

Supporting information

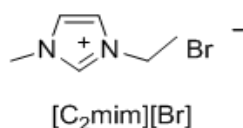
Novel Ionic Liquids and Plastic Crystals utilizing the Cyanate Anion.

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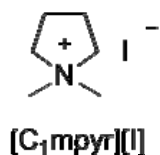
1. Synthesis of the halide salts

1-ethyl-3-methylimidazolium bromide



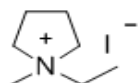
To a solution of 1-methylimidazole (20g, 1.00 eq, 244 mmol) in abs. *i*-propanol (150 mL) a solution of ethyl bromide (27.87 g, 1.05 eq, 256 mmol) in abs. *i*-propanol (50 mL) was added slowly at room temperature. The solution was stirred over a period of 4 days under a nitrogen atmosphere. 150 mL of the solvent was removed under reduced pressure, 100 mL acetonitrile was added and the solution placed in the freezer (-20 °C) to crystallize the product. White crystals were filtered off and dried at high vacuum. The mother liquor was reduced under vacuum, 50 mL acetonitrile added, the solution was seeded with already existing [C₂mim][Br] crystals and placed in the freezer. The crystallization process was repeated twice. The product was obtained in form of white crystals (41 g, 88% yield). MS (m/z) ES+ 111.0; ES- 80.9. ¹H-NMR (400 MHz, d₆-DMSO): δ ppm = 1.41 (t, 3H, J=7.6), 3.86 (s, 3H), 4.21 (q, 2H, J=7.6), 7.75 (s, 1H), 7.84 (s, 1H), 9.30 (s, 1H). ¹³C-NMR (100 MHz, d₆-DMSO): δ ppm = 15.0, 35.6, 43.9, 121.8, 123.4, 136.1.

N,N-dimethylpyrrolidinium iodide



To a solution of N-methylpyrrolidine (20.44g, 1.00 eq., 240 mmol) in ethyl acetate (300 mL) a solution of methyl iodide (35.77g, 1.05 eq., 252 mmol) in 100 mL ethyl acetate was added slowly at 0°C, immediately forming a white precipitate. The reaction mixture was then stirred overnight at room temperature, protected from light by aluminum foil. The white precipitate was filtered off, washed with 200 mL ethyl acetate and the product was recrystallized from acetonitrile/ethyl acetate. The product was obtained in the form of white crystals (50 g, 92% yield). MS (m/z) ES+ 100.1; ES- 127.0. ¹H-NMR (400 MHz, d₆-DMSO): δ ppm = 2.09-2.11 (m, 4H), 3.12 (s, 6H), 3.46-3.50 (m, 4H). ¹³C-NMR (100 MHz, d₆-DMSO): δ ppm = 21.0, 50.6 (t), 64.5 (d).

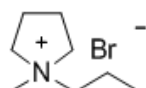
N-ethyl-N-methylpyrrolidinium iodide



[C₂mpyr][I]

To a solution of N-methylpyrrolidine (20.44g, 1.00 eq, 240 mmol) in abs *i*-propanol (150 mL) a solution of ethyl iodide (39.30, 1.05 eq, 252 mmol) in 50 mL *i*-propanol was added slowly while cooling with an ice bath. The reaction mixture was stirred for 3 days under a nitrogen atmosphere at room temperature, protected from light by aluminum foil, during which time a white solid crashed out and was then filtered off. Hexane was added to the mother liquor and the white solid precipitate collected. The product was purified through crystallization out of acetonitrile and ethyl acetate. The product was obtained as off-white crystals (42.8 g, 74 % yield). MS (m/z): Es+ 114.1; Es- 126.9. ¹H-NMR (400 MHz, d₆-DMSO): δ ppm = 1.27 (tt, 3H, J=7.2, J=2), 2.07-2.09 (m, 4H), 2.96 (s, 3H), 3.40-3.45 (m, 6H). ¹³C-NMR (100 MHz, d₆-DMSO): δ ppm = 9.0, 21.0, 46.9 (t), 58.2 (t), 62.8.

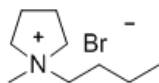
N-methyl-N-propylpyrrolidinium bromide



[C₃mpyr][Br]

To a solution of N-methylpyrrolidine (20.44g, 1.00 eq, 240 mmol) in abs *i*-propanol (150 mL) a solution of propylbromide (31.00, 1.05 eq, 252 mmol) in 50 mL *i*-propanol was added slowly. The reaction mixture was stirred for 3 days under a nitrogen atmosphere. Hexane was then added to the yellow solution and the white solid precipitate collected. The product was purified through crystallization out of acetonitrile and ethyl acetate, giving white crystals (44.5 g, 89 % yield). MS (m/z): Es+ 128.2; Es- 78.9. ¹H-NMR (400 MHz, d₆-DMSO): δ ppm = 0.87 (t, 3H, J=7.2), 1.64-1.74 (m, 2H), 2.06 (s, 4H), 2.94 (s, 3H), 3.20-3.24 (m, 2H) 3.33-3.46 (m, 4H). ¹³C-NMR (100 MHz, d₆-DMSO): δ ppm = 11.0, 17.2, 21.4, 48.0 (t), 64.1 (d), 65.2.

N-butyl-N-methylpyrrolidinium bromide

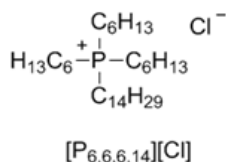


[C₄mpyr][Br]

To a solution of N-methylpyrrolidine (20.44g, 1.00 eq, 240 mmol) in abs *i*-propanol (150 mL) a solution of butyl bromide (34.53 g, 1.05 eq, 252 mmol) in 50 mL *i*-propanol was added slowly. The reaction mixture was stirred for 3 days under a nitrogen atmosphere. Hexane was then added to the yellow solution and the precipitated white solid collected. The product was

purified through crystallization out of acetonitrile and ethyl acetate. The product was obtained as white crystals (42.7 g, 80 % yield). MS (m/z): Es+ 142.2; Es- 80.9. ¹H-NMR (400 MHz, d₆-DMSO): δ ppm = 0.90-0.94 (m, 3H), 1.29-1.35 (m, 2H), 1.64-1.71 (m, 2H), 2.07 (s, 4H), 3.00 (s, 3H), 3.33-3.37 (m, 2H) 3.46-3.50 (m, 4H). ¹³C-NMR (100 MHz, d₆-DMSO): δ ppm = 13.4, 19.2, 21.0, 24.8, 47.4 (t), 62.7 (d), 63.3.

trihexyl(tetradecyl)phosphonium chloride



Trihexyl(tetradecyl)phosphonium chloride was supplied by CYTEC Australia Holdings Pty. and purified as follows; 30g of [P_{6,6,6,14}][Cl] was dissolved in 300 mL acetone and stirred over activated carbon overnight at room temperature. The suspension was then filtered through 200 g basic alumina and washed with 200 mL acetone. The solvent was removed under reduced pressure. The colorless viscous liquid was dried at high vacuum, yielding 29.5 g product. MS (m/z): ES+ 483.6; ES - 35.0.

2. Synthesis of silver cyanate

To a suspension of sodium cyanate (Sigma Aldrich, 96% purity, 13.55 g, 1.0 eq., 200 mmol) in water (200 mL) a silver nitrate (33.97 g, 1.0 eq., 200 mmol) solution in water (200 mL) was added and the suspension stirred overnight at room temperature. The white precipitate was then filtered off, washed with 200 mL water and dried at high vacuum for 24h. The product was obtained as a white solid (29.9 g, yield quantitative).

3. Synthesis of cyanate compounds

General synthetic procedure:

A solution of the appropriate halide salt (1.00 eq. 60 mmol) in water (100 mL) was added to a suspension of silver cyanate (8.99g, 1.00 eq, 60 mmol) in water (200 mL). The reaction mixture was heated to 50 °C for 3h and then stirred overnight at room temperature. The yellow precipitate was then filtered off and the product purified as follows: The product was dissolved in water and the insoluble silver halide impurity was allowed to precipitate out. To encourage Oswald ripening the solution was placed in the fridge for 12 h, followed by filtration and evaporation of the solvent on the rotary evaporator. This process was then repeated twice with acetonitrile. The product was then dried at high vacuum for at least 24h.

***1-ethyl-3-methylimidazolium cyanate*, [C₂mim][OCN].**

The product was obtained as white crystals (9.80 g, 98 % yield). MS (m/z) ES⁺ 111.3; ES⁻ 42.1. HRMS (m/z) ES⁺ 111.0927 (calculated 111.0922); ES⁻ 41.9985 (calculated 41.9980; higher order clusters can be detected in negative mode). ¹H-NMR (400 MHz, d₆-DMSO): δ ppm = 1.41 (t, 3H, J=7.6), 3.86 (s, 3H), 4.21 (q, 2H, J=7.6), 7.73 (s, 1H), 7.82 (s, 1H), 9.29 (s, 1H). ¹³C-NMR (100 MHz, d₆-DMSO): δ ppm = 15.0, 35.6, 44.0, 121.9, 123.5, 126.6, 136.3. IR (cm⁻¹) = 3409, 3313, 3055, 2989, 2140, 1663, 1575, 1457, 1416, 1371, 1337, 1285, 1271, 1174, 1028, 884, 827, 800, 701, 649, 625, 617. Ion selective electrode (ISE): (Ag⁺) < 10 ppm; (Br⁻) < 200 ppm.

***N,N-dimethylpyrrolidinium cyanate*, [C₁mpyr][OCN].**

The product was obtained as an off-white solid (8.35 g, 98 % yield). MS (m/z) ES⁺ 100.1; ES⁻ 42.1. HRMS (m/z) ES⁺ 100.1129 (calculated 100.1126); ES⁻ 41.9981 (calculated 41.9980; higher order clusters can be detected in negative mode). ¹H-NMR (400 MHz, d₆-DMSO): δ ppm = 2.06-2.10 (m, 4H), 3.10 (s, 6H), 3.44-3.48 (m, 4H). ¹³C-NMR (100 MHz, d₆-DMSO): δ ppm = 21.3, 50.8 (t), 64.7 (t), 126.7. IR (cm⁻¹) = 3409, 3321, 3019, 2134, 1661, 1475, 1283, 1196, 1046, 999, 977, 934, 820, 623. ISE: (Ag⁺) < 10 ppm; (I⁻) < 10 ppm.

***N-ethyl-N-methylpyrrolidinium cyanate*, [C₂mpyr][OCN].**

The product was obtained as a very soft yellow solid (8.15 g, 87 % yield). MS (m/z) ES⁺ 114.1; ES⁻ 42.1. HRMS (m/z) ES⁺ 114.1282 (calculated 114.1283); ES⁻ 41.9973 (calculated 41.9980; higher order clusters can be detected in negative mode). ¹H-NMR (400 MHz, d₆-DMSO): δ ppm = 1.26 (tt, 3H, J=7.2, J=2), 2.06-2.08 (m, 4H), 2.96 (s, 3H), 3.39-3.46 (m, 6H). ¹³C-NMR (100 MHz, d₆-DMSO): δ ppm = 8.8, 21.0, 46.8 (t), 58.3 (t), 62.8, 126.7. IR (cm⁻¹) = 3409, 3314, 2983, 2133, 1612, 1463, 1404, 1342, 1280, 1193, 1034, 999, 937, 879, 813, 623. ISE: (Ag⁺) < 20 ppm; (I⁻) < 10 ppm.

***N-methyl-N-propylpyrrolidinium cyanate*, [C₃mpyr][OCN].**

The product was obtained as very soft off-white solid (9.70 g, 95 % yield). MS (m/z) ES⁺ 128.2; ES⁻ 42.1. HRMS (m/z) ES⁺ 128.1441 (calculated 128.1439); ES⁻ 41.9966 (calculated 41.9980; higher order clusters can be detected in negative mode). ¹H-NMR (400 MHz, d₆-DMSO): δ ppm = 0.88 (t, 3H, J=7.2), 1.63-1.73 (m, 2H), 2.06 (s, 4H), 2.93 (s, 3H), 3.18-3.22 (m, 2H) 3.33-3.46 (m, 4H). ¹³C-NMR (100 MHz, d₆-DMSO): δ ppm = 11.0, 17.0, 21.5, 48.0 (t), 64.0 (d), 65.2, 127.3. IR (cm⁻¹) = 3399, 3313, 3013, 2969, 2880, 2137, 2083, 1626, 1475, 1461, 1382, 1278, 1192, 1041, 1007, 972, 940, 907, 835, 758, 683, 621. ISE: (Ag⁺) < 20 ppm; (Br⁻) < 10 ppm.

N-butyl-N-methylpyrrolidinium cyanate, [C₄mpyr][OCN].

The product was obtained as soft yellow solid (10.82 g, 98 % yield). MS (m/z) ES⁺ 142.2; ES⁻ 42.1. HRMS (m/z) ES⁺ 142.1593 (calculated 142.1596); ES⁻ 41.9977 (calculated 41.9980; higher order clusters can be detected in negative mode). ¹H-NMR (400 MHz, d₆-DMSO): δ ppm = 0.93 (t, 3H, J=7.2), 1.27-1.36 (m, 2H), 1.63-1.72 (m, 2H), 2.08 (s, 4H), 2.98 (s, 3H), 3.28-3.32 (m, 2H) 3.38-3.42 (m, 4H). ¹³C-NMR (100 MHz, d₆-DMSO): δ ppm = 13.4, 19.2, 21.0, 24.8, 47.4 (t), 62.9, 63.3 (t), 126.6 (d). IR (cm⁻¹) = 3409, 3313, 2963, 2876, 2135, 2083, 1623, 1475, 1466, 1433, 1364, 1335, 1305, 1281, 1194, 1006, 977, 929, 910, 835, 761, 683, 622. ISE: (Ag⁺) < 10 ppm; (Br⁻) < 800 ppm.

trihexyl(tetradecyl)phosphonium cyanate, [P_{6,6,6,14}][OCN].

A solution of [P_{6,6,6,14}][Cl] (10.38g, 1.00 eq, 20 mmol) in acetone (100 mL) was added to a suspension of silver cyanate (2.99g, 1.00 eq, 20 mmol) in water (100 mL). The reaction mixture was stirred for 48h at room temperature and then the yellow precipitate removed by filtration. For purification, the product was dissolved in chloroform and the insoluble silver halide impurity allowed to precipitate out. To allow Oswald ripening the solution was placed in the fridge for 12 h, followed by filtration and evaporation of the solvent. The same process was repeated twice in acetonitrile. The product was dried at high vacuum for a period of at least 24h. The product was obtained as a yellow viscous liquid (10.20 g, 97 % yield). MS (m/z) ES⁺ 483.6; ES⁻ 42.0. HRMS (m/z) ES⁺ 483.5058 (calculated 483.5059); ES⁻ 41.9988 (calculated 41.9980; higher order clusters can be detected in negative mode). ¹H-NMR (400 MHz, d₆-DMSO): δ ppm = 0.84-0.89 (m, 12H), 1.24-1.30 (m, 16H), 1.35-1.39 (m, 16H), 1.44-1.50 (m, 16H), 2.14-2.21 (m, 8H). ¹³C-NMR (100 MHz, d₆-DMSO): δ ppm = 13.7, 13.8, 17.1, 17.2, 17.5, 17.6, 20.3, 20.4, 20.5, 21.7, 22.0, 28.0, 28.5, 28.6, 28.8, 28.9, 29.6, 29.7, 29.9, 30.3, 31.2, 32.0, 55.7, 68.3, 126.7. IR (cm⁻¹) = 2997, 2921, 2286, 2164, 2138, 2051, 209, 1980, 1480, 1409, 1288, 1253, 1046, 1018, 1002, 981, 935, 898, 871, 820, 766, 726. ISE: (Ag⁺) < 10 ppm; (Cl⁻) < 20 ppm.

Instrumental information

Differential scanning calorimetry (DSC) was performed across the temperature range of -150 °C to 200 °C (with the exception of [C₁mpyr][OCN], which was measured between -150 °C to 230 °C), at a scan rate of 10 °C/min. Transition temperatures were reported using the peak maximum of the thermal transition and entropies of fusion were calculated from the melting endotherm area (ΔH_f) according to ΔS = ΔH_f/T_m.

Decomposition temperatures were determined using a Stuart Scientific melting point apparatus SMP3 at a scan rate of 2.5 °C/min in closed capillaries.

Density measurements were performed using an Anton Paar DMA 5000 density meter; for [P_{6,6,6,14}][OCN] from room temperature (25 °C) to 90 °C; for [C₂mim][OCN] from 70 °C to 90 °C and for [C₃mpyr][OCN] from 80 °C to 90 °C.

The viscosity was measured using an Anton Paar AMVn; for [P_{6,6,6,14}][OCN] from room temperature (25 °C) to 100 °C; for [C₂mim][OCN] from 70 °C to 100 °C and for [C₃mpyr][OCN] from 80 °C to 100 °C.

The ionic conductivity of the samples was evaluated using AC impedance spectroscopy across a frequency range of 0.1 Hz to 10 MHz. The measurements were performed with a frequency response analyser, Solartron 1296, driven by Solartron impedance measurement software version 3.2.0. A barrel cell was used for [C₁mpyr][OCN], across the temperature range -50 °C to 150 °C. A dip cell was used for [C₁mim][OCN], [C₂mpyr][OCN], [C₃mpyr][OCN], [C₄mpyr][OCN] and [P_{6,6,6,14}][OCN], across a temperature range of -50 to 100 °C.

X-ray Crystal Structure Analysis of [C₂mim][OCN].

A colourless prismatic crystal of dimensions 0.25x0.20x0.18 mm was mounted on an Oxford Gemini CCD diffractometer and cooled to 123 K. Data were collected with Mo K α radiation ($\lambda = 0.71073$ Å) to $2\theta_{\max}$ of 64.4° yielding 6769 reflections (Lp and multi-scan absorption corrections applied) using the CrysAlisPro software [S1]. The structure was solved and refined with SHELX-97 [S2] using 1444 unique reflections of which 1189 have $I > 2\sigma I$. All non-hydrogen atoms were located on a crystallographic mirror plane ($y = 0.25$) and were refined with anisotropic thermal parameters. Hydrogen atoms attached to the aromatic C atoms were placed in calculated positions using a riding model with C-H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$. Plausible positions for the remaining hydrogen atoms (located off the mirror plane) were located in the difference Fourier map and were refined with C-H distances restrained to 0.97-0.98 Å. The assignment of the N and O atoms was based on the refinement characteristics; the alternative configuration significantly increased $R1$ to 0.078 and resulted in a high residual electron density peak (0.81 Å⁻³) in the vicinity of the N atom. Reported N-C and N-O bond distances show contradictory trends eg [Me₃Te][OCN] N-C 1.168(4), C-O 1.217(4) Å [S3] and [Me₄N][OCN] N-C 1.219(5) (4); C-O 1.128(5) Å [S4].

C₇H₁₁N₃O *FW* 153.19. Monoclinic, $P2_1/m$. $a = 7.5540(9)$, $b = 6.4305(10)$, $c = 8.6265(11)$ Å, $\beta = 107.468(14)^\circ$. $V = 399.72(9)$ Å³. $Z = 2$. $\rho_{\text{calc}} = 1.273$ g.cm⁻³. $\mu = 0.089$ mm⁻¹. $F(000) = 164$. $R1 = 0.053$, $wR2 = 0.145$ ($I > 2\sigma I$). $R1 = 0.064$, $wR2 = 0.154$ (all data). $GoF = 1.163$. $\Delta e_{\text{max,min}} = 0.38, -0.27$ eÅ⁻³.

References

- S1 CrysAlisPro v 1.171.34.36, Oxford Diffraction Ltd (Agilent Technologies), Oxfordshire UK, 2010.
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