Electron diffraction studies of an elastic molecular crystal

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Methanol-solvated cocrystals of caffeine and 4-chloro-3-nitrobenzoic acid are the earliest known system whose single crystals demonstrate reversible elastic bending [1]. Elastic bending in these crystals is governed by variation in molecular tilt and van der Waals gap between molecules from the tensile to the compressive arc of a mechanically bent crystal [2].

Recent investigations have shown that the crystals undergo a structural transformation $T > 320$ K, which ostensibly marks the loss of flexibility of the system [3]. Heating-cooling cycles from $T = 360$ K, $T = 370$ K, and $T = 380$ K, respectively, to $T = 100$ K led to the discovery of three structurally irreversible states [3]. Furthermore, employing an *in-situ* desolvation-solvation reaction mechanism by heating and cooling the cocrystal sample, single crystals were obtained [4]. The *in-situ* crystals demonstrated excellent flexibility, albeit in this case, the unit cell with orthorhombic *Fdd*2 symmetry was found to be larger than the starting solvent-grown material (prototype). During solvation, the flexible product recrystallized with greater number of methanol molecules in the crystal structure than the prototype which explains the expansion of the unit volume of the *in-situ* crystals [4].

Inspired by the observation on internal flexibility of the crystal packing of the cocrystal solvate, we have successfully grown flexible single crystals by cocystallizing caffeine with 4-bromo-3-nitrobenzoic acid and methanol (CAF-BNB). In-house single-crystal X-ray diffraction experiments revealed that the crystal structure is isomorphous to the prototype. Owing to the greater $d_{C–Br} = 1.89$ Å compared to $d_{C–Cl} = 1.72$ Å covalent bond distance and larger van der Waals radius of bromine atom (= 1.85 Å) than chlorine atom (= 1.75 Å), the unit cell volume is larger ($T = 100$ K: $V_{CAF\text{-}BNB} = 7400$ Å^3 *vs* $V_{prototype} = 7214$ Å^3 [3]).

To map the structural deformations in strained molecular crystals, μ-X-ray diffraction technique employing synchrotron radiation has emerged as an important tool in recent years [5]. However, large-scale facilities are not always accessible. In addition, the present system is not as stable as the prototype, making it difficult to store for extended periods of time and to transport.

We have therefore taken an alternative approach to study the deformation in this material employing continuous rotation 3D electron diffraction (3DED) experiments using the transmission electron microscope FEI Tecnai G2 20. Usage of nano-size electron beam minimizes the contribution of neighbouring domains to the diffraction pattern. Test 3D ED experiments on microcrystals of this system under cryogenic environment at $T = 100$ K demonstrated diffraction up to $d^* = 0.9–1.0$ Å^{-1}. Bragg peaks could be indexed in the *F*-centred orthorhombic lattice suggesting that the interaction of electrons with the crystals does not induce chemical changes to the crystal, *viz.* loss of solvent molecules. This confirms the potential of 3D ED to study flexible molecular multicomponent solvates.

In this contribution, we will present the results of kinematical and dynamical refinements of the 3D ED datasets. We will also present the potential of 3D ED to investigate the strain in this system.

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The authors acknowledge Physics for Future – MSCA COFUND reg. number: 101081515 for funding.