Electronic Supplementary Material (ESI) for CrystEngComm

Supplementary information for

A novel hydrate of α-cyclodextrin crystallised under high-pressure conditions

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Table 1 shows a comparison between hydrogen-bond distances and angles across forms I and Ib. The same donor atoms have been considered for comparison purposes but acceptor atoms can change. Differences are marked by an arrow at the end of the corresponding row.

In line with the hydrophobic effect, the interaction energies of H bonds between included water molecules and CD are usually weaker (up to 18%) than those involving non-included molecules and this is for example reflected in longer donor-acceptor distances.[1] This fact was known for form I and it is also confirmed for form Ib. In form I at 150 K mean hydrogen-acceptor distances where the donor is a water molecule located inside the cavity are 0.22 and 0.15 Å longer than if it is located outisde. In form Ib at high pressure the equivalent mean donor-acceptor distances are 0.28 Å longer (there are not enough values to compare hydrogen-acceptor distances).

[1] H. C. Georg, K. Coutinho and S. Canuto, *Chem. Phys. Lett.*, 2005, **413**, 16-21

Table 1: Comparison between hydrogen-bond distances and angles across forms I and Ib

		form I at 150 K					Form I at 295 K[a]					form Ib at 0.65 GPa					
D	H	A	d(D-H)[b]	d(H-A)	d(D-A)	θ(D-H-A)	A	d(D-H)[c]	d(H-A)	d(D-A)	θ(D-H-A)	A	d(D-H)[b]	d(H-A)	d(D-A)	θ(D-H-A)	
O2_1	H2O_1	OW3_7#1	0.983	1.96	2.806(3)	143	OW3_7#1	1.07	1.76	2.813	166	OW3_7#1	0.983	1.88	2.77(2)	149	
												OWD_7#2	0.983	2.28	2.83(5)	114	←
O3_1	H3O_1	O6_5#2	0.983	1.62	2.597(3)	172	O6_5#2	0.98	1.67	2.606	158	O6_5#2	0.983	1.78	2.589(18)	137	
												O2_1	0.983	2.48	2.884(18)	104	←
O6A_1[d]	H6OA_1[d]	O6_3#3	0.983	1.85	2.784(3)	157	O6_3#3	1.03	1.77	2.807	177	O6_3#3	0.983	2.01	2.85(3)	142	
O6B_1[e]	HO6B_1[e]											OWD_7#3	0.983	1.99	2.79(5)	137	←
O2_2	H2O_2	OW4_7#2	0.983	1.71	2.682(3)	171	OW4_7#2	0.93	1.77	2.692	169	OW4_7#2	0.983	1.66	2.63(2)	170	
O3_2	H3O_2	O2_1	0.983	1.98	2.936(3)	163	O2_1	0.86	2.09	2.949	175	O2_1	0.983	1.91	2.853(19)	161	
O6_2	H6O_2	O3_1#4	0.983	1.83	2.782(3)	161	O3_1#4	0.91	1.89	2.785	171	O3_1#4	0.983	1.97	2.750(18)	135	
O2_3	H2O_3	OW2_7#5	0.983	1.76	2.715(3)	164	OW2_7#5	0.86	1.85	2.718	179	OW2_7#5	0.983	1.70	2.654(17)	162	
O3_3	H3O_3[f]	O2_2	0.983	2.00	2.974(3)	169	O2_2	1.09	1.93	3.016	171	O2_2	0.983	2.05	3.036(17)	177	
O6_3	H6O_3	OW4_7	0.983	1.87	2.834(3)	167	OW4_7	1.04	1.87	2.889	166	OW4_7	0.983	2.12	3.06(2)	159	
												O6_6#11	0.983	2.42	2.956(19)	114	←
O2_4	H2O_4	O4_5	0.983	2.29	2.779(3)	109	O3_5	0.91	2.85	3.367	118	O4_5	0.983	2.28	2.775(19)	110	←
												O5_4#8	0.983	2.27	3.044(15)	134	←
O3_4	H3O_4	O2_3	0.983	1.99	2.812(3)	140	O2_3	0.99	1.86	2.816	161	O2_3	0.983	1.95	2.784(16)	141	
O6_4	H6O_4	O2_2#6	0.983	1.88	2.844(3)	164	O2_2#6	0.94	1.95	2.850	160	O2_2#6	0.983	1.81	2.782(19)	169	
O2_5	H2O_5	O3_3#7	0.983	1.87	2.850(3)	172	O3_3#7	0.97	1-95	2.902	169	O3_3#7	0.983	2.18	2.869(18)	126	
O3_5	H3O_5	O6_4#8	0.983	1.74	2.697(3)	164	O6_4#8	0.96	1.77	2.716	169	O6_4#8	0.983	1.70	2.671(17)	169	
O6_5	H6O_5	OWA_7	0.983	1.84	2.749(4)	153	OWA_7	0.85	1.92	2.773	176	OWA_7	0.983	1.79	2.77(3)	173	
O2_6	H2O_6	O3_1	0.983	2.23	3.009(3)	135	O3_1	0.97	2.14	3.021	150	O3_1	0.983	1.98	2.957(18)	175	
O3_6	H3O_6	O3_4#8	0.983	1.86	2.794(3)	157	O3_4#8	0.93	1.89	2.788	163	O3_4#8	0.983	1.79	2.743(16)	163	
O6_6	H6O_6	OW1_7#9	0.983	1.93	2.861(3)	158	OW1_7#9	0.94	1.97	2.897	169	OW1_7#9	0.983	1.85	2.815(18)	165	
OW1_7	HW1_7	OW2_7	0.983	1.84	2.821(3)	176	OW2_7	1.02	1.84	2.857	176	OW2_7	0.983	2.00	2.832(19)	141	
	HW1'_7	O2_6#10	0.983	1.79	2.722(3)	157	O2_6#10	0.96	1.86	2.747	152	O6_6#11	0.983	2.27	2.815(18)	114	←
OW2_7	HW2_7	O2_5#7	0.983	1.74	2.712(3)	170	O2_5#7	0.97	1.75	2.719	174	O2_5#7	0.983	1.92	2.675(17)	132	
	HW2'_7	O3_6#7	0.983	1.79	2.761(3)	169	O3_6#7	1.03	1.75	2.773	169	O3_6#7	0.983	1.74	2.695(18)	164	
OW3_7	HW3_7	O6_3	0.983	1.87	2.820(3)	162	O6_3	0.91	1.93	2.831	171	O6_3	0.983	1.79	2.77(2)	172	
	HW3'_7	O5_6#11	0.983	1.96	2.945(3)	175	O6_6#11	1.07	2.72	3.339	117	OWD_7#12	0.983	1.74	2.71(5)	165	←
							O6B_1		2.85	3.327	107						
OW4_7	HW4_7	O6_2#12	0.983	1.88	2.819(3)	159	O6_2#12	0.87	1.98	2.840	169	O6_2#12	0.983	2.12	2.74(2)	119	
	HW4'_7	OW1_7	0.983	1.85	2.825(3)	172	OW1_7	1.01	1.87	2.867	171	OW1_7	0.983	2.14	2.99(3)	144	
OWA_7	HWA_7	O6_1	0.983	1.97	2.911(4)	160	O6_1A	1.00	1.98	2.974	173	OWD_7	0.983	2.01	2.41(5)	102	←
	HWA'_7	OWB_7	0.983	1.92	2.884(4)	166	OWB_7	0.89	2.04	2.915	167	OWB_7	0.983	1.95	2.89(3)	158	
OWB_7	HWB_7	O3_5#8	0.983	2.37	3.065(4)	127	O3_5#8	0.96	2.27	3.108	145	O3_5#8			2.95(3)		
	HWB'_7	O2_4#8	0.983	1.97	2.955(4)	175	O2_4#8	0.98	2.05	2.991	160	OWC_7#8			2.28(5)		←
OWC_7												O2_4#8			2.72(5)		←
												O4_1			2.78(5)		←
OWD_7												O3_2#6			2.80(5)		←

Symmetry codes: #1 x+1/2, -y+1/2, -z; #2 x , y , z-1; #3 x+1/2, -y+1/2, -z+1; #4 x-1/2, -y+1/2, -z; #5 -x+1/2, -y, z-1/2; #6 x, y, z+1; #7 -x+3/2, -y, z+1/2; #8 -x+3/2, -y, z-1/2; #9 x+1, y, z; #10 x-1, y, z+1; #11 x-1, y, z; #12 x-1/2, -y+1/2, -z+1.

[a] From Table 3 in Klar *et al.*, *Acta Cryst.*, 1980, **B36**, 1154–1165. [b] Position of hydrogen atoms normalized to neutron values using the program PLATON (Spek, *Acta Cryst.*, 2009, **D65**, 148–155). [c] Position of hydrogen originally determined by neutron diffraction. [d] O6_1 and H6O_1 in form I at 150 K. [e] These atoms do not exist in form I at 150 K. [f] H3OB_3 in form I at 150 K.