

*The high-temperature phases of L-phenylalanine*Carl Henrik Görbitz<sup>1</sup><sup>1</sup>Department Of Chemistry, University Of Oslo, Norway, Oslo, Norway  
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After years of controversy over the solid state structure of the essential amino acid L-phenylalanine (L-Phe), the single crystal and powder X-ray investigations were recently published for no less than four different polymorphs. The common form I has P21 symmetry with four molecules in the asymmetric unit ( $Z' = 4$ ) [1], exactly as form III [2], but with a different arrangement of molecular bilayers. Form II, "stable only under rigorously dry conditions" [3], is unrelated to form I and III, as is the high-density form IV [1].

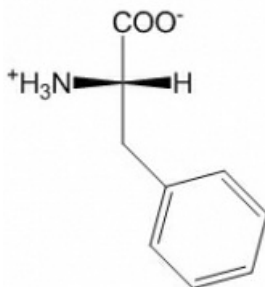
In the present work we add to the structural complexity of this prototype aromatic amino acid by demonstrating that L-Phe has at least three more high-temperature phases. Form Ih and form IIIh (h for high T) can be obtained from form I and form III by heating, which causes pairs of initially conformationally distinct molecules to become indistinguishable. This gives a reduction from 4 to 2 for  $Z'$  and a change of crystal symmetry. For form III this is an irreversible phase transition, as cooling of form IIIh leads not to form III, but to form I as a result of sliding of molecular bilayers in the crystal, a process observed previously for enantiomeric, racemic and quasiracemic structures of amino acids with linear side chains (see ref. [4] and references therein). As for the elusive form V, it is obtained at somewhat lower temperature than form IIIh by heating of some, but not all form I crystals. It is triclinic, P1, with  $Z' = 8$ .

[1] Ihlefeldt, F. S. et al. (2014). *Angew. Chem. Int. Ed.* 53, 13600 –13604

[2] Mossou, E. et al. (2014). *Acta Crystallogr. Sect. C* 70, 326 – 331.

[3] Williams, P. A. et al. (2013). *J. Phys. Chem. C* 117, 12136 – 12145.

[4] Görbitz, C. H. et al. (2016). *IUCrJ* 3, 341 – 353.



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