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Energetic Salts from *N*-Aminoazoles

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New energetic salts (**2**, **3**, **5**, **6**, **13**, **14**, **21**, **22**) were synthesized via the quaternization of derivatives of *N*-aminoazoles with nitric or perchloric acid or with iodomethane followed by metathesis reaction with silver nitrate or silver perchlorate. The structure of 2-amino-4,5-dimethyltetrazolium nitrate (**21**) was confirmed by single-crystal X-ray analysis. Most of the salts exhibit good thermal stabilities and low melting points. By using experimentally determined constant volume combustion energies, the standard molar enthalpies of formation were derived on the basis of designed Hess thermochemical cycles.

Introduction

In recent years, the synthesis of energetic heterocyclic compounds has attracted considerable interest.[1−3] Modern energetic materials derive most of their energy either from oxidation of the carbon backbone as with traditional energetic materials, such as TNT (trinitrotoluene) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane),[4] or from their high positive heats of formation, such as nitrogen-rich compounds including 3,3′-azobis(6-amino-1,2,4,5-tetrazine)[2] and tetrazole azide.[5] The standard heats of formation of the latter two are +862 and +458 kJ/mol, respectively. Recently, the syntheses of new members of heterocyclic-based energetic, low-melting salts were reported.[6] Energetic materials that are salt-based often possess advantages over nonionic molecules since these salts tend to exhibit lower vapor pressure and higher densities than their atomically similar nonionic analogues.

High-energy materials tend to be more sensitive to friction, impact, and heat. From an analysis of the structures of thermally stable explosives, it appears that introduction of amino groups into heterocycles is one of the simplest approaches to enhance their thermal stability.[7] However, until now, most research is based on compounds with both nitro and carbon-amino or nitrogen-amino substitutents.[7] Five-membered nitrogen-containing heterocycles are traditional centers for energetic materials, and considerable attention is currently focused on energetic compounds based on azoles.[8,9] *N*-Aminoazoles are a family of compounds of increasing interest, since these substituted azoles when paired with nitrate or perchlorate anions may well form new, highly energetic salts. Yet the chemistry and properties of *N*-aminoazole energetic salts are rarely discussed in the scientific literature.[6,10] In our current work, energetic salts based on *N*-aminoazoles were synthesized with concomitant determination of structural and thermal properties.

Results and Discussion

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 the order from imidazole ($\Delta H^{\circ}_{\mathrm{f(cryst)}} = 58.5$ kJ/mol)[11] to 1,2,4-triazole ($\Delta H^{\circ}_{\mathrm{f(cryst)}} = 109$ kJ/mol) to tetrazole ($\Delta H^{\circ}_{\mathrm{f(cryst)}} = 237.2$ kJ/mol),[12] the variation in the trend of their heats of formation is increasingly positive. In this research, attention is focused on the energetic *N*-amino derivatives of triazole and tetrazole. The quaternization of 1-amino-1,2,4-triazole to its corresponding salts is given in

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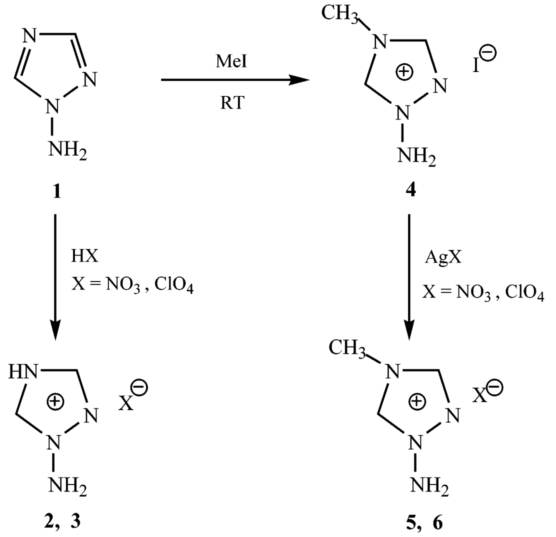
10.1021/ic048890x CCC: $27.50

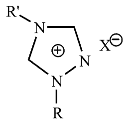
Scheme 1



Scheme 1. 1-Alkyl-1,2,4-triazoles can be quaternized at N-4 by reaction with equivalent amounts of alkyl iodides under neat conditions to produce quaternary salts in >98% isolated yields.[13−17] In this case, 1-amino-1,2,4-triazole, **1**, was readily quaternized at N-4 with a concentrated solution of strong acid[6] (nitric or perchloric acid) using methanol as a solvent to form salts in nearly quantitative yields and in high purity (**2**, **3**). These results are consistent with Drake's results where 4-amino-1,2,4-triazole was quaternized with nitric (or perchloric) acid to form **7** or **8**. The *N*-amino group behaves as an electron-withdrawing group in high-nitrogen heterocycles.[6] Exchanging the position of the amino group from 1 to 4 on the tetrazole ring does effect the physical properties of the resulting salts; e.g., the melting point of the nitrate salt is lowered by 52 °C while having a minimal change in the melting point for the analogous perchlorate (8 °C lower). Concomitantly the thermal stability of the nitrate is improved by 32 °C while that of the perchlorate is lowered by 27 °C. Although crystal structure data for **2** are not available, it is likely that hydrogen bonding between the amino group and the nitrate ion is significantly reduced in **7** relative to **2** (Table 1).

Quaternary salt **4** was obtained from the reaction of **1** with iodomethane at 25 °C. Metathesis of **4** with silver nitrate or silver perchlorate led to the formation of the new quaternary salts **5** and **6** in excellent isolated yields (Scheme 1). 1-Methyl-4-amino-1,2,4-triazolium iodide, **9**, was synthesized in a similar manner by reacting 4-amino-1,2,4-triazole with iodomethane in acetonitrile as solvent. Metathesis of **9** with silver nitrate or silver perchlorate led to the formation of **10** or **11**. The single-crystal X-ray structure of **11** clearly shows significant hydrogen bonding between the perchlorate anion and amino group and that the methyl substitution has occurred at N-1.[17,18] Interestingly, as is the case for **5** ($T_{\mathrm{g}} = -62$ °C), **10** is also a room-temperature ionic liquid with a phase transition temperature (T_{g}) at −60 °C. These results differ significantly for **6** and **11**, the corresponding perchlorate salts, which melt at 108 and 86 °C, respectively. In this case (vide supra), the position of the methyl group seems to make little difference in the properties of 1-amino-4-methyl- and 1-methyl-4-amino-substituted triazolium salts (Table 1).

Table 1. Structures, Phase Transition, and Decomposition Temperatures of Quaternary Triazolium Salts



compd	R	R	X⁻	$T_{\mathrm{m}}/T_{\mathrm{g}}$[a]	T_{d}[b]
2	NH_2	H	NO_3	121	149
3	NH_2	H	ClO_4	91	235
5	NH_2	CH_3	NO_3	−62 (T_{g})	217
6	NH_2	CH_3	ClO_4	108	253
7	H	NH_2	NO_3	69 (69)[c]	181 (180)[c]
8	H	NH_2	ClO_4	83 (84)[c]	208 (210)[c]
10	CH_3	NH_2	NO_3	−60 (T_{g}) (54)[d]	221(185)[d]
11	CH_3	NH_2	ClO_4	86 (83)[d]	259 (250)[d]

[a] Melting point (T_{m})/phase transition temperature (T_{g}), °C. [b] Thermal degradation, °C. [c] Reference 6. [d] Reference 18.

However, the nitrate salts **2** and **7**, where either 4-H or 1-H is present on the triazolium ring, have melting points that are considerably higher than the methyl substituted **5** and **10**. Clearly, the opportunity for hydrogen bonding with the nitrate ion is markedly reduced in these compounds and the result is a lower melting point, T_{g}. The variations in melting points are quite small for the perchlorate salts **3** and **6** or **8** and **11**. Conversely, thermal degradation temperatures for both nitrate and perchlorate salts are increased when a methyl group is present on the ring.

Drake reported that 1,5-diaminotetrazole can be quaternized with perchloric acid directly to form 1,5-diamino-1,2,3,4-tetrazolium perchlorate and determined its structure by single-crystal X-ray diffraction analysis.[10] We also found that 1,5-diamino-1,2,4-triazole, **12**, can be reacted with nitric acid or perchloric acid to form the corresponding quaternary salt **13** or **14** in high yield. The melting points for **13** (159 °C) and **14** (138 °C) are considerably lower than that of the precursor **12** (190 °C).

Since the presence of two amino groups on the tetrazole ring results in undesirably high melting compounds, we prepared amino/methyl tetrazolium compounds to achieve lower melting materials. Thus, 1-amino-5-methyltetrazole, **15**, and 2-amino-5-methyltetrazole, **19**, were synthesized, and their quaternary salts (**17**, **18**, **21**, **22**) were obtained by reaction with methyl iodide (Table 2). The melting points for 2-amino-4,5-methyltetrazolium salts are higher that those for 1-amino-4,5-methyltetrazolium salts. In fact, **17** ($T_{\mathrm{g}} =$

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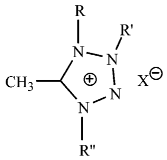
Table 2. Structures, Phase Transition, and Decomposition Temperatures of Quaternary tetrazolium salts



compd	R	R	R	X^-	T_m/T_g[a]	T_d[b]
17	NH_2		CH_3	NO_3	−59 (T_g)	170
18	NH_2		CH_3	ClO_4	51	182
21		NH_2	CH_3	NO_3	94	173
22		NH_2	CH_3	ClO_4	140	238

[a] Melting point (T_m)/phase transition temperature (T_g), °C. [b] Thermal degradation, °C.

Table 3. Densities and Thermochemical Results for Synthesized Salts at 298.15 K

compd	d_{calcd}[a] (g/cm^3)	d[b] (g/cm^3)	$-\Delta_c U_m$[c] (kcal/mol)	$-\Delta_c H_m^\circ$[d] (kJ/mol)	$\Delta_f H_m^\circ$[e] (kJ/mol)
2	1.75	1.69	368.80	1536.24	34.65
3	1.92	1.80	434.49	1807.99	357.01
5	1.60	(1.51[g])	480.84	2006.26	−174.68
6	1.77	1.66	614.43	2562.10	431.78
7	1.75	1.64 (1.60[h])	334.28	1391.81	−109.79
8	1.92		420.49	1749.42	298.43
10	1.60	(1.55[g])	477.81	1993.58	−187.36
11	1.77 (1.70[f])	1.66	562.66	2345.49	215.17
13	1.76	1.65	373.44	1555.02	−89.49
14	1.93	1.83	499.30	2078.54	484.64
17	1.55	(1.50[g])	587.85	2453.37	129.52
18	1.71		672.96	2811.76	538.53
21	1.55 (1.53[f])		595.95	2487.26	163.41
22	1.71	1.65	763.32	3184.44	911.21

[a] Calculated density. [b] Measured density using gas pycnometer. [c] Constant volume combustion energy. [d] Molar enthalpy of combustion. [e] Molar enthalpy of formation. [f] From X-ray structure. [g] Measured density using a pycnometer at 25 °C. [h] Reference 6.

−59 °C) is a room-temperature ionic liquid. But just the opposite is observed for thermal degradation temperatures where higher stabilities are seen, especially for perchlorate salts **22** (T_d = 238 °C) and **18** (T_d = 182 °C). Interestingly, the trends for the triazolium salts appear analogous to the trends for the tetrazolium compounds.

The densities of some of new synthesized salts were calculated by literature methods.[19,20] Some of the measured densities for the new ionic liquids and data from single crystal structures are also listed in Table 3. Several of these new salts have relatively high densities, such as **3**, **8**, and **14**, where values are ~1.90 g/cm^3. For all of the compounds, the densities exceed 1.50 g/cm^3.

Some of the measured densities with helium displacement methods for the new ionic salts and data from single-crystal structures are also listed in Table 3. It is shown that the calculated densities tend to be slightly higher than the experimental values. Several of these new salts have relatively high densities, such as **14** where the calculated value is 1.93 g/cm^3 and the measured value is 1.83 g/cm^3.

The standard enthalpy of formation of an energetic salt is helpful in predicting stability. The heats of formation reported here are based on experimentally determined heats of combustion. Typical experimental results (averaged over three measurements each) of the constant volume combustion energy ($\Delta_c U_m$) of the new salts are given in Table 3. The standard molar enthalpy of combustion ($\Delta_c H_m^\circ$) of the samples can be derived from the constant volume combustion energy by means of the following formula:

$$\Delta_c H_m^\circ = \Delta_c U_m + \Delta nRT$$

$$\Delta n = \sum n_i(\text{products, g}) - \sum n_i(\text{reactants, g})$$

Here $\sum n_i$ is the total molar amount of the gases in products or reactants. The calculated molar enthalpy of formation of the sample, such as for **2**, was calculated from a designed Hess thermochemical cycle according to reaction a as follows:

$$[C_2H_5N_4]^+[NO_3]^-(s) + {}^7/_4O_2 \rightarrow 2CO_2(g) + {}^5/_2H_2O(l) + {}^5/_2N_2(g) \quad (a)$$

$$\Delta_f H_m^\circ([C_2H_5N_4]^+[NO_3]^-, s) = [2\Delta_f H_m^\circ(CO_2, g) + {}^5/_2\Delta_f H_m^\circ(H_2O, l)] - \Delta_c H_m^\circ([C_2H_5N_4]^+[NO_3]^-, s)$$

Using the above formula and the literature values for the standard molar enthalpies of formation of CO_2(g) and H_2O(l) [$\Delta_f H_m^\circ(CO_2,g)$ = −393.51 kJ/mol, $\Delta_f H_m^\circ(H_2O,l)$ = −285.83 kJ/mol],[21,22] $\Delta_c H_m^\circ$ and $\Delta_f H_m^\circ$ for compound **2** were calculated to be −1536.24 and 34.65 kJ/mol, respectively. For perchlorate salts, the heat of formation of hydroxylammonium perchlorate was investigated by using a combustion calorimetric method which showed that 13−17% of the chlorine in the perchlorate anion was found as chlorine gas.[23] The heat of formation of 2,4,6-trimethylpyrylium perchlorate was determined on the basis of the HCl(aq) formed.[24] We also used a similar method.[23] When the gaseous reaction products were condensed into a starch−KI solution to determine the quantity of elemental chlorine formed, it was found that only 0.5% of the chlorine in the perchlorate salt was present as chlorine gas. When the combustion reaction was run with water added to the sample in the calorimeter, the chloride concentration was determined by the Volhard method[25] which indicates nearly quantitative chloride ion formation during combustion. Therefore, for the perchlorate salts, such as **3**, the designed Hess thermochemical cycle was based on reaction b:

$$[C_2H_5N_4]^+[ClO_4]^-(s) + O_2 \rightarrow 2CO_2(g) + 2H_2O(l) + 2N_2(g) + HCl(g) \quad (b)$$

The data for all other samples were calculated and listed in Table 3. The enthalpies of combustion and the standard

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Table 4. Crystal and Structure Refinement Data for **21**

empirical formula	$C_3H_8N_6O_3$
fw	176.15
cryst syst, space group	orthorhombic, $P2_12_12_1$
color, habit	colorless plate
cryst dimens, mm	0.38, 0.19, 0.03
T (°C)	85(2)
a (Å)	6.7172(6)
b (Å)	7.8064(7)
c (Å)	14.633(1)
V (Å^3)	767.3(1)
Z	4
D_{calc} (Mg m^{-3})	1.525
μ (mm^{-1})	0.133
data/restraints/params	1758/0/119
goodness of fit on F^2	1.058
λ (Å)	0.710 73
final R indices [$I > 2\sigma(I)$]^a	R1 = 0.0411, wR2 = 0.0883
R indices (all data)^a	R1 = 0.0524, wR2 = 0.0924

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

enthalpies of formation of dinitrobiuret (DNB) and diaminotetrazolium nitrate were calculated;[26] e.g., the constant volume combustion energy for the latter is 7900 ± 300 kJ/kg (308 ± 12 kcal/mol). From Table 3, it can be seen that our newly synthesized salts have higher constant volume combustion energies. The combustion energies and standard molar enthalpies of formation for perchlorate salts are higher than those of nitrates. Not surprisingly, the standard molar enthalpies of formation for salts from *N*-aminotetrazoles are higher than those of the analogous *N*-aminotriazolium salts. Of the new compounds reported in this work, 2-amino-4,5-dimethyltetrazolium perchlorate, **22**, has the highest standard molar enthalpy of formation, 911.21 kJ/mol.

X-ray Crystallography. The solid-state structure of **21**, which crystallizes in the chiral space group $P2_12_12_1$ (orthorhombic), shows that the N4 atom of the tetrazole was methylated (Table 4). The absolute configuration could not be determined by anomalous scattering. There is extensive, strong hydrogen bonding between the tetrazole cation and the NO_3^- group ranging from 2.857(2) to 3.295(3) Å (donor−acceptor). There is one bifurcated hydrogen bond between N8 and O1, O2 (2.857(2), 2.944(2) Å), and O2 and O3 have three hydrogen bonds each (see Supporting Information). This synthon joins the ions together into a complicated 3D network (Figure 1). Although there are no reported structures of 2-amino-5-methyltetrazolium salts in the Cambridge Database,[27] the structure of 2-methyl-5-aminotetrazole and various derivatives are known.[28] There are a few 5-methyltetrazole examples which show bond lengths and angles similar to those **21**.[29]

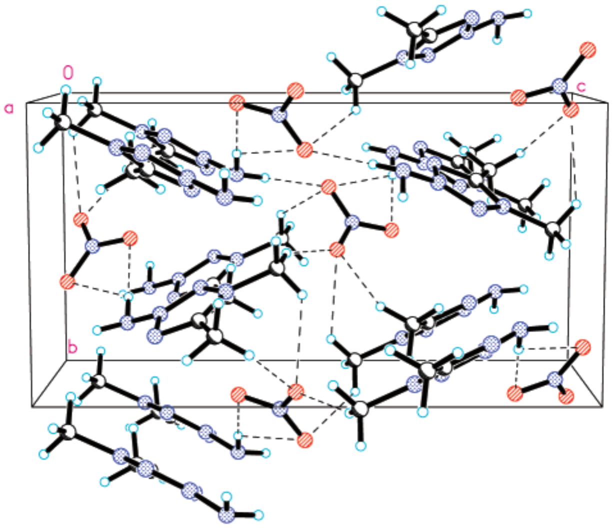

Figure 1. Packing diagram of **21** showing hydrogen bonding between the NO_3^- group and the tetrazolium cation.

Conclusion

Syntheses of *N*-aminoazole precursors and their subsequent quaternization lead to new energetic salts. Most of the new ionic compounds exhibit good physical properties, including high densities (>1.55 g/cm^3), good thermal stabilities, and low melting points (<100 °C). On the basis of the crystal structure data, intermolecular cation/anion hydrogen bonding plays a major role in determining the melting point, T_g. The molar enthalpies of formation of the new salts that were calculated on the basis of the experimentally determined constant volume combustion energy are quite high. Perchlorate salts have higher combustion energies than the analogous nitrates, and tetrazolium salts also exhibit higher ΔH_f's than triazolium compounds. These compounds should be useful in low signature propellant applications.

Experimental Section

Caution! *Although we have not experienced any problems in handling these compounds, on the basis of the high positive heats of formation, all materials should be handled with extreme care.*

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively, using DMSO-d_6 as solvent unless otherwise indicated. Chemical shifts were reported relative to Me_4Si. GC/MS spectra were determined using an appropriate instrument. Mass spectra for ionic salts were determined by using solid probe insertion. M$^+$ is the mass of the cation. The melting and decomposition points were recorded on a differential scanning calorimeter and a thermogravimetric analyzer at a scan rate of 10 °C/min, respectively. IR spectra were recorded using NaCl plates for neat liquids and KBr pellets for solids. Densities of ionic liquids were measured at room temperature using a pycnometer. Densities of solid salts were measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry.

Calorimetry Apparatus and Procedure. The heat of combustion was determined using a Parr (series 1425) semimicro oxygen bomb calorimeter. The substances were burned in an oxygen atmosphere at a pressure of 3.04 MPa. The energy equivalent of the calorimeter was determined with a standard reference sample

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of benzoic acid (SRM 39i, NIST). Since Parr 45C10 alloy fuse wire was used, a correction of 2.3 (IT) calories/cm of wire burned has been applied in all standardization and calorific value determinations. Acid correction has been omitted for all semimicro samples. The bomb was examined for evidence of unburned carbon after each run, and if more than a slight trace was present, the run was discarded. The enthalpy of combustion was determined using the formula $\Delta_c H_m^\circ = \Delta_c U_m + \Delta nRT$, where $\Delta_c U_m$ is the constant volume combustion energy and Δn is the increase in the number of moles of gas during the reaction. The molar enthalpies of formation, $\Delta_f H_m^\circ$ at 298.15 K, of the corresponding ionic salts were calculated by designed Hess thermochemical cycles.

X-ray Crystallographic Studies. Crystals of compound **21** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream.[30] Data for **21** were collected at 85(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using ω scans of 0.3°/frame for 10 s, and a hemisphere of data was collected. A total of 1471 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[31] software and refined using SAINTPlus[32] on all observed reflections. Data reduction and correction for *Lp* and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[33] The structure was solved by direct methods and refined by least-squares method on F^2 using the SHELXTL program package All atoms were refined anisotropically. No decomposition was observed during data collection. The amino hydrogen atoms were located on the difference map and refined. Details of the data collection and refinement are provided in the Supporting Information.

1-Amino-1,2,4-triazole (1). Compound **1** was prepared by a literature procedure:[34] white solid, 55% yield, mp 86 °C; IR (KBr) 3308, 3200, 3128, 1638, 1511, 1462, 1342, 1212, 1137, 1014, 952, 872, 681, 626 cm^{-1}; ^{1}H NMR δ 6.55 (s, 2H), 7.82 (s, 1H), 8.31 (s, 1H); ^{13}C NMR δ 150.18, 143.56.

General Procedure for Preparation of Salts 2 and 3. **1-Amino-1,2,4-triazolium Nitrate (2).** A dried, nitrogen-filled Pyrex glass Schlenk tube was charged with **1** (0.084 g, 1.0 mmol), dry methanol (1 mL), and concentrated nitric acid (70 wt %, 0.09 g, 1.0 mmol). The mixture was stirred for 2 h at 25 °C. The solvent was removed under high vacuum overnight to leave a white solid: 0.144 g, 98% yield, mp 121 °C; IR (KBr) 3239, 3115, 2065, 1761, 1635, 1537, 1321, 991, 829, 650 cm^{-1}; ^{1}H NMR δ 4.53 (s, 2H), 8.49 (s, 1H), 9.25 (s, 1H); ^{13}C NMR δ 146.44, 141.96; MS (solid probe) (EI) *m/z* (%) 85 (M$^+$, 4.8). Anal. Calcd for $C_2H_5N_5O_3$: C, 16.33; H, 3.43. Found: C, 16.28; H, 3.54.

1-Amino-1,2,4-triazolium Perchlorate (3). Compound **3** was prepared as above from **1** and concentrated perchloric acid (70 wt %) to give a white solid: 98% yield, mp 91 °C; IR (KBr) 3246, 3117, 2822, 1634, 1530, 1091, 940, 627 cm^{-1}; ^{1}H NMR δ 6.36 (s, 2H), 8.43 (s, 1H), 9.16 (s, 1H); ^{13}C NMR δ 145.49, 141.54; MS (solid probe) (EI) *m/z* (%) 85 (M$^+$, 5.5). Anal. Calcd for $C_2H_5N_4$-ClO_4: C, 13.02; H, 2.73. Found: C, 12.52; H, 3.00.

1-Amino-4-methyl-1,2,4-triazolium Iodide (4). Compound **4** was obtained from **1** and CH_3I using CH_3CN as solvent at 25 °C for 3 days to give a brown solid: 60.4% yield, mp 142 °C; IR (KBr) 3219, 3095, 3055, 1740, 1572, 1520, 1362, 1062, 1100, 880, 646, 609 cm^{-1}; ^{1}H NMR δ 3.86 (s, 3H), 7.39 (s, 2H), 9.02 (s, 1H), 10.00 (s, 1H); ^{13}C NMR δ 144.73, 142.02, 35.68; MS (solid probe) (EI) *m/z* (%) 99 (M$^+$, 9.5). Anal. Calcd for $C_3H_7N_4I$: C, 15.94; H, 3.12. Found: C, 15.91; H, 3.13.

General Procedure for Preparation of Salts 5 and 6. **1-Amino-4-methyl-1,2,4-triazolium Nitrate (5).** To a magnetically stirred solution of **4** (0.10 g, 0.442 mmol) in water (3 mL) was added silver nitrate ($AgNO_3$, 0.075 g, 0.442 mmol). After 2 h at room temperature, the insoluble silver iodide was removed by filtration and the solution was evaporated in vacuo to give a colorless oil: 0.070 g, 98% yield, $T_g = -62$ °C; IR (NaCl) 3464, 3290, 3130, 2395, 1753, 1580, 1527, 1379, 1240, 1178, 1065, 989, 887, 828, 653 cm^{-1}; ^{1}H NMR δ 3.85 (s, 3H), 7.42 (s, 2H), 9.00 (s, 1H), 9.99 (s, 1H); ^{13}C NMR δ 144.77, 142.09, 35.44; MS (solid probe) (EI) *m/z* (%) 99 (M$^+$, 9.9). Anal. Calcd for $C_3H_7N_5O_3$: C, 22.36; H, 4.38. Found: C, 22.61; H, 4.61.

1-Amino-4-methyl-1,2,4-triazolium Perchlorate (6). Compound **6** was prepared as above from **4** and silver perchlorate to form a white solid: 98% yield, mp 108 °C; IR (KBr) 3219, 3100, 3028, 1572, 1364, 1090, 887, 627 cm^{-1}; ^{1}H NMR δ 3.85 (s, 3H), 7.40 (s, 2H), 8.98 (s, 1H), 9.96 (s, 1H); ^{13}C NMR δ 144.76, 142.08, 35.49; MS (solid probe) (EI) *m/z* (%) 99 (M$^+$, 9.4). Anal. Calcd for $C_3H_7N_4ClO_4$: C, 18.15; H, 3.55. Found: C, 17.93; H, 3.58.

4-Amino-1,2,4-triazolium Nitrate (7). Compound **7** was prepared by a literature procedure[6] to give a white solid: 98% yield, mp 69 °C; IR (KBr) 3202, 3091, 3041, 2977, 1761, 1514, 1375, 1045, 933, 877, 813, 623 cm^{-1}; ^{1}H NMR δ 6.63 (br, 2H), 9.45 (s, 2H); ^{13}C NMR δ 145.37.

4-Amino-1,2,4-triazolium Perchlorate (8). Compound **8** was prepared by a literature procedure[6] to give a white solid: 98% yield, mp 83 °C; IR (KBr) 3202, 3091, 3039, 2977, 1516, 1323, 1095, 936, 878, 812, 627 cm^{-1}; ^{1}H NMR δ 5.24 (br, 2H), 9.54 (s, 2H); ^{13}C NMR δ 145.33.

1-Methyl-4-amino-1,2,4-triazolium Iodide (9). Compound **9** was obtained by a minor modification of the previous syntheses,[35] using acetonitrile as solvent to give a yellow salt **9** in quantitative yield: mp 101 °C; IR (KBr) 3457, 3215, 3127, 1618, 1568, 1441, 1406, 1168, 1069, 979, 865, 734, 609 cm^{-1}; ^{1}H NMR δ 4.04 (s, 3H), 6.96 (s, 2H), 9.14 (s, 1H), 10.14 (s, 1H); ^{13}C NMR δ 146.35, 144.23, 40.66.

1-Methyl-4-amino-1,2,4-triazolium Nitrate (10).[17] Compound **10** was prepared by following the general procedure used for **5** and **6** from **9** and silver nitrate to give a colorless oil: 98% yield, $T_g = -60$ °C; IR (NaCl) 3460, 3287, 3140, 2040, 1750, 1637, 1574, 1350, 1174, 1073, 980, 884, 829, 656 cm^{-1}; ^{1}H NMR δ 4.04 (s, 3H), 6.97 (s, 2H), 9.16 (s, 1H), 10.12 (s, 1H); ^{13}C NMR δ 146.39, 144.35, 40.15; MS (solid probe) (EI) *m/z* (%) 99 (M$^+$, 2.5). Anal. Calcd for $C_3H_7N_5O_3$: C, 22.36; H, 4.38. Found: C, 22.33; H, 4.44.

1-Methyl-4-amino-1,2,4-triazolium Perchlorate (11).[17] Compound **11** was prepared as with **5** and **6** from **9** and silver perchlorate to give a white solid: 98% yield, mp 86 °C; IR (KBr) 3604, 3345, 3244, 3145, 2023, 1725, 1632, 1575, 1445, 1410, 1365, 1171, 1118, 981, 880, 735, 614 cm^{-1}; ^{1}H NMR δ 4.03 (s, 3H), 6.94 (s, 2H),

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9.15 (s, 1H), 10.05 (s, 1H); ^{13}C NMR δ 146.34, 144.27, 40.21; MS (solid probe) (EI) *m*/*z* (%) 99 (M$^+$, 2.6).

1,5-Diamino-1,2,4-triazole (12). Compound **12** was prepared by a literature procedure[36] resulting in a white solid: 32% yield, mp 190 °C; IR (KBr) 3298, 3140, 1672, 1556, 1528, 1439, 1261, 1203, 1143, 1061, 966, 880, 631 cm^{-1}; ^{1}H NMR δ 5.82 (s, 2H), 5.86 (s, 2H), 7.21 (s, 1H); ^{13}C NMR δ 153.41, 144.87.

1,5-Diamino-1,2,4-triazolium Nitrate (13). Compound **13** was prepared using the general procedure for **2** and **3** from **12** and concentrated nitric acid (70 wt %) to give a white solid: 98% yield, mp 159 °C; IR (KBr) 3265, 3150, 2397, 1707, 1610, 1352, 1234, 1115, 914, 750 cm^{-1}; ^{1}H NMR δ 6.34 (s, 2H), 8.05 (s, 2H), 8.22 (s, 1H); ^{13}C NMR δ 149.58, 136.95; MS (solid probe) (EI) *m*/*z* (%) 100 (M$^+$, 20.1). Anal. Calcd for $C_2H_6N_6O_3$: C, 14.82; H, 3.73. Found: C, 14.83; H, 3.69.

1,5-Diamino-1,2,4-triazolium Perchlorate (14). Compound **14** was prepared using the procedure for **2** and **3** from **12** and concentrated perchloric acid (70 wt %) to give a white solid: 98% yield, mp 138 °C; IR (KBr) 3265, 3146, 1709, 1605, 1370, 1090, 848, 626 cm^{-1}; ^{1}H NMR δ 6.37 (s, 2H), 8.05 (s, 2H), 8.22 (s, 1H); ^{13}C NMR δ 149.50, 136.80; MS (solid probe) (EI) *m*/*z* (%) 100 (M$^+$, 22.5). Anal. Calcd for $C_2H_6N_5ClO_4$: C, 12.04; H, 3.03. Found: C, 11.95; H, 3.02.

1-Amino-5-methyltetrazole (15). Compound **15** was prepared by following the literature[37] to give a white solid: 35% yield, mp 45 °C; IR (KBr) 3330, 3213, 3000, 1636, 1530, 1428, 1394, 1267, 1223, 1120, 1078, 1001, 927, 669 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.43 (s, 3H), 5.83 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 151.27, 7.72.

1-Amino-4,5-dimethyltetrazolium Iodide (16).[17] Compound **16** was prepared from **15** and CH$_3$I at 60 °C for 3 days to give a yellow solid: 76% yield, mp 121 °C; IR (KBr) 3228, 3121, 2999, 1643, 1576, 1418, 1375, 1225, 1030, 893, 768, 627 cm^{-1}; ^{1}H NMR δ 7.71 (s, 2H), 4.23 (s, 3H), 2.78 (s, 3H); ^{13}C NMR δ 152.57, 38.40, 10.03; MS (solid probe) (EI) *m*/*z* (%) 114 (M$^+$, 3.9). Anal. Calcd for $C_3H_8N_5I$: C, 14.95; H, 3.35. Found: C, 14.79; H, 3.36.

1-Amino-4,5-dimethyltetrazolium Nitrate (17).[17] Compound **17** was prepared as for **5** and **6** from **16** and silver nitrate to give a colorless oil: 98% yield, $T_g = -59$ °C; IR (NaCl) 3473, 3243, 3137, 1745, 1645, 1579, 1377, 1034, 949, 829, 772, 651 cm^{-1}; ^{1}H NMR δ 7.73 (s, 2H), 4.22 (s, 3H), 2.75 (s, 3H); ^{13}C NMR δ 152.57, 38.08, 9.50; MS (solid probe) (EI) *m*/*z* (%) 114 (M$^+$, 4.2). Anal. Calcd for $C_3H_8N_6O_3$: C, 20.46; H, 4.58. Found: C, 19.98; H, 4.84.

1-Amino-4,5-dimethyltetrazolium Perchlorate (18).[17] Compound **18** was prepared as for **5** and **6** from **16** and silver perchlorate to give a white solid: 98% yield, mp 51 °C; IR (KBr) 3422, 3166, 3085, 1634, 1570, 1381, 1338, 1078, 768, 625 cm^{-1}; ^{1}H NMR δ 7.72 (s, 2H), 4.20 (s, 3H), 2.75 (s, 3H); ^{13}C NMR δ 152.55, 38.03, 9.47; MS (solid probe) (EI) *m*/*z* (%) 114 (M$^+$, 4.0). Anal. Calcd for $C_3H_8N_5ClO_4$: C, 16.87; H, 3.78. Found: C, 16.56; H, 4.01.

2-Amino-5-methyltetrazole (19). Compound **19** was prepared by a procedure similar to that in the literature[38] to give a colorless oil: 12% yield; IR (NaCl) 3317, 3280, 3175, 1620, 1499, 1380, 1354, 1220, 1036, 964, 771, 668 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.35 (s, 3H), 6.54 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 162.38, 11.77.

2-Amino-4,5-dimethyltetrazolium Iodide (20). Compound **20** was prepared from **19** and CH$_3$I at 60 °C for 3 days to obtain a yellow solid: 50% yield, mp 124 °C; IR (KBr) 3441, 3159, 3026, 1592, 1545, 1400, 1177, 1039, 916, 803, 650 cm^{-1}; ^{1}H NMR δ 2.66 (s, 3H), 4.10 (s, 3H), 9.89 (s, 2H); ^{13}C NMR δ 158.71, 114.96, 10.47; MS (solid probe) (EI) *m*/*z* (%) 114 (M$^+$, 2.1). Anal. Calcd for $C_3H_8N_5I$: C, 14.95; H, 3.35. Found: C, 14.92; H, 3.04.

2-Amino-4,5-dimethyltetrazolium Nitrate (21). Compound **21** was prepared by following the method for **5** and **6** from **20** and silver nitrate to give a white solid: 98% yield, mp 94 °C; IR (KBr) 3414, 3002, 2390, 1759, 1632, 1547, 1381, 1240, 1041, 827, 648 cm^{-1}; ^{1}H NMR δ 2.66 (s, 3H), 4.10 (s, 3H), 9.91 (s, 2H); ^{13}C NMR δ 158.70, 36.98, 10.31; MS (solid probe) (EI) *m*/*z* (%) 114 (M$^+$, 1.5).

2-Amino-4,5-dimethyltetrazolium Perchlorate (22). Compound **22** was prepared as for **5** and **6** from **20** and silver perchlorate to give a white solid: 98% yield, mp 140 °C; IR (KBr) 3425, 3147, 3005, 1620, 1546, 1392, 1089, 944, 800, 625 cm^{-1}; ^{1}H NMR δ 9.90 (s, 2H), 4.10 (s, 3H), 2.66 (s, 3H); ^{13}C NMR δ 158.70, 36.98, 10.32; MS (solid probe) (EI) *m*/*z* (%) 114 (M$^+$, 2.0). Anal. Calcd for $C_3H_8N_5ClO_4$: C, 16.87; H, 3.78. Found: C, 17.18; H, 3.43.

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Supporting Information Available: X-ray crystallographic files in CIF format for 2-amino-4,5-dimethyltetrazolium nitrate, **21**. This information is available free of charge via the Internet at http://pubs.acs.org.

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