

**Experiment title:**

Insight into the high-pressure stability of hydrazobenzene and pressure-induced polymerization of azobenzene from crystal structure analysis

Experiment number:

CH-6291

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In recent years, pressure-induced polymerization of aromatic compounds has become a well-established route for the generation of novel carbon nanomaterials containing sp^3 carbon-bonded networks. In earlier high-pressure studies by Dong et al. [1] and our group [2,3], it was found that azobenzene undergoes a reversible phase transition at ca. 10 GPa and irreversible amorphization accompanied by polymerization at above 18–20 GPa. In contrast, hydrazobenzene, which has an N–N single bond instead of the N=N double bond in azobenzene, was reported to be stable up to at least 28 GPa [1]. Recently, we reported the pressure-induced polymerization process of *trans*-stilbene, which is isotypic to azobenzene and has a C=C double bond as linkage between the phenyl rings (Fig. 1) at ca. 16–20 GPa [4]. Hints to a pressure-induced phase transition were observed in stilbene at ca. 8 GPa. For both, azobenzene and stilbene, a polymerization mechanism and a model structure for a 1-dimensionally extending ‘double-core’ polymer was proposed [2–4].

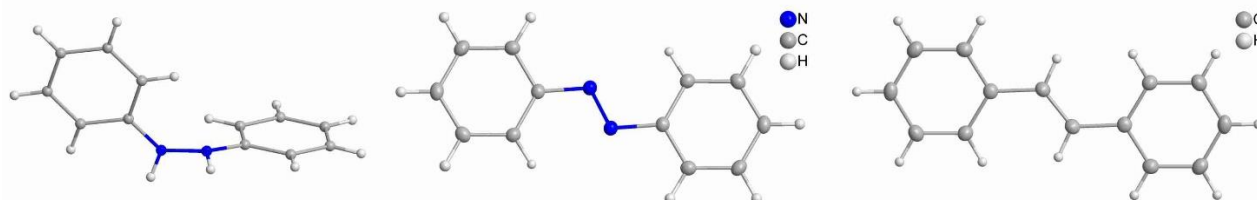


Fig. 1. The molecular structures of (left) hydrazobenzene, (centre) azobenzene, and (right) stilbene at 100 K.

We have grown single crystals of azobenzene and hydrazobenzene. The crystals of hydrazobenzene intrinsically did not have sufficient quality for single-crystal synchrotron X-ray diffraction experiments. Hence, we have collected high-quality single-crystal synchrotron X-ray diffraction data on azobenzene and *trans*-stilbene, which was commercially available, at pressures of up to 33 GPa. Neon was used as the pressure-transmitting medium. Intensity data were collected on two crystals of different orientations of each compound and combined in the crystal structure refinements. This improved the completeness of the high-pressure data, which usually suffer from the restriction of access to the reciprocal space induced by the high-pressure cell, which is especially important for low-symmetry compounds.

Main results

We have determined the crystal structures of azobenzene and stilbene up to polymerization pressure at 28 GPa and 18 GPa, respectively. For azobenzene, the high-pressure phase transition occurred at 13 GPa. It was apparent as a discontinuity in all the cell axes and β angle, while the unit-cell volume compressed uniformly (Fig. 2). We have solved the crystal structure of the high-pressure phase (Fig. 3). While an orientational disorder of one of the symmetry-independent molecules is present in the low-pressure phase of azobenzene, it is completely gone in the high-pressure phase, accompanied by a slight re-orientation of the molecules (Fig. 3). The molecular packing in azobenzene close to polymerization indicates a different polymerization mechanism to what was previously proposed [2,3]. In contrast to azobenzene, stilbene showed a uniform compression of all lattice parameters and the unit cell volume within errors up to the highest pressure of 18 GPa, a pressure stability much lower than for azobenzene crystals. Final data analysis will give important information on the evolution of the azobenzene and stilbene structures prior to polymerization and information on the polymer structures will be complemented by theoretical computations. The results of this experiment promise to contribute to the understanding of pressure-induced polymerization mechanisms for the generation of novel carbon nanomaterials.

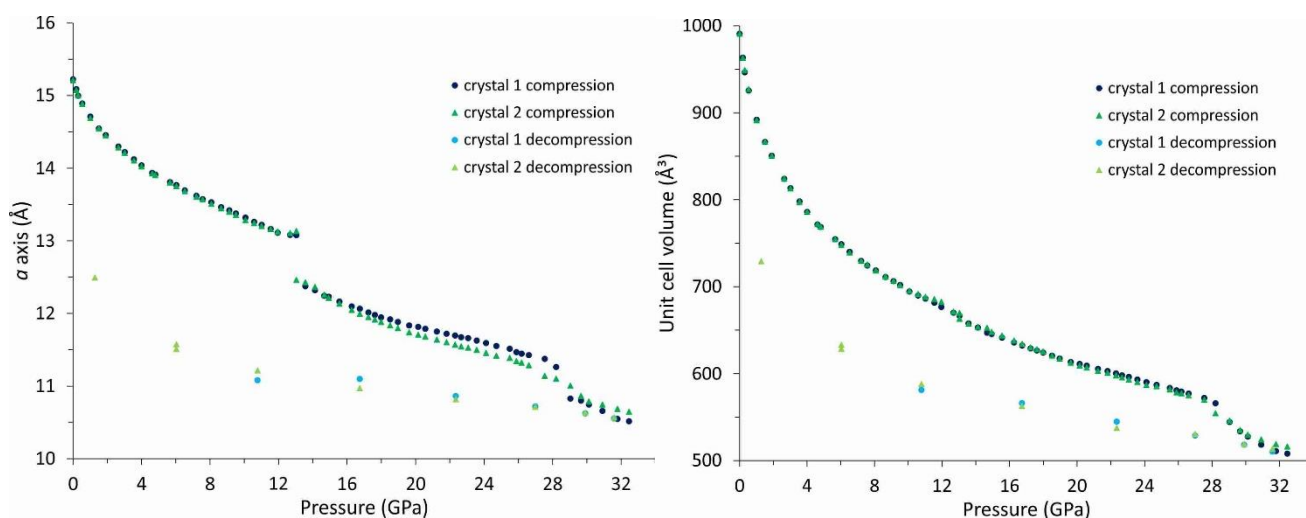


Fig. 2. Pressure evolution of the a axis (left) and the unit cell volume (right) of azobenzene. At ca. 13 GPa a phase transition is apparent in a discontinuity of the cell axes and β angle, while the unit cell volume compresses continuously. The onset of the pressure-induced polymerization is observed at ca. 28 GPa, a much higher pressure than previously reported [1–3]. Decompression data confirm the irreversibility of the reaction.

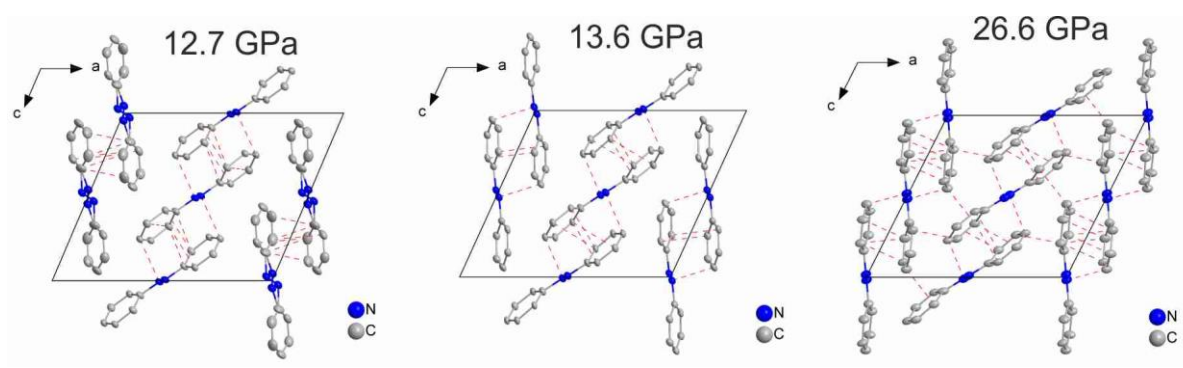


Fig. 3. Crystal structure of the low- (left) and high-pressure (centre and right) phases of azobenzene and close to the polymerization pressure (right) projected along the b axis. Some weak intermolecular C–N and C–C contacts are indicated by red dashed lines. Hydrogen atoms are omitted for clarity. The nitrogen atoms of one of the molecules in the low-pressure phase are disordered in a pedal motion configuration.

References

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