Electronic Supporting Information for

Recent advances in self–assembled amidinium and guanidinium frameworks

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General methodology

The Cambridge Structural Database[S1] Version 5.39 (November 2017 & 2 updates) was searched with the fragments shown in Fig. S1. The database was searched for structures with no errors and no disorder and with R-factors < 10% in order to minimize the number of poorly-defined structures. Only organic structures were considered to avoid large numbers of structures where anions were coordinated to transition metal ions (and thus not free to hydrogen bond in the optimum configuration). Only structures containing acyclic C–N bonds were used, while this means some amidinium/guanidinium groups were overlooked, this was necessary to avoid huge numbers of irrelevant structures, such as those containing benzimidazolium or aminopyridinium groups.

Searches were required to contain an intermolecular short contact between an amidinium/guanidinium hydrogen atom and a negatively-charged oxygen atom with a length between 1.62 and 2.43 Å. These values were chosen as they represent 60–90% of the sum of the van der Waals radii of hydrogen and oxygen.[S2] In the case of the sulfonate anions, triflate anions were manually removed due to the non-coordinating nature of this anion (*i.e.* any anion with a CF_3 bonded to the sulfur atom was excluded).

The results were then visually inspected to remove any unintended structures (*i.e.* where there was no positive charge on the nitrogen component, where the carboxylate anion was coordinated to a calcium or strontium cation, or triflate anions). Histograms of the interaction distances are shown in Fig. S2 and statistics are shown in Table S1.

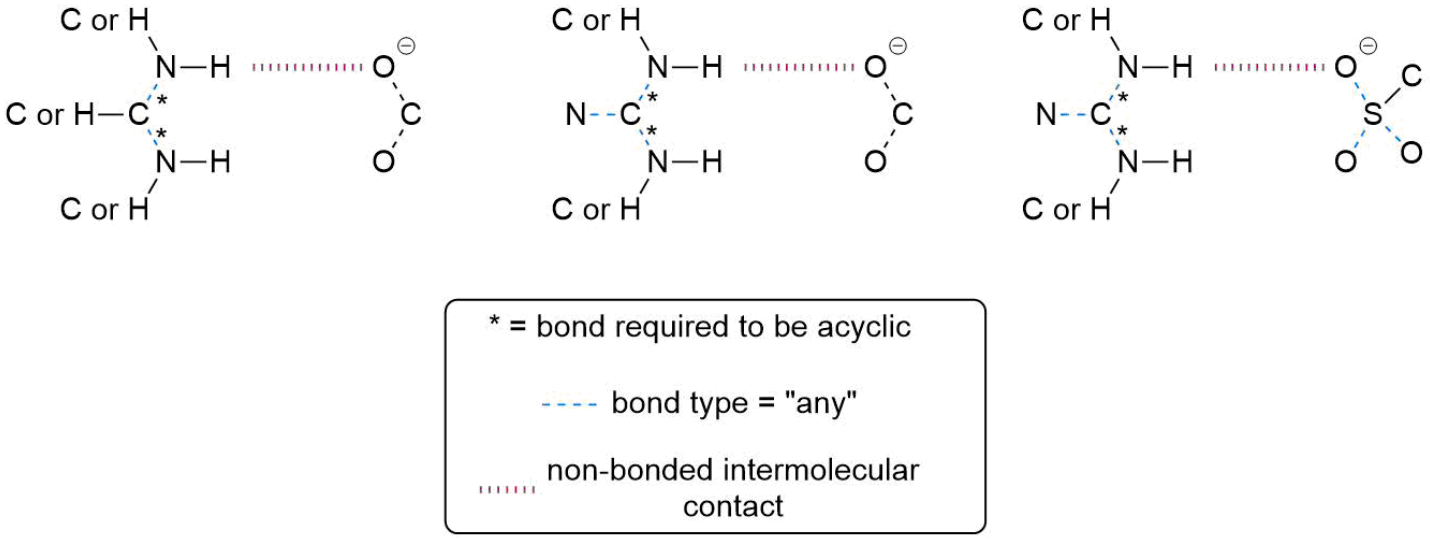

Fig S1. Search fragments used in CSD search.

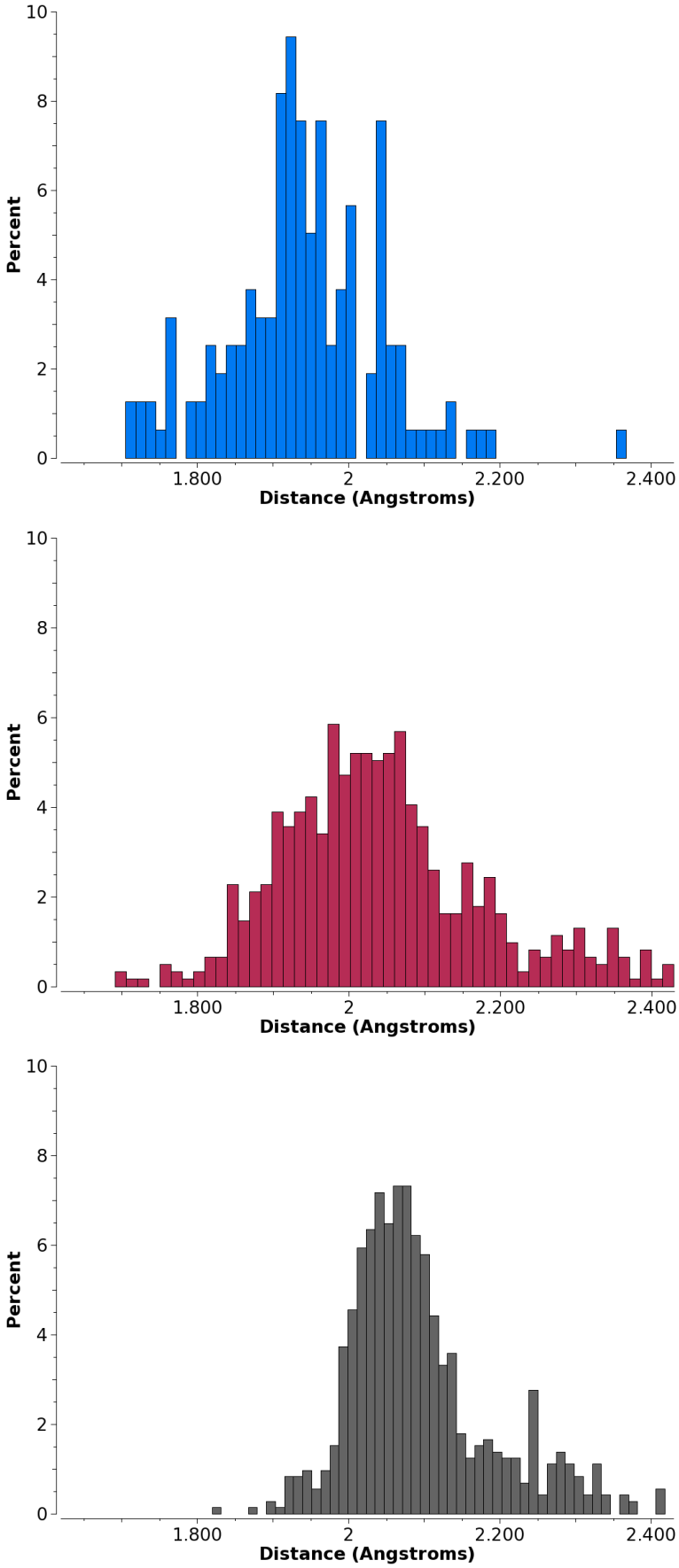

Fig S2. Histograms of hydrogen bonding distances: amidinium and carboxylate/carbonate anions (blue, top); guanidinium and carboxylate/carbonate anions (maroon, middle); guanidinium and sulfonate anions (grey, bottom).

Table S1. Statistics of hydrogen bonding interactions involving amidinium and guanidinium groups.[a]

Amidinium···carboxylate /carbonate anions		***Guanidinium···carboxylate /carbonate anions***		***Guanidinium···sulfonate anions***	
Number of structures	72	Number of structures	262	Number of structures	272
Number of H-bonds	159	Number of H-bonds	616	Number of H-bonds	725
Median distance (Å)	1.934	Median distance (Å)	2.028	Median distance (Å)	2.075
Mean distance (Å)	1.940	Mean distance (Å)	2.041	Mean distance (Å)	2.093
Lower quartile distance (Å)	1.883	Lower quartile distance (Å)	1.952	Lower quartile distance (Å)	2.033
Upper quartile distance (Å)	2.000	Upper quartile distance (Å)	2.105	Upper quartile distance (Å)	2.132
Minimum distance (Å)	1.706	Minimum distance (Å)	1.692	Minimum distance (Å)	1.820
Maximum distance (Å)	2.367	Maximum distance (Å)	2.429	Maximum distance (Å)	2.418

[a] Only structures with H···O distances between 1.62 and 2.43 Å are considered.

References

[S1] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Crystallogr.* **2016**, *B72*, 171–179.

[S2] S. Alvarez, *Dalton Trans.* **2013**, *42*, 8617–8636.