New Energetic Salts Based on Nitrogen-Containing Heterocycles

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New energetic salts (**4**−**9**, **11**, **13**, **16**, **21**, **22**, **29**−**34**, **36**, **37**, **42**, **43**, **46**, **47**) were synthesized via 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. The structures of 1,4-dimethyl-3-azido-1,2,4-triazolium nitrate (**5**), 3-azido-1,2,4-triazolium nitrate (**6**), 1-methyl-4-amino-1,2,4-triazolium perchlorate (**16**), and 1,4-dimethyl-2-H-1,2,4-triazolium triiodide (**20**) were confirmed by single-crystal X-ray analysis. Most of the salts exhibit good thermal stabilities and low melting points. By using constant volume combustion energies that were determined experimentally using an oxygen bomb calorimeter, the standard molar enthalpies of formation were derived based on designed Hess thermochemical cycles.

Introduction

There has been a growing interest in the synthesis of energetic materials with great potential as explosives and propellants in recent years.[1−3] Most of the energy obtained from modern energetic materials results either from oxidation of the carbon backbone as traditionally found for energetic materials, such as HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) and TNT (trinitrotoluene),[4] or from their high positive heats of formation in such nitrogen-rich compounds as tetrazole azide[5] and 3,3′-azobis(6-amino-1,2,4,5-tetrazine)[2] which exhibit standard heats of formation of +458 kJ/mol and +862 kJ/mol, respectively. Heterocycles that contain large amounts of nitrogen are typically relatively dense, and the smaller amounts of hydrogen and carbon enhance good oxygen balance. Normally, they also have higher heats of reaction. Because a higher percentage of the decomposition products will be dinitrogen, these nitrogen-rich compounds are promising high energetic materials with high energy densities that may be more environmentally acceptable.[6]

Recently, the syntheses of new heterocyclic-based energetic, low-melting salts were reported.[7] These materials that are salt-based often possess advantages over nonionic molecules since they tend to exhibit very low vapor pressures essentially eliminating the risk of exposure through inhalation, and ionic compounds often have higher density than their atomically similar nonionic analogues. This results from the influence of Coulombic forces which encourage the formation of ordered and dense lattice structures in molecular assemblies.[7] However, until now, only relatively simple heterocycles, such as 1H-1,2,4-triazole, 4-amino-1,2,4-triazole, and 1H-1,2,3-triazole were utilized to make energetic ionic salts.[7,8] Five-membered nitrogen-containing heterocycles are traditional sources of energetic materials, and considerable attention is currently focused on azoles as energetic compounds, especially the 1,2,4-triazole series.[9,10] Within the series of azoles, the relative energy characteristics ($\Delta H_f°$) are dependent on the ring structures. Hydrogen atoms of azoles can be substituted readily with various energetic functional groups. For example, the standard heat of formation for 3-azido-1,2,4-triazole ($\Delta H_f° = +458$ kJ/mol)[11] is about four times larger than that of 1H-1,2,4-triazole ($\Delta H_f° = +109$ kJ/mol).[7] In addition, the azoles may incorporate not only endothermic moieties, such as the azido group, which significantly increases the enthalpy of formation of the azido azoles, but also the nitro and nitramino groups that substantially improve the oxygen balance of the corresponding derivatives and eventually result in a higher exothermicity of the combustion and detonation processes.[12] These substituted azoles paired with the nitrate or perchlorate anion form new energetic salts.

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The main objective of the work described herein was to design and synthesize new families of nitrogen-containing heterocyclic salts which exhibit suitable characteristics in order to be classified as new highly energetic members of the well-known class of ionic liquids.[7,13−15]

Experimental Section

Caution. Although we experienced no difficulties in handling these materials, with such high positive heats of formation some could be unstable. Therefore, all of them should be treated with care and with appropriate safety precautions.

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer operating at 300.13 and 75.48 MHz, respectively. Chemical shifts were reported relative to Me_4Si. GC/MS spectra were determined using an appropriate instrument. Mass spectra for salts were determined by insertion using solid probe. M^+ is the mass of the cation. The melting and decomposition points were recorded on a differential scanning calorimeter at a scan rate of 10 °C/min. 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) semi-micro oxygen bomb calorimeter. The substances were combusted in an oxygen atmosphere at a pressure of 3.04 Mpa. The energy equivalent of the calorimeter was determined with a standard reference sample of benzoic acid (SRM 39i, NIST). Parr 45C10 alloy fuse wire was used. A correction of 2.3 (IT) calories per cm of wire burned has been applied in all standardization and calorific value determinations. Acid corrections have been omitted for all semi-micro samples. The bomb was examined for evidence of noncombusted carbon for each run. If more than a slight trace was present, the run was discarded. The enthalpy of combustion was determined using the formula $\Delta_c H_m° = \Delta_c U_m + \Delta n RT$, 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 enthalpy of formation, $\Delta_f H_m°$, for each of the corresponding salts was calculated at 298.15 K using designed Hess thermochemical cycles.

X-ray Crystallographic Studies. Crystals of compound **5** (or **6**, **16**, **20**) 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.[16] Data for **5** (or **6**, **16**, **20**) were collected at 83 (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 omega scans of 0.3° per frame for 20 s, and a full sphere of data was collected. A total of 2132 frames were collected with a final resolution of 0.73 Å. The first 50 frames were re-collected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[17] software and refined using SAINTPlus[18] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[19] The structure was solved by direct methods and refined by least-squares method on F^5 using the SHELXTL program package. All atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are provided in the Supporting Information.

3-Azido-1,2,4-triazole (1). Compound **1** was prepared by a literature procedure.[11] White solid, 76.2% yield, mp 120 °C. IR (KBr) 3090, 2897, 2141, 1508, 1450, 1330, 1175, 1085, 1010, 975, 848, 627 cm^{-1}.; ^{1}H NMR (DMSO-d_6) δ 8.54 (s, 1H). ^{13}C NMR (DMSO-d_6) δ 158.48, 146.05.

1-Methyl-3-azido-1,2,4-triazole (2). Compound **2** was prepared by a similar procedure.[20] Colorless oil, 62.5% yield, $R_f = 0.22$ (hexane/ethyl acetate = 2:1), bp 155 °C (755.4 Torr). IR (NaCl) 3465, 3118, 2950, 2415, 2141, 1524, 1457, 1330, 1232, 1191, 1030, 864, 792 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.76 (s, 3H), 7.84 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 159.15, 145.02, 37.41.

1,4-Dimethyl-3-azido-1,2,4-triazolium Iodide (3). Compound **2** (0.16 g, 1.29 mmol) and iodomethane (0.18 g, 1.29 mmol) were placed in a Pyrex glass tube that was evacuated, sealed, and held at 25 °C for 5 days. The brown residue was washed with ether to give a yellow solid (0.21 g), 60% yield, mp 116 °C. IR (KBr) 3460, 3020, 2285, 2424, 2174, 1597, 1545, 1503, 1277, 872, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.87 (s, 3H), 4.16 (s, 3H), 11.11 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 151.29, 145.04, 41.11, 34.32; MS (solid probe) (EI) M/Z (%) 139 (M^+,18). Anal. Calcd for $C_4H_7N_6I$: C, 18.06; H, 2.65. Found: C, 18.37; H, 2.67.

General Procedure for Preparation of Salts 4 and 5. 1,4-Dimethyl-3-azido-1,2,4-triazolium Perchlorate (4). To a magnetically stirred solution of **3** (0.10 g, 0.375 mmol) in water (3 mL) was added silver perchlorate ($AgClO_4$, 0.078 g, 0.375 mmol). After 2 h at room temperature, silver iodide was removed by filtration. The filtrate was dried in vacuo to give a yellow solid (**4**) (0.087 g), 97% yield, mp 68 °C. IR (KBr) 3613, 3099, 2343, 2177, 1600, 1551, 1507, 1455, 1410, 1280, 1186, 1091, 870, 707, 623 cm^{-1}. ^{1}H NMR (acetone-d_6) δ 3.79 (s, 3H), 4.14 (s, 3H), 9.62 (s, 1H). ^{13}C NMR (acetone-d_6) δ 151.16, 143.72, 39.07, 32.16.; MS (solid probe) (EI) M/Z (%) 139(M^+, 6). Anal. Calcd for $C_4H_7N_6ClO_4$: C, 20.14; H, 2.96. Found: C, 20.28; H, 3.17.

1,4-Dimethyl-3-azido-1,2,4-triazolium Nitrate (5). Compound **5** was prepared as above from **3** and silver nitrate to form a yellow solid in 98% yield, mp 98 °C. IR (KBr) 3018, 2178, 1595, 1545, 1507, 1402, 1369, 1335, 1272, 1153, 924, 827, 702, 621 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 3.62 (s, 3H), 4.03 (s, 3H), 9.86 (s, 1H). ^{13}C NMR (DMSO-d_6) δ 151.65, 145.01, 40.34, 33.47. MS (solid probe) (EI) M/Z (%) 139(M^+, 33).

General Procedure for Preparation of Salts 6−9. 3-Azido-1,2,4-triazolium Nitrate (6). A dry, nitrogen-filled Schlenk glass tube was charged with compound **1** (0.11 g, 1.0 mmol), dry methanol (1 mL), and concentrated nitric acid (70 wt %, 0.09 g, 1.0 mmol). The mixture was stirred 2 h at room temperature. The solvent was evacuated under vacuum overnight to give a white solid (**6**) in 98% yield (0.17 g), mp 147 °C. IR (KBr) 3109, 2562, 2160, 1583, 1414, 1319, 1160, 908, 781 cm^{-1}. ^{1}H NMR (acetone-d_6) δ 8.50 (s, 1H). ^{13}C NMR (acetone-d_6) δ 158.26, 145.35; MS (solid probe) (EI) M/Z (%) 111(M^+, 29).

3-Azido-1,2,4-triazolium Perchlorate (7). Compound **7** was prepared as above from **1** and concentrated perchloric acid (70 wt %) to form a white solid in 98% yield, mp 123 °C. IR (KBr) 3150,

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3069, 2935, 2820, 2588, 2158, 1705, 1586, 1453, 1283, 1106, 927, 808, 708, 624 cm^{-1}. ^{1}H NMR (acetone-d_6) δ 9.82 (s, 1H). ^{13}C NMR (acetone-d_6) δ 152.29, 143.09. MS (solid probe) (EI) M/Z (%) 111 (M$^+$, 2.3). Anal. Calcd for $C_2H_3N_6ClO_4$: C, 11.41; H, 1.44. Found: C, 10.97; H, 1.51.

1-Methyl-3-azido-1,2,4-triazolium Nitrate (8). Compound **8** was prepared as above from **2** and concentrated nitric acid (70 wt %) to give a white solid in 97.5% yield, mp 66 °C. IR (KBr) 3061, 2147, 1589, 1433, 1190, 1107, 912, 718, 629 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 8.53 (s, 1H), 3.98(s, 3H). ^{13}C NMR ($CDCl_3$) δ 156.61, 144.31, 38.51. MS (solid probe) (EI) M/Z (%) 125 (M$^+$, 1.2). Anal. Calcd for $C_3H_5N_7O_3$: C, 19.26; H, 2.69. Found: C, 19.21; H, 2.70.

1-Methyl-3-azido-1,2,4-triazolium Perchlorate (9). Compound **9** was prepared as above from **2** and concentrated perchloric acid (70 wt %) to form a white solid in 98% yield, mp 55 °C. IR (KBr) 3116, 2820, 2163, 1587, 1447, 1306, 1264, 1102, 930, 866, 801, 710, 624 cm^{-1}. ^{1}H NMR (acetone-d_6) δ 4.19 (s, 3H), 9.66 (s, 1H). ^{13}C NMR (acetone-d_6) δ 151.79, 142.88, 39.79. MS (solid probe) (EI) M/Z (%) 125(M$^+$, 1.5). Anal. Calcd for $C_3H_5N_6ClO_4$: C, 16.05; H, 2.24. Found: C, 16.36; H, 2.12.

5-Methyl-3-azido-1,2,4-triazole (10). Compound **10** was prepared by a literature procedure.[11] White solid, 80% yield, mp 142 °C. IR (KBr) 3158, 3036, 2928, 2788, 2143, 1713, 1503, 1440, 1222, 1063, 897, 796, 729 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 3H). ^{13}C NMR ($CDCl_3$) δ158.50, 155.53, 13.17.

5-Methyl-3-azido-1,2,4-triazolium Nitrate (11). Compound **11** was prepared as for **6**−**9** from **10** and concentrated nitric acid (70 wt %) to give a white solid in 98% yield, mp 118 °C. IR (KBr) 3070, 2878, 2549, 2157, 1624, 1560, 1521, 1436, 1278, 1181, 997, 792, 713 cm^{-1}. ^{1}H NMR (D_2O) δ 2.35 (s, 3H). ^{13}C NMR (D_2O) δ 158.00, 153.60, 10.33. MS (solid probe) (EI) M/Z (%) 125 (M$^+$, 1.8). Anal. Calcd for $C_3H_5N_7O_3$: C, 19.26; H, 2.69. Found: C, 19.52; H, 2.70.

3,5-Diazido-1,2,4-triazole (12). Compound (**12**) was prepared by a literature procedure.[21] White solid, 38.5% yield, mp 78 °C. IR (KBr) 2359, 2136, 1654, 1566, 1510, 1398, 1200, 1136, 1045, 833, 733 cm^{-1}. ^{13}C NMR (DMSO-d_6) δ 158.19.

3,5-Diazido-1,2,4-triazolium Nitrate (13). Compound **13** was prepared as for **6**−**9** from **12** and concentrated nitric acid (70 wt %) to from a white solid, 78.6% yield, mp 97 °C. IR (KBr) 2529, 2145, 1699, 1573, 1516, 1407, 1300, 1203, 1030, 803 cm^{-1}. ^{13}C NMR (D_2O) δ 154.62. HRMS (EI): M/Z Calcd for cation $C_2H_2N_9$ (M$^+$): 151.0355. Found: 151.0358.

1-Methyl-4-amino-1,2,4-triazolium Iodide (14). Compound **14** was obtained via a minor modification of previous syntheses.[22] A mixture of 4-amino-1,2,4-triazole (0.17 g, 2 mmol) and iodomethane (0.29 g, 2 mmol) in acetonitrile (20 mL) was stirred at room temperature for 5 d. The solvent was then evaporated under reduced pressure to give **14** in essentially 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 (DMSO-d_6) δ 4.04 (s, 3H), 6.96 (s, 2H), 9.14 (s, 1H), 10.14 (s, 1H). ^{13}C NMR (DMSO-d_6) δ 146.35, 144.23, 40.66.

1-Methyl-4-amino-1,2,4-triazolium Nitrate (15). This compound was first synthesized and reported orally by Dr. Gregory Drake.[7] In the meantime, we have also produced it and include our data here. Compound **15** was prepared as for **4** and **5** from **14** and silver nitrate to form 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 (DMSO-d_6) δ 4.04 (s, 3H), 6.97 (s, 2H), 9.16 (s, 1H), 10.12 (s, 1H). ^{13}C NMR (DMSO-d_6) 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 (16). Compound **16** was prepared as for **4** and **5** from **14** and silver perchlorate to form 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 (DMSO-d_6) δ 4.03 (s, 3H), 6.94 (s, 2H), 9.15 (s, 1H), 10.05 (s, 1H). ^{13}C NMR (DMSO-d_6) δ 146.34, 144.27, 40.21. MS (solid probe) (EI) M/Z (%) 99 (M$^+$, 2.6).

3-Nitroamino-1,2,4-triazole (17). Compound **17** was prepared via a literature procedure.[23] White solid, 70% yield, mp 206 °C. IR (KBr) 1750, 1585, 1531, 1438, 1283, 949, 837, 637 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 8.50 (s, 1H).

1-Methyl-3-Nitroamino-1,2,4-triazole (18). A 0.40-g (3.1 mmol) portion of **17** was dissolved in 10 mL of acetone, then 1.2 mL of 10% sodium hydroxide was added, followed by 0.39 g (3.1 mmol) of dimethyl sulfate. After 12 h, the acetone was evaporated and the residue was dissolved in water and extracted with ethyl acetate. The extracts were dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was recrystallized (ethanol) to give a white solid, 40.9% yield (0.18 g), mp 161 °C. IR (KBr) 3206, 1697, 1557, 1463, 1401, 1313, 1257, 1210, 864, 713 cm^{-1}. ^{1}H NMR (acetone-d_6) δ 8.37 (s, 1H), 3.58 (s, 3H). ^{13}C NMR (acetone-d_6) δ 152.93, 141.46, 31.24. Anal. Calcd for $C_3H_5N_5O_2$: C, 25.18; H, 3.52. Found: C, 24.72; H, 3.51.

1-Methyl-3-nitro-1,2,4-triazole (19). Compound **19** was prepared via a literature method to form a white solid, 65% yield,[24] mp 62 °C. IR (KBr) 3119, 1549, 1504, 1446, 1414, 1309, 1204, 1036, 898, 833, 696 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.09 (s, 3H), 8.22 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 162.79, 145.49, 37.84.

1,4-Dimethyl-2-H-1,2,4-triazolium Triiodide (20). Compound **20** was prepared via the procedure for **3** from **19** and CH_3I at 100 °C for 3 days to give a brown solid, 80.4% yield, mp 110 °C. IR (KBr) 3083, 2380, 1582, 1431, 1163, 864, 613 cm^{-1}. ^{1}H NMR (acetone-d_6) δ 4.23 (s, 3H), 4.31 (s, 3H), 9.09 (s, 1H), 10.03 (s, 1H). ^{13}C NMR (acetone-d_6) δ 146.39, 144.34, 39.85, 35.34.

1,4-Dimethyl-2-H-1,2,4-triazolium Nitrate (21). Compound **21** was prepared as for salts **4** and **5** from **20** and silver nitrate to form a yellow liquid in 98% yield, mp 1 °C. IR (NaCl) 3456, 3091, 1642, 1590, 1346, 1169, 890, 621 cm^{-1}. ^{1}H NMR (acetone-d_6) δ 4.15 (s, 3H), 4.24 (s, 3H), 9.15(s, 1H), 10.49(s, 1H). ^{13}C NMR (acetone-d_6) δ146.32, 145.06, 39.27, 34.72, 5. MS (solid probe) (EI) M/Z (%) 99 (M$^+$, 7.8). Anal. Calcd for $C_4H_9N_4O_3$: C, 29.82; H, 5.63. Found: C, 29.32; H, 5.21.

1,4-Dimethyl-2-H-1,2,4-triazolium Perchlorate (22). Compound **22** was prepared as for salts **4** and **5** from **20** and silver perchlorate to get a brown liquid, 98% yield, T_g −34 °C. IR (NaCl) 3539, 2404, 2231, 1591, 1450, 1095, 883, 622 cm^{-1}. ^{1}H NMR (acetone-d_6) δ 4.12 (s, 3H), 4.22 (s, 3H), 8.96(s, 1H), 9.79 (s, 1H). ^{13}C NMR (acetone-d_6) δ 146.16, 144.37, 39.47, 34.90. MS (solid probe) (EI) M/Z (%) 99(M$^+$, 7.9). Anal. Calcd for $C_4H_9N_3ClO_4$: C, 24.19; H, 4.57. Found: C, 24.42; H, 4.32.

1-Methyl-5-nitroimidazole (23). Compound **23** was prepared via a literature method to form a white solid, 77% yield,[25,26] mp135 °C. IR (KBr) 3117, 1528, 1479, 1397, 1322, 1290, 980 cm^{-1}. ^{1}H

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NMR ($CDCl_3$) δ 3.83 (s, 3H), 7.42 (d, *J* = 1.24 Hz, 1H), 7.78 (d, *J* = 1.24 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 148.2, 136.8, 120.4, 34.64.

1,2-Dimethyl-5-nitroimidazole (24). Compound **24** was prepared following a literature method and obtained as a white solid, 75% yield,[25,26] mp 186 °C. IR (KBr) 3050, 2977, 1538, 1499, 1387, 1305, 1298, 997 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.41 (s, 3H), 3.66 (s, 3H), 7.65 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 146.3, 145.1, 120.7, 33.86, 12.94.

1-Ethyl-2-methyl-5-nitroimidazole (25). Compound **25** was prepared via a literature method and obtained as a light orange solid, 70% yield,[25,26] mp 86 °C. IR (KBr): 3110, 2977, 1534, 1500, 1401, 1334, 989. ^1H NMR (D_2O) δ 1.44 (t, *J* = 7.22 Hz, 3H), 2.40 (s, 3H), 3.95 (q, *J* = 7.22 Hz, 2H), 7.68 (s, 1H). ^{13}C NMR (D_2O) δ 146.5 (bs), 144.5, 119.0, 42.12, 15.46, 12.98.

1,3-Dimethyl-5-nitroimidazolium Iodide (26). Compound **26** was prepared as for **3** from **23** and CH_3I at 125 °C for 3 days, yellow solid, 95.4% yield, mp 180 °C. IR (KBr) 3048, 2999, 1526, 1387, 1153, 1065 cm^{-1}. ^1H NMR (D_2O) δ 3.98 (s, 3H), 4.16 (s, 3H), 8.63 (s, 1H). ^{13}C NMR (D_2O) δ 139.5 (t, *J* = 34.40 Hz), 138.1 (bs), 125.9, 37.70, 37.69. MS (solid probe) (EI) M/Z (%) 142 (M^+, 100). Anal. Calcd for $C_5H_8N_3O_2I$: C, 22.32; H, 3.00. Found: C, 22.42; H, 2.97.

1,2,3-Trimethyl-5-nitroimidazolium Iodide (27). Compound **27** was prepared as for **3** from **24** and CH_3I at 125 °C for 3 days, yellow solid, 94.5% yield, mp 191 °C. IR (KBr) 3044, 1531, 1495, 1395, 1310, 1103, 857 cm^{-1}. ^1H NMR (D_2O) δ 2.75 (s, 3H), 3.91 (s, 3H), 4.09 (s, 3H), 8.59 (s, 1H). ^{13}C NMR (D_2O) δ 149.0, 137.4 (bs), 125.4, 36.41 (36.38), 35.40, 10.53. MS (solid probe) (EI) M/Z (%) 156 (M^+, 100). Anal. Calcd for $C_6H_{10}N_3O_2I$: C, 25.46; H, 3.56. Found: C, 25.46; H, 3.50.

1-Ethyl-2,3-dimethyl-5-nitroimidazolium Iodide (28). Compound **28** was prepared as for **3** from **25** and CH_3I, yellow solid, 90% yield, mp 172 °C. IR (KBr): 3057, 1528, 1501, 1329, 1112, 846. ^1H NMR (D_2O) δ 1.50 (t, *J* = 7.36 Hz, 3H), 2.77 (s, 3H), 4.08 (s, 3H), 4.30 (q, *J* = 7.36 Hz, 2H), 8.69 (s, 1H). ^{13}C NMR (D_2O) δ 148.3, 137.7 (bs), 123.8, 45.32 (45.29), 35.21, 13.85, 10.41. MS (solid probe) (EI) M/Z (%) 170 (M^+, 100). Anal. Calcd for $C_7H_{12}N_3O_2I$: C, 28.30; H, 4.07. Found: C, 28.32; H, 4.00.

1,3-Dimethyl-5-nitroimidazolium Perchlorate (29). Compound **29** was prepared as for **4** and **5** from **26** and silver perchlorate, white solid, 98% yield, mp 172 °C. IR (KBr) 3116, 1593, 1531, 1397, 1323, 1089 cm^{-1}. ^1H NMR (D_2O) δ 3.98 (s, 3H), 4.16 (s, 3H), 8.63 (s, 1H). ^{13}C NMR (D_2O) δ 139.5 (t, *J* = 34.40 Hz), 138.1 (bs), 125.9, 37.70, 37.69. MS (solid probe) (EI) M/Z (%) 142 (M^+, 100). Anal. Calcd for $C_5H_8N_3ClO_6$: C, 24.86; H, 3.34. Found: C, 25.07; H, 3.31.

1,3-Dimethyl-5-nitroimidazolium Nitrate (30). Compound **30** was prepared as for **4** from **26** and silver nitrate, colorless solid, 98% yield, mp 163 °C. IR (KBr) 3046, 1589, 1528, 1397, 1348, 1046 cm^{-1}. ^1H NMR (D_2O) δ 3.99 (s, 3H), 4.17 (s, 3H), 8.63 (s, 1H). ^{13}C NMR (D_2O) δ 139.5 (t, *J* = 34.14 Hz), 138.1 (bs), 125.7, 37.28, 37.26. MS (solid probe) (EI) M/Z (%) 142 (M^+, 100). Anal. Calcd for $C_5H_8N_4O_5$: C, 29.42; H, 3.95. Found: C, 29.47; H, 3.99.

1,2,3-Trimethyl-5-nitroimidazolium Perchlorate (31). Compound **31** was prepared as for **4** from **27** and silver perchlorate, colorless solid, 98% yield, mp 186 °C. IR (KBr) 3131, 2943, 1543, 1407, 1321, 1090, 856 cm^{-1}. ^1H NMR (D_2O) δ 2.71 (s, 3H), 3.89 (s, 3H), 4.06 (s, 3H), 8.56 (s, 1H). ^{13}C NMR (D_2O) δ 149.0, 137.3 (bs), 125.2 (125.0, 124.7), 36.07 (36.03), 35.06, 10.00. MS (solid probe) (EI) M/Z (%) 156 (M^+, 100). Anal. Calcd for $C_6H_{10}N_3ClO_6$: C, 28.19; H, 3.94. Found: C, 28.16; H, 3.86.

1,2,3-Trimethyl-5-nitroimidazolium Nitrate (32). Compound **32** was prepared as for **4** from **27** and silver nitrate, colorless solid, 98% yield, mp 161 °C. IR (KBr) 3042, 1603, 1501, 1405, 1337, 825 cm^{-1}. ^1H NMR (D_2O) δ 2.72 (s, 3H), 3.90 (s, 3H), 4.08 (s, 3H), 8.57 (s, 1H). ^{13}C NMR (D_2O) δ 149.0, 137.4 (bs), 125.2, 36.09 (36.05), 35.08, 9.99. MS (solid probe) (EI) M/Z (%) 156 (M^+, 100). Anal. Calcd for $C_6H_{10}N_4O_5$: C, 33.03; H, 4.62. Found: C, 32.86; H, 4.64.

1-Ethyl-2,3-dimethyl-5-nitroimidazolium Perchlorate (33). Compound **33** was prepared as for **4** from **28** and silver perchlorate, colorless solid, 98% yield, mp 146 °C. IR (KBr): 3121, 2958, 1533, 1506, 1402, 1323, 1090 cm^{-1}. ^1H NMR (acetone-*d*$_6$) δ 1.57 (t, *J* = 7.34 Hz, 3H), 2.94 (s, 3H), 4.22 (s, 3H), 4.48 (q, *J* = 7.34 Hz, 2H), 8.60 (s, 1H). ^{13}C NMR (acetone-*d*$_6$) δ 148.8, 138.1 (bs), 123.7, 45.09, 35.01, 13.91, 10.08. MS (solid probe) (EI) M/Z (%) 170 (M^+, 100). Anal. Calcd for $C_7H_{12}N_3ClO_6$: C, 31.18; H, 4.49. Found: C, 31.20; H, 4.42.

1-Ethyl-2,3-dimethyl-5-nitroimidazolium Nitrate (34). Compound **34** was prepared as for **4** from **28** and silver nitrate, colorless solid, 98% yield, mp 65 °C. IR (KBr): 3075, 2986, 1599, 1536, 1506, 1337, 1206, 851 cm^{-1}. ^1H NMR (D_2O) δ 1.40 (t, *J* = 7.36 Hz, 3H), 2.67 (s, 3H), 4.00 (s, 3H), 4.20 (q, *J* = 7.36 Hz, 2H), 8.60 (s, 1H). ^{13}C NMR (D_2O) δ 149.0, 138.4 (bs), 124.4, 45.90, 35.62, 14.38, 10.65. MS (solid probe) (EI) M/Z (%) 170 (M^+, 100). Anal. Calcd for $C_7H_{12}N_4O_5$: C, 36.21; H, 5.21. Found: C, 35.96; H, 5.34.

2-Azidoimidazole (35). Compound **35** was prepared via a literature method and obtained as a colorless solid in 95% yield.[20,27] ^1H NMR (D_2O) δ 6.76 (s, 2H). ^{13}C NMR (D_2O) δ 141.93, 121.7.

2-Azidoimidazolium Perchlorate (36). Compound (**36**) was prepared as for **6** from **35** and concentrated perchloric acid (70 wt %), colorless solid, 98% yield, mp 116 °C. IR (KBr) 3187, 3038, 2181, 1627, 1086 cm^{-1}. ^1H NMR (D_2O) δ 7.04 (s, 2H). ^{13}C NMR (D_2O) δ 117.8. MS (solid probe) (EI) M/Z (%) 110 (M^+, 100). Anal. Calcd for $C_3H_4N_5ClO_4$: C, 17.20; H, 1.92. Found: C, 17.41; H, 2.05.

2-Azidoimidazolium Nitrate (37). Compound **37** was prepared as for salts **6** from **35** and concentrated nitric acid (70 wt %), colorless solid, 98% yield, mp 124 °C. IR (KBr) 3150, 2173, 1618, 1387, 1314 cm^{-1}. ^1H NMR (D_2O) δ 7.05 (s, 2H). ^{13}C NMR (D_2O) δ 117.8. MS (solid probe) (EI) M/Z (%) 110 (M^+, 100). Anal. Calcd for $C_3H_4N_6O_3$: C, 20.94; H, 2.34. Found: C, 21.20; H, 2.41.

1-Methyl-5-nitrotetrazole (38). Compound **38** was prepared following a literature method and obtained as a white solid, 42% yield,[28] mp 41 °C. IR (KBr) 2965, 2907, 2683, 1567, 1500, 1457, 1345, 1262, 1210, 1105, 1024, 833, 800, 700, 638 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.46 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 157.04, 38.94.

1,5-Dimethyltetrazole (39). Compound **39** was prepared following a literature method[28] and obtained as a white solid, 45% yield, mp 70 °C. IR (KBr) 2962, 1533, 1406, 1283, 1248, 1095, 1043, 914, 799, 728, 654 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.56 (s, 3H), 4.00 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 152.75, 34.23, 9.51.

2,5-Dimethyltetrazole (40). Compound **40** was prepared following a literature method[28] and obtained as a colorless oil, 30% yield. IR (NaCl) 2957, 1498, 1451, 1385, 1363, 1187, 1041, 761, 625 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.38 (s, 3H), 4.17 (s, 3H), ^{13}C NMR ($CDCl_3$) δ 163.66, 39.89, 11.44.

2,4,5-Trimethyltetrazolium Iodide (41). Compound **41** was prepared as for **3** from **40** and CH_3I at 60 °C for 24 h, white solid, 80.1% yield, mp 156 °C. IR (KBr) 3005, 1553, 1421, 1338, 1036, 809, 651 cm^{-1}. ^1H NMR (D_2O) δ 4.47 (s, 3H), 4.18 (s, 3H), 2.67-(s, 3H). ^{13}C NMR (D_2O) δ 160.28, 43.71, 37.18, 9.45. MS (solid probe) (EI) M/Z (%) 113 (M^+, 20.05). Anal. Calcd for $C_4H_9N_4I$: C, 20.01; H, 3.78. Found: C, 20.07; H, 3.78.

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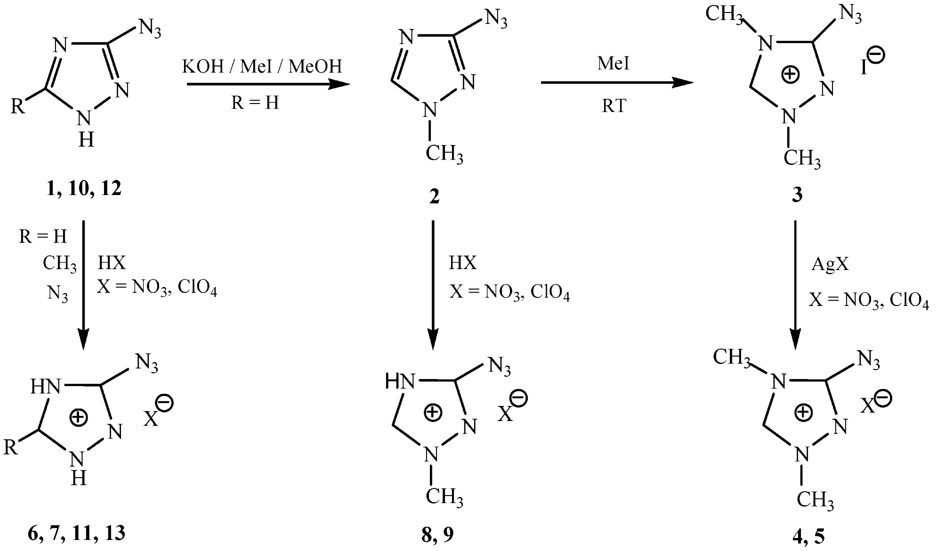
Scheme 1



2,4,5-Trimethyltetrazolium Nitrate (42). Compound **42** was prepared as for **4** from **41** and silver nitrate, white solid, 98% yield, mp 94 °C. IR (KBr) 3428, 3018, 2398, 1762, 1632, 1552, 1336, 1101, 1044, 806, 652 cm^{-1}. ^1H NMR (D_2O) δ 4.51 (s, 3H), 4.22 (s, 3H), 2.71 (s, 3H). ^{13}C NMR (D_2O) δ 160.31, 43.62, 37.07, 9.31. MS (solid probe) (EI) M/Z (%) 113 (M^+, 19.55). Anal. Calcd for $C_4H_9N_5O_3$: C, 27.43; H, 5.18. Found: C, 26.47; H, 5.17.

2,4,5-Trimethyltetrazolium Perchlorate (43). Compound **43** was prepared as for **4** from **41** and silver perchlorate, white solid, 98% yield, mp 133 °C. IR (KBr) 3050, 2029, 1706, 1428, 1378, 1287, 1091, 806, 623 cm^{-1}. ^1H NMR (acetone-d_6) δ 4.75 (s, 3H), 4.50 (s, 3H), 2.95 (s, 3H). ^{13}C NMR (acetone-d_6) δ 160.51, 43.63, 37.35, 9.50. MS (solid probe) (EI) M/Z (%) 113 (M^+, 19.21). Anal. Calcd for $C_4H_9N_4ClO_4$: C, 22.60; H, 4.27. Found: C, 22.80; H, 4.26.

5-Methyl-1-amino-tetrazole (44). Compound **44** was prepared following a literature method[29] and obtained as 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}. ^1H NMR ($CDCl_3$) δ 2.43 (s, 3H), 5.83 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 151.27, 7.72.

4,5-Dimethyl-1-aminotetrazolium Iodide (45). Compound **45** was prepared as for **3** from **44** and CH_3I at 60 °C for 3 days, yellow solid, 76% yield, mp 121 °C. IR (KBr) 3228, 3121, 2999, 1643, 1576, 1418, 1375, 1225, 1030, 893, 768, 627 cm^{-1}. ^1H NMR (DMSO-d_6) δ 7.71 (s, 2H), 4.23 (s, 3H), 2.78 (s, 3H). ^{13}C NMR (DMSO-d_6) 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.

4,5-Dimethyl-1-aminotetrazolium Nitrate (46). Compound **46** was prepared as for **4** from **45** and silver nitrate, colorless oil, 98% yield, T_g −59 °C. IR (NaCl) 3473, 3243, 3137, 1745, 1645, 1579, 1377, 1034, 949, 829, 772, 651 cm^{-1}. ^1H NMR (DMSO-d_6) δ 7.73 (s, 2H), 4.22 (s, 3H), 2.75 (s, 3H). ^{13}C NMR (DMSO-d_6) 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.

4,5-Dimethyl-1-aminotetrazolium Perchlorate (47). Compound **47** was prepared as for **4** from **45** and silver perchlorate, white solid, 98% yield, mp 51 °C. IR (KBr) 3422, 3166, 3085, 1634, 1570, 1381, 1338, 1078, 768, 625 cm^{-1}. ^1H NMR (DMSO-d_6) δ 7.72 (s, 2H), 4.20 (s, 3H), 2.75 (s, 3H). ^{13}C NMR (DMSO-d_6) 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.

Results and Discussion

With the increase in the number of nitrogen atoms, heterocycles demonstrate a considerable gain in standard enthalpies of formation. 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)[30] to 1,2,4-triazole ($\Delta H_f{}^\circ{}_{(cryst)} = 109$ kJ/mol) to tetrazole ($\Delta H_f{}^\circ{}_{(cryst)} = 237.2$ kJ/mol),[12] the variation in the trend of their heats of formation is obvious. In our research, considerable attention is focused on energetic azido and nitro derivatives of azoles. The syntheses of the starting azido derivatives of 1,2,4-triazole, and their subsequent quaternization to corresponding salts are given in Scheme 1.

The 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 yield.[31] Azido derivatives of 1,2,4-triazole (**1**, **2**, **10**, **12**) were readily quaternized with a concentrated solution of strong acid (nitric or perchloric acid) using methanol as solvent. All of the salts were formed in nearly quantitative yield and in high purity (**6**−**9**, **11**, **13**). A single-crystal X-ray study was carried out on 3-azido-1,2,4-triazolium nitrate (**6**). As expected, the proton is attached to N-4 of the 1,2,4-triazole ring. This is consistent with the quaternary results of 1-alkyl-1,2,4-triazoles with alkyl iodide.[31]

Quaternary salt **3** was obtained from compound **2** (1-methyl-1,2,4-triazole) and iodomethane at room temperature. Metathesis of **3** with silver perchlorate or silver nitrate led to the formation of new quaternary salts **4** or **5** in excellent isolated yields. Single-crystal X-ray structure determination

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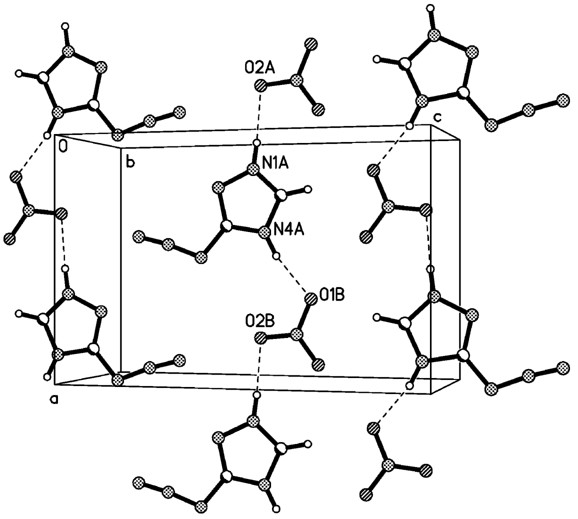
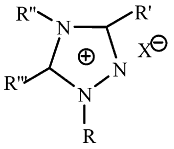


Figure 1. Unit cell of 3-azido-1,2,4-triazolium nitrate (**6**) showing hydrogen bonding.

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

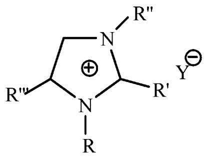


compd	R	R′	R″	R‴	X⁻	T_m/T_g[a]	T_d[b]
4	CH_3	N_3	CH_3	H	ClO_4	68	147
5	CH_3	N_3	CH_3	H	NO_3	98	129
6	H	N_3	H	H	NO_3	147	174
7	H	N_3	H	H	ClO_4	123	154
8	CH_3	N_3	H	H	NO_3	66	139
9	CH_3	N_3	H	H	ClO_4	55	147
11	H	N_3	H	CH_3	NO_3	118	136
13	H	N_3	H	N_3	NO_3	97	136
15	CH_3	H	H	NH_2	NO_3	−60 (T_g)	221
16	CH_3	H	H	NH_2	ClO_4	86	259
21	CH_3	H	CH_3	H	NO_3	1	160
22	CH_3	H	CH_3	H	ClO_4	−34 (T_g)	97

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

of **5** clearly shows methyl substitution at N-4. Examination of the crystal structures of **5** and **6** illustrates the influence of significant hydrogen bonding between the nitrate anion and the protonated 1,2,4-triazolium ring for **6** (Figure 1) which explains its higher density of 1.79 g/cm^3 and melting point of 147 °C compared with that of compound **5** (d = 1.58 g/cm^3, mp 98 °C). By comparing the melting points of **6** and **8**, or **7** and **9** (Table 1), it is seen that the melting points of **8** and **9** are obviously lower than those of **6** and **7**. This may also occur because of the presence of a methyl group at N-1 in **8** or **9**, which lowers the possibility of hydrogen bonding between the nitrate or perchlorate anion and the protonated 1,2,4-triazolium ring. The relative impact of cation and anion on melting points of salts of azido derivatives of 1,2,4-triazole are shown in Table 1. When the anion is perchlorate, the melting points of corresponding compounds are lower than that of the analogous nitrate. Azido derivatives of imidazole also show similar results, e. g., the melting points for **36** and **37** are 116 and 124 °C, respectively (Table 2). 3,5-Diazido-1,2,4-triazolium nitrate (**13**) was synthesized from 3,5-diazido-1,2,4-triazole (**12**) and nitric acid. It is extremely sensitive toward friction, shock and electrostatic impact. The melting point is 97 °C. It was not subjected to elemental analysis because of the detonation risk. The high-resolution mass of cation for **13** is 151.0358 which is nearly equal to the calculated value for the cation (151.0355).

Table 2. Structures and Phase Transition and Decomposition Temperatures of Quaternary Imidazolium Salts



compd	R	R′	R″	R‴	Y⁻	T_m[a]	T_d[b]
29	CH_3	H	CH_3	NO_2	ClO_4	172	259
30	CH_3	H	CH_3	NO_2	NO_3	163	174
31	CH_3	CH_3	CH_3	NO_2	ClO_4	186	307
32	CH_3	CH_3	CH_3	NO_2	NO_3	161	166
33	Et	CH_3	CH_3	NO_2	ClO_4	146	237
34	Et	CH_3	CH_3	NO_2	NO_3	65	146
36	H	N_3	H	H	ClO_4	116	132
37	H	N_3	H	H	NO_3	124	124

[a] Melting point (T_m), °C. [b] Thermal degradation, °C.

1-Methyl-4-amino-1,2,4-triazolium iodide (**14**) was synthesized from 4-amino-1,2,4-triazole and iodomethane by using acetonitrile as solvent. Metathesis of **14** with silver nitrate or silver perchlorate led to the formation of **15**[7] or **16**. The single-crystal X-ray structure of **16** clearly shows the significant hydrogen bonding between the perchlorate anion and amino group, and that the methyl group is attached to N-1 of the 1,2,4-triazolium ring. This is consistent with Drake's results where 4-amino-1,2,4-triazole can be quaternized with nitric (or perchloric) acid because the N-amino group acts as an electron withdrawing group in high nitrogen heterocycles.[7] However, **15**[7] is a room-temperature ionic liquid with a phase transition temperature (T_g) at −60 °C. This is significantly different from **16**—the perchlorate salt—that melts at 86 °C.

Because the presence of the nitroamino and nitro groups can improve the oxygen balance of the corresponding azoles, eventually resulting in a higher exothermicity of the combustion and detonation process, 1-methyl-3-nitroamino-1,2,4-triazole (**18**) and 1-methyl-3-nitro-1,2,4-trizaole (**19**) were also synthesized. Unfortunately, although different solvents and more forcing reaction temperatures were tried, neither **18** nor **19** were quaternizable with either concentrated nitric acid or iodomethane. However, when **19** was heated with iodomethane at 100 °C for 3 days, a brown solid (**20**) was obtained. The proton NMR spectrum of **20** showed the presence of a new methyl group and a new C−H moiety. Moreover, based on the IR spectrum, no nitro group remained. A single-crystal X-ray structure (Figure 2) supports the NMR and IR data, i.e., quaternization had occurred with the nitro group of the 1,2,4-triazolium ring being replaced by a proton at C-3 and a methyl group appearing at N-4. The anion was triiodide. Metathesis of **20** with silver nitrate or silver perchlorate led to the formation of new ionic liquids **21** or **22**.

Some nitro imidazolium salts (**23**−**25**) were also synthesized in our work. In comparison with 1-methyl-3-nitro-1,2,4-

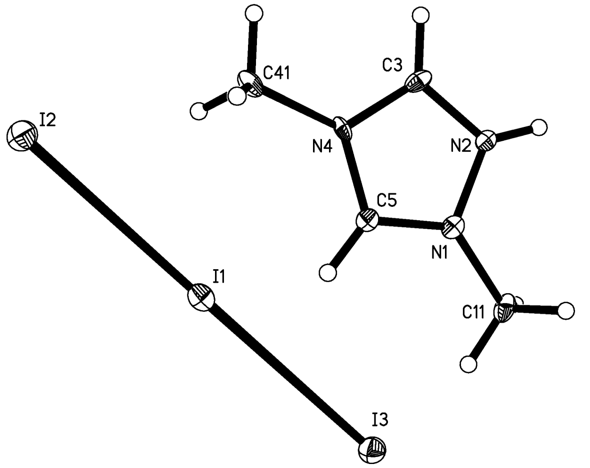
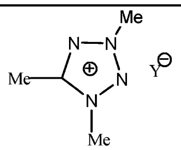
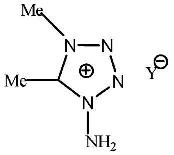


Figure 2. Molecular structure of compound (**20**) as ORTEP plot.

triazole (**19**), the more basic imidazoles, **23**−**25**, were quaternized readily with iodomethane to form the nitro imidazolium iodides **26**−**28**. Metathesis reactions of these iodides with silver nitrate or silver perchlorate led to the formation of new salts (**29**−**34**). With the exception of **34** (mp 65 °C), the melting points of these salts are >100 °C (Table 2). In general, the nitrate salts have lower melting points and thermal stabilities than the corresponding perchlorates.

The increasing interest in tetrazole derivatives is driven not only by their effective use in modern medicine, biochemistry, and agriculture, but by their possible applications as energetic components of propellants and gas-generating systems.[12,32] Yet the problems associated with the chemistry and properties of energetic tetrazolium ionic salts are rarely discussed in the scientific literature.[33,34] In our work, some tetrazole derivatives (**38**−**40**, **44**) were synthesized. As was the case for 1-methyl-3-nitro-1,2,4-triazole (**19**), 1-methyl-5-nitro-tetrazole (**38**) was difficult to quaternize with iodomethane under various conditions. Heating **38** at 50 or 80 °C with nitric acid in methanol gave rise to a brown gas with concomitant decomposition. Whereas alkylation of 1-substituted tetrazoles generally produces a mixture of isomeric 1,4- and 1,3-substituted tetrazolium salts, 2-substituted tetrazoles can be alkylated only at position 4 of the cycle to give 2,4-substituted tetrazolium salts.[35] We also found similar results. An isomeric mixture formed when 1,5-dimethyltetrazole (**39**) was reacted with iodomethane. However, pure 2,4,5-trimethyltetrazolium iodide (**41**) was obtained from **40** and CH_3I when the mixture was heated at 60 °C for 24 h. Metathesis of **41** with silver nitrate or silver perchlorate led to the formation of salts **42** and **43**. As is the case for 4-amino-1,2,4-triazole, 5-methyl-1-amino-tetrazole (**44**) was also quaternized with CH_3I to form **45**. Its subsequent metathesis with silver nitrate or silver perchlorate led to the formation of salts **46** and **47**. When the anion is nitrate, an ionic liquid (**46**) was obtained (T_g −59 °C). In comparison with **42** and **43**, the melting points and thermal degradation temperatures of the amino tetrazoles (**46** and **47**) are lower (Table 3).

Table 3. Structures and Phase Transition and Decomposition Temperatures of Quaternary Tetrazolium Salts

Compd	Structure	Y^-	T_m / T_g [a]	T_d [b]
42		NO_3	94	193
43		ClO_4	133	315
46		NO_3	-59 (T_g)	170
47		ClO_4	51	182

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

Density is one of the important physical properties of energetic salts. The densities of some of the new salts were calculated using literature methods.[36,37] Some of the measured densities obtained by using helium displacement methods for the new ionic salts and data from single crystal structures are also listed in Table 4. It is shown that the calculated densities are slightly higher than observed ones. Several of these new salts have relatively high densities, such as **36** where the calculated value is 1.89 g/cm^3 and the measured value is 1.76 g/cm^3. For all of the compounds except **34**, the densities exceed 1.50 g/cm^3.

The standard enthalpy of formation of an energetic salt is a very important characteristic. Enthalpies of combustion and the standard enthalpies of formation of dinitrobiuret (DNB) and diaminotetrazolium nitrate have been calculated.[34] The heat of formation of hydroxyammonium perchlorate using a combustion calorimetric method was also investigated.[40] Chlorine gas was liberated in the reaction. In our research, typical experimental results (averaged over three measurements each) of the constant volume combustion energy ($\Delta_c U_m$) of some salts are given in Table 4. 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:

$$\Delta_c H_m^\circ = \Delta_c U_m + \Delta n RT,$$
$$\Delta n = \sum n_i \,(\text{products, g}) - \sum n_i \,(\text{reactants, g})$$

where $\sum n_i$ is the total molar amount of the gases in products or reactants. The calculated molar enthalpy of formation of the sample, such as compound **6**, was calculated from a

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Table 4. 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)
6	1.80 (1.79^f)	1.76	345.35	1434.41	218.65
8	1.66	1.63	477.47	1988.46	93.35
9	1.80	1.66	581.17	2419.22	574.73
11	1.68	1.61	492.54	2051.49	156.38
33	1.54		834.79	3489.04	−980.51
34	1.47		929.23	3881.08	−537.86
36	1.89	1.76	454.35	1892.32	140.13
37	1.73	1.64	534.96	2230.84	529.27
43	1.61	1.55	755.97	3155.54	345.88
46	1.55	1.50^g	587.85	2453.37	129.52
47	1.71	1.66	672.96	2811.76	538.53

[a] Calculated density; refs 36 and 37. [b] Measured density using a gas pycnometer at 25 °C. [c] The 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.

designed Hess thermochemical cycle according to the reaction **a** as follows:

$$[C_2H_3N_6]^+[NO_3]^- \text{ (s)} + {}^5/_4{\cdot}O_2 \rightarrow 2CO_2 \text{ (g)} + {}^3/_2{\cdot}H_2O \text{ (l)} + {}^7/_2{\cdot}N_2 \text{ (g)} \quad (\mathbf{a})$$

$$\Delta_f H_m{}^\circ([C_2H_3N_6]^+[NO_3]^-,s) = [2\Delta_f H_m{}^\circ(CO_2,g) + {}^3/_2{\cdot}\Delta_f H_m{}^\circ(H_2O,l)] - \Delta_c H_m{}^\circ([C_2H_3N_6]^+[NO_3]^-, s)$$

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],[38,39] $\Delta_c H_m{}^\circ$ and $\Delta_f H_m{}^\circ$ for compound **6** were calculated to be −1434.41 and 218.65 kJ/mol, respectively.

For perchlorate salts, the heat of formation of hydroxyammonium 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.[40] The heat of formation of 2,4,6-trimethylpyrylium perchlorate was determined on the basis of the HCl (aq) which was formed.[41] We also used a similar method.[40] When the gaseous reaction products were condensed into a starch−KI solution to determine the amount of elemental chlorine formed, it was found to be sufficiently low (<0.5% of total chlorine) that it was neglected. When the combustion reaction was run with water added to the sample in the calorimeter, the chloride concentration was determined by the Volhard method.[42] These results indicate nearly quantitative chloride ion formation during combustion. Therefore, for the perchlorate salts, such as compound **9**, the designed Hess thermochemical cycle was based on reaction **b**:

$$[C_3H_5N_6]^+[ClO_4]^- \text{ (s)} + 2O_2 \rightarrow 3CO_2 \text{ (g)} + 2H_2O \text{ (l)} + 3N_2 \text{ (g)} + HCl \text{ (g)} (\mathbf{b})$$

The data for all other samples were calculated and are listed in Table 4.

Energies of combustion and differential thermograms of organic azides were investigated by Denault,[11] e. g., the constant volume combustion energy for 3-azido-1,2,4-triazole (**1**) is 363.42 kcal/mol. From Table 4, we can see that our newly synthesized salts have higher constant volume combustion energies. The constant volume combustion energies and standard molar enthalpies of formation for perchlorate salts are higher than those of nitrates. Of all of the compounds examined, **9** has the highest standard molar enthalpy of formation, 574.73 kJ/mol.

Conclusion

Syntheses of azido and nitro derivatives of imidazole, 1,2,4-triazole, and substituted derivatives of tetrazole, and their subsequent quaternization led to new energetic salts. The nitro derivatives of triazole and tetrazole are more difficult to quaternize with nitric acid or iodomethane than the analogous azido derivatives of azoles. However, nitro derivatives of imidazole can be readily reacted with iodomethane to form quaternary salts. Most of the new salts exhibit good physical properties, including high densities (>1.50 g/cm^3), good thermal stabilities, and low melting points (<100 °C). The molar enthalpies of formation for some salts were calculated from the combustion energy obtained via oxygen bomb calorimetry. Most of the new salts have high combustion energies and molar enthalpies of formation. Perchlorate salts have higher combustion energies and molar enthalpies of formation than the analogous nitrates.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for 1,4-dimethyl-3-azido-1,2,4-triazolium nitrate (**5**), 3-azido-1,2,4-triazolium nitrate (**6**), 1-methyl-4-amino-1,2,4-triazolium perchlorate (**16**), and 1,4-dimethyl-2-H-1,2,4-triazolium triiodide (**20**) (pdf). This information is available free of charge via the Internet at http://pubs.acs.org.

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