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New energetic compounds based on the nitrogen-rich 5,5′-azotetrazolate anion ($[C_2N_{10}]^{2-}$)†

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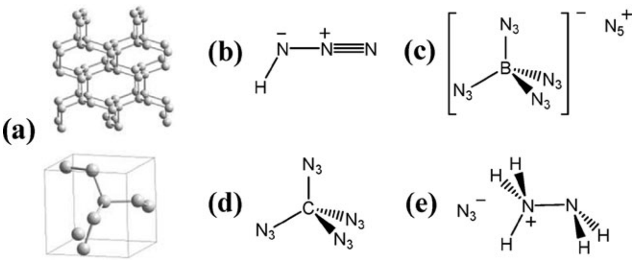
The metathesis reaction between sodium 5,5′-azotetrazolate ($[Na]^+{}_2ZT^{2-}$) pentahydrate and 1,3-dimethyl-5-aminotetrazolium iodide or semicarbazidium chloride in water leads to the formation of the corresponding ZT^{2-} salts as the hydrated species (**2** and **4**). The anhydrous derivatives (**1** and **3**) were synthesized by reaction of silver 5,5′-azotetrazolate with a suitable halogenide salt in methanol. Alternatively, the crystal water in the hydrated salts **2** and **4** was quantitatively removed under vacuum leading to a safe up-scalable synthesis for compounds **1** and **3**, which does not make use of highly sensitive silver salts. The formation of the salts was confirmed by analytical and spectroscopic methods and, in addition, the crystal structures of **2** and **4** were determined using low-temperature X-ray measurements (**2**: monoclinic $P2_1/n$, $a = 9.3101(3)$, $b = 6.5383(2)$, $c = 19.5637(5)$ Å; $\beta = 90.48(1)°$; $V = 1190.84(6)$ Å^3 and **4**: triclinic $P\bar{1}$, $a = 4.563(5)$, $b = 7.362(5)$, $c = 11.334(5)$ Å; $\alpha = 105.125(5)$, $\beta = 90.48(1)$, $\gamma = 102.871(5)°$; $V = 357.2(5)$ Å^3). Although the semicarbazidium salts **3** and **4** have relatively low thermal stabilities (<130 °C), the tetrazolium salts **1** and **2** decompose above 190 °C. All four compounds classify as insensitive, have high performances (**1**: $P = 19.0$ GPa and $D = 7667$ m s^{-1}; **2**: $P = 25.1$ GPa and $D = 8585$ m s^{-1}; **3**: $P = 23.4$ GPa and $D = 8125$ m s^{-1} and **4**: $P = 20.0$ GPa and $D = 7694$ m s^{-1}) and decompose giving (mainly) environmentally friendly gases. Lastly, the properties of salts **1–4** make them attractive for further studies as a new class of high performing, insensitive, environmentally more benign and, in the case of **1** and **2**, also thermally stable energetic materials.

Introduction

In the development of new high energy density materials (HEDMs) more power with lower sensitivity and less pollution is sought.[1] In this context, nitrogen-rich chemistry has emerged as a prospective solution for the development of the HEDMs of the future.[2–5] The average bond energy of the N–N triple bond is exceptionally high for any atom in the periodic system, which makes nitrogen-rich compounds very endothermic and, therefore, very energetic materials. Also, nitrogen-rich materials should ideally decompose giving environmentally benign gases (*i.e.*, mainly N_2). Unfortunately, high performing compounds are often very sensitive[1] and ways of stabilizing them are sought in order to find ways of controlling energy release and avoid accidents.[6] Recently, solid nitrogen was synthesized by Eremets *et al.*[7] and other nitrogen-rich species such as HN_3,[8] $N_5{}^+[B(N_3)_4]^-$,[9] $C(N_3)_4$[10] or $[N_2H_5]^+N_3{}^-$[11] are known, which have nitrogen contents (N) above 93% (Scheme 1). However, all of these compounds suffer of low stability under room conditions and/or elevated toxicity.[6–12] Azole- and in particular tetrazole-based materials seem to show a good compromise of desired properties. On one hand, the relatively large number of inherent C–N and N–N bonds make these compounds fairly non-toxic and highly endothermic (*e.g.*, $\Delta H°_f$ (tetrazole) = +237 kJ mol^{-1}),[13] on the other, their aromatic character accounts for the (generally) low sensitivities and good chemical stabilities. In this regard, we synthesized and fully characterized 5-azido-1*H*-tetrazole ($N = 88.3\%$),[14] however, as many other covalent azides, the compound is very sensitive and difficult to handle.[15] A further example of a tetrazole derivative is bis(hydrazinium) 5,5′-azotetrazolate, which is only slightly nitrogen poorer



Scheme 1 Structures of the five nitrogen-richest, isolated, non-gaseous compounds: (a) cubic gauche nitrogen, (b) hydrazoic acid, (c) pentaaza tetraazidoborate, (d) tetraazidomethane and (e) hydrazinium azide.

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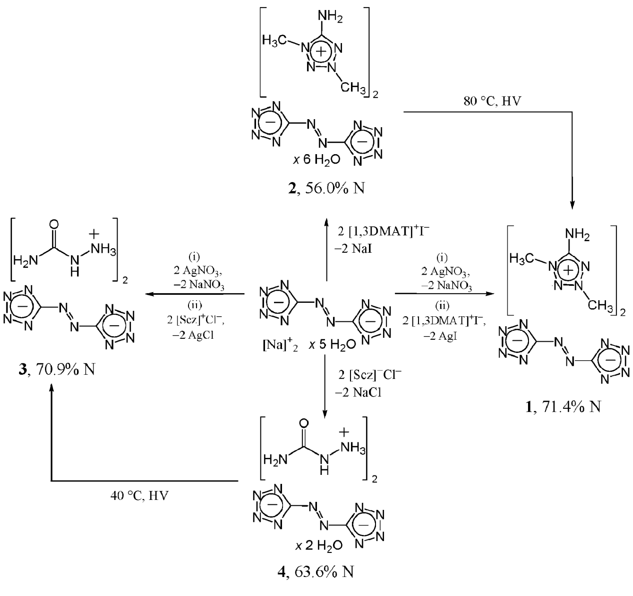
† Electronic supplementary information (ESI) available: X-Ray tables, pictures of the "flame tests" and histograms with the decomposition gases for compounds **1–4**. CCDC reference numbers 707556 (**2**) and 707555 (**4**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b820381d

(*N* = 85.2%), counts as one of the most endothermic compounds reported so far (value) and is fairly insensitive.[16] The 5,5′-azotetrazolate anion (ZT^{2-}) was subsequently the subject of many studies in which the toxic hydrazinium cation was exchanged by more environmentally friendly cations.[17,18] Guanidinium cations are non-toxic, fairly nitrogen-rich and readily available and were combined with the ZT^{2-} anion rendering a new class of HEDMs.[19] Subsequently, guanidinium cations were combined with different anions to form energetic salts.[20] Interestingly, azolate anions in conjunction with azolium cations give compounds with suitable properties for energetic applications.[21] With all this in mind, we decided to study further examples of salt-based materials containing an azolate anion and either an azolium cation or the semicarbazidium cation, which is reminiscent of the aminoguanidinium cation.

Results and discussion

Syntheses

The 1,3-dimethyl-5-aminotetrazolium (**2**) and semicarbazidium (**4**) 5,5′-azotetrazolate salts could be obtained by recrystallization from hot/warm water of equimolar amounts of sodium 5,5′-azotetrazolate pentahydrate and a suitable halogenide salt as the hexahydrate and dihydrate species, respectively (Scheme 2). The incorporation of crystal water is usual for 5,5′-azotetrazolate salts.[17*b*,22] The synthesis of compound **4** needs to be carried out at low temperatures (~50 °C), since the compound readily decomposes in solution. The best yield is attained by slowly cooling the solution and immediate filtration. Compounds **2** and **4** were obtained as a bright yellow and a dark orange solid, respectively. On the other hand, the anhydrous compounds **1** and **3**, were initially synthesized in moderate yield by the metathesis reaction between silver 5,5′-azotetrazolate, formed by addition of silver nitrate to the sodium salt, and a suitable halogenide salt in dry alcohol (*i.e.*, methanol or ethanol). Since the silver salt is a very sensitive compound an alternative procedure was sought that made the synthesis of the compounds more readily available for safe up-scaling and the crystal water in the hydrated salts **2** and **4** was quantitatively removed by heating the compounds for several days under high vacuum, yielding the anhydrous species **1** and **3**. Note that the dehydration of **4** to form **3** should be carried out at lower temperatures (~40 °C) in order to avoid decomposition of the compound.



Scheme 2 Synthesis of nitrogen-rich 5,5′-azotetrazolate salts **1–4**. $[1,3DMAT]^+I^-$ = 1,3-dimethyl-5-aminotetrazolium iodide, $[Scz]^+Cl^-$ = semicarbazidium chloride.

Lastly, all of the compounds are insoluble in acetone and apolar solvents and moderately soluble in water or alcohol. Whereas **1** and **2** are perfectly stable solids (both in the solid state and in solution), the semicarbazidium salts **3** and **4** decompose, as pointed out above, in a variety of polar solvents (*e.g.*, H_2O, DMSO, DMF, ...) and are thermally labile.

Vibrational and NMR spectroscopy

In the Raman spectra of compounds **1–4**, the cation signals are obscured by bands of strong intensity corresponding to the symmetric $C–N_{azo}$ stretching (1384 ± 5 cm^{-1}) and to the $N_{azo}–N_{azo}$ stretching mode (observed at ~1485 cm^{-1} for **1** and **2** and ~1500 cm^{-1} for **3** and **4**). Apart from slight differences in the shifts, the Raman spectra of all four salts have essentially identical shapes. The two bands observed at 1068 and 1099 cm^{-1} for the sodium salt, exchange their relative intensities and are shifted to ~1075 and ~1045 cm^{-1} for the anhydrous species (**1** and **3**) and to ~1080 and ~1065 cm^{-1} for the hydrated salts (**2** and **4**). This shifts are indicative for the formation of the compounds. On the other hand, the IR spectra are dominated by the asymmetric $C–N_3$ and the asymmetric $C–N_2$ stretching modes observed at ~1390 (tetrazolium salts) and ~1405 (semicarbazidium salts) cm^{-1}, and at ~730 (tetrazolium salts) and ~740 (semicarbazidium salts) cm^{-1}, respectively. In the case of the tetrazolium salts **1** and **2**, the most intense peak in the IR spectra corresponds to the $C–NH_2$ stretching mode at ~1675 cm^{-1}, whereas the semicarbazidium salts **3** and **4** show absorptions at ~1680 and ~1580 cm^{-1} for the C=O and $C–NH_2$ stretching vibrations, respectively. Lastly, other bands of lower intensity are also observed, which can be assigned as follows: >3300 cm^{-1} [ν(O–H)], 3300–3100 cm^{-1} [ν(N–H)], 3100–3000 cm^{-1} [ν(C–H)], 1680–1580 [$\delta(NH_2)$], 1580–1350 cm^{-1} [ν(tetrazole ring), $\delta_{as}(CH_3)$], ~1390 cm^{-1} [$\delta(CH_3)$], 1350–700 cm^{-1} [ν(N–C–N), ν(N–N), γ(CN), δ(tetrazole ring)], <700 cm^{-1} [δ out-of-plane bend (N–H), $\omega(NH_2)$].[23,24]

The IR spectra also provide insight into the cation structure.[25] By comparison of the $C–NH_2$ stretching modes in salts **1** and **2** with those observed in the isomeric 1,4-dimethyl-5-aminotetrazolium ($1,4DMAT^+$) salts,[17*b*] the signals of **1** and **2** are observed at lower energies indicating elongation of this bond, in agreement with crystallographic studies.[6,26]

In the ^1H NMR in [D_6]-DMSO the signals corresponding to one of the methyl groups in compounds **1** and **2** are found at ~3.9 ppm ($C3H_3$), whereas the other methyl group resonates at lower field ($C4H_3$, ~4.4 ppm). In the hydrates species **2** and **4** only one broad signal is observed corresponding to the crystal water protons, which exchange fast with those of the amino group in the NMR solvent. In the ^{13}C NMR, the shifts are very similar to the starting materials. The ring carbon resonances for the 5,5′-azotetrazolate anion are observed at ~173 ppm for all four compounds and the tetrazolium and semicarbazidium cations have resonances for the C–NH_2 carbon atom at ~158.0 and ~158.5 ppm, respectively. The resonances for the two methyl groups for compounds **1** and **2** are to be found ~42.5 ppm ($C4H_3$) and to higher field in respect to [D_6]-DMSO at ~34.2 ppm ($C3H_3$). ^{14}N NMR measurements only show broad signals for the nitrogen atoms due to the quadrupole moment of the nucleus. The low solubility of the compounds in any solvent tried did also not allow to record a ^{15}N NMR (natural abundance).

Crystal structures

Single crystals of the hydrated species **2** and **4**, suitable for X-ray analysis were obtained as described in the experimental section. An Oxford Diffraction Xcalibur 3 diffractometer equipped with a CCD detector using the CrysAlis CCD software was used for the measurements[27] and the CrysAlis RED software was used to reduce the data.[28] All data were collected using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by means of full-matrix least-squares procedures using WinGX and the available software in the package.[29–32] Finally, the structures were checked using *PLATON*.[33] The absorption corrections were performed using a *SCALE3 ABSPACK* multi-scan method.[34] All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were located from difference Fourier electron density maps and refined isotropically. The crystal structure solution and refinement data for the two compounds can be found in Table S1 of the ESI.† Table 1 contains a summary of the bond distances and angles for the anion in compounds **2** and **4**. The hydrogen bonding geometry has been tabulated in Table 2, whereas Tables S2 and S3 (ESI†) show a record of the graph-sets of interest found in the crystal structures of **2** and **4**, respectively.[35]

Interatomic distances and angles (Table 1) for the 5,5′-azotetrazolate anion in the ionic salts **2** and **4** are very similar. The N–N distances on the tetrazole rings, between 1.317(3) and 1.345(3) Å, are longer than normal C═N double bonds (1.22 Å) and shorter than normal C–N single bonds (1.47 Å),[36] implying a certain delocalization throughout the tetrazole ring. The azo-bridge N–N distances between 1.250(2) and 1.265(3) Å are slightly longer than a typical N═N double bond showing the aromatic character of the anion.[37] Both distances compare nicely with the values measured for the crystal structures of 5,5′-azotetrazolate salts with alkali and alkaline earth metals[18c] and other salts containing the same anion.[17b,19] The relatively long C–NH_2 distance in salt **1** makes the nomenclature 5-aminotetrazole preferable to 5-iminotetrazole, which is in contrast to other tetrazolium salts.[6,23,38]

Table 1 Bond distances (Å) and angles (°) in the 5,5′-azotetrazole anion of compounds **2** and **4**

	2[a]	**4**[b]	Bond	**2**[a]	**4**[b]
N1–N2	1.342(2)	1.343(3)	N4–C1	1.328(2)	1.332(3)
N1–C1	1.337(2)	1.336(3)	N5–C1	1.406(2)	1.423(3)
N2–N3	1.323(2)	1.320(3)	N5–N5^{i}	1.256(3)	1.233(4)
N3–N4	1.335(2)	1.332(3)	—	—	—
C1–N5–N5^{i}	112.9(2)	111.3(3)	N2–N3–N4	109.1(1)	109.6(2)
C1–N1–N2	103.6(1)	103.9(2)	N4–C1–N1	112.5(1)	112.4(2)
N3–N2–N1	109.8(1)	109.5(2)	N4–C1–N5	119.0(1)	115.5(2)
C1–N4–N3	104.7(1)	104.5(2)	N1–C1–N5	128.3(1)	132.1(2)

[a] **2**: symmetry code: (i) 0.5 − x, −0.5 + y, 0.5 − z. [b] **4**: symmetry code: (i) 2 − x, 1 − y, 1 − z.

Table 2 Hydrogen-bonding geometry in 5,5′-azotetrazolate salts **2** and **4**

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
2				
O3–H32···N6	0.98(3)	1.94(4)	2.899(2)	165(3)
O2–H21···N9	0.83(3)	2.05(3)	2.876(2)	172(3)
O1–H12···O2	0.90(3)	1.88(4)	2.776(2)	174(3)
N1–H1A···N8^{i}	0.96(3)	2.03(3)	2.974(2)	168(2)
N1–H1B···O1^{ii}	0.85(3)	1.95(3)	2.795(2)	176(2)
O1–H11···O2^{ii}	0.83(3)	1.93(3)	2.763(3)	180(3)
O3–H31···N7^{iii}	0.88(3)	2.03(3)	2.894(2)	167(2)
O2–H22···O3^{iv}	0.95(4)	1.74(4)	2.687(2)	176(3)
4				
N8–H8B···O2	0.98(4)	1.75(4)	2.725(3)	174(3)
N6–H6B···N1^{i}	0.84(3)	2.17(3)	3.000(3)	171(3)
N7–H7···N5^{ii}	0.83(3)	2.19(4)	2.998(3)	165(3)
N8–H8C···N4^{ii}	0.98(4)	1.92(4)	2.864(3)	159(3)
N6–H6A···N2^{iii}	0.87(3)	2.22(3)	3.088(4)	173(3)
N8–H8A···O1^{iv}	0.85(3)	2.23(3)	2.957(3)	144(3)
O2–H2B···N3^{iv}	0.93(5)	1.89(5)	2.803(3)	168(4)
N8–H8A···O1^{v}	0.85(3)	2.42(3)	3.038(4)	131(2)
O2–H2A···O1^{vi}	0.88(5)	1.87(5)	2.742(3)	174(4)

Symmetry codes: for **2**: (i) 0.5 − x, −0.5 + y, 0.5 − z; (ii) 1.5 − x, −0.5 + y, 0.5 − z; (iii) −x, 1 − y, 1 − z; (iv) 1 − x, 1 − y, 1 − z. **4**: (i) 1 − x, −y, 1 − z; (ii) −1 + x, −1 + y, z; (iii) 1 + x, y, z; (iv) 1 − x, −y, 2 − z; (v) −1 + x, y, z; (vi) 2 − x, −y, 2 − z.

Compound **2** crystallizes in a monoclinic cell in the space group $P2_1/n$ with two molecules in the unit cell as the hexahydrate species (Fig. 1(a)) and with a crystal density of 1.396 g cm^{-3}. Half of the molecule can be generated by symmetry (symmetry code (i) 1 − x, 1 − y, 1 − z). The molecules pack in the unit cell forming waved layers (Fig. 1(b)), which are connected by strong hydrogen bonds formed by two water molecules (O1···O2^{v} = 2.763(3) Å; symmetry code: (v) 1.5 − x, −0.5 + y, 0.5 − z). In a layer (Fig. 1(b)), there exists extensive hydrogen bonding. Every anion forms a hydrogen bond to the cation amino-group (N10^{ii}···N3 = 2.974(2) Å, symmetry code: (ii) 0.5 − x, 0.5 + y, 0.5 − z) and is surrounded by six water molecules to which it forms hydrogen bonding with distances between donor and acceptor atoms of ~2.9 Å. All nitrogen atoms in the tetrazole rings are involved in hydrogen bonding, only the bridging nitrogen atoms do not participate in any significant interaction.

It is interesting to compare the hydrogen bonding networks formed by **2** with those of the isomeric salt containing the 1,4DMAT$^+$ cation.[17b] Due to the complexity of these networks, graph-set nomenclature[39] is useful here to establish similarities in the hydrogen bonding patterns. The computer program *RPLUTO*[40,41] identifies up to 35 graph-sets formed

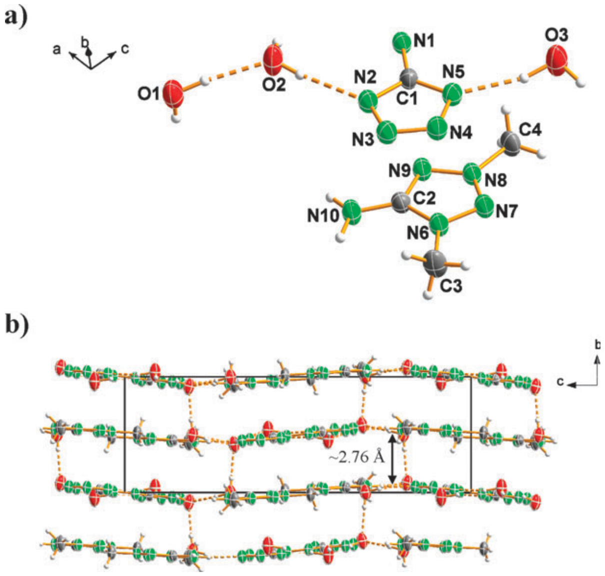


Fig. 1 (a) Asymmetric unit of 5,5′-azotetrazolate salt **2** with the labeling scheme (ellipsoids are represented at the 50% probability) and (b) formation of layers in the unit cell of **2** (view along the *a*-axis).

by the hydrogen bonds summarized in Table 2 (see also Table S2 of ESI†). At the primary level only dimeric interactions of the type **D1,1(2)** are found, which combine at the secondary level to form mainly other finite patterns with the labels **D2,2(X)** (X = 4, 5, 8–10), however, there also exist some **C1,2(4)** and **C2,2(10)** chain patterns and the **R4,4(10)** network represented in Fig. 2, which is formed by the side-on interaction of two 5,5′-azotetrazolate anions over two water molecules (O3···N6 = 2.899(2) Å and O3···$N7^{iii}$ = 2.894(2) Å; symmetry code: (iii) −*x*, 1 − *y*, 1 − *z*). The latter appears to be a common pattern for tetrazolium 5,5′-azotetrazolate salts.[17b] Lastly, the presence of six molecules of water in the crystal structure makes that most of the hydrogen-bonded networks are formed by more than only two hydrogen bonds rendering the standard graph-set nomenclature insufficient since it just describes patterns, which are formed by one or two different hydrogen bonds, thus at the primary or secondary level. Therefore, an extended graph-set nomenclature for more complex hydrogen bonding networks would certainly prove useful (*e.g.*, to describe the **R3,3(11)** ring network represented in Fig. 2 and formed at the tertiary level).

Compound **4** crystallizes with two molecules of crystal water and a relatively high density of 1.638 g cm^{-3} similar to guanadinium salts containing the same anion[19] and higher than tetrazolium 5,5′-azotetrazolate salts.[17b] This high value is explained by the extensive hydrogen bonding found in the structure. Table 2 contains tabulated the nine hydrogen bonds found in the structure. These hydrogen bonds are between N···N, N···O, O···N and O···O and are strong with distances between donor and acceptor atoms in the range ∼2.7–3.1 Å, in general well below the sum of the van der Waals radii (r_N = 1.55 Å; r_O = 1.52 Å).[42]

The compound crystallizes forming layers, which are connected *via* hydrogen bonds to the NH_3^+ moiety in the cation (N8···$O1^v$ = 3.038(4) Å; symmetry code: (v) –1 + *x*, *y*, *z*). Fig. 3 shows the hydrogen bonding in one of these layers. Every single electronegative atom in the structure is involved in the formation of (at least) one hydrogen bond. The reasonably complex hydrogen bonding networks can also be described in terms of graph-set analysis (see above). At the unitary level, the program identifies seven of the hydrogen bridges in the structure as describing **D1,1(2)** finite patterns, five of which combine (still at the primary level) to generate larger **D2,2(X)** (X = 4, 8, 10) dimer graph-sets. In addition, the other two hydrogen bonds form a **C1,1(5)** chain and an **R2,2(10)** ring networks. At the secondary level, two hydrogen bonds combine to form dimeric **D2,2(X)** (X = 4–10), **D2,3(8)**, **D3,3(10)**, chain **C3,3(X)** (X = 10, 14, 16, 18), **C2,2(X)** (X = 9, 10) and more interestingly ring **R2,2(X)** (X = 4, 7, 9, 10, 12) and **R4,4(X)** (X = 10, 14, 16, 18, 20, 26) patterns, whereas three hydrogen bonds combine forming an **R3,3(9)** motif. The **R2,2(7)** and **R2,2(9)** graph-sets are formed both by interaction between one cation and one anion ($N8^{vii}$···N4 = 2.864(3) Å; $N7^{vii}$···N5 = 2.998(3) Å; $N6^x$···N1 = 3.000(3) Å; symmetry codes: (vii) 1 − *x*, −*y*, 1 − *z*; (*x*) 1 + *x*, 1 + *y*, *z*) whereas the **R3,3(9)** network is described by the hydrogen bridges between one cation, one anion and one molecule of crystal water and

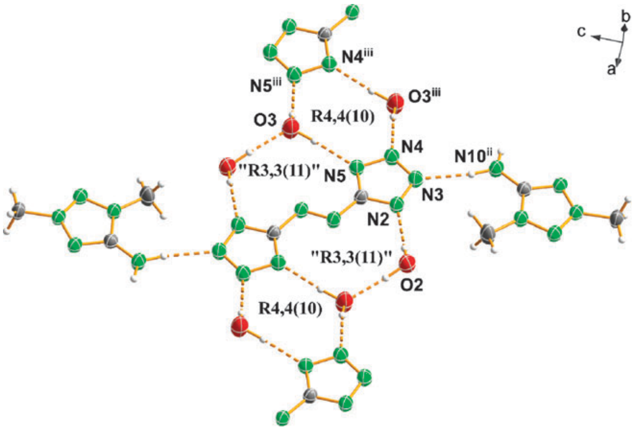


Fig. 2 Hydrogen bonding around the anion in the structure of **2**. Only half of the surrounding anions are represented for clarity purposes. Symmetry codes: (ii) 0.5 − *x*, 0.5 + y, 0.5 − *z*; (iii) *x*, 1 − *y*, 1 − *z*.

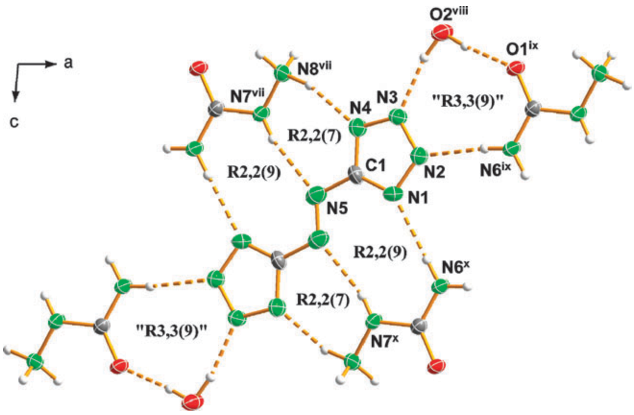


Fig. 3 Hydrogen bonding around the 5,5′-azotetrazolate anion in the crystal structure of **4**. Symmetry codes: (vii) 1 − *x*, −*y*, 1 − *z*; (viii) 1 + *x*, 1 + *y*, −1 + *z*; (ix) 3 − *x*, 1 − *y*, 1 − *z*; (x) 1 + *x*, 1 + *y*, *z*.

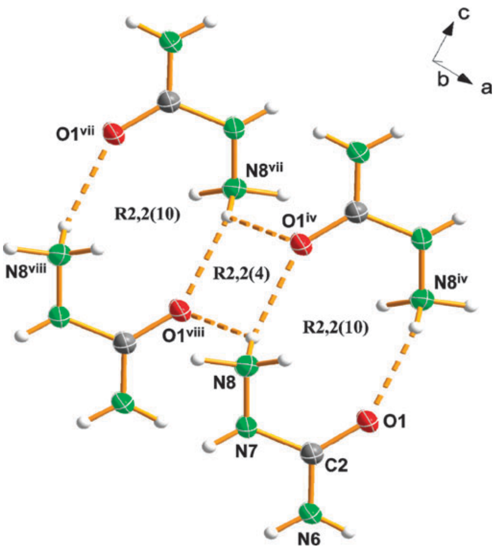


Fig. 4 Hydrogen bonding between cations in the crystal structure of **4**. Symmetry codes: (iv) $1 - x, -y, 2 - z$; (vii) $-x, -y, 2 - z$; (viii) $-1 + x, y, z$.

they are all represented in Fig. 3. Fig. 4 depicts the hydrogen bonding between cations. The hydrogen bond between layers described above describes a small **R2,2(4)** graph-set, whereas two cations interact yielding a larger **R2,2(10)** ring network at the primary level ($N8 \cdots O1^{iv} = 2.957(3)$ Å; symmetry code: (iv) $1 - x, -y, 2 - z$).

Thermal and energetic properties

Electronic energy calculations. The electronic energies of the 5,5′-azotetrazolate anion and of the 1,3-dimethyl-5-aminotetrazolium and semicarbazidium cations were calculated using the Gaussian 03W suite of programs[43] and are tabulated in Table 3. Møller–Plesset perturbation theory truncated at the second order (MP2)[44] was used for the calculations and the values were used unscaled. The correlation consistent polarized valence double-zeta basis set cc-pVDZ was used for all atoms in all calculations.[45,46] A detailed explanation of the method used here has been given in the recent literature and is therefore omitted here.[47]

Differential scanning calorimetry (DSC) measurements were used to study the thermal stability of the compounds in this work and the sensitivities of the materials towards impact, friction and electrostatic discharge were assessed by using standardized procedures.[48–51] In addition, for all four CHN(O) salts the constant volume energies of combustion ($\Delta U_{\text{comb.}}$) were determined experimentally using oxygen bomb calorimetry. The heats and energies of formation were back-calculated from the combustion data and subsequently used in conjunction with the molecular formula and density (from X-ray or picnometer measurements) to predict the detonation performance parameters (pressure and velocity) for each compound using the EXPLO5 computer code.[52] Because of the (in some cases) significant experimental uncertainties obtained in the bomb calorimetry measurements, the validity of the values obtained for the detonation parameters was checked by way of quantum chemical calculation (MP2) of electronic energies and an approximation of lattice enthalpy.

The DSC measurements were carried out at a heating rate of $\beta = 5$ °C min^{-1} on small samples of compounds **1–4** ($\sim$1 mg). The tetrazolium salts **1** and **2** show good thermal stabilities showing highly exothermic peaks up to above 190 °C, whereas the semicarbazidium derivatives **3** and **4** reveal lack of thermal stability, decomposing in two steps at $\sim$125 (sharp exothermic peak) and above 140 °C (slow decomposition), respectively. The low thermal stability of the semicarbazidium salts is in contrast with that of the chemically similar aminoguanidinium salt, which is stable up to 217 °C at the same heating rate.[19] Note that the 5,5′-azotetrazolate anion is expected to provide compounds with high thermal stabilities and the low decomposition temperatures of the semicarbazidium salts is most likely attributable to the cation itself (*e.g.*, many urea derivatives are known to be thermally labile). Although none of the compounds melted in the DSC apparatus prior to decomposition, the hydrated species **2** and **4** show endothermic peaks corresponding to the loss of crystal water at temperatures of $\sim$120 and $\sim$100 °C, respectively. In addition, the response to fast heating was tested by placing a small sample of the salts (typically $\sim$5–10 mg) in the flame. This resulted in smokeless burning in the case of the semicarbazidium salts **3** and **4** and a more vigorous reaction (*i.e.*, deflagration) in the case of **1** and **2**, also with little or no smoke (TNT burns and 1,3,5-trinitroperhydro-1,3,5-triazine, RDX, deflagrates under similar conditions). Fig. S1 (ESI†) shows pictures of a typical "flame test" for compounds **1** and **2**.

Table 4 summarizes the data collected for friction, impact and electrostatic discharge sensitivity of the compounds in this study. Comparison with other ionic salts containing the same cation (**1** and **2**)[26] or the same anion (**1–4**)[17b,19] puts into perspective the low sensitivity of the salts in this work, which, according to standard methods,[51] classify as being insensitive

Table 3 Results of the DFT calculations (MP2/aug-cc-pVDZ)[43]

Species	Formula	p.g[a]	$-E^b$/a.u.	zpe^c/kJ mol^{-1}	$NIMAG^d$
1,3DMAT$^+$	$C_3H_8N_5^+$	C_1	391.577017	347.8	0
Scz$^+$	$CH_6N_3O^+$	C_1	280.234194	247.7	0
ZT^{2-}	$C_2N_{10}^{2-}$	C_1	622.128460	146.7	0
Oxygen	O_2	$D_{\infty h}$	150.320042	41.8	0
Carbon dioxide	CO_2	$D_{\infty h}$	188.580940	127.5	0
Water	H_2O	$D_{\infty h}$	76.419736	234.5	0
Nitrogen	N_2	$D_{\infty h}$	109.524129	61.0	0

[a] Point group symmetry. [b] Energy (in atomic units). [c] Zero point energy. [d] Number of imaginary frequencies.

Table 4 Initial safety testing results and predicted[a] energetic performance of 5,5′-azotetrazolate salts **1–4** using the EXPLO5 code

	T_{ex}[b]/K	V_0[c]/L kg^{-1}	P_{det}[d]/GPa	D[e]/m s^{-1}	Impact[f]/J	Friction[f]/N	ESD (±)[g]	Thermal shock
1	2973 [3530]	783 [783]	19.0 [21.5]	7667 [8089]	>40	>360	—	Deflagrates
2	3931 [4086]	890 [890]	25.1 [25.8]	8585 [8685]	>40	>360	—	Deflagrates
3	2779 [3587]	836 [836]	23.4 [29.7]	8125 [8886]	>40	>360	—	Burns
4	2166 [3862]	879 [879]	20.0 [32.8]	7694 [9258]	>40	>360	—	Burns

[a] Calculated values in square brackets (see ref. 47 for calculation method). [b] Temperature of the explosion gases. [c] Volume of the explosion gases. [d] Detonation pressure. [e] Detonation velocity. [f] Tests according to BAM methods (see refs. 48–51). [g] Rough sensitivity to electrostatic discharge using a Tesla coil (~20 kV), + sensitive, − insensitive.

to both impact (>40 J) and friction (>360 N). The sensitivity of the salts towards friction was also tested by grinding the compounds in a mortar and the sensitivity towards electrostatic discharge was tested by spraying sparks across a small sample of the materials using a Tesla coil. In both cases, no reaction was observed, which is in agreement with the high insensitivity of the materials. In comparison to commonly used high explosives such as TNT or RDX,[53] the compounds in this report are less prone to accidental initiation by impact, friction or an electrostatic discharge (*i.e.*, to classical stimuli). This can be explained in terms of extensive hydrogen bonding (see X-ray discussion above), which seems to diminish the sensitivity of the compounds to classical stimuli. Interestingly, the parameters of which performance is most dependant on (*i.e.*, density and heat of formation) are either favored, in the case of the density, or slightly disfavored, in the case of heat of formation, by strong hydrogen bonding.[54] In this context, nitrogen-rich compounds are envisioned to form extensive hydrogen-bonded networks and are therefore of interest as prospective highly energetic though insensitive materials.[55,56]

Due to the need for more powerful energetic compounds with decreased sensitivity values,[1] performance of new materials has also been at the centre of attention of recent investigations.[4,5] The EXPLO5 software can be used to calculate the performance of a material with a general formula $C_xH_yN_zO_t$, commonly measured by the detonation parameters (*i.e.*, detonation pressure and velocity) by using the molecular formula of the compound, its density (either calculated or experimentally determined) and its heat of formation (ΔU_f). The program is based on the Becker–Kistiakowsky–Wilson (BKWN) rules[12] and uses the following values for the BKWN equation of state: $\alpha = 0.5$, $\beta = 0.176$, $\kappa = 14.71$ and $\theta = 6620$. Some descriptive values of these calculations have been collected in Table 4. Table 5 contains summarized the experimentally determined energies of combustion and back-calculated energies of formation used for the calculations. The (MP2) computed values have also been included in both tables in square brackets.

The energies of formation (ΔU°_f) of salts **1–4** were back-calculated from the energies of combustion on the basis of their combustion equations (see below), Hess's Law, the known standard heats of formation for water and carbon dioxide[58] and a correction for change in gas volume during combustion. No corrections for the non-ideal formation of nitric acid (typically ~5% of the nitrogen content reacts to form HNO_3) were made.

$$\mathbf{1}: [C_3H_8N_5]^+{}_2[C_2N_{10}]^{2-}\,(s) + 12\,O_2 \rightarrow 8\,CO_2\,(g) + 8\,H_2O\,(l) + 10\,N_2\,(g)$$

$$\mathbf{2}: [C_3H_8N_5]^+{}_2[C_2N_{10}]^{2-}\cdot 6H_2O\,(s) + 12\,O_2 \rightarrow 8\,CO_2\,(g) + 14\,H_2O\,(l) + 10\,N_2\,(g)$$

$$\mathbf{3}: [CH_7N_3O]^+{}_2[C_2N_{10}]^{2-}\,(s) + 6\,O_2 \rightarrow 4\,CO_2\,(g) + 6\,H_2O\,(l) + 8\,N_2\,(g)$$

$$\mathbf{4}: [CH_7N_3O]^+{}_2[C_2N_{10}]^{2-}\cdot 2H_2O\,(s) + 8\,O_2 \rightarrow 4\,CO_2\,(g) + 8\,H_2O\,(l) + 8\,N_2\,(g)$$

All materials have high nitrogen contents up to ~71% (**1** and **3**) and even higher combined nitrogen and oxygen balances up to 82% (**4**). The low amount of oxygen present in the compounds accounts for the relatively low (highly negative) oxygen balances (Ω), which are nevertheless comparable to that of TNT ($\Omega = -74.0\%$) or RDX ($\Omega = -21.6\%$). The values for the calculated (from X-ray analysis) or experimentally determined (from picnometer measurements) densities are relatively low in the case of the tetrazolium salts **1** and **2** (ρ ~1.40 g cm^{-3}) and relatively high for the semicarbazidium salts **3** and **4** (ρ ~1.62 g cm^{-3}) in comparison with other salts with the same anion.[17b,19] Despite of the low carbon contents of the compounds, the experimentally determined energies of combustion take highly negative values and account for the highly positive energies of formation back-calculated for **1–3**. The presence of the less endothermic semicarbazidium cation (in comparison to the tetrazolium cation in compounds **1** and **2**) on one hand, and the crystal water (in contrast to the anhydrous compound **3**) account for the negative energy of formation observed for salt **4**, which is, however, more positive than that of TNT.[53] As expected, the highly endothermic character of the cation and the absence of crystal water in compound **1** make it most endothermic ($\Delta U^\circ_f = +3650$ kJ kg^{-1}), with a value comparable to that of bis(hydrazinium) 5,5′-azotetrazolate ($\Delta U^\circ_f = +3700$ kJ kg^{-1}).[16]

Comparison of the experimentally determined (from bomb calorimetry measurements) heats of formation and detonation parameters (see below) with those calculated on the basis of the electronic energies of cation and anion (see above for computational method) gives relatively good agreements in the case of the tetrazolium salts **1** and **2**, as expected from a cation with relatively low possibility to form hydrogen bonds. However, in the case of the semicarbazidium salts, which forms extensive hydrogen bonded patterns (see X-ray discussion), the agreement between semiempirical and computed values is lower. This can be explained by the low capacity of the method used in this work to account for strong

Table 5 Physico-chemical properties of 5,5′-azotetrazole salts **1–4**

	1	**2**	**3**	**4**
Formula	$C_8H_{16}N_{20}$	$C_8H_{28}N_{20}O_6$	$C_4H_{12}N_{16}O_2$	$C_4H_{16}N_{16}O_4$
MW/g mol^{-1}	392.19	500.51	316.25	352.28
$T_m{}^a$/°C	—	∼119 (–H_2O)	121	127, ∼96 (–H_2O)
$T_{decomp}{}^b$/°C	193.2	194.3	121, 145	127, 160
N (%)[d]	71.4	56.0	70.9	63.6
N + O (%)[e]	71.4	75.2	81.0	81.8
Ω^f (%)	–97.9	–76.7	–60.7	–54.5
ρ^g/g cm^{-3}	1.412	1.396	1.614	1.638
$\Delta U_{comb}{}^{hi}$/cal g^{-1}	−4158(20) [−4434]	−4190(15)	−2865(20) [−3282]	−2455(15)
$\Delta U°_f{}^{ij}$/kJ kg^{-1}	+3650(90) [+4821]	+3390(60) [+3781]	+1700(75) [+3445]	−560(60) [+3093]
$\Delta H°_f{}^{ik}$/kJ kg^{-1}	+3475(90) [+4707]	+3220(60) [+3692]	+1527(75) [+3328]	−730(60) [+2987]

[a] Chemical melting point and [b] decomposition point (DSC onsets) from measurement with β = 5 °C min^{-1}. [d] Nitrogen percentage. [e] Combined nitrogen and oxygen contents. [f] Oxygen balance according to ref. 57. [g] Density from picnometer (**1** and **3**) or X-ray (**2** and **4**) measurements. [h] Experimentally determined (oxygen bomb calorimetry) constant volume energy of combustion. [i] Uncertainty in parentheses and calculated values in square brackets (see ref. 47 for calculation method). [j] Experimentally determined (back-calculated from $\Delta U_{comb.}$) energy of formation. [k] Experimentally determined enthalpy of formation.

Table 6 Thermodynamic and explosive properties of formulations of 5,5′-azotetrazolate salts **1–4** with ammonium nitrate (AN)

	AN + **1**[a]	AN + **2**[b]	AN + **3**[c]	AN + **4**[d]
ρ^e/g cm^{-3}	1.669	1.654	1.695	1.699
M/g mol^{-1}	133.09	168.29	139.05	153.49
Ω^f (%)	−0.1	−0.3	−0.2	−0.1
$\Delta U°_f{}^g$/kJ kg^{-1}	−3051	−2784	−2893	−3381
$\Delta H°_f{}^h$/kJ kg^{-1}	−3184	−2917	−3029	−3517
$T_{ex}{}^i$/K	3052	3290	2991	2824
$V_0{}^j$/L kg^{-1}	949	964	948	956
P^k/GPa	24.4	26.4	24.8	24.1
D^l/m s^{-1}	8041	8329	8079	7993

[a] 83% AN + 17% **1**. [b] 79% AN + 21% **2**. [c] 75% AN + 25% **3**. [d] 73% AN + 27% **4**. [e] Density (averaged with EXPLO5). [f] Oxygen balance according to EXPLO5. [g] Calculated energy of formation. [h] Calculated enthalpy of formation. [i] Temperature of the explosion gases. [j] Volume of the explosion gases. [k] Detonation pressure. [l] Detonation velocity.

hydrogen bonding as has been pointed out previously.[59] In any case, the detonation velocities of compounds **1–4** are either comparable to nitroglycerine (D = 7714 m s^{-1}) in the case of compounds **1** (D = 7667 m s^{-1}) and **4** (D = 7694 m s^{-1}) or, more interestingly, comparable to highly energetic secondary explosives such as pentaerytritol tetranitrate (PETN, D = 8400 m s^{-1}) or RDX (D = 8750 m s^{-1}) in the case of salts **2** (D = 8585 m s^{-1}) and **3** (D = 8125 m s^{-1}).[53] In comparison to recently developed oxygen-balanced tetrazolium dinitramide salts in our group,[60] the performances of **2** and **3** are also comparable if not superior. In addition, the low sensitivities towards impact and friction in comparison to nitroglycerine, PETN or RDX make **1–4** of interest as insensitive energetic compounds.

At this point, it must be said that the calculated energies of formation and thus, the detonation parameters, predicted using electronic energies (calculated by the MP2 method), tend to overestimate the real values (see Tables 4 and 5).[61] This is an important issue since most of the performance parameters discussed in the literature are based on calculations and not on experimental data from calorimetric measurements. The result is an overestimation of (in many case) at least ∼5% in the detonation velocities. Thus we conclude that the materials discussed in this work are, at least, as high-performing as those described in the literature. This topic will be more accurately addressed in a future publication of the group.[26]

Since performance of energetic materials is dependant not only on density and heat of formation but also on oxygen balance,[1] and this reaches its maximum value for a neutral oxygen balance, we calculated the detonation parameters of mixtures of compounds **1–4** with an oxidizer, namely ammonium nitrate (AN) and ammonium dinitramide (ADN) in an oxygen neutral ratio in order to further increase the performance of the mixtures in comparison to the stand-alone energetic compounds. Formulations of the 5,5′-azotetrazolate salts with AN (Table 6) show an increase in the performance of compounds **1** and **4** to detonation pressures of ∼24.0 GPa and detonation velocities of ∼8000 m s^{-1}. However, in the case of the more energetic salts **2** and **3**, the detonation parameters are reduced slightly. On the other hand, mixtures of the compounds with ADN (Table 7) show in all four cases a large increase in the detonation parameters to values perfectly comparable to formulations of RDX and ADN (D = 9091 m s^{-1} and P = 34.9 GPa) in the case of salt **2** (D = 8911 m s^{-1} and P = 31.9 GPa) and comparable to the predicted values for mixtures of TNT and ADN (D = 8739 m s^{-1} and P = 31.7 GPa) for the rest of the compounds.

Long term stability and decomposition gases

Although highly energetic, the semicarbazidium salts **3** and **4** might see their use limited in applications requiring materials with a high thermal stability, due to their low thermal stability, however, the 5,5′-azotetrazolate salts **1** and **2** have attractive energetic properties, *i.e.*, high performance, low sensitivity, high thermal stability, *etc*. Due to the prospective interest in these two compounds for energetic applications we became

Table 7 Thermodynamic and explosive properties of formulations of 5,5′-azotetrazolate salts **1–4** with ammonium dinitramide (ADN)

	ADN + **1**[a]	ADN + **2**[b]	ADN + **3**[c]	ADN + **4**[d]
ρ^{e}/g cm^{-3}	1.725	1.705	1.750	1.754
M/g mol^{-1}	180.38	218.16	181.70	197.07
Ω^{f} (%)	−0.2	+0.2	−0.2	+0.1
$\Delta U^{\circ}{}_{\mathrm{f}}{}^{g}$/kJ kg^{-1}	−92	+31	−251	−919
$\Delta H^{\circ}{}_{\mathrm{f}}{}^{h}$/kJ kg^{-1}	−224	−101	−387	−1055
$T_{\mathrm{ex}}{}^{i}$/K	4041	4206	3866	3620
$V_{0}{}^{j}$/L kg^{-1}	885	904	890	900
P^{k}/GPa	31.1	31.9	31.2	30.3
D^{l}/m s^{-1}	8786	8911	8791	8701

[a] 79% ADN + 21% **1**. [b] 75% ADN + 25% **2**. [c] 70% ADN + 30% **3**. [d] 68% ADN + 32% **4**. [e] Density (averaged with EXPLO5). [f] Oxygen balance according to EXPLO5. [g] Calculated energy of formation. [h] Calculated enthalpy of formation. [i] Temperature of the explosion gases. [j] Volume of the explosion gases. [k] Detonation pressure. [l] Detonation velocity.

interested in gaining insight into the long term thermal stability of these two materials. The long term thermal stability of **1** was measured by means of thermal safety calorimetry (TSC) using a Systag FlexyTSC instrument[62] in combination with a RADEX V5 oven and the SysGraph software. A sample of ~300 mg of the salt was filled in a test glass, which was heated at atmospheric pressure to ~40 °C below the decomposition temperature of the compound (*i.e.*, ~150 °C) over a time of 48 h. Since at this temperature the crystal water in compound **2** is lost forming **1**, the test was only conducted for the latter salt. A typical TSC curve is shown in Fig. 5. The sample does not show any sign of decomposition after the measurement time by comparison with the oven curve nor by visually inspecting the color of the sample (before and after the test the sample shows the characteristic bright yellow color of 5,5′-azotetrazolate salts). The results of this test are indicative of the good long term thermal stability of salt **1** and, indirectly, of salt **2**, and can be extrapolated to shelf-lives of over 50 years at room temperature for both compounds.

In addition to stability issues, environmental impact of energetic compounds is also of utmost interest. In this regard, decomposition experiments gives insight into the toxicity of the gases formed upon decomposition of an energetic compound. Once again, the experiments were carried out only for the more thermally stable compounds **1** and **2**. As expected, the experimentally determined decomposition gases as well as their amounts for both compounds are very similar with the exception of water gas, which is only detected for the hydrated salt **2**. As expected, molecular nitrogen ($N_2^{\bullet+}$) dominates the mass spectra (EI$^+$) of the decomposition products of both salts as suggested by the mass peak at m/z = 28. After this, signals at m/z = 15 (CH_3^+), 16 ($CH_4^{\bullet+}$, NH_2^+), 26 (CN^+) and 27 ($HCN^{\bullet+}$) are supportive for the formation of methane, ammonia and hydrogen cyanide, in keeping with the IR measurements (see below). Additionally, other peaks of lower intensity are found at the following masses: m/z = 12 (C^{4+}), 13 (CH^{3+}), 14 (CH_2^{2+}, N^+), 17 ($NH_3^{\bullet+}$), 16 ($CH_4^{\bullet+}$), 18 ($H_2O^{\bullet+}$), 38 (CCN^{3+}), 39 ($CHCN^{2+}$), 40 (CH_2CN^+) and 41 ($CH_3CN^{\bullet+}$).[63–65] Note the formation of minute amounts of acetonitrile as suggested by the signals in the range m/z = 38–41.

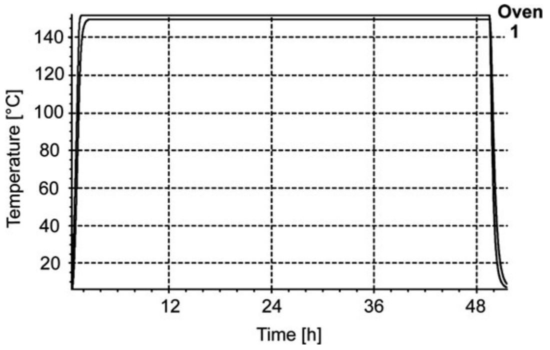


Fig. 5 TSC plot for the long term thermal stability of compound **1**.

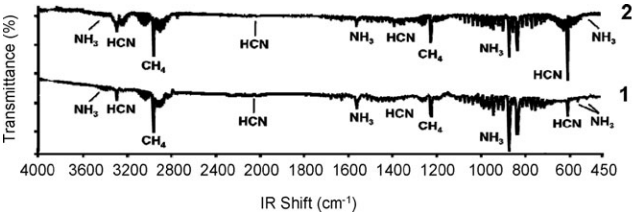


Fig. 6 IR spectra of the gaseous products formed upon decomposition of 5,5′-azotetrazolate salts **1** and **2**.

Fig. 6 shows the IR spectra of the decomposition products detected for compounds **1** and **2**. In contrast to mass spectrometry (MS) measurements where the formation of acetonitrile and water (both in the gas phase) is observed, the IR spectra of compounds **1** and **2** does not support the formation of either of these two species (probably in the liquid phase). This can be explained in terms of the experimental procedure used, *i.e.*, the MS samples were measured first (see general procedure in experimental part). However, apart from molecular nitrogen (IR inactive) the remainder of the decomposition gases analyzed by IR spectroscopy support the MS results. This is, all NH_3, HCN and CH_4 were experimentally detected. Measuring the relative intensities of the gases detected in the EI$^+$ measurements leads to amounts of HCN, which add to almost 1/3 of those of molecular nitrogen. However, it must be taken into consideration that N_2 is much more difficult to ionize than HCN and, therefore, a quantification of the amounts of gases formed based solely on the intensity of the MS peaks does not lead to satisfactory results. No absolute quantification of the amounts of gases formed was performed during our experiments, however, it is clear that the amounts of HCN based on the relative peak intensities would be highly overestimated.

In order to account, to a certain degree, for a quantification of the gases formed upon decomposition of compounds **1** and **2**, the predicted decomposition gases were calculated using the ICT code.[66] The ICT code allows for a fast an inexpensive prediction of the decomposition gases, which were calculated for the decomposition of salts **1** and **2** as well as for compounds **3** and **4**. The computational results have been summarized in Table 8 and, additionally, Fig. S2 of ESI† shows histogram plots of the decomposition gases.

The calculated results are in fair agreement with the experimental values. The main decomposition gas predicted by the

Table 8 Predicted decomposition gases and heats of explosion of 5,5′-azotetrazolate salts **1–4** (using the ICT code)[a]

	CO_2	H_2O	N_2	CO	H_2	NH_3	CH_4	HCN	C	$\Delta H_{ex}{}^c$/ cal g^{-1}
1	—[b]	—[b]	594.7	—[b]	3.7	144.4	46.4	1.1	209.6	967
2	4.8	210.2	452.2	4.0	3.3	130.2	25.6	1.1	169.5	1674
3	1.4	111.6	607.5	1.7	1.7	122.3	9.2	1.0	143.5	871
4	3.8	199.7	540.3	2.6	1.4	116.0	5.5	1.0	129.6	659

[a] The amount of gases formed at 298 K is given in grams of gas per kilogram of energetic compound. [b] Gas not predicted by the code. [c] Heat of explosion.

ICT code is molecular nitrogen, the amount of which increases in the same direction as does the nitrogen content (*i.e.*, **2** < **4** < **3** < **1**). After this, carbon soot is the second expected major product for the anhydrous salts (**1** and **3**) whereas for the hydrated species (**2** and **4**) it is water. The amount of carbon soot diminishes progressively from **1** to **4** and, as expected from nitrogen-rich materials, the figures are far below the values predicted for common energetic materials such as TNT (262.0 g kg^{-1}) and perfectly comparable to those of 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclododecane (TEX, 152.2 g kg^{-1}). Due to the many amino groups present in the cations of compounds **1–4**, NH_3 is also expected to form in relatively large amounts, in the range ~115–145 g kg^{-1}. The small amounts of CO and CO_2 anticipated by the code point at the fact that the oxygen contained in compounds **2–4** does not oxidize the carbon skeleton but is converted to water. On the other hand, the presence of the two methyl groups in the cation of compounds **1** and **2** accounts for the higher amounts of CH_4 in comparison to salts **3** and **4**. H_2 is expected to form in small quantities below 4.0 g kg^{-1}, whereas highly toxic HCN is, for all four compounds, expected to form in only marginal amounts (~1.0 g kg^{-1}). Lastly, the heats of explosions have variable values and that of compound **2** is exceptionally high (1674 cal g^{-1}), even higher than the corresponding computed value for RDX (1593 cal g^{-1}).

Experimental

CAUTION!

Although we experienced no difficulties during the manipulation of the compounds described in this work, tetrazoles and derivatives thereof are potentially energetic compounds, which might detonate under a given stimuli (*e.g.*, impact, friction or electrostatic discharge). We recommend all HEDMs to be treated with respect and with the best safety practice. The use of safety equipment such as a leather jacket, Kevlar gloves, conducting shoes and ear plugs is strongly encouraged, in particular when handling the highly sensitive silver 5,5′-azotetrazolate salt.

General method

All solvents and chemicals were used as supplied by Sigma-Aldrich Inc. without further purification. Disodium 5,5′-azotetrazolate pentahydrate[67] and 1,3-dimethyl-5-aminotetrazolium iodide[21e] were synthesized according to previously reported procedures. A Netsch Simultanous Thermal Analyzer STA 429 machine was used for the CHN analysis and mass spectrometry measurements were recorded on a JEOL MStation JMS 700 machine.[68] DSC measurements (calorimetry (Linseis DSC PT-10 instrument)[69] were used to measure the temperatures of water loss and decomposition points of compounds **1–4**. Measurements were conducted at a heating rate of β = 5 °C min^{-1} in closed aluminum sample pans with a small hole in the top for gas release under a purge of nitrogen (20 mL min^{-1}) and using an empty identical aluminum sample pan as the reference. NMR spectra (^1H and ^{13}C) were measured using a JEOL Eclipse 400 instrument in [D_6]-DMSO and at room temperature. Tetramethylsilane (TMS) was used as an external standard for these measurements. Vibrational spectra were either performed using a Perkin-Elmer Spectrum One FT-IR instrument (IR, KBr pellets)[70] or with a Perkin-Elmer Spectrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (Raman, λ = 1064 nm) at room temperature. Intensity values (IR) are qualitatively described as "very strong" (vs), "strong" (s), "medium" (m) and "weak" (w) and activities (Raman) are given as percentages of the most intense peak.

Decomposition experiments

The explosion gases of salts **1** and **2** were analyzed by IR and mass spectrometry measurements. A sample of the compound (~100 mg) was placed at the bottom of a steel bomb (volume ~100 mL), which had been previously dried in the oven for several days at 100 °C. A valve was attached to the open end and the bomb was evacuated for several minutes at ~10^{-3} mbar. The decomposition of the sample was induced by placing the bottom of the bomb on top of the flame of a Bunsen burner (careful: ear protection!). After 2–3 min a sharp explosion occurred and the explosion gases were left to expand in the steel bomb. At this point, this was attached to a JEOL MStation JMS 700 mass spectrometer.[68] The reservoir of the spectrometer was evacuated during 15 min prior to letting the gases in the bomb to diffuse into the ionization chamber. Mass spectra were recorded using an electron impact mode (EI^+) at 1 scan s^{-1}. The same gases can be analyzed by IR by attaching the bomb to a previously evacuated IR gas cell (NaCl windows) and letting the gases to shortly diffuse in. The empty evacuated IR gas cell was used as the background and the sample was then measured in the range 4000–450 cm^{-1} (5 scans, resolution = 4.0) using a Perkin-Elmer Spektrum One FT-IR machine.[70]

Oxygen bomb calorimetry

A small sample of compounds **1–4** (typically ~200 mg) was carefully mixed with analytical grade benzoic acid (~800 mg) until homogeneous and pressed into a pellet, which was subsequently burned in a 3.05 MPa atmosphere of pure oxygen using a Parr 1356 bomb calorimeter (static jacket) equipped with a Parr 207A oxygen bomb for the combustion of highly energetic materials.[71] A Parr 1755 printer, furnished with a Parr 1356 calorimeter, was used to produce a permanent record of all activities within the calorimeter, which had been calibrated by the combustion of certified benzoic acid. The measurements were repeated five times and the average values were taken.

1,3-Dimethyl-5-aminotetrazolium 5,5′-azotetrazolate (1)

Method 1. Sodium 5,5′-azotetrazolate pentahydrate (0.301 g, 1.00 mmol) was loaded in a plastic test tube and suspended in $\sim$5 mL water. Neat silver nitrate (0.390 g, 2.33 mmol) was then carefully added without stirring producing the precipitation of highly sensitive (**CAUTION!!**) silver 5,5′-azotetrazolate (orange solid). The reaction mixture was then carefully stirred for 15 min under the exclusion of light. At this point the precipitated solid was centrifuged and washed twice with $\sim$5 mL water and twice with $\sim$5 mL dry methanol. The wet silver salt was then suspended in $\sim$5 mL freshly distilled methanol and reacted with 1,3-dimethyl-5-aminotetrazolium iodide (0.372 g, 1.54 mmol) for 15 min in the dark. The insoluble yellow silver iodide was filtered off, washed with methanol and the solvents were left to slowly evaporate, yielding a bright yellow solid. Recrystallization can be carried out from a water–acetonitrile mixture (0.221 g, 73%).

Method 2. Alternatively, drying **2** under high vacuum for four days at 80 °C resulted in the formation of the title compound in quantitative yield. $C_8H_{16}N_{20}$ (392.19 g mol^{-1}, calc./found): C 24.49/24.35, H 4.11/4.16, N 71.40/70.27%; DSC (5 °C min^{-1}, °C, onset): 193.2 (decomp.); m/z (FAB$^+$, xenon, 6 keV, m-NBA matrix): 114.1 (100, cation), (FAB$^-$, xenon, 6 keV, m-NBA matrix): 165.1 (100, $[C_2N_{10}H]^-$); ^{1}H NMR ([D$_6$]-DMSO, 399.78 MHz, TMS) δ/ppm: 8.40 (s, 2H, NH_2), 4.34 (s, 3H, C4H$_3$), 3.92 (s, 3H, C3H$_3$); ^{13}C{^{1}H} NMR ([D$_6$]-DMSO, 100.52 MHz, TMS) δ/ppm: 173.3 (2C, $[N_4C\text{–}N{=}N\text{–}CN_4]^{2-}$), 158.1 (1C, C1–NH$_2$), 42.5 (1C, C4H$_3$), 34.2 (1C, C3H$_3$); Raman $\tilde{\nu}$/cm^{-1} (rel. int.): 2968(2), 1483(57), 1436(2), 1412(6), 1379(100), 1353(3), 1185(1), 1070(11), 1044(41), 1027(7), 918(11), 879(1), 849(2), 629(3), 343(1), 290(1); IR $\tilde{\nu}$/cm^{-1} (KBr, rel. int.): 3434(m), 3360(m), 3245(m), 3059(m), 2791(w), 2732(w), 2516(w), 2401(vw), 2206(vw), 2059(vw), 1675(s), 1622(m), 1451(m), 1430(m), 1385(m), 1367(w), 1289(w), 1248(w), 1185(w), 1151(w), 1114(w), 1070(w), 1035(w), 849(m), 773(w), 730(m), 676(w), 628(w), 561(w).

Decomposition experiments

MS (EI$^+$): m/z = 12 (0.5, C^{4+}), 13 (0.5, CH^{3+}), 14 (3.3, CH_2^{2+}, N^+), 15 (5.3, CH_3^+), 16 (6.9, $CH_4^{\bullet+}$, NH_2^+), 17 (2.1, $NH_3^{\bullet+}$), 26 (6.6, CN^+), 27 (30.6, $HCN^{\bullet+}$), 28 (100.0, $N_2^{\bullet+}$), 38 (0.2, CCN^{3+}), 39 (0.4, $CHCN^{2+}$), 40 (0.9, CH_2CN^+), 41 (1.7, $CH_3CN^{\bullet+}$); IR (gas): $\tilde{\nu}$/cm^{-1} = 3451 (vw, NH$_3$), 3332 (m, HCN), 3283 (m, HCN), 3085 (w, CH$_4$), 3012 (s, CH$_4$), 2950 (w, CH$_4$), 2167 (vw, HCN), 2102 (vw, HCN), 1621 (w, NH$_3$), 1430 (w, HCN), 1382 (vw, HCN), 1300 (m, CH$_4$), 965 (s, NH$_3$), 926 (s, NH$_3$), 731 (s, HCN), 713 (vs, HCN), 684 (m, HCN), 669 (vw, NH$_3$), 625 (vw, NH$_3$).

1,3-Dimethyl-5-aminotetrazolium 5,5′-azotetrazolate hexahydrate (2)

Sodium 5,5′-azotetrazolate pentahydrate (0.611 g, 2.02 mmol) was dissolved in hot water (6 ml) at $\sim$70 °C and 1,3-dimethyl-5-aminotetrazolium iodide (0.970 g, 4.01 mmol) was added to the hot solution, which was heated for 3 h at 100 °C. After cooling slowly in an oil-bath the precipitate was filtered off and washed with acetone and ether giving a yellow solid (0.701 g, 69%). Single crystals of **2** suitable for X-ray analysis were obtained by recrystallization from hot water. $C_8H_{28}N_{20}O_6$ (500.25 g mol^{-1}, calc./found): C 19.20/19.28, H 5.64/5.23, N 55.98/56.18%; DSC (5 °C min^{-1}, °C, onset): $\sim$119 (–H$_2$O), 194.3 (decomp.); m/z (FAB$^+$, xenon, 6 keV, m-NBA matrix): 114.1 (100, cation), (FAB$^-$, xenon, 6 keV, m-NBA matrix): 165.1 (100, $[C_2N_{10}H]^-$); ^{1}H NMR ([D$_6$]-DMSO, 399.78 MHz, TMS) δ/ppm: 8.23 (s, 2H, NH$_2$), 4.48 (s, 3H, C4H$_3$), 3.98 (s, 12H, H$_2$O), 3.85 (s, 3H, C3H$_3$); ^{13}C{^{1}H} NMR ([D$_6$]-DMSO, 100.52 MHz, TMS) δ/ppm: 173.3 (2C, $[N_4C\text{–}N{=}N\text{–}CN_4]^{2-}$), 158.2 (1C, C1–NH$_2$), 42.6 (1C, C4H$_3$), 34.2 (1C, C3H$_3$); Raman $\tilde{\nu}$/cm^{-1} (rel. int.): 2957(1), 1488(48), 1420(5), 1386(100), 1358(2), 1197(1), 1162(1), 1099(2), 1082(19), 1065(26), 919(7), 854(2), 626(3), 346(1), 292(1), 239(1); IR $\tilde{\nu}$/cm^{-1} (KBr, rel. int.): 3429(s), 3291(s), 3225(s), 3061(s), 2725(w), 2215(w), 2075(w), 1675(vs), 1622(s), 1457(m), 1393(s), 1365(m), 1289(m), 1244(m), 1187(w), 1178(w), 1154(w), 1142(w), 1129(w), 1074(w), 1041(w), 1027(w), 1019(w), 853(w), 775(m), 732(m), 674(m), 616(w), 555(w).

Decomposition experiments

MS (EI$^+$): m/z = 12 (0.4, C^{4+}), 13 (0.3, CH^{3+}), 14 (3.5, CH_2^{2+}, N^+), 15 (4.9, CH_3^+), 16 (7.6, $CH_4^{\bullet+}$, NH_2^+, O^{2+}), 17 (2.9, $NH_3^{\bullet+}$, OH^+), 18 (4.1, $H_2O^{\bullet+}$), 26 (5.1, CN^+), 27 (24.6, $HCN^{\bullet+}$), 28 (100.0, $N_2^{\bullet+}$), 38 (0.4, CCN^{3+}), 39 (0.9, $CHCN^{2+}$), 40 (1.6, CH_2CN^+), 41 (1.9, $CH_3CN^{\bullet+}$); IR (gas): $\tilde{\nu}$/cm^{-1}) = 3452 (vw, NH$_3$), 3333 (m, HCN), 3284 (m, HCN), 3084 (w, CH$_4$), 3011 (s, CH$_4$), 2952 (w, CH$_4$), 2166 (vw, HCN), 2103 (vw, HCN), 1621 (w, NH$_3$), 1429 (w, HCN), 1382 (vw, HCN), 1299 (m, CH$_4$), 965 (s, NH$_3$), 925 (s, NH$_3$), 730 (m, HCN), 713 (s, HCN), 686 (m, HCN), 627 (vw, NH$_3$).

Semicarbazidium 5,5′-azotetrazolate (3)

Method 1. A solution of silver nitrate (0.415 g, 2.46 mmol) in 2 mL water was added dropwise into a suspension of sodium 5,5′-azotetrazolate pentahydrate (0.357 g, 1.19 mmol) in 3 mL water. The reaction mixture was carefully stirred for 30 min. in the dark leading to the formation of a highly sensitive compound (silver 5,5′-azotetrazolate). The insoluble orange powder was subsequently washed with water to remove any excess of reactants and the water was removed by washing with dry methanol and subsequently centrifuging. The methanol wet residue was then reacted with a solution of semicarbazidium chloride (0.218 g, 1.96 mmol) in 5 mL dry methanol for 30 min under the exclusion of light, leading to the precipitation of white silver chloride, which was filtered off and discarded. Finally the solvent was stripped under high vacuum ($\sim$10^{-3} mbar) and at room temperature yielding **3** (0.282 g, 91%).

Method 2. The crystal water in **4** could be completely eliminated by heating the compound (0.514 g, 1.58 mmol) at 40 °C under vacuum ($\sim$10^{-3} mbar) over two days yielding **3** in quantitative yield as a slightly brown powder (0.497 g).

$C_4H_{12}N_{16}O_2$ (316.13 g mol^{-1}, calc./found): C 15.18/15.28, H 3.82/3.87, N 70.87/70.57%; DSC (5 °C min^{-1}, °C, onset): 121 (mp + decomp.), ~145 (decomp.); *m*/*z* (FAB$^+$, xenon, 6 keV, m-NBA matrix): 76.1 (100, cation), (FAB$^-$, xenon, 6 keV, m-NBA matrix): 165.1 (100, $[C_2N_{10}H]^-$); ^{1}H NMR ([D$_6$]-DMSO, 400.18 MHz, 25 °C, TMS) δ/ppm: 8.50 (s, 1H, NH), 8.10 (s, 3H, NH_3^+), 6.36 (s, 2H, NH_2); $^{13}C\{^1H\}$ NMR ([D$_6$]-DMSO, 100.63 MHz, 25 °C, TMS) δ/ppm: 159.3 (2C, C = O), 171.2 (2C, $[N_4C\text{–}N = N\text{–}CN_4]^{2-}$); Raman $\tilde{\nu}/\text{cm}^{-1}$ (rel. int.): 1500(46), 1422(14), 1380(100), 1189(2), 1156(2), 1079(10), 1049(51), 1033(19), 923(11), 348(1), 190(1); IR $\tilde{\nu}/\text{cm}^{-1}$ (KBr, rel. int.): 3347(vs), 3234(vs), 2926(s), 2681(m), 2091(w), 2066(w), 2011(w), 1683(vs), 1581(vs), 1536(s), 1459(w), 1404(s), 1396(s), 1267(m), 1202(m), 1188(m), 1173(m), 1151(m), 1133(m), 1081(w), 1056(w), 1036(w), 941(w), 876(w), 767(m), 742(m), 685(m), 612(m), 571(m), 529(m), 511(m).

Semicarbazidium 5,5′-azotetrazolate dihydrate (4)

Sodium 5,5′-azotetrazolate pentahydrate (1.017 g, 3.39 mmol) was suspended in 10 mL water and the suspension was gently warmed up by means of a heat gun until all insoluble material had dissolved. A solution of semicarbazidium chloride (0.752 g, 6.78 mmol) in 5 mL water at room temperature was added at once and the clear dark orange solution was stirred for 2 min. Crystallization was induced by scratching the sides of the flask with a glass stab and the solution was left to stand overnight yielding brown–orange single crystals of the compound. Elemental analysis showed that **4** formed as the dihydrated species and no further purification was necessary (0.578 g, 48%). $C_4H_{16}N_{16}O_4$ (352.15 g mol^{-1}, calc./found): C 13.64/13.75, H 4.58/4.45, N 63.62/63.50%; DSC (5 °C min^{-1}, °C, onset): 96 ($-H_2O$), 127 (mp + decomp.), ~160 (decomp.); *m*/*z* (FAB$^+$, xenon, 6 keV, m-NBA matrix): 76.1 (70, cation), (FAB$^-$, xenon, 6 keV, m-NBA matrix): 165.1 (100, $[C_2N_{10}H]^-$); ^{1}H NMR ([D$_6$]-DMSO, 400.18 MHz, 25 °C, TMS) δ/ppm: 9.48 (s, 3H, NH_3^+), 8.50 (s, 1H, NH), 6.57 (s, 2H, NH_2), 3.89 (s, 4H, H_2O); $^{13}C\{^1H\}$ NMR ([D$_6$]-DMSO, 100.63 MHz, 25 °C, TMS) δ/ppm: 157.9 (2C, C = O), 173.1 (2C, $[N_4C\text{–}N = N\text{–}CN_4]^{2-}$); Raman $\tilde{\nu}/\text{cm}^{-1}$ (rel. int.): 1505(60), 1430(17), 1388(100), 1203(3), 1085(15), 1065(60), 1040(14), 925(15), 357(1); IR $\tilde{\nu}/\text{cm}^{-1}$ (KBr, rel. int.): 3348(vs), 3232(vs), 2924(s), 2638(s), 2089(w), 2066(w), 2012(w), 1683(s), 1577(s), 1537(s), 1454(m), 1405(s), 1396(m), 1267(m), 1202(m), 1163(w), 1147(w), 1130(w), 1081(w), 1055(w), 1035(w), 938(w), 767(w), 742(m), 684(w), 666(w), 614(w), 570(w), 528(m).

Conclusions

Four new energetic salts based on the 5,5′-azotetrazolate anion ($[C_2N_{10}]^{2-}$) and tetrazolium or semicarbazidium cations (**1–4**) have been synthesized and characterized by analytical and spectroscopic methods. Additionally, the molecular structures of the hydrated species **2** and **4** were determined by means of X-ray analysis, showing interesting hydrogen bonding patterns. All four compounds have high performances and are regardless insensitive to classical stimuli, which suggest their potential for application. In particular, the good thermal stability of salt **2** in combination with high nitrogen content and detonation parameters comparable to RDX, make the compound a suitable candidate for further studies as a new low-pollution HEDM.

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