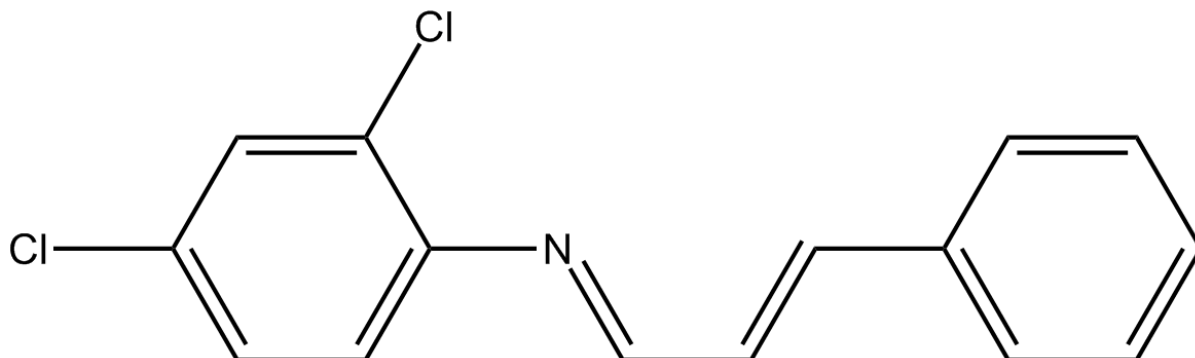


Crystallographic riddle

Known information:

The sample was ground and placed into the 0.3mm borosilicate glass capillary which was measured at room temperature in transmission mode on the PANanalytical Empyrean powder diffractometer from 4° to 80° 2Theta with CuK $\alpha_{1,2}$ radiation ($\lambda = 1.54184 \text{ \AA}$, focusing mirror, step size was 0.013° 2Theta).



Open Fox.exe in the working folder of this example

1. Find the unit cell (indexing)

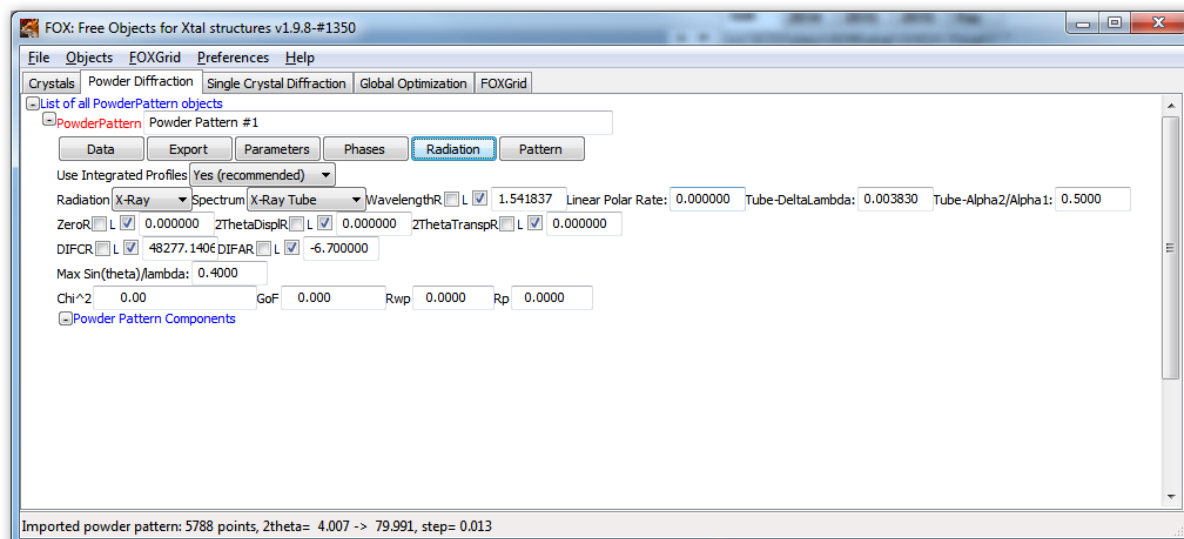
Menu->Objects->New powder pattern

[In the Powder diffraction tab]

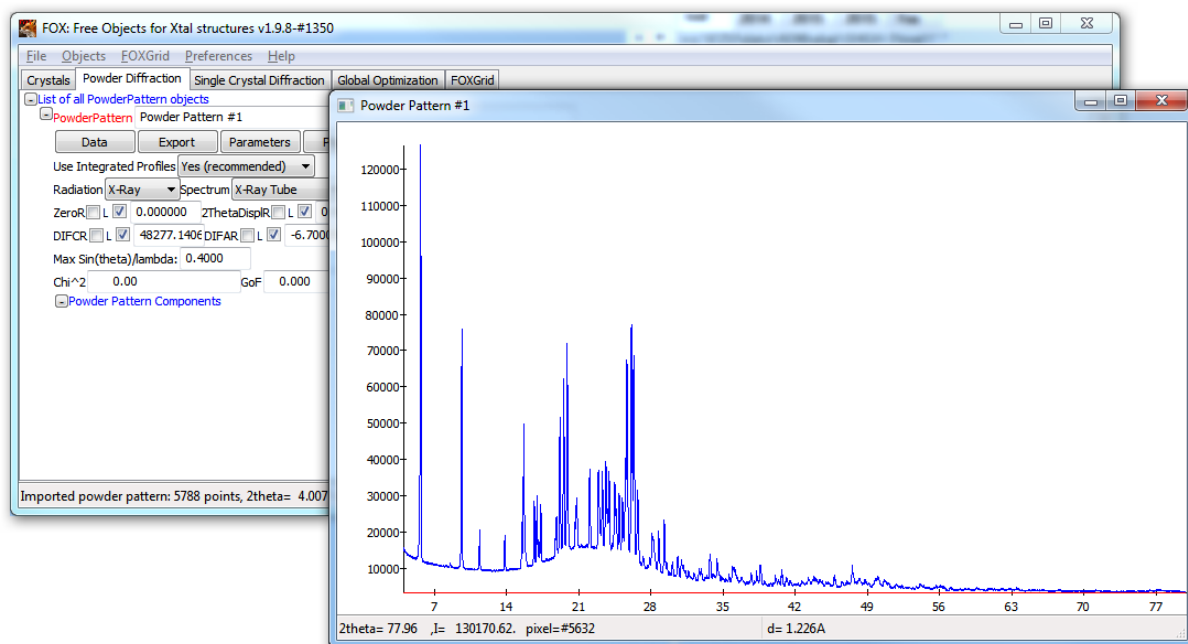
Click Data->Import 2Theta-Obs pattern

Select shgh-3.xy; Open

Click Radiation->X-ray tube CuKa12



Click Pattern->Show graph

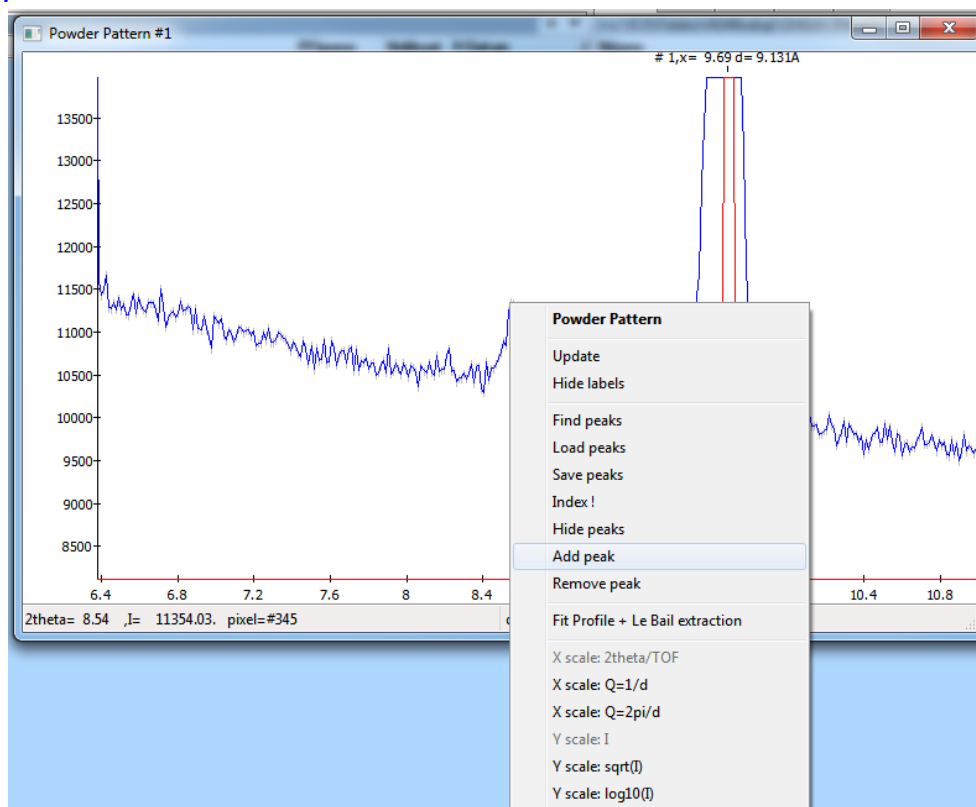


[In the Powder pattern window]

right-click->Find peaks

Enlarge by mouse regions in the powder pattern and check positions of reflections found by Fox.

In the case of a wrongly placed reflection, **right-click** on the reflection and select **remove peak**. The peak will disappear. In the case of missing reflection, add it by **right-clicking** to its position in the pattern and select **add peak**.



Find reflection at 8.55° 2Theta and add it.

Start indexing

Right-click on the pattern and select Index!

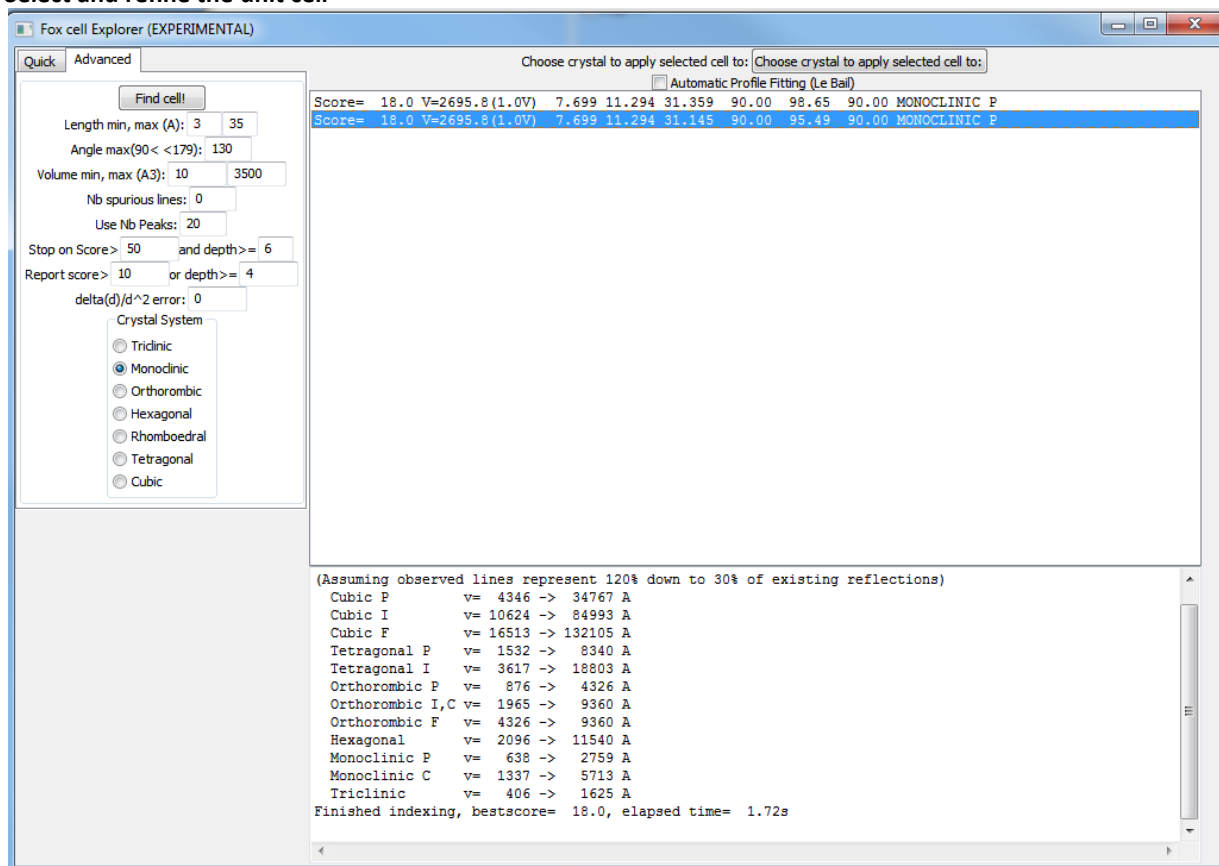
Go to Advanced and set max. length to 35 and max. volume to 3500.

Select orthorombic and click Find cell!

Select monoclinic and click Find cell!

[Optional - This will take several minutes, e.g. 10 minutes!]: Select triclinic and click Find cell!

Select and refine the unit cell



[In the cell explorer]

Select one of the unit cell.

There are probably two monoclinic unit cells with the same volume and differ only in angle and one length. They are probably convertible to each other, so, it does not matter which you select. But select the one which is closer to this 7.7 11.29 3.15 90 95.5 90. It will be better to have the same unit cell as it is described in this example.

Check Automatic profile fitting (Le Bail) at the top of the window; YES; OK

This will perform automatic profile fitting. This will take some time.

[In the powder pattern window]

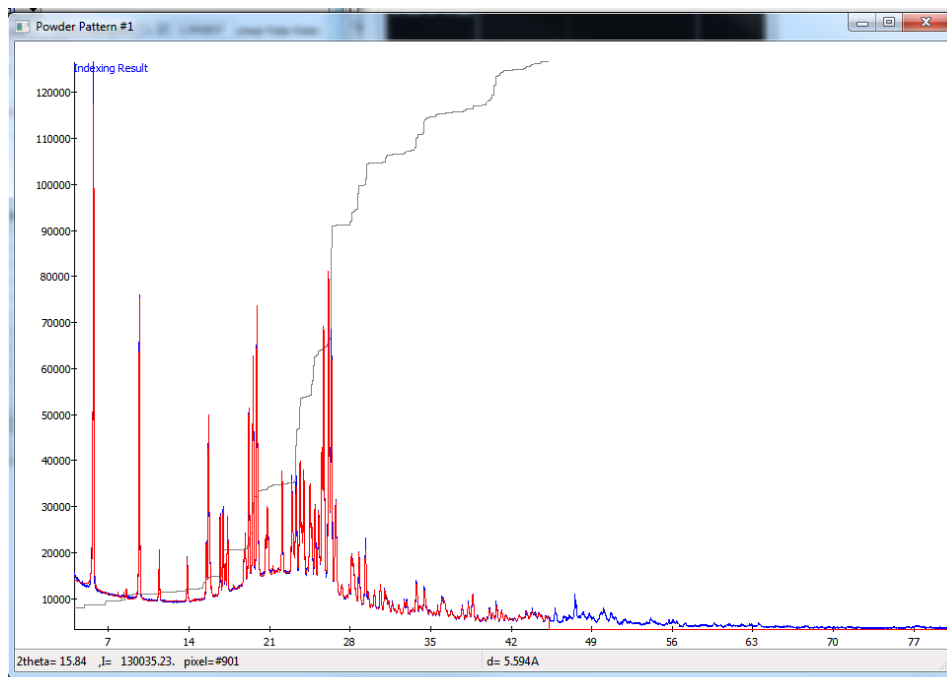
Make the picture more synoptical

Right-click -> Hide labels

Right-click -> Hide peaks

Check if all measured peaks are explained. If yes, close the cell explorer window.

You found the unit cell!:)



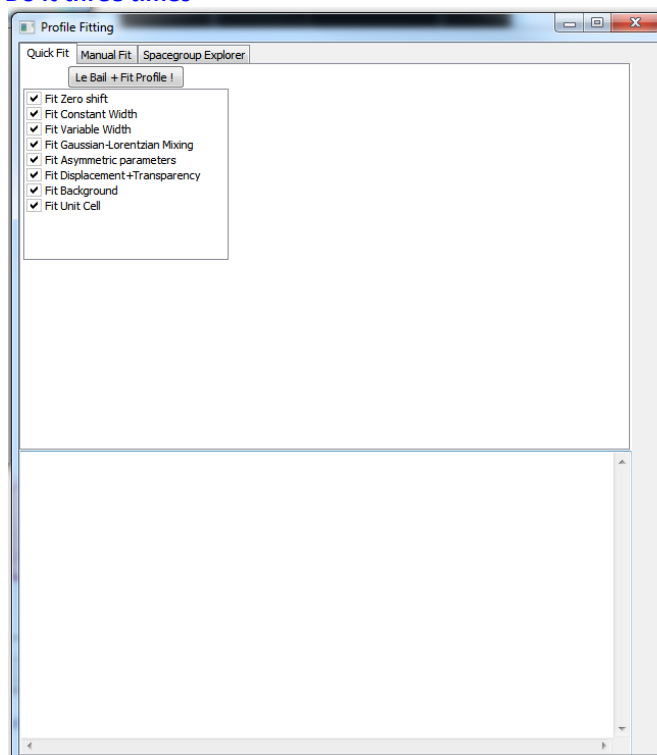
2. Find space group

[In the powder pattern window]

Right-click-> Fit profile + Le Bail extraction

Perform Le Bail extraction by Le Bail + Fit Profile button. Wait, it takes time...

Do it three times



Go to the Space group explorer

Click on **Try all possible spacegroups - Le Bail + Least Squares (SLOW)**.

This will take some time. If you have a slow computer, perform the faster version. In this case, the result will be the same.

The result is a list of best solutions which looks like this:

*Rwp= 4.24% GoF= 26.46: (extinct refls=14)P 1 a 1
Rwp= 4.24% GoF= 26.46: (extinct refls=14)P 1 2/a 1
Rwp= 4.30% GoF= 27.17: (extinct refls=16)P 1 21/a 1
Rwp= 4.40% GoF= 29.03: (extinct refls= 0)P 1 2 1
Rwp= 4.40% GoF= 29.03: (extinct refls= 0)P 1 m 1
Rwp= 4.40% GoF= 29.03: (extinct refls= 0)P 1 2/m 1
Rwp= 4.46% GoF= 29.80: (extinct refls= 2)P 1 21 1
Rwp= 4.46% GoF= 29.80: (extinct refls= 2)P 1 21/m 1
Rwp= 4.40% GoF= 32.94: (extinct refls= 0)P 1
Rwp= 4.40% GoF= 32.94: (extinct refls= 0)P -1*

The P21/a has the highest number of extinct reflections, and the Rwp is almost the same as the first solution Pa. This indicates that the correct space group is P21/a rather than Pa

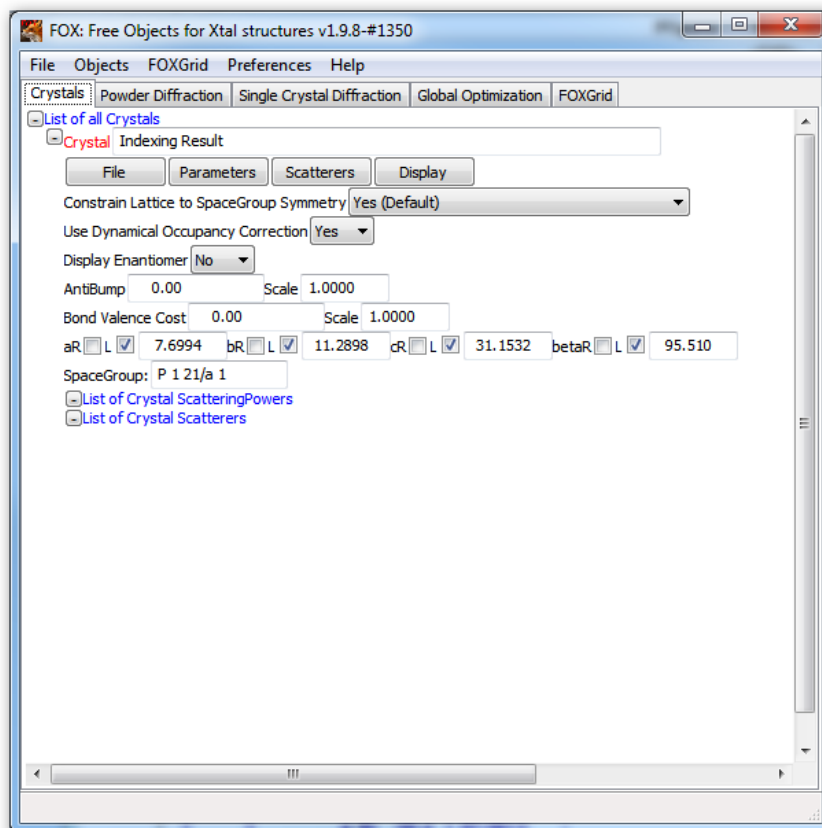
Close Profile fitting window

[In the FOX main window]

Go to Crystal tab. You can see there the new crystal with the found unit cell, which you refined.

Set the space group to P21/a.

Save it by Menu->File->Save as 01.xml.gz



3. Define molecular model

The volume of the unit cell is approximately $2700 \text{ \AA}^3$. The volume of the molecule is approximately $325 \text{ \AA}^3$ (if we assume the volume of $15 \text{ \AA}^3$ for non-hydrogen atoms and $5 \text{ \AA}^3$ for hydrogen atoms). $2700/325 = 8.3$. It means there are probably 8 molecules of the organic compound, but P21/a produces only 4 positions! It means there are probably **2 molecules in the asymmetric part of the unit cell!**

[In the FOX main window]

Go to Crystal tab. (You are probably there)

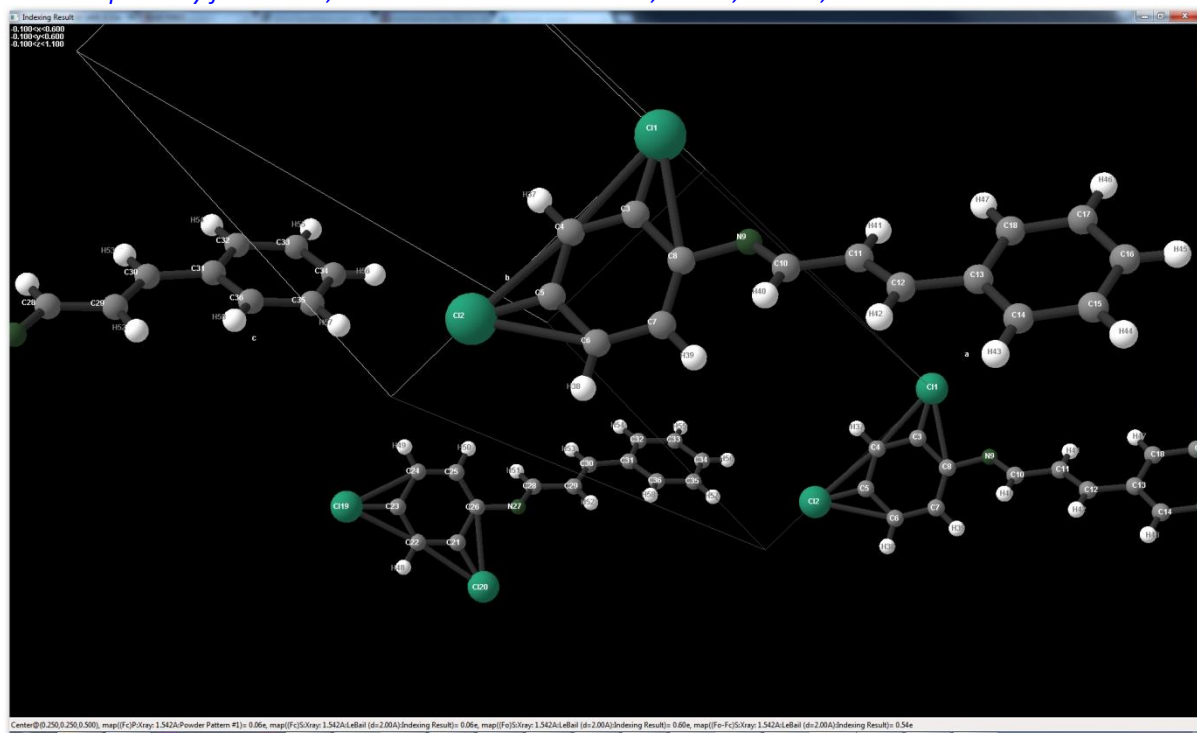
Scatterers->Import molecule from Fenske-Hall z-matrix->Select shgh3.fhz file; Open.

Program will place the molecule randomly to the unit cell. If the picture is strange, change temporarily the space group to P1. Do not forget to set it back to P21/a after you finish the model!

Open the 3D display, if it is not opened, yet (Display->3D display).

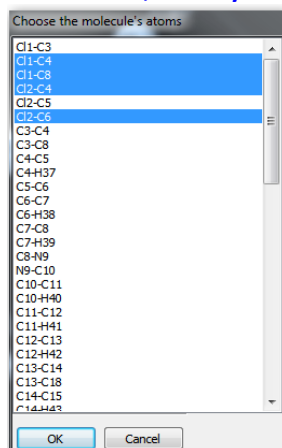
Check the model.

There are probably four bonds, which are not correct. C8-Cl1, C4-Cl1, C4-Cl2, C6-Cl2.



Click Formula and Restraints->Remove bond restraints.

Select bonds, which you want to remove; OK; YES



[In the 3D window]

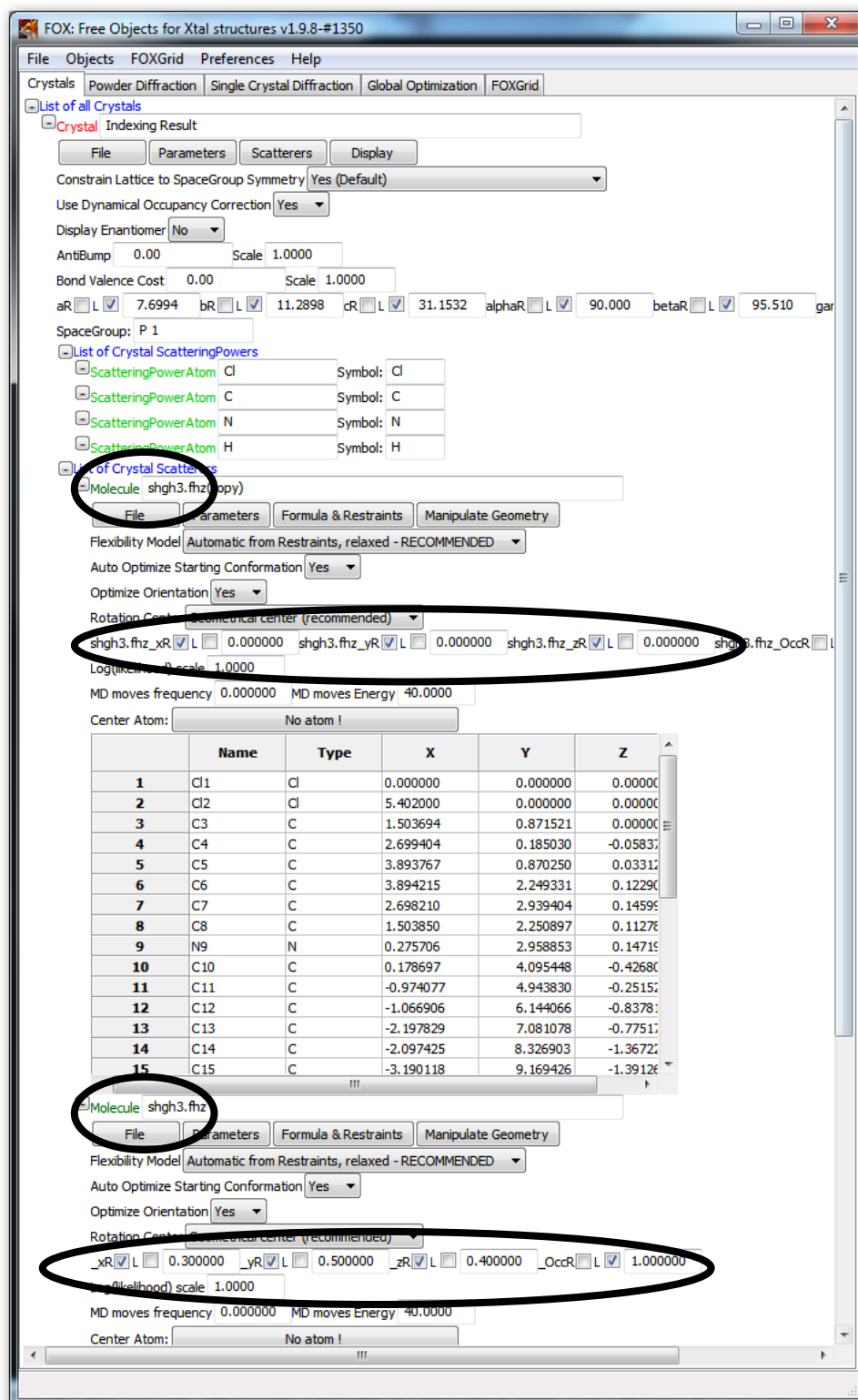
right-click->Update

This will update the model. Strange bonds disappear.

[In the FOX main window]

Scatterers->Duplicate scatterers; OK

This creates a copy of the molecule. The new molecule is in the same position, so it looks like it is not there, but it is there. Just change its position. E.g. set the first coords to 0 0 0 and the second coords to the 0.3 0.5 0.4



Save it by Menu->File->Save as 02.xml.gz

Define the algorithm

Menu->Objects->New Monte-Carlo Object

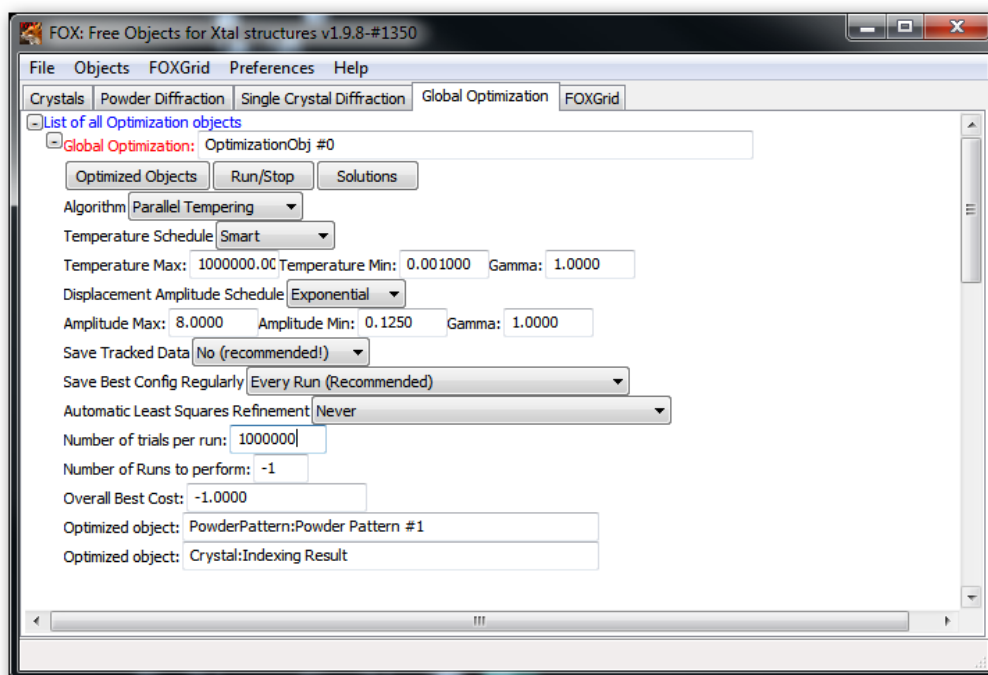
[In the Global Optimization]

Click Optimized Objects->Add object to optimize->Select Powder pattern

Click Optimized Objects->Add object to optimize->Select Crystal

Set the nb of trials per run to 1000000

Set -1 in the Number of Runs to perform (*it means that this will continue until you stop it*).



To speed it up

Go to Crystal tab.

Set Use Dynamical occupancy correction to NO

[In the Powder Diffraction]

Change $\text{Max Sin}(\theta)/\lambda$ to 0.25

Save it by Menu->File->Save as 03.xml.gz

[In the Global Optimization]

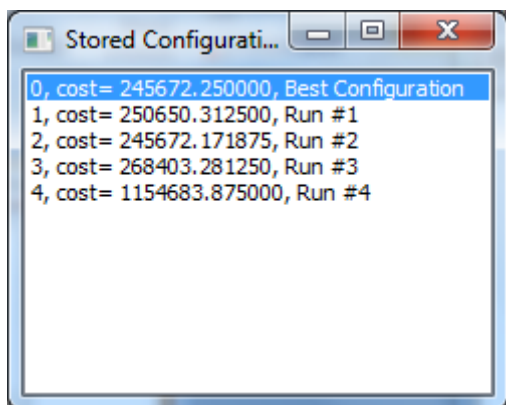
Click Run/Stop->Multiple runs

4. Saving the result

*When the FOX finish the computation, the folder contains several *.xml files. File names contain information about the Run number and also the final value of the cost function. So, if you close the FOX program, your results will still be there. But don't close the FOX at this moment. We will use its solution browser...*

In the „Global optimization tab“

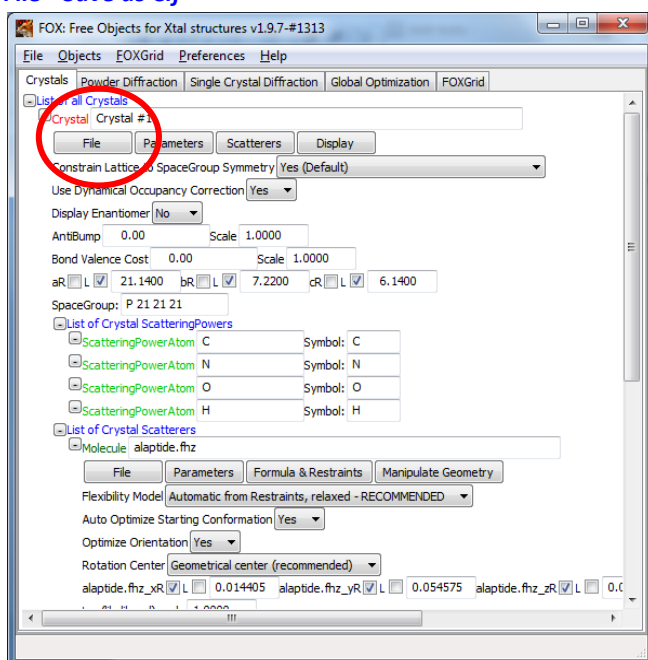
Solutions->Browse solutions



If you click on some row, the FOX will show you immediately the result in the Crystal #1 and powder pattern windows. You can select the result which you find as correct (usually the best one, which is on the top).

In the “Crystals” tab

File->Save as Cif



You can continue, and you can save another solution from the solution Browser as well.