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Nitrogen-Rich Energetic Ionic Liquids Based on the *N*,*N*-Bis(1*H*-tetrazol-5-yl)amine Anion – Syntheses, Structures, and Properties

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Dedicated to Professor Jean'ne M. Shreeve on the occasion of her 80th birthday

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N,N-Bis(1H-tetrazol-5-yl)amine anions (HBTA⁻/BTA²⁻) were used as suitable nitrogen-rich components for the construction of energetic ionic liquids. Seven ionic liquids, namely, 1,3-dimethylimidazolium (1, [C₁mim]HBTA), 1-ethyl-3-methylimidazolium (2, [C₂mim]HBTA), 1-butyl-3-methylimidazolium (3, [C₄mim]HBTA), 1-hexyl-3-methylimidazolium 1-methyl-3-octylimidazolium [C₆mim]HBTA), (5. (4, 1,2,3-trimethylimidazolium (6, [C₈mim]HBTA), and [C₁mmim]HBTA) cations with the HBTA⁻ anion and di-1,2,3trimethylimidazolium *N*,*N*-bis(1*H*-tetrazol-5-yl)amine (7. $[C_1 mmim]_2 BTA)$, were synthesized. All materials were fully characterized by IR and NMR spectroscopy, elemental analysis, and high-resolution mass spectrometry. The crystal structures of 1 and 7 were determined by single-crystal X-ray diffraction [1: monoclinic, $P2_1/n$, a = 14.0653(4) Å, b =

Introduction

In recent years, ionic liquids have received much attention as interesting modifiable soft materials in a wide range of applications as solvents,^[1] catalysts,^[2] electrolytes,^[3] lubricants,^[4] surfactants,^[5] magnetic,^[6] and optical fluids.^[7] Some ionic liquids have interesting properties as green liquid propellants and explosives for application in energetic materials.^[8] Compared with traditional molecular energetic compounds, such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), many energetic ionic liquids have advantages of enhanced thermal stability, negli-

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6.9507(2) Å, c = 22.4699(7) Å, $\beta = 93.996(3)^{\circ}$, V = 2191.38(12) Å³, Z = 8, $\rho = 1.511 \text{ g cm}^{-3}$; **7**: monoclinic, $P2_1/c$, a = 17.5869(3) Å, b = 12.8757(2) Å, c = 21.9203(6) Å, $\beta = 125.0580(10)^{\circ}$, V = 4063.15(15) Å³, Z = 8, $\rho = 1.221 \text{ g cm}^{-3}$]. The nitrogen contents of **1**–**7** exceed 40%, and **1** has the highest value of 61.78%. The ionic liquids **1**–**7** are thermally stable to 220 °C, and **2**–**5** are room-temperature ionic liquids. The heats of formation of **1**–**7** obtained by both experimental and theoretical methods are all positive. The ionic liquids **1**–**7** are insensitive towards impact (>40 J) and friction (>360 N). They can be ignited in air. These new energetic ionic liquids contain only C, H, and N and are of interest as potential propellants with high energy, high thermal stability, low sensitivity to impact and friction, and environmentally friendly decomposition gases.

gible vapor pressure, large liquidus ranges, little or no vapor toxicity, and improved safety issues related to transportation, handling, and processing from production to end use, which originate from the charged structures of the ionic liquids.^[9]

Propellants are the most important application of energetic ionic liquids. To date, several kinds of typical energetic ionic liquid propellants have been reported. Christe and Shreeve have tried to seek suitable monopropellants containing sufficient oxygen.^[10] In contrast, the present work is primarily concerned with bipropellants in which safety and stability are enhanced by the segregation of fuel and oxidizer into separate working fluids. Most known energetic ionic liquids are underoxidized, because small anions such as nitrate (NO₃⁻), perchlorate (ClO₄⁻), and dinitramide [N(NO₂)₂⁻] have insufficient oxygen to completely oxidize the large cations to carbon monoxide.^[11] However, only a part of them may supply energy, as hypergols undergo hypergolic ignition with common propellant oxidizers.^[12]

The common oxidizers for hypergols comprise highly toxic and corrosive chemicals including dinitrogen tetroxide (N_2O_4) and fuming nitric acid (HNO₃), which are still haz-

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ardous and dangerous. Oxygen gas (O_2) is nonhazardous, nonflammable, and unreactive, but is a strong oxidizer. Thus, in consideration of their environmental friendliness, green chemistry, and low vapor toxicity, energetic ionic liquids may also be useful fuels with O_2 as the oxidizer in clean bipropellant applications. Moreover, the propellant applications of combustible energetic ionic liquids that can ignited in air may reduce the oxidizer tank in the atmosphere, which will increase the payload of an aircraft

The dicyanamide anion $[N(CN)_2^-]$ has been studied as a stable anion for the construction of hypergolic ionic liquids with good fluidity and thermal stability.^[13] Nevertheless, the demand for new energetic ionic liquids with higher energy density is constant. Nitrogen-rich anions, including azide (N_3^-) and 5-aminotetrazolate, were used to prepare energetic ionic liquids with high heats of formation and high energy densities.^[14] However, low thermal and impact stabilities limit the applications of N_3^- -containing energetic ionic liquids. In addition, the nitrogen content of polynitrogen heterocyclic ring frameworks and the melting points of the stable energetic salts are directly related, that is, the rigidity of the heterocyclic ring increases the melting point.

Recently, N,N-bis(1H-tetrazol-5-yl)amine (H₂BTA) was considered as an interesting nitrogen-rich framework for energetic salts.^[15] H₂BTA is the product of the reaction between NaN(CN)₂ and NaN₃ under acidic conditions (Scheme 1). The N,N-bis(1H-tetrazol-5-yl)amine anion (HBTA⁻) contains two nitrogen-rich tetrazole rings and may combine the virtues of the $N(CN)_2^-$ and N_3^- anions with a balance of stability and energy. Compared with other sensitive 5-substituted tetrazoles,^[16] including 5-nitrotetrazole, 5-cyanotetrazole, 1,5-diaminotetrazole, 5,5'-azotetrazole, and 5-azidotetrazoles, the neutral H₂BTA possesses high thermal and mechanical stability with a high nitrogen content of 82.34%. Some metallic and nonmetallic BTA salts have been reported as nitrogen-rich compounds/energetic materials with high thermal stability (>200 °C), high heat of formation (> $+600 \text{ kJ mol}^{-1}$), and low impact (>40 J) and friction (>360 N) sensitivities.^[15] However, the melting points of these salts are all higher than 100 °C. To the best of our knowledge, no ionic liquids based on HBTA⁻ or BTA²⁻ anions have been reported.



Scheme 1. Synthesis of *N*,*N*-bis(1*H*-tetrazol-5-yl)amine (H₂BTA).

Herein, we report the synthesis of a series of nitrogenrich ionic liquids based on the HBTA⁻ anion with 1,3-dimethylimidazolium (1, $[C_1mim]HBTA$), 1-ethyl-3-methylimidazolium (2, $[C_2mim]HBTA$), 1-butyl-3-methylimidazolium (3, $[C_4mim]HBTA$), 1-hexyl-3-methylimidazolium (4, $[C_6mim]HBTA$), 1-methyl-3-octylimidazolium (5, [C₈mim]HBTA), and 1,2,3-trimethylimidazolium (6, [C₁mmim]HBTA) cations; the di-1,2,3-trimethylimidazolium BTA^{2–} salt (7, [C₁mmim]₂BTA) was also synthesized. Compounds 1–7 were fully characterized, and singlecrystal X-ray diffraction analysis of 1 and 7 confirmed the structures of these ionic liquids. In addition, their thermal and chemical stabilities and sensitivities along with their combustibility characteristics were also determined.

Results and Discussion

Syntheses

Substituted imidazolium cations are typical cations for the construction of ionic liquids. In this work, we introduced substituted imidazolium cations, especially asymmetric imidazolium cations, to design ionic liquids based on the HBTA⁻ anion. No C_2 -symmetric axis exists in the HBTA⁻ anion, but a C_2 -symmetric axis may be found in H₂BTA or the BTA²⁻ anion. These asymmetric functional groups or frameworks will lead to low melting points for the new salts. The energetic ionic liquids 1-6 with the monoanion HBTA⁻ were obtained directly after anion metatheses (Scheme 2). The starting material, N,N-bis(1H-tetrazol-5-yl)amine monohydrate (H2BTA·H2O), was obtained according to the literature method.^[15] The reaction of H₂BTA·H₂O with silver nitrate (1:1 molar ratio) in water results in the formation of silver N,N-bis(1H-tetrazol-5-yl)amine (AgHBTA) as a white precipitate. Compounds 1-6 were prepared from reactions of their corresponding 1,3-dialkylimidazolium iodide/bromide salt precursors with AgHBTA in methanol.



Scheme 2. Synthesis of the ionic liquids 1–6 with HBTA⁻ monoanion.

The ionic liquid 7 with the BTA^{2-} dianion was obtained by slow recrystallization of the ionic liquid **6** from a methanol/ethyl acetate solution. Neutral H₂BTA was the byproduct and remained in solution after the crystallization (Scheme 3).



Scheme 3. Formation of the ionic liquid 7 with the BTA²⁻ dianion.

All of the ionic liquids 1–7 were characterized by IR and NMR spectroscopy, elemental analysis, and high-resolution mass spectrometry. Typical peaks of the 1-alkyl-3-methyl-imidazolium cations were recorded in the ¹H and ¹³C NMR spectra of all compounds. A signal of HBTA[–] anion at δ = 156.88–160.78 ppm in the ¹³C NMR spectra was found for every HBTA[–] ionic liquid. No hydrated or solvent water molecules were found in the ionic liquids from NMR spectroscopy and elemental analysis.

X-ray Crystallography

In the reported crystal structures of the energetic metallic HBTA⁻ salts and energetic BTA²⁻ salts, ligands such as H_2O , NH_3 , or other organic ligands are necessary to stabilize the crystal structures.^[15] Moreover, the single-crystal structure of a nonmetallic HBTA⁻ salt has not been reported previously. Herein, two crystals of 1 and 7 suitable for X-ray diffraction were obtained by slow recrystallization from methanol/ethyl acetate solutions. Both of them contain no water or solvent molecules. The structure of 1 is the first single-crystal structure of a nonmetallic HBTA⁻ salt. The crystallographic and structural refinement data of 1

Table 1. Selected bond lengths [Å] and angles [°] of 1 and 7.

1	Bond length [Å]	7	Bond length [Å]
N1-C1	1.331(2)	N1C1	1.334(4)
N1-N2	1.353(2)	N1-N2	1.354(4)
N2-N3	1.311(2)	N2-N3	1.303(4)
N3-N4	1.361(2)	N3-N4	1.358(4)
N4C1	1.322(2)	N4C1	1.334(4)
N5C1	1.388(2)	N5C1	1.376(4)
N5-C2	1.347(2)	N5-C2	1.383(4)
N6-C2	1.330(2)	N6-C2	1.334(4)
N15-N16	1.368(2)	N9-C2	1.340(4)
N19-C9	1.465(2)	N16-N17	1.309(4)
N20-C6	1.372(2)	N21-C16	1.466(5)
N20-C8	1.464(2)	N22-C15	1.464(5)
1	Bond angle [°]	7	Bond angle [°]
C1-N1-N2	103.70(14)	C1-N1-N2	104.2(2)
N3-N2-N1	109.31(14)	N3-N2-N1	108.9(2)
N2-N3-N4	109.94(14)	N2-N3-N4	110.9(2)
C1-N4-N3	103.18(14)	N4-C1-N1	113.0(3)
C1-N5-C2	125.67(15)	C1-N5-C2	127.0(3)
C2-N9-N8	107.67(14)	N6-C2-N9	113.3(3)
N4-C1-N5	125.31(16)	C2-N6-N7	103.2(2)
N4-C1-N1	113.86(15)	N6-N7-N8	110.1(2)
N9-C2-N5	127.48(16)	N7-N8-N9	110.3(2)
N20-C5-N19	108.48(16)	C5-N19-C7	109.0(3)
C7-C6-N20	107.41(16)	C5-N20-C6	108.5(3)
C6-C7-N19	106.92(16)	N20-C5-N19	107.6(3)

and 7 are summarized in Table 5. Selected bond lengths [Å] and angles [°] of 1 and 7 are listed in Table 1.

Compound 1 crystallizes in the monoclinic space group $P2_1/n$ and has a density of 1.511 g cm⁻³ and a unit cell volume of 2191.38(12) Å³ (Table 5). In the molecule of 1 (Figure 1), the N1-C1, N4-C1, N6-C2, N20-C5, N20-C6 bond lengths in the tetrazole and imidazole rings are 1.331(2), 1.322(2), 1.330(2), 1.322(2), and 1.372(2) A, respectively (Table 1). These C-N ring bonds are much shorter than classical C-N single bonds (1.47 Å), but are longer than C=N double bonds (1.31 Å),^[17] which suggests that a little multiple bond character is present. A similar trend was observed for the N1–N2 [1.353(2) Å], N2–N3 [1.311(2) Å], and N3-N4 [1.361(2) Å] bonds, which are significantly longer than typical N=N bonds (1.24 Å). Compared with those of the neutral H₂BTA, the bond lengths on the tetrazole rings of 1 are similar.^[15] However, the N5-C1 bond length of 1 is 1.388(2) Å, which is a little longer than that in H₂BTA [1.365(2) Å] and N5–C2 [1.347(2) Å]. This difference originates from the conjugated tetrazolate anion. The N4-C1-N1 angle in the tetrazole ring of 1 is 113.86(15)°, which is bigger than that in H₂BTA $[109.5(2)^{\circ}]$,^[15] but close to that in the structure of the 5-aminotetrazolate anion [112.5(5)°].^[14c] Furthermore, the C2–N5–C1 [125.67(15)°],



Figure 1. Top: molecular structure of 1 (displacement ellipsoids shown at 30% probability). Hydrogen atoms represented by spheres of arbitrary radius. Bottom: packing diagram of 1 viewed down the *b* axis.



N4–C1–N5 [125.31(16)°], and N9–C2–N5 [127.48(16)°] angles suggest that the two tetrazole rings in HBTA⁻ ionic liquids are not coplanar.

The packing structure of 1 viewed along the *b* axis is built up by hydrogen bonding (Figure 1). Each HBTA⁻ anion is surrounded by one 1,3-dimethylimidazolium cation. The imino group and the nitrogen atoms on the tetrazole rings in each HBTA⁻ anion may form intramolecular [N9–H9····N4, 2.898(2) Å] and intermolecular hydrogen bonds between the neighboring HBTA⁻ anions [N5– H5····N15 2.916(2) Å, N9–H9····N10 2.809(2) Å, N14– H14···N1 2.828(2) Å, and N18–H18···N12 2.877(2) Å; Table 2]. Charge delocalization over the whole molecule is accomplished by extensive hydrogen bonding in the extended structure, which may enhance the decrease of C–N bond lengths in the HBTA⁻ anion. The combination of this extensive hydrogen bonding in the extended structure results in a three-dimensional supramolecular network.

Compound 7 crystallizes in the monoclinic space group $P2_1/c$ with a density of 1.221 g cm⁻³ and a unit cell volume of 4063.15(15) Å³ (Table 5). In the crystal structure of 7 (Figure 2), the C–N and N–N bond lengths of the tetrazole rings and imidazole rings also show multiple bond character (Table 1). Compared with the N5–C1 [1.388(2) Å] and

Table 2. Lengths [Å] and angles [°] for hydrogen bonds in 1 and 7.

D–H···A	d(D–H)	<i>d</i> (H•••A)	<i>d</i> (D····A)	D–H–A
1 ^[a]				
N5–H5…N15 ¹	0.88(2)	2.04(2)	2.916(2)	173.2(2)
N9–H9…N4	0.93(2)	2.43(2)	2.898(2)	111.2(18)
N9-H9····N10 ²	0.93(2)	1.99(2)	2.809(2)	146(2)
N14–H14…N1 ³	0.88(2)	1.95(2)	2.828(2)	173.9(2)
N18–H18…N12 ⁴	0.95(2)	1.97(2)	2.877(2)	158.9(18)
7 ^[b]				
N5–H5…N10 ¹	0.86(4)	2.10(4)	2.934(4)	165(3)
N14–H14•••N1 ²	0.86(3)	2.11(3)	2.900(4)	152.5(3)
[a] 1: x , $-1 + y$, z ; 2 x, $1 - y$, $-z$, [b] 1: -	2: $3/2 - x, -1/2 + y$	$\frac{1}{1/2} + y, \frac{1}{2}$	-z; 3: x, 1 -x 1/2 + z	1 + y, z; 4: 2

N5–C2 [1.347(2) Å] bond lengths of the nitrogen atoms linked to the two tetrazole rings in 1, the lengths of those in 7 are nearly the same [N5–C1 1.376(4) Å, N5–C2 1.383(4) Å]. This is maybe because the two tetrazole rings in the BTA^{2–} anion are in similar chemical environments. However, in the HBTA[–] anion, the two tetrazole rings are different and exist as one neutral tetrazole and one tetrazolate anion.



Figure 2. Top: molecular structure of 7 (displacement ellipsoids shown at 30% probability). Hydrogen atoms represented by spheres of arbitrary radius. Bottom: packing diagram of 7 viewed down the *b* axis.

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The packing structure of 7 is built up by hydrogen bonding along the *b* axis (Figure 2). In contrast to the structure of 1, every BTA^{2–} anion is surrounded by two imidazolium cations. There are no intramolecular hydrogen bonds because only one hydrogen atom in each anion is located on the amino group, which is far away from the other nitrogen atoms in the tetrazole rings. Only intermolecular hydrogen bonds exist between the amino group and the neighboring nitrogen atoms of the tetrazole rings [N5–H5···N10 2.934(4) Å, N14–H14···N1 2.900(4) Å; Table 2]. The relatively weaker hydrogen-bond interactions in 7 result in a three-dimensional supramolecular network that is different

NBO Analysis

from that of 1.

H₂BTA is a weak acid that may reversibly release one or two protons to form HBTA- and BTA²⁻ anions (Scheme 4). This reversible ionization can be controlled by the addition of different amounts of base, so that HBTA- can be transformed into BTA²⁻ by the change of the basicity of system.^[15] The natural bond order (NBO) analysis data of six N-substituted imidazolium cations is shown in Table 3. The charge densities of C-2 of the imidazole rings was ca. +0.265 in the five 1-alkyl-3-methylimidazolium cations. No clear difference was found even as the alkyl chain lengthened from methyl to octyl. However, when the hydrogen atom attached to C-2 was substituted by a methyl group ($[C_1 mmim]^+$), its C-2 charge density increased to +0.472 (Figure 3). An obvious increase of the Lewis basicity of the 1,2,3-trimethylimidazolium cation was confirmed compared to the other five 1-alkyl-3-methylimidazolium cations. As ionic liquid 6 slowly recrystallized, the HBTA⁻ ion transformed into BTA²⁻, and a divalent BTA²⁻ salt of 7 was obtained.



Scheme 4. Reversible deprotonation of H₂BTA.

Table 3. The C-2 charge densities of different substituted imidazolium cations.

[C ₁ mim] ⁺	$[C_2 mim]^+$	[C ₄ mim] ⁺	$[C_6 mim]^+$	$[C_8 mim]^+$	[C ₁ mmim] ⁺
0.264	0.265	0.265	0.265	0.265	0.472

Physicochemical Properties

The physicochemical properties of the ionic liquids 1-7 are summarized in Table 4. These nitrogen-rich ionic liquids have high nitrogen contents above 40%. For 1 in particular, the nitrogen content reaches 61.78%. The nitrogen contents of 1-7 are even higher than those of the corresponding ni-



Figure 3. NBO analysis of $[C_1 mim]^+$ and $[C_1 mmim]^+$.

trogen-rich ionic liquids containing the 5-aminotetrazolate anion.^[11d] The high nitrogen content originates from the nitrogen atoms of the HBTA⁻ and BTA²⁻ anions. The densities of 1-7 range from 1.22 to 1.51 g cm⁻³.

Ionic liquids 1–7 are thermally stable to more than 220 °C. No water release was observed in the thermogravimetric analysis (TGA) curves. Their considerable thermal stabilities are comparable to those of neutral H_2BTA and their analogous copper BTA^{2-} salts.^[15] Hydrogen bonding could play the predominant role in determining their thermal decomposition temperatures. As confirmed by the crystal structures, extensive hydrogen bonds exist in the ionic liquids, and these hydrogen bonds can enhance their thermal stabilities.

The melting points/glass transition temperatures $(T_{\rm m}/T_{\rm g})$ were observed by differential scanning calorimetry (DSC) from the first heating cycle. The $T_{\rm m}$ of **1** is 48 °C, which is lower than that of **7** (77 °C). For **2–5**, which are room-temperature liquids, $T_{\rm g}$ values instead of $T_{\rm m}$ values were observed. Their $T_{\rm g}$ values ranged from –31 to –15 °C. The liquidus range of the ionic liquids **2–5** may excess 240 °C. The asymmetry of the cations of these ionic liquids could lead to low $T_{\rm m}/T_{\rm g}$ values. For **6**, no obvious $T_{\rm m}$ or $T_{\rm g}$ was

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Table 4	Physico	ochemical	properties	of	1 - 7
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3	4	5	6	7
3 291.32	319.37	347.42	263.13	373.45
-22	-20	-31	_	77
228	223	223	225	228
2 52.89	48.24	44.35	58.52	48.73
1.42	1.37	1.34	1.44	1.22
9 642.7	614.5	584.6	655.2	791.9
7.1 7050.0	8339.8	9619.7	5663.9	9523.8
.6 7046.9	8339.2	9621.6	5658.3	9570.9
6 682.3	615.9	539.6	652.3	774.7
5 2342	1928	1553	2478	2074
>40	>40	>40	>40	>40
0 >360	>360	>360	>360	>360
; ,	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

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[a] Molecular weight. [b] Melting point. [c] Decomposition temperature. [d] Nitrogen content. [e] Density at 25 °C. [f] Calculated molar enthalpy of formation. [g] Experimental (constant-volume) energy of combustion. [h] Experimental molar enthalpy of combustion. [i] Experimental molar enthalpy of formation. [j] Specific enthalpy of formation. [k] Impact sensitivity. [l] Friction sensitivity.

observed from -80 to 200 °C. The introduction of imidazolium cations improved the properties of the liquids and enhanced their thermal stabilities effectively. The Coulomb interactions and hydrogen-bond network mainly affect their physicochemical property. The high delocalization of the ionic charges and the asymmetry of the cations results in weak Coulomb interactions between anions and cations and, thus, low lattice energies and melting points.

The theoretical heats of formation of the ionic liquids 1– 7 are between 584.6 and 791.9 kJ mol⁻¹. The theoretical heat of formation of 1 is 700.1 kJ mol⁻¹, which is the highest among the six nitrogen-rich ionic liquids with HBTA⁻ monoanions. Their heats of formation decrease when longer alkyl groups are introduced into the structures of the imidazolium cations.

The experimentally determined constant-volume energies of combustion ($\Delta_c U$) of the ionic liquids 1–7 were measured by using oxygen bomb calorimetry. The heat of combustion, $\Delta_c H^{\circ}$, was calculated from $\Delta_c U$ and a correction for change in gas volume during combustion was included: $\Delta_c H_m = \Delta_c U_m + \Delta n RT$, in which Δn is the difference in the number of moles of gas between the products and the reactants. The standard heats of formation of 1–7, $\Delta_f H^{\circ}$, were back-calculated from the heats of combustion on the basis of combustion equations (I)–(VII), Hess's Law as applied to thermochemical equations (1)–(7).^[18]

1:
$$C_7H_{11}N_{11}(s) + 39/4O_2(g) \rightarrow 7CO_2(g) + 11/2H_2O(l) + 11/2N_2(g)$$
 (I)

$$\Delta_{\rm f} H^{\rm o}_{298} (\mathbf{1}, s) = 7 \Delta_{\rm f} H^{\rm o}_{298} (\rm CO_2, g) + 11/2 \Delta_{\rm f} H^{\rm o}_{298} (\rm H_2O, l) - \Delta_{\rm c} H^{\rm o}_{298} (\mathbf{1}, s)$$
(1)

2:
$$C_8H_{13}N_{11}(l) + 45/4O_2(g) \rightarrow 8CO_2(g) + 13/2H_2O(l) + 11/2N_2(g)$$
 (II)

 $\Delta_{\rm f} H^{\rm o}{}_{298} (\mathbf{2}, 1) = 8 \Delta_{\rm f} H^{\rm o}{}_{298} ({\rm CO}_2, g) + 13/2 \Delta_{\rm f} H^{\rm o}{}_{298} ({\rm H}_2 {\rm O}, 1) - \varDelta_{\rm c} H^{\rm o}{}_{298} (\mathbf{2}, 1)$ (2)

3:
$$C_{10}H_{17}N_{11}(l) + 57/4O_2(g) \rightarrow 10CO_2(g) + 17/2H_2O(l) + 11/2N_2(g)$$
 (III)

 $\Delta_{\rm f} H^{\rm o}{}_{298}$ (3, l) = $10\Delta_{\rm f} H^{\rm o}{}_{298}$ (CO₂, g) + $17/2\Delta_{\rm f} H^{\rm o}{}_{298}$ (H₂O, l) – $\Delta_{\rm c} H^{\rm o}{}_{298}$ (3, l) (3)

4: $C_{12}H_{21}N_{11}(l) + 69/4O_2(g) \rightarrow 12CO_2(g) + 21/2H_2O(l) + 11/2N_2(g)$ (IV)

$$\Delta_{\rm f} H^{\rm o}{}_{298} \ (\mathbf{4}, \ \mathbf{l}) = 12 \Delta_{\rm f} H^{\rm o}{}_{298} \ ({\rm CO}_2, \ \mathbf{g}) + 21/2 \Delta_{\rm f} H^{\rm o}{}_{298} \ ({\rm H}_2 {\rm O}, \ \mathbf{l}) - \Delta_{\rm c} H^{\rm o}{}_{298} \ (\mathbf{4}, \ \mathbf{l}) \tag{4}$$

5: $C_{14}H_{25}N_{11}(l) + 81/4O_2(g) \rightarrow 14CO_2(g) + 25/2H_2O(l) + 11/2N_2(g)$ (V)

 $\Delta_{\rm f} H^{\rm o}{}_{298} \ ({\bf 5}, \ {\bf l}) \ = \ 14 \Delta_{\rm f} H^{\rm o}{}_{298} \ ({\rm CO}_2, \ {\rm g}) \ + \ 25/2 \Delta_{\rm f} H^{\rm o}{}_{298} \ ({\rm H}_2 {\rm O}, \ {\bf l}) \ - \ \Delta_{\rm c} H^{\rm o}{}_{298} \ ({\bf 5}, \ {\bf l}) \ ({\bf 5})$

6: $C_8H_{13}N_{11}(s) + 45/4O_2(g) \rightarrow 8CO_2(g) + 13/2H_2O(l) + 11/2N_2(g)$ (VI)

$$\Delta_{\rm f} H^{\rm o}_{298} (\mathbf{6}, {\rm s}) = 8\Delta_{\rm f} H^{\rm o}_{298} ({\rm CO}_2, {\rm g}) + 13/2\Delta_{\rm f} H^{\rm o}_{298} ({\rm H}_2{\rm O}, {\rm l}) - \varDelta_{\rm c} H^{\rm o}_{298} (\mathbf{6}, {\rm s})$$
(6)

7: $C_{14}H_{23}N_{13}(s) + 79/4O_2(g) \rightarrow 14CO_2(g) + 23/2H_2O(l) + 13/2N_2(g)$ (VII)

$$\Delta_{\rm f} H^{\rm o}{}_{298} \ (7, \ {\rm s}) = 14 \Delta_{\rm f} H^{\rm o}{}_{298} \ ({\rm CO}_2, \ {\rm g}) + 23/2 \Delta_{\rm f} H^{\rm o}{}_{298} \ ({\rm H}_2{\rm O}, \ {\rm l}) - \Delta_{\rm c} H^{\rm o}{}_{298} \ (7, \ {\rm s}) \ (7)$$

From the experimentally determined heats of combustion and the known heats of formation of CO₂ $(-393.51 \text{ kJ mol}^{-1})$ and H₂O $(-285.83 \text{ kJ mol}^{-1})$,^[19] the heats of formation of 1–7 are in the range 539.6–774.7 kJ mol⁻¹. The experimental heats of formation of these ionic liquids are in good agreement with the theoretical data. Of these nitrogen-rich ionic liquids, salt 1 possesses the highest specific heat of formation of 3018 kJ kg⁻¹. Although 7 has the highest heat of formation per mole, its specific heat of formation is relatively low at 2074 kJ kg⁻¹ because of its larger molecular weight owing to its two cations.

Ionic liquids 1–7 exhibit positive heats of formation, which illustrates that these ionic liquids may be highly energetic. The high heats of formation of the molecules are derived from the large number of N–N and N–C bonds in the nitrogen-rich HBTA⁻ anions. The molecules with higher nitrogen content have increased heats of formation. The neutral H₂BTA has more than 80% nitrogen content and a high heat of formation (633 kJ mol⁻¹). Therefore, these ionic liquids should have higher values for their heats of formation. These values are substantially higher than that of



TNT (-67 kJ mol⁻¹, -0.29 kJ g⁻¹).^[20] Compared with other 1-alkyl-3-methylimidazolium cation-based energetic salts, the heats of formation of **1**–7 are increased markedly. For instance, the heat of formation of **3** with the 1-butyl-3methylimidazolium cation is $\Delta_{\rm f} H^{\circ} = 638.8$ kJ mol⁻¹, which is much higher than those of the corresponding ionic liquids including dicyanamide (266.4 kJ mol⁻¹), nitrocyanamide (128.5 kJ mol⁻¹), 5-aminotetrazolate (305.9 kJ mol⁻¹), and dinitromethanide (-72.2 kJ mol⁻¹).^[9,14c]

Combustion Test

The ionic liquids 1–7 were examined by the hypergolic ignition test with white fuming nitric acid (WFNA, 100% HNO₃) to monitor their reactivity and evaluate their performance. After the ionic liquids were dropped into WFNA, no flames were observed, which indicates that no hypergolic processes occurred. This result suggests that these ionic liquids cannot be ignited by the WFNA oxidizer.

In 2006, Rogers et al. revealed the combustible characteristic of many energetic ionic liquids.^[21] Combustible ionic liquids may be of interest as propellants that can be ignited in air. Therefore, the combustion tests of 1–7 in air at room temperature were performed. With ignition by flame, the ionic liquids 1–7 ignited in a very short time and self-sustained combustion in air. For example, the combustion behavior of the ionic liquid 2 before and after ignition is shown in Figure 4. These ionic liquids contain only C, H, and N. Thus, no halogen or sulfuric byproducts will be generated during the combustion. These new nitrogen-rich energetic ionic liquids are environmental friendly during their energy release processes and could exhibit good combustible characteristics.



Figure 4. The combustion behavior of the ionic liquid 2.

Impact and Friction Sensitivities

The impact and friction sensitivities of the ionic liquids 1–7 were determined by using the standard BAM method.^[22] The collected impact sensitivity (IS) and friction sensitivity (FS) data are summarized in Table 4. All of the ionic liquids 1–7 are stable at 40 J (10 kg hammer, 40 cm) in fall-hammer experiments. Their friction sensitivities exceed 360 N. Based on the UN standard, these ionic liquids

are insensitive toward impact and friction.^[23] In the presence of dialkylimidazolium cations, HBTA⁻ and BTA²⁻ anions are potential nitrogen-rich structures for the construction of insensitive/safe energetic ionic liquids.

Conclusions

Nitrogen-rich energetic ionic liquids based on dialkylimidazolium cations and N,N-bis(1H-tetrazol-5-yl)amine anions (HBTA⁻/BTA²⁻) were synthesized under mild conditions. Their structures were verified by IR and NMR spectroscopy, elemental analysis, and high-resolution mass spectrometry. The single-crystal data of 1 showed the exact structure of the first nonmetallic salt with the HBTAmonoanion. The crystal structure of 7 reveals that ionic liquids with HBTA- monoanions may convert to those with BTA²⁻ dianions under certain conditions. Ionic liquids 1–7 are thermally stable to more than 220 °C. Among them, 2-5 are liquid at room temperature with liquid ranges exceeding 240 °C. The nitrogen contents of 1-7 are all higher than 40%. Ionic liquid 1 has the highest nitrogen content (61.78%). Their experimental standard heats of formation are between 539.6 and 774.7 kJ mol⁻¹, which are concordant with the theoretical heats of formation. Ionic liquids 1-7 are insensitive to impact (>40 J) and friction (>360 N). These CHN-type ionic liquids showed good combustion characteristics in air after flame ignition. These new nitrogen-rich energetic ionic liquids are of interest as potential safe and environmentally friendly liquid propellants.

Experimental Section

Caution: We have not experienced any problems in handling these compounds. Although they are impact- and friction-insensitive materials, we strongly suggest that they should be handled with extreme care by using all standard safety precautions such as leather gloves, leather coat, face shields, and ear plugs because of their high nitrogen content.

General Methods: All chemicals of analytically pure grade were obtained commercially and used as received. 1-Alkyl-3-methylimidazolium halides and 1,2,3-trimethylimidazolium iodide were prepared according to the literature procedure.^[24] Infrared spectra (IR) were recorded with a NEXUS 670 FT-IR spectrometer by using KBr pellets. ¹H and ¹³C NMR spectra were recorded with a Bruker 400 MHz nuclear magnetic resonance spectrometer with samples in [D₆]dimethyl sulfoxide ([D₆]DMSO). ¹H and ¹³C chemical shifts are reported in ppm relative to tetramethylsilane (TMS). Differential scanning calorimetry (DSC) measurements were performed with a TA DSC Q200 PC calorimeter equipped with an autocool accessory and calibrated by using standard pure indium, which was gently flooded with N_2 with a flow rate of 20 mL min⁻¹. Samples were sealed in aluminum pans with a hole (1 µm) on the top under nitrogen gas. Measurements were performed from -80 to 200 °C at 10 °C min⁻¹. Thermogravimetric analysis (TGA) measurements were accomplished with a NETZSCH TG 209F1 thermogravimetric analyzer by heating samples at 10 °C min⁻¹ from 25 to 500 °C in a dynamic nitrogen atmosphere at a flow rate of 70 mLmin⁻¹. Elemental analyses were performed with a Carlo-Erba 1106 Elemental Analyzer. High-resolution mass spectrometry (HRMS)

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measurements were performed with a Waters Q-TOF Premier mass spectrometer.

Theoretical Study: Computations were performed by the Gaussian03 (Revision E.01) suite of programs.^[25] The geometric optimization, frequency analyses, and NBO analyses were performed by using the popular Becke three-parameter hybrid functional Lee–Yang–Parr (B3LYP) analyses with the 6-31+G** basis set. Single-point energies (of gas-phase geometries) were calculated at the level of Møller-Plesset second-order perturbation theory truncated at the second order (MP2) with the 6-311++G** basis set. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

The theoretical heats of formation of the cations and anions were computed by using the method of isodesmic reactions (Scheme 5). The sources of the energies of the parent ions in the isodesmic reactions were calculated from protonation reactions [$\Delta_{\rm f} H^{\rm o}({\rm H}^+) = +1528.085 \text{ kJ mol}^{-1}$].^[26] The heats of formation of NH₂NH₃⁺ (+770.0 kJ mol⁻¹), the HBTA⁻ anion (+500.1 kJ mol⁻¹), and the BTA²⁻ anion (+630.0 kJ mol⁻¹) were taken from ref.^[15e] The enthalpies of reaction ($\Delta_{\rm r} H^{\rm o}_{298}$) were obtained by combining the MP2/6-311++G** energy differences for the reaction, the scaled zero point energies, and other thermal factors.

The theoretical heats of formation of the ionic liquids at T = 298.15 K were calculated based on a Born–Haber energy cycle (Scheme 6). In a Born–Haber energy cycle, the heat of formation of an ionic liquid can be simplified by the expression:



(a, b, c, d are the number of moles of the respective products)

Scheme 6. Born–Haber cycle for the heats of formation of the ionic liquids 1–7.

$$\Delta_{\rm f} H^{\rm o}(\text{ionic liquid, 298 K}) = \Sigma \Delta_{\rm f} H^{\rm o}(\text{cation, 298 K}) + \Sigma \Delta_{\rm f} H^{\rm o}(\text{anion,} 298 \text{ K}) - \Delta H_{\rm L}$$
(7)

where $\Delta H_{\rm L}$ is the lattice energy of the ionic salt. $\Delta H_{\rm L}$ (kJmol⁻¹) can be predicted by the formula suggested by Jenkins et al.:^[27]

$$\Delta H_{\rm L} = U_{\rm POT} + [p(nM/2-2) + q(n_{\rm X}/2-2)]RT$$
(8)

nM and n_X depend on the nature of the ions M^{p+} and X^{q-} , respectively, and have a value of six for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} has the form:

$$U_{\rm POT} = \gamma(\rho_{\rm m}/M_{\rm m}) \, 1/3 + \delta \tag{9}$$

Scheme 5. The isodesmic and protonation reactions of the ions in ionic liquids 1-7.

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 $\rho_{\rm m}$ is density (gcm⁻³) and $M_{\rm m}$ is the chemical formula mass of the ionic liquid. For MX (1:1) salts, γ is 1981.2 and δ is 103.8. Thus, $U_{\rm POT}$ of ionic liquids 1–6 is given by:

$$U_{\rm POT} = 1981.2(\rho_{\rm m}/M_{\rm m})^{1/3} + 103.8 \tag{10}$$

For M₂X (1:2) salts, γ is 8375.6 and δ is -178.8. Therefore, U_{POT} of ionic liquid 7 is given by:

$$U_{\rm POT} = 8375.6(\rho_{\rm m}/M_{\rm m})\,1/3-178.8\tag{11}$$

X-ray Crystallography: Single crystals of 1 or 7 were removed from the flask, and a suitable crystal was selected and attached to a glass fiber. The data were collected by using an Xcalibur Eos diffractometer with graphite-monochromated Mo- K_a radiation ($\lambda = 0.71073$). A Cryocool NeverIce low-temperature device was used to keep the crystals at a constant 134.95(10) K during data collection.

The data were measured by using omega scans of 0.3° per frame for 5 seconds, and a full sphere of data was collected. By using Olex2,^[28] the structures were solved with the SHELXS structure solution program by direct methods and refined with the SHELXL refinement package by using least-squares minimization.^[29] No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 5.

Table 5. Crystal data and structure refinement for 1 and 7.

	1	7
Formula	C ₇ H ₁₁ N ₁₁	C ₁₄ H ₂₃ N ₁₃
FW [gmol ⁻¹]	249.27	373.45
Size [mm]	$0.34 \times 0.30 \times 0.12$	$0.34 \times 0.30 \times 0.25$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a [Å]	14.0653(4)	17.5869(3)
b [Å]	6.9507(2)	12.8757(2)
<i>c</i> [Å]	22.4699(7)	21.9203(6)
a [°]	90.00	90.00
β [°]	93.996(3)	125.0580(10)
γ [°]	90.00	90.00
$V[Å^3]$	2191.38(12)	4063.15(15)
Z	8	8
$\rho [\text{g cm}^{-3}]$	1.511	1.221
T [K]	134.95(10)	134.95(10)
$\mu [{\rm mm}^{-1}]$	0.111	0.085
F [000]	1040.0	1584.0
λ (Mo- K_{α}) [Å]	0.71073	0.71073
Reflections	8643	15294
$R_{\rm int}$	0.0224	0.0199
Parameters	337	504
S on F^2	1.040	1.103
$R_1 [I > 2\sigma(I)]^{[a]}$	0.0408	0.0747
$wR_2 [I > 2\sigma(I)]^{[b]}$	0.0889	0.1686
R_1 [all data] ^[a]	0.0534	0.0920
wR_2 [all data] ^[b]	0.0953	0.1770
$\Delta \rho_{\min and max} [e Å^{-3}]$	0.19 and -0.24	0.31 and -0.29

[a] $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$. [b] $wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{1/2}$.

CCDC-913585 (for 7) and -913586 (for 1) 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.

Bomb Calorimetry: The calorimetric measurements were performed with a Parr 6725 bomb calorimeter (static jacket) equipped with a Parr 207A oxygen bomb. The samples were carefully dropped into the platinum crucible and were subsequently burned in a 3.05 MPa atmosphere of pure oxygen; Parr 45C10 alloy fuse wire was used for ignition. The experimental heats of combustion were obtained

from the average of three separate measurements with standard deviations calculated as a measure of experimental uncertainty. The bomb was examined for evidence of unburned carbon after each run. In all measurements, the calculater was calibrated by the

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run. In all measurements, the calorimeter was calibrated by the combustion of certified benzoic acid in an oxygen atmosphere at the same pressure of 3.05 MPa combined with a correction for burned wire.

Impact and Friction Sensitivity: Impact tests were performed with a BCJ impact sensitivity instrument. Test specimens were kept between two hardened anvils and a 10 kg drop weight was allowed to fall freely from different heights. Ten tests were conducted for each compound. The results are reported in terms of height for 50% probability of explosion of the sample. The friction tests were performed on a BMJ friction sensitivity instrument. The samples were kept between a fixed corrugated (rough) stainless steel plate and a movable stainless steel plate. Friction was generated by pulling the movable plate at varying lever loads.

1,3-Dimethylimidazolium *N,N-Bis*(1*H*-tetrazol-5-yl)amine (1): 1,3-Dimethylimidazolium iodide (448 mg, 2.0 mmol) was dissolved in methanol (20 mL). Then, silver *N,N*-bis(1*H*-tetrazol-5-yl)amine (AgHBTA, 780 mg, 3.0 mmol) was added to the solution. The resulting mixture was stirred in the dark overnight. Insoluble excess AgHBTA along with the precipitated silver iodide byproduct were removed. The filtrate was collected and dried in vacuo to yield white solid **1** (467 mg, 94%). Clear colorless plate crystals of **1** suitable for X-ray structure determination were obtained after recrystallization from methanol/ethyl acetate. ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 9.38 (s, 1 H), 7.67 (s, 2 H), 3.86 (s, 6 H) ppm. ¹³C NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 160.77, 137.86, 123.61, 35.84 ppm. IR (KBr): \tilde{v} = 3415, 3156, 3111, 1577, 1497, 1415, 1174, 1120, 840, 752, 630 cm⁻¹. C₇H₁₁N₁₁ (249.27): calcd. C 33.73, H 4.41; found C 33.67, H 4.67.

1-Ethyl-3-methylimidazolium *N*,*N*-**Bis(1***H*-**tetrazol-5-yl)amine (2):** A similar procedure was followed as that described above for **1**. 1-Ethyl-3-methylimidazolium bromide (382 mg, 2.0 mmol) and AgHBTA (780 mg, 3.0 mmol) were reacted in methanol to obtain a colorless liquid **2** (505 mg, 96%). ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 9.20 (s, 1 H), 7.78 (s, 1 H), 7.69 (s, 1 H), 4.18 (q, *J* = 7.2 Hz, 2 H), 3.84 (s, 3 H), 1.40 (t, *J* = 7.2 Hz, 3 H) ppm. ¹³C NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 156.97, 137.48, 135.79, 123.73, 122.15, 44.26, 35.85, 15.33 ppm. IR (KBr): \tilde{v} = 3392, 3151, 3105, 2877, 1604, 1571, 1460, 1377, 1256, 1168, 1112, 827, 768, 620 cm⁻¹. HRMS (ESI): calcd. for C₈H₁₃N₁₁ [M]⁺ 111.0917; found 111.0916; [M]⁻ 152.0439; found 152.0440. C₈H₁₃N₁₁ (263.13): calcd. C 36.50, H 4.98; found C 36.17, H 5.02.

1-Butyl-3-methylimidazolium *N*,*N*-Bis(1*H*-tetrazol-5-yl)amine (3): The same procedure was followed as that described above for **1**. 1-Butyl-3-methylimidazolium bromide (438 mg, 2.0 mmol) and AgHBTA (780 mg, 3.0 mmol) were reacted in methanol to obtain a pale yellow liquid **3** (548 mg, 94%). ¹H NMR (400 MHz, [D₆]-DMSO, 25 °C, TMS): δ = 9.37 (s, 1 H), 7.81 (s, 1 H), 7.74 (s, 1 H), 4.19 (t, *J* = 7.2 Hz, 2 H), 3.86 (s, 3 H), 1.78 (m, 2 H), 1.23 (m, 2 H), 0.88 (t, *J* = 6.8 Hz, 3 H) ppm. ¹³C NMR (400 MHz, [D₆]-DMSO, 25 °C, TMS): δ = 159.95, 137.07, 123.78, 122.50, 48.63, 36.01, 31.69, 19.00, 13.55 ppm. IR (KBr): \tilde{v} = 3425, 3141, 3069, 2960, 2871, 1616, 1570, 1464, 1378, 1340, 1170, 1113, 841, 756, 622 cm⁻¹. HRMS (ESI): calcd. for C₁₀H₁₇N₁₁ [M]⁺ 139.1230; found 139.1230; [M]⁻ 152.0439; found 152.0437. C₁₀H₁₇N₁₁ (291.32): calcd. C 41.23, H 5.88; found C 41.17, H 6.25.

1-Hexyl-3-methylimidazolium *N*,*N*-**Bis(1***H***-tetrazol-5-yl)amine (4): The same procedure was followed as that described above for 1**. 1-Hexyl-3-methylimidazolium bromide (495 mg, 2.0 mmol) and

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AgHBTA (780 mg, 3.0 mmol) were reacted in methanol to obtain a colorless liquid 4 (607 mg, 95%). ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 9.32 (s, 1 H), 7.78 (s, 1 H), 7.71 (s, 1 H), 4.18 (t, J = 7.2 Hz, 2 H), 3.86 (s, 3 H), 1.74 (m, 2 H), 1.25 (m, 6 H), 0.86 (t, J = 6.8 Hz, 3 H) ppm. ¹³C NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 159.49, 137.18, 123.80, 122.48, 48.91, 35.97, 30.83, 29.69, 25.39, 22.15, 14.10 ppm. IR (KBr): $\tilde{\nu}$ = 3392, 3147, 3080, 2927, 2856, 1603, 1571, 1464, 1375, 1169, 1114, 841, 754, 654, 623 cm⁻¹. HRMS (ESI): calcd. for C₁₂H₂₁N₁₁ [M]⁺ 167.1543; found 167.1541; [M]⁻ 152.0439; found 152.0440. C₁₂H₂₁N₁₁ (319.37): calcd. C 45.13, H 6.63; found C 45.37, H 6.84.

1-Methyl-3-octylimidazolium *N*,*N*-Bis(1*H*-tetrazol-5-yl)amine (5): The same procedure was followed as that described above for 1. 1-Methyl-3-octylimidazolium bromide (547 mg, 2.0 mmol) and AgHBTA (780 mg, 3.0 mmol) were reacted in methanol to obtain a colorless liquid **5** (667 mg, 96%). ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 9.35 (s, 1 H), 7.78 (s, 1 H), 7.71 (s, 1 H), 4.16 (t, *J* = 7.2 Hz, 2 H), 3.85 (s, 3 H), 1.75 (m, 2 H), 1.23 (m, 10 H), 0.85 (t, *J* = 6.8 Hz, 3 H) ppm. ¹³C NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 159.65, 137.13, 123.79, 122.43, 48.91, 35.97, 31.45, 29.76, 28.78, 25.76, 22.34, 14.21 ppm. IR (KBr): \hat{v} = 3373, 3253, 3134, 3084, 2959, 2863, 1616, 1570, 1464, 1343, 1169, 1110, 837, 760, 656, 623 cm⁻¹. HRMS (ESI): calcd. for C₁₄H₂₅N₁₁ [M]⁺ 195.1856; found 195.1853; [M]⁻ 152.0439; found 152.0440. C₁₄H₂₅N₁₁ (347.42): calcd. C 48.40, H 7.25; found C 48.76, H 7.52.

1,2,3-Trimethylimidazolium *N,N*-Bis(1*H*-tetrazol-5-yl)amine (6): The same procedure was followed as that described above for **1**. 1,2,3-Trimethylimidazolium iodide (476 mg, 2.0 mmol) and AgHBTA (780 mg, 3.0 mmol) were reacted in methanol to obtain a white solid **6** (350 mg, 94%). ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 7.55 (s, 2 H), 3.72 (s, 6 H), 2.51 (s, 3 H) ppm. ¹³C NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 156.88, 145.17, 122.39, 35.12, 9.54 ppm. IR (KBr): \tilde{v} = 3441, 3072, 2904, 1633, 1518, 1414, 1251, 1135, 759, 652, 564 cm⁻¹. HRMS (ESI): calcd. for C₈H₁₃N₁₁ [M]⁺ 111.0917; found 111.0915; [M]⁻ 152.0439; found 152.0438. C₈H₁₃N₁₁ (263.13): calcd. C 36.50, H 4.98; found C 36.82, H 5.20.

Bis(1,2,3-Trimethylimidazolium) *N,N*-**Bis(1***H***-tetrazol-5-yl)amine (7): Transparent colorless plate crystals of 7 suitable for X-ray structure determination were obtained after recrystallization of 6** from methanol/ethyl acetate. ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 7.58 (s, 2 H), 3.74 (s, 6 H), 2.54 (s, 3 H) ppm. ¹³C NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 160.56, 144.63, 121.92, 34.77, 8.93 ppm. IR (KBr): \tilde{v} = 3437, 3081, 2893, 1632, 1517, 1254, 1136, 767, 649 cm⁻¹. C₁₄H₂₃N₁₃ (373.45): calcd. C 45.02, H 6.16; found C 45.13, H 6.02.

Supporting Information (see footnote on the first page of this article): ¹H and ¹³C NMR, IR, MS, TGA, and DSC data of 1–7.

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Energetic Ionic Liquids

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/KAP1

Nitrogen-Rich Energetic Ionic Liquids Based on the *N*,*N*-Bis(1*H*-tetrazol-5-yl)amine Anion – Syntheses, Structures, and Properties

Keywords: Energetic materials / Propellants / Ionic liquids / Nitrogen heterocycles / Heats of formation



Nitrogen-rich energetic ionic liquids based on the N,N-bis(1H-tetrazol-5-yl)amine anion were synthesized. These ionic liquids have high nitrogen contents, high heats of formation, and high stabilities to heat, impact, and friction. These nitrogen-rich energetic ionic liquids combust in air after ignition with a flame. They are potential environmentally friendly liquid propellants.

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