1427 (45), 1377 (27), 1342 (18), 1318 (17), 1305 (15), 1280 (40), 1252 (100), 1215 (21), 1172 (43), 1135 (16), 1092 (13), 1014 (16), 951 (30), 933 (28), 915 (48), 694 (20), 607 (12), 580 (26), 534 (12), 487 (24), 448 (23), 385 (30), 363 (15), 326 (16), 295 (17), 252 (18) cm^{-1} . IR: 3340 (w), 3311 (m), 3275 (m), 3252 (m), 3116 (m), 3004 (w), 2840 (m), 2199 (w), 2128 (w), 1670 (s), 1629 (s), 1586 (vs), 1508 (m), 1481 (m), 1439 (m), 1426 (m), 1378 (w), 1341 (w), 1303 (m), 1283 (m), 1251 (m), 1214 (w), 1180 (w), 1009 (s), 968 (m), 944 (s), 932 (s), 911 (m), 824 (s), 760 (s), 723 (s), 694 (m) cm^{-1} . $\text{C}_4\text{H}_{11}\text{N}_5\text{O}_2$ (161.16 g mol^{-1}): C 29.81, H 6.88, N 43.46; found C 29.89, H 6.61, N 43.44. T_{melt} : 124 °C, Dec. point: 216 °C. Sensitivities (BAM): impact > 40 J; friction > 360 N; ESD > 1.5 J (grain size < 100 μm).

Ammoniumdiacetyl dihydrazinium trinitrate monohydrate (4a): Aminodiacetyl dihydrazide (4, 1.0 g, 6.2 mmol) was dissolved in a small amount of water (2 mL) and diluted nitric acid (60%, 0.63 mL, 20.5 mmol) was added dropwise at -10°C . After 30 minutes, the solvent was removed under reduced pressure as cold as possible. The crude product was washed with methanol and dried again under reduced pressure. This procedure may be repeated until the pure product is obtained. Ammoniumdiacetyl di-

hydrazinium trinitrate (0.6 g, 42%) was isolated as colorless crystalline compound.

^1H NMR (DMSO- D_6): $\delta = 12-9$ (br, 10H, NH, NH_2 , NH_3), 3.99 (s, 4H, CH_2); $^{13}\text{C}\{\text{H}\}$ NMR (DMSO- D_6): $\delta = 164.6$ (CO), 46.0 (CH_2); ^{14}N NMR (DMSO- D_6): $\delta = -4$ (NO_3^-). Raman (800 mW): 2967 (17), 1716 (9), 1587 (7), 1437 (8), 1202 (6), 1103 (9), 1047 (100), 950 (8), 724 (11), 442 (5) cm^{-1} . IR: 2972 (m), 2686 (m), 2126 (w), 1951 (w), 1709 (m), 1539 (m), 1278 (s), 1101 (m), 1033 (s), 926 (m), 852 (m), 819 (s), 729 (m) cm^{-1} . $\text{C}_4\text{H}_{14}\text{N}_8\text{O}_{11} \cdot \text{H}_2\text{O}$ (368.22 g mol^{-1}): C 13.05, H 4.38, N 30.43; found C 13.06, H 4.17, N 29.21. Dec. point: 160 °C. Sensitivities (BAM): impact 10 J; friction 80 N; ESD 0.4 J (grain size < 100 μm).

Ammoniumdiacetyl dihydrazinium trichloride (4b) [21]: Aminodiacetyl dihydrazide (4, 1.0 g, 6.2 mmol) was dissolved in a small amount of water (2 mL) and concentrated hydrochloric acid (0.63 mL, 20.5 mmol) was added dropwise at -10°C . After 30 minutes, the solvent was removed under reduced pressure as cold as possible. The crude product was washed with methanol and dried again under reduced pressure. This procedure may be repeated until the pure product is obtained. Ammoniumdiacetyl dihydrazinium trichloride (1.4 g, 96%) was isolated as colorless crystalline compound.

^1H NMR (DMSO- D_6): $\delta = 13-9$ (br, 10H, NH, NH_2 , NH_3), 3.98 (s, 4H, CH_2); $^{13}\text{C}\{\text{H}\}$ NMR (DMSO- D_6): $\delta = 164.4$ (CO), 45.9 (CH_2). Raman (800 mW): 2949 (100), 1858 (18), 1709 (47), 1520 (25), 1432 (34), 1192 (32), 1170 (26), 1099 (34), 947 (38), 552 (17), 489 (28), 437 (28) cm^{-1} . IR: 4070 (w), 2847 (s), 2642 (s), 2366 (m), 2342 (m), 2184 (m), 1974 (w), 1698 (vs), 1507 (s), 1496 (s), 1434 (s), 1418 (s), 1378 (m), 1348 (s), 1285 (m), 1202 (s), 1102 (m), 1022 (m), 925 (m), 830 (m) cm^{-1} . $\text{C}_4\text{H}_{14}\text{Cl}_3\text{N}_5\text{O}_2$ (270.54 g mol^{-1}): C 17.76, H 5.22, N 25.89; found C 17.55, H 5.63, N 25.01. T_{melt} : 139 °C, Dec. point: 201 °C. Sensitivities (BAM): impact > 40 J; friction > 360 N; ESD 0.6 J (grain size < 100 μm).

Nitraminodiacetic acid diethylester (5): To a solution of aminodiacetic acid diethylester (3, 2.1 g, 11.3 mmol) in acetic anhydride (10 mL), concentrated nitric acid (7.5 mL) was added dropwise at -10°C . The solution was stirred for 2 h at -10°C and another 2 h at room temperature. The reaction mixture was poured on ice (150 mL) and the formed precipitate was filtered and washed with cold water. The yellowish powder turned colorless upon drying on air and nitraminodiacetic acid diethylester (2.5 g, 96%) was obtained.

^1H NMR (Acetone- D_6): $\delta = 4.69$ (s, 4H, CH_2), 4.21 (q, 4H, $^3J(\text{H}, \text{H}) = 7.1$ Hz, CH_2CH_3), 1.25 (t, 6H, $^3J(\text{H}, \text{H}) = 7.1$ Hz, CH_3); $^{13}\text{C}\{\text{H}\}$ NMR (Acetone- D_6): $\delta = 167.6$ (CO), 62.1 (CH_2), 54.0 (CH_2), 14.4 (CH_3); ^{14}N NMR (Acetone- D_6): $\delta = -30$ (NO_2). Raman (800 mW): 3228 (3), 3055 (5), 2991 (52), 2977 (48), 2967 (56), 2939 (56), 2875 (14), 2754 (4), 2724 (4), 2544 (9), 1859 (5), 1757 (7), 1744 (19), 1528 (6), 1457 (21), 1445 (17), 1397 (7), 1378 (14), 1364 (9), 1330 (8), 1306 (18), 1295 (30), 1171 (5), 1125 (16), 1094 (15), 1018 (7), 967 (7), 925 (7), 893 (100), 868 (8), 841 (9), 805 (7), 700 (6), 668 (8), 472 (6), 444

(10), 426 (17), 400 (6), 355 (7), 334 (8), 266 (5) cm^{-1} . IR: 4060 (w), 2987 (w), 2940 (w), 2904 (w), 2838 (w), 2346 (w), 2208 (w), 2173 (w), 2122 (w), 2096 (w), 2053 (w), 1990 (w), 1928 (w), 1838 (w), 1744 (s), 1705 (w), 1521 (m), 1465 (w), 1453 (m), 1405 (m), 1377 (m), 1328 (m), 1297 (m), 1225 (m), 1203 (vs), 1168 (m), 1123 (w), 1094 (m), 1014 (s), 966 (m), 958 (m), 915 (w), 866 (w), 804 (w), 764 (w), 725 (m), 700 (w), 657 (m) cm^{-1} . $\text{C}_8\text{H}_{14}\text{N}_2\text{O}_6$ (234.21 g mol^{-1}): C 41.03, H 6.03, N 11.96; found C 41.16, H 5.94, N 11.99. T_{melt} : 58 °C. Dec. point: 233 °C. Sensitivities (BAM): impact > 40 J; friction > 360 N; ESD > 1.5 J (grain size < 100 μm).

Nitraminodiacetyl dihydrazide (6): Hydrazine monohydrate (5.0 g, 100 mmol) was dissolved in a solvent mixture of methanol (15 mL) and diethyl ether (15 mL). Nitraminodiacetic acid diethylester (**5**, 5.8 g, 25 mmol) was added dropwise at -10°C . The reaction mixture was stirred at -10°C for 2 h and a colorless crystalline precipitate was formed. After filtration the product was washed with diethyl ether and nitraminodiacetyl dihydrazide (3.9 g, 75%) was obtained as a colorless solid.

^1H NMR (D_2O): $\delta = 4.56$ (s, 4H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (D_2O): $\delta = 167.8$ (CO), 54.1 (CH_2); ^{14}N NMR (D_2O): $\delta = -30$ (NO_2). Raman (800 mW): 3353 (10), 3282 (14), 3239 (8), 3200 (16), 3005 (15), 2986 (18), 2949 (35), 1672 (12), 1644 (19), 1553 (13), 1512 (13), 1441 (15), 1413 (20), 1379 (15), 1337 (50), 1318 (39), 1288 (51), 1256 (25), 1207 (11), 1152 (22), 1127 (40), 1110 (39), 1006 (28), 955 (58), 933 (28), 873 (100), 743 (11), 699 (10), 670 (19), 649 (33), 569 (17), 454 (27), 408 (51), 387 (32), 340 (33), 274 (21), 241 (22) cm^{-1} . IR: 3352 (w), 3215 (m), 3004 (m), 1680 (s), 1611 (m), 1550 (s), 1510 (s), 1440 (s), 1408 (m), 1377 (s), 1338 (s), 1285 (s), 1251 (vs), 1100 (s), 994 (s), 952 (vs), 903 (s), 786 (s), 740 (vs), 699 (s) cm^{-1} . $\text{C}_4\text{H}_{10}\text{N}_6\text{O}_4$ (206.16 g mol^{-1}): C 23.30, H 4.89, N 40.76; found C 23.27, H 5.02, N 40.72. Dec. point: 130 °C. Sensitivities (BAM): impact 15 J; friction > 360 N; ESD 1.0 J (grain size < 100 μm).

Nitraminodiacetyl dihydrazinium dinitrate (6a): Nitraminodiacetyl dihydrazide (**6**, 1.0 g, 3.88 mmol) was dissolved in a small amount of water (2 mL) and diluted nitric acid (60%, 0.6 mL, 7.7 mmol) was added dropwise at -10°C . After 30 minutes, the solvent was removed under reduced pressure as cold as possible. The crude product was washed with methanol and dried again under reduced pressure. This procedure may be repeated until the pure product is obtained. Nitraminodiacetyl dihydrazinium dinitrate (0.7 g, 85%) was isolated as colorless compound.

^1H NMR ($\text{DMSO}-d_6$): $\delta = 11.2$ (br, 2H, NH), 11–8.5 (br, 6H, NH_3), 4.68 (s, 4H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$): $\delta = 165.6$ (CO), 53.4 (CH_2); ^{14}N NMR ($\text{DMSO}-d_6$): $\delta = -5$ (NO_3^-), -29 (NO_2). Raman (800 mW): 3000 (14), 2963 (21), 1700 (17), 1601 (9), 1541 (10), 1443 (9), 1409 (10); 1334 (12), 1289 (19), 1203 (10), 1120 (11), 1087 (12), 1048 (100), 958 (12), 935 (20), 880 (30), 728 (14), 668 (8), 446 (13), 364 (12) cm^{-1} . IR: 4337 (w), 3614 (w), 2996 (m), 2706 (w), 2359 (w), 1961 (w), 1698 (m), 1521 (m), 1285 (s), 1183 (s), 1039 (m), 952 (m), 877 (m), 822 (m), 764 (m), 720 (m) cm^{-1} . $\text{C}_4\text{H}_{12}\text{N}_8\text{O}_{10}$ (332.18 g mol^{-1}): C 14.46, H 3.64, N 33.73; found C 14.74, H 3.90, N 33.58. Dec.

point: 131 °C. Sensitivities (BAM): impact 10 J; friction 192 N; ESD 0.4 J (grain size < 100 μm).

Nitraminodiacetyl dihydrazinium dichloride (6b): Nitraminodiacetyl dihydrazide (**6**, 1.0 g, 4.85 mmol) was dissolved in a small amount of water (2 mL) and concentrated hydrochloric acid (0.87 mL, 10.2 mmol) was added dropwise at -10°C . After 30 minutes, the solvent was removed under reduced pressure as cold as possible. The crude product was washed with methanol and dried again under reduced pressure. This procedure may be repeated until the pure product is obtained. Nitraminodiacetyl dihydrazinium dichloride (1.1 g, 73%) was isolated as colorless crystalline compound.

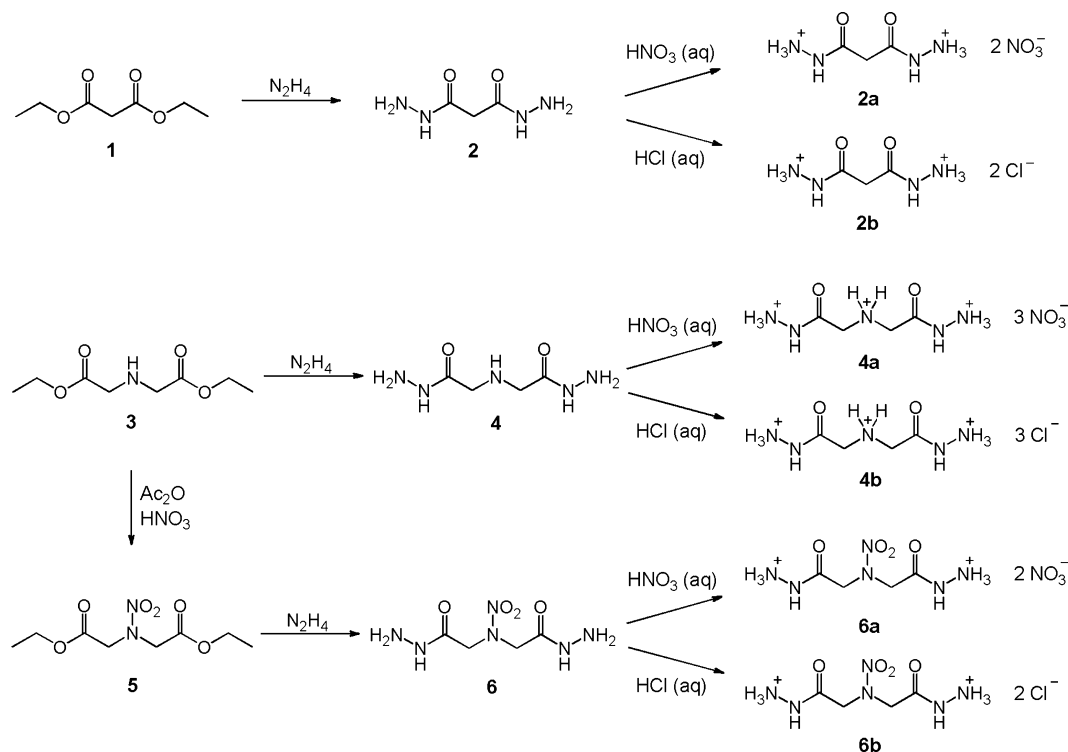
^1H NMR ($\text{DMSO}-d_6$): $\delta = 11.6$ (br, 2H, NH), 11.5–10 (br, 6H, NH_3), 4.71 (s, 4H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$): $\delta = 165.5$ (CO), 53.5 (CH_2); ^{14}N NMR ($\text{DMSO}-d_6$): $\delta = -29$ (NO_2). Raman (800 mW): 2989 (64), 2949 (70), 2904 (45), 2630 (16), 1786 (11), 1720 (82), 1559 (21), 1530 (23), 1481 (25), 1460 (25), 1408 (20), 1390 (41), 1329 (18), 1308 (25), 1288 (36), 1230 (31), 1178 (42), 1168 (37), 1141 (23), 1101 (12), 1085 (26), 959 (31), 935 (53), 887 (100), 669 (27), 574 (11), 492 (16), 483 (14), 433 (20), 416 (20), 402 (21), 308 (30) cm^{-1} . IR: 4077 (w), 3168 (m), 2988 (m), 2834 (m), 2729 (m), 2641 (m), 2348 (w), 2200 (w), 2116 (w), 2084 (w), 2060 (w), 1997 (w), 1928 (w), 1813 (w), 1719 (s), 1710 (s), 1594 (m), 1557 (s), 1542 (s), 1485 (s), 1456 (s), 1408 (w), 1396 (m), 1330 (w), 1307 (s), 1288 (s), 1227 (s), 1167 (vs), 1139 (s), 1079 (m), 952 (m), 934 (m), 886 (w), 828 (w), 769 (w), 668 (m) cm^{-1} . $\text{C}_4\text{H}_{12}\text{Cl}_2\text{N}_6\text{O}_4$ (279.08 g mol^{-1}): C 17.21, H 4.33, N 30.11; found C 17.41, H 4.40, N 30.02. Dec. point: 168 °C. Sensitivities (BAM): impact 10 J; friction > 360 N; ESD 1.0 J (grain size < 100 μm).

3 Results and Discussion

3.1 Synthesis and Characterization

The diethylesters **1** and **3** were either commercially available or synthesized from the corresponding acid according to literature procedures [20]. The dihydrazides **2** and **4** can easily be obtained by the conversion of the diethylesters (**1**, **3**) with hydrazine hydrate described in literature [19,21]. The nitramino compound **5** was obtained from a nitration of **3** in a mixture of acetic anhydride and anhydrous nitric acid. The reaction with hydrazine hydrate at low temperatures yielded the dihydrazide **6** in good yields. The three dihydrazides were converted into their corresponding nitrate (**4a**, **6a**) and chloride salts (**4b**, **6b**) by protonation with diluted nitric acid or hydrochloric acid using different ratios and purification methods (Scheme 1).

All compounds are colorless, crystalline solids. The hydrazides were obtained in good yields and high purity and were used without further purification. The chloride salts are easily obtainable, as some can be precipitated from the aqueous phase. Purification of the nitrates is more challeng-



Scheme 1. Synthesis of the nitrate salts **2a**, **4a** and **6a** from malonic acid diethylester (**1**) and aminodiacetic acid diethylester (**3**).

ing due to their high hygroscopicity, especially regarding the trinitrate **4a**.

3.2 NMR and Vibrational Spectroscopy

All compounds were characterized by 1H and ^{13}C NMR spectroscopy, additionally the ^{14}N NMR spectra for the nitramino containing compounds **5**, **6**, **6a** and **6b** and the nitrates **2a** and **4a** were recorded.

The NMR spectra of nitraminodiacetic acid diethylester (**5**) were recorded in acetone- D_6 . In the 1H NMR spectrum the ethyl moieties are observed as quartet at 4.21 ppm and triplet at 1.25 ppm ($^3J = 7.1$ Hz). The methylene units next to the nitramine group are observed as singlet at 4.69 ppm. In the ^{13}C NMR spectrum the two non-equivalent methylene groups are observed at 62.2 and 54.0 ppm and the methyl group at 14.4 ppm. The carbonyl carbon atoms are observed in the low field at 167.6 ppm. In the ^{14}N NMR spectrum, a single signal for the nitro nitrogen is detected at -30 ppm.

The NMR spectra of the hydrazides and derived salts were recorded in DMSO- D_6 except **6**, which decomposes in DMSO and therefore was recorded in D_2O .

Regarding the 1H NMR spectra of the hydrazides **2** and **4**, the signal for the methylene groups can be observed between 3.06 and 2.90 ppm, while the NH resonance is found as a broad signal around 4.2 ppm and the NH_2 resonances

are more low field shifted at 9.0 ppm. For the hydrazide **6** the methylene signal is observed at 4.56 ppm, whereas the resonances of the hydrazide groups are not detectable in D_2O . In the ^{13}C NMR spectra all dihydrazides show the corresponding resonances for the carbonyl groups (**2**: 166.0 ppm, **4**: 169.9 ppm, **6**: 167.8 ppm) and the methylene groups (**2**: 40.0 ppm, **4**: 51.0 ppm, **6**: 54.1 ppm). The resonance of the nitro group of **6** is visible at -30 ppm in the ^{14}N NMR spectrum, whereas all hydrazine and amino nitrogen resonances are typically not detected.

Concerning the nitrates **2a**, **4a** and **6a**, their 1H NMR spectra show the signals for the methylene groups as sharp signal between 4.68–3.35 ppm. The NH, NH_2 and NH_3^+ resonances are broadened due to the quadrupole influence of the neighboring nitrogen atoms. For the malonyl salt **2a**, the NH signal is observed at 11.2 ppm and the NH_2 signal is observed at 9.7 ppm. In the 1H NMR spectra of the triple protonated salt **4a**, the signals for the NH, NH_2^+ and NH_3^+ groups are very broad and overlap between 12 ppm and 8 ppm. The NH signal for the salt **6a** is found at 11.2 ppm and the NH_3^+ signal is broadened in the area between 11 ppm and 8.5 ppm. In the ^{13}C NMR spectra, the methylene groups are observed at 39.1 (**2a**), 46.0 (**4a**) and 53.4 (**6a**) ppm, and the carbonyl carbon atoms are found between 164.6–165.6 ppm. For the ^{14}N NMR spectra, all compounds show the resonance of the nitrate anion at -4 ppm to -5 ppm, and **6a** shows an additional signal for the nitramine unit at -30 ppm.

In the ^1H NMR spectra of the chloride salts **2b**, **4b** and **6b** the methylene groups are observed at 3.42 ppm (**2b**), 3.98 ppm (**4b**) and 4.71 ppm (**6b**). The NH , NH_2 and NH_3 resonances are broadened and shown between 13 ppm and 9 ppm. In the ^{13}C NMR spectra the compounds show the corresponding signals for the carbonyl (165.5–164.4 ppm) and methylene (53.4–39.0 ppm) carbon groups. In the ^{14}N NMR spectrum of the chloride salt **6b** the nitrogen of the nitramine moiety is observed at -29 ppm.

3.3 Single Crystal Structure Analysis

Single crystals suitable for structure determination were obtained for the ethylester **5**, the dihydrazide **6** and the nitrate salt **6a** recorded at 143 K (Table 1).

Single crystals from **5** were obtained from ethyl acetate by slow evaporation at room temperature. The nitraminodiacetic acid diethylester (**5**) crystallizes in the orthorhombic space group $Pca2_1$ with four molecules of **5** in the unit cell and a density of 1.38 g cm^{-3} at 143 K (Figure 3).

In the crystalline state **5** shows the expected high planarity along the carbonyl units (e.g. torsion angle $\text{C4}–\text{C3}–\text{O1}–\text{O2} = 178.2^\circ$). Rather unusual, the nitramino moiety is in planar alignment $\text{C4}–\text{C5}$ without avoiding any steric hindrance (e.g. torsion angle $\text{O4}–\text{N2}–\text{N1}–\text{C5} = -2.4^\circ$). Regarding the intermolecular structure, the molecules are stacked with the nitramino groups pointing at the amino nitrogen of the neighboring molecule. Weak non-classical hydrogen bonding may explain this molecular grouping. Examples are observed between the nitro oxygens O3 and O4 and the methylene hydrogens $\text{C4}–\text{H7}$ and $\text{C5}–\text{H8}$ (e.g. $\text{DHA } \text{C4}–\text{H7} \cdots \text{O3}$, bond angle $\text{DHA} = 149.6^\circ$, $d(\text{D}–\text{A}) = 3.25\text{ \AA}$, $d(\text{A}–\text{H}) = 2.26\text{ \AA}$) [22].

Single crystals from **6** were obtained from the aqueous work-up by slow evaporation at room temperature. The nitraminodiacetyl dihydrazide (**6**) crystallizes in the monoclinic space group $P2_1/c$ with four molecules of **6** in the unit cell and a density of 1.73 g cm^{-3} at 143 K (Figure 4).

The crystal structure of nitraminodiacetyl dihydrazide (**6**) is much more twisted in comparison to the diethylester precursor **5**. This can be explained with the strong intramolecular hydrogen bonding between the two hydrazide branches ($\text{DHA } \text{N5}–\text{H8} \cdots \text{O1}$, bond angle $\text{DHA} = 170.5^\circ$, $d(\text{D}–\text{A}) = 2.84\text{ \AA}$, $d(\text{H}–\text{A}) = 2.02\text{ \AA}$). As a consequence, the proton donating branch is less planar than the proton accepting one (e.g. torsion angles $\text{C2}–\text{C1}–\text{N2}–\text{H3} = -2.0^\circ$ and $\text{C3}–\text{C4}–\text{N5}–\text{H8} = -8.0^\circ$). Similar to ester **5**, the dihydrazide **6** also shows the high planarity around the nitramino center (torsion angle $\text{C2}–\text{N3}–\text{N4}–\text{O2} = -1.2^\circ$). In combination with the twisted structure, multiple intermolecular hydrogen bonds between the free carbonyl oxygen O4 and neighboring hydrazide groups lead to a significant higher density of compound **6** in comparison with the precursor **5** (**5** = 1.38 g cm^{-3} , **6** = 1.73 g cm^{-3} , at 148 K).

Table 1. Crystal data, details of the structure determinations and refinement of **5**, **6** and **6a**.

	5	6	6a
formula	$\text{C}_8\text{H}_{14}\text{N}_2\text{O}_6$	$\text{C}_4\text{H}_{10}\text{N}_6\text{O}_4$	$\text{C}_4\text{H}_{12}\text{N}_8\text{O}_{10}$ * $2(\text{CH}_3)_2\text{SO}$
$FW [\text{g mol}^{-1}]$	234.21	206.16	488.47
$T [\text{K}]$	143	143	143
$\lambda [\text{\AA}]$	0.71073	0.71073	0.71073
crystal system	orthorhombic	monoclinic	monoclinic
space group	$Pca2_1$	$P2_1/c$	Pn
crystal size [mm]	$0.4 \times 0.21 \times 0.21$	$0.31 \times 0.27 \times 0.04$	$0.23 \times 0.21 \times 0.02$
crystal habit	colorless needle	colorless platelet	colorless platelet
$a [\text{\AA}]$	17.385 (10)	14.672 (6)	8.096 (6)
$b [\text{\AA}]$	5.849 (3)	6.723 (3)	5.652 (4)
$c [\text{\AA}]$	11.049 (7)	8.077 (3)	22.529 (2)
$\alpha [\text{deg}]$	90	90	90
$\beta [\text{deg}]$	90	96.46 (4)	90.41 (8)
$\gamma [\text{deg}]$	90	90	90
$V [\text{\AA}^3]$	1123.5 (11)	791.6 (6)	1030.9 (2)
Z	4	4	2
$\rho_{\text{calc.}} [\text{g cm}^{-3}]$	1.38	1.73	1.57
μ	0.119	0.152	0.333
$F(000)$	496	432	512
2θ range [deg]	4.96–30.62	5.00–31.49	4.48–29.48
index ranges	$-23 \leq h \leq 22$ $-7 \leq k \leq 7$ $-14 \leq l \leq 14$	$-18 \leq h \leq 15$ $-8 \leq k \leq 8$ $-9 \leq l \leq 10$	$-10 \leq h \leq 10$ $-5 \leq k \leq 7$ $-29 \leq l \leq 30$
reflections collected	9423	5663	8916
reflections unique	2719	1610	4661
parameters	145	151	275
Goof	1.041	1.058	1.010
$R_1/wR_2 [I > 2\sigma(I)]$	0.0363/0.0857	0.0311/0.0722	0.0469/0.0773
R_1/wR_2 (all data)	0.0455/0.0920	0.0378/0.0764	0.0657/0.0841
max/min residual electron density [\AA^{-3}]	$-0.259/0.224$	$-0.241/0.294$	$-0.272/0.362$
CCDC	1821952	1821953	1821954

Single crystals from **6a** were obtained from dimethyl sulfoxide by slow evaporation at room temperature. The nitraminodiacetyl dihydrazinium dinitrate (**6a**) crystallizes in the monoclinic space group Pn with two molecules of **6a** and four solvent molecules DMSO in the unit cell and a density of 1.57 g cm^{-3} at 143 K (Figure 5).

The crystal structure of the solvent containing nitrate salt **6a** shows many characteristics of the neutral precursor **6**. The structure is twisted again due to intramolecular hydrogen bonding between the two hydrazinium branches. Here, the proton donating dihydrazinium unit is more planar than the proton accepting one (e.g. torsion angles $\text{C2}–\text{C1}–\text{N2}–\text{H4} = -17.8^\circ$ and $\text{C3}–\text{C4}–\text{N5}–\text{H9} = -1.0^\circ$). In line

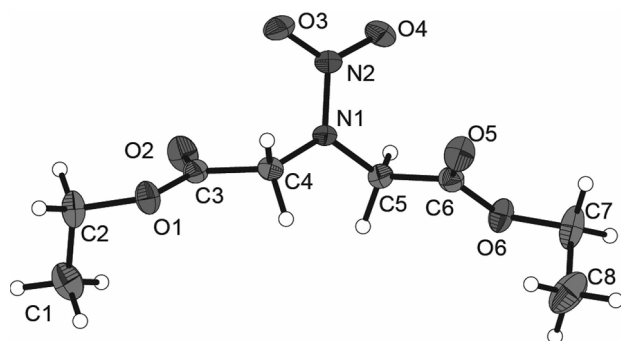


Figure 3. X-ray molecular structure of nitraminodiacetic acid diethylester (**5**). Selected atom distances (Å) and angles (deg.): N1–N2 1.342 (2), N1–C4 1.443 (2), N1–C5 1.447 (2), C3–O2 1.193 (2), C3–O1 1.332 (2), C4–N1–C5 123.9 (1), C4–N1–N2 118.1 (1), C4–C3–O2 125.3 (2), O1–C3–O2 125.9 (1); C4–N1–N2–O3 -9.4 (2), C4–N1–N2–O4 170.7 (1), C5–N1–N2–O3 177.5 (1), C5–N1–N2–O4 -2.4 (2).

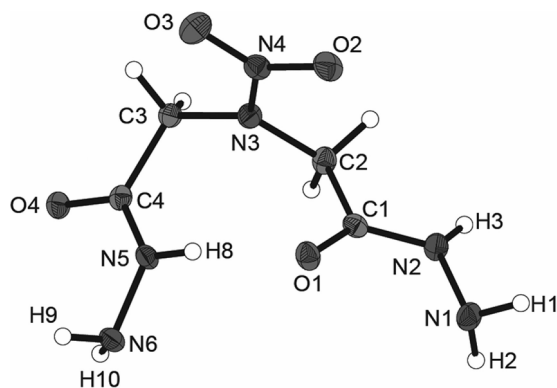


Figure 4. X-ray molecular structure of nitraminodiacetyl dihydrazide (**6**). Selected atom distances (Å) and angles (deg.): N3–N4 1.352 (2), N4–O3 1.229 (2), C1–O1 1.233 (2), C1–N2 1.330 (2), N1–N2 1.418 (2), N1–H1 0.89 (2), N1–H2 0.91 (2), N2–H3 (2); C2–N3–N4 117.5 (1), C3–N3–N4 119.3 (1), C2–C1–O1 121.9 (1), C2–C1–N2 113.1 (1), N2–C1–O1 124.9 (1); C3–N3–N4–O3 5.0 (2), C3–N3–N4–O2 -176.0 (1), C2–N3–N4–O3 179.7 (1), C2–N3–N4–O2 -1.3 (2), C2–C1–O1–N2 178.2 (2), C2–C1–N2–N1 -169.9 (1), O1–C1–N2–N1 8.4 (2), C2–C1–N2–H3 -2.0 (14), O1–C1–N2–H3 176.4 (14), C3–C4–N5–H8 -8.0 (13), O4–C4–N5–H8 172.9 (13).

with compounds **5** and **6** the nitramino moiety of **6a** shows a high planarity with the carbon atoms C2 and C3. The intermolecular structure is dominated by several strong hydrogen bonds between the dihydrazinium moieties and the nitrate anions as well as the DMSO molecules (Figure 6, e.g. DHA N1–H1 \cdots O10, bond angle DHA = 155.4° , $d(\text{D} \cdots \text{A}) = 2.80$ Å, $d(\text{H} \cdots \text{A}) = 1.95$ Å).

3.5 Thermal Stabilities and Energetic Properties

The thermal stabilities of all compounds were determined by Differential Thermal Analysis (DTA) measurements. The

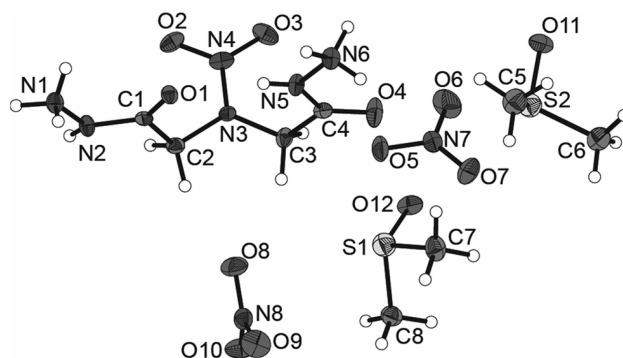


Figure 5. X-ray molecular structure of nitraminodiacetyl dihydrazinium dinitrate (**6a**). Selected atom distances (Å) and angles (deg.): N3–N4 1.343 (3), C1–O1 1.221 (4), C1–N2 1.340 (4), N1–N2 1.419 (3); C2–C1–O1 122.3 (3), N2–C1–O1 124.1 (3), C1–N2–N1 117.0 (2); C2–N3–N4–O2 4.8 (4), C2–N3–N4–O3 -177.2 (2), C3–N3–N4–O2 174.0 (2), C3–N3–N4–O3 -7.9 (4), C2–C1–N2–N1 178.9 (2), O1–C1–N2–N1 1.9 (4), C2–C1–N2–H4 -17.8 (4), O1–C1–N2–H4 165.2 (3), C3–C4–N5–H9 -1.0 (4), O4–C4–N5–H9 179.9 (3).

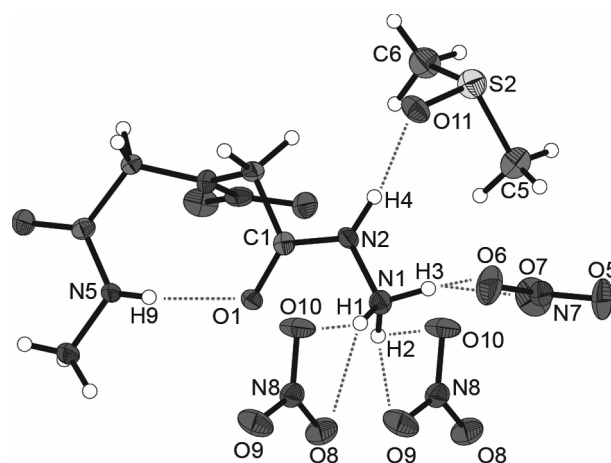


Figure 6. Classical intramolecular and intermolecular hydrogen bonds in the crystal structure of **6a**.

temperature range of $15\text{--}400^\circ\text{C}$ was recorded with a heating rate of 5°C min^{-1} . The nitrate salt of malonyl dihydrazide (**2a**) has a decomposition temperature of 266°C . The trinitrate **4a** decomposes at 160°C and the nitramine containing salt **6a** decomposes at 131°C . The chloride salts have a decomposition temperature of 195°C (**2b**), 201°C (**4b**) and 168°C (**6b**). The neutral hydrazide compounds **2**, **4** and **6** melt at 182°C (**2**) and 124°C (**4**) and the hydrazides decompose at 195°C (**2**), 216°C (**4**) and 130°C (**6**).

Friction and impact sensitivities were evaluated according to BAM standards, additionally the sensitivity towards electrostatic discharge was determined. The nitrates **2a**, **4a** and **6a** are rated sensitive towards impact, with values between 10 J (**4a**, **6a**) and 20 J (**2a**). The chlorides (**2b**, **4b**)

and the neutral hydrazides (**2**, **4**) of malonic acid and aminodiacetic acid are insensitive towards impact. Nitramine containing compounds **5** (15 J) and **6** (10 J) are sensitive towards impact. Regarding friction sensitivities, the nitrates **2a** (324 N), **4a** (80 N) and **6a** (192 N) are rated sensitive. The chlorides (**2b**, **4b**, **6b**) and the neutral hydrazides (**2**, **4**, **6**) are not considered sensitive towards friction.

The physical properties of the nitrate salts **2a** and **6a** were determined and are summarized in Table 2. The densities and cell volumes of malonyl dihydrazinium dinitrate (**2a**) and nitraminodiacetyl dihydrazinium dinitrate (**6a**) were estimated by comparison with the crystal structures of the neutral hydrazides **2** [23] and **6** and the solvent containing crystal structure of compound **6a**. The estimation method is explained in detail in the Supporting Information.

Table 2. Physical and sensitivity data of **2a** and **6a** in comparison with AP.

	2a	6a	AP
Formula	C ₃ H ₁₀ N ₆ O ₈	C ₄ H ₁₂ N ₈ O ₁₀	NH ₄ ClO ₄
FW [g mol ⁻¹]	258.15	332.19	117.49
T _{dec} [°C] ^[a]	266	131	240
IS [J] ^[b]	20	10	20
FS [N] ^[b]	324	192	360
ESD [J] ^[b]	1.5	0.4	–
ρ [g cm ⁻³] ^[c]	1.65	1.65	1.95
O [%] ^[d]	49.6	48.2	54.5
Ω _{CO} [%] ^[e]	0	0	+ 34.0
Ω _{CO2} [%] ^[e]	–18.6	–19.2	+ 34.0
Δ _f H _m ^o [kJ mol ⁻¹] ^[f]	–785.0	–708.9	–295.8
V _{det} [m s ⁻¹] ^[g]	7830	7998	6368
I _{sp} [s] ^[h]	214	231	157
I _{sp} [s] (15 % Al) ^[h]	245	254	235
I _{sp} [s] (15 % Al, 14 % binder) ^[h]	225	227	261

[a] Onset decomposition point T_{dec} from DTA measurements, heating rate 5 °C min⁻¹. [b] Sensitivity towards impact IS, friction FS and electrostatic discharge ESD. [c] Estimated density at room temperature. [d] Oxygen content. [e] Oxygen balance assuming formation of CO and CO₂. [f] Energy of formation calculated by the CBS-4M method using Gaussian 09 [15]. [g] Predicted detonation velocity. [h] Specific impulse I_{sp} of the neat compound and compositions with aluminium or aluminium and binder (6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile and 2% bisphenol A ether) using the EXPLO5 (Version 6.03) program package (70 kbar, isobaric combustion, equilibrium to throat and frozen to exit) [18a].

Both dinitrates **2a** and **6a** develop a detonation velocity of around 8000 m s⁻¹ obtained from theoretical calculations. This value ranges between the secondary explosives TNT and PETN and is inferior to the diaminourea and oxalyl dihydrazide nitrate salts [5,6]. The estimated density of both nitrate salts (**2a**, **6a**) is crucially lower than the density of the compared compounds, hence this result is to be expected. The specific impulse of the neat compound as well as in combination with 15 % aluminum yields superior specific

impulses I_{sp} compared to ammonium perchlorate (AP). By the addition of polymeric binders the composite with ammonium perchlorate clearly shows the highest specific impulse. The oxygen balance of compounds **2a** and **6a** is not sufficient for a complete oxidation, therefore the specific impulse drops by the addition of the carbon based binder system.

4 Conclusions

Three new polynitrate and -chloride hydrazinium salts as well as two new neutral nitramines were synthesized and fully characterized in this study. The investigated syntheses are feasible and cost-efficient through economic starting materials and high yields. Little to none purification is necessary to obtain the final compounds in high purity. Unfortunately, the nitrate salts **2a**, **4a** and **6a** are hygroscopic, which limits their application. The nitrates show some interesting physical properties, e.g. their low sensitivity towards impact and friction and the high thermal stability of malonyl dihydrazide dinitrate (**2a**). Their specific impulse in combination with aluminum exceeds the performance of AP. The addition of high amounts of binder reduces the I_{sp} significantly. The chloride salts in general are interesting precursors, e.g. in metathesis reactions to form the perchlorate and dinitramide salts.

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References

- [1] T. M. Klapötke, *Chemistry of High-Energy Materials*, 4th ed., De Gruyter, Berlin, 2015.
- [2] D. Fischer, T. M. Klapötke, J. Stierstorfer, Potassium 1,1'-Dinitramino-5,5'-bistetrazolate: A Primary Explosive with Fast Detonation and High Initiation Power, *Angew. Chem.* **2014**, 126, 8311–8314; *Angew. Chem. Int. Ed.* **2014**, 53, 8172–8175.
- [3] N. Fischer, D. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, Pushing the Limits of Energetic Materials - the Synthesis and Characterization of Dihydroxylammonium 5,5'-Bistetrazole-1,1'-diolate, *J. Mater. Chem.* **2012**, 22, 20418–20422.
- [4] a) K. O. Christe, W. W. Wilson, M. A. Petrie, H. H. Michels, J. C. Bottaro, R. Gilardi, The Dinitramide Anion, N(NO₂)₂⁻, *Inorg. Chem.* **1996**, 35, 5068–5071. b) J. C. Bottaro, P. E. Penwell, R. J.

- Schmitt, 1,1,3,3-Tetraoxo-1,2,3-triazapropene Anion, a New Oxy Anion of Nitrogen: The Dinitramide Anion and Its Salts, *J. Am. Chem. Soc.* **1997**, *119*, 9405–9410.
- [5] N. Fischer, T. M. Klapötke, J. Stierstorfer, Explosives Based on Diaminourea, *Propellants Explos. Pyrotech.* **2011**, *36*, 225–232.
- [6] D. Fischer, T. M. Klapötke, J. Stierstorfer, Oxalyldihydrazinium Nitrate and Dinitrate - Efficiency Meets Performance, *J. Energ. Mat.* **2014**, *32*, 37–49.
- [7] K. S. Khariton, M. E. Soshkevich, L. V. Kurtev, A. A. Shamshurin, Kinetics of the Solvolysis of Diethyl Dicarboxate (Diethyl Pyrocarbonate). IV. Influence of Pressure on the Rate of Hydrolysis in Water, *Suom. Kemistil. B* **1968**, *41*, 372–374.
- [8] a) Y.-H. Joo, B. Twamley, S. Garg, J. M. Shreeve, Energetic Nitrogen-Rich Derivatives of 1,5-Diaminotetrazole, *Angew. Chem.* **2008**, *120*, 6332–6335; *Angew. Chem. Int. Ed.* **2008**, *47*, 6236–6239 b) O. Diels, Ueber den Stickstofftricarbonsäureester und Einige mit Natriumurethan Ausgeführte Synthesen, *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 736–748.
- [9] Oxford Diffraction Ltd., *CrysAlis CCD*, 1.171.35.11, Abingdon, Oxford (U. K.), **2011**.
- [10] Oxford Diffraction Ltd., *CrysAlis RED*, 1.171.35.11, Abingdon, Oxford (U. K.), **2011**.
- [11] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, SIR97: A New Tool for Crystal Structure Determination and Refinement, *J. Appl. Crystallogr.* **1999**, *32*, 155–119.
- [12] a) G. M. Sheldrick, *Programs for Crystal Structure Determination*, University of Göttingen, Germany, **1997**; b) G. M. Sheldrick, A Short History of SHELX, *Acta Crystallogr.* **2008**, *64 A*, 112–122.
- [13] L. Farrugia, WinGX Suite for Small-molecule Single-crystal Crystallography, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
- [14] A. L. Spek, Structure Validation in Chemical Crystallography, *Acta Crystallogr.* **2009**, *65 D*, 148–155.
- [15] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., *Gaussian 09*, Wallingford, **2009**.
- [16] R. D. Dennington, T. A. Keith, J. M. Millam, *GaussView*, v. 5.08, Semichem, Inc., Wallingford, **2009**.
- [17] J. A. Montgomery, M. J. Frisch, J. W. Ochterski, G. A. Petersson, A Complete Basis Set Model Chemistry. VII. Use of the Minimum Population Method, *J. Chem. Phys.* **2000**, *112*, 6532–6542.
- [18] a) M. Sucasca, *EXPLO5*, v. 6.03, Zagreb, **2015**; b) M. Sucasca, Calculation of the Detonation Properties of CHNO Explosives, *Propellants Explos. Pyrotech.* **1991**, *16*, 197–202.
- [19] A. Alborzi, S. Zahmatkesh, A. Yazdanpanah, L-Lysine-derived Optically Active Poly(hydrazide-imide)s: Synthesis, Characterization and their Application in Removal of Heavy Metal Ions, *Polym. Bull.* **2013**, *70*, 3359–3372.
- [20] H. S. Park, Q. Lin, A. D. Hamilton, Protein Surface Recognition by Synthetic Receptors: A Route to Novel Submicromolar Inhibitors for α -Chymotrypsin, *J. Am. Chem. Soc.* **1999**, *121*, 8–13.
- [21] T. Curtius, O. Hofmann, Hydrazide und Azide Organischer Säuren. XXXIII. Abhandlung. Über die Einwirkung von Hydrazin und Salpetriger Säure auf Di- und Triglykolamidsäureester, *J. Prakt. Chem.* **1917**, *96*, 202–235.
- [22] T. Steiner, The Hydrogen Bond in the Solid State, *Angew. Chem.* **2002**, *114*, 50–80; *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76.
- [23] C. Miravittles, J. L. Brianzo, F. Plana, M. Font-Altaba, Malonic Dihydrazide, *Cryst. Struct. Commun.* **1975**, 81–84.

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