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Azoniaspiro salts: towards bridging the gap between room-temperature ionic liquids and molten salts

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Electronic Supplementary Information

1. General laboratory procedures

All reactions requiring an inert atmosphere were performed under a blanket of nitrogen gas, which was dried through a column of phosphorus pentoxide. All commercially acquired chemicals were obtained from Sigma-Aldrich or Tokyo Chemical Industry, and were used without further purification unless otherwise stated. Anhydrous solvents were dried through an HPLC column on an Innovative Technology Inc. solvent purification system. NMR spectra were recorded on Bruker Avance-400 (^{1}H NMR (400 MHz), ^{13}C (100 MHz), ^{19}F (376 MHz)) NMR spectrometers. Chemical shifts are reported in ppm (relative to the DMSO-d6 residual peak). IR spectra were recorded on a Perkin Elmer spectrum 100 FTIR using an ATR inset with a diamond crystal. LSIMS mass spectrometry was performed on a Micromass AutoSpec Premier mass spectrometer. Melting point measurements were carried out on a Stanford Research Systems 'OptiMelt' automated melting point system, with a heating rate of 1 °C min^{-1}. Melting point values are uncorrected. Elemental analysis experiments were carried out by the London Metropolitan University service.

2. Synthesis of ionic compounds

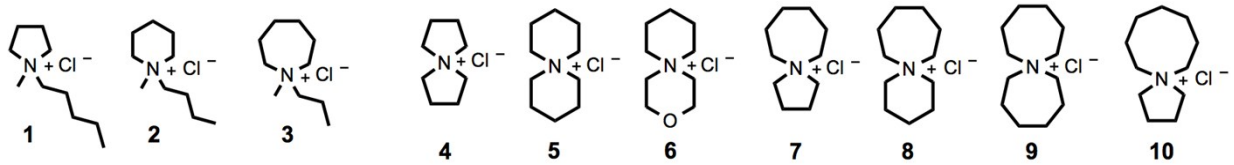


Fig E1: Single-ring (**1**-**3**) and azoniaspiro (**4**-**10**) chloride salts prepared in this investigation.

General Procedure: ***synthesis of single-ring salts*** (**1**-**3**):

1-methyl(*N*-heterocycle) (1 equiv.) was dissolved in toluene. The mixture was heated to a defined temperature (60-90 °C) with vigorous stirring. A 1-chloroalkane (1 equiv.) was then added dropwise slowly, followed by additional 1-chloroalkane where necessary. The solution was maintained at 60-90 °C for one to six days. The solid product was collected by filtration/decanting off the toluene, was washed, and was dried under high vacuum.

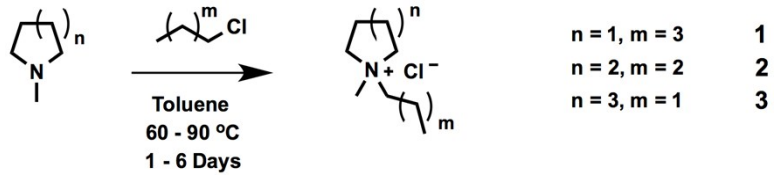


Fig E2: General procedure for synthesis of single-ring tetraalkylammonium chloride salts, **1**-**3**.

1-Methyl-1-pentylpyrrolidinium chloride (**1**).
1-Methylpyrrolidine (22.5 g, 264 mmol) was dissolved in toluene (100 ml) in a 250 ml four-necked round-bottomed flask, fitted with a reflux condenser, dropping funnel, thermometer and stopper. The dropping funnel was charged with 1-chloropentane (30.0 g, 281 mmol). The solution was heated to 90 °C under an argon atmosphere, and the 1-chloropentane was added dropwise to the toluene solution over 15 minutes with vigorous stirring. The solution was maintained at 90 °C for four days, during which time a white precipitate formed. The solution was allowed to cool to room temperature. The solution was filtered under an argon atmosphere, and the solid product was washed with ethyl acetate (20 ml) to yield 1-methyl-1-pentylpyrrolidinium chloride (4.65 g, 9%) as a white solid.
Found: m.p. 127.0-129.0 °C. ^{1}H NMR (400 MHz, DMSO-d6): δ 3.54-3.37 (4H, m), 3.31 (2H, m), 2.99 (3H, s), 2.15-1.99 (4H, s br), 1.75-1.63 (2H, m), 1.40-1.19 (4H, m), 0.89 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz,

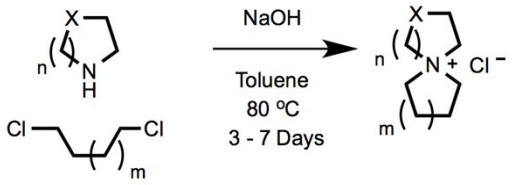
DMSO-d6): *δ* 63.3, 62.9, 47.4, 28.0, 22.6, 21.7, 21.0, 13.8. *ν*(neat)/cm^{-1} 2956 2872 (aliphatic C-H stretch, m), 1467 (aliphatic CH_2 bend, m), 935 (aliphatic C-N stretch, m). *m/z* (LSIMS$^+$): 156 (100%) $[C_5C_1pyrr]^+$. *m/z* (LSIMS$^-$): 35 (100%) $^{35}Cl^-$, 37 (48%) $^{37}Cl^-$. Calc. for $C_{10}H_{22}ClN$: C, 62.64; H, 11.56; N, 7.30%. Found: C, 62.59; H, 11.40; N, 7.19%.

1-Butyl-1-methylpiperidinium chloride (**2**).
Freshly distilled 1-methylpiperidine (48.1 g, 485 mmol) was dissolved in toluene (200 ml) in a two-necked, 500 ml round-bottomed flask fitted with a reflux condenser and a dropping funnel. The dropping funnel was charged with freshly distilled 1-chlorobutane (70.9 g, 766 mmol). The solution was heated to 80 °C under a nitrogen atmosphere and the 1-chlorobutane was added dropwise over 30 minutes, with vigorous stirring. The dropping funnel was replaced with a thermometer, and the solution was maintained at 80 °C for six days, during which time the solution had turned yellow and a white precipitate had formed. The solution was allowed to cool to room temperature, and the toluene solution was carefully decanted off. The white precipitate was washed with toluene (3 × 50 ml), and dried under high vacuum to yield 1-butyl-1-methylpiperidinium chloride (5.3 g, 6%) as a white solid.
Found: m.p. >210 °C *decomposition*. ^{1}H NMR (400 MHz, DMSO-d6): *δ* 3.33-3.23 (6H, m), 2.99 (3H, s), 1.85-1.70 (4H, m), 1.69-1.58 (2H, m), 1.57-1.44 (2H, m), 1.38-1.24 (2H, m), 0.94 (3H, t, J = 8 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): *δ* 62.2, 59.9, 47.0, 23.0, 20.7, 20.4, 19.3, 13.5. *ν*(neat)/cm^{-1} 2941 2876 (aliphatic C-H stretch, w), 1471 (aliphatic CH_2 bend, w), 945 (aliphatic C-N stretch, m). *m/z* (LSIMS$^+$): 72 (100%) $[C_5H_{12}]^+$, 99 (14%) $[(CH_2)_5N(CH_3)]^+$, 156 (12%) $[C_4C_1pip]^+$. *m/z* (LSIMS$^-$): 35 (100%) $^{35}Cl^-$, 37 (30%) $^{37}Cl^-$. Calc. for $C_{10}H_{22}ClN$: C, 62.64; H, 11.56; N, 7.30%. Found: C, 62.56; H, 11.64; N, 7.30%.

1-Methyl-1-propylazepanium chloride (**3**).
1-Methylazepane (5.00 g, 44 mmol) was dissolved in toluene (35 ml) in a four-necked, 100 ml round-bottomed flask, fitted with a reflux condenser, thermometer and dropping funnel. The dropping funnel was charged with 1-chloropropane (7.0 g, 89 mmol). The toluene solution was warmed to 60 °C, followed by dropwise addition of the 1-chloropropane, over 10 minutes. The solution was heated under reflux at 60 °C for 2 hours. The dropping funnel was charged with additional 1-chloropropane (20.0 g, 255 mmol). The solution was then heated to 80 °C, and the 1-chloropropane was dispensed dropwise over 30 minutes. The solution was heated at 80 °C under reflux overnight, during which time a white precipitate had formed. The mixture was filtered under an argon atmosphere, and the solid was washed with ethyl acetate (20 ml), to yield 1-methyl-1-pentylazepanium chloride (0.40 g, 5%) as a white solid.
Found: m.p. 244-245 °C *with decomposition*. ^{1}H NMR (400 MHz, DMSO-d6): *δ* 3.47-3.29 (4H, m), 3.24 (2H, m), 2.98 (3H, s), 1.90-1.75 (4H, s br), 1.76-1.63 (2H, m), 1.63-1.52 (4H, m), 0.90 (3H, t, J = 8 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): *δ* 65.4, 63.4, 49.8, 27.2, 20.8, 15.4, 10.6. *ν*(neat)/cm^{-1} 3008 2966 2931 2861 (aliphatic C-H stretch, w), 1495 (aliphatic CH_2 bend, w), 934 (aliphatic C-N stretch, m). *m/z* (LSIMS$^+$): 156 (100%) $[C_3C_1azp]^+$. *m/z* (LSIMS$^-$): 35 (100%) $^{35}Cl^-$, 37 (24%) $^{37}Cl^-$. Calc. for $C_{10}H_{22}ClN$: C, 62.64; H, 11.56; N, 7.30%. Found: C, 62.49; H, 11.65; N, 7.22%.

General Procedure: ***synthesis of azoniaspiro chloride salts*** (**4**-**10**):

An *N*-heterocycle (1 equiv.) was dissolved in toluene. NaOH (1 equiv.) was dissolved in deionized water, and was added to the toluene solution. The mixture was heated to 80 °C with vigorous stirring. 1 equivalent of 1,(*m*+3)-dichloroalkane was added dropwise, slowly. The solution was maintained at 80 °C for a minimum of three days. The solution was cooled to room temperature, additional deionized water and toluene were added, and the layers were separated. Unreacted *N*-heterocycle and dichloroalkane were removed by washing the aqueous layer with aliquots of toluene. The water was evaporated from the aqueous layer, and the product was extracted into ethanol, in which byproduct NaCl was very insoluble. The solid product was collected by evaporation of the ethanol, and was purified by recrystallization where appropriate.



n = 1, m = 1, X = CH_2	**4**
n = 2, m = 2, X = CH_2	**5**
n = 2, m = 2, X = O	**6**
n = 3, m = 1, X = CH_2	**7**
n = 3, m = 2, X = CH_2	**8**
n = 3, m = 3, X = CH_2	**9**
n = 4, m = 1, X = CH_2	**10**

Fig E3: General procedure for synthesis of azoniaspiro chloride salts, **4**-**10**.

5-Azoniaspiro[4.4]nonanium chloride monohydrate (**4.**H_2O).
Pyrrolidine (10.0 g, 141 mmol) was dissolved in toluene (40 ml) in a 250 ml, three-necked round-bottomed flask, fitted with a reflux condenser, dropping funnel and stopper. Separately, an aqueous solution of NaOH was prepared by dissolving solid NaOH (5.6 g, 141 mmol) in deionized water (20 ml). The NaOH solution was added to the toluene solution, and the dropping funnel was charged with 1,4-dichlorobutane (17.9 g, 141 mmol). The mixture was heated to 80 °C under a nitrogen atmosphere, and 1,4-dichlorobutane was added dropwise to the toluene/water mixture over 30 minutes, with vigorous stirring. The solution was maintained at 80 °C for three days and was then allowed to cool to room temperature. Toluene (50 ml) and deionized water (50 ml) were added, and the layers were separated. The aqueous layer was washed with toluene (3 × 40 ml). The water was removed by rotary evaporation, and to the residue was added cold ethanol (100 ml), in which the product was found to be more soluble than NaCl. The solution was filtered, and the ethanol was removed by rotary evaporation. A portion of the crude product was recrystallised from ethanol/toluene (50:50 vol/vol) (150 ml), followed by cooling of a portion of the mixture in the freezer for five months, during which time crystals had formed. The liquid was carefully decanted off, followed by washing of the product with diethyl ether (4 × 20 ml) to yield 5-azoniaspiro[4.4]nonanium chloride monohydrate as a white crystalline solid.
Found: m.p. 63.0-65.5 °C. ^{1}H NMR (400 MHz, DMSO-d6): *δ* 3.61-3.43 (8H, m), 2.18-1.95 (8H, m). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): *δ* 61.8, 21.5. ***m/z*** (LSIMS^{+}): 126 (100%) $[(CH_2)_4N(CH_2)_4]^{+}$. ***m/z*** (LSIMS^{-}): 35 (100%) $^{35}Cl^{-}$, 37 (33%) $^{37}Cl^{-}$. Calc. for $C_8H_{18}ClNO$: C, 53.47; H, 10.10; N, 7.80%. Found: C, 53.71; H, 10.97; N, 7.73%.

6-Azoniaspiro[5.5]undecanium chloride (**5**).
Piperidine (3.8 g, 44 mmol) was dissolved in toluene (20 ml) in a 100 ml three-necked round-bottomed flask, fitted with a reflux condenser, dropping funnel and stopper. Separately, an aqueous solution of NaOH was prepared by dissolving solid NaOH (1.76 g, 44 mmol) in deionized water (5 ml). The NaOH solution was added to the toluene solution, and the dropping funnel was charged with 1,5-dichloropentane (6.2 g, 44 mmol). The mixture was heated to 80 °C under a nitrogen atmosphere, and the 1,5-dichloropentane was added dropwise to the toluene/water mixture over 10 minutes, with vigorous stirring. The solution was maintained at 80 °C for six days, and was then allowed to cool to room temperature. Toluene (20 ml) and deionized water (20 ml) were added, and the layers were separated. The aqueous layer was washed with toluene (3 × 20 ml). The water was removed by rotary evaporation, and to the residue was added cold ethanol (100 ml), in which the product was found to be more soluble than NaCl. The solution was filtered, and the ethanol was removed

by rotary evaporation. The crude product was recrystallized from ethanol/toluene (50:50 vol/vol), to yield 6-azoniaspiro[5.5]undecanium chloride (2.1 g, 25%) as a white crystalline solid.
Found: m.p. 310-312 °C *with decomposition* (lit. 310-311 °C *with decomposition*).[1] ^{1}H NMR (400 MHz, DMSO-d6): *δ* 3.38 (8H, t, J = 6 Hz), 1.82-1.67 (8H, m), 1.63-1.46 (4H, m). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): *δ* 58.3, 21.3, 18.7. *ν*(neat)/cm^{-1} 2998 2934 2875 (aliphatic C-H stretch, w), 1475 (aliphatic CH_2 bend, w), 893 (aliphatic C-N stretch, m). *m/z* (LSIMS^{+}): 98 (100%) $[C_5H_{10}N{=}CH_2]^{+}$, 154 (85%) $[(CH_2)_5N(CH_2)_5]^{+}$. *m/z* (LSIMS^{-}): 35 (100%) $^{35}Cl^{-}$, 37 (31%) $^{37}Cl^{-}$. Calc. for $C_{10}H_{20}ClN$: C, 63.31; H, 10.63; N, 7.38%. Found: C, 63.24; H, 10.70; N, 7.40%.

3-Oxa-6-azoniaspiro[5.5]undecanium chloride (**6**).
Morpholine (6.18 g, 71 mmol) was dissolved in toluene (20 ml) in a 100 ml, three-necked round-bottomed flask, fitted with a reflux condenser, dropping funnel and stopper. Separately, an aqueous solution of NaOH was prepared by dissolving solid NaOH (2.84 g, 71 mmol) in deionized water (5 ml). The NaOH solution was added to the toluene solution, and the dropping funnel was charged with 1,5-dichloropentane (10.0 g, 71 mmol). The mixture was heated to 80 °C under a nitrogen atmosphere, and the 1,5-dichloropentane was added dropwise to the toluene/water mixture over 10 minutes, with vigorous stirring. The solution was maintained at 80 °C for one week, and was then allowed to cool to room temperature. Toluene (25 ml) and deionized water (25 ml) were added, and the layers were separated. The aqueous layer was washed with toluene (3 × 20 ml). The water was removed by rotary evaporation, and to the residue was added cold ethanol (40 ml), in which the product was found to be more soluble than NaCl. The solution was filtered, and the ethanol was removed by rotary evaporation to yield 3-oxa-6-azoniaspiro[5.5]undecanium chloride (2.13 g, 16%) as a white solid.
Found: m.p. >280 °C *decomposition*. ^{1}H NMR (400 MHz, DMSO-d6): *δ* 3.97 (4H, t br, J = 5 Hz), 3.56 (4H, t br, J = 6 Hz), 3.51 (4H, t br, J = 5 Hz), 1.85-1.69 (4H, m), 1.61-1.50 (2H, m). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): *δ* 59.3, 58.6, 57.3, 21.1, 18.6. *ν*(neat)/cm^{-1} 2987 2966 2943 2877 (aliphatic C-H stretch, w), 1117 (C-O stretch, m), 904 (aliphatic C-N stretch, m). *m/z* (LSIMS^{+}): 156 (100%) $[(CH_2CH_2OCH_2CH_2)N(CH_2)_5]^{+}$, 100 (32%) $[(CH_2CH_2OCH_2CH_2)N{=}CH_2]^{+}$. Calc. for $C_9H_{18}ClNO$: C, 56.39; H, 9.46; N, 7.31%. Found: C, 56.47; H, 9.54; N, 7.27%.

5-Azoniaspiro[6.4]undecanium chloride (**7**).
Azepane (25.0 g, 252 mmol) was dissolved in toluene (80 ml) in a 250 ml, four-necked round-bottomed flask, fitted with a reflux condenser, a dropping funnel, a thermometer and a stopper. Separately, a 25% aqueous solution of NaOH was prepared by mixing 50% aqueous NaOH (20.16 g, 252 mmol) with deionized water (20.16 g). The NaOH solution was added to the toluene solution, and the dropping funnel was charged with 1,4-dichlorobutane (32.02 g, 252 mmol). The mixture was heated to 80 °C under an argon atmosphere, and the 1,4-dichlorobutane was added dropwise to the toluene/water mixture over a period of 15 minutes, with vigorous stirring. The solution was maintained at 80 °C for four days, and was then allowed to cool to room temperature. Toluene (50 ml) and deionized water (250 ml) were added, and the layers were separated. The toluene layer was washed with deionized water (2 × 25 ml), and the aqueous layers were combined. Water was removed by rotary evaporation, and to the residue was added cold ethanol (100 ml), in which the product was found to be more soluble than NaCl. The solution was filtered, and the filtrate was treated with anhydrous $MgSO_4$. The solution was filtered again, and the ethanol was removed by rotary evaporation. The crude product was recrystallized from ethanol/ethyl acetate (30:70 vol/vol) (150 ml) to yield 5-azoniaspiro-[6.4]undecanium chloride (26.50 g, 55%) as a white solid.
Found: m.p. 262-263 °C *with decomposition* (lit. 266-267 °C *with decomposition*).[1] ^{1}H NMR (400 MHz, DMSO-d6): *δ* 3.53-3.37 (8H, m), 2.10-2.00 (4H, s br), 1.88-1.76 (4H, s br), 1.67-1.56 (4H, m). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): *δ* 63.8, 62.3, 26.7, 22.0, 21.0. *ν*(neat)/cm^{-1} 2931 2865 (aliphatic C-H stretch, w), 909 (aliphatic C-N stretch, m). *m/z* (LSIMS^{+}): 154 (100%) $[(CH_2)_6N(CH_2)_4]^{+}$. *m/z* (LSIMS^{-}): 35 (100%) $^{35}Cl^{-}$, 37 (28%) $^{37}Cl^{-}$. Calc. for $C_{10}H_{20}ClN$: C, 63.31; H, 10.63; N, 7.38%. Found: C, 63.30; H, 10.70; N, 7.44%.

6-Azoniaspiro[6.5]dodecanium chloride (**8**).
Azepane (15.0 g, 151 mmol) was dissolved in toluene (70 ml) in a 250 ml, three-necked round-bottomed flask, fitted with a reflux condenser, a dropping funnel and a thermometer. Separately, an aqueous solution of NaOH was prepared by dissolving solid pellets of NaOH (6.05 g, 151 mmol) in deionized water (20 ml). The NaOH solution was carefully added to the toluene solution, and the dropping funnel was charged with

1,5-dichloropentane (21.33 g, 151 mmol). The biphasic mixture was heated to 80 °C under a nitrogen atmosphere, and the 1,5-dichloropentane was added dropwise to the toluene/water mixture over a period of 15 minutes, with vigorous stirring. The solution was maintained at 80 °C for four days and was subsequently allowed to cool to room temperature. Toluene (100 ml) and deionized water (100 ml) were added, and the two layers were separated. The (upper) toluene layer was washed with deionized water (2 × 25 ml), and the three aqueous fractions were combined. Water was removed by rotary evaporation. To the resultant crude residue was added cold ethanol (200 ml), in which the product was found to be more soluble than NaCl. The solution was filtered, and the filtrate was treated with anhydrous $MgSO_4$. The solution was filtered again, and the ethanol was removed by rotary evaporation, to yield 6-azoniaspiro[6.5]dodecanium chloride (18.6 g, 60%) as a white, free-flowing solid.
Found: m.p. 272-273 °C *with decomposition* (lit. 270-272 °C *with decomposition*).[1] ^{1}H NMR (400 MHz, DMSO-d6): *δ* 3.44 (4H, t, J = 5 Hz), 3.34 (4H, t, J = 6 Hz), 1.88-1.68 (8H, m), 1.65-1.47 (6H, m). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): *δ* 61.4, 60.3, 27.1, 20.8, 20.3, 19.4. *ν*(neat)/cm^{-1} 2933 2862 (aliphatic C-H stretch, w), 1449 (aliphatic CH_2 bend, w), 870 (aliphatic C-N stretch, m). *m/z* (LSIMS$^+$): 168 (100%) $[(CH_2)_6N(CH_2)_5]^+$. *m/z* (LSIMS$^-$): 35 (100%) $^{35}Cl^-$, 37 (23%) $^{37}Cl^-$. Calc. for $C_{11}H_{22}ClN$: C, 64.84; H, 10.88; N, 6.87%. Found: C, 64.81; H, 10.77; N, 6.89%.

7-Azoniaspiro[6.6]tridecanium chloride (**9**).
Azepane (15.0 g, 151 mmol) was dissolved in toluene (70 ml) in a 250 ml, three-necked round-bottomed flask, fitted with a reflux condenser, dropping funnel and stopper. Separately, an aqueous solution of NaOH was prepared by dissolving solid NaOH (6.05 g, 151 mmol) in deionized water (25 ml). The NaOH solution was added to the toluene solution, and the dropping funnel was charged with 1,6-dichlorohexane (23.5 g, 151 mmol). The mixture was heated to 80 °C under a nitrogen atmosphere, and the 1,6-dichlorohexane was added dropwise to the toluene/water mixture over a period of 30 minutes, with vigorous stirring. The solution was maintained at 80 °C for one week, during which time the solution had become yellow. The solution was subsequently allowed to cool to room temperature. Toluene (50 ml) and deionized water (50 ml) were added, and the layers were separated. The aqueous layer was washed with toluene (3 × 40 ml). The water was removed by rotary evaporation, and to the residue was added cold ethanol (100 ml), in which the product was found to be more soluble than NaCl. The solution was filtered, and the ethanol was removed by rotary evaporation. A portion of the crude product was recrystallised from ethanol/toluene (50:50 vol/vol), to yield 7-azoniaspiro[6.6]tridecanium chloride (0.7 g, 2%) as an white crystalline solid.
Found: m.p. >305 °C *decomposition*. ^{1}H NMR (400 MHz, DMSO-d6): *δ* 3.32 (8H, t, J = 5 Hz), 1.88-1.68 (8H, s br), 1.66-1.50 (8H, s br). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): *δ* 62.5, 27.4, 20.9. *ν*(neat)/cm^{-1} 2981 2940 2926 2861 (aliphatic C-H stretch, w), 1494 1454 (aliphatic CH_2 bend, m), 987 (aliphatic C-N stretch, w). *m/z* (LSIMS$^+$): 55 (100%) $[C_4H_7]^+$, 112 (66%) $[C_6H_{12}N{=}CH_2]^+$, 182 (32%) $[(CH_2)_6N(CH_2)_6]^+$. *m/z* (LSIMS$^-$): 35 (100%) $^{35}Cl^-$, 37 (29%) $^{37}Cl^-$. Calc. for $C_{12}H_{24}ClN$: C, 66.18; H, 11.11; N, 6.43%. Found: C, 66.02; H, 11.11; N, 6.38%.

5-Azoniaspiro[7.4]dodecanium chloride (**10**).
Heptamethyleneimine (4.50 g, 40 mmol) was dissolved in toluene (20 ml) in a 100 ml, three-necked round-bottomed flask, fitted with a reflux condenser, dropping funnel and stopper. Separately, an aqueous solution of NaOH was prepared by dissolving solid NaOH (1.6 g, 40 mmol) in deionized water (5 ml). The NaOH solution was added to the toluene solution, and the dropping funnel was charged with 1,4-dichlorobutane (5.05 g, 40 mmol). The mixture was heated to 80 °C under a nitrogen atmosphere, and the 1,4-dichlorobutane was added dropwise to the toluene/water mixture over a period of 10 minutes, with vigorous stirring. The solution was maintained at 80 °C for four days, and was then allowed to cool to room temperature. Toluene (10 ml) and deionized water (20 ml) were added, and the layers were separated. The water was removed by rotary evaporation, and to the residue was added cold ethanol (30 ml), in which the product was found to be more soluble than NaCl. The solution was filtered, and the filtrate was treated with anhydrous $MgSO_4$. The solution was filtered, and ethanol was removed by rotary evaporation to yield 5-azoniaspiro[7.4]dodecanium chloride (4.13 g, 51%) as a white solid.
Found: m.p. 256-257 °C with decomposition. ^{1}H NMR (400 MHz, DMSO-d6): *δ* 3.51-3.44 (4H, m), 3.44-3.38 (4H, m), 2.11-1.98 (4H, m), 1.92-1.78 (4H, m), 1.65-1.54 (6H, m). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): *δ* 62.7, 57.2, 25.8, 23.5, 21.7, 21.0. *ν*(neat)/cm^{-1} 2990 2963 2918 2872 (aliphatic C-H stretch, w), 1476

(aliphatic CH_2 bend, w), 863 (aliphatic C-N stretch, w). *m/z* (LSIMS$^+$): 168 (100%) $[(CH_2)_7N(CH_2)_4]^+$. *m/z* (LSIMS$^-$): 35 (100%) $^{35}Cl^-$, 37 (33%) $^{37}Cl^-$. Calc. for $C_{11}H_{22}ClN$: C, 64.84; H, 10.88; N, 6.87%. Found: C, 64.77; H, 10.92; N, 6.79%.

***Synthesis of metathesis salts**:*

6-Azoniaspiro[6.5]dodecanium *bis*(trifluoromethanesulfonyl)imide.
6-Azoniaspiro[6.5]dodecanium chloride (5.00 g, 25 mmol) and lithium *bis*(trifluoromethanesulfonyl)imide (7.05 g, 25 mmol) were carefully weighed into a 250 ml, single-neck round-bottomed flask. Dry CH_2Cl_2 (80 ml) was added, and the solution was stirred at room temperature for three days, during which white fine precipitate had formed. The solution was filtered under gravity followed by filtration through syringe filters to remove fine particulate matter. The CH_2Cl_2 was removed by rotary evaporation to yield 6-azoniaspiro[6.5]dodecanium *bis*(trifluoromethylsulfonyl)imide (7.9 g, 72%) as a white free-flowing solid, which tested negative for Cl^- with aqueous silver(I) nitrate.
Found: m.p. 104.5-106 °C. ^{1}H NMR (400 MHz, DMSO-d6): *δ* 3.42 (4H, t, J = 5 Hz), 3.31 (4H, t, J = 6 Hz), 1.85-1.70 (8H, m), 1.65-1.49 (6H, m). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): *δ* 121.1, 61.4, 60.4, 27.2, 20.8, 20.3, 19.4. ^{19}F NMR (376 MHz, DMSO-d6): δ -78.7. *ν*(neat)/cm^{-1} 2940 (aliphatic C-H stretch, w), 1348 (asym. S=O stretch, m), 1176 (sym. S=O stretch, m), 1050 (aliphatic C-N stretch, m). *m/z* (LSIMS$^+$): 168 (100%) $[(CH_2)_6N(CH_2)_5]^+$. *m/z* (LSIMS$^-$): 280 (100%) $[NTf_2]^-$. Calc. for $C_{13}H_{22}F_6N_2O_4S_2$: C, 34.82; H, 4.94; N, 6.25%. Found: C, 35.02; H, 5.15; N, 6.21%.

6-Azoniaspiro[6.5]dodecanium trifluoromethanesulfonate.
6-Azoniaspiro[6.5]dodecanium chloride (0.910 g, 4.46 mmol) and lithium trifluoromethanesulfonate (0.766 g, 4.91 mmol) were carefully weighed into a 50 ml, single-neck round-bottomed flask. Dry CH_2Cl_2 (25 ml) was added, and the solution was stirred at room temperature for three days, during which white fine precipitate had formed. The solution was filtered under gravity to remove the by-product lithium chloride. The resultant filtrate was washed with distilled water (3 × 5 ml) until the washings tested negative for chloride with 0.1 M aqueous silver(I) nitrate. The CH_2Cl_2 was removed by rotary evaporation to yield 6-azoniaspiro[6.5]dodecanium trifluoromethanesulfonate (0.885 g, 63%) as a white free-flowing solid.
Found: m.p. 115.5-117 °C. ^{1}H NMR (400 MHz, DMSO-d6): *δ* 3.43 (4H, t, J = 5 Hz), 3.32 (4H, t, J = 6 Hz), 1.87-1.70 (8H, m), 1.65-1.49 (6H, m). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): *δ* 61.9, 60.9, 27.6, 21.2, 20.8, 19.9. ^{19}F NMR (376 MHz, DMSO-d6): δ -77.7. *m/z* (LSIMS$^+$): 168 (100%) $[(CH_2)_6N(CH_2)_5]^+$. *m/z* (LSIMS$^-$): 149 (100%) $[OTf]^-$. Calc. for $C_{12}H_{22}F_3NO_3S$: C, 45.41; H, 6.99; N, 4.41%. Found: C, 45.33; H, 7.10; N, 4.43%.

***Synthesis of intermediate**:*

1-Methylazepane. Azepane (300 g, 3.03 mol) was added to a 3 L, three-necked round-bottomed flask, fitted with a dropping funnel, a nitrogen inlet and a stopper. The dropping funnel was charged with 40% aqueous formaldehyde (262 g, 3.49 mol). The formaldehyde solution was added dropwise to the azepane over one hour, with vigorous stirring and under a nitrogen atmosphere. The dropping funnel was then charged with formic acid (146 g, 3.17 mol). The formic acid was added dropwise to the azepane solution over one hour, with vigorous stirring under a nitrogen atmosphere, during which time strong effervescence was observed. The solution was stirred for a further one hour, after which time the effervescence had stopped. The solution was made basic by the addition of 2.5 M aqueous NaOH (150 ml), resulting in a biphasic solution. The upper organic layer was collected by separation. Additional organic material was collected by treating the aqueous fraction with further 2.5 M aqueous NaOH (50 ml), and separating. The organic fractions were combined and were dried with anhydrous $MgSO_4$. The crude product was distilled under nitrogen (b.p. 146 °C) to yield 1-methylazepane (77 g, 23%) as a colourless liquid.
Found: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.54 (4H, t, J = 6 Hz), 2.34 (3H, s), 1.71-1.62 (4H, m), 1.62-1.53 (4H, m). ^{1}H NMR data is consistent with the literature.[2] *ν*(neat)/cm^{-1} 2925 2852 2787 (aliphatic C-H stretch, m), 1451 (aliphatic CH_2 bend, m). Calc. for $C_7H_{15}N$: C, 74.27; H, 13.36; N, 12.37%. Found: C, 74.26; H, 13.49; N, 12.18%.

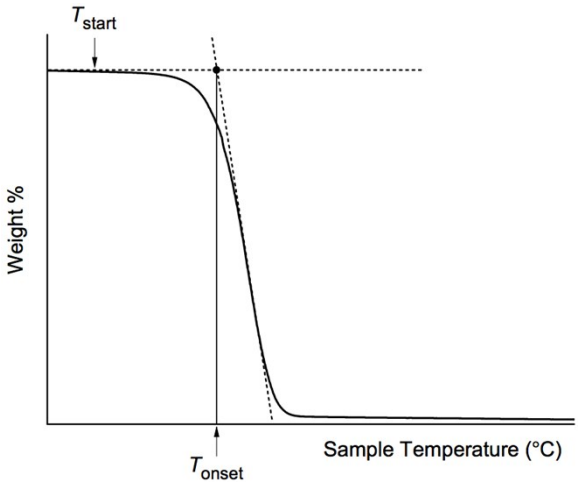
3. TGA procedures

Thermogravimetric Analysis (TGA) spectra were obtained on a PerkinElmer 'Pyris 1 TGA' Thermogravimetric Analyzer, using platinum sample pans of 6 mm diameter.

Scanning TGA experiments were carried out for compounds **1**-**3**, **5**-**10** in the range of 30-700 °C. Between 4-8 mg of the ionic compound was measured into a platinum pan. All compounds were dried thoroughly under high vacuum prior to TGA measurement. However, during the transferal of the hygroscopic compound into the TGA pan, a small quantity of water (≤5 wt%) would be absorbed from the atmosphere. A **drying procedure** was therefore implemented: the compound was heated to 80 °C for 30 minutes in the TGA apparatus, in order to remove water.* The compound was then cooled to room temperature before resetting the sample weight and beginning the scan. A ramping rate of 10 °C min^{-1} and a nitrogen flow of 20 ml min^{-1} were used for all experiments.

Table E1: T_{onset} and T_{start} values for salts **1**-**3**, **5**-**10**. Temperature-ramped TGA experiments were performed with a heating rate of 10 °C min^{-1}, using nitrogen flow rate of 20 ml min^{-1}. T_{onset} values were calculated according to the temperature at the intersection of the 100 wt% baseline with the tangent at the steepest point of weight loss; T_{start} is determined as the point of first measurable weight loss ($d\alpha/dt \neq 0$) (see graphical representation below):

Salt		T_{onset} (°C)	T_{start} (°C)
1	$[C_5C_1pyrr]Cl$	228	198
2	$[C_4C_1pip]Cl$	232	221
3	$[C_3C_1azp]Cl$	254	241
5	[6+6]Cl	245	189
6	[3-oxa-6+6]Cl	330	310
7	[7+5]Cl	286	274
8	[7+6]Cl	323	297
9	[7+7]Cl	304	263
10	[8+5]Cl	263	253



Isothermal TGA experiments were conducted for 6-azoniaspiro[6.5]dodecanium chloride, **8**. Between 6-8 mg of the compound was measured into the platinum pan. A **longer drying period** of 2 hours at 90 °C was employed.** The sample was heated rapidly to the experimental temperature, and was maintained at this temperature for a period of 2-10 hours.

* *The drying procedure was justified on the basis that the onset decomposition temperature of each compound (**1**-**10**) is substantially (>145 °C) higher than the 80 °C drying temperature, and the drying period is short. Therefore actual decomposition of each salt during the drying period is negligible.*

** *This drying period was justified since the T_{onset} temperature of **8** was found to be significantly higher (>200 °C) than the drying temperature. Therefore, thermal decomposition of the salt during the two-hour drying period is negligible.*

The $T_{0.01/10}$ value for [7+6]Cl, **8**, was determined using the following method (Fig. 6 in main manuscript):

(i) Linear decomposition 'curves' are collected at varying temperatures, and the gradients are determined.
(ii) The $t_{0.99}$ value (time taken for 1% weight loss to occur) is extracted from the gradient of the isotherm.
(iii) A plot of $t_{0.99}$ *vs*. temperature gives an exponential relationship, which can be extrapolated or interpolated to give the temperature corresponding to $t_{0.99}$ = 10 hours/600 mins.

$T_{0.01/10}$ was determined as 205 °C for [7+6]Cl, **8**.

4. TGA-MS procedures

Thermogravimetric Analysis-Mass Spectrometry (TGA-MS) data was obtained on a PerkinElmer 'Pyris 1 TGA' Thermogravimetric Analyzer, using ceramic pans. Between 20-60 mg of the salt was measured into the ceramic pan. A heating rate of 10 °C min^{-1} and a CP Grade helium flow of 20 ml min^{-1} were used. The TGA was connected to a 'Hiden Analytical HPR 20' Mass Spectrometer with a ceramic heated capillary. All TGA-MS data was processed in Microsoft Excel. Graphs were prepared using the Origin Pro v. 8.5 package.

5. TGA-GCMS procedures

Thermogravimetric Analysis-Gas Chromatography Mass Spectrometry (TGA-GCMS) results were obtained on a 'Netzsch STA (Simultaneous Thermal Analysis) 409PG Luxx®' analyser, coupled to a heat transfer line at 180 °C (Fig. E4, panel B). Approximately 2 mg of 6-azoniaspiro[6.5]dodecanium chloride, **8**, was loaded into a porcelain crucible (Fig E4, panel A), and was heated from 35-600 °C at a heating rate of 10 °C min^{-1}. Evolved gases were collected onto activated carbon ('Tennax') tubes for periods of 15 seconds (Fig. E4, panel C), at two periods during the temperature-ramped experiment (310 and 340 °C). Tennax tubes were subsequently loaded into a PerkinElmer 'Automated Thermal Desorber Turbomatrix 350' apparatus (Fig. E4, panel D). Thermal decomposition products were evolved from the Tennax tubes, with a tube desorption temperature of 290 °C and column transfer temperature of 225 °C. The PerkinElmer 'Automated Thermal Desorber Turbomatrix 350' apparatus was attached to a PerkinElmer 'Clarus 500' Gas Chromatographer-Mass Spectrometer. Gas chromatography experiments were performed in the temperature range 50-300 °C, with a heating rate of 20 °C min^{-1}, and employing a 'Phase Elite 5MS, L=30 m, ID=0.25 Serial 818753' column.

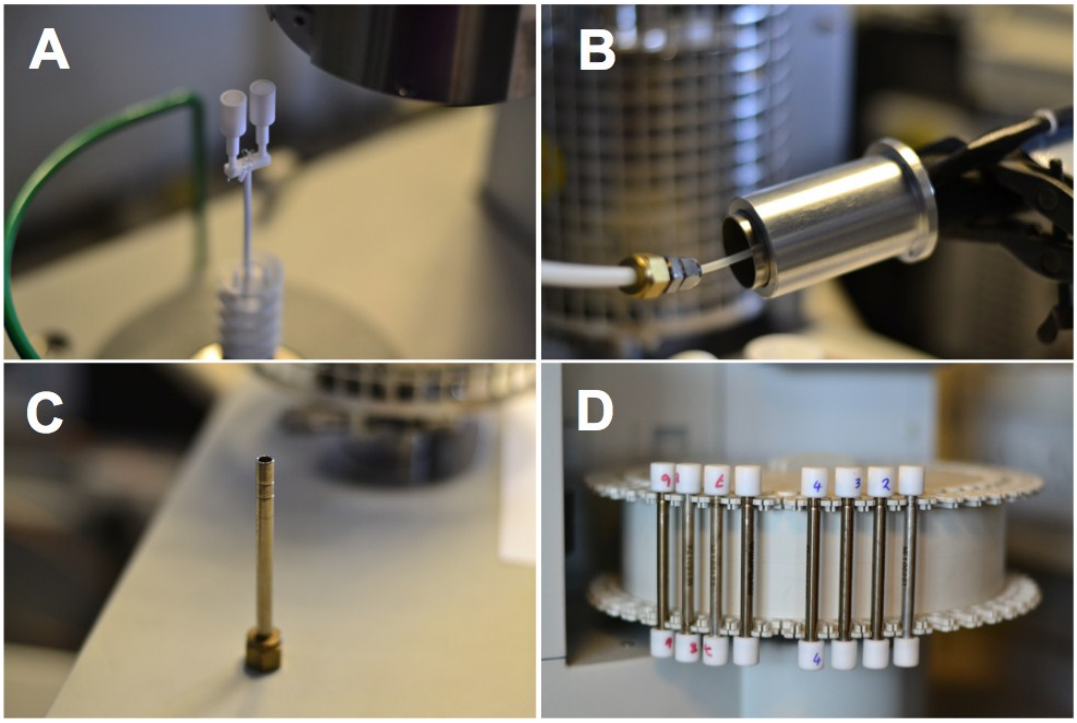


Fig. E4 Photographs representing the TGA-GCMS experimental setup: (A) porcelain sample crucibles of the 'Netzsch STA 409PG Luxx®' analyser; (B) heat transfer line (at 180 °C); (C) example activated carbon (Tennax) tube; (D) Tennax tubes loaded into the PerkinElmer 'Automated Thermal Desorber Turbomatrix 350' apparatus.

6. X-Ray Crystallography procedures and data

The X-ray crystal structure of 4.H_2O.

Crystal data for **4**: $(C_8H_{16}N)(Cl)\cdot H_2O$, M = 179.68, orthorhombic, *Pbca* (no. 61), a = 12.5408(3), b = 11.0072(3), c = 14.1345(4) Å, V = 1951.12(9) Å^3, Z = 8, D_c = 1.223 g cm^{-3}, μ(Mo-Kα) = 0.342 mm^{-1}, T = 173 K, colourless blocks, Agilent Xcalibur 3E diffractometer; 2160 independent measured reflections (R_{int} = 0.0300), F^2 refinement,[1] R_1(obs) = 0.0379, wR_2(all) = 0.0949, 1868 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 56°], 109 parameters. CCDC 1434098.

The H_2O hydrogen atoms of the included water molecule in the structure of **4**.H_2O were located from ΔF maps and refined freely subject to an O–H distance constraint of 0.90 Å.

The X-ray crystal structure of 5.

Crystal data for **5**: $(C_{10}H_{20}N)(Cl)$, M = 189.72, orthorhombic, $P2_12_12_1$ (no. 19), a = 8.1634(3), b = 8.9539(3), c = 14.4292(5) Å, V = 1054.69(6) Å^3, Z = 4, D_c = 1.195 g cm^{-3}, μ(Mo-Kα) = 0.313 mm^{-1}, T = 173 K, colourless blocky needles, Oxford Diffraction Xcalibur 3 diffractometer; 2581 independent measured reflections (R_{int} = 0.0246), F^2 refinement,[3] R_1(obs) = 0.0422, wR_2(all) = 0.1094, 2370 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 59°], 110 parameters. The structure of **5** was shown to be a partial racemic twin by a combination of R-factor tests [R_1^+ = 0.0424, R_1^- = 0.0425] and by use of the Flack parameter [x^+ = +0.47(8), x^- = +0.53(8)]. CCDC 978072.

The Flack parameter of 0.47(8) seen in the final refinement of the structure of **5** indicates a near centrosymmetric arrangement of the atoms in the unit cell. This raises the possibility that the correct space group may well be a centrosymmetric one, and indeed inspection of the data for systematic absences reveals a strong indication of a *c*-glide perpendicular to *b*, and weak signs of an *n*-glide perpendicular to *c*, even though the $|E^2-1|$ statistics strongly favour non-centrosymmetric (0.775). Whilst it is possible to solve and refine the structure using the centrosymmetric space group *Pmcn* (a non-standard setting of *Pnma*), this gives a poor R-factor (0.1324 *cf.* 0.0424 for the $P2_12_12_1$ version) and significant inherent disorder across a mirror plane. As the use of $P2_12_12_1$ gives a much lower R-factor and avoids any disorder we feel that this is the correct space group, despite the pseudo-centrosymmetric atom arrangement.

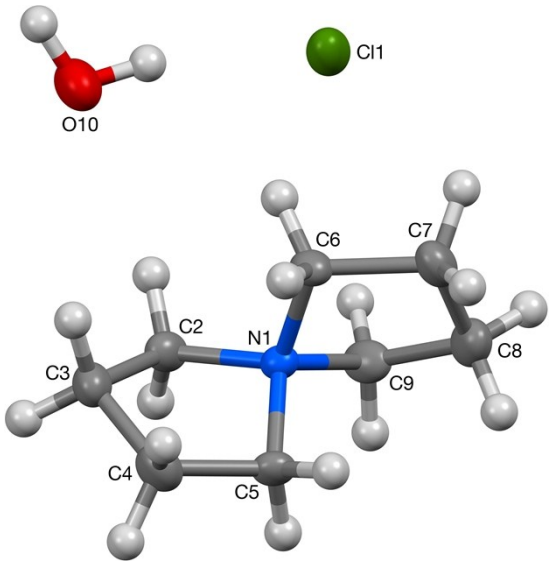


Fig. E5 The crystal structure of **4**.H_2O (50% probability ellipsoids).

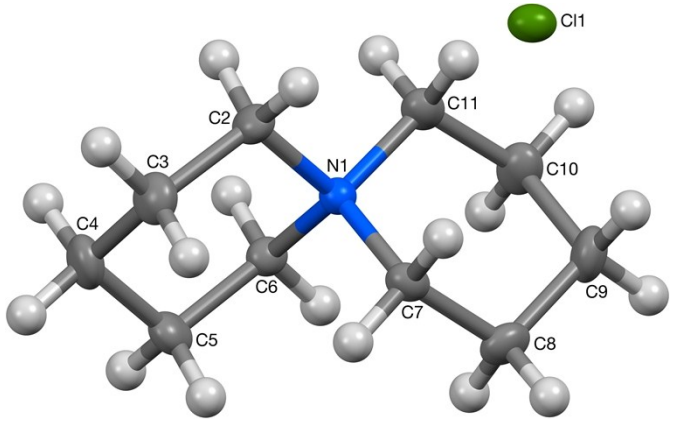


Fig. E6 The crystal structure of **5** (50% probability ellipsoids).

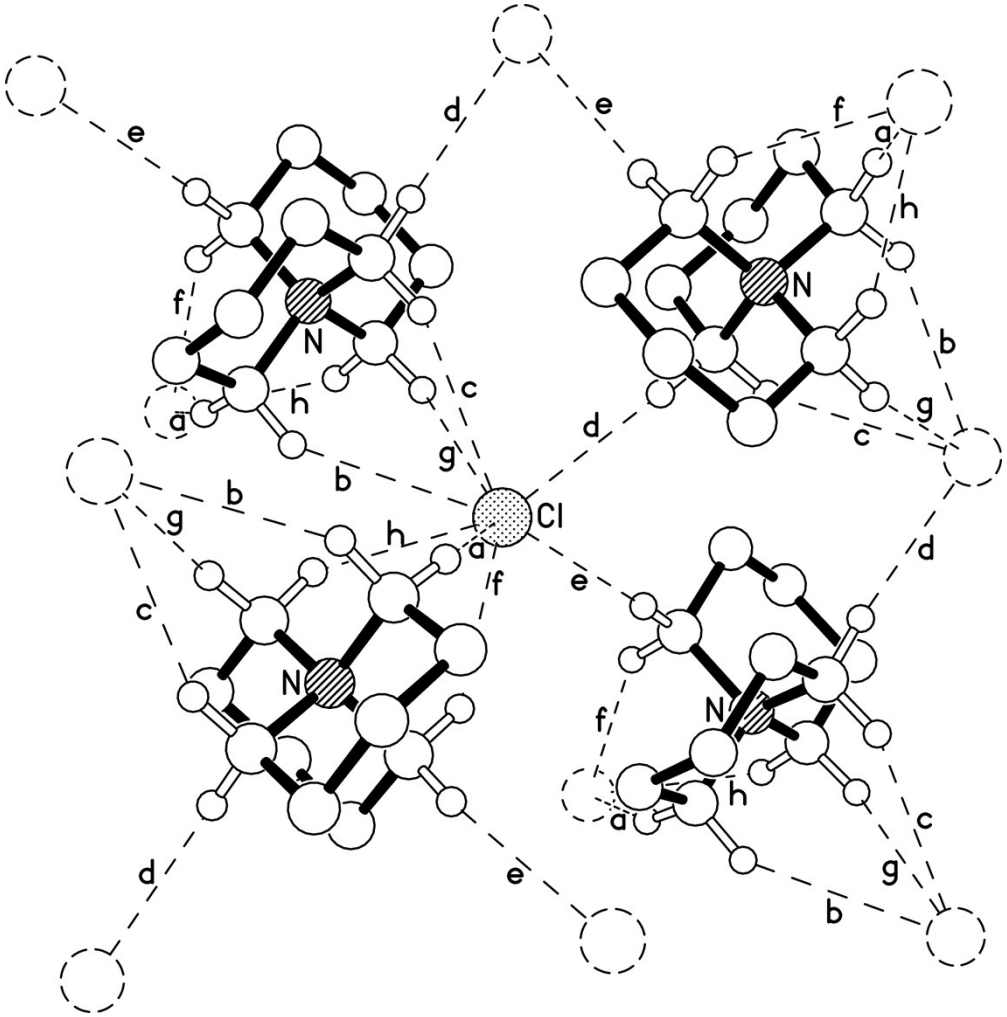


Fig. E7 The crystal structure of **5**, showing the C–H···Cl hydrogen bonds to the chloride anion (only α-hydrogen atoms have been shown for clarity).

7. Computational methods

DFT calculations were performed using the GAUSSIAN 09 suite of programs.[4] The B3LYP (Becke's three-parameter exchange[5] in combination with the Lee, Yang, Parr correlation[6]) functional, including the Grimme empirical dispersion correction (D2)[7], here on referred to as B3LYP-D2, was employed for all calculations together with the 6-311++G(d,p) basis set. The inclusion of dispersion forces has been shown to be necessary when investigating ionic liquid systems.[8] Convergence criteria were tightened above default Gaussian values to 10^{-9} on the RMS density matrix, and to 10^{-7} on the energy. In addition, the numerical integration grid was enhanced from the default, with an optimised grid of 99 radial shells and 590 angular points per shell. These tighter convergence criteria were employed for all optimisation calculations and single-point calculations (*e.g.* frequency calculations). All calculations were performed under no symmetry constraints.

Calculations were performed with the SMD generalised solvent model.[9] Specific parameters for the novel ILs studied here do not exist. Therefore parameters for 1-butyl-1-methylpiperidinium chloride, $[C_4C_1pip]Cl$ were generated from a range of relevant sources: Abraham's hydrogen bond basicity = 0.5985, calculated using the conversion equation[10] employing the Kamlet Taft value of β □ 0.84 reported for $[C_4C_1im]Cl$,[11] □□□□□□□□□□has been assumed that this value is highly dependent on the anion and that any effect on β due to differences between the two cations is minimal; Abraham's hydrogen bond acidity = 0.1375, calculated using the conver-sion equation[10] employing the Kamlet Taft value of α □ 0.32 computed using the α_{EP} method[12]; dielectric con-stant ε = 14, the experimental value reported for $[C_1Him]Cl$[13] (this value was selected because it is the only dielectric constant reported for a chloride-based IL, to the author's best knowledge), and; values suggested for a generic IL[10] – index of refraction = 1.43, macroscopic surface tension = 61.21, fraction of non-hydrogen atoms that are aromatic carbon atoms = 0, fraction of non-hydrogen atoms that are electronegative halogen atoms = 0.08333.

For the majority of structures a multi-stage optimisation process was employed:

(i) initial optimisation was performed using the B3LYP functional and the smaller 6-31G(d) basis set;

(ii) optimisation was then continued using the B3LYP functional and the larger 6-311++G(d,p) basis set;

(iii) the dispersion corrected B3LYP-D2 functional was employed using the 6-311++G(d,p) basis set;

(iv) the gas phase optimised geometries were then re-optimised within an SMD generalised solvent model at the B3LYP-D2/6-311++G(d,p) level.

Cation structures were generated allowing a tetrahedral geometry around the N atom, leading to a variety of ring conformers. For **2**, this resulted in the chair deformation towards or away from the axial (either Me or Bu alkyl) group, to give four possible conformers: C(Me-Ax)-up, C(Me-Ax)-down, C(But-Ax)-up, C(But-Ax)-down. Further conformers can be obtained by rotating the butyl chain about the torsion angles τ1(CNCC) leading to 3 minima, τ2(NCCC) leading to 3 minima and τ3(CCCC), which is an essentially barrierless rotation of the terminal methyl group. For **8**, four cation geometries were obtained from the combination of either a chair or boat deformation at the six-membered ring and the adoption of either of two low-energy deformed seven-membered ring structures. After initial optimisation of the cation structures, the chloride anion was placed in chemically-sensible positions in the proximity of the cation, and the structures were allowed to optimise.

All optimised structures were confirmed as minima or transition states by frequency analysis. All transition states have been confirmed by the presence of a single negative frequency, with the negative mode associated with the reaction coordinate. Intrinsic Reaction Coordinate (IRC) calculations were undertaken to ensure that each TS identified connects the relevant reactants and products.[4] IRC calculations were performed for both the SMD and gas phase optimised transition states.

Population analysis was undertaken using the Natural Bond Orbital (NBO) method (version 5.9).[14] The NBO method was chosen because it is known to be less sensitive to the basis set, compared to (for example) the population analysis method of Mulliken.[15]

8. Ion pair conformers and transition state structures

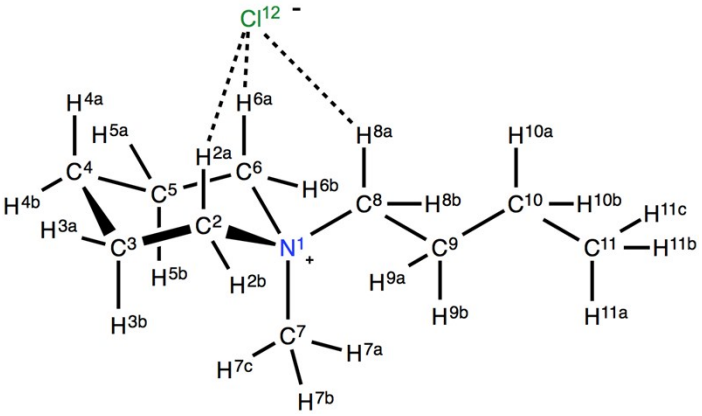
Ion pair geometries were optimised for chair conformation structures of 1-butyl-1-methylpiperidinium chloride, [C_4C_1pip]Cl, **2**, and ion pair structures of 6-azoniaspiro[6.5]dodecanium chloride, [7+6]Cl, **8**. Isolated cations were initially optimised. Subsequently, the chloride anion was placed in chemically sensible positions around the cation, and the structures were optimised. Zero point energy (ZPE) corrections were evaluated. Δ*G*, Δ*H*, *T*Δ*S*, ΔZPE and ΔE_{ZPE} enthalpies and energies (calculated at 298.15 K) are listed below for each compound (Tables E2 and E3), and the NBO charges for the lowest energy conformer of each salt are displayed (Figs. E8 and E9).

Table E2: Gas-phase ion pair energies for 1-butyl-1-methylpiperidinium chloride, [C_4C_1pip]Cl, **2**.

Ion Pair [C_4C_1pip]Cl	Δ*G* (kJ mol^{-1})	Δ*H* (kJ mol^{-1})	*T*Δ*S* (kJ mol^{-1})	Δ*ZPE* (kJ mol^{-1})	ΔE_{ZPE} (kJ mol^{-1})
C (Me-Ax) ααα 1	0.0	0.0	0.0	0.0	0.0
C (Bu-Ax) ααα 1	2.0	1.4	-0.5	0.4	1.8
C (Bu-Ax) ααα 2	4.4	4.3	-0.1	0.5	4.7
C (Me-Ax) ααα 2	5.2	4.9	-0.3	0.1	5.1
C (Me-Ax) ααβγ	16.5	12.3	-4.2	1.1	13.2
C (Bu-Ax) αββ	19.2	17.0	-2.1	-0.4	17.4
C (Bu-Ax) ααβ	21.1	21.5	0.4	-0.8	21.6
B ααβ 1	24.3	24.1	-0.2	-1.2	23.9
B ααα 1	25.9	25.1	-0.9	0.6	25.1
C (Me-Ax) αββ	29.6	29.6	0.0	-1.1	29.7
B ααα 2	31.8	29.9	-1.8	0.7	30.3
B ααα 3	30.8	31.1	0.2	-0.1	31.1
B ααα 4	31.2	31.3	0.1	0.1	31.3
B ααβ 2	45.5	46.6	1.1	-0.7	46.3

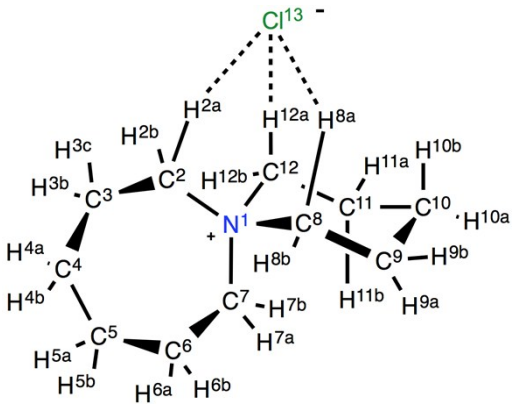
Table E3: Gas-phase ion pair energies for 6-azoniaspiro[6.5]dodecanium chloride, [7+6]Cl, **8**.

Ion Pair [7+6]Cl	Δ*G* (kJ mol^{-1})	Δ*H* (kJ mol^{-1})	*T*Δ*S* (kJ mol^{-1})	Δ*ZPE* (kJ mol^{-1})	ΔE_{ZPE} (kJ mol^{-1})
$7_{chair1}6_{chair}$ ααα	0.0	0.0	0.0	0.0	0.0
$7_{chair2}6_{chair}$ ααα 1	2.0	1.6	-0.4	0.5	1.6
$7_{chair1}6_{chair}$ ααβ 1	4.0	4.4	0.4	-0.9	4.3
$7_{chair2}6_{chair}$ ααα 2	4.1	4.9	0.7	0.4	4.7
$7_{chair1}6_{chair}$ ααβ 2	9.9	10.3	0.4	-0.8	10.2
$7_{chair2}6_{boat}$ ααα	23.8	25.3	1.6	-0.9	24.7
$7_{chair2}6_{chair}$ αββ 1	23.9	26.6	2.6	-1.2	25.9
$7_{chair2}6_{chair}$ αββ 2	24.2	26.7	2.4	-1.7	26.0
$7_{chair2}6_{boat}$ ααβ 1	28.8	31.7	2.8	-1.8	30.7
$7_{chair1}6_{boat}$ ααβ 1	33.9	36.7	2.8	-1.5	35.9
$7_{chair1}6_{boat}$ ααβ 2	33.9	37.3	3.4	-1.1	36.6
$7_{chair2}6_{boat}$ ααβ 2	35.7	39.4	3.7	-2.1	38.2
$7_{chair2}6_{boat}$ αββ	43.4	46.5	3.1	-2.4	45.5



Atom	Charge	Atom	Charge	Atom	Charge
N^1	-0.36	C^6	-0.19	C^{10}	-0.38
C^2	-0.20	H^{6a}	0.29	H^{10a}	0.21
H^{2a}	0.29	H^{6b}	0.20	H^{10b}	0.19
H^{2b}	0.20	C^7	-0.35	C^{11}	-0.57
C^3	-0.40	H^{7a}	0.21	H^{11a}	0.19
H^{3a}	0.23	H^{7b}	0.21	H^{11b}	0.20
H^{3b}	0.18	H^{7c}	0.21	H^{11c}	0.21
C^4	-0.40	C^8	-0.19		
H^{4a}	0.24	H^{8a}	0.29	Cl^{12}	-0.89
H^{4b}	0.20	H^{8b}	0.19		
C^5	-0.40	C^9	-0.40		
H^{5a}	0.23	H^{9a}	0.21		
H^{5b}	0.18	H^{9b}	0.19		

Fig E8: Atomic numbering scheme and NBO charges for the lowest energy 'C (Me-Ax) ααα 1' gas-phase ion pair conformer of 1-butyl-1-methylpiperidinium chloride, $[C_4C_1pip]Cl$, **2**.



Atom	Charge	Atom	Charge	Atom	Charge
N^1	-0.37	C^6	-0.41	C^{10}	-0.40
C^2	-0.19	H^{6a}	0.22	H^{10a}	0.24
H^{2a}	0.29	H^{6b}	0.21	H^{10b}	0.20
H^{2b}	0.20	C^7	-0.17	C^{11}	-0.40
C^3	-0.42	H^{7a}	0.22	H^{11a}	0.23
H^{3a}	0.23	H^{7b}	0.21	H^{11b}	0.18
H^{3b}	0.20	C^8	-0.19	C^{12}	-0.20
C^4	-0.38	H^{8a}	0.29	H^{12a}	0.29
H^{4a}	0.21	H^{8b}	0.20	H^{12b}	0.20
H^{4b}	0.19	C^9	-0.40		
C^5	-0.38	H^{9a}	0.18	Cl^{13}	-0.90
H^{5a}	0.19	H^{9b}	0.23		
H^{5b}	0.21				

Fig E9: Atomic numbering scheme and NBO charges for the lowest energy '$7_{chair1}6_{chair}$ ααα' gas-phase ion pair conformer of 6-azoniaspiro[6.5]dodecanium chloride, [7+6]Cl, **8**.

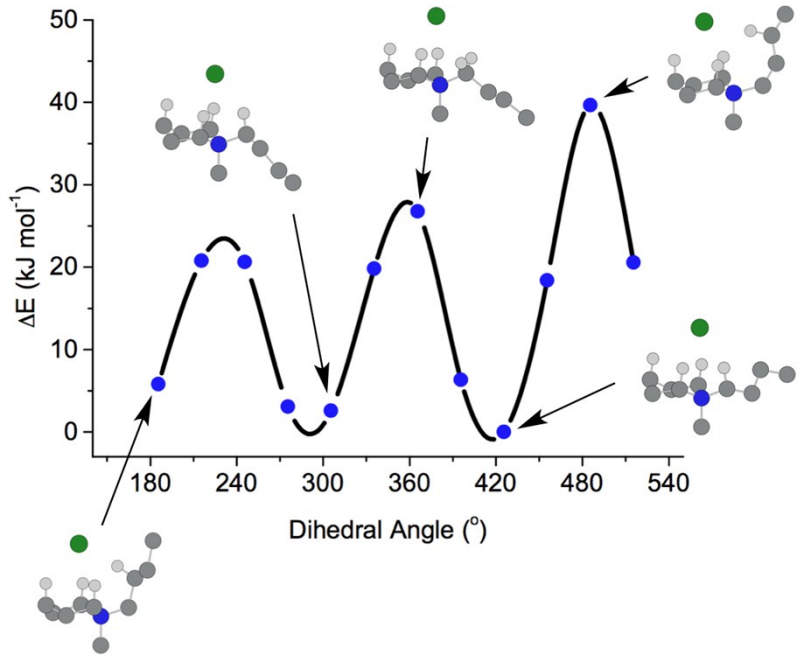


Fig E10: Change in the gas-phase energy and structure of the 'C (Me-Ax) ααβγ' ion pair conformer of 1-butyl-1-methylpiperidinium chloride, $[C_4C_1pip]Cl$, **2**, upon rotation of the C_{Me}-N-C_α-C_β dihedral angle (the butyl side-chain), revealing other energy minima. Energies are uncorrected.

The zero-point-corrected association energies (E_{ass}) for the lowest-energy ion pair geometries of [C_4C_1pip]Cl, **2** and [7+6]Cl, **8** are tabulated below (Table E4), both in the gas-phase and employing the SMD model.[11]

Table E4: *Gas-phase* and *SMD* zero-point-corrected association energies for lowest-energy ion pair conformers of [C_4C_1pip]Cl, **2**, and [7+6]Cl, **8**.

Ion Pair	ΔE_{ass} (gas phase) (kJ mol^{-1})	ΔE_{ass} (SMD) (kJ mol^{-1})
[C_4C_1pip]Cl C (Me-Ax) ααα 1	-519.5	-16.6
[7+6]Cl 7_{chair1} 6_{chair} ααα	-533.0	-17.2

Thermal decomposition pathways investigated in this study are shown in Figures E11 and E12.

Gas-phase energies for transition state/product structures of [C_4C_1pip]Cl, **2** (mechanisms A1-E1) and [7+6]Cl, **8** (mechanisms A2-D2) are displayed in Tables E5 and E6, respectively.

The *SMD* energies for transition state/product structures of [C_4C_1pip]Cl, **2** (mechanisms A1-E1) and [7+6]Cl, **8** (mechanisms A2-D2) are displayed in Tables E7 and E8, respectively.

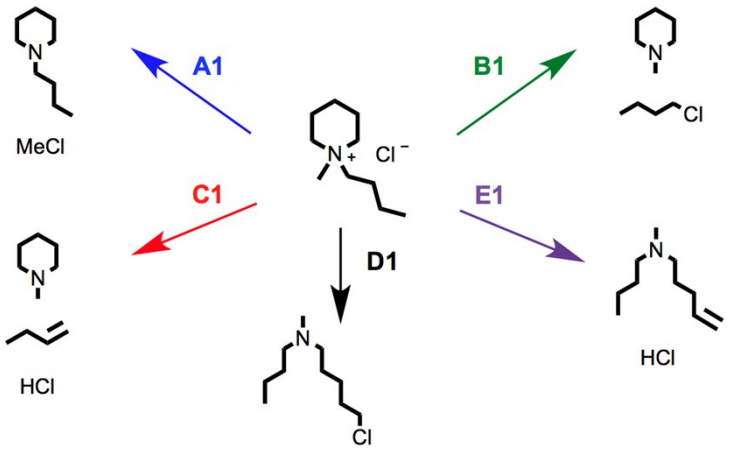


Fig E11: Thermal decomposition routes A1-E1 for 1-butyl-1-methylpiperidinium chloride, [C_4C_1pip]Cl, **2**.

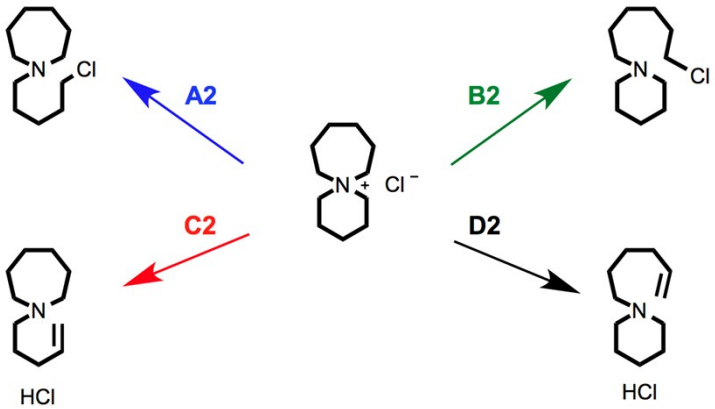


Fig E12: Thermal decomposition routes A2-D2 for 6-azoniaspiro[6.5]dodecanium chloride, [7+6]Cl, **8**.

Table E5: *Gas-phase* transition state energies and product energies for decomposition mechanisms of 1-butyl-1-methylpiperidinium chloride, [C_4C_1pip]Cl, **2**, relative to the lowest energy 'C (Me-Ax) ααα 1' ion pair conformer.

Mechanism	**Ion Pair** (kJ mol^{-1})					**TS** (kJ mol^{-1})					**Product** (kJ mol^{-1})				
	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}
A1	0.0	0.0	0.0	0.0	0.0	86.7	89.0	2.3	-9.5	88.4	-34.4	15.5	49.9	-18.8	13.4
B1	0.0	0.0	0.0	0.0	0.0	91.3	90.0	-1.2	-9.3	90.2	-31.2	21.2	52.4	-17.3	20.4
C1	0.0	0.0	0.0	0.0	0.0	116.0	119.0	3.1	-30.1	117.5	-12.4	83.0	95.4	-39.4	77.4
D1	0.0	0.0	0.0	0.0	0.0	91.5	93.3	1.8	-10.2	92.8	-3.5	12.1	15.5	-14.4	7.8
E1	0.0	0.0	0.0	0.0	0.0	118.1	124.6	6.5	-30.0	122.6	15.6	74.2	58.6	-36.3	65.3

Table E6: *Gas-phase* transition state energies and product energies for decomposition mechanisms of 6-azoniaspiro[6.5]dodecanium chloride, [7+6]Cl, **8**, relative to the lowest energy '$7_{chair1}6_{chair}$ ααα' ion pair conformer.

Mechanism	**Ion Pair** (kJ mol^{-1})					**TS** (kJ mol^{-1})					**Product** (kJ mol^{-1})				
	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}
A2	0.0	0.0	0.0	0.0	0.0	96.0	97.9	1.9	-9.9	97.4	-2.4	14.0	16.4	-14.4	9.6
B2	0.0	0.0	0.0	0.0	0.0	93.3	93.3	0.0	-8.7	93.3	-21.8	-4.4	17.4	-14.2	-8.4
C2	0.0	0.0	0.0	0.0	0.0	122.4	129.5	7.1	-29.5	127.6	16.5	76.2	59.6	-36.3	67.1
D2	0.0	0.0	0.0	0.0	0.0	109.8	117.1	7.3	-27.1	115.3	-2.9	59.3	62.2	-37.1	50.0

Table E7: *SMD* transition state energies and product energies for decomposition mechanisms of 1-butyl-1-methylpiperidinium chloride, [C_4C_1pip]Cl, **2**, relative to the lowest energy 'C (Me-Ax) ααα 1' ion pair conformer.

Mechanism	**Ion Pair** (kJ mol^{-1})					**TS** (kJ mol^{-1})					**Product** (kJ mol^{-1})				
	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}
A1	0.0	0.0	0.0	0.0	0.0	131.8	129.5	-2.3	-12.7	129.4	28.6	71.2	42.6	-17.5	70.5
B1	0.0	0.0	0.0	0.0	0.0	136.4	133.8	-2.6	-13.6	133.8	23.5	70.7	47.2	-16.7	70.8
C1	0.0	0.0	0.0	0.0	0.0	187.2	192.5	5.3	-35.4	190.1	31.4	121.2	89.7	-39.3	116.5
D1	0.0	0.0	0.0	0.0	0.0	139.7	137.1	-2.6	-13.3	137.0	67.5	77.2	9.8	-14.5	73.9
E1	0.0	0.0	0.0	0.0	0.0	177.0	179.1	2.1	-34.4	177.1	74.5	127.5	53.0	-36.9	119.6

Table E8: *SMD* transition state energies and product energies for decomposition mechanisms of 6-azoniaspiro[6.5]dodecanium chloride, [7+6]Cl, **8**, relative to the lowest energy '$7_{chair1}6_{chair}$ ααα' ion pair conformer.

Mechanism	**Ion Pair** (kJ mol^{-1})					**TS** (kJ mol^{-1})					**Product** (kJ mol^{-1})				
	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}
A2	0.0	0.0	0.0	0.0	0.0	146.6	140.0	-6.6	-12.9	140.2	76.1	80.5	4.4	-13.7	77.8
B2	0.0	0.0	0.0	0.0	0.0	142.2	135.7	-6.5	-12.9	135.9	55.4	62.6	7.3	-13.9	60.0
C2	0.0	0.0	0.0	0.0	0.0	180.3	180.6	0.3	-35.1	178.6	81.5	130.7	49.3	-36.6	123.1
D2	0.0	0.0	0.0	0.0	0.0	152.4	153.1	0.7	-34.6	151.0	58.0	107.4	49.5	-36.5	99.9

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