Engineering Short, Strong Hydrogen Bonds in Urea Di-carboxylic Acid Complexes

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Supporting Information

Section 1. Crystallographic Data Tables

Compound	**2:1 Urea : Succinic acid**					
Diffractometer	Rigaku R-AXIS RAPID	VIVALDI	Rigaku R-AXIS RAPID	VIVALDI	Rigaku R-AXIS RAPID	VIVALDI
Radiation	X-ray	Neutron	X-ray	Neutron	X-ray	Neutron
Formula	$C_6H_{14}N_4O_6$	$C_6H_{14}N_4O_6$	$C_6H_{14}N_4O_6$	$C_6H_{14}N_4O_6$	$C_6H_{14}N_4O_6$	$C_6H_{14}N_4O_6$
Molecular weight (g mol^{-1})	238.21	238.21	238.21	238.21	238.21	238.21
T (K)	100	100	200	200	300	300
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
***a* (Å)**	5.7109(7)	5.71	5.6706(5)	5.67	5.6366(6)	5.64
***b* (Å)**	7.9698(11)	7.97	8.1227(7)	8.12	8.2568(10)	8.26
***c* (Å)**	12.1580(15)	12.16	12.2182(10)	12.22	12.2790(13)	12.28
***β* (°)**	96.160(4)	96.16	96.375(3)	96.38	96.659(4)	96.66
Volume (Å^3)	550.17(12)	550.19	559.30(8)	559.13	567.61(11)	568.22
Z	2	2	2	2	2	2
Reflections collected	7014	7869	7340	4829	7067	8028
Independent	1255	1403	1280	826	1293	1049
Observed > 2σ(I)	1085	1087	1065	659	812	791
R_{int}	0.023	-	0.017	-	0.026	-
Parameters	101	137	101	137	101	137
GooF	1.07	1.26	1.09	1.24	1.14	1.37
R_1 (observed)	0.0299	0.0453	0.0315	0.0355	0.0351	0.0423
R_1 (all)	0.0350	0.0734	0.0382	0.0565	0.0621	0.0678
wR_2 (all)	0.0830	0.0800	0.0896	0.0691	0.1074	0.0787
Δρ (max, min) / e$^-$/Å^3 or fm/Å^3	0.30, -0.18	0.65, -0.58	0.23, -0.15	0.41, -0.41	0.14, -0.18	0.39, -0.29

Table S1 Summary of crystallographic data for **US**. No errors are quoted for the neutron data as the unit cell parameters were not refined in the data reduction and taken to be the same as those determined by X-ray diffraction.

Compound	2:1 Urea : Fumaric acid						
Diffractometer	SXD	Rigaku R-AXIS RAPID	SXD	Rigaku R-AXIS RAPID	SXD	Rigaku R-AXIS RAPID	SXD
Radiation	Neutron	X-ray	Neutron	X-ray	Neutron	X-ray	Neutron
Formula	$C_6H_{12}N_4O_6$	$C_6H_{12}N_4O_6$	$C_6H_{12}N_4O_6$	$C_6H_{12}N_4O_6$	$C_6H_{12}N_4O_6$	$C_6H_{12}N_4O_6$	$C_6H_{12}N_4O_6$
Molecular weight (g mol^{-1})	236.18	236.18	236.18	236.18	236.18	236.18	236.18
T (K)	30	100	100	200	200	300	300
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
***a* (Å)**	5.7976(10)	5.764(5)	5.766(2)	5.671(5)	5.676(2)	5.541(5)	5.549(2)
***b* (Å)**	7.5666(10)	7.640(5)	7.666(3)	7.888(5)	7.912(3)	8.214(5)	8.239(3)
***c* (Å)**	12.351(3)	12.283(5)	12.332(5)	12.348(5)	12.366(5)	12.427(5)	12.445(4)
***β* (°)**	97.03(3)	96.901(5)	96.81(3)	96.719(5)	96.66(3)	97.314(5)	97.24(3)
Volume (Å^3)	537.7	537.0(6)	541.2	548.6(6)	551.6	561.0(7)	564.5
Z	2	2	2	2	2	2	2
Reflections collected	5451	6806	3581	7039	3023	7119	2053
Independent	5451	1230	3581	1253	3023	1285	2053
Observed > 2σ(I)	5451	1024	3581	923	3023	1024	2053
R_{int}	-	0.040	-	0.024	-	0.031	-
Parameters	204	97	182	97	193	97	193
GooF	1.12	1.04	1.05	1.13	1.09	1.20	1.10
R_1 (observed)	0.0499	0.0350	0.0552	0.0328	0.0558	0.0577	0.0566
R_1 (all)	0.0499	0.0442	0.0552	0.0481	0.0558	0.0768	0.0566
wR_2 (all)	0.1261	0.0832	0.1144	0.0951	0.1248	0.1114	0.1301
Δρ (max, min) / e$^-$/Å^3 or fm/Å^3	1.73, -1.50	0.25, -0.22	0.91, -0.90	0.17, -0.19	0.61, -0.73	0.15, -0.12	0.42, -0.37

Table S2 Summary of crystallographic data for **UF**.

Compound	**2:1 *N*-Methylurea : Succinic acid**						
Diffractometer	VIVALDI	Rigaku R-AXIS RAPID	VIVALDI	Rigaku R-AXIS RAPID	VIVALDI	Rigaku R-AXIS RAPID	VIVALDI
Radiation	Neutron	X-ray	Neutron	X-ray	Neutron	X-ray	Neutron
Formula	$C_8H_{18}N_4O_6$	$C_8H_{18}N_4O_6$	$C_8H_{18}N_4O_6$	$C_8H_{18}N_4O_6$	$C_8H_{18}N_4O_6$	$C_8H_{18}N_4O_6$	$C_8H_{18}N_4O_6$
Molecular weight (g mol^{-1})	266.26	266.26	266.26	266.26	266.26	266.26	266.26
T (K)	20	100	100	200	200	300	300
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
***a* (Å)**	7.89	8.0244(12)	8.02	8.2868(7)	8.29	8.5398(8)	8.54
***b* (Å)**	5.79	5.7496(7)	5.75	5.6618(3)	5.66	5.5798(4)	5.58
***c* (Å)**	13.65	13.735(2)	13.74	13.7761(11)	13.78	13.838(2)	13.84
***β* (°)**	91.22	91.426(5)	91.43	91.799(4)	91.80	92.921(4)	92.92
Volume (Å^3)	623.4	633.5(2)	633.4	646.03(8)	646.3	658.84(11)	658.7
Z	2	2	2	2	2	2	2
Reflections collected	13957	8408	11410	8559	9049	8658	5368
Independent	2522	1457	1856	1480	1400	1501	893
Observed > 2σ(I)	1945	1304	1410	1147	994	851	636
R_{int}	-	0.023	-	0.018	-	0.038	-
Parameters	163	118	163	118	163	118	163
GooF	1.34	1.09	1.44	1.12	1.47	1.16	1.38
R_1 (observed)	0.0538	0.0334	0.0497	0.0353	0.0530	0.0432	0.0441
R_1 (all)	0.0896	0.0371	0.0800	0.0455	0.0906	0.0773	0.0814
wR_2 (all)	0.0860	0.0918	0.0920	0.1077	0.0983	0.1464	0.0852
Δρ (max, min) / e$^-$/Å^3 or fm/Å^3	0.12,-0.11	0.34, -0.17	0.08,-0.13	0.19, -0.14	0.06,-0.08	0.17,-0.17	0.04,-0.04

Table S3 Summary of crystallographic data for **MUS**. No errors are quoted for the neutron data as the unit cell parameters were not refined in the data reduction and taken to be the same as those determined by X-ray diffraction.

Compound	**2:1 *N*-Methylurea : Fumaric acid**		
Diffractometer	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID
Formula	$C_8H_{16}N_4O_6$	$C_8H_{16}N_4O_6$	$C_8H_{16}N_4O_6$
Molecular weight (g mol^{-1})	264.25	264.25	264.25
T (K)	100	200	300
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
***a* (Å)**	8.3188(10)	8.5509(16)	8.7741(14)
***b* (Å)**	5.6497(5)	5.5691(8)	5.4413(7)
***c* (Å)**	13.8382(13)	13.909(2)	13.930(2)
***β* (°)**	104.156(4)	102.959(7)	100.730(6)
Volume (Å^3)	630.63(11)	645.5(2)	653.44(16)
Z	2	2	2
Reflections collected	8243	8540	8681
Independent	1449	1475	1494
Observed > 2σ(I)	1172	1002	865
R_{int}	0.033	0.043	0.047
Parameters	114	114	115
GooF	1.07	1.07	1.03
R_1 (observed)	0.0327	0.0398	0.0487
R_1 (all)	0.0435	0.0656	0.0949
wR_2 (all)	0.0804	0.1043	0.1168
Δρ (max, min) / e$^-$/Å^3	0.19, -0.17	0.17, -0.15	0.14, -0.12

Table S4 Summary of crystallographic data for **MUF**.

Compound	**2:1 *N*-Methylurea : Oxalic acid**	
Diffractometer	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID
Formula	$C_6H_{14}N_4O_6$	$C_6H_{14}N_4O_6$
Molecular weight (g mol^{-1})	238.21	238.21
T (K)	200	300
Space group	$P2_1/c$	$P2_1/c$
***a* (Å)**	5.1081(8)	5.1464(14)
***b* (Å)**	10.5388(14)	10.555(2)
***c* (Å)**	10.2233(14)	10.313(3)
***β* (°)**	102.717(7)	101.835(13)
Volume (Å^3)	536.85(13)	548.3(2)
Z	2	2
Reflections collected	7002	13815
Independent	1233	1255
Observed > 2σ(I)	816	880
R_{int}	0.034	0.049
Parameters	102	102
GooF	1.17	1.06
R_1 (observed)	0.0432	0.0508
R_1 (all)	0.0696	0.0790
wR_2 (all)	0.1261	0.1231
Δρ (max, min) / e$^-$/Å^3	0.23, -0.24	0.21, -0.16

Table S5 Summary of crystallographic data for **MUOX**.

Compound	**2:1 *N,N*-Dimethylurea : Succinic acid**				
Diffractometer	VIVALDI	VIVALDI	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID
Radiation	Neutron	Neutron	X-ray	X-ray	X-ray
Formula	$C_{10}H_{22}N_4O_6$	$C_{10}H_{22}N_4O_6$	$C_{10}H_{22}N_4O_6$	$C_{10}H_{22}N_4O_6$	$C_{10}H_{22}N_4O_6$
Molecular weight (g mol^{-1})	294.32	294.32	294.32	294.32	294.32
T (K)	20	50	100	200	300
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
***a* (Å)**	8.35	8.40	8.483(3)	8.6629(12)	8.797(2)
***b* (Å)**	5.44	5.47	5.5169(14)	5.6284(6)	5.6934(13)
***c* (Å)**	15.43	15.47	15.415(5)	15.152(2)	15.059(4)
***β* (°)**	101.95	101.95	101.677(8)	100.948(4)	100.764(7)
Volume (Å^3)	685.7	695.4	706.5(4)	725.34(16)	741.0(3)
Z	2	2	2	2	2
Reflections collected	15220	9617	9079	9619	9568
Independent	3055	2549	1611	1664	1700
Observed > 2σ(I)	2334	1931	1468	1468	1410
R_{int}	-	-	0.025	0.017	0.020
Parameters	190	190	135	135	135
GooF	1.28	1.22	1.09	1.08	1.07
R_1 (observed)	0.0502	0.0473	0.0308	0.0373	0.0472
R_1 (all)	0.0871	0.0800	0.0330	0.0408	0.0534
wR_2 (all)	0.0838	0.0838	0.0900	0.1113	0.1435
Δρ (max, min) / e$^-$/Å^3 or fm/Å^3	0.13, -0.13	0.11, -0.10	0.25, -0.19	0.18, -0.19	0.18, -0.19

Table S6 Summary of crystallographic data for **DMUS**. No errors are quoted for the neutron data as the unit cell parameters were not refined in the data reduction and taken to be the same as those determined by X-ray diffraction.

Compound	**2:1 *N,N*-Dimethylurea : Fumaric acid**		
Diffractometer	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID
Formula	$C_{10}H_{20}N_4O_6$	$C_{10}H_{20}N_4O_6$	$C_{10}H_{20}N_4O_6$
Molecular weight (g mol^{-1})	292.3	292.3	292.3
T (K)	100	200	300
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
***a* (Å)**	5.8025(8)	5.8640(5)	5.924(4)
***b* (Å)**	18.158(2)	18.2369(11)	18.376(9)
***c* (Å)**	6.8184(8)	6.8458(4)	6.873(5)
***β* (°)**	101.019(4)	101.330(3)	101.293(5)
Volume (Å^3)	705.15(15)	717.83(9)	733.7(8)
Z	2	2	2
Reflections collected	9285	9445	9713
Independent	1620	1645	1674
Observed > 2σ(I)	1286	1317	1029
R_{int}	0.035	0.021	0.025
Parameters	131	131	131
GooF	1.13	1.08	1.08
R_1 (observed)	0.0417	0.0397	0.0507
R_1 (all)	0.0525	0.0485	0.0802
wR_2 (all)	0.1251	0.1196	0.1693
Δρ (max, min) / e$^-$/Å^3	0.23, -0.22	0.21, -0.14	0.18, -0.17

Table S7 Summary of crystallographic data for **DMUF.**

Section 2. Short, Strong Hydrogen Bond Lengths

Complex	T/K	r(O-H) / Å		r(H···O) / Å		r(O-H···O) / Å	
		X-ray	Neutron	X-ray	Neutron	X-ray	Neutron
US	**100**	0.99(2)	1.041(3)	1.54(2)	1.484(3)	2.5149(10)	2.512(2)
	200	0.99(2)	1.050(4)	1.54(2)	1.481(4)	2.5211(11)	2.520(2)
	300	1.02(3)	1.039(5)	1.52(3)	1.500(4)	2.5298(15)	2.527(3)
UF	**30**	-	1.072(2)	-	1.437(2)	-	2.4983(14)
	100	1.01(2)	1.067(3)	1.49(2)	1.438(2)	2.496(2)	2.494(2)
	200	1.03(2)	1.065(3)	1.48(2)	1.443(3)	2.495(2)	2.498(2)
	300	0.99(3)	1.063(5)	1.52(3)	1.448(5)	2.498(2)	2.501(3)
MUS	**20**	-	1.034(2)	-	1.513(2)	-	2.536(2)
	100	0.92(2)	1.030(2)	1.62(2)	1.521(3)	2.5340(11)	2.540(2)
	200	0.93(3)	1.038(4)	1.64(3)	1.519(4)	2.5488(12)	2.546(3)
	300	0.98(4)	1.019(6)	1.59(4)	1.531(5)	2.553(2)	2.540(4)
MUF	**100**	1.02(2)	-	1.53(2)	-	2.5291(12)	-
	200	1.04(2)	-	1.52(2)	-	2.5333(14)	-
	300	1.07(3)	-	1.48(3)	-	2.536(2)	-
MUOX	**200**	1.06(3)	-	1.43(3)	-	2.458(2)	-
	300	1.03(3)	-	1.45(3)	-	2.461(2)	-
DMUS	**20**	-	1.031(2)	-	1.491(2)	-	2.513(2)
	50	-	1.036(2)	-	1.494(2)	-	2.521(2)
	100	0.94(2)	-	1.60(2)	-	2.5249(11)	-
	200	0.95(2)	-	1.58(2)	-	2.5174(12)	-
	300	0.97(3)	-	1.56(3)	-	2.5234(15)	-
DMUF	**100**	1.01(2)	-	1.50(2)	-	2.5000(15)	-
	200	1.01(2)	-	1.50(2)	-	2.4996(14)	-
	300	1.08(4)	-	1.45(4)	-	2.501(2)	-

Table S8 Lengths of the short, strong O-H···O hydrogen bonds within the U-A-U units at all measured temperatures. Considering the difficulty in locating hydrogen atoms from X-ray techniques, the data show a remarkable agreement of the refined hydrogen atom positions between the X-ray and neutron data sets. The differences between the X-ray and neutron determined values can be attributed to the X-ray data showing the average position of hydrogen electron density (drawn closer to the donor atom in the covalent bond) while the neutron data show the average position of the hydrogen atom nuclei.

Section 3. H Position Variation with Temperature

The position of the hydrogen atom contained within the short, strong O-H···O hydrogen bonds in the U-A-U units is invariant as a function of temperature. There is no evidence of proton migration within these molecular complexes in either the X-ray or neutron data (Figures S1-S4).

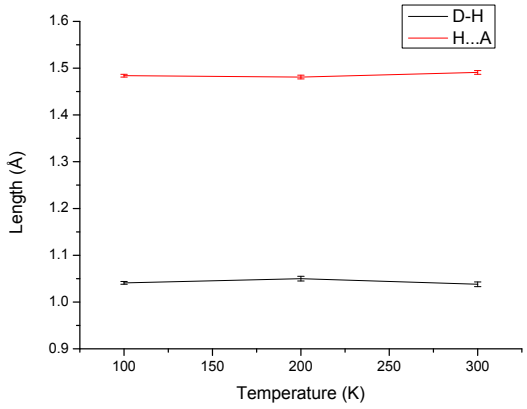

Figure S1 D-H (black) and H···A (red) lengths for the short, strong O-H···O hydrogen bond in **US**, derived from the neutron data.

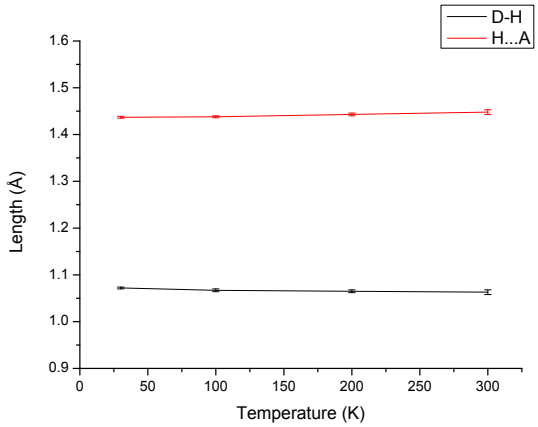

Figure S2 D-H (black) and H···A (red) lengths for the short, strong O-H···O hydrogen bond in **UF**, derived from the neutron data.

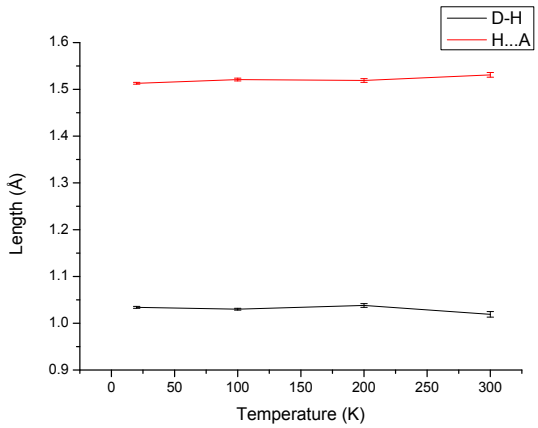

Figure S3 D-H (black) and H···A (red) lengths for the short, strong O-H···O hydrogen bond in **MUS**, derived from the neutron data.

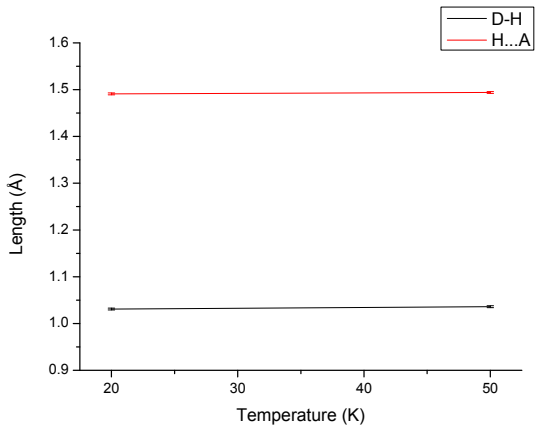

Figure S4 D-H (black) and H···A (red) lengths for the short, strong O-H···O hydrogen bond in **DMUS**, derived from the neutron data.

Section 4. Fourier Difference Maps

Fourier difference maps showing the electronic (derived from the X-ray data) and the nuclear density (derived from the neutron data) associated with the hydrogen atoms located in the short, strong O-H···O hydrogen bonds within the U-A-U units of the seven complexes show a single, well-defined position for the hydrogen atoms at all temperatures (Figure S5 – S9). The maps are generated with the hydrogen atom of interest removed from the structural model so that the peak or trough in the electronic or nuclear density map (from the X-ray and neutron data, respectively) is the density associated with the hydrogen atom removed from the model. The maps show that only in a few cases is the electron density associated with the hydrogen atom smeared out across the hydrogen bond (X-ray data). This smearing out can be indicative of proton migration but this is not reflected in the neutron data. There is good agreement between the X-ray and neutron determined hydrogen atom positions.

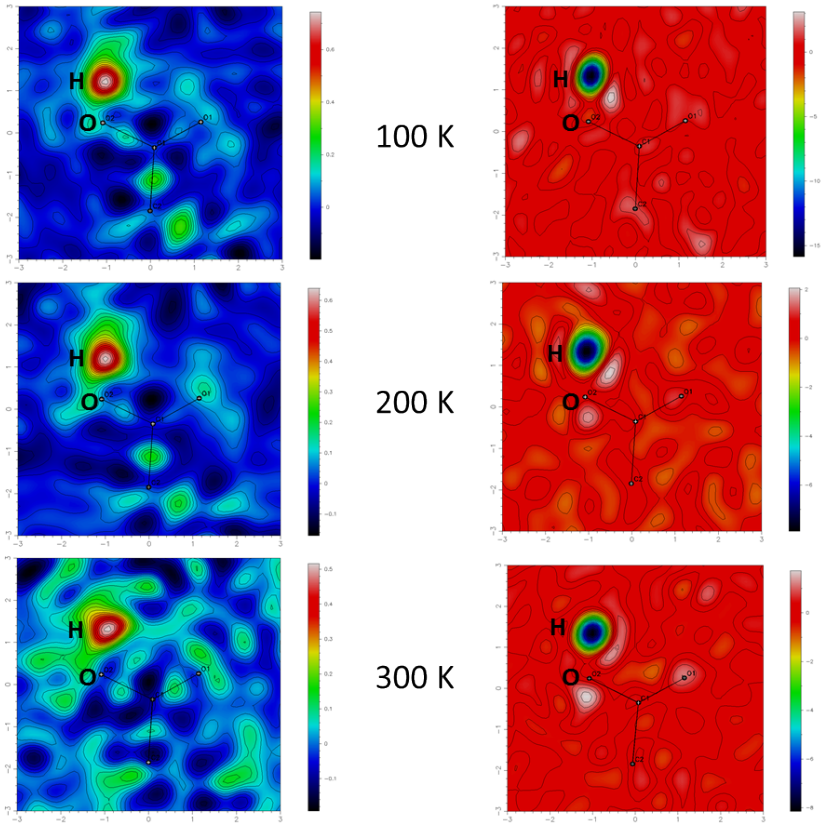

Figure S5 X-ray and neutron Fourier difference maps showing the electronic (left) and nuclear (right) density associated with the hydrogen atom in the short, strong O-H···O hydrogen bond in **US.**

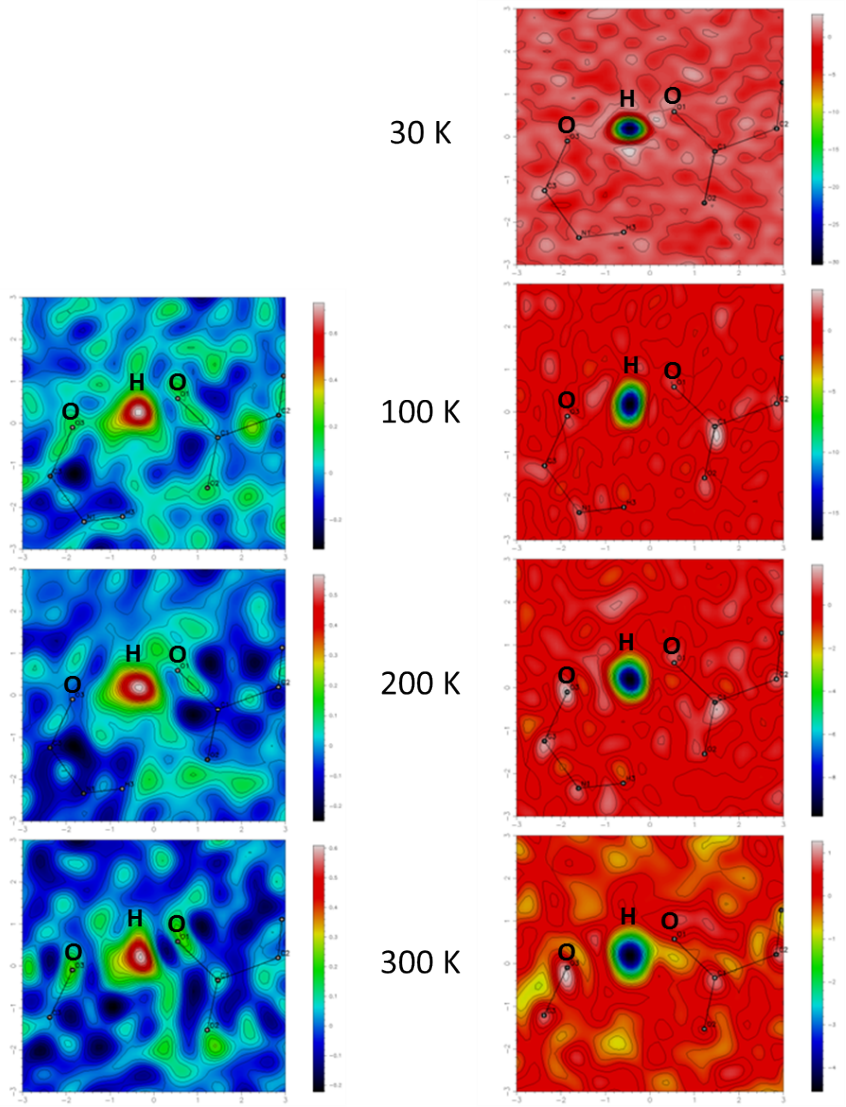

Figure S6 X-ray and neutron Fourier difference maps showing the electronic (left) and nuclear (right) density associated with the hydrogen atom in the short, strong O-H···O hydrogen bond in **UF**.

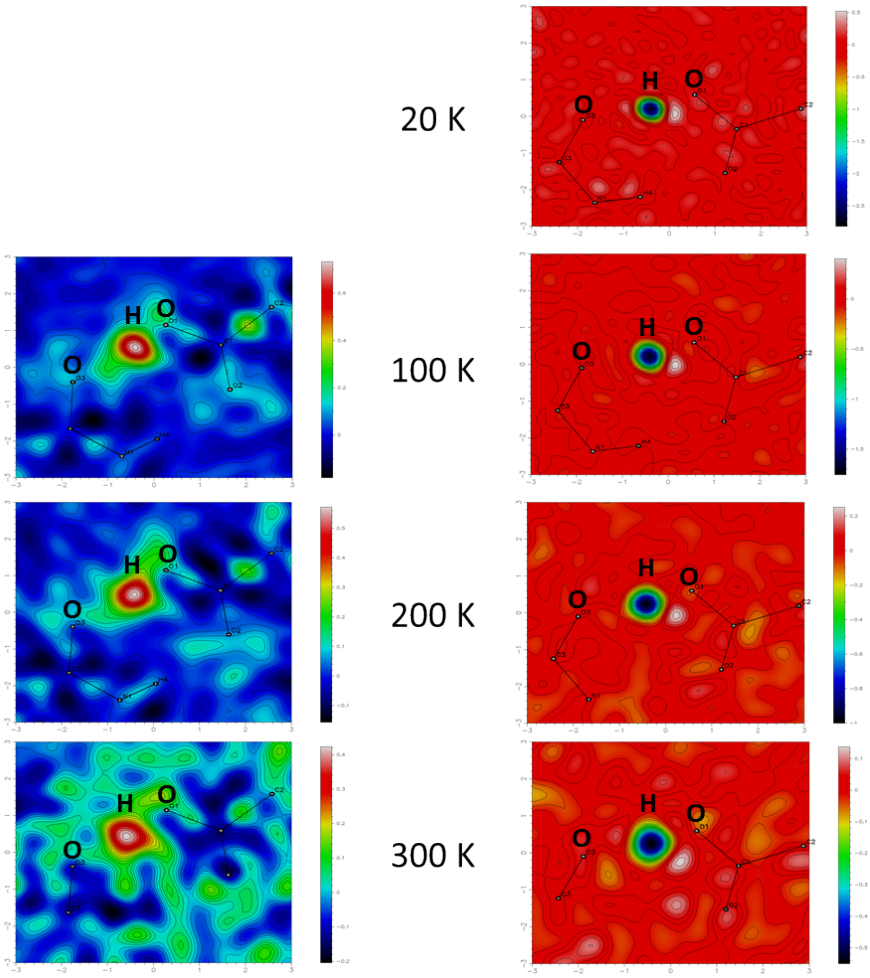

Figure S7 X-ray and neutron Fourier difference maps showing the electronic (left) and nuclear (right) density associated with the hydrogen atom in the short, strong O-H···O hydrogen bond in **MUS.**

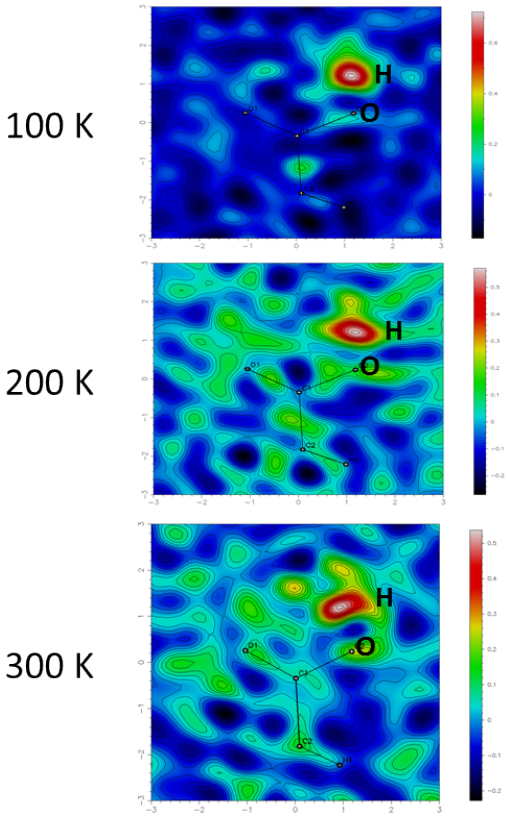

Figure S8 X-ray Fourier difference maps showing the electronic density associated with the hydrogen atom in the short, strong O-H···O hydrogen bond in **MUF**.

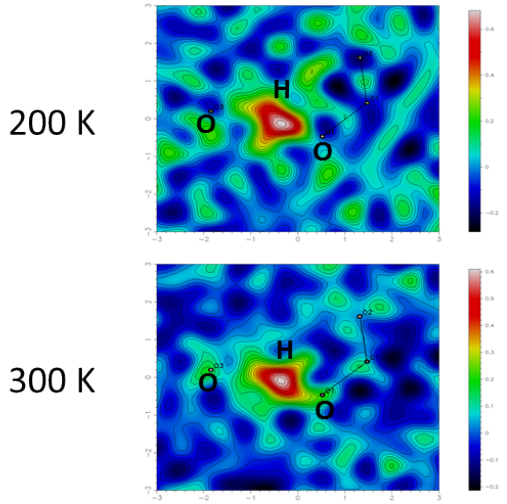

Figure S8 X-ray Fourier difference maps showing the electronic density associated with the hydrogen atom in the short, strong O-H···O hydrogen bond in **MUOX**.

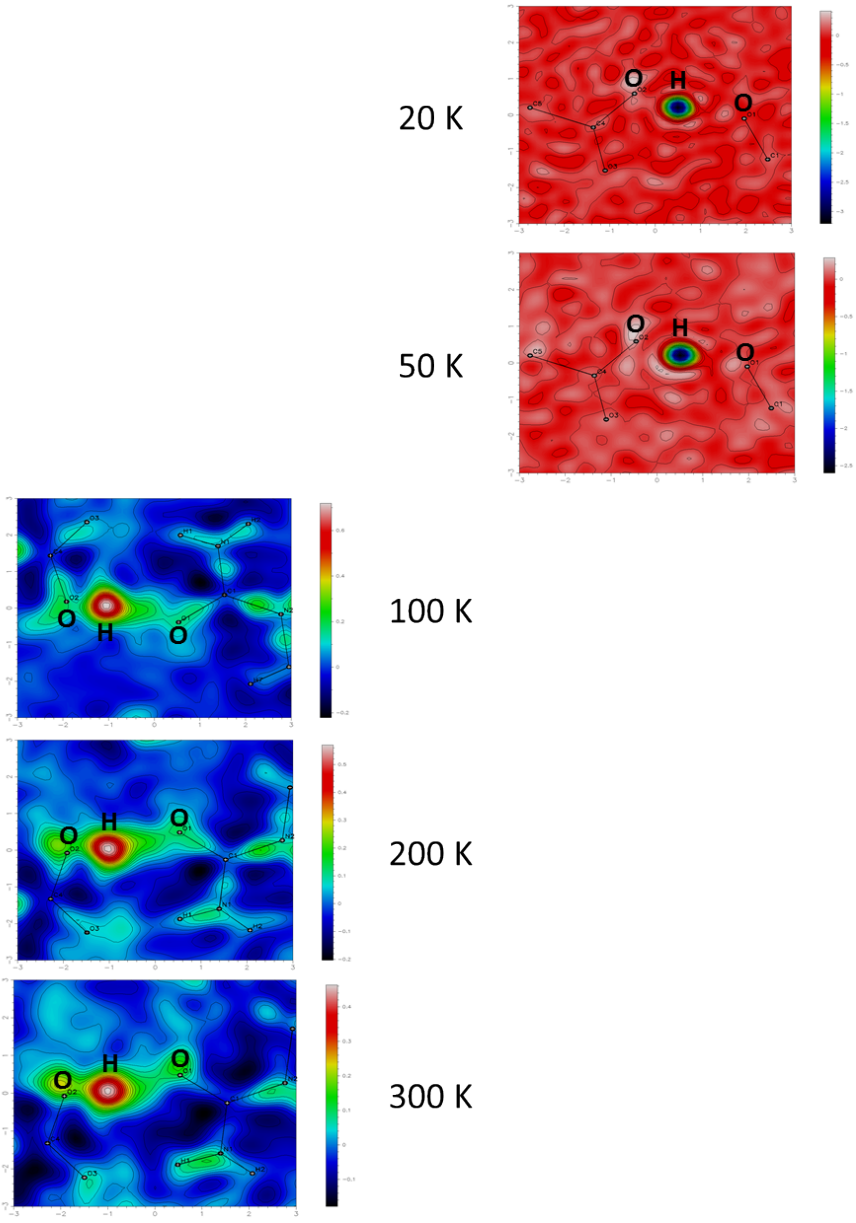

Figure S9 X-ray and neutron Fourier difference maps showing the electronic (left) and nuclear (right) density associated with the hydrogen atom in the short, strong O-H···O hydrogen bond in **DMUS**.

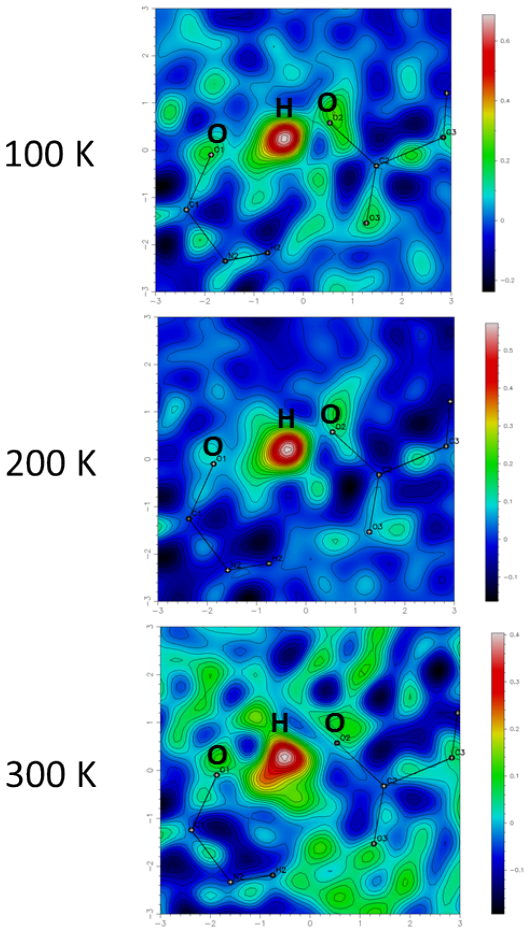

Figure S10 X-ray Fourier difference maps showing the electronic density associated with the hydrogen atom in the short, strong O-H···O hydrogen bond in **DMUF**.