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In situ high pressure study of an elastic crystal by FTIR spectroscopy†

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We performed an *in situ* high pressure FTIR spectroscopic study on a 2,3-dichlorobenzylidene-4-bromoaniline (DBA) crystal at pressures ranging from ambient pressure to 13.8 GPa at room temperature. The variations in the stretching frequency of the aromatic C–H, H–C=N and C–Cl bands on compression showed significant molecular movement in the DBA crystal. Decompression was monitored on the aliphatic and aromatic C–H stretches which clearly show the reversibility of the molecular movements in the crystal lattice.

The mechanical properties of organic crystals have attracted great attention among researchers owing to a wide range of applications in fields like flexible electronics, organic light emitting diodes, solar cells, mimics of natural fibres, *etc.*^{1–7} Mechanical properties refer to both elastic and plastic deformations as well as fractures which occur under the action of applied load on the molecular crystals.^{8–10} Numerous studies established the fact that plastic deformation or irreversible bending in organic crystals is caused by the permanent sliding of molecular planes across the slip planes under load.^{8–14} However, the elastic or reversible bending of organic crystals can be attributed to the presence of multiple weak and dispersive interactions which act as “structural buffers” allowing easy rupture and

reformation of bonds during bending.^{9,15–19} Ghosh and Reddy showed that the elasticity of caffeine–4-chloro-3-nitrobenzoic acid co-crystals is due to the isotropic interlocking nature of weak and dispersive interactions in all directions.¹⁵ However, a number of reports appeared on the elastic behaviour of molecular crystals and these were based on comparable hydrogen bonding and halogen bonding interactions.^{16–19} Crystalline elastic materials have shown clear advantages over polymeric or liquid crystalline materials in actuation behaviour and they also serve as better energy conversion systems.^{1–9} The frequency shifts of solid nitro- and nitrito-cobalt(III) ammine complexes analysed by high pressure-FTIR spectroscopy at static pressures up to 20 kbar demonstrate that sufficient elastic strain can also be observed at relatively low pressures.²⁰ It is well known that small applied pressures generally induce significant changes in intermolecular interactions which are accompanied by dramatic reorganizations of crystal packing in molecular crystals and this subsequently influences the physical and chemical properties. A high pressure FTIR (HP-FTIR) study of energetic 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) crystals showed elastic behaviour wherein the crystals exhibited small structural rearrangements at high pressure.²¹ We have recently utilized variable temperature FTIR spectroscopy to understand the thermo-salient changes in an elastic crystal.²²

To understand the dynamic structural changes that occur under pressure, a systematic study of pressure-induced changes in an elastic crystal is needed. Such an understanding will assist in designing elastic crystals with predictable response behaviour. No such studies have been conducted using FTIR spectroscopy that showed a clear model for structural rearrangements of an elastic crystal at high pressures. Here, in this communication, we report a HP-FTIR study of an elastic organic crystal, 2,3-dichlorobenzylidene-4-bromoaniline (DBA hereafter), which was subjected to compression and decompression in pressures ranging from ambient pressure to 13.8 GPa with gradual increments. The changes in positions, shapes and

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