Synthesis and Characterization of Nitrate Based Energetic Ionic Liquids (EILs)

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ABSTRACT

By definition, salts being liquid (ILs) below 100 °C are defined as ionic liquids [1]. They are receiving an increasing interest due to their unique properties and are under investigation in the field of energetic materials, too. ILs consists out of ions and show good thermal stability, electric conductivity, and extremely low vapor pressure. Potential applications are energetic plasticizers or liquid rocket and gun propellants. This paper presents the synthesis of energetic ionic liquids (EILs) on the base of 4-Amino-1,2,4-Triazole with Nitrate as an anion. The substituents at N1 synthesized are methyl, cyanomethyl, and cyanoethyl resulting in 4-Amino-1-methyl-1,2,4-triazolium nitrate (C1 N), 4-Amino-1-(cyanomethyl)-1,2,4-Triazolium Nitrate (C1CN N), and 4-Amino-1-(cyanoethyl)-1,2,4-Triazolium Nitrate (C2CN N). C1 N is a room temperature EIL and C1CN N and C2CN N are solid at room temperature. The phase stabilization of ammonium nitrate through addition of C1CN N and C2CN (N 5wt%, 10wt% and 15wt%) was studied.

INTRODUCTION

Ionic liquids (ILs) are in the focus of recent research and finding application in more and more fields of life. The applications range from novel reaction media [2], as electrolytes in batteries [3], solar cells [4], gas storing media [5], as lubricants [6] and heat-transfer fluids [7], to mention only a small excerpt of the investigated and in use applications. Remarkable the whole field of ILs began already in 1888 with ethanolammonium nitrate (T_m = 52-54 °C), an energetic protic IL synthesized and characterized by Gabriel [8] and ethylammonium nitrate (T_m = 13-14 °C; Paul Walden 191 [9]). However, the discovery of a new class of liquids did not prompt any significant interest at that time. In general, protic ionic liquids are formed by proton transfer between Brønsted acids and bases like the very first IL, whereas aprotic ILs are usually synthesized through S_N2 alkylation reactions and subsequent anion metathesis.

The properties attributed to aprotic ionic liquids are good thermal stability, very low vapor pressure, electric conductivity, good solvent abilities, and a high heat capacity. Shreeve et al.[10] already investigated a series of new energetic ionic liquids (EILs) but there is still a big undiscovered field due to the great number of possible combinations of energetic anions and cations. The general principle behind EILs is shown in Figure 1.

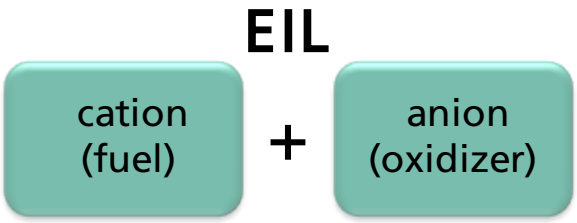
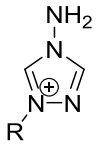


Figure 1: General principle of Energetic Ionic Liquids (EILs).

RESULTS AND DISCUSSION

Alkylation of 4-Amino-1,2,4-Triazole, which contains two C-H linkage in the ring as well as a pendant NH_2 group, performs selectively in the N1 position and breaks the mirror symmetry of the ring. This can be seen in the proton spectra by the disappearance of the singlet derived from the two C-H protons and emergence of two equal downfield C-H singlets. A similar effect can bee seen in the ^{13}C NMR upon alkylation of 4-Amino-1,2,4-Triazole which resulted in two singlets, too. The physical properties of the synthesized compounds are summarized in Table 1. 4-Amino-1-methyl-1,2,4-Triazolium Nitrate (C1 N) is liquid at room temperature (room temperature EIL), has a glass transition point of -54 °C, and shows low sensitivity against impact (20 Nm) and friction (>360 N). 4-Amino-1-(cyanomethyl)-1,2,4-Triazolium Nitrate (C1CN N) and 4-Amino-1-(cyanoethyl)-1,2,4-Triazolium Nitrate (C2CN N) are solid at room temperature, although C1CN N was described as a liquid at room temperature in [11]. Both compounds show very low sensitivity against impact (30 Nm, 50 Nm) and friction (>360 N).

Table 1: Physical data of synthesized compounds C1 N, C1CN N, and C2CN N.

		C1 N	C1CN N	C2CN N
state		liquid	solid	solid
T_g / T_m	[°C]	-54,1	95,4	59,4
T_{dec} (TGA)	[°C]	249,1	210,3	221,0
density	[g/cm^3]	1,44	1,59	1,53
impact sensitivity	[Nm]	20	30	50
friction sensitivity	[N]	360	360	360

By adding a nitrile group to the methyl substituent in N1 the density increases. By increasing the chain length in N1 from cyanomethyl to cyanoethyl the density and the melting point drops. The thermal stability decreases by adding a nitrile group to the methyl substituent in N1 and increases again from cyanomethyl to cyanoethyl, probably due to the increase of electron donating properties of the additional methylene group. An overview for the chloride educts and the synthesized Nitrat based EILs is shown in Figure 2.

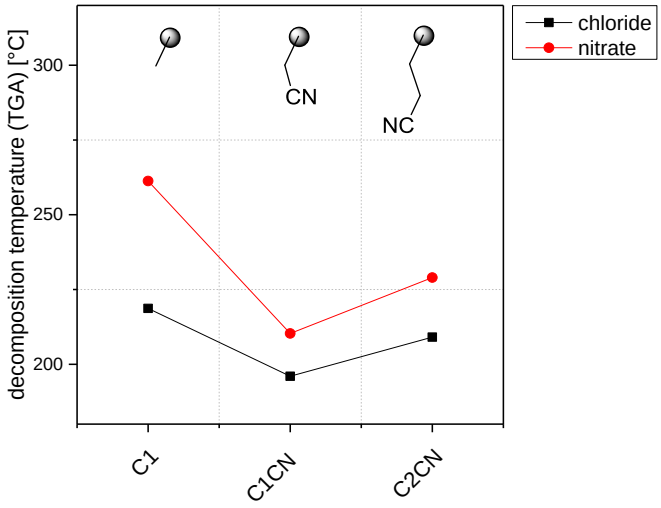
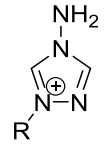


Figure 2: Thermal decomposition temperature (TGA) of 4-Amino-1-R-1,2,4-Triazolium Chlorides and Nitrates (R = methyl, cyanomethyl, cyanoethyl).

The calculated properties of the synthesized EILs are shown in Table 2. The oxygen balance drops by adding a nitrile group to the C1 N resulting in C1CN N from -64,6% to -68,6%. However, the nitrogen content increases and the standard enthalpy of formation rises significantly. The heat of explosion is stays nearly in the same range, whereas the specific energy and produced gasvolume without H_2O at 25 °C is noticeably reduced. Due to the density increase of C1 N (liquid) to C1CN N (solid) a better volume specific impuls is achieved.

Table 2: Calculated properties and performance data of synthesized EILs.

		C1 N	C1CN N	C2CN N
oxygen balance	[%]	-64,6	-68,8	-87,9
nitrogen content	[%]	43,5	45,15	41,99
standard enthalpy of formation	[kJ/mol]	+33	+141	+116
heat of explosion	[J/g]	3467.7	3421.7	3195.2
specific energy	[J/g]	974.9	908.8	819.4
gasvolume (without H_2O at 25 °C)	[cm^3/g]	1048.5	955.4	963.1
mass specific impuls (frz. 70:1)	[N s/kg]	1983	1997	1912
volume specific impuls (frz. 70:1)	[N s/dm^3]	2860	3172	2917

C1CN N and C2CN N were tested as a phase stabilizing additive in ammonium nitrate. In Figure 3 DSC measurements of ammonium nitrate mixtures with C1CN N (left) and C2CN N (right) are shown. However, the ammonium nitrat / C1CN N and ammonium nitrat / C2CN N mixtures still showed polymorphic phase transitions below 60 °C.

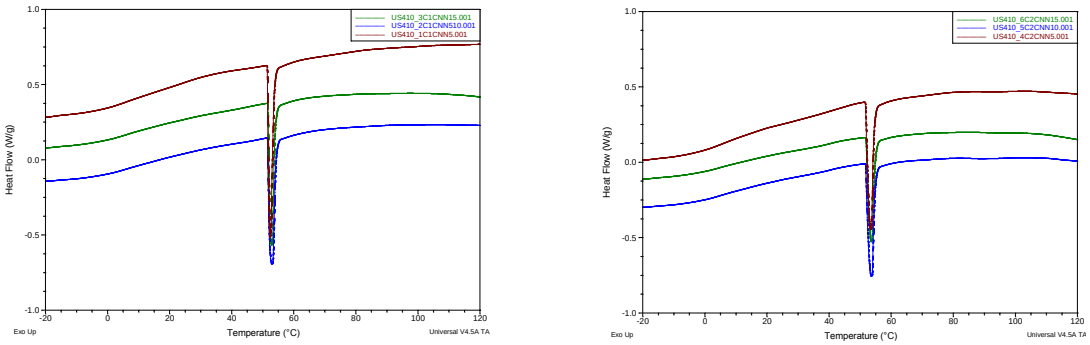
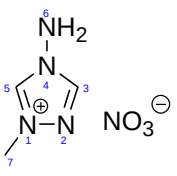


Figure 3: DSC measurements of ammonium nitrate mixtures with C1CN N (left) and C2CN N (right) (5wt% - 15 wt%).

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR were conducted on a 400 MHz Bruker AV-400 spectrometer in DMSO-d_6. Differential scanning calorimetry (DSC) was done by a TA instruments Q 1000 using pierced aluminum pans. Scans were carried out on each sample, at scan rates of 5 °C/min, under argon flux. Glass transition points were measured from the 2nd heating cycle after cooling to -90 °C. Reported values are onset temperatures. Thermogravimetric analysis (TGA) was done by a TA Q500 apparatus with a scan rate of 10 °C/min under nitrogen flux. Reported values are the central points according to DIN EN ISO 11358. Infrared spectroscopy was done on a Nicolet SX 5 spectrometer. Impact sensitivity and friction sensitivity tests were determined according to NATO STANAG 4487 and NATO STANAG 4489 procedures with the BAM-Impact sensitivity tester and the BAM-Friction sensitivity tester made by the former company Julius Peter (Berlin). Synthesis was performed according to published route [12]. Performance data was calculated with ICT Code [13], impulses are calculated with frozen equilibrium with a chamber pressure of 70 bar and an expansion pressure of 1 bar. Ammonium nitrate C1CN N and C2CN N mixtures were prepared by dissolving the salts in methanol p.a. and evaporating the solution.

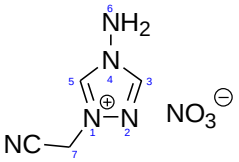
4-Amino-1-methyl-1,2,4-Triazolium Nitrate (C1 N)



Colorless liquid T_g = -54,1 **°C. T_d** = 249,1 °C. **TGA** = 261,3 °C. **Density** = 1,442 g/cm^3. **^{1}H NMR** (DMSO-d_6, 400 MHz): **δ** (ppm) = 4.03 (s, 3H, C7), 7.04 (s, 2H, NH_2), 9.15 (s, 1H, C3), 10.13 (s, 1H, C5). **^{13}C NMR** (DMSO-d_6, 101 MHz): **δ** (ppm) = 38.9 (C7), 143.1 (C3), 145.2 (C5). **FT-IR** (ATR, cm^{-1}) = 3282 (w), 3141 (w), 1637 (w), 1573 (w), 1318 (s), 1171 (m), 1071 (w), 979 (m), 881 (w), 828 (m), 737 (w). **FT-RAMAN** (cm^{-1}) = 3161

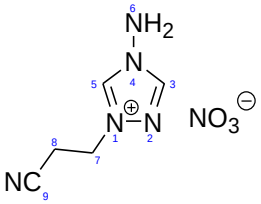
(w), 2963 (w), 1574 (w), 1531 (w), 1411 (m), 1406 (s), 1382 (m), 1325 (m), 1203 (w), 1089 (m), 1075 (m), 981 (w), 740 (w), 711 (w), 616 (w), 456 (w). **η** (20°C) = 454 mPa·s**. Impact sensitivity** = 20 Nm. **Friction sensitivity** = >360 N.

4-Amino-1-(cyanomethyl)-1,2,4-Triazolium Nitrate (C1CN N)



White solid T_m = 95,4 **°C**. **T_d** = 194,5 **°C**. **TGA** = 210,3 **°C**. **Density** = 1,588 g/cm^3. **^{1}H NMR** (DMSO-d_6, 400 MHz): **δ** (ppm) = 5.80 (2H, s, C7), 7.12 (2H, s, NH_2), 9.33 (1H, s, C3), 10. 21 (1H, s, C5). **^{13}C NMR** (d_6-DMSO, 101 MHz): **δ** (ppm) = 39.1 (C7), 113.6 (CN), 144.0 (C3), 145.7 (C5) ppm. **FT-IR** (ATR, cm^{-1}) = 3306 (w), 3132 (w), 3071 (w), 1641 (w), 1564 (w), 1424 (w), 1380 (m), 1316 (vs), 1282 (s), 1168 (s), 1071 (m), 1013 (m), 946 (m), 891 (m), 829 (w), 770 (w). **FT-RAMAN** (cm^{-1}) = 3141 (w), 2958 (w), 2274 (m), 1565 (w), 1424 (m), 1367 (w), 1194 (w), 1073 (m), 1050 (s), 997 (w), 948 (w), 767 (w), 691 (w), 651 (w), 485 (w), 428 (w), 348 (w), 305 (w). **Impact sensitivity** = 30 Nm. **Friction sensitivity** = >360 N.

4-Amino-1-(cyanoethyl)-1,2,4-Triazolium Nitrate (C2CN N)



White solid T_m = 59,4 **°C**. **T_d** = 221,0 °C. **TGA** = 234,0 °C. **Density** = 1, 526 g/cm^3. **^{1}H NMR** (DMSO-d_6, 400 MHz): **δ** (ppm) = 3.23 (2H, t, C8), 4.67 (2H, t, C7), 7.11 (2H, s, NH_2), 9.28 (1H, s, C3), 10.26 (1H, s, C5). **^{13}C NMR** (d_6-DMSO, 101 MHz): **δ** (ppm) = 17.4 (C8), 47.4 (C7), 117.7 (C9), 143.3 (C3) 145.5 (C5). **FT-IR** (ATR, cm^{-1}) = 3276 (w), 3124 (w), 3058 (w), 2257 (w), 1641 (w), 1562 (w), 1449 (w), 1406 (m), 1364 (s), 1329 (s), 1312 (s), 1221 (m), 1162 (m), 1025 (m), 975 (m), 909 (m), 827 (w), 716 (w). **FT-RAMAN** (cm^{-1}) = 2994 (w), 2942 (m), 2256 (m), 1410 (m), 1227 (w), 1069 (m), 1049 (s), 976 (w), 830 (w), 716 (w), 603 (w), 364 (w). **Impact sensitivity** = >50 Nm. **Friction sensitivity** = >360 N.

CONCLUSION

The room temperature EIL 4-Amino-1-methyl-1,2,4-triazolium nitrate (C1 N) and the two energetic salts 4-Amino-1-(cyanomethyl)-1,2,4-Triazolium Nitrate (C1CN N) and 4-Amino-1-(cyanoethyl)-1,2,4-Triazolium Nitrate (C2CN N) were successfully synthesized and characterized. The performance data of the synthesized substances was calculated revealing good energetic properties.

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ABBREVIATIONS

DSC	Differential Scanning Calorimetry
DMSO	Dimethylsulfoxide
EIL	Energetic Ionic Liquid
IL	Ionic Liquid
IR	Infrared Spectroscopy
T_m	Melting Point
T_g	Glass Transition Temperature
T_{dec}	Decomposition Temperature
TGA	Thermogravimetric Analysis

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