

Tutorial: Crystal structure refinement of oxalic acid dihydrate using Jana2006

The aim of this tutorial is to use Jana2006 to locate hydrogen in oxalic acid dihydrate and refine the crystal structure. By no means is it intended to provide a general recipe for structure refinement nor is it claimed the suggested route here is the best possible and only one to take. It serves as a mere example how it can be done. Oxalic acid dihydrate crystallises in the monoclinic space group $P2_1/n$ with lattice parameters $a = 6.1143 \text{ \AA}$, $b = 3.5870 \text{ \AA}$, $c = 12.0109 \text{ \AA}$ and $\beta = 106.127^\circ$. The chemical composition is $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$.

Installing the software

Download Jana2006 from <http://www-xray.fzu.cz/jana/jana.html> and install it (don't forget to set the environment variables as described on the website - you need administrator rights on your computer in order to do this).

Download the structure visualisation program VESTA from http://www.geocities.jp/kmo_mma/crystal/en/vesta.html and install it.

Launch Jana2006 by double-clicking on the icon.

In the Jana2006 menubar, select **Tools**→**Programs**.

- In the dialog box that appears, set both *Graphic viewer* and *3d visualisation of maps* to the full path name of VESTA (e.g. C:\Program Files\VESTA\VESTA.exe). Click to exit.

Preparing the data

The first thing we need to do is to prepare the SXD data. The crystal has been measured at five different omega settings (orientations) for about 1 hour at each setting. The temperature was close to 300 K. The raw data have been indexed and integrated using SXD2001. However, we still need to calculate the absorption correction and convert the files to GSAS histograms. To perform the absorption correction, start SXD2001, load the "SXDII.instr" file and click (Fig. 1).

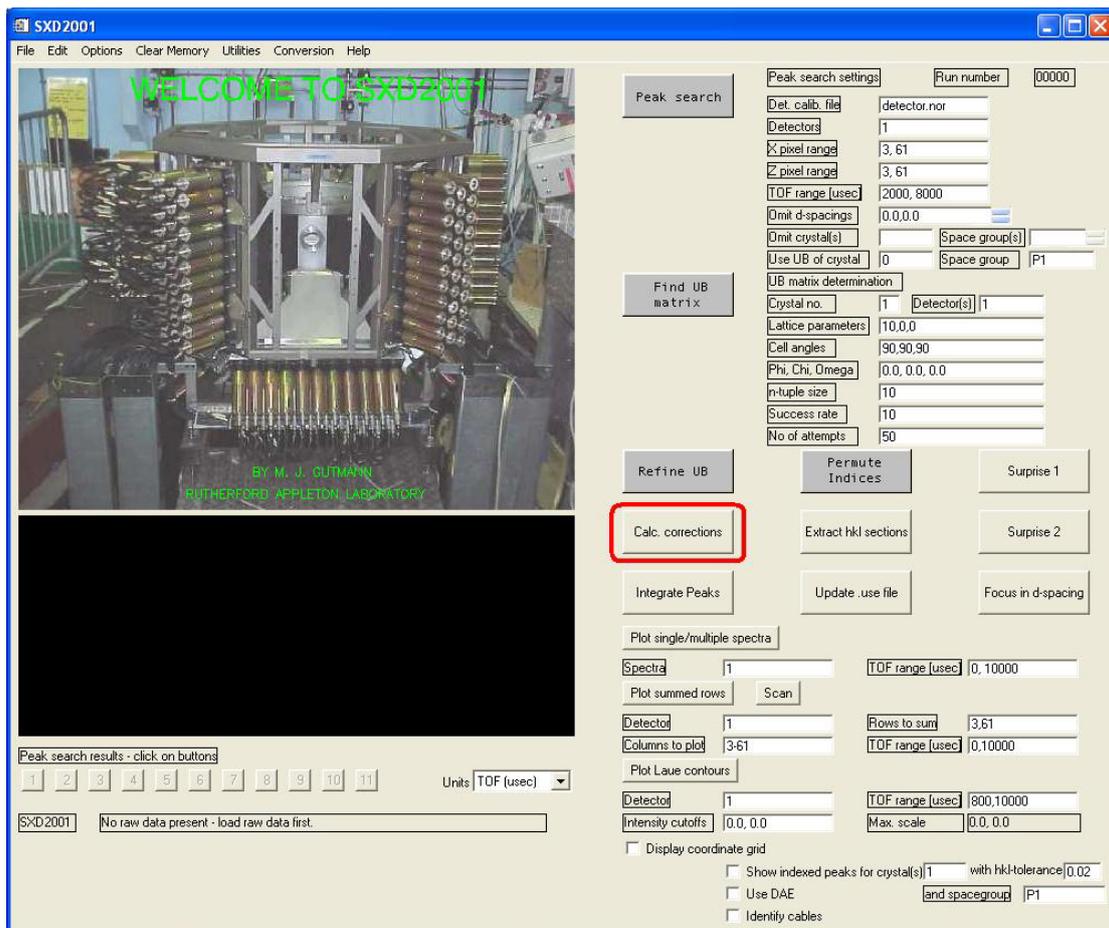


Figure 1: SXD2001 main GUI. The location of the **Calc. corrections** button is indicated.

A GUI similar to the one shown in Figure 2 should appear. The quantities to be specified by the user are the scattering and absorption cross section *per atom* and the number density in units of \AA^{-3} . Information about the cross sections can be found on the internet at <http://www.ncnr.nist.gov/resources/n-lengths/>. They are summarised in Table I.

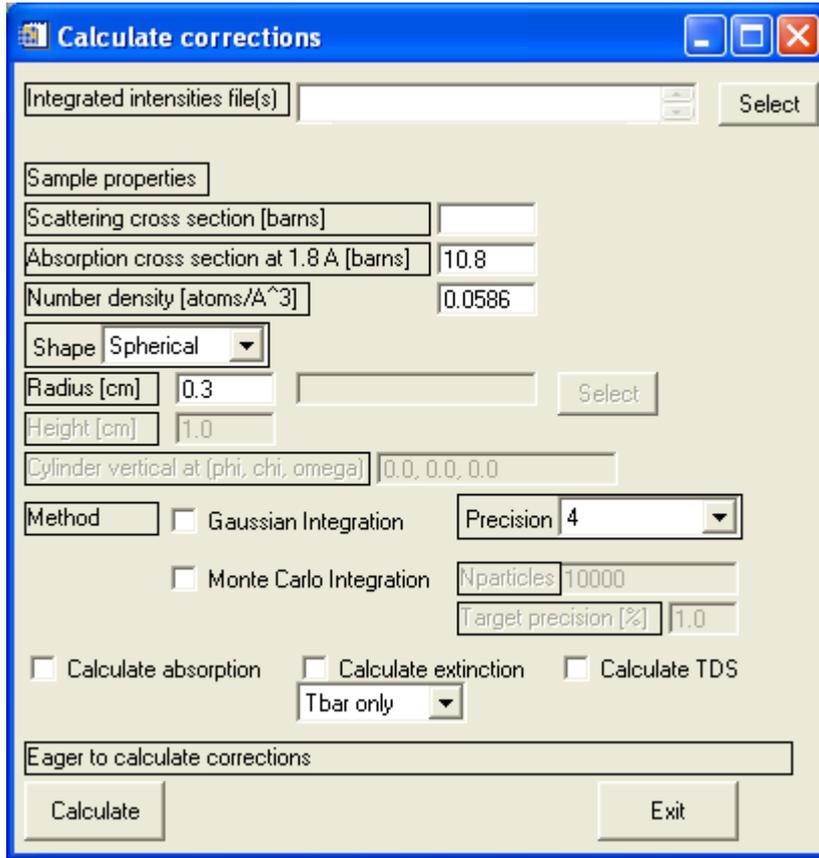


Figure 2: Initial appearance of the calculate corrections GUI.

Table I: Scattering and absorption cross sections of C, O and H (values taken from <http://www.ncnr.nist.gov/resources/n-lengths/>).

Element	Scattering cross section [barns]	Absorption cross section at 1.8 Å [barns]
H	82.02	0.3326
C	5.551	0.0035
O	4.232	0.00019

As can be seen from Table I, the scattering cross section, which is the sum of the coherent and incoherent cross sections is very large for hydrogen. This is mainly due to the large incoherent cross section of hydrogen. This large cross section of hydrogen is often causing a large slowly varying background in the diffraction pattern. A way around this would be to replace deuterium for hydrogen. The scattering cross section is nearly independent of the energy, while the absorption cross section varies linearly with wavelength. Thus, this value is usually quoted for neutrons having a wavelength of 1.8 Å corresponding to a neutron speed of 2200 m/s or a thermal energy of 293 K.

As mentioned in the introduction, the chemical composition of oxalic acid dihydrate is $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$. The scattering and absorption cross section per atom are calculated as follows:

$$\sigma_{abs} = \frac{1}{n} \sum_{i=1}^n \sigma_{abs}^i \quad (1)$$

$$\sigma_{scat} = \frac{1}{n} \sum_{i=1}^n \sigma_{scat}^i \quad (2)$$

where n is the number of atoms in the formula and σ_{abs}^i , σ_{scat}^i are the absorption and scattering cross sections, respectively, for atom i in the chemical formula.

Using the values in Table I compute the absorption and scattering cross section and enter them in the corresponding field in the **Calc. corrections** GUI. If you need a calculator, Window XP usually supplies one in the **Start**→**All programs**→**Accessories** menu.

Next, we calculate the number density. This number is defined as the number of atoms divided by the unit cell volume. This should be straightforward...(Hint: there are $Z = 2$ formula units per unit cell). Insert the result in the corresponding text field in the **Calc. corrections** GUI. The number density can also be derived from the mass density. This is left as an exercise to the reader (Hint: Use Avogadro's number).

Select the intensity files "sxd17210_1sb.int", "sxd17211_1sb.int", "sxd17212_1sb.int", "sxd17213_1sb.int" and "sxd17214_1sb.int" using the **Browse** button in the **Calc. corrections** GUI (Fig. 3). These files contain the results of the peak integration for the runs sxd17210–sxd17214 corresponding to the runs for the present compound. For convenience, these files are located on the desktop.

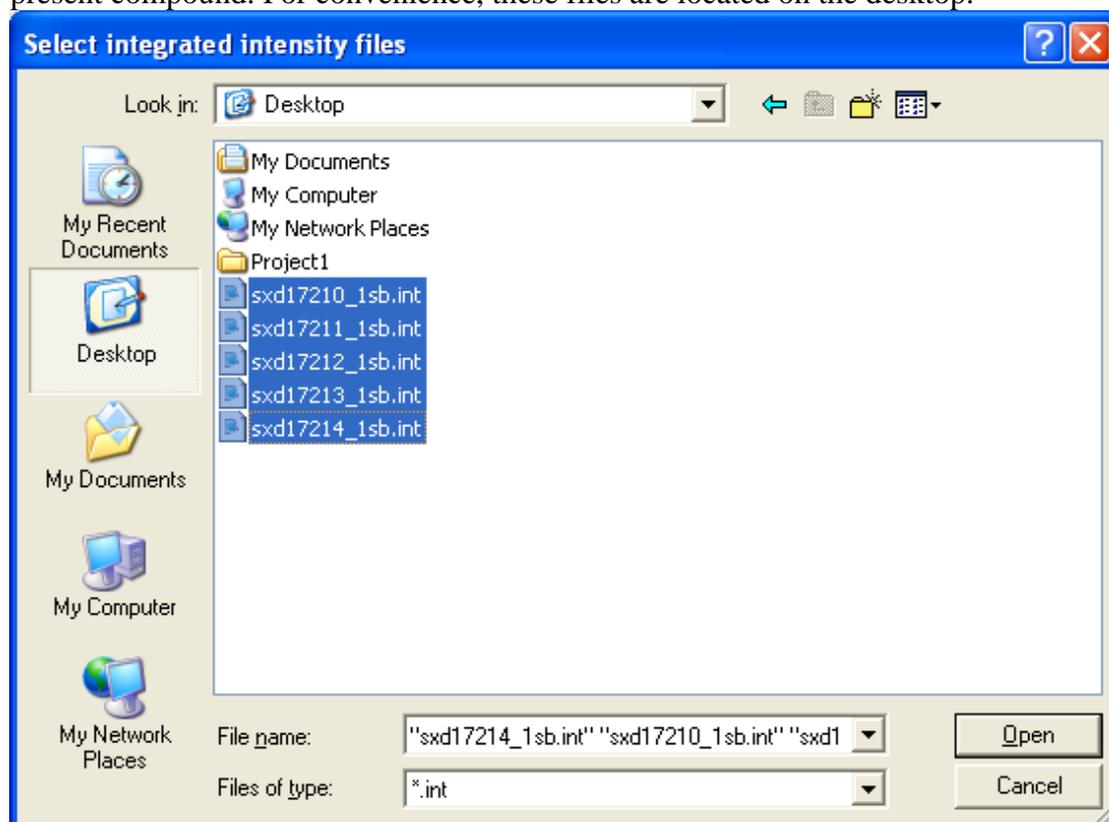


Figure 3: Select the reflection files for use in Jana2006.

Finally, we need to know the sample shape. In our case, a cylindrical shape will be good enough. Specify a radius of 0.2 cm and a height of 0.4 cm. Select 'Gaussian Integration' with a precision of 32 points. The latter parameter corresponds to the

number of grid points used in the numerical integration – the higher, the more precise but also the slower the calculation will be.

Select *Calculate absorption* and *Calculate extinction* but leave the selection at *Tbar only*. This is the absorption weighted path length through the crystal and is needed for the Becker-Coppens type extinction correction (discussed later). The GUI should now appear similar to the one shown in Figure 4. Note, that the absorption and scattering cross section as well as the number density have been omitted and are left to the user to be calculated as an exercise. They are needed, so don't omit them!

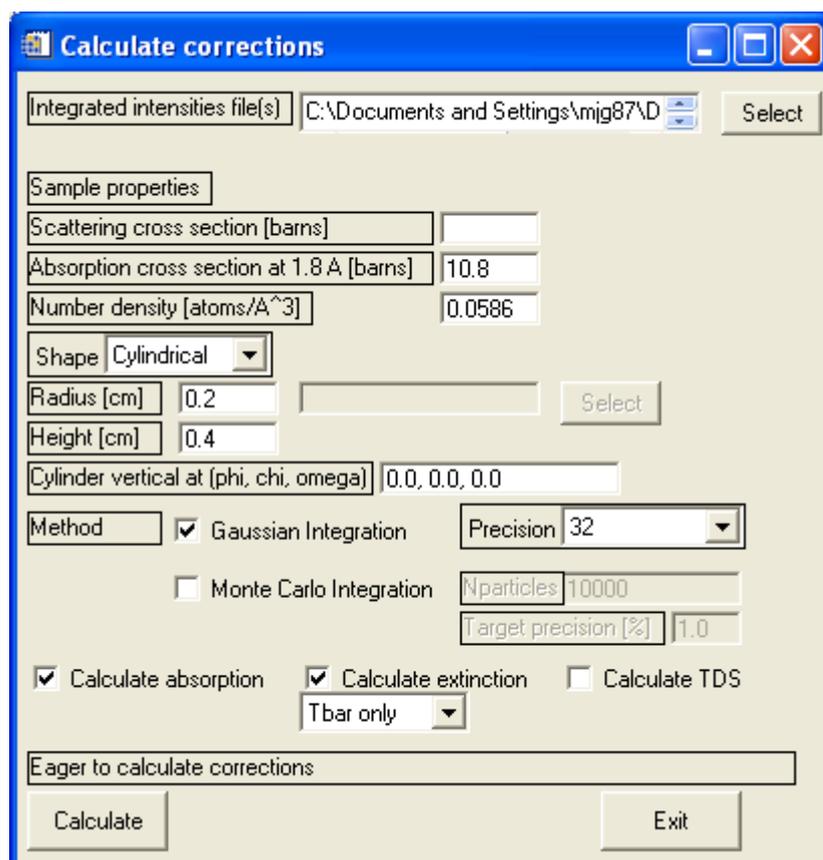


Figure 4: Specify the scattering and absorption cross section as well as the number density.

To calculate the corrections click **Calculate** and wait until the text window just above says that it is done. Then exit.

The reflection files are now ready for importing into Jana2006. In the SXD2001 menubar, select **File**→**Generate Jana2006 reflection file**.

- A dialog box pops up asking for the reflection files. Point the directory path to your desktop and select simultaneously sxd17210_1sb.int – sxd17214_1sb.int as shown in Figure 5. Click **Open**.
- In the dialog box that appears, leave all the options as they are (make sure to retain the default selection of *One histogram per crystal*) and click **OK** to finish the export. Set the exported filename to “Oxalic_acid.int”.

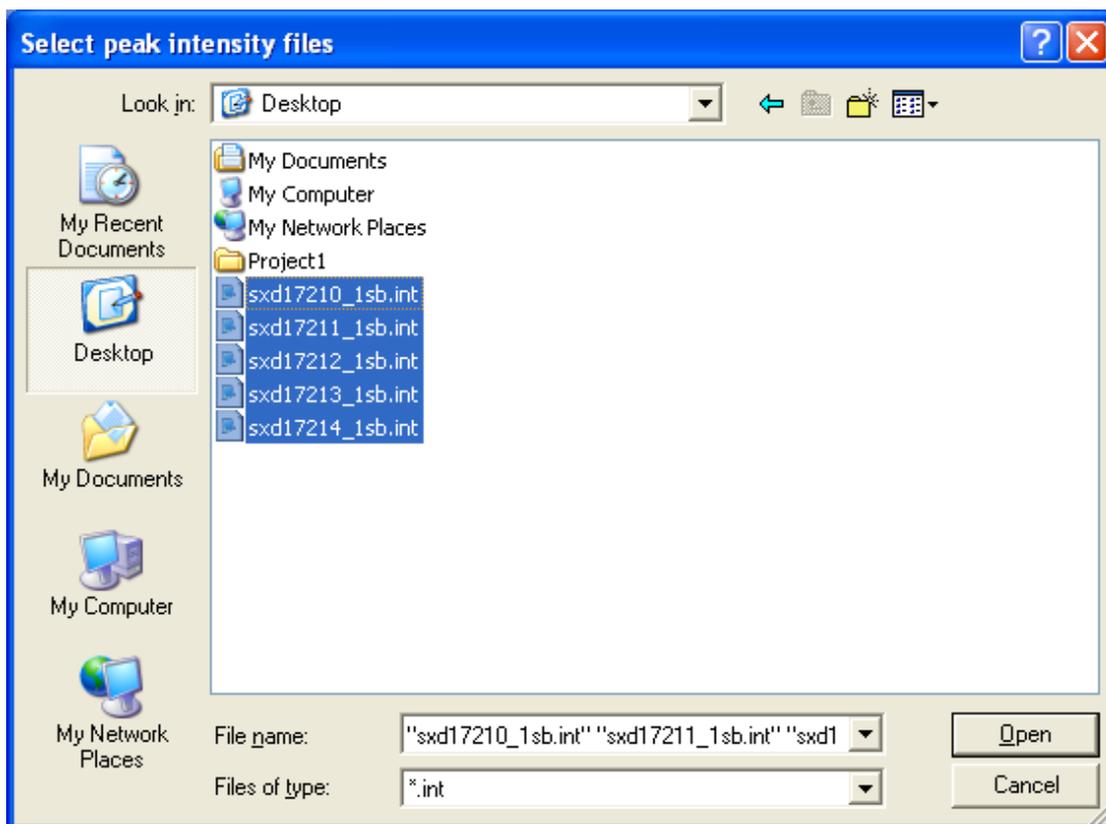


Figure 5: Select the reflection files.

Setting up the refinement

Create a new folder in My Documents (or wherever you wish to work in the Windows directory structure) called (e.g.) “Oxalic acid”. Copy the SXD data file “Oxalic_acid.int” into this directory. This is the only file you need to start with – it contains all the integrated and absorption-corrected data, as well as the unit cell information.

In the Jana2006 menubar, select **File**→**Structure**→**New**.

- In the dialog box that appears, select the directory you just created and enter the filename “Oxalic_acid”. Click on **Next** to continue.
- In the next dialog box, select *Single crystal known diffractometer formats*. Click on **Next** to continue.
- In the next dialog box, select *ISIS SXD* and set *File name* to “Oxalic_acid.int”. Click on **Next** to continue.
- In the next dialog box, make sure that it has read the lattice parameters correctly (see above). Click on **Next** to continue.
- In the next dialog boxes, click on **Next** and **OK** to get through the next couple of dialog boxes (note that the program should have read 1320 reflections), then click on **Finish** to start pre-processing the data.
- In the next dialog boxes, click on **OK** and **Yes** until you get to the symmetry dialog box, then set *Space group* to “P21/n” and click on **Complete the set**. In the dialog box that appears, select the option “P 1 2₁/n 1” (*b*-axis unique, which is the standard setting) and click on **OK** then **Yes**. Click on **Next** to continue.

- In the next dialog box, click on **OK**, then select *Use non-averaged data* (you cannot average the data because you will need to perform a variable-wavelength absorption correction). Click on **Next** to continue.
- In the next dialog box, click on **Finish** to complete data pre-treatment.
- A dialog box now appears that concerns automated structure solution. You do not need to perform this task, so click on **Esc** to exit the last dialog box and return to the Jana2006 desktop.

On the Jana2006 desktop, double-click on icon **EditM50**.

- In the **Composition** tab of the dialog box that appears, set *Formula* to “C2 O6 H6” and *Formula units* to “2”. Click on **Calculate density** to check that it is reasonable (should be 1.6083 g cm⁻³). Click on **OK** then **Yes** to return to the Jana2006 desktop.

Inserting atoms

The (relatively) heavy carbon and oxygen atoms have already been found using X-ray diffraction, and are listed in Table 2.

Table 2: Positions of carbon and oxygen

Atom	x	y	z
C(1)	-0.045	0.054	0.052
O(1)	0.084	-0.059	0.149
O(2)	-0.220	0.231	0.037
O(3)	-0.049	0.112	0.319

In the Jana2006 menubar, select **Parameters**→**Atoms**→**New**. Click on **OK** to proceed by entering the atomic positions from the keyboard.

- In the dialog box that appears, set *Type new atoms coordinates* to “-0.045 0.054 0.052” and hit the “tab” key to move those numbers across to the list on the right. Click on **Use typed in coordinates** then **Include selected peak** to proceed.
- In the next dialog box, set *Name of atom* to “C1” and *Atomic type* to “C”. Click on **OK** to return to the previous dialog box, where you can enter another atom.
- Repeat the last two steps for all atoms in the Table 2, giving them suitable names and atom types.
- When you have finished entering all the atoms and returned to the first dialog box, just click on **OK** without having entered any coordinates in order to exit. Click on **Yes** to enter the atoms and set up the initial structure.

Check that the initial structure looks reasonable

In the Jana2006 menubar, select **Tools**→**Graphic**→**Run viewer** to launch VESTA.

In the VESTA menubar, select **Edit**→**Bonds**. In the dialog box that appears, set *Search mode* to “Search atoms bonded to A1”, set *A1* to “C” and click **Add**. Click **OK** to draw the bonds.

You should see sensible-looking C-C and C-O bonds. Assuming that all is well, exit VESTA (In the VESTA menubar, select **File**→**Exit** and click .)

Initial refinement

We are now ready to start some initial refinements.

On the Jana2006 desktop, Right-click on the icon **Refine**.

- In the dialog box that appears, go to the **Select/Listing** tab. Untick *Use unobserved reflections* and set *Unobserved reflections* to $I < 2 * \text{sig}(I)$. Click on to proceed.
- Click on to start the refinement.

R_w(all) should go down to ~43 %.

It is a good idea to look at the structure again in VESTA again to check that nothing unreasonable happened, then return to Jana2006.

Finding the hydrogens

On the Jana2006 desktop, Right-click on the icon **Fourier**.

- In the dialog box that appears, go to the **Basic** tab. Select *Map type* = “F(obs)-F(calc) - difference Fourier”. Click and then to launch the calculation, then to open the listing (this option disappears after 10 seconds – if you weren't quick enough, go to the Jana2006 menubar and select **Edit/view**→**View of Fourier**.)

Scroll to the bottom of the Fourier output listing, and you should see that there are 3 strong negative peaks. These should correspond to your hydrogen atoms, since H is a negative neutron scatterer.

Write down the fractional coordinates (x, y and z values) of those 3 peaks, and close the window.

[NB: when Jana2006 is updated, it should be possible to visualise these peaks in VESTA by selecting the *Include peaks from Fourier calculation* option, but for the moment this does not work for negative peaks.]

In the Jana2006 menubar, select **Parameters**→**Atoms**→**New**.

- In the dialog box that appears, select *Coordinates from keyboard* and enter the fractional coordinates of the 3 hydrogens, labelling as H1, H2 and H3 with atoms type H (in the same way that you entered the C and O atoms above). [NB: when Jana2006 is updated, it should be possible to use the *Coordinates from last Fourier option*, removing the need to write them down and type them in again, but for the moment this does not work for negative peaks]

Look at the structure again in VESTA to check that these H positions are reasonable. (NB: do not select the *include peaks from Fourier calculation* option, as this will only include the positive ones).

You should see that one of the H atoms is bonded to an O of the oxalic acid molecule, completing the acid; while the other two are bonded to an isolated O to make a water molecule.

Assuming that this is the case, exit VESTA to return to the Jana2006 desktop.

You can now re-refine the structure with the H atoms included.

On the Jana2006 desktop, double-click on icon **Refine**.

$R_w(\text{all})$ should go down to ~26 %.

Extinction correction

A very important correction in neutron single-crystal diffraction is extinction. Compared to X-ray diffraction, crystals for neutron diffraction are quite large. Even in the absence of absorption effects, extinction often still is important. Note that there are different models available to describe extinction, and it is not necessarily clear which model should be used (one might have to try different models). In our case we will use a “Type I” Lorentzian distribution model.

In the Jana2006 menubar, select **Parameters**→**Extinction**.

- In the dialog box that appears, select *Isotropic*, *Type 1* and *Lorentzian*. Set *Radius* to “0.3” cm.
- Although extinction has been “turned on”, it is still set to zero so will have no effect unless it is refined. Make sure the box is ticked to refine the absorption parameter, then click on to return to the Jana2006 desktop.

On the Jana2006 desktop, double-click on icon **Refine**.

$R_w(\text{all})$ should go down to ~12 %.

Finalising the refinement

As a final step, we would like to change the atomic displacement parameters (often loosely referred to as “thermal parameters”) from isotropic spheres to anisotropic ellipsoids.

In the Jana2006 menubar, select **Parameters**→**Atoms**→**Edit/define atoms**.

- In the dialog box that appears, select “harmonic” ADP’s for Atom #1. (Note that “Anharmonic” ADP’s require more data than you have available in this case.)
- Change the atom number to “2” and set it to “harmonic” ADP’s as well.
- Continue until all 7 atoms are “harmonic”, then click , and to return to the Jana2006 desktop.

On the Jana2006 desktop, double-click on icon **Refine**.

$R_w(\text{all})$ should go down to below 9 %.

Extracting the results for publication

You have now taken the refinement as far as it will go using the available data. It is time to extract the results into a standard crystallographic information file (CIF) for publication, and to produce some pretty pictures to go with it.

In the Jana2006 menubar, select **File**→**CIF Utilities**→**Make CIF file** and click on **OK** to create the file “Oxalic_acid.cif” and return to the Jana2006 desktop.

In the Jana2006 menubar, select **Tools**→**Graphic**→**Run viewer** to launch VESTA.

In the VESTA menubar, select **Edit**→**Bonds**. In the dialog box that appears, set *Search mode* to “Search atoms bonded to A1”, set *A1* to “C” and click **Add**, then set *A1* to “O” and click **Add**. Click **OK** to draw the bonds and return to the VESTA desktop.

You should see sensible-looking C–C, C–O and O–H bonds forming the oxalic acid and water molecules. Note that the H on oxalic acid is hydrogen-bonded to the O on the water molecule.

On the VESTA desktop, click on **Properties** and go to the **Atoms** tab of the dialog box that appears. Select *Show as thermal ellipsoids* and tick *Hide nonbonding atoms*, then click **OK** to update the picture and return to the VESTA desktop. Note that the ADP's look quite reasonable in terms of thermal motion perpendicular to covalent bonds.

In the VESTA menubar, select **Boundary**. In the dialog box that appears, set $x(\min)$ to “-0.1”, $x(\max)$ to “1.1”, $y(\min)$ to “-0.1”, $y(\max)$ to “1.1”, $z(\min)$ to “-0.15” and $z(\max)$ to “1.15”. Click **OK** to draw the expanded cell and return to the VESTA desktop.

You should now have a picture that looks something like Fig.6. You can save this file, print out the picture and/or export it to various formats as you like.

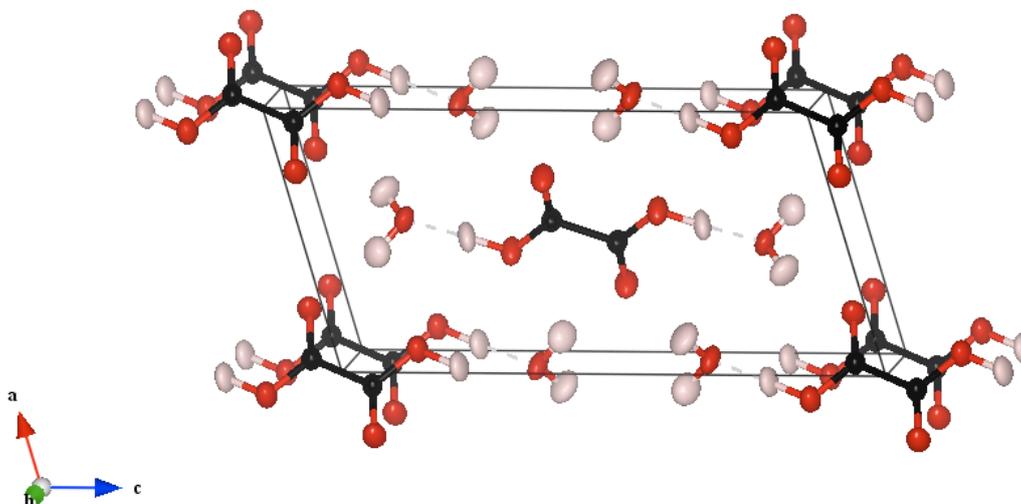


Figure 6: The final structure of oxalic acid dehydrate.