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# Energetic Salts of 3-Nitro-1,2,4-triazole-5-one, 5-Nitroaminotetrazole, and Other Nitro-Substituted Azoles[†]

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Energetic salts comprised of substituted 1,2,4-triazolium and tetrazolium cations and 3-nitro-1,2,4-triazolate-5-one (NTO), 5-nitroimino-tetrazolate, 3-nitro-5-trifluoromethyl-1,2,4-triazolate, 3,5-dinitro-1,2,4-triazolate, 4,5-dinitro-imidazolate, 3,5-dinitro-pyrazolate, and 5-nitro-tetrazolate anions were synthesized and characterized. The structures of 3-amino-1,2,4-triazolium 3-nitro-5-trifluoromethyl-1,2,4-triazolate (**6**), and 1-propyl-1,2,4-triazolium 5-nitroimino-tetrazolate (**20**) were confirmed by X-ray analysis. Standard enthalpies of formation were calculated using the computationally feasible DFT(B3LYP) and MP2 methods in conjunction with an empirical approach based on densities of salts. Cheetah 4.0 was used to calculate detonation properties. Salts **2**, **14**, **20**, and **21** fall into the ionic liquid class (mp < 100 °C).

## Introduction

The synthesis of energetic heterocyclic compounds has attracted considerable interest in recent years,[1−7] especially the syntheses and application of new members of heterocyclic-based energetic, low-melting salts.[8,9] 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. The cation is generally a bulky organic nitrogen-containing heterocycle with low symmetry. The anions most frequently are inorganic, such as nitrate,[8,9,10e] perchlorate,[8,9,10e] dinitramide,[8,9c,10] azide,[10e] and tetraazidoborate.[11] However, reports are available that describe ionic liquids with organic anions, such as α-cyano-4-hydroxycinnamate, anthraquinone-2-sulfonate,[12] salicylate and lactate,[13] imidazolate and triazolate, tetrazolate, and picrate.[9,14,15]

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[†] Dedicated to Prof. Dr. Dieter Naumann of the Universität zu Köln on the occasion of his 65th birthday.

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Some metal salts composed of organic anions, such as lithium 4, 5-dicyano-1,2,3-triazolate, were reported as electrolytes,[16] and alkali metal salts of 5,5′-azotetrazolate were also synthesized as potential explosives.[9d,17]

3-Nitro-1,2,4-triazol-5-one (NTO), an explosive of low sensitivity, has several desirable features, such as a slightly negative heat of formation (−101.1 kJ/mol) and high density (1.93 g/cm$^3$).[18] It is a dibasic acid (p$K_1$ = 3.76, p$K_2$ = 11.25),[5] and because of its acidic nature it is possible to synthesize its salts with metals[18,19] and organic bases.[5,18,20] The main explosive characteristics of NTO salts with ethylenediamine, guanidine, and amino-, diamino-, and triaminoguanidine have been studied in detail.[5,18,20] All these salts are less sensitive than RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane), and triaminoguanidinium nitrate. Another example of a superior precursor to energetic salts is the dibasic acid, 5-nitroaminotetrazole,[21] whose heat of formation is +252.3 kJ/mol[21d] and density is 2.06 g/cm$^3$. Earlier advantage was taken of its acidity (p$K_a$ = −0.72 ± 0.50) to synthesize salts with organic bases, such as pyridine, *N*-diethylaniline, ethylenediamine, and guanidine.[21abe] Few thermodynamic studies on the salts were carried out. Recently, we have reported the syntheses of energetic azolium-azolate salts.[9e,f]

In this work, new energetic salts containing either energetic substituted triazolium or tetrazolium cations and 3-nitro-1,2,4-triazolate-5-one, 5-nitroimino-tetrazolate, 3-nitro-5-trifluoromethyl-1,2,4-triazolate, 3,5-dinitro-1,2,4-triazolate, 4,5-dinitro-imidazolate, 3,5-dinitro-pyrazolate, and 5-nitro-tetrazolate anions were synthesized with concomitant determination of structural and thermal properties.

## Experimental Section

*Caution:* Although we experienced no difficulties in handling these materials that possess positive heats of formation and rather impressive detonation properties, they should be handled in very small amounts using the best safety practices.

**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 are reported relative to $Me_4Si$. The melting and decomposition points were obtained 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 with a pycnometer. Densities of solid salts were obtained at room temperature by employing a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were determined using a CE-440 elemental analyzer.

**X-ray Crystallography.** Crystals of compounds **6** (**20**) were removed from the flask, a suitable crystal was selected and attached to a glass fiber, and data were collected at 89(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low-temperature device.[22] Data were measured using omega scans of 0.3° per frame for 40 s for both, and a full sphere of data was collected. A total of 2400 frames were collected for each structure with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[23] software and refined using SAINTPlus[24] on all observed reflections. Data reduction and correction for Lp and decay were performed using SAINTPlus. Absorption corrections were applied using SADABS.[25] The structures were solved by direct methods and refined by least-squares method on $F^2$ using the SHELXTL program package.[26] The structure of **6** (**20**) was solved in the space group $P2(1)/n$ ($P\bar{1}$) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. Diffraction for **6** was very weak with little high-angle data for the four ion pairs per asymmetric unit. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

1-Propyl-1,2,4-triazole,[27] 1-amino-1,2,4-triazole,[9b] 3-azido-1,2,4-triazole,[9a] 1,5-dimethyl-tetrazole,[9a] 1,5-diamino-tetrazole,[10g] 3-nitro-1,2,4-triazol-5-one,[28] 3,5-dinitro-1,2,4-triazole,[29] 3,5-dinitro-pyrazole,[30] 5-nitro-tetrazole,[31] and 5-nitroamine-tetrazole[21e,f] were synthesized according to literature procedures.

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**Table 1. Crystallographic Data and Structure Refinement Parameters for 6 and 20**

| | 6 | 20 |
|---|---|---|
| formula | $C_5H_5F_3N_8O_2$ | $C_6 H_{11} N_9 O_2$ |
| mol wt | 266.17 | 241.24 |
| cryst syst | monoclinic | triclinic |
| space group | *P*2(1)/*n* | $P\bar{1}$ |
| *a* (Å) | 10.9690(18) | 5.0235(16) |
| *b* (Å) | 32.719(5) | 10.636(3) |
| *c* (Å) | 12.317(2) | 12.018(4) |
| α (deg) | 90 | 106.15(3) |
| β (deg) | 108.898(3) | 98.63(4) |
| γ (deg) | 90 | 100.48(3) |
| *V* (Å$^3$) | 4182.1(12) | 592.7(4) |
| *Z* | 16 | 2 |
| *T* (K) | 89(2) | 89(2) |
| λ (Å) | 0.71073 | 0.71073 |
| $\rho_{calcd}$ (Mg/m$^3$) | 1.691 | 1.352 |
| μ (mm$^{-1}$) | 0.167 | 0.107 |
| *F*(000) | 2144 | 252 |
| crystal size (mm$^3$) | 0.25 × 0.10 × 0.04 | 0.38 × 0.06 × 0.04 |
| θ range (deg) | 1.86 to 25.25 | 1.81 to 25.24 |
| index ranges | $-13 \leq h \leq 13$<br>$-39 \leq k \leq 39$<br>$-14 \leq l \leq 14$ | $-6 \leq h \leq 6$<br>$-12 \leq k \leq 12$<br>$-14 \leq l \leq 14$ |
| refl. collected | 45512 | 12288 |
| indep. reflections | 7565 [*R*(int) = 0.0579] | 2127 [*R*(int) = 0.0270] |
| data/restraints/param. | 7565/0/649 | 2127/0/156 |
| GOF | 1.085 | 1.041 |
| R1 [$I > 2\sigma(I)$][a] | 0.0642 | 0.0365 |
| wR2 [$I > 2\sigma(I)$][a] | 0.1345 | 0.0936 |
| largest diff. peak, <ind:1>hole (e Å$^{-3}$) | 0.640 and −0.402 | 0.238 and −0.188 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

**3-Amino-1,2,4-triazolium 3-Nitro-1,2,4-triazolate-5-one (1).** Compound **1** was synthesized according to the literature,[20b] mp 242 °C; IR (KBr) 3458, 3159, 3043, 2438, 1804, 1689, 1623, 1518, 1381, 1313, 1156, 1114, 1060, 1028, 941, 867, 833, 777, 715, 674, 620 cm$^{-1}$; $^1$H NMR δ 5.86 (s, 2H), 7.51 (s, 1H), 12.66 (s, 3H); $^{13}$C NMR δ 156.71, 156.42, 150.52, 145.68.

**1-Amino-1,2,4-triazolium 3-Nitro-1,2,4-triazolate-5-one (2).** A dry, nitrogen-filled Schlenk glass tube was charged with 1-amino-1,2,4-triazole[9b] (0.084 g, 1.0 mmol), dry methanol (5 mL), and 3-nitro-1,2,4-triazol-5-one[28] (0.130 g, 1.0 mmol). The mixture was stirred 8 h at room temperature. The solvent was evacuated under vacuum overnight to give a white solid (**1**): 95% yield (0.20 g), mp 71 °C; IR (KBr) 3316, 3219, 2809, 2479, 1715, 1548, 1469, 1373, 1206, 1131, 1016, 990, 877, 854, 827, 793, 755, 729, 676, 621 cm$^{-1}$; $^1$H NMR δ 6.53 (s, 2H), 7.81 (s, 1H), 8.29 (s, 1H), 12.81 (s, 2H); $^{13}$C NMR δ 154.21, 148.79, 147.83, 142.17. Anal. Calcd for $C_4H_6N_8O_3$•$0.5H_2O$ (MW = 221.3): C, 21.52; H, 3.14; N, 50.22. Found: C, 21.50; H, 2.39; N, 50.21.

**4-Amino-1,2,4-triazolium 3-Nitro-1,2,4-triazolate-5-one (3).** Compound **3** was prepared the same as **2** from 4-amino-1,2,4-triazole (0.084 g, 1.0 mmol) and 3-nitro-1,2,4-triazol-5-one[28] (0.130 g, 1.0 mmol) to give a yellow solid in 96% yield, mp 131 °C; IR (KBr) 3319, 3215, 3151, 3100, 2951, 2357, 1964, 1908, 1638, 1521, 1383, 1307, 1273, 1213, 1172, 1049, 1022, 987, 897, 773, 740, 665, 621 cm$^{-1}$; $^1$H NMR δ 6.21 (s, 2H), 8.38 (s, 1H), 12.80 (s, 2H); $^{13}$C NMR δ 155.95, 149.61, 145.53. Anal. Calcd for $C_4H_6N_8O_3$ (MW 214.2): C, 22.44; H, 2.82; N, 52.33. Found: C, 22.21; H, 2.53; N, 52.04.

**1-Methyl-5-amino-tetrazolium 3-Nitro-1,2,4-triazolate-5-one (4).** Compound **4** was prepared the same as **2** from 1-methyl-5-amino-tetrazole[9a] (0.099 g, 1.0 mmol) and 3-nitro-1,2,4-triazol-5-one[28] (0.130 g, 1.0 mmol) to give a white solid in 95% yield, mp 187 °C; IR (KBr) 3320, 3158, 2742, 2552, 2455, 2378, 2015, 1716, 1665, 1595, 1547, 1483, 1354, 1321, 1184, 1092, 1007, 827, 789, 756, 729, 677 cm$^{-1}$; $^1$H NMR δ 3.70 (s, 3H), 6.65 (s, 2H), 12.78 (s, 2H); $^{13}$C NMR δ 157.31, 155.91, 149.53, 32.96. Anal. Calcd for $C_4H_7N_9O_3$ (MW 214.2): C, 20.97; H, 3.08; N, 55.01. Found: C, 20.74; H, 3.02; N, 54.51.

**3-Nitro-5-trifluoromethyl-1,2,4-triazole (5).** 3-Amino-5-trifluoromethyl-1,2,4-triazole[5b] (3.04 g, 20 mmol) was slowly added to a solution of sodium nitrite (1.58 g) in concentrated sulfuric acid (7.0 mL) at 0−5 °C. After 1 h, water (50 mL) was added at a temperature not exceeding 5 °C. The mixture was well-stirred and then poured slowly into 50 mL of a 40% aqueous solution of sodium nitrite (20 g) at 35−40 °C. The mixture was set aside at room temperature overnight and then extracted three times with ethyl acetate and dried over $MgSO_4$. A colorless liquid was obtained, 55% yield, $R_f = 0.35$ (hexane/ethyl acetate = 2:1). IR (NaCl) 3080, 2701, 1955, 1711, 1625, 1562, 1479, 1400, 1345, 1311, 1177, 1002, 839, 752, 656 cm$^{-1}$; $^1$H NMR (acetone-*d*$_6$) δ 11.0 (s, 1H); $^{13}$C NMR (acetone-*d*$_6$) δ 158.56, 148.87 (q, $J_{C-C-F} = 41.50$ Hz), 117.38 (q, $J_{C-F} = 272.89$ Hz); $^{19}$F NMR (acetone-*d*$_6$) δ −65.90 (s, 3F); GC-MS (EI) *m*/*z* 182 (M$^+$, 30), 163 (25), 154(13), 137(34), 117 (2), 88 (6), 76 (11), 69 (100), 46 (94), 41 (16). Anal. Calcd for $C_3HN_4O_2F_3$•$0.05CH_3COOC_2H_5$ (MW = 186.4): C, 20.60; H, 0.75; N, 30.04. Found: C, 20.67; H, 0.69; N, 29.89.

**3-Amino-1,2,4-triazolium 3-Nitro-5-trifluoromethyl-1,2,4-triazolate (6).** Compound **6** was prepared the same as **2** from 3-amino-1,2,4-triazole (0.084 g, 1.0 mmol) and 3-nitro-5-trifluoromethyl-1,2,4-triazole (**5**) (0.182 g, 1.0 mmol) to give a white solid in 98% yield, mp 168 °C; IR (KBr) 3468, 2985, 2761, 2597, 1685, 1550, 1510, 1463, 1408, 1357, 1306, 1269, 1199, 1151, 1043, 950, 870, 838, 750, 717,663, 626 cm$^{-1}$; $^1$H NMR δ 8.30 (s, 1H), 8.02 (s, br, 2H); $^{13}$C NMR δ 165.25, 152.44 (q, $J_{C-C-F} = 35.47$ Hz), 150.92, 139.37, 120.61 (q, $J_{C-F} = 269.57$ Hz); $^{19}$F NMR δ −62.32 (s, 3F). Anal. Calcd for $C_5H_5F_3N_8O_2$ (MW 266.2): C, 22.56; H, 1.88; N, 42.11. Found: C, 22.64; H, 1.85; N, 41.88.

**3-Amino-1,2,4-triazolium 3,5-Dinitro-1,2,4-triazolate (7).** Compound **7** was prepared the same as **2** from 3-amino-1,2,4-triazole (0.084 g, 1.0 mmol) and 3,5-dinitro-1,2,4-triazole[29] (0.159 g, 1.0 mmol) to give a yellow solid in 98% yield, mp 149 °C; IR (KBr) 3460, 3379, 3290, 2978, 2750, 1681, 1558, 1493, 1352, 1299, 1253, 1111, 1061, 948, 845, 744, 692, 648 cm$^{-1}$; $^1$H NMR δ 8.25 (s, 1H), 7.70 (s, br, 2H); $^{13}$C NMR δ 162.90, 151.21, 139.73. Anal. Calcd for $C_4H_5N_9O_4$ (MW 243.2): C, 19.76; H, 2.07; N, 51.85. Found: C, 20.10; H, 2.00; N, 51.49.

**1-Amino-1,2,4-triazolium 3,5-Dinitro-1,2,4-triazolate (8).** Compound **8** was prepared the same as **2** from 1-amino-1,2,4-triazole[9b] (0.084 g, 1.0 mmol) and 3,5-dinitro-1,2,4-triazole[29] (0.159 g, 1.0 mmol) to give a yellow solid in 98% yield, mp 167 °C; IR (KBr) 3348, 3129, 3020, 2919, 2837, 2687, 2601, 1637, 1540, 1491, 1448, 1392, 1357, 1300, 1116, 1093, 997, 972, 929, 868, 698, 657, 619 cm$^{-1}$; $^1$H NMR δ 7.75 (s, 2H), 8.46 (s, 1H), 9.20 (s, 1H); $^{13}$C NMR δ 162.74, 144.87, 140.57. Anal. Calcd for $C_4H_5N_9O_4$ (MW 243.2): C, 19.76; H, 2.07; N, 51.85. Found: C, 19.75; H, 1.93; N, 51.47.

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**4-Amino-1,2,4-triazolium 3,5-Dinitro-1,2,4-triazolate (9).** Compound **9** was prepared the same as **2** from 4-amino-1,2,4-triazole (0.084 g, 1.0 mmol) and 3,5-dinitro-1,2,4-triazole[29] (0.159 g, 1.0 mmol) to give a yellow solid in 98% yield, mp 126 °C; IR (KBr) 3326, 3242, 3154, 3001, 2465, 1794, 1639, 1555, 1498, 1384, 1355, 1301, 1205, 1163, 1074, 1028, 993, 930, 871, 842, 648, 613 $cm^{-1}$; $^1H$ NMR $\delta$ 7.51 (s, 2H), 9.43 (s, 2H); $^{13}C$ NMR $\delta$ 162.81, 143.94. Anal. Calcd for $C_4H_5N_9O_4$ (MW 243.2): C, 19.76; H, 2.07; N, 51.85. Found: C, 19.71; H, 1.92; N, 51.25.

**1-Methyl-5-amino-tetrazolium 3,5-Dinitro-1,2,4-triazolate (10).** Compound **10** was prepared the same as **2** from 1-methyl-5-amino-tetrazole (0.099 g, 1.0 mmol) and 3,5-dinitro-1,2,4-triazole[29] (0.159 g, 1.0 mmol) to give a yellow solid in 98% yield, mp 139 °C; IR (KBr) 3372, 3137, 3076, 2708, 2229, 1681, 1550, 1500, 1392, 1357, 1305, 1236, 1122, 1037, 848, 779, 709, 646 $cm^{-1}$; $^1H$ NMR $\delta$ 3.72 (s, 3H), 7.31 (s, 2H); $^{13}C$ NMR $\delta$ 163.39, 155.81, 32.56. Anal. Calcd for $C_4H_6N_{10}O_4$ (MW 258.2): C, 18.61; H, 2.34; N, 54.26. Found: C, 18.88; H, 2.27; N, 53.73.

**3-Amino-1,2,4-triazolium 4,5-Dinitro-imidazolate (11).** Compound **11** was prepared the same as **2** from 3-amino-1,2,4-triazole (0.084 g, 1.0 mmol) and 4,5-dinitro-imidazole[9e] (0.158 g, 1.0 mmol) to give a yellow solid in 98% yield, mp 163 °C; IR (KBr) 3482, 3377, 3152, 2963, 2904, 2743, 2436, 1759, 1681, 1608, 1531, 1455, 1381, 1346, 1303, 1249, 1182, 1033, 948, 881, 852, 751, 719, 623 $cm^{-1}$; $^1H$ NMR $\delta$ 8.24 (s, 2H), 7.10 (s, 1H), 7.02 (s, br, 2H); $^{13}C$ NMR $\delta$ 151.33, 139.90, 139.52, 138.63. Anal. Calcd for $C_5H_6N_8O_4$ (MW 242.2): C, 24.80; H, 2.50; N, 46.27. Found: C, 24.35; H, 2.20; N, 45.50.

**4-Amino-1,2,4-triazolium 3,5-Dinitro-pyrazolate (12).** Compound **12** was prepared the same as **2** from 4-amino-1,2,4-triazole (0.084 g, 1.0 mmol) and 3,5-dinitro-pyrazole[30] (0.158 g, 1.0 mmol) to give a yellow solid in 98% yield, mp 145 °C; IR (KBr) 3437, 3333, 3271, 3144, 3051, 2831, 1965, 1626, 1542, 1487, 1357, 1325, 1186, 1072, 1030, 995, 916, 870, 835, 752, 625 $cm^{-1}$; $^1H$ NMR $\delta$ 4.88 (s, 2H), 7.70 (s, 1H), 8.76 (s, 2H); $^{13}C$ NMR $\delta$ 153.49, 144.07, 99.23. Anal. Calcd for $C_5H_6N_8O_4$ (MW 242.2): C, 24.80; H, 2.50; N, 46.27. Found: C, 24.71; H, 2.46; N, 45.85.

**3-Amino-1,2,4-triazolium 5-Nitro-tetrazolate (13).** Compound **13** was prepared the same as **2** from 3-amino-1,2,4-triazole (0.084 g, 1.0 mmol) and 5-nitro-tetrazole[31] (0.115 g, 1.0 mmol) to give a colorless oil in 98% yield, mp 151 °C; IR (KBr) 3329, 3159, 2981, 2756, 2078, 1690, 1558, 1454, 1428, 1362, 1322, 1250, 1184, 1149, 1076, 1028, 950, 834, 715, 661, 632 $cm^{-1}$; $^1H$ NMR $\delta$ 8.31 (s, 1H), 8.05 (s, br, 2H); $^{13}C$ NMR $\delta$ 168.65, 150.64, 139.05. Anal. Calcd for $C_3H_5N_9O_2$ (MW 199.1): C, 18.10; H, 2.53; N, 63.30. Found: C, 18.21; H, 2.39; N, 62.84.

**1,5-Dimethyl-tetrazolium 5-Nitro-tetrazolate (14).** Compound **14** was prepared the same as **2** from 1,5-dimethyl-tetrazole[9a] (0.098 g, 1.0 mmol) and 5-nitro-tetrazole[31] (0.115 g, 1.0 mmol) to give a colorless oil in 98% yield, $T_g$ −55 °C; IR (NaCl) 3342, 3068, 2839, 2642, 1954, 1558, 1437, 1315, 1192, 1095, 1042, 1015, 963, 836, 725, 662 $cm^{-1}$; $^1H$ NMR (acetone-$d_6$) $\delta$ 2.56 (s, 3H), 4.06 (s, 3H), 11.70 (s, 1H); $^{13}C$ NMR (acetone-$d_6$) $\delta$ 166.13, 151.70, 32.26, 7.14. Anal. Calcd for $C_4H_7N_9O_2$ (MW 213.1): C, 22.53; H, 3.31; N, 59.14. Found: C, 22.43; H, 3.49; N, 57.52.

**5-Amino-tetrazolium 5-nitro-tetrazolate (15).** Compound **15** was prepared the same as **2**, using water as solvent, from 5-amino-tetrazole (0.085 g, 1.0 mmol) and 5-nitro-tetrazole[31] (0.115 g, 1.0 mmol) to give a white solid in 98% yield, mp 159 °C; IR (KBr) 3378, 2474, 1692, 1538, 1481, 1429, 1380, 1317, 1192, 1162, 1078, 1045, 974, 868, 833, 735, 677 $cm^{-1}$; $^1H$ NMR $\delta$ 8.30 (s, 2H); $^{13}C$ NMR $\delta$ 168.46, 155.30. Anal. Calcd for $C_2H_4N_{10}O_2$ (MW 200.1): C, 12.00; H, 2.01; N, 69.99. Found: C, 12.63; H, 2.07; N, 69.57.

**1,5-Diamino-tetrazolium 5-Nitro-tetrazolate (16).** Compound **16** was prepared the same as **2**, using water as solvent, from 1,5-diamino-tetrazole[10g] (0.010 g, 1.0 mmol) and 5-nitro-tetrazole[31] (0.115 g, 1.0 mmol) to give a white solid in 98% yield, mp 128 °C; IR (KBr) 3344, 3267, 3099, 2861, 2660, 2482, 1713, 1634, 1542, 1507, 1446, 1426, 1371, 1321, 1186, 1161, 1125, 1078, 1006, 948, 838, 687 $cm^{-1}$; $^1H$ NMR $\delta$ 6.24 (s, 2H), 6.74 (s, 2H); $^{13}C$ NMR $\delta$ 168.43, 153.50. Anal. Calcd for $C_2H_5N_{11}O_2$ (MW 215.2): C, 11.17; H, 2.34; N, 71.62. Found: C, 11.60; H, 2.35; N, 70.87.

**4-Amino-1,2,4-triazolium 5-Nitroimino-tetrazolate (17).** Compound **17** was prepared the same as **2** from 4-amino-1,2,4-triazole (0.084 g, 1.0 mmol) and 5-nitroamino-tetrazole[21e,f] (0.130 g, 1.0 mmol) to give a white solid in 98% yield, mp 143 °C; IR (KBr) 3289, 3186, 3136, 2840, 2011, 1792, 1619, 1538, 1433, 1328, 1209, 1150, 1070, 1036, 918, 856, 742, 677, 655, 613 $cm^{-1}$; $^1H$ NMR $\delta$ 9.18 (s, 2H), 9.22 (s, 2H); $^{13}C$ NMR $\delta$ 156.03, 143.99. Anal. Calcd for $C_3H_6N_{10}O_2$ (MW 214.2): C, 16.83; H, 2.82; N, 65.41. Found: C, 16.73; H, 2.60; N, 64.03.

**5-Amino-tetrazolium 5-Nitroimino-tetrazolate (18).** Compound **18** was prepared the same as **2** from 5-amino-tetrazole (0.085 g, 1.0 mmol) and 5-nitroamino-tetrazole[21e,f] (0.130 g, 1.0 mmol) to give a white solid in 98% yield, mp 165 °C; IR (KBr) 3428, 3300, 2706, 1703, 1651, 1601, 1539, 1445, 1315, 1237, 1148, 1097, 1059, 974, 871, 740, 692 $cm^{-1}$; $^1H$ NMR $\delta$ 6.27 (s, 2H); $^{13}C$ NMR $\delta$ 156.27, 153.15. Anal. Calcd for $C_2H_5N_{11}O_2$ (MW 215.2): C, 11.17; H, 2.34; N, 71.62. Found: C, 11.44; H, 2.35; N, 69.28.

**1,2,4-Triazolium 5-Nitroimino-tetrazolate (19).** Compound **19** was prepared the same as **2** from 1,2,4-triazole (0.069 g, 1.0 mmol) and 5-nitroamino-tetrazole[21e,f] (0.130 g, 1.0 mmol) to give a white solid in 98% yield, mp 177 °C; IR (KBr) 3140, 2892, 2791, 1942, 1866, 1579, 1535, 1423, 1336, 1281, 1217, 1195, 1150, 1084, 1053, 987, 935, 882, 802, 772, 743, 686, 663, 630 $cm^{-1}$; $^1H$ NMR (acetone-$d_6$) $\delta$ 8.75 (s, 2H), 10.22 (s, 3H); $^{13}C$ NMR (acetone-$d_6$) $\delta$ 154.60, 145.04. Anal. Calcd for $C_3H_5N_9O_2$ (MW 199.1): C, 18.10; H, 2.53; N, 63.30. Found: C, 18.55; H, 2.49; N, 63.02.

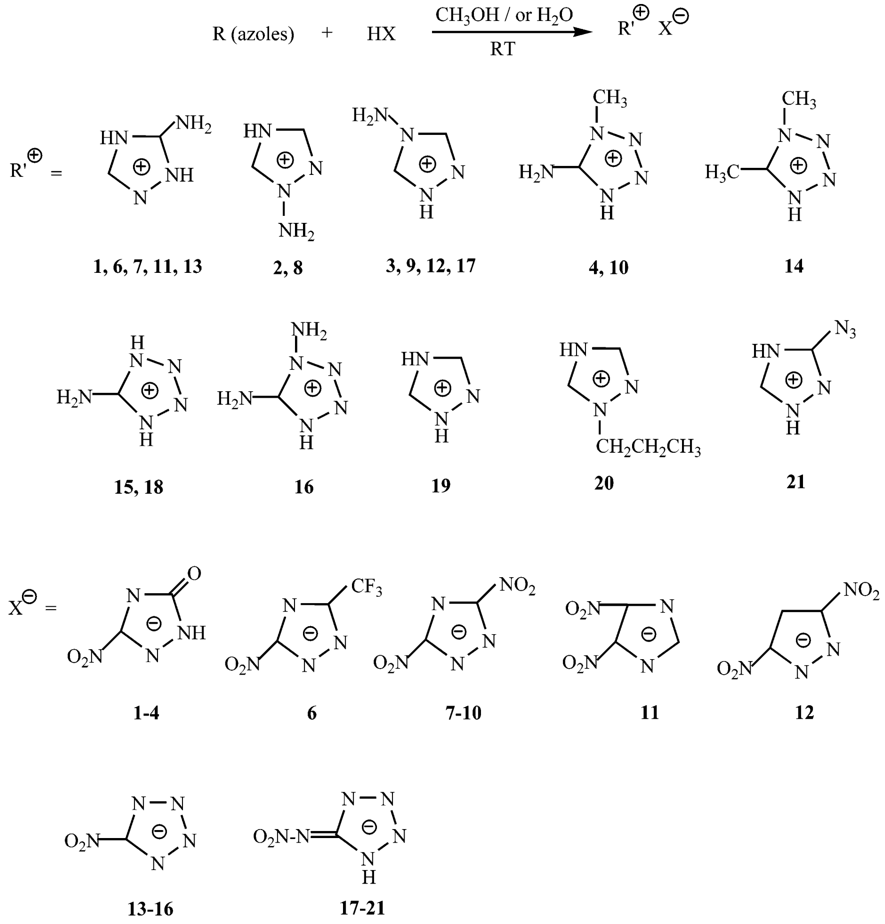
**1-Propyl-1,2,4-triazolium 5-Nitroimino-tetrazolate (20).** Compound **20** was prepared the same as **2** from 1-propyl-1,2,4-triazole[27] (0.111 g, 1.0 mmol) and 5-nitroamino-tetrazole[21e,f] (0.130 g, 1.0 mmol) to give a white solid in 98% yield, mp 69 °C; IR (KBr) 3103, 2752, 1962, 1801, 1701, 1541, 1448, 1354, 1307, 1228, 1167, 1068, 989, 903, 881, 774, 745, 690, 668, 627 $cm^{-1}$; $^1H$ NMR (acetone-$d_6$) $\delta$ 0.91 (t, 3H, $J = 6.0$ Hz), 1.89 (tq, 2H, $J = 7.23$ Hz), 4.25 (t, 2H, $J = 6.0$ Hz), 8.00 (s, 1H), 8.51 (s, 1H), 9.16 (s, 2H); $^{13}C$ NMR (acetone-$d_6$) $\delta$ 153.58, 151.53, 144.36, 51.99, 23.93, 11.28. Anal. Calcd for $C_6H_{11}N_9O_2$ (MW = 241.1): C, 29.88; H, 4.60; N, 52.26. Found: C, 29.51; H, 4.42; N, 51.48.

**3-Azido-1,2,4-triazolium 5-Nitroimino-tetrazolate (21).** Compound **21** was prepared the same as **2** from 3-azido-1, 2, 4-triazole[9a] (0.110 g, 1.0 mmol) and 5-nitroamino-tetrazole[21e,f] (0.130 g, 1.0 mmol) to give a white solid in 98% yield, mp 89 °C; IR (KBr) 3502, 3452, 3117, 2565, 2166, 1847, 1588, 1541, 1510, 1448, 1315, 1224, 1155, 1080, 1057, 991, 868, 775, 744, 709, 620 $cm^{-1}$; $^1H$ NMR (acetone-$d_6$) $\delta$ 8.42 (s, 3H), 10.80 (s, 3H); $^{13}C$ NMR (acetone-$d_6$) $\delta$ 157.29, 151.51, 144.32. Anal. Calcd for $C_3H_4N_{12}O_2 \cdot H_2O$ (MW = 258.1): C, 13.95; H, 2.33; N, 65.11. Found: C, 13.56; H, 2.18; N, 65.33.

## Results and Discussion

Five-membered nitrogen-containing heterocycles are excellent precursors to energetic materials, and considerable attention is currently focused on azoles as energetic compounds, especially the 1,2,4-triazole series.[4,5,9] Within the series of azoles, the relative energy characteristics ($\Delta H_f°$)

**Scheme 1. Syntheses of Triazolium or Tetrazolium Salts of 3-Nitro-1,2,4-triazolate-5-one, 3-Nitro-5-trifluoromethyl-1,2,4-triazolate, 3,5-Dinitro-1,2,4-triazolate, 4,5-Dinitro-imidazolate, 3,5-Dinitro-pyrazolate, 5-Nitro-tetrazolate, and 5-Nitroimino-tetrazolate**



are dependent on the ring structures and their substituents. Both NTO and 5-nitroamino-tetrazole are dibasic acids, and some of their simple salts have been prepared and thermodynamic properties determined, such as the heats of formation of ammonium 3-nitro-1,2,4-triazolate-5-one and guanidinium 5-nitroamino-tetrazole (−47.1 kJ/mol[20c] and +111.3 kJ/mol,[21d] respectively). For the 3-amino-1,2,4-triazolium salt of NTO, the proton is bonded at the 4-position of the triazolium ring, and the charge of the anion is mainly concentrated at the $N_4$ atom of NTO.[20b] However, no thermal properties and energetic characteristics were cited. Here, we report the syntheses of several new salts based on energetic triazolium or tetrazolium cations and azolate anions. Displayed in Scheme 1 are the preparative equation and the cations and anions of the new salts.

Derivatives of 1,2,4-triazole were readily quaternized at N-4 with a concentrated solution of strong acid (nitric or perchloric acid).[8,9a,b,e] 5-Amino-tetrazole was found to react with picric acid to form 5-amino-tetrazolium picrate,[9h] and 1,5-diamino-tetrazole reacted with nitric acid or perchloric acid to form the corresponding energetic quaternary salts.[8e,10g] The azoles chosen for this study that have electron-withdrawing nitro-substituents on the ring are typical NH acids (p$K_a$ = 3.67,[18b] −0.66,[29] −0.8,[31] and −0.72 ± 0.50 for NTO, 3,5-dinitro-1,2,4-triazole, 5-nitro-tetrazole, and 5-nitroamino-tetrazole, respectively) and can be reacted to form derivatives of variously substituted 1,2,4-triazoles or tetrazoles. The salts form in nearly quantitative yields and in high purity (**1**−**4**, **6**−**21**). The structures of **6** and **20** were confirmed by single-crystal X-ray analysis (Table 1, Figures 1 and 2).

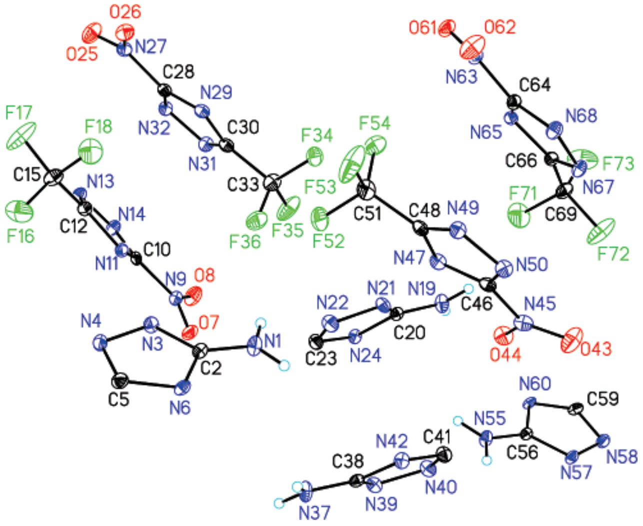


**Figure 1.** Thermal ellipsoid plot (30%) of **6** showing the four independent ion pairs in the asymmetric unit. Hydrogen atoms on the amino groups are shown to illustrate the pseudo planarity of these moieties. All other hydrogen atoms are omitted for clarity.

**Structure Discussion.** Crystals of both **6** and **20** were obtained by slow evaporation of methanolic solutions at room temperature. Compound **6** is shown in Figure 1. As can be

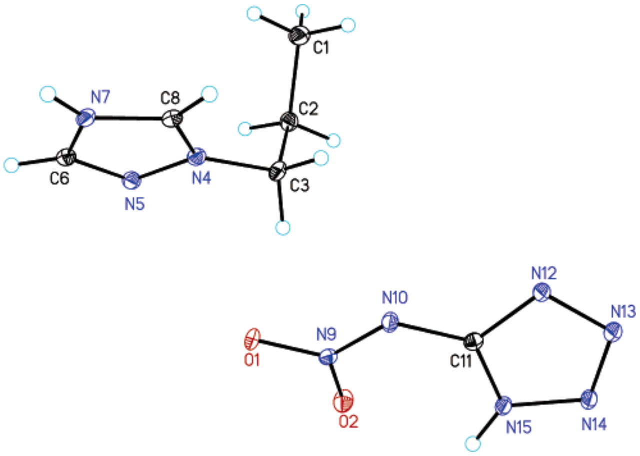


**Figure 2.** Thermal ellipsoid plot (30%) of **20**. Hydrogen atoms included but unlabeled for clarity.

seen, there are four independent ion pairs in the asymmetric unit, indicating the difficulty in crystallization and packing of this compound in the solid state. Stabilization of the negative charge over the whole anion is seen with the "in-plane" arrangement of the nitro groups. The loss of pyramidalization of the exocyclic nitrogen $NH_2$ groups indicates lone pair donation into the ring $\pi$ system to stabilize the cation. The extended structure (see Supporting Information) shows the packing arrangement of **6** where the alternating head to toe anions form stacks perpendicular to the crystallographic 1, 0, 1 direction. Each cation in **6** can form a variety of hydrogen bonds. Each cation forms a contact between adjacent cations via the amino $NH_2$ group and the non-protonated ring nitrogen (N1···N22, 2.968(4); N19···N4, 2.972(4); N37···N58, 3.001(4); N55···N40, 2.994(4) Å) and each cationic protonated ring nitrogen forms hydrogen bonds to two neighboring anionic ring nitrogen atoms (N3···N11, 2.876(3); N6···N49, 2.807(4); N21···N47, 2.889(3); N24···N31, 2.778(4); N39···N29, 2.852(4); N42···N67, 2.787(4); N57···N65, 2.858(4); N60···N13, 2.792(4) Å). There are also weak nonclassical hydrogen bonds between the cationic ring C−H and the nitro group oxygen atoms, e.g., bifurcated C5···O44, 3.291(4); C5···O61, 3.164(4); C23···O7, 3.157(4) Å. There are relatively few structurally characterized compounds containing the 5-amino-1,2,4-triazolium cation,[32] and all display the charge stabilization via lone pair donation seen in **6**. Compound **20** (Figure 2) contains the more unusual anion, 5-nitroimino-tetrazolate. In this moiety, the nitroimino group is twisted ca. 20° from the plane of the ring which is similar to the anion conformation in diammonium 5-nitramino-1,2,4-tetrazoldiide.[33a] Apart from cesium 5-nitramino-tetrazolide[33b] (ca. 10.5° dihedral) all other nitroimino groups are approximately planar.[33] The imino distances (N10−N9, 1.323(1); C11−N10, 1.377(1) Å) are similar to many of the reported structures.[33] The packing of **20** is less complex than **6** (see Supporting Information). There is a strong intramolecular hydrogen bond between the tetrazolate ring N−H and the nitro group oxygen (N15···O2, 2.6326(19) Å) and both nitro group oxygen atoms are acceptor atoms for weak nonclassical hydrogen bonds from the cation C−H groups (C3···O2, 3.426(2); C8···O1, 3.202(2) Å). Another important hydrogen bond is between the cation N−H and the imino nitrogen (N7···N10, 2.789(1) Å) and the cation/anion stacks are weakly associated by a nonclassical C−H···N and C−H···O bonds (C6···N13, 3.401(2); C8···O1, 3.202(2); C3···O2, 3.426(2) Å). It is interesting to note that both monoammonium salts of 5-nitroamino-triazole and 5-nitroamino-tetrazole formerly known as ammonium 5-nitroamino azolates are in fact *N*-nitroimines rather than primary *N*-nitroamines.[34]

The syntheses of salts which contain the NTO or 5-nitroimino-tetrazolate anion are of considerable interest because of the reputation of the precursor as a relatively dense (1.93 or 2.06 g/cm$^3$), insensitive explosive with a first ionization potential at least an order of magnitude larger than that of acetic acid. Density contributes markedly to the magnitudes of the detonation properties of these energetic materials. Therefore, it is worthwhile to synthesize ionic derivatives in an attempt to generate materials that may retain the parent molecule's energetic character as well as its relatively high density.

As is typical of energetic salts, attempts to use our experimental observations as a basis to generalize cation and anion contributions to important properties and thus to assist in the design of materials with a majority of desirable properties is extremely difficult if not impossible! Based on the syntheses and study of a large number of ionic materials, we found that perchlorate ion contributes most positively to the decomposition temperature, density, and most often to the heat of formation (invariably when compared with nitrate but rarely with nitroheterocyclic anions). Perchlorate salts also exhibit the highest decomposition pressures and velocities and values for specific impulse. While polynitroheterocyclic anions are not strictly competitive with perchlorate, they do appear to be superior to other anions. Of course, they are more environmentally friendly than perchlorates. Here we were interested in examining properties of salts where the anions were primarily from the acids NTO, 5-nitroamino-tetrazole, 3,5-dinitrotriazole, and 5-nitrotetrazole, and the cations from triazole and tetrazole bases (Table 2).

Immediately, it is obvious that **14** and **20**, although containing energetic anions, have low thermal stabilities/low melting points as well as noncompetitive density values perhaps due to the lower tendency of the cations to hydrogen bond and thus are of little value for energetic applications. Not surprisingly, because of the azide substituted cation, **21** (3-azidotetrazolium 5-nitroimino-tetrazolate), while having low melting point and thermal stability, exhibits the highest heat of formation (694.2 kJ/mol; 2.89 kJ/g) and good detonation properties. The remaining three 5-nitroimino-

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**Table 2. Phase Transition, Decomposition Temperatures, Densities, Oxygen Balance (OB), Nitrogen Content (N), and Thermochemical Results for Salts (298 K)**

| compd | $T_m/T_g$[a] (°C) | $T_d$[b] (°C) | $d$[c] (g/cm$^3$) | OB[d] (%) | N (%) | $\Delta_f H_c°$[e] (kJ/mol) | $\Delta_f H_a°$[f] (kJ/mol) | $\Delta H_L°$[g] (kJ/mol) | $\Delta_f H_m°$[h] (kJ/mol) | $\Delta_f H_m°$[h] (kJ/g) | $P$[i] (GPa) | $\nu D$[j] (m/s) | $I_{sp}$[k] (s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 242 | 242 | 1.71 | −60 | 52.3 | 804.5 | 63.9 | 504.8 | 363.6 | 1.70 | 24.8 | 8021 | 223.0 |
| **2** | 71 | 188 | 1.67 | −60 | 52.3 | 936.5 | 63.9 | 501.6 | 498.8 | 2.33 | 24.8 | 7973 | 238.3 |
| **3** | 131 | 175 | 1.68 | −60 | 52.3 | 936.3 | 63.9 | 502.4 | 497.8 | 2.32 | 25.1 | 8016 | 238.2 |
| **4** | 187 | 202 | 1.65 | −59 | 55.0 | 929.9 | 63.9 | 491.3 | 502.5 | 2.19 | 24.4 | 8010 | 233.9 |
| **6** | 168 | 216 | 1.63 | −54 | 42.1 | 804.5 | −772.4 | 471.2 | −439.2 | −1.65 | 16.5 | 6808 | 179.9 |
| **7** | 149 | 180 | 1.72 | −43 | 51.9 | 804.5 | −41.2 | 489.1 | 274.1 | 1.13 | 25.2 | 7945 | 219.0 |
| **8** | 167 | 201 | 1.72 | −43 | 51.9 | 936.5 | −41.2 | 489.1 | 406.2 | 1.67 | 26.5 | 8054 | 233.7 |
| **9** | 126 | 176 | 1.69 | −43 | 51.9 | 936.3 | −41.2 | 486.9 | 408.2 | 1.68 | 25.4 | 7930 | 234.0 |
| **10** | 139 | 195 | 1.63 | −43 | 54.3 | 929.9 | −41.2 | 474.9 | 413.7 | 1.60 | 23.5 | 7763 | 229.8 |
| **11** | 163 | 163 | 1.69 | −59 | 46.3 | 804.5 | −103.2 | 487.4 | 213.9 | 0.88 | 21.7 | 7539 | 208.8 |
| **12** | 145 | 212 | 1.64 | −59 | 46.3 | 936.3 | −47.4 | 484.1 | 404.8 | 1.67 | 23.5 | 7519 | 228.7 |
| **13** | 151 | 197 | 1.63 | −52 | 63.3 | 804.5 | 112.8 | 508.0 | 409.2 | 2.06 | 22.6 | 7865 | 219.2 |
| **14** | −55 ($T_g$) | 131 | 1.38[l] | −71 | 59.1 | | | | | | | | |
| **15** | 159 | 163 | 1.75 | −32 | 70.0 | 975.6 | 112.8 | 516.9 | 571.4 | 2.86 | 31.4 | 8843 | 246.0 |
| **16** | 128 | 161 | 1.71 | −33 | 71.6 | 1042. 2 | 112.8 | 504.1 | 650.8 | 3.03 | 30.7 | 8844 | 249.2 |
| **17** | 143 | 184 | 1.72 | −52 | 65.4 | 936.3 | 9.8 | 505.5 | 440.6 | 2.06 | 27.0 | 8506 | 218.9 |
| **18** | 165 | 165 | 1.63 | −33 | 71.6 | 975.6 | 9.8 | 497.9 | 487.5 | 2.27 | 25.5 | 8276 | 229.0 |
| **19** | 177 | 177 | 1.74 | −52 | 63.3 | 835.0 | 9.8 | 516.8 | 328.0 | 1.65 | 26.0 | 8334 | 208.7 |
| **20** | 69 | 122 | 1.48 | −103 | 52.3 | | | | | | | | |
| **21** | 89 | 135 | 1.68 | −40 | 70.0 | 1172.1 | 9.8 | 487.7 | 694.2 | 2.89 | 25.9 | 8230 | 233.5 |
| **22**[m] | 137 | 149 | 1.65 | −59 | 46.3 | 936.3 | −103.2 | 484.9 | 354.4 | 1.48 | 23.6 | 7383 | 221.1 |
| **23**[n] | 102 | 190 | 1.58 | −52 | 63.3 | 936.3 | 112.8 | 503.9 | 545.2 | 2.77 | 23.1 | 7792 | 233.7 |
| **24**[o] | | | 1.65 | −27 | | | | | 83.9 | 0.57 | 27.1 | 8536 | 219.2 |
| NTO | | | 1.93 | −25 | | | | | −101.0 | −0.78 | 33.4 | 8655 | 210.5 |
| 5-nitro-amino-tetrazole | | | 2.06 | −12 | | | | | 252.3 | 1.94 | 48.5 | 10358 | 257.6 |

[a] Melting point/phase transition temperature. [b] Thermal degradation. [c] Density, gas pycnometer, 25 °C. [d] OB(%) is oxygen balance, for $C_aH_bN_cO_d$: OB (%) = 1600($d$ − 2$a$ − $b$/2)/MW, MW = molecular weight of salt. [e] Molar enthalpy of the formation of cation. [f] Molar enthalpy of the formation of anion. [g] Lattice energy. [h] Molar enthalpy of the formation of salt. [i] Detonation pressure. All values given in this column were calculated using Cheetah 4.0.[41] [j] Detonation velocity. All values given in this column were calculated using Cheetah 4.0.[41] [k] Specific impulse. All values given in this column were calculated using Cheetah 4.0.[41] [l] Density, pycnometer, 25 °C. [m] Reference 9e, **22** (4-amino-1,2,4-triazolium 4,5-dinitro-imidazolate). [n] Reference 9e, **23** (4-amino-1,2,4-triazolium 5-nitro-tetrazolate). [o] Reference 33, **24** (ammonium 5-nitroimine-tetrazolate).

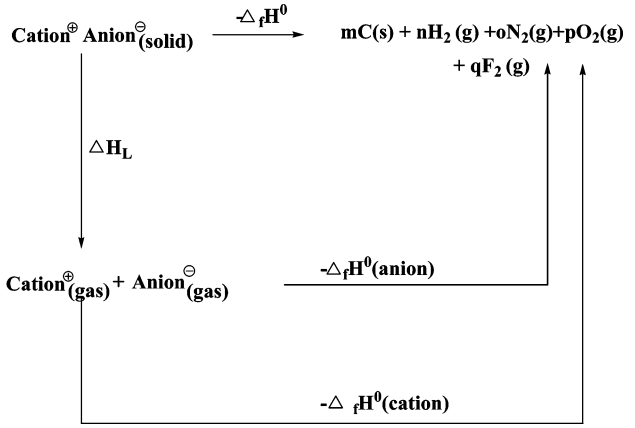
tetrazolate salts where the cations are triazolium (**19**), 4-amino triazolium (**17**), and 5-amino-tetrazolium (**18**) exhibit lower densities by 0.30−0.40 g/cm$^3$ relative to the parent 5-nitroamino-tetrazole, and the magnitude of their detonation properties is much reduced. However, the heats of formation of (**17**) and (**18**) (except **19)** exceed the parent (252.3 kJ/mol; 1.94 kJ/g) with values of (440.6 kJ/mol; 2.06 kJ/g) and (487.5 kJ/mol, 2.27 kJ/g), respectively. The triazolium derivative (**19**) has the highest density of this group. Comparing the four salts which contain the NTO anion shows that their densities are nearly the same (1.65−1.71 g/cm$^3$) but the values are much lower than that of the parent NTO (1.93 g/cm$^3$). Three of the cations are the 1, 3, and 4 isomers of amino-triazole. The 1-amino- and 4-amino-triazolium NTO salts (**2**, **3**) are remarkably lower melting (71 and 131 °C) and thermally decomposing (188 and 175 °C) than the 3-amino-triazolium salt (**1**) which decomposes upon melting at 242 °C. The detonation properties for the four salts are similar but the heats of formation for **2**, **3**, and **4** far outstrip **1**, viz., 498.8 kJ/mol (2.33 kJ/g), 497.8 kJ/mol (2.32 kJ/g), 502.5 kJ/mol (2.19 kJ/g), and 363.6 kJ/mol (1.70 kJ/g), respectively. Compound **4**, 1-methyl-5-amino-tetrazolium NTO salt, melts and decomposes at higher temperatures than **2** and **3**.

Replacing the NTO anion by 3,5-dinitro-triazole in 1-amino- and 4-amino-triazolium salts (**8** and **9)** gives rise to salts with similar detonation property values, but lower heats of formation which again are nearly identical for both salts. As was the case for **4** vis-à-vis **2** and **3**, **10** (1-methyl-5-amino-tetrazolium) is somewhat less energetic and slightly less dense than **8** and **9**. 4,5-Dinitro-imidazolate almost invariably contributes no worthwhile property to energetic materials. This is demonstrated by comparing 3-amino-tetrazolium 4,5-dinitro-imidazolate (**11)** with 4-amino-tetrazolium 3,5-dinitro-pyrazolate (**12)** where the heat of formation of (**11**) is ca. one-half of **12** (0.88 vs 1.67 kJ/g).

Although 5-amino-tetrazolium 5-nitro-tetrazolate (**15**) melts and decomposes at less than 170 °C, it exhibits the highest density and the highest heat of formation (2.86 kJ/g (except azide, **21**) in this group of new salts, and by far the most positive detonation properties. Salt **15** at 70% nitrogen content as well as **16** (71.6%, 3.03 kJ/g), **18** (71.6%, 2.27 kJ/g), and **21** (70%, 2.89 kJ/g) strongly support the view that high nitrogen content contributes markedly to the energy of the system.

From the heats of formation for **1**, **7**, and **11**, it can be seen that, for the same cation (3-amino-1,2,4-triazolium), the impact of the anion on the heats of formation of the salts varies as NTO anion (**1**) > 3,5-dinitro-1,2,4-triazolate (**7**) > 4,5-dinitro-imidazolate (**11**) [363.6 (1.70), 274.1 (1.13), and 213.9 (0.88) kJ/mol (kJ/g)]) respectively. To compare properties with **7**, 3-nitro-5-trifluoromethyl-1,2,4-triazolate was introduced as the anion, primarily to examine the impact on density; however, both the density of **6** (1.63 g/cm$^3$) and its heat of formation [−439.2 kJ/mol (−1.65 kJ/g)] are not competitive with (**7**, 1.72 g/cm$^3$). When 4-amino-1,2,4-triazolium is the cation, anionic impact on the heats of formation of the salts varies as 5-nitro-tetrazolate (**23**) > 3-nitro-1,2,4-triazolate-5-one (NTO) (**3**) > 5-nitroimine-tetrazolate (**17**) > 3,5-dinitro-1,2,4-triazole (**9**) > 3,5-dinitro-pyrazole (**12**) > 4,5-dinitro-imidazolate (**22**) [545.2 (2.77),

**Scheme 2. General Born−Haber Cycle for the Formation of Salts**



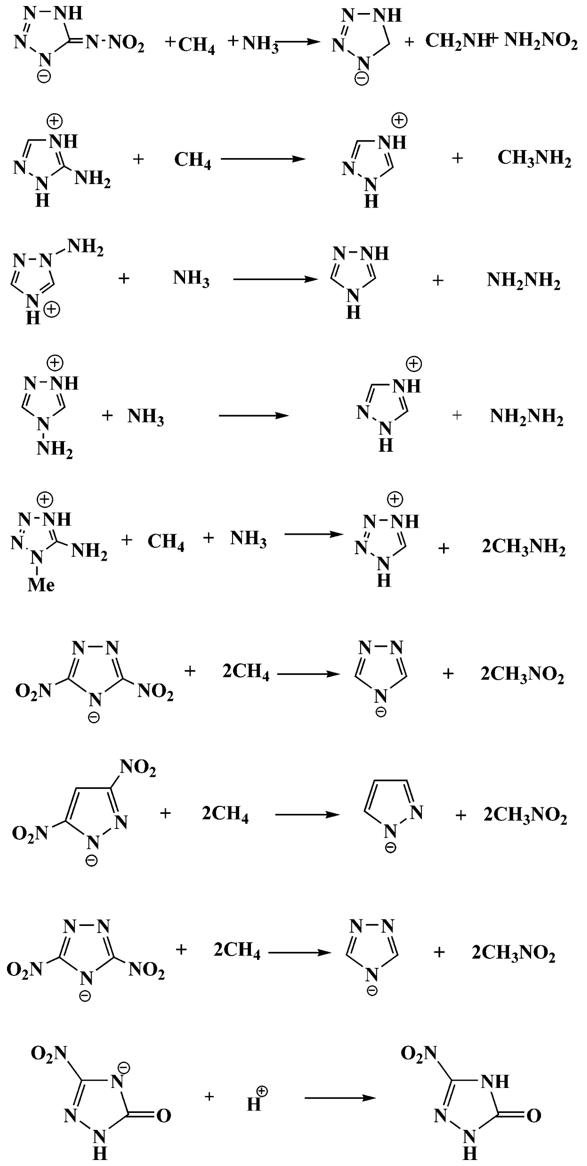
497.8 (2.32), 440.6 (2.06), 408.2 (1.68), 404.8 (1.67), and 354.4 (1.48) kJ/mol (kJ/g)], respectively.

Oxygen balance (OB) values are calculated by a literature method.[35] Energetic salts which incorporate a nitro group can substantially improve the oxygen balance of the corresponding compounds and eventually result in higher exothermicities of the combustion and detonation processes. Most of the OB values for the new salts range from −32 to −71% (Table 2), which are slightly more negative than NTO (−25%) and 5-nitroamino-tetrazole (−12%), but reasonably close to those for TNT (−74%) and tetryl (*N*-methyl-*N*-nitro-2,4,6-trinitroaniline (−47%).

## Calculations

The standard molar enthalpy of formation ($\Delta_f H_m°$) for all the salts (except **14** and **20**) plus NTO and 5-nitroamino-tetrazole were calculated by using Born−Haber energy cycles (Scheme 2). Calculations were performed with the Gaussian03 (Revision D.01) suite of programs.[36] The geometric optimization of the structures based on single-crystal structures, where available, and frequency analyses are carried out using B3-LYP functional with 6-31+G** basis set,[37] and single energy points were calculated at the MP$_2$(full)/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

**Scheme 3. Isodemic Reactions and Protonation Reactions for the Heats of Formation of Both Cations and Anions**



Based on Born−Haber energy cycles (Scheme 2), the heat of formation of an ionic salt can be simplified by the formula

$$\Delta H_f°(\text{ionic salt, 298 K}) = \Delta H_f°(\text{cation, 298 K}) + \Delta H_f°(\text{anion, 298 K}) - \Delta H_L$$

where $\Delta H_L$ is the lattice energy of the ionic salts which could be predicted by the formula suggested by Jenkins et al.[38] as

$$\Delta H_L = U_{POT} + [p(n_M/2-2) + q(n_X/2-2)]RT \qquad (A)$$

where $n_M$ and $n_X$ depend on the nature of the ions $M_p^+$ and $X_q^-$, respectively, and are equal to **3** for monatomic ions, **5** for linear polyatomic ions, and **6** for nonlinear polyatomic ions. The equation for lattice potential energy $U_{POT}$ (eq **B**) has the form

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$$U_{POT}/\text{kJ mol}^{-1} = \gamma(\rho_m/M_m)^{1/3} + \delta \qquad \text{(B)}$$

where $\rho_m$ is density, g/cm$^3$, $M_m$ is the chemical formula mass of the ionic material, *g*, and the coefficients $\gamma$ (kJ/mol cm) and $\delta$ (kJ/mol) take their values from the literature.[38]

Then the heats of formation of the cations and anions are computed using the method of isodesmic reactions or protonation reaction (NTO anion at G2MP2 level, and heat of formation of $H^+$ is 1530 kJ/mol[39]) (Scheme 3).[40] The enthalpy of reaction ($\Delta H_r{^o}_{298k}$) is obtained by combining the MP2(full)/6-311++G** energy difference for the reaction, the scaled zero point energies(B3LYP/6-31+G**), and other thermal factors(B3LYP/6-31+G**). Thus, the heat of formation of the cations and anions being investigated can be readily extracted.

The detonation properties of the new energetic salts, detonation pressure (*P*, Gpa), velocity of detonation ($\nu$D, m/s), and specific impulse ($I_{sp}$, s) were calculated based on traditional Chapman-Jouget thermodynamic detonation theory using Cheetah 4.0 (Table 2).[41] The calculated detonation pressures and detonation velocities range between ($P = 16.5$ GPa, $\nu D = 6808$ m/s (**6**)) and ($P = 31.4$ GPa, $\nu D = 8843$ m/s (**15**)). Although the denotation pressures are lower than the corresponding values for RDX (1,3,5-trinitro-1,3,5-triazacyclohexane, $P = 34.4$ GPa, $\nu D = 8750$ m/s), most of them are superior to TNT ($P = 20.6$ GPa, $\nu D = 6850$ m/s) and may well be of interest as potential solid propellants.

## Conclusions

New energetic salts composed strictly of azolium cations and azolate anions (3-nitro-1,2,4-triazolate-5-one (NTO), 5-nitroimino-tetrazolate, 3-nitro-5-trifluoromethyl-1,2,4-triazolate, 3,5-dinitro-1,2,4-triazolate, 4,5-dinitro-imidazolate, 3,5-dinitro-pyrazolate, and 5-nitro-tetrazolate) were synthesized and characterized. Most of the new salts exhibit good physical properties which include relatively high densities (1.38−1.75 g/cm$^3$) and high positive heats of formation and moderate detonation properties. To design salts with the most attractive energetic properties, both cation and anion should have the highest nitrogen content which in turn enhances the density and concomitantly the detonation characteristics.

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**Supporting Information Available:** X-ray crystallographic information files are available for 5-amino-1,2,4-triazolium 3-nitro-5-trifluoromethyl-1,2,4-triazolate (**6**), and 1-propyl-1,2,4-triazolium 5-nitroimine-tetrazolate (**20**). CCDC 630747 (**6**) and 630748 (**20**) 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. This material is available free of charge via the Internet at http://pubs.acs.org.

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