How subtle differences in organic molecular crystals influence their structural evolution in compression

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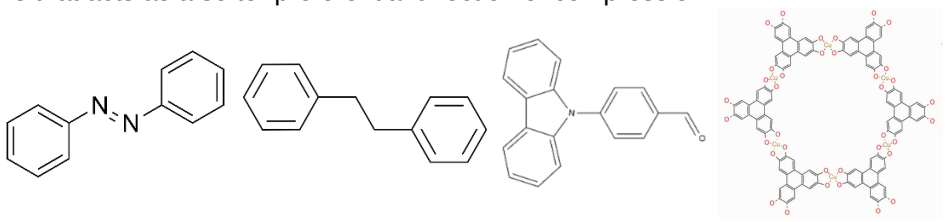
Abstract

Organic molecular crystals are an incredibly interesting class of materials to be studied in compression. Structural evolution under pressure depends on two different contributions: one that comes from the entire molecular unit moving within the unit cell, and the other instead that derives from intra-molecular changes. The most direct approach to observe these changes under pressure is synchrotron powder and single crystal X-ray diffraction, while fine variations in molecular structure and interactions can be complemented with spectroscopic techniques such as IR, Raman, UV-Vis and XAS spectroscopy. Simple molecular systems will be presented to showcase how small differences in chemical formula and conformations can result in very different structural evolution in compression, but also how distinct compounds can have similar features that can dictate how the system ultimately reacts to high pressure. Azobenzene/stilbene and bibenzyl are two closely related molecules differing only in the central chemical bond that links the two phenyl groups. This however makes azobenzene more rigid than bibenzyl, which has instead an additional degree of freedom in the torsional movement of the central bond. This difference plays a huge role in influencing the phase transition path that both undergo around 14 GPa: azobenzene exhibit a more drastic phase transition that needs to involve a greater molecular rearrangement in the structure [1], while bibenzyl is able to release the accumulated stress with molecular distortions that have a much smaller effect on the symmetry and unit cell [2]. N-(4-Formylphenyl)carbazole shares a similar torsional degree of freedom to bibenzyl and as such they share a comparable low pressure behavior where tortional motion provides access to a much softer preferred crystallographic direction of compression. However, an overall lower flexibility leads to rupture of the unit cell symmetry along a specific direction rather than the point group symmetry of the molecule. Lastly, the structural evolution in compression of novel 2D-MOFs composed by metal centers and hexahydroxytriphenylene (HHTP) units is showcased. These MOFs are gaining interest due to their straightforward synthesis procedure and semiconducting properties which arise from intermolecular interactions of stacked two-dimensional extended metal-organic molecules [3]. The nature of these compounds allows for compressions to higher pressure than usual MOFs thanks to the available space between layers that acts as a softer preferential direction of compression.



Left to right: azobenzene, bibenzyl, N-(4-Formylphenyl)carbazole, CuHHTP 2D-MOF

[1] Agati, Milo, et al., Chemical Science 16.21 (2025): 9240-9254

[2] Agati Milo, et al., Crystal Growth & Design (2026) 26 (2), 970-984

[3] Lilia S. Xie, Grigorii Skorupskii, and Mircea Dincă, Chemical Reviews (2020) 120 (16), 8536-8580