Supplementary material (ESI) for Journal of Materials Chemistry

Supporting Information

Belonging to the manuscript

Energetic Nitrogen Rich-Salts and Ionic Liquids: 5-Aminotetrazolate (AT) as a Weak Acid

Guo-Hong Tao, Yong Guo, Young-Hyuk Joo, Brendan Twamley, and Jean'ne M. Shreeve*
Department of Chemistry, University of Idaho, Moscow, Idaho, 83844-2343, USA
jshreeve@uidaho.edu

Table of contents

Table S1 Calculated (B3LYP/6-31+G**//MP2/6-311++G**) Total Energy (E_0), Zero-Point Energy (ZPE), Values of Thermal Correction (H_T), and Heats of Formation (HOF) of the ions.

Name	E_0 (au)	ZPE (au)	H_T (kJ/mol)	HOF (kJ/mol)
Guanidinium cation	-205.2570379	0.088421	16.4	566.7
Aminoguanidinium cation	-260.4513108	0.105672	19.5	646.7
Guanylguanidinium cation	-353.7240685	0.127659	23.3	620.9
4-Amino-1*H*-1,2,4-triazolium cation	-297.2005028	0.089612	15.5	910.7
4-Amino-1-methyl-1,2,4-triazolium cation	-336.4026071	0.116980	18.1	866.6
4-Amino-1-ethyl-1,2,4-triazolium cation	-375.6060696	0.145786	23.2	828.2
1,5-Diamino-4-methyltetrazolium cation	-407.63759	0.121200	23.7	974.3
5-Amino-tetrazolate anion	-312.3505776	0.050441	13.1	183.8
1,2,4-Triazolium cation	-242.00879	0.07324	12.0	835.0[1]
1,2,3,4-Tetrazolium cation	-257.98206	0.06029	11.8	1016.5
1,2,3,4-Tetrazolate anion	-257.12424	0.03382	11.1	170.0
Guanidine	-204.8735031	0.075945	14.4	26.0[2]
CH_4	-40.3796224	0.044793	10.0	-74.6[3]
CH_3NH_2	-95.59384	0.06403	11.5	-23.0[3]
NH_2NH_2	-111.5836915	0.05331	11.0	95.4[3]
NH_3	-56.4154647	0.034384	10.0	-45.9[3]
CH_3CH_3	-79.571631	0.07461	11.6	-84.0[3]

Geometry Coordinates

B3LYP/6-31+G(d,p) optimized geometries (Å)

Guanidinium cation

N	-1.321565	-0.205759	-0.001103
H	-1.712671	-1.117729	-0.190869
H	-1.970964	0.542506	0.196530
N	0.482509	1.247196	-0.000648
H	-0.111583	2.041503	-0.192387
H	1.455076	1.435319	0.197728
C	-0.000067	-0.000207	0.000163
N	0.839274	-1.041242	0.000175
H	0.515935	-1.978052	0.195878
H	1.823085	-0.923670	-0.196822

Aminoguanidinium cation

C	-0.504976	0.010490	-0.000029
N	-1.672119	-0.645757	0.000086
H	-2.552499	-0.151829	0.001064
H	-1.714448	-1.654549	-0.000865
N	-0.450326	1.338155	-0.000108
H	-1.278826	1.913876	0.000001
H	0.468074	1.768621	-0.000311
N	0.648420	-0.687107	-0.000330
H	0.630718	-1.701363	0.001063
N	1.857403	0.016619	0.000051
H	2.395955	-0.194844	0.836789

H	2.397236	-0.196219	-0.835458

Guanylguanidinium cation

N	-2.314538	-0.864119	0.020001
N	-1.290750	1.299628	-0.065131
N	-0.013984	-0.648573	-0.062699
N	2.291511	-0.864577	-0.007758
N	1.323720	1.252320	0.056428
C	-1.271523	0.022110	-0.012483
C	1.216003	-0.060793	0.000652
H	-3.248678	-0.478054	0.035410
H	-2.216260	-1.743927	0.509578
H	-2.215512	1.709109	0.039310
H	-0.038768	-1.614416	-0.363807
H	3.224367	-0.481085	-0.061090
H	2.213614	-1.862354	0.124293
H	0.429349	1.775573	-0.013737
H	2.213295	1.704487	0.215129

4-Amino-1*H*-1,2,4-triazolium cation

C	-0.172838	-1.076494	0.000083
N	0.646548	-0.011281	0.000012
H	0.138613	-2.111769	0.000087
N	-1.420322	0.777774	0.000105
C	-0.158532	1.114920	-0.000022
H	0.217205	2.128611	-0.000051
N	2.040327	-0.142025	-0.000050
H	2.429365	0.280973	-0.840035
H	2.429399	0.280570	0.840123
N	-1.401764	-0.583657	-0.000104
H	-2.279887	-1.094613	-0.000224

4-Amino-1-methyl-1,2,4-triazolium cation

C	0.006248	-0.892372	0.000023
N	1.094927	-0.099125	0.000000
H	0.023968	-1.972845	0.000022
N	-0.672815	1.221604	-0.000062
C	0.633882	1.200485	0.000071
H	1.273413	2.071788	0.000093
N	2.397847	-0.610898	-0.000041
H	2.889464	-0.311583	-0.839054
H	2.889422	-0.311798	0.839074
N	-1.048666	-0.091165	0.000002
C	-2.477522	-0.450248	0.000000
H	-2.708511	-1.025521	-0.897763
H	-2.708536	-1.025431	0.897815
H	-3.033921	0.485286	-0.000055

4-Amino-1-ethyl-1,2,4-triazolium cation

C	-0.453418	-0.887568	-0.137908

N	-1.533490	-0.103428	0.053323
H	-0.465042	-1.967675	-0.154799
N	0.204983	1.230107	-0.213824
C	-1.083823	1.199207	-0.001677
H	-1.720357	2.065219	0.113005
N	-2.816937	-0.624592	0.253783
H	-3.169571	-0.342863	1.165488
H	-3.438629	-0.317566	-0.490684
N	0.581950	-0.079408	-0.297782
C	2.006363	-0.427326	-0.524049
H	2.025570	-1.498340	-0.738854
H	2.307146	0.113529	-1.424300
C	2.877284	-0.063878	0.674751
H	2.578027	-0.615324	1.570632
H	3.913068	-0.326452	0.443355
H	2.835814	1.008113	0.880951

1,5-Diamino-4-methyl-tetrazolium cation

C	0.015400	0.608371	-0.000002
N	1.070948	-0.235973	-0.000003
N	0.625821	-1.539709	0.000001
N	-0.637344	-1.512320	0.000018
N	-1.057975	-0.198681	-0.000015
N	0.084884	1.933576	0.000021
H	1.000085	2.369554	0.000013
H	-0.739521	2.516578	-0.000035
N	2.388355	0.176842	-0.000005
H	2.860771	-0.162415	0.836451
H	2.860759	-0.162380	-0.836482
C	-2.483670	0.137308	-0.000003
H	-2.734056	0.702498	0.900845
H	-2.733930	0.703009	-0.900565
H	-3.027312	-0.807060	-0.000310

5-Aminotetrazolate anion

C	-0.581765	-0.048938	0.000109
N	0.210406	-1.127001	-0.000844
N	0.113966	1.099541	-0.000134
N	1.403651	0.706163	-0.000219
N	1.460917	-0.618158	0.000817
N	-2.012399	-0.124491	0.000111
H	-2.372595	0.369803	0.813530
H	-2.372601	0.371446	-0.812300

S-11 References

[1] M. W. Schmidt, M. S. Gordon and J. A. Boatz, *J. Phys. Chem.*, A, 2005, **109**, 7285−7295.

[2] Y. Guo, H. Gao, B. Twamley, and J. M. Shreeve, *Adv. Mater.*, 2007, **19**, 2884−2888.

[3] D. R. Lide, ed., "Standard Thermodynamic Properties of Chemical Substances" *in CRC Handbook of Chemistry and Physics,Internet Version 2007, (87th Edition),* <*http:/www.hbcpnetbase.com*>, Taylor and Francis, Boca Raton, FL, 2007.

Table S2 Bond lengths [Å] and bond angles [°] in crystal **5**.

C(3)-N(2)	1.3320(18)	N(6)-C(5)-N(7)	118.10(13)
C(3)-N(4)	1.3399(17)	N(6)-C(5)-N(4)	124.45(13)
C(3)-N(1)	1.3459(18)	N(7)-C(5)-N(4)	117.32(13)
C(5)-N(6)	1.3360(18)	N(13)-C(9)-N(10)	112.59(12)
C(5)-N(7)	1.3373(18)	N(13)-C(9)-N(8)	124.66(12)
C(5)-N(4)	1.3432(18)	N(10)-C(9)-N(8)	122.67(13)
C(9)-N(13)	1.3374(18)	C(3)-N(1)-H(1A)	119.7(13)
C(9)-N(10)	1.3403(17)	C(3)-N(1)-H(1B)	117.8(15)
C(9)-N(8)	1.3865(17)	H(1A)-N(1)-H(1B)	118.9(19)
N(1)-H(1A)	0.87(2)	C(3)-N(2)-H(2A)	117.9(12)
N(1)-H(1B)	0.83(2)	C(3)-N(2)-H(2B)	119.6(13)
N(2)-H(2A)	0.90(2)	H(2A)-N(2)-H(2B)	120.3(18)
N(2)-H(2B)	0.87(2)	C(3)-N(4)-C(5)	121.66(12)
N(6)-H(6A)	0.87(2)	C(5)-N(6)-H(6A)	119.9(14)
N(6)-H(6B)	0.88(2)	C(5)-N(6)-H(6B)	118.2(14)
N(7)-H(7A)	0.91(2)	H(6A)-N(6)-H(6B)	122(2)
N(7)-H(7B)	0.86(2)	C(5)-N(7)-H(7A)	116.7(13)
N(8)-H(8A)	0.90(2)	C(5)-N(7)-H(7B)	120.7(15)
N(8)-H(8B)	0.84(2)	H(7A)-N(7)-H(7B)	122.3(17)
N(10)-N(11)	1.3523(16)	C(9)-N(8)-H(8A)	110.3(14)
N(11)-N(12)	1.3107(17)	C(9)-N(8)-H(8B)	111.3(14)
N(12)-N(13)	1.3605(17)	H(8A)-N(8)-H(8B)	114(2)
		C(9)-N(10)-N(11)	104.15(11)
N(2)-C(3)-N(4)	118.31(13)	N(12)-N(11)-N(10)	109.68(11)
N(2)-C(3)-N(1)	118.18(12)	N(11)-N(12)-N(13)	109.83(11)
N(4)-C(3)-N(1)	123.46(13)	C(9)-N(13)-N(12)	103.75(11)

Table S3 Hydrogen bonding geometry in crystal **5** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...N(13)#1	0.87(2)	2.12(2)	2.9687(17)	165(2)
N(1)-H(1B)...N(12)#2	0.83(2)	2.49(2)	3.1442(18)	136.7(18)
N(2)-H(2A)...N(12)#2	0.90(2)	2.23(2)	3.0313(17)	148.4(16)
N(2)-H(2B)...N(11)#3	0.87(2)	2.08(2)	2.9513(17)	171.5(17)
N(6)-H(6A)...N(12)#4	0.87(2)	2.29(2)	3.1498(17)	170.3(18)
N(6)-H(6B)...N(8)#5	0.88(2)	2.24(2)	3.0858(18)	162.0(19)
N(7)-H(7A)...N(10)#6	0.91(2)	2.06(2)	2.9590(18)	169.0(18)
N(7)-H(7B)...N(8)#5	0.86(2)	2.58(2)	3.3181(19)	144.4(18)
N(8)-H(8A)...N(10)#7	0.90(2)	2.43(2)	3.0726(17)	128.9(18)
N(8)-H(8B)...N(4)#8	0.84(2)	2.25(2)	3.0860(17)	169.8(19)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y-1/2,-z+1/2 #2 -x+3/2,-y+1,z+1/2 #3 -x+1,y+1/2,-z+1/2
#4 -x+1/2,-y+1,z+1/2 #5 -x,y-1/2,-z+1/2 #6 x+1,y,z
#7 -x,y+1/2,-z+1/2 #8 x-1,y,z

Figure S1 DSC plots of AT salts, **2**, **3**, **4**, **5**, **6**, and **9**, heating rate 10 °C/min.

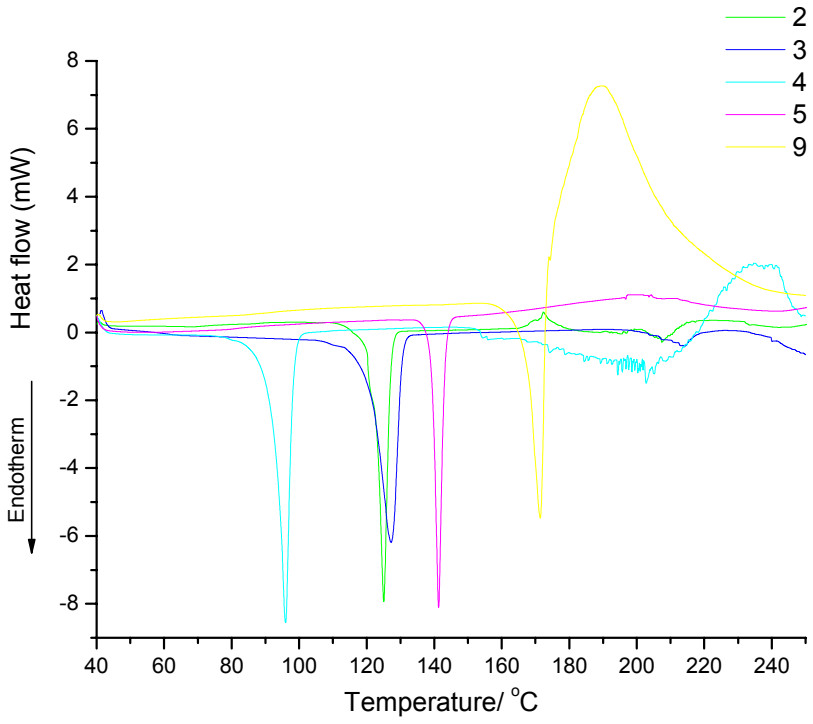

Figure S2 DSC plots of AT ionic liquids, **7**, and **8**, heating rate 10 °C/min.