



2-Tetrazene Derivatives as New Energetic Materials; Synthesis, Characterization and Energetic Properties

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Abstract: The oxidation of 1,1-dimethylhydrazine with aqueous monochloramine yielded (*E*)-1,1,4,4-tetramethyl-2-tetrazene (**1**) as a pale yellow liquid with hypergolic properties. **1** can be oxidized with potassium permanganate to form (*E*)-1-formyl-1,4,4-trimethyl-2-tetrazene (**2**) and (*E*)-1,4-diformyl-1,4-dimethyl-2-tetrazene (**3**). Additionally, **1** reacts with a diethyl ether solution of monochloramine to form a stable 1,1,4,4-tetramethyl-2-tetrazenium chloride salt (**4**). The chloride in salt **4** was exchanged with various energetic anions, such as nitrate (**5**), perchlorate (**6**), 5,5'-azobistetrazolate ($7 \cdot 6\text{H}_2\text{O}$), picrate (**8**) and azide (**9**). All materials were characterized by analytical and spectroscopic methods and the solid state structures of compounds **2-8** were elucidated. Due to the energetic nature of these materials, they were submitted to friction and impact sensitivity tests and DSC analysis was used to assess their thermal stabilities. Furthermore, the heats of formation of compounds **2-8** were computed using quantum mechanical methods (CBS-4M) and their detonation parameters (pressure and velocity) and specific impulses were also calculated. Lastly, the 2-tetrazene derivatives presented here are of potential interest either as building blocks or as a new class of low toxicity, low sensitivity energetic materials.

Keywords: 2-tetrazene, energetic materials, X-ray diffraction, NMR spectroscopy

1 Introduction

Compounds containing several nitrogen-nitrogen bonds are of great interest for energetic applications. The high average two electron bond energy associated

with the nitrogen-nitrogen triple bond provides these materials with high energies. In this context, azole derivatives have often been the focus of attention [1-4] due to their unique combination of high energy content with relatively high chemical/thermal stability. In addition to heterocyclic compounds, acyclic molecules containing multiple nitrogen-nitrogen bonds have also been described as having interesting energetic properties. Recently, salts based on the 2,2-dimethyltriazanium cation were described by Shreeve *et al.* [5], and also by our laboratory [6], and the Klapötke group has reported several functionalized 2-tetrazenes with potential for energetic applications [7-9].

It is known from the literature that some 2-tetrazenes of the type $R^1R^2N-N=N-NR^1R^2$ ($R = H, CH_3$ or NH_2) are unstable under ambient conditions (Figure 1). For example, the simplest 2-tetrazene (N_4H_4 , *i.e.*, $R^1 = R^2 = H$), synthesized by Wiberg *et al.* at $-78\text{ }^\circ\text{C}$, was reported to explode spontaneously at $0\text{ }^\circ\text{C}$, and 1,4-dimethyl-2-tetrazene ($N_4H_2Me_2$, *i.e.* $R^1 = H, R^2 = CH_3$) remains elusive [10].

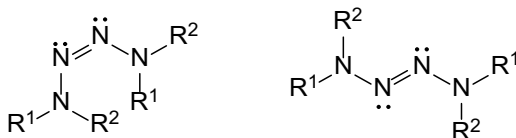


Figure 1. Formula structures of *cis*- and *trans*-2-tetrazenes.

On the other hand, hypergolic systems often use hydrazines as fuels mixed with an oxidizer [11-16]. However, recently, there has been a lot of concern about the acute toxicity and carcinogenic character of this type of hydrazine, monomethylhydrazine and 1,1'-dimethylhydrazine. Consequently ionic molecules were introduced as being advantageous since they have lower vapour pressures (and hence lower toxicities) and they often exhibit higher densities (higher performances) [17].

2 Materials and Methods

Caution!! 2-Tetrazenes, nitrogen-rich heterocycles and in particular silver azide are energetic materials, which might explode under certain conditions. For this reason, we recommend these materials to be handled only by qualified personnel following the methods of best practice and using suitable safety equipment including, but not limited to, Kevlar jackets/gloves, ear plugs, face shields, grounded shoes, *etc.* [18].

2.1 General methods

The chemical products used in this work were purchased from Sigma-Aldrich Inc. or Acros Organics and used without further purification. For the NMR measurements, a JEOL Eclipse 400 instrument was used. For all experiments, CDCl_3 and DMSO-d_6 were used as the solvents and the measurements were conducted at 25 °C. Tetramethylsilane (^1H and ^{13}C NMR) and ammonia (^{15}N NMR) were used as references for the chemical shifts. For the infrared (IR) spectra a Perkin-Elmer Spectrum instrument equipped with a Universal ATR sampling accessory was used. The IR peak intensities are expressed as very weak (vw), weak (w), medium (m), strong (s) and very strong (vs). A SETARAM DSC131 differential scanning calorimetry (DSC) instrument, calibrated with standard pure indium and zinc, was used to measure the melting and decomposition points of all compounds in this work (heating rate $\beta = 5\text{ °C}\cdot\text{min}^{-1}$, open aluminum pans with a hole (1 mm), nitrogen flow = $20\text{ mL}\cdot\text{min}^{-1}$).

2.2 (*E*)-1,1,4,4-Tetramethyl-2-tetrazene (1)

A 0.982 M solution of chloramine in water (50 mL, 49.1 mmol) was added dropwise to a solution of 1,1-dimethylhydrazine (10 mL, 7.900 g, 131.45 mmol) in distilled water (20 mL) at -10 °C. The reaction is exothermic (!). The reaction mixture was stirred for a few minutes at -10 °C and for a further 1.5 h at room temperature. Compound **1** was then extracted with diethyl ether (3×50 mL) and the extracts were dried over sodium sulfate and rotary evaporated to give crude **1** (as a pale yellow liquid). The crude product was then distilled under reduced pressure (0.05 bar, 40 °C) to give pure **1** (2.529 g, 89%). $\text{C}_4\text{H}_{12}\text{N}_4$ (MW = 116.16 g mol^{-1} , calc./found): C 41.35 / 41.38, H 10.42 / 10.34, N 48.23 / 47.88%; DSC (5 °C min^{-1}): 130 °C (endo, b.p.), 170 °C (exo, dec.); m/z (ESI-ToF): 115.1 (12), 116.1 (100, $[\text{M}^{+\cdot}]$), 117.1 (7); ^1H NMR (CDCl_3 , 400.18 MHz, TMS) δ /ppm: 2.76 (12 H, s, - CH_3); ^{13}C NMR (CDCl_3 , 100.52 MHz, TMS) δ /ppm (A_2B_2 spin system): 39.9 (q, $^1\text{J}_{\text{C-H}} = 135.6\text{ Hz}$, N- CH_3), 39.9 (q, $^1\text{J}_{\text{C-H}} = 135.6\text{ Hz}$, N- CH_3); IR $\tilde{\nu}/\text{cm}^{-1}$ (rel. int.): 2996(vw) 2958(w) 2852(w) 2820(w) 2786(vw) 1629(vw) 1587(vw) 1467(m) 1444(w) 1398(vw) 1273(m) 1239(w) 1139(m) 1092(vw) 1035(w) 95(vs) 895(w) 820(m) 590(s).

2.3 (*E*)-1-Formyl-1,4,4-trimethyl-2-tetrazene (2)

The following modified literature procedure was used [19]: potassium permanganate (2.12 g, 26.83 mmol) was added slowly to a solution of compound **1** (1.16 g, 20.0 mmol) in acetone (200 mL) containing calcium sulfate (*ca.* 3 g, as desiccant). The reaction is exothermic (!) and a brown solid

precipitates. The reaction mixture was stirred under ambient conditions for 1 h until it turned colourless and a second portion of potassium permanganate (2.12 g, 26.83 mmol) was then added. After stirring for a further 1 h, the insoluble material was filtered off through *Celite* and the solvents were reduced to dryness to give a pale yellow liquid. **2** precipitated upon standing at room temperature and the solid compound was dried under vacuum (0.581 g, 45%). The precipitation resulted in the formation of single crystals of the compound suitable for the X-ray experiments. C₄H₁₀N₄O (MW = 130.15 g·mol⁻¹, calc./found): C 36.91/36.73, H 7.74/7.63, N 43.05/42.83; DSC (5 °C·min⁻¹): 54 °C (endo, m.p.), 183 °C (exo, dec.); m/z (GC-MS, ESI): 131.1 (7, [M+H]), 130.1 (100, [M]), 101.2 (3, [M-CHO]), 87.1 (15, [M+H-N(CH₃)₂]), 86.1 (7, [M-N(CH₃)₂]), 73.1 (6, [HN=NN(CH₃)₂]), 59.2 (61, [HN(CH₃)(CHO)]), 43.2 (48, [CH₂=N(CH₃)]), 28.2 (28, [N₂]), 15.2 (12, [CH₃]); m/z (CHCl₃/MeOH, ESI-ToF): 283.2 (39, [2M+Na]), 261.2 (41, [2M+H]), 153.1 (22, [M+Na]), 131.1 (100, [M+H]), 130.1 (1, [M]); ¹H NMR (CDCl₃, 400.18 MHz, TMS) δ/ppm: 3.05 (6 H, s, -CH₃), 3.19 (3 H, s, -CH₃), 8.78 (1 H, s, CHO); ¹³C {¹H} NMR (CDCl₃, 100.52 MHz, TMS) δ/ppm: 27.09 (1 C, N-CH₃), 40.19 (2 C, N-CH₃), 163.23 (1 C, CHO); ¹⁵N NMR (CDCl₃, 40.51 MHz, NH₃) δ/ppm: +413.0 (1 N, s, N3), +358.8 (1 N, s, N2), +186.2 (1 N, s, N1), +125.8 (1 N, s, N4); IR $\tilde{\nu}$ /cm⁻¹ (rel. int.): 3032(w) 2972(w) 2944(w) 2893(w) 2890(w) 2801(w) 1749(w) 1663(s) 1472(m) 1443(m) 1409(m) 1400(m) 1385(m) 1368(m) 1298(m) 1227(m) 1204(m) 1140(w) 1093(w) 1052(w) 1027(s) 904(w) 847(m) 738(m) 669(w) 583(m).

2.4 (*E*)-1,4-Diformyl-1,4-dimethyl-2-tetrazene (**3**)

Compound **3** was synthesized by two independent methods as follows.

Method 1. Following the preparation of 2-tetrazene **2** (see above) using the following quantities: **1** (2.32 g, 20.0 mmol), acetone (200 mL), potassium permanganate (8.48 g, 53.66 mmol), no calcium sulfate was added. This method led to the formation of single crystals of compound **3** in low yield (0.451 g, 16%).

Method 2. The following method gave an increased yield of 2-tetrazene **3**: potassium permanganate (14.47 g, 91.56 mmol) was added portion-wise to a solution of 1-formyl-1-methylhydrazine (FMH, see below) (10.00 g, 134.90 mmol) in acetone (150 mL) at 0 °C. The ice bath was then removed and the brown reaction mixture was stirred at room temperature for 6 h. The insoluble material was filtered off through *Celite* and the solvent was stripped off under reduced pressure to give a pale yellow solution. Crystals of compound **3** separated upon standing of the latter solution (5.68 g, 51%). C₄H₈N₄O₂ (MW = 144.13 g·mol⁻¹, calc./found): C 33.33/33.21, H 5.59/5.69,

N 38.87/38.67; DSC (5 °C·min⁻¹): 164 °C (endo, m.p.), 201 °C (exo, dec.); m/z (GC-MS, ESI): 145.1 (5, [M+H]), 144.1 (97, [M]), 87.1 (3, [M+H-N(CH₃)₂]), 86.1 (7, [M-N(CH₃)₂]), 73.1 (20, [HN=NN(CH₃)₂]), 59.2 (31, [HN(CH₃)(CHO)]), 43.2 (100, [CH₂=N(CH₃)]), 28.2 (28, [N₂]), 15.2 (21, [CH₃]); ¹H NMR (CDCl₃, 400.18 MHz, TMS) δ/ppm: 3.32 (6 H, s, -CH₃), 8.94 (2 H, s, CHO); ¹³C {¹H} NMR (CDCl₃, 100.52 MHz, TMS) δ/ppm: 27.11 (1 C, N-CH₃), 163.37 (1 C, CHO); ¹⁵N NMR (CDCl₃, 40.51 MHz, NH₃) δ/ppm: +391.7 (1 N, s, N2), +193.2 (1 N, s, N1); IR $\tilde{\nu}$ /cm⁻¹ (rel. int.): 3035(w) 2996(w) 2955(w) 2918(w) 1756(w) 1665(m) 1647(m) 1467(m) 1445(w) 1410(w) 1400(w) 1390(w) 1338(s) 1272(w) 1226(m) 1128(w) 1087(w) 1031(s) 1021(s) 851(m) 668(m) 604(w) 573(s).

2.5 1-Formyl-1-methylhydrazine (FMH)

FMH was obtained according to the following modified procedure [20]: 97% ethyl formate (16.0 mL, 14.672 g, 192.11 mmol) was added portion-wise to a solution of 1-methylhydrazine (10.5 mL, 9.187 g, 195.44 mmol) in ethanol (15 mL). The reaction is very exothermic (!!). After it had cooled, the reaction mixture was heated under reflux for 6 h to give a bright yellow solution, which was rotary evaporated to dryness. The crude product was then distilled under reduced pressure (0.05 bar, 100 °C) to give pure FMH (10.692 g, 75%). C₂H₆N₂O (MW = 74.08 g mol⁻¹, calc./found): C 32.43/32.25, H 8.16/8.15, N 37.81/37.73%; DSC (5 °C·min⁻¹): >170 (exo, dec.), 199-200 °C (endo, b.p); m/z (GC-MS, ESI): 75.2 (1, [M+H]), 74.2 (25, [M]), 59.2 (3, [M-CH₃]), 46.2 (86), 45.2 (100, [M-CHO]), 44.2 (12), 43.2 (17), 31.2 (24), 30.2 (30, [M-CH₃-CHO]), 29.2 (28, [CHO]), 28.2 (50, [N₂]), 18.1 (22, [H₂O]), 17.1 (4), 16.2 (2, [NH₂]), 15.2 (5, [CH₃]); ¹H NMR (DMSO-d₆, 400.18 MHz, TMS) δ/ppm: 2.86 (3 H, s, -CH₃), 4.11 (2 H, s(br.), -NH₂), 7.98 (1 H, s, CHO); ¹³C NMR (DMSO- d₆, 100.52 MHz, TMS) δ/ppm: 36.85 (1 C, s, -CH₃), 164.32 (1 C, s, CHO); IR $\tilde{\nu}$ /cm⁻¹ (rel. int.): 3446(w) 3315(w) 3213(w) 2924(w) 2882(w) 1652(s) 1484(w) 1418(w) 1398(w) 1359(m) 1234(m) 1081(m) 984(m) 871(m) 849(m) 662(m) 573(w) 563(w).

2.6 (*E*)-1-Aminomethylidene-1,4,4-trimethyl-2-tetrazenium chloride (4)

A pre-cooled solution of chloramine in diethyl ether (90 mL, 34.20 mmol) was added to a solution of compound **1** (2.070 g, 17.83 mmol) in diethyl ether (10 mL) at -10 °C. The reaction mixture was stirred for 2 days under ambient conditions to give a colourless precipitate. The solvent was then decanted (retain!!) and the remaining solid was washed with diethyl ether and dried. The solid was

then extracted three times with 30 mL of an ethanol/acetone solution (1:3). The combined ethanol/acetone extracts were rotary evaporated to dryness to give a pale yellow solid, which was recrystallized from ethanol (0.445 g, 15%). This process allowed single crystals of compound **4** to be obtained, which were used for the X-ray measurements. The yield can be increased if the retained mother liquor (see above) is reacted several times with a freshly prepared chloramine solution (1.249 g, 41%). $C_4H_{12}N_5Cl$ (MW = 165.62 g mol⁻¹, calc./found): C 29.00/28.68, H 7.24/7.19, N 42.30/40.16; DSC (5 °C·min⁻¹): 203 °C (exo, dec.); m/z (ESI⁺, 70 eV, >5%): 129.9 (100, C⁺); ¹H NMR (D₂O/DMSO-d₆, 400.18 MHz, TMS) δ/ppm: 3.33 (6 H, s, -CH₃), 4.13 (3 H, s, -CH₃), 8.01 (1 H, s, C-H), 9.56 (2 H, s(br), -NH₂); ¹³C [¹H] NMR (D₂O/DMSO-d₆, 100.52 MHz, TMS) δ/ppm: 37.9 (2 C, N-CH₃), 39.4 (1 C, N-CH₃), 150.2 (1 C, C-H); IR $\tilde{\nu}/\text{cm}^{-1}$ (rel. int.): 3194(w) 2964(s) 2659(w) 2266(vw) 2059(vw) 1702(s) 1622(m) 1560(w) 1496(m) 1481(m) 1447(w) 1436(m) 1391(s) 1363(m) 1337(m) 1300(w) 1232(w) 1132(m) 1101(m) 1035(s) 905(w) 833(w) 796(m) 748(vs) 640(m) 589(w) [6b].

2.7 (*E*)-1-Aminomethylidene-1,4,4-trimethyl-2-tetrazenium nitrate (**5**)

Chloride **4** (0.075 g, 0.45 mmol) was reacted with silver nitrate (0.077 g, 0.45 mmol) in methanol (5 mL). The reaction mixture was stirred with exclusion of light for 30 min and the insoluble material was filtered off. The filtrate was then rotary evaporated to dryness to give the pure title compound (0.086 g, 99%). Slow evaporation of a methanolic solution of the compound led to the formation of X-ray quality, single crystals. $C_4H_{12}N_6O_3$ (MW = 192.18 g mol⁻¹, calc./found): C 25.00/24.82, H 6.29/6.06, N 43.73/43.29; DSC (5 °C min⁻¹): 164 °C (exo, dec.); m/z (+c ESI): 130.0 (100, C⁺); m/z (-c ESI): 62.0 (88, A⁻); ¹H NMR (DMSO-d₆, 400.18 MHz, TMS) δ/ppm: 10.05 (2 H, s(br), -NH₂), 7.33 (1 H, s, C-H), 4.15 (3 H, s, -CH₃), 3.38 (6 H, s, N-CH₃); ¹³C [¹H] NMR (DMSO-d₆, 100.52 MHz, TMS) δ/ppm: 37.8 (2 C, N-CH₃), 39.2 (1 C, N-CH₃), 150.2 (1 C, C-H); ¹⁴N NMR (DMSO-d₆, 40.51 MHz, NH₃) δ/ppm: +369 (s, NO₃⁻); IR $\tilde{\nu}/\text{cm}^{-1}$ (rel. int.): 3113(m) 3016(m) 2805(w) 2360(vw) 2166(vw) 2081(vw) 2049(vw) 1979(vw) 1751(w) 1704(m) 1627(w) 1480(w) 1438(w) 1388(m) 1324(s) 1223(m) 1122(m) 1103(m) 1043(m) 1022(m) 904(w) 830(m) 757(m) 717(w) 708(w) [6b].

2.8 (*E*)-1-Aminomethylidene-1,4,4-trimethyl-2-tetrazenium perchlorate (**6**)

Silver perchlorate (0.127 g, 0.61 mmol) was reacted with a solution of chloride **4** (0.102 g, 0.61 mmol) in methanol (5 mL). The reaction mixture was stirred

with exclusion of light for 30 min and the insoluble material was filtered off. Slow evaporation of the filtrate led to the formation of X-ray quality, single crystals. The crystals were then washed with diethyl ether and dried to give pure compound **6** (0.137 g, 98%). $C_4H_{12}N_5O_4Cl$ (MW = 229.62 g mol⁻¹, calc./found): C 20.92/20.78, H 5.27/5.07, N 30.50/30.28; DSC (5 °C min⁻¹): >195 °C (exo, dec.); m/z (+c ESI): 130.0 (100, C⁺); m/z (-c ESI): 99.0 (100, A⁻); ¹H NMR (DMSO-d₆, 400.18 MHz, TMS) δ/ppm: 10.35 (2 H, s(br), -NH₂), 7.13 (1 H, s, C-H), 4.21 (3 H, s, -CH₃), 3.39 (9 H, s, N-CH₃); ¹³C [¹H] NMR (DMSO-d₆, 100.52 MHz, TMS) δ/ppm: 37.7 (2 C, N-CH₃), 39.1 (1 C, N-CH₃), 150.1 (1 C, C-H); ³⁵Cl NMR (DMSO-d₆, 49.03 MHz, NaCl) δ/ppm: 1011 (ClO₄⁻); IR $\tilde{\nu}$ /cm⁻¹ (rel. int.): 3384(w) 3312(w) 3251(m) 3175(m) 3104(w) 3050(w) 3019(w) 2937(w) 2809(w) 2236(vw) 2020(vw) 1702(m) 1598(w) 1493(m) 1459(w) 1434(w) 1411(w) 1386(m) 1368(m) 1333(m) 1224(w) 1068(s) 1014(s) 934(w) 901(w) 826(w) 672(w) 635(w) 620(s) [6b].

2.9 (*E*)-1-Aminomethylidene-1,4,4-trimethyl-2-tetrazenium 5,5'-azotetrazolate hexahydrate (7*6H₂O)

Chloride **4** (0.083 g, 0.50 mmol) was dissolved in hot water (*ca.* 1 mL) and added to a solution of sodium 5,5'-azotetrazolate pentahydrate (0.076 g, 0.25 mmol) in hot water (*ca.* 2 mL). The reaction mixture was briefly boiled and left to cool to room temperature to produce single crystals of the compound, which were used for the X-ray experiments (0.097 g, 73%). $C_{10}H_{36}N_{20}O_6$ (MW = 532.52 g mol⁻¹, calc./found): C 22.55/22.90, H 6.81/6.75, N 52.60/52.29; DSC (5 °C min⁻¹): 50-100 (endo, -H₂O), 162 °C (exo, dec.); m/z (+c ESI): 130.0 (100, C⁺); m/z (-c ESI): 165.1 (100, [A²⁺ + H⁺]); ¹H NMR (DMSO-d₆, 400.18 MHz, TMS) δ/ppm: 9.02 (4 H, s(br), -NH₂), 8.08 (2 H, s, C-H), 3.38 (12 H, s(br), H₂O), 3.19 (6 H, s, N⁺-CH₃), 3.00 (6 H, s, -CH₃), 2.98 (6 H, s, -CH₃); ¹³C {¹H} NMR (DMSO-d₆, 100.52 MHz, TMS) δ/ppm: 35.2 (2 C, N-CH₃), 36.8 (2 C, N-CH₃), 42.3 (2 C, N-CH₃), 155.8 (2 C, C-H), 173.2 (2 C, [C₂N₁₀]²⁺); IR $\tilde{\nu}$ /cm⁻¹ (rel. int.): 3249(m) 2932(m) 2436(vw) 2205(vw) 2094(vw) 1978(m) 1712(m) 1484(m) 1429(m) 1398(m) 1384(m) 1340(m) 1232(w) 1200(w) 1180(w) 1166(w) 1132(m) 1105(m) 1050(m) 1029(m) 907(w) 773(m) 735(s) 687(m) 638(m) 620(m) 606(m) [6b].

2.10 (*E*)-1-Aminomethylidene-1,4,4-trimethyl-2-tetrazenium 5,5'-azotetrazolate (7)

Compound 7*6H₂O (0.043 g, 0.12 mmol) was heated at 60 °C under high vacuum for several hours to give the anhydrous material (quantitative yield). $C_{10}H_{24}N_{20}$ (MW = 424.43 g·mol⁻¹, calc./found): C 28.30/28.18, H 5.70/5.66, N

66.00/65.87; DSC (5 °C·min⁻¹): 163 °C (exo, dec.); m/z (+c ESI): 130.0 (100, C⁺); m/z (-c ESI): 165.1 (100, [A²⁻ + H⁺]); ¹H NMR (DMSO-d₆, 400.18 MHz, TMS) δ/ppm: 8.99 (4 H, s(br), -NH₂), 8.09 (2 H, s, C-H), 3.20 (6 H, s, N⁺-CH₃), 3.00 (6 H, s, -CH₃), 2.98 (6 H, s, -CH₃); ¹³C {¹H} NMR (DMSO-d₆, 100.52 MHz, TMS) δ/ppm: 35.2 (1 C, N-CH₃), 36.8 (1 C, N-CH₃), 42.2 (1 C, N-CH₃), 155.7 (1 C, C-H), 173.2 (2 C, [C₂N₁₀]²⁻); IR $\tilde{\nu}$ /cm⁻¹ (rel. int.): 3003(m) 2935(m) 2825(w) 2490(vw) 1704(m) 1646(m) 1567(w) 1489(m) 1457(w) 1439(w) 1424(w) 1407(w) 1388(s) 1367(m) 1341(m) 1231(m) 1182(w) 1155(w) 1127(w) 1107(m) 1050(m) 1034(m) 1013(m) 908(w) 811(w) 774(m) 732(m) 645(w) [6b].

2.11 (*E*)-1-Aminomethylidene-1,4,4-trimethyl-2-tetrazenium picrate (**8**)

A solution of chloride **4** (0.331 g, 2.0 mmol) in distilled water (2 mL) was overlaid with diethyl ether (20 mL) and cooled to 2-3 °C. A previously cooled 20% solution of sodium hydroxide in water (3.30 mL, 0.660 g, 16.5 mmol) was then added and the diethyl ether layer was separated and filtered, through *Drierite*, into a pre-cooled solution of picric acid (0.435 g, 1.9 mmol) in diethyl ether (10 mL). The mixture was stirred for a further 15 min. The yellow solid obtained was filtered off, washed with diethyl ether and dried to give compound **8** (0.601 g, 84%). Slow evaporation of a solution of this compound in methanol led to the formation of X-ray quality, single crystals. C₁₀H₁₄N₈O₇ (MW = 358.10 g·mol⁻¹, calc./found): C 33.52/33.48, H 3.94/3.87, N 31.28/31.12; DSC (5 °C·min⁻¹): 123 °C (m.p.), ³135 °C (exo, dec.), ³225 °C (exo, dec.); m/z (+c ESI): 129.9(56, C⁺), 242.0(100); m/z (-c ESI): 228.1(100, A⁻), 478.9 (11, [2A⁻ + Na⁺]⁻), 729.7(32, [3A⁻ + 2Na⁺]⁻); ¹H NMR (DMSO-d₆, 400.18 MHz, TMS) δ/ppm: 8.59 (2 H, s, H-Ar), 8.21 (1 H, s, C-H), 3.38 (6 H, s, N⁺-CH₃), 3.33 (3 H, s, -CH₃); ¹³C [¹H] NMR (DMSO-d₆, 100.52 MHz, TMS) δ/ppm: 160.7 (1 C, C1), 150.2 (1 C, C-H), 141.7 (2 C, C2), 125.1 (2 C, C3), 124.0 (1 C, C4), 36.7 (3 C, CH₃); IR $\tilde{\nu}$ /cm⁻¹ (rel. int.): 3353(w) 3217(w) 3097(w) 1705(m) 1629(m) 1599(m) 1556(m) 1480(m) 1428(m) 1402(w) 1389(w) 1362(m) 1328(s) 1250(s) 1161(m) 1135(m) 1101(m) 1076(m) 1052(m) 1031(m) 937(w) 925(w) 908(m) 834(w) 787(m) 744(m) 709(s) 642(m) 604(w) 591(m) 541(m) 522(w) [6b].

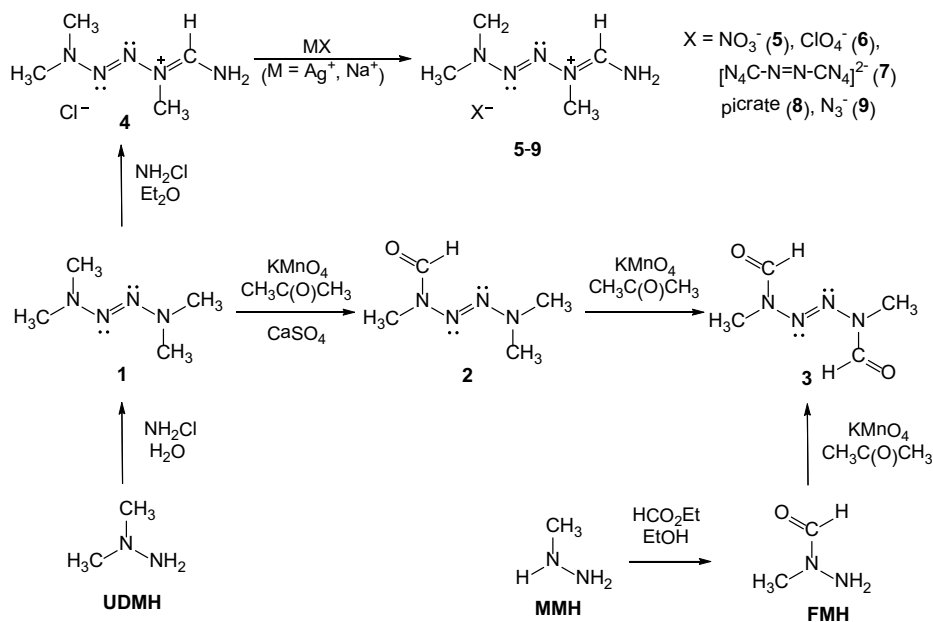
2.12 (*E*)-1-Aminomethylidene-1,4,4-trimethyl-2-tetrazenium azide (**9**)

Silver azide (**very sensitive!!**), prepared from sodium azide (78.5 mg, 1.208 mmol) and silver nitrate (205.2 mg, 1.208 mmol), was reacted overnight in the dark with chloride **4** (100.0 mg, 0.604 mmol) in distilled water (10 mL). The insoluble material was then filtered off and “the excess silver azide was immediately destroyed by adding dilute hydrochloric acid to a suspension of the

silver azide in water containing an excess of sodium nitrite" (!). The filtrate was rotary evaporated to dryness to yield pure compound **9** (93.3 mg, 90%). $C_4H_{12}N_8$ (MW = 172.19 g·mol⁻¹, calc./found): C 27.90/27.80, H 7.02/6.88, N 65.07/64.74; DSC (5 °C·min⁻¹): 189 °C (exo, dec.); m/z (+c ESI): 130.0 (100, C⁺); m/z (-c ESI): 42.1 (100, A⁻); ¹H NMR (DMSO-d₆, 400.18 MHz, TMS) δ/ppm: 8.99 (2 H, s(br.), -NH₂), 7.98 (1 H, s, C-H), 3.17 (3 H, s, +N-CH₃), 3.00 (3 H, s, N-CH₃), 2.98 (3 H, s, N-CH₃); ¹³C [¹H] NMR (DMSO-d₆, 100.52 MHz, TMS) δ/ppm: 35.2 (2 C, N-CH₃), 36.8 (1 C, N-CH₃), 155.6 (1 C, C-H); ¹⁴N NMR (DMSO-d₆, 40.51 MHz, NH₃) δ/ppm: +250 (1 N, N Δ N), +207 (1 N, -N⁺(CH₃)=CHNH₂), +104 (1 N, Δ N Δ); IR $\tilde{\nu}$ /cm⁻¹ (rel. int.): 3344(w) 3165(w) 2964(m) 2030(m) 1702(m) 1634(w) 1485(w) 1447(w) 1438(w) 1425(w) 1407(w) 1393(m) 1352(m) 1240(w) 1133(m) 1104(m) 1044(s) 972(w) 907(w) 833(w) 809(w) 774(m) 660(w) 647(w) 629(m) 624(m) 579(w) 537(s) [6b].

3 Results and Discussion

Sisler *et al.* described the oxidation reaction of 1,1-dimethylhydrazine (UDMH) with chloramine in diethyl ether to form 2,2-dimethyltriazanium chloride [21]. However, we realized that when UDMH is reacted with a buffered solution of chloramine at pH ~10, (*E*)-1,1,4,4-tetramethyl-2-tetrazene (**1**) separates out of the reaction medium in high yield and purity (Scheme 1).



Scheme 1. Scheme for the synthesis of compounds **1-9**.

The oxidation of compound **1** with potassium permanganate to form (*E*)-1-formyl-1,4,4-trimethyl-2-tetrazene (**2**) and (*E*)-1,4-diformyl-1,4-dimethyl-2-tetrazene (**3**) was described by Thun *et al.* [19]. However, the latter report turned out to be irreproducible in our hands and does not provide physical evidence for the structure of the materials. We found that when compound **1** was reacted with one equivalent of potassium permanganate, compound **2** was obtained (Scheme 1). However, the use of a large excess of potassium permanganate still resulted in the formation of compound **2** as the major product and only low yields of the bis-functionalized 2-tetrazene **3** were obtained. We found that **3** can be synthesized best by the oxidation of 1-formyl-1-methylhydrazine (FMH) with potassium permanganate. FMH, in turn, can be formed by the reaction of monomethylhydrazine (MMH) and ethyl formate.

Furthermore, **1** can undergo an oxidation reaction with chloramine to form a stable 2-tetrazenium chloride salt (**4**). The chloride in compound **4** can be exchanged with energetic anions such as nitrate, perchlorate, 5,5'-azobistetrazolate, picrate and azide, to form the stable 2-tetrazenium salts **5-9**.

The two formyl functionalized 2-tetrazenes **2** and **3** were studied by ^{15}N NMR spectroscopy (Figure 2). Derivative **2** displays four distinct N-resonances

$\delta_{N3} = 413.0$, $\delta_{N2} = 358.8$, $\delta_{N4} = 125.8$ and $\delta_{N1} = 186.2$ ppm. The symmetrical derivative **3** shows only two distinctive N-resonances at $\delta_{N2} = 391.7$ and $\delta_{N1} = 193.2$ ppm.

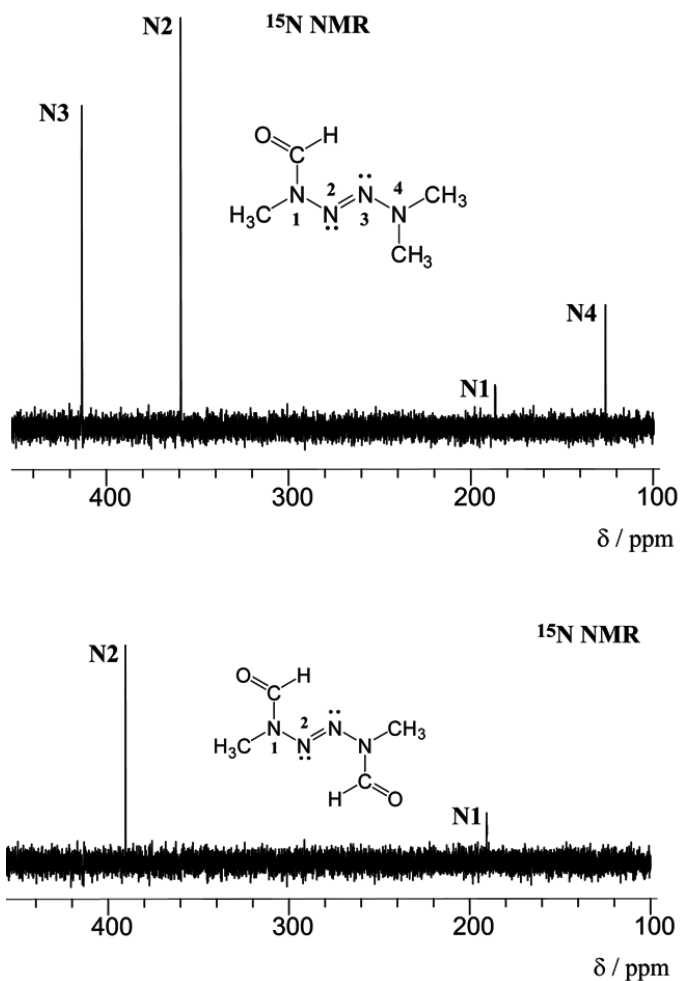


Figure 2. ^{15}N NMR spectra of the formyl 2-tetrazenes **2** and **3**.

The *trans*-geometry of the 2-tetrazene derivatives in this work is supported by the X-ray studies. 2-Tetrazene **2** (CCDC 824059) forms planar layers (Figure 3), which form unclassical hydrogen bonds ($\text{C8}\cdots\text{O5} = 3.791(6)$ Å). In addition, the compound forms **C1,1(8)** infinite chains with $\text{C9}\cdots\text{O5} = 3.477(6)$ and $\text{C18}\cdots\text{O14} = 3.478(6)$ Å.

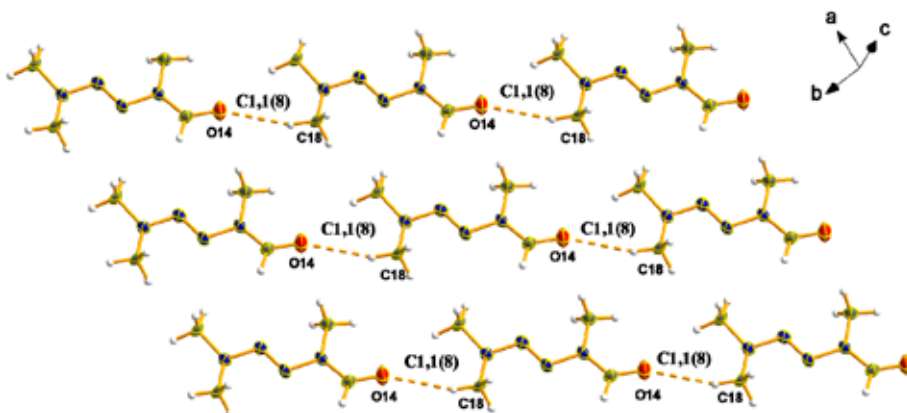


Figure 3. Hydrogen-bonding in the crystal structure of compound 2.

Compound 3 (CCDC 824058) forms two unclassical hydrogen bonds ($C4\cdots O5 = 3.474(2)$ and $C3\cdots O5 = 3.590(2)$ Å), with great directionality and C–H–O angles of $169.0(1)$ and $175.2(1)^\circ$, respectively. These interactions describe different hydrogen-bonding patterns, such as the **R2,2(16)** rings, represented in Figure 4.

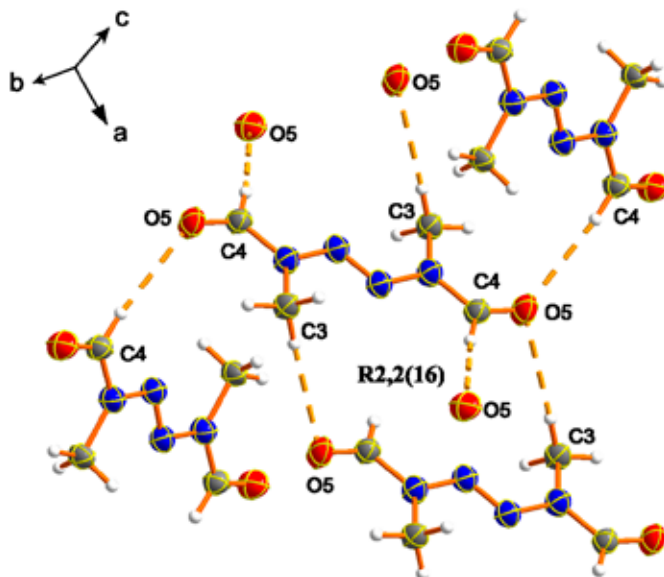


Figure 4. Hydrogen-bonding in the crystal structure of compound 3.

The chloride salt **4** [6b], formed by a coplanar cation and anion, forms planar layers with two hydrogen bonds between the amino groups and the chlorine atoms ($N9 \cdots C11 = 3.293(5)$ and $N9 \cdots C11^i = 3.135(3)$ Å; symmetry code: (i) $0.5+x, 1.5-y, 0.5-z$). These unclassical hydrogen bonds describe infinite **C1,2(4)** chain networks (Figure 5).

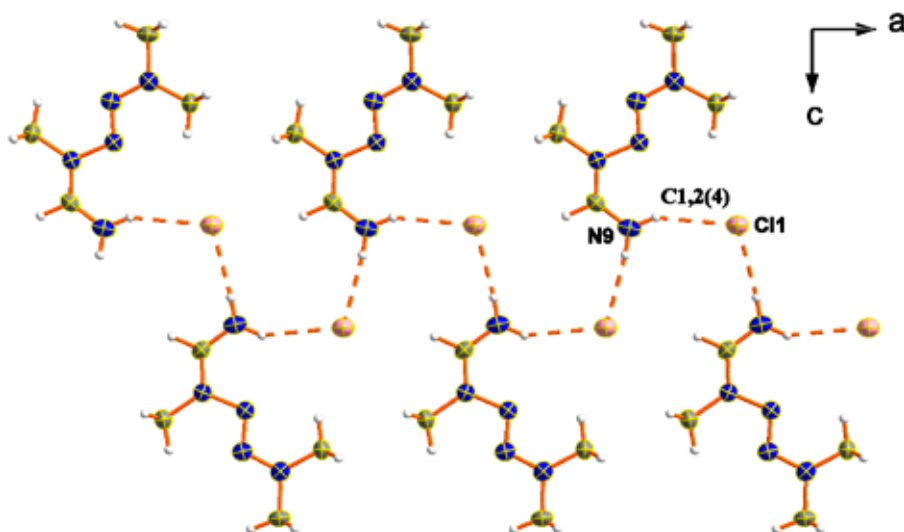


Figure 5. Hydrogen-bonding in the crystal structure of compound **4**. Taken from [6b].

The nitrate and perchlorate salts (compounds **5** and **6**, respectively) [6b] have some similar structural features. Both the nitrate anion in salt **5** (Figure 6) and the perchlorate anion in salt **6** (Figure 7) form three hydrogen bonds with the amino groups, which leads to the formation of infinite **C2,2(6)** chains and **R2,1(4)** ring networks. In the nitrate salt **5**, these latter ring patterns arise from the two hydrogen bonds formed by one hydrogen atom of the cation and two oxygen atoms of the anion ($N1 \cdots O3 = 3.033(3)$ and $N1 \cdots O2 = 3.034(3)$ Å).

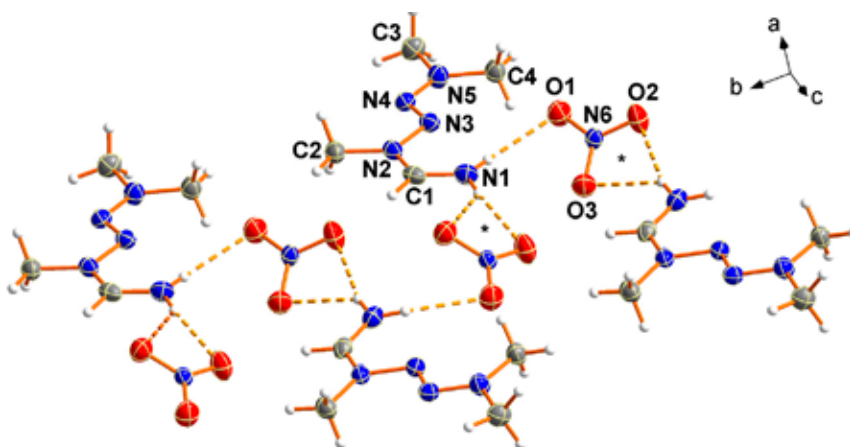


Figure 6. Hydrogen-bonding in the crystal structure of compound **5**. Taken from [6b].

In contrast to the structure of the chloride salt **4**, the nitrate salt **5** does not form planar layers and the anions are slightly out of the plane formed by the cations. The methyl groups of the cations are involved in hydrogen-bonding between layers with $C1 \cdots O2 = 3.132(3)$ and $C3 \cdots O3 = 3.346(3)$ Å. The high directionality of the interactions and the short distances between proton and acceptor atoms, which are below the sum of the van der Waals radii ($r_O + r_H = 2.7$ Å) [22], support the formation of these unclassical hydrogen bonds.

Similar to the situation already encountered for salts **4** and **5**, the cations in the perchlorate salt **6** are almost coplanar. However, the anion is sp^3 -hybridized, thus preventing the layers from being planar. The unclassical hydrogen bonds found in the structure of compound **6** ($C2 \cdots O1 = 3.411(5)$, $C1 \cdots O1 = 3.284(5)$, $C3 \cdots O4 = 3.378(5)$ and $C4 \cdots O1 = 3.384(5)$ Å) lead to the formation of the zig-zag arrangement represented in Figure 7. As for the nitrate salt **5**, the amino groups and the anions form **R2,1(4)** ring structures ($N1 \cdots O3 = 2.986(5)$ and $N1 \cdots O4 = 3.269(5)$ Å).

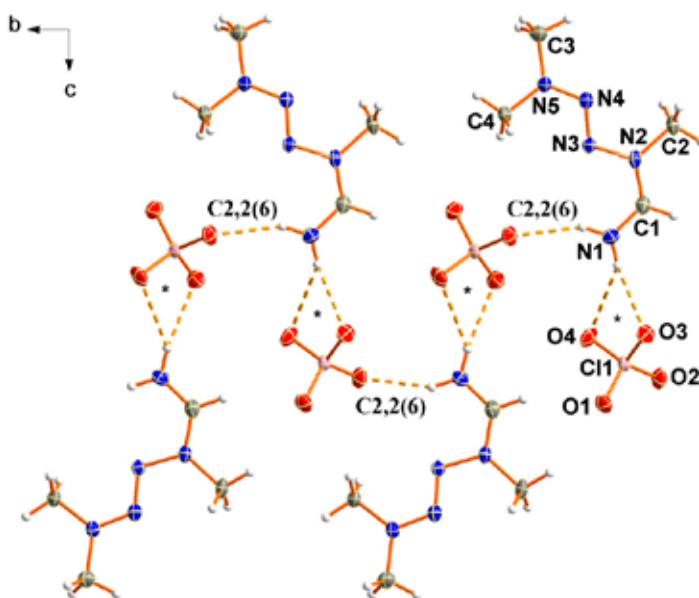


Figure 7. Hydrogen-bonding in the crystal structure of compound **6**. Taken from [6b].

The crystal structure of compound **7**·6H₂O [6b] gave evidence for the presence of six molecules of crystal water in the structure (Figure 8). The structure has a symmetry plane (symmetry code: (i) 1-x, 1-y, 1-z) and the asymmetric unit is formed by one half of a formula unit. All hydrogen bonds in the structure of compound **7**·6H₂O are involved in the formation of finite dimeric interactions, which take the descriptors **D1,1(2)[D2,2(8)]** and **D1,1(2)[D2,2(10)]**. Lastly, the only nitrogen atoms in the anion which do not participate in the formation of hydrogen bonds are those of the N=N bridge.

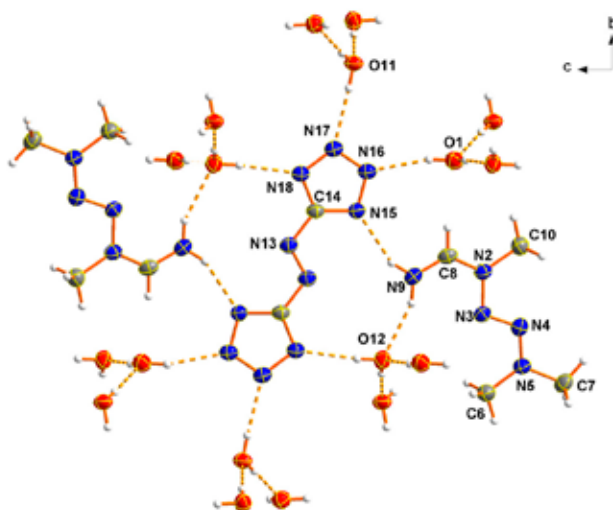


Figure 8. Hydrogen-bonding in the crystal structure of compound **7***6H₂O. Taken from [6b].

The structure of the picrate salt **8** [6b] does not show any evidence for the formation of unclassical C⋯O hydrogen bonds between anions, as is common for azolium picrate salts [23]. However, the cations and anions are involved in the formation of unclassical hydrogen bonds with C1⋯O3 = 3.346(4) Å. These hydrogen bonds lead to the formation of chain **C2,2(X)** (X = 6, 8) and ring **R2,1(6)** hydrogen-bonding patterns. The latter graph-sets are shown in Figure 9 and marked by an asterisk (*).

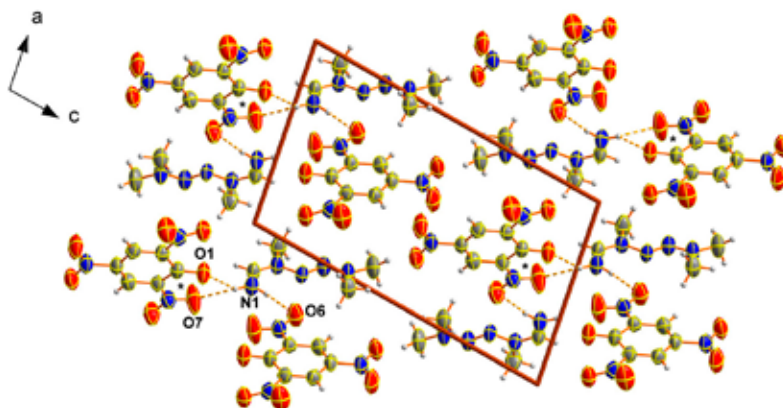


Figure 9. Hydrogen-bonding in the crystal structure of compound **8**. Taken from [6b].

2-Tetrazene **1** was isolated as a pale yellow liquid with a boiling point (with decomposition) at *ca.* 130 °C. **1** exhibited hypergolic character when mixed with strong oxidizers (*e.g.*, red-fuming nitric acid). All of the other compounds in this study (**2-9**) were isolated as solids. The physical and chemical properties of the formyl 2-tetrazenes **2** and **3** have been collected in Table 1. According to the DSC measurements, **2** and **3** melt at *ca.* 54 and 164 °C, respectively and decompose at *ca.* 183 and 201 °C, respectively.

Table 1. Physical and chemical properties of 2-tetrazenes **2** and **3**

	<i>trans-2</i>	<i>trans-3</i>
Formula	C ₄ H ₁₀ N ₄ O	C ₄ H ₈ N ₄ O ₂
Mol. Mass, [g·mol ⁻¹]	130.15	144.13
m.p., [°C] ^[a]	54.0	164.0
Td, [°C] ^[b]	182.5	201.4
N, [%] ^[c]	43.05	38.87
N + O, [%] ^[d]	55.33	61.07
Ω, [%] ^[e]	-147.5	-111.0
ρ, [g·cm ³] ^[f]	1.292	1.396
Δ _f U ^o , [kJ·kg ⁻¹] ^[g]	+495	-747
Δ _f H ^o , [kJ·kg ⁻¹] ^[h]	+352	-867

[a] Melting point and [b] temperature of decomposition; [c] nitrogen content; [d] nitrogen + oxygen content; [e] oxygen balance; [f] density; [g] calculated energy of formation; [h] calculated enthalpy of formation.

Quantum chemical methods were used to calculate the thermodynamic data of compounds **2** and **3**. As shown in Table 2, compound **2** is formed endothermically ($\Delta_f H^\circ(\textit{trans-2}) = +45.8 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H^\circ(\textit{cis-2}) = +108.7 \text{ kJ}\cdot\text{mol}^{-1}$) whereas the diformyl derivative **3** is a slightly exothermic compound ($\Delta_f H^\circ(\textit{trans-3}) = -125.1 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H^\circ(\textit{cis-3}) = -44.2 \text{ kJ}\cdot\text{mol}^{-1}$).

The results of the friction and impact sensitivity tests and the calculated performance data and thermodynamics data of energetic salts **5-9** are summarized in Tables 3 and 4.

According to the DSC measurements, all of the compounds **5-9** decompose without melting except for the picrate salt **8** (m.p. = 123 °C), which exhibits the highest thermal stability at 225 °C. The remainder of the materials *i.e.*, **4**, **5**, **6**, **7**·6H₂O, **7** and **9** show decomposition temperatures varying between 160 and 205 °C. The relatively high thermal stability of these materials might be related to the formation of extensive hydrogen-bonding, as supported by the X-ray crystallographic results (see discussion above).

Table 2. Enthalpies ($\Delta_f H^\circ$) and energies of formation ($\Delta_f U^\circ$) of compounds **2** and **3**.

Salt	$\Delta_f H^\circ(\text{g})$ [kcal·mol ⁻¹]	$\Delta_f H^\circ(\text{s})$ [kcal·mol ⁻¹]	$\Delta_f H^\circ(\text{s})$ [kJ·mol ⁻¹]	$\Delta n^{[a]}$	$\Delta_f U^\circ(\text{s})$ [kcal·mol ⁻¹]	M [g·mol ⁻¹]	$\Delta_f U^\circ(\text{s})$ [kJ·kg ⁻¹]
<i>trans</i> - 2	+25.6	+10.9	+45.8	-7.5	+15.4	130.15	+495.0
<i>trans</i> - 3	-10.2	-29.9	-125.1	-7	-25.7	144.13	-747.7
<i>cis</i> - 2	+40.6	+26.0	+108.7	-7.5	+30.4	130.15	+978.5
<i>cis</i> - 3	+9.0	-10.5	-44.2	-7	-6.4	144.13	-186.8

^[a] Δn = change in number of moles of gaseous components.

The perchlorate salt, which is the compound with the best oxygen balance of the group, is also the most sensitive material. Its impact sensitivity is similar to that of TNT ($i = 15$ J) and its friction sensitivity is lower than that of RDX ($f = 120$ N) [24]. The less oxygen-balanced nitrate salt is significantly less sensitive with $i = 30$ J and $f = 300$ N, and the azide salt is the only compound sensitive to friction with $f = 200$ N. Lastly, the nature of the ions used in this work and the stabilizing role of hydrogen-bonding, might explain the lower sensitivity of the materials in this study compared to commonly used energetic materials.

Table 3. Sensitivity data and computed performance data of salts **5-9**. Taken from [6b].

Salt	T_{ex} [K] ^[a]	V_0 [L·kg ⁻¹] ^[b]	P_{det} [kbar] ^[c]	D [m·s ⁻¹] ^[d]	I_{sp} [s] ^[e]	Impact [J] ^[f]	Friction [N] ^[f]	Thermal shock
5	2815	825	200.8	7598	206	>30	>300	deflagrates
6	3519	786	222.4	7651	225	>15	>150	explodes
7 *6H ₂ O	2815	854	177.2	7371	214	>40	>360	deflagrates
7	1855	751	169.3	7258	207	>25	>360	explodes
8	3233	689	180.0	7080	200	>40	>360	burns slowly
9	2524	800	191.1	7577	223	>30	>200	burns rapidly

[a] temperature (explosion gases); [b] volume (explosion gases); [c] detonation pressure; [d] detonation velocity; [e] specific impulse (isobaric combustion, chamber pressure = 60 bar); [f] impact and friction sensitivities.

The calculated values for the detonation velocities, in the range $D = 7080 \text{ m}\cdot\text{s}^{-1}$ (picrate salt **8**) and $D = 7651 \text{ m}\cdot\text{s}^{-1}$ (perchlorate salt **6**), are higher than that of TNT ($D = 7171 \text{ m}\cdot\text{s}^{-1}$) [24] and the specific impulses vary between $I_{sp} = 200 \text{ s}$ (picrate salt **8**) and $I_{sp} = 225 \text{ s}$ (perchlorate salt **6**).

Compounds **5-9** are highly endothermic with heats of formation in the range between $74 \text{ kJ}\cdot\text{mol}^{-1}$ (nitrate salt **5**) and $695 \text{ kJ}\cdot\text{mol}^{-1}$ (5,5'-azobistetrazolate $7\cdot 6\text{H}_2\text{O}$). The energies of formation vary between $342 \text{ kJ}\cdot\text{kg}^{-1}$ (picrate salt **8**) and $3469 \text{ kJ}\cdot\text{kg}^{-1}$ (azide salt **9**).

Table 4. Physical and chemical properties of salts **5-9**. Taken from [6b].

Salt	5	6	$7\cdot 6\text{H}_2\text{O}$	7	8	9
Formula	$\text{C}_4\text{H}_{12}\text{N}_6\text{O}_3$	$\text{C}_4\text{H}_{12}\text{N}_5\text{O}_4\text{Cl}$	$\text{C}_{10}\text{H}_{36}\text{N}_{20}\text{O}_6$	$\text{C}_{10}\text{H}_{24}\text{N}_{20}$	$\text{C}_{10}\text{H}_{14}\text{N}_8\text{O}_7$	$\text{C}_4\text{H}_{12}\text{N}_8$
Mol. mass [$\text{g}\cdot\text{mol}^{-1}$]	192.18	229.62	532.52	424.43	358.10	172.19
T_m [$^{\circ}\text{C}$] [a]	–	–	–	–	123	–
T_d [$^{\circ}\text{C}$] [b]	164	195	162	163	225	189
Ω [%] [c]	-91	-66	-96	-120	-89	-130
ρ [$\text{g}\cdot\text{cm}^{-3}$] [d]	1.449	1.543	1.320	1.327	1.500	1.373
$\Delta_f H^\circ$ (g, Cat ⁺) [$\text{kJ}\cdot\text{mol}^{-1}$] [e]	+884	+884	+884	+884	+884	+884
$\Delta_f H^\circ$ (g, An ⁻) [$\text{kJ}\cdot\text{mol}^{-1}$] [e]	-312	-276	+773	+773	-369	+191
ΔU_L [$\text{kJ}\cdot\text{mol}^{-1}$] [f]	+492	+477	+955	+1046	+423	+499
ΔH_L [$\text{kJ}\cdot\text{mol}^{-1}$] [f]	+497	+482	+962	+1053	+428	+503
$\Delta_f H^\circ$ (s) [$\text{kJ}\cdot\text{mol}^{-1}$] [g]	+74	+125	+695	+604	+86	+572
$\Delta_f U^\circ$ (s) [$\text{kJ}\cdot\text{kg}^{-1}$] [g]	+524	+787	+1450	+1553	+342	+3469

[a] Melting point; [b] temperature of decomposition; [c] oxygen balance; [d] density; [e] standard (gas phase) heat of formation of the cation (Cat⁺) and anion (An⁻); [f] lattice energy and lattice enthalpy; [g] standard (solid phase) heat and energy of formation of the ionic species.

4 Conclusions

1,1-Dimethylhydrazine can be oxidized with chloramine to form (*E*)-1,1,4,4-tetramethyl-2-tetrazene (**1**). **1** is as a pale yellow liquid with hypergolic properties. The oxidation reactions of **1** with potassium permanganate and chloramine were studied. The reaction of 2-tetrazene **1** with potassium permanganate leads to the formation of functionalized 2-tetrazenes (compounds **2** and **3**). However the reaction of 1-formyl-1-methylhydrazine with potassium permanganate provides a better method for the synthesis of compound **3**. The reaction of 2-tetrazene **1** with chloramine leads to the formation of a stable 2-tetrazenium salt (compound **4**), which can undergo metathesis reactions to form energetic salts (compounds **5-9**). The compounds in this work were characterized analytically and spectroscopically and the structure of the 2-tetrazene fragment was unequivocally identified using X-ray crystallography. DSC data point to high thermal stabilities for all of the compounds except **1**, and all materials exhibit low sensitivities to impact and friction. Furthermore, compounds **5-9** have higher calculated detonation velocities than the commonly used TNT and specific impulses which are similar to those of recently published energetic compounds. Lastly, the functionalized 2-tetrazenes **2** and **3** might be useful starting materials for the synthesis of energetic compounds and the 2-tetrazenium salts **5-9** might be of interest as energetic materials with moderate performance, low sensitivities and low toxicities.

Acknowledgements

We are thankful for financial support from the Centre National de la Recherche Scientifique (CNRS), the Centre National d'Études Spatiales (CNES), Herakles-SAFRAN and the University Claude Bernard of Lyon. The authors would also like to thank Dr. E. Jeanneau for the X-ray crystallographic work.

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