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Liquid Azide Salts

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Ionic liquid azides from azidoethyl, alkyl, and alkenyl substituted derivatives of 1,2,4- and 1,2,3-amino-triazoles were prepared and examined for the first time to investigate their structural and physical properties. All reported salts possess melting points below 100 °C. The unique character of these newly discovered ionic liquid azides is based upon the fact that these molecules are not simple protonated salts like previously reported substituted hydrazinium azides. The presence of quaternary nitrogen confers both thermal stability and negligible volatility.

Introduction

The azide anion was discovered by Curtius in 1890.[1] Ever since, azide chemistry has fascinated generations of chemists. Covalent and ionic azides have been prepared involving almost every single element from the periodic table. Only recently, the chemistry of simple main-group and transition-metal azides have provided another high point in azide chemistry.[2–31] However, so far, azides have found only limited use because of their violent, explosive character, toxic decomposition products, and the attendant danger in handling them. The lately discovered transition-metal azides are no exception to that tendency. A process for the controlled decomposition of azides would be especially valuable because of the high exothermicity of the reaction and the low molecular weight of the decomposition gases (e.g., eq 1).[32]

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$$H_2NNH_3^+N_3^- \xrightarrow[\text{measured after explosion}]{\Delta} 2.18N_2 + 1.52H_2 + 0.65NH_3 \quad (1)$$

Like the azide anion, hydrazinium azide was also discovered by Curtius.[33] The usefulness of hydrazinium azide and other closely related azides as energetic materials has been covered in a series of papers and patents.[34–36] Surprisingly, no comprehensive studies were reported for nearly 30 years, until Klapötke et al. investigated the structural and physical properties of hydrazinium azides in great detail. Unfortunately, these materials are volatile and hygroscopic.[37–44]

Two of the first compounds studied, hydrazinium azide, $[H_2NNH_3]^+[N_3]^-$, and hydrazinium azide hydrazinate, $[H_2NNH_3]^+[N_3]^- \cdot H_2NNH_2$, possess melting points of 75 and 65 °C, respectively. This qualifies them as ionic liquids (ILs) according to the conventional definition (i.e., a salt with a melting point $\leq$ 100 °C). Over the past decade, ILs have received much attention as replacements for common organic solvents and more recently as energetic materials because of their desirable characteristics.[45] The newly discovered IL azides described herein are unique in not being simple, protonated salts like the previously reported substituted and unsubstituted hydrazinium azides. Substitution of the hydrogens of hydrazinium azide with methyl groups leads to an increase in volatility. In addition, the undesirable and dangerous elimination of HN_3 from these molecules becomes more favorable.[37–44] In the compounds presented here, the presence of quaternary nitrogen confers both thermal stability and negligible volatility along with low vapor toxicity. Previously reported azides, particularly urotropinium azide,[46] permethylated hydrazinium azides,[39] and 1,5-diamino-4-methyl-tetrazolium azide,[47] showed melting points exceeding the benchmark for an IL. The salts reported here possess melting points below 100 °C, and some are even room-temperature ILs.

Experimental Section

General Information. ***Caution!*** *None of the prepared triazolium azides appeared to show particular sensitivity toward friction or impact, and no accidents or mishaps occurred during this work. However, the use of appropriate safety precautions (safety shields, face shields, leather gloves, and protective clothing such as heavy leather welding suits and ear plugs) is essential for work with energetic materials, especially when working on a larger scale. Silver azide is a well-known energetic material and can explode violently under certain conditions. Ignoring safety precautions can lead to serious injuries.*

All chemical reagents and solvents were purchased from Aldrich Chemical Co., Inc. and their purities were checked by ^1H and ^{13}C NMR prior to use. The alkyl halides (allyl bromide, 1,2-dibromoethane, methyl iodide), 4-amino-1,2,4-triazole (99%), acetonitrile (99.93+% HPLC grade), methanol (99.93% ACS HPLC grade), diethyl ether (anhydrous, 99+%, ACS reagent), and the azide exchange resin (azide on Amberlite IRA-400, 16–50 mesh, ~3.8 mmol N_3/g) were used as received. 2-Bromoethanol was distilled with the exclusion of light and stored inside a sealed Schlenk vessel under nitrogen in the dark. 1-Amino-1,2,3-triazole[48] and the triazolium halide salts[48,49] were prepared according to literature procedures. Silver azide was prepared according to a literature procedure,[42] but it was thoroughly washed with either ethanol or methanol instead of water. The silver azide was always kept suspended in alcohol and never allowed to dry! Nonvolatile solids were handled in the dry nitrogen atmosphere of a glovebox. Raman spectra were recorded in the range 4000–80 cm^{-1} on a Bruker Equinox 55 FT-RA 106/S spectrometer using a Nd-Yag laser at 1064 nm. Pyrex melting point capillaries or 5 mm glass NMR tubes were used as sample containers. Nuclear magnetic resonance spectra were recorded on a Bruker Spectrospin DRX 400 MHz Ultrashield spectrometer at room temperature with each salt sample being measured as a neat liquid or dissolved in DMSO-d_6 in 5 mm NMR tubes. The ^1H and ^{13}C spectra were referenced to external samples of neat TMS; ^{14}N and ^{15}N (natural abundance) spectra were referenced to external samples of neat nitromethane. Melting points were determined by differential scanning calorimetry using a Thermal Analyst 200, Dupont 910 differential scanning calorimeter. Measurements were carried out at a heating rate of 10 °C/min in sealed aluminum pans with a nitrogen flow rate of 20 mL/min. The reference sample was an empty Al container which was sealed in the nitrogen atmosphere of a glovebox. Impact testing was carried out on an Olin-Mathieson-style drop weight tester where a small sample (20 mg) was placed in a steel cup and a two-kilogram mass was dropped vertically upon a closed sample.[63] The minimum drop height in centimeters was recorded for five consecutive negative tests. A five microgram sample of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) was used as a standard and has a value of 34 kg cm. For friction testing, a Julius-Peters-style friction tester was employed whereby a small amount of sample (20 mg) was placed on a small ceramic square plate, and a steel pin was pushed across the sample under a known load. Any evidence of discoloration, odor, smoke, or spark was considered a positive test.

X-ray Analyses. The single crystal X-ray diffraction data were collected on a Bruker 3-circle platform diffractometer equipped with

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a SMART detector with the χ-axis fixed at 54.74° and using Mo Kα radiation (λ = 0.71073 Å) from a fine-focus tube. The diffractometer was equipped with a KryoFlex apparatus for low temperatures using controlled liquid nitrogen boil off. The goniometer head, equipped with a nylon Cryoloop and magnetic base, was used to mount the crystals using perfluoropolyether oil. Cell constants were determined from 90 ten-second frames. A complete hemisphere of data was scanned on omega (0.3 °) with a run time of ten-seconds per frame at a detector resolution of 512 × 512 pixels using the SMART software.[50,51] A total of 2400 frames were collected in four sets and final sets of 50 frames, identical to the first 50 frames, were also collected to determine any crystal decay. The frames were then processed using the SAINT software[52,53] to give the hkl file corrected for Lp/decay. For the structure of **4**, the absorption correction was performed using the SADABS[54] program. The structures were solved by the direct method using the SHELX-90[55] program and refined by the least-squares method on F^2 using SHELXL-97[56] incorporated in SHELXTL suite 5.10.[57,58] All nonhydrogen atoms were refined anisotropically. For the anisotropic displacement parameters, the U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The hydrogen atoms were located either from difference electron density maps or generated at calculated positions.

1-Methyl-4-amino-1,2,4-triazolium Azide (1a). To a 500 mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 3.97 g (17.56 mmol) of 1-methyl-4-amino-1,2,4-triazolium iodide was added and dissolved in about 200 mL of ethanol. All further handlings were carried out with the exclusion of light. A 19.47 mmol (2.92 g) quantity of freshly prepared silver azide was added to the stirred triazole solution. Stirring was continued for 24 h. The silver iodide formed, together with excess silver azide, was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind an off-white solid. Yield: 74%; melting point (peak): +43 °C; decomp. onset: +129 °C. Raman (200 mW, 25 °C, cm^{-1}) ν = 3251(1), 3150(4), 3060(5), 3021(4), 2952(12), 2821(4), 1621(4), 1573(5), 1539(2), 1433(4), 1405(44), 1330(77), 1262(1), 1244(9), 1226(5), 1177(4), 1093(7), 1075(19), 1029(3), 984(16), 914(0+), 891(0+), 740(2), 657(1), 617(11), 455(7), 332(6), 303(6), 123(100), 102(84), 85(76); δ_{1H} (400 MHz, neat liquid at +50 °C) 9.61 (1H, s, br), 8.55 (1H, s, br), 6.55 (2H, s, br, NH_2), 3.77(3H, s, br, CH_3); δ_{13C} (100 MHz, neat liquid at +50 °C) 145.5, 143.6, 39.1.

1-Amino-3-methyl-1,2,3-triazolium Azide (1b). Method (a). To a 500 mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 4.99 g (22.07 mmol) of 1-amino-3-methyl-1,2,3-triazolium iodide was added and dissolved in about 40 mL of methanol. All further handlings were carried out with the exclusion of light. 30.04 mmol (4.50 g) of freshly prepared silver azide was added to the stirred triazole solution. Stirring was continued for 24 h. The silver iodide formed, together with excess silver azide, was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind a white solid. Raman and NMR spectroscopies revealed product contamination by NaN_3 which remained from the AgN_3 preparation.

Method (b). To a 250 mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 1.92 g (8.49 mmol) of 1-amino-3-methyl-1,2,3-triazolium iodide was added and dissolved in about 30 mL of acetonitrile. A 11.18 g quantity of azide exchange resin (3.8 mmol N_3/g = 42.48 mmol) was added to the stirred solution. Stirring was continued for 16 h. The insoluble polymeric reagent was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind a white crystalline solid. Yield 98%; melting point (peak): +50 °C; decomp. onset +156 °C. Raman (200 mW, 25 °C, cm^{-1}) ν = 3150(4), 3143(6), 3013(17), 2953(15), 2938(14), 2866(4), 2821(2), 2782(1), 1536(5), 1480(4), 1469(4), 1449(2), 1418(3), 1398(7), 1332(29), 1256(4), 1225(0+), 1199(1), 1093(13), 1049(5), 1037(3), 983(0+), 942(4), 750(2), 732(2), 635(5), 626(4), 488(6), 462(1), 452(3), 333(2), 322(3), 102(56), 84(100); δ_{1H} (400 MHz, DMSO) 8.80 (1H, s), 8.58 (1H, s), 8.49 (2H, s, NH_2), 4.23(3H, s, CH_3); δ_{13C} (100 MHz, DMSO) 131.9, 127.1, 40.05.

1-(2-Hydroxyethyl)-4-amino-1,2,4-triazolium Azide (2). To a 500 mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 4.13 g (19.74 mmol) of 1-hydroxyethyl-4-amino-1,2,4-triazolium bromide was added and dissolved in about 50 mL of ethanol. All further handlings were carried out with the exclusion of light. A 23.85 mmol (3.58 g) quantity of freshly prepared silver azide was added to the stirred triazole solution. Stirring was continued for 36 h. The silver bromide formed, together with excess silver azide, was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind a pale yellow liquid. Yield: 92%; glass transition: −50 °C; decomp. onset: +129 °C.

In a modification of the above procedure, water was used instead of methanol as a solvent. An isolated yield of the pure product, 83%, was achieved. Raman (500 mW, 25 °C, cm^{-1}) ν = 3147(5), 3010(6), 2961(18), 2884(8), 2731(2), 1628(2), 1563(4), 1524(4), 1465(6), 1442(6), 1409(24), 1331(36), 1247(7), 1190(4), 1161(3), 1076(16), 989(8), 947(5), 871(7), 723(4), 676(2), 630(5), 606(9), 501(5), 451(5), 347(4), 306(3), 261(7), 104(78), 84(100); δ_{1H} (400 MHz, neat liquid) 9.48 (1H, s, br), 8.45 (1H, s, br), 6.30 (2H, s, br, NH_2), 4.71 (1H, s, OH), 4.00 (2H, s, br, $-CH_2CH_2OH$), 3.36 (2H, s, br, $-CH_2CH_2OH$); δ_{13C} (100 MHz, neat liquid) 145.8, 143.4, 59.0, 55.5.

1-Allyl-4-amino-1,2,4-triazolium Azide (3a). To a 250 mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 0.83 g (4.08 mmol) 1-allyl-4-amino-1,2,4-triazolium bromide was added and dissolved in about 30 mL of acetonitrile. A 5.19 g quantity of azide exchange resin (3.8 mmol N_3/g = 19.72 mmol) was added to the stirred solution. Stirring was continued for 16 h. The insoluble polymeric reagent was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind an amber liquid. Yield 97%; glass transition: −57 °C; decomp. onset: +109 °C. Raman (500 mW, 25 °C, cm^{-1}) ν = 3136(5), 3121(7), 3087(11), 3023(14), 2984(15), 2942(16), 2876(2), 1647(16), 1559(4), 1519(2), 1413(13), 1328(19), 1293(8), 1247(2), 1202(0+), 1073(9), 998(4), 946(3), 920(2), 697(1), 652(2), 618(1), 573(3), 505(1), 456(2), 400(2), 289(0+), 107(48), 84(100); δ_{1H} (400 MHz, DMSO) 10.24 (1H, s), 9.22 (1H, s), 7.06 (2H, s, NH_2), 6.02 (1H, m, $CH_2CH{=}CH_2$), 5.38 (2H, m, $CH_2CH{=}CH_2$), 5.02 (2H, d, $CH_2CH{=}CH_2$); δ_{13C} (100 MHz, DMSO) 145.8, 143.3, 130.8, 121.4, 54.3.

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Table 1. ^{15}N, ^{14}N NMR Chemical Shifts (ppm), Coupling Constants (J, Hz), ^{14}N Half-Width ($\Delta_{1/2}$, Hz) for the Compounds Studied[f,g]

compd		N1	N2	N3	N4	Nα′	Nβ′	Nγ′	Nα	Nβ
4AT[60]	^{15}N[c]	−198.2	−66.1	−66.1	−315.5					
1AT[h]	^{15}N[c]	−129.3	−39.7	−22.8	−300.6 ^{1}J (69)					
	^{14}N[a]	−128 $\Delta_{1/2}$ (700)	[d]	−23 $\Delta_{1/2}$ (1600)	−313 $\Delta_{1/2}$ (2000)					
1a	^{15}N[a]	−187.8 (10.4)	−86.5 (−20.4)	−169.3 (−103.2)	−303.9 (11.6) ^{1}J (70)				−277.3	−132.8
	^{14}N[b]	−190 $\Delta_{1/2}$ (350)	−85 $\Delta_{1/2}$ (800)	−170 $\Delta_{1/2}$ (200)	[e]				−283 $\Delta_{1/2}$ (150)	−133 $\Delta_{1/2}$ (45)
1b	^{15}N[c]	−119.2 (10.1)	−48.2 (−8.5)	−151.6 (−128.8)	−284.6 (16.0) ^{1}J (73)				−278.5	−133.2
	^{14}N[c]	[d]	[e]	∼−140 $\Delta_{1/2}$ (1700)	[e]				−276 $\Delta_{1/2}$ (200)	−132 $\Delta_{1/2}$ (70)
2	^{15}N[a]	−189.2 (9.0)	−89.7 (−23.6)	−164.0 (−97.9)	−306.1 (9.4) ^{1}J (72)				−279.6	−134.7
	^{14}N[b]	−188 $\Delta_{1/2}$ (500)	[e]	−161 $\Delta_{1/2}$ (300)	[e]				−283 $\Delta_{1/2}$ (200)	−133 $\Delta_{1/2}$ (60)
3a	^{15}N[a]	−187.2 (11.0)	−87.6 (−21.5)	−160.9 (−94.8)	−301.3 ^{1}J (71)				−276.1	−132.0
	^{14}N[c]	[e]	[e]	[e]	[e]				−277 $\Delta_{1/2}$ (40)	−131 $\Delta_{1/2}$ (75)
3b	^{15}N[c]	−121.0 (8.3)	−47.4 (−7.7)	−141.4 (−118.3)	−283.4 (17.2) ^{1}J (64)				−277.6	−133.4
	^{14}N[c]	[e]	[e]	[e]	[e]				−279 $\Delta_{1/2}$ (800)	−134 $\Delta_{1/2}$ (400)
5	^{15}N[c]	−187.8 (10.4)	−89.5 (−23.4)	−166.0 (−99.9)	−305.0 (10.5) ^{1}J (73)	−172.0	−132.1	−319.1	−277.2	−134.9
	^{14}N[c]	[d]	[e]	−170 $\Delta_{1/2}$ (700)	[e]	[e]	−133 $\Delta_{1/2}$ (140)	[d]	−276 $\Delta_{1/2}$ (130)	−132 $\Delta_{1/2}$ (30)

[a] Neat liquid. [b] d_4-MeOH solution. [c] DMSO solution. [d] Overlapping with N3. [e] Not observed. [f] PIS effect in parentheses. [g] Shifts were referenced to an external sample of neat CH_3NO_2. [h] This work.

1-Amino-3-allyl-1,2,3-triazolium Azide (3b). To a 250 mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 1.83 g (8.97 mmol) 1-allyl-4-amino-1,2,4-triazolium bromide was added and dissolved in about 30 mL of acetonitrile. A 12.83 g quantity of azide exchange resin (3.8 mmol N_3/g = 48.75 mmol) was added to the stirred solution. Stirring was continued for 16 h. The insoluble polymeric reagent was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind an amber liquid. Yield 97%; glass transition: −62 °C; decomp. onset: +114 °C. Raman (500 mW, 25 °C, cm^{-1}) ν = 3089(8), 3027(13), 2987(14), 2948(15), 1669(3), 1646(14), 1529(4), 1420(8), 1331(24), 1295(7), 1248(3), 1219(3), 1086(5), 1052(14), 950(4), 921(2), 775(1), 754(0+), 703(4), 663(3), 634(3), 579(3), 482(2), 396(2), 84(100); δ_{1H} (400 MHz, DMSO) 8.85 (1H, s), 8.58 (1H, s), 8.57 (2H, s, NH_2), 6.01 (1H, m, $CH_2CH{=}CH_2$), 5.33 (2H, m, $CH_2CH{=}CH_2$), 5.22 (2H, d, $CH_2CH{=}CH_2$); δ_{13C} (100 MHz, DMSO) 130.9, 130.3, 127.1, 122.0, 55.2.

1-(2-Bromoethyl)-4-amino-1,2,4-triazolium Bromide (4). To a 500 mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 9.89 g (117.63 mmol) 4-amino-1,2,4-triazole was added and dissolved in about 100 mL of acetonitrile at +80 °C. Twenty mL (232 mmol) of 1,2-dibromoethane were added dropwise to the stirred solution. Stirring was continued for about 3 h. The mixture was cooled and the precipitate was removed by filtration and dried in a dynamic vacuum. The precipitate consisted of 68.4% (based on 4-amino-1,2,4-triazole) 1,1-ethylene-bis-(4-amino-1,2,4-triazolium) dibromide. The mother liquor was transferred to a Schlenk flask, and the volatiles were removed in a dynamic vacuum leaving behind a crystalline white solid. Yield of the desired product 29.9% (based on 4-amino-1,2,4-triazole); melting point: +131 °C; decomp. onset: 154 °C. Raman (500 mW, 25 °C, cm^{-1}) ν = 3176(13), 3129(15), 3110(20), 3071(12), 3012(33), 2980(32), 2958(73), 2940(77), 2833(5), 2730(4), 1564(13), 1522(9), 1424(27), 1405(22), 1376(9), 1332(10), 1309(9), 1256(10), 1200(7), 1179(7), 1129(5), 1077(16), 1044(8), 984(13), 931(11), 887(4), 869(4), 709(7), 625(5), 602(10), 561(71), 459(10), 434(8), 333(10), 283(7), 209(17), 171(16), 120(29), 85(100), 70(42); δ_{1H} (400 MHz, DMSO) 10.41 (1H, s), 9.33 (1H, s), 7.16 (2H, s, NH_2), 4.84 (1H, t, $-CH_2CH_2Br$), 3.99 (2H, t, CH_2CH_2Br); δ_{13C} (100 MHz, DMSO) 146.0, 143.7, 53.5, 30.4.

1-(2-Azidoethyl)-4-amino-1,2,4-triazolium Azide (5). To a 500 mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 0.51 g (1.88 mmol) 1-(2-bromoethyl)-4-amino-1,2,4-triazolium bromide was added and dissolved in about 150 mL of acetonitrile. A 2.95 g quantity of azide exchange resin (3.8 mmol N_3/g = 11.21 mmol) was added to the stirred solution. Stirring was continued for about 16 h. The insoluble polymeric reagent was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind a dark amber liquid. Yield 98%; glass transition: not observed; decomp. onset: +106 °C. Raman (500 mW, 25 °C, cm^{-1}) ν = 3088(7), 2955(19), 2875(6), 2743(3), 2249(5), 2109(6), 1647(5), 1561(7), 1522(6), 1443(11), 1410(24), 1327(32), 1245(10), 1191(5), 1073(15), 1021(7), 983(9), 944(4), 836(7), 724(4), 675(4), 631(8), 603(9), 489(4), 447(4), 84(100); δ_{1H} (400 MHz, DMSO) 10.33 (1H s,), 9.28 (1H, s,), 7.14 (2H, s, NH_2), 4.56 (1H, t, $-CH_2CH_2N_3$), 3.92 (2H, t, $CH_2CH_2N_3$); δ_{13C} (100 MHz, DMSO) 145.9, 143.8, 51.6, 48.9.

Results and Discussion

Synthesis. The different azide salts (**1a**−**3b**, **5**) were readily prepared by exchange of the halide for the azide using silver azide. The insoluble silver azide can be used in excess assuring essentially complete conversion and can be separated together with the silver halide formed during the metathesis. This process guarantees a highly pure IL azide product. To avoid the cumbersome handling

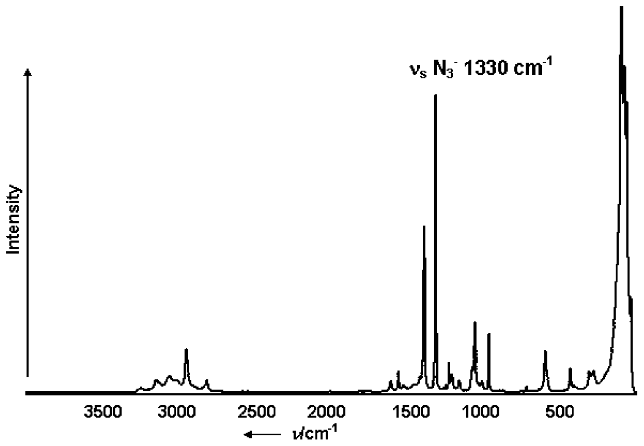


Figure 1. Raman spectrum of 1-methyl-4-amino-1,2,4-triazolium azide (**1a**).

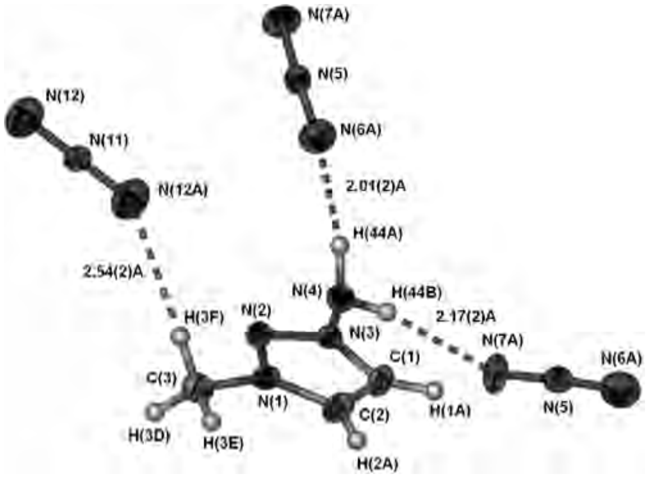


Figure 2. ORTEP (Oak Ridge thermal ellipsoid plot) diagram showing the conformation, the atom numbering scheme, and the hydrogen bond network of 1-amino-3-methyl-1,2,3-triazolium azide (disorder removed for clarity) (**1b**).

of silver azide, an alternative route was developed employing a polymeric quaternary ammonium azide exchange resin (eqs 2−6).

The exchange resin method is easier to perform, but a small contamination from the polymeric reagent cannot be easily avoided, giving the isolated products, especially in the case of liquids, a very distinctive, amine-like smell. ^{1}H NMR spectroscopy showed amounts of less than 2% contamination. All salts are soluble in polar solvents such as acetonitrile, methanol, and water but are insoluble in diethyl ether, hexane, dichloromethane, and ethyl acetate. This can be used for further purification if required. All salts were characterized by ^{1}H, ^{13}C, ^{14}N and ^{15}N NMR, Raman spectroscopy and differential scanning calorimetry (DSC) analysis, and salt **1b** was additionally characterized by single crystal X-ray analysis. For the preparation of **5**, a simple two-step route was employed (eqs 7, 8).

In the first step, compound **4** was prepared in reasonable yield by alkylating 4-amino-1,2,4-triazole with 1,2-dibromoethane. It was identified by Raman and NMR spectroscopy and by X-ray crystallography. In a second step, **4** was treated with an azide exchange resin yielding **5** in a straightforward manner.

Vibrational Spectroscopy. Raman spectroscopy proved very useful for the qualitative analysis of these compounds. The symmetric stretch band for the azide anion, ν_s, is very prominent in the Raman spectra and is observed around 1330 cm^{-1}(e.g., Figure 1).

In the IL azides, the strong hydrogen-bond network seen in the X-ray crystal structure of **1b** (Figure 2) and discussed below causes a shift of the ν_s azide vibration to lower wavenumbers, about 30 cm^{-1} from ν_s in sodium azide.[59]

A comparison of the Raman spectra of **4** and **5** was used to check that **4** was completely converted into **5**. Halogen-carbon vibrations are usually very intense within Raman spectra, and the major contribution to the vibration at 561 cm^{-1} apparently comes from C−Br vibration in the bromoethyl group. This band is entirely missing from the spectrum of **5** which indicates a quantitative exchange.

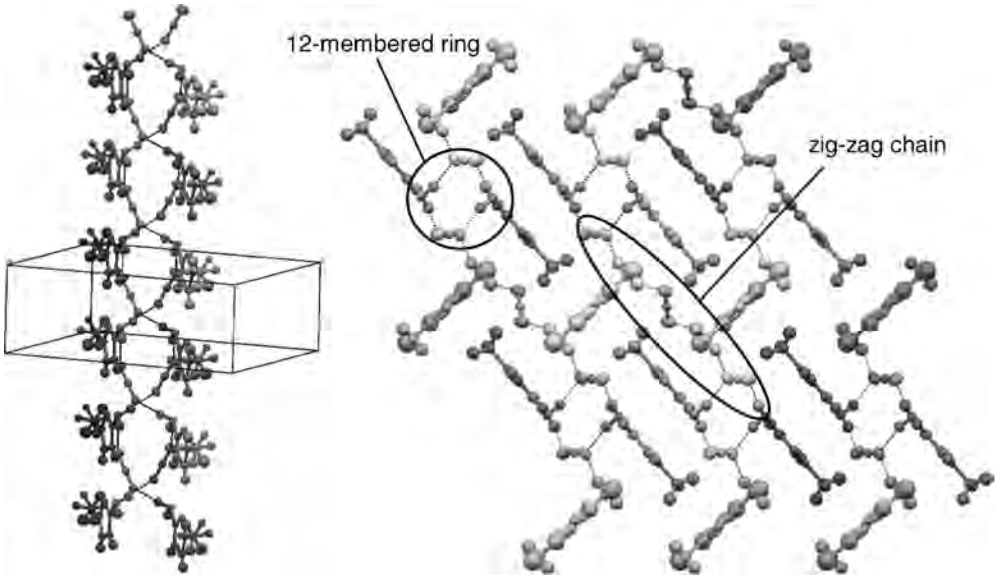
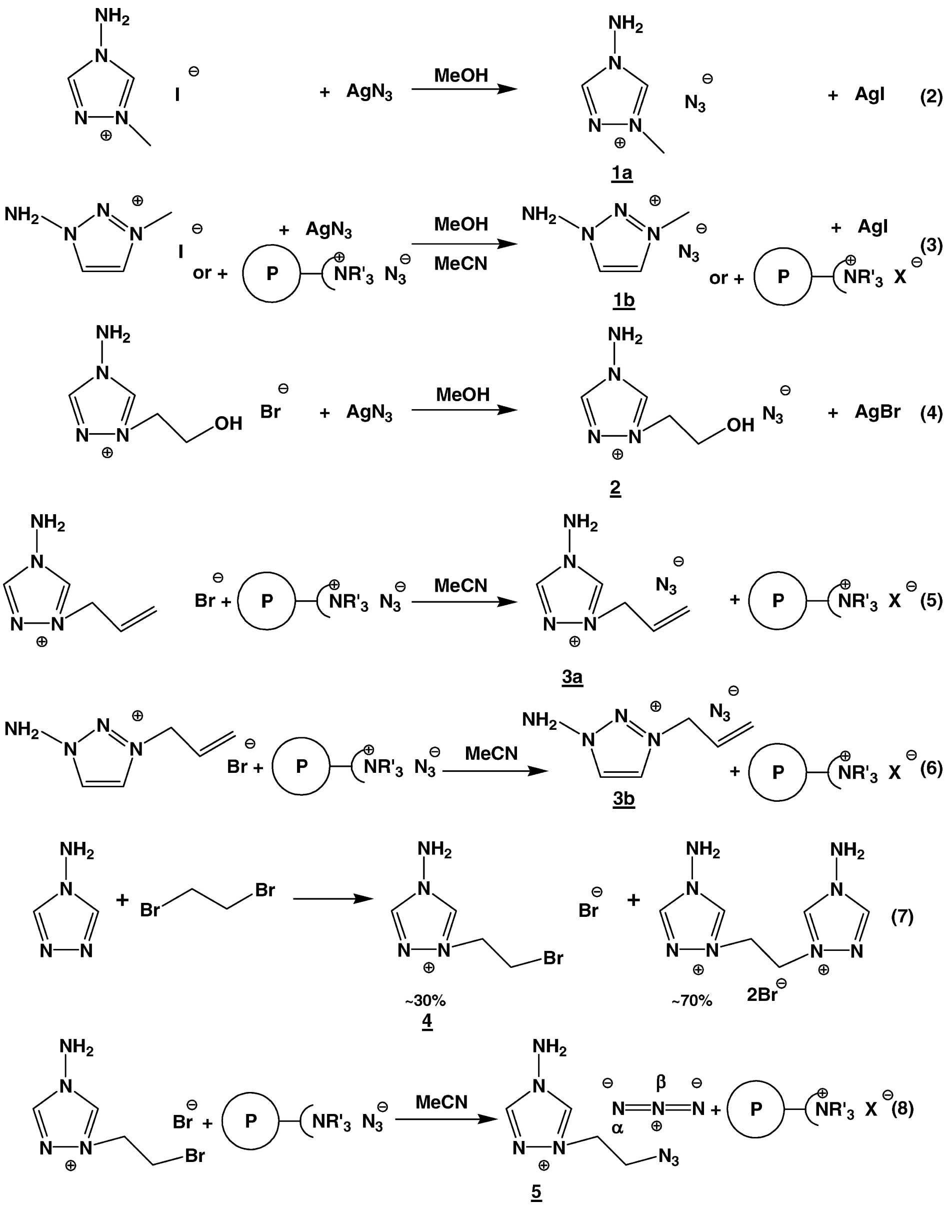


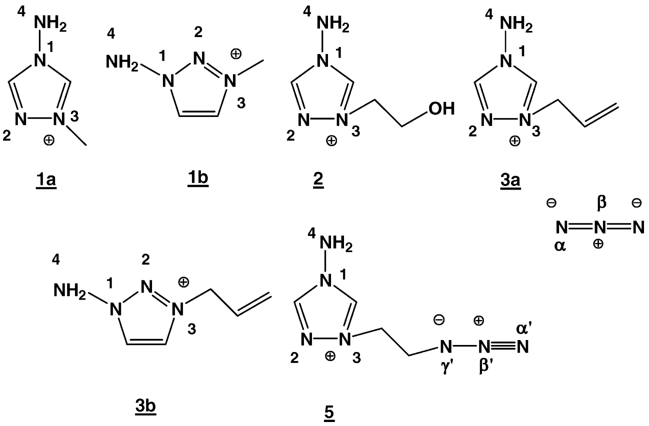
Figure 3. (left) Right handed helix formed by two hydrogen bonded chains of alternating triazole group and azide ions. These helixes run along the *b-axis* and are ~3.8 Å apart. (right) Packing diagram including hydrogen bonding along the *b-axis* of **1b**.



^{14}N and ^{15}N NMR Spectra. ^{15}N NMR spectroscopy is the only suitable method of accounting for all nitrogens in the compounds. The ^{14}N and ^{15}N NMR chemical shifts of the neutral and alkylated compounds are listed in Table 1, and nitrogen atoms are assigned according to Scheme 1.

In the ^{14}N NMR spectra, signals for the non azide nitrogens were either not at all or only partially observable because of line broadening. In 1-amino-1,2,3-triazoles, alkylation can take place either on the N2 or on the N3 position. To determine the site of alkylation, a study of the ^{15}N protonation-induced shift (PIS), here actually alkylation-induced, has been a useful method in the past.[47,60] It has been found that the protonated/alkylated nitrogen is marked by the greatest PIS. For this purpose, the ^{14}N and ^{15}N data for 1-amino-1,2,3-triazole were recorded, and comparison with the corresponding 4-amino-1,2,4-triazoles clearly indicates on which nitrogen alkylation occurs. The largest PIS is observed for the N3 nitrogen in the alkylated 4-amino-1,2,4-triazolium azides and is negative (~100 ppm upfield shift). In the 1-amino-1,2,3-triazoles, **1b** and **3b**, alkylation takes place

Scheme 1



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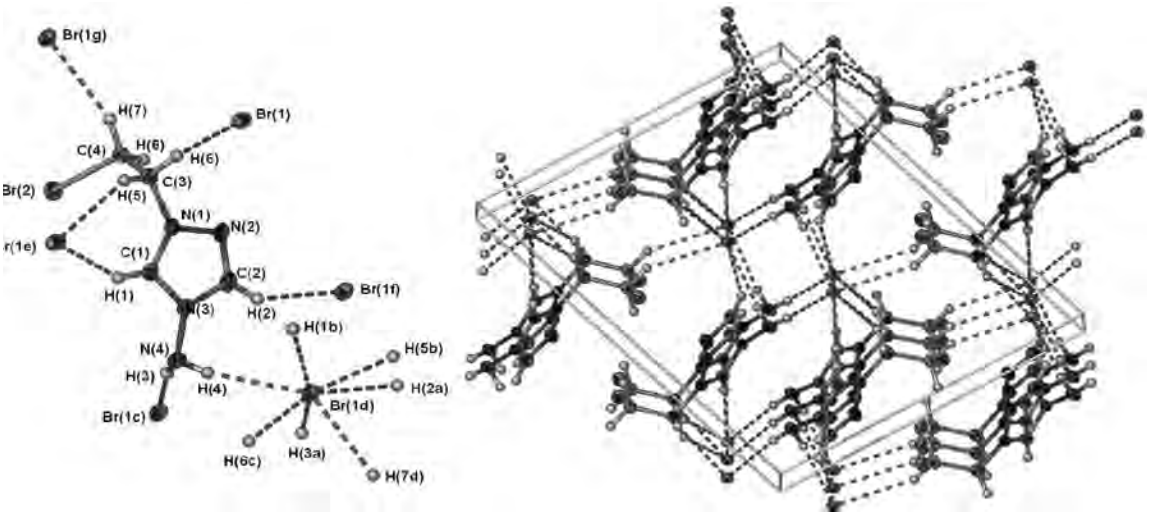

Figure 4. ORTEP diagram showing the conformation and the atom numbering scheme of the individual cations and anions (left) and the packing diagram of 1-(2-bromoethyl)-4-amino-1,2,4-triazolium bromide (**4**) along the *b*-axis (right).

Table 2. Crystal and Structure Refinement Data for **1b** and **4**

compound	1b	4
formula	$C_3H_7N_7$	$C_4H_8BrN_4$, Br
space group	$P2/c$ monoclinic	$P2_1/n$ monoclinic
a (Å)	11.453(3)	11.531(2)
b (Å)	5.531(1)	5.540(1)
c (Å)	15.252(4)	13.941(2)
β (°)	95.385(4)	106.231(2)
V (Å^3)	961.9(4)	855.1(2)
$\rho_{calc.}$ (g cm^{-3})	1.462	2.112
Z	6	4
formula weight	141.16	271.94
μ (mm^{-1})	0.110	9.416
temperature (K)	173	173
λ (Mo Kα)	0.71073	0.71073
crystal size	0.97 × 0.21 × 0.12	0.67 × 0.04 × 0.01
reflection collected	9035	9604
independent [R(int)]	1762 [0.025]	2057 [0.05]
obs. refl. ([$I > 2.0\ \sigma(I)$])	1620	1805
F(000)	444	520
GooF (S)	1.07	1.06
R_1, wR [I > 2σ(I)]	0.0326, 0.0928	0.0288, 0.0688
R_1, wR_2 (all data)[a,b]	0.0350, 0.0951	0.0341, 0.0711
L.diff. peak/hole (e•Å^3)	0.23 and −0.20	0.75 and −0.39
absorption correct.	none	SADABS
no. parameters	185	123
refinement method	full-matrix least-squares on F^2	

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma(w(|F_o|^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.2056P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 3. Thermophysical Properties of Triazolium Azides and Reference Compounds

compound	$T_{g(peak)}$ (°C)	$T_{m(peak)}$ (°C)	$T_{dec(onset)}$ (°C)	$\Delta_fH°$ (kcal mol^{-1})	$\Delta_cH°$ (kcal g^{-1})
1a		+43	+129	+136	−4.66
1b		+50	+156	+149	−4.76
2	−50		+129	+93	−4.54
3a	−57		+109	+161	−5.62
3b	−62		+114	+173	−5.69
5	[a]		+106	+223	−4.46
H_2NNH_2[71]				+12	−4.64
MeN_3[70]				+57	−4.45
$HOCH_2CH_2N_3$[70]				+23	−4.39

[a] Not observed.

Table 4. Initial Safety Test Results for IL Triazolium Azides[a]

azide	impact[a] drop height (kg cm)	friction[b] (N)
1a	>200	>360
1b	>200	>360
2	176	353
3a	132	n.d.[c]
3b	<60	n.d.[c]
5	>150 < 200	n.d.[c]

[a] Insensitve, >200 kg cm; sensitive, ≥40 kg cm. [b] Insensitive, >360N; sensitive, <360N and >80N. [c] n.d. = not determined.

at the N3 positions which show the largest PIS of −128.8 ppm and −118.3 ppm, respectively. The PIS for the amino groups is positive, which is in agreement with the effects observed by other groups.[47,60]

Crystal Structures of 1-Amino-3-methyl-1,2,3-triazolium Azide (1b) and 1-Bromoethyl-4-amino-1,2,4-triazolium Bromide (4). 1b crystallized in the centrosymmteric monoclinic space group, $P2/c$. The asymmetric unit contains two ion pairs, one of which suffers from substantial disorder in the cation as well as the azide anion (see also Supporting Information).

The two crystallographically independent cationic triazole rings are nearly planar and are arranged almost perpendicular to each other, with a mean plane angle of 88.6°. Hydrogen bonding between the individual azide anions and different cations is especially pronounced. All contacts lie within the sum of the van der Waals radii of 2.75 Å (Figure 2).[61] The hydrogen bonding network within the crystal lattice is composed of two components—a helix formation of one of the triazole rings and azide ions progressing clockwise along the *b*-axis with N−H•••N(azide) distances of 2.01(2) and 2.17(2) Å (Figure 3 left).

When viewed along the *b*-axis, this helix appears as a quasi-twelve-membered ring. The second crystallographically independent triazole rings are connected to each other through hydrogen bonding via azide anions forming a zigzag chain (Figure 3 right). The N−H•••N(azide) chains run along the *c*-axis and are at a distances of 2.33(2), which shows that these interactions are relatively weaker compared to the other ion pair. Finally, the helixes are linked to the chains via a weak N−H•••N(azide) bond of 2.54(2) Å.

4 crystallized in the monoclinic space group, $P2_1/n$. Figure 4 shows the asymmetric unit and the packing arrangement

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[61] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

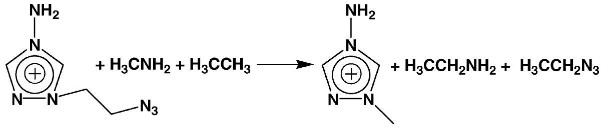
along the *b* axis. The overall packing is dominated by attractive Coulomb forces accompanied by substantial hydrogen bonding involving hydrogens from the amino group, from the triazole ring, and from the bromoethyl group to the bromide anion forming a three-dimensional network.

The triazole ring shows no abnormalities within the lengths and angles.[49] The ring is planar with the attached exocyclic nitrogen atom N(4) and C(3) atom from the bromoethyl group lying within the plane (the maximum torsion angle of N(4) from this plane is 1.9(2)° and 1.7(2)° for C3, respectively). The amino group is pyramidal and staggered with respect to C(2), which has been frequently observed in other structures.[47–49,62] The pendant alkyl group is curved by C(4)−C(3)−N(1), 112.4(2)°, and C(3)−C(4)−Br(2), 111.6(2)°, with the bromine atom pointing back to the ring, but being dihedrally twisted outward from the plane by 71.0(3)°. The bromide anion shows extensive hydrogen bonding with different cations, giving it a coordination number of seven (Figure 4). Connections range from a very strong Br(1)•••H(3) amino group bond with 2.58(4) Å to a relatively weak Br(1)•••H(6) alkyl group bond of 2.99(3) Å, just below the sum of the van der Waals radii of 3.05 Å.[61]

Thermal Stability, Sensitivity Investigations, and Theoretical Calculations. Phase transition and thermal decomposition temperatures were determined by DSC analysis (Table 3). For energetic materials key features are thermal stability and desirable physical properties. In this case, the ultimate goal was preparing room temperature IL azides with a long liquid range. The azide anion offers a rich platform for hydrogen bonding through both terminal nitrogen atoms, as is evident in the crystal structure of **1b**. Therefore, the discovery of relatively low-melting azide salts was unexpected. Introducing allyl-, 2-hydroxyethyl- and 2-azidoethyl-functionalities clearly promoted liquefying the ionic system. The drawback of more energetic side chain functionalities is reflected in lower decomposition onsets for **3a**, **3b**, and **5**.

Initial safety studies were carried out with the aminotriazolium azides. Generally, the salts are less sensitive to impact than RDX (∼50 kg cm, Table 4). The relative insensitivity of these IL azides is somewhat surprising, especially given the explained reputation of covalent azides as notorious explosives. This can be justified by the nominally linear azide anions which exhibit symmetric *N*═N double bonds in contrast to an unsymetrical N−N single and triple bonds arrangement found in covalent azides.

Another key feature is the heat of formation of the compounds. Theoretical performance can be estimated from calculated heats of formation. In general, a promising compound should possess a high positive heat of formation without inducing thermal instability or shock sensitivity. Table 3 lists the calculated heats of formation for the compounds investigated. With one exception, gas-phase heats of formation for all the separate ions of the compounds in Table 3 were calculated by the G2 method[64] using Gaussian 98.[65] For the cation of **5**, this value was derived from the homodesmic[66] reaction of eq 9 and from MP2/6–31G(d)//HF/6–31G(d) enthalpies[67] from GAMESS.[68]



(9)

The sum of the enthalpies of the ions was then corrected by the lattice enthalpy of the solid as estimated using the procedures described by Jenkins[69] with the individual crystal ion volumes approximated by the volumes enclosed by the 0.001 electron contour of the HF/6–31G(d) electron density in the isolated species. The heats of (oxygen) combustion (Table 3) were calculated according to eq 10.

$$C_aH_bN_cO_d(\text{l or s}) + \left(a + \frac{b}{4} - \frac{d}{2}\right)O_2(\text{g}) \rightarrow aCO_2(\text{g}) + \frac{b}{2}H_2O(\text{l}) + \frac{c}{2}N_2(\text{g}) \quad (10)$$

For an easier comparison, data for known compounds, CH_3N_3,[70] $HOCH_2CH_2N_3$,[70] and H_2NNH_2[71] are given as well.

Conclusion

It has been demonstrated that true room-temperature IL azides can be obtained. The azide anion did not cause the compounds to become too sensitive to be handled safely and an alternative preparative route has been described avoiding silver azide. This would seem to indicate that these new, less volatile, less sensitive, liquid azides may hold great potential as energetic materials. Certainly there would be a need for further characterization (e.g., vacuum thermal stability, Henkin time to explosion, and adiabatic compressibility) of these new materials when considering their development for specific applications.

Acknowledgment. The financial support of the AFOSR (Mike Berman) is gratefully acknowledged.

Supporting Information Available: Crystallographic data for **1b** and **4** in CIF format and additional information for structure **1b.** This material is available free of charge via the Internet at http://pubs.acs.org.

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