Mono and Bridged Azolium Picrates as Energetic Salts

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The energetic mono and bridged imidazolium, triazolium and tetrazolium picrates **7–10**, **14**, and **16**, the dipicrates **23**, **25**, and **26** and the dinitrates **24**, and **27** were synthesized by the quaternization of azolium derivatives (**1**, **2**, **13**, **15**, **19** and **20**) with picric acid and nitric acid or by metathesis of the corresponding quaternary salts (**3**, **6**, **21** and **22**) with silver picrate or silver nitrate. The structures of **14** and **16** were determined by single-crystal X-ray diffraction analysis confirming quaterization on the triazolium and tetrazolium rings.

Their physical and thermodynamic properties were determined. In some cases, the salts are thermally stable to ca. 300 °C and they exhibit densities averaging ca. 1.6 g/cm^3. Nearly all have positive heats of formation with the highest calculated value, $\Delta_f H^\circ_m$ = 611.6 kJ/mol, found for 3-azido-1,4-dimethyl-1,2,4-triazolium picrate (**10**).

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Introduction

Energetic materials are used extensively for both civilian and military applications. There are ongoing research programs worldwide to develop such new materials with higher performance or enhanced insensitivity to thermal or shock insults. In recent years, the synthesis of energetic, heterocyclic compounds have attracted considerable interest. Heterocycles generally have higher heats of formation, density, and oxygen balance than their carbocyclic analogues.[1–3]

Recently, a new class of energetic compounds containing a large number of nitrogen atoms has been studied. These high-nitrogen compounds form a unique class of energetic materials whose energy is derived from their very high positive heats of formation rather than from the combustion of the carbon backbone or the ring/cage strain. The high heat of formation is directly attributable to the large number of inherently energetic N–N and C–N bonds.[4–8]

Most often molecular compounds have been utilized in an energetic role, whereas we and others have recently demonstrated that heterocyclic-based energetic, low-melting salts appear to be of considerable value in this area.[9–13] Energetic materials that are salt-based often possess advantages over non-ionic molecules since these salts tend to exhibit lower vapor pressures and higher densities than their atomically similar non-ionic analogues. Five-membered nitrogen-containing heterocycles are traditional centers for energetic materials, and considerable attention is currently focused on energetic compounds based on azoles.[14,15] N-Aminoazolium salts are a family of compounds of increasing interest, since these substituted hetero rings when paired with nitrate or perchlorate anions form new, highly energetic salts.

We have synthesized energetic salts based on N-aminoazoles with concomitant determination of structural and thermal properties.[16–18] Increasing the number of nitrogen atoms in heterocycles results in considerable gain in the standard enthalpy of formation in the resulting compounds. The enthalpy criteria of energetic chemical systems are governed by their molecular structure. In moving from imidazole ($\Delta H_f^\circ{}_{(cryst)}$ = 58.5 kJ/mol)[19] to 1,2,4-triazole ($\Delta H_f^\circ{}_{(cryst)}$ = 109 kJ/mol) to tetrazole ($\Delta H_f^\circ{}_{(cryst)}$ = 237.2 kJ/mol),[20] the variation in the trend of the heats of formation is increasingly positive The N-amino group behaves as an electron-withdrawing group in high-nitrogen heterocycles.[9]

High-nitrogen compounds containing polyazides possess even more positive heats of formation because their energy content rapidly increases with the number of energetic azido groups in the molecule. However, they tend to be extremely sensitive to spark, friction, and impact as well as to heat.[8] We have reported new energetic salts obtained by the quaternization of azido or nitro derivatives of imidazole, 1,2,4-triazole and substituted derivatives of tetrazole with nitric or perchloric acid or with iodomethane followed by metathesis reaction with silver nitrate or silver perchlorate.[17] While these compounds with azide-containing triazolium cations (nitrate or perchlorate anion) do exhibit marginally high positive heats of formation, recently reported molecular azides of triazine are considerably more energetic with considerably higher heats of formation, e. g., 2,4,6-triazido-1,3,5-triazine (+1053 kJ/mol) and 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine (+2171 kJ/mol).[8]

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Another area of increasing interest is based on high-energy salts where both the cation and anion are high-nitrogen species.[8,21,22] This is a relatively new area where only a very few such compounds have been studied.[5,10b,22c] One of the more recent and exciting developments in high energy dense materials is salts with high-nitrogen content and with very high positive heats of formation which show remarkable insensitivity to electrostatic discharge, friction, and shock.

We have now extended our studies to salts with energetic mono and bridged azolium cations with picrate as the anion, and have determined their physical and thermodynamic properties. While the typical anions used in these systems are for example, nitrate, perchlorate, and dinitramide, until now their picrate analogues have not been synthesized. In our work, the physical and energetic properties of new picrate salts are compared with those of the salts formed with the former anions. The new salts reported here contain mono or dications and consequently, are either mono or dipicrates. These picrate salts combine an oxygen-rich anion with a high-nitrogen azolium cation thus providing the opportunity for high positive heats of formation. Although anhydrous picric acid tends to be unstable, and its impact and friction sensitivities are higher than that of TNT, many organic and inorganic picrate salts have been created and studied;[23] however, none consists of diazolium cations combined with picrate. The successful syntheses and characterization of these rather stable salts with moderately high positive enthalpies of formation are now reported.

Results and Discussion

Energetic salts, some of which are ionic liquids, have been prepared that contain substituted azolium cations (e. g., imidazolium, triazolium and tetrazolium) in combination with usually small energetic inorganic anions [e. g., NO_3^-, ClO_4^-, and $N(NO_2)_2^-$].[9,10c,16–18,24] Now we have replaced these simple inorganic species by introducing picrate as the energetic anion.
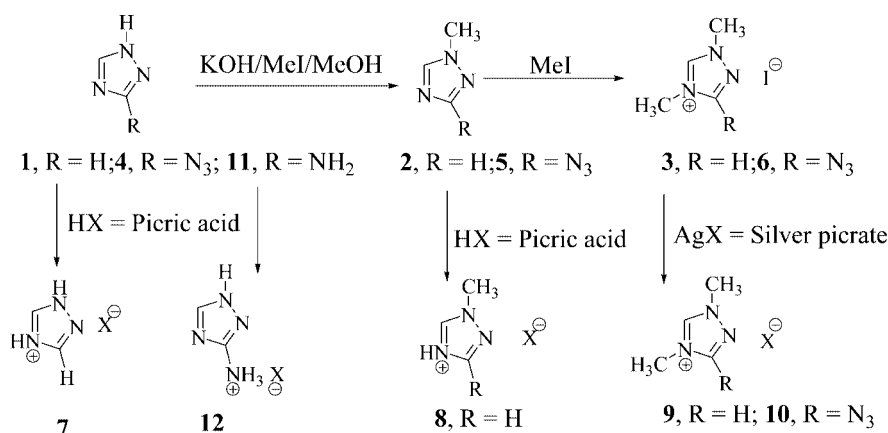
Triazolium or substituted triazolium picrates were prepared either by direct reaction with picric acid in methanol

(7, 8) or metathesis with silver picrate after quaternization of the parent triazole with methyl iodide (9, 10) (Scheme 1). The triazolium iodides, 3 and 6, were prepared based on the literature.[17,25] Although earlier we were able to quaternize azido-substituted triazoles with concentrated nitric or perchloric acid,[17] the analogous reactions of 4 and 5 with picric acid failed under a variety of conditions. This likely arises from the lower acidity of picric acid (pK_a of 0.3) compared to nitric acid (pK_a of –1.44) and with the concomitant decrease in the basicity of the triazolium ring because of the presence of the azide group. However, 3-azido-1,4-dimethyl-1,2,4-triazolium picrate (10) can be readily obtained from 6 which was metathesized with silver picrate (Scheme 1).
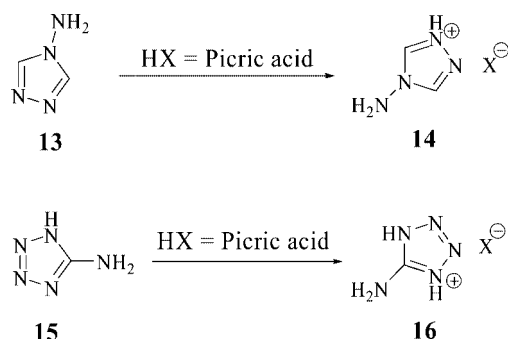
In their ^{1}H NMR spectra, all of the compounds 3, 6, 7, and 8–10, with the exception of 12 (shift at δ = 8.3 ppm), have chemical shifts downfield from δ = 9.3 ppm. The latter shifts indicate that these compounds were comprised of quaternized triazolium rings. However, quaternization of 3-amino-1,2,4-triazole (11) did not occur at the N-4 position in the triazolium ring, but rather compound 12 resulted from the ready protonation of the 3-amino group (Scheme 1). This same phenomenon was observed when concentrated nitric or perchloric acid was used, that is, a substituted ammonium salt ($RNH_3^+X^-$, X = NO_3^-, ClO_4^-) was formed analogous to 12.

However, 4-amino-1,2,4-triazole (13) was readily quaternized with picric acid in methanol by protonating the ring at N-1 to give the triazolium salt 14 in high yield (Scheme 2). This is supported by signals at δ = 9.5 ppm and δ = 144.1 ppm in the ^{1}H NMR and ^{13}C NMR spectra, respectively. Additionally, the single-crystal X-ray structure corroborates the quaternization at N-1 (Figure 1).

These results are consistent with the literature where *N*-amino groups in nitrogen-rich heterocycles were quaternized in the ring, not at the *N*-amino group.[9,16,26] This apparently arises because the *N*-amino group acts as an electronegative, electron-withdrawing group in these triazolium systems in contrast to the cases where the triazolium derivatives contain *C*-amino group (s). However, surprisingly, quaternization of 5-amino-tetrazole (*C*-amino group)

1, R = H;**4**, R = N$_3$; **11**, R = NH$_2$ **2**, R = H;**5**, R = N$_3$ **3**, R = H;**6**, R = N$_3$

7   **12**   **8**, R = H   **9**, R = H; **10**, R = N$_3$

Scheme 1.

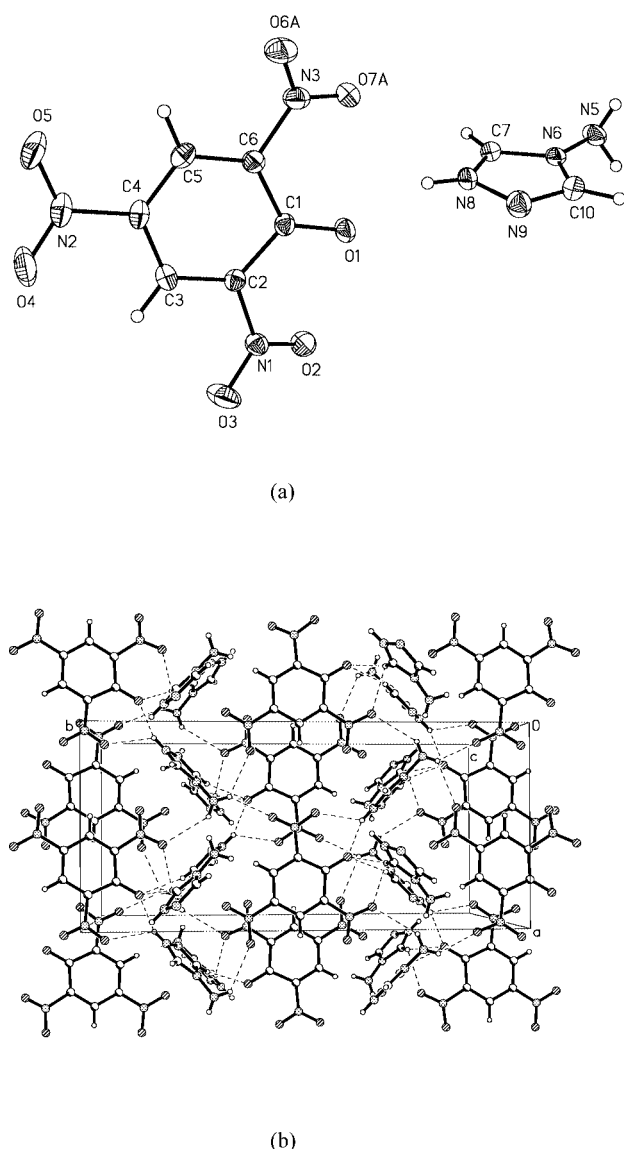C.-M. Jin, C. Ye, C. Piekarski, B. Twamley, J. M. Shreeve

Scheme 2.

(a)

(b)

Figure 1. (a) 30% Probability thermal ellipsoid plot of **14**. Only one conformation for the disordered NO₂ group is shown. Hydrogen atoms are shown but are unlabelled for clarity. (b) A packing diagram of **14**. Dashed lines indicate hydrogen bonding. Zig-zag sheets of triazolium cations tie the rows of picrates into a crosslinked 3D array.

(**15**) (Scheme 2) occurs at the N-4 position in the tetrazolium ring in high yield, and not at the amino group at C-5, to form the salt 5-amino-1,2,4-tetrazolium picrate (**16**). The single-crystal X-ray structure of compound **16** is given in Figure 2.

There is a paucity of energetic salts with bridged cations.[5] In order to examine the physical and thermodynamic properties of mono and diazolium salts containing a common anion, bridged bis(imidazolium) or bis(triazolium) methane compounds were obtained from the reaction of imidazole or triazole with dibromo- or dichloromethane under basic conditions and in the presence of a phase-transfer catalyst (Scheme 3).[27] These bridged azolium species, **19** and **20**, were either: 1) Reacted with picric or nitric acid to form the picrate **23**, or the nitrate **24**; however, compound **20** did not react with picric acid to give the corresponding dipicrate; or 2) quaternized with methyl iodide to give compound **21** and **22**,[27c] which were subsequently metathesized with silver picrate or nitrate forming compound **25**, **26** and **27**. Each of the picrate or nitrate salts was isolated in a yield >88%. Compound **27** is readily soluble in water, but **23**–**26** are not miscible with water. In general, all of these new picrate and nitrate salts are hydrolytically stable.

Physical characteristics and thermochemical properties of the new energetic ionic salts are given in Table 1. The effectiveness of an energetic compound is a function of many properties. Density is crucial since the more grams (mol) of material that can be loaded in a given space, the more efficient the energetic species is. High oxygen balance and a positive, Scheme 3, heat of formation increase the sensitivity of the material as well as performance since the specific impulse is proportional to the square root of heat of formation. For example, the heat of formation is 1075 kJ/mol, the density, 1.60 g/cm³, and the oxygen balance, –56% are reported for an highly energetic salt, triaminoguanidinium 5,5′-azobis(1*H*-tetrazolate).[8]

Most of the picrates have good thermal stabilities ranging between 176 °C (**10**) and 313 °C (**25**) (TGA), melting points between 91 °C (**8**) and 215 °C (**23**) (DSC), and relatively high densities between 1.48 (**10**) and 1.85 (**16**) g/cm³ (gas pycnometer). In fact, the latter approaches the density of HMX at 1.91 g/cm³. However, in general, the bridged azolium picrates are somewhat more stable thermally than their monocationic picrate analogues as shown by their decomposition temperatures, e. g., **26**, T_d = 242 °C, is higher than **8**, T_d = 185 °C. Also, the picrates are more thermally stable than nitrates or perchlorates, e. g., 4-amino-1,2,4-triazolium picrate (**14**) decomposes at 228 °C compared with the nitrate and perchlorate which decompose at 181 °C and 208 °C, respectively.[18]

Similarly, compound **26** (picrate) decomposes at 242 °C, and compound **27** (nitrate) at 162 °C. However, while triazolium picrate (**7**) is thermally unstable at 196 °C, and the nitrate is stable only upto 182 °C, the perchlorate decomposes at 285 °C.[9] Compound **27**, a nitrate salt, exhibits properties of an energetic ionic liquid (T_g –15 °C). In general, the nitrate salt with same azolium cation has a lower
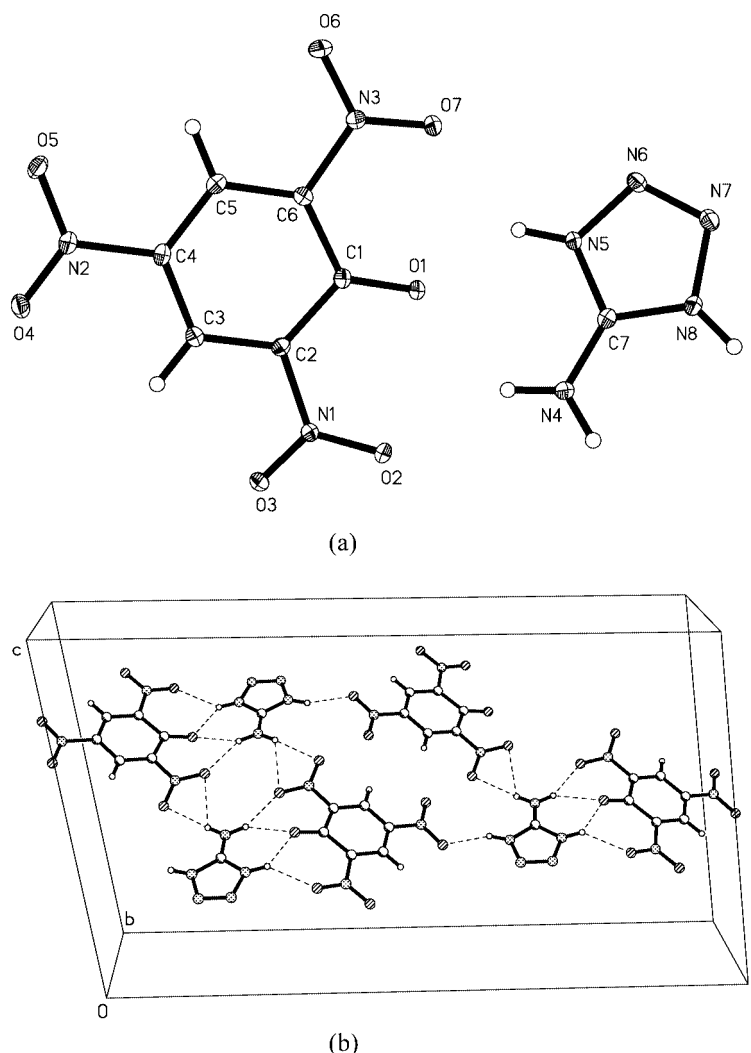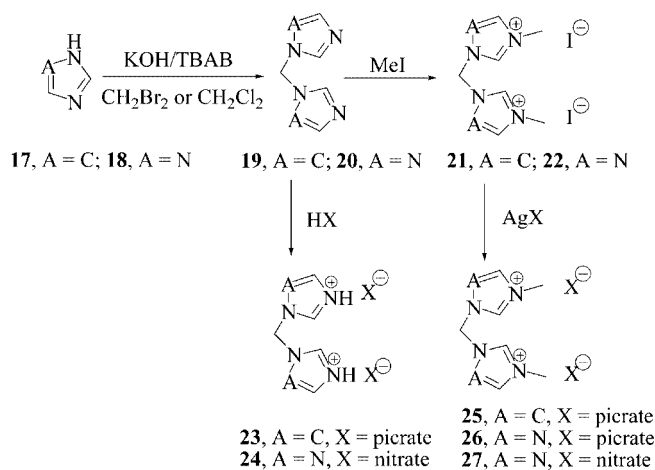
(a)

(b)

Figure 2. (a) 30% Probability thermal ellipsoid plot of **16**. Hydrogen atoms are shown but are unlabelled for clarity. (b) A packing diagram of **16**. Only one sheet section is shown. Hydrogen bonding is indicated by dashed lines.

17, A = C; **18**, A = N   **19**, A = C; **20**, A = N   **21**, A = C; **22**, A = N

23, A = C, X = picrate
24, A = N, X = nitrate

25, A = C, X = picrate
26, A = N, X = picrate
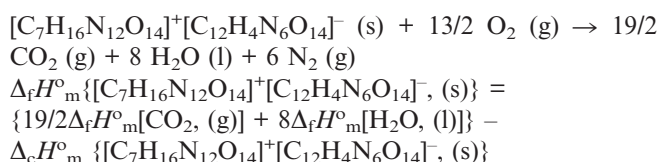**27**, A = N, X = nitrate

Scheme 3.

melting point than its picrate or perchlorate; e. g. compound **27** is liquid and compound **26** with T_m 216 °C.

4-Amino-1,2,4-triazolium picrate (**14**) with T_m = 197 °C is higher than the nitrate with T_m = 69 °C.[18] Unfortunately, we did not obtain ionic liquids based on picrate; only 1-methyl-1,2,4-triazolium picrate (**8**) with a melting point 91 °C falls into the ionic liquid class. The calculated oxygen balance values range from –36 to –93% which are reasonably close to those for TAG-AT (–73%), TNT (–74%) and picric acid (–43%) (Table 1) and slightly more negative than for HMX (–21%) and RDX (–22%). The molar enthalpy of formation for each sample, e. g., for compound **26**, was derived from the constant volume combustion energy using the following equation:

$$\Delta_c H^{\circ}_m = \Delta_c U_m + \Delta nRT \, [\Delta n = \sum n_i \, (\text{products, g}) - \sum n_i \, (\text{reactants, g})]$$

where $\sum n_i$ is the total molar amount of the gases in products or reactants.

The calculated heat of formation was based on the following reaction:

$[C_7H_{16}N_{12}O_{14}]^+[C_{12}H_4N_6O_{14}]^-$ (s) + 13/2 O_2 (g) → 19/2 CO_2 (g) + 8 H_2O (l) + 6 N_2 (g)

$\Delta_f H^o_m\{[C_7H_{16}N_{12}O_{14}]^+[C_{12}H_4N_6O_{14}]^-, (s)\} = \{19/2\Delta_f H^o_m[CO_2, (g)] + 8\Delta_f H^o_m[H_2O, (l)]\} - \Delta_c H^o_m \{[C_7H_{16}N_{12}O_{14}]^+[C_{12}H_4N_6O_{14}]^-, (s)\}$

Using the above formula and the literature values for the standard molar enthalpies of formation of CO_2 (g) and H_2O (l) [$\Delta_f H^o_m$ [CO_2, (g)] = –393.5 kJ/mol, $\Delta_f H^o_m$ [H_2O, (l)] = –285.8 kJ/mol],[28] $\Delta_f H^o_m$ for compound **26** was calcu-

lated to be 520.4 kJ/mol. All of the quaternary salts have positive heats of formation (ranging from 177.3 kJ/mol to 611.4 kJ/ mol) except for the imidazolium picrate deriva-tives **23** and **25** with heats of formation at –213.6 kJ/mol and –538.1 kJ/mol, respectively, and 1,1′-methylbis(4-meth-yltriazolium) dinitrate, and compound **27** with the heat of formation at –195.7 kJ/mol. Not surprisingly, picrate salts have higher heats of formation than the nitrate analogs, for example, $\Delta_f H^o_m$ of compound **26** is 520.4 kJ/mol and that of compound **27** is –195.7 kJ/mol; 4-amino-1,2,4-triazolium

Table 1. Phase transition and decomposition temperatures, densities and thermochemical results of picrates, nitrates and perchlorates.

Compound	Picrate T_m[a]	d[b]	OB[d]	T_d[e]	$\Delta_f H^o_m$[f]	Nitrate T_d[e]	$\Delta_f H^o_m$[f]	Perchlorate T_d[e]	$\Delta_f H^o_m$[f]
7	169	1.77	–67	196	497.7	182	–	285[g]	–
8	91	1.72	–79	185	409.6				
9	141	1.80	–91	271	340.1	160[h]	–	97[h]	–
10	106	1.48	–78	176	611.4	129[h]	–	147[h]	–
12	235	1.60	–66	244	513.2	HMS[i]			
14	197	1.64[c]	–66	228	468.8	181[j]	–109.7	208[j]	298
16	147	1.85[c]	–53	214	198.1				
23	215	1.52	–36	283	–213.6				
24	153	1.54	–46			188	177.3		
25	184	1.63	–93	313	–538.1				
26	216	1.67	–81	242	520.4				
27	–15 (T_g)		–74			162	–195.7		
TAG-AT		1.60	–73		1075[k]				
HMX		1.91	–21		75[k]				
TNT		1.65	–74		–64[k]				
Picric acid		1.77	–43		–213.6				
RDX		–	–22		83.8				

[a] Melting point (T_m) (°C)/phase transition temperature (T_g) (°C). [b] Measured density using pycnometer (g/cm³). [c] Density from crystal structure for **14** is 1.72 and **16** is 1.84. [d] OB (%) is oxygen balance which was calculated from $OB = 1600[(a + b/2 – d)/FW]$ for a compound with the molecular formula of $C_aH_bN_cO_d$. [e] Thermal degradation temperature (T_d) (°C). [f] Molar enthalpy of formation (kJ/mol). [g] Ref.[9]. [h] Ref.[17]. [i] High melting salt. [j] Ref.[18]. [k] Ref.[8].

Table 2. Crystallographic data for compounds **14** and **16**.

Compound	**14**	**16**
Formula	$C_8H_7N_7O_7$	$C_7H_6N_8O_7$
Mol. mass	313.21	314.20
Crystal system	orthorhombic	monoclinic
Space group	$Pbcn$	$C2/c$
a [Å]	9.1757(9)	25.4959(13)
b [Å]	19.8568(18)	6.1793(3)
c [Å]	13.2656(12)	14.5863(8)
β [°]	–	98.069(1)
V [Å³]	2417.0 (4)	2275.3(2)
Z	8	8
T [K]	297 (2)	86 (2)
λ [Å]	0.71073	0.71073
$\rho_{calcd.}$ [mg/m³]	1.721	1.834
μ [mm⁻¹]	0.153	0.165
$F(000)$	1280	1280
Crystal size [mm]	0.62×0.61×0.29	0.43×0.40×0.26
θ range [°]	2.05 to 25.25	1.61 to 25.25
Index ranges	$-11 \leq h \leq 9, -23 \leq k \leq 23, -10 \leq l \leq 15$	$-30 \leq h \leq 30, -7 \leq k \leq 7, -17 \leq l \leq 17$
No. refl. collected	21722	16834
No. indep. reflections	2184 [R(int) = 0.0222]	2059 [R(int) = 0.0226]
Data/restraints/param.	2184/6/229	2059/0/199
GOF	1.048	1.010
R_1 [$I > 2\sigma(I)$]	0.0419	0.0282
wR_2 [$I > 2\sigma(I)$]	0.1126	0.0787
Largest diff. peak, hole [e·Å⁻³]	0.230, –0.269	0.239, –0.284
$R_1 = \Sigma|F_o| – |F_c|/\Sigma|F_o|$; w$R_2 = \{\Sigma[w(F_o^2 – F_c^2)^2]/ \Sigma [w(F_o^2)^2]\}^{1/2}$		

picrate (**14**) at 468.8 kJ/mol is significantly more positive than the nitrate and the perchlorate salts at –109.7 and 298 kJ/mol, respectively.[17] Not unexpectedly 3-azido-1,4-dimethyl-1,2,4-triazolium picrate (**10**) with $\Delta_f H^\circ_m$ = 611.6 kJ/mol exhibits the most positive heat of formation in this group of energetic salts.

X-ray Crystallography

Compound **14** crystallizes in an orthorhombic space group, *Pbcn*, and compound **16** in the monoclinic *C2/c* space group. Both have eight formula units in the cell and in spite of the different space groups, display similar characteristics. Both consist of discrete crystallographically independent picrate anions and 4-amino-triazolium (**14**) or 5-imino-tetrazolium (**16**) cations. The protonation in compound **14** (part a in Figure 1), has occurred on one of the ring nitrogen atoms, N8, instead of the amino group. This NH$^+$ is involved in an asymmetric bifurcated hydrogen bond; N8···O1, 2.653(1) and N8···O7a, 2.950(5) Å. The double bonds appear to be localized in the triazolium in spite of the protonation, C7–N8, 1.297(2) Å and N9–C10, 1.296(2) Å. The dihedral angle between the triazolium group and the picrate is 78.4°. The packing diagram (part b in Figure 1) is more complex with rows of picrate anions hydrogen-bonded together by zig-zag sheets of triazolium cations into a cross-linked array. In **16**, the tetrazole double bonds also appear distinct, with N6–N7, 1.269(1) Å and an exocyclic amino C7–N4, 1.310(1) Å, (part a in Figure 2). The picrate and tetrazolium species have a much shallower angle to each other (dihedral angle of 21.9°) compared to **14**. The orientation of the tetrazolium cation to the anion also leads to an asymmetric bifurcated hydrogen bond between N5···O1, 2.624(1) Å, and N5···O7, 2.873(1) Å. Both amino hydrogen atoms are also involved in bifurcated hydrogen bonding, which help extend the system into isolated buckled sheets (part b in Figure 2). Although there are many picrate salts in the literature, there are relatively few associated with triazoles and tetrazoles. Only two of the four examples of each[29–32] display similar asymmetric bifurcated bonding between the tri/tetrazolium and the picrate (N···O, 2.62, 2.64 Å and 2.85, 2.90 Å). Crystallographic data for compounds **14** and **16** were listed in Table 2.

Conclusions

In summary, mono and bridged azolium picrate and nitrate salts were synthesized and their physical and thermochemical properties compared. The thermal stabilities of the salts are dipicrates > picrates > perchlorates > nitrates while the densities are found to average ca. 1.60 g/cm³. Although it is not possible to quaternize 3-*C*-aminotriazole, the 4-aminotriazole easily reacted at N-1. In contrast, the 5-aminotetrazole (C-5) was readily quaternized at N-4. Their structures were confirmed by single-crystal X-ray analysis. The heats of formation values for picrates are more positive than for analogous nitrates and perchlorates. Oxygen bal-

ance values for the mono and bridged azolium picrates and dipicrates fall in the range of many common energetic materials.

Experimental Section

Caution: Although we have not experienced any problems in handling these compounds, their shock and impact sensitivity has not been determined. They should be handled with extreme care.

General Methods: The chemicals were obtained commercially. Silver picrate was prepared based on the literature.[33] A standard Schlenk line system was used for various manipulations. ^{1}H and ^{13}C NMR spectra were recorded on a spectrometer operating at 300 and 75 MHz, respectively, using [D$_6$]DMSO as solvent unless otherwise indicated. Chemical shifts are reported in ppm relative to TMS. DSC data were recorded by heating from 20 °C to 400 °C at 10 °C/min using a differential scanning calorimeter equipped with auto-cool and calibrated using indium. Thermogravimetric analysis (TGA) measurements were made by heating samples at 10 °C/min from 20 °C to 450 °C in a dynamic nitrogen atmosphere. Densities of solid salts were measured at room temperature using a gas pycnometer. The heat of combustion was determined using a semimicro oxygen bomb calorimeter. Elemental analyses were performed commercially. Electrospray mass spectra were recorded using Micromass LCT equipment.

Crystallography: Crystals of compound **14** and **16** were removed from the flasks. A suitable crystal was selected, attached to a glass fiber and placed in the low-temperature nitrogen stream. Data for **14** were collected at 297(2) K and for **16** were collected at 86(2) K using a Bruker/Siemens SMART APEX instrument (Mo-K_α radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3° per frame for 5 seconds, and a hemisphere of data was collected for compound **14**. A total of 1471 frames were collected with a final resolution of 0.81 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. And a full sphere of data was collected for **16**. A total of 2400 frames were collected with a final resolution of 0.77 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART software[34] and refined using SAINTPlus[35] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[36] The structure was solved by direct methods and refined by least-squares method on F^2 using the SHELXTL program package.[37] The structure was solved in the space group *Pbcn* (no. 60) for **14** and *C2/c* (no. 15) for **16** by analysis of systematic absences. CCDC-271202 (for **14**) and CCDC-271203 (for **16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1,2,4-Triazolium Picrate (7): In 20 mL methanol were mixed 1,2,4-triazole (0.113 g, 1.6 mmol) and picric acid (0.373 g, 1.6 mmol). The mixture was stirred for 10 hours at 25 °C, and the solvent was removed under reduced pressure. The solid was washed with water (20 mL) and acetone (20 mL) to yield a dark-yellow solid **7** (0.453 g) in 95% yield. M.p. 169 °C. IR (KBr): ṽ = 3153, 3068, 2887, 1607, 1571, 1350, 1203, 628 cm^{-1}. ^{1}H NMR: δ = 11.8 (br. s, 2 H), 9.34 (s, 1 H), 9.32 (s, 1 H), 8.60 (s, 2 H) ppm. ^{13}C NMR: δ = 160.8, 143.3, 141.9, 125.3, 124.5 ppm. C$_8$H$_6$N$_6$O$_7$ (298.1): calcd. C 32.23, H 2.03, N 28.19; found C 31.99, H 2.06, N 28.43.

1-Methyl-1,2,4-triazolium Picrate (8): The procedure was the same as for compound **7** using **2** (0.083 g, 1.0 mmol) and picric acid (0.229 g, 1.0 mmol) at 25 °C for 8 hours. The residue was washed with water (20 mL) and dichloromethane (20 mL) to leave a light-yellow solid **8** (0.291 g) in 93% yield. M.p. 91 °C. IR (KBr): ṽ = 3143, 3074, 1608, 1538, 1322, 1274, 664 cm⁻¹. ¹H NMR ([D₆]acetone): δ = 9.42 (s, 1 H), 8.88 (s, 2 H), 8.66 (s, 1 H), 8.18 (br. s, 1 H), 4.21 (s, 3 H) ppm. ¹³C NMR δ = 158.2, 145.4, 142.1, 140.6, 130.2, 124.9, 3.69 ppm. C₉H₈N₆O₇ (312.2): calcd. C 34.62, H 2.58, N 26.92; found C 34.25, H 2.61, N 27.26.

1,4-Dimethyl-1,2,4-triazolium Picrate (9): Silver picrate (0.336 g, 1.0 mmol) was added to **3** (0.225 g, 1.0 mmol) in 20 mL DMF to give a yellow precipitate. The mixture was filtered and solvent was removed from the filtrate under vacuum to leave a yellow solid. The latter was recrystallized from methanol and acetone (1:2) to give a pure yellow solid **9** (0.287 g) in 88% yield. M.p.141 °C. IR (KBr): ṽ = 3081, 2953, 1634, 1561, 1337, 1278, 786, 634 cm⁻¹. ¹H NMR δ = 9.97 (s, 1 H), 9.08 (s, 1 H), 8.58 (s, 2 H), 4.06 (s, 3 H), 3.89 (s, 3 H) ppm. ¹³C NMR δ = 160.9, 145.3, 143.4, 141.8, 125.3, 124.4, 38.6, 34.0 ppm. C₁₀H₁₀N₆O₇ (326.2). MS (ESI): (+v e): m/z = 97.9 [M − Picrate] ⁺; (−v e): m/z = 227.9 [picrate] ⁻.

3-Azido-1,4-dimethyl-1,2,4-triazolium Picrate (10): The procedure was as used for **9** using **6** (0.18 g, 0.68 mmol) and silver picrate (0.224 g, 0.68 mmol) in 20 mL DMF to form a yellow solid. After removal of solvent, the residue was washed with acetone (30 mL) to leave a dark-yellow solid **10** (0.227 g) in 91% yield. M.p.106 °C. IR (KBr): ṽ = 3194, 3095, 2183, 1636, 1550, 1327, 1282, 702, 615 cm⁻¹. ¹H NMR: δ = 9.83 (s, 1 H), 8.59 (s, 2 H), 4.02 (s, 3 H), 3.62 (s, 3 H) ppm. ¹³C NMR: δ = 161.3, 150.8, 144.1, 142.3, 125.6, 124.7, 39.5, 32.6 ppm. C₁₀H₉N₉O₇ (367.2): calcd. C 32.71, H 2.47, N 34.33; found C 32.45, H 2.40, N 33.50.

3-Amino-1,2,4-triazolium Picrate (12): The procedure was as used for **7** from **11** (0.084 g, 1.0 mmol) and picric acid (0.229 g, 1.0 mmol) in 40 mL methanol for 3 h at 45 °C to give a yellow powder **12** (0.298 g) in 95% yield. M.p. 235 °C. IR (KBr): ṽ = 3450, 3344, 3098, 1701, 1641, 1551, 1337, 1276, 708, 603 cm⁻¹. ¹H NMR: δ = 8.60 (s, 2 H), 8.32 (s, 1 H), 8.05 (br. s) ppm. ¹³C NMR: δ = 160.9, 150.8, 141.9, 139.2, 125.3, 124.4 ppm. C₈H₇N₇O₇ (313.2): calcd. C 30.68, H 2.25, N 31.31; found C 30.52, H 2.11, N 31.89.

4-Amino-1,2,4-triazolium Picrate (14): Procedure was as used for **12** from **13** (0.094 g, 1.1 mmol) and picric acid (0.26 g, 1.1 mmol) at 45 °C for 6 h to give a yellow solid. Recrystallization from methanol (20 mL) to gave pure **14** (0.317 g) in 92% yield. M.p. 197 °C. IR (KBr): ṽ = 3363, 3260, 3122, 2988, 1610, 1543, 1336, 1266, 710, 619 cm⁻¹. ¹H NMR: δ = 9.49 (s, 1 H), 9.48 (s, 1 H), 8.60 (s, 2 H), 6.26 (br. s) ppm. ¹³C NMR: δ = 160.9, 144.1, 141.9, 125.3, 124.4 ppm. C₈H₇N₇O₇ (313.2): calcd. C 30.68, H 2.25, N 31.31; found C 30.64, H 2.09, N 32.36.

5-Aminotetrazolium Picrate (16): Procedure was as used for **8** from **15** (0.124 g, 1.5 mmol) and picric acid (0.345 g, 1.5 mmol) in methanol (20 mL) at 50 °C for 12 h to form a yellow solid. Recrystallization from methanol and dichloromethane (1:2) produced pure **16** (0.424 g) in 90% yield. M.p. 147 °C. IR (KBr): ṽ = 3416, 3331, 3209, 2931, 1647, 1587, 1334, 1265, 734, 677 cm⁻¹. ¹H NMR δ = 8.60 (s, 2 H), 7.70 (br. s) ppm. ¹³C NMR: δ = 160.8, 156.3, 141.9, 125.3, 124.4 ppm. C₇H₆N₈O₇ (314.2). MS (ESI): (+v e): m/z = 84.0 [M − Picrate − 2H] ⁺; (−v e): m/z = 227.9 [picrate] ⁻.

1,1′-Methylenebis(imidazolium) Dipicrate (23): Procedure was as for **7** from **19** (0.064 g, 0.5 mmol) and picric acid (0.229 g, 1.0 mmol) to give a yellow solid which was washed with acetone (10 mL) and dichloromethane (15 mL) to give a yellow powder **23** (0.288 g) in

95% yield. M.p. 215 °C. IR (KBr): ṽ = 3133, 3066, 1611, 1563, 1320, 1272, 709, 621 cm⁻¹. ¹H NMR: δ = 9.34 (s, 2 H), 8.60 (s, 4 H), 7.97 (s, 2 H), 7.74 (s, 2 H), 6.67 (s, 2 H) ppm. ¹³C NMR: δ = 160.9, 141.9, 137.2, 125.3, 124.5, 121.6, 121.1, 58.0 ppm. C₁₉H₁₄N₁₀O₁₄ (606.4): calcd. C 37.63, H 2.33, N 23.10; found C 37.57, H 2.45, N 23.54.

1,1′-Methylenebis(triazolium) Dinitrate (24): Procedure was as for **7** from **20** (0.26 g, 2.0 mmol) and concentrated nitric acid (1.1 g, 70%wt) The solvent was removed in vacuo, the solid was washed with methanol (20 mL) to form a white solid **24** (0.536 g) in 97% yield. M.p. 153 °C. IR (KBr): ṽ = 3142, 3029, 1609, 1549, 1309, 1232, 715 cm⁻¹. ¹H NMR: δ = 10.22 (br. s), 9.25 (s, 2 H), 8.32 (s, 2 H), 6.78 (s, 2 H) ppm. ¹³C NMR: δ = 150.6, 145.4, 60.0 ppm. C₅H₈N₈O₆ (276.2): calcd. C 21.75, H 2.92, N 40.37; found C 21.72, H 2.84, N 41.91.

1,1′-Methylenebis(3-methylimidazolium) Dipicrate (25): Procedure was as for **9** from **21** (0.13 g, 0.3 mmol) and silver picrate (0.2 g, 0.6 mmol) in 20 mL DMF to give a yellow solid. Recrystallization from methanol and acetone (1:3) gave pure **25** (0.172 g) in 90% yield. M.p. 184 °C. IR (KBr): ṽ = 3104, 3029, 1618, 1567, 1367, 1271, 734, 619 cm⁻¹. ¹H NMR: δ = 9.34 (s, 2 H), 8.60 (s, 4 H), 7.94 (s, 2 H), 7.79 (s, 2 H), 6.64 (s, 2 H), 3.91 (s, 6 H) ppm. ¹³C NMR: δ = 160.7, 141.7, 137.9, 125.1, 124.4, 124.2, 121.9, 58.2, 36.2 ppm. C₂₁H₁₈N₁₀O₁₄ (634.4). MS (ESI): (+v e): m/z = 178.8 [M − Picrate] ⁺, 89 [M − 2 picrate] ²⁺/2; (−v e): m/z = 227.9 [picrate] ⁻.

1,1′-Methylenebis(4-methyltriazolium) Dipicrate (26): Procedure was as used for **9** from **22** (0.086 g, 0.2 mmol) and silver picrate (0.134 g, 0.4 mmol) to give an orange-yellow solid. Recrystallization from methanol (10 mL) gave pure **23** (0.114 g) in 89% yield. M.p. 216 °C. IR (KBr): ṽ = 3060, 1630, 1556, 1313, 1266, 705, 613 cm⁻¹. ¹H NMR: δ = 10.41 (s, 2 H), 9.29 (s, 2 H), 8.60 (s, 4 H), 7.19 (s, 2 H), 3.99 (s, 6 H) ppm. ¹³C NMR: δ = 160.9, 146.6, 145.7, 141.9, 125.3, 124.3, 62.3, 34.7 ppm. C₁₉H₁₆N₁₂O₁₄ (636.4). MS (ESI): (+v e): m/z = 90.0 [M − 2 picrate] ²⁺/2; (−v e): m/z = 227.9 [picrate] ⁻.

1,1′-Methylenebis(4-methyltriazolium) Dinitrate (27): Compound **22** (0.189 g, 0.44 mmol) was mixed with silver nitrate (0.148 g, 0.88 mmol) in water (20 mL) to form a yellow precipitate. The suspension was filtered. The solvent was removed from the filtrate in vacuo to leave a colorless wax **27** (0.127 g) in 95% yield. M.p. − 15.2 °C. IR (KBr): ṽ = 3116, 2986, 1637, 1588, 1352, 1233, 760, 617 cm⁻¹. ¹H NMR: δ = 10.46 (s, 2 H), 9.29 (s, 2 H), 7.17 (s, 4 H), 3.97 (s, 6 H) ppm. ¹³C NMR: δ = 146.6, 145.9, 62.6, 34.6 ppm. C₇H₁₂N₈O₆ (304.2). MS (ESI): (+v e): m/z = 90.0 [M − 2NO₃ ⁻]²⁺/2; (−v e): m/z = 62.0 [NO₃] ⁻.

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