Energetic salts of azotetrazolate, iminobis(5-tetrazolate) and 5, 5′-bis(tetrazolate)†

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Energetic ionic salts of azotetrazolate (AT), iminobis(5-tetrazolate) (IBT) and 5, 5′-bis(tetrazole) (BT) were synthesized; 1-methyl-4-aminotriazolium azotetrazolate has a layered structure and exhibits a heat of formation of +4360 kJ kg^{-1}.

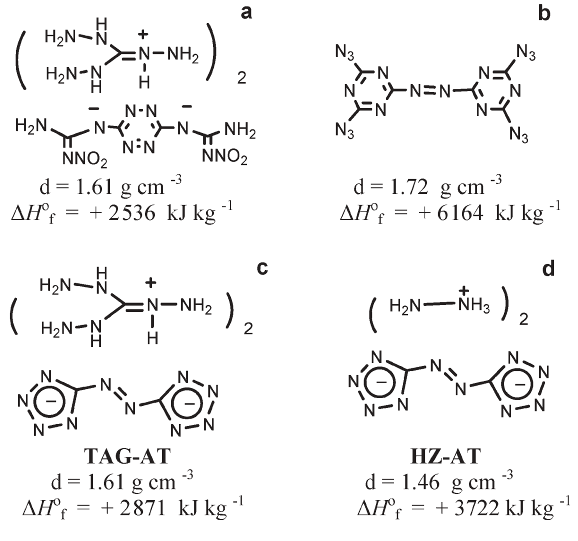
Interest in modern high-energy density materials (HEDM) continues.[1–5] One of the most recent and exciting developments are salts with a high nitrogen content and with very high positive heats of formation that show remarkable insensitivity to friction, electrostatic discharge, and shock. The high heats of formation are directly attributable to the large number of inherently energetic N–N and C–N bonds. For example, triaminoguanidinium azotetrazolate[1] and nitroguanyl-substituted tetrazine[6] salts exhibit potentially useful energetic properties with high heats of formation (ΔH°_f) of +2871 kJ kg^{-1} and +2536 kJ kg^{-1}, respectively. At this time, the highest heat of formation reported is +6164 kJ kg^{-1} for 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine.[7] The presence of azo and hydrazo links dramatically increases the melting points of the polyazido products while concomitantly giving rise to much higher positive heats of formation compared with polynitro and other high nitrogen compounds.

5,5′-Azotetrazolate salts are considered to be energetic materials. Since the first report of these metal salts, *e.g.*, alkali metal and alkaline earth, and of protonated nitrogen bases, *e.g.*, ammonium and hydrazinium in the 1890s,[8] guanidinium,[9] triaminoguanidinium,[10] and others have been well documented.[11] Heats of formation of hydrazinium,[11*a*] guanidinium,[1] and ammonium 5,5′-azotetrazolates[1] were measured as ΔH°_f = +3722, +1442, and +2213 kJ kg^{-1}, respectively. These high nitrogen-containing salts have been widely used as gas generators for airbags, initiators and additives in solid rockets as low-smoke propellant ingredients (Scheme 1).

While our work was underway, reports in a similar area appeared.[6,7] Now we report on the synthesis and characterization of imidazolium, triazolium and tetrazolium azotetrazolates which exhibit very positive high heats of formation, while the analogous salts IBT and BT show relatively lower heats of formation and the IBT salt exhibits different thermal behaviour.

Sodium and barium 5,5′-azotetrazolates were used as starting materials and were synthesized according to the literature.[11*b*] Initially, an effort was made to metathesize triazolium nitrate[12] or sulfate directly with barium 5,5′-azotetrazolate, but decomposition of the azotetrazolate anion to give nitrogen gas occurred due to its instability in the presence of acid. However, the use of quaternized imidazolium iodide salts followed by two metathetical reaction steps[11] readily gave the desired azotetrazolate. Thus, compound **1** (Scheme 2) was readily prepared, which was an ionic liquid at room temperature melting at 3 °C similar to 1-butyl-3-methylimidium 3,5-dinitrotriazolate.[13] This is unprecedented since most of the known azotetrazolates are solid with melting points higher than 160 °C. However, the heat of formation for compound **1** is −2273 kJ kg^{-1}. For comparison, 1-methyl-4-nitroimidazole was quaternized with methyl iodide at 90 °C,[14] followed by a metathesis reaction resulting in salt **2** which exhibits a heat of formation of +2999 kJ kg^{-1}. The latter is higher than that of TAG-AT.[7] Encouraged by this result, we prepared some substituted triazolium and azido-triazolium azotetrazolate salts.

4-Amino-1,2,4-triazole itself has a rather high calculated heat of formation at +318 kJ mol^{-1}. Although its azotetrazolate salts have a lower nitrogen content than TAG-AT, its two quaternized salts, **5** and **6**, exhibit very high heats of formation, at +4360 kJ kg^{-1} and +4679 kJ kg^{-1}, respectively. The structure of **5** is further supported by X-ray single crystal analysis.‡ The hydrogen atoms on N7 were disordered over the mirror plane. Interestingly, the unit cell packs as a layered structure with hydrogen bonds; the distance between the two layers is 3.04 Å , and as shown in Fig. 1, there are hydrogen bonds between the cation and anion; the hydrogen atom on C(12) participates in two hydrogen bonds (see ESI for more information†).



Scheme 1 Structures of some known energetic compounds. a, ref. 6; b, ref. 7; c, ref. 10; d, ref. 11*a*.

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b5/b502583d/
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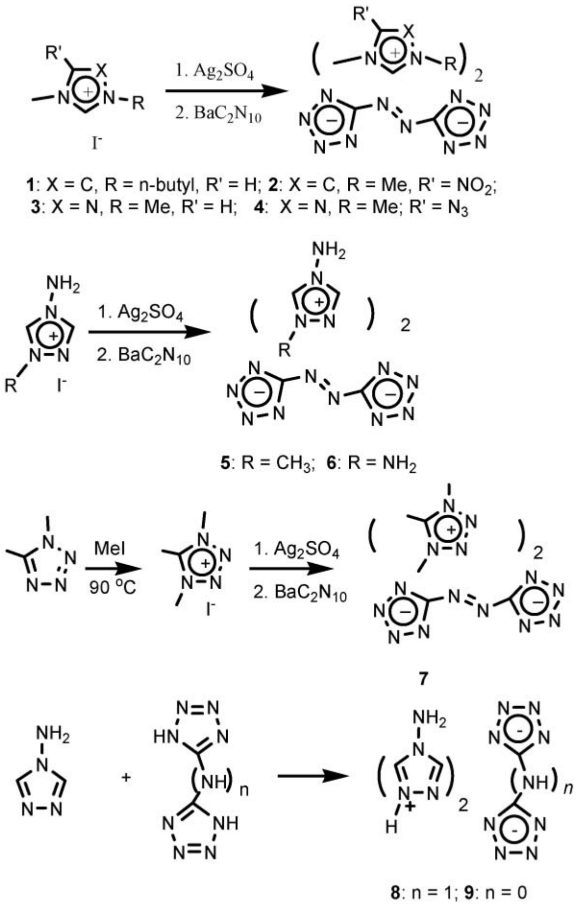


Scheme 2 Synthesis of energetic salts.

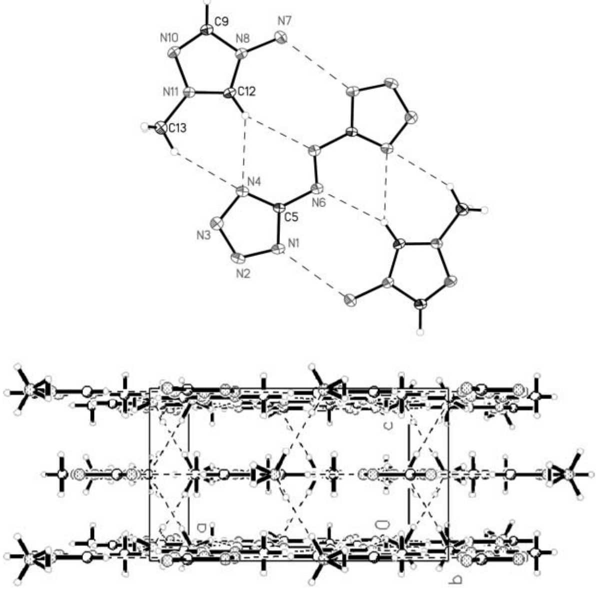


Fig. 1 Thermal ellipsoid (30%) plot of **5**. Only unique atoms are labelled. Disordered hydrogen atoms have been removed for clarity (upper) and a packing diagram is shown (lower).

A trimethyltetrazolium salt was also obtained by quaternization of 1, 5-dimethyltetrazole with methyl iodide at 90 °C. Frequently the quaternized products of 1,5-disubstituted tetrazoles give rise to two isomers, but in this case, under higher reaction temperature, only the 1,2,5-quaternized azotetrazolate salt, **7**, was obtained. This was found to have a relatively low positive heat of formation, +1547 kJ kg^{-1}. Although there are several reports of the salts of iminobis(5-tetrazolate) (IBT)[15] and 5,5′-bis(tetrazolate) (BT),[16] most of them are described in patents or unpublished documents, and there is a paucity of data available for comparison. Therefore, we prepared the salts of IBT and BT. In refluxing methanol, they can readily quaternize 4-amino-1,2,4-triazole to give the corresponding energetic salts **8** and **9**. With regard to the heats of formation of the salts of these three dianions, BT ranks lower than AT but much higher than IBT. Interestingly, in sharp contrast, the BT salt has a much lower melting point.

Density is an important physical property of any new energetic material. As shown in Table 1, the densities of most of the salts range from 1.5 to 1.6 g cm^{-3}. It is noteworthy that, with the exception of compound **7**, none of azotetrazolate salts contains water of hydration or solvent as determined by NMR and elemental analysis. Decomposition of azotetrazolate salts **2–7** occurs violently at the melting point. In contrast to AT salts, the IBT salt, **9**, evolved gas gently at its melting point, and the BT salt, **8**, is stable at its melting point of 131 °C, but decomposes violently at 182 °C, shown by DSC. Most of the salts are stable for storage at room temperature for 2 months, except for **6**, which spontaneously evolves N_2 gas.

Explosives such as TNT have been successfully used in the detonation synthesis of nanodiamond,[17] and these energetic compounds could be the precursors of nanomaterials. Recently, 3,6-di(azido)-1,2,4,5-tetrazine (DiAT)[18] was found to undergo decomposition to give carbon nanospheres or carbon nitride depending on the different heating process. In our work, microwave radiation[19] was used to study the thermal behavior of **5**, **8** and **9** in air. Under microwave radiation, **5** and **9** decomposed violently to give carbon black powder while compound **8** gently decomposed to 1,2,4-triazole, which sublimes on the wall of the reaction tube, and forms a yellowish nanopowder (Fig. 2) on the bottom of the tube with empirical formula of $C_3N_{4.7}H_4$ (Scheme 3) as determined by elemental analysis. The yellow material is insoluble in any solvent tried.

In conclusion, ionic salts of AT and BT exhibit high heats of formation compared to IBT salt, and IBT salt shows markedly different thermal behavior from AT and BT on microwave heating.

Table 1 Properties of the energetic salts

Compound	mp/°C	Density[a]/ g cm^{-3}	ΔH°_f/ kJ mol^{-1}	ΔH°_f/ kJ kg^{-1}
1	3	1.26	−1006	−2273
2	145	1.54	1345	2999
3	182	1.42	1216	3374
4	155	1.55	1429	3230
5	180	1.57[b]	1580	4360
6	—[c]	1.59	1705	4679
7	189	1.46	604	1547
8	175	1.59	496	1543
9	131	1.61	948	3095

[a] Gas pycnometer method. [b] X-Ray density is 1.61 g cm^{-3}. [c] Melting point not observed, decomposes violently at 134 °C.

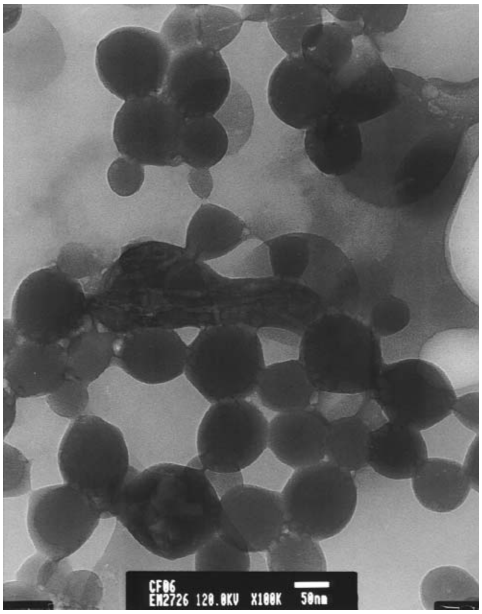
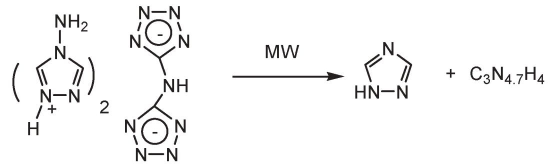


Fig. 2 TEM image of the nano powder. Bar represents 50 nm.



Scheme 3 Decomposition of **8** on microwave heating.

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Notes and references

‡ Crystal data for **5**, $C_8H_{14}N_{18}$, $M = 362.37$, orthorhombic, $a = 10.4301(13)$ Å, $b = 23.494(3)$ Å, $c = 6.0885(7)$ Å, $V = 1491.9(3)$ Å^3, $T = 86(2)$ K, space group *Ibam*, $Z = 4$, μ(Mo-Kα) = 0.122 mm^{-1}, $R1 = 0.0515$, $wR2 = 0.1089$ ($I > 2\sigma(I)$); $R1 = 0.0776$, $wR2 = 0.1210$ (all data). CCDC 265160. See http://www.rsc.org/suppdata/cc/b5/b502583d/ for crystallographic data in CIF or other electronic format.

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19 Using a CEM discovery microwave oven, 30 mg sample for each run, 2 min ramp to 200 °C, and held at this temperature for 10 min. Caution! A large amount of energetic salts for each run would result in destructive explosion.