

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

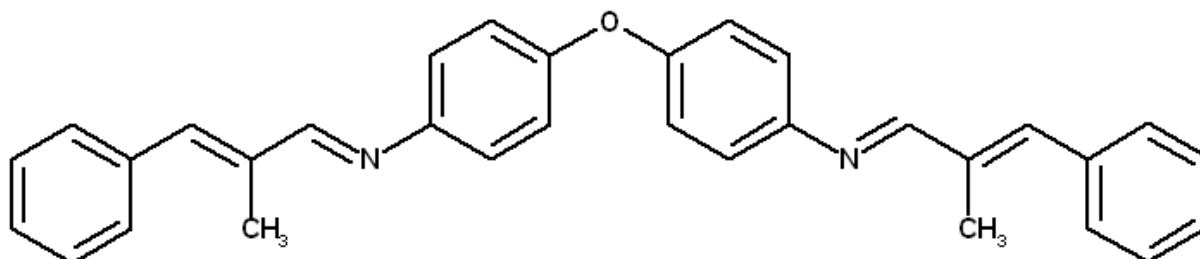
Input files:

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

I.	Data import.....	95
1.	Creating new jobname	95
2.	Import wizard	95
3.	Data Repository	96
II.	Symmetry and data merging.....	97
1.	Symmetry wizard	97
2.	Creating refinement reflection file.....	98
III.	Structure solution.....	99
3.	Structure solution wizard	99
4.	Verification of the structure solution	101
5.	Assignment of correct chemical types	103
IV.	Refinements and model improvement	104
1.	Refinement	104
2.	Twin volume fraction.....	105
3.	Adding of hydrogen atoms & Final refinement.....	106
V.	Creating CIF file	107
	References	110

Instructions

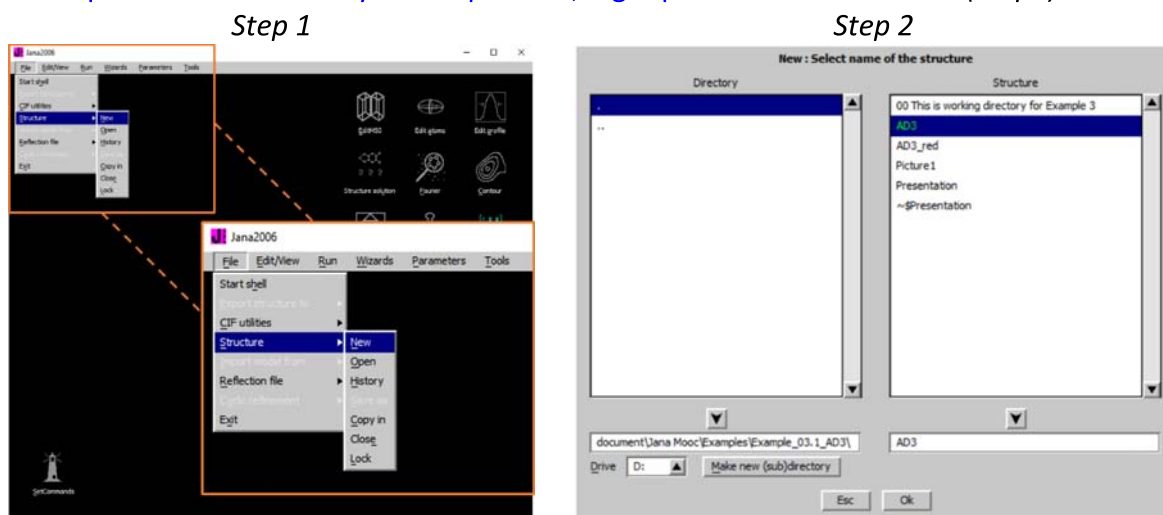
I. Data import

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*)

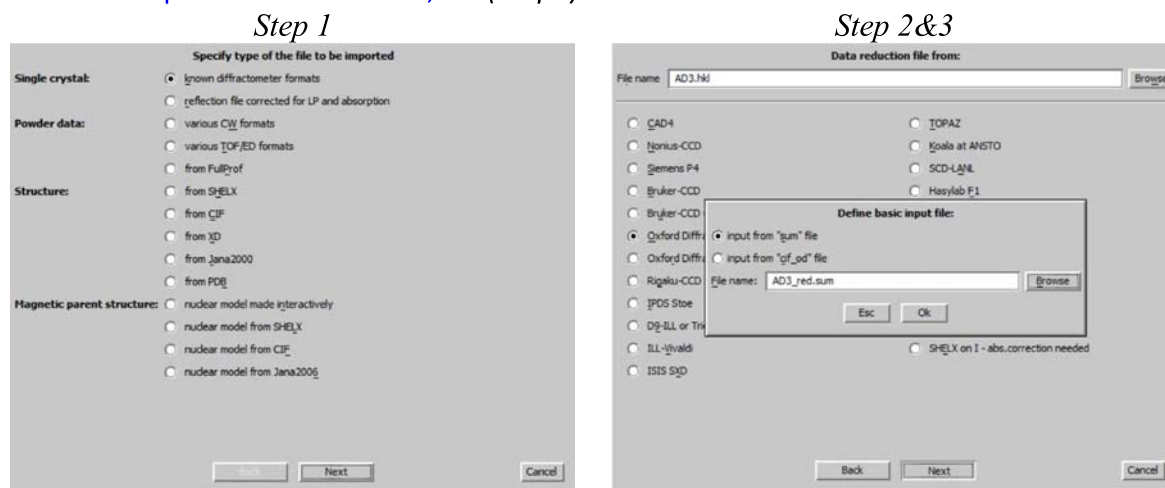


2. Import wizard

Select “Known diffractometer formats”; NEXT (*Step1*)

Select “Oxford Diffraction → CCD”; NEXT (*Step2*)

Select “Input from “sum” file”; OK (*Step3*)



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

Complete/correct experimental parameters

Cell parameters: 6.01853 7.46668 55.84393 90.0468 90.01671 89.95836

Number of input indices: 3

1st modulation vector:

2nd modulation vector:

3rd modulation vector:

X-ray tube

Wave length: 1.541837

Temperature: 293

Polarization correction:

☐ Circular polarization

☒ Perpendicular setting

☐ Parallel setting

☐ Guinier camera

☐ Linearly polarized beam

Monochromator parameters:

Perfectioness: 0.5

Glancing angle: 13.28847

Define the reference cell/split by twinning

Cell parameters: 6.0185 7.4667 55.8439 90.047 90.017 89.958

Target dimension: 3

☐ Twinning

1st modulation vector:

2nd modulation vector:

3rd modulation vector:

Index: satellite index:

Accuracy:

Number of domains:

Data related to domain:

Multiply input F(hkl)/I(hkl) by: 1

INFORMATION

All 15611 input reflections were properly handled

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

Step 6

Define parameters for absorption and scaling procedure

☒ None or done before importing

☐ Correction for spherical sample radius of the sphere [mm]

☐ Gaussian integration method integration grid

☐ Empirical correction and/or frame scaling

☐ Define absorption coefficient =>

☐ Define formula =>

Number of formula units:

Step 7

INFORMATION

The import wizard is complete. As a next step you can import another file or modify the previously imported ones.

3. Data Repository

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

Step 1

Data repository

File	Type	Radiation
AD3.Hkl	Single crystal	X-rays Cu K(alpha)

Step 2

INFORMATION

Now the program will open a wizard for a space group test which can determine interactively the symmetry. In the case that later you will need to modify your first choice the same procedure can be run by the command "File->Reflection file->Make space group test" without necessity to reimport the data.

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

Tolerances for crystal system recognition:
Original cell parameters: 6.018 7.467 55.844 90.05 90.02 89.96
Maximal deviation for cell lengths in [Å] 0.02
Maximal deviation for cell angles in deg 0.2

Tolerances for space group recognition:
Maximal ave(I/sig(I)) for centering 5
Maximal ave(I/sig(I)) for extinctions 10

☒ Search for higher symmetry
☒ Introduce twin laws
☐ Use old twin laws

☒ look for centering vectors composed from 0 and 1/2
☐ look for centering vectors composed from 0, 1/3 and 2/3

INFORMATION
No supercell having a higher cell symmetry has been found.
Ok

Back Next Cancel

Step 2

Select Laue symmetry

Crystal system	Point group	Rint(obs/all)	#averaged	Redundancy
Tridinic	-1	1.48/1.51	6452/7492	2.084
Monoclinic-setting "a"	2/m	17.37/17.38	3713/4225	3.695
Monoclinic-setting "b"	2/m	17.34/17.36	3582/4161	3.752
Monoclinic-setting "c"	2/m	1.59/1.61	3454/3910	3.993
Orthorhombic	mmm	17.88/17.90	2041/2345	6.657

☒ ordered by Laue symmetry
☐ ordered by Rint

Averages made from 13102/15611 reflections

Details

Back Next Cancel

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

Select cell centering

Centering	obs/all	ave(I/sig(I))
<input checked="" type="radio"/> P	0/0	0.000/0.000
<input type="radio"/> A	6526/7811	37.641/31.643
<input type="radio"/> B	5745/7825	26.467/19.737
<input type="radio"/> C	6531/7812	37.053/31.175
<input type="radio"/> I	6606/7818	36.164/30.748
n.a. R-observe	5755/6944	37.705/31.452
n.a. R-reverse	5755/6944	37.705/31.452
<input type="radio"/> F	9401/11724	34.023/27.514

Warning: The cell centering need not be one you expect from collection as the program first transform the cell to the reduced form.
Moreover after your selection the program makes another transformation whenever the centering is not the standard one.

Back Next Cancel

Step 4

Select space group

Space group	obs/all	ave(I/sig(I))	FOM
P21/n	46/170	6.025/2.272	0.40433
P2/n	21/94	5.666/1.950	0.50411
Pn	21/94	5.666/1.950	0.50411
P2/m	0/0	0.000/0.000	1.00000
Pm	0/0	0.000/0.000	1.00000
P2	0/0	0.000/0.000	1.00000
P21/m	25/76	6.327/2.670	1.27704
P21	25/76	6.327/2.670	1.27704

Details

Back Next Cancel

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

Jana2006

Print Find next Go to Print PgUp Open in editor Close

List of strongest reflections contradicting the space group P21/n structure:

Original cell parameters: 6.018 7.467 55.844 90.05 90.02 99.94

Transformation matrix:

0.000	0.000	-1.000
1.000	0.000	0.000
0.000	-1.000	0.000

Actual cell parameters: 7.467 55.844 6.018 90.00 90.04 90.00

Centrosymmetric space group: P21/n

List of centering vectors:

0.000000 0.000000 0.000000

Symmetry operators:

```

x y z
-x+1/2 -y+1/2 z+1/2
-x -y z
-x+1/2 -y+1/2 z+1/2

```

* List of strongest reflections contradicting the space group P21/n *

h	k	l	I	sig(I)	I/sig(I)
0	-45	0	200.4	12.4	16.2
0	45	0	223.1	14.9	15.0
0	-47	0	129.9	13.6	9.4
0	47	0	135.7	13.2	9.1
8	0	2	202.0	23.8	8.4
8	0	2	140.8	20.2	8.0
4	0	1	189.7	23.9	7.9
0	-21	0	183.0	19.3	9.4
8	0	4	77.3	9.9	7.8
0	21	0	146.9	19.1	7.7
4	0	1	223.0	30.4	7.3
8	0	0	94.0	13.3	7.2
1	0	-2	135.4	19.0	7.1
8	0	-2	224.5	31.9	7.1
8	0	1	70.5	10.0	7.0
0	21	0	220.5	17.7	6.8
0	-45	0	41.3	9.1	6.7
4	0	-1	148.4	24.7	6.7
0	45	0	70.9	11.4	6.5
0	29	0	101.4	16.7	6.5
0	-29	0	204.1	31.7	6.2
0	11	0	74.9	12.2	6.1
0	29	0	111.6	18.6	6.0

Step 6

Final step of the space group test

☒ accept the space group in the standard setting:

Space group: P21/n
Cell parameters: 7.4667 55.8439 6.0185 90 90.042 90
Transformation matrix: a' = 0.000*a +1.000*b +0.000*c
b' = 0.000*a +0.000*b -1.000*c
c' = -1.000*a +0.000*b +0.000*c

☐ accept the space group transformed into the original cell:

Space group: P21/n
Cell parameters: 6.0185 7.4667 55.8439 90 90 89.958

☐ discard the changes

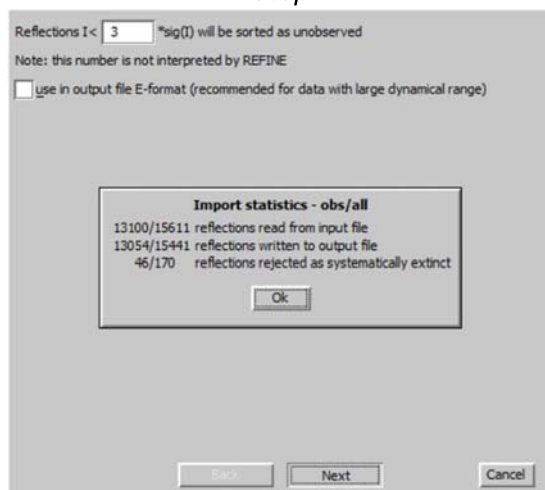
☒ Accept twinning matrices induced by the space group test

Back Finish Cancel

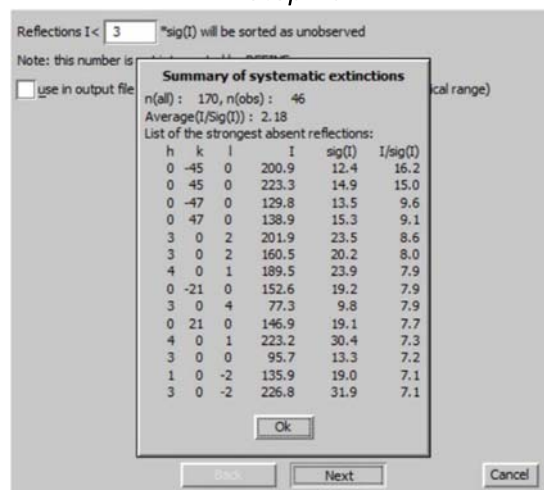
2. Creating refinement reflection file

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

Step 1



Step 1b

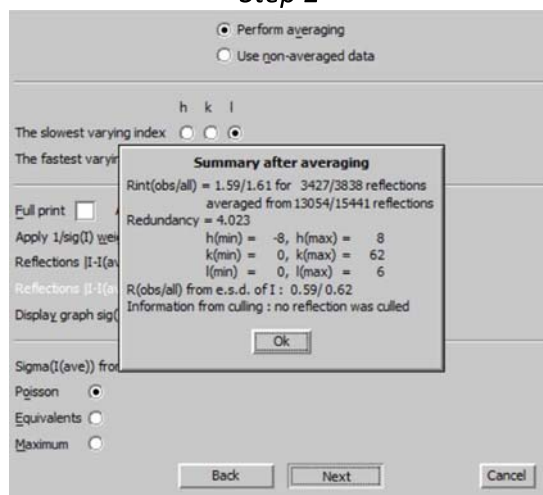


[On the screen: settings for merging of reflections]

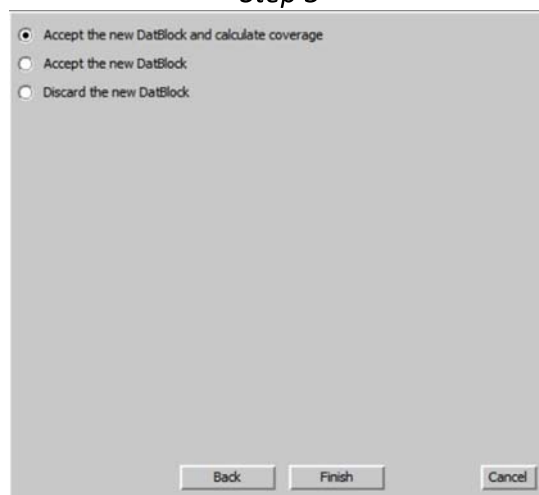
Leave all settings default; NEXT (Step2)

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

Structure solution

☐ use SJR 2011 ☒ use Superflip

Formula:

Formula units:

Actual space group: P21/n

☐ allow manual editing of the command file before start

☐ use previously prepared input file for Superflip

☐ use old solution and reinterpret it

☐ Repeat Superflip: Until the convergence detected

☒ Repeat Superflip: Number of runs =>

☐ Use local normalization

☐ Use a specific random seed

☐ Define explicitly delta value

Iteration scheme: ☒ CF ☐ LDE ☐ AAR

For peak search use: ☐ EDMA - fixed composition ☐ EDMA - fixed number of atoms
☐ EDMA - peak interpretation by Jana2006 ☒ Peaks from Jana2006

Starting model: ☒ Random phases ☐ Patterson superposition map

[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 extinctions. 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

Structure solution

☐ use S_{IR} 2014
☒ use Superflip
☐ use Shelx

Formula: CNOH
 Formula units: 4
 Actual space group: P21/n

☐ allow manual editing of the command file before start
☐ use previously prepared input file for Superflip
☐ use old solution and reinterpret it
☐ Repeat Superflip: Until the convergence detected
☒ Repeat Superflip: Number of runs => 15
☐ Use local normalization
☐ Use a specific random seed
☐ Define explicitly delta value

Iteration scheme: ☒ CF
☐ LDE
☐ AAR

For peak search use: ☐ EDMA - fixed composition
☐ EDMA - fixed number of atoms
☐ EDMA - peak interpretation by Jana2006
☒ Peaks from Jana2006
☐ Peaks from Jana2006 but first run Fourier

Starting model: ☒ Random phases
☐ Patterson superposition map

Quit Diamond without saving changes

In case of doubts repeat structure solution and plotting

Finally press "Accept last solution" to close the structure solution wizard

4. Verification of the structure solution

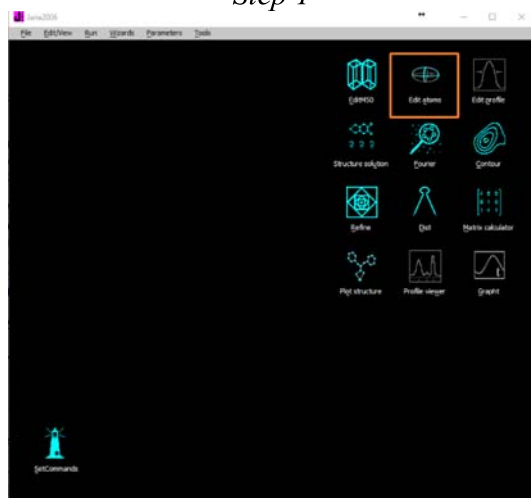
Start "Edit atoms" (Step1)

[On the screen: list of atoms]

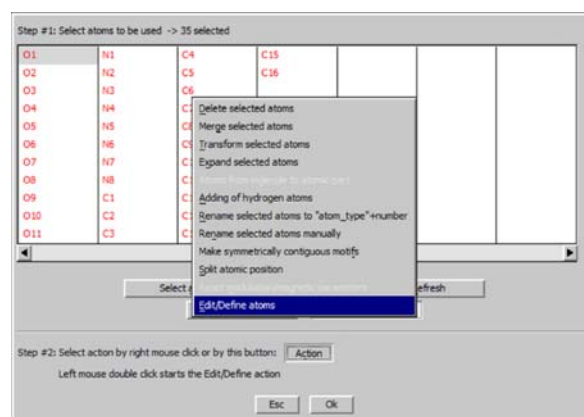
Press "Select all"

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.

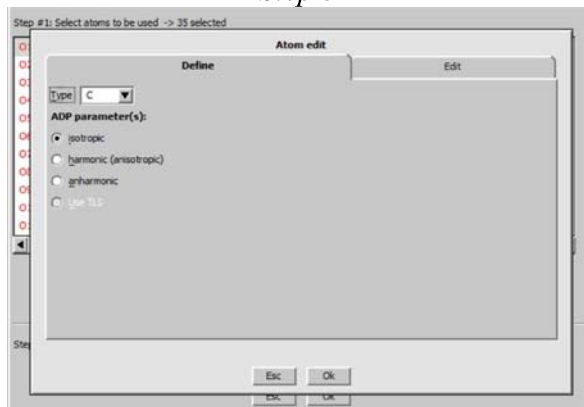
Select Carbon, OK (Step3)

[On the screen: list of atoms.]

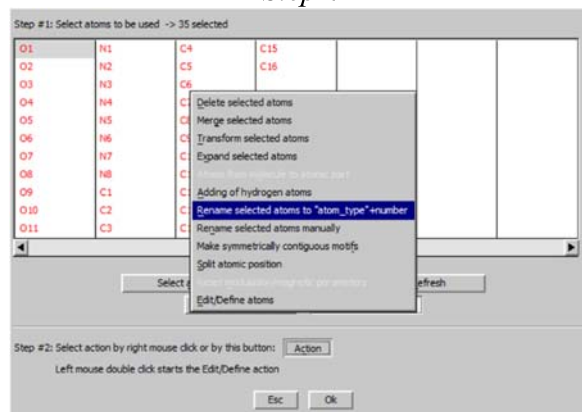
The labels are still the original ones but the chemical type of all atoms is carbon

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"

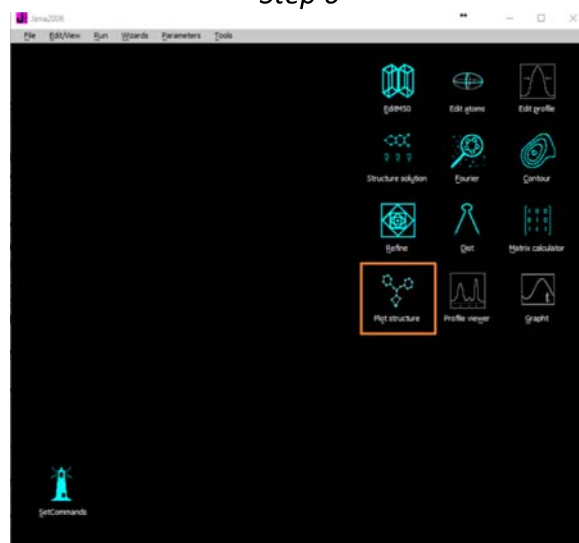
Notes

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

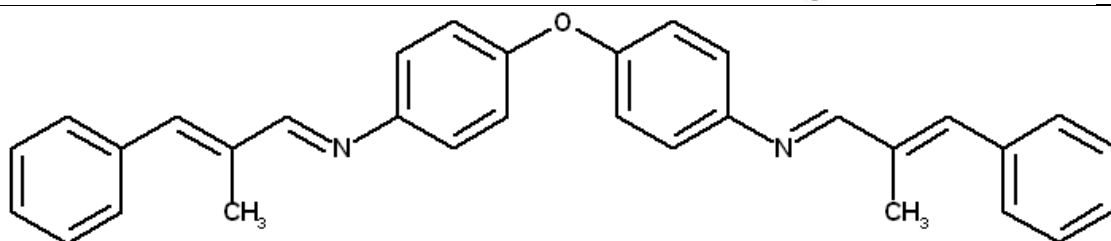
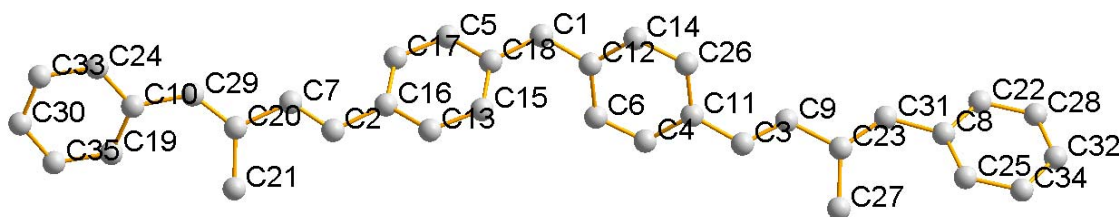
Define text size ~0.8Å; OK

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

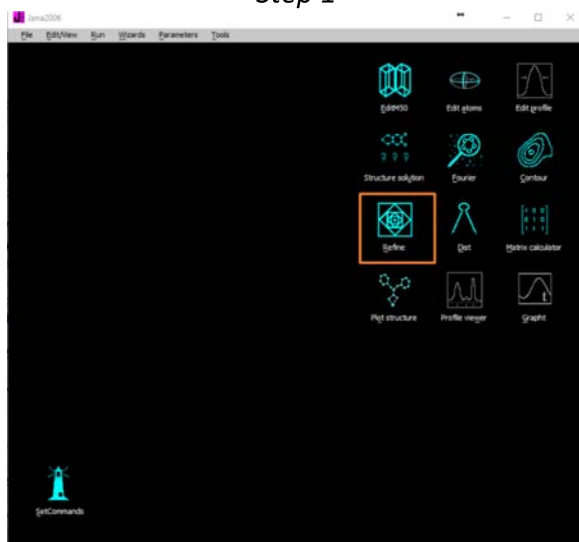
[On the screen: basic window of Jana]
 Right-click the icon of Refine. (Step1)
 [On the screen: refinement options]
 Define 100 of cycles, Instability factor 0.02; OK (Step2)

Notes

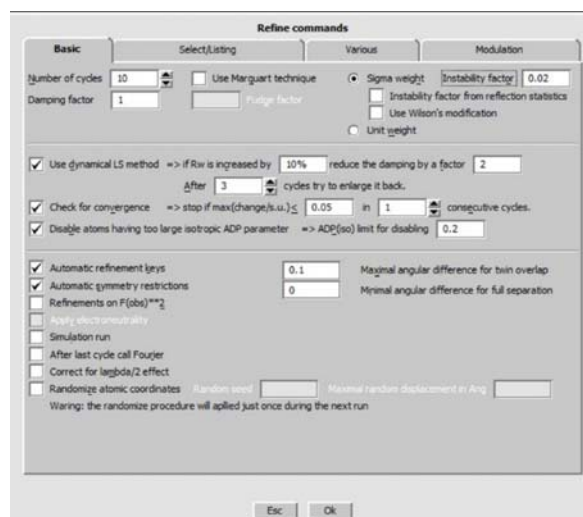
This instability factor slightly lowers goodness of fit, which makes happy editors used for SHELX. However, we cannot change this number arbitrarily because values below 0.01 or above 0.02 are usually in contradiction with the instrument characteristics.

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

Step 1



Step 2



2. Twin volume fraction

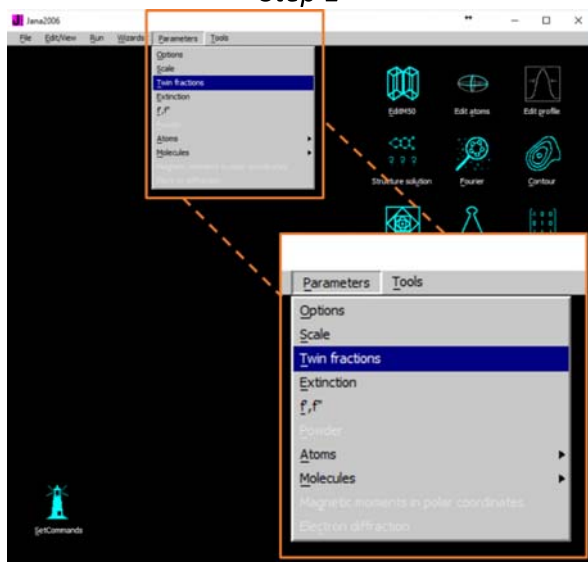
Start “parameters → Twin fractions” (Step1)

Notes

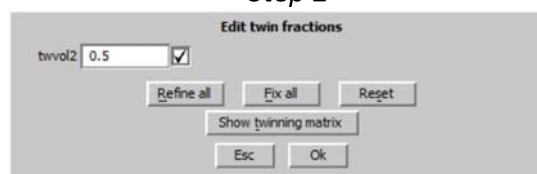
The volume fraction of the twin domain introduced by the Symmetry wizard is 0.5 and twinning matrix relating the monoclinic and orthorhombic symmetry is $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$.

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]

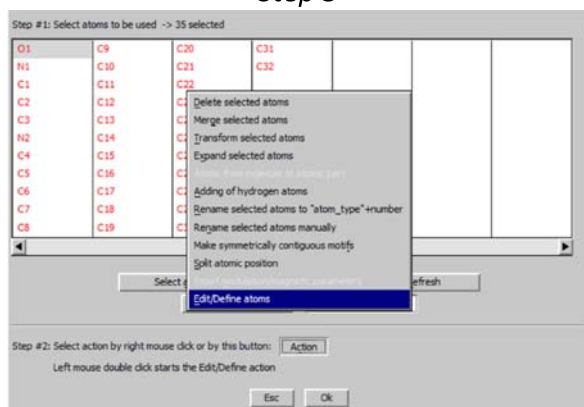
Press “Select all” and “Action → Edit/define” (Step3)

Choose “harmonic” for ADP parameters. (Step4)

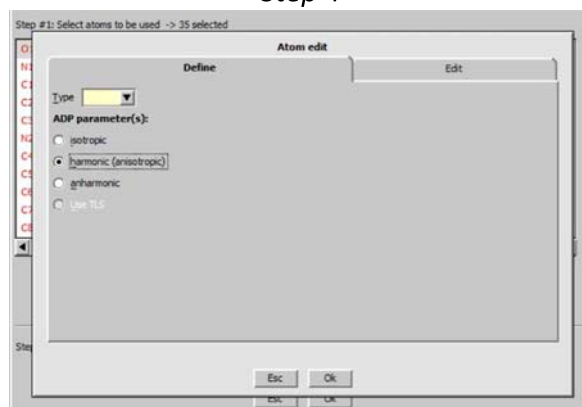
This defines anisotropic temperature parameters for all atoms.

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"

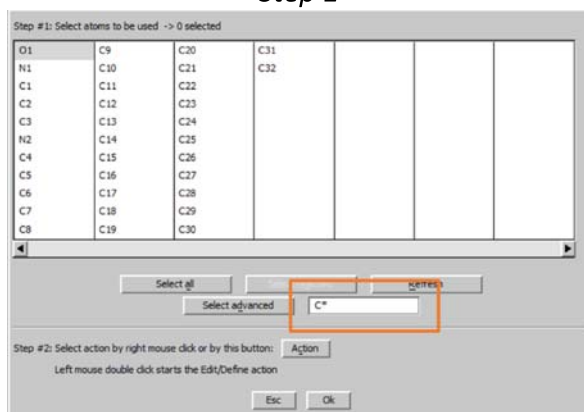
In the textbox type "C*"; TAB. (Step1)

Notes

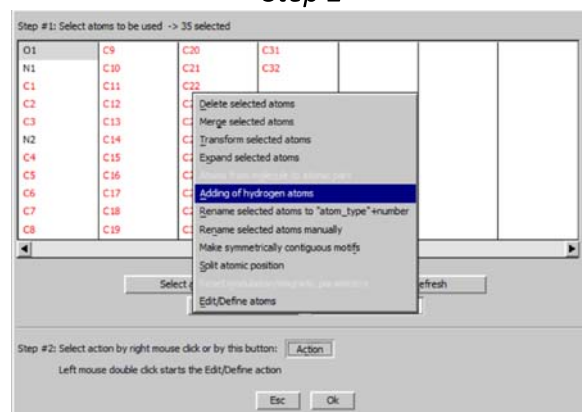
This will select atoms starting with C, i.e. carbons

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)

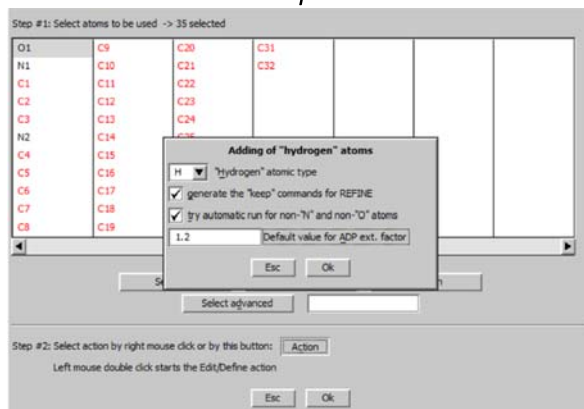
[On the screen: list of atoms with new hydrogens]

Notes

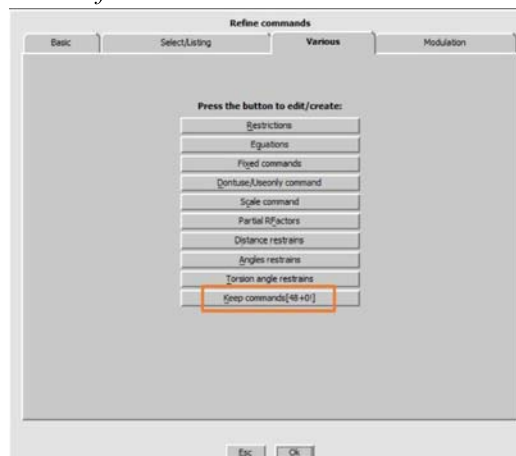
Total number of atoms should be 63 (can be verified using "Select All")

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

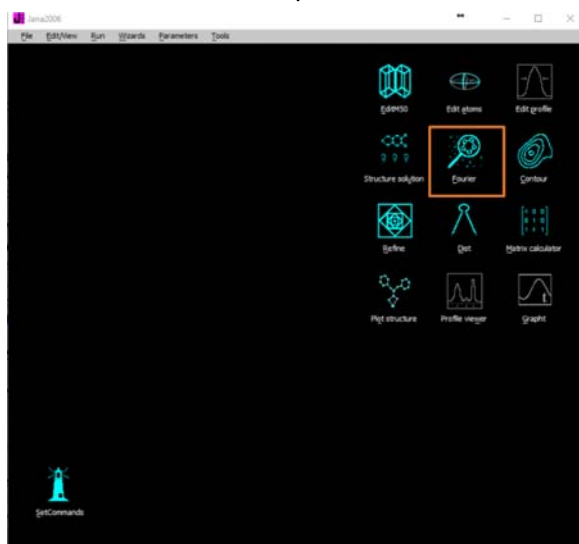
Notes

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

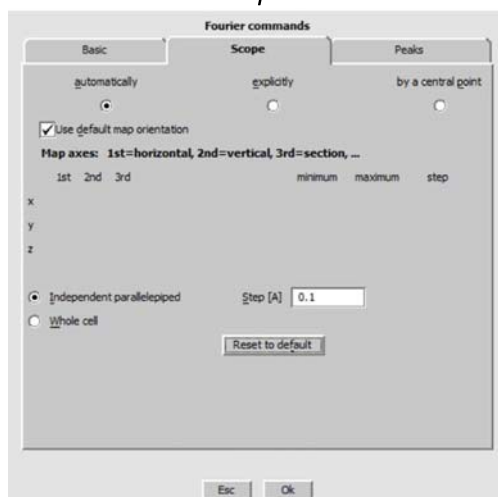


Step 2



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

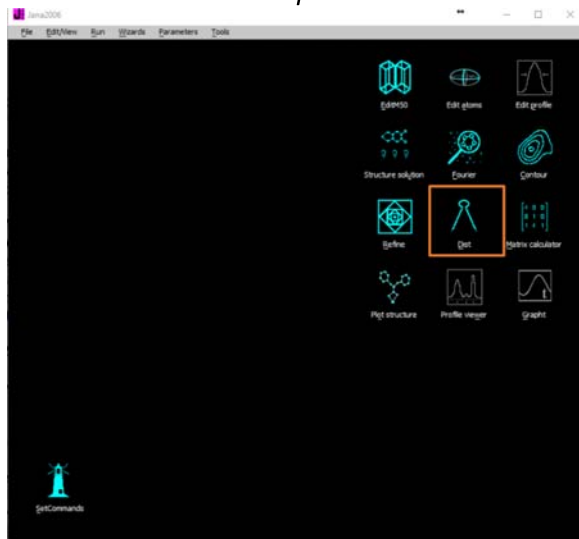


OK; YES+START; NO to include new atoms; NO to see the listing

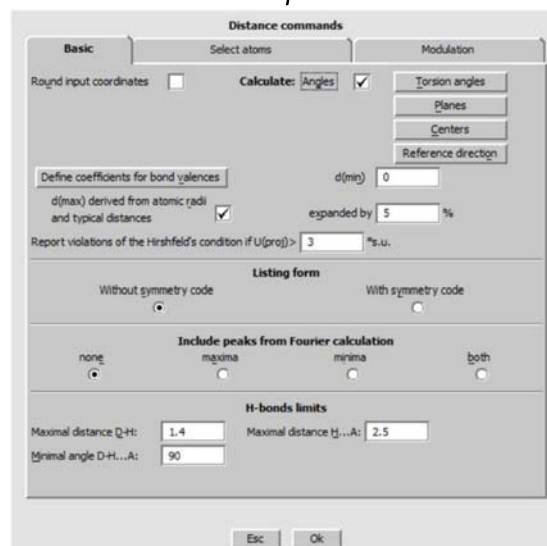
Right-click Dist icon (Step5)

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)

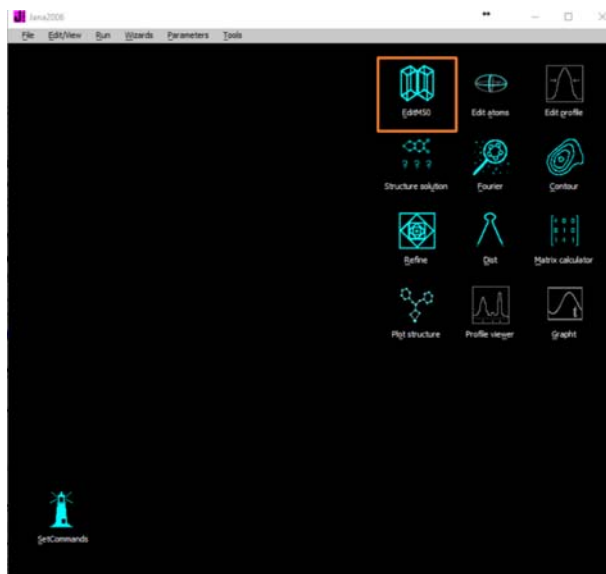
OK; YES+START; Close;

Start EditM50; (Step8)

Step 7



Step 8



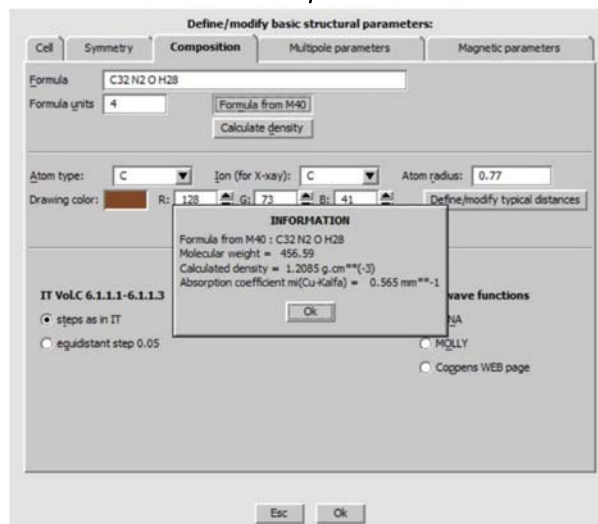
Go to page Composition; enter 4 for “Formula units”, press “Formula from M40” (Step9)

OK; YES for updating the formula.

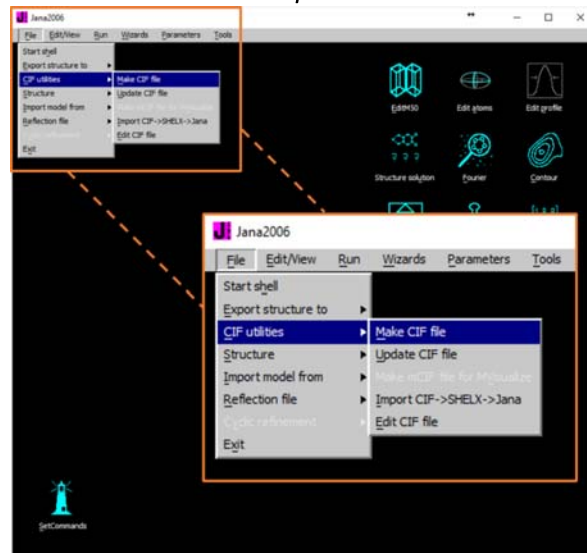
OK; YES to rewrite M50zn

Start “File → CIF utilities → Make CIF file” (Step10)

Step 9



Step 10



References