Electronic Supporting Information (ESI) for

Unusual polymorphs of *rac*-3-phenylpyrrolidine-2,5-dione with Z' = 1, 2, and 3

Tatiana V. Timofeeva, Victoria Sena, Boris B. Averkiev, Shabari N. Bejagam, Muhammad Usman, and Arcadius V. Krivoshein

Table S1 Crystallization conditions for Polymorphs II and III

Trial	Solvent	*rac*-PPD conc. (mg/ml)	Temp. (°C)	Vessel (sample vol.)	Desiccation?	Resulting polymorph
A1	hexanes/acetone (2:1)	15	20-22	10×75 mm glass tube (2 ml)	Yes	II
A2	hexanes/acetone (2:1)	15	20-22	10×75 mm glass tube (2 ml)	Yes	II
F1	abs. EtOH	40	20-22	10×75 mm glass tube (2 ml)	Yes	II
F2	abs. EtOH	40	20-22	10×75 mm glass tube (2 ml)	Yes	II
F3	abs. EtOH	40	20-22	10×75 mm glass tube (2 ml)	Yes	II
F5	abs. EtOH	40	20-22	12×75 mm glass tube (2 ml)	Yes	III
F9	abs. EtOH	40	-12	10×75 mm glass tube (3 ml)	No	II
F10	abs. EtOH	40	20-22	10×75 mm glass tube (3 ml)	Yes	II
F13	95% EtOH	40	3	10×75 mm glass tube (2 ml)	No	II
F14	95% EtOH	100	3	50-ml polypropylene conical centrifuge tube (20 ml)	No	II

Table S2 Crystallographic and refinement data for Polymorph II crystals at different temperatures

Parameter	Temperature at which the structures were determined			
	100 K	175 K	215 K	298 K
λ, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	15.5(1)	15.575(6)	15.563(3)	15.57(4)
b, Å	5.64(5)	5.711(2)	5.711(1)	5.72(1)
c, Å	20.5(2)	20.567(8)	20.574(4)	20.69(6)
α, deg.	90	90	90	90
β, deg.	108.1(1)	107.533(5)	107.435(3)	107.77(2)
γ, deg.	90	90	90	90
V, Å^3	1704(25)	1744(1)	1745(1)	1754(8)
Z; Z'	8; 2	8; 2	8; 2	8; 2
d_c, g/cm^3	1.366	1.334	1.334	1.327
F(000)	736	736	736	736
Index range	$-13 \le h \le 13$ $-4 \le k \le 4$ $-17 \le l \le 17$	$-17 \le h \le 17$ $-6 \le k \le 6$ $-23 \le l \le 23$	$-22 \le h \le 22$ $-8 \le k \le 8$ $-29 \le l \le 29$	$-13 \le h \le 14$ $-5 \le k \le 5$ $-18 \le l \le 15$
No. of reflections collected	2613	15783	25756	4381
No. of unique reflections	1071	2756	5178	1331
No. of reflections with $I > 2s(I)$	473	2158	2869	971
Data/restraints/parameters	1071/0/235	2756/0/243	5178/0/243	1331/0/235
R_1; wR_2 ($I > 2s(I)$)	0.0691; 0.1326	0.0331; 0.0772	0.0505; 0.0999	0.0368; 0.0846
Goodness-of-fit on F^2	0.866	1.026	1.001	0.988
T_{min}; T_{max}	0.3098; 0.7442	0.6463; 0.7450	0.6544; 0.7460	0.5908; 0.7443

Table S3 N-H...O hydrogen bond parameters in structures in Polymorph II determined at different temperatures

D-H...A	Geometric parameter	Temperature at which the structure was determined			
		100 K	175 K	215 K	298 K
N1A-H1A…O2A*	d (D-H), Å	0.88(2)	0.86(2)	0.87(2)	0.86(2)
	d (H...A), Å	1.93(2)	1.97(2)	1.97(2)	1.97(2)
	d (D...A), Å	2.812(2)	2.834(2)	2.835(2)	2.833(2)
	∠ (D-H...A), deg.	178(2)	179(2)	179(2)	179(2)
N1B-H1B…O1A	d (D-H), Å	0.88(2)	0.87(2)	0.91(2)	0.86(2)
	d (H...A), Å	2.04(2)	2.06(2)	2.02(2)	2.08(2)
	d (D...A), Å	2.893(2)	2.911(2)	2.910(2)	2.919(2)
	∠ (D-H...A), deg.	162(2)	166(2)	165(2)	166(2)

* Symmetry transformations used to generate equivalent atoms: -x+1, y+1/2, -z+1/2

Table S4 Weak C-H...O hydrogen bond distances (Å) and angles (deg.) in Polymorphs I-III

Polymorph	D-H...A	d (D-H)	d (H...A)	d (D...A)	∠ (D-H...A)
I	C3-H2…O1[1]	0.90(2)	2.61(2)	3.420(2)	151(2)
	C6-H5...O2[2]	0.99(2)	2.59(2)	3.238(2)	123(2)
IIA	C3A-H3AB...O1A[3]	0.96(2)	2.51(2)	3.289(2)	138(1)
	C2B-H2B...O2A[4]	0.95(2)	2.60(2)	3.476(2)	155(1)
IIB	C6B-H6B...O1B[5]	0.96(2	2.64(2)	3.543(2)	157(2)
	C10A-H10A...O1B[6]	0.96(2)	2.49(2)	3.427(2)	164(1)
IIIA	C10B-H10B...O1A[7]	0.97(2)	2.64(2)	3.604(2)	169(1)
	C9C-H9C...O1A[3]	0.99(2)	2.62(2)	3.477(3)	146(1)
IIIB	C3A-H3AA…O1B[8]	0.94(2)	2.38(2)	3.189(2)	144(1)
	C6C-H6C…O1B[7]	0.99(2)	2.65(2)	3.500(2)	144(1)
	C3C-H3CA...O2B[9]	0.96(2)	2.49(2)	3.414(2)	160(1)
IIIC	C10A-H10A...O1C	1.04(2)	2.55(2)	3.557(2)	162(1)
	C6B-H6B...O1C[10]	0.97(2)	2.70(2)	3.431(2)	133(1)
	C2B-H2B...O2C[11]	1.02(2)	2.56(2)	3.379(2)	138(1)
	C10C-H10C...O2C[9]	0.98(2)	2.57(2)	3.546(2)	172(1)

Symmetry transformations used to generate equivalent atoms:
[1] -x+1, -y, z+1/2; [2] x+1/2, -y+1/2, z-1; [3] x, y-1, z; [4] -x+1, y+3/2, -z+1/2; [5] x, y+1, z; [6] -x+1, y-1/2, -z+1/2; [7] -x+1, -y+1, -z; [8] -x+2, -y+1, -z; [9] -x+1, -y, -z; [10] -x+2, -y, -z; [11] x+1, y, z.

Table S5 Vibrational modes of *rac*-PPD

Vibrational mode	IR frequency, cm^{-1}		
	Polymorph II (ground crystals)	Polymorph III (ground crystals)	In solution
ν(N-H) (free)	3468	3468	n.a.
ν(N-H) (H-bonded)	3228, ~3150sh	3227, ~3150sh	n.a.
ν_s(C=O)	1786, 1774	1786, 1773	1780
ν_{as}(C=O)	1738sh, 1721, 1697sh, 1687	1738sh, 1721, 1696sh, 1687	1707

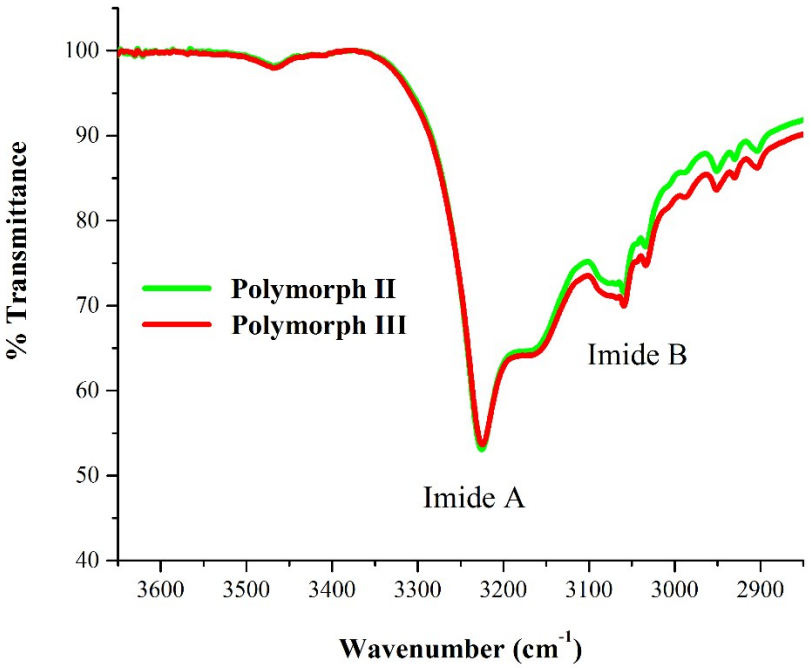

Fig. S1 ATR IR spectra in the N-H stretch region of Polymorphs II and III in the crystalline state. To facilitate the comparison, the spectra were normalized based on the area between 1520 and 1880 cm^{-1} (imide I envelope).