Supporting Information for the article

Exploiting Supramolecular Synthons in Cocrystals of Two Racetams with 4-Hydroxybenzoic Acid and 4-Hydroxybenzamide Coformers

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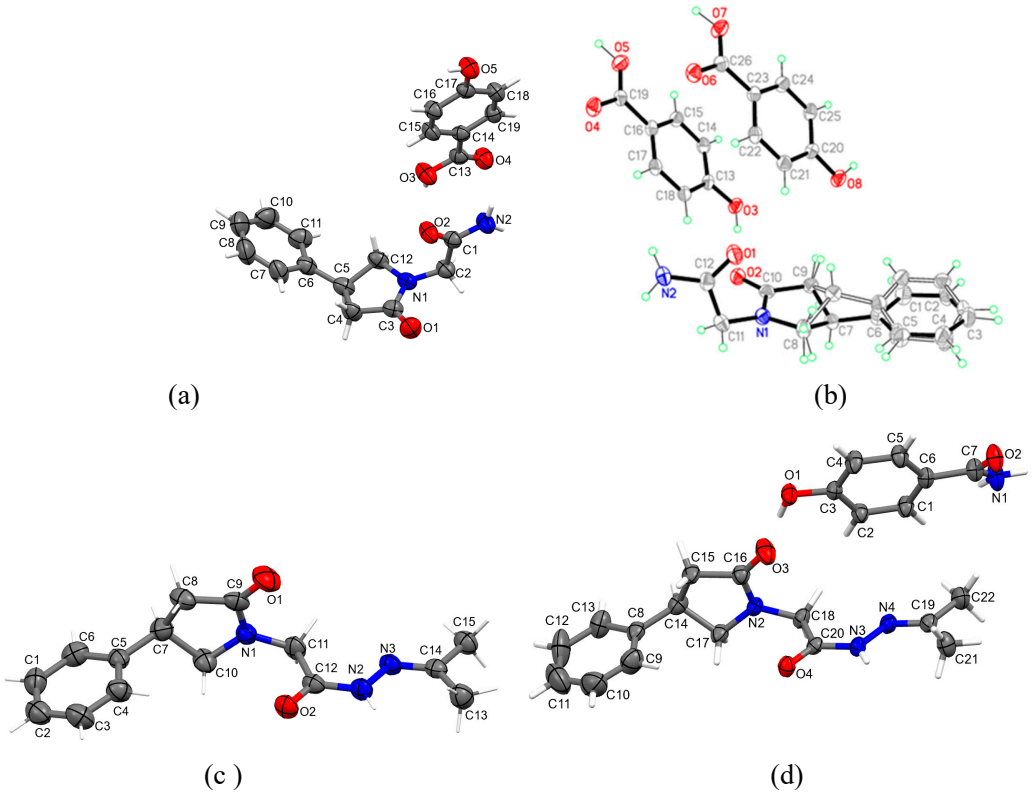


Figure S1. ORTEP drawings with labelling schemes for (a) **PPA·HBA**; (b) **PPA·2HBA** – with indication of disorder; (c) **PPAH** and (d) **PPAH·HBD**.

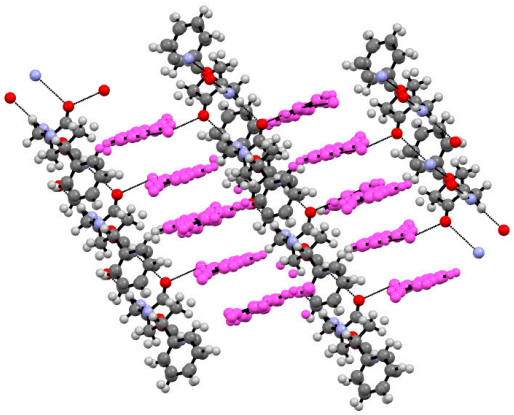


Figure S2. Alternation of homomeric **PPA** and **HBA** (pink) H-bonded layers in cocrystal **PPA**·**2HBA**.

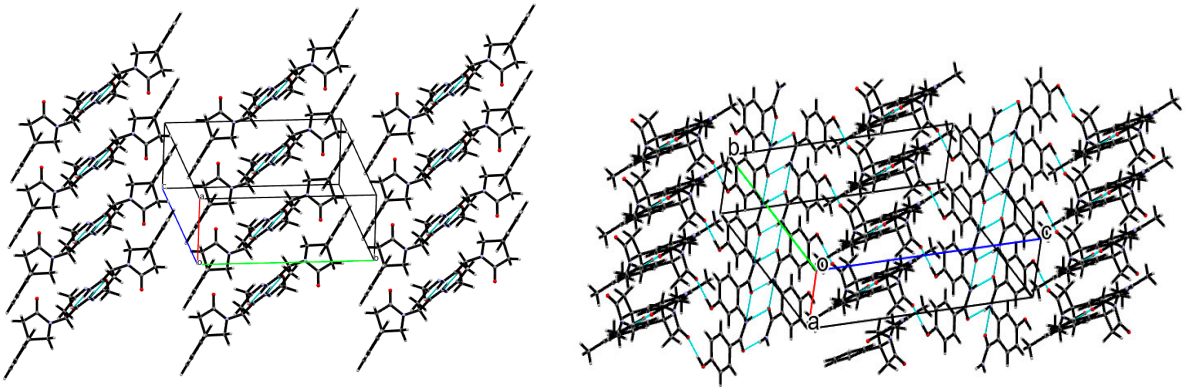


Figure S3. (a) Similar packing motifs in **PPAH** and **PPAH**·**HBD** cocrystal: (a) Stacking columns of the **PPAH** dimers along the shortest *a*-axis; (b) Stacking columns of the **PPAH** dimers along the shortest *a*-axis in cocrystal separated by double chains of coformer.

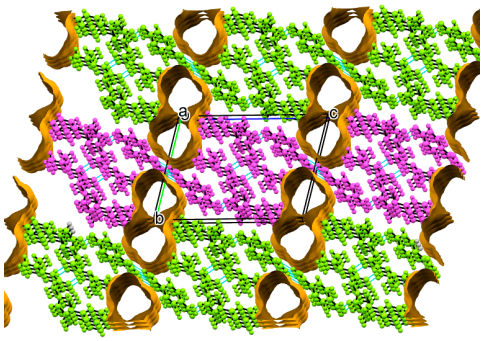
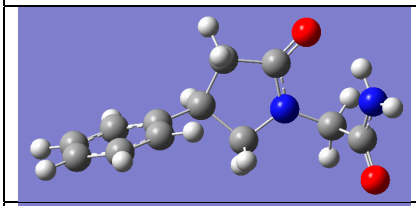
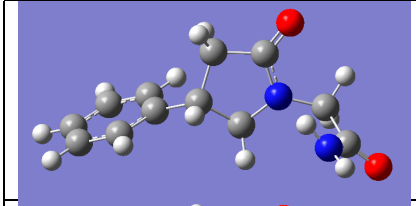
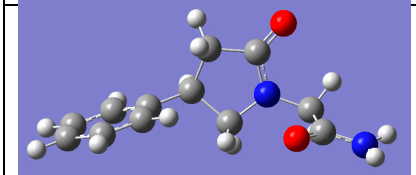
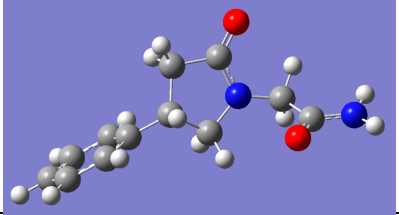
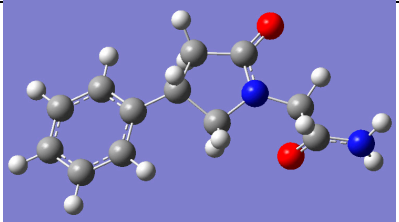
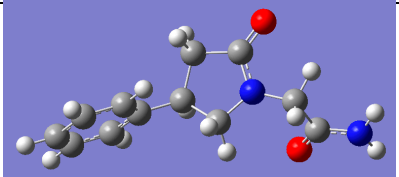
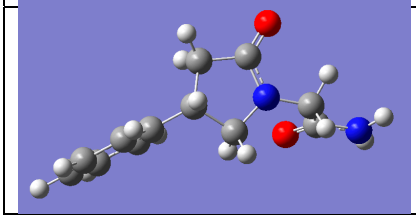


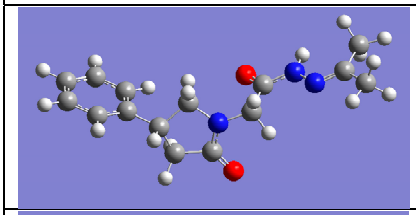
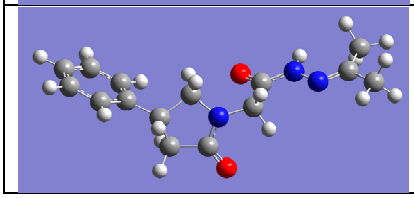
Figure S4. Packing of **PPAH**·**HBD** H-bonded layers with voids filled by the disordered acetone solvent molecules.

Table S1. Relative energies of **PPA** enantiomers with different conformations according to DFT calculations on B3LYP/6-311++(d,p) level of theory, kcal/mol

Molecular structure	Molecular and enantiomer ID	ΔE, kcal/mol
	**PPA**(*S*)-A	0.00
	**PPA**(*R*)-A	1.24
	**PPA**(*S*)-B	1.62
	**PPA**(*R*)-B	1.78
	**PPA·2HBA**(*R*)	3.14
	**PPA·2HBA**(*S*)	1.78
	**PPA·HBA**(*R;S*)	1.63

The most favorable phenypiracetam (**PPA**) structure is one of the conformers found in **PPA** crystal. Other three conformers in **PPA** crystal are less favorable from 1.24 to 1.78 kcal/mol according to calculations on B3LYP/6-311++G(d,p) level of theory. The differences between conformers **PPA**(*S*)-A and **PPA**(R)-A is in rotation of amid functional group around C-C bond (torsion angles O-C-C-N for **PPA**(S)-A is 115.0° and for **PPA**(R)-A is 153.8°). The same torsion angle for conformations **PPA**(S)-B and **PPA**(R)-B is more close to 0 (5.2° and 13.8° respectively). For conformers **PPA**(S)-A and **PPA**(R)-B torsion angles (N)C-C-C-C(Ph) of phenyl ring are very similar (60.5° and 59.0° respectively). Molecules **PPA**(R)-A and **PPA**(S)-B have different orientations of phenyl group characterized with torsion angles (117.2° and 118.0° respectively).

Table S2. Relative energies of **PPAH** enantiomers with different conformations according to DFT calculations on B3LYP/6-311++(d,p) level of theory, kcal/mol

Molecular structure	Molecular and enantiomer ID	ΔE, kcal/mol
	**PPAH**	0.00
	**PPAH·HBD**	0.00

Geometry parameters of molecule in pure material and cocrystal are very similar and there is no difference in their conformational energies.