Pressure-induced collapse of H-bonded structures
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Transformations of hydrogen bonds, their braking and formation in new molecular aggregates are frequent elements of chemical or biological processes. Studies of such transformations in simple molecular model compounds provide useful understanding of their mechanism.

Benzene belongs to the most common and best known organic compounds. Its simple and highly symmetric molecular structure inspired the concept of aromaticity. Molecular arrangements of benzene have been determined at the lowest limits of pressure ranges of phase I, at 0.15 GPa, and phase II at 0.91 and 0.97 GPa, all at 295 K. Benzene molecules in both phases interact by specific C–H⋯π(arene) hydrogen bonds. In phase I the they are bonded approximately perpendicular into sheets and there are substantial voids between the molecules within the sheets. The mechanism of benzene I/II phase transition can be described as a collapse of the voids between C–H⋯π(arene) bonded molecules in phase I, and shifts of the neighboring sheets. Due to the elimination of the voids, the interpenetration of molecules into the neighboring voids decreases, which increases the thickness of the sheets, and partly compensates the volume change of the voids collapse. In the result a small transition volume change between benzene I and II, the sluggish mechanism.

Guanidinium nitrate, C(NH$_2$)$_3$NO$_3$, is regarded as a model system for N–H⋯O hydrogen-bonded structures and their transformations. The guanidinium cation and nitrate anion are ideal H-donor and H-acceptor of six H-bonds, respectively. Highly favoured N–H⋯O bonded honeycomb layers in guanidinium nitrate is destabilized by pressure of 0.6 GPa, and the novel motif of 3-dimensional N–H⋯O bonded aggregation in high-pressure phase IV have been determined for in situ grown single-crystal by X-ray diffraction. The mechanism of the transition involves the collapse of voids present in phases I, II and III. The established P/T phase diagram of guanidinium nitrate illustrates a considerable hysteresis of the phase IV boundaries, caused by the strongly reconstructive character of the transition [2].

In conclusion, the benzene and guanidinium nitrate crystals reveal typical features of hydrogen-bonded aggregates containing voids at normal conditions.

References:

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