Supplementary Information

Relative Stability of Pyrazinamide Polymorphs Revisited, a Computational Study of Bending and Brittle Forms Phase Transitions in a Broad Temperature Range

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Relative Gibbs free energies should be calculated with care, taking into account the need to use a supercell. Otherwise, it may lead to inconsistent data as presented below. Both methods incorrectly show lower stability of α, γ and δ form in relation to β with temperature increase.

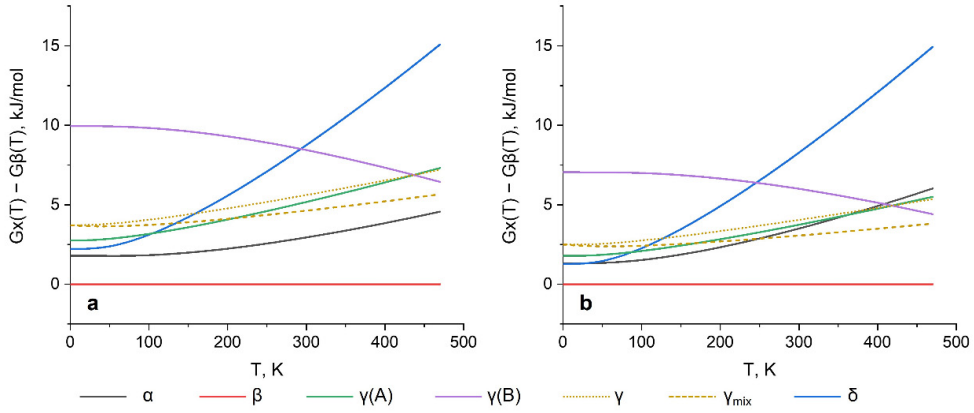

Figure S1: Calculated relative Gibbs free energies using full unit cell (no supercell) (a) finite difference approach using PBE-D3BJ functional, (b) DFPT approach using nonlocal rev-vdW-DF2 functional.

As it can be seen from Table S1, the optimized structures are almost identical to the initial geometries (volume deviation <2%, RMSD of atomic positions < 0.1 Å), except for the disorder state γ(B), which is quite close.

Table S1: Comparison between initial parameters of experimental crystallographic data and optimized crystal structures for the of α(PYRZIN22), β(PYRZIN18), γ(PYRZIN19) and δ form (PYRZIN16) calculated using DFT-PBE-D3BJ level of theory . Difference in % is given in brackets.

	α		β		γ			δ	
	Exp.	Opt.	Exp.	Opt.	Exp.	Opt.(A)	Opt.(B)	Exp.	Opt.
a, Å	3.617	3.621 (0.09%)	14.315	14.208 (-0.75%)	7.176	7.120 (-0.78%)	6.953 (-3.11%)	5.119	5.132 (+0.26%)
b, Å	6.741	6.693 (-0.71%)	3.624	3.644 (+0.56%)	3.651	3.690 (+1.09%)	3.756 (+2.89%)	5.705	5.659 (-0.81%)
c, Å	22.463	22.280 (-0.81%)	10.616	10.481 (-1.27%)	10.663	10.449 (-2.00%)	10.153 (-4.79%)	9.857	9.791 (-0.67%)
α, °	90.000	90.000 (0.00%)	90.000	90.000 (0.00%)	90.000	90.000 (0.00%)	90.000 (0.00%)	97.463	97.692 (+0.24%)
β, °	92.395	92.622 (0.25%)	101.119	100.794 (-0.32%)	106.337	105.860 (-0.45%)	104.805 (-1.44%)	98.173	97.888 (-0.29%)
γ, °	90.000	90.000 (0.00%)	90.000	90.000 (0.00%)	90.000	90.000 (0.00%)	90.000 (0.00%)	106.473	107.035 (+0.53%)
Volume, Å^3	547.276	539.342 (-1.45%)	540.354	533.054 (-1.35%)	268.057	264.100 (-1.48%)	256.341 (-4.37%)	268.818	264.716 (-1.53%)
RMSD, Å		0.049		0.058		0.088	0.533		0.053