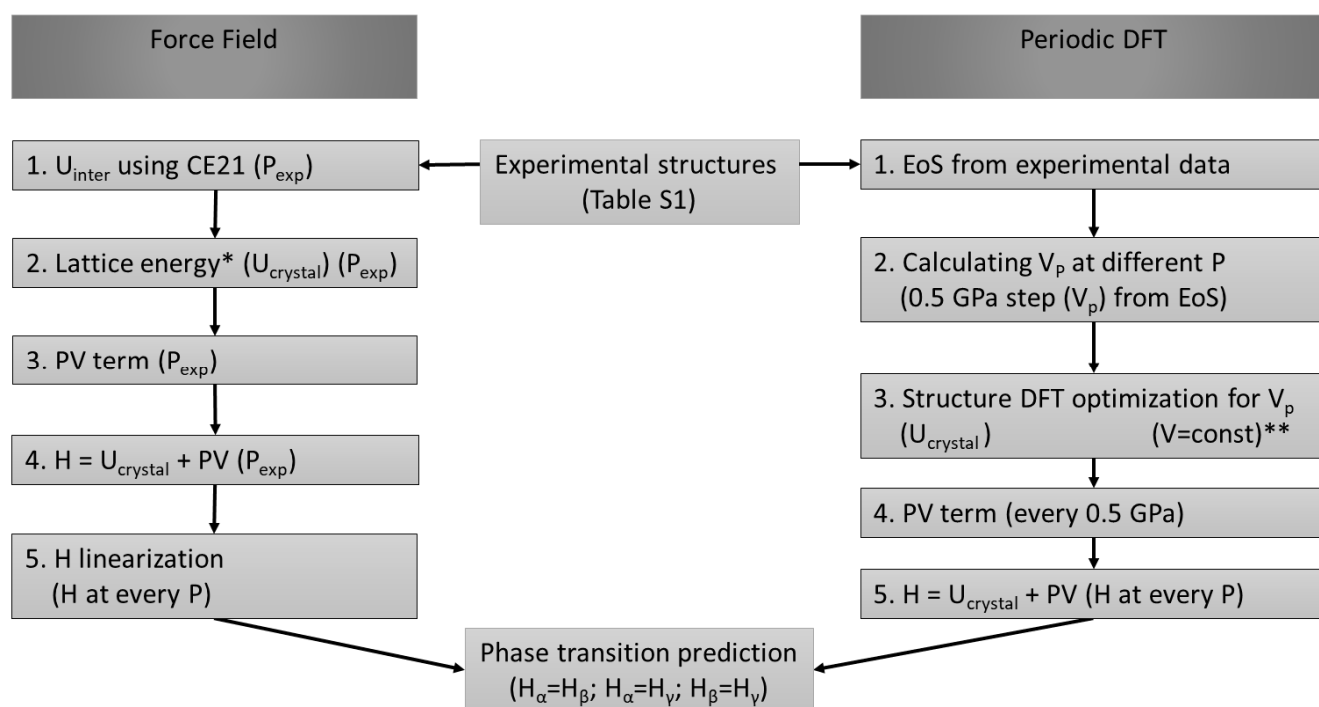


Computational Investigation of the Stability of Di-*p*-Tolyl Disulfide “Hidden” and “Conventional” Polymorphs at High Pressures

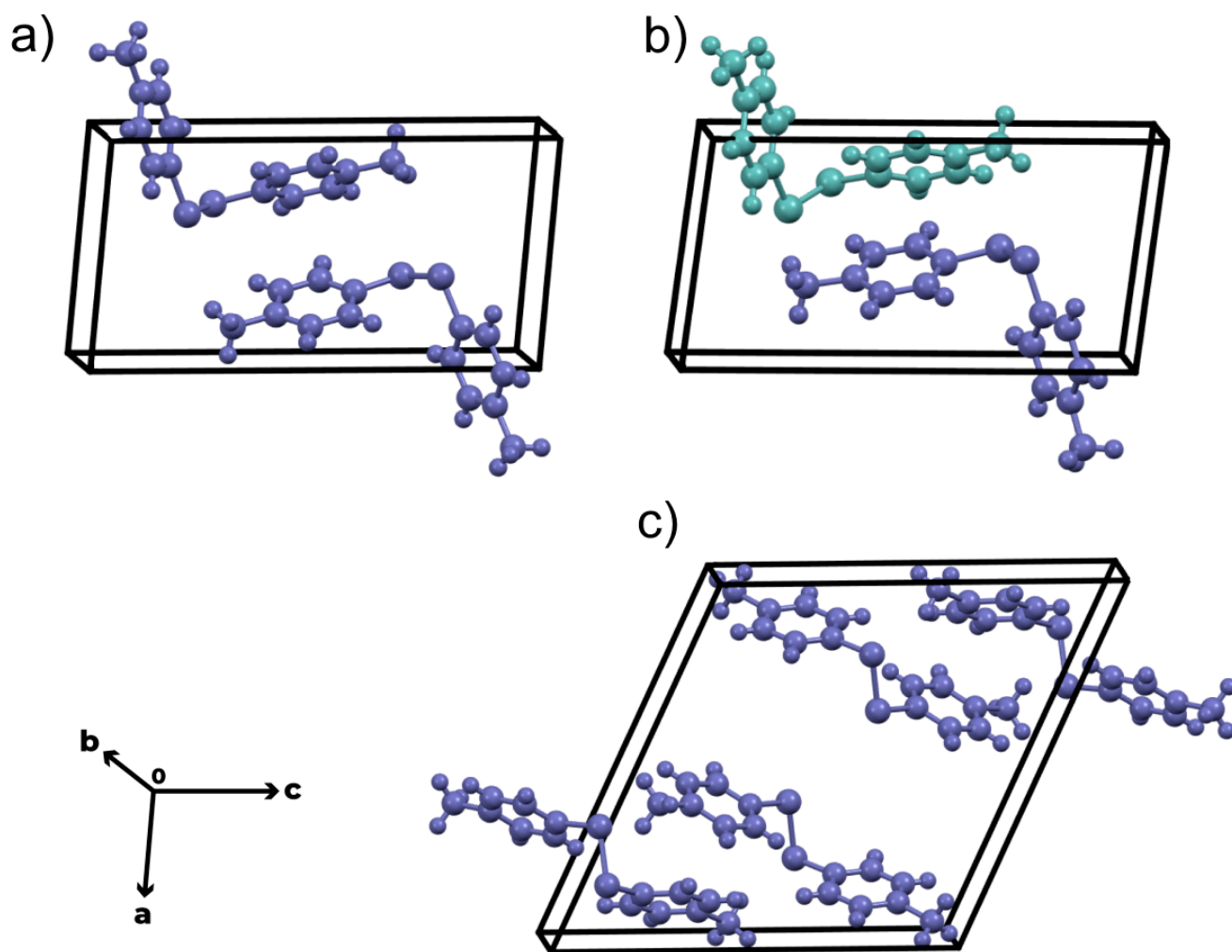
Supplementary Information



Scheme S1. An overall workflow of computational procedures. *Lattice energy can either be calculated as U_{inter} or $U_{\text{inter}} + U_{\text{intra}}$, where U_{intra} is calculated in CE21, while U_{intra} from ref. [14]. **V = const means that unit cell volume is fixed, while cell parameters and atom positions are optimized using DFT (ISIF = 4). For FF methods experimental structures are used at steps 1–4, while for periodic DFT only at step 1.

Table S1. Summarized structural data for *p*-Tol₂S₂ polymorphs used in CE21 and EoSFit7 calculations.

Polymorph	CCDC Refcode	Pressure, GPa	a, Å	b, Å	c, Å	α , °	β , °	γ , °	Volume, Å ³	Space group
α	IPIXUB06	0.0001	7.593(<1)	5.713(<1)	14.722(<1)	90	94.76(<1)	90	636.414	P21
α	IPIXUB02	0.15	7.570(5)	5.667(2)	14.710(80)	90	94.90(20)	90	628.741	P21
α	IPIXUB03	0.6	7.483(3)	5.588(1)	14.530(60)	90	94.83(15)	90	605.436	P21
α	IPIXUB04	1.38	7.346(4)	5.441(3)	14.400(80)	90	94.56(16)	90	573.74	P21
α	IPIXUB11	1.28	7.344(1)	5.467(<1)	14.360(40)	90	94.50(7)	90	574.806	P21
α	IPIXUB05	1.52	7.319(1)	5.428(1)	14.370(30)	90	94.93(7)	90	568.764	P21
β	IPIXUB14	1.72	7.306(1)	5.509(1)	14.038(3)	95.14(3)	97.23(3)	85.36(3)	556.885	P1
β	IPIXUB13	1.85	7.285(<1)	5.518(<1)	14.024(5)	95.30(1)	97.37(1)	85.32(<1)	555.359	P1
β	IPIXUB07	2.2	7.247(<1)	5.500(<1)	13.926(4)	95.54(1)	97.67(1)	85.03(<1)	545.963	P1
β	IPIXUB15	2.8	7.193(<1)	5.469(<1)	13.814(4)	95.92(1)	98.14(1)	84.70(<1)	533.389	P1
γ	IPIXUB08	0.45	15.260(20)	5.962(<1)	14.615(10)	90	115.56(14)	90	1199.544	P21/c
γ	IPIXUB09	0.71	15.020(30)	5.931(<1)	14.587(14)	90	115.73(19)	90	1170.522	P21/c
γ	IPIXUB16	1.38	14.720(30)	5.810(<1)	14.362(11)	90	114.98(16)	90	1113.442	P21/c
γ	IPIXUB12	2.15	14.360(80)	5.759(1)	14.260(30)	90	114.90(50)	90	1069.725	P21/c
γ	IPIXUB10	2.8	14.090(60)	5.703(1)	14.180(20)	90	114.80(30)	90	1034.338	P21/c

**Figure S1.** Crystal structures of (a) alpha, (b) beta and (c) gamma polymorphs of *p*-Tol₂S₂. Colors according to symmetry equivalence in corresponding crystal structures.

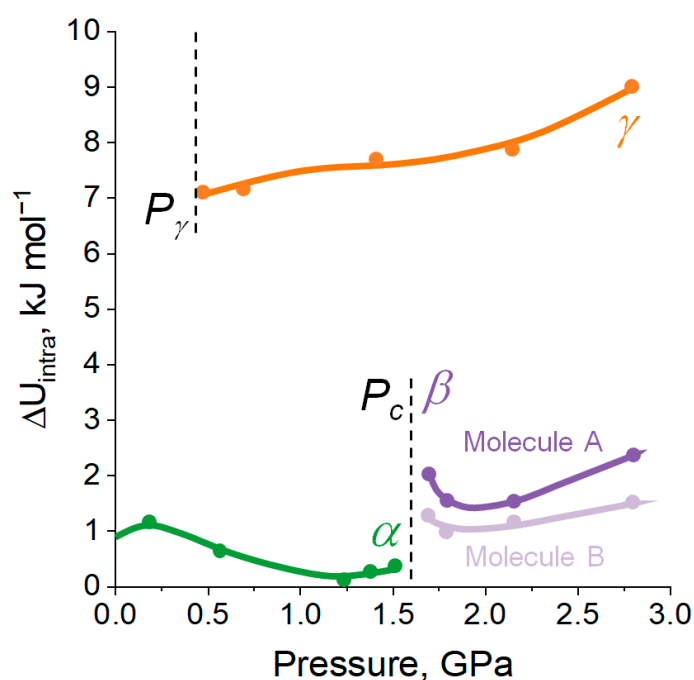


Figure S2. Potential energy changes (ΔE_p) calculated by Gaussian (Experimental Section of [14]) for the isolated molecule in its conformation, experimentally determined in the *p*-TolS₂ structures of phases α , β , and γ . The atomic coordinates determined by the diffraction measurements reported as the starting models. Full optimizations, except for soft torsion angles $\tau/\tau_1/\tau_2$ fixed at the values present in phases $\alpha/\beta/\gamma$, were performed in the original study [14]. For all the quantum mechanical calculations, the program Gaussian09 was applied. Figure adapted from [14], keeping the original designations.

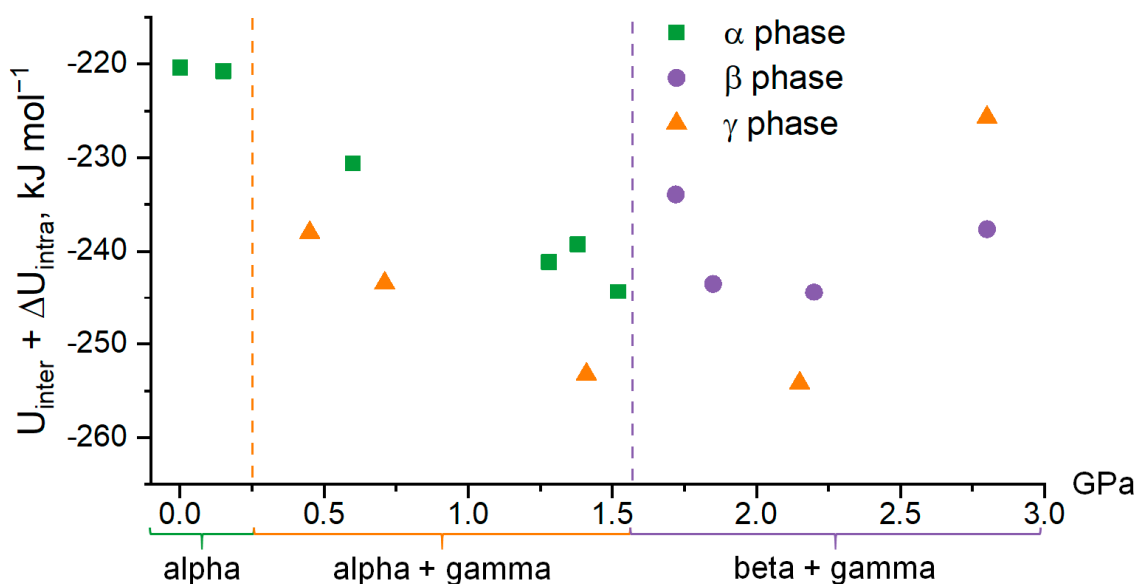


Figure S3. Lattice energies (the sum of U_{inter} and U_{intra}) of phases α , β , and γ as a function of pressure calculated based on experimental data. Regions of structural stability according to experimental data are shown with dashed lines. U_{intra} is reproduced from work [14], Figure S2.

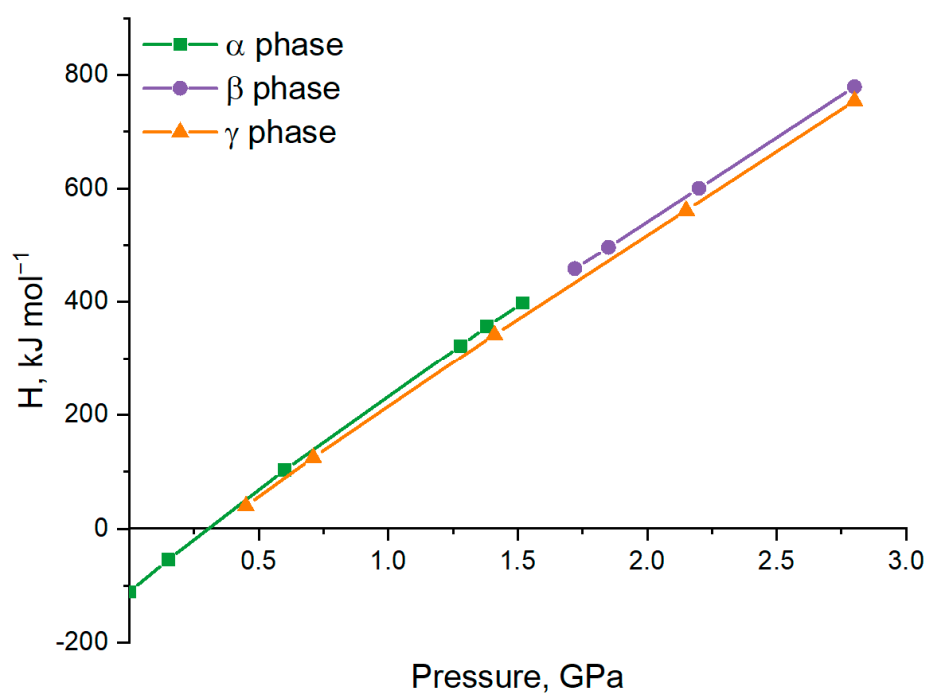


Figure S4. Enthalpies of phases α , β , and γ as a function of pressure calculated based on experimental data using CE21.

Table S2. Predicted by FF and experimental phase transition pressures.

Phase transition	Calculated from FF method (CE21)	Reported experimental data
$\alpha \rightarrow \beta$	1.45	1.60
$\alpha \rightarrow \gamma$	0.44	0.45
$\gamma \rightarrow \beta$	6.12	no data

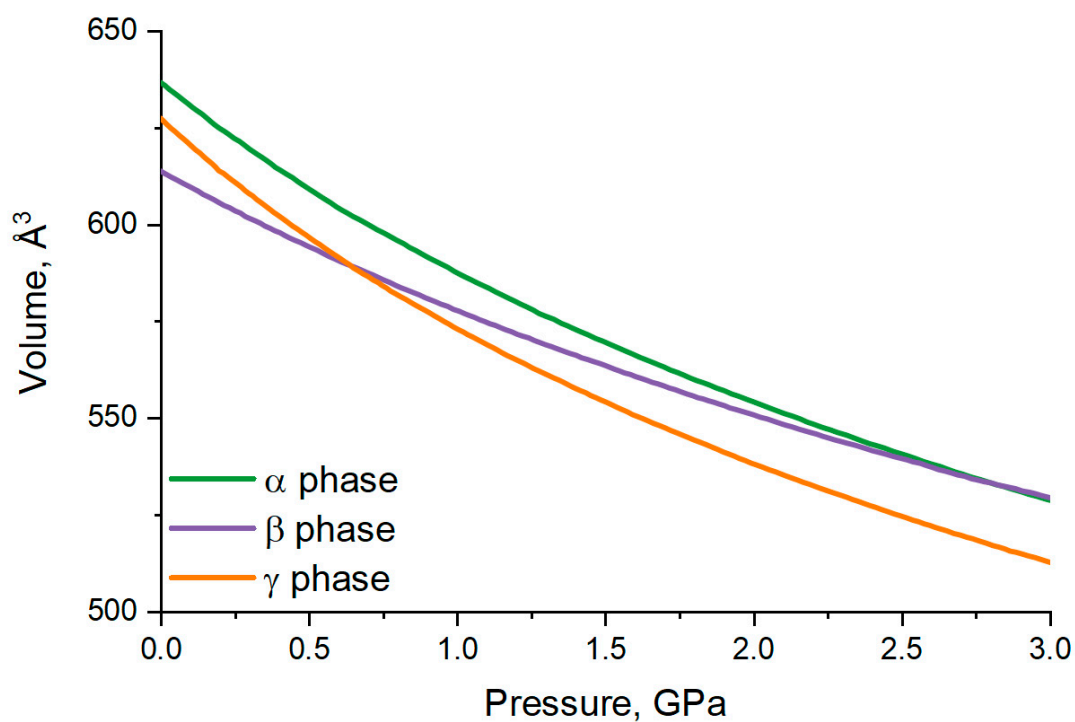


Figure S5. *p*-Tol2S₂ volume-pressure dependence based on calculated EoS.

Table S3. EoS Birch-Murnaghan 3rd order coefficients. V_0 — reference pressure volume at ambient pressure, K_0 — bulk modulus, K_p — derivative of Bulk Modulus (dK/dP).

Polymorph	$V_0, \text{\AA}^3$	K_0, GPa	K_p
α	636.414	10.242	4.9360
β	613.579	14.401	4.6549
γ	627.144	8.695	5.3616

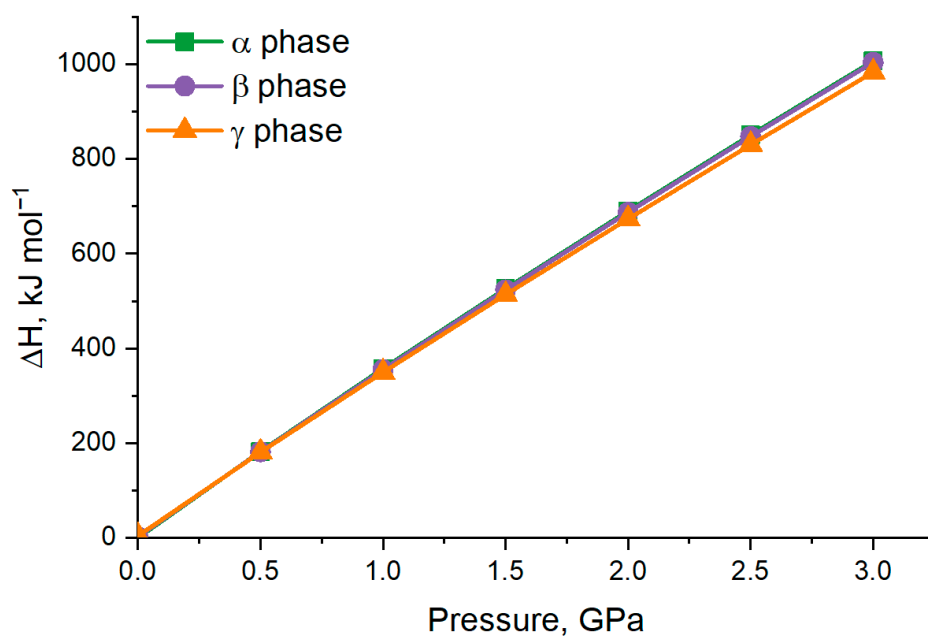


Figure S6. Enthalpies of phases α , β , and γ as a function of pressure calculated using periodic DFT and EoS. No linearization was applied. Please see Figure S7 and Table S5 for estimation of linearization accuracy to calculate relative phase stability.

Table S4. Relative stability of *p*-Tol₂S₂ polymorphs in different pressure ranges calculated by periodic DFT.

Pressure range, GPa	Stability rank		
	1 (Most stable)	2 (Intermediate)	3 (Less stable)
0.00–0.33	α	β	γ
0.33–0.34	α	γ	β
0.34–0.36	γ	α	β
0.36–3.00	γ	β	α

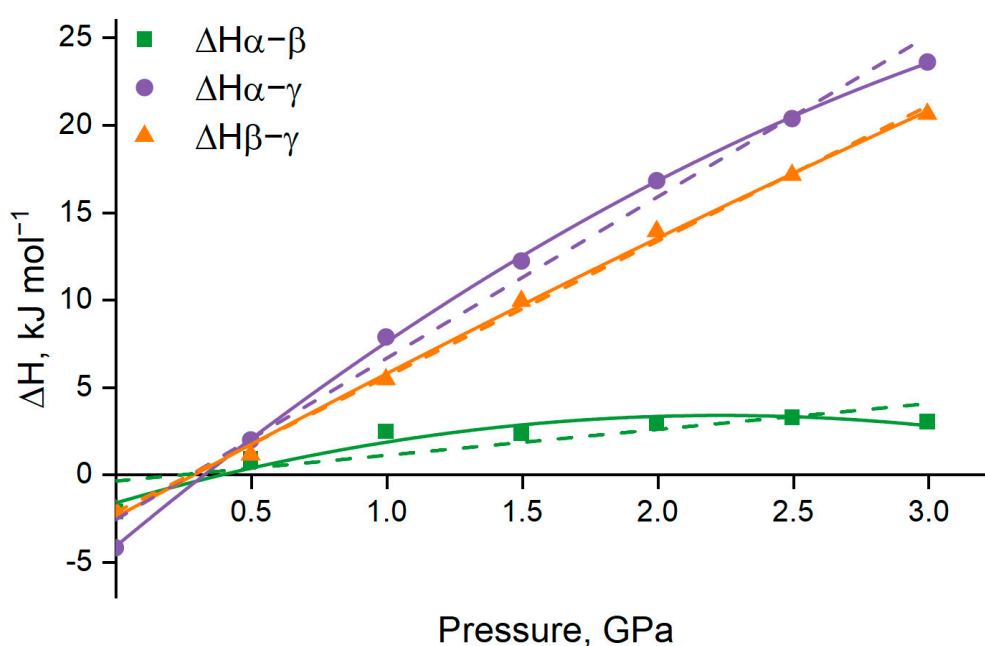


Figure S7. ΔH differences between *p*-Tol₂S₂ polymorph α and γ (green), α and β (purple), β and γ (orange) as a function of pressure (i.e. $\Delta U_{\alpha-\beta} = U_{\alpha} - U_{\beta}$, $\Delta PV_{\alpha-\beta} = PV_{\alpha} - PV_{\beta}$, $\Delta H_{\alpha-\beta} = H_{\alpha} - H_{\beta}$, etc.). Phase transition between the involved polymorphs can be expected when their enthalpy difference is equal to zero. Dashed lines are given as a linearization of the calculated data (see Table S5).

Table S5. Linear equations for Enthalpies with R^2 coefficients calculated for enthalpy difference data calculated using periodic DFT.

Phase transition	Number of points at different pressures	Equation	R^2 coefficient
$\alpha \rightarrow \beta$	7	$y = 1.4791x - 0.429$	0.6975
$\alpha \rightarrow \gamma$	7	$y = 9.2378x - 2.6462$	0.9865
$\beta \rightarrow \gamma$	7	$y = 7.7587x - 2.2171$	0.9973

Table S6. Phase transitions of *p*-Tol₂S₂ polymorphs under pressure according to various experimental and computational techniques.

Phase Transition	Pressure, GPa		
	Experimental data	FF based	Periodic DFT based
$\alpha \rightarrow \beta$	1.60	1.45	Do not occur*
$\alpha \rightarrow \gamma$	0.45	0.44	0.34
$\gamma \rightarrow \beta$	Beyond 0.0–3.0 GPa, if any occur	6.12**	Do not occur

*Do not occur based on thermodynamic approach, but happens due to high transition state energies of $\alpha \rightarrow \gamma$ transformation.

**Based on linearization of polymorphs enthalpies.

Important to note that direct comparison of methods regarding phase transitions should be avoided, due to different limitations of these techniques: periodic DFT shows thermodynamic (but not kinetic) factors, FF approach is linearized to access predictive options and contain significant uncertainties outside experimental range, experimental data provide limited information from one experimental technique.