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Direct lock-in transition in 4-biphenylcarboxy substituted L-phenylalaninate crystals

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Protection of amino acids is an essential aspect for peptide synthesis.[1] Recently, crystals of 4-biphenylcarboxy substituted *L*-serine, *L*-tyrosine, *L*-alanine, *L*-leucine and *L*-phenylalanine methyl esters have been demonstrated to possess diverse supramolecular assembly governed by C–H···π and π···π interactions between biphenyl fragments and intermolecular N–H···O interactions between the amide O=C–N–H groups.[2,3] Amongst them, 4-biphenylcarxy-*L*-phenylalaninate is elusive because it crystallizes in monoclinic space group symmetry P21 within a pseudo-orthorhombic lattice[3] [a = 5.0748(2) Å, b = 8.7658(3) Å, c = 42.4828(13) Å, β = 90.038(3)°] at ambient conditions (phase **I**). The crystal comprises of two independent molecules (Z' = 2) with disparate molecular torsion and the monoclinic distortion is retained up to its melting temperature.
Temperature dependent single crystal X-ray diffraction experiments revealed a reversible structural phase transition at Tc ≈ 124 K upon cooling. Below Tc (phase **II**), satellite reflections in addition to main reflections were observed. **q** remains invariant as function of temperature that can be indexed with a modulation wave vector, **q** = (½, 0, ½) with respect to the basic monoclinic lattice. The crystal structure is described as a (3+1)D commensurately modulated structure in superspace group P21(σ10σ3)0 (σ1 = ½, σ3 = ½). The equivalent 3D superstructure [space group monoclinic (b–unique) B21] comprises of four independent molecules in the asymmetric unit.
Here we present the phase relations between **I** and **II**. The phase transition at Tc is primarily characterized by evolution of torsional modulation within the biphenyl fragments that are unequal for the two independent molecules. The origin of the torsional modulation is argued to lie in the competition between possible steric hindrance between the ortho-hydrogens of the biphenyl fragment that favors torsion and intermolecular C–H···π interactions that favors planar biphenyl moiety. Stabilized by weak C–H···O hydrogen bonds, short H–C···C–H interactions involving the biphenyl fragment suppresses the torsion for one independent molecule while longer H–C···C–H contacts allows larger torsional amplitude for the other.

References:

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