

*Mapping the trajectory of proton transfer via experimental electron density.*Lorraine Andrade Malaspina¹, Kunihisa Sugimoto², Alison J. Edwards³, Simon Grabowsky¹¹University Of Bremen, Institute For Inorganic Chemistry And Crystallography, Bremen, Germany, ²Japan Synchrotron Radiation Research Institute (JASRI) - SPring-8, Sayo-cho, Japan, ³Bragg Institute, Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia

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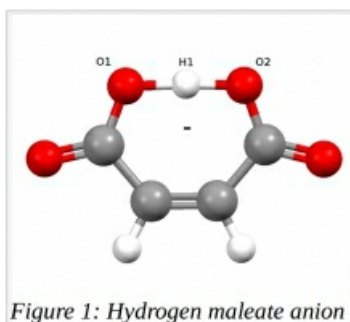
Hydrogen maleate (HM) salts offer the unique opportunity to follow a pseudo-reaction pathway of a proton transfer not only in theoretical simulations but also experimentally because the position of the hydrogen atom inside the strong and short intramolecular O-H...O hydrogen bond (low-barrier hydrogen bond [1]) is highly flexible dependent on the cation and/or crystalline environment (Figure 1). There is a great number of crystal structures of hydrogen maleate salts in the Cambridge Structural Database (CSD) (303 entries) which show that the O...O distance varies from 2.361 Å to 2.540 Å with a large variety of intermediate distances. Neutron diffraction studies establish that the O-H distances vary from 1.079 Å up to 1.215 Å. This means that snapshots along a pseudo-reaction pathway can be measured and, with the symmetric hydrogen bonds, even a model for a possible transition state is accessible.

In this study nine different hydrogen maleate salts (4-aminopyridinium HM, 8-hydroxyquinolinium HM, barium bis-HM tetrahydrate, calcium bis-HM pentahydrate, potassium HM, lithium HM dihydrate, magnesium bis-HM hexahydrate, sodium HM trihydrate and L-phenylalaninium HM [2]) that span the whole range from perfectly symmetric to highly asymmetric intramolecular hydrogen bonds are presented. The trajectory of the proton transfer is mapped through experimental electron density (ED) studies using high-resolution low-temperature synchrotron X-ray diffraction, data measured at the beamline BL02B1 of SPring-8, Japan. For this aim, it is crucial to obtain the precise and accurate position and displacement parameters of the hydrogen atom in the low-barrier hydrogen bond. Therefore the position of the proton in all compounds presented is supported by low-temperature neutron diffraction, data measured at the beamline KOALA of the Bragg Institute of ANSTO, Australia [3]. The response of the hydrogen atom in question to various properties, such as the experimentally derived electric field imposed by the crystallographic environment, will be discussed.

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