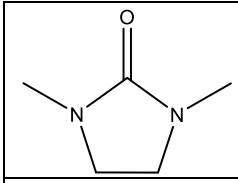
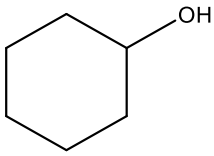
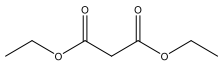
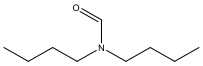
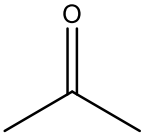
Electronic Supplementary Information

S1. Summary of the multi-component sulfathiazole crystals

Co-crystals (total: 59)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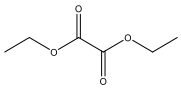	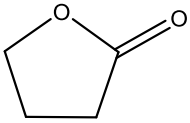	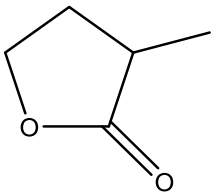	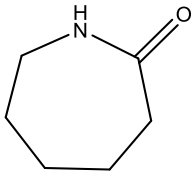	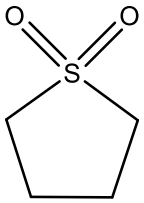
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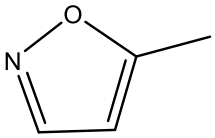	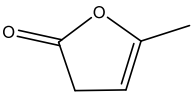	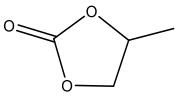	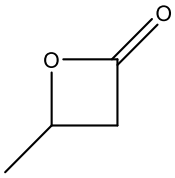	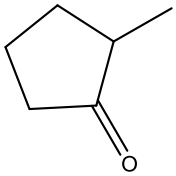
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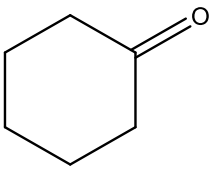	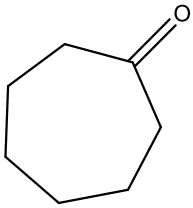	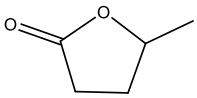	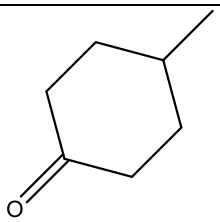	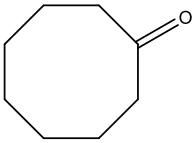
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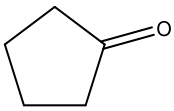	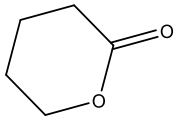	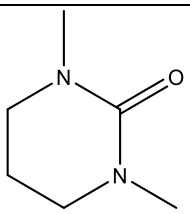	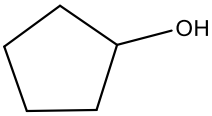	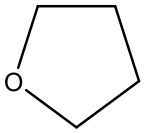
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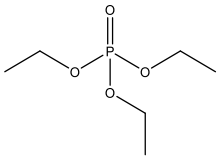	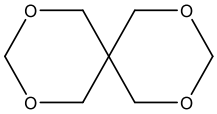	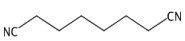	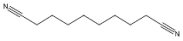	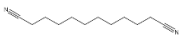
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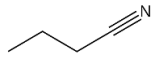
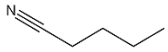
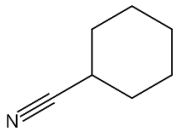
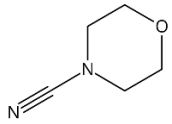
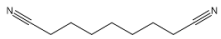
S1. Summary of the multi-component sulfathiazole crystals

Co-crystals (total: 59)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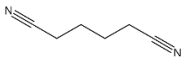	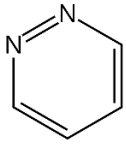	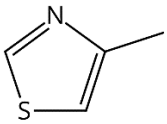	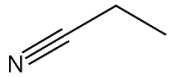	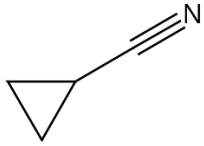
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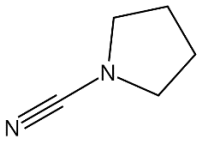
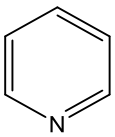
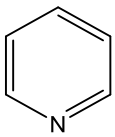
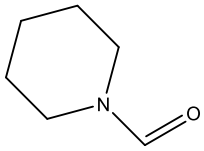
			CH_3—CN	
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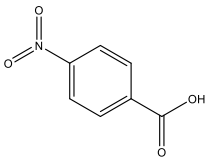
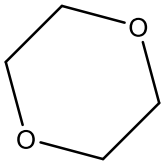
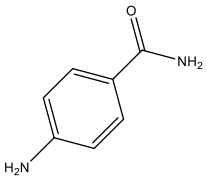
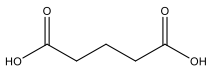
		18-CROWN-6 + ACETONITRILE		
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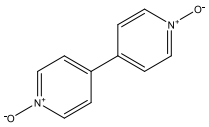
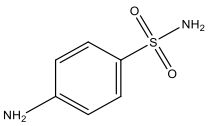
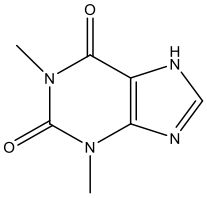
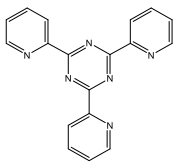
	Me_2N—COMe			
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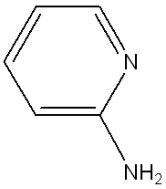
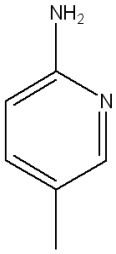
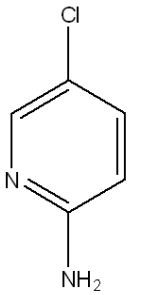
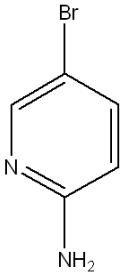
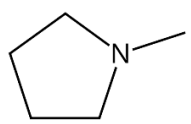
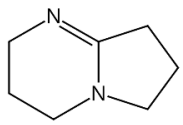
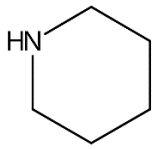
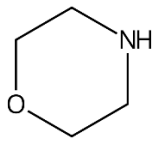
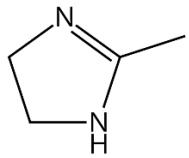
				
56	**57**	**58**	**59**	

S1. Summary of the multi-component sulfathiazole crystals

Salts (total: 29)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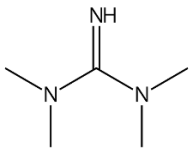
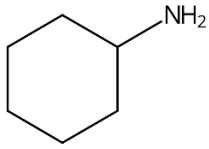
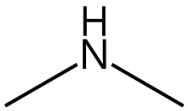
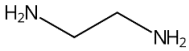
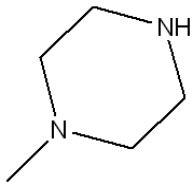
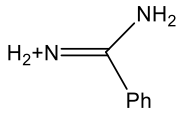
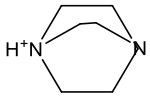
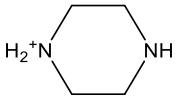
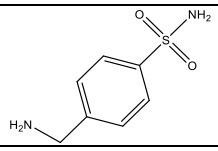
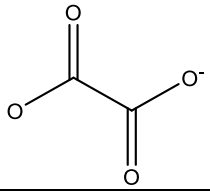
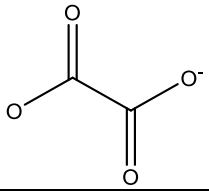
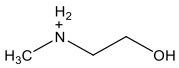
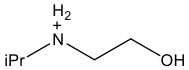
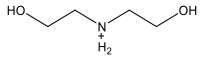
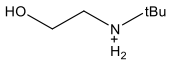
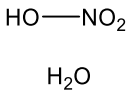
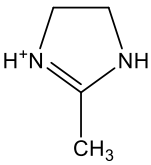
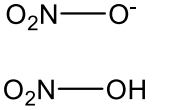
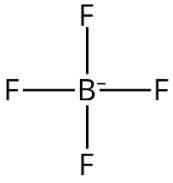
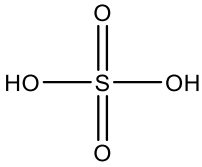
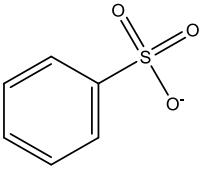
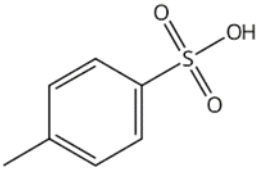
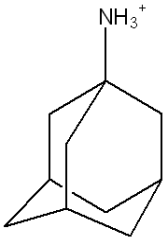
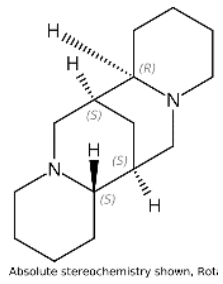
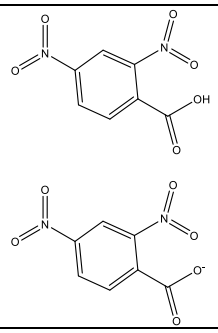
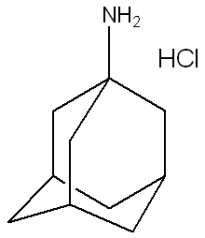
				
65	**66**	**67**	**68**	**69**
	$[SiF_6]^{2-}$			
70	**71**	**72**	**73**	**74**
				
75	**76**	**77**	**78**	**79**
				
80	**81**	**82**	**83**	**84**
				
85	**86**	**87**	**88**	

S1. Summary of the multi-component sulfathiazole crystals

Other (total: 3)

		
89	**90**	**91**

Notes on the following table

(i) **25**: the SLFZ positions approximate Pbca (Z′ = 1), but the P212121 (Z′ = 2) description is retained in the structure set containing only SLFZ molecules for consistency with the full structure set.

(ii) **35**: included in the DFT-optimised set in P21 (Z′ = 2) to accommodate the azelanitrile molecules without disorder. The SLFZ molecules actually define P21/n (Z′ = 1) (used for refinement of the X-ray structure) and the P21/n structure is included in the structure set containing only SLFZ molecules.

(iii) **41**: the SLFZ molecules approximate P21/n (Z′ = 1) with unit-cell parameters 8.559, 20.550, 9.673, 90, 96.13, 90 (comparable to **28**–**35**). The larger unit cell in P21/c (Z′ = 2) accommodates the N-cyanopyrrolidine molecules without disorder. The transformation matrix from the larger to smaller cell is [½ 0 ½ / 0 –1 0 / ½ 0 –½]. The larger P21/c (Z′ = 2) structure is included in the structure set containing only SLFZ molecules for consistency with the full structure set.

(iv) **43**: ADEDIX02 is published in space group P41. This is converted to P43 in the DFT-optimised set to produce the “R” conformation for SLFZ.

(v) **52**: SOGSEO in the CSD has one H atom missing from SLFZ. The structure contains the $R_2^2(8)$ H-bonded dimer, so it is clear that the missing H atom is attached to N13. The corrected structure is included in the DFT-optimised set.

(vi) **85**: VEYRAZ is reported (correctly) in C2/c, but the structure is included in the DFT-optimised set in Cc (Z′ = 2) to accommodate $[SO_4]^{2-}$ / H_2O without disorder. The higher symmetry C2/c (Z′ = 1) structure is included in the set containing only SLFZ molecules.

(vii) **86**: VEYYEG is reported (correctly) as an average structure in Pbcn (Z′ = 1), but the symmetry is reduced to Pna21 (Z′ = 2) (with a change of unit-cell setting) to accommodate the benezenesulfonate anions without disorder. The DFT-optimised structure shows some distortion from Pbcn, so the Pna21 (Z′ = 2) structure is retained in both the DFT-optimised set and the set containing only SLFZ molecules.

(viii) **87**: FIFWOJ is reported (incorrectly) in the CSD in space group P–1 with Z′ = 2. The space group is actually P21/n with Z′ = 1. The P21/n version is included in the DFT-optimised set.

(ix) **89**: the structure closely resembles P21/c, but the symmetry is broken by the non-centrosymmetric sparteine molecules. The P21 version is retained in the structure set containing only SLFZ molecules for consistency with the full structure set.

S1. Summary of the multi-component sulfathiazole crystals

Co-crystals (total: 59)

	CSD Refcode	Space Group	Solvent	Partner	Stoichiometry	Cell dimensions						Z	V
						a	b	c	α	β	γ		
1	2120788	P–1	dimethylethyleneurea	$C_5H_{10}N_2O$	2:1	8.051	11.492	15.552	77.45	88.64	88.64	2	1403.9
2	2120806	P21	cyclohexanol	$C_6H_{12}O$	1:1	8.541	12.401	8.836	90	102.96	90	2	912.0
3	2120768	Pc	diethylmalonate	$C_7H_{12}O_4$	2:1	8.409	16.640	11.274	90	101.37	90	2	1546.6
4	2120769	Cc	N,N-dibutylformamide	$C_9H_{19}NO$	2:1	16.616	16.088	12.630	90	110.69	90	4	3158.5
5	2120801	P21/c	acetone	C_3H_6O	1:1	8.322	16.020	11.352	90	100.29	90	4	1489.1
6	2120771	P21/c	diethyloxalate	$C_6H_{10}O_4$	1:1	8.416	17.394	10.342	90	104.70	90	4	1464.4
7	2120781	P21/c	γ-butyrolactone	$C_4H_6O_2$	1:1	8.636	19.187	9.354	90	91.03	90	4	1549.7
8	2120770	P21/n	α-Me-γ-butyrolactone	$C_5H_8O_2$	1:1 (disorder)	8.392	21.207	9.302	90	93.12	90	4	1653.0
9	2120775	P21/n	ε-caprolactam	$C_6H_{11}NO$	1:2	11.448	14.224	15.323	90	111.60	90	4	2319.9
10	2120772	P21/n	sulfalone	$C_4H_8O_2S$	1:1	6.036	21.020	12.791	90	94.44	90	4	1618.0
11	2120773	P21/n	methylisoxazole	C_4H_5NO	1:1 (disorder)	8.366	21.353	9.097	90	93.37	90	4	1622.3
12	2120774	P21/n	α-angelica lactone	$C_5H_6O_3$	1:1	8.194	21.111	9.570	90	94.20	90	4	1651.0
13	2120787	P21/n	propylene carbonate	$C_4H_6O_3$	1:1	8.628	21.151	9.135	90	97.70	90	4	1652.0
14	2120776	P21/n	β-butyrolactone	$C_4H_6O_2$	1:1	8.606	21.643	8.735	90	98.76	90	4	1608.0
15	2120777	P21/n	(±)2-methylcyclopentanone	$C_6H_{10}O$	1:1 (disorder)	8.550	21.491	9.215	90	89.73	90	4	1693.2
16	2120778	P21/n	cyclohexanaone	$C_6H_{10}O$	1:1 (disorder)	6.487	12.332	22.259	90	94.19	90	4	1775.9
17	2120779	P21/n	cycloheptanone	$C_7H_{12}O$	1:1 (disorder)	6.613	12.074	22.085	90	93.44	90	4	1760.2
18	2120780	P21/n	γ-valerolactone	$C_5H_8O_2$	1:1	8.417	20.975	9.472	90	93.83	90	4	1668.5
19	2120783	P21/n	4-methylcyclohexanone	$C_7H_{12}O$	1:1	6.572	12.959	21.553	90	92.48	90	4	1832.2
20	2120782	P21/n	cyclooctanone	$C_8H_{14}O$	2:1	8.783	14.728	23.800	90	98.46	90	4	3045.2
21	2120803	P21/n	cyclopentanone	C_5H_8O	1:1	8.454	20.699	9.487	90	92.37	90	4	1658.7
22	2120800	P21/n	δ-valerolactone	$C_5H_8O_2$	1:1	8.583	20.652	9.520	90	93.66	90	4	1684.0
23	2120784	P21/n	N,N-dimethylpropyleneurea	$C_6H_{12}N_2O$	2:1	16.553	9.996	19.810	90	112.26	90	4	3029.9
24	2120785	C2/c	cyclopentanol	$C_5H_{10}O$	1:1	20.705	11.385	14.136	90	99.02	90	8	3291.0
25[i]	2120786	P212121	tetrahydrofuran	C_4H_8O	2:2	9.515	16.675	19.249	90	90	90	8	3054.1
26	2120792	Aba2	triethylphosphate	$C_6H_{15}O_4P$	1:1	19.639	8.864	24.612	90	90	90	8	4284.5

S1. Summary of the multi-component sulfathiazole crystals

Co-crystals (total:59)

	CSD Refcode	Space Group	Partner	Partner	Stoichiometry	Cell dimensions						Z	V
						a	b	c	α	β	γ		
27	2120799	Pbca	tetraoxaspiroundecane	$C_7H_{12}O_4$	1:1	20.406	9.016	20.494	90	90	90	8	3770.5
28	2120789	P21/n	suberonitrile	$C_8H_{12}N_2$	1:0.5	8.010	20.820	8.990	90	94.65	90	4	1494.3
29	2120790	P21/n	sebaconitrile	$C_{10}H_{16}N_2$	1:0.5	8.523	21.073	9.0867	90	96.54	90	4	1621.5
30	2120791	P21/n	dodecanedinitrile	$C_{12}H_{20}N_2$	1:0.5	8.679	19.911	10.022	90	97.78	90	4	1715.8
31	2120793	P21/n	butyronitrile	C_4H_7N	1:1	8.248	21.019	9.074	90	96.53	90	4	1562.8
32	2120794	P21/n	valeronitrile	C_5H_9N	1:1	8.476	20.718	9.611	90	97.84	90	4	1671.9
33	2120807	P21/n	cyanocyclohexane	$C_7H_{11}N$	1:1	9.112	18.994	10.590	90	101.37	90	4	1796.9
34	2120795	P21/n	N-cyanomorpholine	$C_5H_8N_2O$	1:1	8.355	18.880	10.776	90	96.79	90	4	1687.9
35[ii]	2120796	P21	azelanitrile	$C_9H_{14}N_2$	2:1	8.363	21.146	9.116	90	95.76	90	2	1604.0
36	2120797	P21/c	adiponitrile	$C_6H_8N_2$	1:0.5	8.154	17.399	10.077	90	101.32	90	4	1401.8
37	2120798	P21/c	pyridazine	$C_4H_4N_2$	1:1	8.390	18.813	9.540	90	102.54	90	4	1469.9
38	2120804	P21/c	4-methylthiazole	C_4H_5NS	1:1	8.167	12.443	15.632	90	96.88	90	4	1577.1
39	2120805	Pbca	propionitrile	C_3H_5N	2:2	9.045	16.864	39.421	90	90	90	8	6013.0
40	2120802	Pbca	cyanocyclopropane	C_4H_5N	2:2	9.179	16.907	39.202	90	90	90	8	6083.7
41[iii]	2120819	P21/c	N-cyanopyrrolidine	$C_5H_8N_2$	2:2	12.213	20.550	13.583	90	97.03	90	8	3383.4
42	ADEDIX	P21/c	pyridine	C_5H_5N	1:1	8.385	9.272	20.704	90	100.10	90	4	1584.7
43[iv]	ADEDIX02	P43	pyridine	C_5H_5N	1:1	8.651	8.651	20.538	90	90	90	4	1573.2
44	BABYIN	P21/c	acetonitrile	C_2H_3N	1:1	10.741	7.592	16.748	90	103.99	90	4	1325.2
45	BABYOT	P–1	N-formylpiperidine	$C_6H_{11}NO$	2:2	10.539	12.189	13.981	95.29	107.38	90.63	4	1705.3
46	FIZFUR	P21/n	4-nitrobenzoic acid	$C_7H_5NO_4$	1:1	6.631	15.014	17.708	90	94.55	90	4	1757.4
47	FURDIF	Pbca	1,4-dioxan	$C_4H_8O_2$	1:1	9.424	17.195	19.560	90	90	90	8	3169.6
48	HADMUU	P21/n	(18-crown-6) / acetonitrile	$C_{12}H_{24}O_6$ / C_2H_3N	1:1:1	8.355	40.104	9.339	90	111.13	90	4	2918.8
49	KUFWOZ	P21/c	4-aminobenzamide	$C_7H_8N_2O$	1:1	10.171	10.865	16.134	90	105.05	90	4	1721.6
50	LOFLUP	P21/n	pentanedioic acid	$C_5H_8O_4$	1:1	8.885	13.323	14.740	90	101.16	90	4	1712.0
51	OXIDEG02	P21/n	4,4′-bipyridine-1,1′-dioxide	$C_{10}H_8N_2O_2$	1:1	10.532	8.551	21.750	90	91.06	90	4	1958.4
52[v]	SOGSEO	P21/c	N,N-dimethyl propanamide	C_4H_9NO	1:1	8.258	12.153	16.561	90	98.79	90	4	1642.5

S1. Summary of the multi-component sulfathiazole crystals

Co-crystals (total: 59)

	CSD Refcode	Space Group	Partner	Partner	Stoichiometry	Cell dimensions						Z	V
						a	b	c	α	β	γ		
53	STHSAM01	P21/c	sulfanilamide	$C_6H_8N_2O_2S$	1:1	9.135	5.379	36.633	90	91.17	90	4	1799.7
54	SULTHE01	P21/c	theophylline	$C_7H_8N_4O_2$	1:1	11.020	9.010	20.186	90	113.68	90	4	1835.5
55	WIYLAT	P–1	2,4,6-tris(pyridine-2-yl)-1,3,5-triazine	$C_{18}H_{12}N_6$	1:1	8.811	12.722	13.170	66.23	73.80	88.07	2	1292.1
56	JUVFOY	P21/n	2-aminopyridine	$C_5H_6N_2$	1:1	8.501	18.841	10.507	90	104.51	90	4	1629.1
57	JUVFUE	P21/n	2-amino-5-methylpyridine	$C_6H_8N_2$	1:1	8.358	19.281	10.997	90	105.06	90	4	1711.2
58	JUVGAL	P21/n	2-amino-5-chloropyridine	$C_5H_5ClN_2$	1:1	8.403	19.276	10.962	90	106.2	90	4	1704.9
59	JUVGEP	P21/n	2-amino-5-bromopyridine	$C_5H_5BrN_2$	1:1	8.379	19.645	11.117	90	106.9	90	4	1751.0

Salts (total: 29)

	CSD Refcode	Space Group	Partner	Partner	Stoichiometry	Cell dimensions						Z	V
						a	b	c	α	β	γ		
60	2120818	Pna21	n-methylpyrrolidine	$[C_5H_{12}N]^+$	1:1	13.943	9.260	12.698	90	90	90	4	1639.5
61	2120809	Pna21	1,5-diazabicyclo[4.3.0]non-5-ene (DBN)	$[C_7H_{13}N_2]^+$	1:1	15.807	10.126	10.754	90	90	90	4	1721.3
62	2120808	P212121	piperidine	$[C_5H_{12}N]^+$	1:1	6.948	14.868	15.958	90	90	90	4	1648.5
63	2120814	P212121	morpholine	$[C_4H_{10}NO]^+$	1:1	6.592	15.155	15.689	90	90	90	4	1567.4
64	2120812	Fdd2	2-methyl-2-imidazoline	$[C_4H_9N_2]^+$	1:1	17.562	42.270	8.291	90	90	90	16	6220.3
65	2120810	P21	1,1,3,3-teytramethylguanidine	$[C_5H_{14}N_3]^+$	2:2	10.449	13.331	13.664	90	110.38	90	4	1784.2
66	2120816	P21/c	cyclohexylamine	$[C_6H_{14}N]^+$	1:1	8.081	16.676	13.169	90	104.56	90	4	1717.7
67	2120811	P21/c	N,N-dimethylamine	$[C_2H_8N]^+$	2:2	20.623	8.320	18.157	90	115.64	90	4	2808.5
68	2120817	C2/c	ethylenediamine	$[C_2H_9N_2]^+$	1:1	10.838	11.826	22.321	90	90.14	90	8	2860.9
69	2120813	P212121	methylpiperazine	$[C_5H_{13}N_2]^+$	1:1	8.401	11.142	17.746	90	90	90	4	1661.1
70	BUHMOI	P21/c	amino (phenyl) methamininium	$[C_7H_9N_2]^+$	1:1	13.949	8.327	16.944	90	113.29	90	4	1807.9
71	BUWDUT	C2/c	hexafluorosilicate	$[SiF_6]^{2-}$	1:0.5	17.723	11.684	11.938	90	91.78	90	4	1235.4
72	DOWPUC	P212121	4-aza-1-azoiabicyclo-2,2-octane	$[C_6H_{13}N_2]^+$	1:1	15.349	6.620	17.148	90	90	90	4	1742.4

S1. Summary of the multi-component sulfathiazole crystals

Salts (total: 29)

	CSD Refcode	Space Group	Partner	Partner	Stoichiometry	Cell dimensions						Z	V
						a	b	c	α	β	γ		
73	DOWQAJ	P212121	piperazin-1-ium	$[C_4H_{11}N_2]^+$	1:1	8.416	10.181	17.941	90	90	90	4	1537.2
74	HSLSTZ	P–1	mafenide	$[C_7H_{11}N_2O_2S]^+$	1:1	12.106	10.421	8.284	102.98	903	107.72	2	967.4
75	LOFMAW	P21/c	oxalic acid	$[C_2HO_4]^-$	1:1	8.039	19.934	8.636	90	97.72	90	4	1371.4
76	LOFMAW01	P21/c	oxalic acid	$[C_2HO_4]^-$	1:1	10.692	10.546	13.213	90	112.41	90	4	1377.2
77	OHUWAR	P21/n	2-hydroxy-N-methylethaniniumazanide	$[C_3H_{10}NO]^+$	1:1	7.877	12.109	16.048	90	102.69	90	4	1493.4
78	OHUWEV	P21/c	N-(2-hydroxyethyl)-propan-2-aminiumazanide	$[C_5H_{14}NO]^+$	1:1	8.976	11.444	17.367	90	99.30	90	4	1760.6
79	OHUWIZ	P21/c	2-hydroxy-N-(2-hydroxyethyl) ethaniniumazanide	$[C_4H_{12}NO_2]^+$	1:1	8.012	12.743	16.799	90	102.20	90	4	1676.5
80	QEDWAZ	P21/c	1-butyl(2-hydroxyethyl)ammonium	$[C_6H_{16}NO]^+$	2:2	13.893	11.771	22.191	90	91.40	90	4	3627.9
81	UDAKOA	P21/c	nitrate monohydrate	$[NO_3]^-$ / H_2O	1:1:1	12.192	7.635	15.389	90	107.47	90	4	1366.4
82	XIFPEI01	P21/n	lysidine	$[C_4H_9N_2]^+$	1:1	12.179	9.610	13.353	90	101.92	90	4	1529.1
83	VEYQUO	P21/n	nitric acid / nitrate	HNO_3 / $2[NO_3]^-$	2:1:2	14.948	8.259	22.962	90	100.82	90	4	2784.3
84	VEYRAV	P21/c	tetrafluoroborate	$[BF_4]^-$	1:1	8.056	9.942	17.209	90	90.57	90	4	1378.2
85[vi]	VEYREZ	Cc	sulfate monohydrate	$[SO_4]^{2-}$ / H_2O	2:1:1	17.473	11.624	11.756	90	90	90	4	2387.8
86[vii]	VEYYEG	Pna21	besylate	$[C_6H_5O_3S]^-$	2:2	15.530	8.145	28.496	90	90	90	8	3604.2
87[viii]	FIFWOJ	P21/n	tosylate	$[C_7H_7O_3S]^-$	1:1	14.639	5.984	20.927	90	94.78	90	4	1826.6
88	RUMXAB	P21/c	1-admantylammonium	$[C_{10}H_{18}N]^+$	1:1	8.810	17.171	13.250	90	101.1	90	4	1966.9

Other (total: 3)

	CSD Refcode	Space Group	Partner	Partner	Stoichiometry	Cell dimensions						Z	V
						a	b	c	α	β	γ		
89[ix]	2120815	P21	(-)sparteine	$[C_{15}H_{27}N_2]^+$	2(SLFZ):2(SLFZ$^-$):2	16.676	11.771	19.062	90	111.71	90	2	3476.3
90	KUFWIT	P–1	2,4-dinitrobenzoic acid	$[C_7H_3N_2O_6]^-$ / $C_7H_4N_2O_6$	1:1:1	8.184	13.358	13.519	86.79	79.56	76.49	2	1413.0
91	VUKTAZ	P21/n	1-admantylammonium chloride	$[C_{10}H_{18}N]^+$ / Cl^-	1:1:1	6.511	19.151	17.662	90	98.69	90	4	2176.9

S2. Crystallographic information for the new crystal structures

	1	**2**	**3**	**4**	**5**	**6**
CCDC number	2120788	2120806	2120768	2120769	2120801	2120771
Moiety formula	$2(C_9H_9N_3O_2S_2)$, $C_5H_{10}N_2O$	$C_9H_9N_3O_2S_2$, $C_6H_{12}O$	$2(C_9H_9N_3O_2S_2)$, $C_7H_{12}O_4$	$2(C_9H_9N_3O_2S_2)$, $C_9H_{19}NO$	$C_9H_9N_3O_2S_2$, C_3H_6O	$2(C_9H_9N_3O_2S_2)$, $C_6H_{10}O_4$
Total formula	$C_{23}H_{28}N_8O_5S_4$	$C_{15}H_{21}N_3O_3S_2$	$C_{25}H_{30}N_6O_8S_4$	$C_{27}H_{37}N_7O_5S_4$	$C_{12}H_{15}N_3O_3S_2$	$C_{24}H_{28}N_6O_8S_4$
Formula weight	624.77	355.47	670.79	667.87	313.39	656.76
Temperature / K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P -1	P 21	P c	C c	P 21/c	P 21/c
a / Å	8.051(2)	8.541(2)	8.409(2)	16.616(3)	8.322(1)	8.416(2)
b / Å	11.492(2)	12.401(2)	16.640(1)	16.088(3)	16.020(1)	17.394(3)
c / Å	15.552(3)	8.836(2)	11.274(1)	12.630(3)	11.352(1)	10.342(2)
α / °	77.45(3)	90	90	90	90	90
β / °	88.64(2)	102.96(3)	101.37(2)	110.69(3)	100.29(1)	104.70(3)
γ / °	88.64(2)	90	90	90	90	90
Unit-cell volume / $Å^3$	1403.9(5)	912.0(3)	1546.6(4)	3158.5(13)	1489.1(2)	1464.4(6)
Z	2	2	2	4	4	2
Calc. density / g cm^{-3}	1.478	1.294	1.440	1.405	1.398	1.489
F(000)	652	376	700	1408	656	684
Radiation type	Mo Kα	Mo Kα	Cu Kα	Mo Kα	Mo Kα	Mo Kα
Absorption coefficient / mm^{-1}	0.389	0.308	3.313	0.350	0.367	0.382
Crystal size / mm^3	0.30 x 0.20 x 0.15	0.30 x 0.10 x 0.10	0.30 x 0.20 x 0.20	0.20 x 0.20 x 0.15	0.30 x 0.10 x 0.10	0.20 x 0.20 x 0.20
2θ range / °	4.02-43.93	4.73-43.91	5.31-88.78	5.24-55.02	4.45-43.93	4.68-43.92
Completeness to max 2θ	0.999	0.969	0.998	0.998	0.929	0.945
No. of reflections measured	10840	3242	1335	13211	4319	4521
No. of independent reflections	3429	1960	1335	6380	1687	1686
R(int)	0.1093	0.1004	0.0213	0.0366	0.1333	0.0855
No. parameters / restraints	376 / 6	210 / 31	388 / 78	388 / 2	190 / 15	191 / 0
Final *R*1 values [$I > 2\sigma(I)$]	0.0498	0.0472	0.0396	0.0356	0.0516	0.0605
Final $wR(F^2)$ values (all data)	0.1069	0.0891	0.1141	0.0859	0.1167	0.1296
Goodness-of-fit on F^2	0.949	0.683	1.055	1.026	0.836	0.791
Largest difference peak & hole / e $Å^{-3}$	0.275, -0.278	0.259, -0.195	0.356, -0.239	0.236, -0.365	0.333, -0.338	0.490, -0.290
Flack parameter		0.6(2) [undetermined]	0.03(4)	0.02(4)		

S2. Crystallographic information for the new crystal structures

	7	**8 [SQUEEZE]**	**9**	**10**	**11**	**12**	**13**
CCDC number	2120781	2120770	2120775	2120772	2120773	2120774	2120787
Moiety formula	$C_9H_9N_3O_2S_2$, $C_4H_6O_2$	$C_9H_9N_3O_2S_2$, $[C_5H_8O_4]$	$C_9H_9N_3O_2S_2$, $2(C_6H_{11}NO)$	$C_9H_9N_3O_2S_2$, $C_4H_8O_2S$	$C_9H_9N_3O_2S_2$, C_4H_5NO	$C_9H_9N_3O_2S_2$, $C_5H_6O_2$	$C_9H_9N_3O_2S_2$, $C_4H_6O_3$
Total formula	$C_{13}H_{15}N_3O_4S_2$	$C_{14}H_{17}N_3O_4S_2$	$C_{21}H_{31}N_5O_4S_2$	$C_{13}H_{17}N_3O_4S_3$	$C_{13}H_{14}N_4O_3S_2$	$C_{14}H_{15}N_3O_4S_2$	$C_{13}H_{15}N_3O_5S_2$
Formula weight	341.40	355.42	481.63	375.47	338.40	353.41	357.40
Temperature / K	293(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P 21/c	P 21/n	P 21/n	P 21/n	P 21/n	P 21/n	P 21/n
a / Å	8.636(2)	8.392(2)	11.448(2)	6.036(1)	8.366(2)	8.194(2)	8.628(2)
b / Å	19.187(4)	21.207(4)	14.224(3)	21.020(4)	21.353(4)	21.111(4)	21.151(4)
c / Å	9.354(2)	9.302(2)	15.323(3)	12.791(3)	9.097(2)	9.570(2)	9.135(2)
α / °	90	90	90	90	90	90	90
β / °	91.03(3)	93.12(3)	111.60(3)	94.44(3)	93.37(3)	94.20(3)	97.70(3)
γ / °	90	90	90	90	90	90	90
Unit-cell volume / $Å^3$	1549.7(6)	1653.0(6)	2319.9(9)	1618.0(6)	1622.3(6)	1651.0(6)	1652.0(6)
Z	4	4	4	4	4	4	4
Calc. density / g cm^{-3}	1.463	1.428	1.379	1.541	1.386	1.422	1.437
F(000)	712	744	1024	784	704	736	744
Radiation type	Cu Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Absorption coefficient / mm^{-1}	3.318	0.345	0.268	0.481	0.345	0.345	0.350
Crystal size / mm^3	0.30 x 0.30 x 0.30	0.30 x 0.30 x 0.30	0.30 x 0.30 x 0.30	0.30 x 0.10 x 0.10	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20	0.30 x 0.30 x 0.20
2θ range / °	9.22-148.46	4.79-49.96	6.25-61.05	3.74-50.16	3.81-43.92	3.86-43.93	3.85-43.93
Completeness to max 2θ	0.968	0.997	0.957	0.844	0.952	0.960	0.956
No. of reflections measured	3240	9723	13166	6447	5049	5433	5401
No. of independent reflections	3059	2893	6771	2422	1891	1932	1929
R(int)	0.0174	0.0861	0.0348	0.1754	0.1113	0.0819	0.1218
No. parameters / restraints	206 / 3	145 / 0	296 / 3	108 / 18	183 / 19	209 / 0	209 / 0
Final *R*1 values [$I > 2\sigma(I)$]	0.0554	0.0523	0.0552	0.0678	0.0594	0.0473	0.0474
Final $wR(F^2)$ values (all data)	0.1754	0.1554	0.1520	0.1551	0.1440	0.1035	0.0981
Goodness-of-fit on F^2	1.118	1.000	1.029	0.814	0.791	0.698	0.802
Largest difference peak & hole / e $Å^{-3}$	0.394, -0.405	0.231, -0.357	0.767, -0.790	0.735, -0.673	0.339, -0.267	0.198, -0.168	0.263, -0.185
Flack parameter							

S2. Crystallographic information for the new crystal structures

	14	**15**	**16**	**17**	**18**	**19**	**20**
CCDC number	2120776	2120777	2120778	2120779	2120780	2120783	2120782
Moiety formula	$C_9H_9N_3O_2S_2$, $C_4H_6O_2$	$C_9H_9N_3O_2S_2$, $C_6H_{10}O$	$C_9H_9N_3O_2S_2$, $C_6H_{10}O$	$C_9H_9N_3O_2S_2$, $C_7H_{12}O$	$C_9H_9N_3O_2S_2$, $C_5H_8O_2$	$C_9H_9N_3O_2S_2$, $C_7H_{12}O$	$2(C_9H_9N_3O_2S_2)$, $C_8H_{14}O$
Total formula	$C_{13}H_{15}N_3O_4S_2$	$C_{15}H_{19}N_3O_3S_2$	$C_{15}H_{19}N_3O_3S_2$	$C_{16}H_{21}N_3O_3S_2$	$C_{14}H_{17}N_3O_4S_2$	$C_{16}H_{21}N_3O_3S_2$	$C_{26}H_{32}N_6O_5S_4$
Formula weight	341.40	353.45	353.45	367.48	355.42	367.48	636.81
Temperature / K	150(2)	150(2)	150(2)	150(2)	293(2)	150(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P 21/n	P 21/n	P 21/n	P 21/n	P 21/n	P 21/n	P 21/n
a / Å	8.606(2)	8.550(2)	6.487(3)	6.613(3)	8.417(2)	6.572(1)	8.783(1)
b / Å	21.643(4)	21.491(4)	12.332(4)	12.074(3)	20.975(4)	12.959(3)	14.728(4)
c / Å	8.735(2)	9.215(2)	22.259(3)	22.085(3)	9.472(2)	21.533(4)	23.800(5)
α / °	90	90	90	90	90	90	90
β / °	98.76(3)	90.27(3)	94.19(3)	93.440(1)	93.83(3)	92.48(3)	98.46(1)
γ / °	90	90	90	90	90	90	90
Unit-cell volume / $Å^3$	1608.0(6)	1693.2(6)	1775.9(10)	1760.2(9)	1668.5(6)	1832.2(6)	3045.2(11)
Z	4	4	4	4	4	4	4
Calc. density / g cm^{-3}	1.410	1.387	1.322	1.387	1.415	1.332	1.389
F(000)	712	744	744	776	744	776	1336
Radiation type	Mo Kα	Mo Kα	Mo Kα	Cu Kα	Cu Kα	Mo Kα	Cu Kα
Absorption coefficient / mm^{-1}	0.351	0.332	0.316	2.914	3.103	0.309	3.257
Crystal size / mm^3	0.30 x 0.10 x 0.10	0.30 x 0.30 x 0.30	0.20 x 0.20 x 0.20	0.30 x 0.10 x 0.10	0.20 x 0.20 x 0.20	0.30 x 0.10 x 0.10	0.30 x 0.30 x 0.30
2θ range / °	6.04-60.99	4.81-50.05	3.67-41.62	8.02-94.27	8.43-133.18	4.92-43.93	7.08-114.37
Completeness to max 2θ	0.972	0.996	0.971	0.903	0.935	0.999	0.726
No. of reflections measured	9351	13217	5034	1473	2941	15682	3082
No. of independent reflections	4773	2980	1803	1428	2751	2226	2999
R(int)	0.0435	0.0666	0.1050	0.0248	0.0398	0.1329	0.1543
No. parameters / restraints	221 / 17	272 / 55	169 / 15	178 / 0	253 / 54	218 / 0	370 / 0
Final *R*1 values [$I > 2\sigma(I)$]	0.0534	0.0493	0.0832	0.1159	0.0494	0.0494	0.0691
Final $wR(F^2)$ values (all data)	0.1381	0.1359	0.2309	0.2878	0.1265	0.1220	0.1863
Goodness-of-fit on F^2	1.029	1.031	0.818	1.124	0.968	1.035	0.918
Largest difference peak & hole / e $Å^{-3}$	0.498, -0.294	0.344, -0.371	0.487, -0.375	0.879, -0.632	0.236, -0.273	0.190, -0.302	0.465, -0.412

S2. Crystallographic information for the new crystal structures

	21	**22**	**23**	**24**	**25**	**26**	**27**
CCDC number	2120803	2120800	2120784	2120785	2120786	2120792	2120799
Moiety formula	$C_9H_9N_3O_2S_2$, C_5H_8O	$C_9H_9N_3O_2S_2$, $C_5H_8O_2$	$2(C_9H_9N_3O_2S_2)$, $C_6H_{12}N_2O$	$C_9H_9N_3O_2S_2$, $C_5H_{10}O$	$C_9H_9N_3O_2S_2$, C_4H_8O	$C_9H_9N_3O_2S_2$, $C_6H_{15}O_4P$	$C_9H_9N_3O_2S_2$, $C_7H_{12}O_4$
Total formula	$C_{14}H_{17}N_3O_3S_2$	$C_{14}H_{17}N_3O_4S_2$	$C_{24}H_{30}N_8O_5S_4$	$C_{14}H_{19}N_3O_3S_2$	$C_{13}H_{17}N_3O_3S_2$	$C_{15}H_{24}N_3O_6PS_2$	$C_{16}H_{21}N_3O_6S_2$
Formula weight	339.42	355.42	638.80	341.44	327.41	437.46	415.48
Temperature / K	293(2)	293(2)	293(2)	293(2)	150(2)	150(2)	150(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	P 21/n	P 21/n	P 21/n	C 2/c	P 21 21 21	A b a 2	P b c a
a / Å	8.454(1)	8.583(1)	16.533(3)	20.705(4)	9.515(2)	19.639(4)	20.406(4)
b / Å	20.699(2)	20.652(2)	9.996(1)	11.385(2)	16.675(3)	8.864(2)	9.016(2)
c / Å	9.487(1)	9.520(4)	19.810(2)	14.136(3)	19.249(4)	24.612(5)	20.494(4)
α / °	90	90	90	90	90	90	90
β / °	92.37(1)	93.66(3)	112.26(2)	99.02(3)	90	90	90
γ / °	90	90	90	90	90	90	90
Unit-cell volume / Å^3	1658.7(3)	1684.0(8)	3029.9(8)	3291.0(11)	3054.1(11)	4284.5(16)	3770.5(13)
Z	4	4	4	8	8	8	8
Calc. density / g cm^{-3}	1.359	1.402	1.400	1.378	1.424	1.356	1.464
F(000)	712	744	1336	1440	1376	1840	1744
Radiation type	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Mo Kα	Mo Kα	Mo Kα
Absorption coefficient / mm^{-1}	3.048	3.075	3.295	3.073	0.362	0.358	0.321
Crystal size / mm^3	0.30 x 0.30 x 0.30	0.30 x 0.10 x 0.10	0.30 x 0.30 x 0.30	0.30 x 0.10 x 0.10	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.15	0.30 x 0.10 x 0.10
2θ range / °	8.54-148.48	8.56-108.47	5.96-148.42	8.89-133.09	3.23-61.03	4.15-54.96	3.97-43.91
Completeness to max 2θ	0.968	1.000	0.969	0.923	0.967	0.984	0.984
No. of reflections measured	3468	2205	6197	2756	20973	19195	12363
No. of independent reflections	3275	2047	5994	2682	8806	4688	2266
R(int)	0.0141	0.0297	0.0232	0.0335	0.0576	0.0705	0.1350
No. parameters / restraints	207 / 3	263 / 111	386 / 6	199 / 0	393 / 6	281 / 7	251 / 3
Final *R*1 values [$I > 2\sigma(I)$]	0.0538	0.0687	0.0493	0.0479	0.0456	0.0451	0.0446
Final $wR(F^2)$ values (all data)	0.1658	0.2147	0.1536	0.1266	0.0987	0.1059	0.0873
Goodness-of-fit on F^2	1.127	1.026	1.097	1.004	1.018	0.994	0.762
Largest difference peak & hole / e Å^{-3}	0.308, -0.265	0.260, -0.306	0.276, -0.406	0.232, -0.344	0.372, -0.407	0.456, -0.389	0.292, -0.314
Flack parameter					0.46(7) [inv. twin]	-0.04(5)	

S2. Crystallographic information for the new crystal structures

	28	**29**	**30**	**31**	**32**	**33**
CCDC number	2120789	2120790	2120791	2120793	2120794	2120807
Moiety formula	$2(C_9H_9N_3O_2S_2)$, $C_8H_{12}N_2$	$2(C_9H_9N_3O_2S_2)$, $C_{10}H_{16}N_2$	$2(C_9H_9N_3O_2S_2)$, $C_{12}H_{20}N_2$	$C_9H_9N_3O_2S_2$, C_4H_7N	$C_9H_9N_3O_2S_2$, C_5H_9N	$C_9H_9N_3O_2S_2$, $C_7H_{11}N$
Total formula	$C_{26}H_{30}N_8O_4S_4$	$C_{28}H_{34}N_8O_4S_4$	$C_{30}H_{38}N_8O_4S_4$	$C_{13}H_{16}N_4O_2S_2$	$C_{14}H_{18}N_4O_2S_2$	$C_{16}H_{20}N_4O_2S_2$
Formula weight	646.82	674.87	702.92	324.42	338.44	364.48
Temperature / K	150(2)	150(2)	120(2)	150(2)	120(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P 21/n	P 21/n	P 21/n	P 21/n	P 21/n	P 21/n
a / Å	8.010(2)	8.523(2)	8.6785(2)	8.2478(2)	8.4758(3)	9.112(2)
b / Å	20.820(4)	21.073(4)	19.9110(6)	21.0191(6)	20.7179(9)	18.994(4)
c / Å	8.990(2)	9.087(2)	10.0217(3)	9.0739(3)	9.6108(5)	10.590(2)
α / °	90	90	90	90	90	90
β / °	94.65(3)	96.54(3)	97.776(1)	96.534(1)	97.840(2)	101.37(3)
γ / °	90	90	90	90	90	90
Unit-cell volume / $Å^3$	1494.3(6)	1621.5(6)	1715.80(8)	1562.85(8)	1671.89(13)	1796.9(7)
Z	2	2	2	4	4	4
Calc. density / g cm^{-3}	1.438	1.382	1.361	1.379	1.345	1.347
F(000)	676	708	740	680	712	768
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Cu Kα
Absorption coefficient / mm^{-1}	0.366	0.340	0.324	0.350	0.330	2.825
Crystal size / mm^3	0.20 x 0.15 x 0.02	0.15 x 0.10 x 0.02	0.15 x 0.10 x 0.02	0.30 x 0.25 x 0.02	0.30 x 0.25 x 0.02	0.30 x 0.20 x 0.10
2θ range / °	7.11-43.08	7.23-61.13	7.13-54.97	7.09-60.63	7.17-50.05	16.40-108.46
Completeness to max 2θ	0.931	0.858	0.988	0.832	0.995	0.907
No. of reflections measured	4276	13649	12957	9149	11011	2116
No. of independent reflections	1607	4261	3882	3897	2937	1983
R(int)	0.0435	0.0596	0.0672	0.0471	0.1204	0.0584
No. parameters / restraints	203 / 3	212 / 3	221 / 3	204 / 3	233 / 15	217 / 0
Final *R*1 values [$I > 2\sigma(I)$]	0.0391	0.0495	0.0397	0.0537	0.0509	0.0585
Final $wR(F^2)$ values (all data)	0.0930	0.1188	0.1035	0.1486	0.1250	0.1602
Goodness-of-fit on F^2	1.072	0.988	1.023	1.041	0.978	0.922
Largest difference peak & hole / e $Å^{-3}$	0.227, -0.320	0.251, -0.424	0.262, -0.458	0.365, -0.566	0.251, -0.414	0.275, -0.378

S2. Crystallographic information for the new crystal structures

	34	**35**	**36**	**37**	**38**	**39**	**40**
CCDC number	2120795	2120796	2120797	2120798	2120804	2120805	2120802
Moiety formula	$C_9H_9N_3O_2S_2$, $C_5H_8N_2O$	$2(C_9H_9N_3O_2S_2)$, $C_9H_{14}N_2$	$2(C_9H_9N_3O_2S_2)$, $C_6H_8N_2$	$C_9H_9N_3O_2S_2$, $C_4H_4N_2$	$C_9H_9N_3O_2S_2$, C_4H_5NS	$C_9H_9N_3O_2S_2$, C_3H_5N	$C_9H_9N_3O_2S_2$, C_4H_5N
Total formula	$C_{14}H_{17}N_5O_3S_2$	$C_{27}H_{32}N_8O_4S_4$	$C_{24}H_{26}N_8O_4S_4$	$C_{13}H_{13}N_5O_2S_2$	$C_{13}H_{14}N_4O_2S_3$	$C_{12}H_{14}N_4O_2S_2$	$C_{13}H_{14}N_4O_2S_2$
Formula weight	367.44	660.84	618.77	335.40	354.46	310.39	322.40
Temperature / K	120(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	P 21/n	P 21/n	P 21/c	P 21/c	P 21/c	P b c a	P b c a
a / Å	8.3551(9)	8.3630(17)	8.154(2)	8.390(2)	8.167(2)	9.045(2)	9.179(2)
b / Å	18.880(3)	21.146(4)	17.399(3)	18.813(4)	12.443(2)	16.864(3)	16.907(3)
c / Å	10.7764(17)	9.1160(18)	10.077(2)	9.540(2)	15.632(3)	39.421(8)	39.202(8)
α / °	90	90	90	90	90	90	90
β / °	96.790(9)	95.76(3)	101.32(3)	102.54(3)	96.88(3)	90	90
γ / °	90	90	90	90	90	90	90
Unit-cell volume / $Å^3$	1688.0(4)	1604.0(6)	1401.8(5)	1469.9(6)	1577.1(6)	6013(2)	6084(2)
Z	4	2	2	4	4	16	16
Calc. density / g cm^{-3}	1.446	1.368	1.466	1.516	1.493	1.371	1.408
F(000)	768	692	644	696	736	2592	2688
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Absorption coefficient / mm^{-1}	0.339	0.342	0.386	0.377	0.481	0.360	0.359
Crystal size / mm^3	0.30 x 0.20 x 0.10	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20	0.35 x 0.20 x 0.20	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20
2θ range / °	7.27-55.01	7.23-50.05	7.53-50.03	7.29-61.03	7.06-50.09	7.08-50.08	4.82-49.82
Completeness to max 2θ	0.985	0.980	0.996	0.993	0.991	0.950	0.850
No. of reflections measured	15509	8090	12559	38391	10089	21487	17034
No. of independent reflections	3826	2768	2466	4455	2770	5055	4506
R(int)	0.1556	0.0560	0.0370	0.0378	0.0913	0.0881	0.0964
No. parameters / restraints	226 / 3	208 / 17	194 / 3	212 / 3	213 / 3	363 / 0	379 / 8
Final *R*1 values [$I > 2\sigma(I)$]	0.0611	0.1259	0.0331	0.0360	0.0458	0.0548	0.0446
Final $wR(F^2)$ values (all data)	0.1436	0.3033	0.0864	0.0964	0.1092	0.1368	0.0803
Goodness-of-fit on F^2	0.933	1.216	1.057	1.042	0.979	1.000	0.660
Largest difference peak & hole / e $Å^{-3}$	0.352, -0.337	0.519, -0.686	0.251, -0.397	0.357, -0.500	0.308, -0.394	0.593, -0.389	0.596, -0.362

S2. Crystallographic information for the new crystal structures

	41	**60**	**61**	**62**	**63**	**64**
CCDC number	2120819	2120818	2120809	2120808	2120814	2120812
Moiety formula	$C_9H_9N_3O_2S_2$, $C_5H_8N_2$	$[C_9H_8N_3O_2S_2]^-$, $[C_5H_{12}N]^+$	$[C_9H_8N_3O_2S_2]^-$, $[C_7H_{13}N_2]^+$	$[C_9H_8N_3O_2S_2]^-$, $[C_5H_{12}N]^+$	$[C_9H_8N_3O_2S_2]^-$, $[C_4H_{10}NO]^+$	$[C_9H_8N_3O_2S_2]^-$, $[C_4H_9N_2]^+$
Total formula	$C_{14}H_{17}N_5O_2S_2$	$C_{14}H_{20}N_4O_2S_2$	$C_{16}H_{21}N_5O_2S_2$	$C_{14}H_{20}N_4O_2S_2$	$C_{13}H_{18}N_4O_3S_2$	$C_{13}H_{17}N_5O_2S_2$
Formula weight	351.44	340.46	379.50	340.46	342.43	339.43
Temperature / K	293(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	P 21/c	P n a 21	P n a 21	P 21 21 21	P 21 21 21	F d d 2
a / Å	12.213(3)	13.943(3)	15.807(3)	6.948(1)	6.592(1)	17.562(4)
b / Å	20.550(5)	9.260(2)	10.126(2)	14.868(1)	15.155(3)	42.720(9)
c / Å	13.583(3)	12.698(3)	10.754(2)	15.958(1)	15.689(3)	8.291(2)
α / °	90	90	90	90	90	90
β / °	97.03(2)	90	90	90	90	90
γ / °	90	90	90	90	90	90
Unit-cell volume / Å^3	3383.4(14)	1639.5(6)	1721.3(6)	1648.5(3)	1567.4(5)	6220(2)
Z	8	4	4	4	4	16
Calc. density / g cm^{-3}	1.380	1.379	1.464	1.372	1.451	1.450
F(000)	1472	720	800	720	720	2848
Radiation type	Cu Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Absorption coefficient / mm^{-1}	2.999	0.337	0.331	0.335	0.357	0.357
Crystal size / mm^3	0.30 x 0.20 x 0.10	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20
2θ range / °	7.29-101.28	7.32-60.93	7.56-49.96	7.49-50.26	7.22-52.50	7.23-59.48
Completeness to max 2θ	0.739	0.945	0.992	0.879	0.986	0.829
No. of reflections measured	2791	4499	11570	6723	6371	13502
No. of independent reflections	2642	4499	2977	2457	3109	3364
R(int)	0.0306	0.0325	0.0465	0.1056	0.0302	0.0491
No. parameters / restraints	415 / 0	227 / 14	226 / 1	199 / 0	217 / 6	217 / 6
Final *R*1 values [$I > 2\sigma(I)$]	0.0455	0.0475	0.0338	0.0368	0.0343	0.0388
Final $wR(F^2)$ values (all data)	0.1290	0.1026	0.0828	0.0694	0.0744	0.0898
Goodness-of-fit on F^2	1.025	1.083	1.066	0.803	1.065	1.040
Largest difference peak & hole / e Å^{-3}	0.235, -0.229	0.267, -0.332	0.209, -0.343	0.307, -0.190	0.201, -0.237	0.288, -0.482
Flack parameter		0.47(11) [inv. twin]	-0.05(3)	0.03(6)	-0.01(4)	-0.06(4)

S2. Crystallographic information for the new crystal structures

	65	**66**	**67**	**68**	**69**	**89**
CCDC number	2120810	2120816	2120811	2120817	2120813	2120815
Moiety formula	$[C_9H_8N_3O_2S_2]^-$, $[C_5H_{14}N_3]^+$	$[C_9H_8N_3O_2S_2]^-$, $[C_6H_{14}N]^+$	$[C_9H_8N_3O_2S_2]^-$, $[C_2H_8N]^+$	$[C_9H_8N_3O_2S_2]^-$, $[C_2H_9N_2]^+$	$[C_9H_8N_3O_2S_2]^-$, $[C_5H_{13}N_2]^+$	$C_9H_9N_3O_2S_2$, $[C_9H_8N_3O_2S_2]^-$, $[C_{15}H_{27}N_2]^+$
Total formula	$C_{14}H_{22}N_6O_2S_2$	$C_{15}H_{22}N_4O_2S_2$	$C_{11}H_{16}N_4O_2S_2$	$C_{11}H_{17}N_5O_2S_2$	$C_{14}H_{21}N_5O_2S_2$	$C_{33}H_{44}N_8O_4S_4$
Formula weight	370.49	354.48	300.40	315.41	355.48	745.00
Temperature / K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	P 21	P 21/c	P 21/c	C 2/c	P 21 21 21	P 21
a / Å	10.449(2)	8.081(2)	20.623(4)	10.838(2)	8.401(2)	16.676(3)
b / Å	13.331(3)	16.676(2)	8.3200(17)	11.826(2)	11.142(2)	11.771(2)
c / Å	13.664(3)	13.1690(7)	18.157(4)	22.321(4)	17.746(4)	19.062(4)
α / °	90	90	90	90	90	90
β / °	110.38(3)	104.56(2)	115.64(3)	90.14(3)	90	111.71(3)
γ / °	90	90	90	90	90	90
Unit-cell volume / $Å^3$	1784.2(7)	1717.6(5)	2808.7(12)	2860.9(9)	1661.1(6)	3476.3(13)
Z	4	4	8	8	4	4
Calc. density / g cm^{-3}	1.379	1.371	1.421	1.465	1.421	1.423
F(000)	784	752	1264	1328	752	1576
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Absorption coefficient / mm^{-1}	0.319	0.325	0.383	0.381	0.337	0.325
Crystal size / mm^3	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20
2θ range / °	7.06-52.72	7.14-49.86	2.19-50.16	7.13-55.07	7.31-42.06	7.29-50.09
Completeness to max 2θ	0.894	0.817	0.983	0.985	0.987	0.993
No. of reflections measured	15098	6680	15775	12059	6966	27570
No. of independent reflections	6430	2450	4914	3207	1772	11517
R(int)	0.0896	0.0939	0.1094	0.0467	0.0822	0.0409
No. parameters / restraints	441 / 1	218 / 3	348 / 0	211 / 12	226 / 6	883 / 1
Final *R*1 values [$I > 2\sigma(I)$]	0.0652	0.0399	0.0869	0.0371	0.0317	0.0413
Final $wR(F^2)$ values (all data)	0.1059	0.0945	0.2265	0.0877	0.0671	0.1026
Goodness-of-fit on F^2	1.066	0.941	1.046	1.064	1.037	1.028
Largest difference peak & hole / e $Å^{-3}$	0.305, -0.398	0.248, -0.288	0.841, -0.432	0.238, -0.431	0.175, -0.178	0.320, -0.347
Flack parameter	-0.06(6)				-0.06(7)	0.00(4)

S3. Details of DFT-D minimisation

Prior to energy minimisation, the positions of all H atoms in the X-ray structures were normalised using the default settings in *Mercury* to produce starting positions close to nuclear positions. DFT-D calculations were then made using *CASTEP via* the interface in *Materials Studio*. The PBE exchange-correlation functional was applied, with a dispersion correction according to Grimme. The plane-wave basis-set cut-off was set to 340 eV and all other parameters were set to the "Fine" defaults in *Materials Studio*. Unit-cell parameters were constrained in each case to those from the reported crystal structure and the space-group symmetry was imposed. In the structures showing solvent disorder, models were constructed for each disorder component and minimised separately. One structure was then chosen for subsequent analysis, as described below. Structures in centred space groups were converted to a primitive setting for efficient minimisation, then subsequently restored to the centred space group. Minimised structures were compared to the starting structures using the method described by van de Streek and Neumann, confirming that the changes in atomic positions do not significantly distort the crystal structure (results are included in the optimised CIFs).

6: the solvent molecules lie on inversion centres in space group $P2_1/c$, so the symmetry was reduced to *Pc* to produce complete molecules. The minimised structure in *Pc* was confirmed to conform to $P2_1/c$ (*i.e.* the diethyloxalate molecule and its environment retains inversion symmetry) and subsequently restored to that group.

8: although the location of the solvent molecule was clear from the X-ray data, the electron density comprised an overlay of several orientations that could not easily be resolved. The most prominent set of peaks in the electron density was modelled with restraints to provide a starting set for energy minimisation. Small changes in atomic positions on minimisation suggest that the result is a satisfactory representation of the X-ray structure.

11, 14: one disorder component of the solvent molecule was clearly dominant (75-80%) in the X-ray structure, and in both cases the structure containing only this component led to satisfactory minimisation. The minor disorder component led to significantly larger atomic displacements on minimisation, consistent with a less well-defined starting model. The structure containing the major component was retained in the standardised set.

15, 18, 22, 26, 60: two disorder components of the solvent molecule have close to equal occupancy in the X-ray refinements and both disorder components led to satisfactory minimisation. The orientation of the solvent has no impact on the resulting analysis, so one structure was chosen arbitrarily in each case to be retained in the standardised set.

S3. Details of DFT-D minimisation

28, 29, 30: the solvent molecules lie on inversion centres in space group $P2_1/n$, so the symmetry was reduced to $P2_1$ to produce complete molecules. The minimised structure in $P2_1$ was confirmed to conform to $P2_1/n$ and subsequently restored to that group.

32: the solvent molecule shows a consistent position for the nitrile group, but apparent disorder of the alkyl chain. The major occupancy component (*ca* 63%) was chosen arbitrarily as the starting position for the alkyl chain and minimisation proceeded satisfactorily.

35: the X-ray structure in space group $P2_1/n$ includes disorder of the non-centrosymmetric azelanitrile molecules around crystallographic inversion centres. The symmetry was reduced to space group $P2_1$ to accommodate the azelanitrile molecules without disorder and the $P2_1$ model is retained in the standardised set. The SLFZ molecules alone define space group $P2_1/n$ (comparable to the structures of **1n**–**7n**) and the minimised structure was restored to $P2_1/n$ in the structure set containing SLFZ molecules only.

50: the structure in the CSD (LOFLUP) shows disorder of the pentanedioic acid molecule. The two disorder components show different hydrogen-bond patterns at one end of the carboxylic acid molecule, forming either an O—H···O interaction to one SLFZ molecule or an O—H···N interaction to a neighbouring SLFZ. The two components were extracted and minimised separately, and the structure containing the O—H···O interaction was found to be lower in energy. Hence, this structure was retained in the DFT-optimised set.

52: the structure in the CSD (SOGSEO) has one H atom missing from SLFZ. The structure contains the prominent centrosymmetric $R_2^2(8)$ H-bonded dimer, so it is evident that the missing H atom should be attached to N13. The corrected structure is included in the DFT-optimised set.

53: the structure in the CSD (STHSAM01) contains one rogue H atom position, which should be part of the SLFZ NH_2 group. The H atom was placed on N11 prior to minimisation and the corrected structure is included in the DFT-optimised set.

71: the structure in the CSD (BUWDUT) shows disorder of $[SiF_6]^{2-}$ around a crystallographic 2-fold axis. The structure was reduced to space group *Cc* and only the major component of $[SiF_6]^{2-}$ was kept. After minimisation, the structure could be restored to space group *C*2/*c*, without imposing disorder on $[SiF_6]^{2-}$ (i.e. the optimised position of $[SiF_6]^{2-}$ conforms to the 2-fold symmetry).

83: the structure (VEYQUO) includes disorder of the $(H)NO_3$ molecules, in a ratio of approximately 82:18%. The atoms of the minority component were deleted, and minimisation proceeded satisfactorily to give the structure included in the DFT-optimised set.

S3. Details of DFT-D minimisation

85: the published structure (VEYREZ) in space group *C*2/*c* imposes disorder on the SO_4^{2-}/H_2O molecules, and the thiazole ring of sulfathiazole is split into two closely-spaced positions. The structure was converted to space group *Cc*, with two independent sulfathiazole molecules, to permit an ordered arrangement to be defined for SO_4^{2-} and H_2O. The two independent thiazole rings in the minimised structure in *Cc* reproduce the split-site model when averaged back to space group *C*2/*c*. The minimised model in *Cc* is retained in the full standardised set to eliminate the SO_4^{2-}/H_2O disorder. However, given the closeness of the SLFZ molecules to *C*2/*c*, the higher-symmetry model was used for the purposes of comparing SLFZ molecules only.

86: the published structure in *Pbcn* (VEYYEG) includes overlaid positions for the benzenesulfonate anions, which can be separated into two different ordered structures in space groups $Pca2_1$ and $Pna2_1$. The structures contain identical positions for SLFZ, so the choice does not affect the subsequent analysis. The $Pna2_1$ structure is included in the full DFT-optimised set. For the structure set containing SLFZ molecules only, the minimised structure was restored to the centrosymmetric group *Pnab* (retaining correspondence of the unit cell with the $Pna2_1$ version).

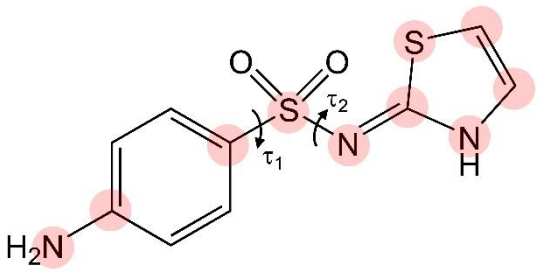
87: the structure in the CSD (FIFWOJ) is reported in space group *P*–1 with Z′ = 2. The correct space group is actually $P2_1/n$ with Z′ = 1. The $P2_1/n$ version was constructed for minimisation, and is included in the DFT-optimised set.

References

- **Materials Studio**: Accelrys, *Materials Studio v. 6.0*, San Diego, California, USA, 2011.
- **CASTEP**: S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson and M. C. Payne, *Z. Kristallogr.*, 2005, **220**, 567.
- **PBE functional**: J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- **Dispersion correction**: S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787.
- **Structure Comparison**: J. Van de Streek and M. A. Neumann, *Acta Cryst. Sect. B*., 2010, **66**, 544.

S4. Molecular conformation and torsion angles

Based on the analysis by Kálmán *et al.* (*Acta Cryst.* 1981, **B37**, 868-977), the molecular conformation of SLFZ is described principally by two torsion angles:



τ_1 = N12—S11—C14—(C13 or C15)

τ_2 = C14—S11—N12—C17

The *R* conformation shows a negative value for τ_2 in the range 0 to –180°.

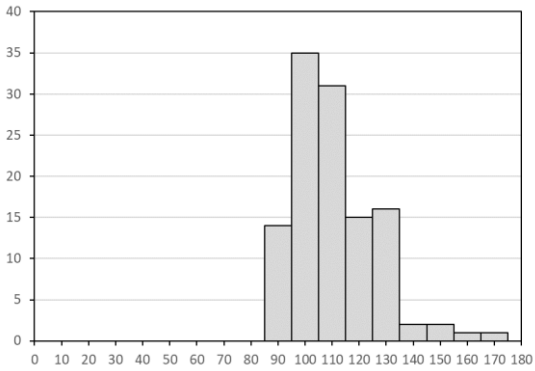
The *S* conformation shows a positive value for τ_2 in the range 0 to +180°.

In both cases, C13 or C15 is selected to give the largest absolute value of τ_1.

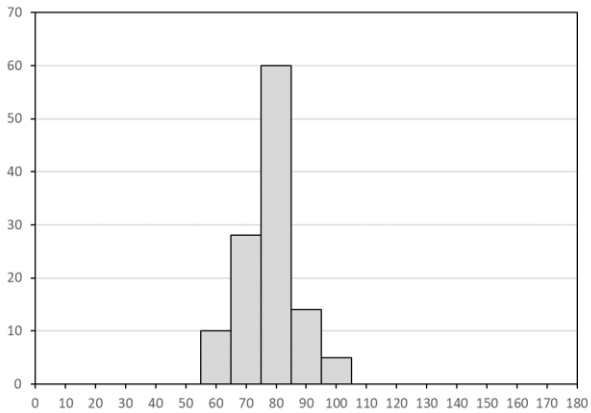
To compare molecules, both τ_1 and τ_2 are considered as absolute values.

<u>Histograms of $|\tau_1|$ and $|\tau_2|$ values for all 96 structures</u>:

Values are grouped at 10° intervals with a range ±5° (*e.g.* the bin centred at 110° contains values in the range 105–115°).



$|\tau_1|$



$|\tau_2|$

The tail to the right of the distribution for $|\tau_1|$ is populated principally by salts.

S4. Molecular conformation and torsion angles

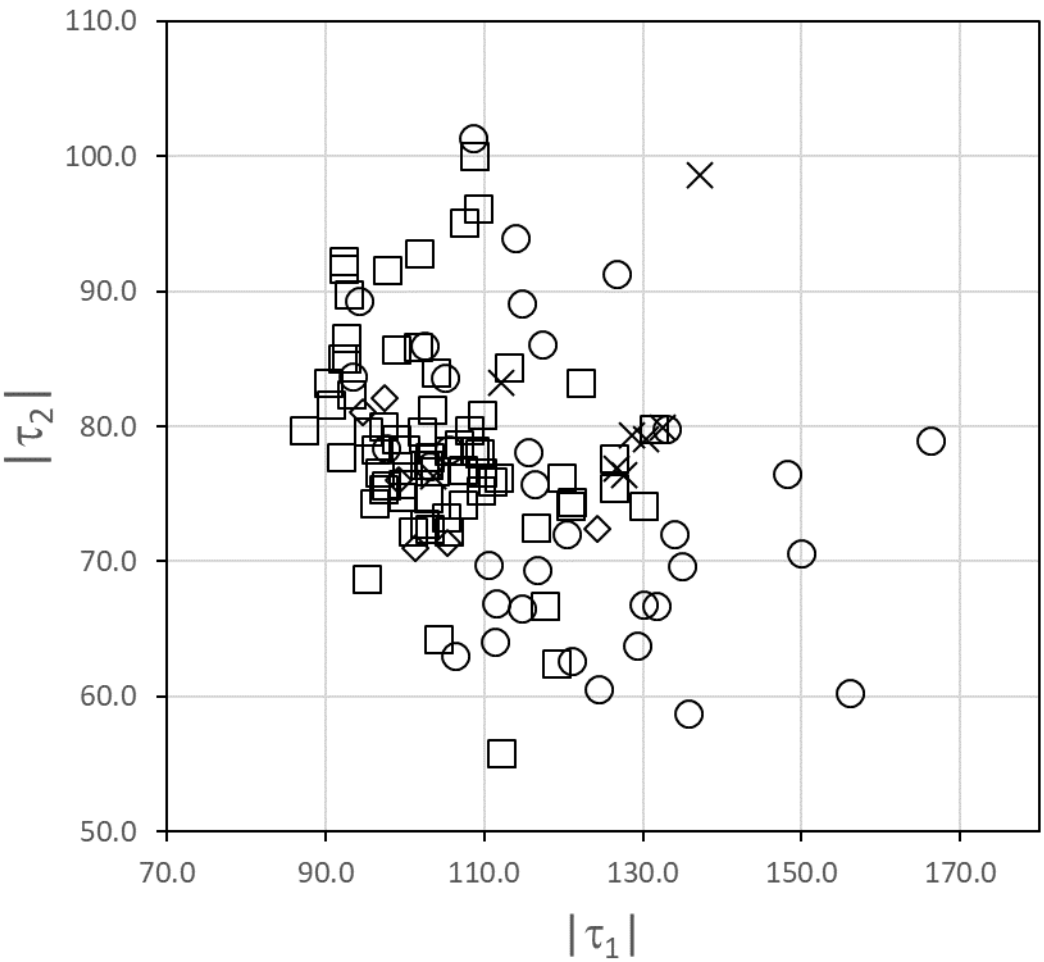
Scattergram of $|\tau_2|$ vs $|\tau_1|$ values for all 96 structures:

× = polymorphs

□ = co-crystals

○ = salts

◊ = other



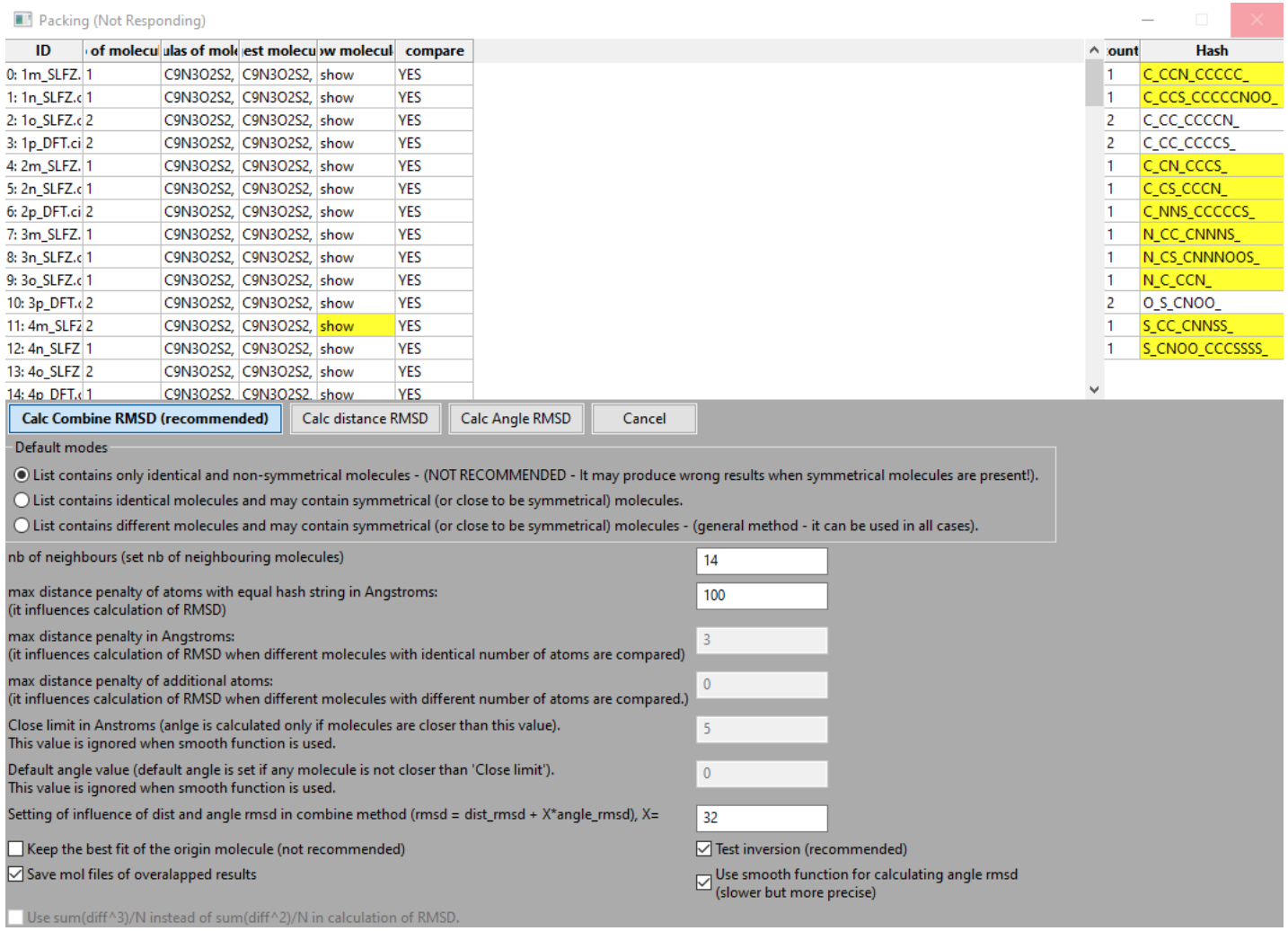
The outlier amongst the polymorphs (τ_1 = 137.2, τ_2 = 98.6°) is molecule 1 in **2p**.

S4. Molecular conformation and torsion angles

			τ_1	τ_2					τ_1	τ_2
1p	01	R	112.2	−83.2		**43**	01	R	117.6	−66.7
	02	R	103.6	−76.3		**44**	01	R	92.6	−85.0
2p	01	R	137.2	−98.6		**45**	01	R	92.0	−77.7
	02	S	−132.5	79.9			02	R	104.0	−84.0
3p	01	R	127.7	−76.4		**46**	01	R	120.8	−74.1
	02	R	128.6	−79.3		**47**	01	R	100.0	−78.3
4p	01	R	126.7	−76.9		**48**	01	R	122.1	−83.2
5p	01	R	130.4	−79.1		**49**	01	R	103.4	−81.2
1	01	R	95.2	−68.7		**50**	01	R	92.3	−91.7
	02	R	121.0	−74.4		**51**	01	R	−107.5	−95.1
2	01	R	111.9	−76.2		**52**	01	R	−101.9	−92.8
3	01	R	−108.7	−100.0		**53**	01	R	131.3	−79.8
	02	R	109.7	−80.9		**54**	01	R	90.3	−83.2
4	01	R	96.9	−76.6		**55**	01	R	107.4	−76.8
	02	R	119.1	−62.5		**56**	01	R	109.4	−78.0
5	01	R	-109.2	−96.1		**57**	01	R	108.8	−78.2
6	01	R	119.8	−76.2		**58**	01	R	109.8	−76.6
7	01	R	109.5	−75.3		**59**	01	R	111.1	−75.9
8	01	R	97.3	−75.4		**60**	01	R	120.4	−72.0
9	01	R	101.0	−72.2		**61**	01	R	150.0	−70.6
10	01	R	130.1	−74.1		**62**	01	R	116.7	−69.4
11	01	R	97.7	−75.6		**63**	01	R	114.7	−66.5
12	01	R	103.0	−74.7		**64**	01	R	111.5	−66.9
13	01	R	103.1	−72.4		**65**	01	R	105.1	−83.6
14	01	R	105.3	−73.3			02	R	135.7	−58.8
15	01	R	96.2	−74.3		**66**	01	R	129.2	−63.8
16	01	R	126.3	−75.5		**67**	01	R	103.1	−77.1
17	01	R	126.4	−77.6			02	S	−97.6	78.4
18	01	R	103.1	−77.7		**68**	01	R	130.0	−66.8
19	01	R	116.6	−72.5		**69**	01	R	106.3	−63.0
20	01	R	104.3	−64.3		**70**	01	R	116.3	−75.7
	02	S	−106.8	78.7		**71**	01	R	−113.9	−94.0
21	01	R	96.4	−78.3		**72**	01	R	111.4	−64.1
22	01	R	99.7	−74.8		**73**	01	R	110.5	−69.8
23	01	R	90.7	−81.6		**74**	01	R	131.7	−66.7
	02	S	−113.2	84.4		**75**	01	R	93.4	−83.7
24	01	R	112.2	−55.8		**76**	01	R	102.4	−86.0
25	01	R	87.3	−79.7		**77**	01	R	121.1	−62.6
	02	S	−102.2	79.6		**78**	01	R	105.6	−78.3
26	01	R	92.3	−92.3		**79**	01	R	124.5	−60.6
27	01	R	97.8	−91.6		**80**	01	R	134.9	−69.7
28	01	R	103.8	−76.7			02	R	−94.2	−89.3
29	01	R	105.5	−72.2		**81**	01	R	115.6	−78.1
30	01	R	97.3	−80.0		**82**	01	R	156.1	−60.3
31	01	R	105.6	−78.2		**83**	01	R	148.2	−76.5
32	01	R	102.9	−77.2			02	R	133.0	−79.8
33	01	R	92.1	−85.0		**84**	01	R	166.3	−79.0
34	01	R	−92.7	−86.6		**85**	01	R	−126.7	−91.3
35	01	R	102.4	−72.8		**86**	01	R	114.8	−89.1
36	01	R	101.6	−85.9			02	R	117.4	−86.1
37	01	R	108.1	−79.7		**87**	01	R	−108.6	−101.4
38	01	R	−92.9	−89.8		**88**	01	R	133.9	−72.0
39	01	R	95.3	−79.6		**89**	01	R	105.4	−71.4
	02	R	102.4	−77.2			02	S	−94.7	81.1
40	01	R	93.3	−82.4			03	R	97.5	−82.1
	02	R	99.0	−79.1			04	S	−99.3	76.0
41	01	R	99.8	−75.7		**90**	01	R	124.3	−72.4
	02	R	98.9	−85.7		**91**	01	R	101.4	−71.0
42	01	R	107.4	−74.2						

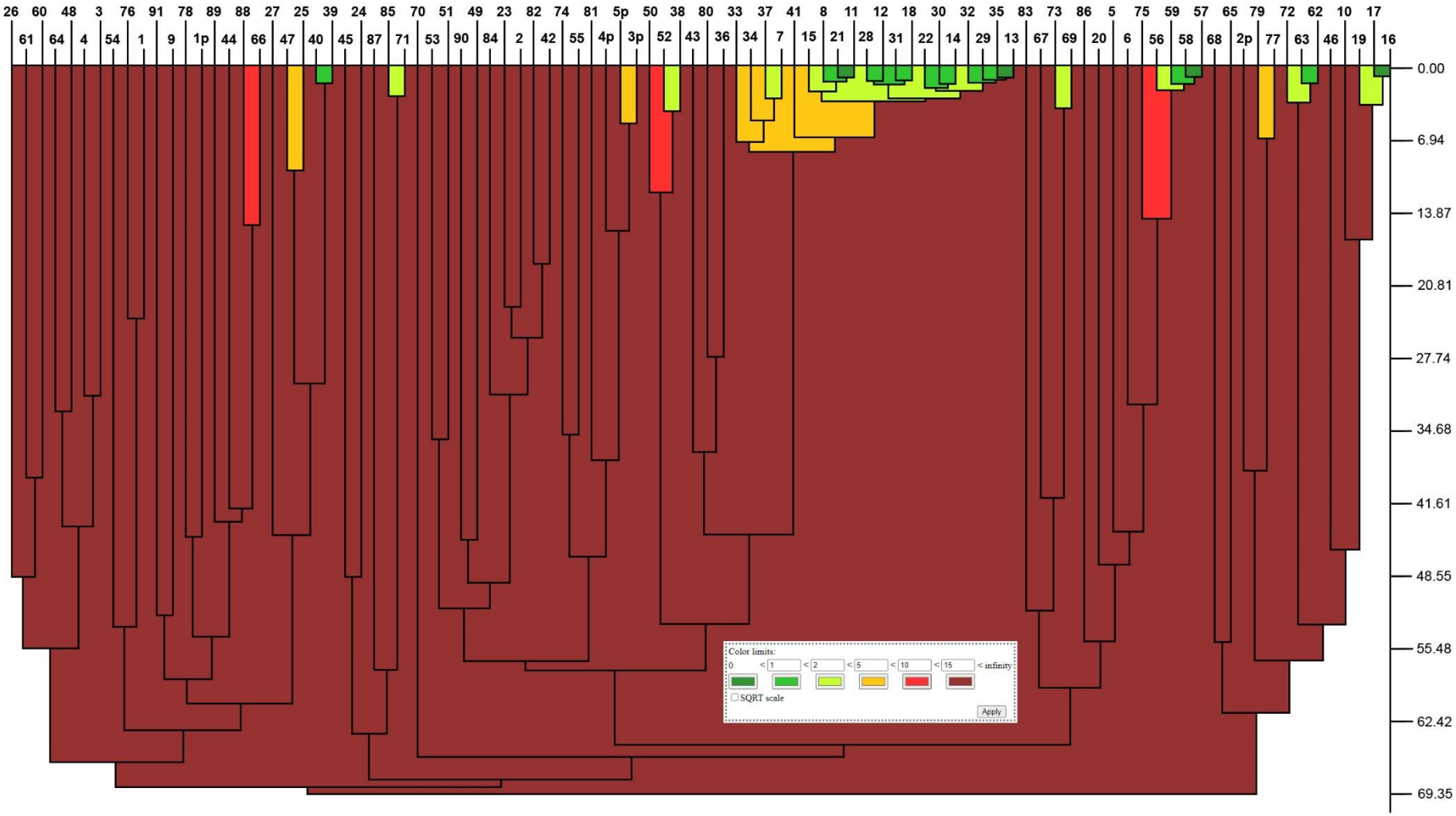
S5. *CrystalCMP*

CrystalCMP rev. 111 (1st April 2020). 96 *vs* 96 Packing Similarity with the following settings:



S5. *CrystalCMP*

***CrystalCMP* dendrogram calculated using WPGMA method (weighted pair group method with arithmetic mean):**



S5. *CrystalCMP*

***CrystalCMP* similarity matrices for clusters linked at PS_{AB} < 15:**

Groups 1 and 2

	8	11	12	13	14	15	18	21	22	28	29	30	31	32	33	34	35	41		7	37
8		1.1557	3.5342	2.5501	2.5711	1.7395	2.0638	1.3893	1.8075	4.1215	3.662	3.1305	3.1052	3.7156	6.3709	3.6061	2.8737	6.0247		7.1301	7.8110
11			2.7861	2.2016	2.6276	2.5689	1.2545	0.8835	2.0243	2.5838	2.5417	2.7387	1.7811	2.8482	5.8113	3.5656	1.9132	6.0991		6.2087	6.7172
12				2.6077	3.516	4.8128	1.9265	2.9925	3.5647	1.3286	2.4386	3.9837	1.296	3.0255	8.3533	6.2879	2.0584	7.1957		9.1357	9.4570
13					1.5728	3.3836	1.9591	2.639	1.653	3.1346	1.144	2.0302	1.9075	1.4625	6.1065	6.2719	0.8764	6.6737		8.7697	7.9609
14						3.1466	3.2276	3.5747	2.0257	3.8435	1.9895	1.4833	2.8022	1.7384	4.9982	6.025	1.9926	6.7133		7.8377	7.7251
15							3.4473	2.7568	2.4901	5.1375	4.1277	3.2595	4.1311	4.1077	5.4617	3.6868	3.5994	6.5793		6.7601	7.0738
18								1.4088	2.1897	2.2201	2.4008	2.9845	1.2221	2.8341	6.6154	4.425	1.7018	6.3347		7.4309	7.4515
21									2.2845	3.0591	3.2774	3.1774	2.2822	3.608	6.2046	3.3632	2.5849	6.1063		6.2138	6.6221
22										4.1467	2.4898	1.7487	2.8609	2.4608	5.5242	4.5525	2.023	5.7391		8.3089	7.2815
28											3.062	5.2706	1.3308	3.8012	11.1075	7.7501	2.603	7.4974		10.2857	10.6814
29												2.7282	1.6611	1.1785	7.8386	7.572	1.0789	7.0872		12.6719	11.6972
30													2.7417	2.0874	4.9129	5.112	2.5465	7.3701		8.8904	6.6281
31														2.6965	9.0394	6.4166	1.5071	6.9327		9.8519	9.6402
32															6.9291	7.2322	1.6585	7.5033		11.328	10.0407
33																5.821	6.824	9.7267		10.4137	7.4806
34																	6.2587	6.6166		4.9535	5.5669
35																		6.6492		11.0657	10.4111
41																				9.7865	10.2171
7																					2.8882
37																					

S5. *CrystalCMP*

***CrystalCMP* similarity matrices for clusters linked at PS_{AB} < 15:**

Group 3 (co-crystals)

	56	57	58	59
56		1.3479	1.7304	2.6460
57			0.8054	1.7462
58				1.2605
59				

Group 4 (salts)

	62	63	72
62		1.4198	3.7785
63			2.7226
72			

Group 5 (co-crystals)

	16	17	19
16		0.7764	3.7061
17			3.3173
18			

Group 6 (salts)

	71	85
71		2.6403
85		

Group 7 (salts)

	69	73
69		3.8504
73		

Group 8 (co-crystals)

	25	47
25		9.7542
47		

Group 9 (salts)**

	38	52
38		4.1144
52		

Group 10 (co-crystals)

	39	40
39		1.4640
40		

Group 11 (salts)

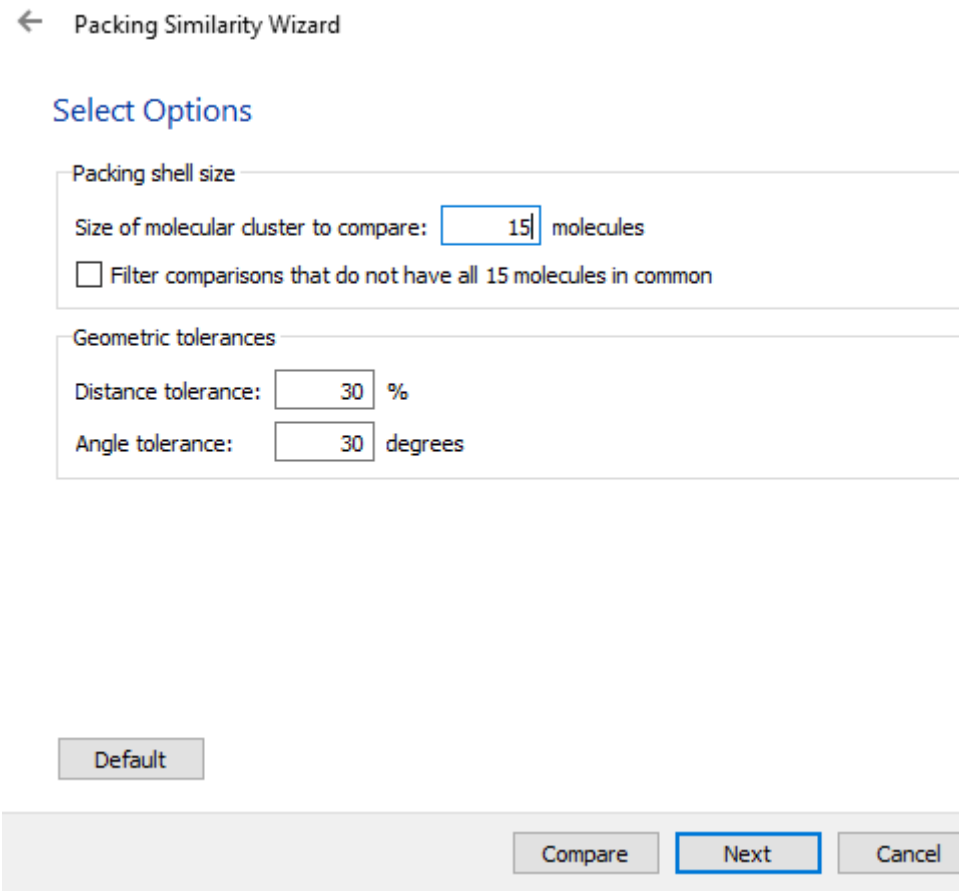
	77	79
77		6.7122
79		

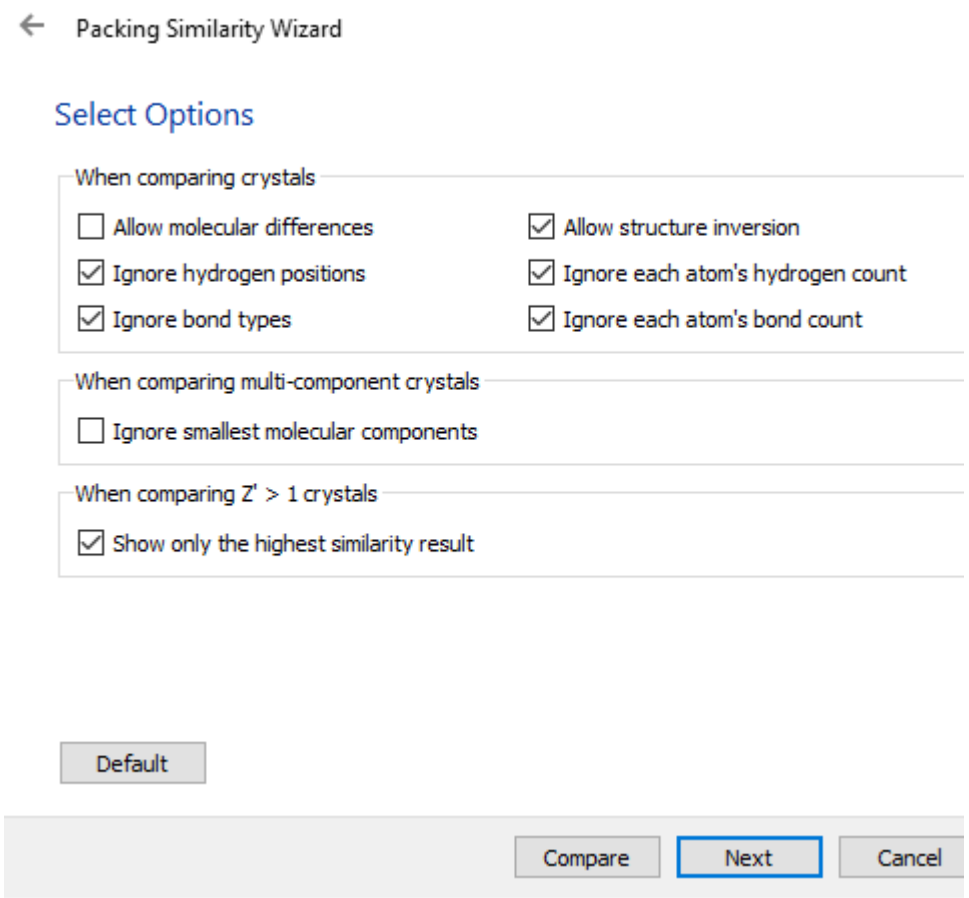
Group 12 (salts)

	66	88
66		14.9780
88		

** Structure **50** is linked to Group 9 in the dendrogram, but is not considered to belong to this group – see main text.

S6. *COMPACK*


Packing Similarity Wizard
Select Options
Packing shell size
Size of molecular cluster to compare: 15 molecules
Filter comparisons that do not have all 15 molecules in common
Geometric tolerances
Distance tolerance: 30 %
Angle tolerance: 30 degrees
Default
Compare
Next
Cancel


Packing Similarity Wizard
Select Options
When comparing crystals
Allow molecular differences
Allow structure inversion
Ignore hydrogen positions
Ignore each atom's hydrogen count
Ignore bond types
Ignore each atom's bond count
When comparing multi-component crystals
Ignore smallest molecular components
When comparing Z' > 1 crystals
Show only the highest similarity result
Default
Compare
Next
Cancel

S6. *COMPACK*

COMPACK (30%, 30°): full list of results is provided as an *Excel* archive.

Automatic grouping of 15-molecule similarity:

(Group numbers generated by *COMPACK* are not those in Table 2 in the manuscript, but the results are consistent).

COMPACK_96_vs_96_30_30 Options

group	spacegroup	density (g/cc)	a	b	c	alpha	beta	gamma
group1								
66_SLFZ	P21/c	0	8.081	16.676	13.169	90	104.56	90
88_SLFZ	P21/c	0	8.8101	17.1707	13.2499	90	101.1	90
group2								
69_SLFZ	P212121	0	8.401	11.142	17.746	90	90	90
73_SLFZ	P212121	0	8.4158	10.181	17.941	90	90	90
group3								
37_SLFZ	P21/c	0	8.39	18.813	9.54	90	102.54	90
7_SLFZ	P21/c	0	8.636	19.187	9.354	90	91.03	90
group4								
38_SLFZ	P21/c	0	8.167	12.443	15.632	90	96.88	90
52_SLFZ	P21/c	0	8.2576	12.1531	16.5609	90	98.785	90
group5								
39_SLFZ	Pbca	0	9.045	16.864	39.421	90	90	90
40_SLFZ	Pbca	0	9.179	16.907	39.202	90	90	90
group6								
19_SLFZ	P21/n	0	6.572	12.959	21.533	90	92.48	90
16_SLFZ	P21/n	0	6.487	12.332	22.259	90	94.19	90
17_SLFZ	P21/n	0	6.613	12.074	22.085	90	93.44	90
group7								
25_SLFZ	P212121	0	9.515	16.675	19.249	90	90	90
47_SLFZ	Pbca	0	9.424	17.195	19.56	90	90	90
group8								
71_SLFZ	C2/c	0	17.723	11.684	11.938	90	91.78	90
85_SLFZ	C2/c	0	17.4737	11.624	11.7557	90	90.072	90
group9								
63_SLFZ	P212121	0	6.592	15.155	15.689	90	90	90
72_SLFZ	P212121	0	6.62	15.349	17.148	90	90	90
62_SLFZ	P212121	0	6.948	14.868	15.958	90	90	90
group10								
77_SLFZ	P21/c	0	7.8774	12.109	16.2492	90	105.532	90
79_SLFZ	P21/c	0	8.0122	12.7431	16.7992	90	102.2	90
group11								
56_SLFZ	P21/n	0	8.5007	18.8407	10.5066	90	104.507	90
57_SLFZ	P21/n	0	8.3577	19.2806	10.9972	90	105.064	90
58_SLFZ	P21/n	0	8.4031	19.2762	10.9624	90	106.229	90
59_SLFZ	P21/n	0	8.3786	19.6447	11.1172	90	106.885	90
group12								
33_SLFZ	P21/n	0	9.112	18.994	10.59	90	101.37	90
34_SLFZ	P21/n	0	8.3551	18.88	10.7764	90	96.79	90
21_SLFZ	P21/n	0	8.454	20.699	9.487	90	92.37	90
22_SLFZ	P21/n	0	8.583	20.652	9.52	90	93.66	90
13_SLFZ	P21/n	0	8.628	21.151	9.135	90	97.7	90
14_SLFZ	P21/n	0	8.606	21.643	8.735	90	98.76	90
15_SLFZ	P21/n	0	8.55	21.491	9.215	90	90.27	90
18_SLFZ	P21/n	0	8.417	20.975	9.472	90	93.83	90
28_SLFZ	P21/n	0	8.01	20.82	8.99	90	94.65	90
29_SLFZ	P21/n	0	8.523	21.073	9.087	90	96.54	90
30_SLFZ	P21/n	0	8.6785	19.911	10.0217	90	97.776	90
31_SLFZ	P21/n	0	8.2478	21.0191	9.0739	90	96.534	90
32_SLFZ	P21/n	0	8.4758	20.7179	9.6108	90	97.84	90
8_SLFZ	P21/n	0	8.392	21.207	9.302	90	93.12	90
11_SLFZ	P21/n	0	8.366	21.353	9.097	90	93.37	90
12_SLFZ	P21/n	0	8.194	21.111	9.57	90	94.2	90
35_SLFZ	P21/n	0	8.363	21.146	9.116	90	95.76	90
41_SLFZ	P21/c	0	12.213	20.55	13.583	90	97.03	90

S6. *COMPACK*

COMPACK (30%, 30°): full list of results is provided as an *Excel* archive.

Similarity matrices (RMSD. Not highlighted = 15 matched molecules matched. Highlighted = no. of matched molecules in parentheses):

Group 1

	8	11	12	13	14	15	18	21	22	28	29	30	31	32	33	34	35	41
8		0.3179	0.4932	0.5115	0.6968	0.3362	0.4173	0.4292	0.2638	0.7475	0.5461	0.6864	0.6323	0.4785	1.0798 (13)	1.1039	0.4477	0.7871
11			0.3684	0.3416	0.6330	0.5542	0.2789	0.3545	0.3657	0.4856	0.3461	0.7120	0.3697	0.4896	1.1877 (13)	1.2576 (10)	0.2628	0.7989
12				0.4891	0.8659	0.7550	0.2170	0.3465	0.4210	0.4488	0.4563	0.6227	0.4081	0.4669	1.2181 (13)	1.1785 (10)	0.3883	0.8031
13					0.4578	0.7562	0.4433	0.5634	0.4810	0.5164	0.1334	0.6736	0.3267	0.3753	1.1200 (13)	1.3423 (10)	0.1834	1.0096
14						0.8472	0.8342	0.9385	0.7851	0.8259	0.4995	0.9938	0.6594	0.6188	1.2717 (13)	1.5916 (10)	0.5046	1.2710
15							0.6679	0.631	0.4779	0.9983	0.7776	0.7679 (8)	0.9043	0.7425	1.2220 (13)	1.2918 (10)	0.7023	0.7263
18								0.1751	0.3041	0.5125	0.4437	0.5445	0.4151	0.4678	1.0934 (13)	1.1098 (10)	0.3914	0.7185
21									0.2966	0.6210	0.5704	0.5568	0.5499	0.5737	1.0309 (13)	1.0108	0.5182	0.6183
22										0.7272	0.5085	0.4830	0.6078	0.3963	0.9174 (13)	1.0053	0.4504	0.6944
28											0.4376	0.7049 (8)	0.2368	0.6868	1.4423 (13)	1.4529 (10)	0.4177	1.0089
29												0.7221	0.2877	0.4114	1.1890 (13)	1.3839 (10)	0.1359	0.9869
30													0.7574	0.4501	0.6516	0.7836	0.7074	0.9986
31														0.5241	1.2803 (13)	1.3625 (10)	0.2780	0.9979
32															0.9815 (14)	1.0920	0.3735	0.9850
33																0.6485	1.1914 (13)	1.2906 (14)
34																	1.3322 (10)	1.2830 (10)
35																		0.9437
41																		

S6. *COMPACK*

COMPACK (30%, 30°): full list of results is provided as an *Excel* archive.

Similarity matrices (RMSD, 15 molecules matched):

Group 2 (co-crystals)

	7	37
7		0.9113
37		

Group 3 (co-crystals)

	56	57	58	59
56		0.2955	0.2971	0.4661
57			0.0937	0.2334
58				0.1900
59				

Group 4 (salts)

	62	63	72
62		0.3177	0.8474
63			0.7503
72			

Group 5 (co-crystals)

	16	17	19
16		0.1676	0.5991
17			0.6199
18			

Group 6 (salts)

	71	85
71		0.2950
85		

Group 7 (salts)

	69	73
69		0.5222
73		

Group 8 (co-crystals)

	25	47
25		0.6716
47		

Group 9 (salts)

	38	52
38		0.5869
52		

Group 10 (co-crystals)

	39	40
39		0.1477
40		

Group 11 (salts)

	77	79
77		0.5568
79		

Group 12 (salts)

	66	88
66		1.1390
88		

S7. *XPac*

Summary of supramolecular constructs (SCs) identified in the polymorphs using "high" tolerances (δ_{ang} = 12, δ_{dhd} = 18°).

Symmetry operators/axis directions refer to the structure indicated in the row (e.g. **1p**:1555_01,3676_01 matches to **3p**:1555_01,3657_01)

Key: 0-D = pink, 1-D = amber, 2-D = blue, 3-D = green

	1p	2p	3p	4p	5p
1p		—	1555_01 3676_01	1555_01 3676_01	—
2p	—		1555_02 3667_02	1555_02 3667_02	1555_02 3667_02
3p	1555_01 3657_01	1555_01 4555_02		[010] [001]	[010] [001]
4p	1555_01 3676_01	1555_01 3576_01	[010] [001]		[010] [001]
5p	—	1555_01 3677_01	[010] [101]	[010] [101]	

S7. *XPac*

Comparison of the 91 multi-component structures vs the polymorphs using "high" tolerances (δ_{ang} = 12, δ_{dhd} = 18°).

Symmetry codes of the matching molecules refer to the structures of the polymorphs. Key: 0-D = pink, 1-D = amber, 2-D = blue, 3-D = green

	1p_01	1p_02	2p_01	2p_02	3p_01	3p_02	4p	5p
1	1555_01 3776_01	1555_02 3755_02	1555_01 3666_01	1555_02 3567_02		1555_02 3767_02		1555_01 3577_01 1555_01 3676_01
2					1555_01 2646_02		[100] 1555_01 1455_01 1655_01	
3					1555_01 2646_02		[100] 1555_01 1455_01 1655_01	
4	NO MATCH							
5	1555_01 3776_01	1555_02 3755_02					[100] 1555_01 1455_01 1655_01	
6	1555_01 3776_01	1555_02 3755_02						
7	1555_01 3776_01	1555_02 3755_02						
8	1555_01 3776_01	1555_02 3755_02						
9	1555_01 3776_01	1555_02 3755_02						
10							1555_01 3666_01	
11	1555_01 3776_01	1555_02 3755_02						

Comparison of the 91 multi-component structures vs the polymorphs using "high" tolerances (δ_{ang} = 12, δ_{dhd} = 18°).

Symmetry codes of the matching molecules refer to the structures of the polymorphs. Key: 0-D = pink, 1-D = amber, 2-D = blue, 3-D = green

	1p_01	1p_02	2p_01	2p_02	3p_01	3p_02	4p	5p
12	1555_01 3776_01	1555_02 3755_02						
13	1555_01 3776_01	1555_02 3755_02						
14	1555_01 3776_01	1555_02 3755_02						
15	1555_01 3776_01	1555_02 3755_02						
16	1555_01 3776_01	1555_02 3755_02						
17	1555_01 3776_01	1555_02 3755_02						
18	1555_01 3776_01	1555_02 3755_02						
19	1555_01 3776_01	1555_02 3755_02						
20	1555_01 3776_01	1555_02 3755_02	1555_01 3666_01	1555_02 3567_02				
21	1555_01 3776_01	1555_02 3755_02						
22	1555_01 3776_01	1555_02 3755_02						
23	1555_01 3776_01	1555_02 3755_02 1555_02 3655_02	1555_01 3666_01		1555_01 3657_01		1555_01 3676_01	
24	1555_01 3776_01	1555_02 3755_02						
25	1555_01 3776_01	1555_02 3755_02						
26	NO MATCH							

Comparison of the 91 multi-component structures vs the polymorphs using "high" tolerances (δ_{ang} = 12, δ_{dhd} = 18°).

Symmetry codes of the matching molecules refer to the structures of the polymorphs. Key: 0-D = pink, 1-D = amber, 2-D = blue, 3-D = green

	1p_01	1p_02	2p_01	2p_02	3p_01	3p_02	4p	5p
27	1555_01 3776_01	1555_02 3755_02						
28	1555_01 3776_01	1555_02 3755_02						
29	1555_01 3776_01	1555_02 3755_02						
30	1555_01 3776_01	1555_02 3755_02						
31	1555_01 3776_01	1555_02 3755_02						
32	1555_01 3776_01	1555_02 3755_02						
33	1555_01 3776_01	1555_02 3755_02						
34	1555_01 3776_01	1555_02 3755_02						
35	1555_01 3776_01	1555_02 3755_02						
36	1555_01 3776_01	1555_02 3755_02			[100] 1555_01 2746_02 2646_02 1655_01		[100] 1555_01 1455_01 1655_01	[100] 1555_01 1455_01 1655_01
37	1555_01 3776_01	1555_02 3755_02						
38	1555_01 3776_01	1555_02 3755_02			1555_01 2646_02		[100] 1555_01 1455_01 1655_01	
39		1555_02 3655_02						
40	NO MATCH							

Comparison of the 91 multi-component structures vs the polymorphs using "high" tolerances (δ_{ang} = 12, δ_{dhd} = 18°).

Symmetry codes of the matching molecules refer to the structures of the polymorphs. Key: 0-D = pink, 1-D = amber, 2-D = blue, 3-D = green

	1p_01	1p_02	2p_01	2p_02	3p_01	3p_02	4p	5p
41	1555_01 3776_01	1555_02 3755_02						
42		1555_02 3655_02	1555_01 3666_01		1555_01 2646_02		[100] 1555_01 1455_01 1655_01	
43					1555_01 2646_02		[100] 1555_01 1455_01 1655_01	
44	1555_01 3776_01	1555_02 3755_02				1555_02 3767_02		1555_01 3676_01
45		1555_02 3655_02						
46	1555_01 3776_01	[010] [001] 1555_02 2745_02 2755_02 3755_02						
47	1555_01 3776_01	1555_02 3755_02						
48					1555_01 2646_02		[100] 1555_01 1455_01 1655_01	
49	1555_01 3676_01				1555_01 3657_01		1555_01 3676_01	
50	1555_01 3776_01	1555_02 3755_02			1555_01 2646_02		[100] 1555_01 1455_01 1655_01	
51	NO MATCH							

Comparison of the 91 multi-component structures vs the polymorphs using "high" tolerances (δ_{ang} = 12, δ_{dhd} = 18°).

Symmetry codes of the matching molecules refer to the structures of the polymorphs. Key: 0-D = pink, 1-D = amber, 2-D = blue, 3-D = green

	1p_01	1p_02	2p_01	2p_02	3p_01	3p_02	4p	5p
52	1555_01 3776_01	1555_02 3755_02			1555_01 2646_02		[100] 1555_01 1455_01 1655_01	
53	1555_01 3776_01	1555_02 3755_02			1555_01 4565_02		1555_01 3566_01	1555_01 3667_01
54	1555_01 3776_01	1555_02 3755_02				1555_02 3767_02		1555_01 3676_01
55				1555_02 3567_02				
56		1555_02 3655_02	1555_01 3666_01	1555_02 3567_02	1555_01 2646_02		[100] 1555_01 1455_01 1655_01	
57		1555_02 3655_02	1555_01 3666_01		1555_01 2646_02		[100] 1555_01 1455_01 1655_01	
58		1555_02 3655_02	1555_01 3666_01	1555_02 3567_02	1555_01 2646_02		[100] 1555_01 1455_01 1655_01	
59		1555_02 3655_02	1555_01 3666_01	1555_02 3567_02	1555_01 2646_02		[100] 1555_01 1455_01 1655_01	
60	**NO MATCH**							
61	**NO MATCH**							
62	**NO MATCH**							
63	**NO MATCH**							

Comparison of the 91 multi-component structures vs the polymorphs using "high" tolerances (δ_{ang} = 12, δ_{dhd} = 18°).

Symmetry codes of the matching molecules refer to the structures of the polymorphs. Key: 0-D = pink, 1-D = amber, 2-D = blue, 3-D = green

	1p_01	1p_02	2p_01	2p_02	3p_01	3p_02	4p	5p
64					1555_01 2646_02		**[100]** 1555_01 1455_01 1655_01	
65	**[010]** 1555_01 2645_01 2655_01		**[100]** 1555_01 1455_01 1655_01					
66					**[010]** 1555_01 1565_01 1545_01	**[010]** 1555_02 1565_02 1545_02 3777_02 3767_02	**[010]** 1555_01 1545_01 1565_01	**[010]** 1555_01 1545_01 1565_01 3666_01 3676_01
67					1555_01 2646_02 4464_02		**[100]** 1555_01 1455_01 1655_01	1555_01 3666_01
68			1555_01 3766_01	1555_02 3667_02	**[010] ++** 1555_01, 1545_01 1565_01, 4555_02 4565_02, 4545_02		**[010]** 1555_01 1545_01 1565_01 3566_01 3576_01	**[010]** 1555_01 1545_01 1565_01 3667_01 3677_01
69					1555_01 2646_02		**[100]** 1555_01 1455_01 1655_01	
70						1555_02 3767_02		1555_01 3676_01
71					1555_01 2746_02			**[100]** 1555_01 1455_01 1655_01

Comparison of the 91 multi-component structures vs the polymorphs using "high" tolerances (δ_{ang} = 12, δ_{dhd} = 18°).

Symmetry codes of the matching molecules refer to the structures of the polymorphs. Key: 0-D = pink, 1-D = amber, 2-D = blue, 3-D = green

	1p_01	1p_02	2p_01	2p_02	3p_01	3p_02	4p	5p
72	**NO MATCH**							
73					1555_01 2646_02		**[100]** 1555_01 1455_01 1655_01	
74			1555_01 3766_01	1555_02 3667_02	**[010] [001]** 1555_01, 1565_01 1545_01, 3767_01 3757_01, 4555_02 4565_02, 4545_02 2747_02, 2737_02		**[010]** 1555_01 1545_01 1565_01 3566_01 3576_01	**3-D** The mafenide sulfathiazole cations occupy comparable crystallographic sites to SLFZ. Hence, the SLFZ molecules in **74** overlay half of the molecules in **5p**.
75			1555_01 3666_01		1555_01 2646_02		**[100]** 1555_01 1455_01 1655_01	
76				1555_02 3567_02	1555_01 4565_02		1555_01 3566_01	1555_01 3667_01
77					1555_01 4565_02		1555_01 3566_01	1555_01 3667_01
78			1555_01 3666_01	1555_02 3567_02				
79					1555_01 4565_02		1555_01 3566_01	1555_01 3667_01
80	1555_01 3676_01							
81			1555_01 3766_01	1555_02 3667_02	**[010]** 1555_01, 1545_01 1565_01, 4555_02 4565_02, 3767_02 3777_02, 3757_02 2757_01, 2747_01		**[010]** 1555_01 1545_01 1565_01 3566_01 3576_01	**[010] [101]** 1555_01, 1545_01 1565_01, 2646_01 2656_01, 3667_01 3677_01, 4465_01 4564_01

Comparison of the 91 multi-component structures vs the polymorphs using "high" tolerances (δ_{ang} = 12, δ_{dhd} = 18°).

Symmetry codes of the matching molecules refer to the structures of the polymorphs. Key: 0-D = pink, 1-D = amber, 2-D = blue, 3-D = green

	1p_01	1p_02	2p_01	2p_02	3p_01	3p_02	4p	5p
82	**NO MATCH**							
83			1555_01 3766_01	1555_02 3667_02	1555_01 2646_02 3657_01 4555_02 1555_01 2646_02		[100] 1555_01 1455_01 1655_01 3576_01 3676_01	1555_01 3677_01
84				1555_02 3567_02	1555_01 4565_02		1555_01 3566_01	1555_01 3677_01
85					1555_01 2746_02			[100] 1555_01 1455_01 1655_01
86					1555_01 2646_02		[100] 1555_01 1455_01 1655_01	
87	**NO MATCH**							
88					[010] 1555_01 1545_01 1565_01	[010] 1555_02 1545_02 1565_02 3767_02	[010] 1555_01 1545_01 1565_01	[010] 1555_01 1545_01 1565_01 3676_01
89		1555_02 3655_02			1555_01 3767_01			1555_01 3567_01
90			1555_01 3666_01	1555_02 3567_02	1555_01 2646_02		[100] 1555_01 1455_01 1655_01	1555_01 3577_01
91	**NO MATCH**							

S8. Unit-cell parameters for the largest isostructural group in the multi-component crystals

	Space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Vol (Å^3)	Solvent	*Z′* (SLFZ:solv)
8	$P2_1/n$	8.392	21.207	9.302	90	93.12	90	1653.0	$C_5H_8O_2$	1:1
11	$P2_1/n$	8.366	21.353	9.097	90	93.37	90	1622.3	C_4H_5NO	1:1
12	$P2_1/n$	8.194	21.111	9.570	90	94.20	90	1651.0	$C_5H_6O_3$	1:1
13	$P2_1/n$	8.628	21.151	9.135	90	97.70	90	1652.0	$C_4H_6O_3$	1:1
14	$P2_1/n$	8.606	21.643	8.735	90	98.76	90	1608.0	$C_4H_6O_2$	1:1
15	$P2_1/n$	8.550	21.491	9.215	90	89.73	90	1693.2	$C_6H_{10}O$	1:1
18	$P2_1/n$	8.417	20.975	9.472	90	93.83	90	1668.5	$C_5H_8O_2$	1:1
21	$P2_1/n$	8.454	20.699	9.487	90	92.37	90	1658.7	C_5H_8O	1:1
22	$P2_1/n$	8.583	20.652	9.520	90	93.66	90	1684.0	$C_5H_8O_2$	1:1
28	$P2_1/n$	8.010	20.820	8.990	90	94.65	90	1494.3	$NC(CH_2)_6CN$	1:0.5
29	$P2_1/n$	8.523	21.073	9.0867	90	96.54	90	1621.5	$NC(CH_2)_8CN$	1:0.5
30	$P2_1/n$	8.679	19.911	10.022	90	97.78	90	1715.8	$C_{12}H_{20}N_2$	1:0.5
31	$P2_1/n$	8.248	21.019	9.074	90	96.53	90	1562.8	$CH_3(CH_2)_2CN$	1:1
32	$P2_1/n$	8.476	20.718	9.611	90	97.84	90	1671.9	$CH_3(CH_2)_3CN$	1:1
33	$P2_1/n$	9.112	18.994	10.590	90	101.37	90	1796.9	$C_6H_{11}CN$	1:1
34	$P2_1/n$	8.355	18.880	10.776	90	96.79	90	1687.9	$C_5H_8N_2O$	1:1
35	$P2_1/n$	8.363	21.146	9.116	90	95.76	90	1604.0	$C_9H_{14}N_2$	1:0.5
41	P21/c	12.213	20.550	13.583	90	97.03	90	3383.4	$C_5H_8N_2$	2:2
7	$P2_1/c$	8.636	19.187	9.354	90	91.03	90	1549.7	$C_4H_6O_2$	1:1
37	$P2_1/c$	8.390	18.813	9.540	90	102.54	90	1469.9	$C_4H_4N_2$	1:1

S9. Pairwise PIXEL energies (kJ mol^{-1}) derived from the DFT-minimised polymorphs, listing |*E*(total)| > 5 kJ mol^{-1}

[Centroid-centroid distances (Å) are geometric (not mass-weighted), and calculated using all atoms in the molecule (including H).
Frequency refers to no. of structures (out of 96) in which the pair is identified using the "Crystal Packing Feature" search in Mercury, tol: 30%, 30°]

Polymorph 1 ($P2_1/c$, $Z' = 2$)

Molecule 1, ARU: 1_555_01, centroid: 0.7561, 0.7992, 0.3688

Symmetry operators: [1] x,y,z; [2] -x,1/2+y,1/2-z; [3] -x,-y,-z; [4] x,1/2-y,1/2+z

	ARU	Centroid x	Centroid y	Centroid z	Cent-cent distance (Å)	Coulomb	Polarisation	Dispersion	Repulsion	Total	Frequency (Mercury)
[1]	3_776_01	0.7561	1.2008	0.6312	7.720	-176.2	-100.7	-55.7	+185.3	-147.3	42
[2]	2_645_01	1.2439	0.2992	0.1312	8.613	-41.6	-16.5	-19.4	+39.2	-38.2	6
[3]	2_655_01	0.2439	1.2992	0.1312	8.613	-41.6	-16.5	-19.4	+39.2	-38.2	3
[4]	4_555_02	0.2439	0.2869	0.5481	7.260	-16.3	-6.5	-25.6	+13.4	-35.0	2
[5]	2_655_02	0.8066	0.7131	0.4519	6.602	-20.9	-6.8	-19.0	+12.6	-34.0	1
[6]	3_665_02	0.1934	0.7869	-0.0481	7.785	-18.3	-9.1	-29.4	+26.2	-30.6	1
[7]	4_565_01	0.1934	0.7008	0.8688	8.689	-24.5	-9.9	-20.2	+25.5	-29.1	4
[8]	4_564_01	0.7561	0.7008	-0.1312	8.689	-24.5	-9.9	-20.2	+25.5	-29.1	4
[9]	4_565_02	0.7561	1.2869	0.5481	6.970	-10.4	-8.1	-27.4	+19.7	-26.1	1
[10]	2_755_02	0.8066	0.7131	0.4519	4.526	-4.2	-8.5	-43.8	+31.4	-25.0	1
[11]	1_555_02	1.1934	0.2131	0.0481	9.483	-27.3	-12.3	-14.7	+32.4	-21.9	3
[12]	3_766_02	0.8066	0.7869	0.9519	9.671	-5.2	-2.8	-9.4	+2.5	-14.9	1
[13]	1_565_02	1.1934	1.2131	0.0481	7.819	-1.6	-6.9	-17.9	+12.3	-14.1	1
[14]	2_665_02	0.1934	1.7131	0.4519	13.496	+5.6	-0.2	-0.1	0.0	+5.3	2
[15]	3_676_01	0.8066	1.2008	0.6312	9.556	+20.0	-2.3	-2.0	0.0	+15.7	9

S9. Pairwise PIXEL energies (kJ mol^{-1}) derived from the DFT-minimised polymorphs, listing |*E*(total)| > 5 kJ mol^{-1}

[Centroid-centroid distances (Å) are geometric (not mass-weighted), and calculated using all atoms in the molecule (including H).
Frequency refers to no. of structures (out of 96) in which the pair is identified using the "Crystal Packing Feature" search in Mercury, tol: 30%, 30°]

Polymorph 1 ($P2_1/c$, $Z' = 2$)

Molecule 2, ARU: 1_555_02, centroid: 0.8066, 0.2131, 0.0481

Symmetry operators: [1] x,y,z; [2] -x,1/2+y,1/2-z; [3] -x,-y,-z; [4] x,1/2-y,1/2+z

	ARU	Centroid x	Centroid y	Centroid z	Cent-cent distance (Å)	Coulomb	Polarisation	Dispersion	Repulsion	Total	Frequency (Mercury)
[1]	3_755_02	1.1934	-0.2131	-0.0481	7.339	-174.9	-98.7	-53.8	+190.6	-136.7	42
[2]	4_554_01	0.7561	-0.2992	-0.1312	7.260	-16.3	-6.5	-25.6	+13.4	-35.0	2
[3]	2_645_01	0.2439	0.2992	0.1312	6.602	-20.9	-6.8	-19.0	+12.6	-34.0	1
[4]	3_665_01	0.2439	0.2008	-0.3688	7.785	-18.3	-9.1	-29.4	+26.2	-30.6	1
[5]	2_745_02	1.1934	-0.2869	0.4519	9.453	-24.2	-11.0	-15.7	+20.2	-30.6	5
[6]	2_755_02	1.1934	0.7131	0.4519	9.453	-24.2	-11.0	-15.7	+20.2	-30.6	5
[7]	4_564_01	0.7561	0.7008	-0.1312	6.970	-10.4	-8.1	-27.4	+19.7	-26.1	1
[8]	2_745_01	1.2439	0.2992	0.1312	4.526	-4.2	-8.5	-43.8	+31.4	-25.0	1
[9]	1_555_01	0.7561	0.7992	0.3688	9.483	-27.3	-12.3	-14.7	+32.4	-21.9	3
[10]	3_655_02	0.1934	-0.2131	-0.0481	8.267	-11.1	-4.7	-8.4	+3.2	-21.0	13
[11]	3_766_01	1.2439	0.2008	0.6312	9.671	-5.2	-2.8	-9.4	+2.5	-14.9	2
[12]	1_545_01	0.7561	-0.2008	0.3688	7.819	-1.6	-6.9	-17.9	+12.3	-14.1	1
[13]	4_555_02	0.8066	0.2869	0.5481	8.648	-4.8	-5.8	-14.8	+17.3	-8.1	5
[14]	4_554_02	0.8066	0.2869	-0.4519	8.648	-4.8	-5.8	-14.8	+17.3	-8.1	5
[15]	2_635_01	0.2439	-0.7008	0.1312	13.496	+5.6	-0.2	-0.1	0.0	+5.3	2

S9. Pairwise PIXEL energies (kJ mol^{-1}) derived from the DFT-minimised polymorphs, listing |*E*(total)| > 5 kJ mol^{-1}

[Centroid-centroid distances (Å) are geometric (not mass-weighted), and calculated using all atoms in the molecule (including H).
Frequency refers to no. of structures (out of 96) in which the pair is identified using the "Crystal Packing Feature" search in Mercury, tol: 30%, 30°]

Polymorph 2 ($P2_1/n$, *Z'* = 2)

Molecule 1, ARU: 1_555_01, centroid: 0.7461, 0.4793, 0.6110

Symmetry operators: [1] x, y, z; [2] 1/2-x,1/2+y,1/2-z; [3] -x,-y,-z; [4] 1/2+x,1/2-y,1/2+z

	ARU	Centroid x	Centroid y	Centroid z	Cent-cent distance (Å)	Coulomb	Polarisation	Dispersion	Repulsion	Total	Frequency (Mercury)
[1]	1_655_02	1.2234	0.4496	0.8943	6.353	-54.8	-31.9	-33.6	+64.3	-56.1	1
[2]	3_666_01	0.2539	0.5207	0.3890	5.996	-22.7	-10.3	-52.1	+34.7	-50.4	9
[3]	1_555_02	0.2234	0.4496	0.8943	6.859	-37.2	-21.4	-17.8	+35.2	-41.2	1
[4]	3_766_01	1.2539	0.5207	0.3890	6.247	-26.0	-13.8	-38.3	+37.8	-40.2	6
[5]	2_656_01	0.7539	0.9793	0.8890	8.544	-44.4	-25.8	-28.8	+59.3	-39.7	1
[6]	2_646_01	0.7539	-0.0207	0.8890	8.544	-44.4	-25.8	-28.8	+59.3	-39.7	1
[7]	2_646_02	1.2766	-0.0504	0.6057	9.732	-38.8	-13.5	-16.8	+29.5	-39.5	15
[8]	2_656_02	1.2766	0.9496	0.6057	9.005	-25.7	-13.4	-21.0	+27.8	-32.4	5
[9]	3_666_02	0.7766	0.5504	0.1057	7.310	-9.2	-5.7	-16.2	+9.0	-22.2	1
[10]	3_667_02	0.7766	0.5504	1.1057	7.145	-10.3	-5.7	-17.5	+14.2	-19.4	1
[11]	2_556_02	0.2766	0.9496	0.6057	8.629	-4.7	-4.4	-11.9	+7.8	-13.2	2
[12]	4_554_02	0.7234	0.0504	0.3943	7.192	-0.3	-2.8	-15.2	+7.2	-11.1	1
[13]	4_464_01	0.2461	1.0207	0.1110	11.981	-5.9	-1.2	-1.4	0.0	-8.5	5
[14]	4_565_01	1.2461	1.0207	1.1110	11.981	-5.9	-1.2	-1.4	0.0	-8.5	5
[15]	1_655_01	1.7461	0.4793	0.6110	10.399	-4.8	-0.5	-0.9	0.0	-6.3	1
[16]	1_455_01	-0.2539	0.4793	0.6110	10.399	-4.8	-0.5	-0.9	0.0	-6.3	1
[17]	4_664_02	1.7234	1.0504	0.3943	13.742	-5.8	-0.2	-0.2	0.0	-6.3	5
[18]	4_565_02	0.7234	1.0504	1.3943	14.141	+5.5	-0.1	-0.1	0.0	+5.3	3

S9. Pairwise PIXEL energies (kJ mol^{-1}) derived from the DFT-minimised polymorphs, listing |*E*(total)| > 5 kJ mol^{-1}

[Centroid-centroid distances (Å) are geometric (not mass-weighted), and calculated using all atoms in the molecule (including H).
Frequency refers to no. of structures (out of 96) in which the pair is identified using the "Crystal Packing Feature" search in Mercury, tol: 30%, 30°]

Polymorph 2 ($P2_1/n$, $Z' = 2$)

Molecule 2, ARU: 1_555_02, centroid: 0.2234, 0.4496, 0.8943

Symmetry operators: [1] x, y, z; [2] 1/2-x,1/2+y,1/2-z; [3] -x,-y,-z; [4] 1/2+x,1/2-y,1/2+z

	ARU	Centroid x	Centroid y	Centroid z	Cent-cent distance (Å)	Coulomb	Polarisation	Dispersion	Repulsion	Total	Frequency (Mercury)
[1]	1_455_01	-0.2539	0.4793	0.6110	6.353	-54.8	-31.9	-33.6	+64.3	-56.1	1
[2]	3_567_02	-0.2234	0.5504	1.1057	5.797	-23.5	-11.5	-52.7	+39.5	-48.2	17
[3]	2_556_02	0.2766	0.9496	0.6057	8.640	-37.8	-15.7	-24.8	+31.8	-46.4	2
[4]	2_546_02	0.2766	-0.0504	0.6057	8.640	-37.8	-15.7	-24.8	+31.8	-46.4	2
[5]	1_555_01	0.7461	0.4793	0.6110	6.859	-37.2	-21.4	-17.8	+35.2	-41.2	1
[6]	2_656_01	0.7539	0.9793	0.8890	9.732	-38.8	-13.5	-16.8	+29.5	-39.6	15
[7]	3_667_02	0.7766	0.5504	1.1057	6.618	-17.6	-8.7	-24.6	+14.2	-36.7	8
[8]	2_646_01	0.7539	-0.0207	0.8890	9.005	-25.7	-13.4	-21.0	+27.8	-32.4	5
[9]	3_666_01	0.2539	0.5207	0.3890	7.310	-9.2	-5.7	-16.2	+9.0	-22.2	1
[10]	3_667_01	0.2539	0.5207	1.3890	7.145	-10.3	-5.7	-17.5	+14.2	-19.4	1
[11]	2_546_01	-0.2461	-0.0207	0.8890	8.629	-4.7	-4.4	-11.9	+7.8	-13.2	2
[12]	4_455_01	0.2461	0.0207	1.1110	7.192	-0.3	-2.8	-15.2	+7.2	-11.1	1
[13]	1_655_02	-0.7766	0.4496	0.8943	10.399	-6.8	-0.5	-0.7	0.0	-7.9	3
[14]	1_455_02	1.2234	0.4496	0.8943	10.399	-6.8	-0.5	-0.7	0.0	-7.9	3
[15]	4_365_01	-0.7539	1.0207	1.1110	13.742	-5.8	-0.2	-0.2	0.0	-6.3	5
[16]	4_465_02	-0.2766	1.0504	1.3943	12.737	-4.6	-0.6	-0.6	0.0	-5.8	3
[17]	4_564_02	0.7234	1.0504	0.3943	12.737	-4.6	-0.6	-0.6	0.0	-5.8	3
[18]	4_464_01	0.2461	1.0207	0.1110	14.141	+5.5	-0.1	-0.1	0.0	+5.3	6

S9. Pairwise PIXEL energies (kJ mol^{-1}) derived from the DFT-minimised polymorphs, listing |*E*(total)| > 5 kJ mol^{-1}

[Centroid-centroid distances (Å) are geometric (not mass-weighted), and calculated using all atoms in the molecule (including H).
Frequency refers to no. of structures (out of 96) in which the pair is identified using the "Crystal Packing Feature" search in Mercury, tol: 30%, 30°]

Polymorph 3 ($P2_1/c$, $Z' = 2$)

Molecule 1, [ARU: 1_555_01, centroid: 0.7272, 0.2737, 0.9869

Symmetry operators: [1] x,y,z; [2] -x,1/2+y,1/2-z; [3] -x,-y,-z; [4] x,1/2-y,1/2+z

	ARU	Centroid x	Centroid y	Centroid z	Cent-cent distance (Å)	Coulomb	Polarisation	Dispersion	Repulsion	Total	Frequency (Mercury)
[1]	1_555_02	0.7807	0.7848	0.7766	5.721	-112.1	-61.5	-59.7	+155.9	-77.5	3
[2]	1_545_02	0.7807	-0.2152	0.7766	5.580	-94.3	-50.8	-62.8	+131.9	-76.1	3
[3]	4_555_02	0.7807	-0.2848	1.2766	6.352	-28.0	-10.8	-33.2	+24.1	-48.0	6
[4]	3_767_02	1.2193	0.2152	1.2234	7.938	-37.5	-15.7	-28.1	+34.9	-46.3	11
[5]	3_667_01	0.2728	0.7263	1.0131	8.962	-28.5	-8.1	-30.4	+22.6	-44.5	3
[6]	4_565_02	0.7807	0.7152	1.2766	5.648	-16.5	-10.7	-47.6	+38.0	-36.8	10
[7]	2_646_02	0.2193	0.2848	0.7234	8.195	-32.4	-16.3	-21.6	+37.2	-33.2	21
[8]	1_565_01	0.7272	1.2737	0.9869	8.498	-24.6	-4.6	-7.5	+4.9	-31.9	10
[9]	1_545_01	0.7272	-0.7263	0.9869	8.498	-24.6	-4.6	-7.5	+4.9	-31.9	10
[10]	4_555_01	0.7272	0.2263	1.4869	7.766	-15.8	-4.7	-13.7	+7.2	-26.9	3
[11]	4_554_01	0.7272	0.2263	0.4869	7.766	-15.8	-4.7	-13.7	+7.2	-26.9	3
[12]	3_757_01	1.2728	-0.2737	1.0131	10.461	-14.0	-1.9	-9.1	+3.1	-21.8	3
[13]	3_667_02	0.2193	0.2152	1.2234	10.837	-4.7	-1.2	-5.2	+1.8	-9.3	8
[14]	2_636_02	0.2193	-0.7152	0.7234	11.738	-5.0	-0.3	-0.2	0.0	-5.5	31

S9. Pairwise PIXEL energies (kJ mol^{-1}) derived from the DFT-minimised polymorphs, listing |*E*(total)| > 5 kJ mol^{-1}

[Centroid-centroid distances (Å) are geometric (not mass-weighted), and calculated using all atoms in the molecule (including H).
Frequency refers to no. of structures (out of 96) in which the pair is identified using the "Crystal Packing Feature" search in Mercury, tol: 30%, 30°]

Polymorph 3 ($P2_1/c$, $Z' = 2$)

Molecule 2, ARU: 1_555_02, centroid: 0.7807, 0.7848, 0.7766

Symmetry operators: [1] x,y,z; [2] -x,1/2+y,1/2-z; [3] -x,-y,-z; [4] x,1/2-y,1/2+z

	ARU	Centroid x	Centroid y	Centroid z	Cent-cent distance (Å)	Coulomb	Polarisation	Dispersion	Repulsion	Total	Frequency (Mercury)
[1]	1_555_01	0.7272	0.2737	0.9869	5.721	-112.1	-61.5	-59.7	+155.9	-77.5	3
[2]	1_565_01	0.7272	1.2737	0.9869	5.580	-94.3	-50.8	-62.8	+131.9	-76.1	3
[3]	4_554_01	0.7272	0.2263	0.4869	6.352	-28.0	-10.8	-33.2	+24.1	-48.0	6
[4]	3_767_01	1.2728	0.7263	1.0131	7.938	-37.5	-15.7	-28.1	+34.9	-46.3	11
[5]	4_564_01	0.7272	1.2263	0.4869	5.648	-16.5	-10.7	-47.6	+38.0	-36.8	10
[6]	2_656_01	0.2728	0.7737	0.5131	8.195	-32.4	-16.3	-21.6	+37.2	-33.2	21
[7]	1_565_02	0.7807	1.7848	0.7766	8.498	-24.0	-4.6	-8.3	+5.6	-31.3	10
[8]	1_545_02	0.7807	-0.2152	0.7766	8.498	-24.0	-4.6	-8.3	+5.6	-31.3	10
[9]	4_564_02	0.7807	0.7152	0.2766	7.778	-12.4	-3.6	-12.3	+6.1	-22.2	3
[10]	4_565_02	0.7807	0.7152	1.2766	7.778	-12.4	-3.6	-12.3	+6.1	-22.2	3
[11]	3_777_02	1.2193	1.2152	1.2234	8.880	-19.0	-1.3	-1.9	0.0	-22.2	8
[12]	2_746_02	1.2193	0.2848	0.7234	9.067	+0.8	-6.5	-19.2	+8.2	-16.7	3
[13]	2_756_02	1.2193	1.2848	0.7234	9.067	+0.8	-6.5	-19.2	+8.2	-16.7	3
[14]	3_667_01	0.2728	0.7263	1.0131	10.837	-4.7	-1.2	-5.2	+1.8	-9.3	8
[15]	2_666_01	0.2728	1.7737	0.5131	11.738	-5.0	-0.3	-0.2	0.0	-5.5	31
[16]	3_767_02	1.2193	0.2152	1.2234	9.428	+25.8	-4.6	-4.7	+3.0	+19.5	11

S9. Pairwise PIXEL energies (kJ mol^{-1}) derived from the DFT-minimised polymorphs, listing |*E*(total)| > 5 kJ mol^{-1}

[Centroid-centroid distances (Å) are geometric (not mass-weighted), and calculated using all atoms in the molecule (including H).
Frequency refers to no. of structures (out of 96) in which the pair is identified using the "Crystal Packing Feature" search in Mercury, tol: 30%, 30°]

Polymorph 4 ($P2_1/c$, $Z' = 1$)

ARU: 1_555_01, centroid: 0.0515, 0.7261, 0.3686
Symmetry operators: [1] x,y,z; [2] -x,1/2+y,1/2-z; [3] -x,-y,-z; [4] x,1/2-y,1/2+z

	ARU	Centroid x	Centroid y	Centroid z	Cent-cent distance (Å)	Coulomb	Polarisation	Dispersion	Repulsion	Total	Frequency (Mercury)
[1]	2_555_01	-0.0515	1.2261	0.1314	5.649	-105.2	-56.7	-60.0	+144.3	-77.6	3
[2]	2_545_01	-0.0515	0.2261	0.1314	5.649	-105.2	-56.7	-60.0	+144.3	-77.5	3
[3]	3_576_01	-0.0515	1.2739	0.6314	6.287	-28.9	-11.2	-35.5	+26.9	-48.7	6
[4]	3_666_01	0.9485	0.2739	0.6314	9.011	-27.1	-7.8	-28.3	+19.5	-43.7	3
[5]	3_566_01	-0.0515	0.2739	0.6314	5.706	-13.8	-8.7	-43.7	+30.2	-35.9	14
[6]	1_655_01	1.0515	0.7261	0.3686	8.193	-35.0	-17.7	-22.3	+40.7	-34.4	25
[7]	1_455_01	-0.9485	0.7261	0.3686	8.193	-35.0	-17.7	-22.3	+40.7	-34.4	25
[8]	1_565_01	0.0515	1.7261	0.3686	8.538	-23.0	-4.1	-7.0	+4.0	-30.1	11
[9]	1_545_01	0.0515	-0.2739	0.3686	8.538	-23.0	-4.1	-7.0	+4.0	-30.1	11
[10]	4_564_01	0.0515	0.7739	-0.1314	7.729	-15.1	-5.1	-15.3	+9.5	-26.0	3
[11]	4_565_01	0.0515	0.7739	0.8686	7.729	-15.1	-5.1	-15.3	+9.5	-26.0	3
[12]	4_464_01	-0.9485	0.7739	-0.1314	10.864	-4.8	-1.1	-4.7	+1.5	-9.1	6
[13]	4_665_01	1.0515	0.7739	0.8686	10.864	-4.8	-1.1	-4.7	+1.5	-9.1	6
[14]	1_665_01	1.0515	1.7261	0.3686	11.833	-5.0	-0.2	-0.2	0.0	-5.5	33
[15]	1_445_01	-0.9485	-0.2739	0.3686	11.833	-5.0	-0.2	-0.2	0.0	-5.5	32

S9. Pairwise PIXEL energies (kJ mol^{-1}) derived from the DFT-minimised polymorphs, listing |*E*(total)| > 5 kJ mol^{-1}

[Centroid-centroid distances (Å) are geometric (not mass-weighted), and calculated using all atoms in the molecule (including H).
Frequency refers to no. of structures (out of 96) in which the pair is identified using the "Crystal Packing Feature" search in Mercury, tol: 30%, 30°]

Polymorph 5 ($P2_1/n$, $Z' = 1$)

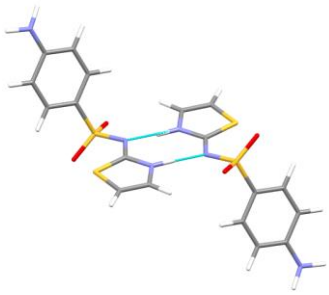
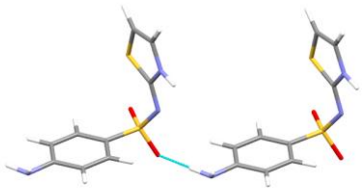
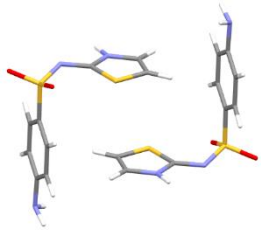
ARU: 1_555_01, centroid: 0.3948, 0.7109, 0.8431
Symmetry operators: [1] x, y, z; [2] 1/2-x,1/2+y,1/2-z; [3] -x,-y,-z; [4] 1/2+x,1/2-y,1/2+z

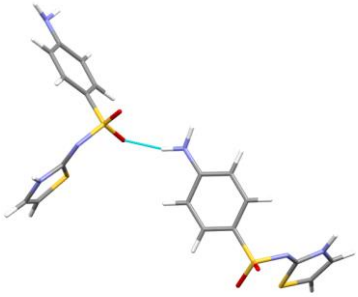
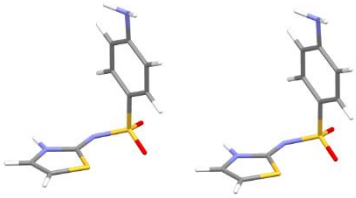
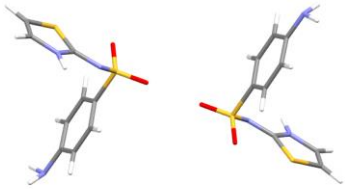
	ARU	Centroid x	Centroid y	Centroid z	Cent-cent distance (Å)	Coulomb	Polarisation	Dispersion	Repulsion	Total	Frequency (Mercury)
[1]	2_556_01	0.1052	1.2109	0.6569	5.636	-93.5	-50.0	-61.1	+132.7	-72.0	3
[2]	2_546_01	0.1052	0.2109	0.6569	5.636	-93.5	-50.0	-61.1	+132.7	-72.0	3
[3]	3_677_01	0.6052	1.2891	1.1569	6.431	-27.6	-10.8	-32.2	+23.5	-47.0	6
[4]	4_465_01	-0.1052	0.7891	1.3431	7.970	-37.8	-16.7	-28.9	+37.7	-45.6	7
[5]	4_564_01	0.8948	0.7891	0.3431	7.970	-37.8	-16.7	-28.9	+37.7	-45.6	5
[6]	3_667_01	0.6052	0.2891	1.1569	5.491	-23.0	-15.5	-55.7	+58.5	-35.7	10
[7]	1_565_01	0.3948	1.7109	0.8431	8.467	-23.9	-4.5	-8.0	+5.5	-30.9	9
[8]	1_545_01	0.3948	-0.2891	0.8431	8.467	-23.9	-4.5	-8.0	+5.5	-30.9	9
[9]	4_464_01	-0.1052	0.7891	0.3431	7.746	-12.7	-3.3	-11.3	+4.5	-22.9	3
[10]	4_565_01	0.8948	0.7891	1.3431	7.746	-12.7	-3.3	-11.3	+4.5	-22.9	3
[11]	3_666_01	0.6052	0.2891	0.1569	8.930	-19.2	-1.3	-1.9	0.0	-22.4	8
[12]	3_577_01	-0.3948	1.2891	1.1569	10.527	-14.2	-2.1	-9.9	+3.8	-22.3	3
[13]	2_656_01	1.1052	1.2109	0.6569	9.050	+0.1	-6.6	-19.9	+9.2	-17.1	3
[14]	2_646_01	1.1052	0.2109	0.6569	9.050	+0.1	-6.6	-19.9	+9.2	-17.1	3
[15]	3_676_01	0.6052	1.2891	0.1569	9.537	+25.6	-4.5	-4.7	+3.1	+19.6	11

S10. Pairwise motifs in the polymorphs and multi-component structures

The range of interaction energies is taken from the *PIXEL* tables in Section S9.

Due to borderline tolerance judgements, frequency values are indicative rather than absolute. Where the same motif in different structures shows a different frequency of occurrence, the **largest** frequency value is shown.

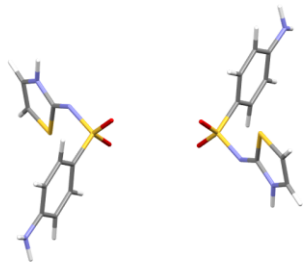
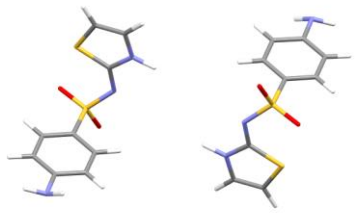
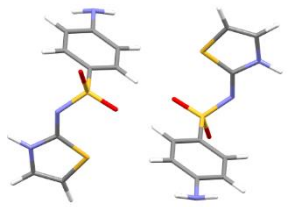
Motif A (Freq = 42)	**Motif B (Freq = 25)**	**Motif C (Freq = 17)**
		
1p:1_555_01:3_776_01 1p:1_555_02:3_755_02	4p:1555_01:1655_01 4p:1555_01:1455_01 3p:1555_01:2646_02	5p:1555_01:3667_01 4p:1555_01:3566_01 3p:1555_01:4565_02 2p:1555_01:3666_01 2p:1555_02:3567_02
-147.3 ≤ *E* ≤ -136.7 kJ mol^{-1} H-bonded = YES	**-33.2 ≤ *E* ≤ -30.1 kJ mol^{-1} H-bonded = YES**	**-50.4 ≤ *E* ≤ -35.9 kJ mol^{-1} H-bonded = NO**

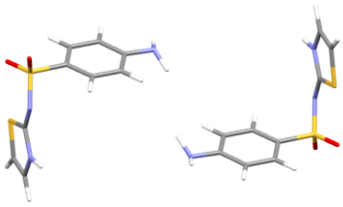
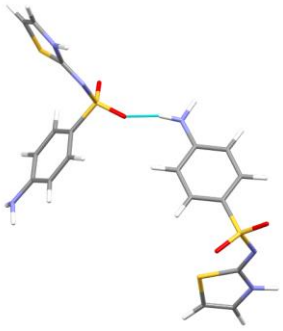
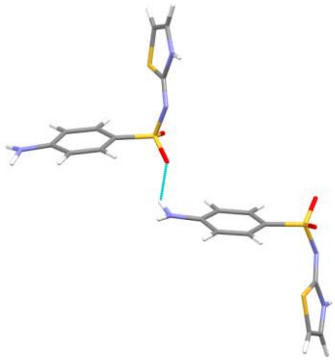
Motif D (Freq = 15)	**Motif E (Freq = 11)**	**Motif F (Freq = 11)**
		
2p:1555_01:2646_02 2p:1555_02:2656_01	5p:1555_01:1545_01 5p:1555_01:1565_01 4p:1555_01:1545_01 4p:1555_01:1565_01 3p:1555_01:1545_01 3p:1555_01:1565_01 3p:1555_02:1545_02 3p:1555_02:1565_02	5p:1555_01:3676_01 3p:1555_02:3767_02
-39.6 ≤ *E* ≤ -39.5 kJ mol^{-1} H-bonded = YES	**-31.9 ≤ *E* ≤ -30.1 kJ mol^{-1} H-bonded = NO**	**+19.5 ≤ *E* ≤ +19.6 kJ mol^{-1} H-bonded = NO**

S10. Pairwise motifs in the polymorphs and multi-component structures

The range of interaction energies is taken from the *PIXEL* tables in Section S9.

Due to borderline tolerance judgements, frequency values are indicative rather than absolute. Where the same motif in different structures shows a different frequency of occurrence, the **largest** frequency value is shown.

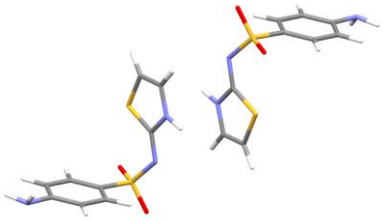
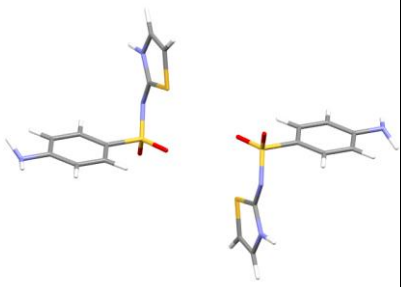
Motif G (Freq = 9)	**Motif H (Freq = 8)**	**Motif I (Freq = 8)**
		
1p:1555_01:3676_01	5p:1_555_01:3_666_01 3p:1_555_02:3_777_02	5p:1555_01:3677_01 4p:1555_01:3576_01 3p:1555_01:4555_02 2p:1555_01:3766_01 2p:1555_02:3667_02
+15.7 kJ mol^{-1} H-bonded = NO	**-22.4 ≤ *E* ≤ -22.2 kJ mol^{-1} H-bonded = NO**	**-48.7 ≤ *E* ≤ -36.7 kJ mol^{-1} H-bonded = NO**

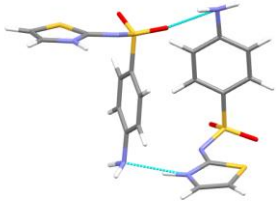
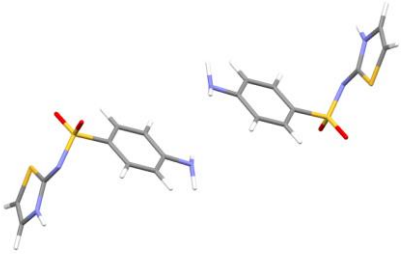
Motif J (Freq = 6)	**Motif K (Freq = 6)**	**Motif L (Freq = 5)**
		
5p:1555_01:3567_01 3p:1555_01:3767_01	1p:1555_01:2645_01 1p:1555_01:2655_01	1p:1_555_02:2_745_02 1p:1_555_02:2_755_02
+1.4 ≤ *E* ≤ +1.9 kJ mol^{-1} H-bonded = NO	**-38.2 kJ mol^{-1} H-bonded = YES**	**-30.6 kJ mol^{-1} H-bonded = YES**

S10. Pairwise motifs in the polymorphs and multi-component structures

The range of interaction energies is taken from the *PIXEL* tables in Section S9.

Where the same motif in different structures shows a different frequency of occurrence (due to borderline tolerance judgements), the **largest** frequency value is shown.

Motif M (Freq = 5)	**Motif N (Freq = 3)**	**Motif O (Freq = 3)**
		
5p:1555_01:1655_01 5p:1555_01:1455_01 3p:1555_01:2746_02	4p:1555_01:3666_01	4p:1555_01:3676_01 3p:1555_01:3657_01
+4.5 ≤ *E* ≤ +4.7 kJ mol^{-1} H-bonded = NO	**-43.7 kJ mol^{-1} H-bonded = NO**	**+1.1 ≤ *E* ≤ +3.2 kJ mol^{-1} H-bonded = NO**

Motif P (Freq = 3)	**Motif Q (Freq = 3)**	
		
5p:1555_01:2546_01 5p:1555_01:2556_01 4p:1555_01:2545_01 4p:1555_01:2555_01 3p:1555_01:1555_02 3p:1555_01:1545_02 3p:1555_02:1555_01 3p:1555_02:1565_01	5p:1555_01:3577_01	
-77.6 ≤ *E* ≤ -72.0 kJ mol^{-1} H-bonded = YES	**-22.3 kJ mol^{-1} H-bonded = NO**	