Electronic Supplementary Material (ESI) for CrystEngComm.

Crystallization and disorder of the polytypic α_1 and α_2 polymorphs of piroxicam

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S1. Details of the DFT-D energy minimisation

Minimisations were performed as described in the Experimental section, in three successive steps:

(1) Allowing only H atoms to move.

(2) Allowing all atoms to move within a constrained unit cell.

(3) Allowing all atoms to move, with optimisation of the unit-cell parameters.

In all three cases, the specified space group symmetry was imposed. Minimisation steps (2) and (3) produced only very small geometrical deviations compared to the result of step (1), as expected for high-quality single-crystal structures. The log files from *CASTEP* are provided within the ESI as a record of the input parameters, convergence conditions, final forces on atoms, *etc*. The minimised structures from step (3) are also compiled in CIF format in the file *minimised.cif*.

S2. Details of the *PIXEL* calculations

From the DFT-D minimised structures produced in step (3), intermolecular interaction energies were calculated using the *PIXEL* method (Gavezzotti, 2011). A summary of the interaction energies is given in the following tables, partitioned into interactions between molecules within the hydrogen-bonded sheets, molecules in adjacent sheets where the pyridyl groups interact, and molecules in adjacent sheets where the benzothiazine groups interact. The tables and corresponding energy-vector diagrams shown in the main paper are produced from the *PIXEL* output files using the *processPIXEL* program. Electronic versions of these files are included with the ESI.

α_1: BIYSEH02 (DFT-D optimised), *Pbc*2_1 (*a* = 17.2547, *b* = 11.5746, *c* = 6.7892 Å)

Estimated totals (kJ mol^{-1}) from 12 most stabilising interactions: in-layer –53.7; pyridyl –53.4; benzo –38.9 (factor ½ applied to deal with "double counting")

		Mol 1	Mol 2	Mol 2 Operator	Distance	Coulomb	Polarisation	Dispersion	Repulsion	Total	
A0	A63	1	1	x,0.5-y,-0.5+z	4.956	-11.1	-5.8	-63.1	38.9	-41.0	In-layer
A0	A3	1	1	x,0.5-y,0.5+z	4.956	-11.1	-5.8	-63.1	38.9	-41.0	In-layer
A0	A45	1	1	2-x,1-y,-0.5+z	8.910	-11.1	-5.8	-32.8	21.5	-28.2	Pyridyl
A0	A46	1	1	2-x,1-y,0.5+z	8.910	-11.1	-5.8	-32.8	21.5	-28.2	Pyridyl
A0	A98	1	1	2-x,0.5+y,z	9.829	-10.3	-10.0	-35.5	30.7	-25.2	Pyridyl
A0	A93	1	1	2-x,-0.5+y,z	9.829	-10.3	-10.0	-35.5	30.7	-25.2	Pyridyl
A0	A86	1	1	1-x,0.5+y,z	10.962	-16.1	-8.5	-25.5	30.0	-20.1	Benzo
A0	A81	1	1	1-x,-0.5+y,z	10.962	-16.1	-8.5	-25.5	30.0	-20.1	Benzo
A0	A31	1	1	1-x,1-y,-0.5+z	10.145	-12.6	-6.9	-36.8	37.4	-18.8	Benzo
A0	A32	1	1	1-x,1-y,0.5+z	10.145	-12.6	-6.9	-36.8	37.4	-18.8	Benzo
A0	A14	1	1	x,y,-1+z	6.789	-8.0	-2.8	-10.1	8.3	-12.7	In-layer
A0	A15	1	1	x,y,1+z	6.789	-8.0	-2.8	-10.1	8.3	-12.7	In-layer
A0	A69	1	1	x,1.5-y,0.5+z	8.657	4.1	-1.8	-7.5	1.6	-3.6	
A0	A68	1	1	x,1.5-y,-0.5+z	8.657	4.1	-1.8	-7.5	1.6	-3.6	
A0	A92	1	1	2-x,-0.5+y,-1+z	11.946	-1.8	-0.2	-0.8	0.0	-2.8	
A0	A99	1	1	2-x,0.5+y,1+z	11.946	-1.8	-0.2	-0.8	0.0	-2.8	
A0	A87	1	1	1-x,0.5+y,1+z	12.894	-1.1	-0.1	-0.5	0.0	-1.7	
A0	A80	1	1	1-x,-0.5+y,-1+z	12.894	-1.1	-0.1	-0.5	0.0	-1.7	
A0	A41	1	1	2-x,-y,0.5+z	12.766	-0.6	-0.1	-1.0	0.0	-1.6	
A0	A40	1	1	2-x,-y,-0.5+z	12.766	-0.6	-0.1	-1.0	0.0	-1.6	

Interaction energies with absolute value less than 1 kJ mol^{-1} are not listed

α_2: BIYSEH05 (DFT-D optimised), $P2_1/c$ (a = 17.4669, b = 11.6561, c = 6.7665 Å, β = 98.721°)

Estimated totals (kJ mol^{-1}) from 12 most stabilising interactions: in-layer –52.7; pyridyl –57.1; benzo –39.9 (factor ½ applied to deal with "double counting").

		Mol 1	Mol 2	Mol 2 Operator	Distance	Coulomb	Polarisation	Dispersion	Repulsion	Total	
A0	A69	1	1	2-x,2-y,1-z	8.406	-24.4	-7.7	-45.8	29.9	-48.0	Pyridyl
A0	A91	1	1	x,2.5-y,-0.5+z	4.990	-11.0	-5.9	-63.1	39.6	-40.4	In-layer
A0	A92	1	1	x,2.5-y,0.5+z	4.990	-11.0	-5.9	-63.1	39.6	-40.4	In-layer
A0	A46	1	1	2-x,0.5+y,0.5-z	9.927	-12.9	-8.9	-33.8	27.2	-28.3	Pyridyl
A0	A41	1	1	2-x,-0.5+y,0.5-z	9.927	-12.9	-8.9	-33.8	27.2	-28.3	Pyridyl
A0	A57	1	1	1-x,2-y,1-z	10.634	-16.3	-3.7	-24.2	16.0	-28.2	Benzo
A0	A28	1	1	1-x,-0.5+y,0.5-z	11.093	-13.1	-7.7	-22.4	25.0	-18.3	Benzo
A0	A33	1	1	1-x,0.5+y,0.5-z	11.093	-13.1	-7.7	-22.4	25.0	-18.3	Benzo
A0	A56	1	1	1-x,2-y,-z	9.865	-8.5	-6.1	-45.2	44.8	-15.0	Benzo
A0	A14	1	1	x,y,-1+z	6.766	-8.3	-3.0	-10.3	9.3	-12.3	In-layer
A0	A15	1	1	x,y,1+z	6.767	-8.3	-3.0	-10.3	9.3	-12.3	In-layer
A0	A68	1	1	2-x,2-y,-z	9.525	-0.1	-3.8	-23.4	17.7	-9.6	Pyridyl
A0	A85	1	1	x,1.5-y,-0.5+z	8.675	3.8	-1.8	-7.2	1.8	-3.5	
A0	A86	1	1	x,1.5-y,0.5+z	8.675	3.8	-1.8	-7.2	1.7	-3.5	
A0	A42	1	1	2-x,-0.5+y,1.5-z	11.147	-1.5	-0.2	-0.9	0.0	-2.7	
A0	A47	1	1	2-x,0.5+y,1.5-z	11.147	-1.5	-0.2	-0.9	0.0	-2.7	
A0	A74	1	1	2-x,3-y,1-z	12.497	-1.7	-0.1	-0.9	0.0	-2.7	
A0	A34	1	1	1-x,0.5+y,1.5-z	13.587	-1.6	-0.1	-0.3	0.0	-2.0	
A0	A29	1	1	1-x,-0.5+y,1.5-z	13.587	-1.6	-0.1	-0.3	0.0	-2.0	
A0	A73	1	1	2-x,3-y,-z	13.275	-0.5	0.0	-0.8	0.0	-1.3	
A0	A58	1	1	1-x,2-y,2-z	14.847	-0.8	0.0	-0.1	0.0	-1.0	

Interaction energies with absolute value less than 1 kJ mol^{-1} are not listed