Understanding the Teaching Subset

Purpose of this guide

This guide is written for educators with little or no experience of crystallography but with some knowledge of chemistry, who wish to make use of the CSD Teaching Subset. As the subset is built up of real data, it is important to know that experimental structures can show real, but potentially confusing features such as disorder, and that models can show imperfections or be incomplete. Neither of these reduce the usefulness of crystal structures for teaching but a basic understanding of these features and problems can help avoid confusion. This guide provides basic explanations of why hydrogen atoms may not appear in an experimental model, and what disorder is. Suggestions for how to deal with such issues when presenting crystal structures to audiences by using Mercury are given. A more comprehensive guide to structure visualization using Mercury is available here.

What are crystal structures?

Crystals are ordered materials, formed out of atoms, ions or molecules that are arranged in a regular or "periodic" way. Periodic structures have the property that in certain circumstances, they interact with light in a way that produces a pattern with a definite relationship to the structure. We call this phenomenon diffraction; it is a characteristic behaviour of waves. In the case of atoms, they are so close together that X-rays[1], which have a very short wavelength, have the right properties to produce a diffraction pattern when a crystal is irradiated with them. This means that a crystal with an unknown structure can have its structure solved, revealing the 3D arrangement of atoms, molecules and ions, which helps us to understand the underlying chemistry. The experimental technique is called *X-ray diffraction* or *X-ray crystallography*.

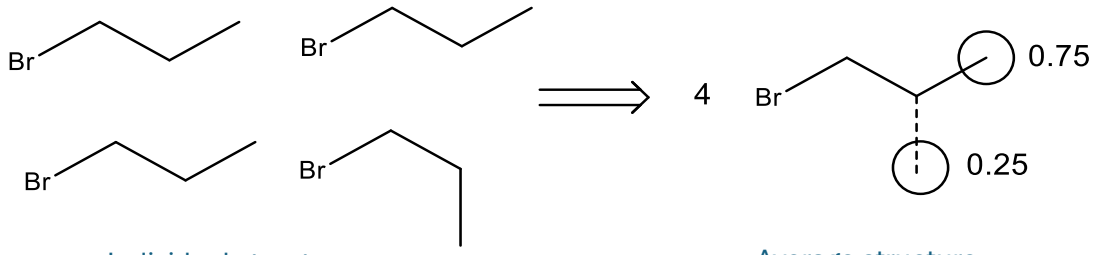
Hydrogen atoms

It is the electrons of atoms that cause X-rays to diffract. As some atoms have more electrons than others, the contribution to the diffraction pattern can vary a lot. Hydrogen atoms have only one electron and contribute relatively little to the diffraction pattern. This means that they can be hard to find. This is particularly the case for older structures which were determined when the experimental instruments (called diffractometers) were not a good as they are today. Hydrogen atoms might be omitted from the model structure if they cannot be located from the data available. Such structures appear to be missing hydrogen but it important to remember that it is just the *model*, not the actual molecules, that are missing hydrogen atoms. Fortunately, we can easily predict where the hydrogen atoms should be just based on chemical knowledge, and it is possible in most cases to add hydrogen atoms to a structural model in which they are missing using Mercury.

[1] Sometimes, neutrons and electrons are used instead of X-rays, but the experiments are more complicated and so you will see them less often.

Disorder

Although crystals show long-range order, they are not always perfect at shorter length scales. Let's say we have four molecules of the same type but that a small portion of one molecule points in a different direction to the other three molecules. We call this *disorder*. Diffraction experiments give an average structure, so if we average all four molecules, we can say that per molecule the disordered bit occupies a different region of the crystal to the rest 25% of the time; its occupancy is said to be 0.25. In the CSD, this minor part (occupancy 0.25) would still be represented in the structure.



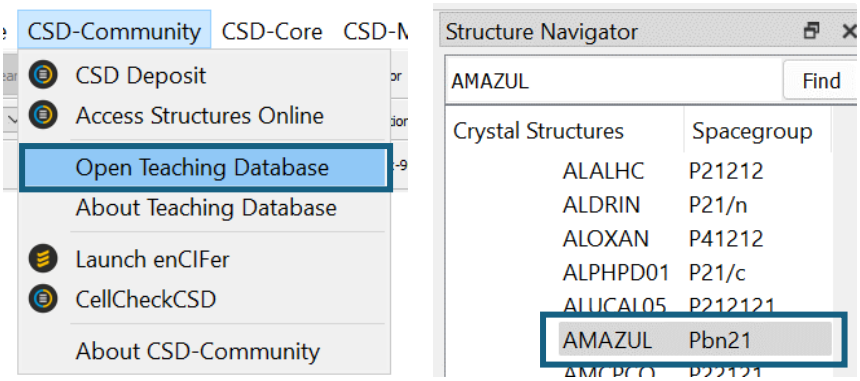
Individual structures

Average structure

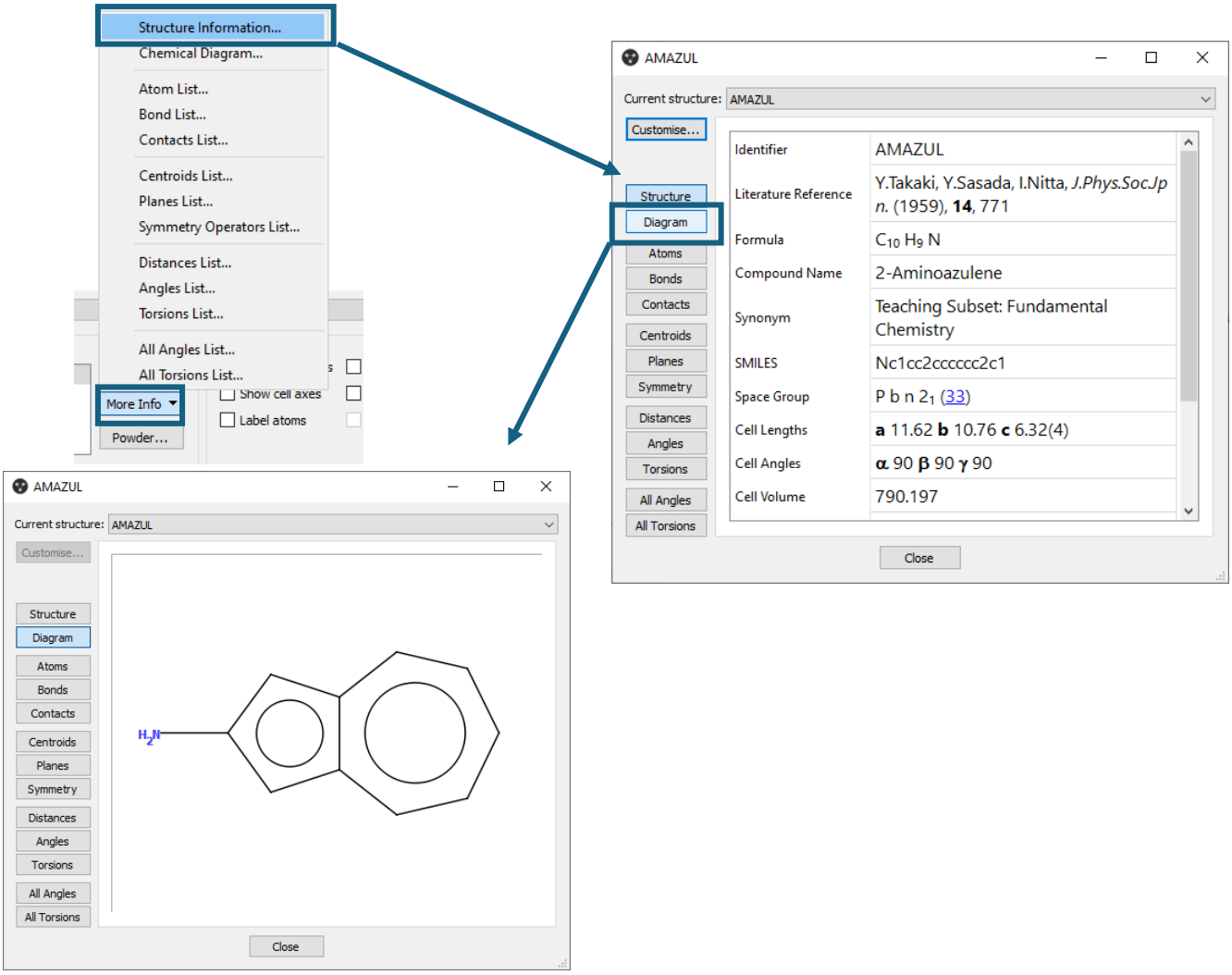
Opening a structure in Mercury

1. Open Mercury from the start menu or by clicking the desktop icon

2. Open the *Teaching Database* from the *CSD-Community* menu, and select the structure you want from the **Structure Navigator** (in this case "AMAZUL")

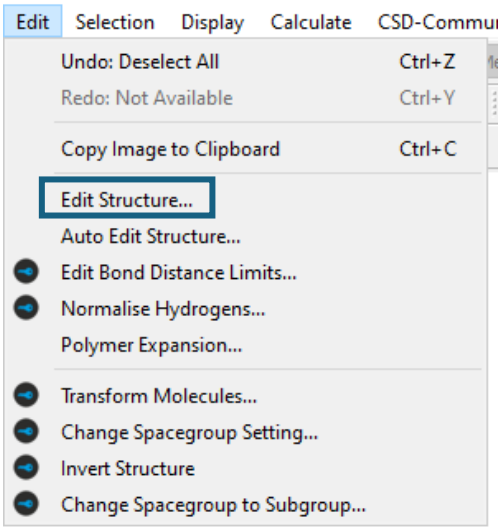


3. You can find out more about a structure by clicking *More Info* > *Structure Information*... in the **Display Options** toolbar. Click **Diagram** to see a structural diagram.

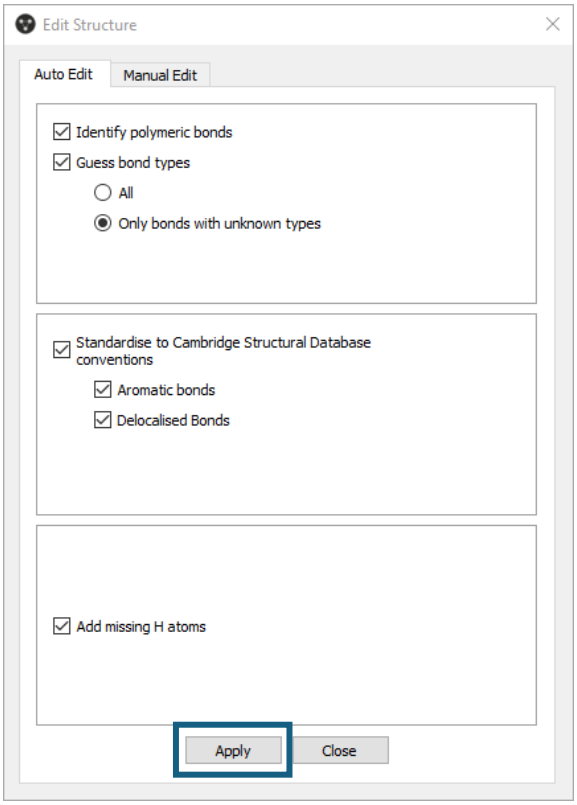


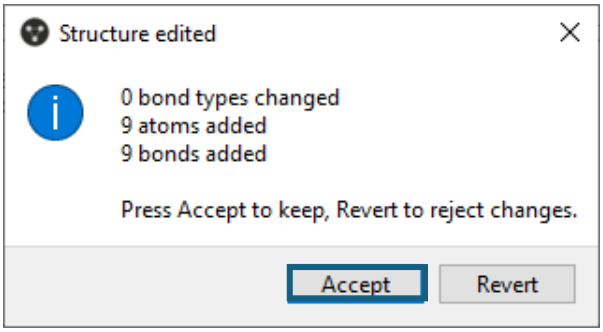
Adding hydrogen atoms in Mercury

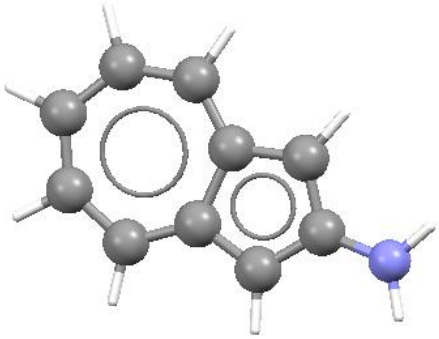
1. To Edit a structure, from the top menu, go to *Edit* > *Edit Structure*...



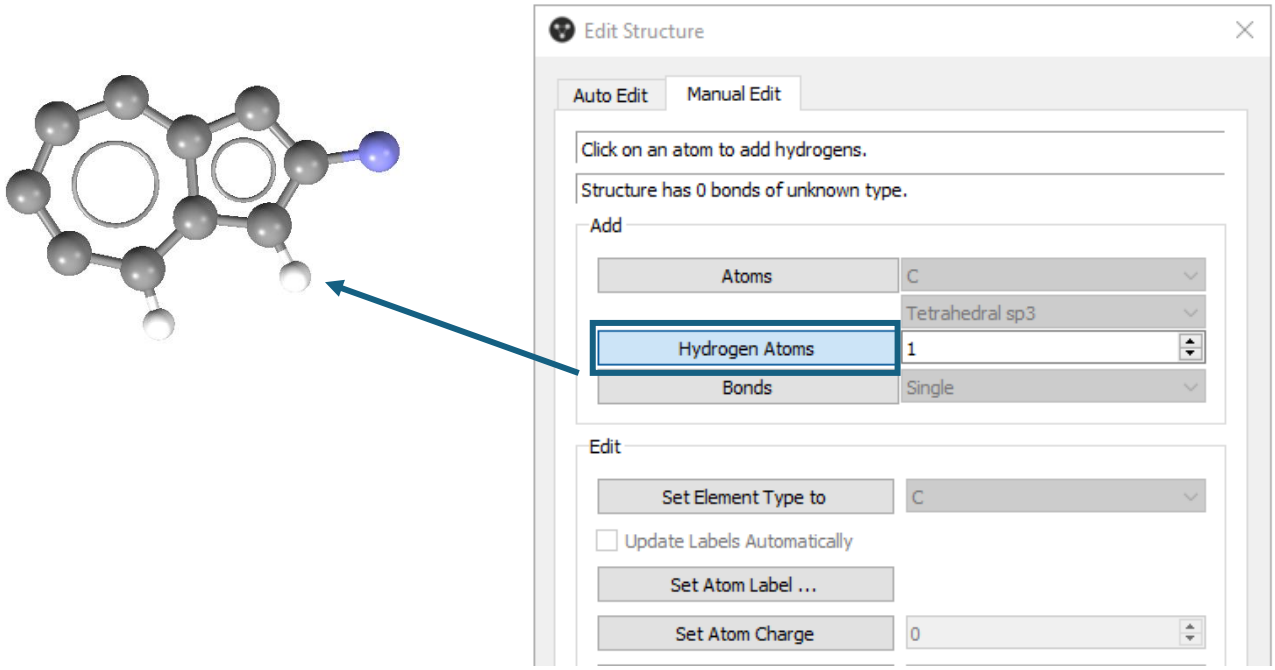
2. In most cases, Auto Edit can add missing hydrogens and fix other issues. In the **Auto Edit** tab of the **Edit Structure** window, leave all the default options ticked and press **Apply**. A dialogue will appear reporting the changes that have been made. Confirm that these are as expected, and press **Accept** to keep the changes. Otherwise, revert and edit manually as in step 3.





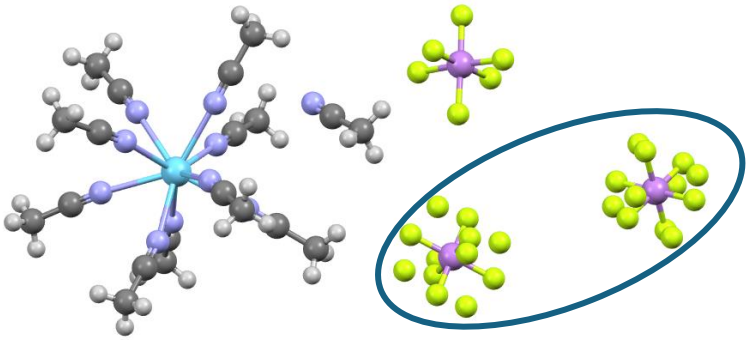


3. To edit manually, in the **Edit** window, in the *Add* section of the **Manual Edit** tab click **Hydrogen Atoms**. Ensure that the correct number of hydrogen atoms to add is selected from the drop-down options next to the button, then click on an atom to add the hydrogen.



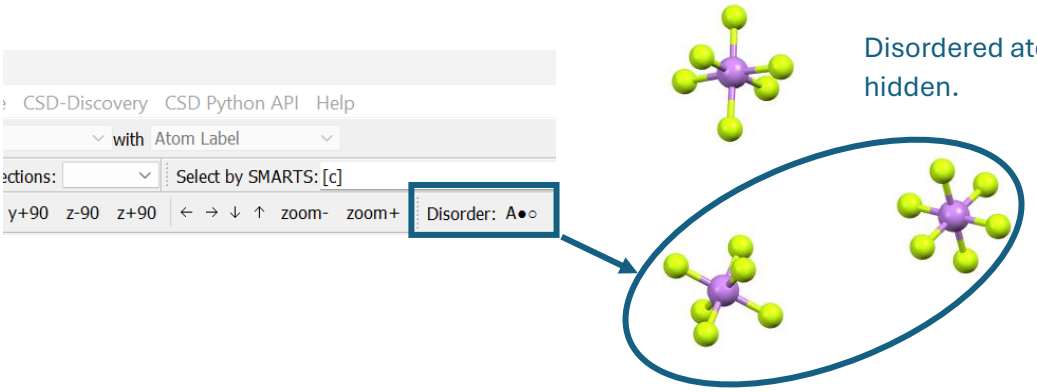
Hiding disorder in Mercury

1. If a structure is disordered, there will usually be disconnected atoms in the vicinity of a molecule or molecular fragment.



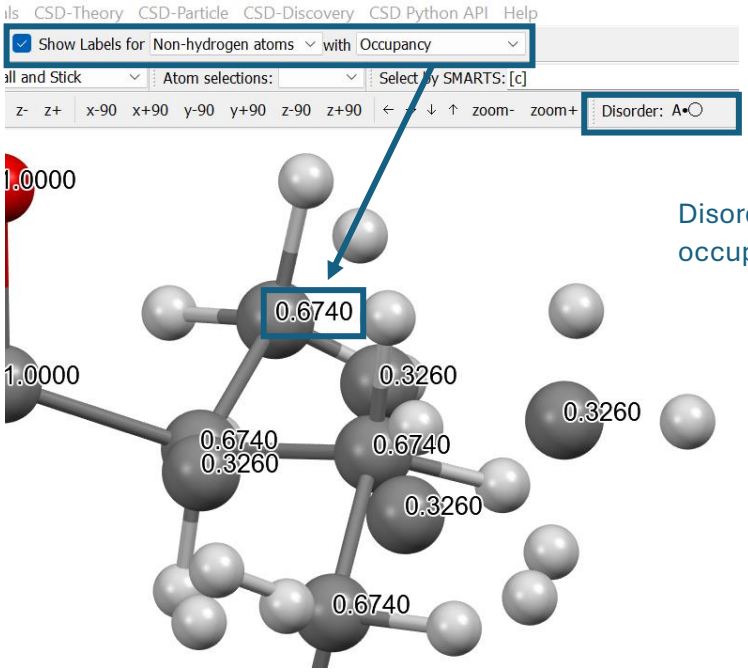
Disordered atoms in AsF_6^- ions (from CSD entry GIWVUD)

2. In the *Disorder* section of the top toolbar, click the two dots to toggle the display of the disorder on and off.



Disordered atoms are now hidden.

3. If you see that one of the two disorder dots is much bigger than the other, it means that one disorder group has much higher occupancy than the other (>0.6). You can label the atoms by occupancy if you want to: tick *Show Labels for* **All atoms** *with* **Occupancy**.



Disordered atoms are labelled with the occupancies in CSD entry SUGXAU.