

Understanding Siloxane Functionalised Ionic Liquids

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Supplementary Material

Details for the estimation of the viscosity difference between bmim and Si-O-Si-mim based ILs

$$\eta = \frac{m\bar{c}}{2\sqrt{2}\pi\sigma^2}$$

from the kinetic theory of gases (hard spheres with a Maxwell distribution of velocities, \bar{c} is the average velocity)

an increased mass will increase the viscosity, but at the same time the volume is increased which will reduce the viscosity.

the atomic mass of:

$$\text{mim} = (4 \times 12) + (2 \times 14) + (6 \times 1) = 82 \text{ amu}$$

$$\text{but} = (4 \times 12) + (9 \times 1) = 57 \text{ amu}$$

$$\text{siloxane group} = (2 \times 28) + (16) + (6 \times 12) + (17 \times 1) = 161 \text{ amu}$$

$$[\text{C}_4\text{C}_1\text{im}]^+ = 139 \text{ amu}$$

$$[(\text{SiOSi})\text{C}_1\text{C}_1\text{im}]^+ = 243 \text{ amu}$$

the "volume" of each ion:

Si is $\approx 50\%$ larger than C (Van der Waals radius 1.70 vs 2.17 Å) and the electron cloud is more diffuse, Si has a much larger dipole polarizability than C (11.8 vs 36.6 a.u.)

Taking a "radial" measurement from C² to the furthest C atom and adding 1.1 Å for the C-H bond,

$$r_{\text{bmim}} = 5.06, r_{\text{Si-O-Si-mim}} = 6.88 \text{ Å}$$

produces volume $\frac{4}{3}\pi r^3$

$$V[\text{C}_4\text{C}_1\text{im}]^+ = 543, V[(\text{SiOSi})\text{C}_1\text{C}_1\text{im}]^+ = 1364 \text{ Å}^3$$

the ratio is $543/1364 = 40\%$

The electronic spacial extent of $[\text{C}_4\text{C}_1\text{im}]^+$ (2374 au²) is 39% of $[(\text{SiOSi})\text{C}_1\text{C}_1\text{im}]^+$ (6118 au²).

the volume of $[\text{C}_4\text{C}_1\text{im}]^+$ is therefore 40% of $[(\text{SiOSi})\text{C}_1\text{C}_1\text{im}]^+$, and a similar number is obtained when the computed electronic spatial extent is used.

$$\eta \propto m/\sigma^2 \quad \eta_{\text{bmim}} \propto 139/(10.12)^2 = 1.36 \quad \eta_{\text{Si-O-Si-mim}} \propto 243/(13.76)^2 = 1.28$$

$$\eta_{\text{bmim}}/\eta_{\text{Si-O-Si-mim}} = 1.36/1.28 = 1.06$$

$$\eta_{\text{bmim}} = 52 \quad \therefore \eta_{\text{Si-O-Si-mim}} = \eta_{\text{bmim}}/1.06 = 49$$

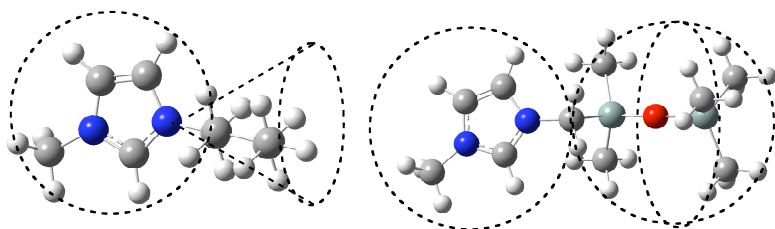


Figure S1: (a) $[\text{C}_4\text{C}_1\text{im}]^+$ the alkyl chain sweeps out an excluded volume on the end of an essentially stationary imidazolium ring, (b) $[(\text{SiOSi})\text{C}_1\text{C}_1\text{im}]^+$ is a dumb-bell shape, two large groups connected via the N¹-C⁷ bond

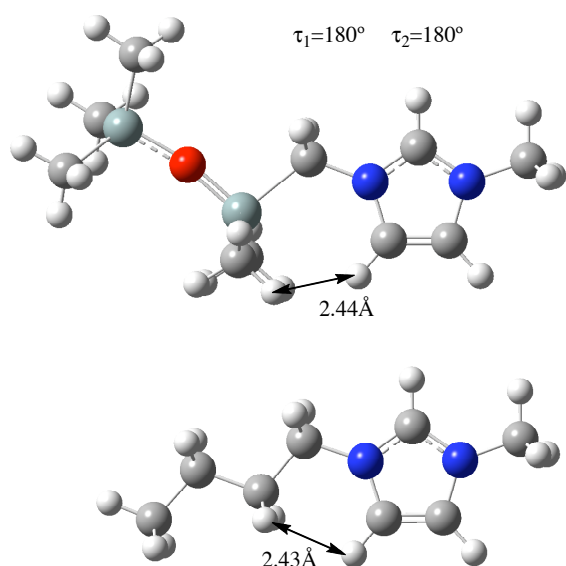


Figure S2: Structures of $[\text{C}_4\text{C}_1\text{im}]^+$ and $[(\text{SiOSi})\text{C}_1\text{C}_1\text{im}]^+$, showing steric interactions between substituents on the chain and the imidazolium H atoms at the rear of the ring, similar interactions occur with the front of the ring.

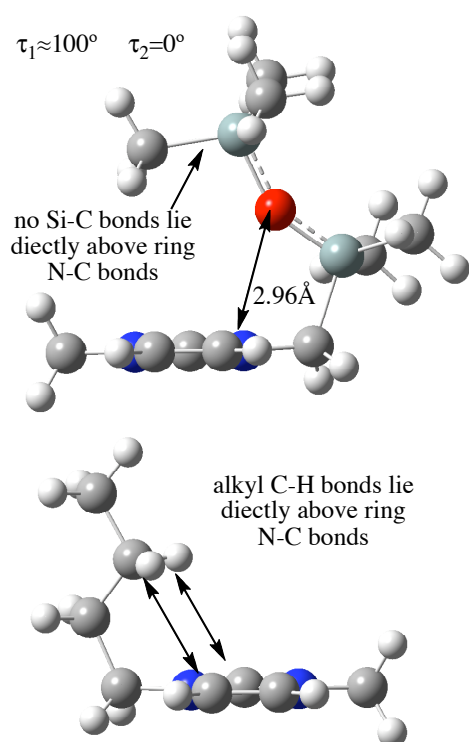


Figure S3: Structure of $[(\text{SiOSi})\text{C}_1\text{C}_1\text{im}]^+$, showing that the siloxane SiMe_3 group sitting above the center of the imidazolium ring and thus avoiding a repulsive through space bond overlap, which is evident in the structure of $[\text{C}_4\text{C}_1\text{im}]^+$ where both $\text{C}^9\text{-H}$ bonds of align exactly over the $\text{N}^1\text{-C}^{2/5}$ bonds of the ring.

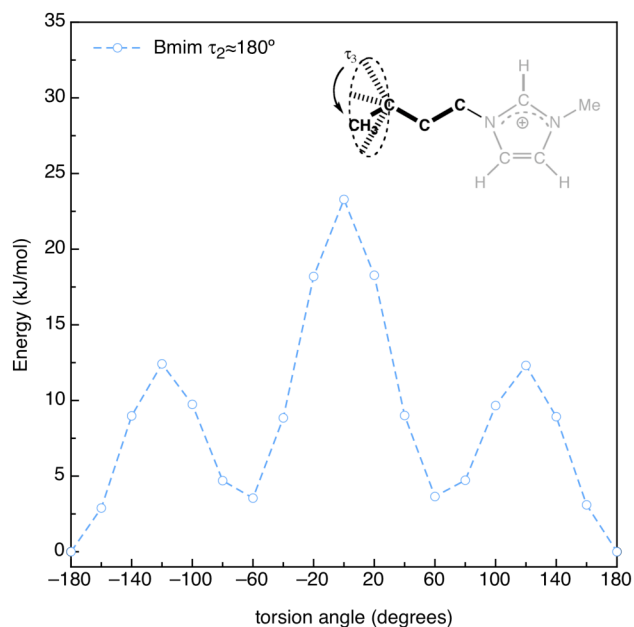


Figure S4: Relaxed scan of the τ_3 rotation for $[\text{C}_4\text{C}_1\text{im}]^+$ dashed blue line and open circles.

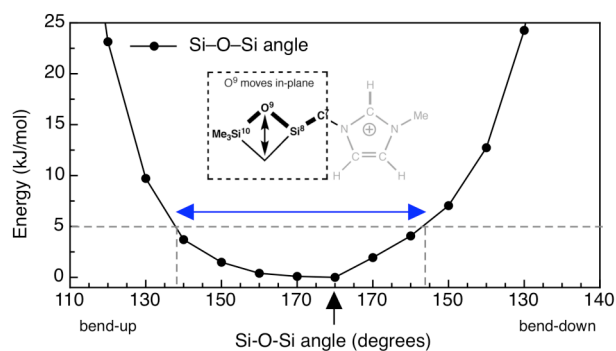


Figure S5: Potential energy scan for $[(\text{SiOSi})\text{C}_1\text{C}_1\text{im}]^+$ obtained by bending the $\alpha=\text{Si-O-Si}$ angle forward and backward from 180° while holding the $\text{N}^1\text{-C}^7\text{-Si}^8\text{-O}^9$ and $\text{C}^7\text{-Si}^8\text{-O}^9\text{-Si}^{10}$ torsion angles fixed ($\approx 180^\circ$), solid line with closed circles.

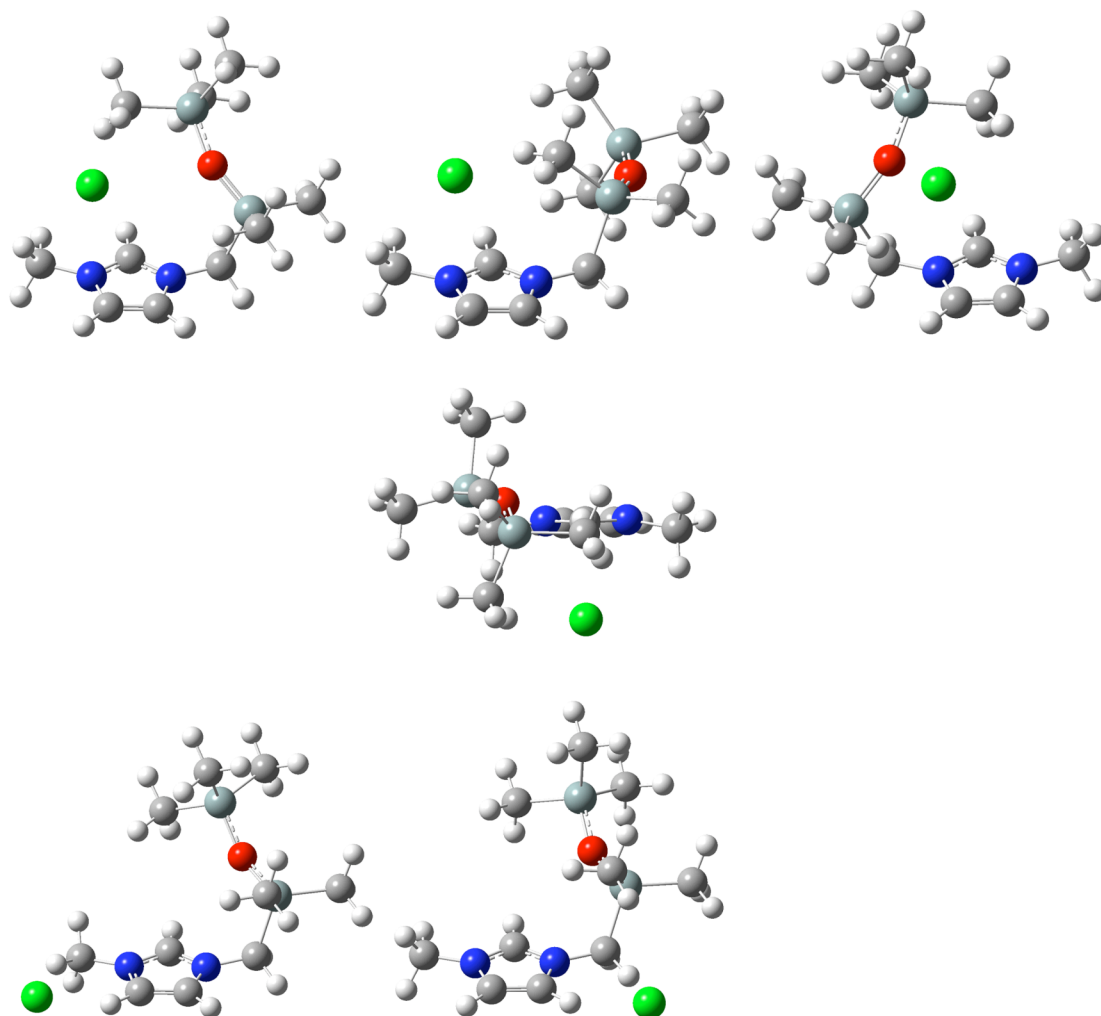


Figure S6: A selection of structures showing the different Cl anion positions for the C_{forward} cation, front-Me (0.00 kJ/mol), front-Me(+0.64), front-R (+0.83), bottom (7.73), side-Me (=38.98), side-R (+27.72).

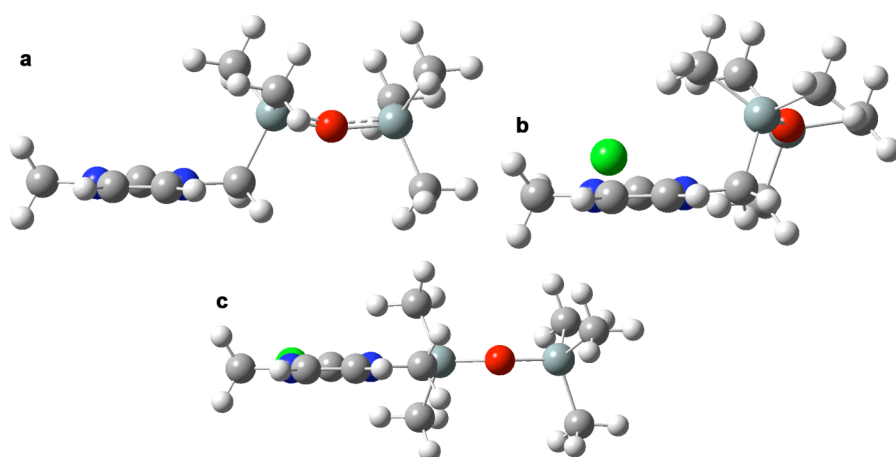


Figure S7: Stable C_{linear} structures with the Cl anion in the front position, (a) stable cation, (b) presence of Cl induces $\approx 50^\circ$ rotation in τ_2 , (c) presence of Cl stabilizes the "unstable" $\tau_1 \approx 0^\circ$ conformer.

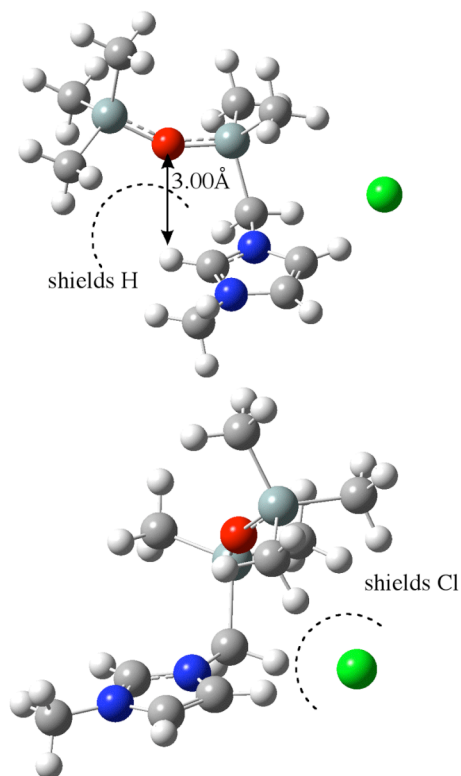


Figure S8: structures where the siloxy chain shields key H-bonding sites from further interaction

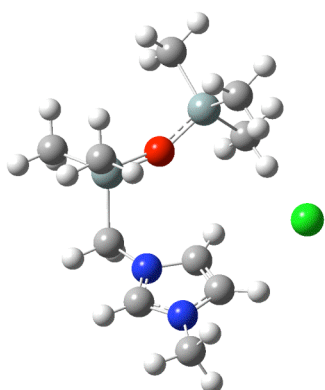


Figure S9: The reach of the siloxane chain has resulted in the stabilisation of a "back" structure.

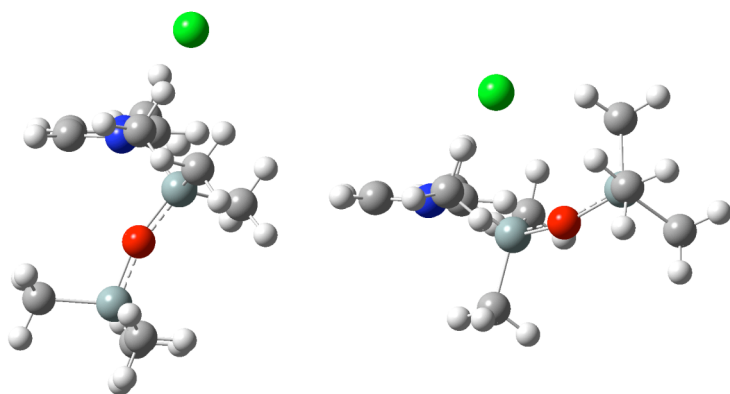


Figure S10: placing the Cl in the "top" position has resulted in substantial movement of the siloxane chain.

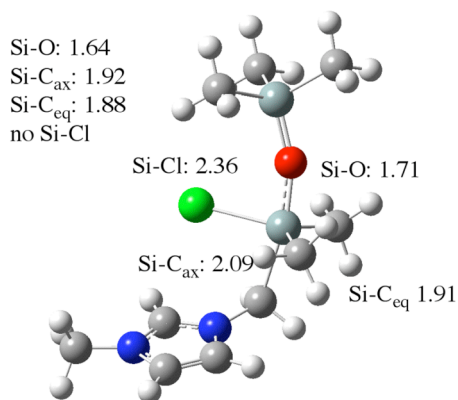


Figure S11: coordination of the Cl anion to the cation forming a neutral species

Crystal data for 1: (C₁₀H₂₃N₂OSi₂)(Cl), *M* = 278.93, monoclinic, *P*2₁/*c* (no. 14), *a* = 15.1593(3), *b* = 8.54934(14), *c* = 12.6684(3) Å, β = 103.130(2)°, *V* = 1598.93(6) Å³, *Z* = 4, *D*_c = 1.159 g cm⁻³, μ(Mo-Kα) = 0.375 mm⁻¹, *T* = 173 K, colourless blocks, Oxford Diffraction Xcalibur 3 diffractometer; 4574 independent measured reflections (*R*_{int} = 0.0175), *F*₂ refinement, *R*₁(obs) = 0.0317, *wR*₂(all) = 0.0914, 3707 independent observed absorption corrected reflections [*|F_o*| > 4σ(*|F_o*)], 2θ_{max} = 63°, 151 parameters. CCDC 750136.

The chloride anion in the structure of 1 was found to be disordered. Two partial occupancy sites were identified of ca. 97 and 3% occupancy. The chlorine atom at the major occupancy site was refined anisotropically, whilst that at the minor occupancy site was refined isotropically. The C–H protons were placed in calculated positions, assigned isotropic thermal parameters, *U*(H) = 1.2*U*_{eq}(C) [*U*(H) = 1.5*U*_{eq}(C–Me)], and allowed to ride on their parent carbon atoms.

	C···Cl (Å)	H···Cl (Å)	C–H···Cl (°)
C(2)–H(2A)···Cl	3.4309(13)	2.55	152
C(4)–H(4A)···Cl	3.5519(15)	2.66	154
C(5)–H(5A)···Cl	3.6171(14)	2.82	142
C(6)–H(6A)···Cl	3.8499(18)	3.11	135
C(6)–H(6B)···Cl	3.6361(13)	2.75	154
C(10)–H(10A)···Cl	3.7499(18)	2.87	152
C(10)–H(10C)···Cl	3.8066(17)	3.02	140
C(15)–H(15A)···Cl	3.9363(19)	3.02	161

Table S1: The closest C–H···Cl separations in 1. For the purposes of the hydrogen bonding analysis all of the C–H distances were normalised to 0.96 Å

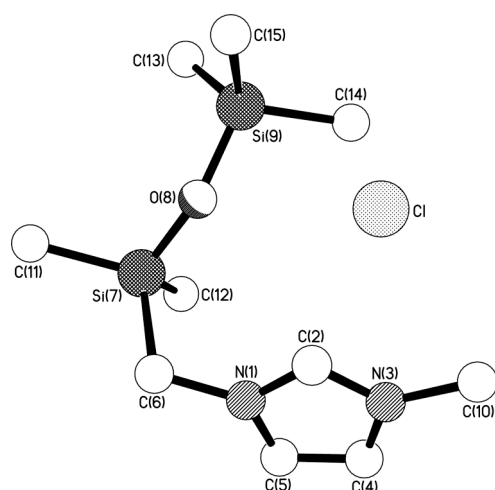


Figure S12: The molecular structure of 1 (50% probability ellipsoids).

	C _{linear}	C _{forward}	C _{backward}	Bmim [*]	Si-O-Si- mim [†]	C _{crystal}	Bmim
C ² -H	1.077	1.078	1.077	1.077	1.112	-	1.122
C ⁴ -H	1.077	1.077	1.077	1.077	1.076	-	1.076
C ⁵ -H	1.076	1.076	1.076	1.077	1.076	-	1.076
N ¹ -C ²	1.335	1.337	1.336	1.336	1.338	1.335	1.339
N ³ -C ²	1.341	1.339	1.339	1.338	1.339	1.329	1.337
C ⁴ -C ⁵	1.362	1.361	1.362	1.361	1.361	1.349	1.360
N ³ -C ⁶	1.470	1.469	1.469	1.471	1.470	1.466	1.470
N ¹ -C ⁷	1.478	1.480	1.478	1.485	1.473	1.471	1.475
C ⁷ -Si ⁸	1.942	1.932	1.935	-	1.927	1.886	-
Si ⁸ -O	1.628	1.655	1.647	-	1.632	1.628	-
Si ¹⁰ -O	1.689	1.697	1.694	-	1.687	1.635	-
Si ⁸ -O- Si ¹⁰	170.1	147.3	149.9	-	159.0	145.9	-
N ¹ -C ² -N ³	109.1	108.8	109.1	109.0	108.2	108.0	108.0
N ³ -C ⁴ -C ⁵	107.1	106.9	107.2	107.1	106.9	106.7	106.9
N ¹ -C ⁵ -C ⁴	107.4	107.4	107.2	107.3	107.0	107.3	106.9
τ _a	-0.2	0.2	-0.2	-0.1	-0.2	-0.2	-0.2
τ ₁	96.5	47.1	124.2	107.5	90.5	76.6	101.4
τ ₂	-177.5	-55.9	60.8	64.3	-54.3	-60.9	63.1

Table S2 Selected structural parameters from the computed cations, most stable ion-pair, and the crystal structure of 1, in addition to comparative values from calculations on a bmim cation and [C₄C₁im]Cl ion-pair. ^{*}C_{forward} [†]C_{forward}Cl_{front-Me} [§]τ_a= N¹-C⁵-C⁴-N³

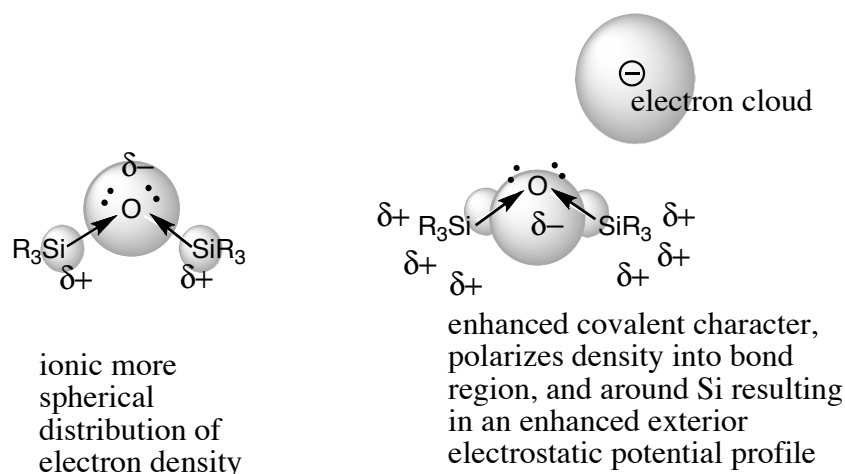


Figure S13: Diagram showing the polarisation of electron density due to the presence of the Cl anion and resulting in reduced NBO charges, while at the same time increasing the CHelpG charges.

$$R_{cq} = \frac{\sum_{i=1}^n q_i r_i}{\sum_{i=1}^n q_i} \quad R_{cm} = \frac{\sum_{i=1}^n m_i r_i}{\sum_{i=1}^n m_i} \quad R_{ca} = |R_{cm} - R_{cq}|$$

Equation S1: equation defining the charge arm.

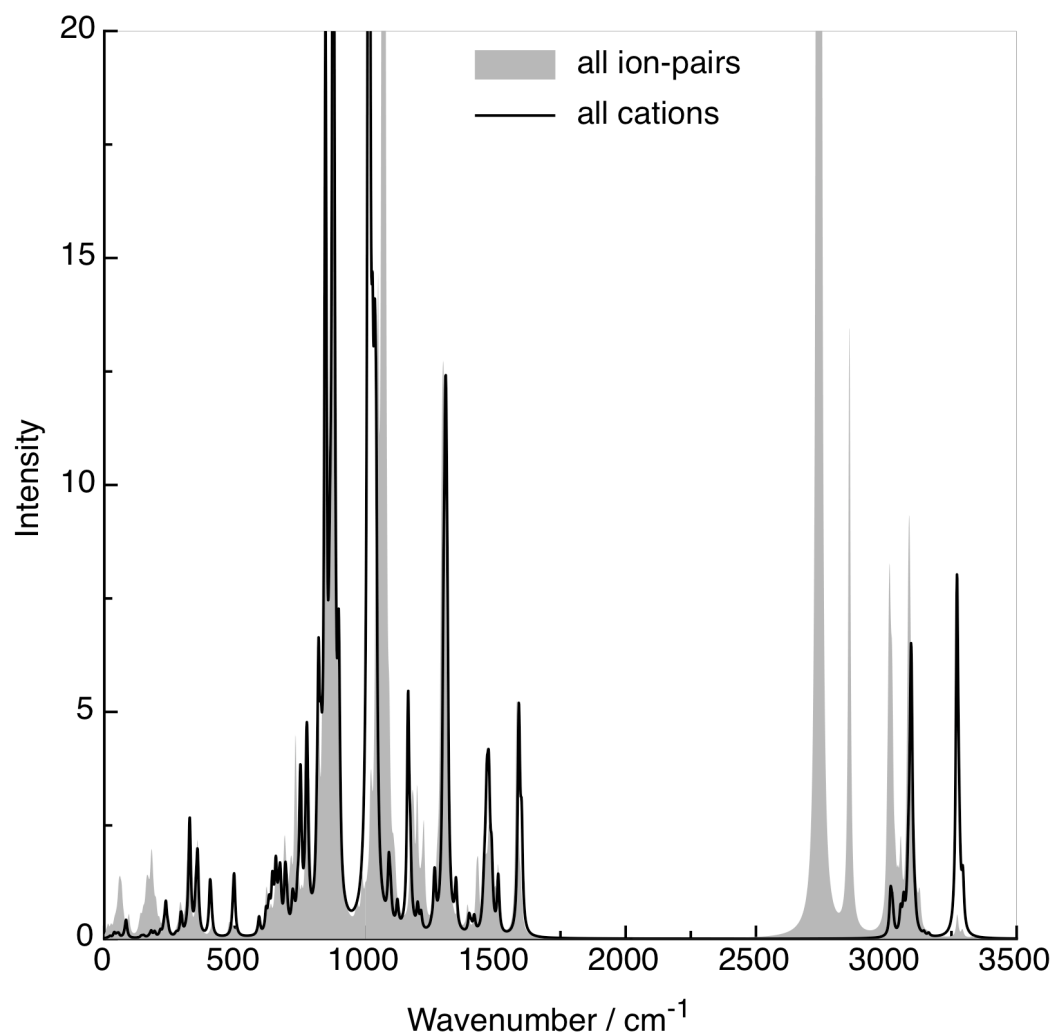


Figure S9 Simulated IR spectrum for all ion-pairs (filled grey) and cations (black line), no scaling factor has been employed.

	BSSE (kJ/mol)	ZPE (kJ/mol)
[C _{forward}]Cl _{front-Me}	3.36	839.44
[C _{forward}]Cl _{front-R}	3.54	839.46
[C _{backward}]Cl _{front-Me}	2.77	838.62
[C _{linear}]Cl _{front-R}	3.86	839.55

Table S3: BSSE evaluated for a subset of ion-pairs using the counterpoise method.