

## **ESI material for the manuscript:**

### **A new polymorph of the common coformer isonicotinamide**

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Table S1: The conditions limiting possible reflections for the crystal of polymorph 6.

Number	Conditions limiting possible reflections*	Deduction
1	hkl: none	Primitive lattice
2	0kl: $k = 2n$	b-glide plane perpendicular to the a-axis
3	h0l: $l = 2n$	c-glide plane perpendicular to the b-axis
4	hk0: none	no glide plane perpendicular to the c-axis
5	h00: $h = 2n$ ( <i>apparent initially</i> )	Screw axis parallel to the a-axis
6	0k0: $k = 2n$	Redundant condition (from 2 above)
7	00l: $l = 2n$	Redundant condition (from 3 above)

\*The conditions listed above refer to the original setting of the crystal unit cell, namely that with  $a = 7.9929(9)$ ,  $b = 9.888(1)$ ,  $c = 15.162(2)$  Å, corresponding to the space group setting  $Pbc2_1$ . Transformation to the standard setting,  $Pca2_1$  (No. 29), required application of the matrix  $\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$  to the original unit cell vectors.

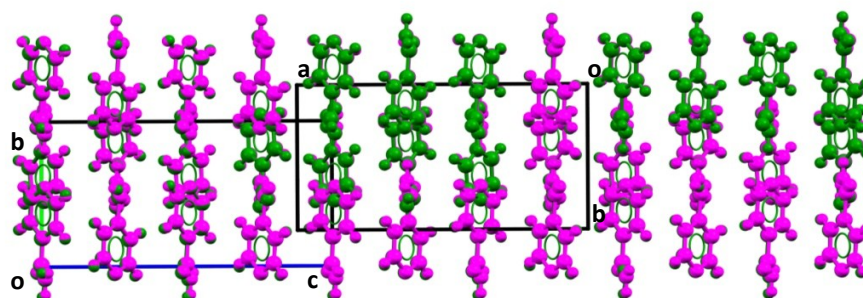


Figure S1: The molecular overlay of polymorph 2 (green) and polymorph 6 (pink), derived from Figure 5 by a 90° rotation around the c-axis of the orthorhombic polymorph.

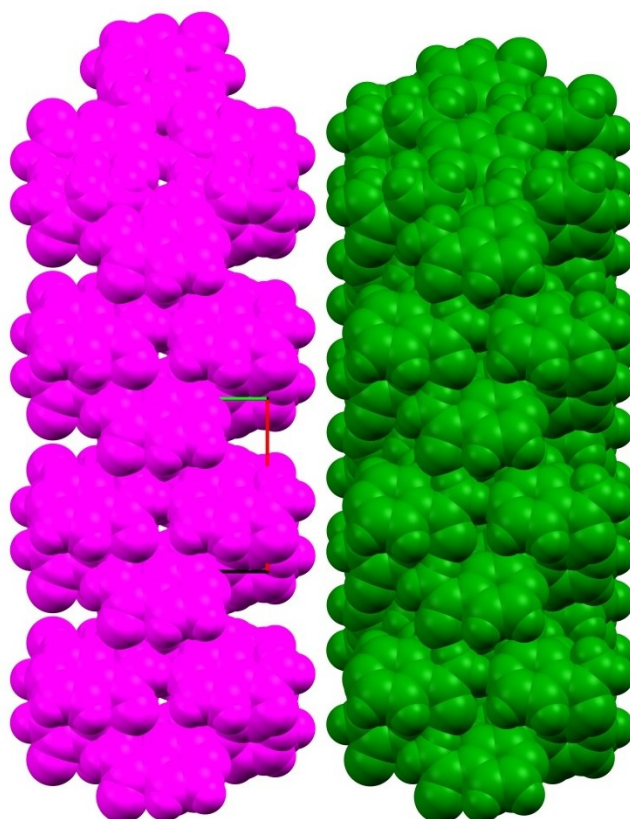
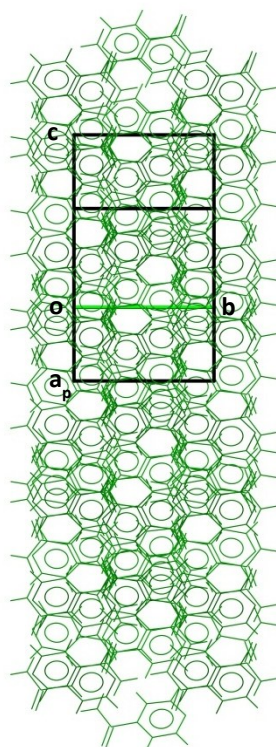
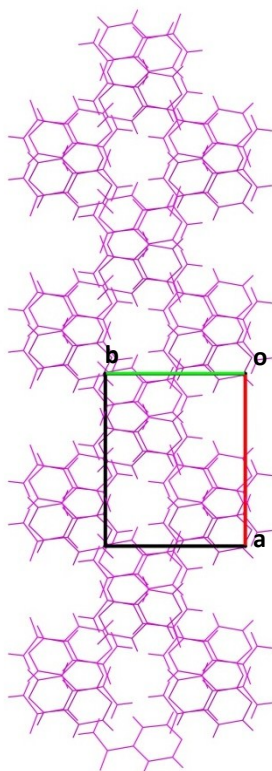


Figure S2a: A wireframe representation of the molecular overlay of polymorph 2 (green) and polymorph 6 (pink), derived from Figure 5 by a 90° rotation around the a-axis of the orthorhombic polymorph.

Figure S2b: A space-filling representation of the molecular overlay shown in Figure S2a.

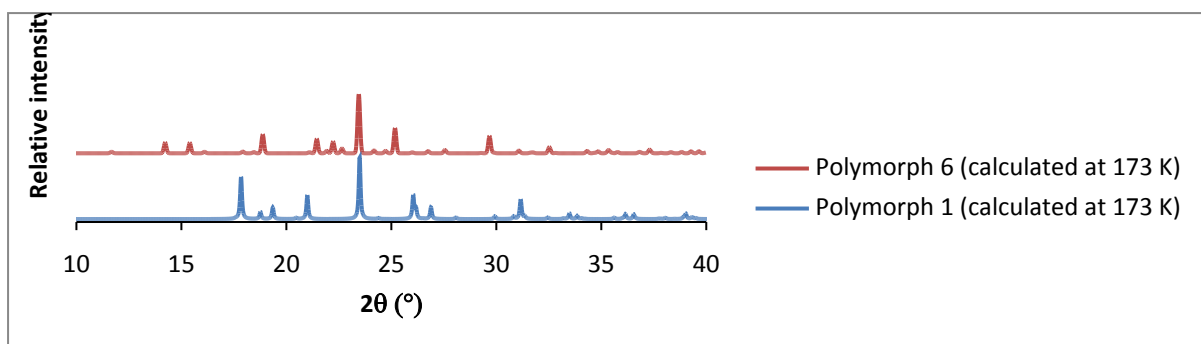


Figure S3a: The calculated PXRD patterns of polymorph 1 and 6.

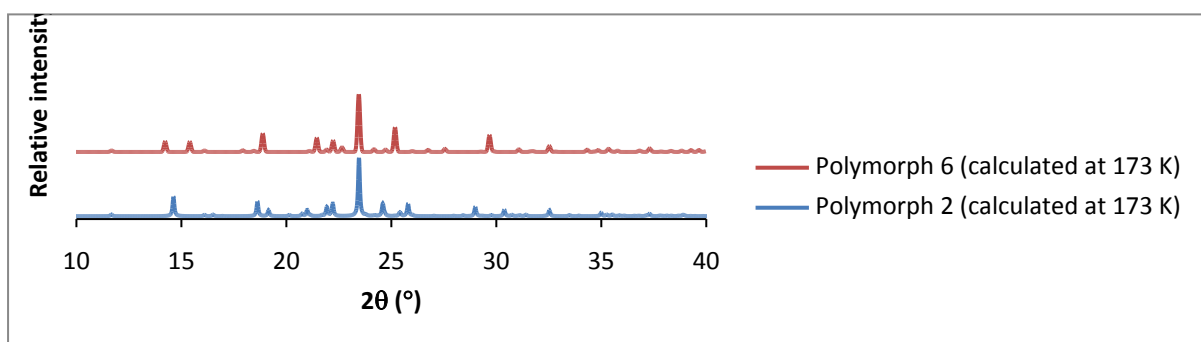


Figure S3b: The calculated PXRD patterns of polymorph 2 and 6.

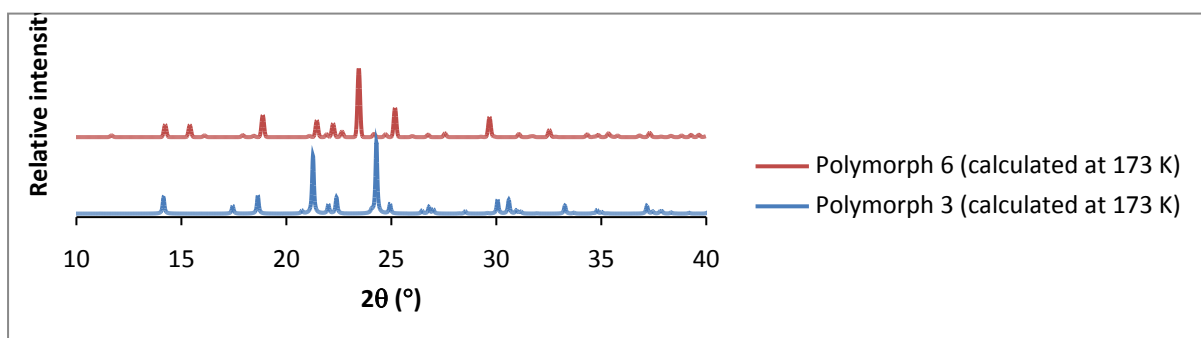


Figure S3c: The calculated PXRD patterns of polymorph 3 and 6.

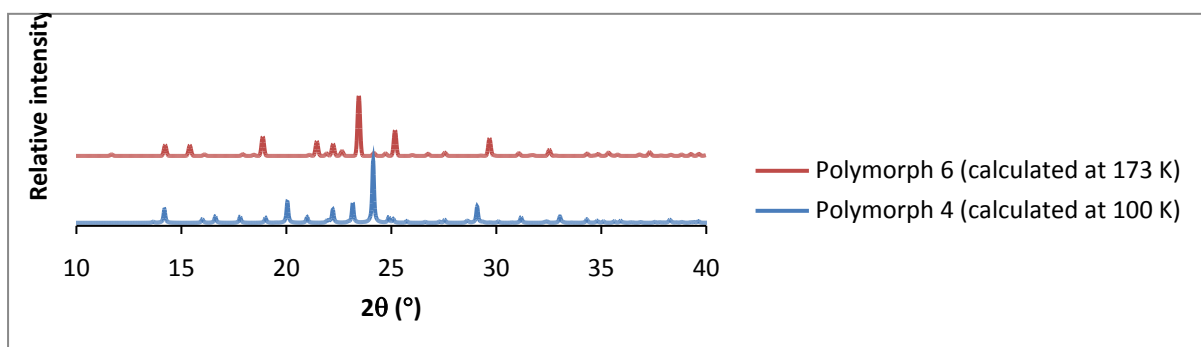


Figure S3d: The calculated PXRD patterns of polymorph 4 and 6.

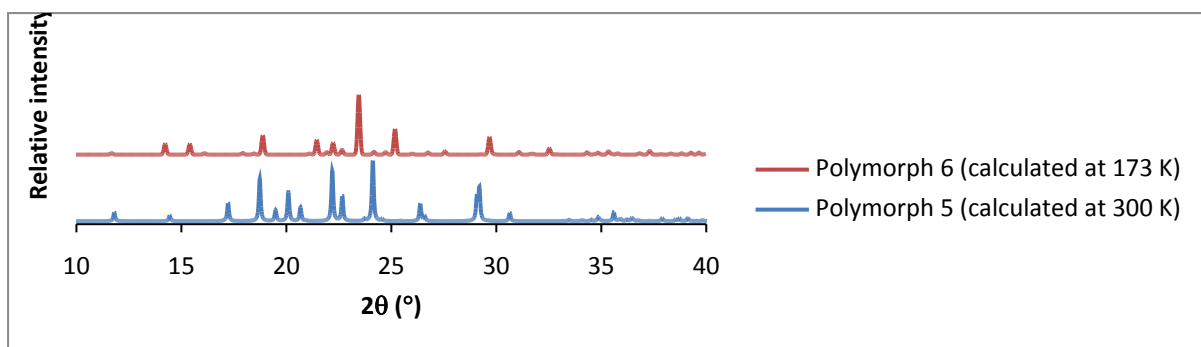


Figure S3e: The calculated PXRD patterns of polymorph 5 and 6.

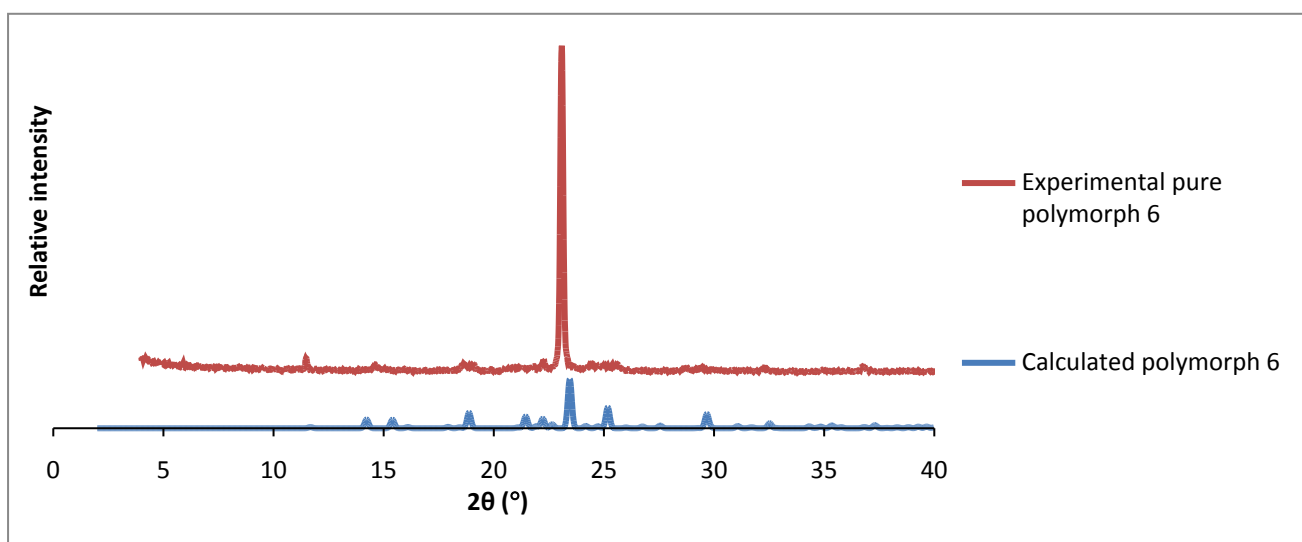


Figure S4a: The experimental PXRD pattern of pure polymorph 6 and the calculated PXRD pattern of polymorph 6.

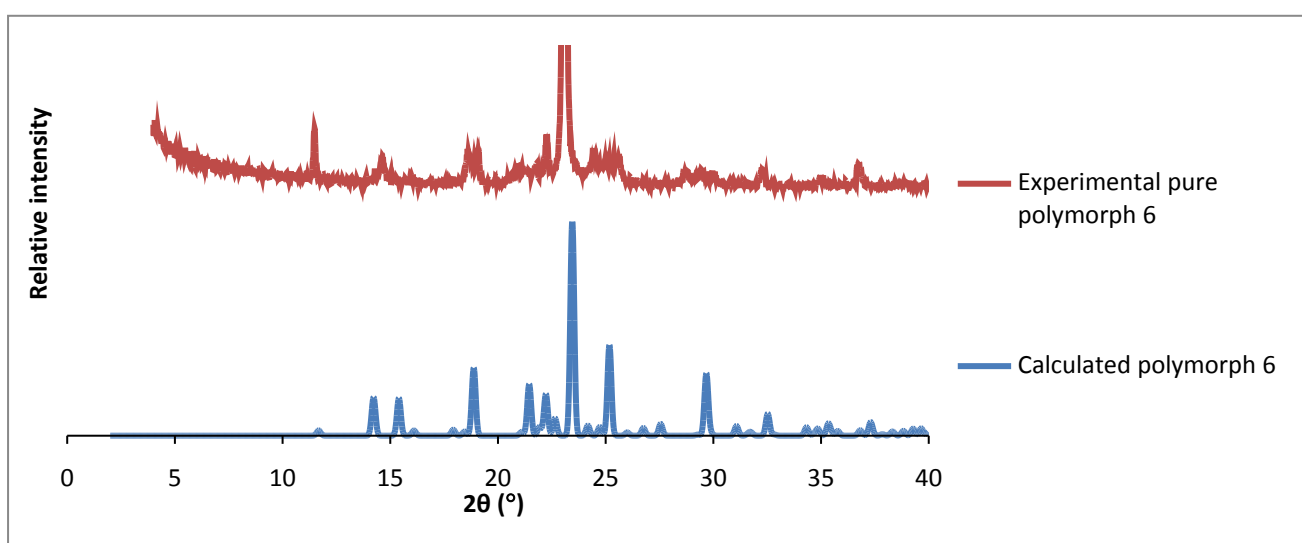


Figure S4b: Intensity-enhanced representations of the PXRD patterns shown in Figure S3a.

Figure S5: A series of HSM micrographs which display the thermal progression of polymorphs 1, 2, 3, 4 and 6 of isonicotinamide from 27.5 °C – 161.0 °C.

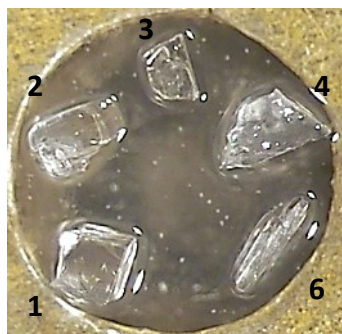


Image 1: The initial appearance of the polymorphs at 27.5 °C.



Image 2: At 122.8 °C the onset of opacity occurred within polymorph 3.



Image 3: At 128.9 °C the onset of the melt occurred for polymorph 6.



Image 4: At 132.1 °C the remaining polymorphs began to melt.



Image 5: At 141.9 °C the onset of opacity occurred within polymorph 4.

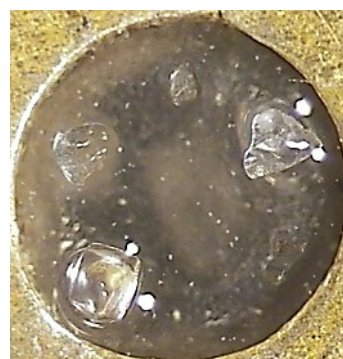


Image 6: At 151.3 °C the melting rate increased and polymorph 6 completely melted.



Image 7: At 155.1 °C polymorphs 1, 2 and 3 had melted, while the melting rate of polymorph 4 decreased significantly.



Image 8: At 161.0 °C all the crystals had fully melted.



Table S2: The results from selected crystals of the recrystallization of isonicotinamide from acetone, acetonitrile and isopropanol.

<b>Solvent</b>	<b>Product characteristics</b>	<b>Method of analysis</b>	<b>Results</b>
Acetone	Large, rectangular, transparent crystals.	SCXRD	Polymorphs 6, 4 and 2 were found in approximately equal ratios by mass.
Acetonitrile	Medium to large, rectangular, transparent crystals.	SCXRD	Polymorphs 6, 4, 2 were found in approximately equal ratios by mass.
Isopropanol	Medium-sized, transparent crystals in the shape of parallelograms.	SCXRD and PXRD	A fair amount of single crystals of polymorph 6 was obtained (majority). However, a few of the other polymorphs (except for polymorph 5) were occasionally found (minority).