CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600354

Energetic Bicyclic Azolium Salts

Ye Gao, Chengfeng Ye, Brendan Twamley, and Jean′ne M. Shreeve*[a]

Abstract: Bicyclic azoles, 2-methyl-5-(imidazol-1-yl)-2*H*-tetrazole (**1**), 2-methyl-5-(1,2,4-triazol-1-yl)-2*H*-tetrazole (**4**), 1-methyl-5-(imidazol-1-yl)-1*H*-tetrazole (**7**), 1-methyl-5-(1,2,4-triazol-1-yl)-1*H*-tetrazole (**10**), 1-methyl-4-nitro-2-(imidazol-1-yl)-1*H*-imidazole (**13**), and 1-methyl-4-nitro-2-(1,2,4-triazol-1-yl)-1*H*-imidazole (**16**) were prepared. Their thermally stable azolium salts, **3**, **6**, **9**, **12**, **15**, and **18**–**21**, with densities ranging between 1.519–1.674 $g\,cm^{-3}$, were synthesized by quaternization with nitric or perchloric acid or with iodomethane followed by metathesis reactions with silver nitrate and silver perchlorate. The structures of **12b** and **21b** were confirmed by single-crystal X-ray analysis. The standard enthalpies of formation for some of the new salts were calculated by using the computationally feasible DFT-(B3LYP) and MP2 methods in conjunction with an empirical approach based on densities of salts. The calculated values range from $\Delta H_f^\circ = 209.9$ (**21a**) to 412.3 (**12b**) $kJ\,mol^{-1}$ in which the experimental densities are $> 1.515\ g\,cm^{-3}$.

Keywords: azolium compounds · bicyclic azoles · energetic salts · heats of formation · heterocycles

Introduction

In recent years, the syntheses of energetic heterocyclic compounds have attracted considerable interest.[1–5] New heterocyclic-based energetic salts have become increasingly important.[6–8] Energetic materials that are salt-based often possess advantages over nonionic molecules as these salts tend to exhibit lower vapor pressures and higher densities than their atomically similar nonionic analogues. One of the most recent and exciting developments are salts with a high nitrogen content and with high positive heats of formation that show remarkable insensitivity to friction, electrostatic discharge, and shock.[7a,9] 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. Within the series of azoles, the relative energy characteristics (molar enthalpy of formation, ΔH_f°) are dependent on ring structures.[9–12]

Our earlier work focused on studies of the properties of high-energy ionic liquids comprised of azido-, nitro-, N-amino-substituted azolium and guanidinium cations with nitrate, perchlorate, dinitramide, azolate, or substituted azolate as anion.[8] In this paper, we report a straightforward syntheses of several new bicyclic N−C bonded (nonbridged) azoles, with subsequent formation of quaternary bicyclic azolium salts by means of reactions with acids or alkyl iodides. The latter are then converted to nitrate and perchlorate salts. Their thermal, physical, and energetic properties are studied in detail.

Results and Discussion

A few N−N-bridged azoles or azolium salts have been examined as energetic materials, including 1,3-bis(4-nitroimido-1,2,4-triazoliium-1-yl)ethane, −2-oxapropane and −3-oxapentane (no physical or thermal properties were reported),[5b] and bisazolium dipicrate and dinitrate salts in which the azolium rings are linked via a methylene moiety.[13] These picrate salts have been well characterized and, in fact, the bridged bisazolium picrates are somewhat more stable thermally than their monocationic picrate analogues. Even a smaller number of N−C-bonded (nonbridged) bicyclic azoles have been synthesized and none have been suggested as a suitable source for energetic bicyclic azolium salts.[14–16]

To determine the energies associated with compounds that contain two linked azole or azolium rings and to compare them with the bridged bicyclic azolium salts, we have prepared several nitrate and perchlorate salts with linked

---

[a] Dr. Y. Gao, Dr. C. Ye, Dr. B. Twamley, Prof. Dr. J. M. Shreeve
Department of Chemistry, University of Idaho
Moscow, Idaho (USA)
Fax: (+1) 208-885-9146
E-mail: jshreeve@uidaho.edu

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

identical and different five-membered nitrogen heterocycles. In the past, preparation of N–C bicyclic azoles or bicyclic azolium salts was accomplished frequently by using precursor rings substituted with a halogen,[14] nitro,[15] or methylsulfonyl[16] moiety as the leaving group. Replacement of the halogen often required high temperatures.[14] When the nitro group was replaced, the composition and the ratio of reaction products were a function of the pK_a of the azole.[15] In this paper, we have prepared methylsulfonyl-substituted imidazole, triazole, and tetrazole species, followed by reaction with sodium imidazolate or sodium triazolate under mild conditions to obtain a series of N–C-biazoles.

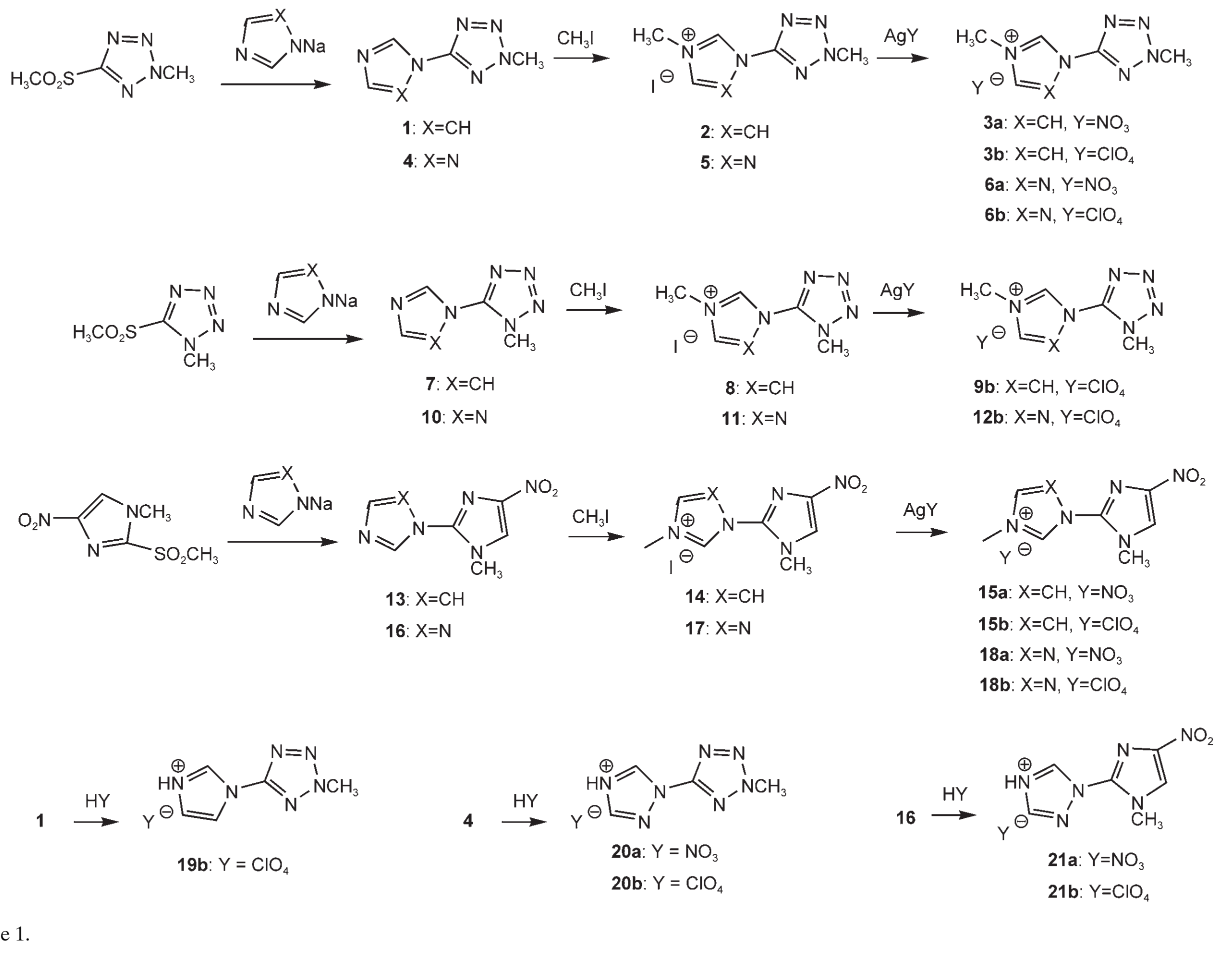
The bicyclic azoles, **1**, **4**, **7**, **10**, **13**, and **16**, were obtained from sodium imidazolate or sodium 1,2,4-triazolate[17] in reaction with methylsulfonyl-substituted azoles, for example, 1-methyl-5-(methylsulfonyl)-1*H*-tetrazole, 2-methyl-5-(methylsulfonyl)-2*H*-tetrazole,[18] and 1-methyl-2-(methylsulfonyl)-5-nitro-1*H*-imidazole.[19] Bicyclic azoles when quaternized with methyl iodide produced iodide salts, **2**, **5**, **8**, **11**, **14**, and **17**, which were further metathesized with silver nitrate or silver perchlorate to give energetic salts, **3**, **6**, **9**, **12**, **15**, and **18**. Bicyclic azoles, **1**, **4**, and **16**, when reacted with nitric or perchloric acid, yielded salts, **19**, **20**, and **21** (Scheme 1).

Phase-transition temperatures (midpoints of melting points, T_m) for all the salts were determined by differential scanning calorimetry (DSC) as given in Table 1. With a common cation, the nitrates with the exception of **6** invariably had lower melting points than the perchlorates. The decomposition temperatures of the perchlorates ranged from 255 to 295 °C (except **12b** at 240 °C, **20b** at 229 °C, and **21b** at 175 °C), while for nitrates the range was from 145 for **18a** to 190 °C for **15a**, invariably lower than perchlorates.

Density 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.[20]

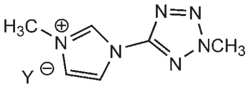
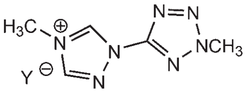
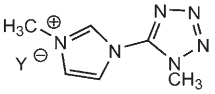
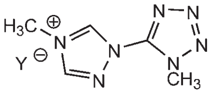
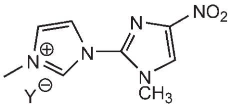
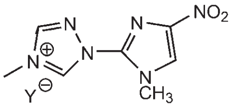
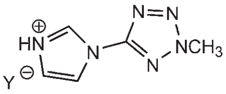
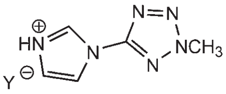
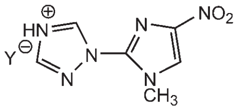
The measured (calculated)[21,22] densities of the nitrate and perchlorate salts fall between 1.519 (1.531) g cm^{-3} for **3a** to 1.674 (1.784) g cm^{-3} for **21b**. The densities which were calculated for the single-crystal structures of **12b** and **21b** are also listed in Table 1. The calculated and experimentally determined densities agree reasonably closely to within 0.4 to 7.6%. The calculated values for **12b** and **21b** and those obtained from single-crystal structure calculations agree within 1.0 and 0.4%, respectively.

Thermochemistry: Computations were performed with the Gaussian 03 (Revision D.01) suite of programs.[23] The geometric optimization of the structures based on single-crystal structures, where available, and frequency analyses are carried out by using B3LYP functional with 6-31+G** basis



Scheme 1.

Table 1. Structures and properties of bicyclic azolium salts.

Compound	Y	No	T_m [°C][a]	T_d [°C][b]	ρ_calcd [g cm^{-3}][c]	ρ_meas [g cm^{-3}][d]	$\Delta_\mathrm{f}H_\mathrm{L}$ [kJ mol^{-1}][e]	$\Delta_\mathrm{f}H_\mathrm{m}$ [kJ mol^{-1}][f]
	NO_3	**3a**	79	175	1.531	1.519	–	–
	ClO_4	**3b**	110	283	1.653	1.631	–	–
	NO_3	**6a**	151	151	1.574	1.515	489.1	310.8
	ClO_4	**6b**	141	293	1.695	1.639	472.2	357.7
	ClO_4	**9b**	159	295	1.653	1.648	–	–
	ClO_4	**12b**	152	240	1.695/1.678[g]	1.645	475.0	412.3
	NO_3	**15a**	125	190	1.574	1.581	–	–
	ClO_4	**15b**	169	289	1.678	1.641	–	–
	NO_3	**18a**	–	145	1.612	1.566	–	–
	ClO_4	**18b**	227	282	1.716	1.652	–	–
	ClO_4	**19b**	150	255	1.725	1.623	–	–
	NO_3	**20a**	154	166	1.644	1.565	493.2	341.8
	ClO_4	**20b**	128	229	1.773	1.648	479.5	385.5
	NO_3	**21a**	153	165	1.676	1.617	474.4	209.9
	ClO_4	**21b**	–	175	1.784/1.767[g]	1.674	468.7	245.6
TNT[h]								−64
HMX[i]								75
TATB[j]								−154

[a] Melting point. [b] Thermal degradation. [c] Calculated density, references [21] and [22]. [d] Measured density by using a gas pycnometer at 25 °C. [e] Molar lattice energy, calcd. [f] Molar enthalpy of formation, calcd. [g] From X-ray structure. [h] 2,4,6-Trinitrotoluene, reference [7a]. [i] Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, reference [7a]. [j] 1,3,5-Triamino-2,4,6-trinitrobenzene, reference [7a].

set,[24] and single energy points were calculated at the MP2-(full)/6-311++G** level.[25,26] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

According to Born–Haber energy cycles, heats of formation of ionic salts could be simplified by the formula:

$$\Delta H_\mathrm{f}^\circ(\text{ionic salts, 298 K}) = \Delta H_\mathrm{f}^\circ(\text{cation, 298 K}) + \Delta H_\mathrm{f}^\circ(\text{anion, 298 K}) - \Delta H_\mathrm{L}$$

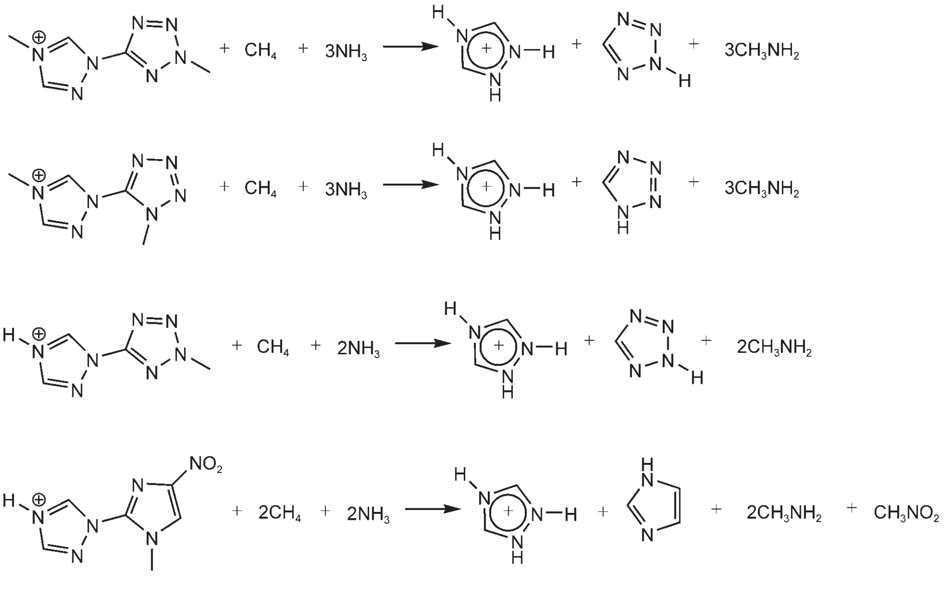
in which ΔH_L was the lattice energy of the ionic salts. For 1:1 salts and considering the nonlinear nature of the cation and anion we currently used, ΔH_L (kJ mol^{-1}) could be predicted by the formula suggested by Jenkins et al. [27] as:

$$\Delta H_\mathrm{L} = 1981.2{*}(\rho_\mathrm{m}/M_\mathrm{m})^{1/3} + 108.8$$

Heats of formation of the NO_3^- and ClO_4^- anions can easily be obtained from the reactions below:

$$NO_3^- + H^+ \xrightarrow{PA^1} HNO_3$$

$$ClO_4^- + H^+ \xrightarrow{PA^2} HClO_4$$



Scheme 2.

The proton affinities (PA) were taken from literature results calculated by using the G2 or G3 method.[10d] A value of 1528.085 kJ mol^{-1} with correction of 6.197 kJ mol^{-1} was adopted for $\Delta H_f^\circ(H^+, 298\,K)$.[28,29] The heat of formation of HNO_3 in the gas phase is experimentally available (−134.3 kJ mol^{-1}), while the heat of formation of $HClO_4$ (g) is a little uncertain. In this work, 0.6 kcal mol^{-1} was used, which was derived from computation by using W1 and W2 methods developed by Martin.[30] As noted in this reference, $HClO_4$ exhibits particularly severe degrees of inner polarization, and as such obtaining a basis-set limit SCF component to the total atomization energy becomes a challenge, although the G2 calculation result is 10.8 kcal mol^{-1}.[30] Thus, heats of formation of NO_3^- and ClO_4^- were calculated to be −307.8 and −277.8 kJ mol^{-1}, respectively.

Thus, the remaining task was to determine the heats of formation of the cations, which were computed by using the method of isodesmic reactions (Scheme 2) in which the 1,2,4-triazolium species was purposely conserved, as its heat of formation has been experimentally determined to be 835 kJ mol^{-1}.[28] The enthalpies of reactions (ΔH_{r298}°) are obtained by combining the MP2(full)/6-311++G** energy difference for the reaction, the scaled zero point energies, and other thermal factors. Thus, the heats of formation of the cations being investigated can be readily extracted. The results are listed in the Table 1.

The calculated results for enthalpies of formation ($\Delta_f H_m$) are listed in Table 1. They range from 209.9 kJ mol^{-1} to 412.3 kJ mol^{-1}, all are higher than the values of TNT, HMX, and TATB.[9a] Comparing the standard molar enthalpies of formation ($\Delta_f H_m$) values for compounds **6**, **20**, and **21**, it is seen that the heats of formation of perchlorates vary from 245.6 for **21b** to 385.5 kJ mol^{-1} for **20b**. They were obviously higher than those of the nitrates, which were from 209.9 for **21a** to 341.8 kJ mol^{-1} for **20a**. Comparing **6** and **20** shows that the heat of formation increased when the methyl group was replaced by hydrogen. For **6b** and **12b**, the heat of formation is higher for 1-methyl tetrazolyl than for the 2-methyl tetrazolyl group.

Molecular structure: Solid-state structures were obtained for **12b** and **21b**. Data (Table 2) for both structures were obtained at 185 K due to crystal instabilities at lower temperatures. The asymmetric unit for each ion pair, **12b** and **21b**, is shown in Figures 1 and 2. The perchlorate anion in both structures displays no unusual features, with Cl−O bond lengths at approximately 1.41 Å and O-Cl-O angles in the range of 106–112°. In both examples, the rings are not coplanar and have dihedral angles of 164 and 73.9°, respectively. Methylation of the triazolium ring in **12b** has delocalized the multiple bonding over N5–C6 and N2–C6 (Table 3), and the bonding pattern in this ring is similar to that in 1,1′-

Table 2. Crystallographic data for **12b** and **21b**.

	12b (bt794)	**21b** (bt795)
formula	$C_5H_8ClN_7O_4$	$C_6H_7ClN_6O_6$
F_w	265.63	294.63
crystal system	monoclinic	monoclinic
crystal size [mm^3]	0.28×0.25×0.13	0.38×0.24×0.21
space group	$P2_1/c$	$P2_1/n$
F (000)	544	600
a [Å]	10.4680(6)	8.2452(4)
b [Å]	10.6844(6)	10.9077(5)
c [Å]	9.4003(6)	12.9611(6)
α [°]	90	90
β [°]	90.870(1)	108.131(1)
γ [°]	90	90
V [Å^3]	1051.25(11)	1107.79(9)
ρ_{calcd} (mg m^{-3})	1.678	1.767
Z	4	4
μ [mm^{-1}]	0.383	0.384
reflns collected/unique	15632/1895	16465/2010
R_{int}	0.0304	0.0216
data/restraints/parameters	1895/0/156	2010/0/173
index ranges	$-12 \le h \le 12$ $-12 \le k \le 12$ $-11 \le l \le 11$	$-9 \le h \le 9$ $-13 \le k \le 13$ $-15 \le l \le 15$
$R1$, $wR2$ ($I > 2\sigma(I)$)[a]	0.0489, 0.1324	0.0404, 0.1099
$R1$, $wR2$ (all data)[a]	0.0503, 0.1339	0.0420, 0.1115
GOF on F^2	1.061	1.063
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ [e Å^{-3}]	0.819 and −0.400	0.507 and −0.508

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

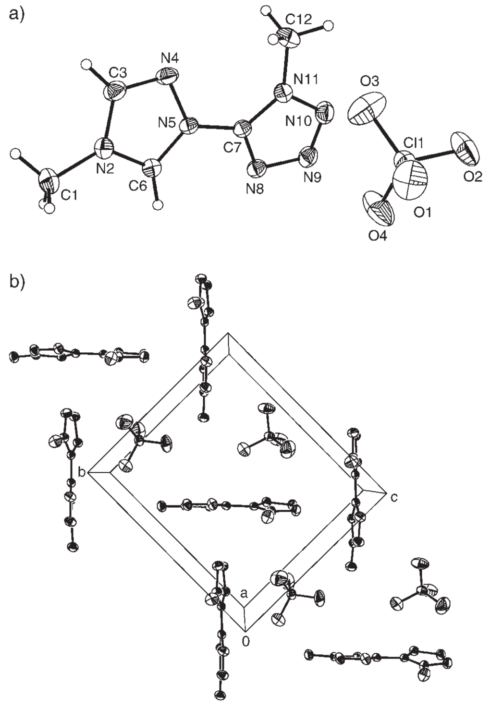


Figure 1. a) A thermal ellipsoid (30%) drawing of **12b**. b) Ball and stick packing diagram of one layer in **12b** viewed down the *a* axis, showing the alternating perpendicular cation motif held together by weak hydrogen bonding.

Table 3. Selected bond lengths [Å] and angles [°] for **12b** and **21b**.

12b		**21b**	
bond lengths [Å]			
C3–N4	1.292(3)	C7–N6	1.314(3)
C3–N2	1.369(3)	C7–N8	1.347(2)
C6–N2	1.315(3)	C7–N10	1.410(2)
C6–N5	1.325(3)	N12–C13	1.352(3)
C7–N8	1.311(3)	N14–C13	1.297(3)
C7–N11	1.320(3)	N10–C11	1.329(3)
C7–N5	1.397(3)	C11–N12	1.315(3)
bond angles [°]			
N8-C7-N11	111.5(2)	N6-C7-N8	114.1(2)
N8-C7-N5	122.4(2)	N6-C7-N10	125.0(2)
N11-C7-N5	126.1(2)	N8-C7-N10	120.8(2)
C6-N5-N4	111.5(2)	C11-N10-N14	111.1(2)
C6-N5-C7	126.1(2)	C11-N10-C7	129.9(2)
N4-N5-C7	122.4(2)	N14-N10-C7	119.0(2)

bis(4-methyl-1,2,4-triazolium-1-ylmethyl)ferrocene iodide monohydrate.[31] Protonation of the tetrazole ring in **21b** leads to a bonding pattern seen previously in these systems.[32] The NO_2 group has a dihedral angle of 8.2° to the imidazole ring indicating some degree of electronic conjugation. There are relatively few heterobicyclic (for example, triazole-imidazole, triazole-triazole or triazole-tetrazole) systems in the literature[33] and due to protonation and differences in substitution no direct comparisons can be made.

The 3D packing of **12b** and **21b** are quite different. In **12b**, an alternating perpendicular cation layer motif is seen (Figure 1b). This is held together by weak hydrogen bonding between the cation and the perchlorate oxygen atoms (3.1–3.4 Å, 138–151°). There is also weak hydrogen bonding between the cations (C1···N9^{i}, 3.449(3) Å, 158.2°; i = symmetry transformation, $x+1,-y+2,-z$). In **21b**, a more regular array is seen with the cations forming a rigid lattice encapsulating the perchlorate anion (Figure 2b). The hydrogen bonding is stronger in this case with cation-perchlorate interactions of 3.0–3.2 Å, 121–151° and cation–cation interactions of 2.7–3.3 Å, 144–156°. The layers in both **12b** and **21b** are held together by hydrogen bonding between cations and also between cations and perchlorate anions.

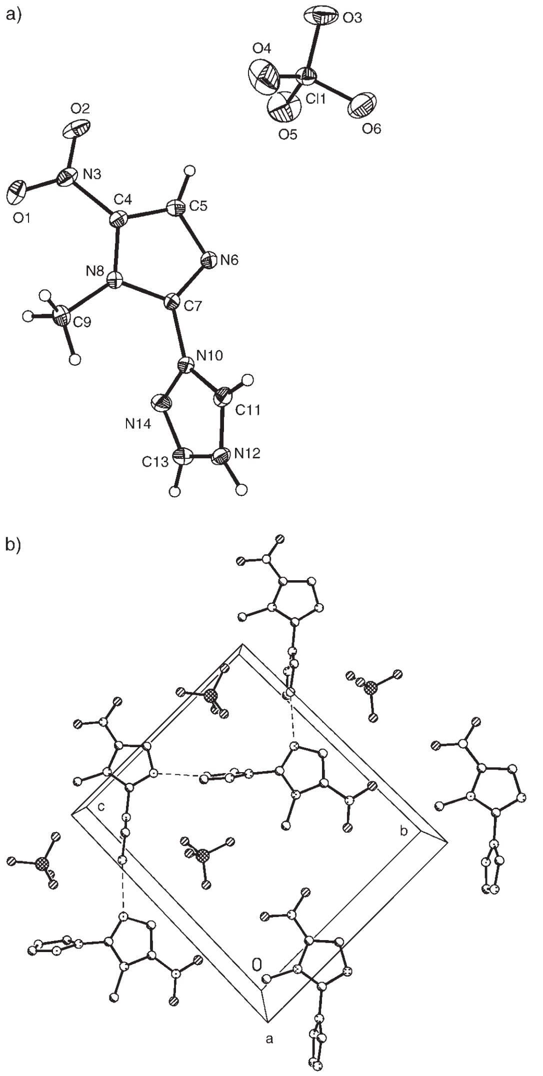


Figure 2. a) A thermal ellipsoid (30%) drawing of **21b**. b) Ball and stick packing diagram of one layer of **21b** viewed down the *a* axis. Dashed lines indicate strong hydrogen bonding.

Conclusion

Bicyclic azoles **1**, **4**, **7**, **10**, **13**, and **16** and bicyclic azolium salts **2**, **3**, **5**, **6**, **8**, **9**, **11**, **12**, **14**, **15**, and **17**–**21** were synthesized and characterized. The structures of **12b** and **21b** were confirmed by single-crystal X-ray analysis. Most of the nitrate and perchlorate salts exhibited good thermal stabilities and showed medium densities ranging from 1.519–1.674 g cm^{-3}. Computations of heats of formation of ionic salts were performed with the Gaussian 03 (Revision D.01) suite of programs.

Experimental Section

Caution: While we have experienced no difficulties with shock and friction sensitivity of these compounds with high nitrogen content and rather high heats of formation, they must be synthesized in mmole amounts and handled with extreme care.

General: ^{1}H and ^{13}C NMR spectra were recorded in [D$_6$]acetone unless otherwise indicated on a 300 MHz (Bruker AMX 300) spectrometer operating at 300.1 and 75.5 MHz, respectively. Chemical shifts are reported in parts per million relative to the appropriate standard (Me$_4$Si for ^{1}H and ^{13}C NMR spectra). Phase-transition temperatures were determined by using a differential scanning calorimeter (DSC, TA Instruments TA10) at a scan rate of 10 °C min^{-1}. TGA (TA Instruments TA50) measurements were recorded as 5 % weight loss temperature at a scan rate of 10 °C min^{-1}. IR spectra (BioRad FTS 3000 Excalibur series infrared spectrometer) were obtained by using KBr pellets. Densities were determined at 24 °C by using a gas pycnometer. Elemental analyses were obtained by using a CE-440 elemental analyzer (EAI Exeter Analytical).

X-ray crystallographic studies: Crystals of compounds **12b** and **21b** 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.[34] Data were collected at 185(2) K (attempts at lowering the temperature any further led to fractures and destruction of the crystal) by using a Bruker/Siemens SMART APEX instrument (Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured by using omega scans of 0.3° per frame for 30 seconds, and a full sphere of data were collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved by using SMART[35] software and refined by using SAINTPlus[36] on all observed reflections. Data reduction and correction for Lp and decay were performed by using the SAINTPlus software. Absorption corrections were applied by using SADABS.[37] The structure was solved by direct methods and refined by the least-squares method on F^5 by using the SHELXTL[38] program package. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are provided in Table 2 and in the CCDC information.

Bicyclic azoles **1**, **4**, **7**, **10**, **13**, and **16** were obtained by reacting sodium imidazolate or sodium 1,2,4-triazolate with methylsulfonyl-substituted azoles including 2-methyl-5-(methylsulfonyl)-2*H*-tetrazole, 1-methyl-5-(methylsulfonyl)-1*H*-tetrazole, and 1-methyl-2-(methylsulfonyl)-5-nitro-1*H*-imidazole. Bicyclic azoles when quaternized with methyl iodide produced diiodide salts, **2**, **5**, **8**, **11**, **14**, and **17**, which then were metathesized with silver nitrate or silver perchlorate to give compounds **3**, **6**, **9**, **12**, **15**, and **18**. Bicyclic azoles (**1**, **4**, and **16**) reacted with nitric acid and perchloric acid to form salts (**19**, **20**, and **21**).

Bicyclic azole syntheses: Sodium hydride (25 mmol, 1.00 g, 60 %) in dry DMF (40 mL) was added to a two-necked round-bottomed flask (100 mL) maintained under N$_2$ and containing a magnetic stirbar. Imidazole (25 mmol, 1.70 g) in DMF (5 mL) was then added slowly to the stirring solution and the mixture was warmed to 90 °C for 1 h and then cooled to RT. 2-Methyl-5-(methylsulfonyl)-2*H*-tetrazole (20 mmol, 3.24 g) in DMF (10 mL) was then added and the mixture was heated to 65 °C for 3 d. After this time, the mixture was cooled to RT, diluted with methylene chloride (100 mL), and filtered. The filtrate was concentrated under vacuum then recrystallized with DMF to give compound 2-methyl-5-(imidazol-1-yl)-2*H*-tetrazole (**1**). Colorless solid; yield: 1.35 g, 45 %; m.p. 141 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 4.37$ (s, 3H), 7.21 (t, $J = 1.4$ Hz, 1H), 7.62 (t, $J = 1.4$ Hz, 1H), 8.28 ppm (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 160.2$, 136.3, 131.8, 117.7, 41.0 ppm; IR (KBr): $\tilde{\nu} = 3113$, 1591, 1521, 1437, 1097, 842 cm^{-1}; elemental analysis calcd (%) for C$_5$H$_6$N$_6$: C 40.00, H 4.03, N 55.97; found: C 39.88, H 4.15, N 56.06.

2-Methyl-5-(1,2,4-triazol-1-yl)-2*H*-tetrazole (4): The procedure was similar to **1**, just after 1-methyl-5-(methylsulfonyl)-1*H*-tetrazole was added, the reaction mixture was heated to 120 °C for 3 d and the product was recrystallized with ethyl acetate. Colorless solid; yield: 0.85 g, 28 %; m.p. 116 °C; ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 4.53$ (s, 3H), 8.26 (s, 1H), 9.11 ppm (s, 1H); ^{13}C NMR (75 MHz, [D$_6$]acetone): $\delta = 158.7$, 153.1, 143.7, 39.5 ppm; IR (KBr): $\tilde{\nu} = 3114$, 1589, 1506, 1431, 1326, 1201, 1123, 1020, 974 cm^{-1}; elemental analysis calcd (%) for C$_4$H$_5$N$_7$: C 31.79, H 3.33, N 64.88; found: C 31.85, H 3.41, N 64.95.

1-Methyl-5-(imidazol-1-yl)-1*H*-tetrazole (7): The procedure was similar to **4**, just after 2-methyl-5-(methylsulfonyl)-2*H*-tetrazole was added, the reaction mixture was kept at RT for 36 h. Colorless solid; yield: 1.26 g, 42 %; m.p. 103 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 4.13$ (s, 3H), 7.27 (t, $J = 1.3$ Hz, 1H), 7.40 (t, $J = 1.3$ Hz, 1H), 7.99 ppm (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 49.0$, 136.6, 131.8, 118.3, 34.5 ppm; IR (KBr): $\tilde{\nu} = 3134$, 3108, 1586, 1479, 1308, 1260, 1061, 953 cm^{-1}; elemental analysis calcd (%) for C$_5$H$_6$N$_6$: C 40.00, H 4.03, N 55.97; found: C 40.01, H 4.10, N 55.85.

1-Methyl-5-(1,2,4-triazol-1-yl)-1*H*-tetrazole (10): The procedure was similar to **7**. Colorless solid; yield: 1.21 g, 40 %; m.p. 98 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 4.41$ (s, 3H), 8.26 (s, 1H), 9.04 ppm (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 154.4$, 148.2, 144.9, 36.2 ppm; IR (KBr): $\tilde{\nu} = 3105$, 1597, 1513, 1381, 1287, 1207, 1122, 984 cm^{-1}; elemental analysis calcd (%) for C$_4$H$_5$N$_7$: C 31.79, H 3.33, N 64.88; found: C 31.72, H 3.38, N 64.64.

1-Methyl-4-nitro-2-(imidazol-1-yl)-1*H*-imidazole (13): The procedure was similar to **7**, except the product was isolated by silica-gel column chromatography (hexanes/diethyl ether 1:1). Yellow solid; yield: 0.69 g, 18 %; m.p. 160 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 3.91$ (s, 3H), 7.27 (t, $J = 1.3$ Hz, 1H), 7.29 (t, $J = 1.3$ Hz, 1H), 7.88 (s, 1H), 7.98 ppm (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 140.5$, 138.0, 136.9, 130.6, 130.5, 118.8, 33.7 ppm; IR (KBr): $\tilde{\nu} = 3124$, 1547, 1476, 1379, 1261, 1162, 1059, 826 cm^{-1}; elemental analysis calcd (%) for C$_7$H$_7$N$_5$O$_2$: C 43.53, H 3.65, N 36.26; found: C 43.32, H 3.45, N 35.50.

1-Methyl-4-nitro-2-(1,2,4-triazol-1-yl)-1*H*-imidazole (16): The procedure was similar to **7**, except the product was isolated by silica-gel column chromatography (hexanes/ethyl acetate 1:1) then recrystallized with acetonitrile. Yellow solid; yield: 1.44 g, 37 %; m.p. 156 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 4.24$ (s, 3H), 7.99 (s, 1H), 8.21 (s, 1H), 8.85 ppm (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 153.6$, 145.5, 139.9, 138.6, 130.8, 34.9 ppm; IR (KBr): $\tilde{\nu} = 3148$, 3115, 1540, 1531, 1470, 1370, 1330, 1263, 1221, 1161, 1130, 1076, 988 cm^{-1}; elemental analysis calcd (%) for C$_6$H$_6$N$_6$O$_2$: C 37.12, H 3.11, N 43.29; found: C 36.94, H 2.92, N 43.17.

A typical preparation of iodide salt was to dissolve **1** (3 mmol) and methyl iodide (6 mmol) in ethyl acetate (2 mL) in a pyrex glass tube (10 mL) that was subsequently evacuated, sealed, and stirred at 60 °C for 24 h. The precipitate was washed with ethyl acetate (3×5 mL) and dried under vacuum for 24 h to give 3-methyl-1-(2-methyl-2*H*-tetrazol-5-yl)imidazolium iodide (2). Yellow solid; yield: 0.81 g, 92 %; m.p. 171 °C; ^{1}H NMR (300 MHz, D$_2$O/H$_2$O): $\delta = 4.09$ (s, 3H), 4.50 (s, 3H), 7.78 (s, 1H), 8.18 (s, 1H), 9.71 ppm (s, 1H); ^{13}C NMR (75 MHz, D$_2$O/H$_2$O): $\delta = 156.4$, 135.6, 124.9, 119.9, 40.5, 36.5 ppm; IR (KBr): $\tilde{\nu} = 3071$, 3117, 1592, 1517, 1447, 1381, 1285, 1137, 1037, 957 cm^{-1}; elemental analysis calcd (%) C$_6$H$_9$N$_6$I: C 24.67, H 3.11, N 28.77; found: C 24.43, H 2.94, N 28.33.

4-Methyl-1-(2-methyl-2*H*-tetrazol-5-yl)-1,2,4-triazolium iodide (5): The procedure was similar to **2**, except the reaction mixture was heated to 70 °C for 3 d. Colorless solid; yield: 0.75 g, 85 %; m.p. 194 °C; ^{1}H NMR (300 MHz, D$_2$O/H$_2$O): $\delta = 4.20$ (s, 3H), 4.55 (s, 3H), 9.24 (s, 1H), 10.87 ppm (s, 1H); ^{13}C NMR (75 MHz, D$_2$O/H$_2$O): $\delta = 156.4$, 146.6, 143.8, 40.7, 34.8 ppm; IR (KBr): $\tilde{\nu} = 3117$, 3071, 1592, 1516, 1447, 1285, 1137, 1037, 957 cm^{-1}; elemental analysis calcd (%) for C$_5$H$_8$N$_7$I: C 20.49, H 2.75, N 33.46; found: C 20.43, H 2.49, N 33.36.

3-Methyl-1-(1-methyl-1*H*-tetrazol-5-yl)imidazolium iodide (8): The procedure was similar to **2**. Yellow solid; yield: 0.83 g, 95 %; m.p. 143 °C; ^{1}H NMR (300 MHz, D_2O/H_2O): $\delta=4.07$ (s, 3H), 4.21 (s, 3H), 7.85 (s, 1H), 8.06 (s, 1H), 9.62 ppm (s, 1H); ^{13}C NMR (75 MHz, D_2O/H_2O): $\delta=$ 147.7, 138.1, 125.8, 122.5, 37.2, 35.2 ppm; IR (KBr): $\tilde{\nu}=3131$, 3065, 1591, 1530, 1496, 1448, 1232, 1075, 957 cm^{-1}; elemental analysis calcd (%) for $C_6H_9N_6I$: C 24.67, H 3.11, N 28.77; found: C 24.59, H 2.84, N 28.09.

4-Methyl-1-(1-methyl-1*H*-tetrazol-5-yl)-1,2,4-triazolium iodide (11): The procedure was similar to **5**. Yellow solid; yield: 0.70 g, 80 %; m.p. 142 °C; ^{1}H NMR (300 MHz, D_2O/H_2O): $\delta=4.18$ (s, 3H), 4.35 (s, 3H), 9.32 (s, 1H), 10.95 ppm (s, 1H); ^{13}C NMR (75 MHz, D_2O/H_2O): $\delta=147.6$, 147.4, 146.1, 36.7, 35.5 ppm; IR (KBr): $\tilde{\nu}=3078$, 3012, 1605, 1504, 1445, 1341, 1218, 1061, 963 cm^{-1}; elemental analysis calcd (%) for $C_5H_8N_7I$: C 20.49, H 2.75, N 33.46; found: C 20.41, H 2.55, N 33.40.

3-Methyl-1-(1-methyl-4-nitroimidazol-2-yl)imidazolium iodide (14): The procedure was similar to **2**, except the reaction solvent was ethyl acetate/DMF 2:1. Yellow solid; yield: 0.87 g, 87 %; m.p. 194 °C; ^{1}H NMR (300 MHz, D_2O/H_2O): $\delta=3.90$ (s, 3H), 4.05 (s, 3H), 7.77 (d, $J=2.1$ Hz, 1H), 7.94 (d, $J=2.1$ Hz, 1H), 8.11 (s, 1H), 9.42 ppm (s, 1H); ^{13}C NMR (75 MHz, D_2O/H_2O) $\delta=140.3$, 139.4, 138.4, 131.5, 126.3, 124.3, 38.1, 35.6 ppm; IR (KBr): $\tilde{\nu}=3078$, 1562, 1508, 1476, 1384, 1264, 1158, 1082, 828 cm^{-1}; elemental analysis calcd (%) for $C_8H_{10}N_5O_2I$: C 28.67, H 3.01, N 20.90; found: C 28.46, H 2.81, N 20.57.

4-Methyl-1-(1-methyl-4-nitroimidazol-2-yl)-1,2,4-triazolium iodide (17): The procedure was similar to **5**, except the reaction solvent was ethyl acetate/DMF 2:1. Yellow solid; yield: 0.81 g, 80 %; m.p. 187 °C; ^{1}H NMR (300 MHz, D_2O/H_2O): $\delta=4.11$ (s, 3H), 4.21 (s, 3H), 8.19 (s, 1H), 9.27 (s, 1H), 10.67 ppm (s, 1H); ^{13}C NMR (75 MHz, D_2O/H_2O): $\delta=148.1$, 147.4, 140.7, 137.8, 131.7, 36.5, 36.2 ppm; IR (KBr): $\tilde{\nu}=3087$, 2993, 1587, 1536, 1474, 1377, 1266, 1239, 1157, 1064, 976 cm^{-1}; elemental analysis calcd (%) for $C_7H_9N_6O_2I$: C 25.02, H 2.70, N 25.01; found: C 24.88, H 2.50, N 24.66.

All metathesis reactions were carried out by using iodide salts (1 mmol) titrated with silver nitrate or silver perchlorate (1 mmol) in water (40 mL) in a test tube (100 mL), then the mixture was filtered, the water pumped off, and the remaining residue dried under vacuum at 40 °C for 24 h.

3-Methyl-1-(2-methyl-2*H*-tetrazol-5-yl)imidazolium nitrate (3a): Colorless solid; yield: 0.22 g, 97 %; m.p. 79 °C; ^{1}H NMR (300 MHz, D_2O/H_2O): $\delta=4.06$ (s, 3H), 4.46 (s, 3H), 7.75 (s, 1H), 8.15 (s, 1H), 9.67 ppm (s, 1H); ^{13}C NMR (75 MHz, D_2O/H_2O): $\delta=156.4$, 135.6, 124.8, 119.9, 40.4, 36.3 ppm; IR (KBr): $\tilde{\nu}=3121$, 3059, 1590, 1517, 1376, 1286, 1138, 957 cm^{-1}; elemental analysis calcd (%) for $C_6H_9N_7O_3$: C 31.72, H 3.99, N 43.16; found: C 31.34, H 3.87, N 43.02.

3-Methyl-1-(2-methyl-2*H*-tetrazol-5-yl)imidazolium perchlorate (3b): Colorless solid; yield: 0.26 g, 99 %; m.p. 110 °C; ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): $\delta=4.01$ (s, 3H), 4.42 (s, 3H), 7.66 (t, $J=1.8$ Hz, 1H), 8.00 (t, $J=1.8$ Hz, 1H), 9.31 ppm (s, 1H); ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): $\delta=157.9$, 136.7, 126.5, 121.2, 41.8, 37.8 ppm; IR (KBr): $\tilde{\nu}=3142$, 3088, 1593, 1519, 1449, 1382, 1285, 1096, 957 cm^{-1}; elemental analysis calcd (%) for $C_6H_9N_6O_4Cl$: C 27.23, H 3.43, N 31.76; found: C 27.17, H 3.25, N 31.90.

4-Methyl-1-(2-methyl-2*H*-tetrazol-5-yl)-1,2,4-triazolium nitrate (6a): Colorless solid; yield: 0.22 g, 96 %; m.p. 151 °C (dec.); ^{1}H NMR (300 MHz, D_2O/H_2O): $\delta=4.12$ (s, 3H), 4.48 (s, 3H), 9.17 (s, 1H), 10.81 ppm (s, 1H); ^{13}C NMR (75 MHz, D_2O/H_2O): $\delta=156.4$, 146.6, 143.8, 40.6, 34.6 ppm; IR (KBr): $\tilde{\nu}=3082$, 2963, 1603, 1385, 1056, 824 cm^{-1}; elemental analysis calcd (%) for $C_5H_8N_8O_3$: C 26.32, H 3.53, N 49.11; found: C 26.15, H 3.41, N 48.72.

4-Methyl-1-(2-methyl-2*H*-tetrazol-5-yl)-1,2,4-triazolium perchlorate (6b): Colorless solid; yield: 0.26 g, 98 %; m.p. 141 °C; ^{1}H NMR (300 MHz, [D$_3$]acetonitrile) $\delta=4.09$ (s, 3H), 4.50 (s, 3H), 8.92 (s, 1H), 10.17 ppm (s, 1H); ^{13}C NMR (75 MHz, [D$_3$]acetonitrile) $\delta=158.1$, 147.8, 144.7, 42.0, 36.1 ppm; IR (KBr): $\tilde{\nu}=3096$, 2963, 1607, 1422, 1223, 1100, 966 cm^{-1}; elemental analysis calcd (%) for $C_5H_8N_7O_4Cl$: C 22.61, H 3.04, N 36.91; found: C 22.54, H 2.79, N 36.87.

3-Methyl-1-(1-methyl-1*H*-tetrazol-5-yl)imidazolium perchlorate (9b): Colorless solid; yield: 0.26 g, 99 %; m.p. 159 °C; ^{1}H NMR (300 MHz, [D$_3$]acetonitrile) $\delta=4.01$ (s, 3H), 4.09 (s, 3H), 7.70 (t, $J=1.8$ Hz, 1H), 7.84 (t, $J=1.8$ Hz, 1H), 9.07 ppm (s, 1H); ^{13}C NMR (75 MHz, [D$_3$]acetonitrile) $\delta=148.4$, 138.7, 126.6, 123.7, 38.0, 35.7 ppm; IR (KBr): $\tilde{\nu}=3144$, 3088, 1593, 1532, 1498, 1464, 1233, 1097 cm^{-1}; elemental analysis calcd (%) for $C_6H_9N_6O_4Cl$: C 27.23, H 3.43, N 31.76; found: C 27.00, H 3.25, N 31.45.

4-Methyl-1-(1-methyl-1*H*-tetrazol-5-yl)-1,2,4-triazolium perchlorate (12b): Colorless solid; yield: 0.26 g, 98 %; m.p. 152 °C; ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): $\delta=4.11$ (s, 3H), 4.24 (s, 3H), 9.03 (s, 1H), 10.26 ppm (s, 1H); ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): $\delta=148.3$, 148.2, 146.5, 37.0, 36.4 ppm; IR (KBr): $\tilde{\nu}=3111$, 3018, 1607, 1506, 1451, 1342, 1217, 1097, 964 cm^{-1}; elemental analysis calcd (%) for $C_5H_8N_7O_4Cl$: C 22.61, H 3.04, N 36.91; found: C 22.44, H 2.79, N 36.63.

3-Methyl-1-(1-methyl-4-nitroimidazol-2-yl)imidazolium nitrate (15a): Colorless solid; yield: 0.26 g, 96 %; m.p. 125 °C; ^{1}H NMR (300 MHz, D_2O/H_2O): $\delta=3.96$ (s, 3H), 4.12 (s, 3H), 7.85 (s, 1H), 8.00 (s, 1H), 8.16 (s, 1H), 9.47 ppm (s, 1H); ^{13}C NMR (75 MHz, D_2O/H_2O): $\delta=139.2$, 138.4, 137.4, 130.4, 125.2, 123.2, 36.9, 34.2 ppm; IR (KBr): $\tilde{\nu}=3106$, 3076, 1562, 1474, 1383, 1265, 1159, 1084, 829 cm^{-1}; elemental analysis calcd (%) for $C_8H_{10}N_6O_5$: C 35.56, H 3.73, N 31.10; found: C 34.77, H 3.76, N 30.44.

3-Methyl-1-(1-methyl-4-nitroimidazol-2-yl)imidazolium perchlorate (15b): Colorless solid; yield: 0.29 g, 94 %; m.p. 169 °C; ^{1}H NMR (300 MHz, [D$_3$]acetone): $\delta=4.04$ (s, 3H), 4.24 (s, 3H), 8.04 (t, $J=1.8$ Hz, 1H), 8.07 (s, 1H), 8.19 (t, $J=1.8$ Hz, 1H), 9.60 ppm (s, 1H); ^{13}C NMR (75 MHz, [D$_3$]acetone): $\delta=140.7$, 140.1, 138.8, 131.0, 126.3, 124.4, 38.0, 35.3 ppm; IR (KBr): $\tilde{\nu}=3136$, 3108, 1565, 1509, 1477, 1264, 1155, 1086, 829 cm^{-1}; elemental analysis calcd (%) for $C_8H_{10}N_5O_6Cl$: C 31.23, H 3.28, N 22.76; found: C 31.23, H 3.17, N 22.42.

4-Methyl-1-(1-methyl-4-nitroimidazol-2-yl)-1,2,4-triazolium nitrate (18a): Colorless solid; yield: 0.26 g, 96 %; m.p. 145 °C (decomp); ^{1}H NMR (300 MHz, D_2O/H_2O): $\delta=4.10$ (s, 3H), 4.21 (s, 3H), 8.18 (s, 1H), 9.26 (s, 1H), 10.66 ppm (s, 1H); ^{13}C NMR (75 MHz, D_2O/H_2O): $\delta=148.1$, 147.3, 140.5, 137.7, 131.5, 36.4, 36.2 ppm; IR (KBr): $\tilde{\nu}=3079$, 3019, 1589, 1536, 1476, 1381, 1350, 1263, 1156, 1065, 974 cm^{-1}; elemental analysis calcd (%) for $C_7H_9N_7O_5$: C 31.00, H 3.35, N 36.15; found: C 31.17, H 3.12, N 36.09.

4-Methyl-1-(1-methyl-4-nitroimidazol-2-yl)-1,2,4-triazolium perchlorate (18b): Colorless solid; yield: 0.29 g, 94 %; m.p. 227 °C; ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): $\delta=3.99$ (s, 3H), 4.06 (s, 3H), 8.03 (s, 1H), 8.92 (s, 1H), 10.01 ppm (s, 1H); ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): $\delta=$ 147.7, 146.9, 141.0, 137.7, 131.1, 36.2, 35.8 ppm; IR (KBr): $\tilde{\nu}=3125$, 3029, 1591, 1537, 1479, 1385, 1263, 1240, 1155, 1097, 978 cm^{-1}; elemental analysis calcd (%) for $C_7H_9N_6O_6Cl$: C 27.24, H 2.94, N 27.23; found: C 26.98, H 2.77, N 26.64.

Nitric acid (1 mmol) or perchloric acid (1 mmol) was added to compound **1**, **4**, or **16** (1 mmol) in acetonitrile (2 mL), this mixture was stirred for 24 h at RT and then the solvent was pumped and the remaining residue dried under vacuum at 40 °C for 24 h.

3-Hydro-1-(2-methyl-2*H*-tetrazol-5-yl)imidazolium perchlorate (19b): Colorless solid; yield: 0.25 g, 100 %; m.p. 150 °C; ^{1}H NMR (300 MHz, [D$_3$]acetone): $\delta=4.01$ (s, 3H), 4.55 (s, 3H), 8.06 (t, $J=1.8$ Hz, 1H), 8.36 (t, $J=1.8$ Hz, 1H), 9.84 ppm (s, 1H); ^{13}C NMR (75 MHz, [D$_8$]acetone): $\delta=158.4$, 136.6, 123.0, 121.5, 41.6 ppm; IR (KBr): $\tilde{\nu}=3101$, 3010, 2887, 2756, 2698, 2585, 1593, 1433, 1110, 838 cm^{-1}; elemental analysis calcd (%) for $C_5H_7N_6O_4Cl$: C 23.96, H 2.82, N 33.54; found: C 23.75, H 2.64, N 33.26.

4-Hydro-1-(2-methyl-2*H*-tetrazol-5-yl)-1,2,4-triazolium nitrate (20a): Colorless solid; yield: 0.21 g, 98 %; m.p. 154 °C; ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): $\delta=4.39$ (s, 3H), 8.28 (s, 1H), 9.11 (s, 1H), 10.08 ppm (brs, 1H); ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): $\delta=158.2$, 145.9, 143.7, 42.0 ppm; IR (KBr): $\tilde{\nu}=3066$, 2989, 1598, 1558, 1504, 1421, 1353, 1309, 1104, 1018, 962 cm^{-1}; elemental analysis calcd (%) for $C_4H_6N_8O_3$: C 22.44, H 2.82, N 52.33; found: C 22.39, H 2.54, N 52.04.

4-Hydro-1-(2-methyl-2*H*-tetrazol-5-yl)-1,2,4-triazolium perchlorate (20b): Colorless solid; yield: 0.25 g, 99%; m.p. 128°C; ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): $\delta = 4.46$ (s, 3H), 8.78 (brs, 1H), 8.93 (s, 1H), 10.10 ppm (s, 1H); ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): $\delta = 159.3$, 152.7, 144.4, 40.8 ppm; IR (KBr): $\tilde{\nu} = 3096$, 2989, 1595, 1562, 1476, 1417, 1325, 1100, 962 cm^{-1}; elemental analysis calcd (%) for $C_4H_6N_7O_4Cl$: C 19.10, H 2.40, N 38.97; found: C 19.20, H 2.15, N 38.95.

4-Hydro-1-(1-methyl-4-nitroimidazol-2-yl)-1,2,4-triazolium nitrate (21a): Yellow solid; yield: 0.25 g, 97%; m.p. 153°C; ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): $\delta = 3.98$ (s, 3H), 8.00 (s, 1H), 8.36 (s, 1H), 9.04 (s, 1H), 11.76 ppm (s, 1H); ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): $\delta = 152.8$, 147.1, 140.5, 140.3, 131.2, 35.4 ppm; IR (KBr): $\tilde{\nu} = 3145$, 3083, 1571, 1537, 1477, 1383, 1265, 1228, 1158, 1070, 978 cm^{-1}; elemental analysis calcd (%) for $C_6H_7N_7O_5$: C 28.02, H 2.74, N 38.13; found: C 27.88, H 2.55, N 38.79.

4-Hydro-1-(1-methyl-4-nitroimidazol-2-yl)-1,2,4-triazolium perchlorate (21b): Colorless solid; yield: 0.29 g, 98%; m.p. 175°C (decomp); ^{1}H NMR (300 MHz, [D$_3$]acetonitrile): $\delta = 4.00$ (s, 3H), 7.05 (brs, 1H), 8.04 (s, 1H), 8.95 (s, 1H), 9.95 ppm (s, 1H); ^{13}C NMR (75 MHz, [D$_3$]acetonitrile): $\delta = 146.0$, 145.8, 137.9, 131.0, 35.7 ppm; IR (KBr): $\tilde{\nu} =$ 3159, 3084, 1569, 1533, 1470, 1381, 1260, 1076, 980 cm^{-1}; elemental analysis calcd (%) for $C_6H_7N_6O_6Cl$: C 24.46, H 2.39, N 28.53; found: C 24.34, H 2.25, N 28.03.

Acknowledgements

The authors gratefully acknowledge the support of AFOSR (F49620-03-1-0209), NSF (CHE0315275), and ONR (N00014-02-1-0600). We are grateful to Dr. Alex Blumenfeld for NMR analyses. The Bruker (Siemens) SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA.

[1] M. X. Zhang, P. E. Eaton, R. D. Gilardi, *Angew. Chem.* **2000**, *112*, 422–426; *Angew. Chem. Int. Ed.* **2000**, *39*, 401–404.

[2] D. E. Chavez, M. A. Hiskey, R. D. Gilardi, *Angew. Chem.* **2000**, *112*, 1861–1863; *Angew. Chem. Int. Ed.* **2000**, *39*, 1791–1793.

[3] D. E. Chavez, M. A. Hiskey, R. D. Gilardi, *Org. Lett.* **2004**, *6*, 2889–2891.

[4] A. Hammerl, T. M. Klapötke, M. Warchhold, *Inorg. Chem.* **2001**, *40*, 3570–3575.

[5] a) M. S. Pevzner, *Russ. Chem. J.* **1997**, *41*, 73–81; b) O. P. Shitov, V. L. Korolev, V. S. Bogdanov, V. A. Tartakovsky, *Russ. Chem. Bull.* **2003**, *52*, 695–699.

[6] R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, *Angew. Chem.* **2006**, *118*, 3664–3682; *Angew. Chem. Int. Ed.* **2006**, *45*, 3584–3601, and references therein.

[7] a) M.-H. V. Huynh, M. A. Hiskey, E. L. Hartline, D. P. Montoya, R. Gilardi, *Angew. Chem.* **2004**, *116*, 5032–5036; *Angew. Chem. Int. Ed.* **2004**, *43*, 4924–4928, and references therein; b) G. Drake, US 6509473, **2003**; c) G. Drake, T. Hawkins, AFOSR Ionic Liquids Workshop, Dulles, VA, **2002**; d) G. Drake, AFOSR Ionic Liquids Workshop, Aberdeen, MD, September **2003**; e) G. Kaplan, G. Drake, K. Tollison, L. Hall, T. Hawkins, *J. Heterocycl. Chem.* **2005**, *42*, 19–27; f) G. W. Drake, T. W. Hawkins, J. Boatz, L. Hall, A. Vij, *Propellants Explos. Pyrotech.* **2005**, *30*, 156–163; g) G. W. Drake, T. W. Hawkins, L. A. Hall, J. A. Boatz, A. J. Brand, *Propellants Explos. Pyrotech.* **2005**, *30*, 329–327.

[8] a) H. Xue, Y. Gao, B. Twamley, J. M. Shreeve, *Chem. Mater.* **2005**, *17*, 191–198; b) H. Xue, S. W. Arritt, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2004**, *43*, 7972–7977; c) Y. Gao, S. W. Arritt, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2005**, *44*, 1704–1714; d) C. Ye, J-. C. Xiao, B. Twamley, J. M. Shreeve, *Chem. Commun.* **2005**, 2750–2752; e) H. Xue, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2005**, *44*, 5068–5072; f) H. Xue, B. Twamley, J. M. Shreeve, *Adv. Mater.* **2005**, *17*, 2142–2146; H. Xue, B. Twamley, J. M. Shreeve, *J. Mater. Chem.* **2005**, *15*, 3459–3465.

[9] D. E. Chavez, M. A. Hiskey, D. L. Naud, *Propellants Explos. Pyrotech.* **2004**, *29*, 209–215, and references therein.

[10] a) A. Hammerl, T. M. Klapötke, *Inorg. Chem.* **2002**, *41*, 906–912; b) A. Hammerl, G. Holl, M. Kaiser, T. M. Klapötke, H. Piotrowski, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2117–2121; c) M. von Denffer, T. M. Klapötke, G. Kramer, G. Spiess, J. Welch, *Propellants Explos. Pyrotech.* **2005**, *30*, 191–195; d) J. C. Gálvez-Ruiz, G. Holl, K. Karaghiosoff, T. M. Klapötke, K. Löhnwitz, P. Mayer, H. Nöth, K. Polborn, C. J. Rohbogner, M. Suter, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 4237–4253.

[11] M. A. Hiskey, D. E. Chavez, D. L. Naud, S. F. Son, H. L. Berghout, C. A. Bolme, *Proc. Int.* **2000**, *27*, 3–14.

[12] M. A. Hiskey, M. M. Stinecipher, J. E. Brown, *J. Energ. Mater.* **1993**, *11*, 157–166.

[13] C. M. Jin, C. Ye, C. Piekarski, B. Twamley, J. M. Shreeve, *Eur. J. Inorg. Chem.* **2005**, 3760–3767.

[14] M. Aouial, A. Bernardini, Ph. Viallefont, *J. Heterocycl. Chem.* **1977**, *14*, 397–400.

[15] T. P. Kofman, *Russ. J. Org. Chem.* **2001**, *37*, 1158–1168.

[16] K. Nagarajan, V. P. Arya, R. K. Shah, S. J. Shenoy, G. A. Bhat, *Indian J. Chem. Sect. B* **1982**, *21*, 945–948.

[17] B. A. Omotowa, J. M. Shreeve, *Organometallics* **2004**, *23*, 783–791.

[18] R. Spear, *Aust. J. Chem.* **1984**, *37*, 2453–2468.

[19] G. Chauvière, B. Bouteille, B. Enanga, C. Albuquerque, S. L. Croft, M. Dumas, J. Périé, *J. Med. Chem.* **2003**, *46*, 427–440.

[20] V. A. Ostrovskii, M. S. Pevzner, T. P. Kofman, I. V. Tselinskii, *Targets Heterocycl. Syst.* **1999**, *3*, 467–526.

[21] J. P. Ritchie, S. M. Bachrach, *J. de Physique. C4*, Suppl. 9, **1987**, 48, 377–391.

[22] H. L. Ammon, S. Mitchell, *Propellants Explos. Pyrotech.* **1998**, *23*, 260–265.

[23] Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford, CT, **2004**.

[24] R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**.

[25] C. M. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618.

[26] J. A. Pople, J. S. Binkely, R. Seeger, *Int. J. Quantum Chem.* **1976**, *10*, 1.

[27] H. D. B. Jenkins, D. Tudeal, L. Glasser, *Inorg. Chem.* **2002**, *41*, 2364.

[28] M. W. Schmidt, M. S. Gordon, J. A. Boatz, *J. Phys. Chem. A* **2005**, *109*, 7285–7295.

[29] M. W. Chase, C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald, A. N. Syverud, *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. I.

[30] J. M. L. Martin *J. Mol. Struct. THEOCHEM* **2006**, in press.

[31] Y. Gao, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2004**, *43*, 3406–3412.

[32] a) O. M. Peeters, G. S. Schuerman, N. M. Blaton, C. J. De Ranter, *Acta Crystallogr. Sect. C* **1993**, *49*, 1958–1961; b) F. Baert, L. Devos, J.-P. Henichart, R. Houssin, B. Lablanche, *Cryst. Struct. Commun.* **1977**, *6*, 511–516; c) V. B. Arion, E. Reisner, M. Fremuth, M. A. Jakupec, B. K. Keppler, V. Yu. Kukushkin, A. J. L. Pombeiro, *Inorg.*

Chem. **2003**, *42*, 6024–6031; d) S. Kiviniemi, M. Nissinen, M. T. Lämsä, J. Jalonen, K. Rissanen, J. Pursiainen, *New J. Chem.* **2000**, *24*, 47–52; e) C. W. Glynn, M. M. Turnbull, *Inorg. Chim. Acta* **2002**, *332*, 92–100; f) O. M. Peeters, N. M. Blaton, C. J. De Ranter, *Acta Crystallogr. Sect. E* **2001**, *57*, 655–657.

[33] a) E. V. Treryakov, G. V. Romanenko, V. I. Ovcharenko, *Tetrahedron* **2004**, *60*, 99–103; b) G. L. Starova, O. V. Frank-Kamenetskaya, O. A. Usov, A. M. Kuz′min, M. S. Pevzner, *Zh. Strukt. Khim.* **1982**, *23*, 171–173.

[34] H. Hope, *Prog. Inorg. Chem.* **1994**, *41*, 1–19.

[35] SMART: version 5.626, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, **2002**.

[36] SAINTPlus: version 6.45a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2003**.

[37] SADABS: version 2.01, an empirical absorption correction program, Bruker AXS, Madison, WI, **2004**.

[38] SHELXTL: version 6.10, Structure Determination Software Suite, G. M. Sheldrick, Bruker AXS Inc., Madison, WI, **2001**.

Received: March 13, 2006