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Supporting information for article:

Supramolecular hydrogen bonding patterns of co-crystals containing the Active Pharmaceutical Ingredient (API) Phloroglucinol and N-heterocycles

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Table S1 Selected geometric parameters (Å, º) for (1)

N1—C7	1.365 (8)	C5—C6	1.359 (8)
N1—C11	1.368 (8)	C7—C8	1.406 (9)
N2—C13	1.339 (10)	C8—C9	1.357 (11)
N2—C17	1.402 (11)	C9—C10	1.384 (12)
N3—C19	1.359 (8)	C10—C11	1.350 (10)
N3—C23	1.372 (8)	C11—C12	1.457 (10)
O1—C1	1.374 (7)	C13—C14	1.444 (11)
O2—C3	1.371 (7)	C14—C15	1.299 (12)
O3—C5	1.346 (7)	C15—C16	1.446 (13)
O4—C7	1.272 (7)	C16—C17	1.300 (11)
O5—C13	1.383 (10)	C17—C18	1.470 (12)
O6—C19	1.262 (8)	C19—C20	1.421 (9)
C1—C2	1.380 (8)	C20—C21	1.345 (9)
C1—C6	1.387 (8)	C21—C22	1.391 (10)
C2—C3	1.393 (8)	C22—C23	1.373 (9)
C3—C4	1.371 (8)	C23—C24	1.472 (10)
C4—C5	1.400 (8)		
C7—N1—C11	125.0 (6)	C10—C11—N1	117.0 (7)
C13—N2—C17	122.6 (8)	C10—C11—C12	125.5 (7)
C19—N3—C23	125.9 (6)	N1—C11—C12	117.5 (7)
O1—C1—C2	121.8 (6)	N2—C13—O5	115.9 (9)
O1—C1—C6	117.5 (5)	N2—C13—C14	118.1 (8)
C2—C1—C6	120.7 (6)	O5—C13—C14	126.0 (8)

C1—C2—C3	118.6 (5)	C15—C14—C13	118.1 (8)
O2—C3—C4	121.6 (5)	C14—C15—C16	122.8 (10)
O2—C3—C2	117.4 (5)	C17—C16—C15	118.7 (10)
C4—C3—C2	121.0 (5)	C16—C17—N2	119.6 (9)
C3—C4—C5	119.3 (6)	C16—C17—C18	125.0 (10)
O3—C5—C6	118.3 (6)	N2—C17—C18	115.2 (9)
O3—C5—C4	121.5 (6)	O6—C19—N3	120.5 (6)
C6—C5—C4	120.2 (5)	O6—C19—C20	125.2 (7)
C5—C6—C1	120.1 (5)	N3—C19—C20	114.2 (7)
O4—C7—N1	118.0 (6)	C21—C20—C19	121.6 (7)
O4—C7—C8	125.7 (7)	C20—C21—C22	121.6 (7)

Table S2 Selected geometric parameters (Å, º) for (2)

O1—C1	1.372 (2)	C1—C6	1.387 (3)
O2—C3	1.360 (2)	C1—C2	1.391 (3)
O3—C5	1.360 (2)	C2—C3	1.387 (3)
O5—C15	1.241 (2)	C3—C4	1.386 (3)
O4—C9	1.241 (2)	C4—C5	1.389 (3)
O6—C19	1.243 (2)	C5—C6	1.392 (3)
N1—C10	1.303 (3)	C7—C8	1.358 (3)
N1—C7	1.379 (3)	C7—C11	1.502 (3)
N2—C10	1.353 (2)	C8—C9	1.426 (3)
N2—C9	1.383 (3)	C10—C12	1.495 (3)
N3—C16	1.306 (2)	C13—C14	1.352 (3)
N3—C13	1.378 (3)	C13—C17	1.498 (3)

N4—C16	1.352 (2)	C14—C15	1.426 (3)
N4—C15	1.384 (2)	C16—C18	1.493 (3)
N5—C20	1.305 (2)	C19—C22	1.426 (3)
N5—C21	1.377 (3)	C20—C24	1.491 (3)
N6—C20	1.350 (2)	C21—C22	1.354 (3)
N6—C19	1.381 (2)	C21—C23	1.494 (3)
C10—N1—C7	117.54 (17)	N2—C9—C8	113.98 (18)
C10—N2—C9	123.14 (17)	N1—C10—N2	122.70 (19)
C16—N3—C13	117.22 (16)	N1—C10—C12	121.25 (18)
C16—N4—C15	123.48 (16)	N2—C10—C12	116.05 (18)
C20—N5—C21	117.60 (16)	C14—C13—N3	122.65 (17)
C20—N6—C19	123.30 (16)	C14—C13—C17	122.44 (19)
O1—C1—C6	117.65 (17)	N3—C13—C17	114.90 (18)
O1—C1—C2	121.02 (18)	C13—C14—C15	120.47 (19)
C6—C1—C2	121.32 (18)	O5—C15—N4	119.73 (17)
C3—C2—C1	119.21 (17)	O5—C15—C14	126.75 (18)
O2—C3—C4	117.59 (18)	N4—C15—C14	113.52 (16)
O2—C3—C2	121.80 (17)	N3—C16—N4	122.62 (18)
C4—C3—C2	120.61 (17)	N3—C16—C18	120.69 (17)
C3—C4—C5	119.23 (19)	N4—C16—C18	116.69 (17)
O3—C5—C4	115.78 (19)	O6—C19—N6	119.56 (17)
O3—C5—C6	122.94 (18)	O6—C19—C22	126.37 (18)
C4—C5—C6	121.27 (18)	N6—C19—C22	114.07 (17)
C1—C6—C5	118.33 (17)	N5—C20—N6	122.45 (17)

C8—C7—N1	122.36 (19)	N5—C20—C24	119.83 (17)
C8—C7—C11	121.9 (2)	N6—C20—C24	117.71 (17)
N1—C7—C11	115.7 (2)	C22—C21—N5	122.52 (18)
C7—C8—C9	120.2 (2)	C22—C21—C23	122.7 (2)
O4—C9—N2	119.53 (18)	N5—C21—C23	114.81 (19)
O4—C9—C8	126.5 (2)	C21—C22—C19	120.05 (19)

Table S3 Selected geometric parameters (Å, º) for (3)

O1—C1	1.367 (2)	C13—C14	1.367 (4)
O2—C3	1.369 (2)	C14—C15	1.355 (5)
O3—C5	1.353 (2)	C15—C16	1.372 (5)
C1—C2	1.383 (3)	C16—C17	1.394 (4)
C1—C6	1.384 (3)	N2—C18	1.331 (4)
C2—C3	1.386 (3)	N2—C22	1.342 (4)
C3—C4	1.378 (3)	C18—C19	1.363 (4)
C4—C5	1.391 (3)	C19—C20	1.390 (3)
C5—C6	1.389 (3)	C20—C21	1.389 (3)
N1—C7	1.322 (4)	C20—C23	1.470 (3)
N1—C11	1.329 (3)	C21—C22	1.372 (4)
C7—C8	1.385 (4)	C23—C28	1.390 (3)
C8—C9	1.382 (3)	C23—C24	1.391 (3)
C9—C10	1.392 (3)	C24—C25	1.381 (4)
C9—C12	1.478 (3)	C25—C26	1.376 (4)
C10—C11	1.374 (3)	C26—C27	1.373 (4)
C12—C17	1.387 (3)	C27—C28	1.385 (4)
C12—C13	1.394 (3)		
O1—C1—C2	121.15 (17)	C13—C12—C9	120.2 (2)
O1—C1—C6	117.79 (17)	C14—C13—C12	121.3 (3)
C2—C1—C6	121.05 (17)	C15—C14—C13	120.2 (3)
C1—C2—C3	118.69 (19)	C14—C15—C16	120.2 (3)
O2—C3—C4	122.60 (18)	C15—C16—C17	120.6 (3)

O2—C3—C2	115.87 (18)	C12—C17—C16	119.4 (3)
C4—C3—C2	121.53 (17)	C18—N2—C22	115.9 (2)
C3—C4—C5	118.99 (18)	N2—C18—C19	124.2 (3)
O3—C5—C6	122.09 (18)	C18—C19—C20	120.3 (3)
O3—C5—C4	117.46 (17)	C21—C20—C19	115.9 (2)
C6—C5—C4	120.44 (18)	C21—C20—C23	122.3 (2)
C1—C6—C5	119.29 (18)	C19—C20—C23	121.8 (2)
C7—N1—C11	116.4 (2)	C22—C21—C20	120.1 (2)
N1—C7—C8	124.6 (2)	N2—C22—C21	123.7 (3)
C9—C8—C7	119.0 (2)	C28—C23—C24	117.7 (2)
C8—C9—C10	116.3 (2)	C28—C23—C20	120.80 (19)
C8—C9—C12	121.7 (2)	C24—C23—C20	121.5 (2)
C10—C9—C12	122.04 (19)	C25—C24—C23	120.8 (2)
C11—C10—C9	120.5 (2)	C26—C25—C24	120.6 (3)
N1—C11—C10	123.2 (2)	C27—C26—C25	119.5 (3)
C17—C12—C13	118.3 (2)	C26—C27—C28	120.0 (3)
C17—C12—C9	121.5 (2)	C27—C28—C23	121.3 (2)

Table S4 Selected geometric parameters (Å, º) for (4)

O1—C1	1.369 (4)	C3—C4	1.377 (6)
O2—C3	1.378 (5)	C4—C5	1.374 (5)
O3—C5	1.372 (5)	C5—C6	1.389 (5)
O4—C7	1.273 (5)	C7—C8	1.421 (6)
O5—C12	1.273 (5)	C8—C9	1.349 (7)
N1—C11	1.346 (6)	C9—C10	1.382 (7)
N1—C7	1.353 (6)	C10—C11	1.326 (6)
N2—C16	1.346 (5)	C12—C13	1.401 (6)
N2—C12	1.349 (5)	C13—C14	1.344 (6)
C1—C2	1.384 (6)	C14—C15	1.377 (7)
C1—C6	1.392 (6)	C15—C16	1.335 (6)
C2—C3	1.374 (6)		
C11—N1—C7	123.4 (4)	O4—C7—N1	119.6 (4)
C16—N2—C12	124.0 (4)	O4—C7—C8	125.2 (5)
O1—C1—C2	121.7 (4)	N1—C7—C8	115.2 (5)
O1—C1—C6	117.1 (4)	C9—C8—C7	120.3 (5)
C2—C1—C6	121.2 (4)	C8—C9—C10	121.5 (5)
C3—C2—C1	118.9 (4)	C11—C10—C9	117.8 (5)
C4—C3—C2	121.7 (4)	C10—C11—N1	121.7 (5)
C4—C3—O2	117.1 (4)	O5—C12—N2	119.4 (4)
C2—C3—O2	121.1 (4)	O5—C12—C13	125.6 (5)
C3—C4—C5	118.3 (4)	N2—C12—C13	115.1 (5)
O3—C5—C4	116.6 (4)	C14—C13—C12	120.8 (5)

O3—C5—C6	121.1 (4)	C13—C14—C15	121.7 (5)
C4—C5—C6	122.3 (4)	C16—C15—C14	117.6 (5)
C5—C6—C1	117.5 (4)	C15—C16—N2	120.8 (5)

Table S5 Selected geometric parameters (Å, º) for (5)

O1—C1	1.370 (3)	C7—C8	1.393 (4)
O2—C3	1.365 (4)	C7—C11	1.492 (4)
O3—C5	1.368 (3)	C8—C12	1.496 (4)
O4—C31	1.369 (3)	C9—C10	1.386 (4)
O5—C33	1.365 (3)	C9—C13	1.496 (5)
O6—C35	1.358 (4)	C10—C14	1.499 (4)
N1—C10	1.334 (4)	C15—C16	1.381 (4)
N1—C7	1.340 (4)	C15—C19	1.498 (5)
N2—C8	1.333 (4)	C16—C20	1.505 (5)
N2—C9	1.340 (4)	C17—C18	1.390 (4)
N3—C18	1.332 (4)	C17—C21	1.500 (5)
N3—C15	1.341 (4)	C18—C22	1.505 (5)
N4—C17	1.336 (4)	C23—C24	1.390 (4)
N4—C16	1.338 (4)	C23—C27	1.496 (4)
N5—C26	1.334 (4)	C24—C28	1.501 (4)
N5—C23	1.339 (4)	C25—C26	1.397 (4)
N6—C25	1.333 (4)	C25—C29	1.490 (4)
N6—C24	1.336 (4)	C26—C30	1.488 (4)
C1—C2	1.385 (4)	C31—C36	1.374 (4)
C1—C6	1.387 (4)	C31—C32	1.382 (4)
C2—C3	1.390 (4)	C32—C33	1.382 (4)
C3—C4	1.382 (4)	C33—C34	1.379 (4)
C4—C5	1.391 (4)	C34—C35	1.385 (4)
C5—C6	1.386 (4)	C35—C36	1.388 (4)

C10—N1—C7	119.8 (2)	N4—C16—C15	120.8 (3)
C8—N2—C9	119.1 (3)	N4—C16—C20	116.7 (3)
C18—N3—C15	119.2 (3)	C15—C16—C20	122.5 (3)
C17—N4—C16	118.8 (3)	N4—C17—C18	120.5 (3)
C26—N5—C23	119.2 (2)	N4—C17—C21	117.0 (3)
C25—N6—C24	118.6 (3)	C18—C17—C21	122.6 (3)
O1—C1—C2	121.9 (3)	N3—C18—C17	120.4 (3)
O1—C1—C6	117.0 (3)	N3—C18—C22	117.3 (3)
C2—C1—C6	121.1 (3)	C17—C18—C22	122.3 (3)
C1—C2—C3	118.4 (3)	N5—C23—C24	120.5 (3)
O2—C3—C4	117.0 (3)	N5—C23—C27	116.9 (3)
O2—C3—C2	120.9 (3)	C24—C23—C27	122.6 (3)
C4—C3—C2	122.1 (3)	N6—C24—C23	120.7 (3)
C3—C4—C5	117.9 (3)	N6—C24—C28	116.9 (3)
O3—C5—C6	115.9 (3)	C23—C24—C28	122.4 (3)
O3—C5—C4	122.5 (3)	N6—C25—C26	121.1 (3)
C6—C5—C4	121.6 (3)	N6—C25—C29	117.2 (3)
C5—C6—C1	118.8 (3)	C26—C25—C29	121.7 (3)
N1—C7—C8	119.6 (3)	N5—C26—C25	119.8 (3)
N1—C7—C11	117.8 (3)	N5—C26—C30	117.1 (3)
C8—C7—C11	122.6 (3)	C25—C26—C30	123.0 (3)
N2—C8—C7	120.8 (3)	O4—C31—C36	123.0 (3)
N2—C8—C12	117.5 (3)	O4—C31—C32	115.8 (3)
C7—C8—C12	121.7 (3)	C36—C31—C32	121.2 (3)

N2—C9—C10	120.5 (3)	C31—C32—C33	119.3 (3)
N2—C9—C13	117.3 (3)	O5—C33—C34	122.2 (3)
C10—C9—C13	122.3 (3)	O5—C33—C32	117.3 (3)
N1—C10—C9	120.2 (3)	C34—C33—C32	120.5 (3)
N1—C10—C14	117.3 (3)	C33—C34—C35	119.3 (3)
C9—C10—C14	122.5 (3)	O6—C35—C34	121.4 (3)
N3—C15—C16	120.3 (3)	O6—C35—C36	117.8 (3)
N3—C15—C19	116.7 (3)	C34—C35—C36	120.8 (3)
C16—C15—C19	123.0 (4)	C31—C36—C35	118.8 (3)

Table S6 CSD codes, Donor…acceptor distances , coformer name and stoichiometric ratio in PHL-cocrystals

CSD code	H-bond	D...A distance (Å)	Coformer	Stoichiometric PHL/coformer/solvent ratio
Water solvated				
APAMEK	O-H...N O-H...N O-H...Ow	2.705 2.833 2.800	1,5-bis(4-Pyridyl)-1,4-pentadiene-3-one	1:2:4
APAMIO	O-H...N O-H...N O-H...N O-H...N O-H...N O-H...N O-H...Ow O-H...Ow	2.816 2.751 2.648 2.672 2.631 2.714 2.735 2.680 2.641	1,5-bis(Pyridin-4-yl)penta-1,4-dien-3-one	3:4:4
EBIMOS	O-H...N O-H...N O-H...Ow	2.653 2.673 2.639	3,3',5,5'-Tetramethyl-4,4'-bipyrazole	1:2:1
HODLES	O-H...N O-H...N O-H...O	2.636 2.595 2.658	1,1'-(Butane-1,4-diyl)bis(1H-imidazole)	1:1:1
MORVIZ	O-H...N O-H...N	2.842 2.949	phenazine	1:2:1

	O-H...N	2.765		
PUPGOX	O-H...N O-H...Ow O-H...Ow	2.846 2.710 2.716	caffeine	1:1:2
VAKVEJ	O-H...N O-H...N O-H...Ow	2.795 2.756 2.628	isonicotinamide	1:2:2
WAJWIP	O-H...O O-H...O O-H...O O-H...O O-H...O O-H...Ow	2.631 2.604 2.656 2.657 2.895 2.678	4,4'-(1,3,4-Oxadiazole-2,5-diylidene)dipyridin-1(4H)-ol	1:1:0.5
WAJWOV	O-H...N O-H...O O-H...Ow	2.743 2.717 2.750	4-(5-(Pyridin-4-yl)-1,3,4-oxadiazol-2-yl)-1λ^5-pyridin-1-ol	1:1:1
WOCGUS	O-H...O O-H...O O-H...Ow	2.720 2.747 2.640	theophylline	1:1:1
Solvated				
GEKSOG	O-H...O O-H...O O-H...O	2.649 2.772 2.753	dimethylsulfoxide	1:1
HAHNOU	O-H...N	2.741	(6,13,20-tris((5'-Methyl-2,2'-bipyridin-5-yl)methyl)-4,11,18-tri-isopropyl-7,14,21-trimethyl-3,6,10,13,17,20,22,23,24-nona-azatetracyclo(17.2.1.15,8.112,15)tetracosa-	1:1:2

			1(21),5(24),7,12(23),14,19(22)-hexaene-2,9,16-trione) bis(dichloromethane) clathrate	
KOLSIO	O-H...N O-H...N O-H...N	2.828 2.803 2.761	1,5-Di(pyridin-4-yl)penta-1,4-dien-3-one Acetonitrile solvate	1:1:1
KOLSOU	O-H...N O-H...N O-H...N	2.811 2.772 2.747	4,5,9,10-tetrakis (Pyridin-4-yl) tricyclo decane-2,7-dione Acetonitrile solvate	2:1:2
KONBUL	O-H...N O-H...N O-H…N	2.755 2.765 2.810	4,5,9,10-tetrakis(Pyridin-4-yl)tricyclo[6.2.0.03,6]decane-2,7-dione acetonitrile solvate	2:1:2
QUSXE1	O-H...N O-H...N O-H...N	2.688 2.711 2.732	(N-Methyl-2-imidazolyl) methoxy) cyclotriguaiacylene acetonitrile solvate	1:1:2
Not solvated				
HIBHEF	O-H…O O-H…O O-H…O	2.714 2.723 2.690	2,8-Dimethyl tricyclo(5.3.1.13,9)dodecane-syn-2,syn-8-diol	1:2
HIMGAL	O-H...N	2.741	4-methylpyridine	1:3
HIMGEP	O-H...N O-H...N O-H...N	2.740 2.746 2.728	2,4-dimethylpyridine	1:3
HOPKAZ	O-H...O O-H...O	2.606 2.635	4,4'-bipyridine-N,N'-dioxide	2:3

	O-H...O	2.673		
KIHZEH	O-H...N O-H...N O-H...N	2.721 2.795 2.784	4-cyanopyridine	1:3
MORVEV	O-H...N O-H...N O-H...N	2.834 2.873 2.785	phenazine	2:3
MORVOF	O-H...N O-H...N O-H…O	2.624 2.703 2.726	acridine	1:2
MORVUL	O-H...N O-H...N O-H...N O-H...N O-H...N	2.865 2.815 2.801 2.778 2.768	phenazine	2:3.5
PUVMIC	O-H...N O-H...N O-H...N	2.785 2.834 2.776	2,2'-Bipyridine	1:2
RAWDIC01	O-H...N O-H...N O-H...N	2.725 2.714 2.712	Urotropine	2:3
TEKKOJ	O-H...N O-H...N O-H...N O-H...N O-H...N O-H...N	2.747 2.710 2.793 2.714 2.728 2.755	4,4’-bipyridine	2:3
ULAZEM	O-H...O	2.706	N-(2-Hydroxyethyl) phthalimide	1:1

	O-H...O O-H...O	2.709 2.756		
XIBQUU	O-H...O O-H...O O-H...O	2.711 2.710 2.693	Trimesic acid	1:2
PHGLOL (phloroglucinol)	O-H...O O-H...O O-H...O	2.763 2.750 2.730		
PHGLOHO2 (hydrate phloroglucinol)	O-H...Ow O-H...Ow O-H...Ow	2.742 2.706 2.706		