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Chemical reactivity at high pressure: the ordered polymerization of oxalic acid

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Pressure is known to trigger unusual chemical reactivity in molecular solids. In particular, small molecules containing unsaturated bonds are subject to oligo- or polymerization, effectively synthesizing new compounds. These are typically energetic materials which can be amorphous, as in the case of carbon monoxide,\textsuperscript{[1]} or crystalline, as for carbon dioxide phase V.\textsuperscript{[2]} In more complex molecular systems, where unsaturated bonds can be only one of the present moieties, stereo-controlled reactivity can be exploited to synthesize topo-tactic structures. We performed a synchrotron single crystal experiment on oxalic acid dihydrate up to 54.7 GPa, using He as pressure transmitting medium to ensure hydrostatic behavior. This is, to the best of our knowledge, the highest pressure ever achieved in a single crystal study on an organic molecule. It had been reported that the species undergoes a proton transfer at mild pressures,\textsuperscript{[3]} and further compression confirms the major role played by hydrogen bonds. After the proton transfer, the species undergoes two phase transitions, caused mainly by a rearrangement of hydrogen bonding patterns, that does not damage the singly crystal nature of the sample. At ~40 GPa an initial bending of the flat oxalic molecule is observed, sign of an enhanced nucleophilic interaction between one oxygen and the carbon of a neighbor molecule. At the highest pressure achieved, a further phase transition is observed. Although the crystallinity is decreased, the new unit cell shows a drastic shrinking in one specific direction. Periodic DFT calculations reveal this metric is compatible with an ordered polymerization of the oxalic acid created by a nucleophilic addition: a monodimensional covalent organic framework is the resulting material (figure). This observation, unique up to now in its kind, is of high relevance for crystal engineering and highlights the potential of high pressure to stimulate new chemistry.


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