Electronic Supporting Information for

A systematic study of the crystallisation products of a series of diacids with imidazole derivatives.

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			2MI		DMI		4MI		1MI		Im	
	pK_a	1	7.88		7.76		7.49		7.01		6.95	
	1	2	-		-		-		-		-	
OxA	1.23	4.19	6.65	3.69	6.53	3.57	6.26	3.30	5.78	2.82	5.72	2.76
MeA	1.83	6.07	6.05	1.81	5.93	1.69	5.66	1.42	5.18	0.94	5.12	0.88
MnA	2.83	5.69	5.05	2.19	4.93	2.07	4.66	1.80	4.18	1.32	4.12	1.26
FmA	3.03	4.44	4.85	3.44	4.73	3.32	4.46	3.05	3.98	2.57	3.92	2.51
ScA	4.20	5.61	3.68	2.27	3.56	2.15	3.29	1.88	2.81	1.40	2.75	1.34
GlA	4.31	5.41	3.57	2.47	3.45	2.35	3.18	2.08	2.70	1.60	2.64	1.54
AdA	4.43	5.41	3.45	2.47	3.33	2.35	3.06	2.08	2.58	1.60	2.52	1.54
PmA	4.48	5.42	3.40	2.46	3.28	2.34	3.01	2.07	2.53	1.59	2.47	1.53
SbA	4.52	5.40	3.36	2.48	3.24	2.36	2.97	2.09	2.49	1.61	2.43	1.55

Table S1 pK_a values of the diacids and Im derivatives, together with their respective pK_a differences (pK_a values from ACD/I-Lab:[1] literature pK_a values were used where possible, the remainder were calculated).

Maleic acid-1-methylimidazole combination

Crystallisation of maleic acid and 1-methylimidazole (0.1M methanol solutions[†]) formed a zwitterion, (Figure S1). The components reacted via a 1,4-Michael addition reaction, linking them by means of the alkene double bond of the acid and the non-methylated nitrogen of the imidazole. Data are available on e-crystals.[2]

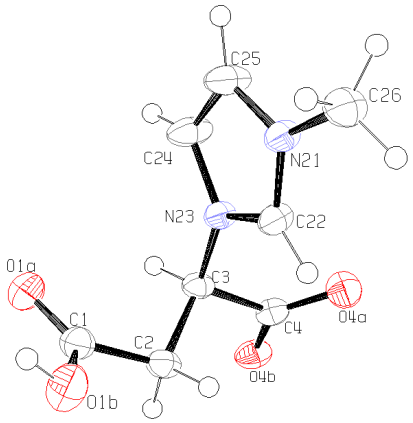

Figure S1 The zwitterion product resulting from the reaction of maleic acid with 1-methylimidazole.

Imidazolium oxalate[3]

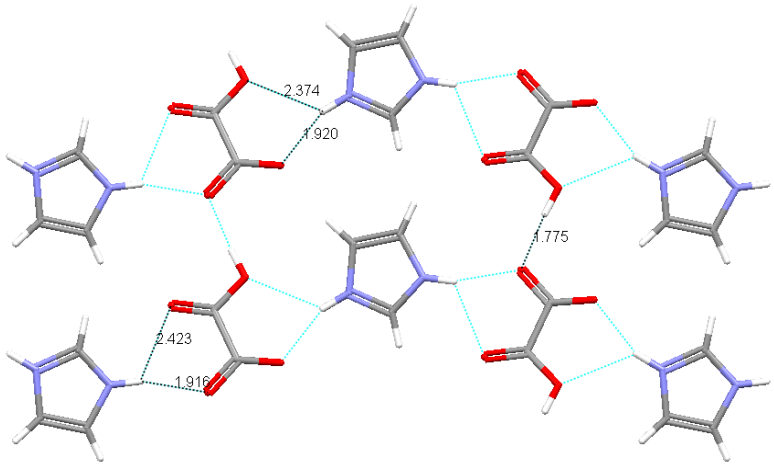

Figure S2 The hydrogen bonded sheets of imidazolium oxalate incorporating synthons I and IV, viewed down the *c*-axis.

Further Details of Crystal Structures and Crystallographic Refinement

Di-imidazolium di-suberate suberic acid (1)

Although ADDSYM suggests an additional (pseudo) symmetry element Z, the conformation of the acid molecule carbon chain prevents such a symmetry element from occurring.

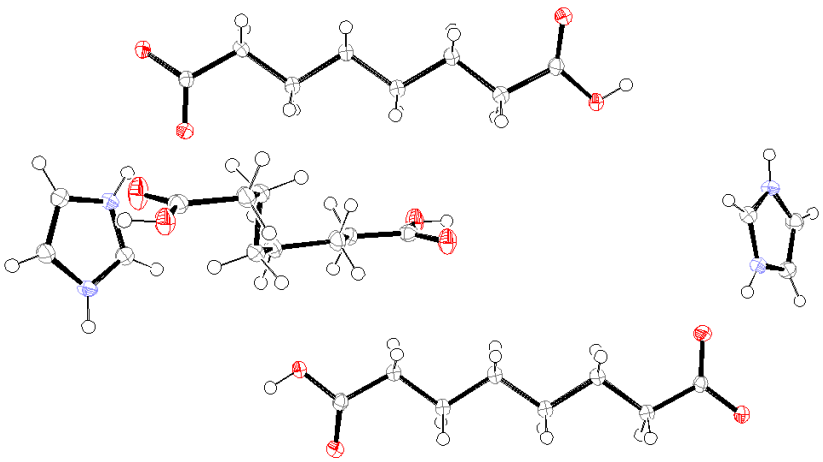

Figure S3 Ortep diagram for the asymmetric unit of **1**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

Di-1-methylimidazolium glutarate glutaric acid (2)

This structure was tested for merohedral twinning using ROTAX which suggested the twinning matrix -1 0 0, 0 -1 0, 0 0 1. This was applied and the structure refined resulting in a batch scale factor of 0.17826, reducing the R1 (obsd data) from 13.81% to 7% and making it possible to locate the transferable hydrogens.

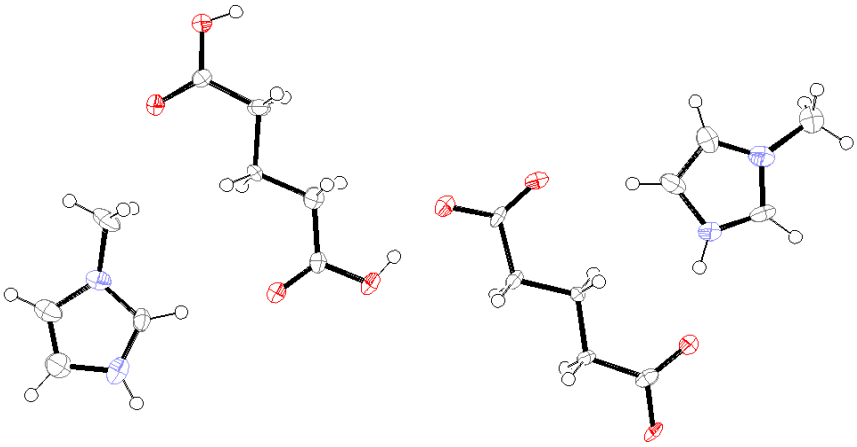

Figure S4 Ortep diagram for asymmetric unit of **2**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

Di-4-methylimidazolium succinate succinic acid (3)

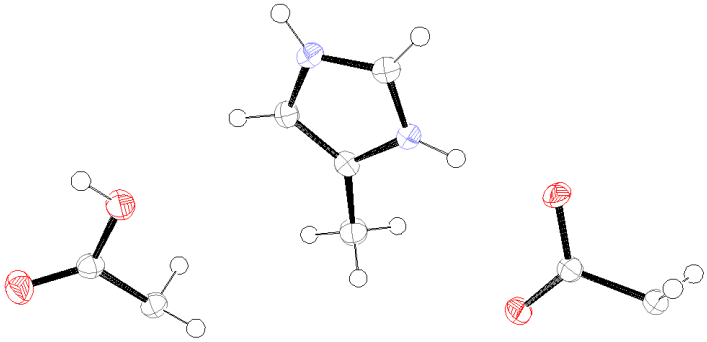

Figure S5 Ortep diagram for the asymmetric unit of **3**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

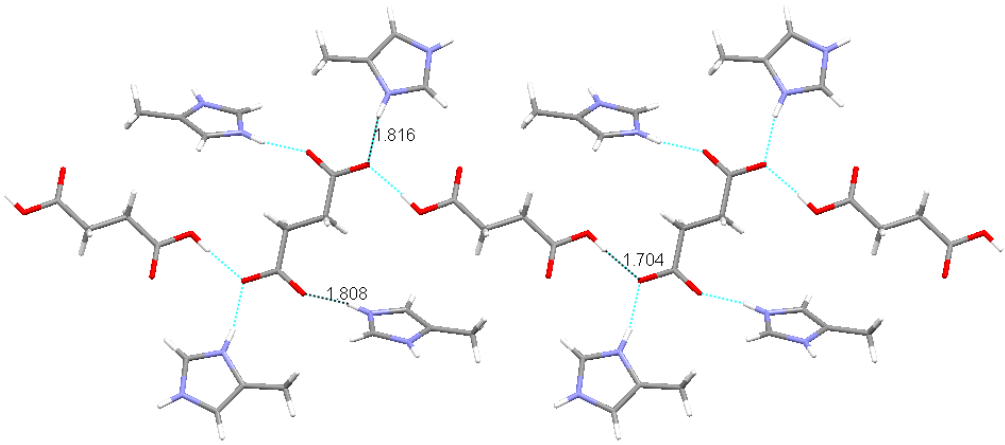

Figure S6 Hydrogen bonded chain structure seen in **3**, hydrogen bond distances marked.

2-Methylimidazolium glutarate (4)

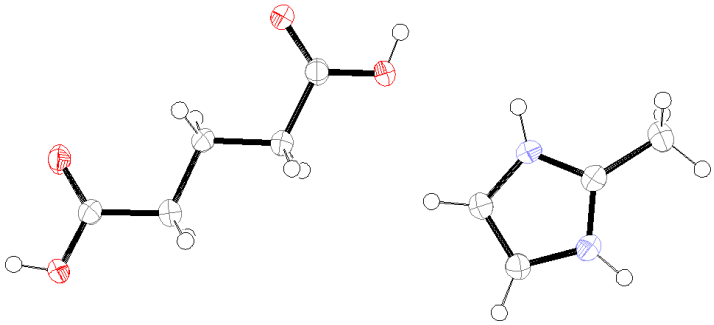

Figure S7 Ortep diagram for the asymmetric unit of **4**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

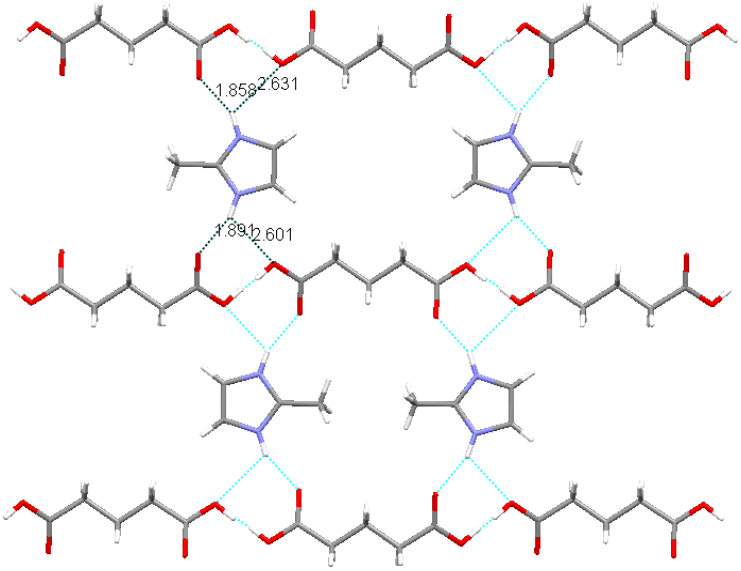

Figure S8 Arrangement of ions in **4** to form Sheet **5** (note hydrogens are half occupancy).

Di-2-methylimidazolium adipate adipic acid dihydrate (5)

Due to the small size and poor quality of the crystals, this sample was sent to Station 9.8 at Daresbury for data collection. Here it was possible to collect data although reflections were still weak at high 2theta resulting in a slightly lower diffrn_measured_fraction_theta_full value than is ideal. We do not feel, however, that this reduction is significant enough to detract from the data.

One of the hydrogen atoms on the water molecule was found to be disordered over two positions (H1w and H1b) which were modelled with arbitrary half occupancy. While the O-H bond distances were restrained using DFIX and DANG, the thermal parameters of the water molecule hydrogen atoms were left to refined freely. The reason for the disorder is due to hydrogen bonding between the water molecules.

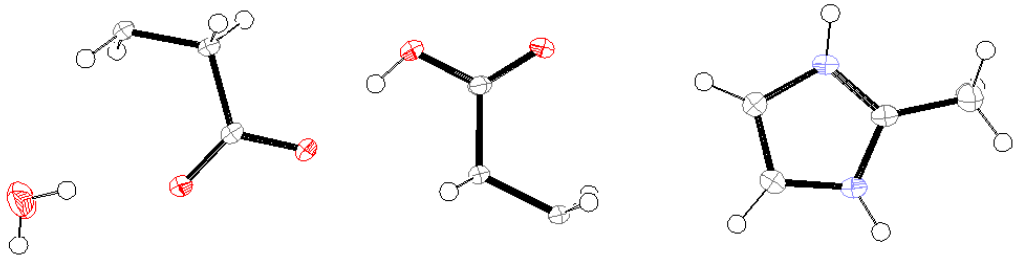

Figure S9 Ortep diagram for the asymmetric unit of **5**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

2-Methylimidazolium succinate (6)

The ions in **6** are both situated on a mirror plane and therefore have half occupancy (hence Z'=0.5, znd Z=2 in $P2_1/m$). The hydrogens on the methyl group of the 2-methylimdiazolium ion have been modelled accordingly; the checkcif alerts regarding short contacts are incorrect.

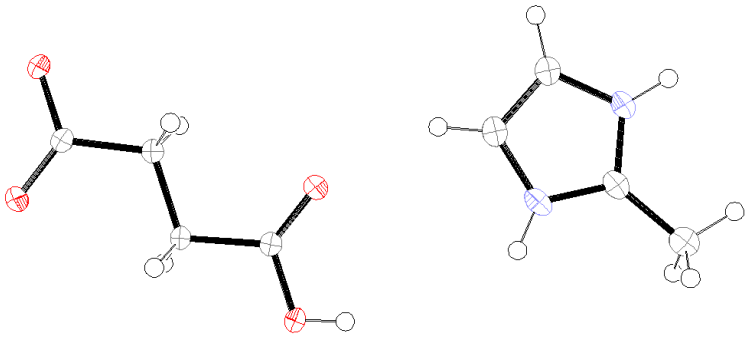

Figure S10 Ortep diagram for the asymmetric unit of **6**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

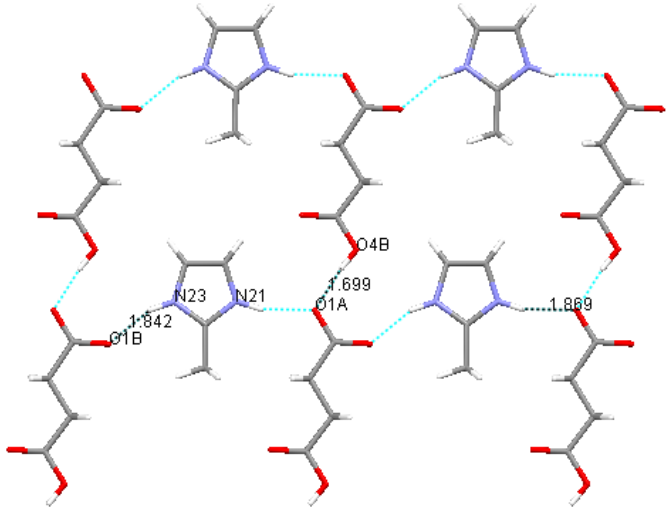

Figure S11 Sheet **7** formed by **6**, viewed down the *b*-axis. Hydrogen bond distances marked.

2-Methylimidazolium fumarate (7)

As **6** and **7** are isostructural, the same notes from above apply here. The ions in **7** are both situated on a mirror plane and therefore have half occupancy (hence Z'=0.5, znd Z=2 in

$P2_1/m$). The hydrogens on the methyl group of the 2-methylimdiazolium ion have been modelled accordingly; the checkcif alerts regarding short contacts are incorrect.

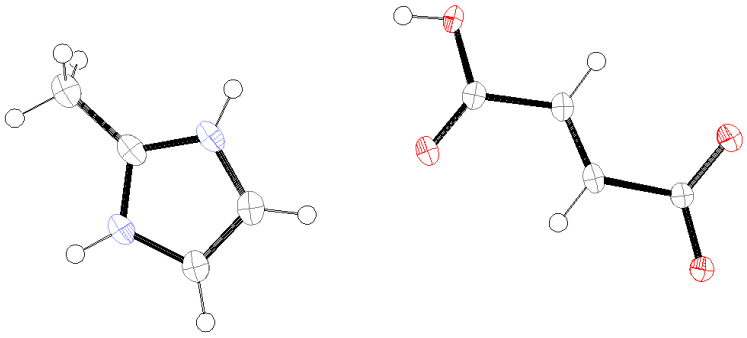

Figure S12 Ortep diagram for the asymmetric unit of **7**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

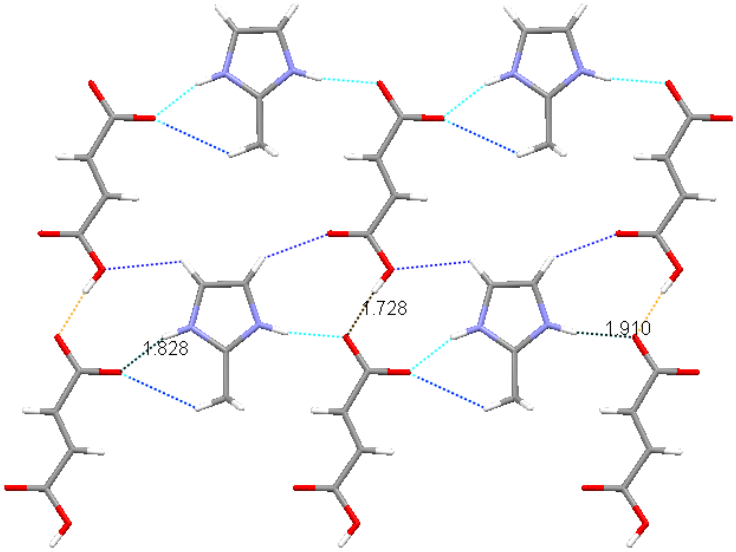

Figure S13 Sheet **7** adopted by **7**, O-H···O hydrogen bonds shown in orange, N-H···O in light blue, C-H···O in dark blue.

2-Methylimidazolium suberate (8)

The carboxyl group of the monoanion was found to be disordered. When refined using PARTs it was found that the group occupies position 8 41.26% of the time and position 9 58.74%.

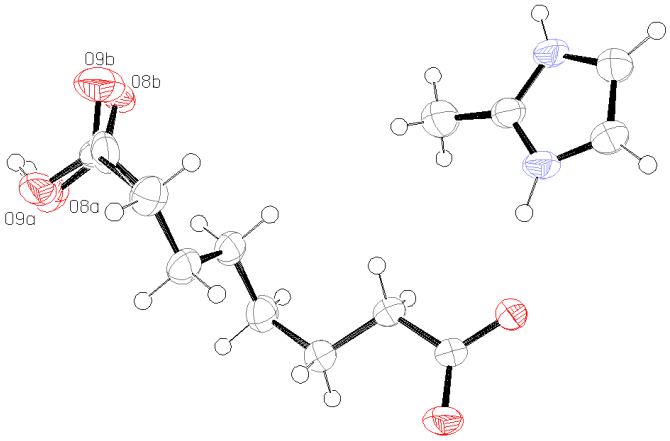

Figure S14 Ortep diagram for the asymmetric unit of **8**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

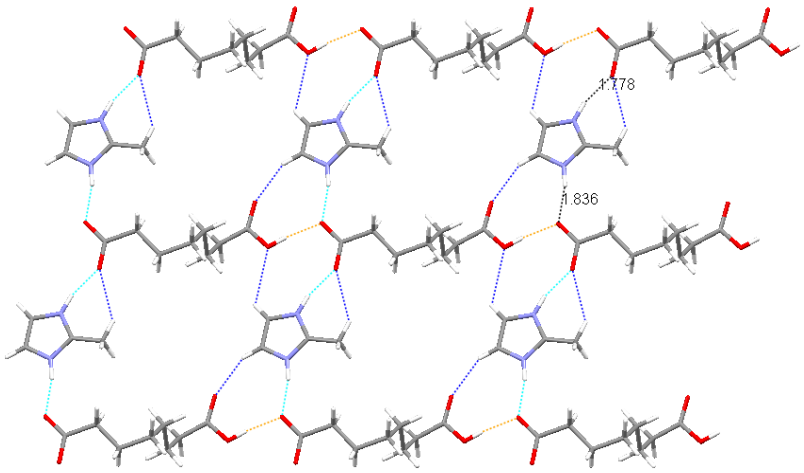

Figure S15 The stepped hydrogen bonded sheet (Sheet **7**) formed by **8**, O-H···O hydrogen bonds shown in orange, N-H···O shown in light blue, C-H···O shown in dark blue.

1,2-Dimethylimidazolium fumarate (9)

The Rint is higher than usual due to the small crystal size. However, all of the hydrogens were found easily and their positions confirmed.

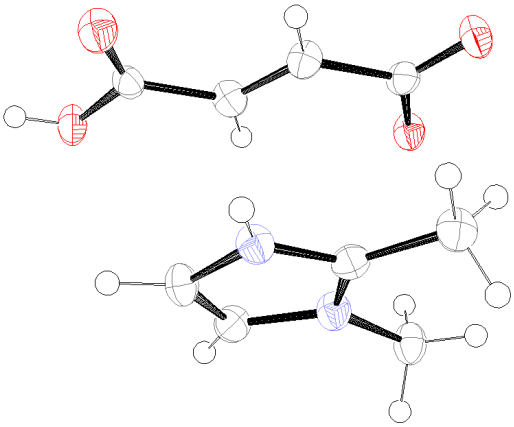

Figure S16 Ortep diagram for the asymmetric unit of **9**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

4-Methylimidazolium suberate (10)

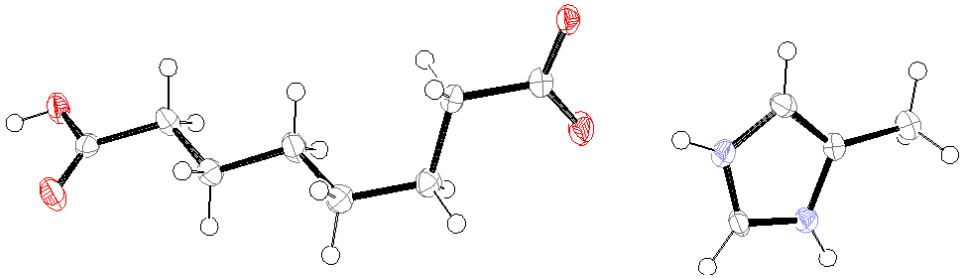

Figure S17 Ortep diagram for the asymmetric unit of **10**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

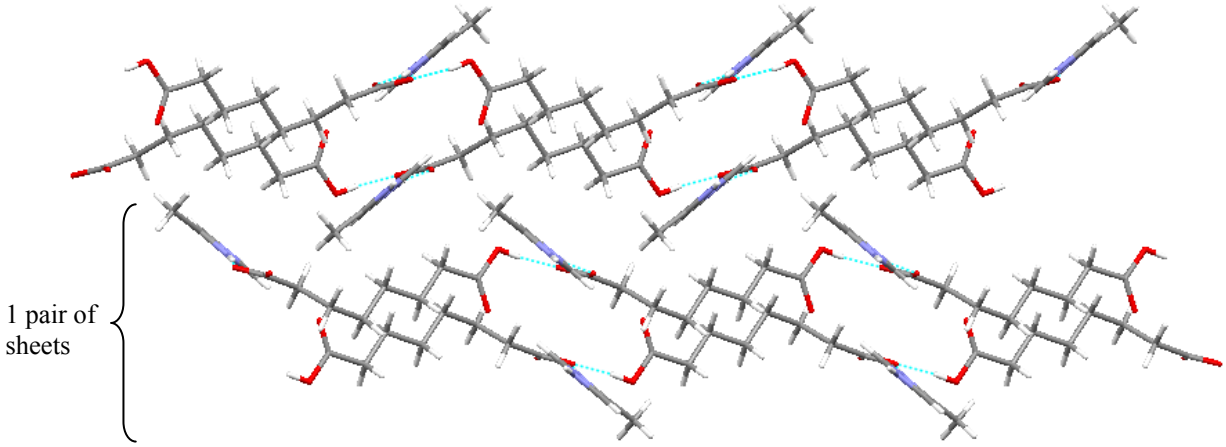

Figure S18 Stacking of the sheets in **10** so as the methyl groups on the cations fill the voids in the adjacent pair of sheets.

4-Methylimidazolium glutarate (11)

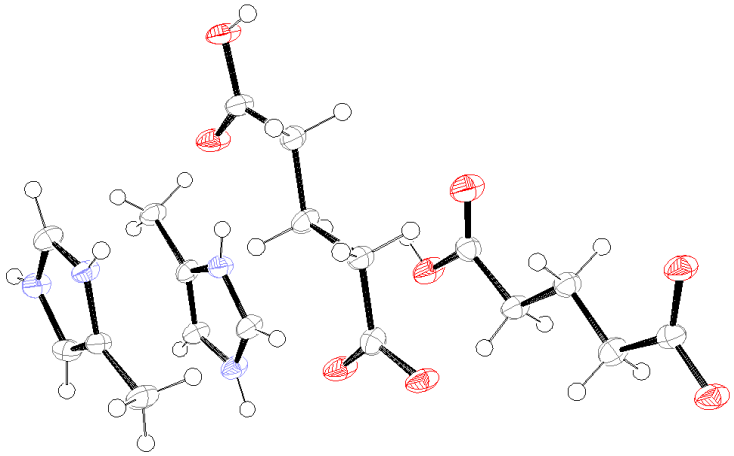

Figure S19 Ortep diagram for the asymmetric unit of **11**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

1,2-Dimethylimidazolium succinate (12)

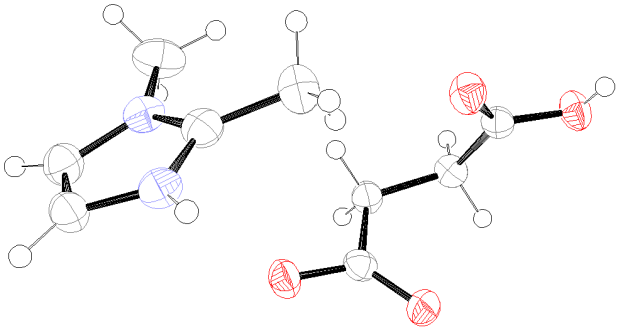

Figure S20 Ortep diagram for the asymmetric unit of **12**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

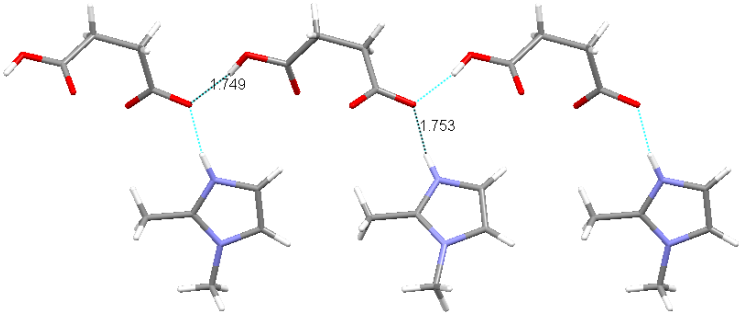

Figure S21 Chain structure of **12** with the anion backbone and subtended cations, hydrogen bond distances marked.

1,2-Dimethylimidazolium succinate (13)

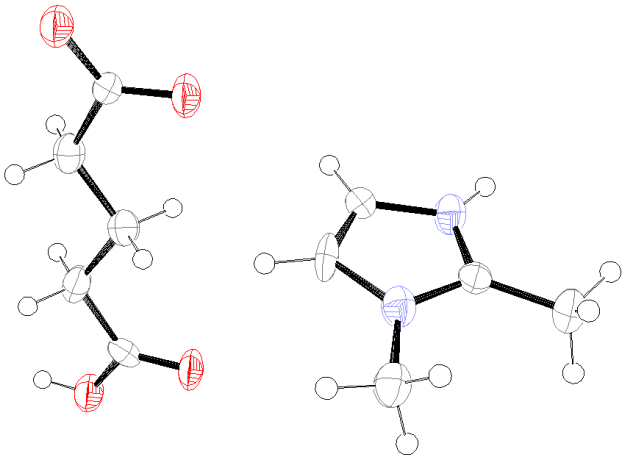

Figure S22 Ortep diagram for the asymmetric unit of **13**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

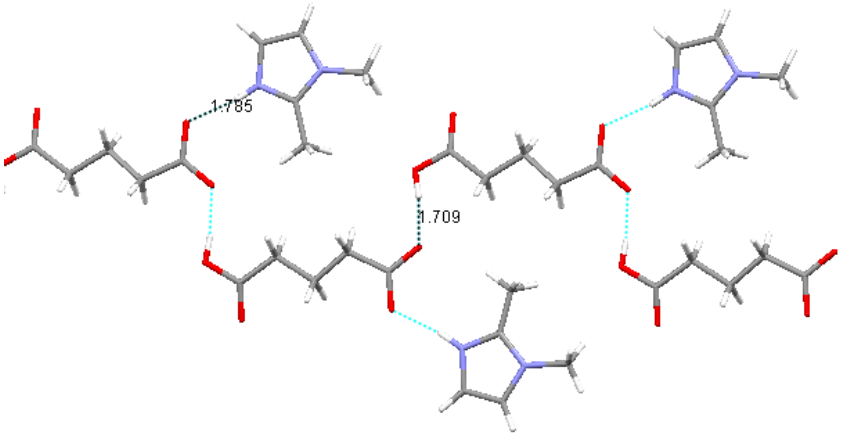

Figure S23 The hydrogen bonded chain of anions and cations in **13**, hydrogen bond distances marked.

1-Methylimidazolium methyloxalate (14)

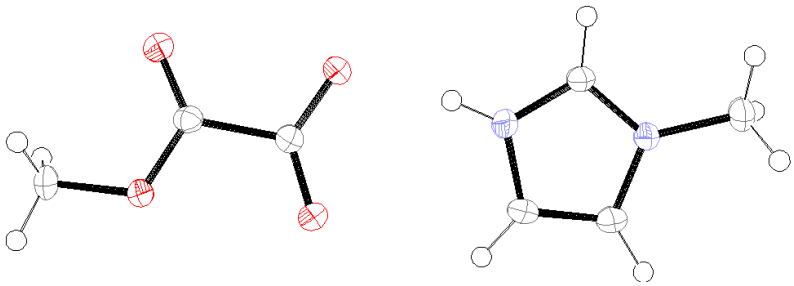

Figure S24 Ortep diagram for the asymmetric unit of **14**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

Di-2-methylimidazolium oxalate (15)

In spite of the higher R-values due to the small crystal size, there were no problems during solving and refining the structure. The transferable hydrogens were found easily and their positions confirmed by testing the hydrogens in their alternative location.

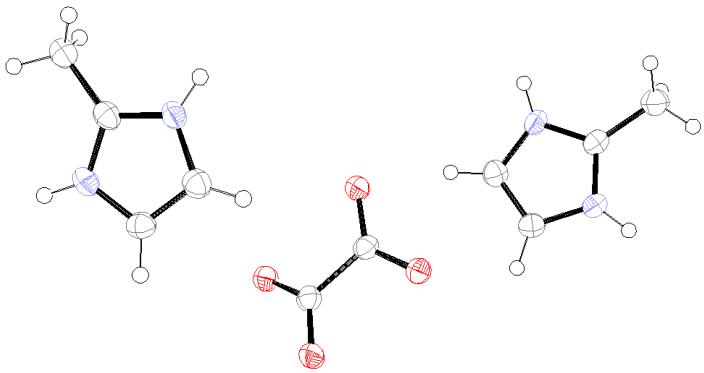

Figure S25 Ortep diagram for the asymmetric unit of **15**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

Di-4-methylimidazolium oxalate dihydrate (16)

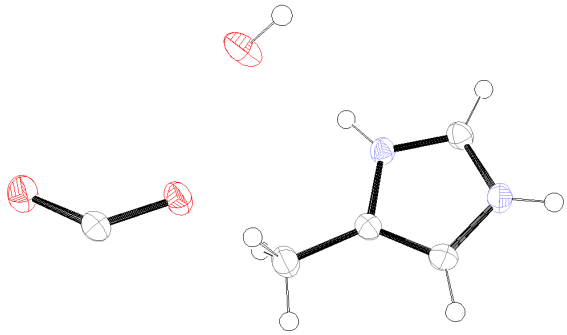

Figure S26 Ortep diagram for the asymmetric unit of **16**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

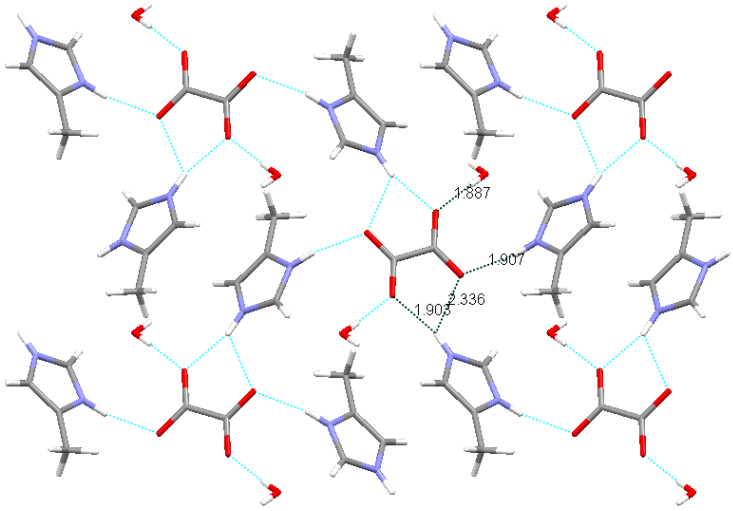

Figure S27 Hydrogen bonded arrangement in **16** where one anion is hydrogen bonded to the surrounding four cations and two water molecules.

Tri-imidazolium di-malonate (17)

While short contact O1B···C35 is a C-H···O hydrogen bond, the particularly short distance of the interaction may be partially due to the disorder seen in the cation. (Therefore disordered C-H···O distances were not included in the C-H···O hydrogen bond distance comparisons).

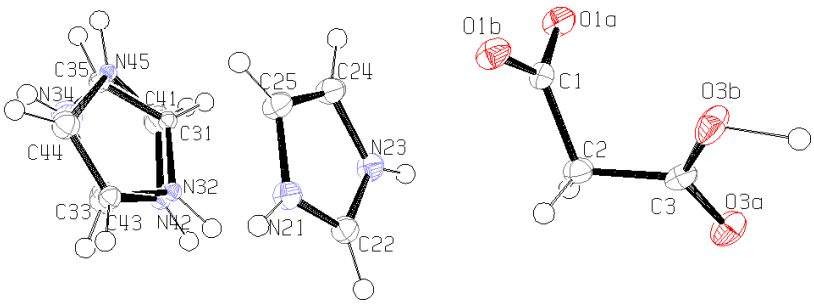

Figure S28 Ortep diagram showing the molecules present in the asymmetric unit of **17** with 50% probability displacement ellipsoids and hydrogens shown as spheres. The position of the disordered cation on an inversion centre creates a further two orientations of the molecule in the disorder assembly. Note that the hydrogen on O3b is only half occupancy.

2-Methylimidazolium malonate (18)

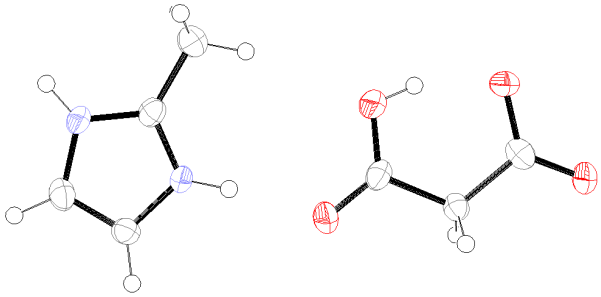

Figure S29 Ortep diagram for the asymmetric unit of **18**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

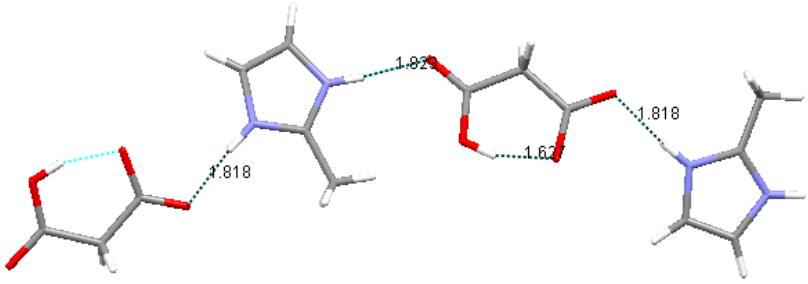

Figure S31 Hydrogen bonded chain of anions and cations in **19**, hydrogen bond distances marked.

4-Methylimidazolium maleate (19)

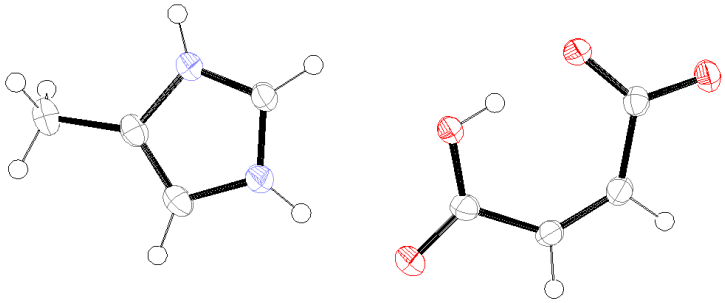

Figure S31 Ortep diagram for the asymmetric unit of **19**. Ellipsoids shown at 50% probability, hydrogen atoms shown as spheres.

References:

1. *ACD/I-Labs Web Service (ACD/pKa 8.03), Advanced Chemistry Development Inc.,*
2. S. K. Callear, M. B. Hursthouse, National Crystallography Service, 2008, University of Southampton, Crystal Structure Report Archive, (doi:10.3737/ecrystals.chem.soton.ac.uk/523).
3. J. C. MacDonald, P. C. Dorrestein, M. M. Pilley, *Cryst. Growth Des.,* 2001, **1,** 29-38.