SUPPORTING INFORMATION

Experimental Section

Single crystals of nicotinamide cocrystal with salicylic acid and salt with oxalic acid were grown using 1:1 stoichiometric ratio of the corresponding coformers in methanol solvent at room temperature by slow evaporation technique. High resolution X-ray data sets up to $(\sin\theta/\lambda)_{max}$ =1.08Å^{-1} with 100% completeness and good redundancy were collected on a Bruker Kappa Apex II CCD diffractometer with MoKα radiation at 100K (Oxford Cryosystems N_2 open flow cryostat). Integration and data reduction was carried out using SAINTPLUS [25] program. The absorption correction, sorting, scaling and merging were carried out by SORTAV.[26] The structures were solved by direct methods using SHELXS97[21] and refined in the spherical atom approximation (based on F^2) by using SHELXL97[21] using the WinGX package.[27] Charge density analysis and refinements were carried out using the XD package.[23] The scattering factors were obtained from wave function models using values from Su, Coppen and Macchi (SCM) data bank[28] and the multipolar ρ(r) model was expanded up to octupolar level for non hydrogen atoms and only bond directed dipole (d_z) and quadrupole (q_{3z^2-1}) components were allowed to refine for hydrogen atoms. Atomic displacement parameters for hydrogen atoms were obtained by SHADE2 approach.[13] The module XDPROP was used to obtain the quantitative picture of the electronic structure.

Theoretical calculations

Single point periodic quantum calculations were carried out using *CRYSTAL06*[20] based on the experimentally determined starting geometries. The optimizations were performed

using density functional theory (DFT) method using the B3LYP/6-31G** level of theory. This basis set provides more reliable and consistent results in studying the intermolecular interactions.[29] The shrinking factors (IS1, IS2 and IS3) along with the reciprocal lattice vectors were set to 4 (30 K-points in irreducible Brillouin zone). The truncation parameters, which control the accuracy of the calculation of the bielectronic Coulomb and exchange series were set as ITOL1 = ITOL2 = ITOL3 = ITOL4 = 8 and ITOL5 = 17. The level shifter was set to 0.7 hartree for better convergence. Upon convergence on energy (~10^{-6}), the periodic wave functions based on optimized geometries were obtained and the option XFAC was used to generate the theoretical structure factors at the same resolutions as observed from the experiments. The atomic positions were held fixed to the values obtained from the geometry optimization during the multipolar refinement with theoretical structure factors. The thermal displacement parameters were set to zero to consider a static model and the same multipoles as refined in experiment were allowed to refine for all atoms to compare the obtained results with experimental structure factors.

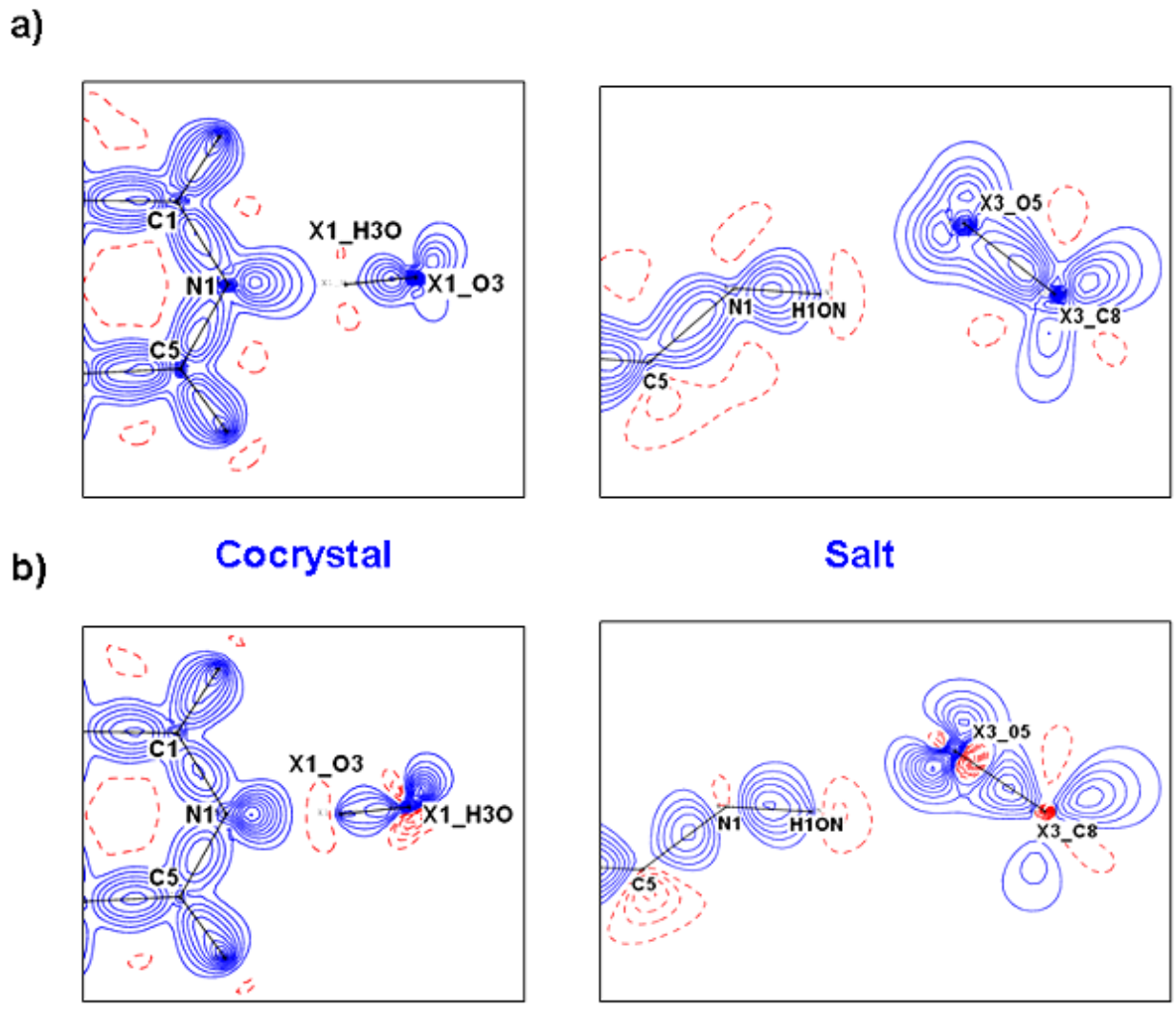
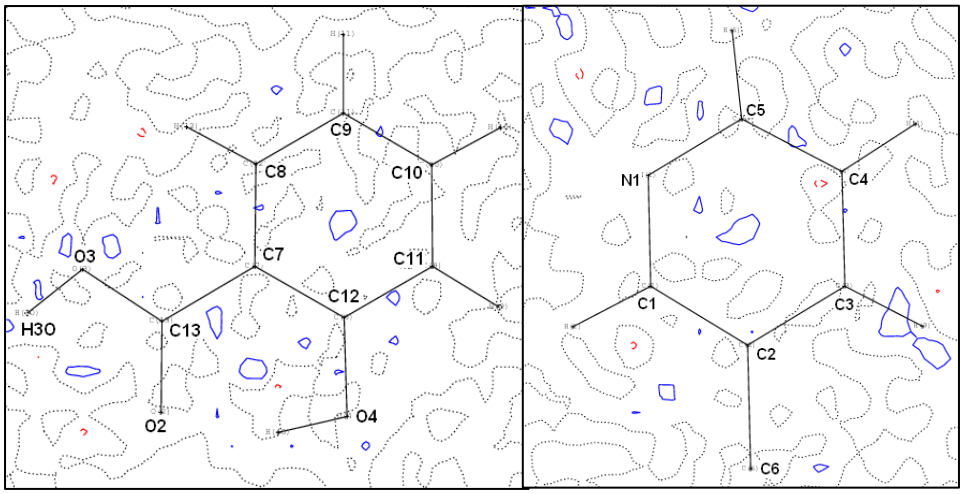


Figure S1. a) Static deformation density maps from the experimental charge density analysis depicting the proton transfer region in a cocrystal and a salt. b) Static deformation density maps from the theoretical charge density analysis for the corresponding regions. Solid blue lines indicate positive contours and dashed red lines negative contours. The contour intervals are at ±0.10 eÅ^{-3}. In the figure, X1 and X3 represent symmetry codes x, y-1, z and –x+1, -y+1, z respectively.

In the following figures (a) refers to experimental and (b) to theoretical charge density analysis of nicotinamide and salicylic acid cocrystal

(a)



(b)

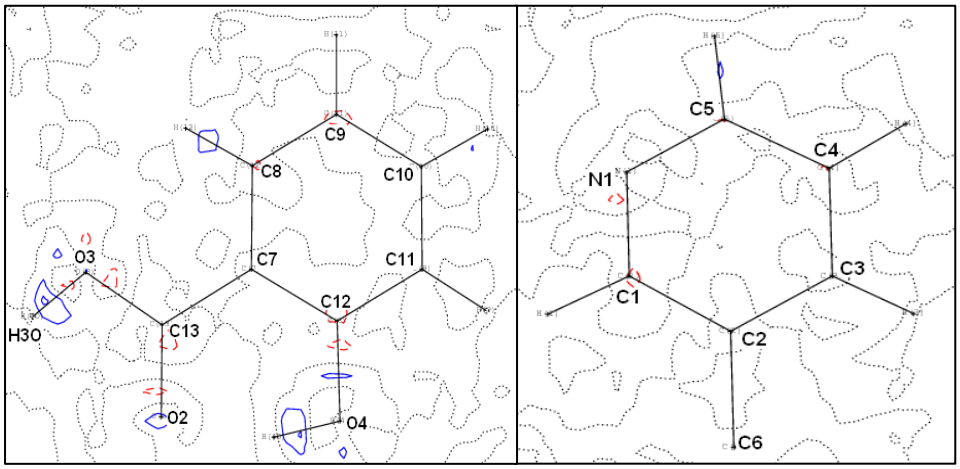
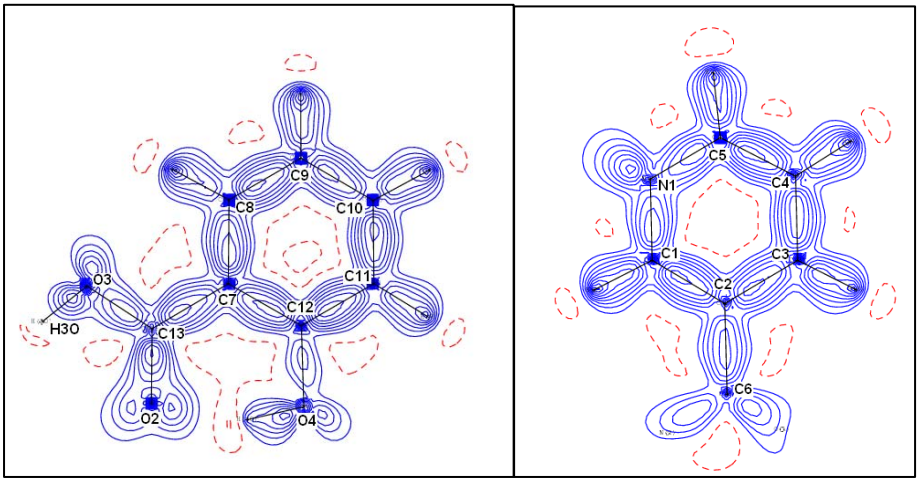


Figure S2. Residual electron density in the molecular plane defined by C7, C9 and C11 and C1, C3 and C5 for salicylic acid (left) and nicotinamide (right) respectively. Solid blue lines indicate positive contours, dashed red lines negative contours and dotted black lines zero contours. The contour intervals are at ±0.10 eÅ^{-3}.

(a)



(b)

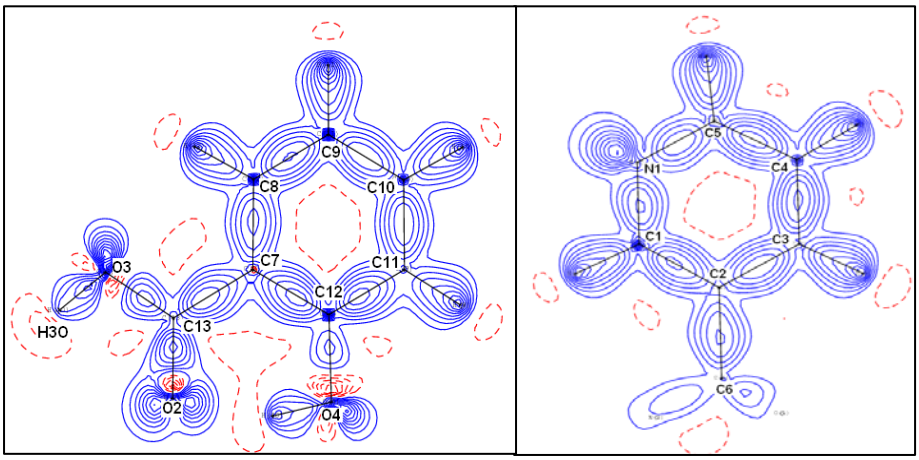
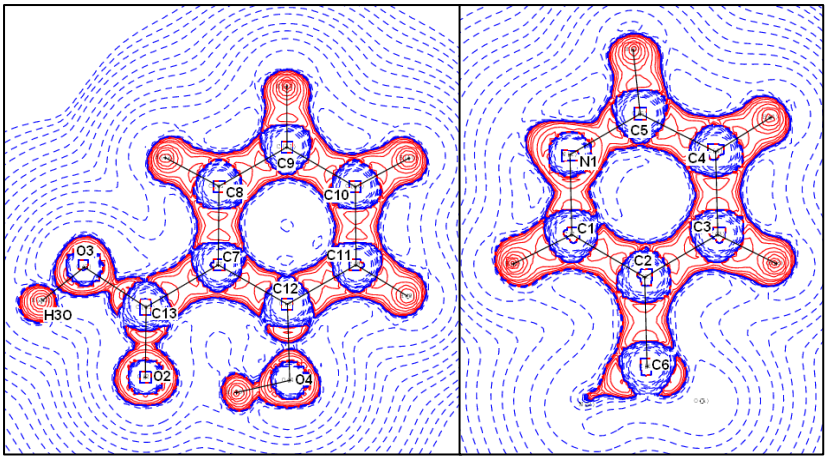


Figure S3. Static deformation density map in molecular planes defined by C7, C9 and C11 and C1, C3 and C5 for salicylic acid (left) and nicotinamide (right) respectively. Solid lines indicate positive contours, dashed lines negative contours. The contour intervals are at ±0.10 eÅ^{-3}.

(a)



(b)

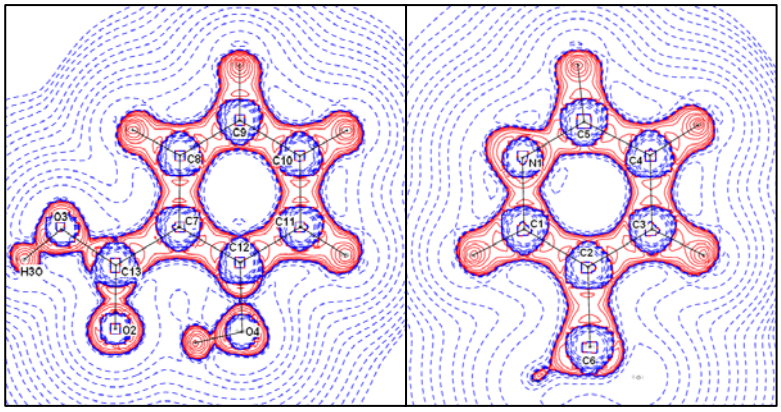
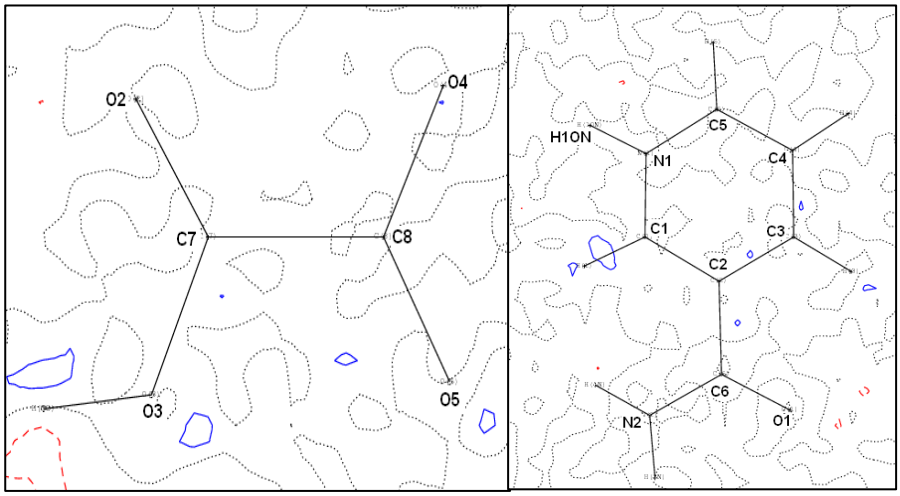


Figure S4. Laplacian distribution map in molecular planes defined by C7, C9 and C11 and C1, C3 and C5 for salicylic acid (left) and nicotinamide (right) respectively. Contours are drawn at logarithmic intervals in $\nabla^2\rho_b$, eÅ^{-5}. Blue lines indicate positive contours and red lines indicate negative contours.

In the following figures (a) refers to experimental and (b) to theoretical charge density analysis of nicotinamide and oxalic acid salt

(a)



(b)

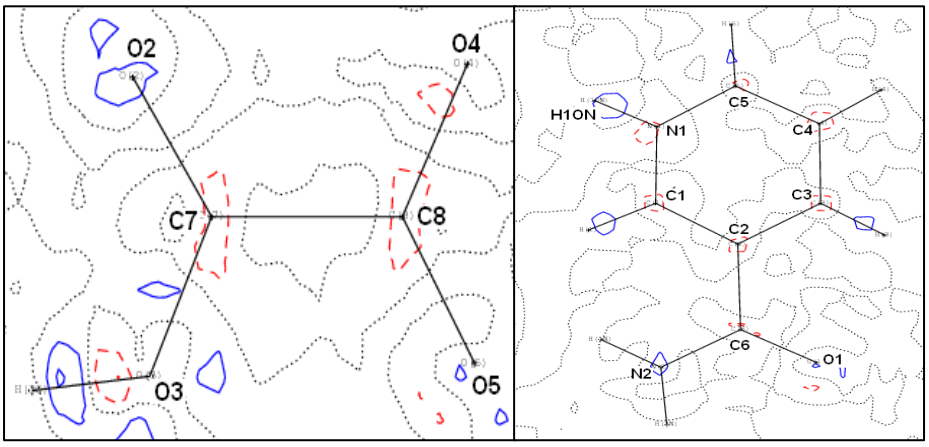
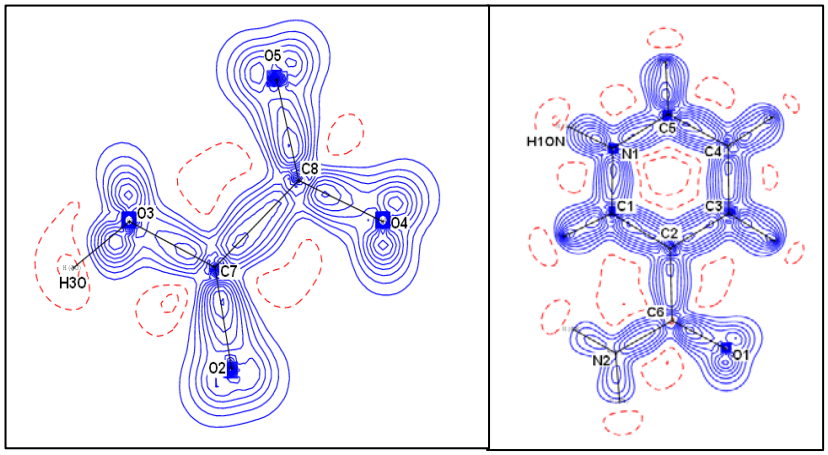


Figure S5. Residual electron density in the molecular plane defined by C7, C8 and O2 and C1, C3 and C5 for oxalic acid (left) and nicotinamide (right) respectively. Solid blue lines indicate positive contours, dashed red lines negative contours and dotted black lines zero contours. The contour intervals are at ±0.10 eÅ^{-3}.

a)



(b)

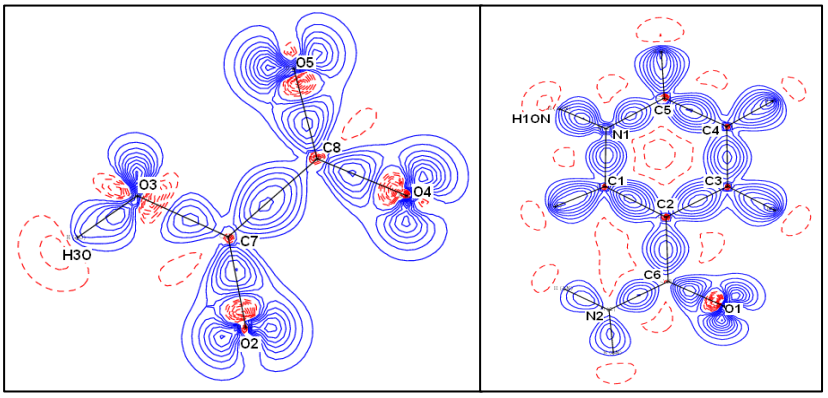
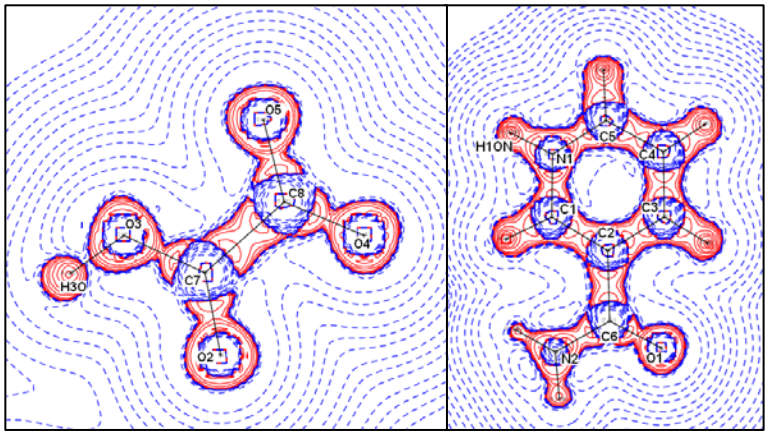


Figure S6. Static deformation density map in molecular planes defined by C7, C8 and O2 and C1, C3 and C5 for oxalic acid (left) and nicotinamide (right) respectively. Solid lines indicate positive contours, dashed lines negative contours. The contour intervals are at ±0.10 eÅ^{-3}.

(a)



(b)

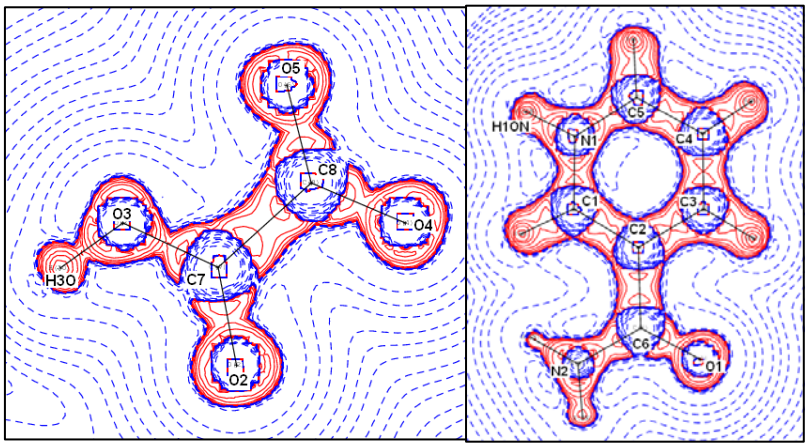


Figure S7. Laplacian distribution map in molecular planes defined by C7, C8 and O2 and C1, C3 and C5 for oxalic acid (left) and nicotinamide (right) respectively. Contours are drawn at logarithmic intervals in $\nabla^2\rho_b$, eÅ^{-5}. Blue lines indicate positive contours and red lines indicate negative contours.

Table S1. Crystallographic and experimental details

Compound	**Cocrystal**	**salt**
Formula	$C_6H_6N_2O.C_7H_6O_3$	$(C_6H_7N_2O)^+.(C_2HO_4)^-$
Formula weight	260.25	212.16
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	11.0518(4)	13.1212(8)
b (Å)	4.9428(2)	6.1094(4)
c (Å)	22.8108(9)	11.1874(9)
β (º)	97.485(2)	105.826(4)
Volume ($Å^3$), Z	1235.46(8), 4	862.82(10), 4
Calculated density	1.399	1.633
F(000)	544	440
Absorption coefficient (mm^{-1})	0.106	0.138
T (K)	100(2)	100(2)
λ (Å)	0.71073	0.71073
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	1.08	1.08
Number of collected reflections	146769	119531
Symmetry independent reflections	13034	9068
Completeness	100 %	99.6 %
Redundancy after integration	11.26	13.18
R_{int}	0.0414	0.0443
Spherical atom refinement		
$R(F^2)$	0.0467	0.0361
$wR(F^2)$	0.1299	0.1027
GoF	1.024	1.075
Multipole refinement		

Total number of parameters	352	274
R(F), R(F^2)	0.025, 0.034	0.018, 0.023
w R(F^2)	0.040	0.032
GoF	1.379	1.361
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e$Å^{-3}$)	-0.136, 0.167	-0.133, 0.141
CCDC Number	CCDC-767113	CCDC-767114

Table S2. Topological properties of hydrogen bonds at BCP in a cocrystal and a salt molecular complexes. The values from periodic calculations using B3LYP/6-31G method are given in italics.**

Compound	Bond	R_{ij}(Å)	ρ_b (e$Å^{-3}$)	$\nabla^2\rho_b$ (e$Å^{-5}$)	λ_1	λ_2	λ_3	ε
Cocrystal	O4…X4_H2N	1.9657	0.082	2.637	-0.43	-0.38	3.44	0.14
	(x+1/2, -y+1, z+1/2	*1.9619*	*0.099*	*2.574*	*-0.51*	*-0.49*	*3.58*	*0.03*
	O1…X1_H1N	1.8363	0.141	3.473	-0.76	-0.73	4.97	0.03
	(x, y+1, z)	*1.8352*	*0.126*	*3.363*	*-0.66*	*-0.64*	*4.66*	*0.02*
	O2…X1_H5	2.4944	0.044	0.740	-0.21	-0.17	1.12	0.28
	(x, y+1, z)	*2.4639*	*0.041*	*0.755*	*-0.19*	*-0.16*	*1.10*	*0.20*
	O1…X3_H3	2.4620	0.040	0.740	-0.17	-0.15	1.06	0.13
	(-x+1, -y+2, -z)	*2.4782*	*0.038*	*0.731*	*-0.18*	*-0.14*	*1.05*	*0.28*
Salt	O3…X3_H1ON	2.2465	0.073	1.124	-0.34	-0.32	1.78	0.07
	(-x+1, -y+1, -z)	*2.2304*	*0.065*	*1.128*	*-0.30*	*-0.27*	*1.70*	*0.12*
	O1…X3_H2N	1.9181	0.100	2.863	-0.53	-0.52	3.91	0.03
	(-x+2, -y, -z)	*1.9170*	*0.110*	*3.032*	*-0.56*	*-0.56*	*4.15*	*0.01*
	O4…X4_H3O	1.5544	0.416	2.813	-3.12	-3.09	9.03	0.01
	(x, -y+1/2, z+1/2)	*1.5543*	*0.316*	*6.339*	*-2.18*	*-2.15*	*10.67*	*0.02*

	O2…X4_H1	2.2197	0.047	1.388	-0.20	-0.18	1.77	0.06
	(x, -y+1/2, z+1/2)	*2.2095*	*0.052*	*1.425*	*-0.21*	*-0.20*	*1.84*	*0.07*
	O1…X2_H3	2.4857	0.042	0.710	-0.17	-0.16	1.04	0.07
	(-x+2, y-1/2, -z+1/2)	*2.4901*	*0.043*	*0.705*	*-0.18*	*-0.16*	*1.05*	*0.14*
	O2…X1_H5	2.3263	0.050	1.011	-0.23	-0.19	1.43	0.19
	(x, y-1, z)	*2.3310*	*0.041*	*0.962*	*-0.23*	*-0.18*	*1.34*	*0.27*
	O…X4_H5	2.4761	0.041	0.701	-0.17	-0.15	1.03	0.11
	(x, -y+3/2, z+1/2)	*2.4805*	*0.041*	*0.680*	*-0.20*	*-0.17*	*1.03*	*0.17*
	O1…X2_H4	2.5394	0.039	0.644	-0.16	-0.15	0.95	0.05
	(-x+2, y-1/2, -z+1/2)	*2.5412*	*0.040*	*0.648*	*-0.16*	*-0.15*	*0.96*	*0.10*