Poster Presentation

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The Only N-H…O Hydrogen Bond - Two Ways to Build a Structure of Dimethylglycine

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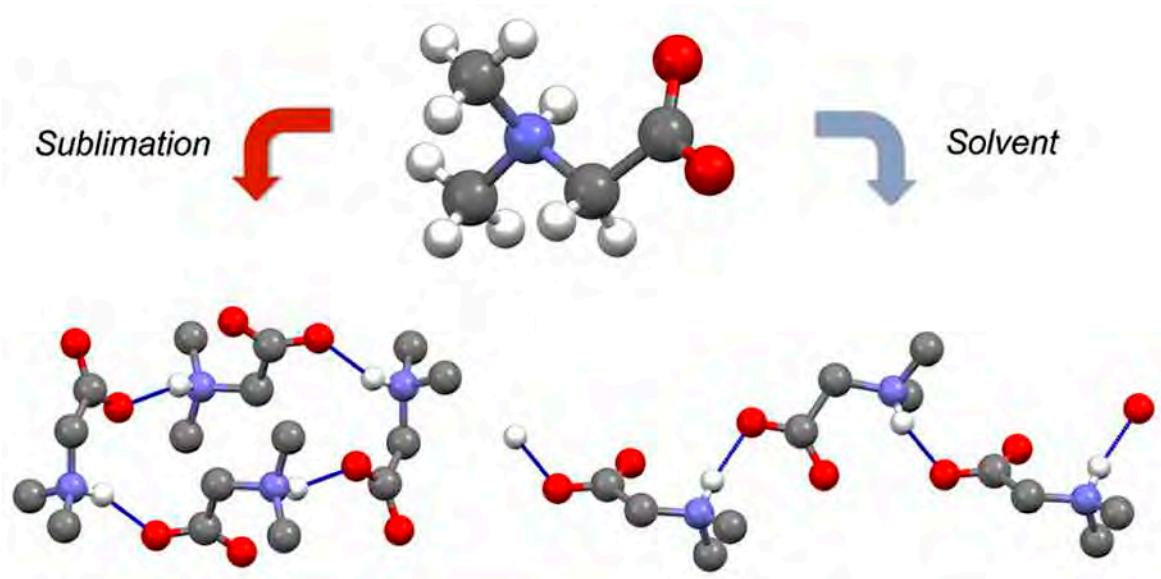
Crystalline amino acids are considered to mimic important interactions in peptides, therefore the studies of the structure-forming factors in these systems attract much attention. N,N-dimethylglycine is an interesting model compound that was used to test the role of the N-H…O H-bonds in forming the head-to-tail chains – the main structural unit in the crystals of amino acids. It was hypothesized previously that additional side N-H…O H-bonds play an important role in forming the head-to-tail chains of amino acid zwitterions linked via N-H…O H-bonds between the charged -NH3 and -COO terminal groups. Twice methylated amino group of N,N-dimethylglycine is able to form only one N-H...O H-bond in the crystal structure, so that this hypothesis could be tested. There are two polymorphs of N,N-dimethylglycine, in which the zwitterions are packed in two different ways. In one polymorph (orthorhombic, Pbca) they form finite four member ring motifs not linked to each other via any H-bonds, but only by weak van der Waals interactions. However, in the second polymorph (monoclinic, P21/n) the zwitterions do form infinite head-to-tail chains though the N-H…O H-bond is the only one and is not assisted via any additional H-bonds. The effect of cooling on the two crystal structures was followed by single-crystal X-ray diffraction combined with polarized Raman spectroscopy of oriented single crystals, in order to compare the response of the N-H…O H-bonds to temperature variations. The crystal structure of the monoclinic polymorph compresses anisotropically on cooling, whereas that of the orthorhombic polymorph undergoes a reversible single-crystal to single-crystal phase transition at ~200 K accompanied by non-merohedral twinning, reducing the space symmetry to monoclinic (P21/b), and doubling the asymmetric unit from 2 to 4 molecules. This phase transition could not be detected by Raman spectroscopy and DSC because of the subtle related changes in intermolecular energies.



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