Tuning protons in hydrogen bonds: diffraction + temperature = chemistry?, Chick Wilson, *Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK, and ISIS Facility, CCLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK*. E-mail: C.C.Wilson@chem.gla.ac.uk

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We have been interested for several years in apparently "anomalous" behaviour of hydrogen atoms in molecular systems [1]. In particular we have been examining structural evolution, where we look for changes in a structure at a range of temperatures (or pressures), to allow us better to image, model and understand these changes. Using a combination of X-ray and neutron single crystal diffraction we have been able to identify many systems in which there is disorder of hydrogen atoms in hydrogen bonds, and have been able to characterise these successfully. In addition, we have identified a range of candidate systems where the position of a hydrogen atom in a hydrogen bond, particularly short, strong hydrogen bonds, appears to change as a function of temperature. A comprehensive multiple temperature/pressure study can allow this proton migration effect to be identified unambiguously (ideally by neutron diffraction, but also by careful X-ray diffraction) and to be followed as it evolves. In such cases, the nature of the hydrogen bond can be said to be changing as the position of the hydrogen atom changes, in essence changing the underlying chemistry of the system. Using neutron and X-ray diffraction, we will discuss examples in which the hydrogen atom migrates towards the mid-point of the hydrogen bond, and also in which the hydrogen atom moves from a position close to the "donor" atom, to a position closer to the "acceptor" atom, thus changing the nature of the hydrogen bond and thus the chemistry. In discussing these systems, we will emphasise: the added value of using both X-ray and neutron methods; the power of imaging through evolutionary Fourier maps; the caution required in using X-ray refinements in modelling subtle hydrogen atom behaviour in such cases; the vital complementary role of computation chemistry methods in understanding these effects.

[1] C C Wilson (2002). Recent Res Devel Chem Phys, 3, 119-147