Instructions Workshop Part 1 – HAR through Olex2

In this part you will perform a Hirshfeld atom refinement (HAR) on the ammonia and the epoxide molecules. This involves refining the atom positions and the atomic anisotropic displacement parameters (ADPs) especially for the hydrogen atoms. Performing HAR is the first step of X-ray wavefunction refinement (XWR).

Preparation

1) Extract the olex2-tonto-win32.zip. Do not just double click!
2) Go into the folder olex2-tonto-win32 and double-click on the executable olex2. → The program will open and show the sucrose molecule.
3) Make a copy of the ammonia and epoxide folders. Call them ammonia_HAR and epoxide_HAR. You need to do this because the input files will be changed and overwritten during the refinements.
   - Ammonia data come from R. Boese et al., J. Phys. Chem. B 1997, 101, 5794
   - Benzene data come from Grabowsky et al., Acta Cryst. A 2008, 64, 397.

Ammonia

4) Back in the Olex2 program, go to the menu bar and open the nh3.res file from the "ammonia_HAR" folder. You will see a N-H bond and some residual density (Q) peaks. Only a third of the molecule is in the asymmetric unit.
5) You can turn your mouse wheel to make the Q peaks appear and disappear. Alternatively press ctrl-Q to see what happens. Make the Q peaks disappear.
6) Right mouse click on the nitrogen atom, select "grow" to see the full ammonia molecule.
7) By holding the right mouse button and moving the mouse you can change the zoom factor.
8) Do a spherical refinement using olex2.refine:
   a. Click on "work" in the right panel.
   b. Click on the down-arrow next to the word "Refine" to see the refinement options.
   c. As refinement program, choose "olex2.refine"; as method, choose "Gauss-Newton". These may already be the default options.
   d. Now press "Refine".
   e. Press "Refine" again.
   f. What is the R1 value that you observe?

   g. Where does the Q peak of highest residual electron density appear (the one that disappears last when you turn the mouse wheel), and what does it mean?

   h. What is the N-H bond distance? It should appear if you just hold your mouse arrow above one of the equivalent bonds. The N-H bond distance obtained by neutron diffraction is 0.989 Å.

i. Currently, by default, the nitrogen atom's displacement parameters are refined anisotropically, those of the hydrogen isotropically.
What happens if you try to refine the hydrogen displacements anisotropically, too?
In order to do that, type "anis –h" into the command line and enter. Then press "Refine" again.

What is the N-H bond length now? Did it change significantly towards the neutron result?
What happens to the R-value?

j. Try to reproduce the result with nitrogen being anisotropic and hydrogen being isotropic. Press "Model" in the upper menu bar, and then "ISOT All". A refinement will start automatically. Wait for it to finish. Then press "Model", and then "Anis All", which will only refine the nitrogen anisotropically.

9) Do an aspherical HAR using Tonto.
   a. As refinement program option, choose "Tonto" instead of olex2.refine; as method, choose "HAR".
   b. Expand the "Refinement Settings Extra" dialogue.
   c. As options for Tonto, choose "DZP" as basis set, "Restricted Hartee-Fock" as method. Have a look which other options are available for basis set and method. Use the pre-selected methods "hirshfeld" for thermal smearing and "mulliken" for the partitioning. Optimise the scale factor, but don't set the other ticks into the boxes. Change the convergence presets to "loose". This will save time.
   -The DZP basis set describes the set of functions used to model the wavefunction.
   -Hartree Fock is the simplest type of wavefunction that you can use.
   -Restricted means that the up (alpha) and down (beta) spin electrons are restricted to be in the same orbital.
   d. Start the refinement by pressing "Refine". Be patient: the refinement should not take more than a couple of minutes. Ignore the warning. Have a look into the "ammonia_HAR" folder in the meantime and observe which files are produced as the program runs. You should get new cif files, and output files such as "stdout".
   e. After the refinement has finished, in the Olex2 GUI you will have to "grow" the molecule again.
   f. How do the anisotropic hydrogen atoms look?

   g. What is the N-H bond distance now? And how big is the improvement relative to the neutron result?

   h. What is the R-value?

Epoxide

10) Repeat the same steps and answer the same questions for the epoxide molecule.
    -Try to remember what you did for ammonia!
    -Don't forget to choose the "loose" convergence options.
    -Be patient with the refinement, it can take 15 minutes. If the refinement takes too long on your computer, you can use results in the given folder "epoxide_HAR_results" to start with Part 2. However, in this case you won't be able to answer the questions.

    You will be surprised about the large R-value after HAR. This is due to different weighting schemes used.

    Open the output file "stdout" in the "epoxide_HAR" folder and have a look. Can you understand its contents? The weighted R-value Rw(F) can be found in the "structure refinement results" section.