Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

for

Systematic coformer contribution to cocrystal stabilization: energy and packing trends

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Total number of pages 9,
13 Figures, 2 Tables

Table of content

Thermal Analysis

Differential Scanning Calorimetry: Differential Scanning Calorimetry data were collected for Acr:Thy 1:1 and Acr:Car 1:2 on a Perkin-Elmer 6000 DSC. Thermograms were registered and elaborated with Pyris Software.

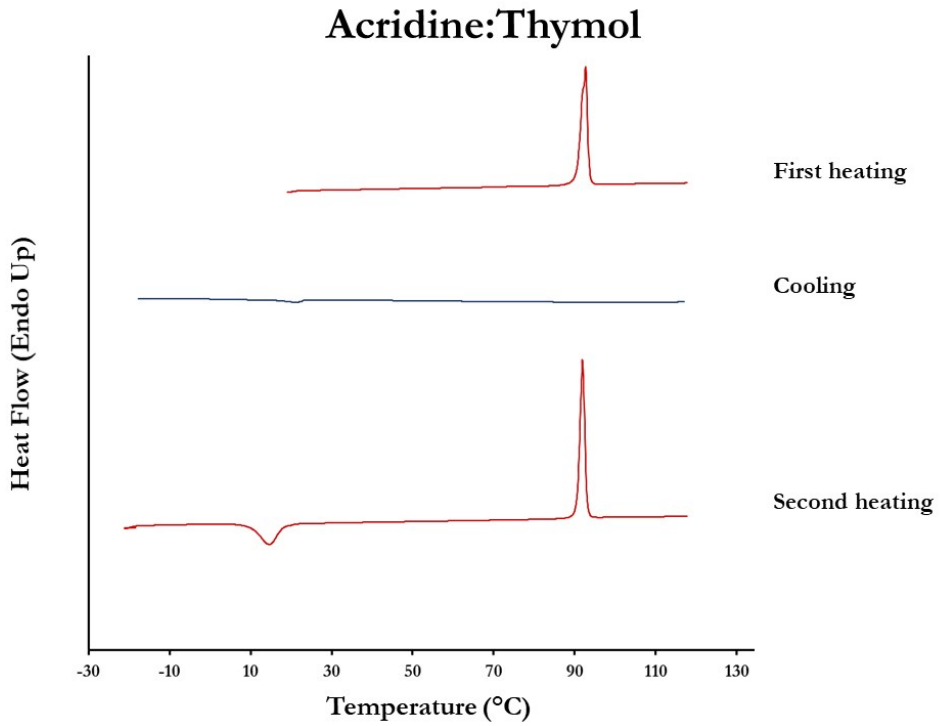

Figure SI *1*. Thermograms registered for Acr:Thy 1:1. Red line: 1st heating from 25 °C to 120 °C; blue line: cooling from 120 °C to -25 °C; red line: 2nd heating from -25 °C to 120 °C. Data were collected at 5 °C/min.

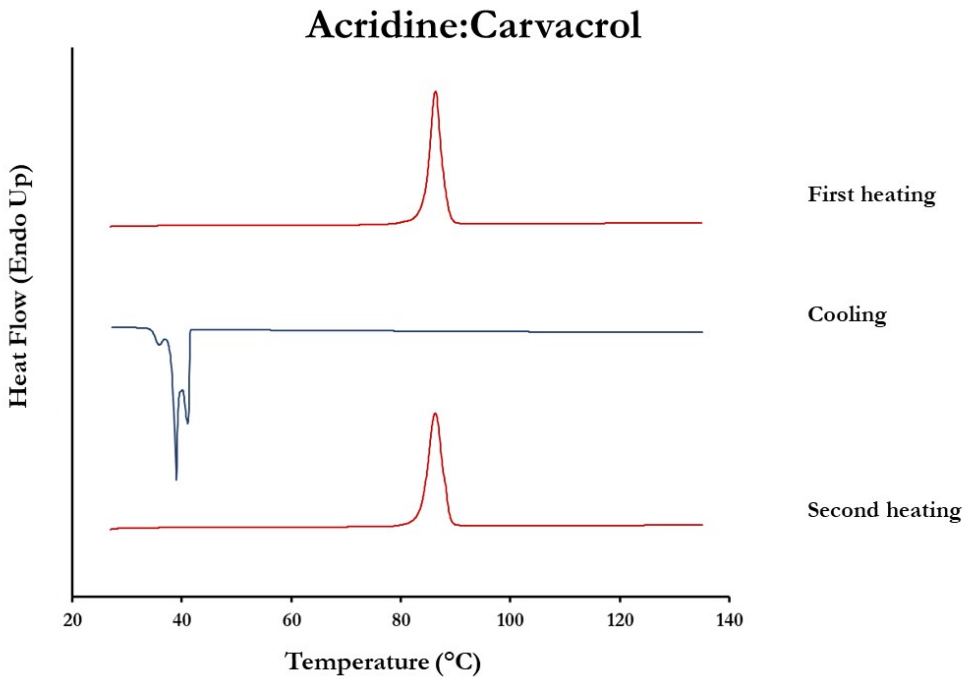

Figure SI *2*. Thermograms registered for Acr:Car 1:2. Red line: 1st heating from 25 °C to 140 °C; blue line: cooling from 140 °C to 25 °C; red line: 2nd heating from 25 °C to 140 °C. Data were collected at 5 °C/min.

Table SI 1. Summary of the thermal events occurring for each cocrystals as reported above.

Cocrystal	Run	Thermal Event	Peak height °C	ΔH (J/g)
Acridine:Thymol 1:1	First Heating	Endothermic	92.70	117.83
	Cooling	---	---	---
	Second Heating - 1st peak	Exothermic	14.67	-56.95
	Second Heating - 2st peak	Endothermic	91.92	120.30
Acridine:Carvacrol 1:2	First Heating	Endothermic	86.34	122.94
	Cooling - 1st peak	Exothermic	41.15	-12.83
	Cooling - 2st peak	Exothermic	39.00	-24.58
	Cooling - 3st peak	Exothermic	35.82	-2.00
	Second Heating	Endothermic	86.31	121.38

X-Ray Powder Diffraction

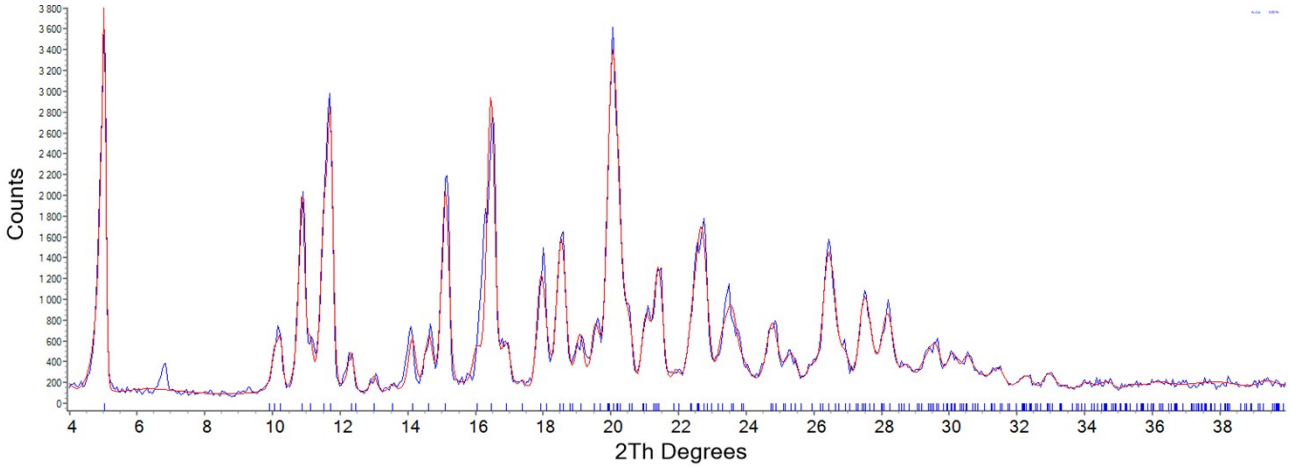

Figure SI 3. Pawley fit of Acr:Car 1:2 obtained after grinding (red line) against experimental data (blue dots). Additional peaks at 6.78 was also detected due to impurities.

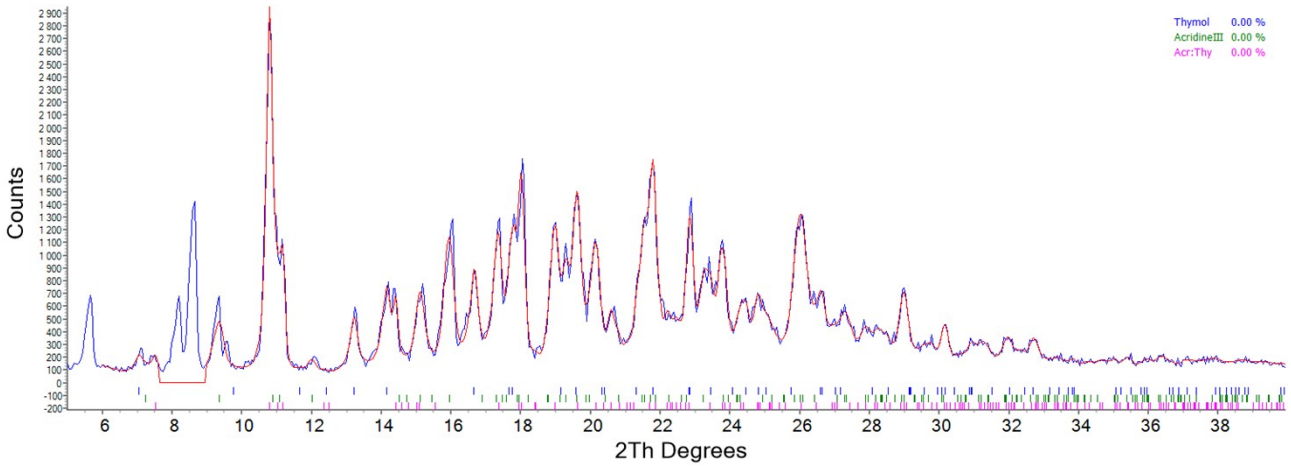

Figure SI 4. Pawley fit of Acr:Thy 1:1 obtained after grinding (red line) against experimental data (blue dots). Blue and green stick respectively refer to unreacted Thymol and Acridine. Pink sticks refer to the title compound. Additional peaks due to impurities at 5.62, 8.19 and 8.60 were also detected thus 2theta range from 5 to 6 and from 7.7 to 8.4 were excluded from the refinement.

Crystallography

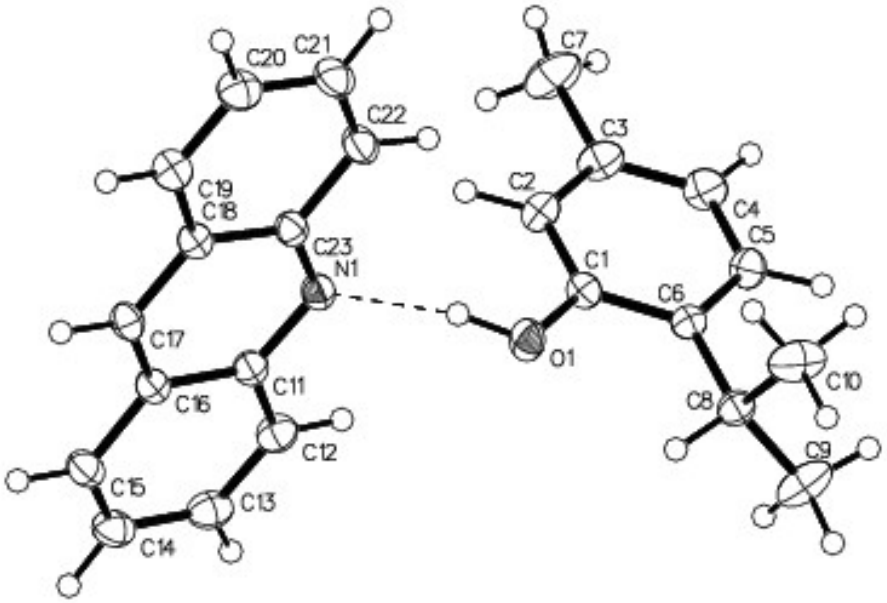

Figure SI 5. ORTEP drawing of Acr:Thy 1:1. All non-hydrogen atoms shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style for sake of clarity.

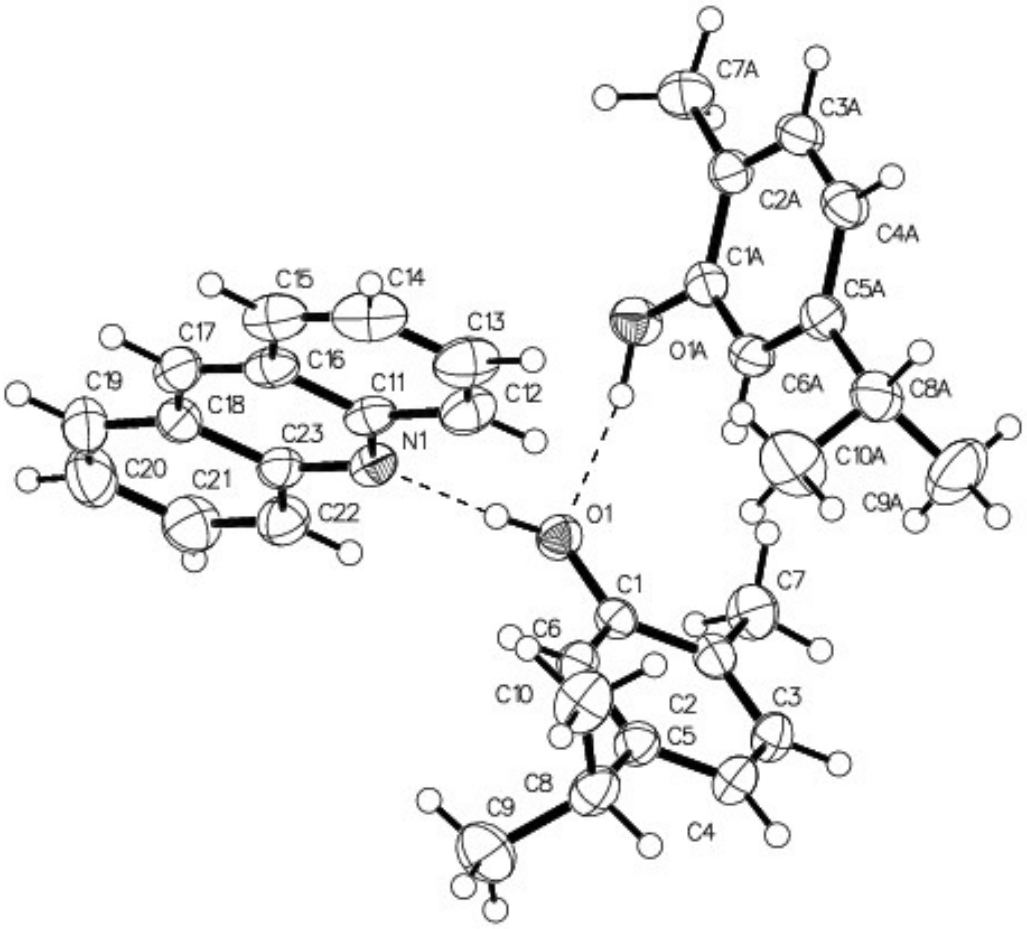

Figure SI 6. ORTEP drawing of Acr:Car 1:2. All non-hydrogen atoms shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style for sake of clarity.

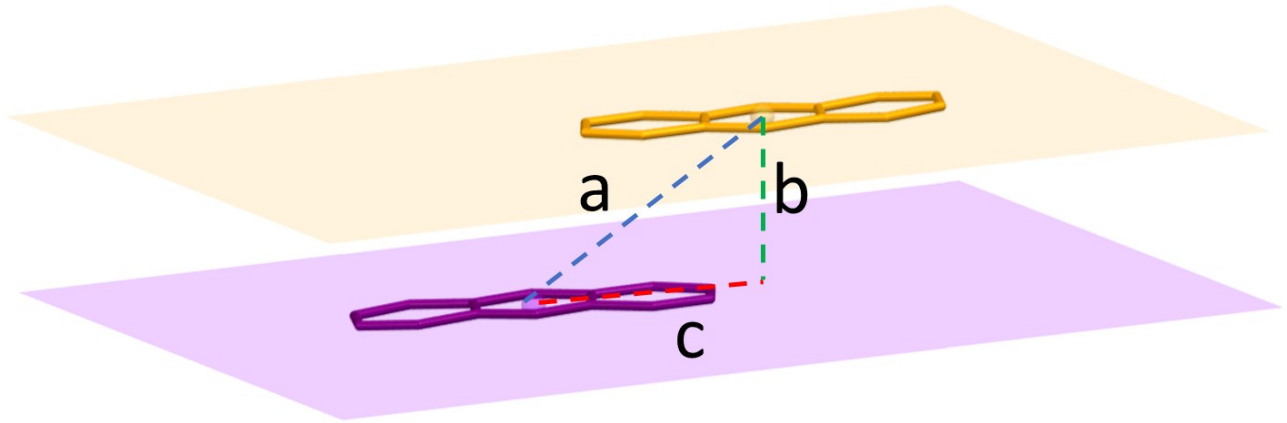

Figure SI 7. Schematic representation of coformer offset calculation: a) centroid-centroid distance, b) interplanar distance, c) molecular offset.

Table 1. Crystal data and structure refinement for Acr:Thy 1:1 and Acr:Car 1:2

	Acr:Thy	**Acr:Car**
Empirical formula	$C_{23}H_{23}NO$	$C_{33}H_{37}NO_2$
Formula weight	329.45	479.63
Temperature/K	100	200
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	12.1372(1)	9.5596(4)
b/Å	9.1209(1)	34.544(1)
c/Å	17.2439(2)	9.0322(3)
α/°	90	90
β/°	108.629(1)	113.902(5)
γ/°	90	90
Volume/Å^3	1808.92(3)	2726.9(2)
Z	4	4
ρ_{calc}g/cm^3	1.2096	1.168
μ/mm^{-1}	0.071	0.071
F(000)	704.2	1032.0
Crystal size/mm^3	0.3 × 0.2 × 0.2	1.0 × 0.5 × 0.5
Radiation	synchrotron (λ = 0.7)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.48 to 57.28	4.66 to 61.01
Index ranges	-16 ≤ h ≤ 16, -12 ≤ k ≤ 12, -23 ≤ l ≤ 23	-13 ≤ h ≤ 13, -47 ≤ k ≤ 49, -12 ≤ l ≤ 12
Reflections collected	29477	30462
Independent reflections	4784 R_{int} = 0.0378, R_{sigma} = 0.0175	8320 R_{int} = 0.0396, R_{sigma} = 0.0345
Data	4784	8320
Restraints	0	0
parameters	319	340
Goodness-of-fit on F^2	1.104	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0617, wR_2 = 0.1611	R_1 = 0.0570, wR_2 = 0.1202
Final R indexes [all data]	R_1 = 0.0629, wR_2 = 0.1627	R_1 = 0.0896, wR_2 = 0.1359
Largest DF max/min /e Å^{-3}	0.46/-0.51	0.23/-0.19

Energy Frameworks

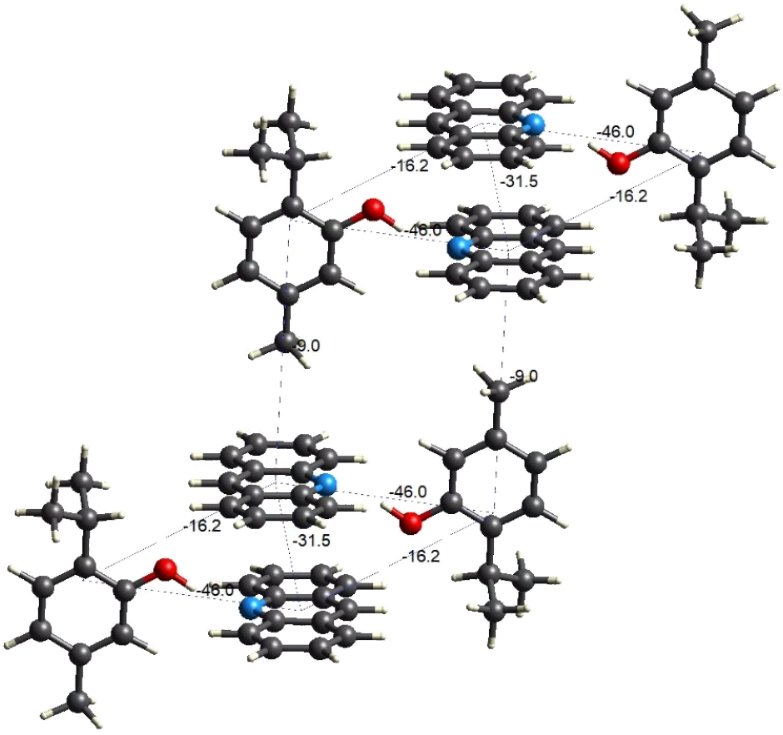

Figure SI 8. Energy Framework calculated for Acr:Thy 1:1 at the B3LYP/6-31G(d,p) level of theory: Annotated total energy. (threshold = -6 kJ/mol).

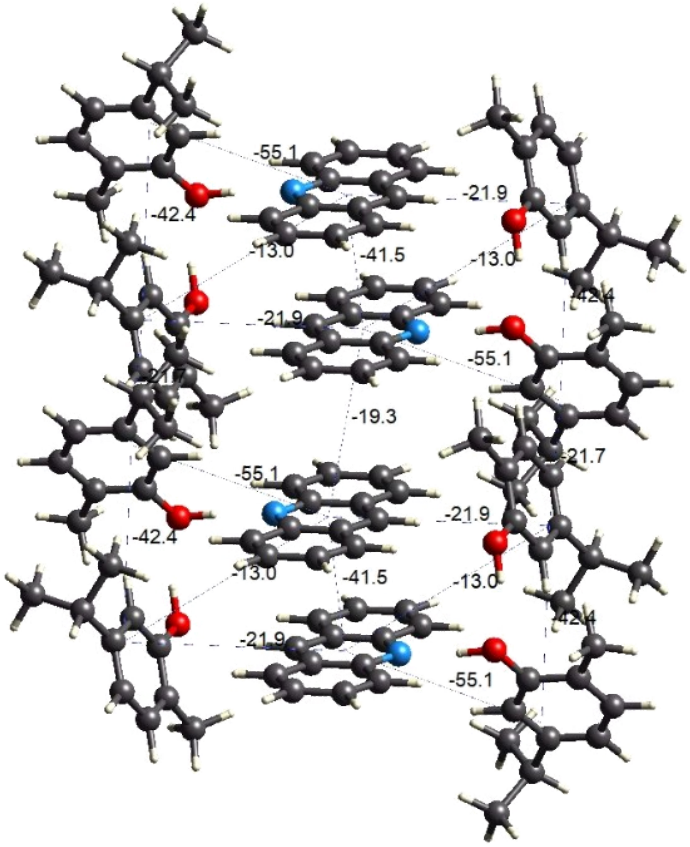

Figure SI 9. Energy Framework calculated for Acr:Car 1:2 at the B3LYP/6-31G(d,p) level of theory: Annotated total energy. (threshold = -6 kJ/mol).

Statistical Analyses

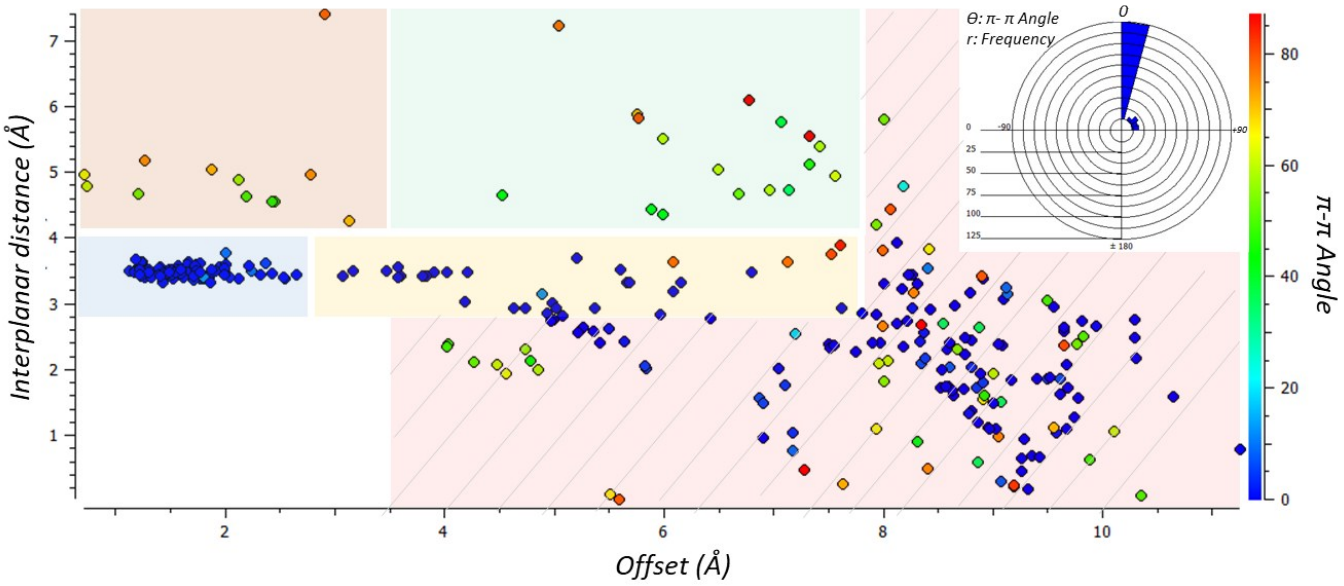

Figure SI 10. Acridine-acridine (A-A) reciprocal orientation observed in analysed cocrystals. Molecular offset (Å) vs molecular interplanar distance (Å) scatter plot. Records are coloured according to the angles registered between the molecular planes going from blue (parallel molecular orientation) to red (orthogonal molecular orientation).

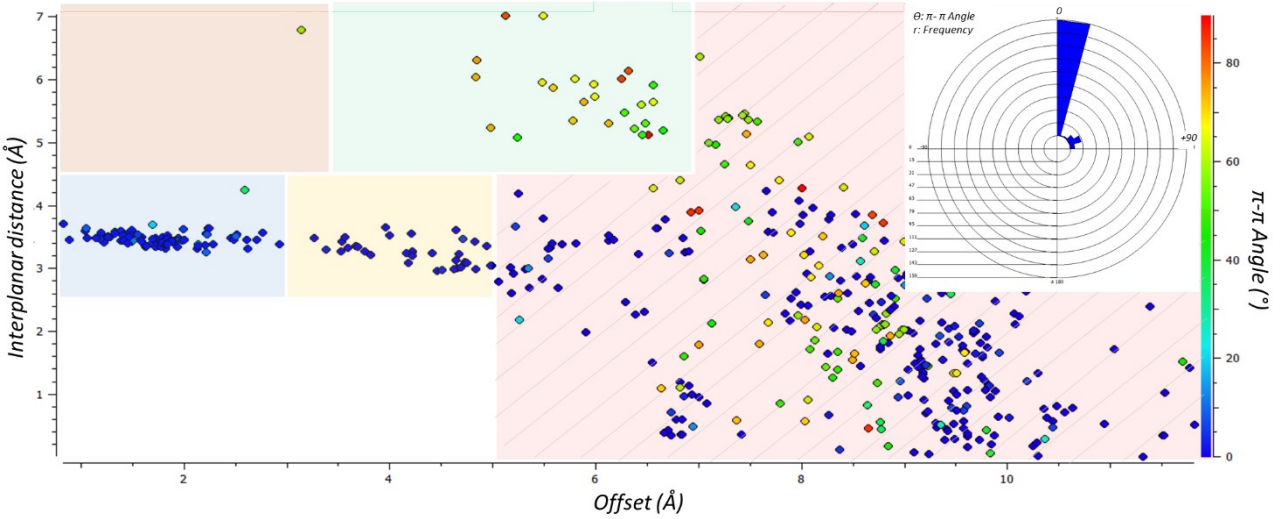

Figure SI 11. Phenazine (P-P) reciprocal orientation observed in analysed cocrystals. Molecular offset (Å) vs molecular interplanar distance (Å) scatter plot. Records are coloured according to the angles registered between the molecular planes going from blue (parallel molecular orientation) to red (orthogonal molecular orientation).

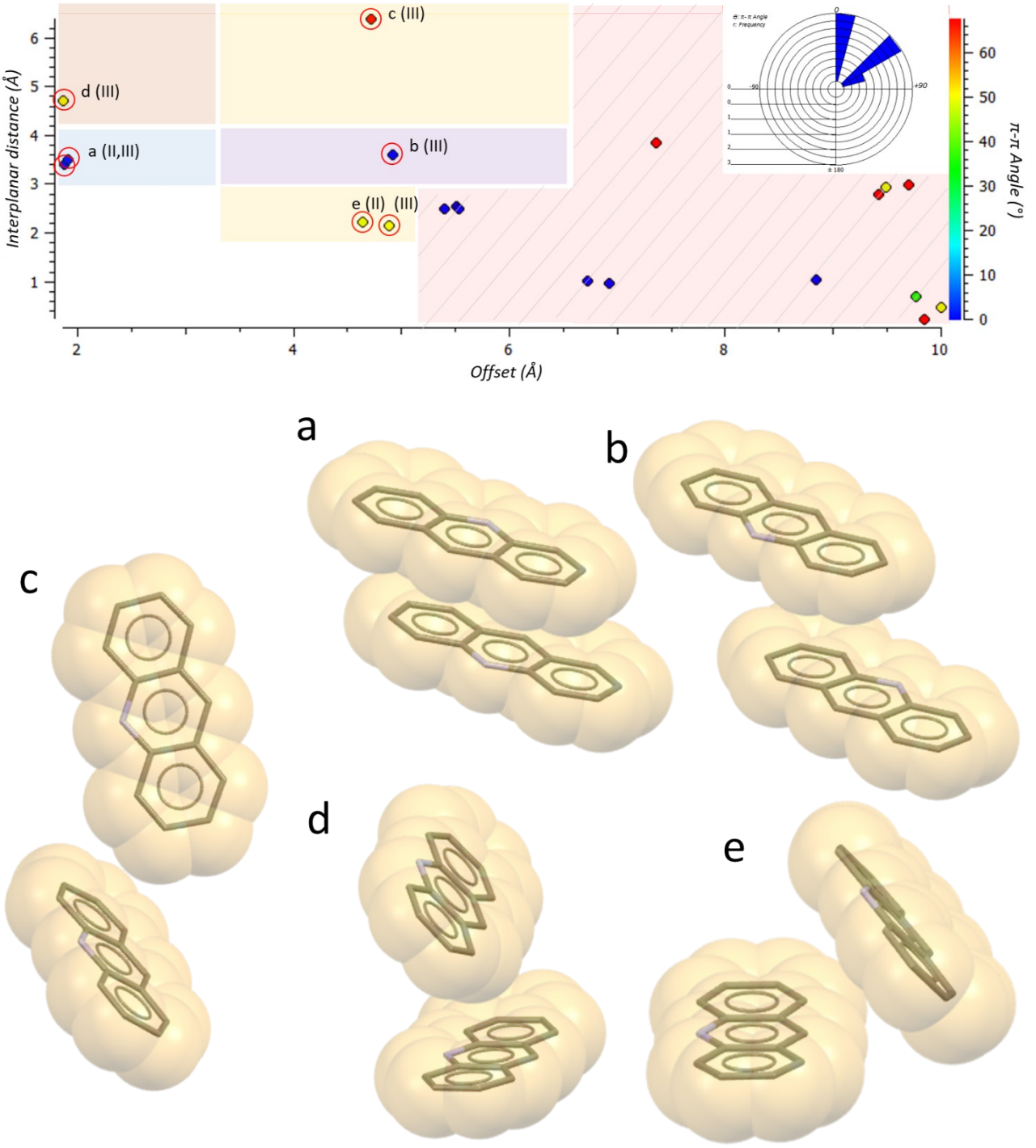

Figure SI 12. Acridine-acridine (A-A) orientations observed in acridine-based cocrystals. Offset (Å) vs π-π interplanar distance (Å) scatter plot. Records are coloured according to the angles registered between the molecular planes ranging from blue (parallel molecular orientation) to red (orthogonal molecular orientation). Exemplificative records labelled in the scatter plot are reported underneath. a) Blue zone represents short interplanar distance and modest A-A offset. b) Purple zone represents short interplanar distance and large A-A offset. c). Yellow zone represents large offset and noticeable π-π interplanar angle (c, very large interplanar distance; e, very short interplanar distance). d) Orange zone represents modest A-A offset and a large π-π interplanar distance. Hydrogen atoms are omitted for the sake of clarity. Inset: Polar histogram plot of the π-π interplanar angle of the above described records only.

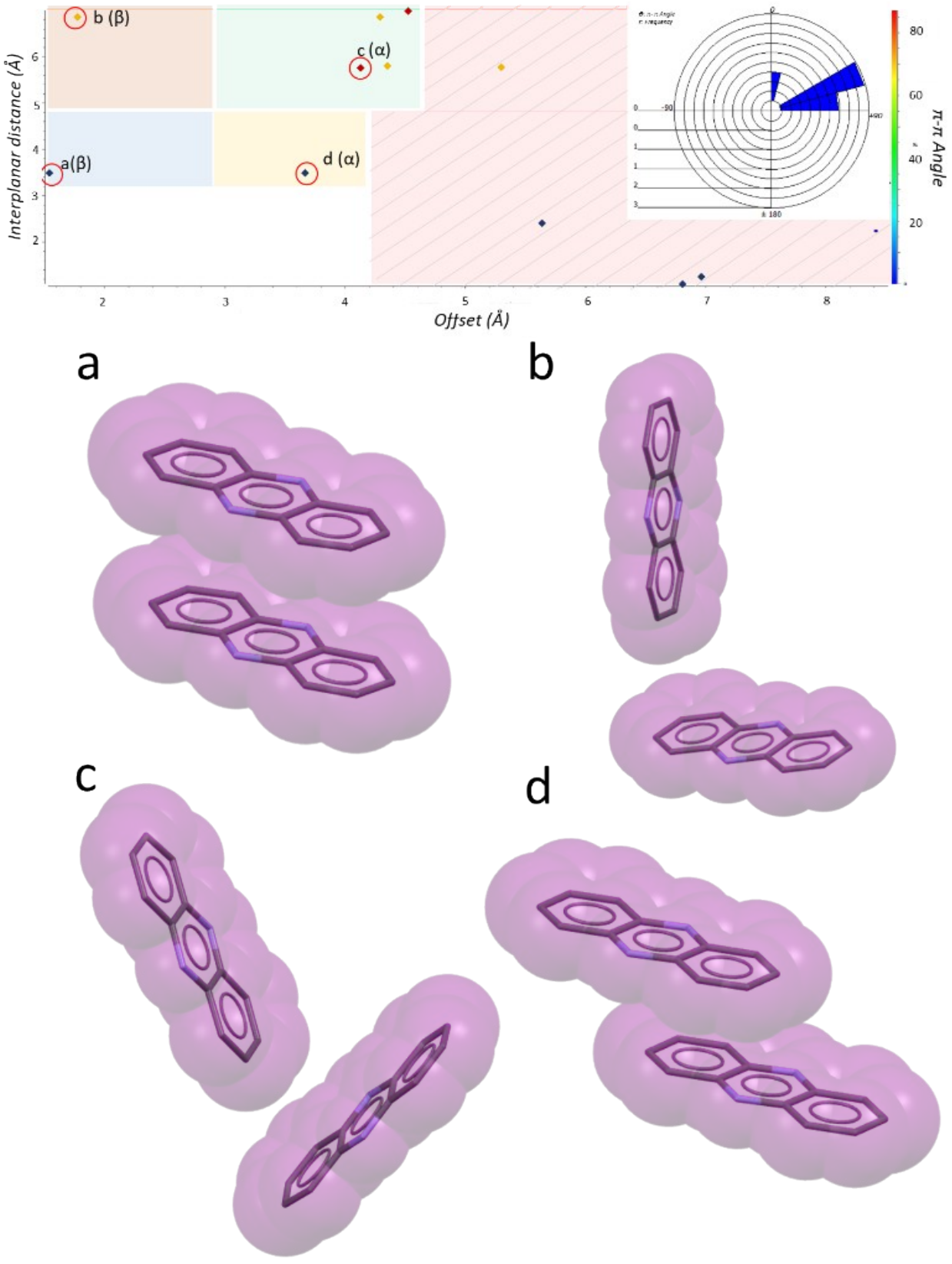

Figure 13. Phenazine-phenazine (P-P) orientations observed in acridine-based cocrystals. Offset (Å) vs π-π interplanar distance (Å) scatter plot. Records are coloured according to the angles registered between the molecular planes ranging from blue (parallel molecular orientation) to red (orthogonal molecular orientation). a) Blue zone represents short interplanar distance and modest P-P offset. b) Orange zone represents short offset and noticeable π-π interplanar distance. c) Green zone represents large interplanar distance and large P-P offset. d) Yellow zone represents short interplanar distance and large P-P offset. Hydrogen atoms are omitted for the sake of clarity. Coloured dotted lines represent H-bond between phenazine and the relative coformer. Inset: Polar histogram plot of the π-π interplanar angle of the above described records only.