The work described in my thesis aimed to understand the structural responses of simple, molecular crystal structures when exposed to extreme pressures and temperatures. The systems selected for study were of fundamental academic appeal as they each demonstrated different aspects of interesting phase behaviour. The investigations, outlined below, either pushed the boundaries of existing scattering techniques or demonstrated the potential for high pressure as tool in crystal engineering. It is for this reason that I would like to be considered for the PANalytical thesis prize.

The crystal structure of the smallest non-chiral amino acid, L-alanine, was studied at very high pressure (*ca.* 15 GPa) using neutron powder and X-ray single crystal diffraction; pressure studies on these types of systems are often limited to 10 GPa. With the exception of benzene, this is the highest pressure study for which *in-situ* diffraction data have been measured on a 'sizeable' organic molecule. Only by exploring this, ordinarily inaccessible, pressure regime could it be shown that L-alanine undergoes a reversible amorphisation above 13.6 GPa, making it the only known amino acid to show a transition of this type. Two manuscripts on this work have been published in CrystEngComm.

4-methylpyridine pentachlorophenol (MPPCP) presents an example where the PV term in the Gibbs free energy equation was effectively used as a crystal engineering tool. MPPCP exhibits a rare case of isotopic polymorphism by deuteration, where the deuterated crystalline form is denser. Crystals of isotopically normal MPPCP were grown in the unit cell of the deuterated analogue when crystallised *in-situ* at high pressure. Furthermore, the crystal demonstrated stability at ambient conditions when recovered from the pressure cell, highlighting the potential for pressure as a route to new, more stable crystalline forms that are inaccessible by conventional means.

In aniline, high-pressure neutron powder and single crystal X-ray diffraction experiments showed that a less dense form, only previously observed at low temperatures, could be obtained on decompression of the high-pressure form. Energetic analysis of intermolecular contacts revealed that one of the hydrogen bonds became destabilising at high pressure, becoming compressed into a repulsive region of its potential — a phenomena that has previously been thought to not occur in organic molecular systems. A paper on aniline has been published in CrystEngComm.

The cyclohexane and oxalyl chloride systems both exhibit order–disorder solid–solid transitions. In order to gain a clearer understanding of *how* phase transitions occur (as opposed to *why*), the local structures of these were measured with neutron total scattering and modelled using a reverse Monte Carlo (RMC) procedure. Both these systems are among the most challenging to have been attempted with RMC modelling; they are relatively complex structures with respect to other molecules that have been studied to date (e.g. SF_6 and CBr_4). These experiments represent a step towards a broader aim of RMC modelling of pharmaceutical molecules in order to understand how phase transitions propagate through a lattice and additionally how molecules behave in the amorphous state. The work on cyclohexane has been submitted for publication.