Electronic Supplementary Information

Design of 4-aminobenzoic acid two-component molecular crystals: prediction and experiments

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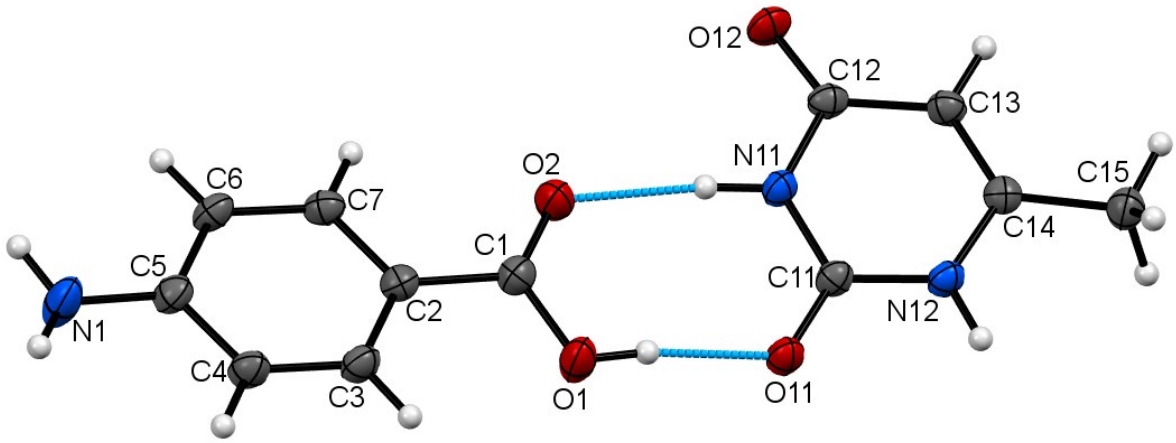
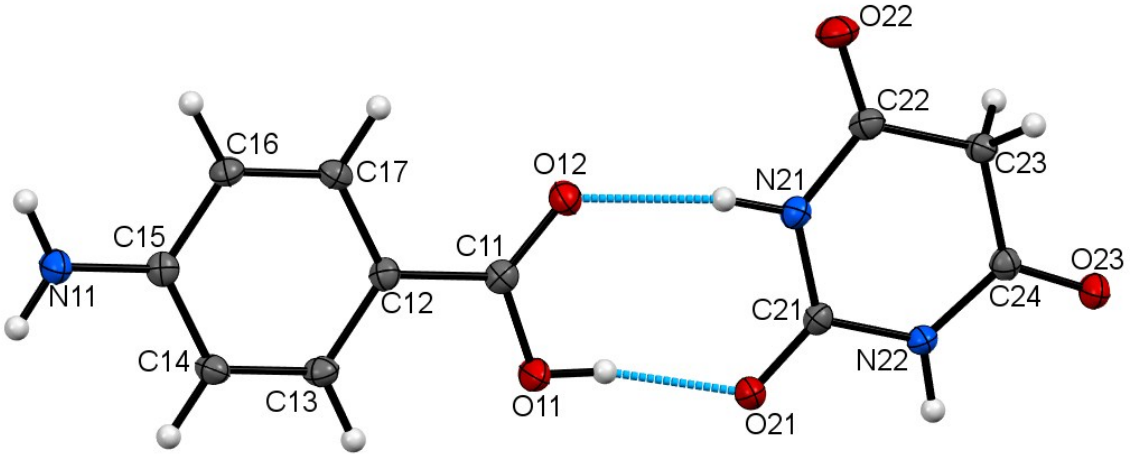
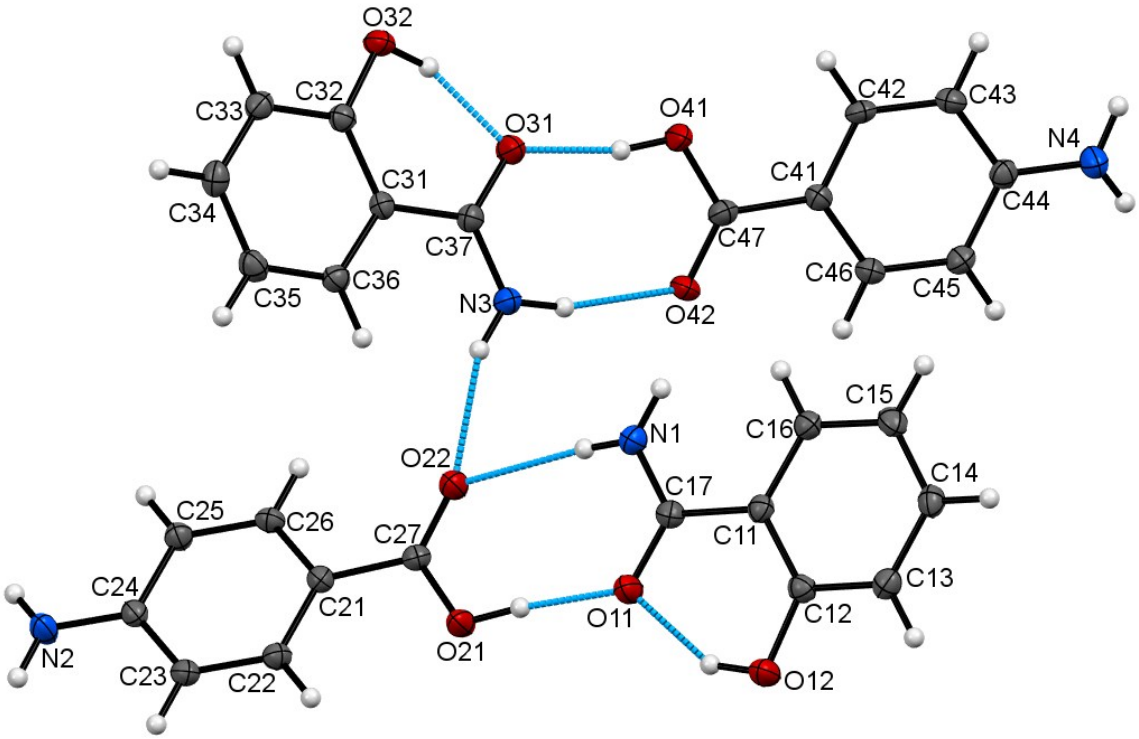
Figure S1. ORTEP drawings of PABA multi-component crystals. The displacement ellipsoids are shown at the 50% probability level.



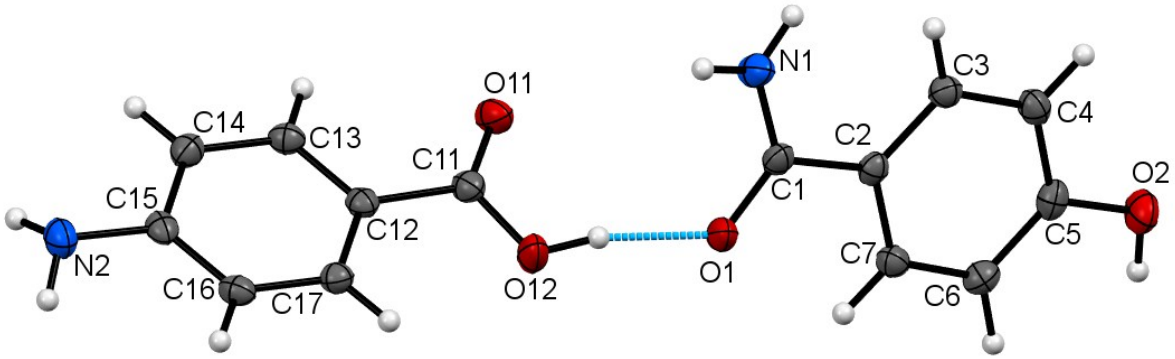
[PABA+6-MeUr]



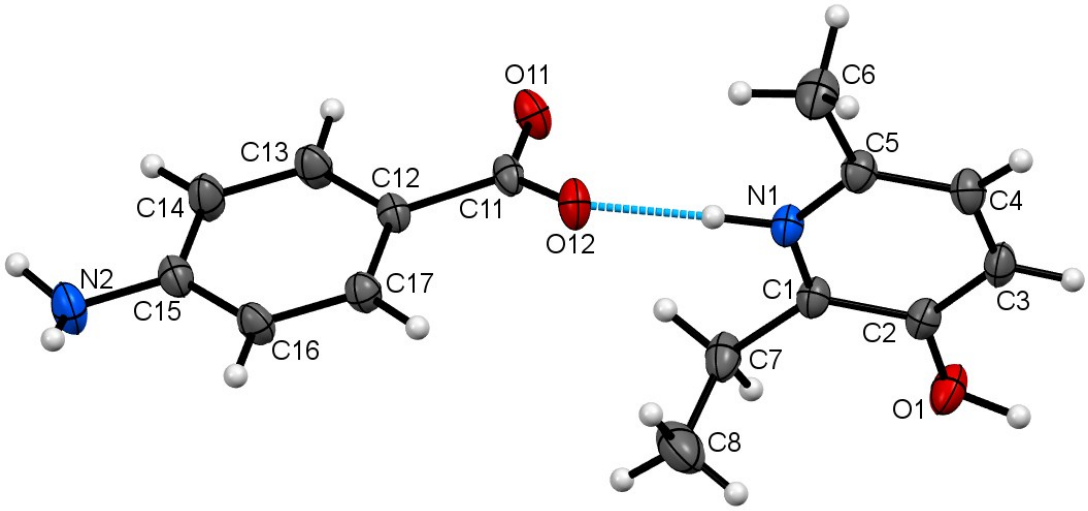
[PABA+BarbAc]



[PABA+2-OHBZA]



[PABA+4-OHBZA]



[PABA+EMX]

Figure S2. Orientation of molecules in the asymmetric unit of [PABA+4-OHBZA].

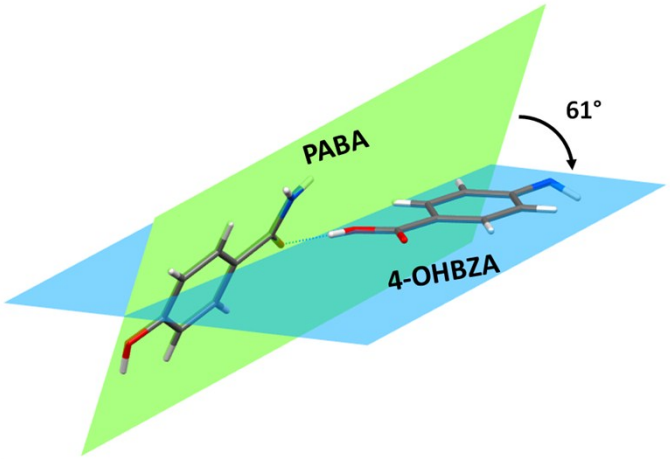


Figure S3. Comparison of the experimental PXRD patterns of the [PABA+6-MeUr] cocrystal prepared by solvent drop grinding (green) of PABA (black) and 6-MeUr (red) and calculated (blue) using single crystal X-ray diffraction data.

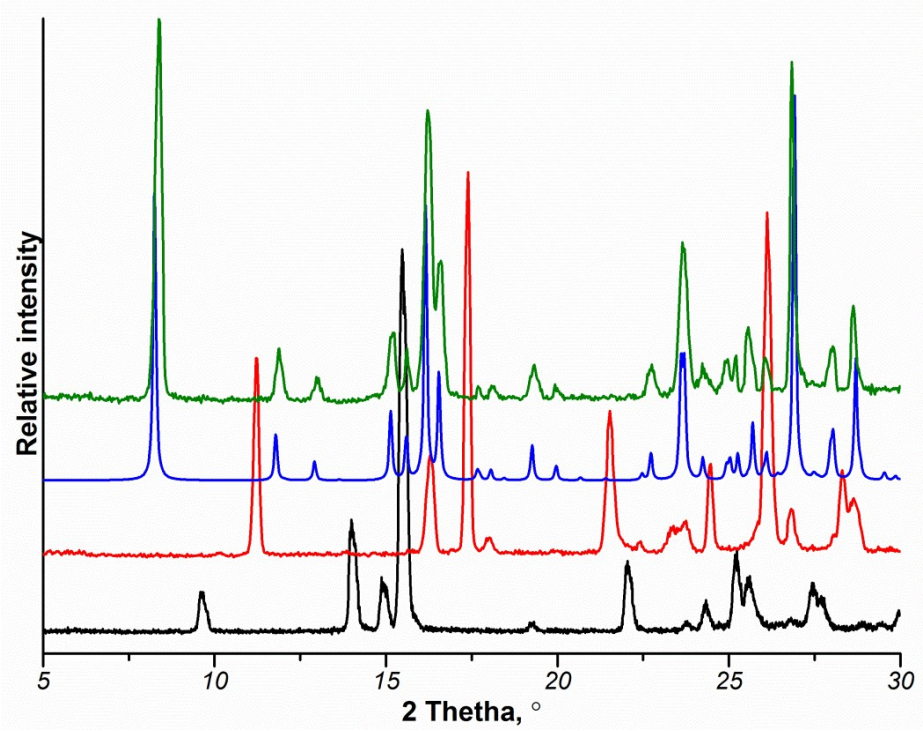


Figure S4. Comparison of the experimental PXRD patterns of the [PABA+BarbAc] cocrystal prepared by solvent drop grinding (green) of PABA (black) and BarbAc (red) and calculated (blue) using single crystal X-ray diffraction data.

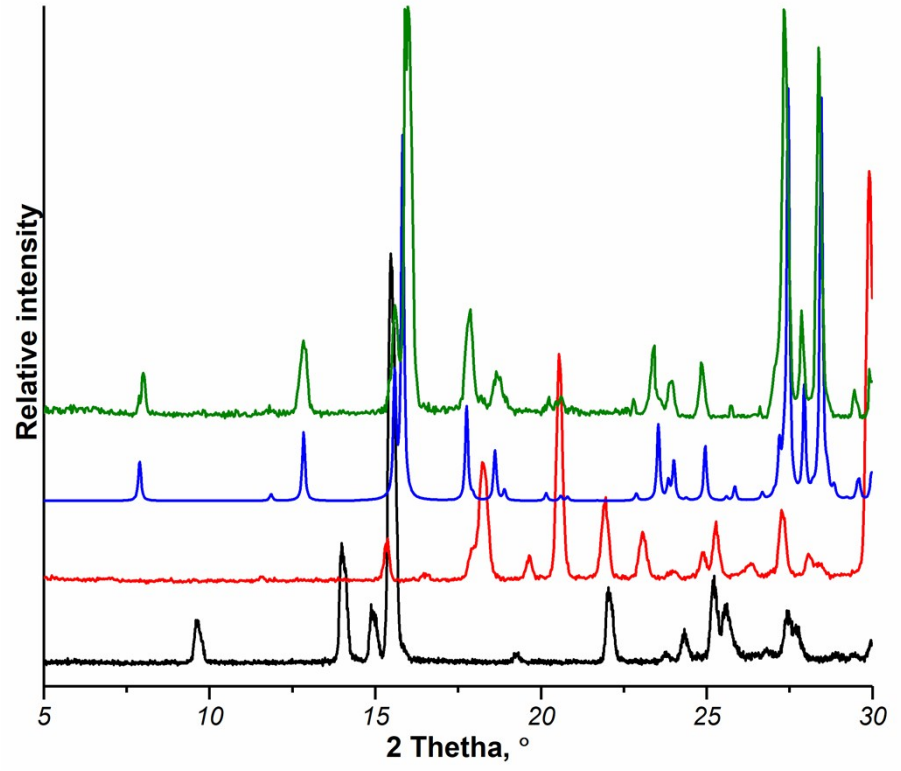


Figure S5. Comparison of the experimental PXRD patterns of the [PABA+2-OHBZA] cocrystal prepared by solvent drop grinding (green) of PABA (black) and 2-OHBZA (red) and calculated (blue) using single crystal X-ray diffraction data.

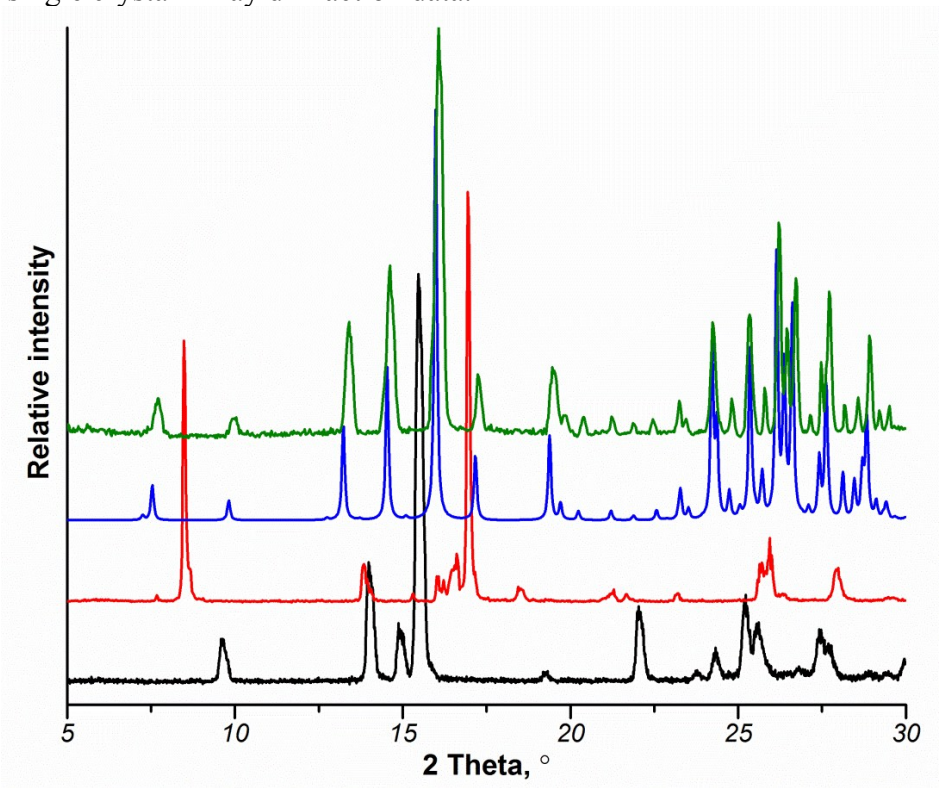


Figure S6. Comparison of the experimental PXRD patterns of the [PABA+4-OHBZA] cocrystal prepared by solvent drop grinding (green) of PABA (black) and 4-OHBZA (red) and calculated (blue) using single crystal X-ray diffraction data.

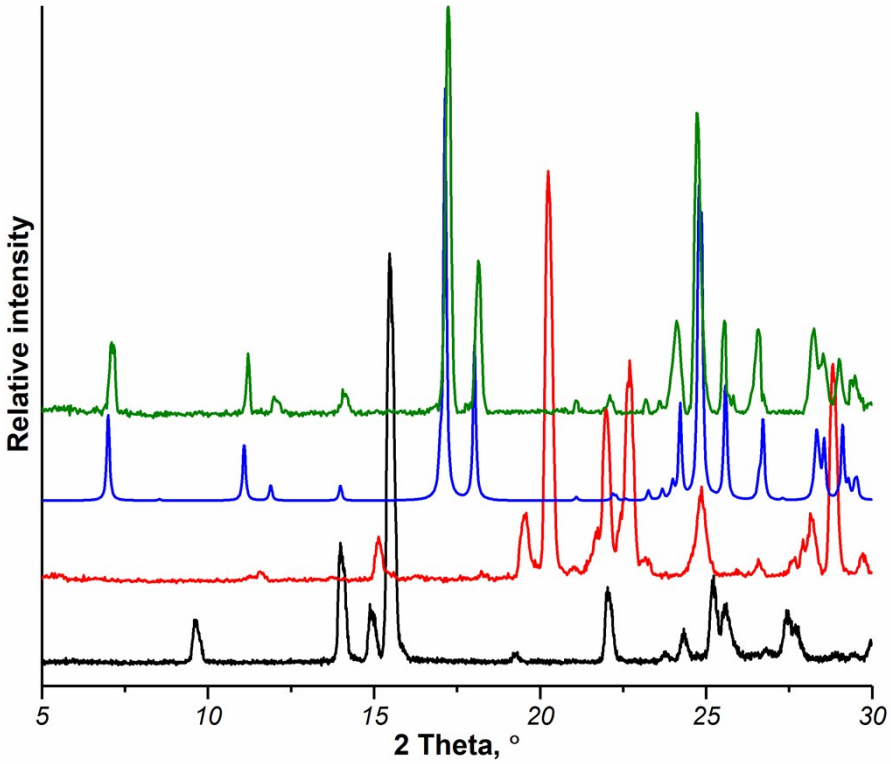


Figure S7. Comparison of the experimental PXRD patterns of the [PABA+EMX] salt prepared by solvent drop grinding (green) of PABA (black) and EMX (red) and calculated (blue) using single crystal X-ray diffraction data.

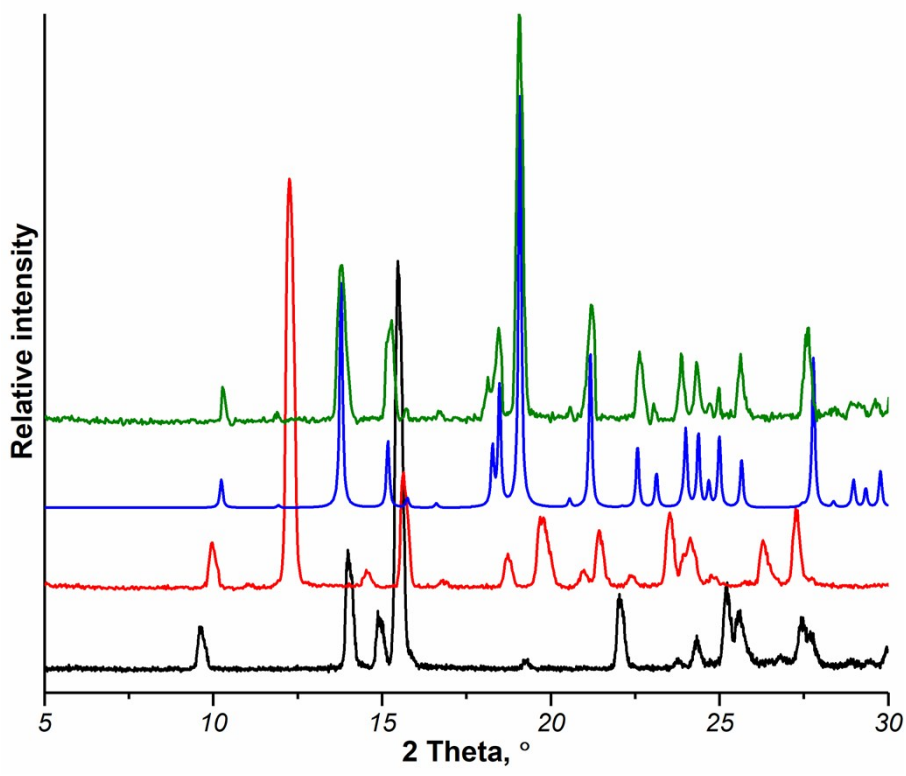
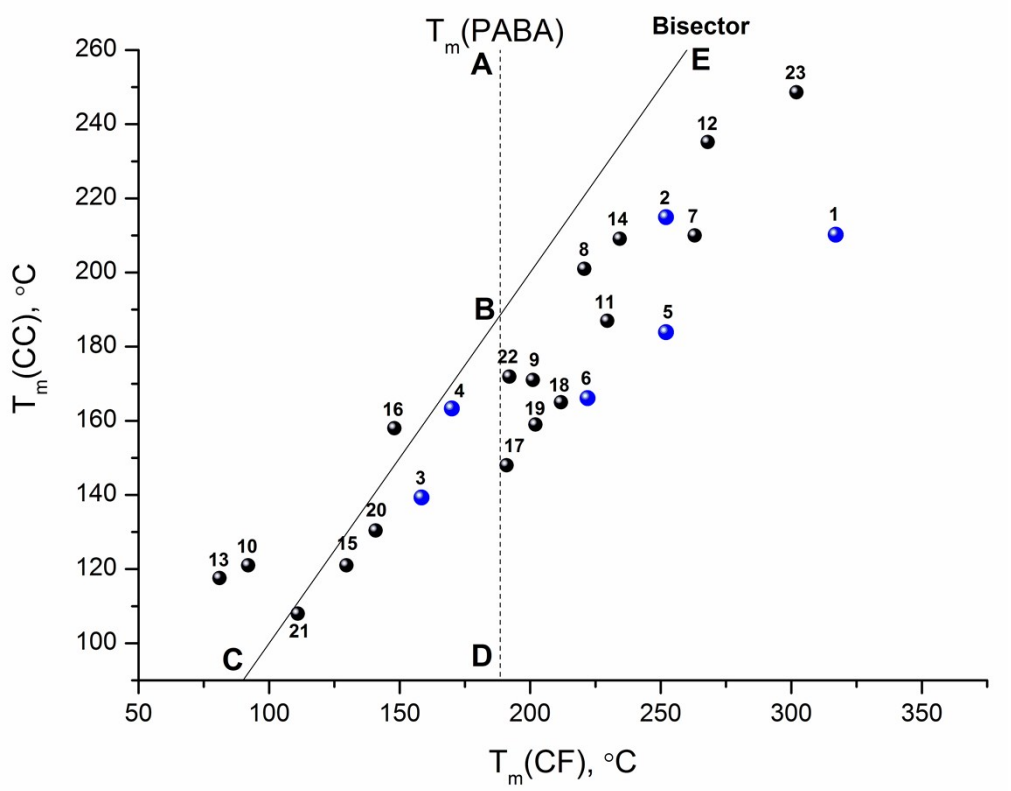


Figure S8. Experimental data of the melting temperatures of the PABA multi-component crystals versus coformers.



[a] The points corresponding to the novel PABA multi-component crystals studied in this paper are colored blue.

[b] The numbering corresponds to the following coformers: 1 - 6-Methyluracil; 2 - Barbituric acid; 3 - 4-OH-BZA; 4 – Emoxypine; 5 - Dipicolinic acid; 6 - Pyrazinoic acid; 7 – Nitrofurantoin; 8 – Furosemide; 9 – Febuxostat; 10 - Gababentin lactam; 11 – Niclosamide; 12 – Nitrofurantoin; 13 - 2,4,6-trinitrotoluene; 14 – Bumetanide; 15 – Voriconazole; 16 – Ketoconazole; 17 – CBZ; 18 – Diflunisal; 19 – Nitazoxanide; 20 - 2-OH-BZA; 21 – Antipyrine; 22 – Pyrazinamide; 23 - 4,4'-Bipyridine N,N'-dioxide.

[c] The points located within Sector **ABC** correspond to $T_{fus}(CC) < T_{fus}(CF)$ and $T_{fus}(PABA)$; the points located within Sector **CBD** correspond to $T_{fus}(CF) < T_{fus}(CC) < T_{fus}(PABA)$; the points located within Sector **DBE** correspond to $T_{fus}(PABA) < T_{fus}(CC) < T_{fus}(CF)$.

Figure S9. Dependence of $\Delta H_{sub}^{0,298}$ versus $\Delta G_{sub}^{0,298}$ for compounds structurally related to 6-MeUr. The numbering corresponds to Table S4.

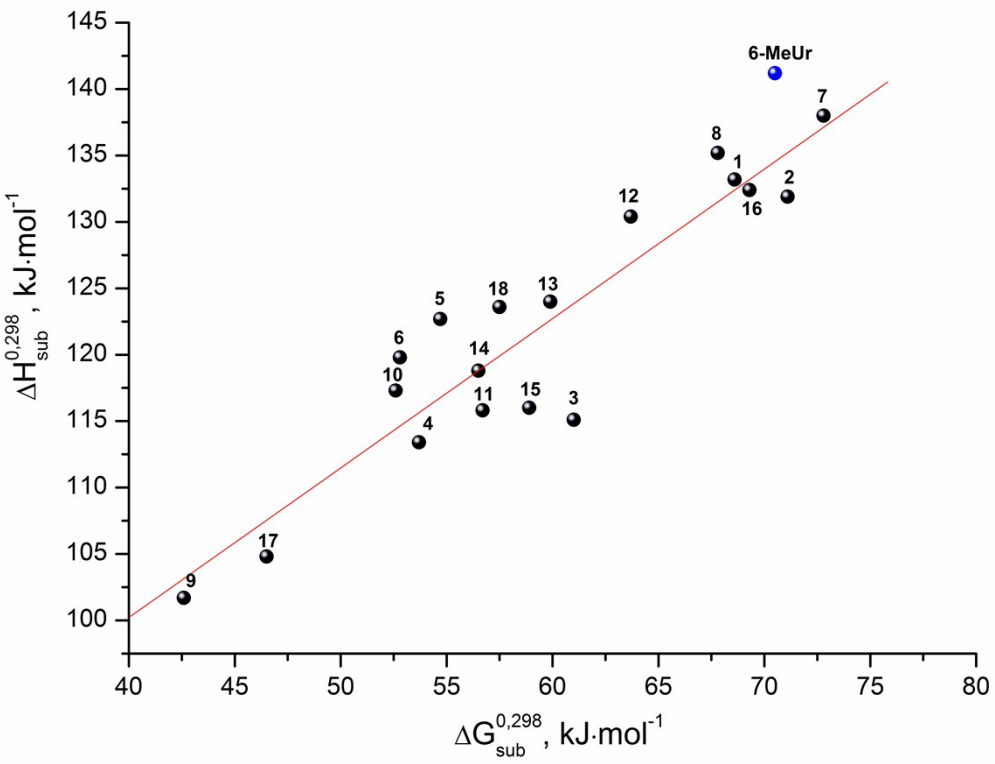


Figure S10. Dependence of $\Delta H_{sub}^{0,298}$ versus $\Delta G_{sub}^{0,298}$ for compounds structurally related to EMX. The numbering corresponds to Table S5.

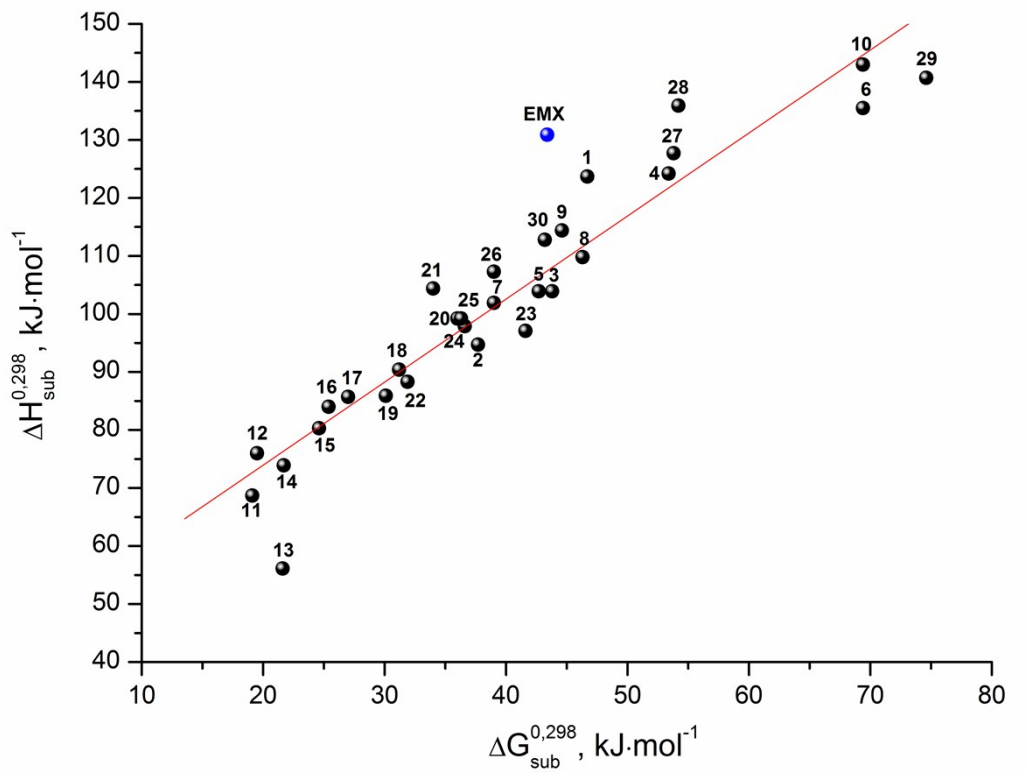
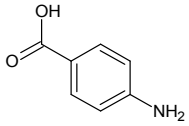
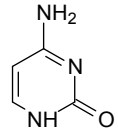
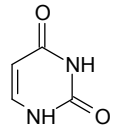
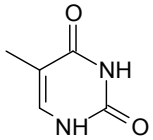
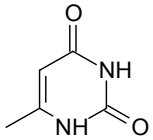
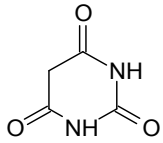
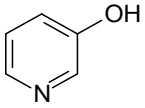
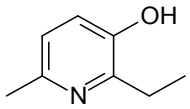
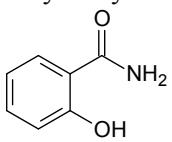
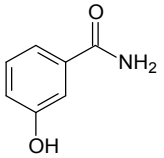
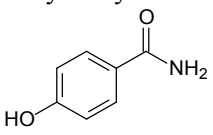
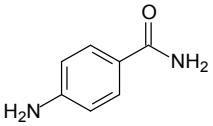


Table S1. Results of the screening for the formation of PABA cocrystals.

N	Compound	CSD ref. code	Ref	N_D/N_A[a]	Strongest H-bond	Number of unique H-bond	Result
1	PABA 	AMBNAC13	[1]	3/3(2)[b]	O-H…O 1.775 Å	2	
2	Cytosine 	CYTSIN01	[2]	3/2	N-H…O 1.897 Å	4	no
3	Uracil 	URACIL	[3]	2/2	N-H…O 1.995 Å	2	no
4	Thymine 	THYMIN02	[4]	2/2	N-H…O 1.985 Å	2	no
5	6-Methyluracul 	CEWVOP02	[5]	2/2	N-H…O 1.859 Å	2	Cocrystal (1:1)
6	Barbituric acid 	BARBAC01	[6]	2/3	N-H…O 1.983 Å	2	Cocrystal (1:1)
7	3-Hydroxypyridine 	BIRYIK11	[7]	1/1	O-H…N 1.645 Å	1	no
8	Emoxypine 	BECYEP	[8]	1/1	O-H…N 1.917 Å	1	Salt (1:1)
9	2-Hydroxybenzamide 	SALMID01	[9]	3/2	N-H…O 2.003 Å	3	Cocrystal (1:1)
10	3-Hydroxybenzamide 	HXBMZM01	[10]	3/2	-		no

11	4-Hydroxybenzamide 	VIDMAX	[11]	3/2	O-H…O 1.839 Å	3	Cocrystal (1:1)
12	4-Aminobenzamide 	AMBZAM11	[12]	4/2	N-H…O 2.017 Å	4	no

[a] the ratio of donors and acceptors of hydrogen bonds in the pure compound
[b] only two acceptors take part in hydrogen bonding

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11 L. K. Hansen, G. L. Perlovich and A. Bauer-Brandl, *Acta Cryst.*, 2007, E**63**, o2362.
12 A. N. Manin, K. V. Drozd, A. V. Churakov and G. L. Perlovich, *Cryst. Growth Des.*, 2018, **18**, 5254-5269.

Table S2. Geometry of intermolecular interactions in the PABA multi-component crystal structures.

D–H…A	d(H…A), Å	d(D...A), Å	D–H…A, °	Symmetry code
[PABA+6-MeUr]				
O1–H10···O11	1.76(2)	2.6466(12)	172.4(19)	x, y, z
N1–H1···O12	2.071(18)	2.9763(15)	174.4(15)	x-1/2, -y+3/2, z-1/2
N1–H2···O12	2.132(18)	3.0035(14)	164.3(15)	-x+1/2, -y+3/2, -z+1
N11–H11···O2	1.925(17)	2.8305(13)	170.0(14)	x, y, z
N12–H12···O11	1.930(17)	2.8251(12)	175.0(15)	-x+2, -y+1, -z+1
[PABA+BarbAc]				
O11–H1···O21	1.81(2)	2.6669(12)	169.2(18)	x, y, z
N21–H21···O12	1.974(18)	2.8928(13)	170.1(15)	x, y, z
N22–H22···O23	2.009(18)	2.8993(13)	171.1(16)	-x+1, -y+3, -z+1
N11–H11···O23	2.197(18)	3.0477(13)	163.7(16)	x+1, y-2, z
N11–H12···O22	2.089(19)	2.9850(14)	172.3(17)	-x+3/2, y-3/2, -z+1/2
[PABA+2-OHBZA]				
O12–H1···O11	1.76(4)	2.576(2)	149(4)	x, y, z
N1–H10···O22	2.17(3)	2.980(3)	174(3)	x, y, z
N1–H11···O42	2.18(3)	3.011(3)	162(3)	x, y+1, z
O21–H2···O11	1.70(4)	2.624(2)	173(4)	x, y, z
N2–H20···O41	2.16(4)	3.035(3)	174(3)	-x+1, -y, z-1/2
N2–H21···O12	2.55(3)	3.351(3)	154(3)	x+1/2, -y+1/2, z
O32–H3···O31	1.72(4)	2.568(2)	153(3)	x, y, z
N3–H30···O42	2.07(3)	3.017(3)	167(3)	x, y, z
N3–H31···O22	2.15(3)	3.007(3)	162(3)	x, y, z
O41–H4···O31	1.70(4)	2.593(2)	167(4)	x, y, z
N4–H40···O21	2.32(4)	3.188(3)	162(3)	-x+1/2, y-1/2, z+1/2
N4–H41···O32	2.63(3)	3.410(3)	162(3)	x-1/2, -y-1/2, z
[PABA+4-OHBZA]				
O2–H5···N2	1.89(2)	2.7828(16)	167.0(19)	x, y-1, z
N1–H1···O11	2.158(19)	3.0030(15)	159.4(16)	x-1, y, z
N1–H2···O11	2.133(19)	2.9827(15)	163.8(16)	-x+1, -y+1, -z+1
O12–H12···O1	1.66(2)	2.5588(13)	167.1(19)	x, y, z
N2–H22···O2	2.222(19)	3.0946(17)	161.2(16)	x+1, y+1, z
[PABA+EMX]				
N1–H1···O12	1.73(2)	2.6666(17)	178(2)	x, y, z
O1–H2···O11	1.57(3)	2.5051(17)	177(3)	-x+1, -y+1, z+1/2
N2–H21···O1	2.60(3)	3.442(2)	176(2)	x-1, y, z
N2–H22···O11	2.36(3)	3.242(2)	156(2)	x-1/2, -y+1/2, z

Table S3. Dependence of the compounds saturated vapour pressure on temperature

N	6-MeUr [a]		EMX [b]	
	T, °C	*P*, Pa	*T*, °C	*P*, Pa
1	121	$3.76 \cdot 10^{-2}$	50	$1.34 \cdot 10^{-1}$
2	122	$4.16 \cdot 10^{-2}$	51	$1.54 \cdot 10^{-1}$
3	123	$4.55 \cdot 10^{-2}$	52	$1.81 \cdot 10^{-1}$
4	124	$5.08 \cdot 10^{-2}$	53	$2.14 \cdot 10^{-1}$
5	125	$5.61 \cdot 10^{-2}$	54	$2.51 \cdot 10^{-1}$
6	126	$6.14 \cdot 10^{-2}$	55	$2.90 \cdot 10^{-1}$
7	127	$6.79 \cdot 10^{-2}$	56	$3.33 \cdot 10^{-1}$
8	128	$7.73 \cdot 10^{-2}$	57	$3.88 \cdot 10^{-1}$
9	129	$8.63 \cdot 10^{-2}$	58	$4.37 \cdot 10^{-1}$
10	130	$9.54 \cdot 10^{-2}$	59	$4.99 \cdot 10^{-1}$
11	131	$1.05 \cdot 10^{-1}$	60	$5.78 \cdot 10^{-1}$
12	132	$1.18 \cdot 10^{-1}$	61	$6.51 \cdot 10^{-1}$
13	133	$1.29 \cdot 10^{-1}$	62	$7.72 \cdot 10^{-1}$
14	134	$1.42 \cdot 10^{-1}$	63	$8.87 \cdot 10^{-1}$
15	135	$1.60 \cdot 10^{-1}$	64	1.03
16	136	$1.75 \cdot 10^{-1}$	65	1.14
17	137	$1.94 \cdot 10^{-1}$		
18	138	$2.14 \cdot 10^{-1}$		
19	139	$2.32 \cdot 10^{-1}$		
20	140	$2.57 \cdot 10^{-1}$		
21	141	$2.86 \cdot 10^{-1}$		

[a] 6-MeUr: $\ln(P[\text{Pa}]) = (39.1 \pm 0.2) - (16702 \pm 67)/T$; $\sigma = 2.48 \cdot 10^{-3}$; $r = 0.99969$; $F = 61859$; $n = 21$

[b] EMX: $\ln(P[\text{Pa}]) = (46.4 \pm 0.3) - (15625 \pm 104)/T$; $\sigma = 4.39 \cdot 10^{-3}$; $r = 0.99932$; $F = 22163$; $n = 16$

Table S4. Structurally similar compounds ($0.8 < T_c < 1$) for 6-MeUr, selected from the literature.

N	Compound	CAS Number	$\Delta G_{sub}^{0,298}$ / kJ·mol^{-1}	$\Delta H_{sub}^{0,298}$ / kJ·mol^{-1}	T_m / °C	Ref
1	5-Fluorouracil	51-21-8	68.6	133.2 ± 1.5	282 ± 2	[1]
2	Uracil	66-22-8	71.1	131.9 ± 0.5	338.9 ± 0.2	[2]
3	Barbituric acid	67-52-7	61.0	115.1 ± 0.7	253.2 ± 0.5	[3]
4	Tetrahydro-2-pyrimidone	1852-17-1	53.7	113.4 ± 0.7	250.0 ± 0.2	[4]
5	1-Methyluracil	615-77-0	54.7	122.7 ± 4.0	237 ± 1	[5]
6	3-Methyluracil	608-34-4	52.8	119.8 ± 3.0	178.9 ± 0.4	[5]
7	5-Methyluracil	65-71-4	72.8	138.0 ± 0.4	326 ± 1	[6]
8	6-Chlorouracil	4270-27-3	67.8	135.2 ± 2.7	295 ± 1	[1]
9	1,3,5,6-Tetramethyluracil	59264-09-4	42.6	101.7 ± 0.9	136.6 ± 0.3	[7]
10	Barbital	57-44-3	52.6	117.3 ± 0.6	190 ± 2	[8]
11	5,5-Dimethylbarbituric acid	24448-94-0	56.7	115.8 ± 0.6	278.5 ± 0.5	[9]
12	DL-alanine anhydride;	5625-46-7	63.7	130.4 ± 1.0	283 ± 1	[10]
13	5,6-Dihydro-5-methyluracil	696-04-8	59.9	124.0 ± 0.7	264 ± 1	[11]
14	5,6-Dihydro-6-methyluracil	2434-49-3	56.5	118.8 ± 0.8	219 ± 1	[11]
15	5,6-dihydrouracil	504-07-4	58.9	116.0 ± 1.2	280 ± 1	[12]
16	5,6-Dimethyluracil	26305-13-5	69.3	132.4 ± 1.4	300.9 ± 0.3	[7]
17	4(3H)-pyrimidinone	4562-27-0	46.5	104.8 ± 0.8	165.5 ± 1.5	[13]
18	5-Isopropylbarbituric acid	7391-69-7	57.5	123.6 ± 0.6	214.5 ± 1.5	[14]

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Table S5. Structurally similar compounds ($0.8 < T_c < 1$) for EMX, selected from the literature.

N	Compound	CAS Number	$\Delta G_{sub}^{0,298}$ / kJ·mol^{-1}	$\Delta H_{sub}^{0,298}$ / kJ·mol^{-1}	T_m / °C	Ref
1	Propyl Paraben	000094-13-3	46.7	123.7 ± 0.6	96.1 ± 0.5	[1]
2	1,3-dihydroxybenzene	108-46-3	37.7	94.7 ± 0.2	109.4 ± 0.4	[2]
3	1,4-dihydroxybenzene	123-31-9	43.8	103.9 ± 0.4	172.4 ± 0.3	[2]
4	1,2,3-trihydroxybenzene	533-73-3	53.4	124.2 ± 0.6	140.1 ± 0.2	[3]
5	1,2,3-trihydroxybenzene	87-66-1	42.7	103.9 ± 0.4	132.5 ± 0.2	[3]
6	1,3,5-trihydroxybenzene	108-73-6	69.4	135.5 ± 1.3	218.7 ± 0.5	[3]
7	Methylhydroquinone	95-71-6	39.0	101.9 ± 0.3	126.5 ± 0.5	[2]
8	4-phenylphenol	92-69-3	46.3	109.8 ± 1.0	170.0 ± 0.2	[4]
9	2,2'-dihydroxybiphenyl	1806-29-7	44.6	114.4 ± 1.2	113.6 ± 0.2	[4]
10	4,4'-dihydroxybiphenyl	92-88-6	69.4	143 ± 2	287.6 ± 0.2	[4]
11	Phenol	108-95-2	19.1	68.7 ± 0.5	40.89 ± 0.02	[5]
12	2-methylphenol	95-48-7	19.5	76.0 ± 0.8	31.03 ± 0.02	[5]
13	3-methylphenol	108-39-4	21.6	56.1 ± 0.8	12.24 ± 0.02	[6]
14	4-methylphenol	106-44-5	21.7	73.9 ± 1.5	34.77 ± 0.02	[5]
15	4-ethylphenol	123-07-9	24.6	80.3 ± 0.5	45.0 ± 0.2	[7]
16	2,3-dimethylphenol	526-75-0	25.4	84 ± 1	72.54 ± 0.05	[7]
17	3,4-dimethylphenol	95-65-8	27.0	85.7 ± 0.1	65.08 ± 0.05	[7]
18	2-methyl-8-hydroxyquinoline	826-81-3	31.2	90.4 ± 0.7	73.8 ± 0.2	[8]
19	4-tert-butylphenol	98-54-4	30.1	85.9 ± 0.5	100.1 ± 0.2	[9]
20	4-tert-butyl-1,2-dihydroxybenzene	98-29-3	36.0	99.2 ± 0.9	57.3 ± 0.2	[10]
21	2-tert-butyl-1,4-dihydroxybenzene	1948-33-0	34.0	104.4 ± 1.3	128.5 ± 0.5	[11]
22	4-tert-amylphenol	80-46-6	31.9	88.3 ± 0.5	95.0 ± 0.2	[9]
23	4-benzylphenol	101-53-1	41.6	97.1 ± 0.6	85.1 ± 0.2	[12]
24	4-tert-octylphenol	124765-79-3	36.6	97.9 ± 0.9	84.5 ± 0.2	[9]
25	2-Methylresorcinol	608-25-3	36.3	99.2 ± 2.3	116.9 ± 0.2	[13]
26	4-Methylresorcinol	496-73-1	39.0	107 ± 3	106 ± 2	[13]
27	4-Butoxybenzoic acid	1498-96-0	53.8	127.7 ± 0.8	160.6 ± 0.2	[14]
28	4-Pentyloxybenzoic acid	15872-42-1	56.1	134.5 ± 0.8	125 ± 2	[14]
29	6-Methyl-2-thiouracil	56-04-2	74.6	140.7 ± 0.9	330 ± 1	[15]
30	4-Phenoxyphenol	831-82-3	43.2	112.8 ± 0.4	82.0 ± 0.2	[16]

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Table S6. Two-component crystals selected for estimation of formation thermodynamics and some of their characteristics.

N	Coformer (CF)[a]	Molar ratio (PABA:CF)	$T_{fus}(CF)$ [b] / °C	$T_{fus}(CC)$ / °C	$\Delta G_{sub}^{0,298}(CF)$ [c] / kJ·mol^{-1}	$\Delta H_{sub}^{0,298}(CF)$ [d] / kJ·mol^{-1}	$\Delta G_{f}^{0,298}(CC)$ / kJ·mol^{-1}	$\Delta H_{f}^{0,298}(CC)$ / kJ·mol^{-1}	$T\Delta S_{f}^{0,298}(CC)$ / kJ·mol^{-1}	Ref
1	TNT	1:1	81.0	117.6	46.3	112.4	1.0	0.9	-0.1	[1]
2	TNT	1:2	81.0	175.2	46.3	112.4	-2.3	-2.1	0.2	[1]
3	Diflunisal	1:1	211.8	165.0	57.6	120.1	1.0	0.4	-0.6	[2]
4	Phenazine	1:2	174.0	174.5	41.8	96.8	3.2	6.3	3.1	[3]
5	Isoniazid	1:1	170.5	152.9	49.5	101.0	4.4	25.1	20.7	[4, 5]
6	CBZ	1:1	164.0	148.0	58.5	114.2	-6.9	4.4	11.3	[6]
7	CBZ	1:4	164.0	120.0	58.5	114.2	-12.0	7.6	19.6	[6]
8	CBZ	1:2	164.0	157.0	58.5	114.2	-3.7	2.4	6.1	[7]
9	6-MeUr	1:1	317.1	210.2	70.5	141.2	2.7	2.8	0.1	tw
10	BarbAc	1:1	251.6	214.9	61.0	115.1	0.7	-0.3	-1.0	tw
11	**2-OHBZA**	**1:1**	**140.8**	**130.4**	**44.4**	**106.9**	**5.8**	**8.0**	**2.2**	**tw**
12	4-OHBZA	1:1	158.4	139.3	58.9	117.8	-7.3	0.2	7.5	tw
13	EMX	1:1	168.8	163.3	43.4	130.9	2.1	-3.0	-5.1	tw

[a] TNT – 2,4,6-Trinitrotoluene; CBZ – Carbamazepine

[b] $T_{fus}(PABA)$ = 188.5°C (α-form); For Diflunisal, 6-MeUr and EMX $T_{fus}(PABA)$ = 145°C (β-form);

[c] $\Delta G_{sub}^{0,298}(PABA)$ = 52.5 kJ·mol^{-1};

[d] $\Delta H_{sub}^{0,298}(PABA)$ = 118.0 kJ·mol^{-1}.

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