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Electron density of molecular crystals at high pressure from synchrotron data

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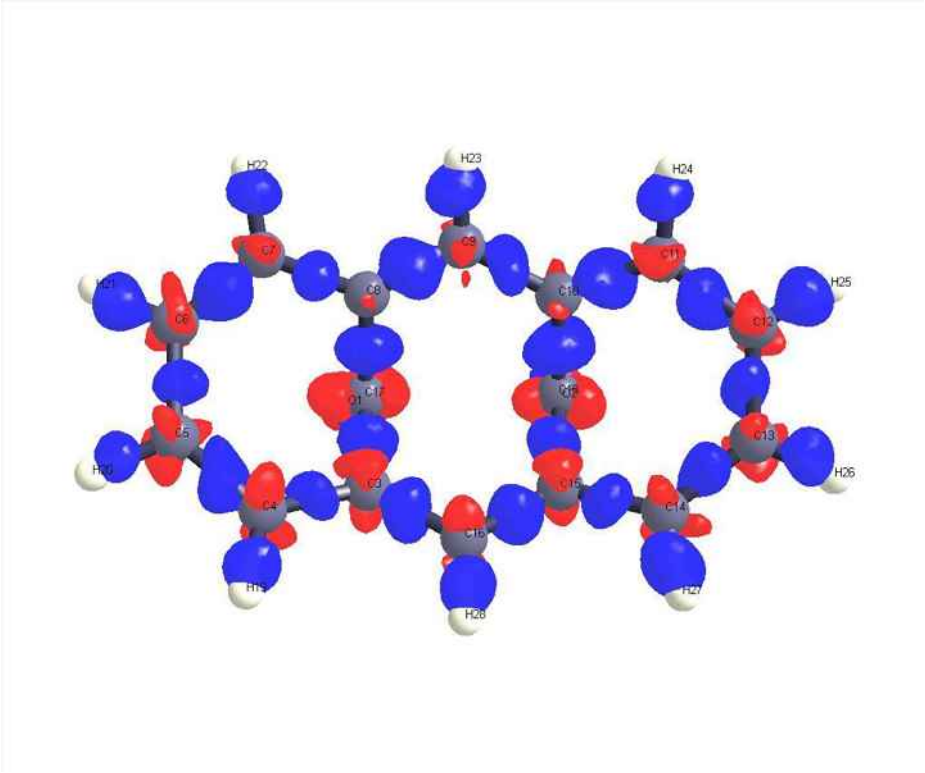
Accurate electron density mapping is quite a common practice for crystals cooled at low temperature and accurately measured. This is not true for species under external perturbation, due to complicated experimental conditions. Studying molecular crystals in excited states is a challenge, Coppens(2009), and a purely experimental electron density mapping is not possible at present. So far, the same limitation affected molecular crystals at high pressure, with only few attempts to use theoretical multipoles to fit experimental data, Fabbiani (2011). Here we report on the first unconstrained multipolar model, refined for syn-l,6;8,13 biscarbonyl[14]annulene (BCA) at P=7.7 GPa. BCA was the subject of a low temperature data collection by Destro (1995). The molecule (close to C2v symmetry) has a fair aromaticity, but it progressively localizes double and single bonds as a function of pressure. At 7.7 GPa the geometrical distortion is quite evident and mirrored by the electron density. The experiment, carried out at Diamond Light Source, was possible combining: a) high energy (40 Kev) to overcome the resolution problems caused by diamond anvil cells and reduce absorption and extinction; b) microfocused beam (30 micron) to minimize spurious X-ray diffusion; c) two crystals in the DAC, to increase data coverage; d) sufficient pressure to quench atomic motion. The final agreement is obviously worse than what typically obtained at ambient pressure. However, the model is satisfactory because: a) the deformation density is sensible and in agreement with the calculated one; b) the distribution of residuals is normal and no significant error is evident. The study proves that aromatic molecules are more reactive when squeezed, in keeping with the recent theoretical study by Hoffmann et al. on benzene. The Figure shows the static deformation density of BCA in 3D, obtained from a multipolar model refined against the experimental structure factors.

[1] *P. Coppens Angew. Chem. int. Ed. Engl., 2009, 48, 4280-4281,* ***[2]*** *F. Fabbiani, B. Dittrich, C. R. Pulham et al. Acta Cryst Sect. A, 2011, 67, C376,* ***[3]*** *R. Destro, F. Merati. Acta Cryst. Sect. B, 1995, 51, 559-570*



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