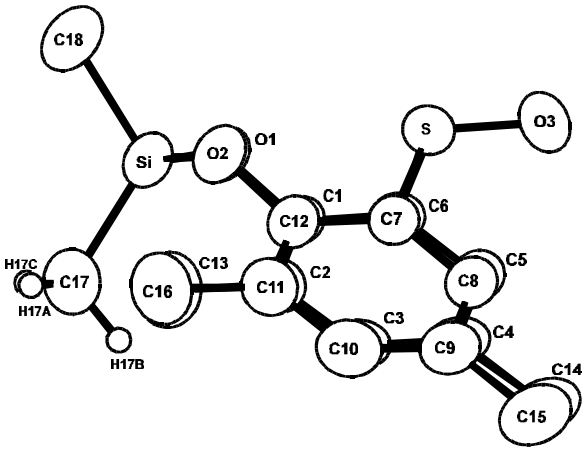
SINGLE CRYSTAL
X-RAY CRYSTALLOGRAPHY

A PRACTICAL GUIDE



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AN OUTLINE

I. CRYSTALS

Select

Mount

Measure density

II. CAD4

Center the crystal

Find cell

Find the space group

Trial data and Good cell

Data collection

III. COMPUTING

Structure solution

Refinement

Tables & figures

I. CRYSTALS

1. Select regular shaped, homogeneously transparent CRYSTALS free from crack and crystallites.

2. Beware of twin crystals.

3. Crystal size better be less than 0.5 mm on any side. Bigger crystals can be cut with good BLADE with care.

4. Select 2 or 3 such crystals.

5. Mount the crystals on a fiber or in a Lindemann capillary. Fix a glass fiber (1.4 cm long) in a metal PIP. Then touch a PASTE with the fiber and touch the crystal so that the crystal is fixed firmly; you can slightly align the crystal before the paste sets.

Put the crystal in a proper sized capillary and place it few mm from the closed end using a glass fiber. Then pick little PASTE in the fiber and apply it in the capillary till the crystal's place and make the crystal stick to it; you can slightly align the crystal. Fuse the capillary about 1.4 cm from the crystal carefully (do not allow the crystal to get heated!). Fix this capillary in a metal PIP.

6. Place the PIP in a GONIOMETER and tighten the screw.

7. Select some bigger crystals and measure density (if possible).

II. CAD4

1. CENTER THE CRYSTAL

A. Check: Water cooler; X-rays on; Interface & Computer on.

B. Give the following commands in the computer
(from **CD0>** prompt)

KP↵
60 11 35 0↵

C. Mount the goniometer in the diffractometer.

D. Switch on the lamp and focus it on the crystal.

E. In the pocket terminal give -60 <move> <kappa>

F. Center the crystal by first adjusting the sides. Then press 101 <move> <psi> in the pocket terminal of CAD4. Again center the sides. Now center the height and then sides. Press 191 <move> <psi> and check/center. Press 281 <move> <psi> and check/center. You can check many times by pressing these angles (11, 101, 191, 281).

G. Switch off the lamp and close the CAD4 sliding doors.

H. Go to the computer.

2. GETTING THE CELL

For data collection we need to have three files. They are *.CRY, *.DAT & *.HKL; the last file is used only when we need to do an absorption correction. The *.CRY file will have the cell, data collection related information. The collected data will be stored in the *.DAT file. You should OPEN a new *.CRY file and a dummy DUM.DAT file (to keep the trial data) at the beginning.

GONCON↵
FCRYST↵
Y↵
*.CRY↵
Y↵ (if a file is there with this name, press Y↵ and give another *.CRY↵)
FILDAT↵

Y↵
DUM.DAT↵
Y↵ (if a file is there with this name, press Y↵ and give another *.DAT↵)
Q↵
LK↵ (to kill the old crystal information)
1 25↵
SEARCH↵
10 0 90↵
12 2↵

(It will search and center a maximum of 25 reflections. You can stop with less reflections and proceed to INDEX↵ or SEARCH↵ in different angles such as 10 20 90 or 10 -20 90. About 20 reflns will be good enough to give a cell. To stop in between: ^C, /S↵, / ↵ and N ↵).

INDEX ↵↵

(Mostly you will get the cell. Even if you have 25 reflns and still do not get cell, call someone else. The crystal may not be good also. See APPENDIX 1)

TRANS ↵↵↵

(You will get a list of systems with NUMBER and Figure Of Merit. Look for the highest system with FOM <0.007)

Number ↵

[You get the new cell parameters. Variations <0.1° & 0.02 Å from ideal system is OK. If it is fairly good press S↵ and Y↵, else Q↵].

TRY VARIOUS SYSTEMS and if you dont get any good one, use the old system itself.

3. FINDING THE SPACE GROUP

Collect trial data for only the required reflns and find the space group; use the DATCIN parameters as noted in the `refining the cell'. Use the following:

THLIM↵
2 21↵
MODE↵
ZIGZAG↵
0 0 0 5 0 5↵

0 0 0↵
LKH↵ (This is to check 0KL reflns. Similarly use the following)

0 5 0 0 0 5↵ (These are for
0 0 0↵ H0L reflns)

0 5 0 5 0 0↵ (These are for
0 0 0↵ HK0 reflns)

Using all these (0KL, H0L, HK0) absences, find the space group.

4. REFINING THE CELL

(To get a good cell, you need to use higher angle reflns with good intensities and with more dispersed indices. To get these, you need to collect a trial data at a fairly high angle range.)

TH↵
10 12↵

(You get the HMAX, KMAX & LMAX. Use them below in the DATCIN data. DATCIN is the DATa Collection INstructions. It is part of the CRY file.)
(KMIN=-KMAX and LMIN=-LMAX for triclinic)
(KMIN=0 and LMIN=-LMAX for monoclinic)
(KMIN=0 and LMIN=0 for orthorhombic)

DATCIN↵
M↵
TEXT↵
CHANDRA'S 100th CRYSTAL P21/N↵
THLIM↵
10 12↵
SCAN↵
0.8 0.35 2.0 1.0 6↵
INT↵
0.5 2 1 5 0↵
PSI↵
BISECT↵
MODE↵
ZIGZAG↵
0 HMAX KMIN KMAX LMIN LMAX↵

0 KMIN LMIN↵
LKH↵
ABSENT↵ (refer CAD4 manual)
1↵
H=0 L<0↵
INTCR↵
0 0.03 0.50↵
Q↵
S↵

DATCOL↵

After this data collection is over, Select 25 good reflections: **Select 3** fairly strong reflections with one of each indices high and also **select 2** strong refln(s) with all indices high. Select 3 sets of 5 reflns with each indices high and select 5 more with all high or medium high indices to make up to 25 total reflns.

LK↵
1 25↵
LH↵
H K L 0↵ (25 times; last number is zero)(give the first five first)

SETANG↵
LS↵
LCA↵
1 25↵
AAAAAAAAAAAAAAAAAAAAAAAAA↵ (25 times)
Y↵
SETANG↵
LS↵

(Now you will be having a good cell, actually good orientation matrix, to start the data collection.)

5. DATA COLLECTION

LO↵
1 25↵

You get the intensities and peakwidths. The last parameter is the intensity (you should divide this by the last-but-two number) and the last-but-one is the peakwidth.

DATCIN↵
M↵
THLIM↵
1.5 21.5↵
SCAN↵
X 0.35 2.0 1.0 6↵
(X is 0.85 times of mean peakwidth of the 25 reflns)
INT↵
0.5 0.05 2 50 0↵
MODE↵
ZIGZAG↵
0 HMAX KMIN KMAX LMIN LMAX↵
0 KMIN LMIN↵
LKH↵ (longest, medium & shortest axes order)
ABSENT↵ (refer CAD4 manual)
1↵
H=0 L<0↵
INTCR↵
10800 0.03 0.50↵
Q↵
S↵

(KMIN=-KMAX and LMIN=-LMAX for triclinic)
(KMIN=0 and LMIN=-LMAX for monoclinic)
(KMIN=0 and LMIN=0 for orthorhombic)

LCI↵
1 5↵
IIIII↵
Y↵

DATCOL↵
(If there was any problem, restart by DATCON↵; you can use DATCOL↵ also. If the PC was down, reboot the PC and give \CAD4↵ as the command in the C:\CAD4\DATA0> prompt to get the CD0> prompt and then give DATCON↵).

When it comes back to CD0> prompt, your data collection is over.

Then give LCA↵ and AAA... ↵(25 times) and Y↵. Give DETTH↵ and when it finishes, give LS↵ to get the final cell & esd.

III. COMPUTING

1. DATA REDUCTION

The data what we have got should now be reduced; The data reduction means applying Lorentz and polarisation corrections (after the raw measurements have been converted to intensity) to get the structure factor amplitude (F or F^2) and its error.

This can be done with the XRAYACS program. The input files needed are ***.CEL and ***.CAD, where *** means any name. The ***.CEL file should have A.F. (21.586), M.A. (6.0), Wavelength (0.71073) and a,b,c,alpha,beta,gamma and the number of intensity controls. ***.CAD is the file we obtain from the other PC after data collection. The program is self explanatory.

Then you get ***.FF2 (or ***.FF1) as the output file. Also check the ***.OUT file to get more idea about the data quality (See APPENDIX 2).

2. STRUCTURE SOLUTION (by SHELXS-86):

Create a file ***.INS with the following:
(free format but first 4 characters are commands).

```
TITL ACS100  P21/n
CELL LAMBDA A B C ALPHA BETA GAMMA
ZERR    (Z and errors of the above)
LATT 1  (see SHELXS or SHELXL manual)
SYMM    (see the manuals and Int. Tables).
SYMM
SFAC C H O
UNIT 10 10 10 (No of atoms in 1 unit cell)
TREF 100
```

Save this file and give the following commands.

```
COPY  ***.INS+***.FF2  ***.INS↵
Y↵
SHELXS  ***↵
```

After the program finishes the structure solution, edit the ***.LST file, find all the atoms and assign correct number of SFAC for each atoms in the ***.RES file

(earlier every atom will be considered as carbon and a number of 1 will be there after the atom number). If there is NO good looking molecule or a part of it, something is wrong!. (see Appendices 2 and 3)

3. STRUCTURE REFINEMENT (by SHELXL-93):

```
COPY  ***.RES  ***.INS↵
Y↵
```

After correcting all the atoms' SFAC number, as much as possible, delete the TREF line and include the following:

```
FMAP 2     (to do a difference Fourier)
PLAN -10    (to get the plot, with ten new peaks)
L.S. 2     (number of cycles of refinement)
```

Delete any MOLE line. Include the following line before the last END command:

```
+***.FF2
```

Save this file and run the refinement program.

```
SHELXL ***↵
DEL  ***.INS↵          (delete the old file)
REN  ***.RES  ***.INS↵
SHELXL  ***↵
```

See the outputs written on the screen, the output file ***.LST and also the Thermal Parameters (TP) of all the atoms. Remove all the atoms with TP higher than 0.2; then take a plot of the molecule and assign atoms unambiguously. Delete wrong atoms or look and include missing atoms. Then continue refinement until the max shift/esd comes to 0.3 or below. Then give a command line ANIS below the FVAR line and run the program. Now, everytime replace the top WGHT line with the WGHT line in the bottom of the file. Refine again and again until the max shift/esd becomes less.

Always watch for the TP and R-factor. If you find some high TP for any correct atoms, check back the ***.LST file and you may be asked to use two positions for that atom(s). Use these positions with a number 10.5000 (instead of 11.0000; these are occupancy + 10) and with one thermal parameter (6 is aniso and 1 is iso). After the refinement if the atoms behave well (the TP are better) then go to hydrogen fixing; you can not fix H for these disordered atoms.

Then FIX the hydrogens using any of the following instructions (** atom names; do not go beyond 80 columns).

```
HFIX 43 ** ** **    (for aryl hydrogens)
HFIX 13 ** ** **    (for tertiary hydrogen)
HFIX 23 ** ** **    (for CH2 hydrogens)
```

HFIX 33 ** ** ** (for CH3 hydrogens) [or HFIX 137]
HFIX 147 ** ** ** (for OH hydrogens)
HFIX ********** (for more see SHELXL manual)

Continue the refinement again (until the max shift/esd becomes less than 0.1).

Now the structure solution & refinement are over.

Also, you might need to do some PLANE calculations which you might do in the SHELXL by using

MPLA N ** ** ** **

(N number of atoms defining the plane; you can give more ** to get the deviation of the latter atoms from the plane)

Give the ACTA command after PLAN command and run the refinement once more (last time!). If your atoms are not matching with the UNIT cell atoms given by you, the program will inform you. Now you copy the CIFTAB.DEF file to your current directory and run CIFTAB program; this converts the output produced by the ACTA command to table form.

Get a ORTEX (or SNOOPI or ORTEP) diagram of the molecule with thermal ellipsoids. If necessary, take some views of rings and other interesting features separately. See APPENDICES 4 and 5.

FOR MORE INFORMATION, SEE THE APPENDICES

APPENDIX-1

GETTING THE CELL

If you have problem in getting the cell, you can try two things.

LCA↵
1 25↵
AAAAAAAAAAAAAAAAAAAAAA ↵ (25 times)
Y↵
SETANG↵
INDEX ↵↵

OR

LO↵
1 25↵

Now you will get a column of numbers. First is the serial number. The next third are H,K,L values; if you did not get the cell, these will be zeros. Next one is theta value. Next three are crystal orientation angles. The last three are about the reflections; The last one is intensity and it should be divided by the first of these. The middle of these is peak width. If it is too broad (>1.0), the crystal quality is not that good but still up to 1.5 we can get the cell (if there is no other problem). If only some are very broad (nearly double than others), it is not good but try to delete them using LK command and their serial number and try INDEX↵↵.

Or delete the reflections which are having three angles too close and then try INDEX↵↵.

Or delete all of them and do SEARCH↵ again in different regions as mentioned in page 5 and try all the above in that list.

If the peaks are broad (>1.5) and have too many close angles and gives some horrible CELL (with a volume in >10,000 or with one length >40) even after all the above checking, you may discard the crystal and try new one or obtain new batch. It may be of some help to ask an experienced person.

APPENDIX-2

DATA REDUCTION

In CAD4 give EXIT↵ command to go to the PC prompt. Then give XRAYACS↵. For the first question give Y↵ and for other(s) give N↵. Then give the first part of the filename; (the filename should have an extension .DAT in contrast to the same program in other PC where it should be .CAD). Copy the .DRD file to a floppy (and take it to the structure solution & refinement PC). Give \CAD4 ↵ in the CAD4 PC before leaving.

Now copy the ***.DRD file into the other PC and run XRAYACS program after making the ***.CEL file(see page 9). Now give Y↵ only to the second question (and also a 2↵ to select F^2) and N↵ for other three (1st, 3rd & 4th) questions. Now you will get the ***.FF2 file which is important and also ***.OUT file which will have some useful information. Now go back to page 9 and proceed.

SOME HINTS ON STRUCTURE SOLUTION

When the SHELXS program is over, edit and look into the ***.LST file. There will be a list consisting of FOM (Figure Of Merit). If any number is smaller than 0.1, you have got your structure for sure. If it is less than 0.2 you may get. If it is more than 0.3, not much hope!.

If your FOM is high and you have not got the structure, check the space group, symmetry lines and also the UNIT cell contents. If you are sure that all these are correct, then use TREF 200 600 (first number is the number of trials and next is the number of E-values to be used). Now run the job again. It may take long time to finish. Sometimes you can increase the number of trials to 500 or 1000 if your computer is fast! If you had ambiguity in space group, then you should try with various space groups. The correct space group will give the structure, if all other things are fine.

APPENDIX-3

SHORT-CUT STRUCTURE SOLUTION

Run the SHELXS program as described in page 9. And copy the file to ***.INS file. Edit the ***.INS file

After correcting the first few Big atoms' SFAC number, (if there is any), delete the TREF line and include the following:

FMAP 2 (to do a difference Fourier)
PLAN -10 (to get the plot, with ten new peaks)
L.S. 3 (number of cycles of refinement)

Delete any MOLE line. Include the following line before the last END command:

+***.FF2

Save this file and run the refinement program.

SHELXL ***↵
DEL ***.INS↵ (delete the old file)
REN ***.RES ***.INS↵
SHELXL ***↵

Now edit the ***.INS file and delete all the atoms with Thermal Parameters above 0.25 and run again. Edit the ***.LST file and see if any of the new peaks has proper distances (not too close or not too far) with other peaks or with the old atoms. If so, edit the ***.INS file (after renaming) and add them above the +***.FF2 line with different names. Also watch for the R1; if it is below 0.20 and there is no new peak with proper distances, ORTEX program can be used to view and rename them. Then it will be easy to look for new atoms and proper atom assignment. Then rename the ***.EDT file as ***.INS file and refine. If any atom was missing, now you can find out from the ***.LST file and include them before the +***.FF2 line. This will make the structure solution free of printouts and is called paperless shelx according to ORTEX author. Go back to refinement.

APPENDIX-4

GETTING A SNOOPI DIAGRAM

COPY ***.RES S80.SHX

Then edit the S80.SHX file and delete the lines other than coordinates and CELL; you can delete all hydrogens also. Delete all the AFIX lines also.

SNPI↵ **(all CAPS locked)**

$DATA↵
SHELX↵
$CONN↵
$↵
$ELLIPSE↵ (or SOLID and then skip BOUND)
BOUND↵
BOND 1 0.08 3 0.16↵
$↵
$VIEW↵
NOFR↵
$↵

Now you get a view of the molecule in the screen. If you press <print screen> key(after switching on the printer) you will get the rough plot. You can change the view using the following commands.

PLANE ALL↵ (default)
PLANE ** ** ** ** **↵ (atleast three atoms)
ALONG ** **↵ (any two atoms; or AO, BO, CO)
VERT ** ** ↵ (any two atoms)
HORIZ ** ** ↵(any two atoms)
XROT XX ↵ (some angle)
YROT XX↵
ZROT XX↵

$END↵

DRAW↵↵↵

goto windows and Corel Draw. Import the HP1.PLT and HP2.PLT with 80% compression in horizontal points. Play with the options and print from there to get a good diagram. Change the thickness of lines to 0.018 inch. You can label the atoms manually; use ARIAL or TIMES NEW ROMAN font, 13 to 15 point size and BOLD characters. Then delete the old labels.

APPENDIX-5

GETTING AN ORTEX DIAGRAM

ORTEX is the best program to see the molecule; it also lets you edit (delete or rename) the atoms and it reads the SHELXL program input file. So any time in between the refinement you can see the molecule and name the atoms in the screen. BUT MOUSE IS MUST!. Just follow the following instructions.
[IMPORTANT: When ever there is a question, the default answer will be displayed in brackets. If you want to choose the default, you MUST press ↵ only!!!! If you type any other key, it will be taken as other answer. If the default is Y, even if you press Y, it will be taken as N.]

COPY ***.INS DUM*.INS↵
EDIT DUM*.INS ↵ (delete the +***.FF2 command line and save)
ORTEX↵
DUM*↵
N↵
4 ↵↵
↵
X↵ (If the maximum bond length is less than X Å, X<2.0)
0, 1 or 2↵↵ (number of Big atoms)
** ↵↵↵↵ (** the last atom bonded to any of the Big atoms; they should follow the Big atoms, in INS file; otherwise wrong bonds will be drawn)
Y↵
4 ↵↵
4 ↵↵
↵

Now you will get a stick diagram

You can rotate the molecule using the mouse; click on the STEP 10 (or 5 or 1 degree) and click on the +X or -X or +Y or -Y or +Z or -Z. When you are satisfied with the view you can EDIT the molecule (DELETE the unwanted atoms and Rename the good ones, if you are in the beginning stage of the structure solution). After EDITing is complete, you can click the END and in the stick diagram click the Label to see whether the labels are OK. If not OK, go back to EDIT mode and RENAME (or DELETE) again, and come back to stick diagram. When done, click EXIT (and one ↵ if you are asked a question).

(continued…)

APPENDIX-5 (…continued)

Now you will have the renamed atoms list in a file DUM*.EDT. You can edit this file and make as ***.INS file. You can continue the refinement.

If you have completed the refinement and want to take the final Figure, proceed as above and don't go to the EDIT mode; instead go to (click) Atom mode. Now you will get a better diagram.

Click the Atoml (small L); the figure will get labels with bigger atoms and bonds. Now click Plot and press ↵ ↵, DUM*.PLT, ↵ ↵.

Click the Outln; the figure will have no labels now.
Now click Plot and press ↵↵, ***.PLT, ↵↵.

Now click Stick and EXIT.

These two files can be plotted either from Word for Windows' Draw program or from CORELDRAW. The DUM.PLT will have poor quality labels and can be used as a guide to label the second file's figure; use ARIAL or TIMES NEW ROMAN font, 13 to 15 point size and BOLD characters. You will have the best Figure.

APPENDIX-6

GETTING THE TABLES

```
COPY \EXE\CIFTAB.DEF↵

CIFTAB↵
***↵                    (***.INS file's first name)
T↵
↵↵ ↵↵↵
N↵
↵↵
Q↵

FOFC↵          (this is to convert the Fo-Fc
***.FCF↵       table to a short and nice form)
FOFC.*** ↵
```

Your ***.TEX and FOFC.*** files are the final tables. So keep them safely. Edit the ***.TEX and add your flavor, if you want to decorate it. The FOFC.*** file should be edited through WINWORD and the guide lines in the beginning of the file to be followed.

APPENDIX-7

THE NECESSARY TABLES ARE: (always with esd)

1. Crystallographic data
2. Coordinates with Ueq for non-Hydrogens
3. Anisotropic thermal parameters for non-Hydrogens
4. Bond Lengths and Bond Angles involving non-Hydrogens
5. Hydrogen coordinates
6. Fo-Fc table

7. Planes & Torsion angles (if important)
8. H-bonds & other interactions (both intra- & inter- molecular)

FIGURE

1. Single molecule (with or without **thermal motion)**
2. Stereoview & Packing diagram.

THE PROGRAMS NEEDED:

1. XRAYACS.EXE (Does all the manipulation of the DATA)
2. SHELXS.EXE (Solves the structure)
3. SHELXL.EXE (Refines, finalizes and calculates bond parameters….)
4. CIFTAB.EXE & CIFTAB.DEF (Makes table from the SHELXL's output)
5. ORTEX program files (or SNOOPI.EXE) (Makes Figure)
6. FOFC.EXE (Makes a compact table for FoFc data)
7. WORD for Windows (Helps to edit and print the tables and Figure)
8. CORELDRAW program (Helps to edit and print the Figure)