Electronic Supplementary Information

For the publication "Thermodynamics by synchrotron X-ray diffraction: Phase relationships and crystal structure of L*-tyrosine ethyl ester form III"*

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Alternative calculation of equilibrium lines and triple points supposing form I is stable at 100 K

If one considers that absence of an observation of form III at 100 K indicates that form I is the stable phase at this temperature, the following approach may be used to obtain the expression for the phase equilibria and the triple points.
The position of the III-I equilibrium must lie between 0 and 100 K at 0 Pa and between 400 and 500 MPa at 337 K. Most simple is to average the limiting values resulting in the following coordinates (***50 K, 0 Pa***), (***337 K, 450 MPa***). It leads to the expression for the pressure (MPa) of the III-I equilibrium as a function of temperature (K):

$$\boldsymbol{P = -78.4 + 1.57\,T} \qquad \text{(SI.1)}$$

Obviously, this expression intersects the temperature axis at 50 K, however also the ***triple point coordinates for III-I-L*** change.
Using equation 2 in the paper together with SI.1, one finds ***425.6 K, 588.9 MPa***. Also the enthalpy change for the III-I equilibrium will be different. Evaluating the slope of 1.57 MPa K^{-1} at 293 K, because the volume change is known at 293 K (9.6 cm^{3}mol^{-1}), leads to $\boldsymbol{\Delta_{I \rightarrow III}H = 4.426\ \mathrm{kJ\ mol^{-1}}}$.

Using equation 6 of the paper, results subsequently in the temperature of fusion at ordinary pressure for form III of $\boldsymbol{T_{III \rightarrow L} = 209.5\ \mathrm{K}}$.

This leads together with the coordinates of the triple point III-I-L above to the expression for the equilibrium III-L of:

$$\boldsymbol{P = -571 + 2.73\,T} \qquad \text{(SI.2)}$$

Equation SI.1 should be compared against equation 5 and equation SI.2 against equation 7. It is clear that the slopes in the paper are much steeper, however the ratio of the slopes remains approximately the same and thus the topological layout does not change. Form III remains the low-temperature, high-pressure form and form I the high-temperature, low-pressure form.
The resulting coordinates of the triple points are compiled in Table SI.1, which can be compared to Table 4 in the paper.

Table ESI.1 Alternative triple point coordinates supposing that form I is stable at 100 K

Triple point	*T* (K)	*P* (Pa)
I-L-V	376.4	57
III-L-V	209.5	4×10^{-6}
III-I-V	50	0
III-I-L	425.6	589×10^{6}

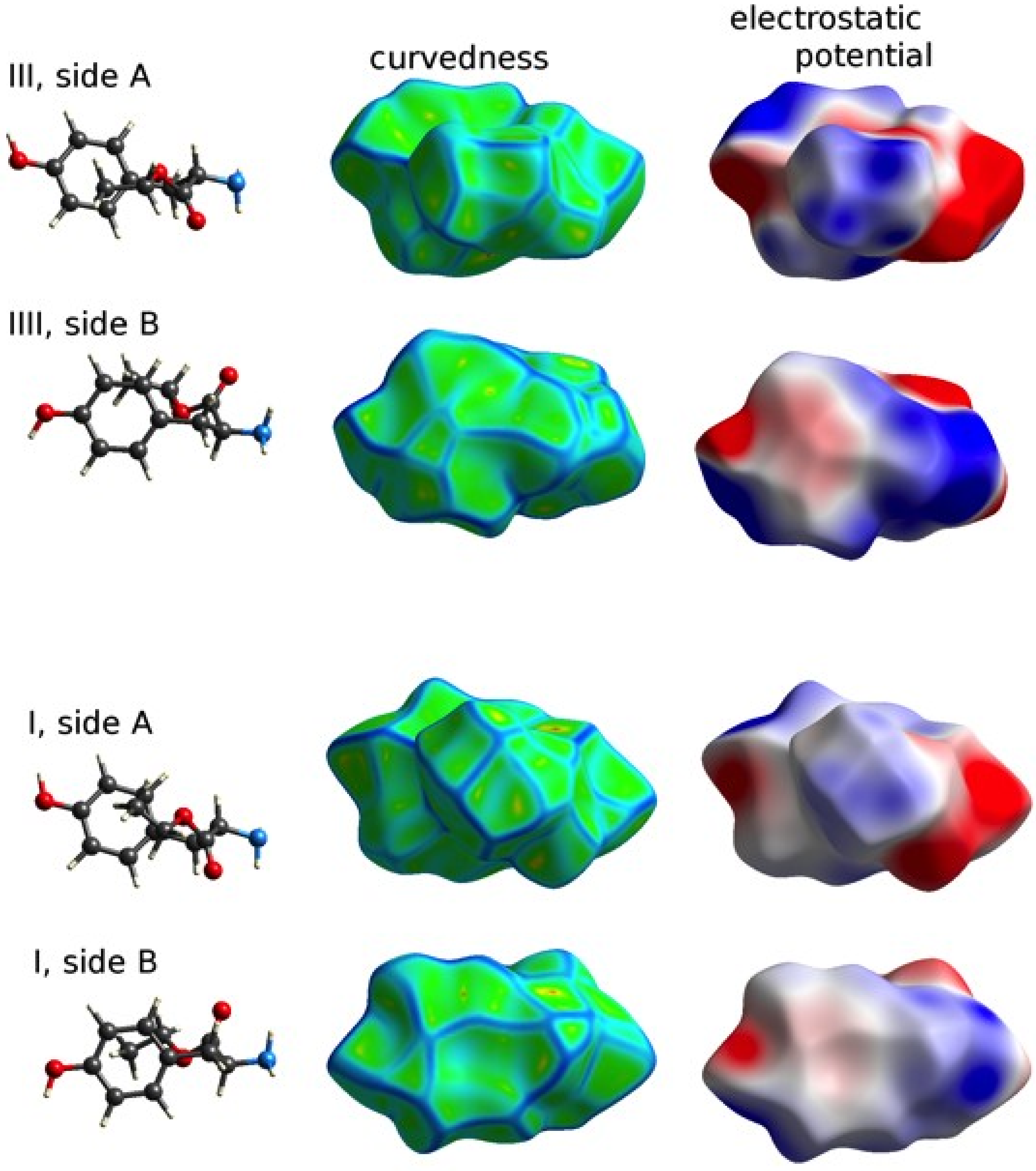

Figure ESI.1. Hirshfeld surfaces of L-tyrosine ethyl ester forms I and III, center: curvedness increases from red to green to blue, right-hand side: electrostatic potential with red a negative potential and blue a positive potential.

Step by step construction of the topological temperature-pressure phase diagram discussed in the article

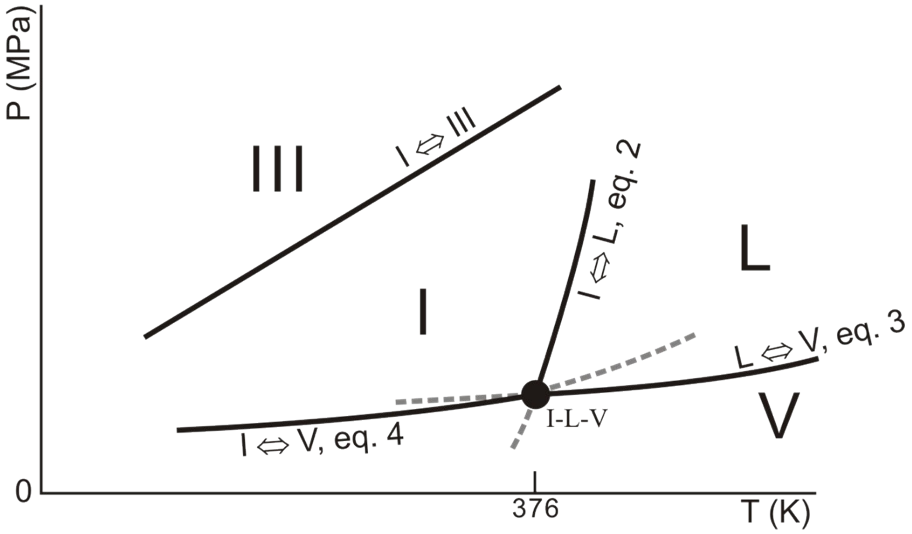

Figure ESI.2a. Topological pressure-temperature phase diagram of form I, the liquid (L) and the vapour phase (V) presenting the phase equilibria between I-L (eq. 1 in main article), L-V (eq. 2), and I-V (eq. 3). The triple point I-L-V, where the three equilibria cross, has coordinates 376 K, 57 Pa (Table 4 in main article). The positive slope of the equilibrium between I and III is indicated with form III above this equilibrium (high pressure, low temperature) and form I below the equilibrium (low pressure, high temperature). Temperature and pressure not to scale.

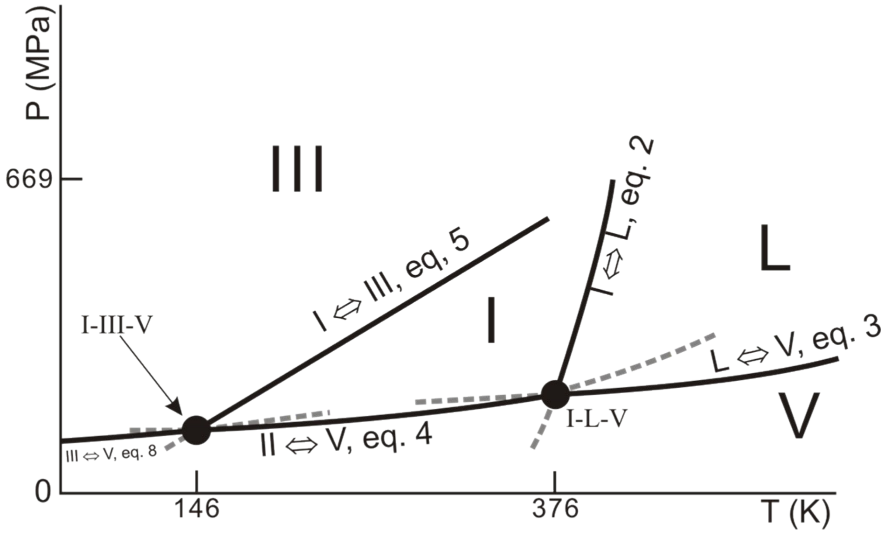

Figure ESI.2b. Triple point I-III-V (146 K, 0 Pa, Table 4) obtained by extrapolation of equation 5, the I-III equilibrium to the intersection with the II-V equilibrium (eq. 3). As phase III is in equilibrium with the vapour phase below triple point I-III-V, equilibrium II-V becomes metastable (grey broken line just above the black line left of the triple point) and equilibrium III-V becomes stable (solid black line).

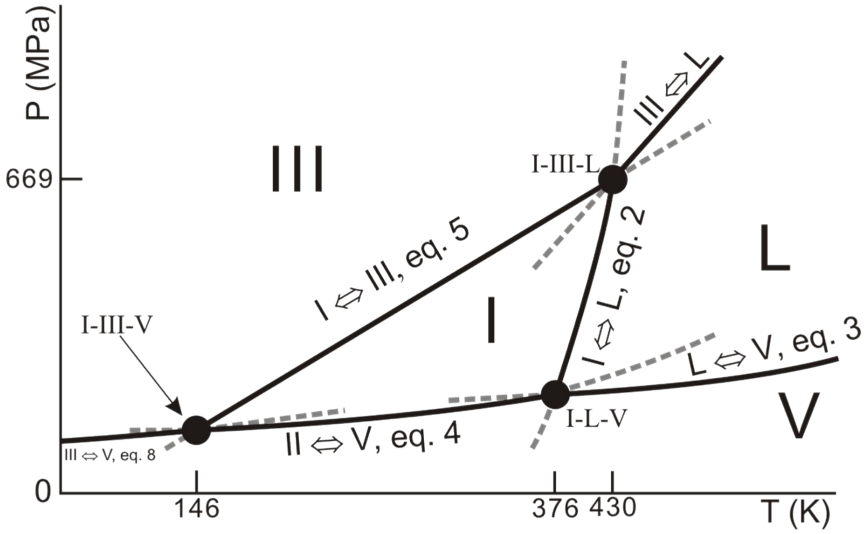

Figure ESI.2c. Triple point I-III-L (430 K, 669 MPa, Table 4) by extrapolating equation 5 (equilibrium I-III) to the intersection with equilibrium I-L (eq. 2). Take note of the alternating stable (solid black lines) and metastable (grey broken lines) equilibria around the triple points.

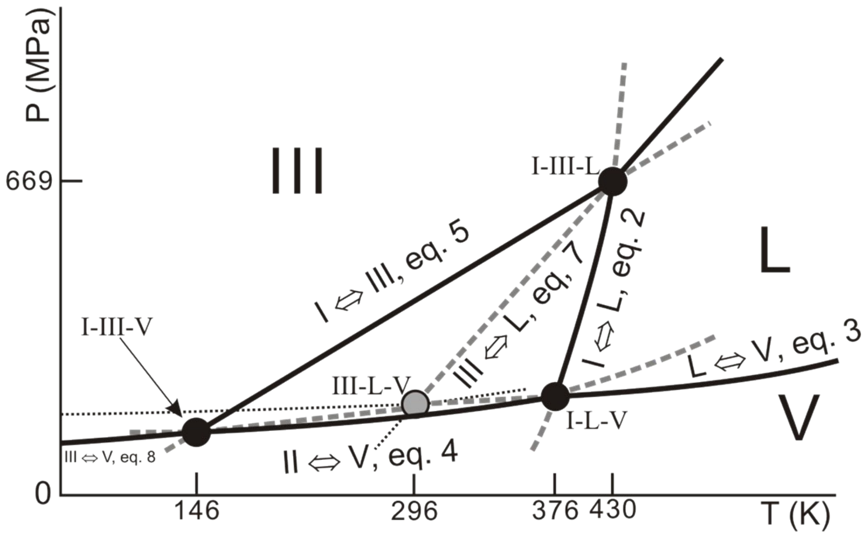

Figure ESI.2d. Metastable triple point III-L-V (grey circle, 296 K, 0.2 Pa, Table 4) by equation 6 for the temperature and equation 3 (metastable extension of the L-V equilibrium, grey broken line) for the pressure. With two points (triple points I-III-L and III-L-V), the position of equilibrium III-L is defined. The equilibrium III-V (equation 8) also crosses the III-L-V triple point. On the right of the triple point III-L-V it is supermetastable (dotted line), on its left it becomes metastable (grey broken line) and once it crosses triple point I-III-V it becomes stable (solid black line).

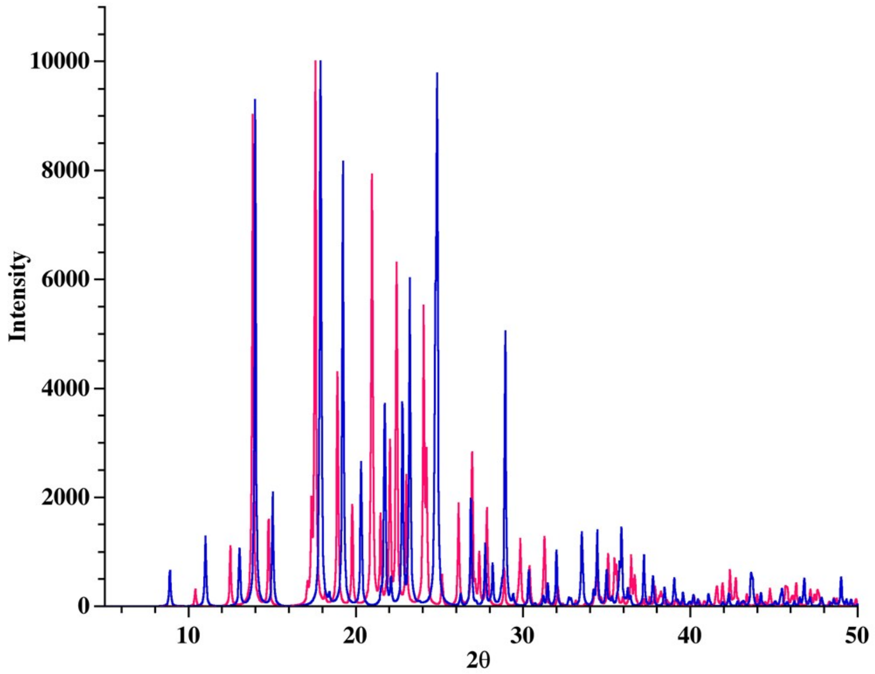

Figure ESI.3. Calculated powder diffraction patterns for form I (red, ambient conditions) and form III (blue, 323 K, 580 MPa)