A pressure induced phase transition of 4-iodobenzonitrile

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The non-covalent interaction between donor atoms and halogen acceptors can be used in crystal engineering to promote chain formation. In the case of 4-iodobenzonitrile, a strong cyano donor aligns with the σ-hole, a region of positive electrostatic potential, in the highly polarizable iodine atom, causing structure-directing N…I interactions resulting in an *I2/a* (Z=4) crystal structure where antiparallel stacked linear chains form along the b-axis with layers along the *ab* plane. The N…I intermolecular distance is shorter than the sum of van der Waals radii, and it is therefore of interest to investigate the chemical effect of pressure-induced shortening on this intermolecular interaction.[1]

High-pressure experiments were performed with single-crystal X-ray diffraction (XRD) to 8 GPa and with Raman spectroscopy to 9.7 GPa using the diamond anvil cell. Compression was performed using pre-grown single crystals as well as crystals grown *in situ* at high pressure. Figure 1 shows the ambient pressure and new high-pressure phase of 4-iodobenzonitrile as determined by single crystal XRD.

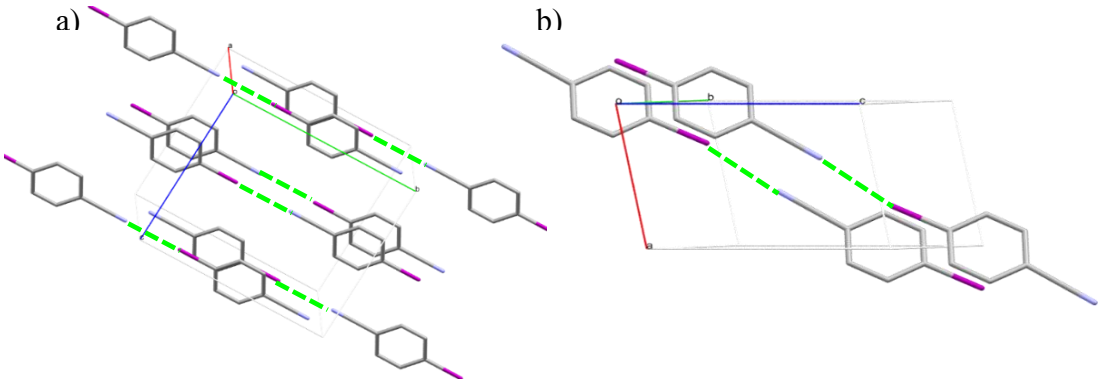

Figure 1 The ambient pressure I2/a phase (a) and the new high pressure P-1 phase (b). Iodine shown in purple, nitrogen in blue, carbon in grey. Hydrogen has been omitted for clarity. Intermolecular attractions shown in green.

Shortening of the I…I distance by pressure in elemental iodine results in a semi-conductor to metallic phase transition at 3.5 GPa,[2] a fairly modest pressure compared to other main-group elements that exhibit similar phase transitions e.g. S (83 GPa)[3] and Br (25 GPa).[4] In 4-iodobenzonitrile, the polarizability of I leads to a pressure induced phase transition from *I2/a* (Z=4) to *P-1 (Z=2)*, consisting of shortening of the N…I distance and possible out-of-plane bending of the I relative to the benzene ring at a modest pressure of 5 GPa.

References:

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