IUCrJ

Volume 6 (2019)

Supporting information for article:

Direct air capture of CO2 – topological analysis of the experimental electron density (QTAIM) of the highly insoluble carbonate salt of a 2,6-pyridine-bis(iminoguanidine), (PyBIGH2)(CO3)(H2O)4

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SUPPLEMENTARY MATERIAL

CONTENTS

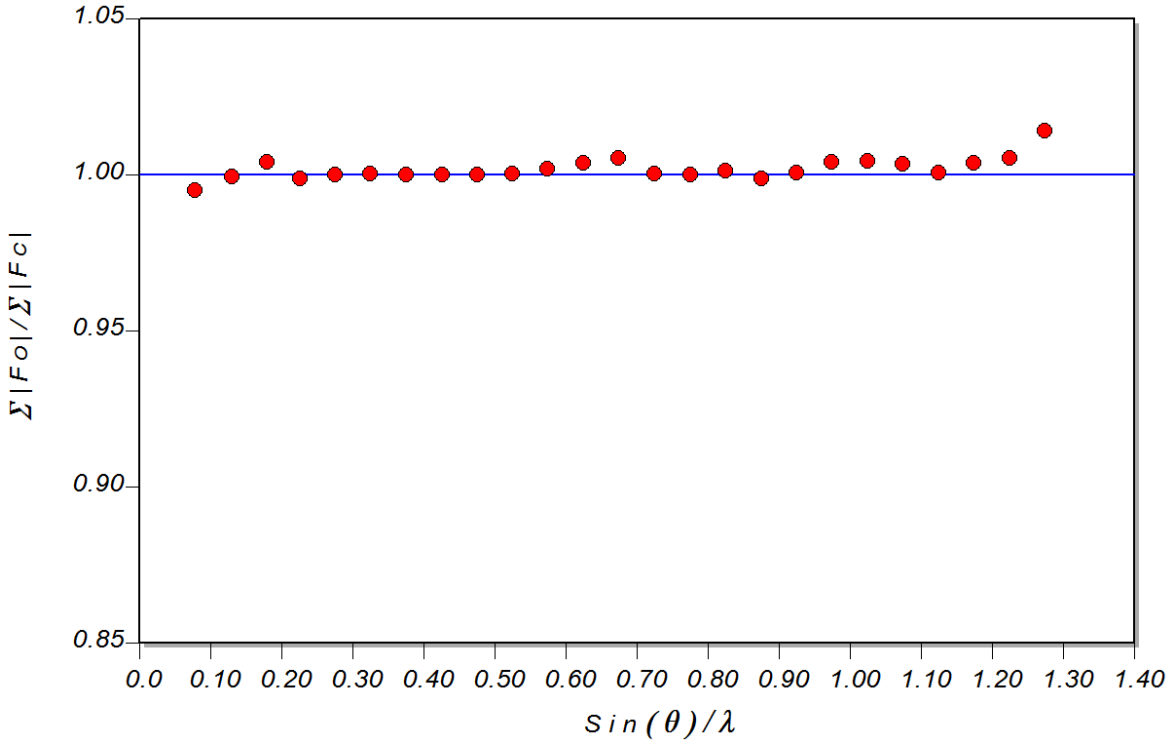

Fig. S1 Averaged ratios (in 0.05 Å^{-1} bins) of observed and calculated structure factors

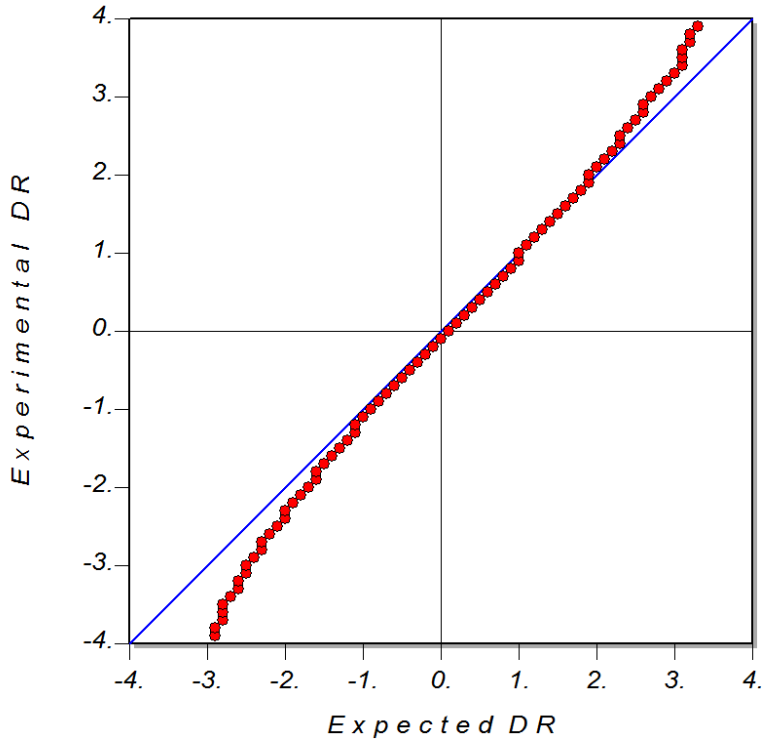

Fig. S2 Normal probability plot

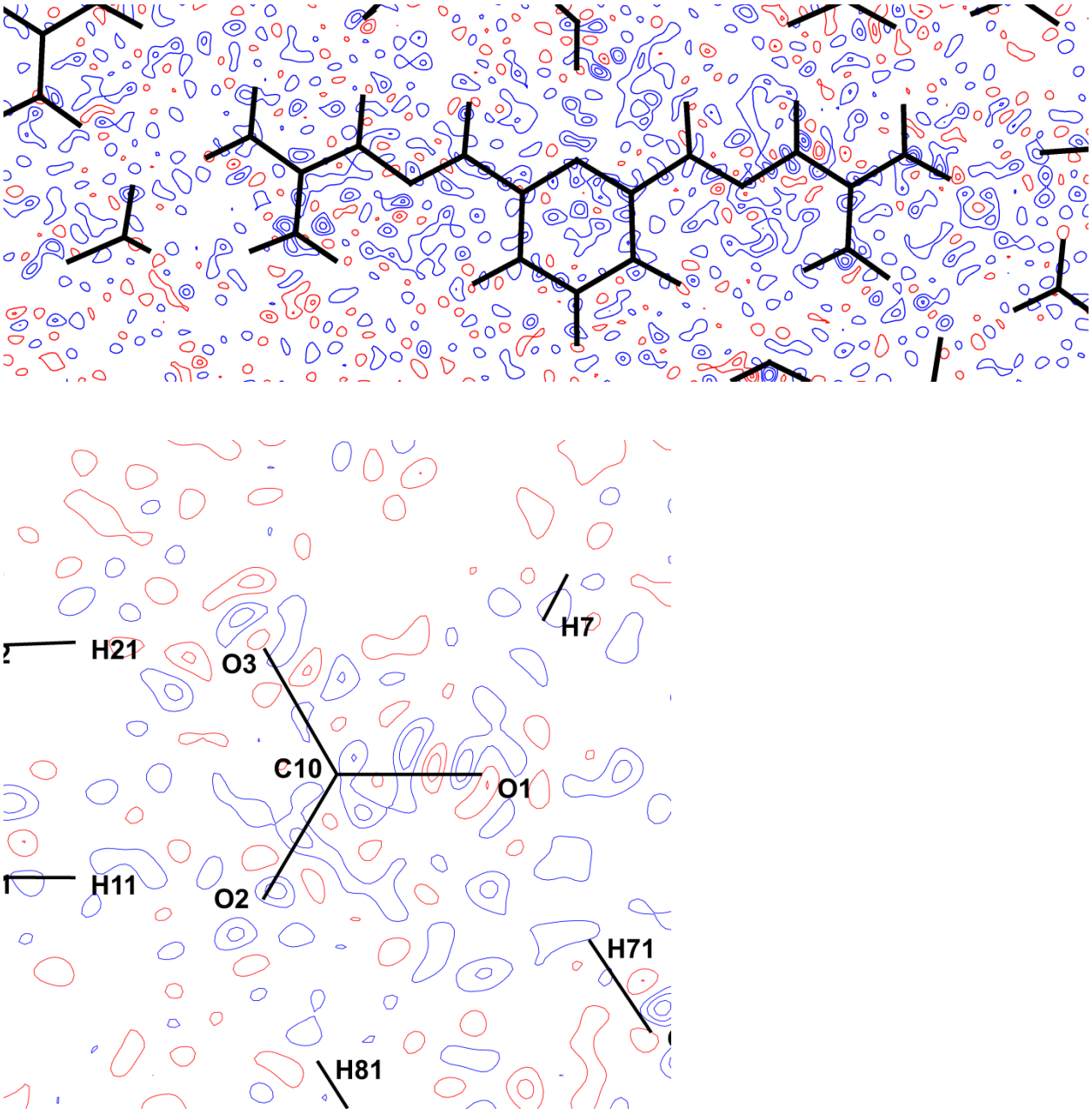

Fig. S3 Residual electron density maps in the plane of the cation (top) and anion (bottom). Contours at the 0.05 e/ang3 level; blue, positive – red, negative.

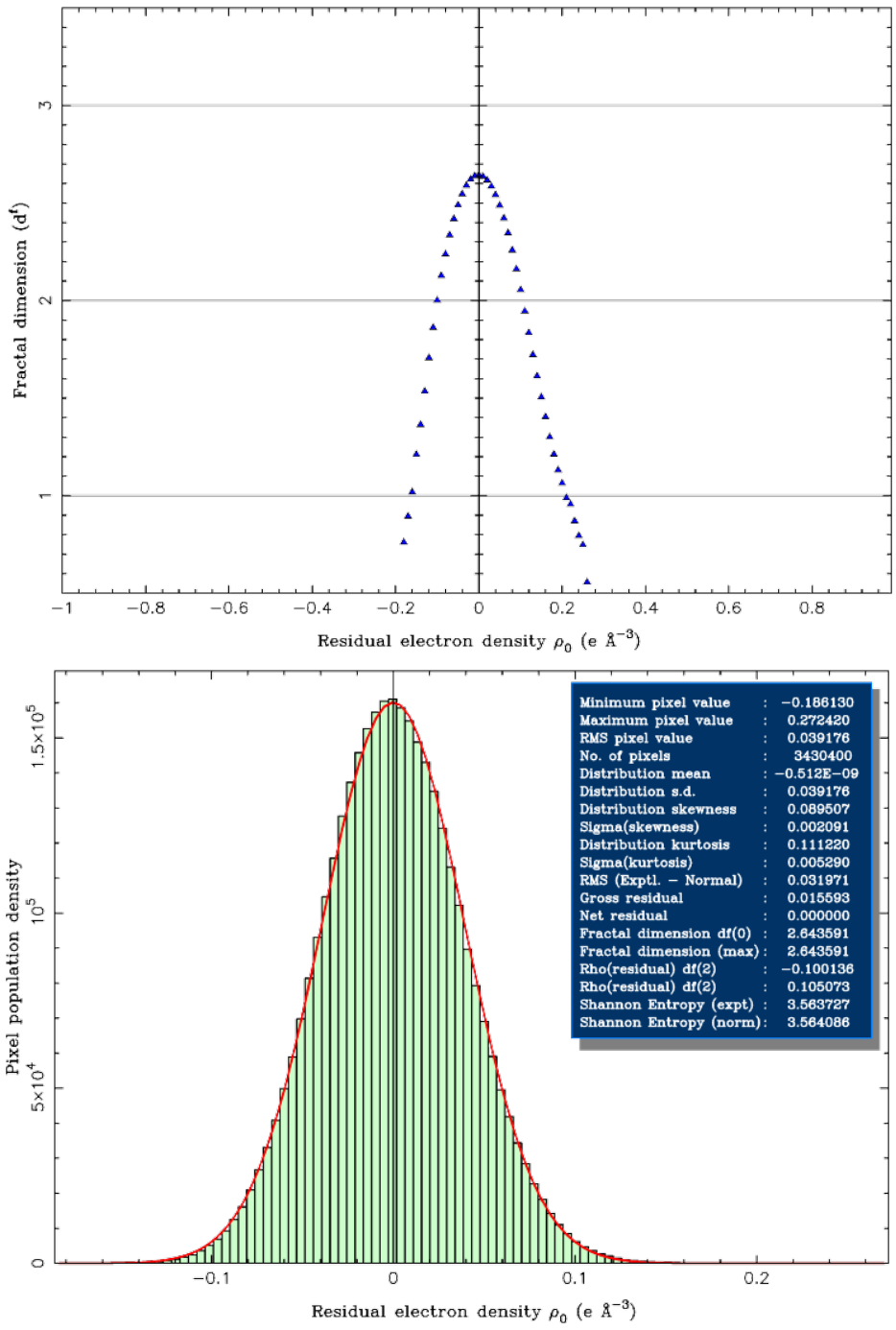

Fig. S4 Fractal dimension plot and probability distribution histogram

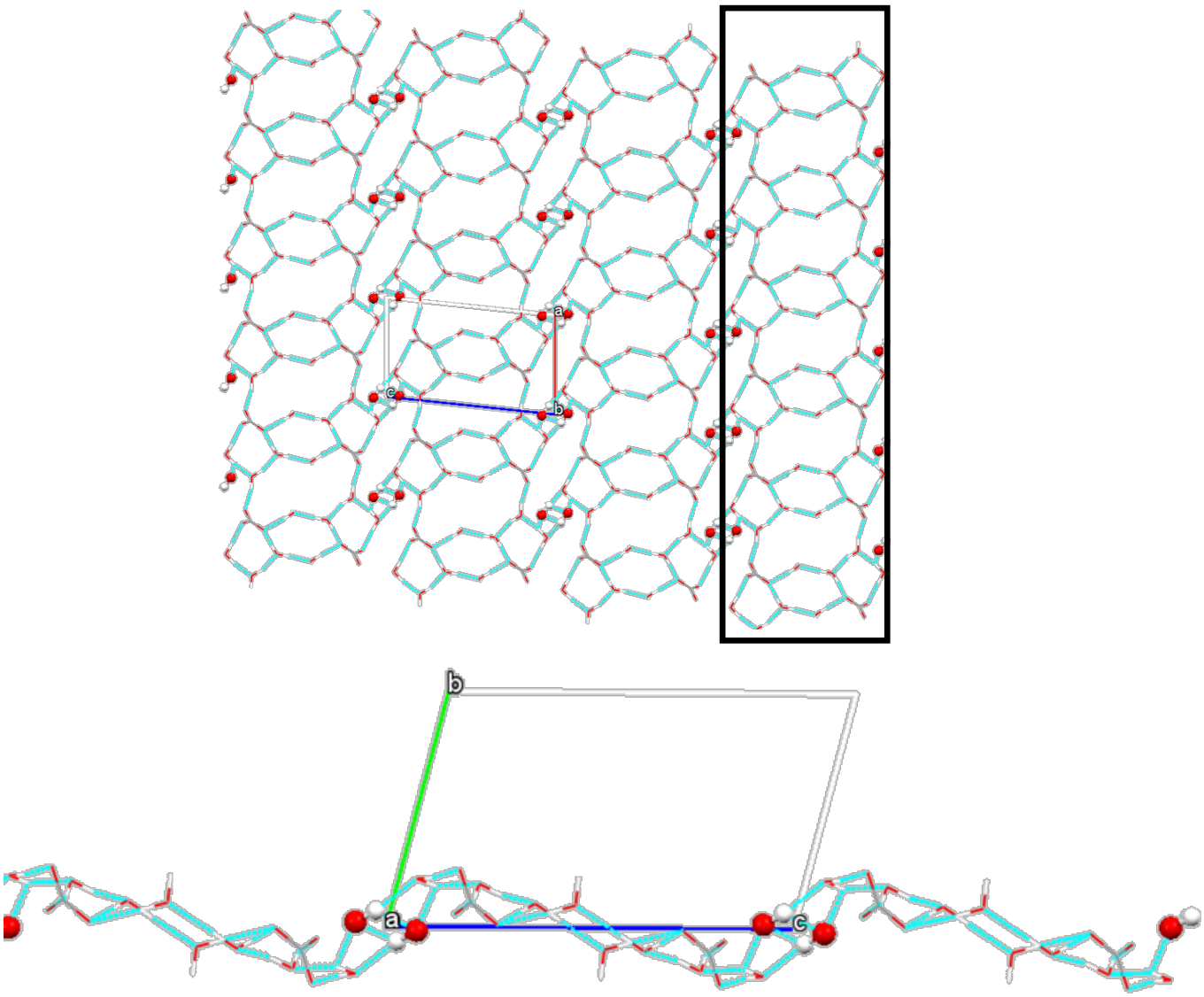

Fig. S5. Packing of anion-water ribbons. In the above figure, four ribbons are depicted from the perspective of looking down the *b*-axis. The ribbons extend infinitely along the *a*-axis, a portion of one these ribbons is highlighted by the black box. The disordered OH^- ions are depicted as balls, while the ordered anion water-ribbons are depicted in wireframe, blue lines denote short contacts (H-bonds). The bottom figure illustrates the canting of the ribbons above and below the *ac*-plane as viewed from the perspective of looking down the *a*-axis.

The anion-water ribbon is canted at an angle of ~23.6° above and below the *ac*-plane, and extends about 1.91 Å above and below the plane. In this context it is unsurprising that the sites of the partially occupied hydroxide ions fall in this cavity and are suggestive of a stabilizing interaction between neighboring ribbons

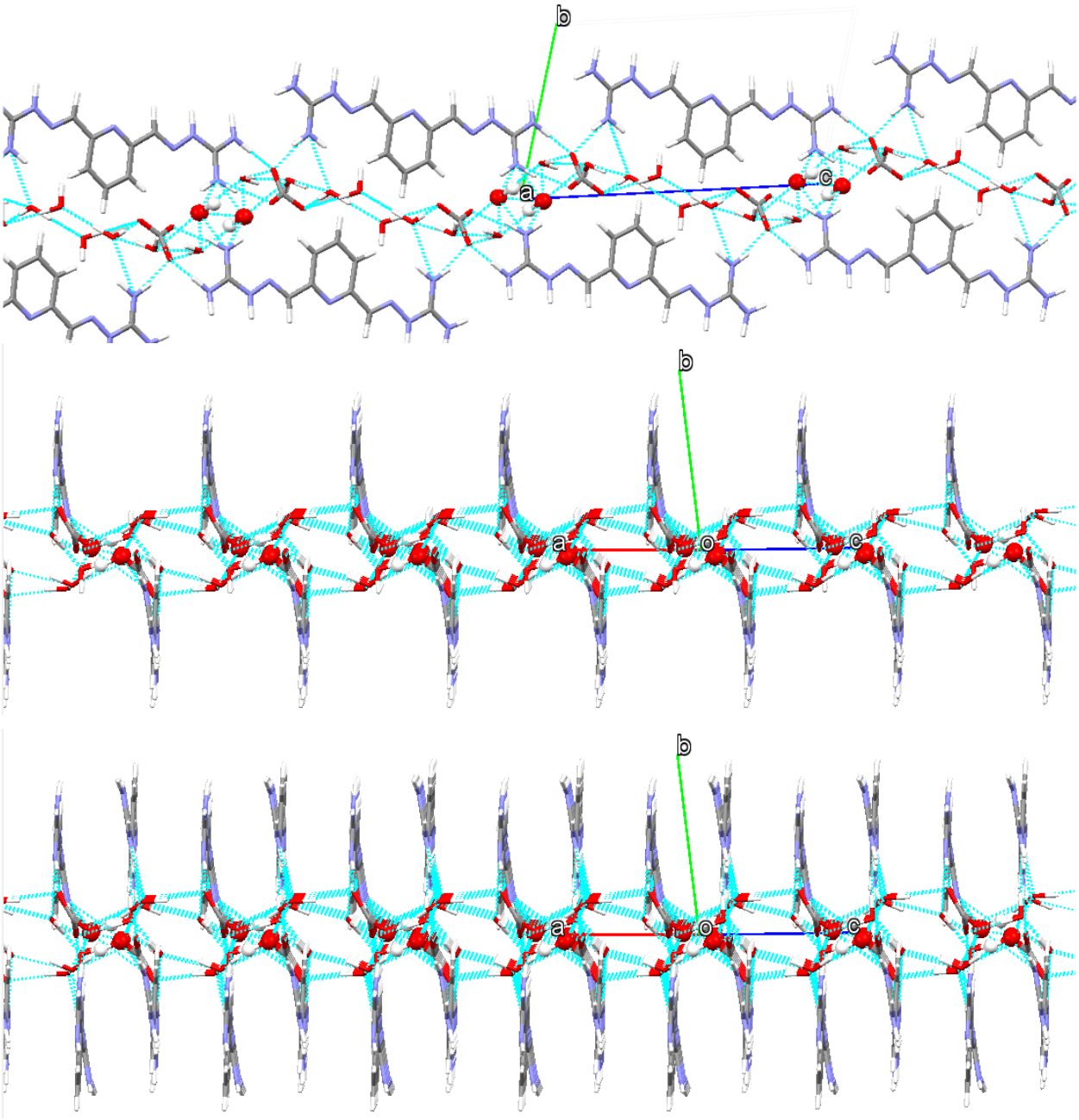

Fig. S6a, S6b, S7 Packing of cations about the anion-water ribbons. There are two differing types of interactions between the cation arrays and the anion-water ribbons. The nearest cation arrays (which pack infinitely along the [101] direction) to the ribbons participate as H-bond donors (see above and middle figures which provide two perspectives of the same diagram, and wherein all cation Npy point away from the anion-water ribbon). Slightly further away from the ribbons are cation arrays wherein the H-bond accepting pyridine N5 atom is oriented towards the ribbon. Both figures are from the perspective of looking down the [101] direction. Cations are depicted as sticks, the anion-water ribbons are depicted in wireframe and the disordered OH^- ions are shown as balls.

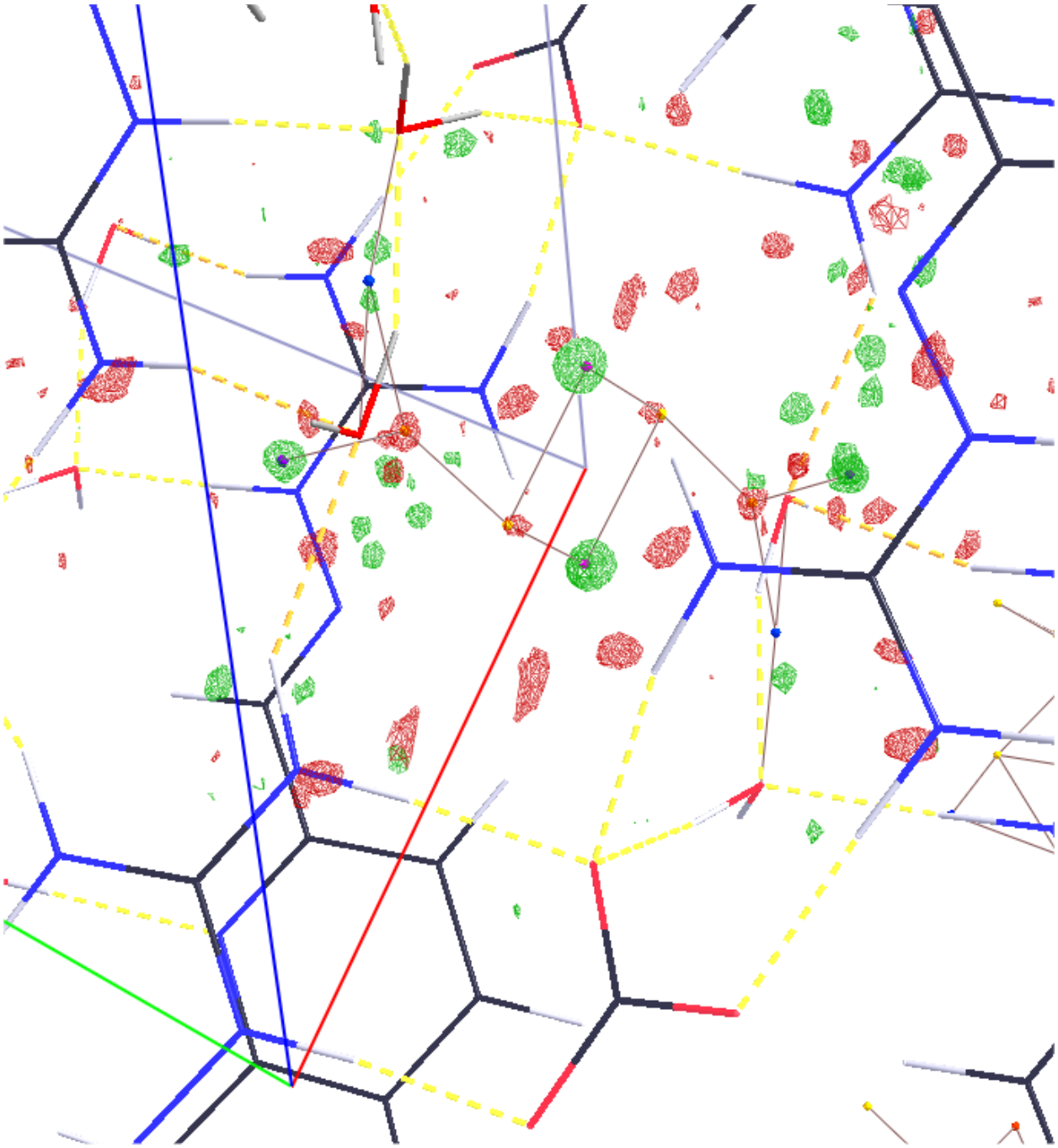

Figure S8. Residual density map from preliminary neutron refinement excluding the partially occupied OH group. The maximum is 1.40 fm Å^{-3}, nearby minimum -0.78 fm Å^{-3} and 1-sigma level 0.205 fm Å^{-3}.
Maximum coordinates; peak height: 0.9747 -0.0200 0.0794; 1.40 fm Å^{-3}
Minimum coordinates; peak height: 1.0980 -0.0779 0.0280; -0.78 fm Å^{-3}

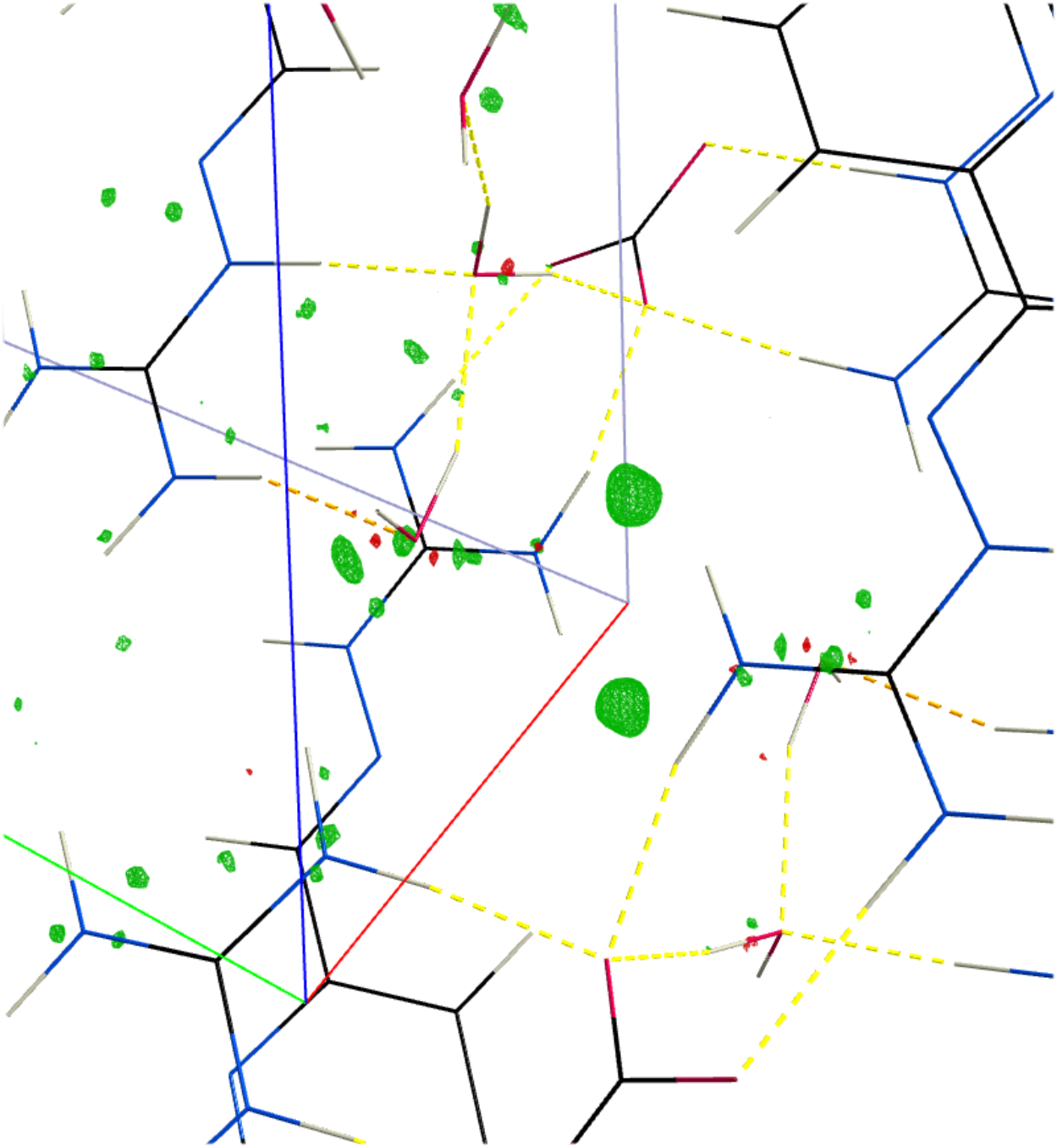

Figure S9. Residual density map from preliminary multipole refinement excluding the partially occupied OH group. The maximum is 0.44 e Å^{-3} while residual density sigma is ~0.04 e Å^{-3} (where sigma is estimated on residual density analysis of the final model).

Maximum coordinates; peak height: 0.9764 -0.0205 0.0792; 0.44 e Å^{-3}

Table S1. Critical point properties of covalent bonds. R_{ij}, d_1 and d_2 (Å); ρ (e Å^{-3}); $\nabla^2\rho$, λ_1, λ_2, λ_3 (e Å^{-5}); g, v, h (au).

Atom 1	Atom 2	R_{ij}	d_1	d_2	ρ	$\nabla^2\rho$	λ_1	λ_2	λ_3	g	v	h	ε	n_{topo}
PyBig														
C1	N1	1.325	0.749	0.576	2.49	-26.40	-21.23	-18.20	13.03	0.3631	-1.0000	-0.6370	0.17	1.26
C1	N2	1.327	0.543	0.785	2.46	-30.35	-22.18	-18.20	10.03	0.3225	-0.9599	-0.6374	0.22	1.16
C1	N3	1.352	0.560	0.792	2.37	-28.05	-20.98	-17.89	10.82	0.3087	-0.9085	-0.5997	0.17	1.10
C2	H2	1.095	0.744	0.350	1.83	-19.78	-18.49	-17.67	16.38	0.1899	-0.5850	-0.3951	0.05	0.89
C2	C3	1.468	0.731	0.737	1.91	-16.05	-14.20	-12.88	11.03	0.2390	-0.6444	-0.4055	0.10	1.08
C2	N4	1.286	0.509	0.778	2.64	-31.84	-23.05	-18.91	10.11	0.3793	-1.0889	-0.7096	0.22	1.34
C3	C4	1.398	0.704	0.694	2.14	-20.07	-16.60	-13.92	10.45	0.2841	-0.7764	-0.4923	0.19	1.26
C3	N5	1.347	0.582	0.766	2.35	-22.86	-19.26	-17.32	13.72	0.3366	-0.9103	-0.5737	0.11	1.17
C4	H4	1.088	0.727	0.361	1.88	-20.42	-18.61	-17.98	16.17	0.1993	-0.6104	-0.4112	0.03	0.93
C4	C5	1.391	0.692	0.699	2.16	-20.02	-16.31	-14.34	10.63	0.2921	-0.7920	-0.4998	0.14	1.31
C5	H5	1.086	0.724	0.363	1.87	-20.25	-18.36	-17.97	16.07	0.1983	-0.6066	-0.4083	0.02	0.93
C5	C6	1.388	0.698	0.690	2.17	-20.32	-16.59	-14.26	10.53	0.2923	-0.7953	-0.5030	0.16	1.30
C6	H6	1.085	0.730	0.355	1.89	-20.85	-18.92	-18.41	16.48	0.2005	-0.6174	-0.4168	0.03	0.92
C6	C7	1.402	0.684	0.718	2.11	-19.48	-16.24	-13.72	10.48	0.2791	-0.7604	-0.4812	0.18	1.26
C7	N5	1.345	0.771	0.574	2.37	-23.75	-19.50	-17.55	13.30	0.3391	-0.9246	-0.5855	0.11	1.18
C7	C8	1.470	0.736	0.734	1.90	-15.87	-14.20	-12.71	11.04	0.2372	-0.6391	-0.4018	0.12	1.08
C8	N6	1.284	0.790	0.494	2.64	-31.87	-22.81	-19.13	10.07	0.3794	-1.0894	-0.7100	0.19	1.34
C8	H8	1.096	0.738	0.358	1.84	-19.56	-18.35	-17.39	16.18	0.1927	-0.5882	-0.3956	0.06	0.91
C9	N7	1.358	0.777	0.581	2.35	-25.50	-20.58	-17.35	12.43	0.3194	-0.9034	-0.5839	0.19	1.12
C9	N8	1.322	0.760	0.563	2.49	-28.67	-22.03	-18.23	11.60	0.3452	-0.9878	-0.6426	0.21	1.21

C9	N9	1.326	0.556	0.770	2.45	-27.40	-21.12	-17.78	11.51	0.3421	-0.9685	-0.6263	0.19	1.21
N1	H12	1.037	0.781	0.256	2.13	-32.37	-29.72	-28.53	25.88	0.1960	-0.7277	-0.5317	0.04	0.69
N1	H11	1.005	0.765	0.240	2.13	-31.95	-30.95	-29.88	28.89	0.2004	-0.7323	-0.5319	0.04	0.64
N2	H22	1.013	0.757	0.257	2.16	-30.16	-29.38	-28.12	27.35	0.2197	-0.7522	-0.5325	0.05	0.73
N2	H21	1.029	0.778	0.251	2.09	-31.28	-29.40	-28.37	26.49	0.1910	-0.7066	-0.5155	0.04	0.66
N3	H3	1.057	0.806	0.252	2.03	-31.38	-28.83	-27.63	25.08	0.1711	-0.6677	-0.4967	0.04	0.63
N3	N4	1.362	0.689	0.673	2.38	-7.05	-20.15	-18.58	31.68	0.4550	-0.9830	-0.5281	0.08	1.38
N6	N7	1.357	0.669	0.688	2.41	-7.88	-20.54	-19.13	31.79	0.4602	-1.0022	-0.5420	0.07	1.37
N7	H7	1.041	0.791	0.250	2.04	-30.49	-29.14	-27.84	26.49	0.1797	-0.6756	-0.4959	0.05	0.62
N8	H82	0.998	0.758	0.240	2.20	-32.86	-31.44	-30.33	28.90	0.2171	-0.7750	-0.5580	0.04	0.69
N8	H81	1.030	0.781	0.249	2.09	-30.96	-29.29	-28.58	26.91	0.1935	-0.7082	-0.5147	0.03	0.66
N9	H92	1.045	0.786	0.259	2.08	-30.10	-28.34	-27.23	25.47	0.1953	-0.7028	-0.5076	0.04	0.69
N9	H91	1.015	0.768	0.247	2.12	-31.53	-30.18	-28.93	27.58	0.2001	-0.7272	-0.5272	0.04	0.66
Carbonate														
C10	O1	1.289	0.475	0.814	2.51	-30.38	-22.95	-20.66	13.23	0.3407	-0.9965	-0.6558	0.11	1.31
C10	O2	1.289	0.476	0.813	2.48	-30.03	-22.64	-20.35	12.97	0.3323	-0.9760	-0.6438	0.11	1.29
C10	O3	1.292	0.491	0.801	2.47	-29.83	-22.36	-19.81	12.34	0.3305	-0.9705	-0.6400	0.13	1.30
Waters														
O4	H42	0.971	0.768	0.203	2.25	-41.79	-38.91	-37.99	35.11	0.1727	-0.7789	-0.6062	0.02	0.55
O4	H41	0.980	0.755	0.225	2.27	-36.72	-36.60	-35.01	34.89	0.2144	-0.8097	-0.5953	0.05	0.59
O5	H52	0.973	0.761	0.212	2.25	-37.03	-36.90	-36.59	36.45	0.2034	-0.7909	-0.5875	0.01	0.53
O5	H51	0.967	0.761	0.205	2.22	-33.49	-36.55	-35.97	39.03	0.2194	-0.7863	-0.5668	0.02	0.45
O6	H62	0.980	0.779	0.201	2.21	-41.44	-38.21	-38.01	34.78	0.1600	-0.7499	-0.5899	0.01	0.53
O6	H61	0.981	0.771	0.211	2.21	-36.63	-36.77	-35.99	36.13	0.1918	-0.7636	-0.5718	0.02	0.51

O7	H72	0.984	0.785	0.199	2.16	-37.75	-37.17	-36.44	35.86	0.1687	-0.7290	-0.5603	0.02	0.47
O7	H71	0.973	0.765	0.208	2.24	-38.56	-37.61	-37.42	36.47	0.1911	-0.7823	-0.5911	0.00	0.52

Table S2. Properties of bond critical points for intermolecular interactions. R_{ij}, d and d_2 (Å); ρ (e Å^{-3}); $\nabla^2\rho$, λ_1, λ_2, λ_3 (e Å^{-5}); g, v, h (au); D_e (kJ/mol).

Atom 1	Atom 2	ORTEP Atom 2	ρ	$\nabla^2\rho$	R_{ij}	d_1	d_2	g	v	h	D_e	λ_1	λ_2	λ_3
O1	H7	46401	0.358	2.09	1.698	1.122	0.577	0.0360	-0.0503	-0.0143	66.0	-2.441	-2.387	6.921
H11	O2	55501	0.354	2.21	1.725	0.596	1.129	0.0364	-0.0499	-0.0135	65.5	-2.312	-2.297	6.817
O3	H91	46401	0.317	2.53	1.725	1.131	0.596	0.0350	-0.0438	-0.0088	57.5	-2.039	-1.960	6.526
O6	H3	65501	0.299	2.47	1.724	1.152	0.572	0.0330	-0.0404	-0.0074	53.1	-2.008	-1.970	6.445
O3	H61	66502	0.296	2.59	1.727	1.134	0.596	0.0336	-0.0403	-0.0067	52.8	-1.875	-1.809	6.275
O2	H81	45401	0.279	2.70	1.751	1.153	0.598	0.0329	-0.0378	-0.0049	49.6	-1.742	-1.713	6.154
O1	H71	56502	0.266	2.17	1.790	1.171	0.619	0.0281	-0.0337	-0.0056	44.2	-1.669	-1.644	5.483
H62	O7	55501	0.258	2.54	1.766	0.594	1.175	0.0300	-0.0337	-0.0036	44.2	-1.657	-1.573	5.774
O2	H41	56502	0.251	2.07	1.798	1.181	0.618	0.0262	-0.0310	-0.0047	40.6	-1.595	-1.579	5.249
O5	H72	65602	0.237	2.56	1.797	1.188	0.611	0.0285	-0.0305	-0.0020	40.0	-1.427	-1.420	5.407
H21	O3	55501	0.244	2.18	1.830	0.635	1.195	0.0264	-0.0302	-0.0038	39.7	-1.489	-1.421	5.089
H42	O6	55501	0.2	2.17	1.868	0.639	1.230	0.0232	-0.0239	-0.0007	31.3	-1.162	-1.149	4.482
O1	H51	56502	0.187	2.29	1.897	1.223	0.676	0.0231	-0.0224	0.0007	29.4	-0.958	-0.943	4.193

H52	N5	55501	0.201	1.61	1.963	0.674	1.290	0.0193	-0.0220	-0.0026	28.8	-1.131	-1.114	3.854
O4	H12	65501	0.154	1.48	2.003	1.291	0.714	0.0155	-0.0156	-0.0002	20.5	-0.814	-0.749	3.037
O7	H82	66602	0.108	1.72	2.115	1.338	0.780	0.0148	-0.0118	0.0030	15.5	-0.481	-0.363	2.561
O4	H92	55401	0.092	1.71	2.129	1.344	0.794	0.0141	-0.0104	0.0037	13.6	-0.405	-0.256	2.369
O7	H6	66602	0.055	0.53	2.561	1.520	1.043	0.0046	-0.0037	0.0009	4.9	-0.191	-0.179	0.897
O5	H5	54501	0.047	0.65	2.647	1.535	1.119	0.0052	-0.0037	0.0015	4.9	-0.141	-0.104	0.893
N1	N3	56502	0.051	0.56	3.256	1.623	1.649	0.0047	-0.0036	0.0011	4.8	-0.122	-0.078	0.763
C3	C9	66602	0.057	0.46	3.280	1.667	1.666	0.0042	-0.0036	0.0006	4.7	-0.097	-0.026	0.586
C7	N6	66602	0.054	0.50	3.267	1.665	1.623	0.0044	-0.0036	0.0008	4.7	-0.071	-0.035	0.604
C3	C7	56602	0.056	0.46	3.295	1.642	1.653	0.0041	-0.0035	0.0006	4.6	-0.075	-0.027	0.562
O4	O8	55601	0.045	0.56	2.131	1.558	0.573	0.0046	-0.0033	0.0013	4.4	-0.257	-0.250	1.072
N3	C9	56602	0.049	0.46	3.398	1.730	1.676	0.0039	-0.0031	0.0008	4.1	-0.050	-0.026	0.534
O5	C5	56602	0.042	0.45	3.216	1.579	1.637	0.0037	-0.0028	0.0010	3.6	-0.084	-0.074	0.612
O7	H4	64501	0.034	0.51	2.807	1.639	1.228	0.0040	-0.0026	0.0014	3.4	-0.074	-0.057	0.643
O6	H4	64501	0.028	0.51	2.807	1.659	1.150	0.0039	-0.0024	0.0015	3.2	-0.073	-0.055	0.641
O1	H8	46401	0.03	0.45	2.796	1.627	1.172	0.0035	-0.0023	0.0012	3.0	-0.088	-0.036	0.577
O4	N2	64501	0.026	0.48	3.366	1.654	1.719	0.0036	-0.0022	0.0014	2.9	-0.076	-0.061	0.615
O8	H22	64501	0.027	0.34	1.738	0.702	1.039	0.0026	-0.0018	0.0009	2.3	-0.130	-0.129	0.596
O4	N2	66502	0.021	0.28	3.550	1.725	1.830	0.0021	-0.0013	0.0008	1.8	-0.047	-0.042	0.366
O6	N8	66602	0.019	0.28	3.535	1.739	1.799	0.0021	-0.0013	0.0008	1.7	-0.046	-0.030	0.359
O7	H8	65602	0.02	0.23	3.138	1.849	1.324	0.0018	-0.0012	0.0006	1.5	-0.053	-0.010	0.297
O1	C5	57502	0.015	0.17	3.867	1.904	1.970	0.0013	-0.0008	0.0005	1.1	-0.012	-0.009	0.187
O4	O8	75502	0.008	0.12	2.876	1.931	0.947	0.0009	-0.0005	0.0004	0.6	-0.023	-0.018	0.159
O1	N2	47502	0.008	0.09	4.214	2.228	2.079	0.0006	-0.0004	0.0003	0.5	-0.010	-0.007	0.104

Table S3-S4. Reflection statistics

Cumulative resolution subsets [s = sin(theta)/lambda , d = 1/(2*s) ; s .le. s_max , d .ge. d_min]

	Nmeasrd	Nunique	<N>	R1	R2	RW	Z	V
d > 10	1	1	1	0	0	0	0	0
d > 8	1	1	1	0	0	0	0	0
d > 6	143	10	14.3	0.0075	0.0098	0.0109	1.092	0.009
d > 4	528	29	18.2	0.0108	0.019	0.0112	1.412	0.014
d > 3.5	834	43	19.4	0.0098	0.0178	0.0105	1.394	0.012
d > 3	1428	70	20.4	0.0191	0.0395	0.0131	1.892	0.024
d > 2.5	2579	121	21.3	0.016	0.0383	0.0123	1.836	0.02
d > 2	4882	226	21.6	0.014	0.0366	0.0121	1.797	0.018
d > 1.5	11964	549	21.8	0.0123	0.035	0.0119	1.66	0.015
d > 1	39636	1836	21.6	0.0136	0.0339	0.0148	1.564	0.017
d > 0.75	84593	4346	19.5	0.0166	0.0337	0.0177	1.391	0.02
d > 0.5	144502	13615	10.6	0.0203	0.0338	0.0197	1.232	0.031
d > 0.4	183602	23751	7.7	0.0226	0.0338	0.0206	1.17	0.039
d > 0.35	189348	25805	7.3	0.0228	0.0338	0.0208	1.165	0.04
d > 0	0	0	0	0	0	0	0	0

Distribution of measured and missing reflections in cumulative fixed resolution subsets [s = sin(theta)/lambda , d = 1/(2*s) ; s .le. s_max , d .ge. d_min]

	n_hkl measured	n_hkl missing	percent completeness
d > 10	1	0	100
d > 8	1	0	100
d > 6	10	0	100
d > 4	29	0	100
d > 3.5	43	0	100
d > 3	70	0	100
d > 2.5	121	0	100
d > 2	226	0	100

d > 1.5	549	0	100
d > 1	1836	0	100
d > 0.75	4346	5	99.9
d > 0.5	13615	1156	92.2
d > 0.4	23751	5356	81.6
d > 0.35	25805	6451	80
d > 0	0	0	0