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With the notable exceptions of water, ammonia and a very limited number of other examples, there have been relatively few high-pressure structural studies of simple molecular compounds. Such studies can provide fascinating information about intermolecular interactions and pressure-induced phase transition, in particular hydrogen-bonding interactions. Recent results for thiourea and urea obtained from the experiments on neutron beamlines at the UK ISIS facilities have shown a very rich high-pressure behaviour [1].

In the light of these results, we have undertaken neutron and synchrotron studies on thiourea dioxide, which has been selected by virtue of its interesting ambient pressure structure [2].

We report a phase transition between a powder sample of orthorhombic phase I of thiourea dioxide to a new monoclinic phase II at a pressure of 0.54 GPa. This transition has also been observed in a single crystal sample at a pressure of 0.45 GPa. We also report an unusual isostructural transformation in thiourea dioxide at 6.8 GPa that involves the formation of a new hydrogen bond.

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Keywords: polymorphism, high pressure phase transitions, hydrogen bonding polymorphism

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The Effect of Pressure, and Formation of new Polymorphs of the Amino Acids L-cysteine and L-serine

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The application of pressure (<10 GPa) has proved a successful way of probing materials, particularly biologically important building blocks such as amino acids to understand the significance of hydrogen bonding interactions in these simple organic molecules [1].

On application of pressure, even systems comparable to each other have been shown to have remarkably different properties. Orthorhombic L-cysteine and L-serine-I, both of which have similar packing arrangements are examples of this. Under pressure, L-cysteine initially undergoes a much larger reduction in volume than L-serine-I, until at much higher pressure (c.a. 4 GPa) a single-crystal to single-crystal phase transition was observed. L-serine-I also undergoes a similar phase transition (c.a. 5 GPa) [2], however, although both phase transitions in L-serine-I and orthorhombic L-cysteine occur through the compressibility of soft interactions, the resulting high-pressure polymorphs are far different.

Pressure studies between ambient and 10 GPa are not only providing a useful way to investigate polymorphism of materials, but the information obtained on increasing pressure is beginning to give us an appreciation of the compressibility of intermolecular interactions under these pressure.

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Absence of Halogen Bonding in the High-pressure Structure of Chlorotrimethylsilane

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Halogen...halogen interactions are usually considered as the next most important cohesion forces, apart from the hydrogen bonds, governing the arrangement of molecules in crystals [1]. Such interactions are observed in many compounds containing halogens.

The interactions of one halogen atom with the lone pair of another halogen atom forms intermolecular bridges. The chlorine...chlorine interactions belong to the most fundamental supramolecular synthons [2].

Meanwhile in the structure of chlorotrimethylsilane determined at low temperature [3] no halogen...halogen interactions are observed. Therefore we have undertaken the high-pressure study of this compound to check if short chlorine...chlorine contacts would exist in the compressed crystal. We have determined the crystal structure of chlorotrimethylsilane at 0.3 and 0.6 GPa. At these pressures the crystal is orthorhombic, space group Pmn₂1, whereas the crystal frozen at low temperature crystallized in monoclinic space group P2₁/m. It occurs that also in this new high-pressure phase of C₃H₉ClSi no close chlorine...chlorine contacts are observed.

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High-pressure Crystal Phase of 1,2-ethylenediamine

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1,2-Ethylenediamine (H₂N CH₂ CH₂ NH₂) is the simplest of α,ω -alkanediamines. Its m.p. is 284.29 K [1], and it was crystallized at low temperature and its structure determined at 213 K [2] and 130 K [3]. The crystals are monoclinic, space group P2₁/c, $a = 5.047(2)$, $b = 7.14(2)$, $c = 5.475(2)$ and $\beta = 115.36(3)$ [3] (hereafter phase II).

In our study we have crystallized C₂H₈N₂ by pressure-freezing in Merrill-Bassett diamond-anvil cell. In this way three distinct phases of C₂H₈N₂ have been obtained and their structures determined: phase II with the unit cell parameters similar to those listed above for the low-temperature phase; phase I (which is stable at lower pressure and higher temperature, than for phase II) – monoclinic, space group P2₁/c $a = 5.031(10)$, $b = 5.132(3)$, $c = 7.167(5)$, $\beta = 110.60(12)^\circ$ at 0.3 GPa and 293(2) K; at 1.5 GPa the crystal is transformed to phase III with the unit-cell doubled.

The structures have been solved by direct methods and refined by full matrix least squares.

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Probing Polymorphism with High Pressure

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In recent years, work at Edinburgh has shown that pressure-induced crystallisation of simple organic compounds from the pure liquid results in the generation of new polymorphs [1]. Attempts to induce polymorphism in more complex, higher melting compounds (such as pharmaceuticals) have been much less successful. This is because thermal decomposition usually occurs long before the pressure-elevated melting temperature is reached.

We have instead developed a technique for growing single crystals from solution at high pressure that removes excessively high temperatures and provides an opportunity to study high-pressure crystallisation from different solvent systems [2]. We report how the power of this technique, in combination with ambient-pressure conventional polymorph screening processes, is not only successful in