Example 3.1: AD3

Revised: 07 March 2018

Data	Topic	Level
X-ray single crystal data	structure with pseudo-merohedric twinning	Basic

Tasks

Solving structure with pseudo-merohedric twinning and unequal twin volume fractions using Jana2006 software

- **Finding twinning matrix using Symmetry wizard**
- **Creating publication CIF.**

Initial data

Data

Single crystal data measured with Oxford Diffraction four-circle diffractometer

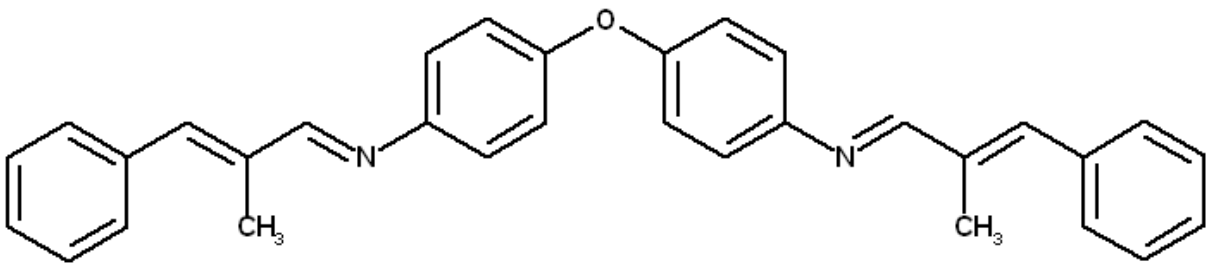
Input files:

AD3.hkl, AD3_red.sum

Additional information:

Frame scaling, absorption correction: done by the diffractometer software

Chemical formula: **Bis[N-(2-benzylidenepropylidene)phenyl]ether**



Contents

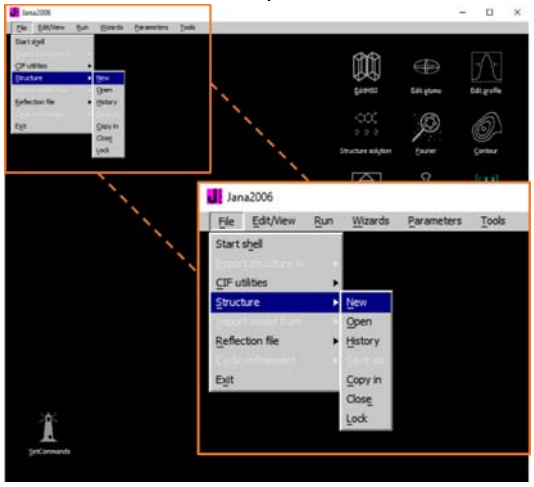
Instructions

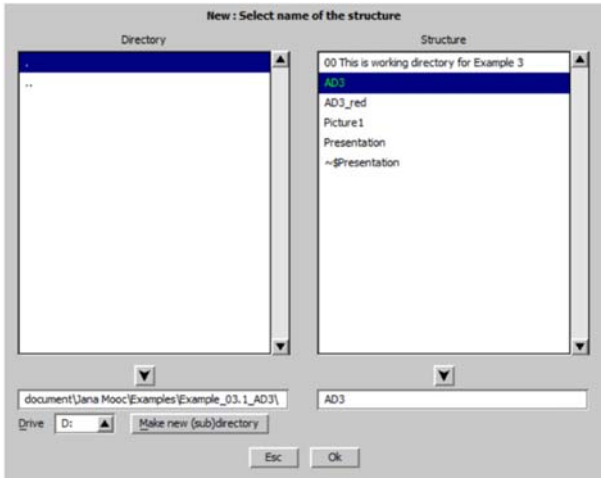
I. Data import

1. Creating new jobname

Start Jana2006
"File → Structure → New" opens a file manager *(Step1)*
Left pane: locate directory with input files; Right pane: double-click AD3 *(Step2)*

Step 1 *Step 2*

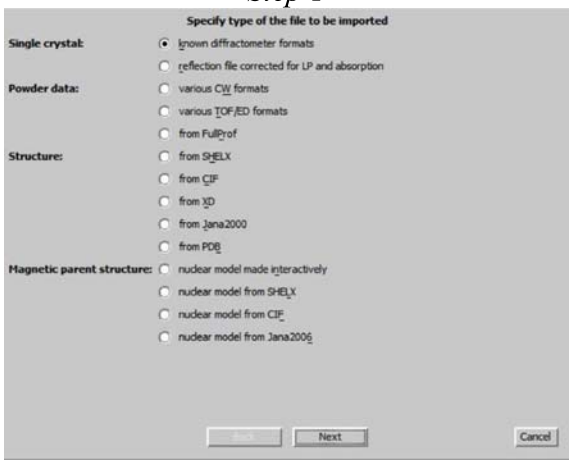


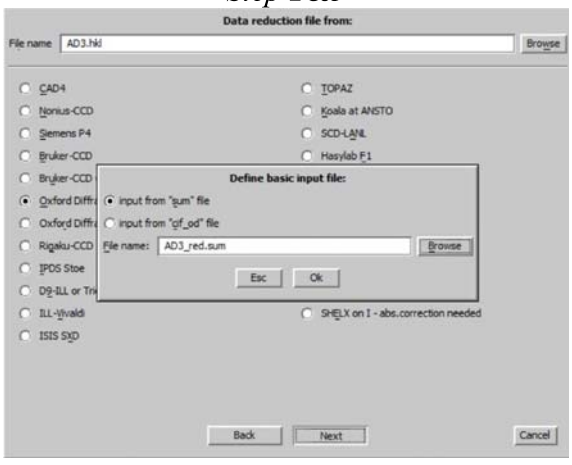


2. Import wizard

Select "Known diffractometer formats"; NEXT *(Step1)*
Select "Oxford Diffraction → CCD"; NEXT *(Step2)*
Select "Input from "sum" file"; OK *(Step3)*

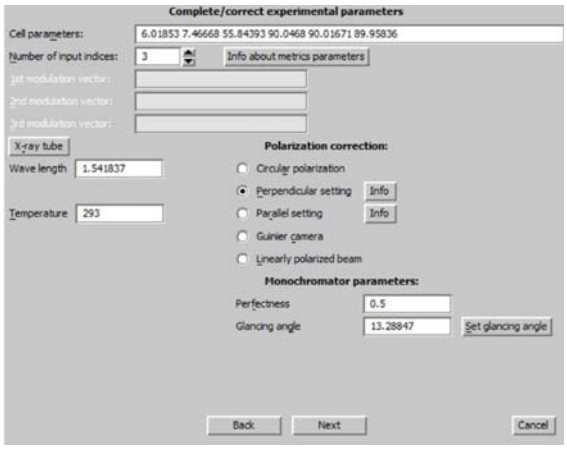
Step 1 *Step 2&3*

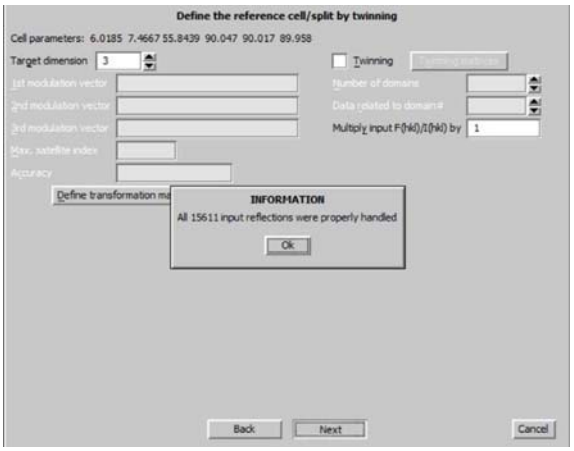




Leave all settings unchanged; NEXT *(Step4)*
Leave all settings unchanged; NEXT; OK; *(Step5)*
The program reads 15611 reflections from hkl file

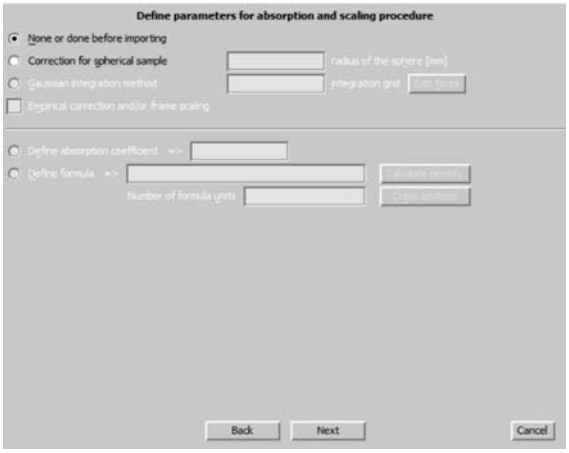
Step 4 *Step 5*





For absorption correction select "None or done before importing"; NEXT *(Step6)*
FINISH *(Step7)*

Step 6

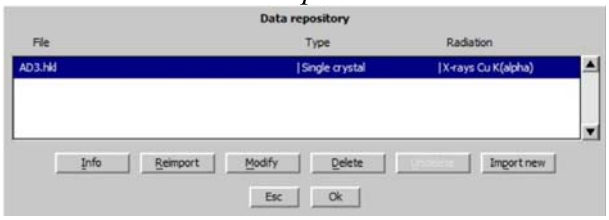


Step 7

3. Data Repository

OK; YES to accept the data set *(Step1)*
Nest; *(Step2)*

Step 1



Step 2

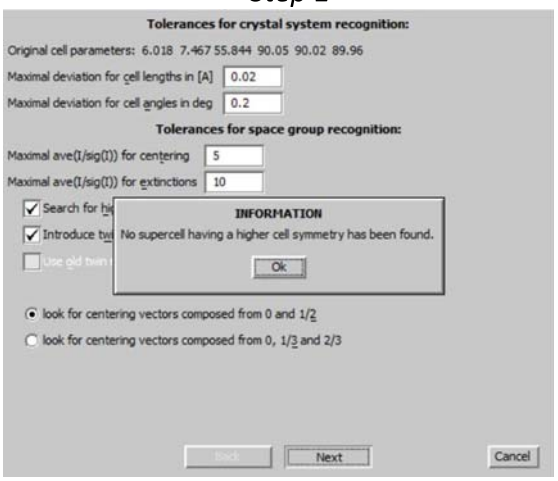
II. Symmetry and data merging

1. Symmetry wizard

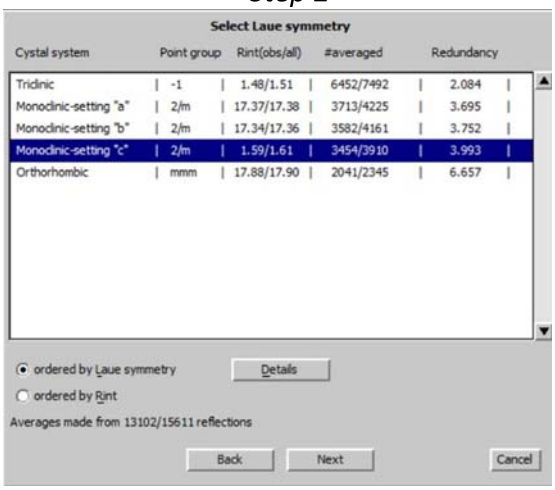
[On the screen: "Tolerances for crystal system recognition".]
Select "Introduce twin laws in case of subgroups"
Leave all other settings default; NEXT *(Step1)*
[On the screen: Select Laue symmetry]
Select Monoclinic – setting "c"; NEXT *(Step2)*

Notes
The highest Laue symmetry consistent with cell parameters is orthorhombic. It has rather high R_{int} (~17%) which indicates that orthorhombic symmetry is violated. Typical reason for such violation is presence of twinning where the structure of twins has lower symmetry and the twin domain fractions are not equal. *The selected Laue symmetry is monoclinic. In the previous step, we have activated an option "Introduce twin laws in case of subgroups". This means that the symmetry operation generating the orthorhombic symmetry from the selected monoclinic symmetry will be used as the twinning operation.*

Step 1

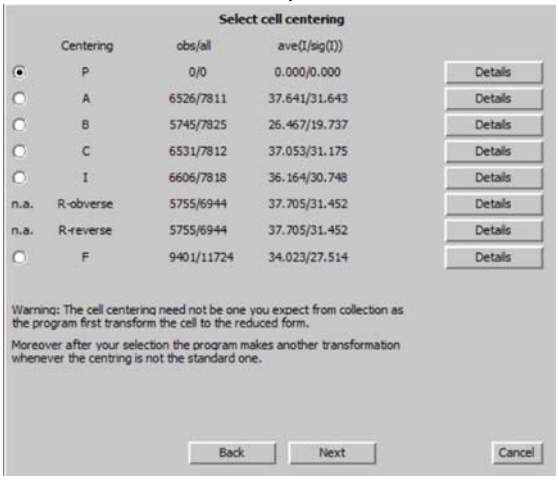


Step 2

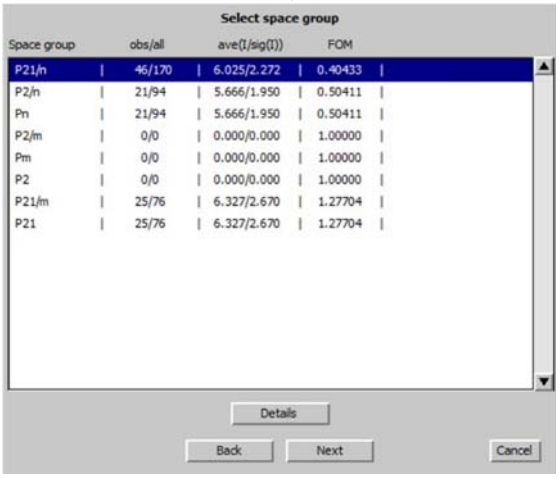


Select primitive unit cell; NEXT *(Step3)*
[On the screen: Select space group]
Using the criteria described in the first example select P21/n, *(Step4)*

Step 3



Step 4

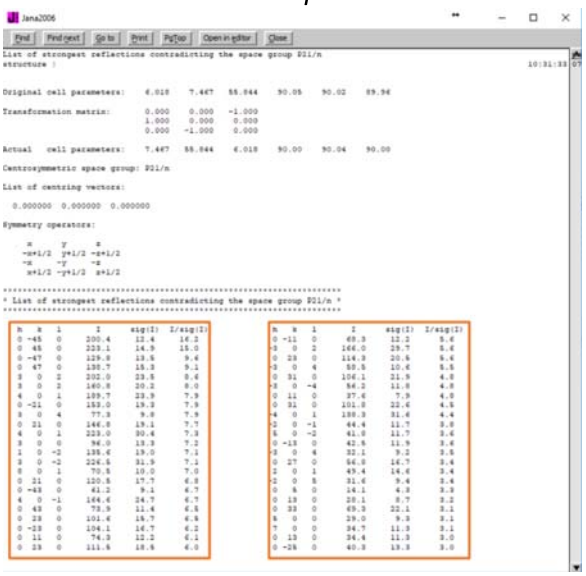


Press "Details" to verify it is really acceptable; NEXT *(Step5)*

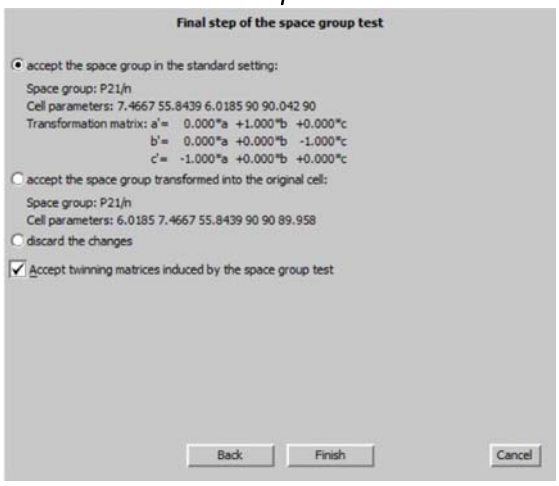
Notes
The 46 reflections violating the extinction rules have mostly low I/p. Some additional spots in the diffraction pattern from e.g. a small crystal attached at the surface of the measured sample might cause the violations. Without seeing the CCD frames we cannot be sure that the 46 reflections are really spurious, but P21/n is the most probable symmetry.

Select "Accept twinning matrices induced by the space group test"
Select "Accept the space group in the standard setting"; FINISH *(Step6)*

Step 5



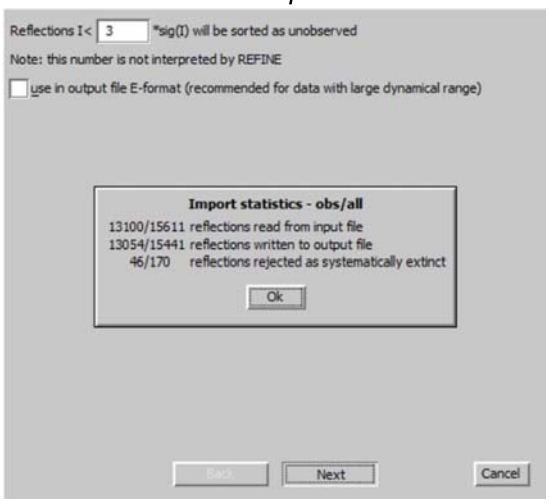
Step 6



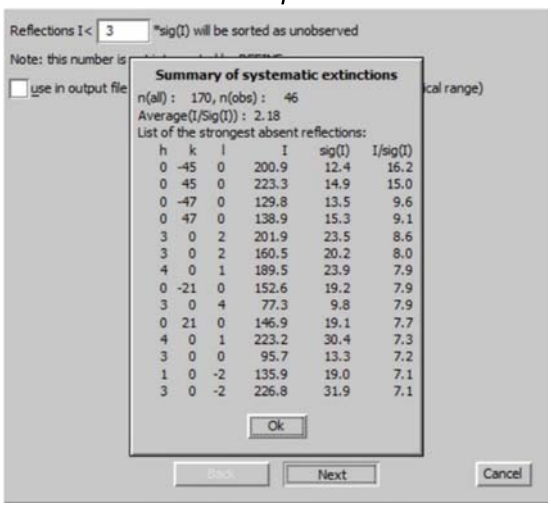
2. Creating refinement reflection file

NEXT to confirm threshold 3sigma*; OK; OK* *(Step1)*

Step 1

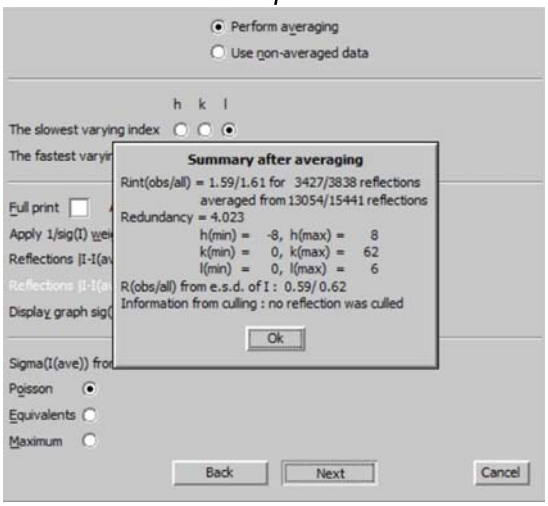


Step 1b

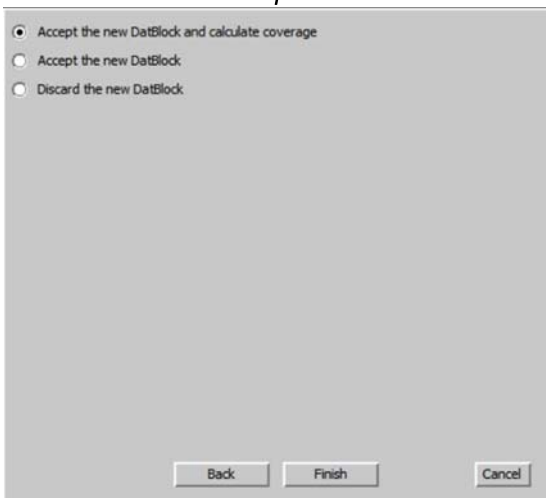


[On the screen: settings for merging of reflections]
Leave all settings default; NEXT *(Step2)*
Accept the new DatBlock and calculate coverage; FINISH *(Step3)*

Step 2



Step 3

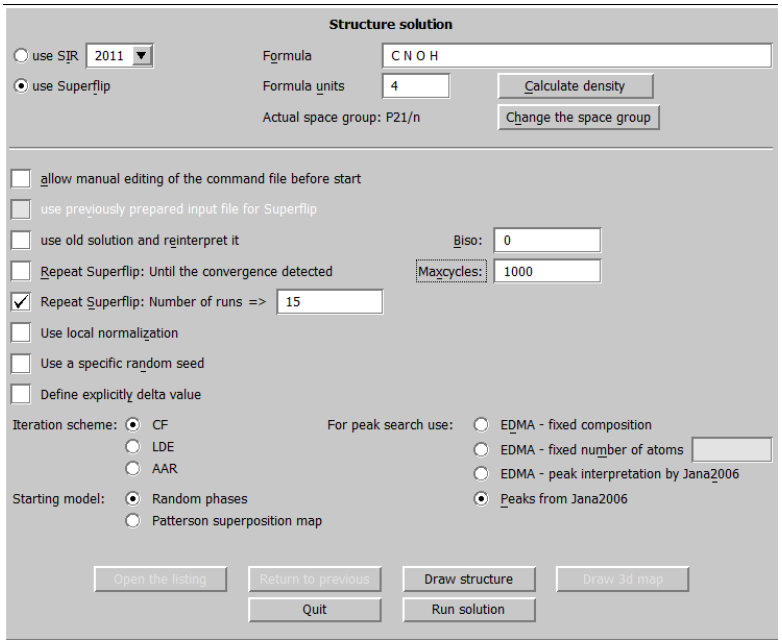


III. ***Structure solution***

3. Structure solution wizard

[On the screen: window of Structure solution]
In "Formula" textbox type list of chemical elements for AD3: C N O H
Select "Superflip", "Peaks from Jana2006"; "Repeat Superflip: Number of runs" and 15 for number of runs; limit Maxcycles to 1000; leave other settings default
Press "Run Solution" *(Step1)*

Step 1



[On the screen: listing of Superflip]

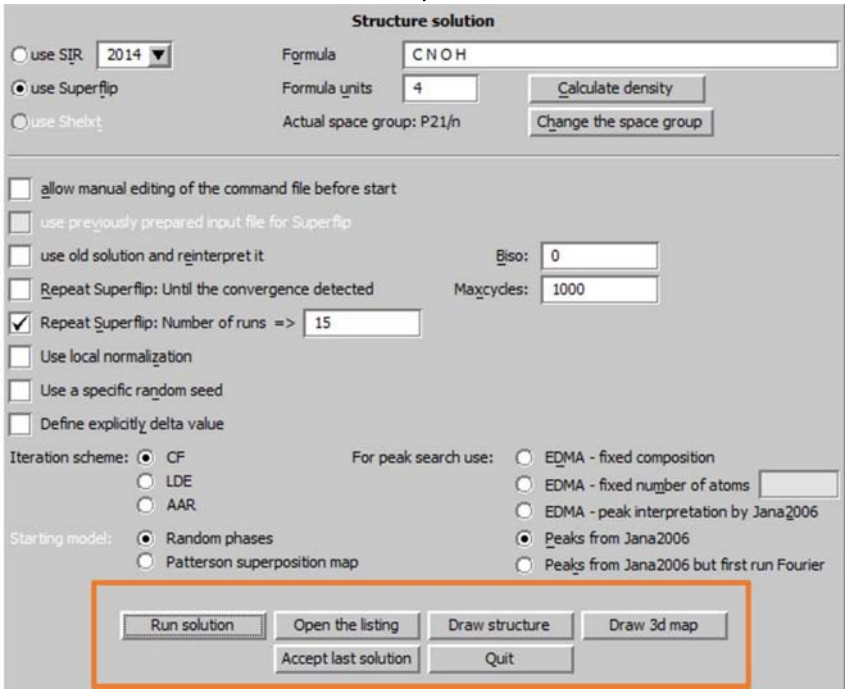
Notes
With this setting Superflip repeats calculation 15 times (from different randomly generated set of phases) and returns the result with the best fit between the electron density map and the user-defined symmetry. Because of twinning the fit of symmetry generators is worse and it may happen that Superflip suggests $P2_1$ instead of $P2_1/n$ - please ignore this fact, "n" is confirmed by systematic extictions. With this structure, the results of Superflip are significantly better when "Biso" is set to 3 in the charge flipping options; however, this would be an empirical step useless for other structures.

Close listing of Superflip

Press “Draw structure” to see result of charge flipping *(Step2)*

Notes
It may happen that Diamond shows two molecules instead of one. This is because twinning also biases the bond lengths, some distances are too long and some atoms are not properly assigned

Step 2

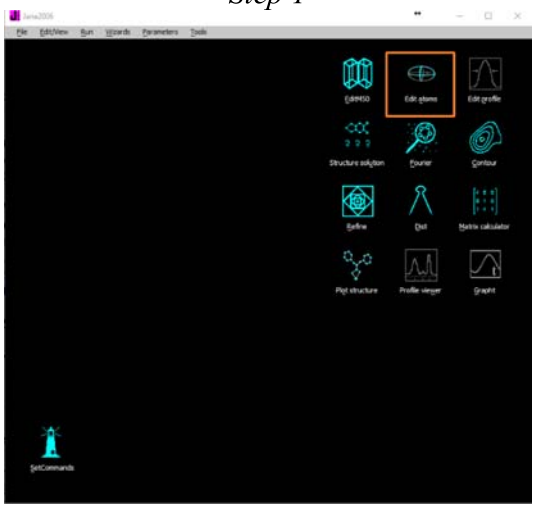


Quit Diamond without saving changes
In case of doubts repeat structure solution and plotting
Finally press "Acccept last solution" to close the structure solution wizard

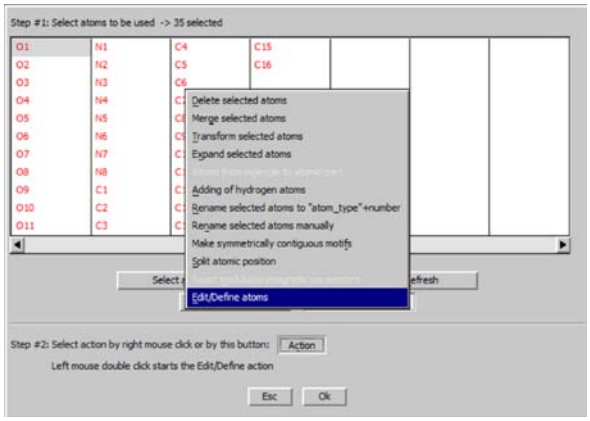
4. Verification of the structure solution

Start "Edit atoms" *(Step1)*
[On the screen: list of atoms]
Press "Select all"
Start "Action → Edit/define" *(Step2)*

Step 1



Step 2



Double-click "Type" textbox

Notes
Double-click unlocks the "Type" textbox. This is locked for security reasons because the selected atoms have different chemical types.

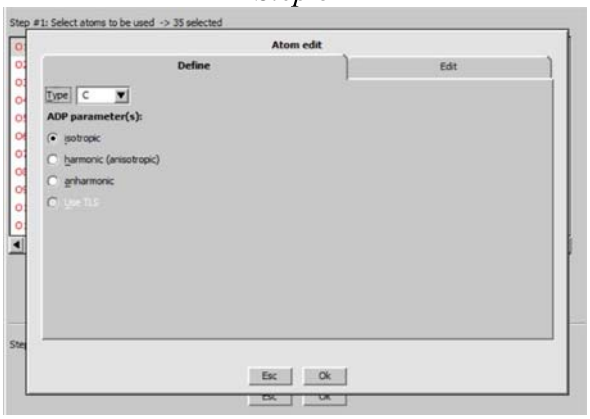
Select Carbon, OK *(Step3)*

[On the screen: list of atoms.]

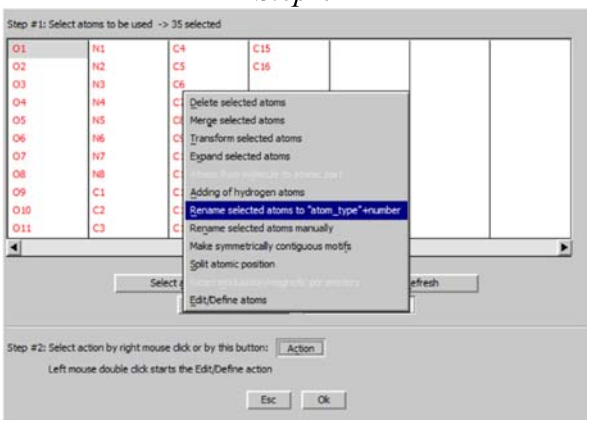
The labels are still the original ones but the chemical type of all atoms is carbon

Start "Action → Rename selected atoms to atom type + number" *(Step4)*

Step 3



Step 4



Press "Select all"

Start "Action → Make symmetrically contiguous motifs" *(Step5)*

OK; YES to save changes

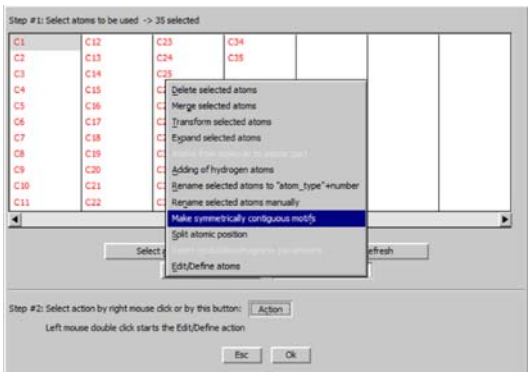
Notes
These steps help to get a reasonable plot in Diamond (next step) even with biased distances and improper chemical types

Start "Plot structure" *(Step6)*

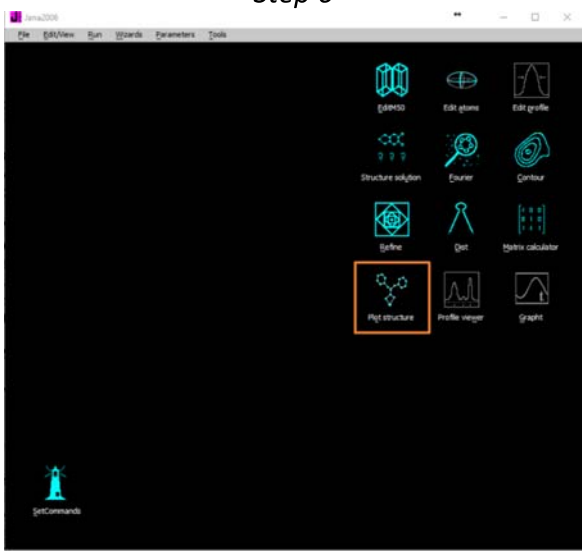
Press "Draw+continue"

Notes
In this mode Jana will launch Diamond but it will not wait for its end

Step 5



Step 6

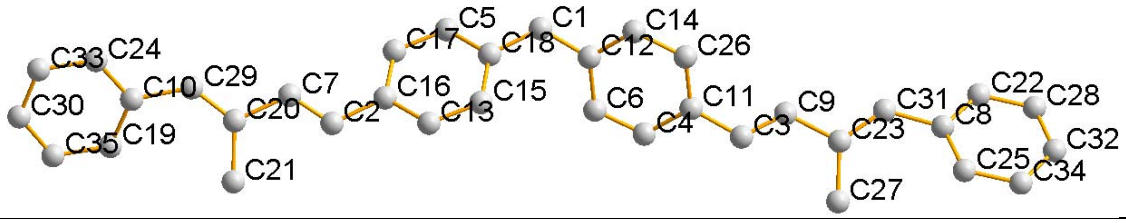


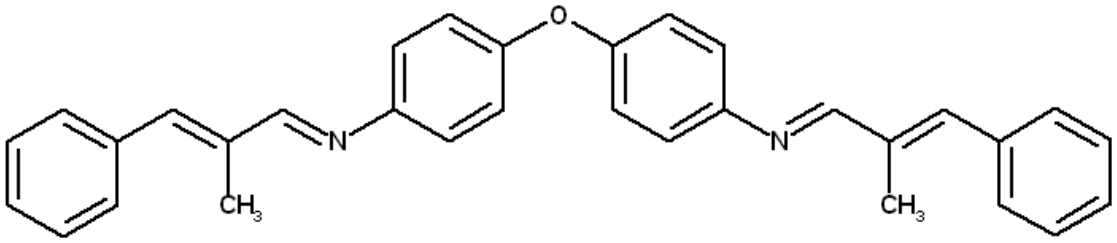
[On the screen: window of Diamond]

Start "Build → Molecules → Get molecules → OK" ***or*** use  on the bottom toolbar
Rotate the molecule ( and  on the bottom toolbar) to get an optimal view
Draw rectangle to select all atoms of the molecule or press Ctrl-A
Right-click on one of the selected atoms, choose "Add → Atom labels"

[On the screen: dialogue of Diamond for atom labeling]
For "Content" select: "Atom symbol"
Define relative position of labels 0.3,0.3,10
Define text size ~0.8Å; OK
Rotate the molecule to similar orientation like has the chemical scheme
[On the screen: plot of the molecule with atom labels]

Notes
The results may be slightly different for each run of Superflip. This is because Superflip starts from random phases and the resulting electron density map differs for each run. In our case the assignment of chemical types is wrong for many atoms of the structure.





Compare the plot with the chemical scheme **and note labels of atoms**, which must be oxygen or nitrogen.

Notes
In our example, C2 and C3 should be nitrogen and C1 should be oxygen.

Quit Diamond

5. Assignment of correct chemical types

[On the screen: basic Jana window]
Start "Edit atoms"
[On the screen: list of atoms]
Select the atom which should be oxygen (C1 in our example)

Editing of one atom can be also started by right mouse button or by double-click
Start "Action → Edit/define" and choose chemical type "O"; OK
Press "Refresh"
Hold Ctrl and select atoms which should be nitrogen (C2,C3 in our example)
Start "Action → Edit/define" and choose chemical type "N"; OK
[On the screen: list of atoms, labels are still the original ones but chemical types are correct]
Press "Select All"
Press "Action" or right-click on one of the selected atoms
Choose "Rename selected atoms to atom_type + number"
[On the screen: list of atoms with labels corresponding to chemical types]

Notes
You should see one oxygen, two nitrogens and carbons. If not press ESC and start again ☺

OK; YES to save the changes
Check chemical types with Diamond

IV. Refinements and model improvement

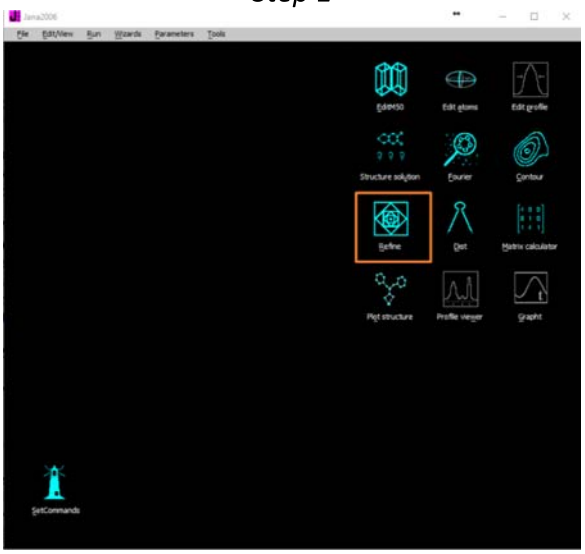
1. Refinement

[On the screen: basic window of Jana]
Right-click the icon of Refine. *(Step1)*
[On the screen: refinement options]
Define 100 of cycles, Instability factor 0.02; OK *(Step2)*

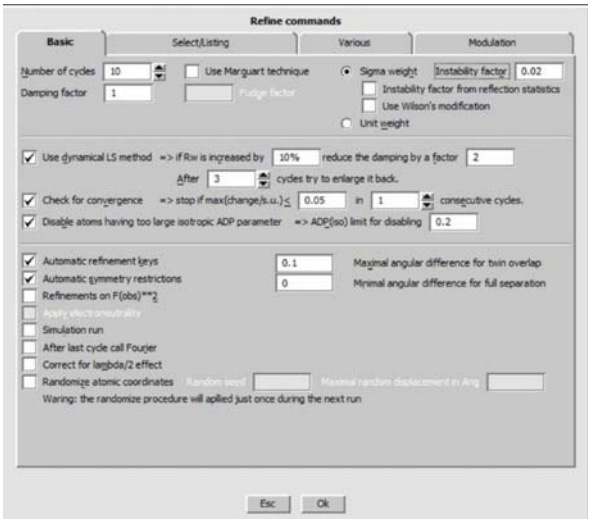
Notes
This instability factor slightly lowers goodness of fit, which makes happy editors used for SHELX. However, we cannot change this number arbitrarily because values below 0.01 or above 0.02 are usually in contradiction with the instrument characteristics.

Choose "YES+START"
Refinement converges with R value about 16%, GOF about 8, 141 refined parameters

Step 1



Step 2



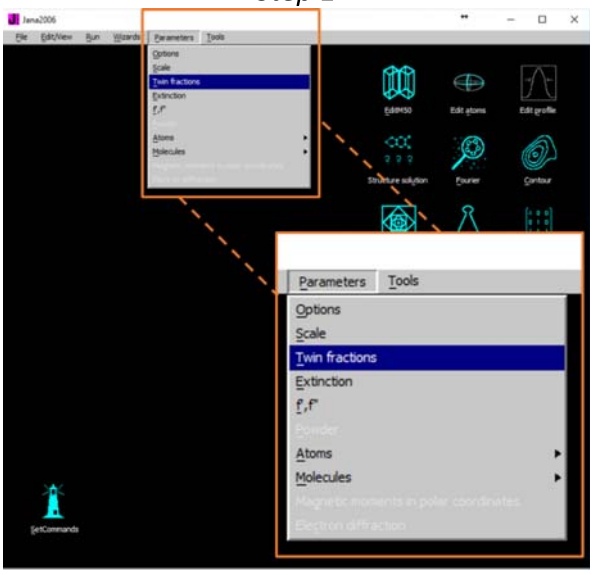
2. Twin volume fraction

Start "parameters → Twin fractions" *(Step1)*

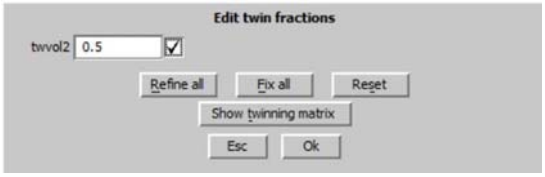
Notes
The volume fraction of the twin domain introduced by the Symmetry wizard is 0.5 and twinning matrix relating the monoclinic and orthorhombic symmetry is (1 0 0 | 0 1 0 | 0 0 -1).

Activate refinement of the twin fraction *(Step2)*

Step 1



Step 2



Repeat refinement

Refinement converges with R value about 11%, GOF about 7

Twin volume fraction drops to 0.29.

Start "Edit atoms"

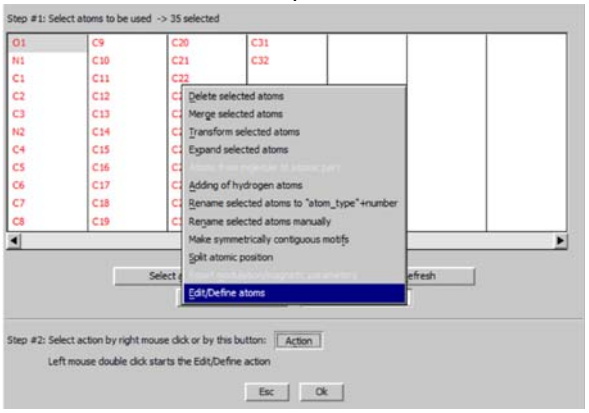
[On the screen: list of atoms]

Press "Select all" and "Action → Edit/define" *(Step3)*

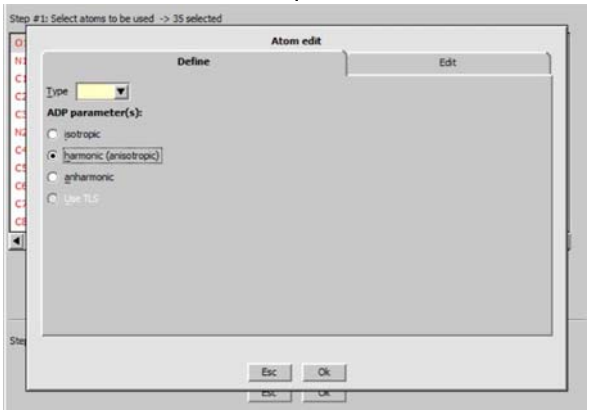
Choose "harmonic" for ADP parameters. *(Step4)*

This defines anisotropic temperature parameters for all atoms.
OK, OK, YES to save changes

Step 3



Step 4



Double-click the icon Refine.
Refinement converges with R value about 9%, GOF about 6, 317 refined parameters.

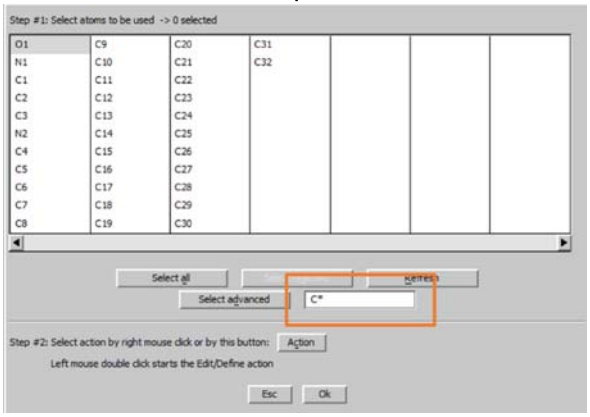
3. Adding of hydrogen atoms & Final refinement

[On the screen: basic window of Jana]
Start "Edit atoms"
In the textbox type "C*"; TAB. *(Step1)*

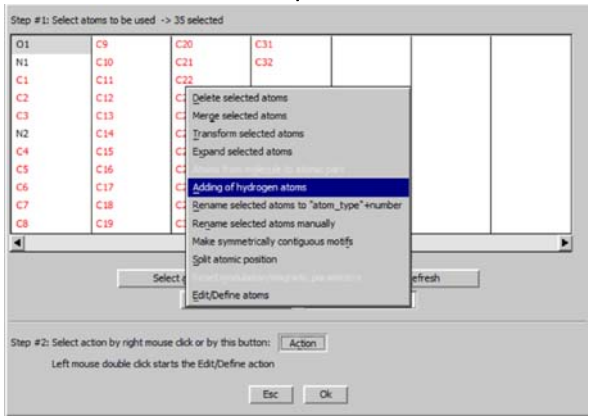
Notes
This will select atoms starting with C, i.e. carbons

Start "Action → Adding of hydrogen atoms" *(Step2)*

Step 1



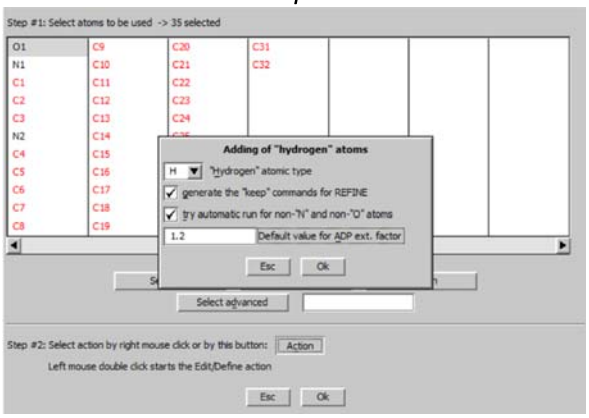
Step 2



[On the screen: Adding of hydrogen atoms dialogue]
Leave all settings default; OK *(Step3)*
[On the screen: list of atoms with new hydrogens]

Notes
Total number of atoms should be 63 (can be verified using "Select All") *The hydrogens are kept in ideal geometry by commands which can be viewed or edited in "Refinement commands → Various → Keep commands".*

Step 3



Refinement commands → Various

OK to close "Edit atoms"; Yes to save changes
"Plot structure" to check results of automatic hydrogen assignment
Make refinement of the final structure

Notes
Oscillation may occur during the refinement. In such case do not break refinement, press Parameters, change Damping factor to 0.5 and close the dialogue. Refinement will continue with damping. *Refinement converges with R value 3.7%, GOF 2.7, 317 refined parameters.*

V. Creating CIF file

Notes
*The information for the CIF file is cumulated in the file M70 during the data processing as well as solution and refinement steps. For creating a publication CIF, repetition of the basic steps is recommended in order to refresh the information in M70. In our case, we have started from the *.sum file so M70 does not contain any information about the experiment*

Start "File → Reflection file → Create refinement reflection file"

Notes
In our case this step is not necessary because it has been already done

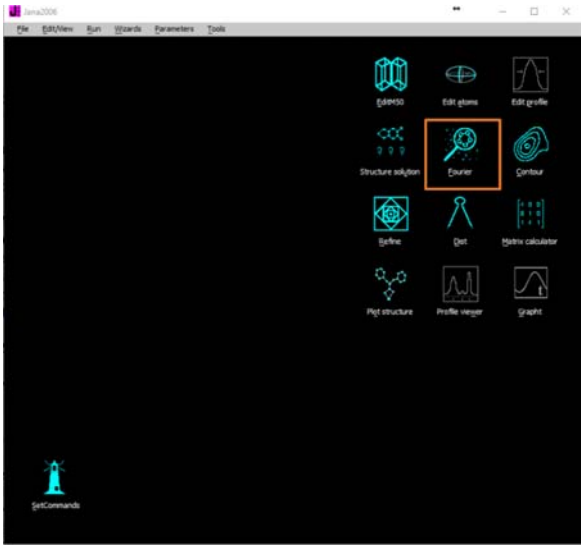
Repeat refinement

Notes
In our case this step is not necessary because it has been already done

Right-click Fourier; *(Step1)*

Select "F(obs)-F(calc) - difference Fourier"; make sure that "Weighting of reflections" is checked and "Apply sin(th)/lambda limits" unchecked; *(Step2)*

Step 1



Step 2

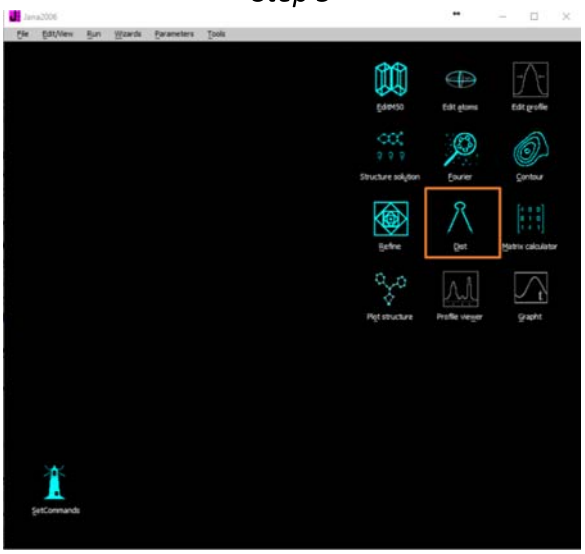
In the page "Scope" press "Reset to default"; *(Step3)*
in the page "Peaks" choose "in a fixed sphere of radius 0.8" *(Step4)*

Step 3

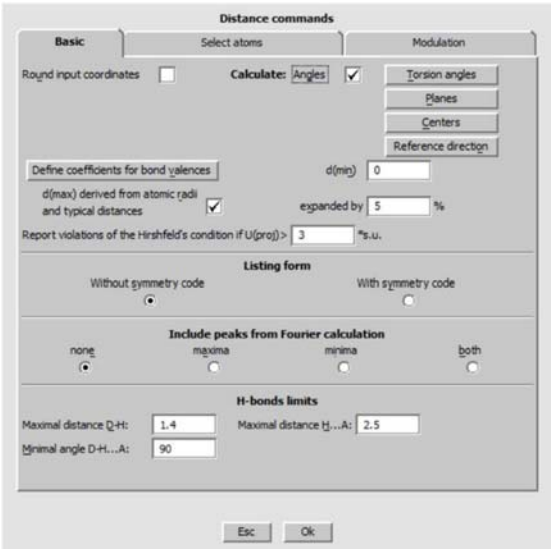
Step 4

OK; YES+START; NO to include new atoms; NO to see the listing
Right-click Dist icon *(Step5)*
Select "d(max) derived from atomic radii and typical distances and adjust "expanded by" value" when needed; check "Calculate angles"; in needed, adjust limits for H-bonds; *(Step6)*

Step 5

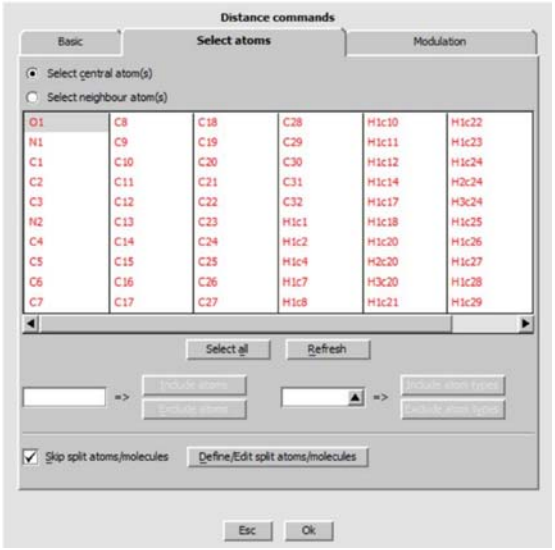


Step 6

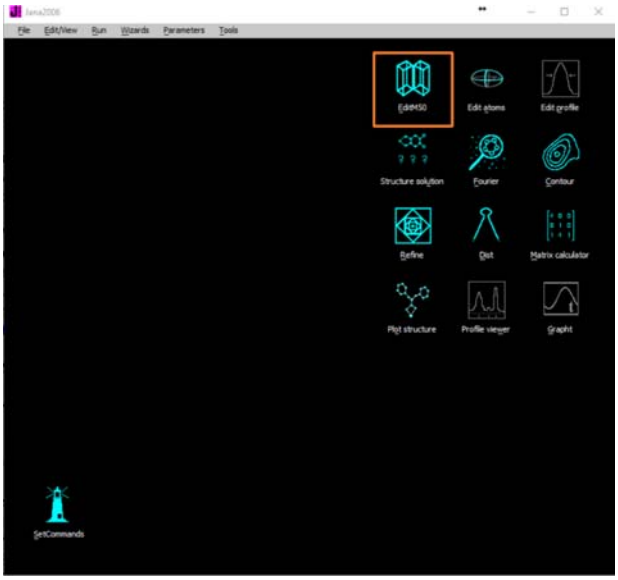


In the page "Select atoms" check central atoms and neighbor atoms – usually we want to have all atoms in both roles; *(Step7)*
OK; YES+START; Close;
Start EditM50; *(Step8)*

Step 7

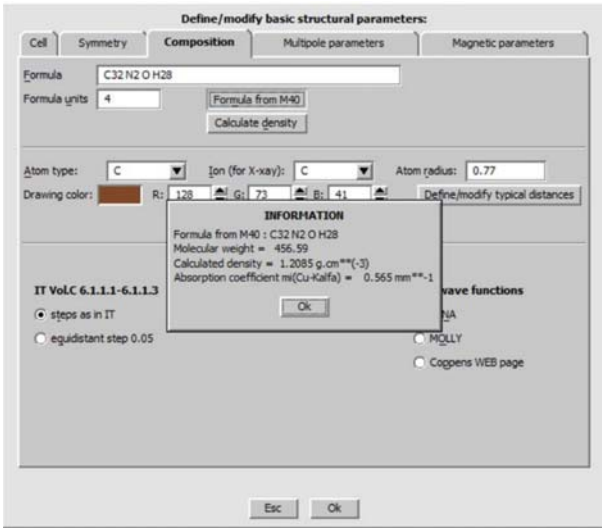


Step 8

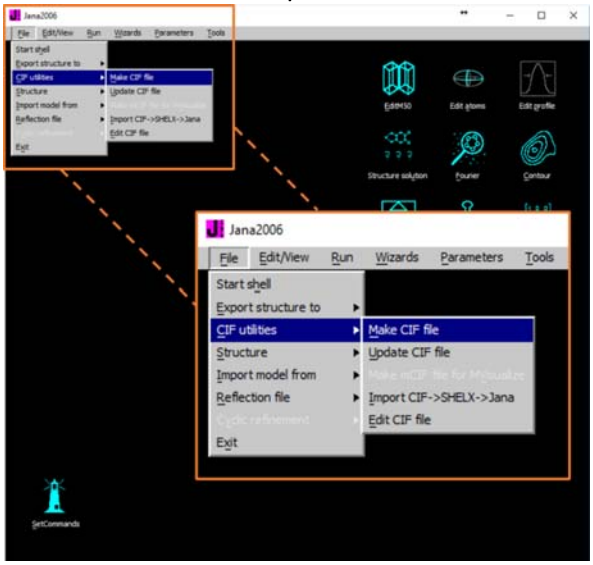


Go to page Composition; enter 4 for "Formula units", press "Formula from M40" *(Step9)*
OK; YES for updating the formula.
OK; YES to rewrite M50Zn
Start "File → CIF utilities → Make CIF file" *(Step10)*

Step 9



Step 10



References