Accurate and Precise Hydrogen Atom Parameters from X-ray Diffraction Data using Hirshfeld Atom Refinement

Simon Grabowsky[1], *Magdalena Woinska*[2], *Paulina Dominiak*[2], *Krzysztof Wozniak*[2], *Dylan Jayatilaka*[3]

1. Department 2 – Biology/Chemistry, The University of Bremen, Leobener Str. NW2, 28359 Bremen, Germany
2. Chemistry Department, University of Warsaw, ul. Pasteura 1, 02-093 Warsaw, Poland
3. School of Chemistry and Biochemistry, The University of Western Australia, 35 Stirling Highway, Crawley WA 6009, Australia

It is one of the most challenging problems in crystallography to accurately and precisely determine the positions and anisotropic displacement parameters for hydrogen atoms from X-ray diffraction data alone. Here we show how Hirshfeld Atom Refinement (HAR, [1]) solves this problem by using tailor-made aspherical atomic scattering factors from molecular wavefunction calculations in a regular least-squares refinement procedure.[2]

We present a statistical analysis of C-H, N-H and O-H bonds in over 80 organic compounds refined with HAR and compare to averaged bond distances determined by neutron diffraction as reference values. The results agree within a single standard deviation. The precision of determination of the mean bond distance per bond type as defined by Allen and Bruno [3] is about the same for X-ray HAR and neutron results. However, for the O-H bonds in water HAR is significantly more precise. These results were obtained for low-resolution data (cut-off 0.8 Å) at temperatures of 140 K or lower at the BLYP/cc-pVDZ level of theory, which means that the method is applicable to data from routine in-house structure determination. HAR is now embedded in the widely used software Olex2.[4]

We will also show first results of free refinements of hydrogen atoms in more unusual bonding situations. Symmetric hydrogen bonds in hydrogen maleate salts are discussed, where the hydrogen atom is in a general position.[5] Moreover, various transition metal hydrides are investigated, where the hydrogen atoms need to be located accurately from the X-ray diffraction data next to a heavy element.

References:

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