Practical Guide to Stucture Solution, Refinement and Publication.

SHELXTL

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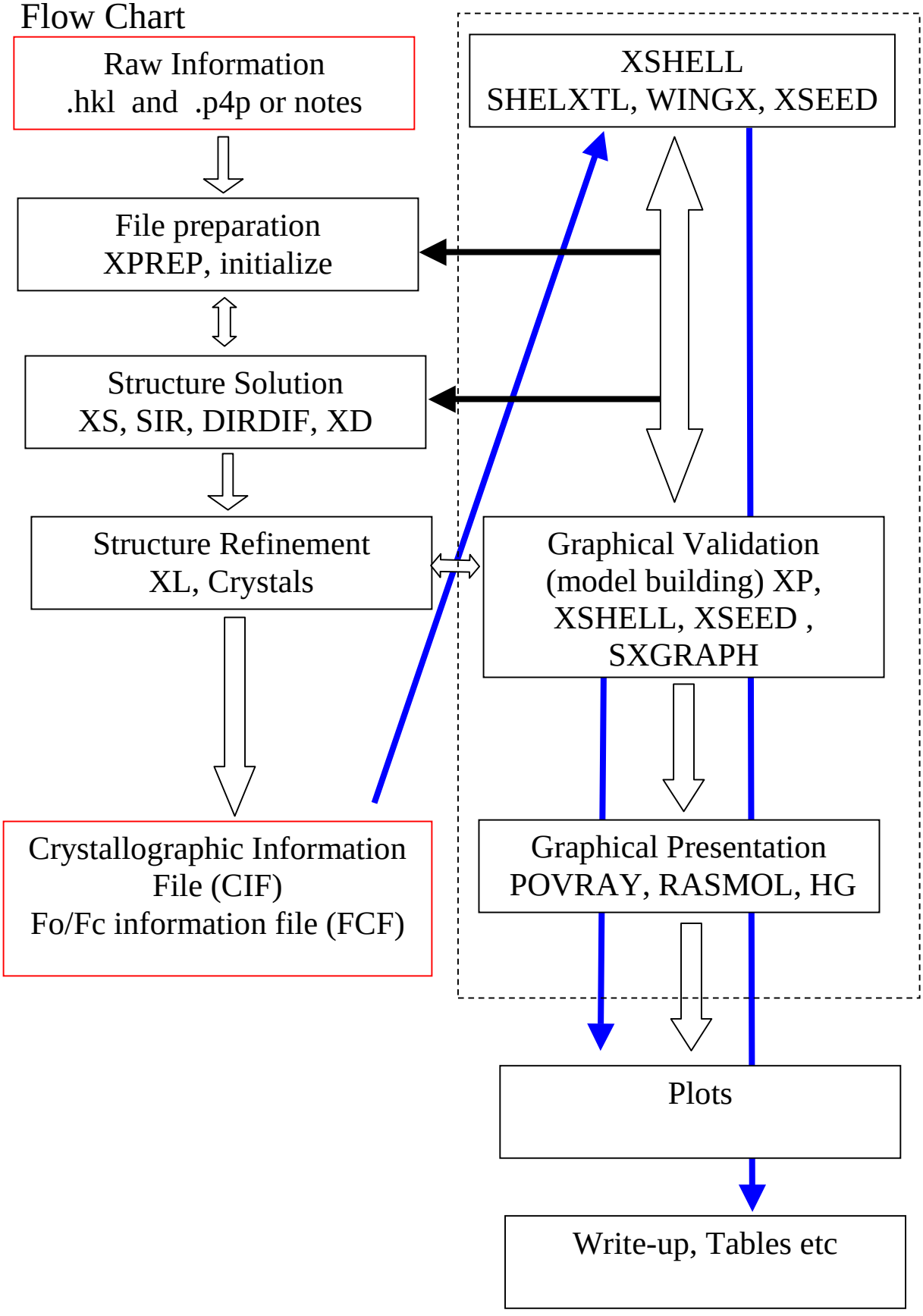
Version 1.0.0

Flow Chart


Raw Information
.hkl and .p4p or notes
File preparation
XPREP, initialize
Structure Solution
XS, SIR, DIRDIF, XD
Structure Refinement
XL, Crystals
Crystallographic Information
File (CIF)
Fo/Fc information file (FCF)
XSHELL
SHELXTL, WINGX, XSEED
Graphical Validation
(model building) XP,
XSHELL, XSEED ,
SXGRAPH
Graphical Presentation
POVRAY, RASMOL, HG
Plots
Write-up, Tables etc

Shell Programs

SHELXTL – BRUKER

a) license stipulates that program can be loaded only on computers owned by the university.

XSEED – L. Barbour

a) license stipulates that program must be used by university employees. If you leave the university then your license is no longer valid.

WINGX – L. Farrugia

a) Freeware, must register with Farrugia.

Other programs

SHELXS, SHELXL - Free must register with G. Sheldrick
SIR88,SIR97,SIR2002 – Free must sign license with C. Giacovazzo
RASMOL, POVRAY, MERCURY

Data Input: 3I4, 2F8.2 $h,k,l, I, \sigma(I)$ [*.hkl]

Parameter file from SMART [*.p4p]

Information required :

a) Molecular Formula (unit cell contents)
b) Anticipated structure

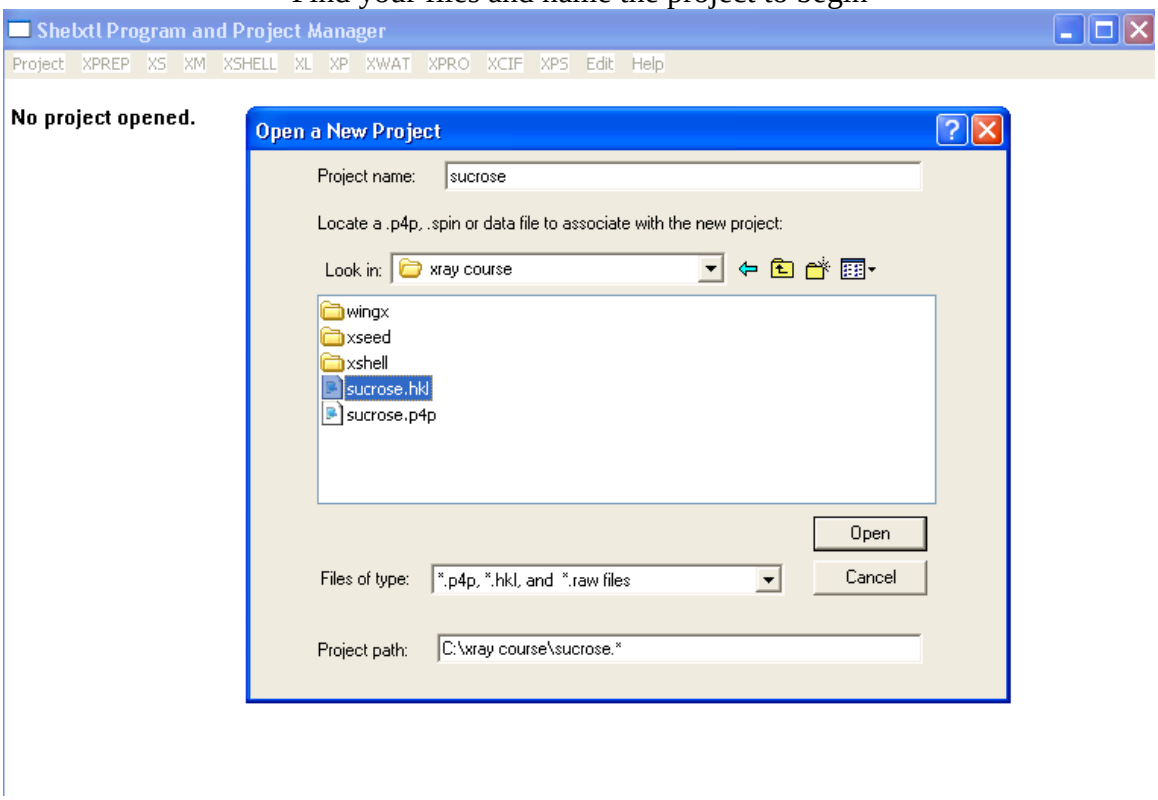
Output crystallographic information file CIF

Crystal Data
Coordinates
Bond lengths and angles
Thermal parameters
Hydrogen atoms

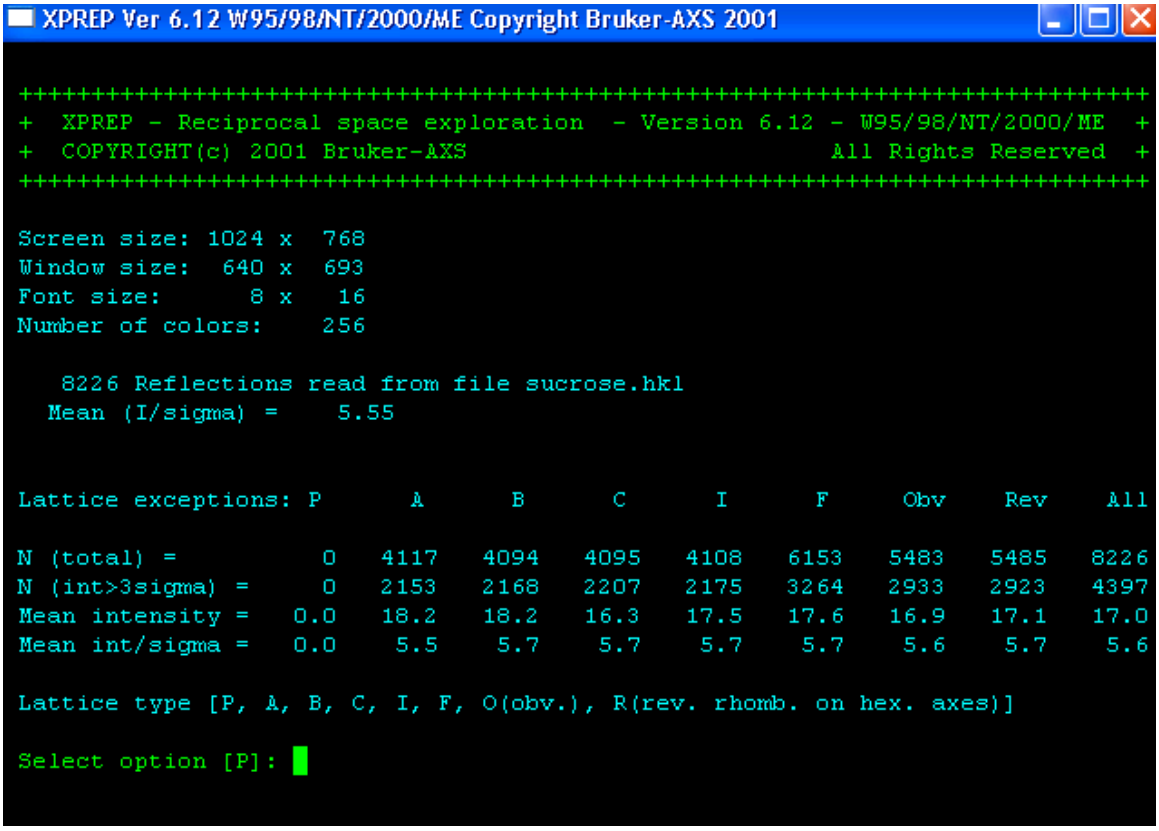
Fo/Fc information FCF

Getting Started. SHELXTL

- Move the *.hkl and *.p4p file to a new directory
- Start SHELXTL
    - Point to PROJECT and then NEW.
        - Find your files and name the project to begin



    - Point to XPREP and start program
        - A new widow will appear

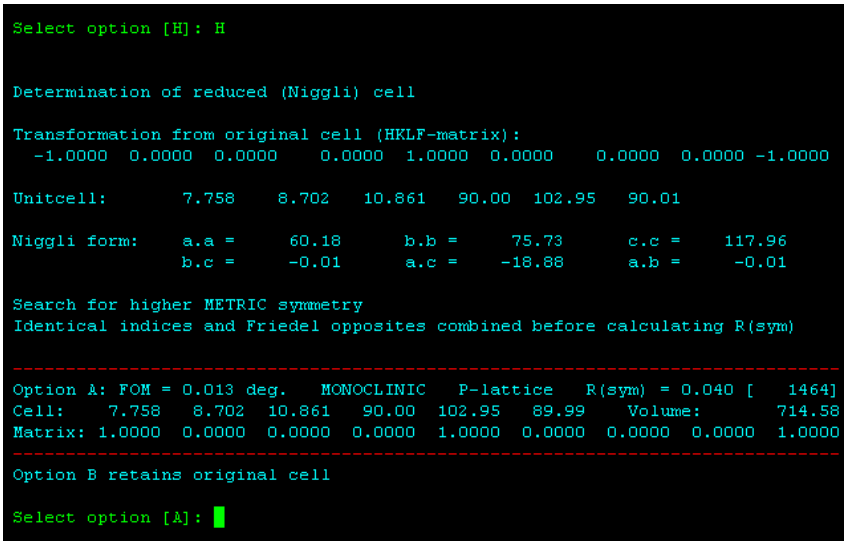


in this case choose the primitive cell (based on the statistics)

Mean Intensity >> mean I/sigma(I) for A,B,C,I, F etc.

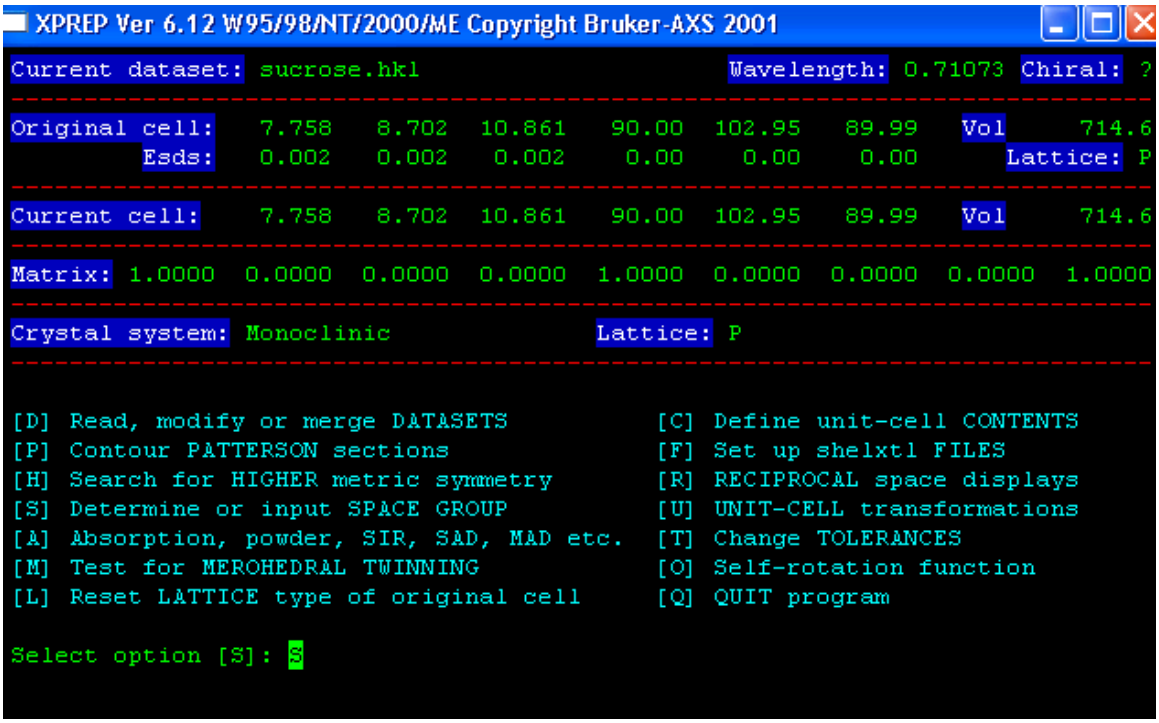
Number of I > 3 sigma(I) is large for A,B,C,I,F, etc.

Search for Higher Symmetry.

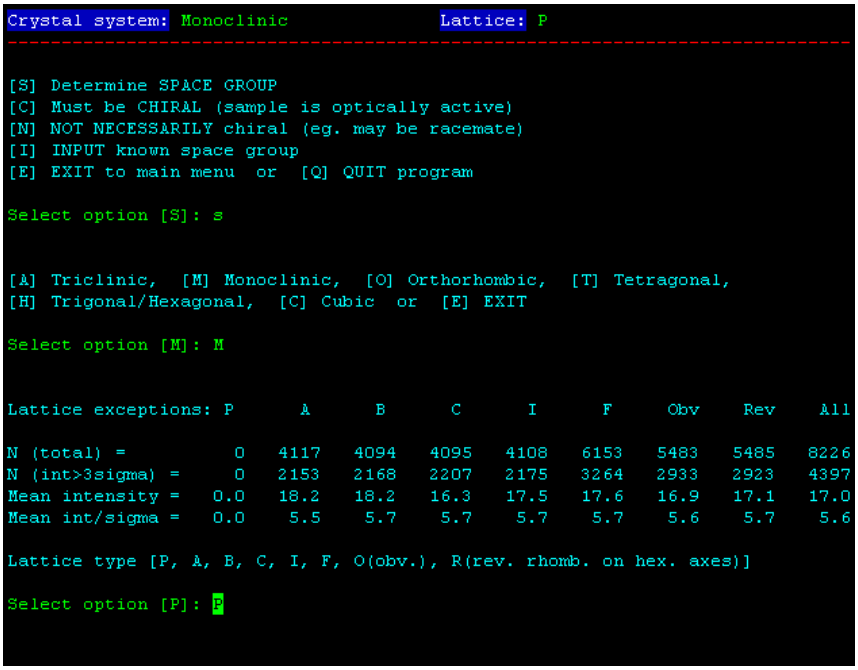


In this case the Monoclinic Cell is chosen (notice an Rsym > .1 may indicate that the choice of the cell is wrong)

Select Determine or Select Space Group from main menu.



Now set up the automatic space group determination



```
Lattice exceptions: P      A      B      C      I      F     Obv    Rev    Al

N (total) =          0   4117   4094   4095   4108   6153   5483   5485   822
N (int>3sigma) =     0   2153   2168   2207   2175   3264   2933   2923   439
Mean intensity =   0.0   18.2   18.2   16.3   17.5   17.6   16.9   17.1   17.
Mean int/sigma =   0.0    5.5    5.7    5.7    5.7    5.7    5.6    5.7    5.

Lattice type [P, A, B, C, I, F, O(obv.), R(rev. rhomb. on hex. axes)]

Select option [P]: P


Mean |E*E-1| = 0.792 [expected .968 centrosym and .736 non-centrosym]


Systematic absence exceptions:

       -21-   -a-   -c-   -n-

N        18   304   301   297
N I>3s    0   164   156   154
<I>     0.1  37.6  35.4  36.9
<I/s>   0.4   6.8   6.0   6.5


Identical indices and Friedel opposites combined before calculating R(sym)

Option  Space Group  No.  Type  Axes  CSD  R(sym) N(eq)  Syst. Abs.   CFOM

[A] P2(1)          #  4  chiral   1  3543  0.040   1464  0.4 /  5.6   2.11
[B] P2(1)/m        # 11  centro   1   402  0.040   1464  0.4 /  5.6   5.13

Select option [A]:
```

notes :

The E^2*-1* statistics predict a non-centrosymmetric space group
I > I/sigma(I) for the a,c and n glides
I < I/sigma(I) for 2_1 screw axis
N (I>3 sigma(I)) is 0 for 2_1

Space group can be P 2_1 and P 2_1/m
P2_1/m is a centrosymmetric space group and not consistent with the E^2*-1* statistics. The structure has a known chrial carbon center (i.e. the space group cannot contain a mirror plane or an inversion center)

Space P 2_1 is chosen.

(see the attached handout for help in choosing space groups)

```
[D] Read, modify or merge DATASETS          [C] Define unit-cell CONTENTS
[P] Contour PATTERSON sections              [F] Set up shelxtl FILES
[H] Search for HIGHER metric symmetry       [R] RECIPROCAL space displays
[S] Determine or input SPACE GROUP          [U] UNIT-CELL transformations
[A] Absorption, powder, SIR, SAD, MAD etc.  [T] Change TOLERANCES
[M] Test for MEROHEDRAL TWINNING            [O] Self-rotation function
[L] Reset LATTICE type of original cell     [Q] QUIT program

Select option [D]: C
```

Skip D (for now) and define unit-cell contents

```
Enter formula; numbers follow elements or brackets, 2nd character of element
name must be lower case, may include: Me, Et, Pp, Bu, Ph, or Cp:
C12 H22 O11


Tentative Z (number of formula units/cell) =   2.0  giving rho = 1.591,
non-H atomic volume =  15.5  and following cell contents and analysis:

C      24.00    42.10 %              H      44.00     6.48 %
O      22.00    51.42 %

[Z] change Z,  [F] new FORMULA,   [R] change RADIATION,
[E] EXIT to main menu  or  [Q] QUIT program

Select option [E]:
```

Enter the formula $C_{12}H_{22}O_{11}$ for sugar. Check the Tentative Z value (should be near 2 for this space group) and the density (see density handout for more information)
If ok choose E and return to main menu.

Choose F from the main menu and write the SHELXTL files.

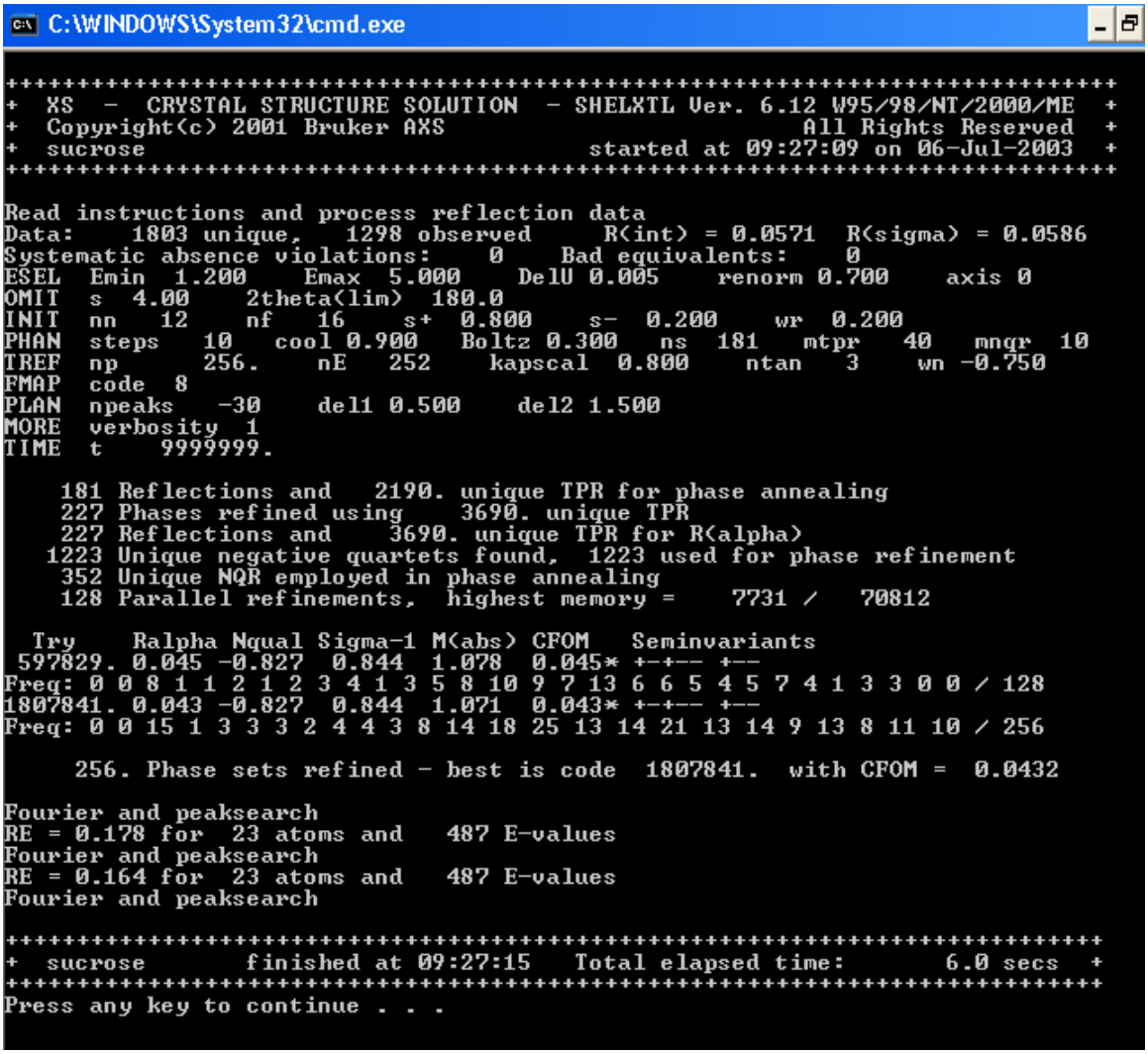
```
Select option [D]: F

Output file name (without extension) [sucrose]:


File sucrose.ins set up as follows:

TITL sucrose in P2(1)
CELL 0.71073   7.7576   8.7022  10.8611  90.000 102.946  90.000
ZERR    2.00   0.0018   0.0020   0.0025   0.000   0.004   0.000
LATT -1
SYMM -X, 0.5+Y, -Z
SFAC C H O
UNIT 24 44 22
TEMP 0
TREF
HKLF 4
END

Do you wish to (over)write the intensity data file sucrose.hkl ? [N]:
```

You may need to write a new file/project name if the program has transformed the unit cell. If you have a backup copy of the HKL file then overwrite the old file here.

Quit the program now and go back to the SHELXTL program

Point to XS to get started (If you had to generate a new file in xprep then go back to project and start a new project)

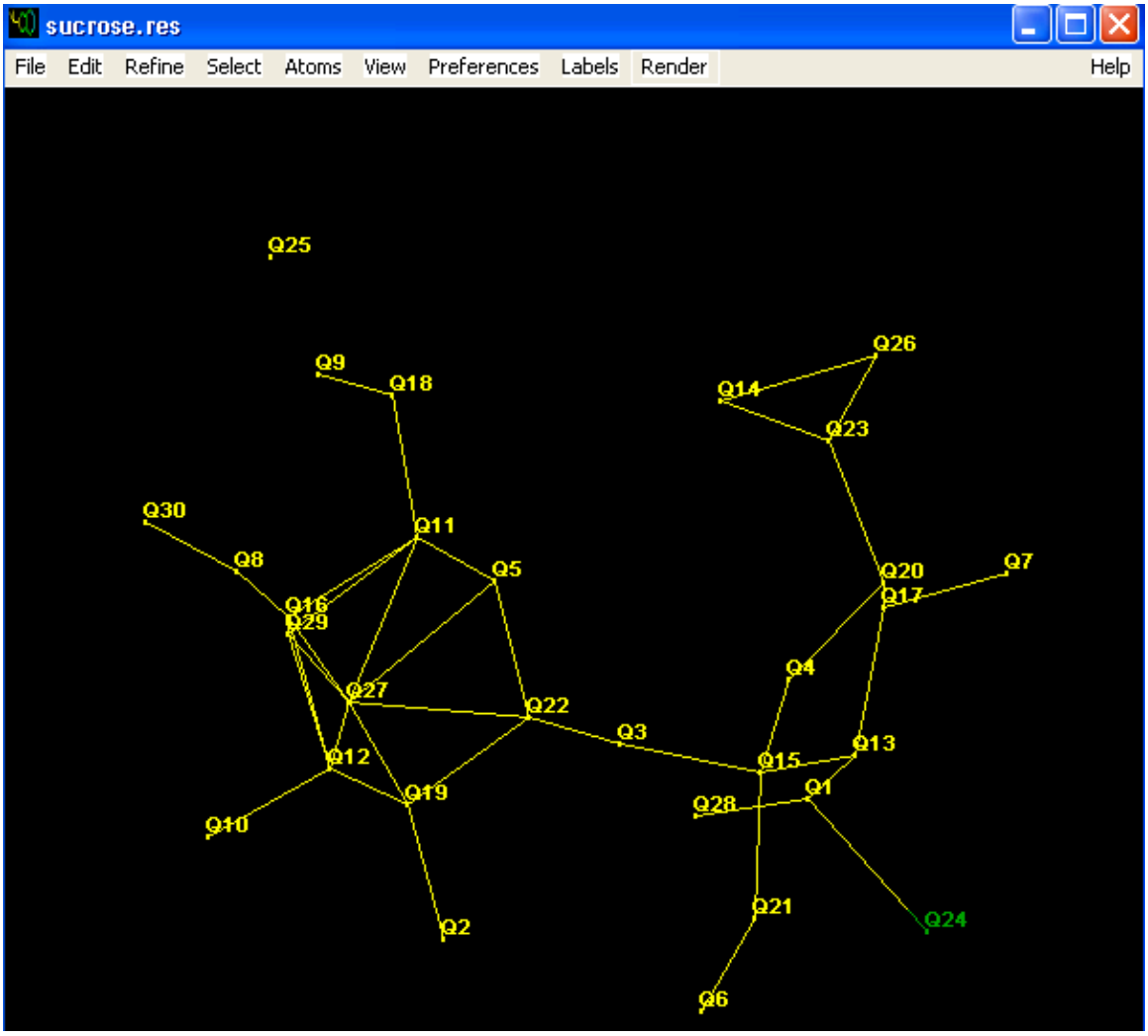
The XS window will start



notes :

The Rint and Rmerge is low (structure is solvable!)
CFOM is low (below 0.1 structure is solved!)
RE is low (below 20%)

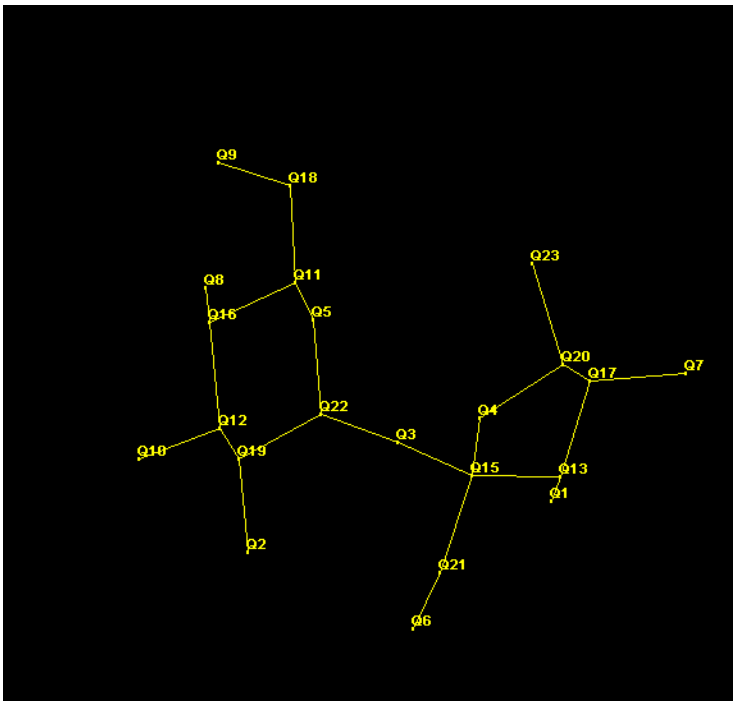
Point to XSHELL



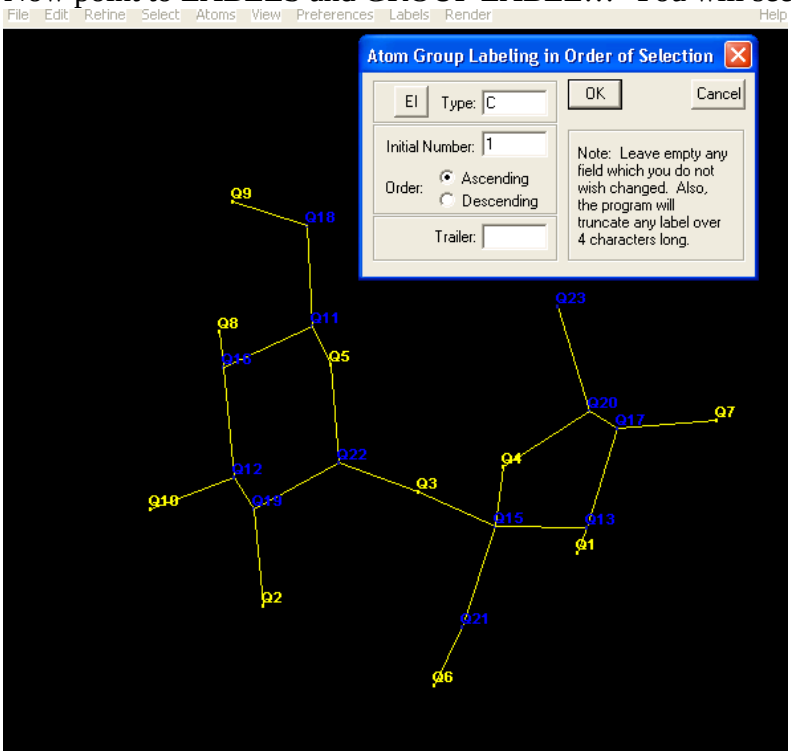
Here is the solution with a few false peaks (Q29, Q27, Q26 etc)

Move the cursor over a false peak (say Q29) and type K. Repeat for each false peak until basic structure (or fragment) is seen. Not all of the atoms may be present in this run. For example Q14 and Q26 in the example above may be misplaced. Let us delete both of them and see if one of them returns in the next run.

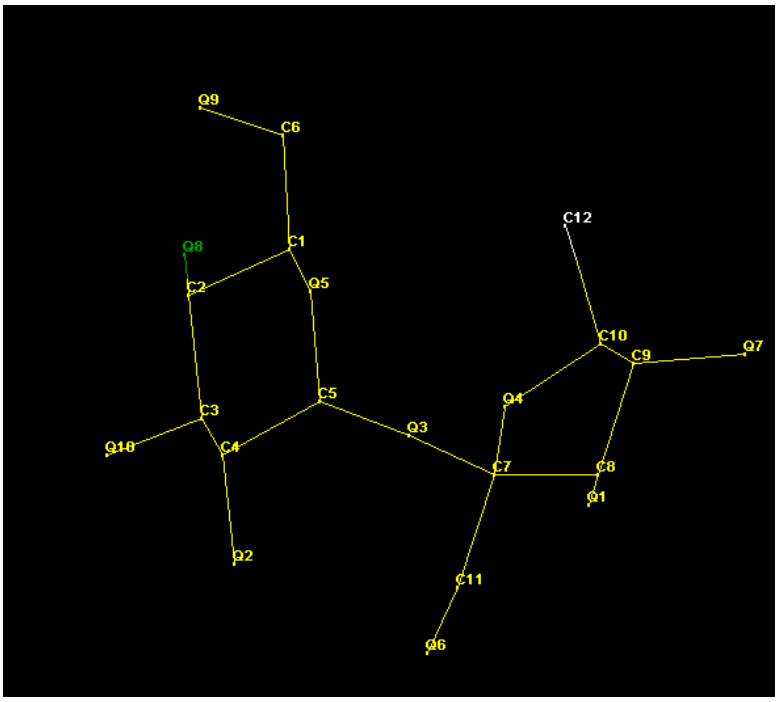
When finished it should look like this.



Now use the select command to choose atoms. Let us choose carbon atoms first. Move cursor to Q11 and type S: Q11 will turn blue. Repeat for Q16, Q12, Q19, Q22, Q18, Q15, Q13, Q17, Q20, Q21 and Q23 (in that order).
Now point to LABELS and GROUP LABEL… You will see



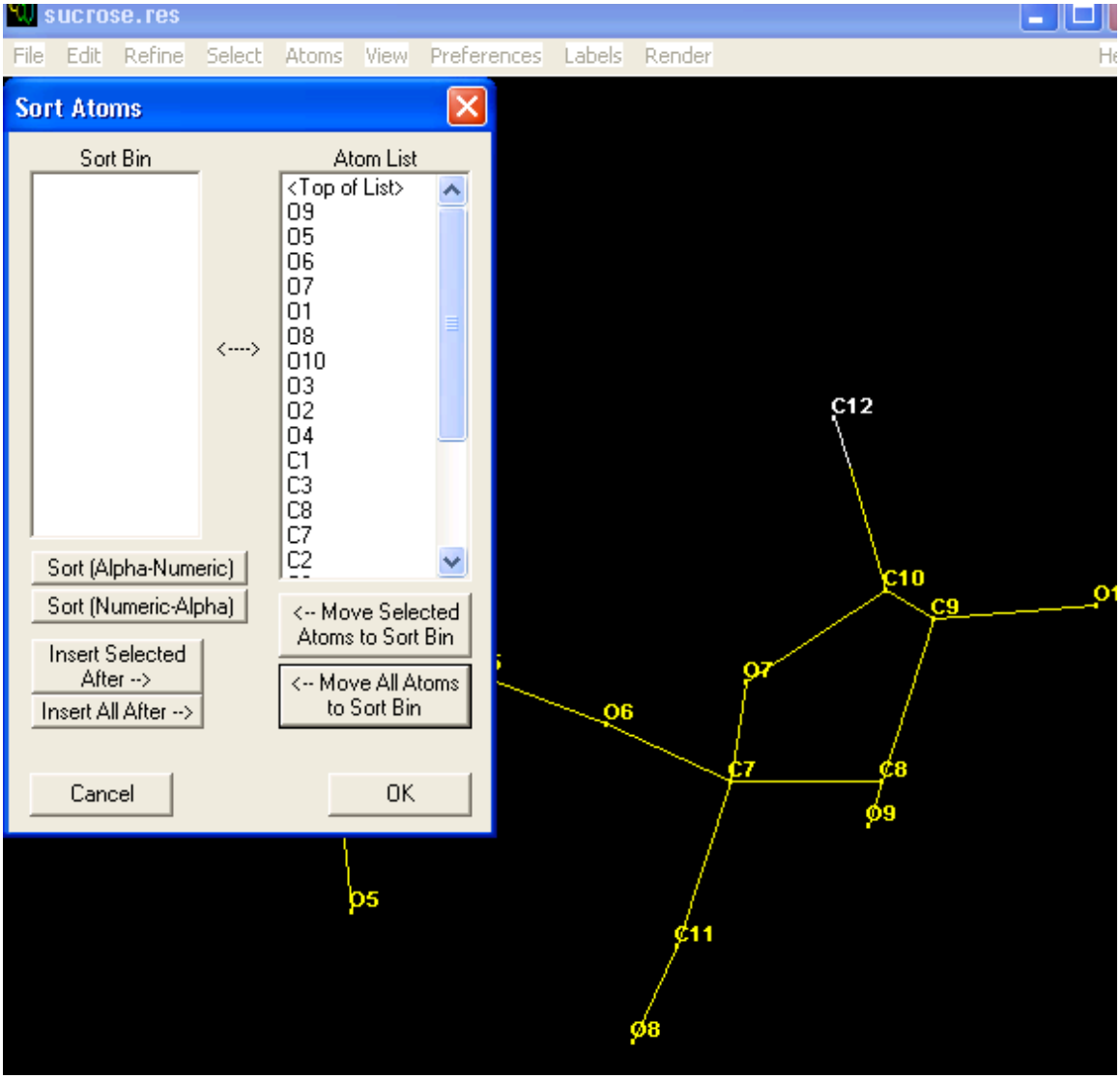
Select type C and initial number as 1 and OK. This will label the carbons(starting a Q11)



Repeat for Oxygens starting at Q5 (Q5, Q9,Q8,Q19,Q2,Q3,Q4,Q6,Q1,Q7)

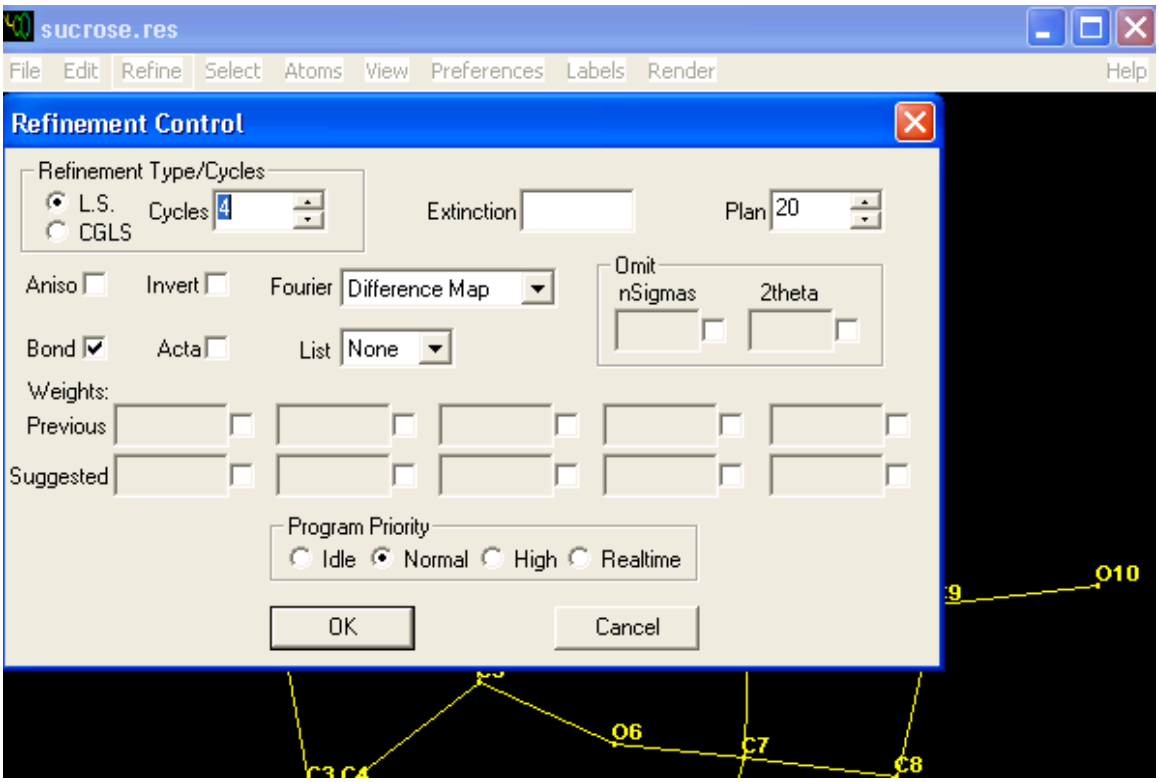
Point to LABELS and GROUP LABEL… and change type to O and type OK.

Now sort the atoms. Point to ATOMS and SORT… you will see

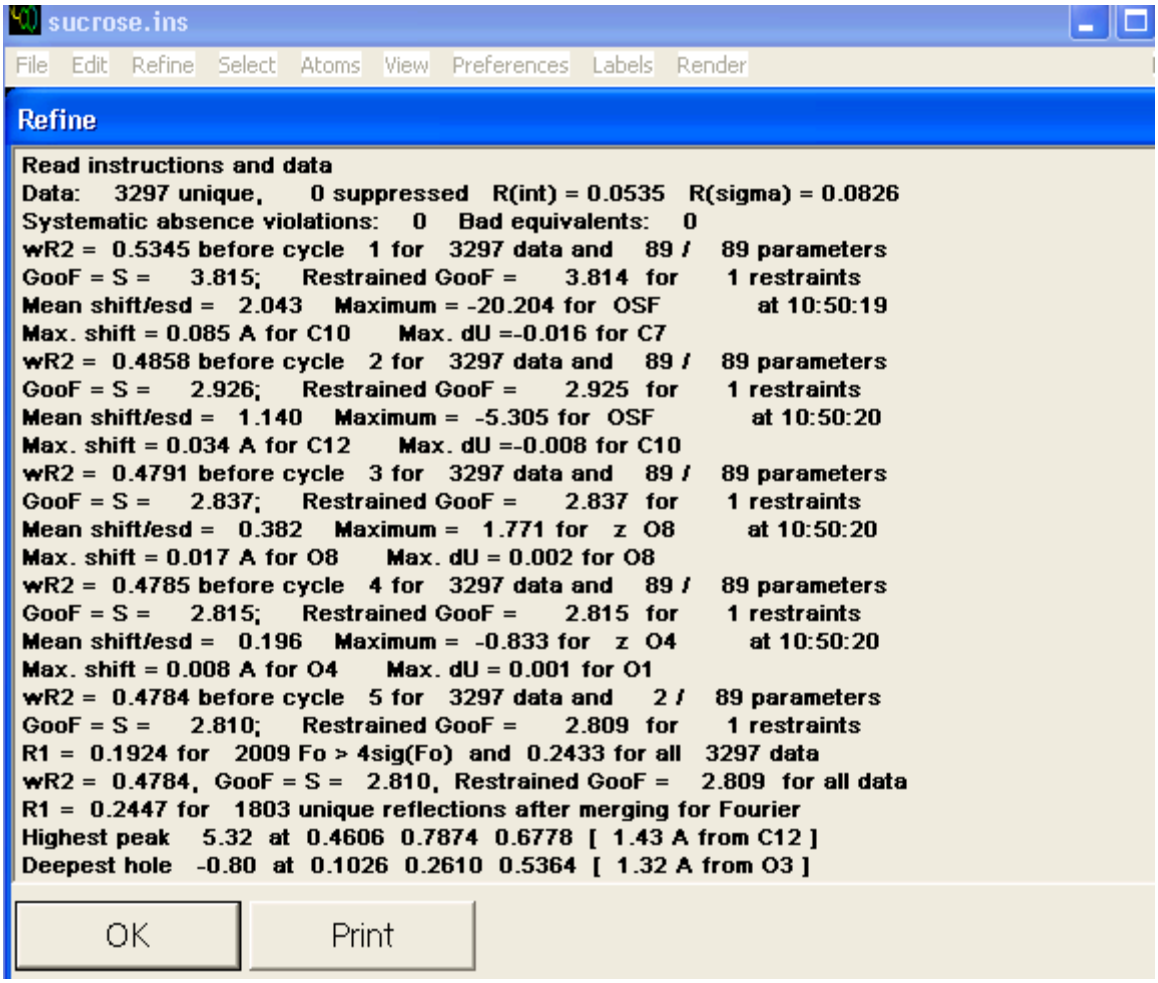


Move all atoms to sort bin. Sort alpha numeric and insert all after <Top of List> (select <Top of List> to proceed). Type OK.

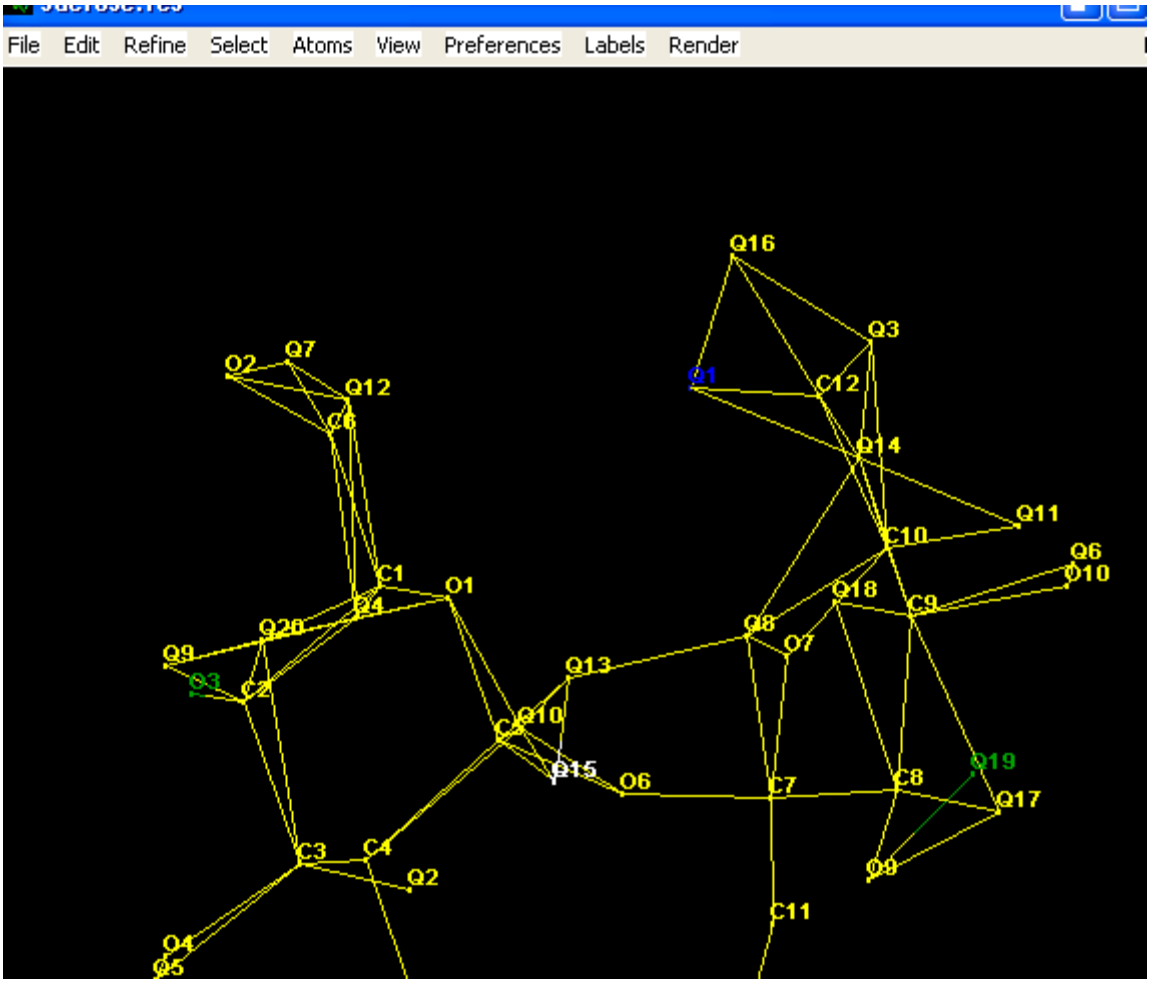
Point to Refine



point to OK and proceed.



Notice the R1 is large (.1924) we are still missing an atom (the peak that is 1.43 A from C12). Point to OK



Select Q1 by moving the cursor over it and typing S. Use Group Label to Label it O11. Kill the remaining Q peaks by pointing to EDIT this Kill all Q peaks. Point to atoms and sort to resort atom list.

Point to refine again and repeat refinement.

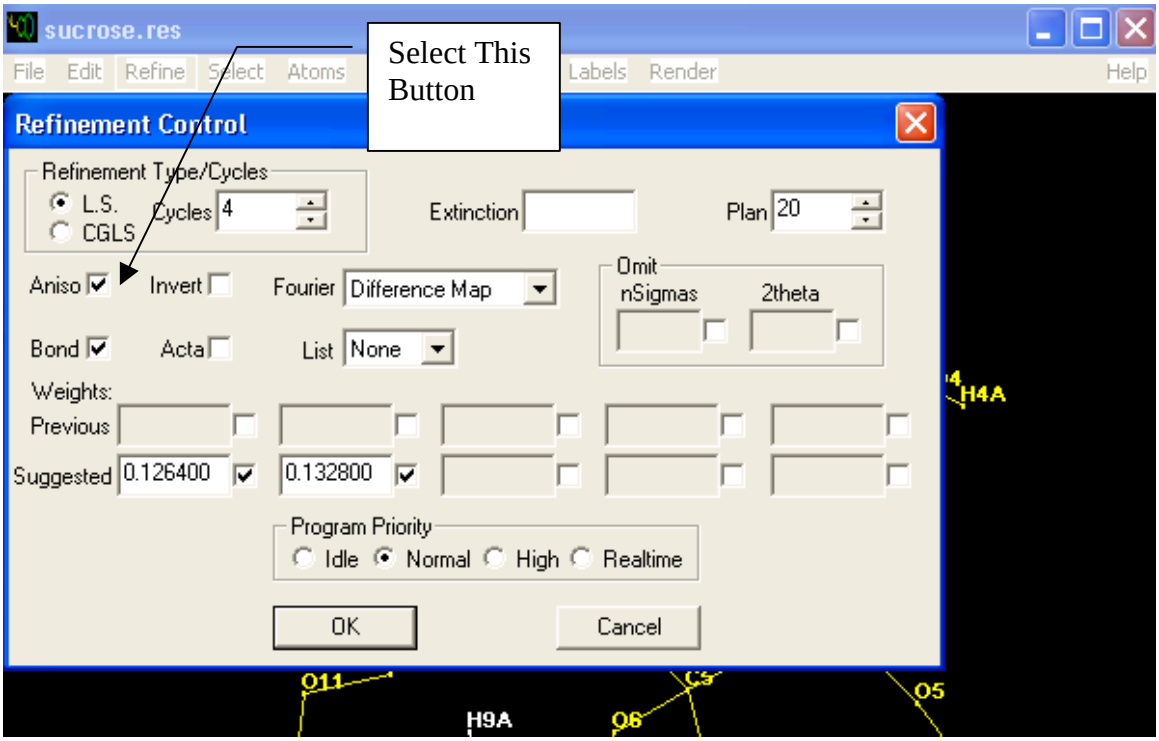
The R1 should now be R1 = 0.0986. All non hydrogen atoms are now located. Find the highest Q peak by moving the cursor over Q1 (find it near C11) and reading the Peak height value in the upper left hand corner. If this is less than 2 than it is most likely a Hydrogen or residual peak. If greater than 2 then you have missed a non hydrogen atom.

Kill and Q-peaks (point to edit/Kill Q-peaks) and add hydrogen atoms.

Point to ATOMS/Hybridize ALL and then ATOMS/Calculate Hydrogens. You will see warning about HFIX 83 type OK.

Now point to refine again and repeat refinement. The R1 = 0.0775 now.

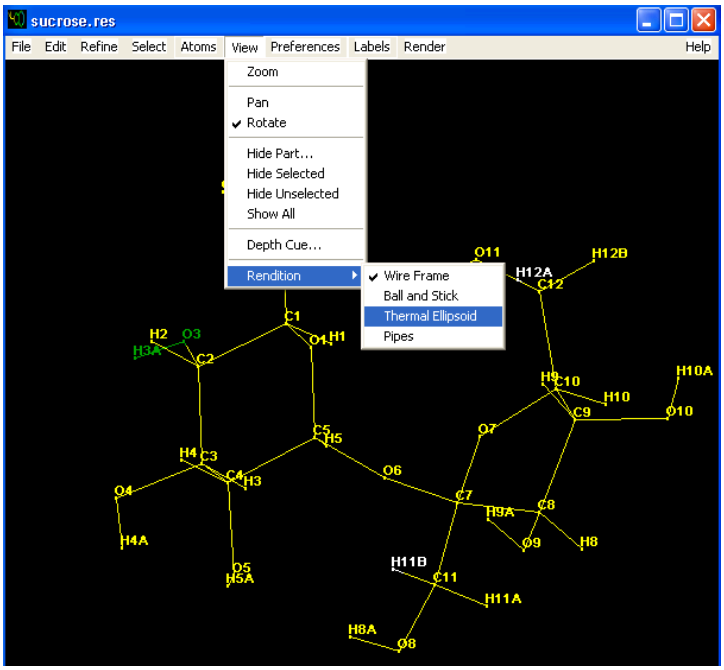
The final step will be the go anisotropic on all non-hydrogen atoms.



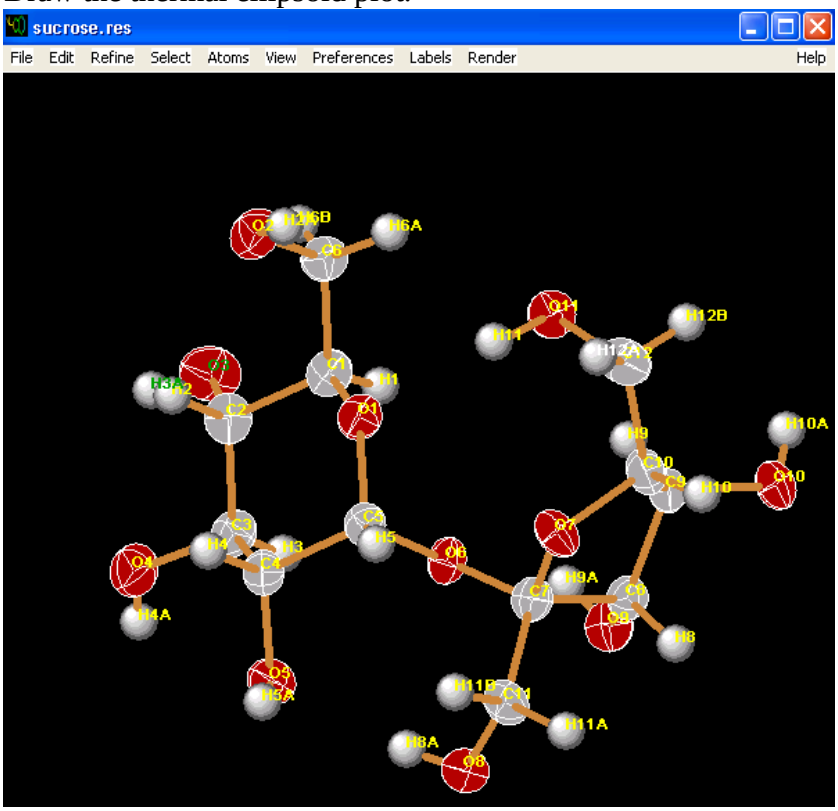
Press OK. The R1 = 0.0613

```
GooF = S =    0.873;    Restrained GooF =    0.873  for     1 restraints
Mean shift/esd =  0.018    Maximum =  -0.155 for tors H8A       at 18:43:58
Max. shift = 0.009 A for H8A      Max. dU = 0.000 for C5
wR2 =  0.1897 before cycle   5 for   3297 data and     2 /   216 parameters
GooF = S =    0.873;    Restrained GooF =    0.873  for     1 restraints
R1 =  0.0613 for   2009 Fo > 4sig(Fo)  and  0.1103 for all   3297 data
wR2 =  0.1897,  GooF = S =   0.873,  Restrained GooF =    0.873  for all data
R1 =  0.0999 for   1803 unique reflections after merging for Fourier
Highest peak    0.36  at  0.1916  0.9207  0.7949  [  0.13 A from O7 ]
Deepest hole   -0.30  at  0.4470  0.3450  0.2406  [  1.16 A from O11 ]

++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
+  sucrose          finished at 18:43:58   Total CPU time:      4.2 secs  +
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
```

Draw the structure, kill all Q-peaks (EDIT/KILL ALL Q-PEAKS) . Point to View/Rendition/Thermal Ellipsoid



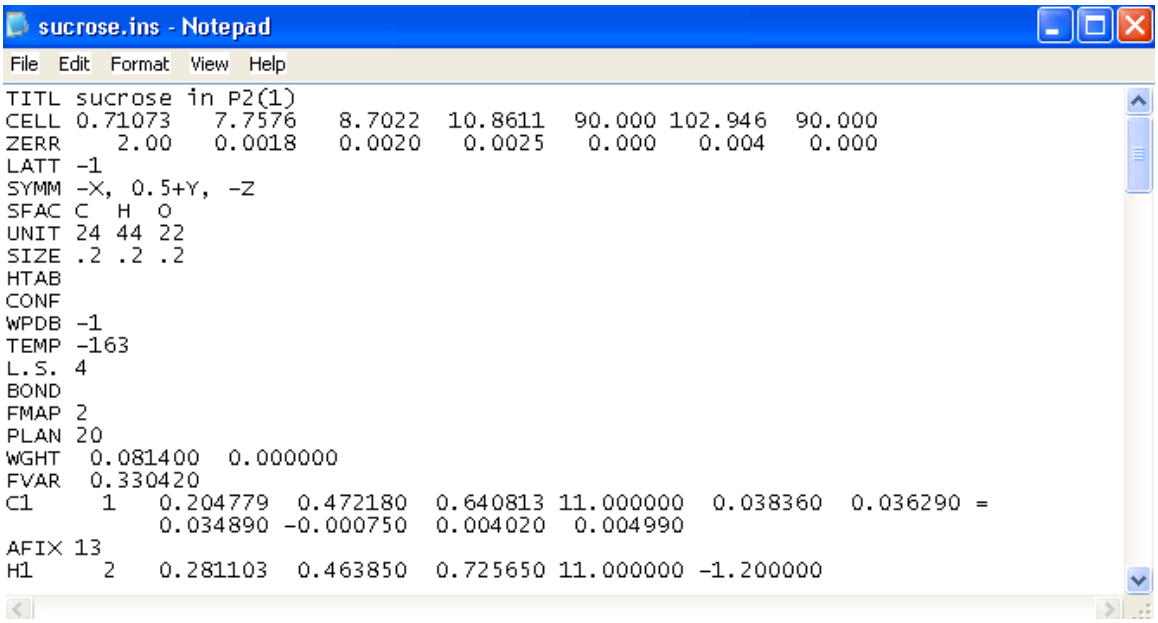
Draw the thermal ellipsoid plot.



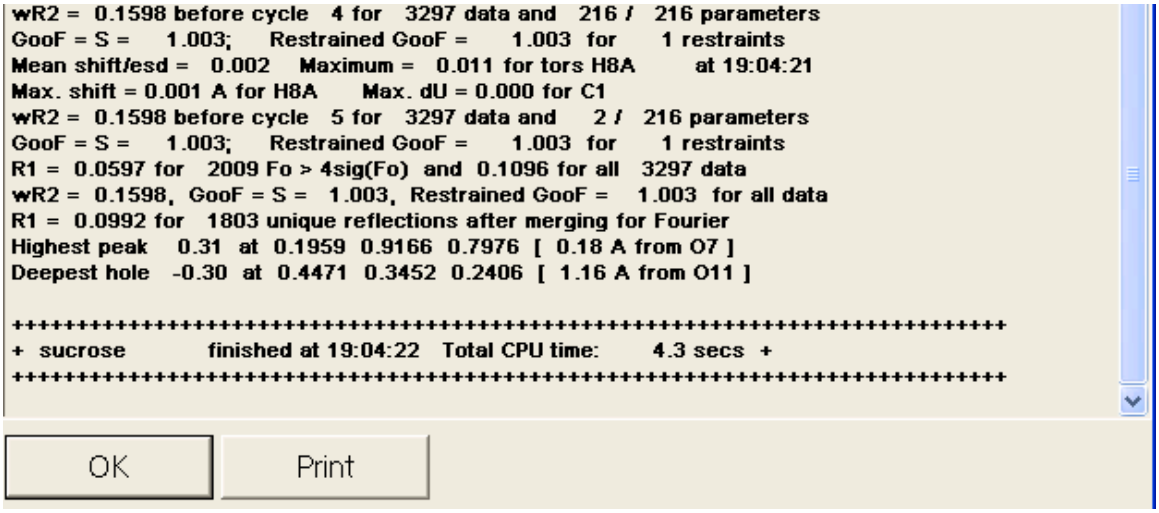
The ellipsoids should be football shaped, not disks or saucers. Non Positive Definite atoms will appear as regular shaped round gray spheres (like those seen for hydrogens and isotropic atoms).

Run the final refinement. First edit the INS file. Point to EDIT/EDIT CURRENT FILE and add

SIZE .2 .2 .2
TEMP –163
HTAB
CONF
WPDB -1



Save bye closing file and keep the changes. Point to refine and choose the ACTA button and start the refinement.

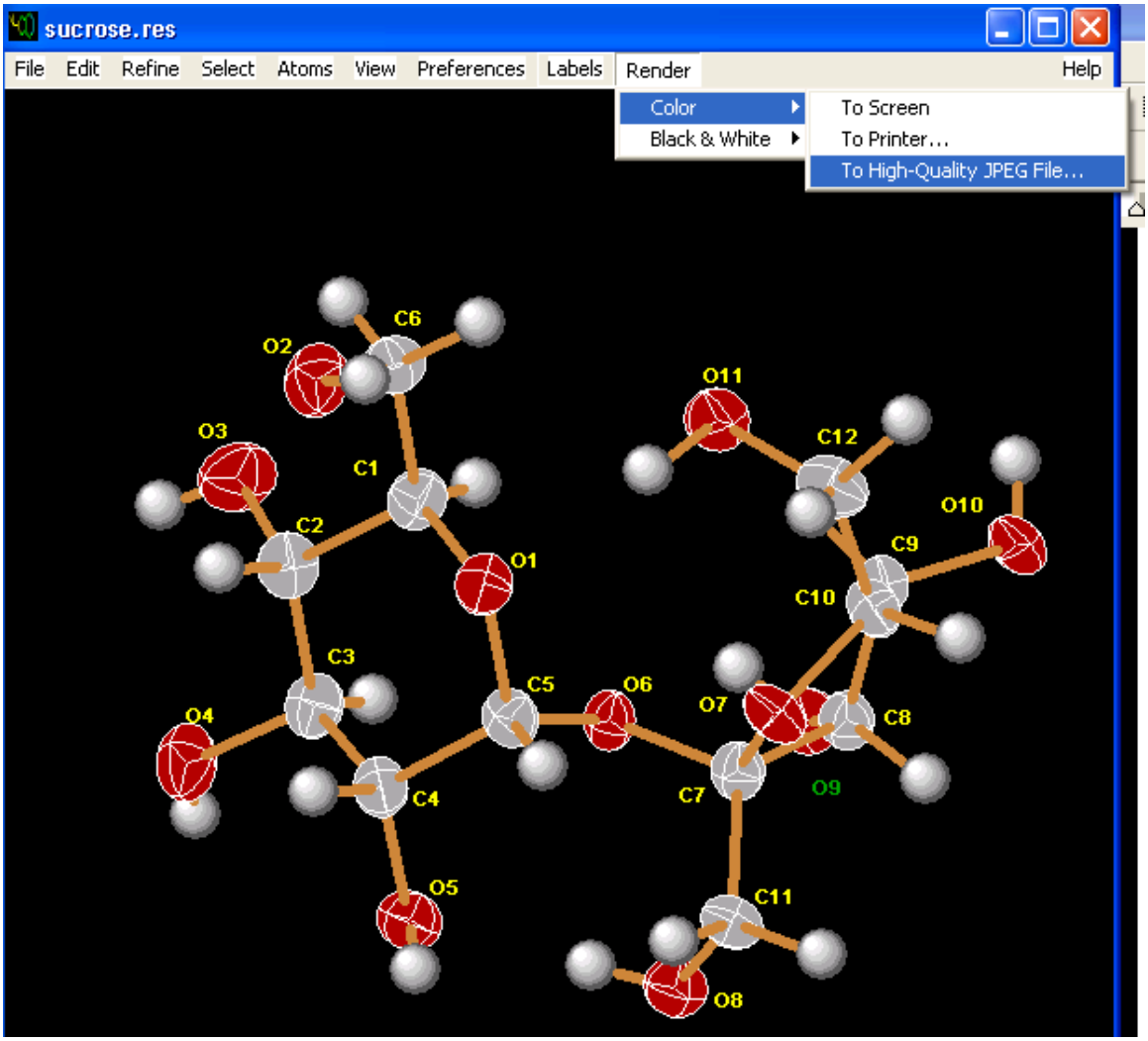


The final results can be examined in detail.

1) The R1 = 0.0597 (for Strong reflections) should be less than 0.10
2) The wR2 should be about 2 times R1 for all unique reflections, in this case R1=0.0992. wR2 should be less than 2 * .099 or 0.198
3) The Goof (1.003) should be greater than 1.0 and less than 2.0
4) The Maximum = 0.011 is the max. shift and should be less than 0.2
5) The highest peak (unassigned) is 0.31 electrons and should be less than 1.00 and the absolute value should be about equal to the absolute value of the deepest hole.

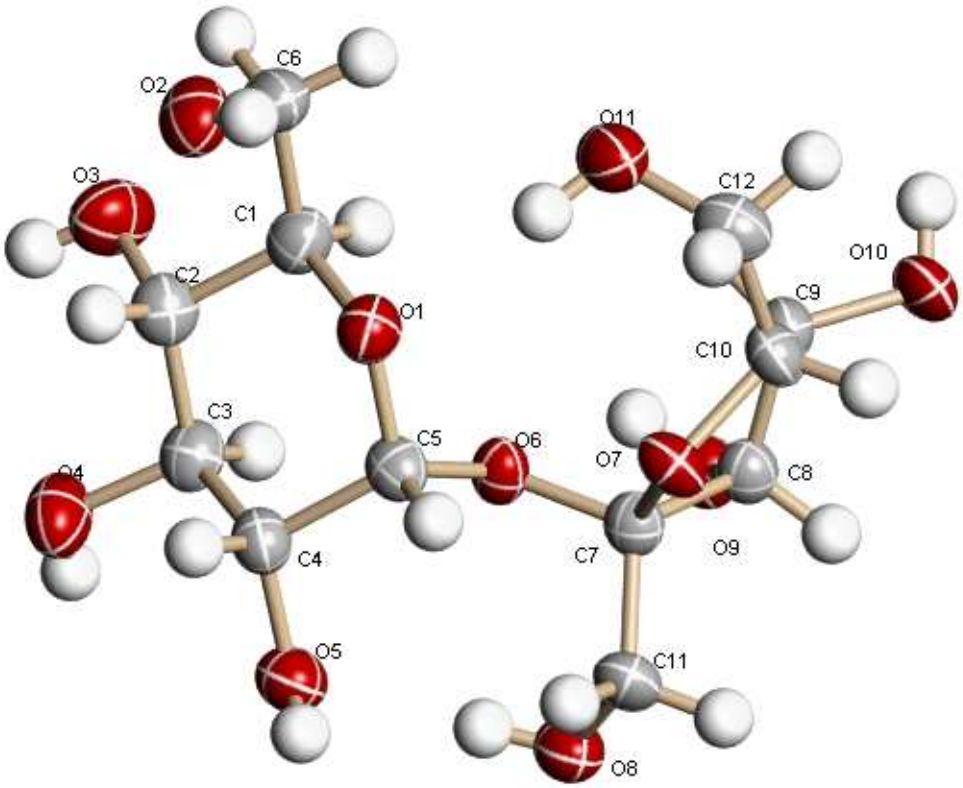
All parameters indicate that this refinement is finished.

Press ok and redraw the structure. Again kill the q-peaks. Redraw the thermal parameters. Point to label and turn off Hydrogen labels. Now move the cursor over an atom and type P. The label now will move with the cursor. Move it to a free area and click the mouse. Repeat for all atoms.

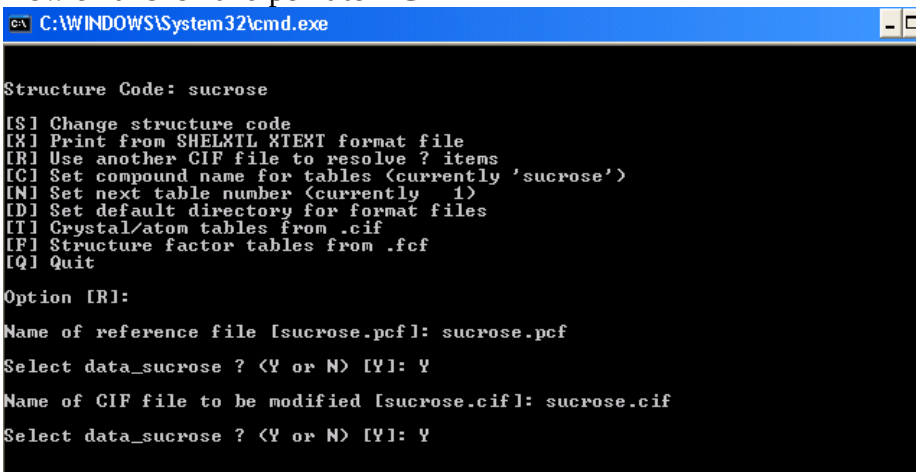


Point to render/color/to high-quality JPEG file and name the file sucrose.jpg.

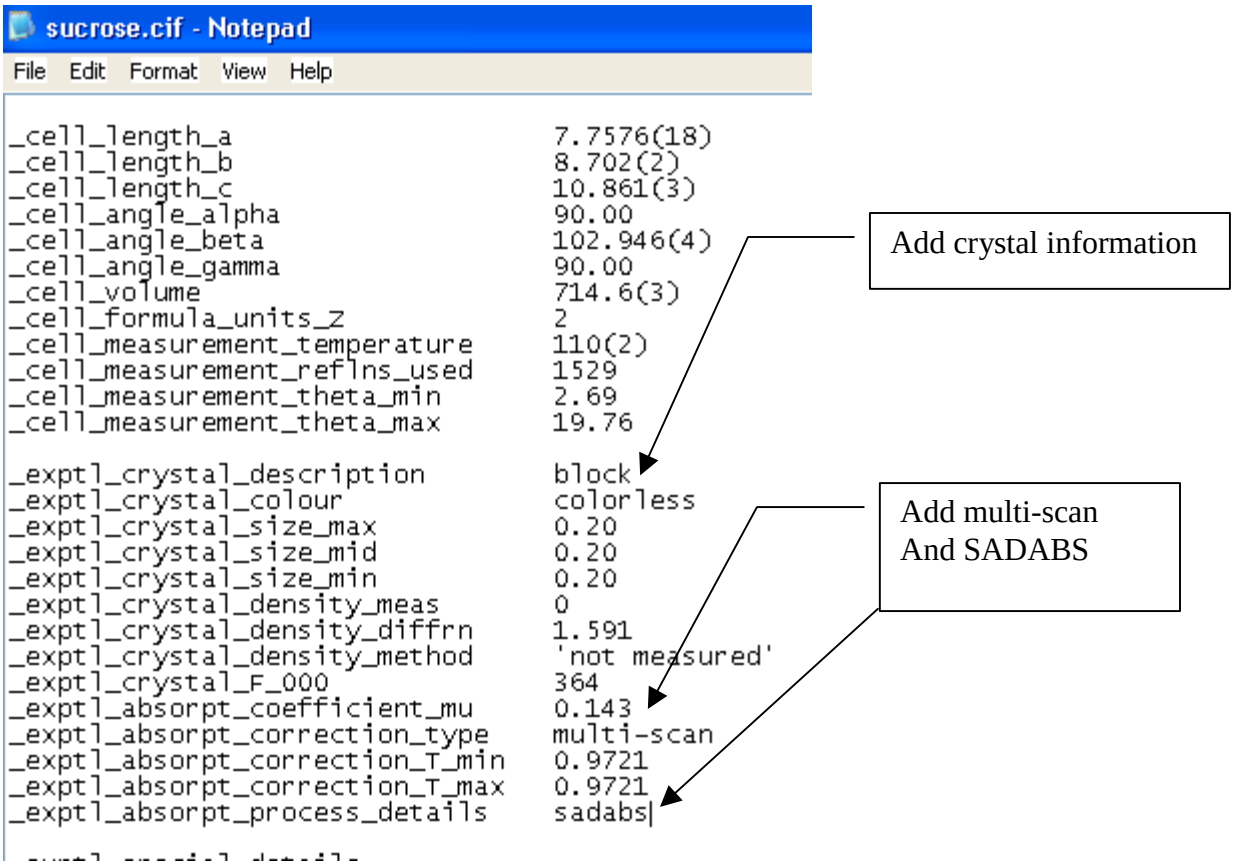
Use the anti-aliasing for best pictures



Now exit xshell and point to XCIF



Follow the defaults and write a new Crystallographic Information File
Exit XCIF and return to SHELXTL. Point to EDIT/EDIT .CIF and edit the CIF file.



Finally change fine-focus to normal-focus

The CIF is now ready for publication.

At this point your structure is finished. You should have three files

Sucrose.CIF, Sucrose.FCF and Sucrose.JPG.

To write a table for WORD return to XCIF. Follow the menu for crystal/atom tables. For the filename type Sucrose.RTF. For filename extension type RTA. Choose the crystal table, the atomic coordinate table, full bond lengths/angles, aniostropic table and the hydrogen atom table. Say no (N) to all other questions.

The rich text file Sucrose.RTF can now be read into any word processing program.

Sucrose

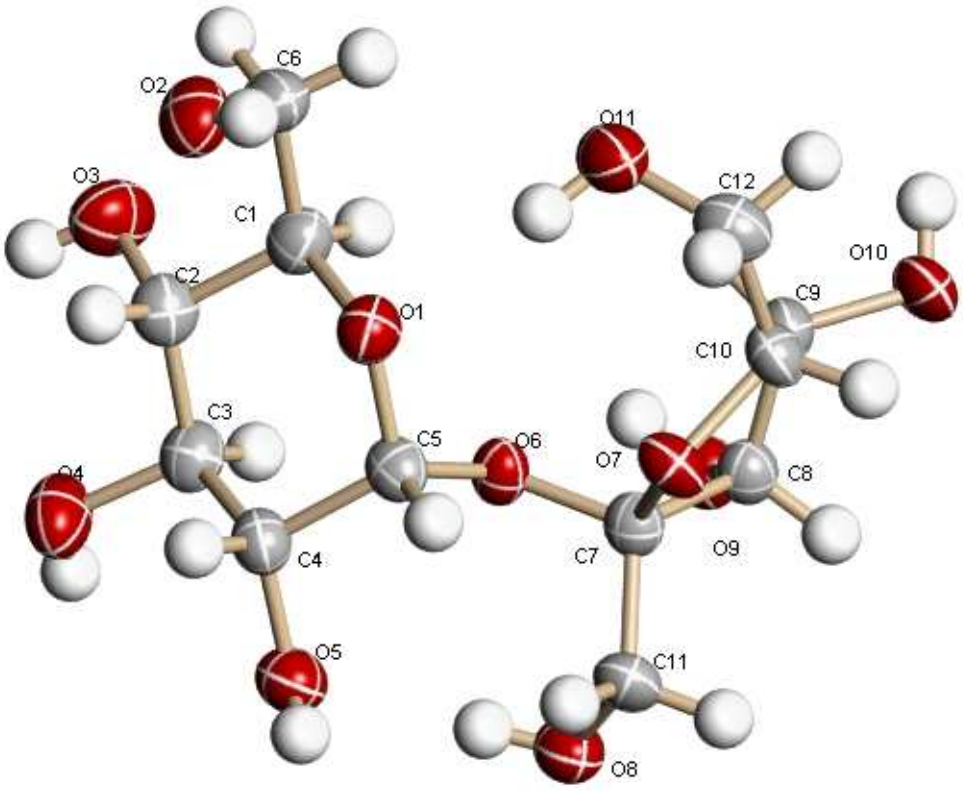

C6
O2
O11
O3
C12
C1
O10
C2
C9
O1
C10
C3
C5
O6
O7
C8
O4
C4
C7
O9
O5
C11
O8

Table 1. Crystal data and structure refinement for sucrose.

Identification code	sucrose	
Empirical formula	C12 H22 O11	
Formula weight	342.30	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 7.7576(18) Å	α= 90°.
	b = 8.702(2) Å	β= 102.946(4)°.
	c = 10.861(3) Å	γ = 90°.
Volume	714.6(3) $Å^3$	
Z	2	
Density (calculated)	1.591 Mg/m^3	
Absorption coefficient	0.143 mm^{-1}	
F(000)	364	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Theta range for data collection	1.92 to 28.37°.	
Index ranges	-10<=h<=10, -11<=k<=11, -14<=l<=14	
Reflections collected	8208	
Independent reflections	3297 [R(int) = 0.0535]	
Completeness to theta = 28.37°	94.3 %	
Absorption correction	None	
Max. and min. transmission	0.9721 and 0.9721	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3297 / 1 / 216	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0594, wR2 = 0.1278	
R indices (all data)	R1 = 0.1095, wR2 = 0.1543	
Absolute structure parameter	0.8(16)	
Largest diff. peak and hole	0.303 and -0.296 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sucrose. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2046(5)	4721(5)	6407(4)	37(1)
C(2)	569(5)	3548(5)	6266(4)	39(1)
C(3)	-632(5)	3899(5)	7141(4)	37(1)
C(4)	-1357(5)	5506(4)	6877(4)	35(1)
C(5)	152(5)	6689(5)	6993(3)	33(1)
C(6)	3160(5)	4537(5)	5438(3)	42(1)
C(7)	1303(5)	8332(4)	8754(3)	32(1)
C(8)	2868(5)	8352(4)	9930(3)	33(1)
C(9)	4439(5)	8582(5)	9334(3)	35(1)
C(10)	3712(5)	9643(5)	8233(4)	36(1)
C(11)	-427(5)	8942(5)	8975(4)	39(1)
C(12)	4528(5)	9434(5)	7115(4)	44(1)
O(1)	1315(3)	6272(3)	6227(2)	37(1)
O(2)	2138(4)	4789(4)	4190(3)	50(1)
O(3)	1445(4)	2120(4)	6519(3)	57(1)
O(4)	-2027(4)	2773(4)	6914(3)	52(1)
O(5)	-2479(4)	5893(4)	7705(3)	42(1)
O(6)	1088(3)	6783(3)	8289(2)	32(1)
O(7)	1837(3)	9310(3)	7875(2)	35(1)
O(8)	-1210(4)	7903(4)	9701(2)	44(1)
O(9)	2958(4)	7074(3)	10737(2)	40(1)
O(10)	5891(3)	9280(4)	10216(2)	43(1)
O(11)	4601(4)	7885(4)	6732(3)	49(1)

Table 3. Bond lengths [Å] and angles [°] for sucrose.

C(1)-O(1)	1.460(5)
C(1)-C(6)	1.512(5)
C(1)-C(2)	1.516(5)
C(2)-O(3)	1.414(5)
C(2)-C(3)	1.504(5)
C(3)-O(4)	1.440(5)
C(3)-C(4)	1.511(6)
C(4)-O(5)	1.425(5)
C(4)-C(5)	1.543(5)
C(5)-O(1)	1.405(4)
C(5)-O(6)	1.434(4)
C(6)-O(2)	1.426(4)
C(7)-O(7)	1.409(4)
C(7)-O(6)	1.436(4)
C(7)-C(11)	1.511(5)
C(7)-C(8)	1.553(5)
C(8)-O(9)	1.408(4)
C(8)-C(9)	1.515(5)
C(9)-O(10)	1.440(4)
C(9)-C(10)	1.516(5)
C(10)-O(7)	1.448(4)
C(10)-C(12)	1.501(5)
C(11)-O(8)	1.422(5)
C(12)-O(11)	1.416(6)

O(1)-C(1)-C(6)	105.7(3)
O(1)-C(1)-C(2)	110.3(3)
C(6)-C(1)-C(2)	113.3(3)
O(3)-C(2)-C(3)	113.3(3)
O(3)-C(2)-C(1)	104.6(3)
C(3)-C(2)-C(1)	111.1(3)
O(4)-C(3)-C(2)	107.6(3)
O(4)-C(3)-C(4)	111.3(3)
C(2)-C(3)-C(4)	109.0(3)

O(5)-C(4)-C(3)	110.7(3)
O(5)-C(4)-C(5)	110.5(3)
C(3)-C(4)-C(5)	111.0(3)
O(1)-C(5)-O(6)	110.2(3)
O(1)-C(5)-C(4)	110.8(3)
O(6)-C(5)-C(4)	109.1(3)
O(2)-C(6)-C(1)	111.2(3)
O(7)-C(7)-O(6)	110.9(3)
O(7)-C(7)-C(11)	107.6(3)
O(6)-C(7)-C(11)	110.4(3)
O(7)-C(7)-C(8)	104.9(3)
O(6)-C(7)-C(8)	107.9(3)
C(11)-C(7)-C(8)	115.1(3)
O(9)-C(8)-C(9)	116.0(3)
O(9)-C(8)-C(7)	115.1(3)
C(9)-C(8)-C(7)	101.9(3)
O(10)-C(9)-C(8)	110.9(3)
O(10)-C(9)-C(10)	111.4(3)
C(8)-C(9)-C(10)	103.0(3)
O(7)-C(10)-C(12)	109.8(3)
O(7)-C(10)-C(9)	105.3(3)
C(12)-C(10)-C(9)	114.5(3)
O(8)-C(11)-C(7)	111.7(3)
O(11)-C(12)-C(10)	113.9(3)
C(5)-O(1)-C(1)	116.2(3)
C(5)-O(6)-C(7)	113.0(3)
C(7)-O(7)-C(10)	111.7(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sucrose. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	38(2)	36(2)	35(2)	-2(2)	4(2)	5(2)
C(2)	43(2)	34(2)	37(2)	5(2)	6(2)	0(2)
C(3)	44(2)	36(2)	31(2)	0(2)	7(2)	-2(2)
C(4)	35(2)	36(2)	34(2)	-2(2)	6(2)	-5(2)
C(5)	33(2)	40(2)	26(2)	1(2)	4(2)	-3(2)
C(6)	37(2)	48(3)	41(2)	-8(2)	9(2)	2(2)
C(7)	31(2)	32(2)	30(2)	0(2)	2(2)	1(2)
C(8)	32(2)	32(2)	34(2)	0(2)	3(2)	1(2)
C(9)	30(2)	37(2)	35(2)	-7(2)	4(2)	-4(2)
C(10)	29(2)	37(2)	41(2)	-2(2)	6(2)	-6(2)
C(11)	26(2)	44(2)	45(2)	-2(2)	6(2)	3(2)
C(12)	36(2)	52(3)	42(2)	8(2)	8(2)	2(2)
O(1)	41(2)	35(2)	35(1)	-1(1)	9(1)	-3(1)
O(2)	58(2)	54(2)	39(2)	-7(1)	12(2)	-8(2)
O(3)	60(2)	40(2)	74(2)	4(2)	23(2)	8(2)
O(4)	64(2)	45(2)	49(2)	-6(2)	19(2)	-18(2)
O(5)	36(2)	48(2)	44(2)	0(1)	11(1)	-1(1)
O(6)	32(1)	31(2)	29(1)	-2(1)	-1(1)	1(1)
O(7)	25(1)	40(2)	39(1)	9(1)	3(1)	-2(1)
O(8)	38(2)	52(2)	43(2)	-5(2)	12(1)	-4(1)
O(9)	41(2)	41(2)	36(2)	6(1)	3(1)	2(1)
O(10)	24(1)	56(2)	46(2)	-9(1)	0(1)	-4(1)
O(11)	40(2)	62(2)	47(2)	-11(2)	9(2)	-2(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for sucrose.

	x	y	z	U(eq)
H(1)	2823	4636	7273	44
H(2)	-135	3557	5374	46
H(3)	48	3826	8037	44
H(4)	-2079	5537	5990	42
H(5)	-369	7718	6718	40
H(6A)	4153	5278	5621	50
H(6B)	3665	3488	5498	50
H(8)	2748	9294	10431	40
H(9)	4812	7581	9024	42
H(10)	3879	10733	8528	43
H(11A)	-215	9940	9422	46
H(11B)	-1254	9121	8151	46
H(12A)	3839	10036	6398	52
H(12B)	5743	9856	7325	52
H(2A)	2312	5687	3961	75
H(3A)	694	1410	6435	85
H(4A)	-2358	2606	7587	77
H(5A)	-3153	6616	7391	63
H(8A)	-1537	7107	9275	65
H(9A)	3082	6269	10338	60
H(10A)	6845	8874	10142	65
H(11)	3569	7534	6508	74