Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supporting Information

Structural Origin of Physicochemical Properties Differences upon Dehydration and Polymorphic Transformation of Ciprofloxacin Hydrochloride Revealed by Structure Determination from Powder X-ray Diffraction Data

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Table S1 Crystallographic data for CIP 1.43 Hydrate and AH2

Parameter	**CIP 1.43 Hydrate**	**CIP AH2**
Empirical formula	C_{17} $H_{21.86}$ Cl F N_3 $O_{4.43}$	C_{17} H_{19} Cl F N_3 O_3
Formula weight	393.56	367.80
Temperature (K)	173(2)	173(2)
Wavelength (Å)	1.54186	
Crystal system	Monoclinic	
Space group	*P* $2_1/a$	*P* $2_1/c$
a (Å)	7.02521(13)	12.4523(2)
b (Å)	19.6681(4)	6.91819(13)
c (Å)	12.9331(2)	19.4137(4)
ϑ (°)	90.7338(7)	101.2940(9)
Volume (Å^3)	1786.85(6)	1640.05(5)
Z, Z'	4, 1	
D (Mg/m^3)	1.463	1.490
Absorption coefficient (mm^{-1})	2.271	2.368
F(000)	825	768
Crystal size (mm^3)	0.115 x 0.095 x 0.062	0.152 x 0.052 x 0.031
θ range for data collection (°)	3.418 to 68.206	3.620 to 68.240
Index ranges	-8<=*h*<=8, -22<=*k*<=23, -15<=*l*<=15	-14<=*h*<=14, -8<=*k*<=8, -23<=*l*<=23
Reflections collected	20568	17887
Independent reflections	3247 [$R_{(int)}$ = 0.0302]	2980 [$R_{(int)}$ = 0.0438]
Max. and min. transmission	0.869 and 0.657	0.929 and 0.781
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3247 / 3 / 268	2980 / 0 / 239
Goodness-of-fit on F^2	1.090	1.141
Final *R* indices [*I>2sigma(I)*]	R_1 = 0.0388, wR_2 = 0.1040	R_1 = 0.0497, wR_2 = 0.1284
R indices (all data)	R_1 = 0.0413, wR_2 = 0.1068	R_1 = 0.0624, wR_2 = 0.1396
Largest diff. peak and hole (e.Å^{-3})	0.487 and -0.373	0.326 and -0.317

Table S2 Crystallographic data for CIP AH1

Empirical formula	C_{17} H_{19} Cl F N_3 O_3
Formula weight	367.80
Temperature (K)	298
Pressure (kPa)	101.3
Wavelength	1.19621 Å (synchrotron radiation)
Crystal system	Orthorhombic
Space group	*P*bca
a (Å)	18.1041(6)
b (Å)	7.3009(17)
c (Å)	26.2525(10)
Volume (Å^3)	3469.96 Å^3
Z, Z'	8, 1
D (Mg/m^3)	1.408
ϑ range for data collection (°)	1 to 70°.
Increment	0.01°
Restraints / parameters	145 / 174
R_p	0.0530
R_{wp}	0.0746
R_{exp}	0.0467
S	1.74
$(\Delta/\sigma)_{max}$	0.04

Table S3 Hydrogen bond details for CIP 1.43 Hydrate

D-H...A	***d*(D-H)**	***d*(H...A)**	***d*(D...A)**	**<(DHA)**
N1-H10...Cl1	0.91(2)	2.17(2)	3.0847(15)	175.5(18)
N1-H18...O2[1]	0.87(2)	2.57(2)	3.2023(17)	130.2(18)
N1-H18...O4	0.87(2)	2.05(2)	2.835(2)	148(2)
C11-H11...Cl1[2]	1	2.78	3.7800(16)	173.9
C12-H12B...O1[3]	0.99	2.47	3.388(2)	154
C14-H14B...F1	0.99	2.39	2.9753(19)	117.2
C15-H15A...O3[1]	0.99	2.58	3.1188(19)	113.8
C16-H16B...F1[3]	0.99	2.4	3.2395(19)	142.4
O4-H1...Cl1[4]	0.88(3)	2.29(3)	3.1721(15)	172(3)
O4-H2...O3[5]	0.86(3)	1.97(3)	2.8312(19)	179(3)
C5-H5...O3	0.95	2.47	2.8025(18)	100.2
O2-H3…O1	0.89(3)	1.68	2.5212(16)	156

Symmetry transformations used to generate equivalent atoms:

[1] *x*+1/2,-*y*+1/2,*z*-1; [2] -*x*,-*y*+1,-*z*+1;[3] *x*+1/2,-*y*+1/2,*z*; [4] *x*+1,*y*,*z*; [5] *x*+1,*y*,*z*-1

Table S4 Hydrogen bond details for CIP AH1

D-H...A	***d*(D-H)**	***d*(H...A)**	***d*(D...A)**	**<(DHA)**
N16-H32 ...Cl1[1]	0.879	2.171	2.994	155.7
N16-H33...Cl1[2]	0.879	2.412	3.198	148.9
C15-H30...O2[3]	0.961	2.545	3.453	157.5
C23-H42…Cl1[4]	0.961	*2.873*	*3.311*	108.8
C18-H37…Cl1[5]	0.959	*2.778*	*3.566*	139.9

Symmetry transformations used to generate equivalent atoms:

[1] -1+*x*,*y*,*z*; [2] 1-*x*,-1/2+*y*,3/2-*z*; [3] -1/2-*x*,-*y*,-1/2+*z*; [4]-1+*x*,1/2-*y*,1/2+*z*

Table S5 Hydrogen bond details for CIP AH1

D-H...A	***d*(D-H)**	***d*(H...A)**	***d*(D...A)**	**<(DHA)**
N3-H1A...Cl1[1]	0.96(3)	2.11(4)	3.069(3)	174(3)
N3- H1A...Cl1[1]	0.93(3)	2.13(4)	3.0587(1)	174(3)
O2-H3...O1	0.97(4)	1.57(4)	2.509(2)	161(3)
C12-H12A...O1[2]	0.99	2.47	3.324(3)	143.8
C14-H14A...F1	0.99	2.19	2.868(3)	124.6
C9-H9...O3	0.95	2.52	2.833(3)	99.5
C14-H14B...O3[3]	0.99	2.57	3.079(3)	111.8

Symmetry transformations used to generate equivalent atoms:

[1] *x*,-*y*+1/2,*z*-1/2; [2] *x*,-*y*+3/2,*z*-1/2; [3] *x*+1,*y*,*z*

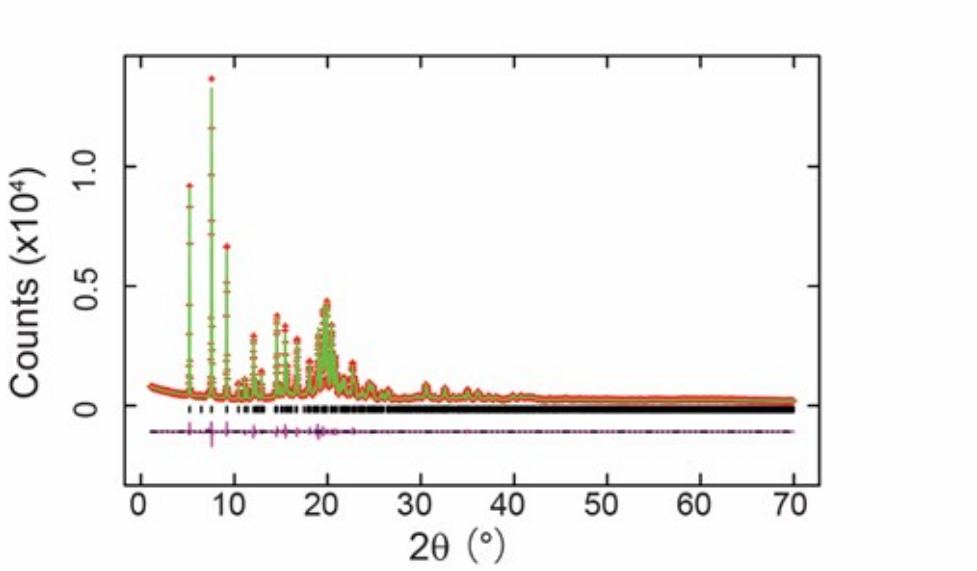

Fig S1. Le Bail fitting of CIP AH1. The experimental powder X-ray diffraction data (red + marks), calculated powder X-ray diffraction pattern (green solid line) and difference profile (magenta line) are shown. The peak positions are indicated by black magenta tick marks.