Experimental

High-Pressure Crystallisation Procedure

Naphthalene

Recrystallisation experiments

A ca. 2.2 M solution of naphthalene (BDH, used as received) in dichloromethane (Fisher) was loaded at 293 K into a DAC equipped with 800 µm culet diamonds and a tungsten gasket with a 300 µm gasket hole. On sealing the cell and pressurising to ca. 0.4 GPa precipitation of polycrystalline material occurred. The temperature was then cycled near ca. 343 K using a hot-air gun in order to dissolve all but one of the crystallites and on slow cooling to 293 K a single crystal grew from solution to fill ca. 70 % of the gasket hole (Figure 2). This crystal was identified as the ambient-pressure phase by single-crystal diffractometry. Subsequent to the identification of the ambient-pressure phase, the pressure inside the DAC was increased from 0.4 GPa to ca. 0.6 GPa. The single crystal grown previously was redissolved by gentle heating, and on cooling precipitation of polycrystalline material was observed. The temperature was then cycled near ca. 353 K in order to dissolve all but one of the crystallites and on slow cooling to 293 K a single crystal grew from solution to fill almost 50 % of the gasket hole. A single-crystal diffraction experiment showed this to correspond to the ambient-pressure phase. Single-crystal diffraction data were then collected as described below.
Compression studies

Dissolution of naphthalene from dichloromethane at pressures higher than 0.6 GPa could not be induced by the current heating method. With a maximum attainable temperature of ca. 423 K, heating with a hot-air gun imposes a limit on the highest pressures at which a compound can be recrystallised from solution. Alternative heating methods, e.g. resistance heating, high-temperature ovens, or laser heating, were not attempted in this series of experiments.

High-pressure recrystallisation of naphthalene from a more dilute methanol (ca. 1.5 M) solution did not increase the working range of pressure for successful dissolution and so further studies of naphthalene were performed by compression of the single crystal grown at 0.6 GPa from dichloromethane. Single-crystal diffraction data were collected at 1.0 GPa and 2.1 GPa. Broad ruby fluorescence lines indicated that above 1.0 GPa the quality of the crystal was deteriorating and that the conditions inside the DAC were non-hydrostatic (the freezing pressure of dichloromethane is 1.33 GPa, Podsiadlo et al., 2005). This is not necessarily an undesirable situation for inducing phase transformations for although non-hydrostatic stresses can in some cases suppress a phase transition (Angel et al., 2001), on other occasions uneven compression can also cause structural strain that can ultimately lead to a phase transition (Resel et al., 2004). No transition for naphthalene was observed up to 2.1 GPa. Above this pressure the “super-pressed” dichloromethane solvent froze and no single-crystal data suitable for analysis could be collected.

Since the principal scope of this work was to induce the formation of a new modification of naphthalene by crystallisation from solution at high pressure, no other pressure transmitting media that would allow carrying out a compressibility study to higher pressures than 2.1 GPa were investigated in this instance. Due to the relatively high solubility of naphthalene in a variety of common pressure transmitting solvents, e.g. methanol and ethanol, it is however foreseen that a careful choice of pressure-transmitting fluid should be considered for future experiments.

Pyrene

Recrystallisation at 0.3 GPa

A ca. 0.5 M solution of pyrene (BDH, used as received) in dichloromethane (Fisher) was loaded at 293 K into a DAC as described for naphthalene. On sealing the cell and pressurising to ca. 0.3 GPa precipitation of polycrystalline material occurred. The temperature was then cycled near ca. 303 K in order to dissolve all but one of the crystallites and on slow
cooling to 293 K a single crystal grew from solution to fill ca. 50 % of the gasket hole. Several temperature-annealing cycles were necessary to grow a single crystal of reasonably large size and prevent the growth of a large number of smaller single crystals nucleating from the edge of the gasket. Notwithstanding this, two smaller single crystals were also allowed to grow in the pressure cell. The pressure within the gasket hole was determined as ca. 0.3 GPa.

Indexing of the reflections obtained from a single-crystal X-ray diffraction experiment gave a unit cell with dimensions substantially different from either of the two known polymorphs of pyrene corresponding to a volume decrease of ca. 6 % with respect to the structure of form II at ambient pressure and temperature.

Recrystallisation at 0.5 GPa

Subsequent to the identification of a new high-pressure phase at 0.3 GPa, here denoted as form III, our attention focussed on whether further new phases could be accessed by recrystallisation at higher pressures. Four temperature-annealing cycles near ca. 303 K were needed to grow a single crystal that filled ca. 50 % of the gasket hole at ca. 0.5 GPa. Despite the ease and low temperatures with which the material could be dissolved, only multiple crystals could be grown at higher pressures and diffraction data were not collected. This could be caused by the intrinsic properties of pyrene-III, although it should be noted that there is little or no control over the number of nucleation sites inside the high-pressure cell and that these may affect the kinetics of the crystallisation process.

Results and Discussion

Naphthalene

The plots illustrated in Figure 1 show the variation of unit-cell volume, density and cell parameters with pressure. The gradient of the graphs of lattice parameters vs. pressure decrease markedly at pressures above 1.0 GPa and this could be attributed to the non-hydrostatic conditions present in the high-pressure cell above this pressure, or could be an indication that the structure is reaching the limit of compression.
Figure s1 Change in (a) unit-cell volume, (b) density and (c, d, e, f) lattice parameters of naphthalene with applied pressure. Open squares: Alt & Kalus (1982) at 0.01 GPa, 0.22 GPa, 0.42 GPa and 0.52 GPa. Filled diamonds: this work at 0.4 GPa, 0.6 GPa, 1.0 GPa and 2.1 GPa. The estimated standard deviations are smaller than the plotted symbols.