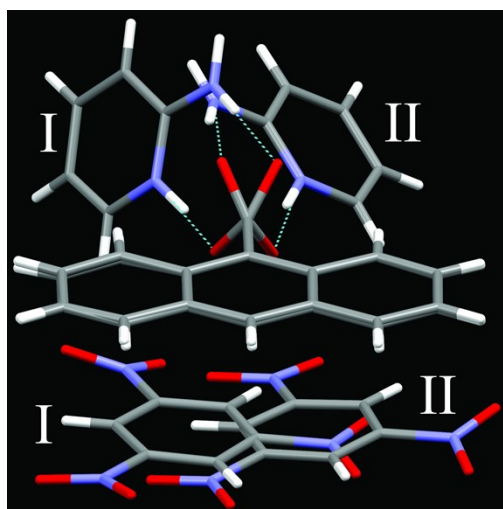


Supplementary Information

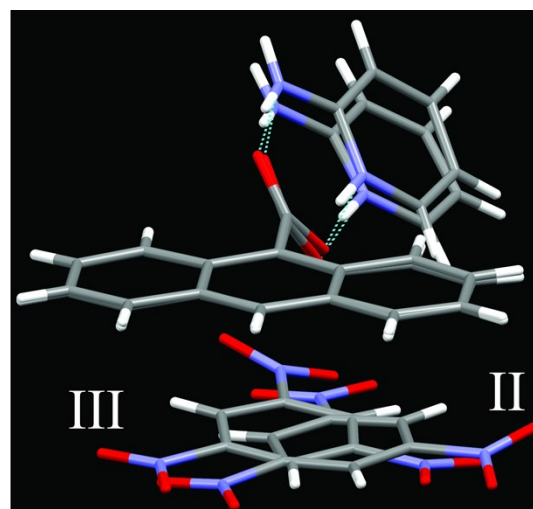
All good things come in threes: an example of a trimorphic, ternary molecular salt complex

Andreas Lemmerer

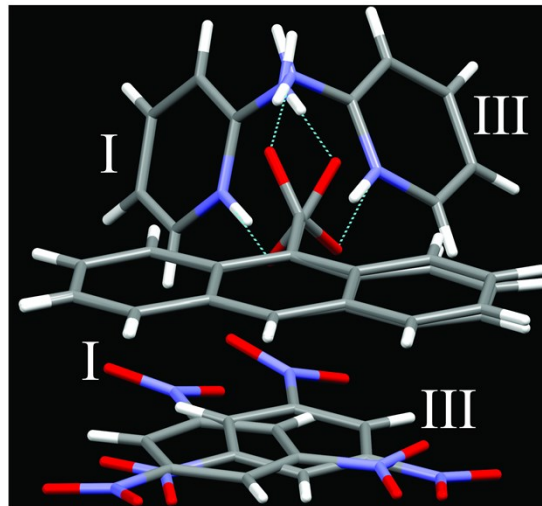
A. Molecular Overlay



(a) Form I and II



(b) Form II and III



(c) Form I and III

Figure S1. Overlays of pairs of polymorphs showing the relative positions to the common 9-ap anion.

B. Intermolecular Potentials

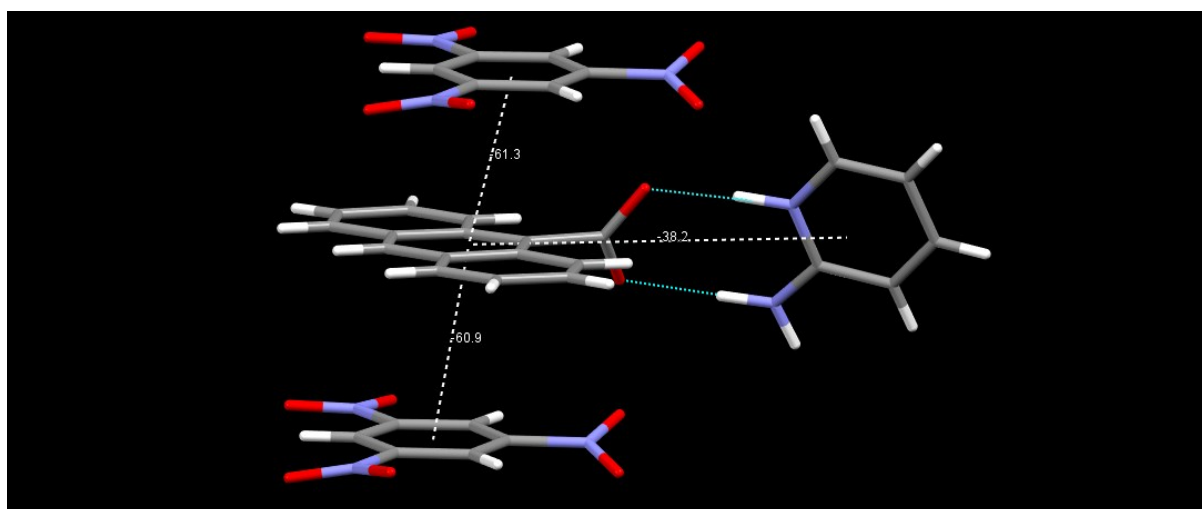


Figure S2. Calculated intermolecular potentials using the UNI force field for Form I. Only the strongest three are shown.

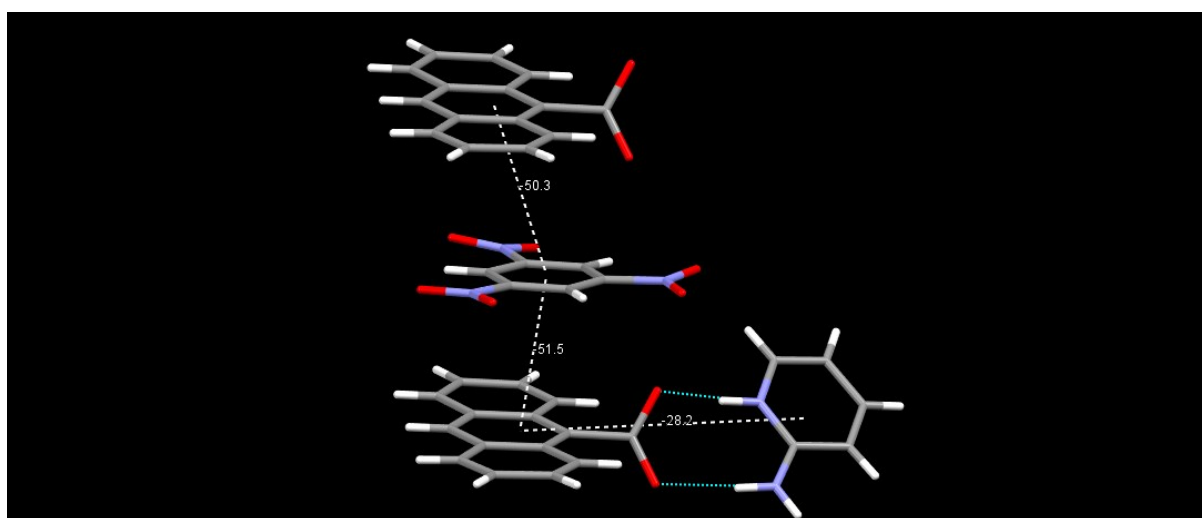


Figure S3. Calculated intermolecular potentials using the UNI force field for Form II. Only the strongest three are shown.

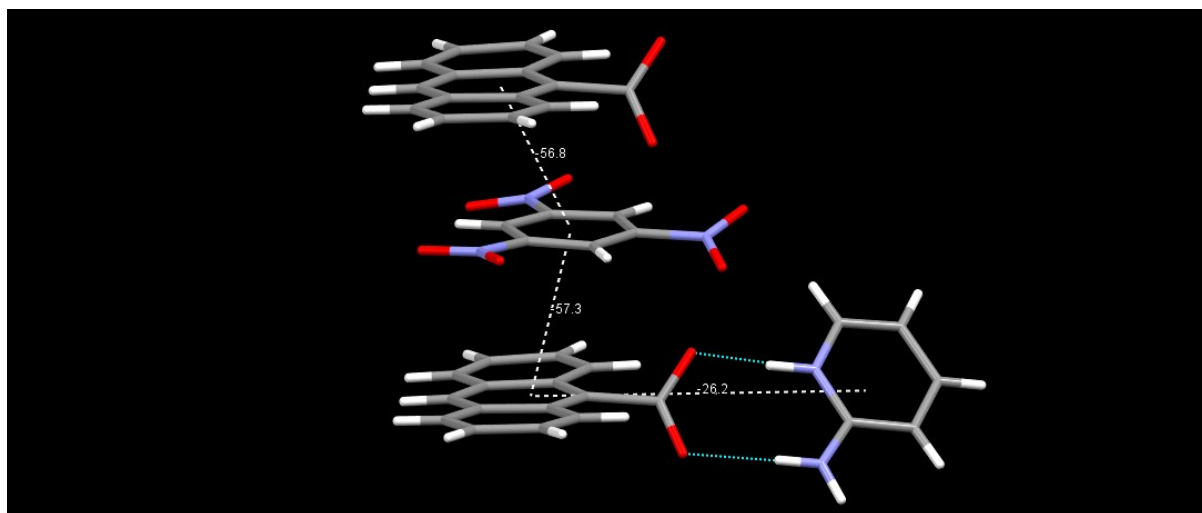


Figure S4. Calculated intermolecular potentials using the UNI force field for Form **III**. Only the strongest three are shown.

C. Experimental Setup

All reagents used for synthesis and characterization were of analytical grade, purchased from Sigma-Aldrich, unless otherwise stated. Reagents were used as received, without further purification. In all experiments, 0.020 g of trinitrobenzene (0.094 mmol), 0.020 g of 9-anthracenecarboxylic acid (0.090 mmol) and 0.010 g of 2-aminopyridine (0.106 mmol) were weighed out. All solutions were heated and stirred and filtered through a 0.45 micron syringe filter.

Slow Evaporation Experiments

acetone	Form I
acetonitrile	Form II and III (repeating this experiment only resulted in form II again)
ethanol	Form I
2-propanol	Form I
acetonitrile	Form I (solution placed in fridge)
dichloromethane	Form I and II
1-butanol	Form I
acetonitrile	Form I and Form II (needle in lid)
ethylacetate	Form I and Form III

Fast Evaporation Experiments (in fume hood)

2-butanone	Form I
bromoform	Form I
acetone	Form I
acetonitrile	Form I
ethanol	Form I
toluene	Form I
ethylacetate	Form I

Vapour Diffusion

acetone/hexane	Form I and II
acetonitrile/hexane	Form II mainly and Form I a little
ethanol/hexane	Form II only
ethylacetate/hexane	Form I and III

D. Single Crystal Diffraction Data

All data collections were obtained on a Bruker Venture D8 Photon CMOS diffractometer with graphite-monochromated $\text{MoK}\alpha_1$ ($\lambda = 0.71073 \text{ \AA}$) radiation at 173 K using an Oxford Cryostream Plus cooler. The collection method involved ω -scans with a 0.5° width. SAINT+ version 6.02.6¹ software was used for data reduction and *SADABS*² was used to make empirical absorption corrections. The crystal structures were solved using direct methods on *SHELXS-97*.³ Non-hydrogen atoms were first refined isotropically, followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using *SHELXL-2017*.³ C-bound H atoms were located in the difference map, then positioned geometrically and were allowed to ride on their respective parent atoms, with thermal displacement parameters 1.2 times of the parent C atom. The coordinates and isotropic displacement parameters of the N-bound H atoms involved in hydrogen bonding interactions were allowed to refine freely. Diagrams and publication material were generated using *WinGX*,⁴ *ORTEP-3*,⁴ *PLATON*⁵ and *MERCURY*.⁶

1. SAINT+, Version 6.02 (Includes XPREP and SADABS); Bruker AXS Inc: Madison, Wisconsin, USA, 2004.
2. Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* 48, 3–10.
3. Sheldrick, G. M., *Acta Crystallogr., Sect. C.* 2015, 71 (Pt 1), 3-8.
4. Farrugia, L., *J. Appl. Crystallogr.* 2012, 45 (4), 849-854.
5. Spek, A., *Acta Crystallogr., Sect. D.* 2009, 65 (2), 148-155.
6. C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J. Appl. Cryst.* 2020, 53, 226-235.

CCDC 2001329 (Form **I**), 2001329 (Form **II**), and 2001329 (Form **III**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures."

Table S1. Crystal data and structure refinement for **Form I**

Identification code	CSD: 2001329	
Empirical formula	C ₂₆ H ₁₉ N ₅ O ₈	
Formula weight	529.46	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 6.8892(2) Å	$\alpha = 90^\circ$.
	b = 13.9675(3) Å	$\beta = 93.5340(10)^\circ$.
	c = 24.3771(6) Å	$\gamma = 90^\circ$.
Volume	2341.22(10) Å ³	
Z	4	
Density (calculated)	1.502 Mg/m ³	
Absorption coefficient	0.114 mm ⁻¹	
F(000)	1096	
Crystal size	0.386 x 0.127 x 0.084 mm ³	
Theta range for data collection	1.674 to 28.000°.	
Index ranges	-9 ≤ h ≤ 9, -18 ≤ k ≤ 18, -32 ≤ l ≤ 31	
Reflections collected	46569	
Independent reflections	5639 [R(int) = 0.0282]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5639 / 0 / 364	
Goodness-of-fit on F ²	1.043	
Final R indices [I > 2σ(I)]	R1 = 0.0401, wR2 = 0.1026	
R indices (all data)	R1 = 0.0561, wR2 = 0.1112	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.297 and -0.216 e.Å ⁻³	

Table S2. Hydrogen bonds for **Form I** [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N(5)-H(5A)...O(8)	0.97(2)	1.89(2)	2.8563(19)	178(2)
N(5)-H(5B)...O(8)#1	0.92(3)	1.96(3)	2.8588(18)	166(2)
N(4)-H(4)...O(7)	1.01(2)	1.72(2)	2.7098(16)	168(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

Table S3. Crystal data and structure refinement for **Form II**

Identification code	CSD: 2001330	
Empirical formula	C ₂₆ H ₁₉ N ₅ O ₈	
Formula weight	529.46	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 7.8923(11) Å	α = 90°.
	b = 18.908(3) Å	β = 95.838(5)°.
	c = 15.969(2) Å	γ = 90°.
Volume	2370.7(6) Å ³	
Z	4	
Density (calculated)	1.483 Mg/m ³	
Absorption coefficient	0.113 mm ⁻¹	
F(000)	1096	
Crystal size	0.68 x 0.44 x 0.26 mm ³	
Theta range for data collection	2.976 to 27.999°.	
Index ranges	-10 ≤ h ≤ 10, -24 ≤ k ≤ 24, -21 ≤ l ≤ 21	
Reflections collected	104798	
Independent reflections	5709 [R(int) = 0.0293]	
Completeness to theta = 25.242°	99.5 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5709 / 0 / 364	
Goodness-of-fit on F ²	1.019	
Final R indices [I > 2σ(I)]	R1 = 0.0377, wR2 = 0.0984	
R indices (all data)	R1 = 0.0419, wR2 = 0.1022	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.395 and -0.227 e.Å ⁻³	

Table S4. Hydrogen bonds for form **II** [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
C(23)-H(23)...O(1)#1	0.95	2.56	3.3786(16)	144
N(4)-H(4A)...O(7)	0.960(17)	1.657(17)	2.6121(12)	172(2)
N(5)-H(5A)...O(8)	0.894(18)	1.959(19)	2.8385(14)	168(2)
N(5)-H(5B)...O(1)#1	0.864(18)	2.490(18)	3.2899(14)	154(1)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y, -z+1$

Table S5. Crystal data and structure refinement for **Form III**

Identification code	CSD: 2001331	
Empirical formula	C ₂₆ H ₁₉ N ₅ O ₈	
Formula weight	529.46	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.0834(5) Å	$\alpha = 77.196(2)^\circ$.
	b = 12.8271(9) Å	$\beta = 85.946(2)^\circ$.
	c = 13.8555(9) Å	$\gamma = 81.281(2)^\circ$.
Volume	1212.51(14) Å ³	
Z	2	
Density (calculated)	1.450 Mg/m ³	
Absorption coefficient	0.110 mm ⁻¹	
F(000)	548	
Crystal size	0.895 x 0.346 x 0.120 mm ³	
Theta range for data collection	3.018 to 28.000°.	
Index ranges	-9<=h<=9, -16<=k<=16, -18<=l<=18	
Reflections collected	40646	
Independent reflections	5832 [R(int) = 0.0345]	
Completeness to theta = 25.242°	99.5 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5832 / 0 / 364	
Goodness-of-fit on F ²	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0445, wR2 = 0.1079	
R indices (all data)	R1 = 0.0555, wR2 = 0.1144	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.282 and -0.255 e.Å ⁻³	

Table S6. Hydrogen bonds for 19va_np908_p [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N(4)-H(4A)...O(7)	0.969(18)	1.648(19)	2.5993(14)	166(2)
N(5)-H(5A)...O(8)	0.886(19)	1.986(19)	2.8570(15)	167(2)
N(5)-H(5B)...O(8)#3	0.860(18)	2.271(17)	2.9147(14)	132(1)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,-y+1,-z #3 -x,-y+1,-z

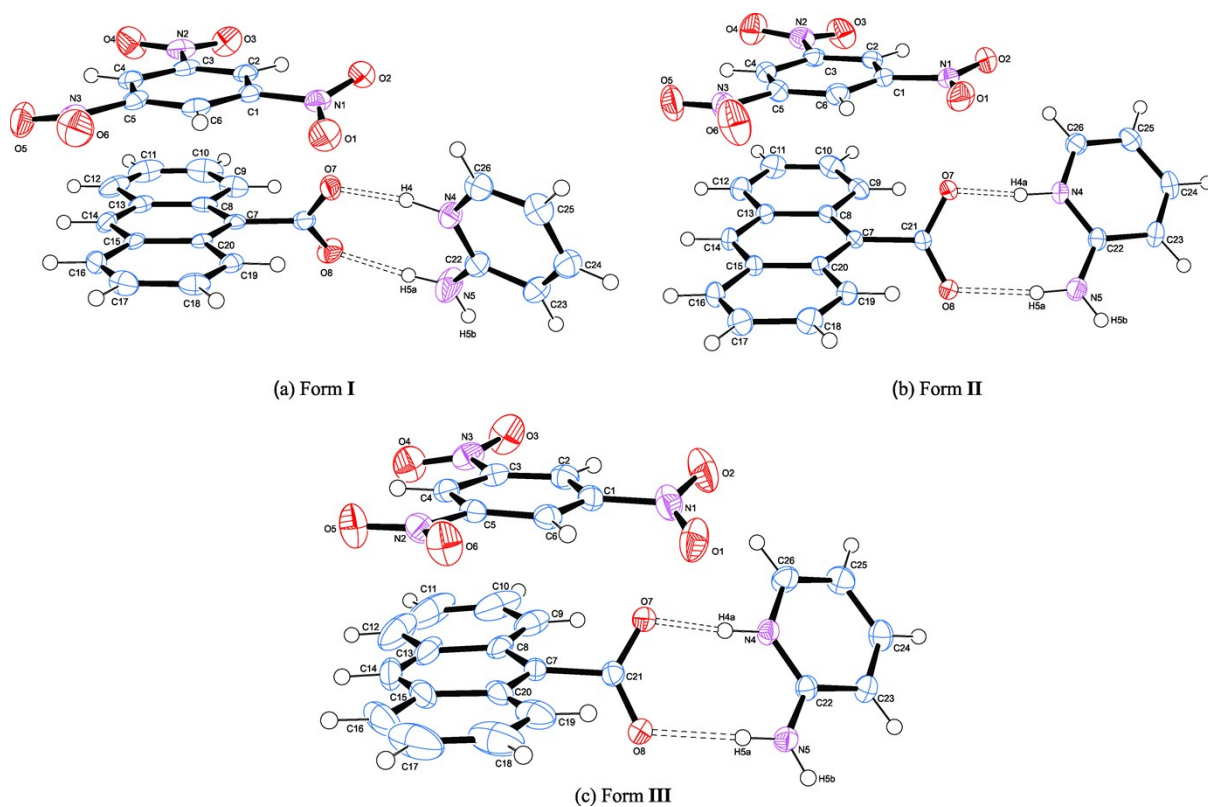


Figure S5. Asymmetric unit of (2-aminopyridinium)·(9-anthracenecarboxylate)·(trinitrobenzene), indicating the numbering scheme, ellipsoids at 50 % probability. Hydrogen bonding interactions shown with a dashed bond.

E. Powder X-ray Diffraction

Powder X-ray diffraction data patterns were collected at 293 K on a Bruker D2 Phaser diffractometer which employed a sealed tube Co X-ray source ($\lambda = 1.78897 \text{ \AA}$), operating at 30 kV and 10 mA, and LynxEye PSD detector in Bragg-Brentano geometry. The calculated powder diffraction patterns were computed from the single crystal data which was collected at 173 K using Mercury. The peak positions are shifted resulting from the different temperatures at which the samples were measured. The peak intensities vary due to preferred orientation. For form III, the sample consisted of a few crystals gently crushed on a zero-background holder and so there is significant preferred orientation.

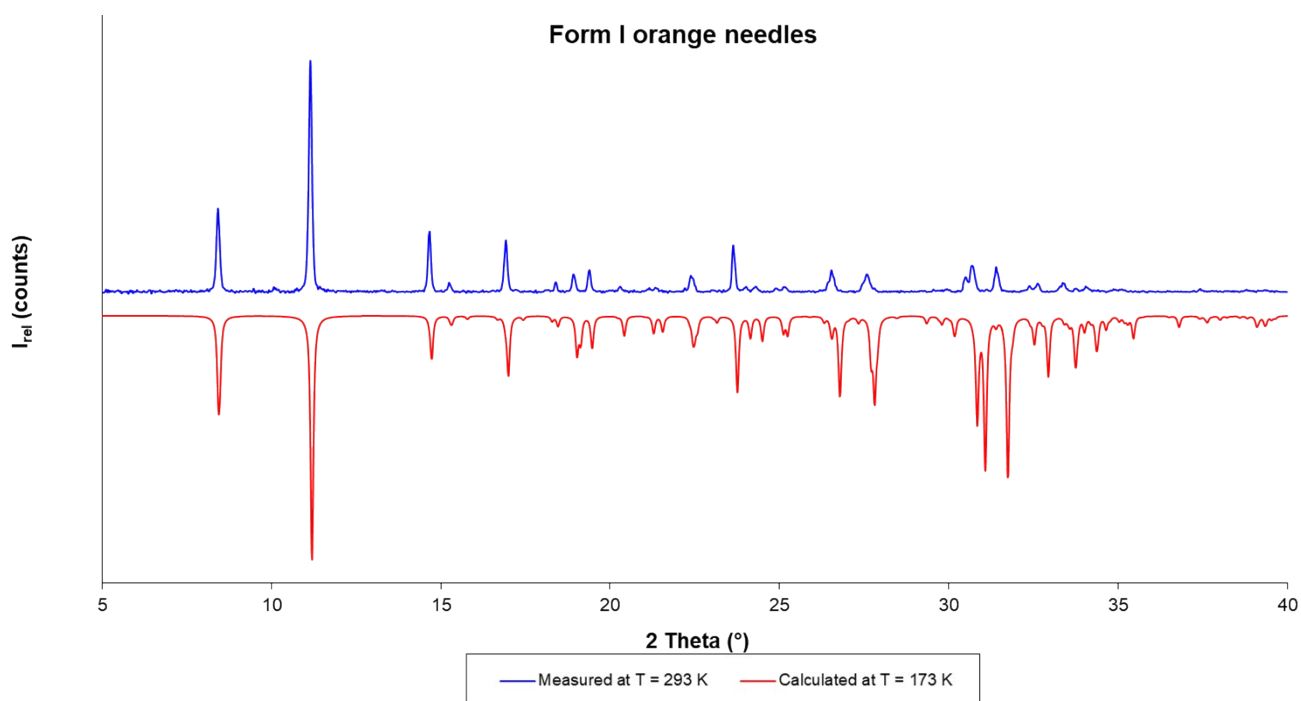


Figure S6 Measured vs. calculated PXRD of the orange form I

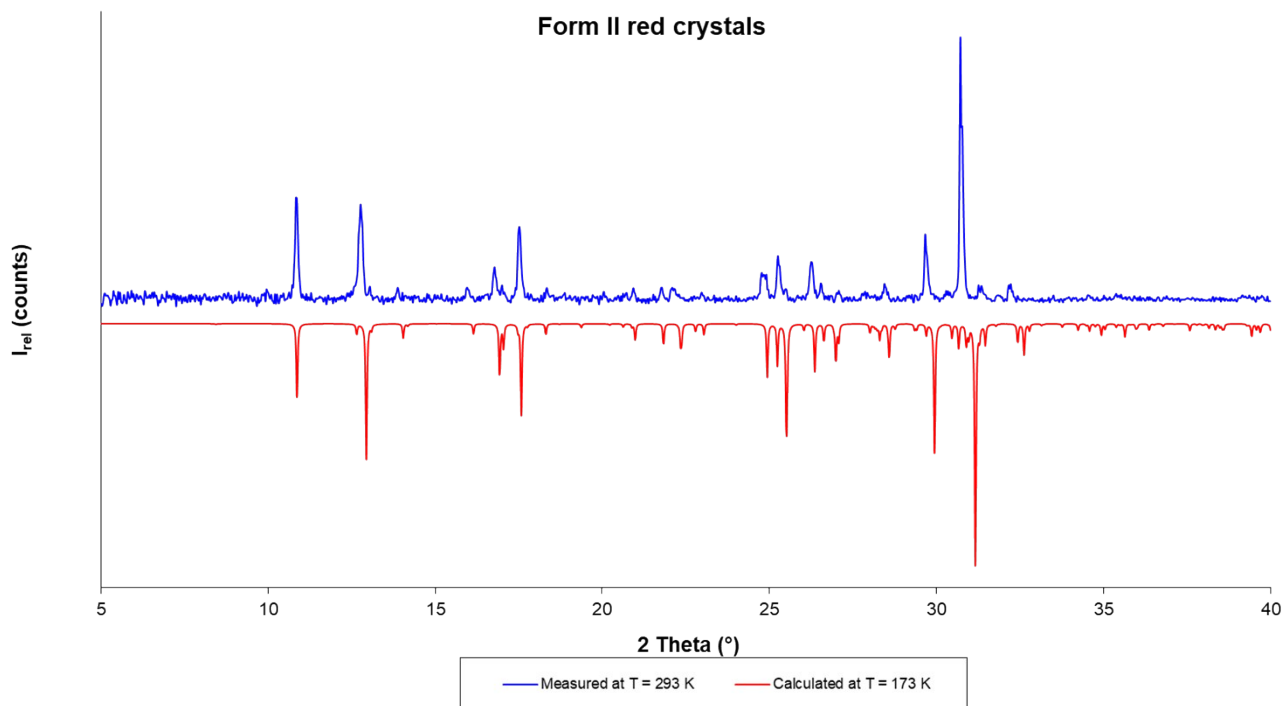


Figure S7 Measured vs. calculated PXRD of the red form **II**.

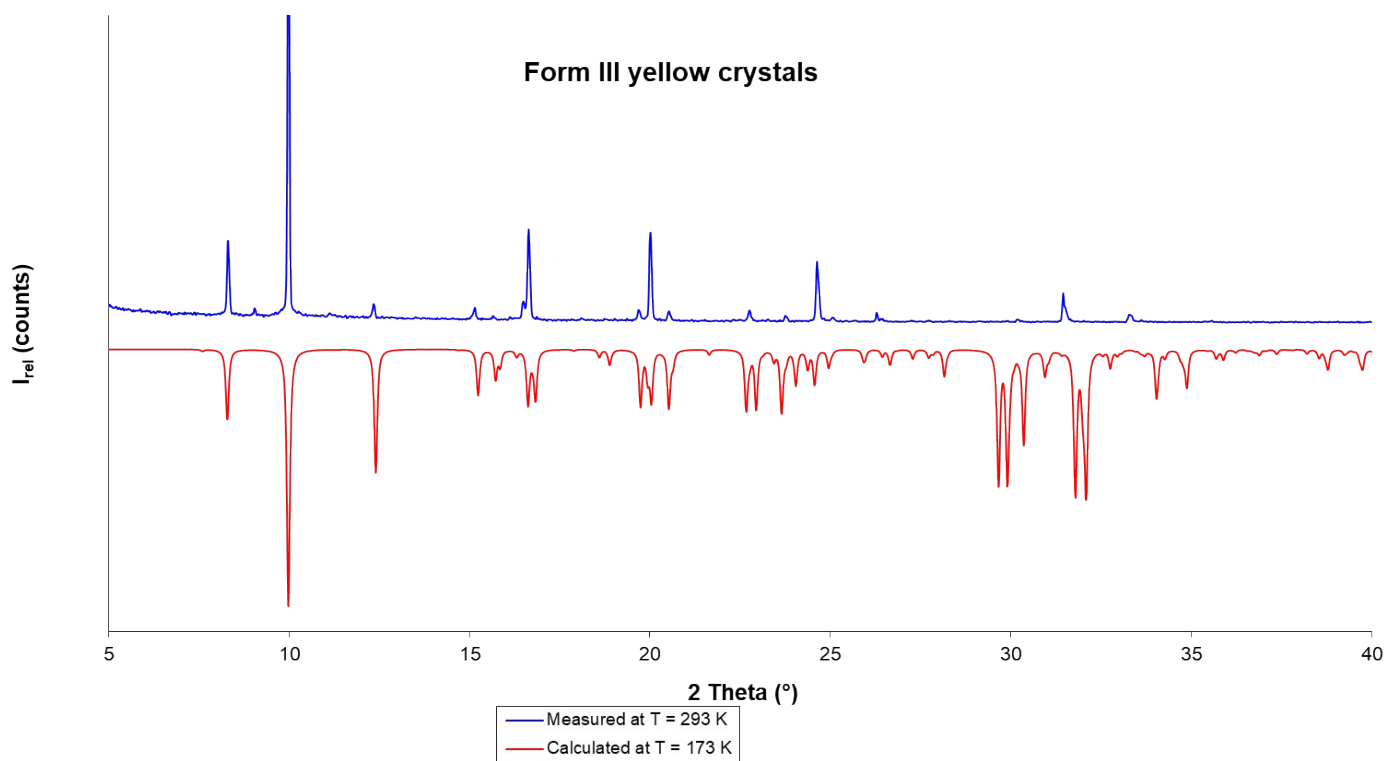


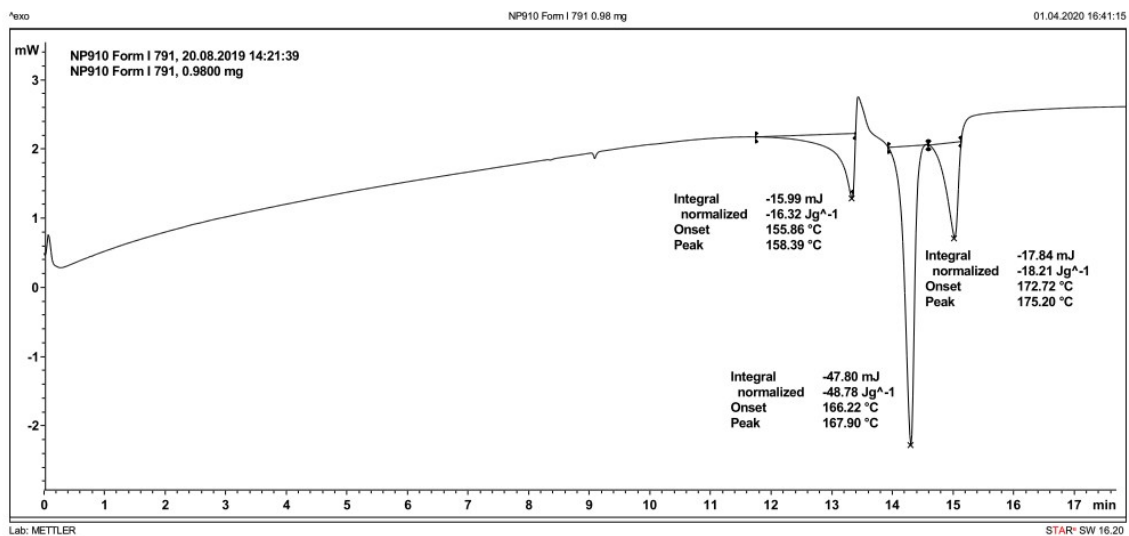
Figure S8 Measured vs. calculated PXRD of the yellow form **III**. The samples of a few crystals were gently crushed on a zero-background holder and so there is significant preferred orientation.

F. DSC Results and Traces

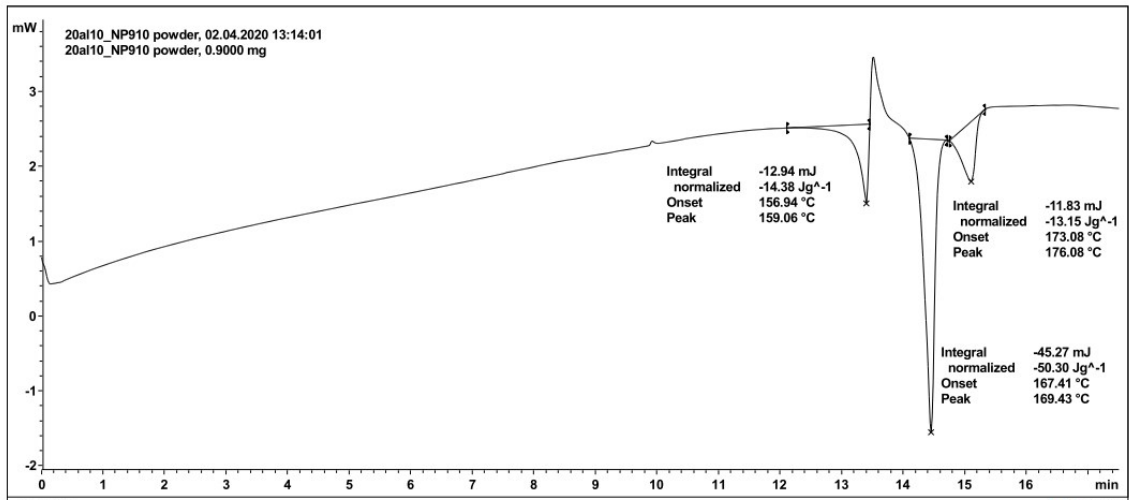
Differential scanning calorimetry data (Table S7-9) were collected using a Mettler Toledo 822e with aluminium pans under N₂ gas purge (10 mL/min). *Star SW 16.20* was used for instrument control and data analysis. Exothermic events were shown as peaks. The temperature and energy calibrations were performed using pure indium (purity 99.99%, m.p. 156.6 °C, heat of fusion 28.45 J g⁻¹).

Table S7. Results of DSC traces for **Form I**.

Polymorph at Start	Sample State	Code	Heating Rate / K min ⁻¹	Sample Code	T _{onset} / °C	T _{peak} / °C	Integral / J g ⁻¹
Form 1	Powder PXRD	DSC 4	10	NP910	155.86	158.39	-16.32
Form 1	Powder PXRD	20a110	10	NP910	156.94	159.06	-14.38
Form 1	Powder PXRD	20a111	10	NP910	156.88	159.16	-10.45
				Average	156.6	158.9	-13.7
				Standard Deviation	0.5	0.3	2.4



exo



exo

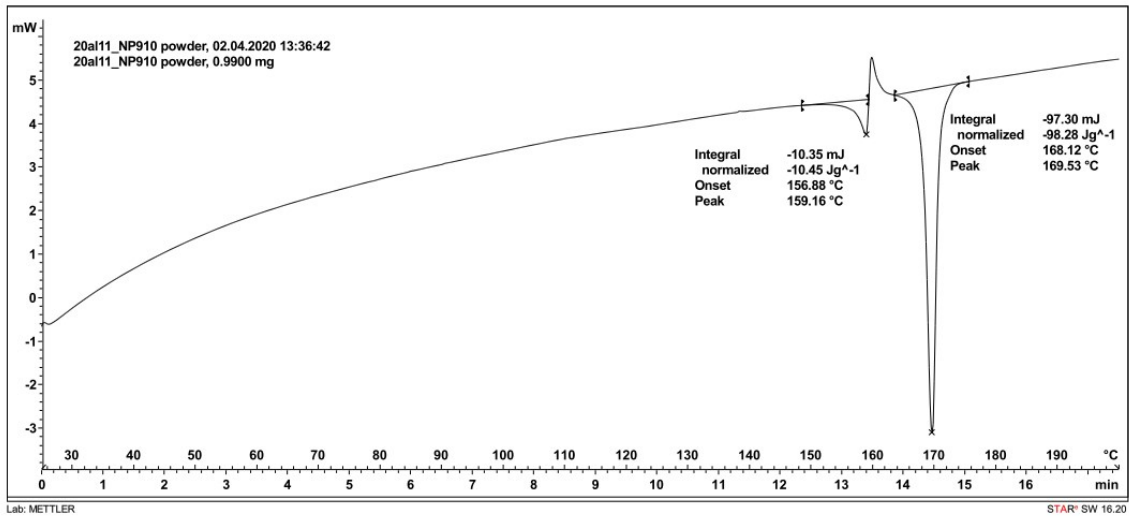
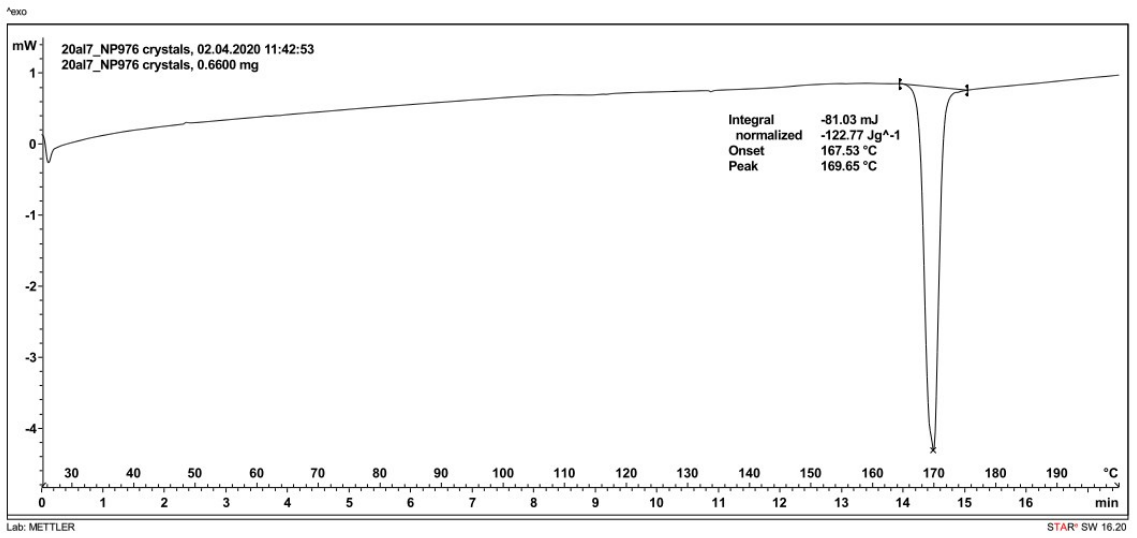
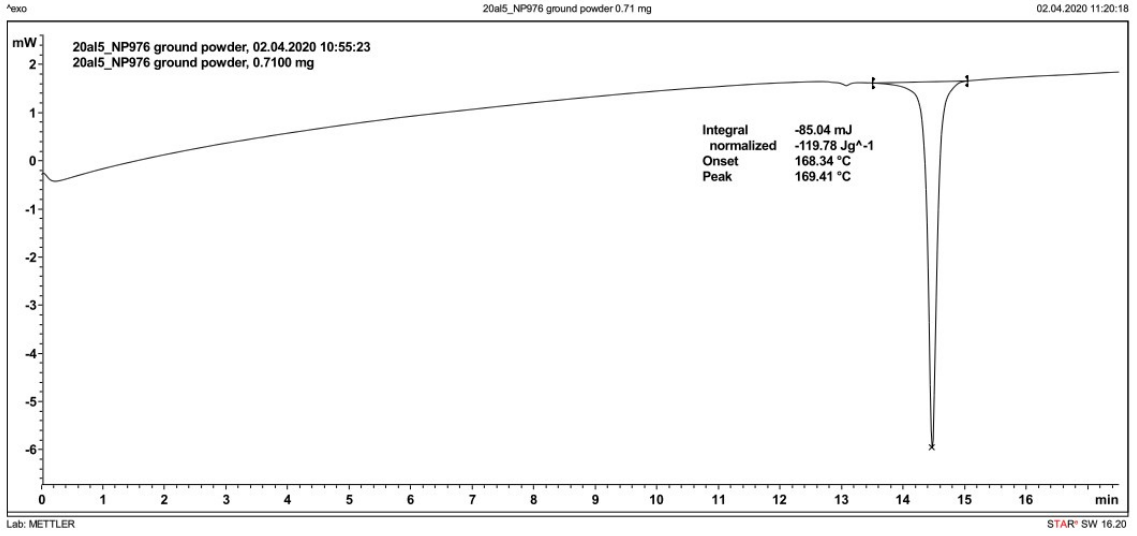


Table S8. Results of DSC traces for **Form II**.

Polymorph at Start	Sample State	Code	Heating Rate / K min ⁻¹	Sample Code	T _{onset} / °C	T _{peak} / °C	Integral / J g ⁻¹
Form 2	ground powder	20a15	10	NP976	168.34	169.41	-119.78
Form 2	crystals	20a17	10	NP976	167.53	169.65	-122.77
Form 2	crystals	20a19	10	NP976	168.10	169.63	-120.29
				Average	168.0	169.6	-120.9
				Standard Deviation	0.3	0.1	1.3



^exo

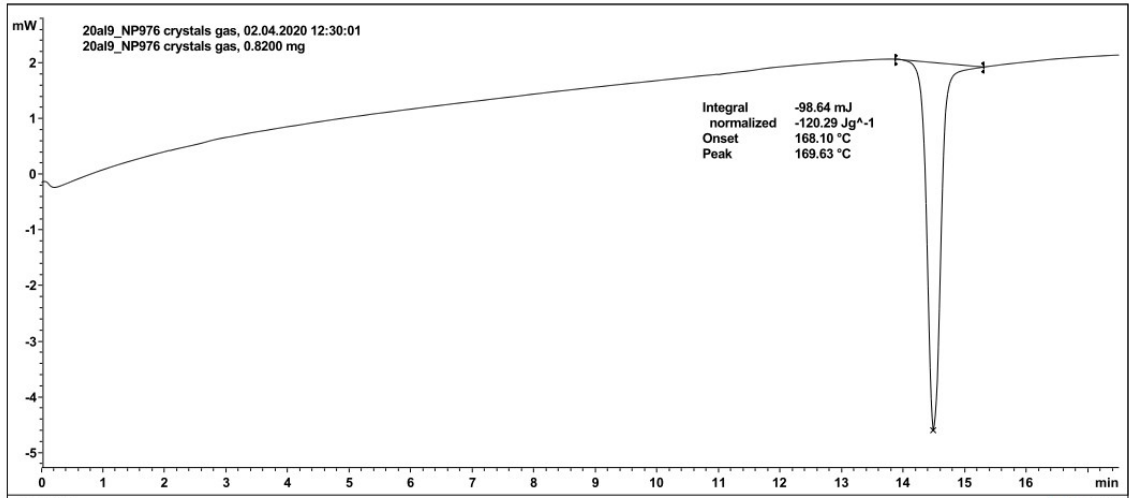
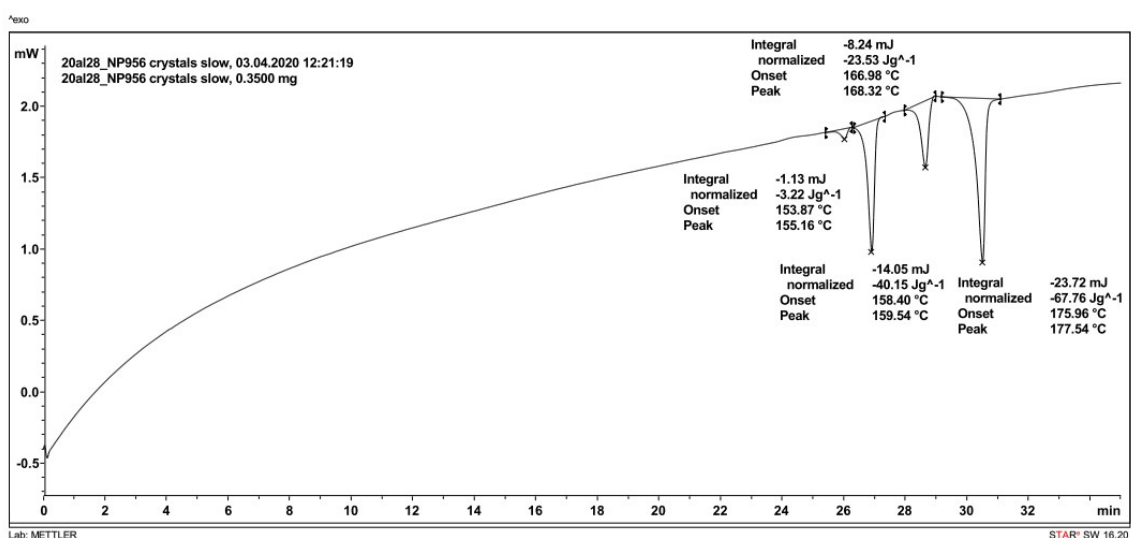
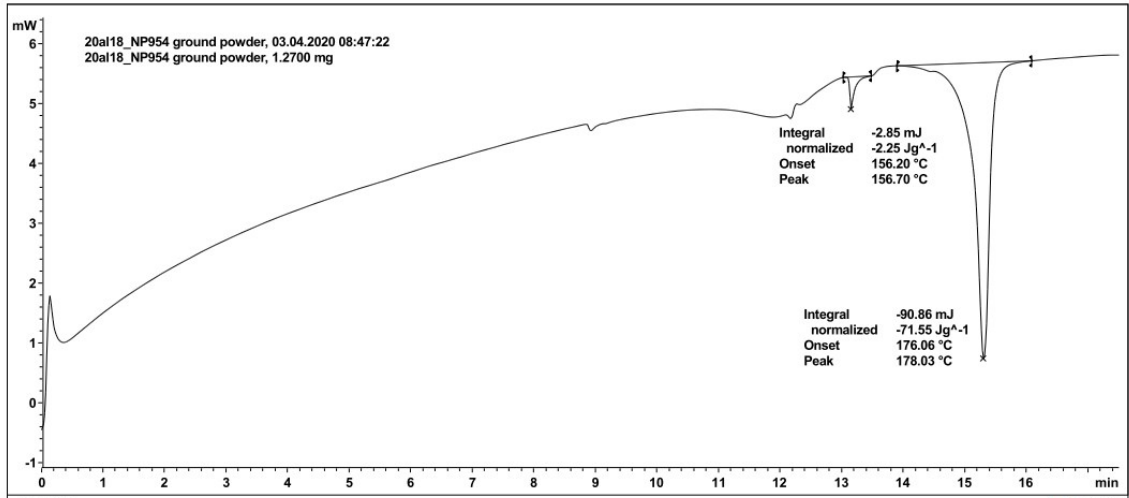


Table S9. Results of DSC traces for **Form III**.

Polymorph at Start	Sample State	Code	Heating Rate / K min ⁻¹	Sample Code	T _{onset} / °C	T _{peak} / °C	Integral / J g ⁻¹
Form 1	crystals	20a128	10	NP956	175.96	177.54	-67.76
Form 1	crystals	20a118	10	NP954	176.06	178.03	-71.55
Form 1	crystals	20a122	10	NP956	177.53	178.99	-62.97
				Average	176.5	178.0	-67.4
				Standard Deviation	0.7	0.7	3.5



exo



exo

