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Lyotropic Liquid Crystals in Amino acid derived Protic Ionic Liquids: Physicochemical Properties and Behaviour as Amphiphile Self-Assembly Media

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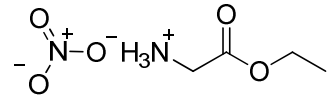
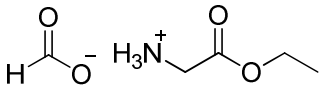
Characterization of PILs

glycine ethyl ester nitrate (2-ethoxy-2-oxoethanaminium nitrate, **GlyEN**)



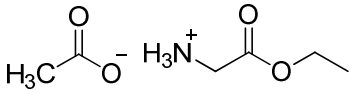
^{1}H NMR (d_6-DMSO, 200 MHz): δ 8.28 (s, broad, 3H, NH_3), 4.10-4.20 (m, 2H, OCH_2), 3.77 (d, J = 2.6 Hz, 2H, CH_2), 1.18 (t, J = 8 Hz, 3H, CH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 168.0 (COOH), 62.0 (O$\underline{C}H_2CH_3$), 40.2 (CH_2), 14.3 ($OCH_2\underline{C}H_3$) ppm; Calc. for $C_4H_{10}N_2O_5$ C 28.92, H 6.07, N 16.86; Found C 27.55, H 5.98, N 17.38.

glycine ethyl ester formate (2-ethoxy-2-oxoethanaminium formate, **GlyEF**)



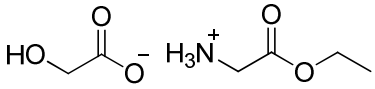
^{1}H NMR (d_6-DMSO, 200 MHz): δ 8.30 (s, 2H), 7.57 (s, 3H, NH_3^+), 4.07-4.17 (m, 2H, OCH_2), 3.56 (s, 2H, CH_2), 1.18 (t, J = 8Hz, 3H, CH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 170.4 (HCO_2^-), 165.9 (cation C=O), 61.3 (O$\underline{C}H_2CH_3$), 41.2(CH_2), 14.4($OCH_2\underline{C}H_3$); Calc. For $C_5H_{11}NO_4$ C 40.27, H 7.43, N 9.39; Found C 40.38, H 7.02, N 11.78.

glycine ethyl ester acetate (2-ethoxy-2-oxoethanaminium acetate, **GlyEA**)



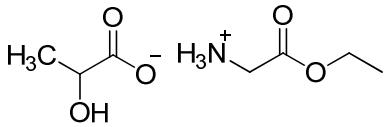
^{1}H NMR (d_6-DMSO, 200 MHz): δ 5.37 (s, 3H, NH_3^+), 4.01-4.12 (m, 2H, OCH_2), 3.28 (s, 2H, CH_2), 1.85 (s, 3H, anion CH_3), 1.17 (t, J = 6 Hz, 3H, cation CH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 173.9 (anion C=O), 172.7(cation C=O), 60.5 (O$\underline{C}H_2CH_3$), 43.5 (CH_2), 21.9 ($\underline{C}H_3CO_2^-$), 14.5 ($OCH_2\underline{C}H_3$) ppm; Calc. Rapid decomposition at room temperature prohibited the microanalysis of this material.

glycine ethyl ester (2-ethoxy-2-oxoethanaminium glycolate, **GlyEG**)



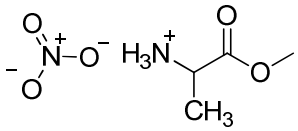
^{1}H NMR (d_6-DMSO, 200 MHz): δ 4.73 (s, 3H, NH_3^+), 4.00-4.24 (m, 2H, OCH_2), 3.65 (m, 1H), 3.53 (s, 2H), 3.40-3.52 (m, 2H), 1.18 (t, J = 9Hz, 3H) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 170.6 (C=O), 170.8 (C=O), 61.2 (CH_2), 61.0 (CH_2), 41.5 (CH_2), 14.4 ($OCH_2\underline{C}H_3$); Calc. For $C_6H_{13}NO_5$ C 40.22, H 7.31, N 7.82; Found C 39.32, H 7.25, N 7.88.

glycine ethyl ester lactate (2-ethoxy-2-oxoethanaminium lactate, **GlyEL**)



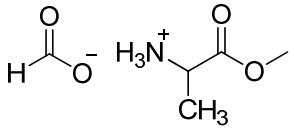
^{1}H NMR (d_6-DMSO, 200 MHz): δ 5.1 (s, broad, 3H, NH_3^+), 4.05-4.16 (m, 2H, OCH_2), 3.77-3.84 (m, 1H, CH), 3.65 (s, 2H, CH_2), 3.40-3.52 (m, 2H, OCH_2), 1.03-1.30 (m, 6H, CH_3 anion and cation) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 178.1 (C=O), 174.5(C=O), 66.9 (CH), 61.1 ($O\underline{C}H_2CH_3$), 41.6 (CH_2), 21.3 (anion CH_3), 14.4 ($OCH_2\underline{C}H_3$); Calc. For $C_7H_{15}NO_5$ C 43.52, H 7.83, N 7.25; Found C 42.36, H 7.68, N 6.91.

Alanine methyl ester nitrate (1-methoxy-1-oxopropan-2-aminium nitrate, **AlaMN**)



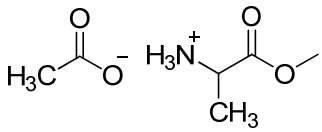
^{1}H NMR (d_6-DMSO, 200 MHz): δ 7.20 (s, broad, 3H, NH_3^+), 3.99-4.10 (m, 1H, CH), 3.71 (s, 3H, OCH_3), 1.35 (d, J = 4Hz, 3H, CH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 171.3 (C=O), 53.2 (CH), 48.4 (CH_3), 16.5 (OCH_3) ppm; Calc. For $C_4H_{10}N_2O_5$ C 28.92, H 6.07, N 16.86; Found C 29.83, H 6.17, N 16.44.

Alanine methyl ester formate (1-methoxy-1-oxopropan-2-aminium formate, **AlaMF**)



^{1}H NMR (d_6-DMSO, 200 MHz): δ 9.31 (s, 1H, HCO_2^-), 7.34 (s, 3H, NH_3^+), 3.69-3.80 (m, 1H, CH), 3.65 (s, 3H, OCH_3), 1.27 (d, J = 3.6 Hz, 3H, CH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 173.7 (C=O), 165.6 (C=O), 52.5 (CH), 48.8 (CH_3), 18.3 (OCH_3) ppm; Calc. For $C_5H_{11}NO_4$ C 40.27, H 7.43, N 9.39; Found C 39.82, H 7.55, N-9.37.

Alanine methyl ester acetate (1-methoxy-1-oxopropan-2-aminium acetate, **AlaMA**)



^{1}H NMR (d_6-DMSO, 200 MHz): δ 5.47 (s, 1H NH_3^+), 3.60 (s, 3H, OCH_3), 3.40-3.51 (m, 1H, CH), 1.85 (s, 3H, anion CH_3), 1.17 (d, J = 3.4 Hz, 3H, CH_3)) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 176.3 (C=O), 172.7 (C=O), 52.0 (CH), 49.6 (CH_3), 21.9 ($\underline{C}H_3CO_2^-$), 20.4 (OCH_3) ppm; rapid conversion to the corresponding amide at room temperature prohibited the microanalysis of this material. NMR initially and after 3

months at 5 ºC shown below, Figure S1.

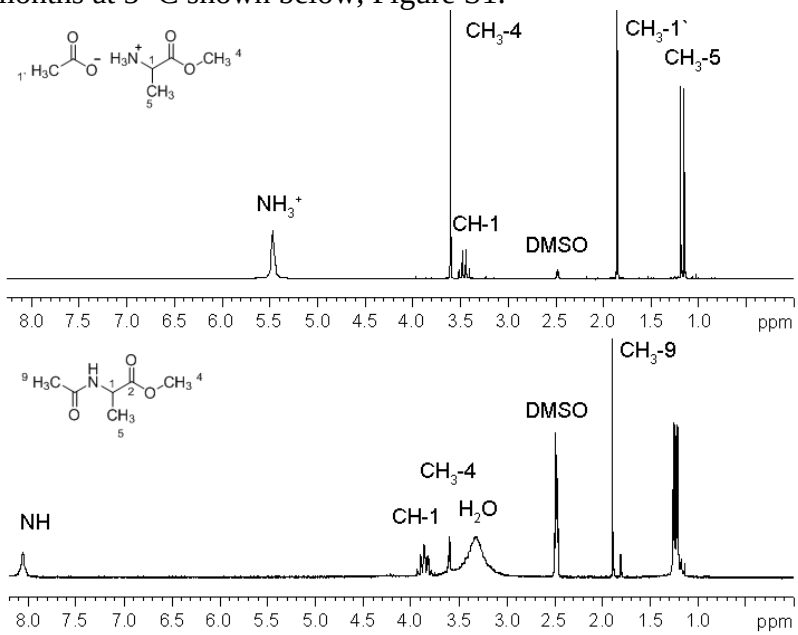
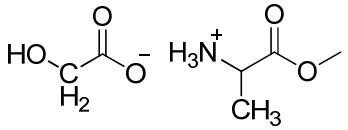


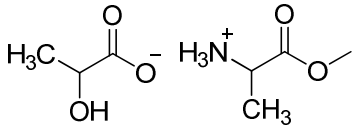
Figure S1 ^{1}H NMR spectra of AlaMA initially and after 3 months of storage.

Alanine methyl ester glycolate (1-methoxy-1-oxopropan-2-aminium glycolate, **AlaMG**)



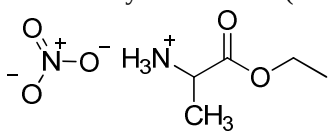
^{1}H NMR (d_6-DMSO, 200 MHz): δ 5.82 (s, broad, 3H, NH_3^+), 3.71-3.82 (m, 1H, CH), 3.65 (s, 3H, CH_2 and OH), 3.14 (s, 3H, OCH_3), 1.28 (d, J = 4 Hz, 3H, CH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 175.7(C=O), 173.6 (C=O), 61.1 (CH_2), 52.5 (CH), 48.8 (CH_3), 18.1 (OCH_3); Calc. For $C_6H_{13}NO_5$ C 40.22, H 7.31, N 7.82; Found C 39.09, H 7.28, N 7.35 ppm.

Alanine methyl ester lactate (1-methoxy-1-oxopropan-2-aminium lactate, **AlaML**)



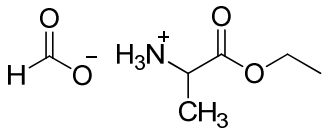
^{1}H NMR (d_6-DMSO, 200 MHz): δ 5.40 (s, broad, 3H, NH_3^+), 3.67-3.86 (m, 2H, anion and cation CH), 3.64 (s, 1H, anion OH), 3.15 (s, 3H, OCH_3), 1.25 (d, J = 3.5 Hz, 3H, anion CH_3), 1.14 (d, J = 3.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 177.9 (C=O), 174.3 (C=O), 66.8 (CHOH), 52.4 (CH_2), 49.0 (CH_3), 21.3 (anion CH_3), 18.8 (OCH_3); Calc. For $C_7H_{15}NO_5$ C 43.52; H 7.83; N 7.25; Found C 42.54, H 7.89, N 6.82 ppm.

Alanine ethyl ester nitrate (1-ethoxy-1-oxopropan-2-aminium nitrate, **AlaEN**)



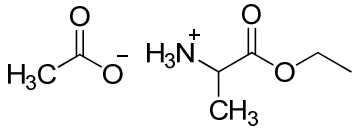
^{1}H NMR (d_6-DMSO, 200 MHz): δ 7.35 (s, broad, 3H, NH_3^+), 4.11-4.22 (m, 2H, CH_2), 3.94-4.04 (m, 1H, CH), 1.34 (d, J = 4Hz, 3H, CH_3), 1.20 (t, J = 7.2Hz, 3H, OCH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 171.0 (C=O), 62.0 ($O\underline{C}H_2CH_3$), 48.5 (CH_2), 16.6 (CH_3), 14.3 ($OCH_2\underline{C}H_3$) ppm.

Alanine ethyl ester formate (1-ethoxy-1-oxopropan-2-aminium formate, **AlaEF**)



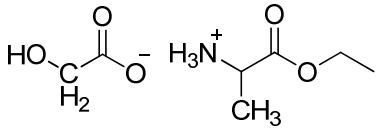
^{1}H NMR (d_6-DMSO, 200 MHz): δ 8.30 (s, 1H, HCO_2^-), 7.22 (s, 3H, NH_3^+), 4.05-4.16 (m, 2H), 3.65-3.76 (m, 1H, CH), 1.26 (d, J = 3.6Hz, 3H), 1.18 (t, J = 7Hz, 3H, OCH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 173.4 (C=O), 165.6 (C=O), 61.2 ($O\underline{C}H_2CH_3$), 48.9 (CH_2), 18.45(CH_3), 14.4 ($OCH_2\underline{C}H_3$) ppm.

Alanine ethyl ester acetate (1-ethoxy-1-oxopropan-2-aminium acetate, **AlaEA**)



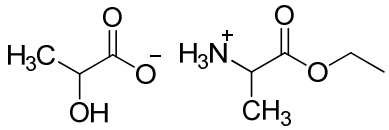
^{1}H NMR (d_6-DMSO, 200 MHz): δ 5.21 (s, 3H, NH_3^+), 4.00-4.11 (m, 2H, OCH_2), 3.38-3.49 (m, 1H, CH), 1.85 (s, 3H, CH_3), 1.13-1.20 (m, 6H, OCH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 175.85 (C=O), 172.78 (C=O), 60.5 ($O\underline{C}H_2CH_3$), 49.7 (CH_2), 21.9 ($\underline{C}H_3CO_2^-$), 20.4 (CH_3), 14.47 ($OCH_2\underline{C}H_3$) ppm.

Alanine ethyl ester glycolate (1-ethoxy-1-oxopropan-2-aminium glycolate, **AlaEG**)



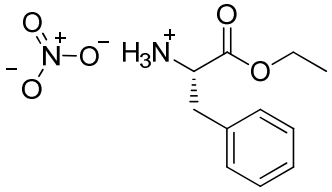
^{1}H NMR (d_6-DMSO, 200 MHz): δ 5.09 (s, broad, 3H, NH_3^+), 4.04-4.15 (m, 2H, OCH_2), 3.73 (s, 2H, anion CH_2), 3.57-3.68 (m, 1H, CH), 1.16-1.25 (m, 6H, OCH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 174.9 (C=O), 174.2 (C=O), 61.0 (CH_2 or CH), 60.6 (CH_2 or CH), 49.2 ($O\underline{C}H_2CH_3$), 19.1 (CH_3), 14.5 ($OCH_2\underline{C}H_3$) ppm.

Alanine ethyl ester lactate (1-ethoxy-1-oxopropan-2-aminium lactate, **AlaEL**)



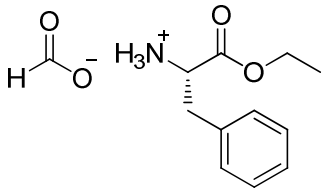
^{1}H NMR (d_6-DMSO, 200 MHz): δ 5.62 (s, broad, 3H, NH_3^+), 4.05-4.15 (m, 2H, CH_2), 3.79-3.89 (m, 1H, anion or cation CH), 3.61-3.71 (m, 1H, anion or cation CH), 3.15 (s, 1H, OH), 1.14-1.26 (m, 9H , OCH_3, anion CH_3 and cation CH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 177.6 (C=O), 173.9 (C=O), 66.7 (CHOH), 61.1 ($O\underline{C}H_2CH_3$), 49.0 (CH), 21.3 (anion CH_3), 18.8 (CH_3), 14.4 ($OCH_2\underline{C}H_3$) ppm; Calc. For $C_8H_{17}NO_5$ C 46.37; H 8.27; N 6.76; Found C 45.70, H 8.28, N 6.08.

Phenylalanine ethyl ester nitrate ((S)-1-ethoxy-1-oxo-3-phenylpropan-2-aminium nitrate**, PheEN)**



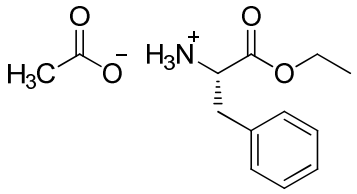
^{1}H NMR (d_6-DMSO, 200 MHz): δ 7.99 (s, broad, 3H, NH_3^+), 7.18-7.37 (m, 5H, Ph), 4.17-4.24 (m, 1H, CH), 4.03-4.13 (m, 2H, OCH_2), 2.93-3.15 (m, 2H, CH_2Ph), 1.07 (t, J = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 169.9(C=O), 135.3 (quat Ph), 129.82 (*o* or *m* -Ph), 128.98 (*o* or *m* -Ph), 127.6 (*p*-Ph), 62.0 ($O\underline{C}H_2CH_3$), 53.9 (CH), 37.0 (CH_2Ph), 14.2 ($OCH_2\underline{C}H_3$); Calc. For $C_{11}H_{16}N_2O_5$ C 51.56; H 6.29; N 10.93; Found C 52.61, H 6.53, N 10.87.

Phenylalanine ethyl ester formate ((S)-1-ethoxy-1-oxo-3-phenylpropan-2-aminium formate**, PheEF)**



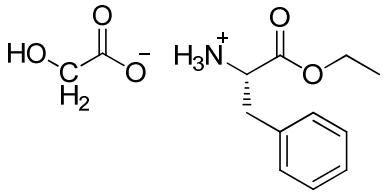
^{1}H NMR (d_6-DMSO, 200 MHz): δ 8.22 (s, 1H, HCO_2^-), 7.14-7.31 (m, 5H, Ph), 4.67 (s, 3H, NH_3^+), 3.96-4.07 (m, 1H, CH), 3.70 (t, J = 7.2 Hz, 2H, OCH_2), 2.87 (d, J = 3.4 Hz, 2H, CH_2), 1.07 (t, J = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 173.8 (C=O), 164.5 (C=O), 137.5 (quat Ph), 129.69 (*o* or *m*-Ph), 128.62 (*o* or *m* -Ph), 126.9 (*p*-Ph), 60.7 ($O\underline{C}H_2CH_3$), 55.5 (CH), 14.4 ($OCH_2\underline{C}H_3$) ppm N.B. $\underline{C}H_2Ph$ peak not observed, under solvent peak; Calc. For $C_{12}H_{17}NO_4$ C 60.24; H 7.16; N 5.85; Found C 62.01, H 7.20, N 6.15.

Phenylalanine ethyl ester acetate ((S)-1-ethoxy-1-oxo-3-phenylpropan-2-aminium acetate**, PheEA)**



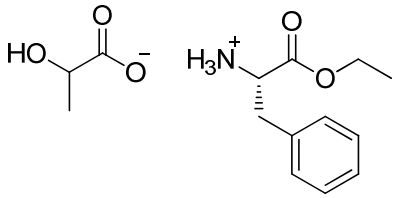
^{1}H NMR (d_6-DMSO, 200 MHz): δ 7.14-7.28 (m, 5H, Ph), 3.9-4.05 (m, 5H, NH_3^+ and CH_2Ph), 3.53 (t, J = 6.8 Hz, 2H, OCH_2), 2.77-3.82 (m, 1H, CH), 1.88 (s, 3H, anion CH_3), 1.08 (t, J = 6.8 Hz, 3H, $OCH_2C\underline{H_3}$) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 175.2 (C=O), 172.5 (C=O), 138.3 (quat Ph), 129.7 (*o* or *m* -Ph), 128.5 (*o* or *m* -Ph), 126.7 (*p*-Ph), 60.3 ($O\underline{C}H_2CH_3$), 56.1 (CH), 21.6 ($\underline{C}H_3CO_2^-$), 14.4 ($OCH_2\underline{C}H_3$) ppm N.B. $\underline{C}H_2Ph$ peak not observed, under solvent peak; Calc. For $C_{13}H_{19}NO_4$ C 61.64; H 7.56; N 5.53; Found C 61.98, H 7.81, N 5.66.

Phenylalanine ethyl ester glycolate ((S)-1-ethoxy-1-oxo-3-phenylpropan-2-aminium glycolate**, PheEG)**



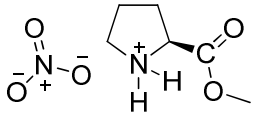
^{1}H NMR (d_6-DMSO, 200 MHz): δ 7.14-7.31 (m, 5H, Ph), 4.68 (s, 3H, NH_3^+), 3.95-4.05 (m, 2H, OCH_2), 3.78 (s, 2H, CH_2 anion), 3.72 (t, J = 6.8 Hz, 1H, CH), 2.88 (d, J = 3.4 Hz, 2H, CH_2Ph), 1.07 (t, J = 6.8 Hz, 3H, $OCH_2C\underline{H_3}$) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 175.1 (C=O), 173.7 (C=O), 137.4 (quat Ph), 129.7 (*o* or *m* -Ph), 128.6 (*o* or *m* -Ph), 126.9 (*p*-Ph), 60.8 (anion CH_2 or $O\underline{C}H_2CH_3$), 60.6 (anion CH_2 or $O\underline{C}H_2CH_3$), 55.4 (CH), 14.3 ($OCH_2\underline{C}H_3$) ppm N.B. $\underline{C}H_2Ph$ peak not observed, under solvent peak; Calc. For $C_{13}H_{19}NO_5$ C 57.98; H 7.11; N 5.20; Found C 58.01, H 7.19, N 5.29.

Phenylalanine ethyl ester lactate ((S)-1-ethoxy-1-oxo-3-phenylpropan-2-aminium lactate**, PheEL)**



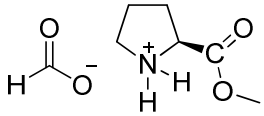
^{1}H NMR (d_6-DMSO, 200 MHz): δ 7.14-7.23 (m, 5H, Ph), 4.48 (s, broad, 3H, NH_3^+), 3.90-4.11 (m, 3H, OCH_2 and CHMe), 3.63 (t, J = 6.8 Hz, 1H, CH), 2.84 (d, J = 3.4 Hz, 2H, CH_2Ph), 1.17-1.36 (m, 3H, anion CH_3), 1.07 (t, J = 6.8 Hz, 3H, $OCH_2C\underline{H_3}$) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 177.1 (C=O), 174.4 (C=O), 137.8 (quat Ph), 129.7 (*o* or *m* -Ph), 128.6 (*o* or *m* -Ph), 126.8 (*p*-Ph), 66.4(anion CH_2 or $O\underline{C}H_2CH_3$), 60.6 (anion CH_2 or $O\underline{C}H_2CH_3$), 55.7 (CH), 21.0 (anion CH_3), 14.4 ($OCH_2\underline{C}H_3$) ppm N.B. $\underline{C}H_2Ph$ not observed, under solvent peak; Calc. For $C_{14}H_{21}NO_5$ C 59.35; H 7.47; N 4.94; Found C 60.09, H 7.63, N 5.13.

Proline methyl ester nitrate ((S)-2-(methoxycarbonyl)pyrrolidin-1-ium nitrate**, ProMN)**



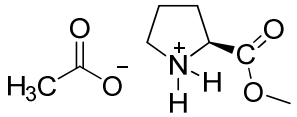
^{1}H NMR (d_6-DMSO, 200 MHz): δ 9.53 (s, 1H, N-H), 8.96 (s, 1H, N-H), 4.40 (t, J = 7.6 Hz, 1H, CH), 3.73 (s, 3H, CH_3), 3.18-3.28 (m, 2H, CH_2), 2.14-2.34 (m, 1H, CH_2), 1.81-2.06 (m, 2H, CH_2) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 169.6 (C=O), 59.1 (CH), 53.4 (CH_3), 46.0 (CH_2), 28.1 (CH_2), 23.5 (CH_2) ppm; Calc. For $C_6H_{12}N_2O_5$ C 37.50; H 6.29; N 14.58; Found C 37.12, H 6.53, N 14.21.

Proline methyl ester formate ((S)-2-(methoxycarbonyl)pyrrolidin-1-ium formate**, ProMF)**



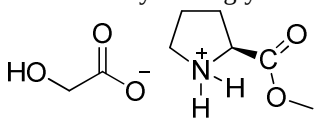
^{1}H NMR (d_6-DMSO, 200 MHz): δ 8.97 (s, 2H), 8.27(s, 1H, HCO_2^-), 3.97-4.04 (m, 1H), 3.66 (s, 3H), 2.91-3.06 (m, 2H), 2.04-2.14 (m, 1H), 1.70-1.88 (m, 3H) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 172.8 (C=O), 165.4 (C=O), 58.9 (CH), 52.6 (CH_3), 46.0 (CH_2), 29.1 (CH_2), 24.6 (CH_2); Calc. For $C_7H_{13}NO_4$ C 47.99; H 7.48; N 8.00; Found C 51.47, H 7.18, N 9.25.

Proline methyl ester acetate ((S)-2-(methoxycarbonyl)pyrrolidin-1-ium acetate**, ProMA)**



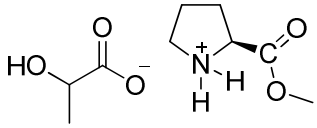
^{1}H NMR (d_6-DMSO, 200 MHz): δ 7.25 (s, 2H), 3.67-3.74 (m, 1H), 3.61 (s, 3H), 2.76-2.91 (m, 2H), 1.92-2.03 (m, 1H), 1.85 (s, 3H), 1.53-1.80 (m, 3H) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 175.04(C=O), 172.78(C=O), 59.2 (CH), 52.0 (CH_3), 46.6 (CH_2), 29.8 (CH_2), 25.4 (CH_2), 21.8 ($\underline{C}H_3CO_2^-$); Calc. For $C_8H_{15}NO_4$ C 50.78; H 7.99; N 7.40; Found C 50.11, H 7.69, N- 8.46.

Proline methyl ester glycolate ((S)-2-(methoxycarbonyl)pyrrolidin-1-ium glycolate**, ProMG)**



^{1}H NMR (d_6-DMSO, 200 MHz): δ 5.62 (s, 2H), 3.83-3.90 (m, 1H), 3.63 (s, 3H), 3.15 (s, 1H), 2.83-2.99 (m, 2H), 1.98-2.09 (m, 1H), 1.85 (s, 3H), 1.65-1.86 (m, 3H) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 174.9 (C=O), 173.9 (C=O), 60.4 (CH_2 anion), 59.1 (CH), 52.4 (CH), 46.3 (CH_2), 29.4 (CH_2), 25.0 (CH_2); Calc. For $C_8H_{15}NO_5$ C 46.82; H 7.37; N 6.83; Found C 44.20, H 7.46, N 6.78.

Proline methyl ester glycolate ((S)-2-(methoxycarbonyl)pyrrolidin-1-ium glycolate**, ProMG)**



^{1}H NMR (d_6-DMSO, 200 MHz): δ 5.73 (s, 2H), 3.85-3.95 (m, 2H), 3.64 (s, 3H), 3.15 (s, 1H), 2.85-3.00 (m, 2H), 1.99-2.10 (m, 1H), 1.66-1.84 (m, 3H), 1.17 (d, J = 3.4Hz, 3H) ppm; ^{13}C NMR (d_6-DMSO, 50 MHz): δ 174.9 (C=O), 173.9 (C=O), 60.4 (CH anion), 59.1 (CH), 52.4 (CH_2), 46.4 (CH_2), 29.5 (CH_2), 25.0 (CH_2); Calc. For $C_9H_{17}NO_5$ C 49.31; H 7.82; N 6.39; Found C 47.98, H 7.84, N 6.23.