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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 $\cdots\pi$ (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 $\cdots\pi$ (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 nature of the phase transition and its large pressure hysteresis have been observed [1].

Guanidinium nitrate, C(NH₂)₃⁺NO₃⁻, is regarded as a model system for N–H \cdots 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 \cdots O bonded honeycomb layers in guanidinium nitrate is destabilized by pressure of 0.6 GPa, and the novel motif of 3-dimensional N–H \cdots 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.

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Study of Palladium Thioether Complexes at High Pressure

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This study builds on the work of Allan *et al* [1], which reports structural change in the square planar mononuclear complex *cis*-[PdCl₂([9]aneS₃)] ([9]aneS₃ = 1,4,7-trithiacyclononane). At 44 kbar this complex changes to give an intensely coloured chain polymer with the metal centre adopting a distorted octahedral coordination. We have examined related Pd(II) thioether complexes of the form [PdXY([9]aneS₃)]PF₆, where X and Y represent different electron-withdrawing ligands.

At ambient pressure it is known [2] that by using π -acceptor ligands such as phosphines the apical Pd \cdots S bond contracts to around 2.8 Å. π -donor ligands as shown in the chloride have longer apical Pd \cdots S distances (3.16 Å for chloride). We argue that using by π acceptor ligands we might induce phenomena to occur at lower pressures than otherwise, including higher coordination numbers.

We can control the extent of π - π stacking interactions in [Pd([9]ane S₃)(PPh₃)₂][PF₆]₂ as a function of pressure. Unusually, this also causes a deformation of the internal structure of the cation, with pyramidalisation at the *ipso* carbon of one phenyl ring (Figure 1). With increasing pressure, the P1–C11 \cdots C14 angle (α) decreases significantly, from 169.8° at ambient pressure and 149.3° at 65.5 kbar.

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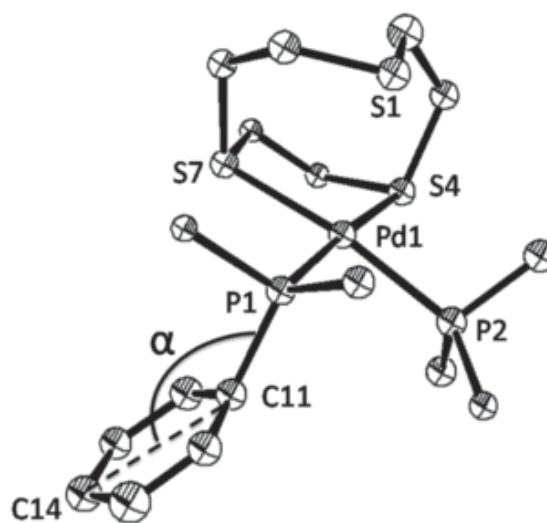


Figure 1. [Pd([9]aneS₃)(PPh₃)₂][PF₆]₂ at 65.5 kbar (H atoms and anions omitted for clarity, only *ipso* C atoms of other phenyl rings shown).

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