Polymorphism in urea

Subjecting simple organic molecular systems in condensed form to external constraints such as changes of temperature or pressure reveals much about the interactions between the molecular constituents. In cases where the interactions are mainly attractive, long-range van der Waals and repulsive, short-range forces, effective pairwise potentials model these interactions quite adequately. In cases where hydrogen bonding is present, however, modelling techniques are not yet as successful, and experimental confirmation of the expected structures is mandatory. Urea is one example, and experiments on POLARIS using the Paris-Edinburgh pressure cell have allowed *ab-initio* structure determination of one of its high-pressure phases.

Urea, NH_2-CO-NH_2 (also called carbamide), is of importance to many areas of chemistry. It is most often remembered as the end product of protein breakdown in the metabolism of many animals. Its historic importance derives mainly from the fact that urea was the first organic chemical ever synthesized commercially; its present commercial relevance stems from its use in plastics (e.g. in amino resins) and as the source of nitrogen in fertilizers.

The phase diagram of urea has not been explored much since the times of Bridgman (figure F4.1). Attention has focused in the meantime solely on the details of its crystal structure between room and low temperature. Its crystal structure at zero pressure, urea I, consists of ribbons of molecules linked in a head-to-tail fashion along the tetragonal *c*-axis (figure F4.2). Each ribbon is surrounded by four identical orthogonally oriented ribbons pointing in the opposite sense along the *c*-axis. The urea molecule is planar and retains its full molecular point symmetry. Each carbonyl oxygen atom accepts four N-H···O hydrogen
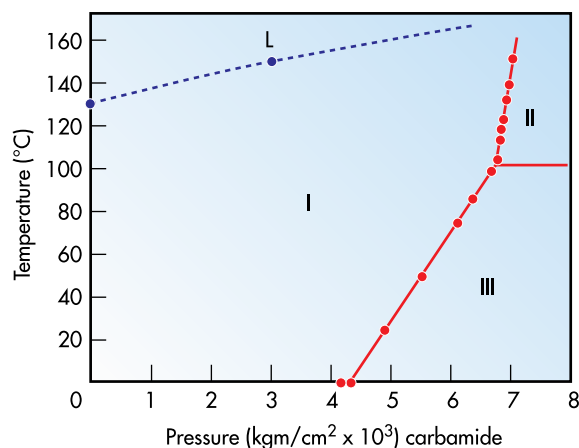

Figure F4.1. Phase diagram of urea (P.W. Bridgman, Proc. Amer. Acad. Arts & Sci. 52 (1916) 91-187

bonds, a very unusual feature for such a bond type. This dense (and energetically quite favourable) hydrogen bond network is probably established at the cost of efficient molecular packing: the structure is quite open, the ribbons forming tunnels with square cross-section 3.94 Å x 3.94 Å. As revealed by multipolar analysis of the electron density, the strongest interaction involves the double H-bond in the head-to-tail arrangement of urea dimers, while the single H-bond linkage between anti-parallel ribbons yields about half as much. The hydrogen bonds are thus all of similar strength, as reflected also by their nearly identical length (2.00 Å and 2.07 Å).

We have now determined the structure of urea phase III just above the phase transition (p=0.48 GPa) and at several pressures above, from powder neutron diffraction data collected on POLARIS. The experiment confirmed that the unit cell of this phase is orthorhombic, as originally reported almost forty years ago. As before, the cell indexing was not unique in that one of the lattice constants could only be determined within a factor of two. Initially, molecular packing arguments appeared to favour the larger unit cell which should contain eight urea molecules. Surprisingly, the smaller four-fold unit cell was eventually

shown to be correct and the space group was quickly established as $P2_12_12_1$. A major step in the *ab initio* structure solution of urea phase III was the development of a sophisticated search procedure to match structure factors extracted by the Pawley method against those of a candidate structure. For a given space group, the program translated and rotated a planar urea molecule (an assumption) about the asymmetric unit, looking for reasonable matches with the extracted structure factors. The best-fit atomic coordinates from this procedure were then used as the starting point of a standard Rietveld refinement to yield the final structure solution (figure F4.2). To our knowledge, this is the most complex *ab initio* structure solution yet obtained from neutron powder diffraction data collected using the Paris-Edinburgh cell.

It is evident that the same strong interactions found in urea phase I prevail in the high-pressure modification, resulting in the same structural units: ribbons of double hydrogen-bonded molecules, linked head-to-tail, with neighbouring ribbons running in opposite directions. Molecular packing in phase III is evidently more efficient. The
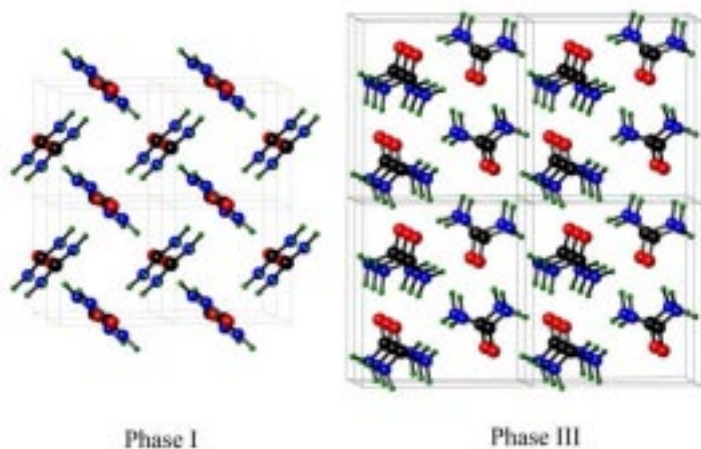

Figure 4.2. The crystal structures of urea phases I and III. The viewing directions are almost parallel to the c-axis (phase I) and to the short orthorhombic b-axis (phase III).
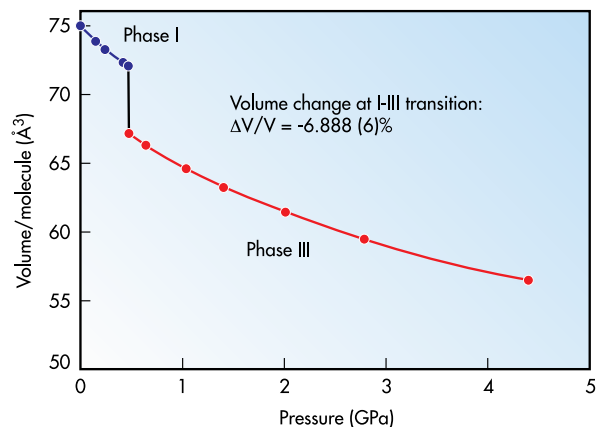

Figure F4.3. Urea equation of state at room temperature as determined from data collected using a mixed-phase sample of deuterated urea and NaCl – a suitable pressure calibrant.

empty tunnels have been filled, and the urea molecules have lost their plane of symmetry to adapt to their new cavity. Each carbonyl oxygen now accepts only three hydrogen bonds instead of four, with N-H···O contact distances varying from 1.84 Å A to 2.30 Å. This is an exception to the commonly held notion that hydrogen bonding increases with pressure. Compared to the zero pressure structure, the chains in the high-pressure structure are noticeably strained. This is evidenced by a larger deviation of the H-bonds from co-linearity as well as by a larger spread of the intra-chain H-bond distances.

The mechanism of the transformation is likely to be a rotation of neighbouring chains around the chain axis, with the goal of better packing. This is energetically not so costly as only one of the two weaker inter-chain H bonds needs to be broken. The lattice of urea phase III appears to be related to that of urea phase I by the relationships $a_{III} = \sqrt{2}a_I$, $b_{III} = a_I / \sqrt{2}$ and $c_{III} = 2c_I$.

The results obtained for the urea equation of state are shown in figure F4.3. The transition pressure of 0.47 GPa is rather modest, and this leads one to predict a phase diagram rich in additional structural modifications, not unlike thiourea.

Michel Bonin (ESRF, Grenoble), W G Marshall (ISIS), Hans-Peter Weber (ESRF, Grenoble), P Toledano (ESRF, Grenoble and Université de Picardie Jules-Verne, Amiens)