Structural origin of anisotropic thermal expansion of molecular crystals and implication for the density rule probed with four ROY polymorphs

Supporting Information

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1. Crystal structure solutions of ROY polymorphs

For each polymorph, a suitable single crystal was fixed onto the tip of a 0.1 mm diameter glass fiber with epoxy (~5 min drying time) and mounted on a Bruker Apex II CCD area detector diffractometer (Bruker AXS, Madison, WI) for data collection using MoKα radiation (graphite monochromator). Data processing was accomplished with the SAINT processing program. The structure was solved using Bruker SHELXTL and refined using Bruker SHELXTL. A direct-methods solution was calculated, which provided all non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located at their general positions. Key crystal data and data collection parameters are summarized in Tables S1-S13.

Table S1. Crystal data and structure refinement for polymorph Y at 123K.

Identification code	y123	
Empirical formula	C12 H9 N3 O2 S	
Formula weight	259.28	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.4794(5) Å	α = 90°
	b = 16.0479(9) Å	β = 91.4120(10)°
	c = 8.4869(5) Å	γ = 90°
Volume	1154.52(12) Å^3	
Z	4	
Density (calculated)	1.492 Mg/m^3	
Absorption coefficient	0.277 mm^{-1}	
F(000)	536	
Crystal color, morphology	yellow, block	
Crystal size	0.42 x 0.35 x 0.30 mm^3	
Theta range for data collection	2.54 to 27.55°	
Index ranges	$-11 \le h \le 11$, $-20 \le k \le 20$, $-10 \le l \le 11$	
Reflections collected	26058	
Independent reflections	2650 [R(int) = 0.0283]	
Observed reflections	2428	
Completeness to theta = 27.56°	99.3%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9215 and 0.8925	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2650 / 0 / 163	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0861	
R indices (all data)	R1 = 0.0356, wR2 = 0.0889	
Largest diff. peak and hole	0.304 and -0.353 e.Å^{-3}	

Table S2. Crystal data and structure refinement for polymorph Y at 173K.

Identification code	y173	
Empirical formula	C12 H9 N3 O2 S	
Formula weight	259.28	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.4847(4) Å	α = 90°
	b = 16.1377(8) Å	β = 91.5450(10)°
	c = 8.5031(4) Å	γ = 90°
Volume	1163.85(10) Å^3	
Z	4	
Density (calculated)	1.480 Mg/m^3	
Absorption coefficient	0.275 mm^{-1}	
F(000)	536	
Crystal color, morphology	yellow, block	
Crystal size	0.42 x 0.35 x 0.30 mm^3	
Theta range for data collection	2.52 to 27.58°	
Index ranges	$-11 \le h \le 11$, $-20 \le k \le 20$, $-10 \le l \le 11$	
Reflections collected	26296	
Independent reflections	2673 [R(int) = 0.0314]	
Observed reflections	2396	
Completeness to theta = 27.61°	99.1%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9221 and 0.8933	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2673 / 0 / 163	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0896	
R indices (all data)	R1 = 0.0400, wR2 = 0.0945	
Largest diff. peak and hole	0.255 and -0.325 e.Å^{-3}	

Table S3. Crystal data and structure refinement for polymorph Y at 223K.

Identification code	y223	
Empirical formula	C12 H9 N3 O2 S	
Formula weight	259.28	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.4866(5) Å	α= 90°.
	b = 16.2347(10) Å	β= 91.6590(10)°.
	c = 8.5160(5) Å	γ = 90°.
Volume	1172.82(12) $Å^3$	
Z	4	
Density (calculated)	1.468 Mg/m^3	
Absorption coefficient	0.273 mm^{-1}	
F(000)	536	
Crystal color, morphology	yellow, block	
Crystal size	0.42 x 0.35 x 0.30 mm^3	
Theta range for data collection	2.51 to 27.57°.	
Index ranges	-11<=h<=11, -20<=k<=20, -11<=l<=10	
Reflections collected	13254	
Independent reflections	2688 [R(int) = 0.0317]	
Completeness to theta = 27.58°	99.2 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9227 and 0.8941	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2688 / 0 / 163	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.0984	
R indices (all data)	R1 = 0.0441, wR2 = 0.1046	
Largest diff. peak and hole	0.213 and -0.315 $e.Å^{-3}$	

Table S4. Crystal data and structure refinement for polymorph Y at 273K.

Identification code	y273	
Empirical formula	C12 H9 N3 O2 S	
Formula weight	259.28	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.477(19) Å	α= 90°.
	b = 16.35(4) Å	β= 91.63(3)°.
	c = 8.532(19) Å	γ = 90°.
Volume	1182(5) $Å^3$	
Z	4	
Density (calculated)	1.457 Mg/m^3	
Absorption coefficient	0.270 mm^{-1}	
F(000)	536	
Crystal color, morphology	yellow, block	
Crystal size	0.42 x 0.35 x 0.30 mm^3	
Theta range for data collection	2.39 to 27.52°.	
Index ranges	-11<=h<=11, -21<=k<=21, -10<=l<=11	
Reflections collected	13237	
Independent reflections	2702 [R(int) = 0.0352]	
Completeness to theta = 27.55°	99.3 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9233 and 0.8949	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2702 / 0 / 163	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.1023	
R indices (all data)	R1 = 0.0492, wR2 = 0.1109	
Largest diff. peak and hole	0.191 and -0.319 $e.Å^{-3}$	

Table S5. Crystal data and structure refinement for polymorph OP at 123K.

Identification code	op123	
Empirical formula	C12 H9 N3 O2 S	
Formula weight	259.28	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.7350(19) Å	α= 90°.
	b = 13.284(3) Å	β= 104.090(3)°.
	c = 11.634(3) Å	γ = 90°.
Volume	1159.5(5) $Å^3$	
Z	4	
Density (calculated)	1.485 Mg/m^3	
Absorption coefficient	0.276 mm^{-1}	
F(000)	536	
Crystal color, morphology	orange, prism	
Crystal size	0.30 x 0.20 x 0.10 mm^3	
Theta range for data collection	2.37 to 27.58°.	
Index ranges	-9<=h<=10, -17<=k<=17, -15<=l<=15	
Reflections collected	13065	
Independent reflections	2673 [R(int) = 0.0319]	
Completeness to theta = 27.64°	99.4 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9729 and 0.9218	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2673 / 0 / 163	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0340, wR2 = 0.0916	
R indices (all data)	R1 = 0.0422, wR2 = 0.0979	
Largest diff. peak and hole	0.271 and -0.313 $e.Å^{-3}$	

Table S6. Crystal data and structure refinement for polymorph OP at 173K.

Identification code	op173	
Empirical formula	C12 H9 N3 O2 S	
Formula weight	259.28	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.7952(11) Å	α= 90°.
	b = 13.2970(19) Å	β= 104.191(2)°.
	c = 11.6398(17) Å	γ = 90°.
Volume	1169.7(3) $Å^3$	
Z	4	
Density (calculated)	1.472 Mg/m^3	
Absorption coefficient	0.273 mm^{-1}	
F(000)	536	
Crystal color, morphology	orange, prism	
Crystal size	0.30 x 0.20 x 0.10 mm^3	
Theta range for data collection	2.37 to 27.55°.	
Index ranges	-10<=h<=10, -17<=k<=17, -15<=l<=15	
Reflections collected	13186	
Independent reflections	2696 [R(int) = 0.0282]	
Completeness to theta = 27.61°	99.6 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9732 and 0.9225	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2696 / 0 / 163	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0340, wR2 = 0.0932	
R indices (all data)	R1 = 0.0414, wR2 = 0.0996	
Largest diff. peak and hole	0.238 and -0.315 $e.Å^{-3}$	

Table S7. Crystal data and structure refinement for polymorph OP at 223K.

Identification code	op223 (11151_0m)	
Empirical formula	C12 H9 N3 O2 S	
Formula weight	259.28	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.8617(9) Å	α= 90°.
	b = 13.3040(15) Å	β= 104.3590(10)°.
	c = 11.6499(13) Å	γ = 90°.
Volume	1180.4(2) $Å^3$	
Z	4	
Density (calculated)	1.459 Mg/m^3	
Absorption coefficient	0.271 mm^{-1}	
F(000)	536	
Crystal color, morphology	orange, prism	
Crystal size	0.30 x 0.20 x 0.10 mm^3	
Theta range for data collection	2.37 to 27.51°.	
Index ranges	-10<=h<=10, -17<=k<=17, -15<=l<=15	
Reflections collected	13344	
Independent reflections	2719 [R(int) = 0.0347]	
Completeness to theta = 27.60°	99.3 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9734 and 0.9231	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2719 / 0 / 163	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.1063	
R indices (all data)	R1 = 0.0537, wR2 = 0.1163	
Largest diff. peak and hole	0.253 and -0.337 $e.Å^{-3}$	

Table S8. Crystal data and structure refinement for polymorph OP at 273.

Identification code	op273	
Empirical formula	C12 H9 N3 O2 S	
Formula weight	259.28	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.9380(6) Å	α= 90°.
	b = 13.3105(10) Å	β= 104.5710(10)°.
	c = 11.6658(9) Å	γ = 90°.
Volume	1192.95(16) $Å^3$	
Z	4	
Density (calculated)	1.444 Mg/m^3	
Absorption coefficient	0.268 mm^{-1}	
F(000)	536	
Crystal color, morphology	orange, prism	
Crystal size	0.30 x 0.20 x 0.10 mm^3	
Theta range for data collection	2.37 to 26.67°.	
Index ranges	-10<=h<=10, -17<=k<=17, -15<=l<=15	
Reflections collected	13509	
Independent reflections	2764 [R(int) = 0.0362]	
Completeness to theta = 27.61°	99.6 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9737 and 0.9239	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2764 / 0 / 163	
Goodness-of-fit on F^2	1.072	
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.1163	
R indices (all data)	R1 = 0.0615, wR2 = 0.1273	
Largest diff. peak and hole	0.250 and -0.351 $e.Å^{-3}$	

Table S9. Crystal data and structure refinement for polymorph R at 123K.

Identification code	r123	
Empirical formula	C12 H9 N3 O2 S	
Formula weight	259.28	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	P-1	
Unit cell dimensions	a = 7.3167(5) Å	α= 75.6110(10)°.
	b = 7.6810(5) Å	β= 77.4730(10)°.
	c = 11.8714(7) Å	γ = 64.4440(10)°.
Volume	578.40(6) $Å^3$	
Z	2	
Density (calculated)	1.489 Mg/m^3	
Absorption coefficient	0.276 mm^{-1}	
F(000)	268	
Crystal color, morphology	red, block	
Crystal size	0.30 x 0.20 x 0.15 mm^3	
Theta range for data collection	2.99 to 27.57°.	
Index ranges	-9<=h<=9, -9<=k<=9, -15<=l<=15	
Reflections collected	13346	
Independent reflections	2625 [R(int) = 0.0187]	
Completeness to theta = 27.57°	98.1 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9597 and 0.9217	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2625 / 0 / 163	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0334, wR2 = 0.0887	
R indices (all data)	R1 = 0.0359, wR2 = 0.0919	
Largest diff. peak and hole	0.406 and -0.398 $e.Å^{-3}$	

Table S10. Crystal data and structure refinement for polymorph R at 173K.

Identification code	r173	
Empirical formula	C12 H9 N3 O2 S	
Formula weight	259.28	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	P-1	
Unit cell dimensions	a = 7.3603(6) Å	α= 75.5880(10)°.
	b = 7.7084(6) Å	β= 77.5530(10)°.
	c = 11.8814(10) Å	γ = 64.2470(10)°.
Volume	583.57(8) $Å^3$	
Z	2	
Density (calculated)	1.476 Mg/m^3	
Absorption coefficient	0.274 mm^{-1}	
F(000)	268	
Crystal color, morphology	red, block	
Crystal size	0.30 x 0.20 x 0.15 mm^3	
Theta range for data collection	2.98 to 27.61°.	
Index ranges	-9<=h<=9, -9<=k<=9, -15<=l<=15	
Reflections collected	6728	
Independent reflections	2654 [R(int) = 0.0198]	
Completeness to theta = 27.61°	97.8 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9601 and 0.9223	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2654 / 0 / 163	
Goodness-of-fit on F^2	0.975	
Final R indices [I>2sigma(I)]	R1 = 0.0341, wR2 = 0.0931	
R indices (all data)	R1 = 0.0385, wR2 = 0.0976	
Largest diff. peak and hole	0.372 and -0.362 $e.Å^{-3}$	

Table S11. Crystal data and structure refinement for polymorph R at 223K.

Identification code	r223	
Empirical formula	C12 H9 N3 O2 S	
Formula weight	259.28	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	P-1	
Unit cell dimensions	a = 7.4072(6) Å	α= 75.5590(10)°.
	b = 7.7365(7) Å	β= 77.6470(10)°.
	c = 11.8875(10) Å	γ = 64.0160(10)°.
Volume	588.71(9) $Å^3$	
Z	2	
Density (calculated)	1.463 Mg/m^3	
Absorption coefficient	0.272 mm^{-1}	
F(000)	268	
Crystal color, morphology	red, block	
Crystal size	0.30 x 0.20 x 0.15 mm^3	
Theta range for data collection	2.98 to 27.56°.	
Index ranges	-9<=h<=9, -9<=k<=9, -15<=l<=15	
Reflections collected	6797	
Independent reflections	2668 [R(int) = 0.0194]	
Completeness to theta = 27.56°	98.0 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9604 and 0.9230	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2668 / 0 / 163	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0961	
R indices (all data)	R1 = 0.0417, wR2 = 0.1017	
Largest diff. peak and hole	0.263 and -0.299 $e.Å^{-3}$	

Table S12. Crystal data and structure refinement for polymorph R at 273K.

Identification code	r273	
Empirical formula	C12 H9 N3 O2 S	
Formula weight	259.28	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	P-1	
Unit cell dimensions	a = 7.4662(10) Å	α= 75.5160(10)°.
	b = 7.7727(10) Å	β= 77.7670(10)°.
	c = 11.8977(15) Å	γ = 63.7330(10)°.
Volume	595.39(13) $Å^3$	
Z	2	
Density (calculated)	1.446 Mg/m^3	
Absorption coefficient	0.269 mm^{-1}	
F(000)	268	
Crystal color, morphology	red, block	
Crystal size	0.30 x 0.20 x 0.15 mm^3	
Theta range for data collection	2.97 to 27.70°.	
Index ranges	-9<=h<=9, -10<=k<=10, -15<=l<=15	
Reflections collected	6871	
Independent reflections	2717 [R(int) = 0.0198]	
Completeness to theta = 27.70°	96.9 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9608 and 0.9238	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2717 / 0 / 163	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.1028	
R indices (all data)	R1 = 0.0427, wR2 = 0.1097	
Largest diff. peak and hole	0.286 and -0.274 $e.Å^{-3}$	

Table S13. Crystal data and structure refinement for polymorph ON at 123K.

Identification code	on123	
Empirical formula	C12 H9 N3 O2 S	
Formula weight	259.28	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	P2(1)/c	
Unit cell dimensions	a = 3.8652(15) Å	α= 90.00°.
	b = 18.528(7) Å	β= 92.653(6)°.
	c = 16.391(6) Å	γ = 90.00°.
Volume	1172.6(8) $Å^3$	
Z	4	
Density (calculated)	1.469 Mg/m^3	
Absorption coefficient	0.273 mm^{-1}	
F(000)	536	
Crystal color, morphology	orange, needle	
Crystal size	0.10 x 0.05 x 0.03 mm^3	
Theta range for data collection	2.97 to 27.70°.	
Index ranges	-4<=h<=4, -21<=k<=22, -19<=l<=19	
Reflections collected	9783	
Independent reflections	1888 [R(int) = 0.1353]	
Completeness to theta = 24.99°	91.2 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9919 and 0.9732	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1888 / 0 / 163	
Goodness-of-fit on F^2	0.959	
Final R indices [I>2sigma(I)]	R1 = 0.0630, wR2 = 0.1554	
R indices (all data)	R1 = 0.1138, wR2 = 0.1854	
Largest diff. peak and hole	0.462 and -0.491 $e.Å^{-3}$	