Pushing the 10 GPa Pressure Boundary for Organic Solids: Crystal Structure Determination of α-Glycine Above a Megabar

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Abstract

Survey of the Cambridge Structural Database (CSD) shows almost 93% of high-pressure depositions (only accounting for 0.36% of the database) to be reported at pressures below 10 GPa.[1] The range of molecular solids studied under pressure encompass not only incredibly common chemical reagents and solvents, but also classes of biomolecules that make up the fundamental building blocks of life. These organic molecular crystals often have extensive networks of non-covalent intermolecular interactions, which play a significant role in the relative arrangement of molecules to form the overall crystal packing.

It is hypothesised that past the 10 GPa (equivalent to 100,000 bar) pressure, intermolecular void space in organic molecular crystals approaches zero, requiring modifications in the network of intra and intermolecular bonding interactions to accommodate for further compression.[2] The lack of single-crystal X-ray diffraction (SCXRD) data on such solids past this pressure threshold presents a clear gap in our understanding of the impact of pressure on interactions that govern the formation of molecular crystals and contribute to the structure-function relationship in biological macromolecules.

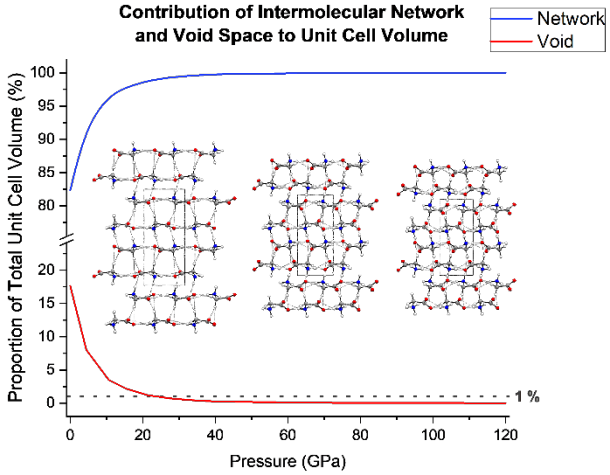

Figure 1. Plot of the contribution of the intermolecular network and void space to the total unit cell volume of α-glycine with increasing pressure. Marked by the grey dashed line is the point at which the proportion of total unit cell volume corresponding to void space is less than 1%. A section of the crystal structure of α-glycine at increasing pressure intervals is shown in the centre of the plot (from left to right: 0.0 GPa, 60.0 GPa, and 120.0 GPa).

Here we will present the results of SCXRD experiments at pressures in excess of a megabar, surpassing the so-called '10 GPa pressure boundary' by over tenfold. The simplest proteinogenic amino acid, glycine, was chosen for the incredible robustness of the α-phase at high pressures. Our SCXRD experiments yielded high quality diffraction data allowing the structure of α glycine to be fully solved and refined up to 120.0 GPa. This far exceeds both the previous highest pressure single crystal structure of α glycine, and the typical pressure range for organic molecular crystals. From these data, the evolution of the intermolecular hydrogen bonding network as a response to pressure has been tracked, and calculations of geometric and energetic data will be presented. Of particular note is the remarkable ability of this crystal structure to accommodate pressure even after the point where void space accounts for less than 1% of the total unit cell volume, found to occur after 21.5 GPa. The data presented will provide insight into the structural modifications undergone by the intermolecular bonding network as a direct response to compression, and highlight the value of studying molecular solids up to this new 1.2 megabar threshold.

[1] C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, The Cambridge Structural Database, *Acta Cryst B*, 2016, **72**, 171–179.

[2] C. J. G. Wilson, T. Cervenka, P. A. Wood and S. Parsons, Behavior of Occupied and Void Space in Molecular Crystal Structures at High Pressure, *Crystal Growth & Design*, 2022, **22**, 2328–2341.