

# Energetic nitrogen-rich salts and ionic liquids: 5-aminotetrazole (AT) as a weak acid†

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5-Aminotetrazole (AT) behaves as a weak acid and can be used to obtain nitrogen-rich energetic salts and ionic liquids. These AT salts have been characterized by IR, NMR, elemental analysis, thermal stability, phase behavior, and density. The salt **2** contains 82% nitrogen, and **7** has the highest nitrogen content (68%) of any known room temperature ionic liquid. Compound **5** crystallizes in the chiral orthorhombic system  $P2(1)2(1)2(1)$ . Based on their calculated heats of formation, detonation properties, and thermal and hydrolytic stabilities, these stable AT compounds hold promise for energetic applications.

## Introduction

Modern high-energy density materials continue to attract considerable interest.<sup>1</sup> Energetic nitrogen-rich salts are among the most recent and exciting developments. The large number of N–N and C–N bonds in the energetic nitrogen-rich salts results directly in high heats of formation and high densities.<sup>2</sup> Their low carbon and hydrogen contents also gives rise to good oxygen balance. The decomposition of these compounds results predominantly in the generation of dinitrogen, which gives rise to very promising candidates for applications requiring environmentally friendly highly energetic materials.<sup>1a</sup> However, the poor stability of many nitrogen-rich compounds—such as hydrazoic acid, tetraazidomethane, and hydrazinium azide<sup>3</sup>—toward friction, impact, and heat often limits their potential applications. Energetic ionic liquids in particular combine the virtues of energetic salts (including enhanced thermal stability, higher densities, negligible vapor pressure, and little or no vapor toxicity) and improved safety issues related to transportation, handling, and processing from production to end-use.<sup>2,4</sup> In addition, the nitrogen content of a polynitrogen heterocyclic ring framework and the melting point of the stable energetic salt are directly related, *i.e.*, as the percentage of nitrogen becomes larger, the melting point increases; heretofore, the nitrogen content in known stable room temperature ionic liquids has not been very large. Therefore, there is need to develop new stable energetic salts that have high nitrogen content and are liquid at room temperature.

Recently the 5-substituted tetrazole anion derivatives,<sup>5</sup> such as 5-nitrotetrazolate,<sup>6</sup> 5,5'-azotetrazolate,<sup>7</sup> 5,5'-bis(tetrazolate),<sup>7c</sup> and iminobis(5-tetrazolate),<sup>7c,8</sup> have received considerable attention due to their high nitrogen contents and the outstanding

thermal stability that results from the aromatic ring system. 5-Aminotetrazole (AT), a simple, commercially available, nitrogen-rich (~82%) compound, has also been utilized as a precursor of energetic salts (alkali metal salts and nitration products).<sup>9</sup> AT and its mono- and dimethyl derivatives have most often been employed as cations in energetic salts because they behave as weak bases with strong inorganic acids.<sup>5b,8,10</sup> There are very few reports on the role of AT as a weak acid and thus as an anion in salts.<sup>11</sup> Herein we report the synthesis and characterization of energetic nitrogen-rich salts based on AT in anionic form which demonstrates that AT is indeed amphoteric. Some of these salts are stable nitrogen-rich ionic liquids that contain the AT anion for the first time.

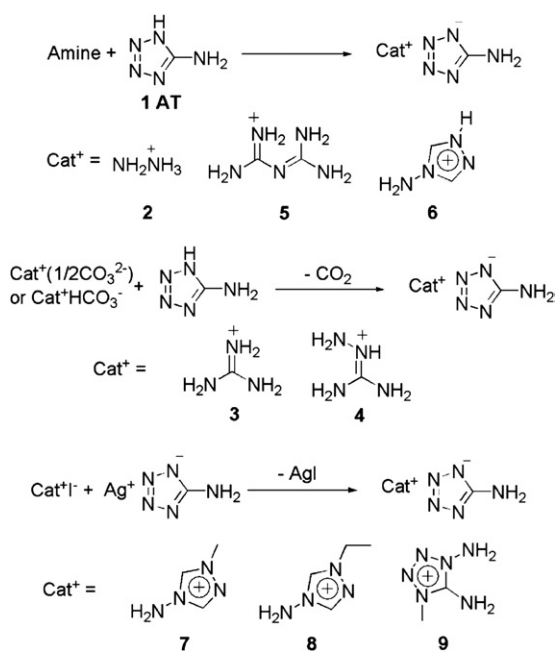
## Results and discussion

The AT anionic salts and ionic liquids were prepared by using three different methodologies (Scheme 1). Compounds **2**<sup>11a</sup> and **6** were synthesized by taking advantage of the acidity of AT (**1**) in reaction with strong bases in methanol; **5** was formed when **1** was reacted with biguanidine in aqueous solution; guanidine carbonate and aminoguanidine bicarbonate with **1** in methanol resulted in **3** and **4**,<sup>11a</sup> respectively, with concomitant release of carbon dioxide; and **7**, **8** and **9** were prepared from AgAT (silver 5-aminotetrazolate) and the corresponding iodide salts. It is noteworthy that none of the resulting AT salts contains water of hydration or solvent as determined by NMR spectral and elemental analysis.

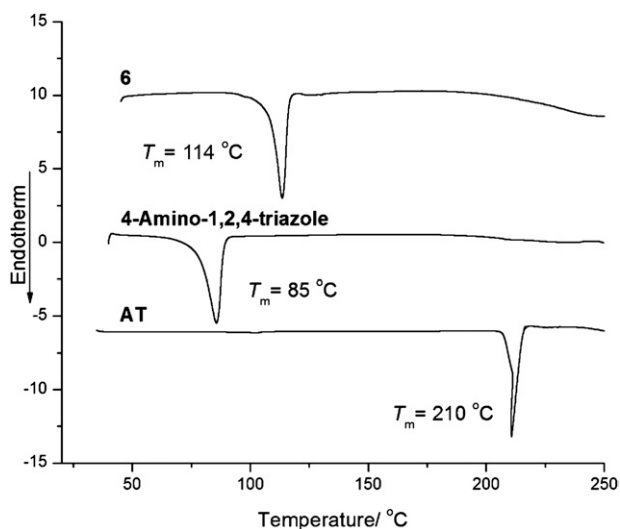
Compounds **2–9** are stable at 25 °C and can be stored at room temperature for at least several months. Their thermal stabilities range between 164 to 220 °C in ambient nitrogen. In these salts, the cations play the predominant role in determining decomposition temperatures because they are less stable than the AT anion. The melting points/glass transition temperatures ( $T_m/T_g$ ) were obtained using differential scanning calorimetry (DSC) from the first heating cycle. The solid samples exhibit distinct melting points ( $T_m$ ). In Fig. 1, the DSC curve of **6** ( $T_m$  114 °C) is compared with the analogous curves of the two starting materials, 4-amino-1,2,4-triazole ( $T_m$  85 °C) and AT ( $T_m$  210 °C). It is obvious that the product obtained is significantly different from

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† Electronic supplementary information (ESI) available: Tables of hydrogen bond geometry, bond lengths, and bond angles in **5**, DSC plots of **2–8**, **10**, *ab initio* computational data. CCDC reference number 690394. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b811506k



**Scheme 1** Synthesis routes of energetic nitrogen-rich AT salts.



**Fig. 1** DSC plots of **6**, 4-amino-1,2,4-triazole and **AT** (heating rate  $10\text{ }^{\circ}\text{C min}^{-1}$ ).

the starting materials (Table 1). DSC curves of other products also confirm the synthesis of new compounds, *i.e.*, the melting points of the products are very different from those of the neutral components (see ESI†). While  $T_m$  and  $T_g$  have no clear linear relationship with the lattice energies of the salts, different cations distinctly affect these properties. The melting points of the AT cationic salts (*e.g.*, compounds **A–C**, Table 1) are higher than most of the AT anionic salts, probably due to the presence of a larger number of hydrogen bonds. Compounds **7** and **8** are room temperature ionic liquids. Each of them displays a gradual step associated with a phase transition temperature,  $T_g$ , at  $-24$  and  $-38\text{ }^{\circ}\text{C}$ , respectively, which was assigned to the glass transition temperatures similar to those of conventional ionic liquids.<sup>12</sup> The asymmetry of the 4-amino-1-alkyl-1,2,4-triazolium

cation contributes to the low melting points of these AT ionic liquids.

Density is one of the most important physical properties of any energetic material. As can be seen in Table 1, the densities of **2–9** range between  $1.39$  and  $1.62\text{ g cm}^{-3}$ . Experimental values and calculated values using a semi-empirical method<sup>13</sup> are in reasonable agreement. These AT compounds have rather high nitrogen content and, especially for the salt **2**, the nitrogen content exceeds 82%. It should be noted that **7**, in which the nitrogen content reaches 68%, contains the highest percentage found in any room temperature ionic liquid to date.

Polynitrogen compounds are of considerable interest as high energy materials for propellant or explosive applications.<sup>14</sup> Synthesis and study of the  $\text{N}_5^+$  cation has been one of the most important breakthroughs in the past several years.<sup>15</sup> A large number of high nitrogen content salts with polyazide anions compete very well as energetic materials.<sup>14</sup> However, compared to such compounds, the AT salts have superior thermal and hydrolytic stabilities, making them more suitable for practical applications. These salts are stable in water even when heated to  $100\text{ }^{\circ}\text{C}$ . The ionic nature of the AT salts contributes to their densities and to their good thermal stabilities especially when coupled with the salt's aromatic ring system. Impact sensitivity tests were carried out using a BAM Fellhammer method.<sup>16</sup> With the exception of the ionic liquids, **7** and **8**, the impact sensitivities of **2–6**, and **9**, were determined to have values  $>60\text{ J}$  (10 kg hammer, 60 cm). Based on the classification standard of sensitivities,<sup>14</sup> these salts are classified as impact insensitive energetic materials.

### X-Ray crystallography

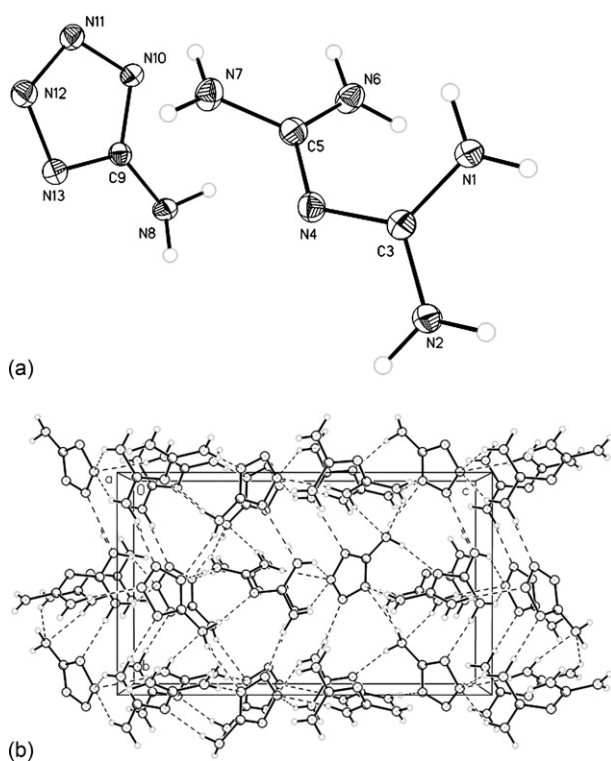
Crystals of the nitrogen-rich AT salt **5** suitable for X-ray diffraction were obtained by slow recrystallization from acetonitrile solution. The structure is shown in Fig. 2 and crystallographic data are summarized in Table 2. Compound **5** crystallizes in the chiral orthorhombic system  $P2(1)2(1)2(1)$ , however, not enough anomalous diffraction was obtained to determine the direction of the polar axis. Selected bond distances and angles are given in Table 3. The cation in **5** has a twist at N4 with a dihedral angle of *ca.*  $127^{\circ}$  between the two guanidinium planes (alternatively a torsion angle of *ca.*  $25^{\circ}$  for N1–C3–N4–C5). The C3–N4 and N4–C5 bond lengths are basically equivalent and both guanidinium moieties are planar which indicates a delocalization of the positive charge. Only N1–C3 shows a slight lengthening compared to the other amino groups. The AT anion also displays delocalization of the negative charge due to bond homogenization (reference bond lengths: C–N,  $1.47\text{ \AA}$ ;<sup>17</sup> N=N,  $1.24\text{ \AA}$  and N–N,  $1.47\text{ \AA}$ <sup>18</sup>).

The packing structure of **5** is built up by hydrogen bonds (Fig. 2b). Each cation forms moderate hydrogen bonds to five anions *via* the terminal amino groups ( $\text{D}\cdots\text{A}$  *ca.*  $2.95$  to  $3.318\text{ \AA}$ ) and also *via* the central linking nitrogen atom ( $\text{N}8\cdots\text{N}4\#1$ ,  $3.0860(17)\text{ \AA}$ ;  $\#1 = x - 1, y, z$  symmetry transformation). Each anion also forms hydrogen bonds to five cations. N8 and N10 form a donor ( $\text{N}8\cdots\text{N}4\#1$ , see above) and acceptor ( $\text{N}7\cdots\text{N}10\#2$ ,  $2.9590(18)\text{ \AA}$ ;  $\#1 = x + 1, y, z$ ) complex to the same cation. The combination of all these hydrogen bonds forms a complex 3D network.

**Table 1** Properties of energetic nitrogen-rich AT salts

Compd	$T_m^a$ ( $T_g$ )/°C	$T_d^b$ /°C	$d^c$ (calcd)/g cm <sup>-3</sup>	$\Delta H_f^{d,e}$ (cation)/kJ mol <sup>-1</sup>	$\Delta H_L^f$ /kJ mol <sup>-1</sup>	$\Delta H_f^g$ /kJ mol <sup>-1</sup>	$\Delta H_f^g$ /kJ g <sup>-1</sup>	$P^h$ /GPa	$D^i$ /m s <sup>-1</sup>
<b>2</b>	125	164	1.48 (1.55)	770.0	570.2	383.6	3.28	24.8	8786
<b>3</b>	126	220	1.54 (1.46)	566.7	545.1	205.4	1.43	19.4	8055
<b>4</b>	96	211	1.51 (1.49)	646.7	528.2	302.3	1.90	20.1	8149
<b>5</b>	141	207	1.41 (1.44)	620.9	497.8	306.9	1.65	16.3	7529
<b>6</b>	114	217	1.62 (1.55)	910.7	529.5	565.0	3.34	23.3	8360
<b>7</b>	(-24)	174	1.46 (1.49)	866.7	504.5	546.0	2.98	18.9	7334
<b>8</b>	(-38)	171	1.39 (1.44)	828.2	488.6	523.4	2.65	16.4	7397
<b>9</b>	171	190	1.57 (1.56)	974.3	503.0	655.1	3.29	23.2	8385
<b>A<sup>j</sup></b>	159	163	1.75		516.9	571.4	2.86	31.4	8843
<b>B<sup>j</sup></b>	165	165	1.63		497.9	487.5	2.27	25.5	8276
<b>C<sup>k</sup></b>	147	214	1.85		466.5	400.6	1.28	29.5	8182

<sup>a</sup> Melting point/phase transition temperature. <sup>b</sup> Thermal degradation. <sup>c</sup> Density, gas pycnometer, 25 °C. <sup>d</sup> Molar enthalpy of the formation of cation. <sup>e</sup> Molar enthalpy of the formation of AT anion, 183.8 kJ mol<sup>-1</sup>. <sup>f</sup> Lattice energy. <sup>g</sup> Molar enthalpy of the formation of salt. <sup>h</sup> Detonation pressure. <sup>i</sup> Detonation velocity. <sup>j</sup> A: 5-Aminotetrazolium 5-nitrotetrazolate; B: 5-aminotetrazolium 5-nitroiminotetrazolate; ref. 5b. <sup>k</sup> C: 5-Aminotetrazolium picrate; ref. 10b.



**Fig. 2** (a) Molecular structure of **5** (displacement ellipsoids shown at 30% probability). Hydrogen atoms represented by spheres of arbitrary radius. (b) Packing diagram of **5** viewed down the *a*-axis. Unit cell is indicated and dashed lines represent hydrogen bonding.

### Theoretical study

Computations were performed by using the Gaussian03 (Revision D.01) suite of programs.<sup>19</sup> The geometric optimization and the frequency analyses were carried out using B3-LYP functional analyses with the 6-31+G\*\* basis set.<sup>20</sup> Single energy points were calculated at the MP<sub>2</sub>/6-311++G\*\* level.<sup>21</sup> All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

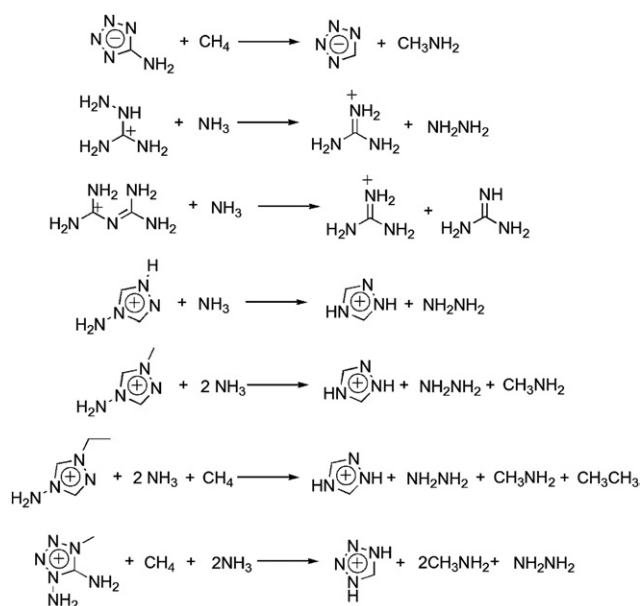
**Table 2** Crystal data and structure refinement for compound **5**

<b>5</b>	
Formula	C <sub>3</sub> H <sub>10</sub> N <sub>10</sub>
FW	186.21
Crystal size/mm	0.50 × 0.28 × 0.22
Crystal system	Orthorhombic
Space group	<i>P</i> 2(1)2(1)2(1)
<i>a</i> /Å	5.6667(6)
<i>b</i> /Å	9.4916(11)
<i>c</i> /Å	15.9768(18)
<i>V</i> /Å <sup>3</sup>	859.33(17)
<i>Z</i>	4
$D_c$ /g cm <sup>-3</sup>	1.439
$\mu$ /mm <sup>-1</sup>	0.110
<i>T</i> /K	90(2)
$\lambda$ (MoK $\alpha$ )/Å	0.71073
Reflections collected	12696
Unique reflections	1343
$R_{int}$	0.0249
Parameters	158
<i>S</i> on $F^2$	1.073
$R_1$ ( $I > 2\sigma(I)$ )	0.0291
$wR_2$ ( $I > 2\sigma(I)$ )	0.0758
$R_1$ (all data)	0.0299
$wR_2$ (all data)	0.0767
$\Delta\rho_{min, max}/e \text{ \AA}^{-3}$	0.262, -0.163

**Table 3** Selected bond lengths [Å] and angles [°] for **5**

C(3)–N(2)	1.3320(18)	C(9)–N(8)	1.3865(17)
C(3)–N(4)	1.3399(17)	N(10)–N(11)	1.3523(16)
C(3)–N(1)	1.3459(18)	N(11)–N(12)	1.3107(17)
C(5)–N(6)	1.3360(18)	N(12)–N(13)	1.3605(17)
C(5)–N(7)	1.3373(18)		
C(5)–N(4)	1.3432(18)	N(2)–C(3)–N(1)	118.18(12)
C(9)–N(13)	1.3374(18)	C(3)–N(4)–C(5)	121.66(12)
C(9)–N(10)	1.3403(17)	N(6)–C(5)–N(7)	118.10(13)

The heats of formation of the cations and anions were computed by using the method of isodesmic reactions (Scheme 2).<sup>22</sup> The sources of the energies of the parent ions in the isodesmic reactions were calculated from protonation reactions ( $\Delta H_f^\circ(H^+) = 1530 \text{ kJ mol}^{-1}$ ).<sup>22,23</sup> The heats of formation of the  $NH_2NH_3^+$  (770.0 kJ mol<sup>-1</sup>) and guanidinium cations



**Scheme 2** Isodesmic reactions of ions.

(566.7 kJ mol<sup>-1</sup>) were taken from the literature.<sup>8</sup> The enthalpy of reaction ( $\Delta H_{r,298}^\circ$ ) was obtained by combining the MP<sub>2</sub>/6-311++G\*\* energy difference for the reaction, the scaled zero point energies, and other thermal factors. The enthalpy of an isodesmic reaction ( $\Delta H_{r,298}^\circ$ ) was obtained by combining the MP<sub>2</sub>/6-311++G\*\* energy difference for the reaction, the scaled zero-point energies (B3LYP/6-31+G\*\*), and other thermal factors (B3LYP/6-31+G\*\*) (see ESI†).

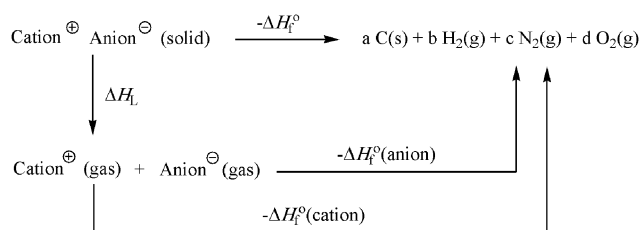
Based on a Born–Haber energy cycle (Fig. 3), heats of formation of ionic salts can be simplified by the expression:

$$\Delta H_f^\circ(\text{ionic salts, 298 K}) = \sum \Delta H_f^\circ(\text{cation, 298 K}) + \sum \Delta H_f^\circ(\text{anion, 298 K}) - \Delta H_L$$

where  $\Delta H_L$  is the lattice energy of the ionic salt. For 1 : 1 salts and considering the nonlinear nature of the cation and anions used,  $\Delta H_L$  (kJ mol<sup>-1</sup>) can be predicted by the formula suggested by Jenkins *et al.*<sup>24</sup> as:

$$\Delta H_L = U_{\text{POT}} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (1)$$

where  $n_M$  and  $n_X$  depend on the nature of the ions  $M_p^+$  and  $X_q^-$ , respectively, and have a value of 6 for nonlinear polyatomic ions. The equation for lattice potential energy  $U_{\text{POT}}$  (eqn 2) has the form



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

**Fig. 3** Born–Haber cycle for the formation of energetic salts.

$$U_{\text{POT}} (\text{kJ mol}^{-1}) = 1981.2(\rho_m/M_m)^{1/3} + 103.8 \quad (2)$$

where  $\rho_m$  is density (g cm<sup>-3</sup>) and  $M_m$  is the chemical formula mass of the ionic material (g).<sup>24</sup>

The heats of formation for compounds **2–9** are summarized in Table 1. All the salts exhibit positive heats of formation with **9** having the highest value (655.1 kJ mol<sup>-1</sup>). Salts **2**, **6**, and **9** have the highest energy densities, 3.28, 3.34, and 3.29 kJ g<sup>-1</sup>, respectively. The energy density values for these salts are higher than those of the known AT cation salts with organic anions (Table 1).

By using the calculated values of the heats of formation and the experimental values for the densities of the new compounds, **2–9**, the detonation pressures ( $P$ ) and detonation velocities ( $D$ ) were calculated based on traditional Chapman–Jouget thermo-dynamic detonation theory using Cheetah 4.0 (Table 1).<sup>25</sup> The calculated detonation pressures lie in the range between  $P = 16.3$  GPa (**5**) and  $P = 24.8$  GPa (**2**). Detonation velocities lie between  $D = 7334$  m s<sup>-1</sup> (**7**) and  $D = 8786$  m s<sup>-1</sup> (**2**). Salt **2** with >82% nitrogen content has the highest detonation pressure and velocity. The ionic liquid **7**, with the highest nitrogen content, also demonstrates moderate detonation pressure ( $P = 18.9$  GPa) and velocity ( $D = 7334$  m s<sup>-1</sup>). All of the new salts have detonation properties similar to the known AT cation salts with organic anions<sup>5b,10b</sup> and higher detonation velocities than TNT ( $D = 6881$  m s<sup>-1</sup>).<sup>26</sup> These properties, coupled with their intrinsic rather high thermal and hydrolytic stabilities, make these high-nitrogen materials attractive candidates for future applications.

## Experimental

**Caution:** We have not experienced any problems in handling these compounds. Though they are impact insensitive materials, their friction sensitivities have not been determined. Therefore, they should be handled with extreme care using all of the standard safety precautions.

## X-Ray crystallography

Crystals of compound **5** were removed from the flask; a suitable crystal was selected, attached to a glass fiber; and data were collected at 90(2) K 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 using omega scans of 0.3° per frame for 5 s, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.73 Å. Cell parameters were retrieved using SMART<sup>27</sup> software and refined using SAINT-Plus<sup>28</sup> on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.<sup>29</sup> The structure was solved by direct methods and refined by least squares method on  $F^2$  using the SHELXTL program package.<sup>30</sup> The structure was solved in the space group  $P2(1)2(1)2(1)$  (no. 19) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and refined. In this all-light-atom structure the value of the Flack parameter did not allow the direction of the polar axis to be determined, and Friedel opposites were merged for the final refinement. No decomposition was observed during data



collection. Details of the data collection and refinement are given in Table 2. Further details are provided in the ESI.† CCDC reference number 690394.

### General methods

All chemicals were pure analytical grade materials obtained commercially and used as received. IR spectra were recorded using KBr plates for neat liquids and KBr pellets for solids using a Biorad Model 3000 FTS spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance spectrometer operating at 300 and 75 MHz, respectively, by using  $d_6$ -DMSO as a locking solvent. Chemical shifts are reported in ppm relative to TMS. The densities of the solid salts were measured at 25 °C using a Micromeritics Accucyc 1330 gas pycnometer. Differential scanning calorimetry (DSC) measurements were performed using a TA DSCQ10 calorimeter equipped with an autocool accessory and calibrated using indium. The following procedure was used in experiments for each sample: cooling from 40 °C to –80 °C and heating to 400 °C at 10 °C min<sup>-1</sup>. Thermogravimetric analysis (TGA) measurements were carried out on a TA TGAQ50 by heating samples at 10 °C min<sup>-1</sup> from 25 to 400 °C in a dynamic nitrogen atmosphere (flow rate 70 mL min<sup>-1</sup>). Elemental analyses (C, H, N) were performed on a CE-440 Elemental Analyzer.

### Compound synthesis

**Hydrazinium 5-aminotetrazolate (2).** The preparation of **2** is based on the literature method.<sup>11a</sup> Hydrazine hydrate (50 mg, 1 mmol) and **1** (85 mg, 1 mmol) were stirred in 20 mL methanol for 3 h, giving a white solid after the solvent was removed under a stream of air. The crude salts were washed with 20 mL ethanol–ether (1 : 3). Yield 111 mg (95%). IR (KBr): 3405, 3352, 3290, 3200, 1632, 1604, 1531, 1443, 1406, 1236, 1105, 1005, 939, 756, 659, 471, 425 cm<sup>-1</sup>;  $^1\text{H}$  NMR:  $\delta$  4.08 (br, 7H);  $^{13}\text{C}$  NMR:  $\delta$  159.85. Calcd for  $\text{CH}_7\text{N}_7$  (117.11): C 10.26, H 6.02, N 83.72; found: C 10.61, H 6.04, N 82.28%.

**Guanidinium 5-aminotetrazolate (3).** The synthesis of **3** is based on the literature method.<sup>11a</sup> A mixture of guanidine carbonate (450 mg, 5 mmol) and **1** (425 mg, 5 mmol) was heated gently to 50 °C in 30 mL methanol for 8 h, giving a white solid after concentration. The crude salt was recrystallized from methanol–ether (1 : 3). Yield 669 mg (93%). IR (KBr): 3420, 3402, 3375, 3175, 1665, 1513, 1443, 1202, 1138, 1118, 1008, 939, 769 cm<sup>-1</sup>;  $^1\text{H}$  NMR:  $\delta$  7.42 (br, 2H), 3.45 (br, 6H);  $^{13}\text{C}$  NMR:  $\delta$  164.05, 158.22. Calcd for  $\text{C}_2\text{H}_8\text{N}_8$  (144.14): C 16.67, H 5.59, N 77.74; found: C 16.76, H 5.66, N 76.89%.

**Aminoguanidinium 5-aminotetrazolate (4).** The preparation of **4** is based on the literature method.<sup>11a</sup> A mixture of aminoguanidine bicarbonate (408 mg, 3 mmol) and **1** (255 mg, 3 mmol) was gently heated to 50 °C in 30 mL methanol for 8 h, giving a white solid after concentration. The crude salt was recrystallized from ethanol–ether (1 : 3). Yield 452 mg (95%). IR (KBr): 3448, 3393, 3364, 3330, 3200, 1689, 1615, 1518, 1434, 1242, 1136, 1106, 1060, 979, 950, 756, 706, 523, 434 cm<sup>-1</sup>;  $^1\text{H}$  NMR:  $\delta$  7.44 (s, 2H), 5.73 (s, 2H), 3.97 (br, 5H);  $^{13}\text{C}$  NMR:  $\delta$  163.24, 159.00.

Calcd for  $\text{C}_2\text{H}_9\text{N}_9$  (159.15): C 15.09, H 5.70, N 79.21; found: C 15.43, H 5.65, N 78.80%.

**Guanylguanidinium 5-aminotetrazolate (5).** Biguanidinium sulfate dihydrate was prepared using a literature method.<sup>31</sup> Biguanidinium sulfate dihydrate (235 mg, 1 mmol) was stirred with barium hydroxide octahydrate (316 mg, 1 mmol) in 30 mL water; then the solution was filtered and **1** (85 mg, 1 mmol) was added. After stirring for 6 h, a white solid was obtained after concentration. Yield 174 mg (93%). After recrystallization from acetonitrile, clear colorless needle crystals suitable for X-ray structure determination were obtained. IR (KBr): 3451, 3418, 3373, 3319, 3115, 1637, 1539, 1510, 1440, 1213, 1146, 1118, 1051, 1011, 911, 745, 722, 615, 571, 505, 440 cm<sup>-1</sup>;  $^1\text{H}$  NMR:  $\delta$  6.96 (br, 3H), 3.38 (br, 7H);  $^{13}\text{C}$  NMR:  $\delta$  163.98, 159.81. Calcd for  $\text{C}_3\text{H}_{10}\text{N}_{10}$  (186.18): C, 19.35; H, 5.41; N, 75.23; found: C, 19.42; H, 5.39; N, 74.70%.

**4-Amino-1*H*-1,2,4-triazolium 5-aminotetrazolate (6).** A mixture of 4-amino-1*H*-1,2,4-triazole (168 mg, 2 mmol) and **1** (170 mg, 2 mmol) was heated gently at reflux in 50 mL methanol for 1 d, giving a white solid after concentration. The crude salts were recrystallized from ethanol–ether (1:3). Yield 310 mg (92%). IR (KBr): 3451, 3369, 3314, 3184, 3130, 3090, 1668, 1612, 1539, 1524, 1440, 1383, 1277, 1193, 1138, 1074, 1050, 993, 955, 874, 845, 737, 687, 621, 465 cm<sup>-1</sup>;  $^1\text{H}$  NMR:  $\delta$  8.38 (s, 1H), 6.41 (s, 1H), 6.19 (s, 1H), 3.36 (br, 4H);  $^{13}\text{C}$  NMR:  $\delta$  156.70, 144.12. Calcd for  $\text{C}_3\text{H}_7\text{N}_9$  (169.15): C 21.30, H 4.17, N 74.53; found: C 21.15, H 4.01, N 74.47%.

**Silver 5-aminotetrazolate (AgAT).** **1** (851 mg, 10 mmol) was reacted with sodium hydroxide (400 mg, 10 mmol) in 50 mL water. After filtration, the solution was added in 20 mL  $\text{AgNO}_3$  (1.70 g, 10 mmol) solution. The precipitate was filtered and washed by water. A white solid was obtained after drying. Yield 1.88 g (98%).

**4-Amino-1-methyl-1,2,4-triazolium 5-aminotetrazolate (7).** 4-Amino-1-methyl-1,2,4-triazolium iodide was prepared using a literature method.<sup>32</sup> A mixture of 4-amino-1-methyl-1,2,4-triazolium iodide (226 mg, 1 mmol) and AgAT (192 mg, 1 mmol) was stirred in 50 mL methanol overnight with complete exclusion of light. After the silver iodide was filtered off, the filtrate was concentrated. After washing with methanol–ether, a colorless liquid was obtained after the solvent was removed. Yield 166 mg (91%). IR (KBr): 3305, 3211, 3140, 1625, 1574, 1514, 1440, 1407, 1374, 1211, 1175, 1130, 1105, 1072, 981, 825, 745, 657, 616, 455 cm<sup>-1</sup>;  $^1\text{H}$  NMR:  $\delta$  10.27 (br, 1H), 9.21 (s, 1H), 7.39 (s, 2H), 4.44 (br, 2H), 4.04 (s, 3H);  $^{13}\text{C}$  NMR:  $\delta$  163.93, 144.93, 142.96, 38.84. Calcd for  $\text{C}_4\text{H}_9\text{N}_9$  (183.17): C 26.23, H 4.95, N 68.82; found: C 26.12, H 4.94, N 68.41%.

**4-Amino-1-ethyl-1,2,4-triazolium 5-aminotetrazolate (8).** The same procedure was used as for **7**. 4-Amino-1-ethyl-1,2,4-triazolium iodide was prepared using a literature method.<sup>32</sup> 4-Amino-1-ethyl-1,2,4-triazolium iodide (240 mg, 1 mmol) and AgAT (192 mg, 1 mmol) were reacted in methanol to obtain a colorless liquid **8**. Yield 171 mg (87%). IR (KBr): 3308, 3216, 3134, 1626, 1566, 1514, 1444, 1406, 1387, 1356, 1212, 1169, 1109,

1078, 993, 965, 870, 801, 747, 623, 465  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  10.26 (br, 1H), 9.19 (s, 1H), 7.24 (s, 2H), 4.36 (q, 2H,  $J = 7.2$  Hz), 3.82 (s, 2H), 1.45 (t, 3H,  $J = 7.2$  Hz);  $^{13}\text{C}$  NMR:  $\delta$  163.36, 145.10, 142.38, 47.41, 13.70. Calcd for  $\text{C}_5\text{H}_{11}\text{N}_9$  (197.20): C 30.45, H 5.62, N 63.92; found: C 30.40, H 5.57, N 63.94%.

**1,5-Diamino-4-methyl-1,2,3,4-tetrazolium 5-aminotetrazolate (9).** The same procedure was used as for 7. 5-Amino-4-methyl-1,2,3,4-tetrazolium iodide was prepared using a literature method.<sup>33</sup> 1,5-Diamino-4-methyl-1,2,3,4-tetrazolium iodide (242 mg, 1 mmol) and AgAT (192 mg, 1 mmol) were reacted in methanol to obtain a white solid 10. Yield 178 mg (89%). IR (KBr): 3409, 3277, 3167, 1718, 1624, 1509, 1442, 1405, 1215, 1118, 1045, 1010, 899, 782, 685, 415  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  6.18 (s, 2H), 4.05 (br, 4H), 3.52 (s, 3H);  $^{13}\text{C}$  NMR:  $\delta$  157.68, 148.33, 32.41. Calcd for  $\text{C}_3\text{H}_9\text{N}_{11}$  (199.18): C 18.09, H 4.55, N 77.36; found: C 17.79, H 4.54, N 77.58%.

## Conclusions

The syntheses of AT salts provide a new and straightforward approach to energetic salts and ionic liquids. These salts exhibit desirable physical properties, such as high nitrogen content ( $\leq 82\%$ ), high densities ( $\leq 1.64$   $\text{g cm}^{-3}$ ), and good hydrolytic and thermal stabilities (164–220  $^{\circ}\text{C}$ ). A combination of theoretical and empirical calculations shows that these materials have reasonably high heats of formation and high energy densities (more than 3.0  $\text{kJ g}^{-1}$ ). Furthermore, they are all impact insensitive energetic materials with good calculated detonation properties. These AT salts and ionic liquids may be potential safe and “green” energetic materials for commercial applications.

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