

## Space Group & Structure Solution

### Determine the Space Group

Space group determination can always be performed by examining the intensity data. A program that can facilitate this step is the command-prompt program `xprep`. Typical input is *project* name where the intensity data are in the file *project.hkl* and the cell parameters and chemical formula are in the file *project.p4p*.

To determine the space group by hand, perform the following steps:

- First be sure that the original unit cell is *reduced*.<sup>1,2</sup>
- From the reduced cell, search for possible higher symmetry, centered cells. This can be done using the Bravais routine in the `APEX3` program<sup>3</sup> or using table 9.2.5.1 of the *Int'l Tables for Crystallography*, Vol. A.<sup>4</sup> Note that the cell parameters must plausibly match the values expected for the crystal system. For each of these plausible higher-symmetry cells, transform the (*hkl*) values and check the intensities to see if the data meets the Laue symmetry for that crystal system. These tests should begin with the plausible, highest-symmetry, centered cells. When the Laue symmetry is matched, you have found the appropriate crystal system and Laue symmetry for the sample.
- For this crystal system, check the intensities for possible reflection conditions (systematic absences), paying the greater attention to glide planes rather than screw axes because a glide plane affects an entire plane of the reciprocal lattice, while a screw axis affects only data on a single line. Once the reflection conditions are determined, the cell may need to be rotated using Table 4.3.2.1 of the *Int'l Tables for Crystallography*, Vol A,<sup>5</sup> to put the cell into a standard orientation.

Before running the `xprep` program, be sure that the \*.p4p and the \*.hkl or \*.raw files have the same root file name.

Typical input is *project* name where the intensity data are in the file *project.hkl* and the cell parameters and chemical formula are in the file *project.p4p*. The program presents the results of different calculations asking the user to either accept their results or pick another option. For most selections, hit <enter> to accept the default.

```

XPREP Version 2014/2 for Windows Copyright(C) Bruker-AXS 2014

+++++
+ XPREP - Reciprocal space exploration - Version 2014/2 for Windows +
+ COPYRIGHT(c) 2014 Bruker-AXS All Rights Reserved +
+++++

Screen size: 1920 x 1080
Window size: 640 x 979
Font size: 8 x 16 ( 125 x 168 )
Number of colors: 256

When xprep is started without a filename on the command line, the filename
is prompted for and then the type of data (SHELX, SCALEPACK, XDS etc.)
requested. XPREP without a filename is also required to read HKLF3 format data.
To generate ideal data, a SHELX .ins or .res file should be given. To determine
the Flack parameter by the Parsons' quotient method, these data are used to
find the space group, then the observed intensities are read in.

Alternatively xprep may be started by 'xprep name.xyz' where xyz is hkl, HKL
(for a XDS_ASCII.HKL format file), res, ins, fco (for a file written by XD),
or fcf for a CIF file written by SHELXL or from the IUCr or COD servers. If a
fco or fcf file contains both Fo^2 and Fc^2, both datasets will be read in:
first Fc^2, then Fo^2. After defining the space group in the usual way,
the Flack x may then be determined by the Parsons' quotient method.

'xprep name' reads a SHELX HKLF 4 format file name.hkl, then tries to find
name.spin or name.p4p to extract the cell dimensions and their esds.

'xprep name1 name2' reads name1.hkl and name2.p4p (or name2.spin).

-Ln on the command line allocates space for 1000000n data (default n=4).

13986 reflections read from file ylid20.hkl
Mean (I/sigma) = 23.73

Lattice exceptions: P A B C I F Obv Rev All
N (total) = 0 6953 6984 7025 6970 10481 9306 9304 13986
N (int>3sigma) = 0 6509 6484 6571 6437 9782 8640 8631 12991
Mean intensity = 0.0 27.3 26.1 25.7 27.3 26.4 26.9 27.0 26.7
Mean int/sigma = 0.0 23.9 22.9 23.8 23.7 23.5 23.6 23.7 23.7

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

```

The program calculates an average (or mean)  $\langle F^2/\sigma(F^2) \rangle$  for the entire data set. Values of 10 or greater for the average  $\langle F^2/\sigma(F^2) \rangle$  suggest that the structure determination is very likely to succeed. The program then presents a table of statistics to determine the current lattice centering. The statistics displayed by the program are the total number of data that should systematically absent if that condition existed, the number of the systematically-absent data that are observed, an average intensity of the proposed systematically-absent data, and finally the  $F^2/\sigma(F^2)$  of the systematically-absent data. The default choice is based on the  $F^2/\sigma(F^2)$  results ( $> 3.87$ ); however, be sure to look at the average intensity data as well. If the cell is found to be a centered lattice, the primitive cell is determined and the primitive cell is reduced.

```

XPREP Version 2014/2 for Windows Copyright(C) Bruker-AXS 2014
Current dataset: ylid20.hkl          Wavelength: 0.71073 Chiral: ?
-----
Original cell:  5.966  9.045 18.408  90.00  90.00  90.00  Vol  993.3
                Esds:  0.000  0.000  0.001  0.00  0.00  0.00  Lattice: P
-----
Current cell:   5.966  9.045 18.408  90.00  90.00  90.00  Vol  993.3
-----
Matrix: 1.0000  0.0000  0.0000  0.0000  1.0000  0.0000  0.0000  0.0000  1.0000
-----

[D] Read, modify or merge DATASETS          [C] Define unit-cell CONTENTS
[P] Contour PATERSON 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 [H]:

Determination of reduced (Niggli) cell

Transformation from original cell (HKLF-matrix):
  1.0000  0.0000  0.0000  0.0000  1.0000  0.0000  0.0000  0.0000  1.0000

Unitcell:      5.966   9.045  18.408  90.00  90.00  90.00

Niggli form:   a.a =    35.59      b.b =    81.81      c.c =   338.85
                b.c =     0.00      a.c =     0.00      a.b =     0.00

Search for higher METRIC symmetry
Identical indices and Friedel opposites combined before calculating R(sym)

-----
Option A: FOM = 0.000 deg.  ORTHORHOMBIC P-lattice  R(sym) = 0.011 [ 3218]
Cell:   5.966  9.045 18.408  90.00  90.00  90.00  Volume:   993.27
Matrix: 1.0000  0.0000  0.0000  0.0000  1.0000  0.0000  0.0000  0.0000  1.0000
-----
Option B retains original cell

Select option [A]: █

```

Higher-symmetry, centered cells are considered by calculating the cell parameter fit to the transformed cells and then calculating the merging R for the crystal system. The program stops looking for lower crystal symmetry groups when the merging R is found to be reasonably low. The combination of lattice type and crystal class is selected.

```

XPREP Version 2014/2 for Windows Copyright(C) Bruker-AXS 2014
Current dataset: ylid20.hkl          Wavelength: 0.71073 Chiral: ?
-----
Original cell:  5.966  9.045  18.408  90.00  90.00  90.00  Vol  993.3
Esds:          0.000  0.000  0.001  0.00  0.00  0.00  Lattice: P
-----
Current cell:   5.966  9.045  18.408  90.00  90.00  90.00  Vol  993.3
-----
Matrix: 1.0000  0.0000  0.0000  0.0000  1.0000  0.0000  0.0000  0.0000  1.0000
-----
Crystal system: Orthorhombic      Lattice: P
-----

[S] Determine SPACE GROUP
[C] Must be CHIRAL (sample is optically active)
[N] NOT NECESSARILY chiral (eg. may be racemate)
[I] INPUT known space group
[E] EXIT to main menu or [Q] QUIT program

Select option [S]:

[A] Triclinic, [M] Monoclinic, [O] Orthorhombic, [T] Tetragonal,
[H] Trigonal/Hexagonal, [C] Cubic or [E] EXIT

Select option [O]:

Lattice exceptions: P      A      B      C      I      F      Obv  Rev  All
N (total) =           0  6953  6984  7025  6970  10481  9306  9304  13986
N (int>3sigma) =      0  6509  6484  6571  6437  9782  8640  8631  12991
Mean intensity =     0.0  27.3  26.1  25.7  27.3  26.4  26.9  27.0  26.7
Mean int/sigma =     0.0  23.9  22.9  23.8  23.7  23.5  23.6  23.7  23.7

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

Select option [P]:

Mean |E*E-1| = 0.696 [expected .968 centrosym and .736 non-centrosym]

Systematic absence exceptions:

      b--  c--  n--  21--  -c-  -a-  -n-  -21-  --a  --b  --n  --21
N      723  706  697  12  464  480  464  21  239  238  229  37
N I>3s 636  615  593  2  379  385  328  2  205  212  183  4
<I>    31.1 32.8 38.6 0.1 53.3 48.7 27.0 0.0 39.1 41.1 33.9 0.1
<I/s>  27.0 26.4 27.7 1.5 29.8 28.0 20.4 1.1 26.9 28.7 26.6 1.6

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)2(1)2(1) # 19 chiral 1 5917 0.011 3218 1.6 / 20.4 0.70

Select option [A]: █

```

The  $\langle |E^2 - 1| \rangle$  for all data is calculated to test for a center of symmetry. From the lattice and crystal system the reflection conditions (systematic absences) for the glide planes and screw axes

of the possible space groups are tested. Note that the tests for glide planes and screw axes are not perfect. These tests can make mistakes, so carefully review the statistics. The program then lists either no space group, a unique space group, or a small list of possible space groups. If a more likely space group is not listed, then end this routine and select Input Space Group to put in your preferred choice.

XPREP Version 2014/2 for Windows Copyright(C) Bruker-AXS 2014

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.64	22	23	95.7	7.39	200.36	151.12	0.0200	0.0046
3.64 - 2.31	47	47	100.0	11.53	133.50	189.60	0.0152	0.0043
2.31 - 1.78	69	69	100.0	11.78	59.75	153.97	0.0153	0.0052
1.78 - 1.51	68	68	100.0	12.94	63.39	158.83	0.0156	0.0051
1.51 - 1.38	68	68	100.0	12.47	35.87	125.61	0.0166	0.0063
1.38 - 1.26	74	74	100.0	12.30	25.60	114.27	0.0192	0.0073
1.26 - 1.18	66	66	100.0	11.65	27.54	104.67	0.0192	0.0077
1.18 - 1.12	65	65	100.0	11.34	21.25	87.69	0.0226	0.0092
1.12 - 1.06	81	81	100.0	11.04	12.51	65.82	0.0294	0.0114
1.06 - 1.02	58	58	100.0	11.10	11.19	62.29	0.0344	0.0133
1.02 - 0.98	73	73	100.0	9.90	12.54	58.07	0.0363	0.0143
0.98 - 0.95	69	69	100.0	9.86	9.11	49.73	0.0374	0.0166
0.95 - 0.92	71	71	100.0	9.94	7.44	43.14	0.0448	0.0194
0.92 - 0.89	81	81	100.0	9.36	6.50	35.68	0.0482	0.0214
0.89 - 0.87	63	63	100.0	8.98	5.69	33.43	0.0553	0.0252
0.87 - 0.85	56	56	100.0	8.73	4.63	29.85	0.0635	0.0288
0.85 - 0.83	72	72	100.0	8.50	4.50	27.51	0.0638	0.0315
0.83 - 0.81	89	89	100.0	8.42	4.59	25.61	0.0685	0.0310
0.81 - 0.80	40	40	100.0	8.32	3.64	22.54	0.0722	0.0356
0.80 - 0.78	88	88	100.0	8.23	3.46	21.23	0.0789	0.0390
0.78 - 0.77	58	58	100.0	7.57	3.51	20.36	0.0755	0.0419
-----								
0.87 - 0.77	403	403	100.0	8.30	4.09	24.52	0.0696	0.0340
Inf - 0.77	1378	1379	99.9	10.14	23.89	70.99	0.0216	0.0084

Merged [A], lowest resolution = 9.20 Angstroms

Graphical output: 1=<I/s>, 2=Rmerge, 3=Rsigma, <Enter>=none: █

The program then asks if you want to display statistics for the whole data set; select the defaults, unless you want more details about the data. An option to display layers of the diffraction data is available and is often checked when the subsequent refinement has problems.

```
XPREP Version 2014/2 for Windows Copyright(C) Bruker-AXS 2014

Current formula is:
C11H10O2S

Tentative Z (number of formula units/cell) = 4.0 giving rho = 1.379,
non-H atomic volume = 17.7 and following cell contents and analysis:

C      44.00    64.05 %      H      40.00    4.89 %
O       8.00    15.51 %      S       4.00    15.55 %

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

Select option [E]: █
```

The default path through the program asks about the chemical formula and calculates a possible Z for the given formula. If the radiation used is not the default Mo  $K\alpha$ , then select the appropriate radiation.

```

XPREP Version 2014/2 for Windows Copyright(C) Bruker-AXS 2014
Current dataset: ylid20.hkl          Wavelength: 0.71073 Chiral: ?
-----
Original cell:  5.966  9.045  18.408  90.00  90.00  90.00  Vol  993.3
                Esds:  0.000  0.000  0.001  0.00  0.00  0.00  Lattice: P
-----
Current cell:  5.966  9.045  18.408  90.00  90.00  90.00  Vol  993.3
-----
Matrix: 1.0000  0.0000  0.0000  0.0000  1.0000  0.0000  0.0000  0.0000  1.0000
-----
Crystal system: Orthorhombic Space group: P2(1)2(1)2(1) # 19 [chi] Laue: 3
-----
Formula: C11H10O2S          Formula wt: 206.26
Z: 4.00 Density: 1.379 At.vol: 17.7 F(000): 432.00 Mu[mm-1]: 0.29
-----

[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 [Q]: f

Output file name (without extension) [ylid20]:

XM/SHELXD (M) or XS/SHELXS (S) format [S]:

File ylid20.ins set up as follows:

TITL ylid20 in P2(1)2(1)2(1)
CELL 0.71073  5.96570  9.04490  18.40780  90.0000  90.0000  90.0000
ZERR  4.00  0.00020  0.00030  0.00060  0.0000  0.0000  0.0000
LATT -1
SYMM 0.5-X, -Y, 0.5+Z
SYMM -X, 0.5+Y, 0.5-Z
SYMM 0.5+X, 0.5-Y, -Z
SFAC C H O S
UNIT 44 40 8 4
TEMP 0.000
SIZE 0.40 0.40 0.40
TREF
HKLF 4
END

Do you wish to (over)write the intensity data file ylid20.hkl ? [Y]: █

```

Finally, an option to set up data files for structure solution is presented.

## Structure Solution

The recommended program for structure solution is `xt` or `shelxt` (these are the same program). This program uses a combination of Patterson map and direct methods with some quick structure factor calculations to produce a model. Note that several space groups may be considered, although only the space groups with the same crystal system and cell centering are attempted.

```
Command Prompt
E:\dpowell\ylid20>xt ylid20
+*****+
+ SHELXTL XT - CRYSTAL STRUCTURE SOLUTION  VERSION 2014/4  +
+ Copyright(c) Bruker AXS 2010-2014 All Rights Reserved  +
+ Started at 11:10:24 on 20 Jul 2017  +
+*****+
Command line parameters:  ylid20
 4 threads running in parallel
Unit-cell:  5.966  9.045 18.408  90.00  90.00  90.00
Laue group identified as number 3:  mmm
13986 reflections read from file ylid20.hkl
R(sym) = 0.0189, R(crim) = 0.0199, R(pim) = 0.0063
Highest resln. = 0.768 Å. For 1.2>d>1.1, <I/sig> = 169.9 and <F>4sig = 98.3
1378 unique reflections converted to 4076 with d > 0.800 Å in P1
 1 data added to fill out missing data to 0.9000 in P1
Fourier grid:  24 x 36 x 72:  0.249 x 0.251 x 0.256 Å
Mean |E^2-1| 0kl 0.850  h0l 0.934  hk0 0.924  Rest 0.682
436 Reflections with E < 0.310 employed for R(weak)
40 unique Patterson peaks with heights greater than 28 selected as
superposition vectors
Setup:  0.153 secs
Try N(iter)  CC  R(weak)  Chem  CFOM  best  Sig(min)  N(CP1)  Vol/N
1 100 96.33 0.0777 0.9787 0.8855 0.8855 2.425 57 17.43
2 100 96.29 0.0793 1.0000 0.8836 0.8855 2.459 57 17.43
3 100 96.41 0.0756 1.0000 0.8884 0.8884 2.317 57 17.43
4 100 96.32 0.0777 0.9800 0.8855 0.8884 2.500 57 17.43
4 attempts, solution 3 selected with best CFOM = 0.8884, Alpha0 = 0.571
Structure solution:  0.266 secs
0 Centrosymmetric and 56 non-centrosymmetric space groups evaluated
Space group determination:  0.517 secs
R1  Rweak Alpha  Orientation  Space group  Flack x  File  Formula
0.089 0.030 0.002  as input  P2(1)2(1)2(1) 0.04  ylid20_a  C11 O2 S
Assign elements and isotropic refinement  0.088 secs
+*****+
+ XT finished at 11:10:25 Total time:  1.025 secs +
+*****+
E:\dpowell\ylid20>_
```

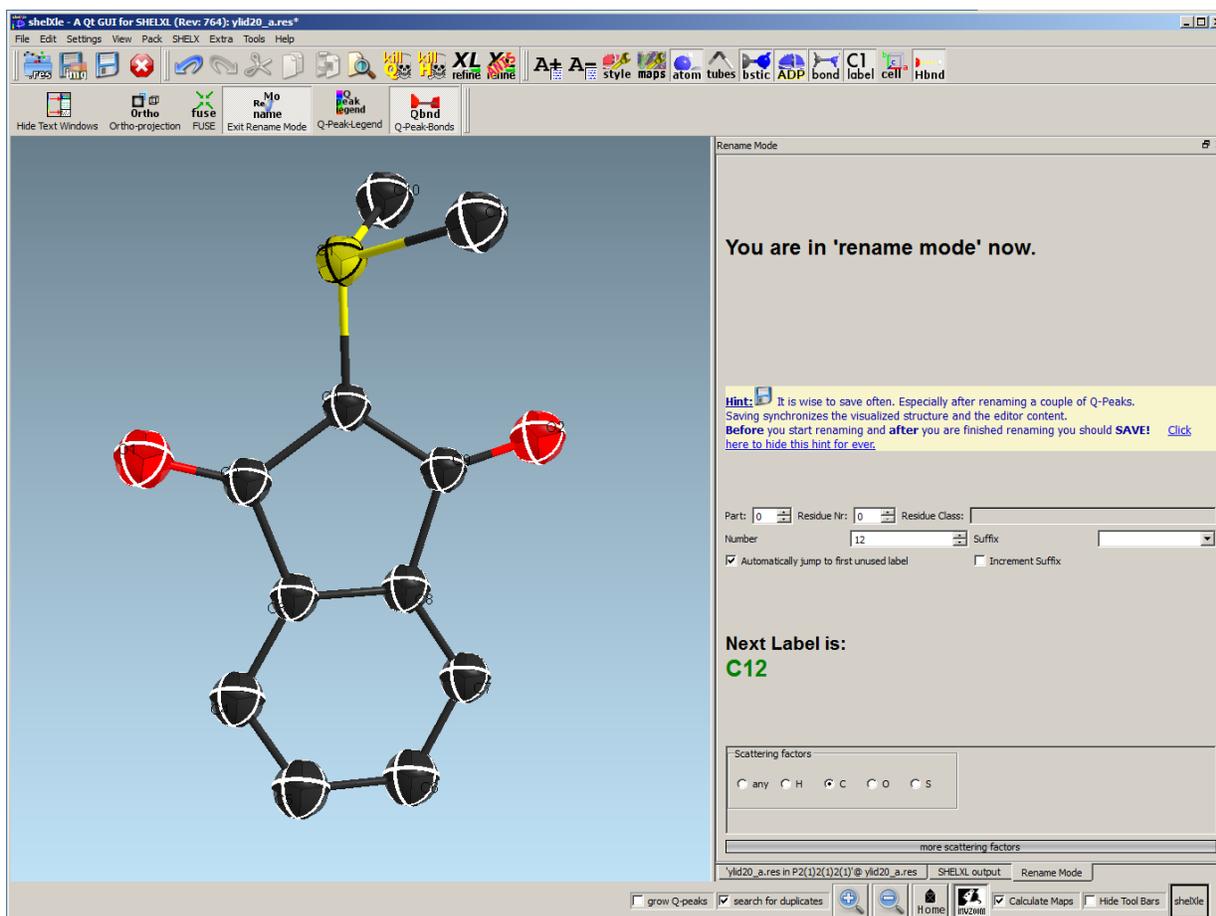
The programs `xt` or `shelxt` require no additional input from the user other than a *project.hkl* file and a *project.ins* file that contains the wavelength of the radiation, the cell parameters, space group symmetry, and atom types and numbers. This program will also handle non-merohedrally twinned data sets, where the multiple domains are still retained in the data set. Because different space groups are tried the output files are renamed as *project\_a.res* (and *project\_a.hkl*), *project\_b.res* (and *project\_b.hkl*) ... , where the *\_a*, *\_b*, ... refer to different space groups.

Other programs for solving structures include the older `xs` or `shelxs`, that solves structures by either direct methods or Patterson (single superposition) methods, `patsee` a molecular replacement program. The program `olex2` contains a link to a charge-flipping routine. The program `shelxd` uses a dual space method to solve macromolecular structures or structures with poor resolution.

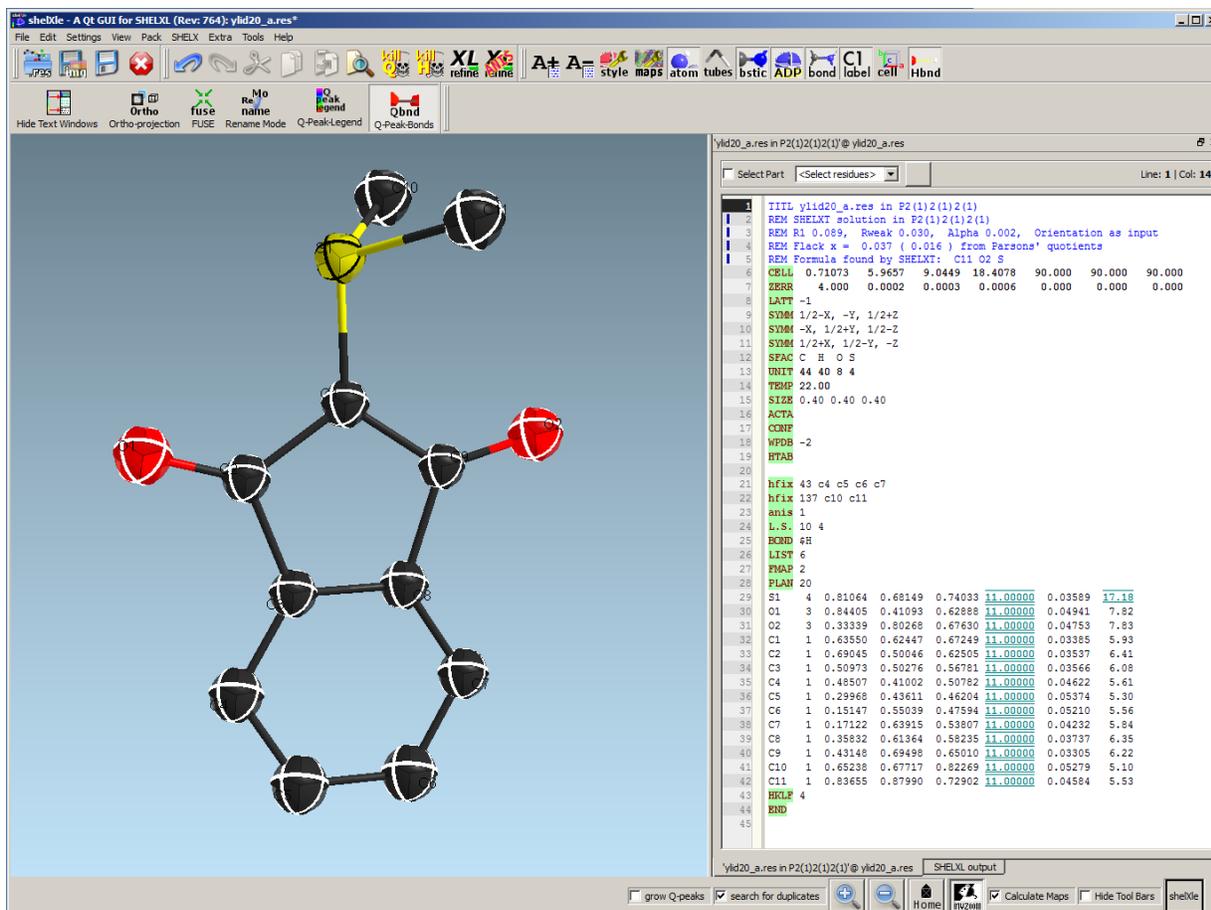
## Model Building

This is most easily accomplished using a graphics program such as [shelxle](#), [olex2](#), or [ortep3](#). The [shelxle](#) offers simple options to not only build the molecules, but also modify the current output data file, and refine the structure, so this program will be described. Also, this program has been built into the program [APEX3](#).

The input file is read in through the “.res” button. Some atom types may be incorrect. Most of the atoms in the structure should be shown.



Select the rename mode and in the right-side menu select the “Automatically jump to first unused label” check box. Then select the atom type to label and, if needed, select a letter label to append to the atom number, and begin selecting atoms to change their labels. Repeat this process for all atom types. The orientation of the view can be changed by moving the mouse to any point on the display away from an atom, holding down the left mouse button, and moving the mouse to rotate the view.



After labeling all atoms, select SHELX > Sort atoms. Add the following lines to the \*.res file between the Unit instruction and the atoms:

```

ACTA
CONF
WPDB -2
HTAB

```

Then select the SHELX > Copy current file and refine button. The refinement run is shown in the right-side panel. Click the “Load refinement results” button.

Instructions for finishing refinement are in the next document.

### References

1. A. D. Mighell, *J. Appl. Cryst.*, **1976**, 9, 491-498.
2. B. Gruber, *Acta Cryst.*, **1989**, A45, 123-131.
3. APEX3, **2007**, Bruker AXS Inc., Madison, Wisconsin, U.S.A.
4. Table 9.2.5.1, *Int'l Tables for Crystallography*, Vol A, **2005**, 5<sup>th</sup> Ed., Springer, 753.
5. Table 4.3.2.1, *Int'l Tables for Crystallography*, Vol A, **2005**, 5<sup>th</sup> Ed., Springer, 63-69.