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Article

Energetic Azolium Azolate Salts

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Energetic salts comprising substituted imidazolium and 1,2,4-triazolium cations and 4,5-dinitro-imidazolate and 5-nitrotetrazolate anions were synthesized and characterized. On the basis of experimentally obtained heats of combustion, the calculated heats of formation range from $\Delta H_f^\circ = 80$ (**3**) to 1071 kJ/mol (**13**). Imidazolate salts are more dense but have lower heats of formation than their tetrazolate analogues. Salts **4**, **5**, **8**, and **11**–**14** fall into the ionic liquid class (mp < 100 °C). The structure of 1,2,4-triazolium 5-nitrotetrazolate (**10**) was confirmed by X-ray analysis.

Introduction

In recent years, the synthesis of energetic heterocyclic compounds has attracted considerable interest.[1−5] 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)[6] 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.[7] The 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.[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 species with low symmetry; nitrogen-containing heterocyclic-based salts predominate. The most frequent anion is inorganic, such as nitrate,[8,9] perchlorate,[8,9] dinitramide,[8,9c,10] and tetraazidoborate.[11] However, reports are already available that describe ionic liquids with organic anions, such as α-cyano-4-hydroxy-cinnamate, anthraquinone-2-sulfonate[12] salicylate, and lactate.[13] While this work was being completed, three imidazole-only triazolates or tetrazolates were reported,[14,15] but no energetic characterization was cited. 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.[17]

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(1) Zhang, M. X.; Eaton, P. E.; Gilardi, R. D. *Angew. Chem., Int. Ed.* **2000**, *39* (2), 401−404.

(2) Chavez, D. E.; Hiskey, M. A.; Gilardi, R. D. *Angew. Chem., Int. Ed.* **2000**, *39* (10), 1791−1793; Chavez, D. E.; Hiskey, M. A.; Gilardi, R. D. *Org. Lett.* **2004**, *6*, 2889−2891.

(3) Hammerl, A.; Klapötke, T. M.; Warchhold, M. *Inorg. Chem.* **2001**, *40*, 3570−3575.

(4) Ou, Y.; Chen, B.; Li, J.; Jia, H. *Heterocycles* **1994**, *38*, 1651−1664; Lee, K. Y.; Kennedy, J. E.; Asay, B. W.; Son, S. F.; Martin, E. S. Shock Compression of Condensed Matter-2003, Part 2. *AIP Conference Proceedings*; Springer-Verlag: New York, 2004; Vol. 706, pp 855−858; Bottaro, J. C.; Schmitt, R. J.; Petrie, M. A.; Penwell, P. E. U.S. Patent 6,255,512, July 3, 2001; Pevzner, M. S. *Russ. Chem. J.* **1997**, *41*, 73−81; Shitov, O. P.; Korolev, V. L.; Bogdanov, V. S.; Tartakovsky, V. A. *Russ. Chem. Bull.* **2003**, *52*, 695−699.

(5) Ostrovskii, V. A.; Pevzner, M. S.; Kofman, T. P.; Tselinskii, I. V. *Targets Heterocycl. Syst.* **1999**, *3*, 467−526.

(6) Köhler, J.; Meyer, R. *Explosives*, 9th ed.; Wiley-VCH: Weinheim, Germany, 1998.

(7) Hammerl, A.; Klapötke, T. M.; Warchhold, M. *Propellants, Explos., Pyrotech.* **2003**, *28* (4), 163−173.

(8) Drake, G.; Hawkins, T.; Brand, A.; Hall, L.; Mckay, M.; Vij, A.; Ismail, I. *Propellants, Explos., Pyrotech.* **2003**, *28* (4), 174−180; Drake, G. U.S. Patent 6,509,473, Jan. 21, 2003; Drake, G.; Hawkins, T. AFOSR Ionic Liquids Workshop, Dulles, VA, October 2002; Drake, G. AFOSR Ionic Liquids Workshop, Aberdeen, MD, September 2003.

(9) (a) Xue, H.; Gao, Y.; Twamley, B.; Shreeve, J. M. *Chem. Mater.* **2005**, *17*, 191−198. (b) Xue, H.; Arritt, S. W.; Twamley, B.; Shreeve, J. M. *Inorg. Chem.* **2004**, *43*, 7972−7977. (c) Gao, Y.; Arritt, S. W.; Twamley, B.; Shreeve, J. M. *Inorg. Chem.* **2005**, *44*, 1704−1714.

(10) Petrie, M. A.; Sheehy, J. A.; Boatz, J. A.; Rasul, G.; Surya Prakash, G. K.; Olah, G. A.; Christe, K. O. *J. Am. Chem. Soc.* **1997**, *119*, 8802−8808.

(11) Fraenk, W.; Habereder, T.; Hammerl, A.; Klapötke, T. M.; Krumm, B.; Mayer, P.; Nöth, H.; Warchhold, M. *Inorg. Chem.* **2001**, *40*, 1334−1340.

(12) Armstrong, D. W.; Zhang, L. K.; He, L. F.; Gross, M. L. *Anal. Chem.* **2001**, *73*, 3679−3686.

(13) Pernak, J.; Goc, I. *Pol. J. Chem.* **2003**, 975−984.

(14) Ogihara, W.; Yoshizawa, M.; Ohno, H. *Chem. Lett.* **2004**, *33*, 1022−1023.

(15) Katritzky, A. R.; Singh, S.; Kirichenko, K.; Holbrey, J. D.; Smiglak, M.; Reichert, W. M.; Rogers, R. D. *Chem. Commun.* **2005**, 868−870.

(16) Egashira, M.; Scrosati, B.; Armand, M.; Béranger, S.; Michot, C. *Electrochem. Solid-State Lett.* **2003**, *6*, A71−A73.

10.1021/ic050284u CCC: $30.25

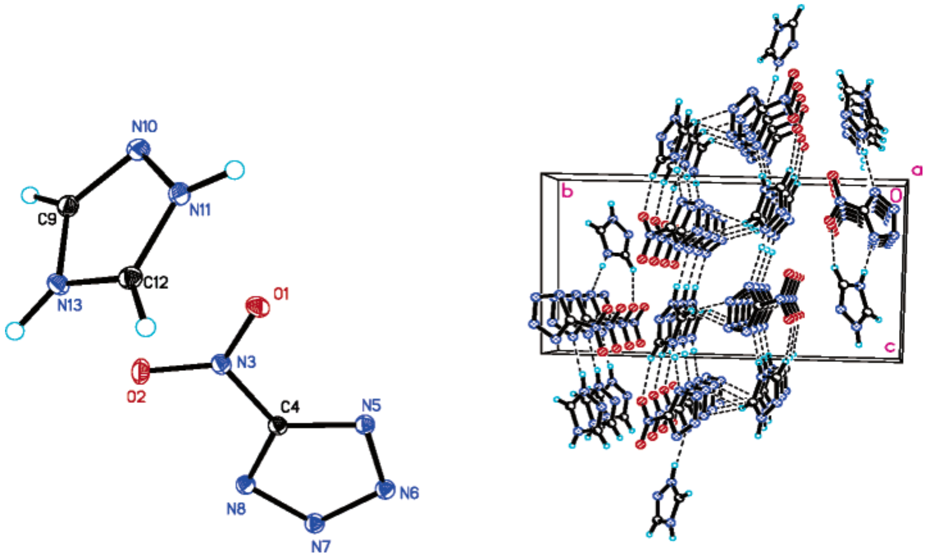
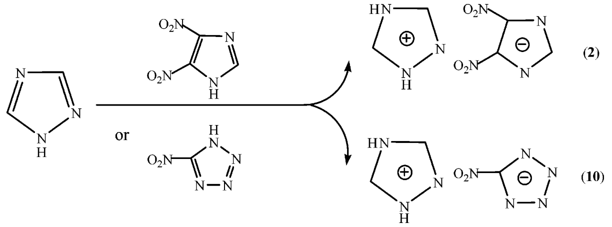


Figure 1. Thermal ellipsoid (30%) drawing of compound **10**. Unit cell of 1,2,4-triazolium 5-nitro-tetrazolate (**10**) showing hydrogen bonding (dashed lines) between anion and cation.

Scheme 1. Synthesis of 1,2,4-triazolium 4,5-dinitro-imidazolate (**2**) or 1,2,4-triazolium 5-nitro-tetrazolate (**10**)



However, to our knowledge, no report has appeared telling of salts containing only energetic azolium cations and azolate anions. These nitrogen-rich azole salts, free from halogens, sulfur, and phosphorus, may be more environmentally acceptable in their practical applications.

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.[4,5,9ab] Within the series of azoles, the relative energy characteristics ($\Delta H_f°$) are dependent on the ring structures. We now report the syntheses of several new ionic salts based on energetic azole-type cations (2-azido-imidazolium and several substituted triazolium derivatives) and anions (4,5-dinitro-imidazolate, 3-nitro-triazolate, and 5-nitro-tetrazolate). Typical examples for preparation of such salts are given in Scheme 1. It has been found that derivatives of 1,2,4-triazole were readily quaternized at N-4 with a concentrated strong acid (nitric or perchloric acid) in methanol.[8,9a,9b] Both 4,5-dinitro-imidazole and 5-nitro-tetrazole, with electron-withdrawing nitro substituents on the ring, are strong NH acids ($pK_a = 0.8$ for 5-nitro-tetrazole).[18] In our case, 4,5-dinitro-imidazole and 5-nitro-tetrazole reacted to quaternize derivatives of variously substituted 1,2,4-triazoles at N-4 and also readily quaternized 2-azido-imidazole using methanol as solvent. The salts were formed in nearly quantitative yields and in high purity (**1**, **2**−**7**, and **9**−**15**).

The single-crystal X-ray structure determination of **10** clearly shows proton substitution at N-4 (N-13 in the structure). It also illustrates the influence of significant hydrogen bonding between the anion and the protonated 1,2,4-triazolium ring of **10** (Figure 1), forming hydrogen-bonded ribbons. Because of the hydrogen bonding arrangement, that is, each triazolium ring has a bifurcated C−H, a single C−H, and a N−H hydrogen bond with each nitrotetrazolate, a series of channels are formed along the *a*-axis, between the ribbons, as shown in the packing diagram (Figure 1). The channel dimensions are ca. 3 Å × 3.5 Å.

In Table 2, it is seen that the melting point of **11** (62 °C) is considerably lower than that of **10** (137 °C). This likely occurs because a methyl group at N-1 in **11** has replaced a hydrogen atom in **10**, reducing the possibility of hydrogen bonding between the anion and the protonated 1,2,4-triazolium ring. 4-Amino-1,2,4-triazole also can react with 3-nitro-1,2,4-triazole in CH_3CN to form 4-amino-1,2,4-triazolium 3-nitro-1,2,4-triazolate (**8**) in high yield. The structural formulas of the new salts are shown in Table 1. The relative impact of cation and anion on properties of the new salts is shown in Table 2. By comparing the melting points of **1** and **9**, **2** and **10**, **3** and **11**, **4** and **12**, **5** and **13**, and **6** and **15**, it is seen that, when 5-nitro-tetrazolate was used as anion, the melting points of **9**−**13** and **15** are obviously lower than those of the corresponding compounds of 4,5-dinitro-imidazolate as the anion (**1**−**6**); for example, the melting points are 127 °C (**1**), 112 °C (**9**), 80 °C (**5**), and −38 °C (T_g) (**13**). The decomposition temperatures for most of the compounds with 5-nitro-tetrazolate as the anion are higher than those of the analogous 4,5-dinitro-imidazolate salts. Comparison of the melting points of **2** and **3**, **4** and **5**, **10** and **11**, and **12**−**14**, clearly illustrates the influence of the cation, for example, the melting point for **2** is 156 °C, which is considerably higher than the methyl group substituted **3** (102 °C).

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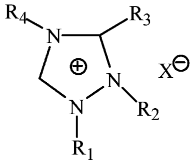
(17) Hammer, A.; Holl, G.; Klapötke, T. M.; Mayer, P.; Nöth, H.; Piotrowski, H.; Warchhold, M. *Eur. J. Inorg. Chem.* **2002**, 834−845.

(18) Ostrovskii, V. A.; Koldobskii, G. I.; Shirokova, N. P.; Poplavskii, V. S. *Khim. Geterotsikl. Soedin.* **1981**, *4*, 559−562.

Table 1. Structural Formulas of Ionic Salts Composed of Substituted Azolium Azolate ions



compd	R_1	R_2	R_3	R_4	X^-
1[a]					NImi[b]
2	H		H	H	NImi[b]
3	CH_3		H	H	NImi[b]
4	H		N_3	H	NImi[b]
5	CH_3		N_3	H	NImi[b]
6	H		H	NH_2	NImi[b]
7		NH_2	NH_2	H	NImi[b]
8	H		H	NH_2	NTri[c]
9[a]					NTet[d]
10	H		H	H	NTet[d]
11	CH_3		H	H	NTet[d]
12	H		N_3	H	NTet[d]
13	CH_3		N_3	H	NTet[d]
14	n-C_3H_7		N_3	H	NTet[d]
15	H		H	NH_2	NTet[d]

[a] **1** and **9** are 2-azido-imidazolium 4,5-dinitro-imidazolate and 2-azido-imidazolium 5-nitro-tetrazolate, respectively. [b] 4,5-Dinitro-imidazolate. [c] 3-Nitro-1,2,4-triazolate. [d] 5-Nitro-tetrazolate.

Table 2. Phase Transition, Decomposition Temperatures, Densities, Oxygen Coefficient (α), Nitrogen Content (N), and Thermochemical Results for Synthesized Salts (at 298.15 K)

compd	T_m/T_g (°C)[a]	T_d (°C)[b]	d[c] (g/cm^3)	α[e] (%)	N (%)	$-\Delta_c U_m$[f] (kcal/mol)	$\Delta_f H_m°$[g] (kJ/mol)
1	127	127	1.64	27.59	47.18	882.55	603.92
2	156	165	1.73	32.00	43.17	763.83	503.21
3	102	150	1.66	25.81	40.66	824.79	80.17
4	92	158	1.70	33.33	52.23	706.49	401.85
5	80	145	1.60	26.67	49.64	939.98	700.69
6	137	149	1.65	30.77	46.27	789.41	466.70
7	153	165	1.64	29.63	49.02	809.14	405.71
8	64	198	1.50	18.18	56.55	617.01	141.38
9	112	112	1.51	20.00	62.49	691.50	735.14
10	137	183	1.53	25.00	60.86	519.06	409.64
11	62	163	1.52	18.18	56.55	776.44	808.42
12	−35 (T_g)	161	1.53[d]	26.67	68.44	618.72	965.20
13	−38 (T_g)	141	1.45[d]	19.05	64.42	806.00	1070.68
14	−45 (T_g)	153	1.40[d]	12.12	57.66	1028.84	646.84
15	102	190	1.58	23.53	63.30	555.21	701.95

[a] Melting point (T_m)/phase transition temperature (T_g). [b] Thermal degradation. [c] Measured density using gas pycnometer at 25 °C. [d] Measured density using a pycnometer at 25 °C. [e] For $C_aH_bO_cN_d$, $\alpha = c/(2a + b/2)$. [f] The constant volume combustion energy. [g] Molar enthalpy of formation.

Obviously, the opportunity for hydrogen bonding with the anion is markedly reduced in methylated compounds. Salts **12**−**14** are room-temperature ionic liquids. For *N*-amino-1,2,4-triazolium salts, the melting point for **7** (T_m 153 °C) is higher than **6** (T_m 137 °C), and in comparing melting points of **6**, **8**, and **15**, compound **8**, with 3-nitro-1,2,4-triazolate as the anion, has the lowest melting point (T_m 64 °C).

Density, oxygen coefficient, and enthalpy of formation are important characteristics of energetic compounds and are governed by their molecular structures. Increasing the number of nitrogen atoms in a heterocycle results in a considerable gain in the heat of formation.[5] Density, oxygen coefficients, nitrogen content, and the heat of formation obtained for the energetic salts are listed in Table 2. It can be seen that the densities for compounds with 4,5-dinitro-imidazolate as the anion are higher than those of the analogous 5-nitro-tetrazolate. For all of the compounds, densities are in excess of 1.40 g/cm^3.

Oxygen coefficients (α), defined as $\alpha = c/(2a + b/2)$ for molecular formula $C_aH_bO_cN_d$, are calculated by a literature method.[19] 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. The oxygen coefficient values of C, H, O, and N-containing energetic compounds belong to the classes of fuels ($\alpha < 0.4$), explosives ($0.4 \leq \alpha \leq 1.0$), and oxidants ($\alpha > 1.0$).[20] The oxygen coefficients for the new salts, which are <0.4, are between 0.12 and 0.33 (Table 2) and are where the majority of the known energetic compounds fall.[20] These salts are nitrogen-rich energetic materials with calculated nitrogen contents between 40 and 68% (Table 2). The typical experimental results of constant volume combustion energy ($\Delta_c U_m$) and the calculated standard molar enthalpy of formation ($\Delta_f H_m°$) using a standard literature method[9] for the new salts are given in Table 2. Comparing the standard molar enthalpy of formation ($\Delta_f H_m°$) values of **1** and **9**, **3** and **11**, **4** and **12**, **5** and **13**, and **6** and **15**, it is seen that, when 5-nitro-tetrazolate was used as the anion, the heats of formation of **9**, **11**−**13**, and **15** are obviously higher than those of the corresponding compounds with 4,5-dinitro-imidazolate as the anion (with the exception **2** and **10**); for example, the $\Delta_f H_m°$ values for **4** and **12** are +401.85 and +965.20 kJ/mol, respectively. The marked influence of the cation is easily observed by comparing these values between corresponding compounds, such as the $\Delta_f H_m^\circ$ values for **3** and **5**, which are +80.17 and +808.42 kJ/mol, respectively, and clearly illustrates the enhancement achieved by the presence of the azido group on the triazolium ring. Of all of the compounds examined, **13**, exhibits the highest positive heat of formation at +1070.68 kJ/mol.

In conclusion, we have synthesized new energetic salts composed strictly of azolium cations and azolate anions. Some of the salts are room-temperature ionic liquids. Compounds with 5-nitro-tetrazolate as the anion have lower melting points and higher molar enthalpies of formation than those of the analogous 4,5-dinitro-imidazolate. Most of the new salts exhibit good physical properties, including relatively high densities (>1.40 g/cm^3) and high positive heats of formation.

Experimental Section

Caution: Although we experienced no difficulties in handling these materials, with such relatively high positive heats of formation, they should be handled with 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. Chemical shifts were reported relative to Me_4Si. MS and electrospray MS spectra were determined

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(19) Martin, A. R.; Yallop, H. J. *Trans. Faraday Soc.* **1958**, *54*, 257−267.

(20) Krukovskii, I. M.; Molchanova, M. S.; Evtushenko, A. V.; Shlyapochnikov, V. A. *Russ. Chem. Bull.* **1998**, *47*, 1266−1273.

using appropriate instruments. 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) semi-micro 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 of benzoic acid (SRM 39i, N.I.S.T.). Since Parr 45C10 alloy fuse wire was used, a correction of 2.3 (IT) cal/cm of wire burned has been applied in all of the standardization and calorific value determinations. Acid correction has been omitted for all of the semi-micro 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 $\Delta_c H_m° = \Delta_c U_m + \Delta nRT$, 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, $\Delta_f H_m°$ at 298.15 K, of the corresponding ionic salts were calculated by designed Hess thermochemical cycles.

2-Azido-imidazole,[9,21,22] 1-methyl-1,2,4-triazole,[23] 3-azido-1,2,4-triazole,[9,24] 1-methyl-3-azido-1,2,4-triazole,[9,21] 1,5-diamino-1,2,4-triazole,[9,25] 4,5-dinitro-imidazole,[26] and 5-nitro-tetrazole[27] were synthesized according to literature procedures.

1-Propyl-3-azido-1,2,4-triazole. The compound was prepared by a similar literature procedure.[9,21] Colorless oil, 41.5% yield, $R_f = 0.50$ (hexane/ethyl acetate, 2:1). IR (NaCl): 3117, 2970, 2412, 2138, 1519, 1458, 1331, 1228, 1188, 1021, 864, 807, 731, 640 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H, $J = 6.0$ Hz), 1.86 (tq, 2H, $J = 7.23$ Hz), 4.00 (t, 2H, $J = 6.0$ Hz), 7.87 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 159.25, 144.24, 52.65, 23.62, 11.69. GC/MS (EI) *m/z*: 152 (M$^+$, 15), 124 (4), 97 (3), 68 (2), 53 (13), 43 (100), 41 (44).

2-Azido-imidazolium 4,5-Dinitro-imidazolate (1). A dry, nitrogen-filled Schlenk Pyrex glass tube was charged with 2-azido-imidazole (0.109 g, 1.0 mmol), dry methanol (5 mL), and 4,5-dinitro-imidazole (0.158 g, 1.0 mmol). The mixture was stirred 4 h at room temperature. The solvent was evacuated under vacuum overnight to give a brown solid (**1**): 96% yield (0.26 g), mp 127 °C. IR (KBr): 3160, 2894, 2689, 2383, 2166, 1894, 1791, 1707, 1626, 1509, 1461, 1387, 1309, 1266, 1195, 1098, 997, 893, 808, 755, 688, 669, 621 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 7.04 (s, 2H), 7.92 (s, 1H), 11.10 (s, 2H). ^{13}C NMR (acetone-d_6): δ 140.62, 136.44, 135.02, 121.13. MS (solid probe) (EI) *m/z* (%): 110 (M$^+$, 35.6). Anal. Calcd for $C_6H_5N_9O_4$: C, 26.97; H, 1.89; N, 47.18. Found: C, 26.96; H, 1.88; N, 46.11.

1,2,4-Triazolium 4,5-Dinitro-imidazolate (2). 2 was prepared as above from 1,2,4-triazole and 4,5-dinitro-imidazole to form a yellow solid: 98% yield, mp 156 °C. IR (KBr): 3140, 1921, 1760, 1531, 1505, 1458, 1346, 1307, 1252, 1190, 1028, 878, 802, 748, 551, 631 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.01 (s, 1H), 8.40 (s, 2H), 11.82 (s, 2H). ^{13}C NMR (acetone-d_6): δ 147.52, 136.70, 135.27. MS (solid probe) (EI) *m/z* (%): 70 (M$^+$, 11.3). Anal. Calcd for $C_5H_5N_7O_4$: C, 26.44; H, 2.22; N, 43.17. Found: C, 26.33; H, 2.14; N, 42.81.

1-Methyl-1,2,4-triazolium 4,5-Dinitro-imidazolate (3). 3 was prepared as above from 1-methyl-1,2,4-triazole and 4,5-dinitro-imidazole to form a yellow solid: 98% yield, mp 102 °C. IR (KBr): 3144, 2460, 1911, 1538, 1488, 1350, 1077, 804, 741, 652, 621 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 3.99 (s, 3H), 7.98 (s, 1H), 8.03 (s, 1H), 8.47 (s, 1H), 11.42 (s, 1H). ^{13}C NMR (acetone-d_6): δ 151.52, 144.85, 136.54, 135.09, 36.55; Electrospray MS (+ve) $C_3H_6N_3$ *m/z:* (M$^+$), 84. MS (−ve) $C_3HN_4O_4$ *m/z*: (M$^-$), 157.

3-Azido-1,2,4-triazolium 4,5-Dinitro-imidazolate (4). 4 was prepared as above from 3-azido-1,2,4-triazole and 4,5-dinitro-imidazole to form a yellow solid: 95% yield, mp 92 °C. IR (KBr): 3140, 2941, 2812, 2144, 1913, 1537, 1493, 1457, 1352, 1219, 1176, 1090, 978, 850, 805, 734, 625 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.05 (s, 1H), 8.39 (s, 1H), 12.08 (s, 2H). ^{13}C NMR (acetone-d_6): δ 158.13, 145.12, 135.72, 134.27. MS (solid probe) (EI) *m/z* (%): 111 (M$^+$, 2.3). Anal. Calcd for $C_5H_4N_{10}O_4$: C, 22.40; H, 1.50; N, 52.23. Found: C, 22.19; H, 1.48; N, 51.95.

1-Methyl-3-azido-1,2,4-triazolium 4,5-Dinitro-imidazolate (5). 5 was prepared as above from 1-methyl-3-azido-1,2,4-triazole and 4,5-dinitro-imidazole to form a yellow solid: 98% yield, mp 80 °C. IR (KBr): 3124, 2804, 2225, 2145, 1931, 1768, 1535, 1491, 1431, 1350, 1305, 1275, 1180, 1047, 1014, 879, 850, 802, 731, 659 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 3.88 (s, 3H), 8.04 (s, 1H), 8.23 (s, 1H). ^{13}C NMR (acetone-d_6): δ 158.77, 146.05, 136.53, 134.90, 36.84. MS (solid probe) (EI) *m/z* (%): 125 (M$^+$, 13.2). Anal. Calcd for $C_6H_6N_{10}O_4$: C, 25.54; H, 2.14; N, 49.64. Found: C, 25.53; H, 2.06; N, 49.04.

4-Amino-1,2,4-triazolium 4,5-Dinitro-imidazolate (6). 6 was prepared as above from 4-amino-1,2,4-triazole and 4,5-dinitro-imidazole to form a yellow solid: 98% yield, mp 137 °C. IR (KBr): 3304, 3153, 2438, 1940, 1753, 1645, 1530, 1456, 1355, 1297, 1261, 1035, 976, 877, 810, 752, 664, 619 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.18 (s, 2H), 7.53 (s, 1H), 8.96 (s, 2H). ^{13}C NMR (DMSO-d_6): δ 145.48, 139.20, 138.41. MS (solid probe) (EI) *m/z* (%): 85 (M$^+$, 5.8). Anal. Calcd for $C_5H_6N_8O_4$: C, 24.80; H, 2.50; N, 46.27. Found: C, 24.77; H, 2.69; N, 45.97.

1,5-Diamino-1,2,4-triazolium 4,5-Dinitro-imidazolate (7). 7 was prepared as above from 1, 5-diamino-1,2,4-triazole and 4,5-dinitro-imidazole to form a yellow solid: 98% yield, mp 153 °C. IR (KBr): 3447, 3252, 3012, 1696, 1633, 1537, 1508, 1462, 1354, 1304, 1262, 1186, 964, 923, 850, 808, 704, 671, 618 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 6.21 (s, 2H), 7.13 (s, 1H), 7.57 (s, 2H), 8.01 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 150.58, 140.90, 140.17, 138.45. MS (solid probe) (EI) *m/z* (%): 100 (M$^+$, 4.8). Anal. Calcd for $C_5H_7N_9O_4$: C, 23.35; H, 2.74; N, 49.02. Found: C, 24.04; H, 3.41; N, 49.09.

4-Amino-1,2,4-triazolium 3-Nitro-1,2,4-triazolate (8). 8 was obtained from 4-amino-1,2,4-triazole and 3-nitro-1,2,4-triazole using CH_3CN as the solvent at 25 °C for 3 days to give a white solid: 98% yield, mp 64 °C. IR (KBr): 3329, 3132, 2856, 1969, 1632, 1558, 1480, 1417, 1377, 1305, 1257, 1192, 1074, 972, 866, 836, 659, 620 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 6.08 (s, 2H), 8.29 (s, 2H),

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(21) Granados, R. *J. Heterocycl. Chem.* **1976**, *13*, 281−284.

(22) Weinmann, H.; Harre, M.; Koenig, K.; Merten, E. *Tetrahedron Lett.* **2002**, *43*, 593−595.

(23) Mirzaei, Y. R.; Twamley, B.; Shreeve, J. M. *J. Org. Chem.* **2002**, *67*, 9340−9345.

(24) Denault, C. C.; Marx, P. C.; Takimoto, H. H. *J. Chem. Eng. Data* **1968**, *13*, 514−516.

(25) Salazar, L.; Espada, M.; Avendano, C. *J. Heterocycl. Chem.* **1990**, *27*, 1109−1110.

(26) Novikov, S. S.; Khmel'nitskii, L. I.; Lebedev, O. V.; Sevast'yanova, V. V.; Epishina, L. V. *Chem. Heterocycl. Compd.* **1970**, *6*, 503−507.

(27) Koldobskii, G. I.; Soldatenko, D. S.; Gerasimova, E. S.; Khokhryakova, N. R.; Shcherbinin, M. B.; Lebedev, V. P.; Ostrovskii, V. A. *Russ. J. Org. Chem.* **1997**, *33*, 1771−1783.

8.50 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 164.13, 145.97, 144.77. MS (solid probe) (EI) m/z (%): 85 (M^+, 8.7). Anal. Calcd for $C_4H_6N_8O_2$: C, 24.25; H, 3.05; N, 56.55. Found: C, 24.19; H, 3.40; N, 56.74.

2-Azido-imidazolium 5-Nitro-tetrazolate (9). A dry, nitrogen-filled Schlenk glass tube was charged with 2-azido-imidazole (0.109 g, 1.0 mmol), dry methanol (5 mL), and 5-nitro-tetrazole (0.115 g, 1.0 mmol). The mixture was stirred 4 h at room temperature. The solvent was evacuated under vacuum overnight to give a brown solid: 97% yield (0.22 g), mp 112 °C. IR (KBr): 3106, 2942, 2914, 2749, 2640, 2180, 2152, 1708, 1628, 1543, 1455, 1421, 1378, 1315, 1191, 1024, 904, 833, 747, 685 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 7.44 (s, 2H), 12.12 (s, 2H). ^{13}C NMR (acetone-d_6): δ 168.57, 140.89, 118.98. MS (solid probe) (EI) m/z (%): 110 (M^+, 2.2). Anal. Calcd for $C_4H_4N_{10}O_2$: C, 21.43; H, 1.80; N, 62.49. Found: C, 21.45; H, 2.15; N, 62.58.

1,2,4-Triazolium 5-Nitro-tetrazolate (10). 10 was prepared as above from 1,2,4-triazole and 5-nitro-tetrazole to form a white solid: 98% yield, mp 137 °C. IR (KBr): 3130, 3071, 2908, 2812, 2730, 2633, 1875, 1578, 1545, 1456, 1423, 1321, 1280, 1171, 1118, 1026, 943, 885, 833, 663, 627 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.30 (s, 2H), 12.24 (s, 2H). ^{13}C NMR (DMSO-d_6): δ 169.41, 144.04. MS (solid probe) (EI) m/z (%): 70 (M^+, 4.8). Anal. Calcd for $C_3H_4N_8O_2$: C, 19.57; H, 2.19; N, 60.86. Found: C, 19.64; H, 2.72; N, 61.45.

1-Methyl-1,2,4-triazolium 5-Nitro-tetrazolate (11). 11 was prepared as above from 1-methyl-1,2,4-triazole and 5-nitro-tetrazole to form a white solid: 98% yield, mp 62 °C. IR (KBr): 3147, 2517, 1541, 1441, 1416, 1362, 1316, 1269, 1170, 1120, 988, 883, 836, 662, 626 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 4.18 (s, 3H), 8.58 (s, 1H), 9.31 (s, 1H), 11.96 (s, 1H). ^{13}C NMR (acetone-d_6): δ 168.06, 147.26, 143.32, 37.41. Electrospray MS (+ve) $C_3H_6N_3$ m/z: (M^+), 84. MS (−ve) CN_5O_2 m/z: (M^-), 114.

3-Azido-1,2,4-triazolium 5-Nitro-tetrazolate (12). 12 was prepared as above from 3-azido-1,2,4-triazole and 5-nitro-tetrazole to form a yellow oil: 98% yield, T_g −35 °C. IR (NaCl): 3143, 2926, 2530, 2148, 1939, 1688, 1521, 1454, 1318, 1267, 1213, 1174, 1083, 978, 836, 778, 667, 627 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.41 (s, 1H), 11.94 (s, 2H). ^{13}C NMR (acetone-d_6): δ 167.28, 157.99, 145.06. MS (solid probe) (EI) m/z (%): 111 (M^+, 3.5). Anal. Calcd for $C_3H_3N_{11}O_2$ $0.5H_2O$: C, 15.38; H, 1.71; N, 65.81. Found: C, 15.23; H, 2.21; N, 65.69.

1-Methyl-3-azido-1,2,4-triazolium 5-Nitro-tetrazolate (13). 13 was prepared as above from 1-methyl-3-azido-1,2,4-triazole and 5-nitro-tetrazole to form a yellow oil: 98% yield, T_g −38 °C. IR (NaCl): 3123, 2932, 2660, 2147, 1946, 1556, 1429, 1315, 1190, 1043, 995, 836, 792, 667, 627 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 3.89 (s, 3H), 8.25 (s, 1H), 11.94 (s, 1H). ^{13}C NMR (acetone -d_6): δ 167.30, 158.11, 145.42, 36.27. MS (solid probe) (EI) m/z (%): 125 (M^+, 1.5). Anal. Calcd for $C_4H_5N_{11}O_2$ $0.5H_2O$: C, 19.35; H, 2.42; N, 62.10. Found: C, 19.81; H, 2.90; N, 62.50.

1-Propyl-3-azido-1,2,4-triazolium 5-Nitro-tetrazolate (14). 14 was prepared as above from 1-propyl-3-azido-1,2,4-triazole and 5-nitro-tetrazole to form a yellow oil: 98% yield, T_g −45 °C. IR (NaCl): 3138, 2973, 2654, 2522, 2147, 1938, 1558, 1460, 1315, 1189, 1090, 1042, 1003, 836, 665, 627 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 0.91 (t, 3H, J = 6.0 Hz), 1.89 (tq, 2H, J = 7.23 Hz), 4.14 (t, 2H, J = 6.0 Hz), 8.30 (s, 1H), 10.60 (s, 1H). ^{13}C NMR (acetone-d_6): δ 167.06, 158.11, 144.87, 51.61, 22.99, 10.54. Electrospray MS (+ve) $C_5H_9N_6$ m/z: (M^+), 153, m/z (−ve) CN_5O_2 m/z (M^-), 114.

4-Amino-1,2,4-triazolium 5-Nitro-tetrazolate (15). 15 was prepared as above from 4-amino-1,2,4-triazole and 5-nitro-tetrazole to form a white solid: 98% yield, mp 102 °C. IR (KBr) 3318, 3136, 2588, 1631, 1540, 1417, 1317, 1171, 1025, 924, 837, 669, 619 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.45 (s, 2H), 9.46 (s, 2H). ^{13}C NMR (DMSO-d_6): δ 168.95, 144.87. MS (solid probe) (EI) m/z (%): 85 (M^+, 3.3). Anal. Calcd for $C_3H_5N_9O_2$: C, 18.10; H, 2.53; N, 63.30. Found: C, 17.97; H, 2.65; N, 63.66.

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Supporting Information Available: General methods, single crystal structure, and single crystal data are available for 1,2,4-triazolium 5-nitrotetrazolate (**10**). This information is available free of charge via the Internet at http://pubs.acs.org.

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