TUTORIAL

DISORDER REFINEMENT USING **CRYSTALS** SOFTWARE

by

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Disorder

There are two type of disorder which should be considered: substitutional and positional. The first one corresponds to an occupation of an identical position in a unit cell by two different atoms. The second corresponds to the partial occupation of two or more positions in the unit cell by the same atom or group of atoms. For substitutional disorder, coordinates and atomic displacement parameters (ADP) of the all atoms occupying same position should be restrained to be same within error (0.001). This can be achieved via SUM commands in LIST 16. For example, substitutional disorder of the Na, Rb, K metals on a single site could be modeled as a follow:
Restrain occupation factors:

```
\list 16
sum 0.001 Na(1,occ) Rb(2,occ) K(3,occ)
\end
```

or put the string

sum 0.001 Na(1,occ) Rb(2,occ) K(3,occ)

into LIST 16 manually (useful if you already have some record in that file, otherwise LIST16 file will be overwritten). Use the ***Restrain tab →Edit Restraints*** button. Restrain positions:

```
\list 12
equiv Na(1,x’s) Rb(2,x’s) K(3,x’s)
\end
```

or put the string

equiv Na(1,x’s) Rb(2,x’s) K(3,x’s)

into LIST 12 manually (useful if you already have some record in that file, otherwise, LIST12 file will be overwritten). Use the ***Constrain tab →Edit Constraints*** button. For positional disorder first of all, make sure you have correct order of the atoms in LIST 5 and reorder them if need. It it really recommended to put disordered atoms in the end of LIST 5. Reordering or renumbering could be done via GUI: ***Structure →Renumber atoms***. Positional disorder may be classified as a disorder over special positions or disorder over general positions. The disorder over special position will be considered first below.

Tricyanoferroceneethylene Disorder over special a position

As example, we can consider the compound tricyanoferrocenylethene published by Victor Nemykin (Nemykin *et al*, Organometallics, **2007**, 26, 3138) kindly provided by author. The compound crystallizes in monoclinic symmetry with point group $P2_1/m$ (Figure 1).

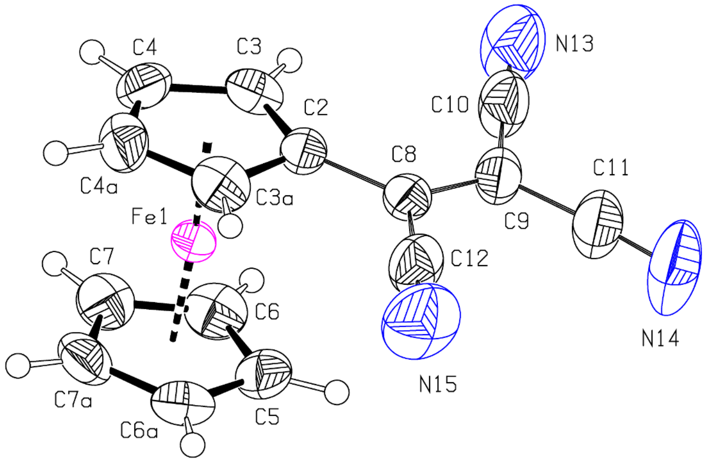
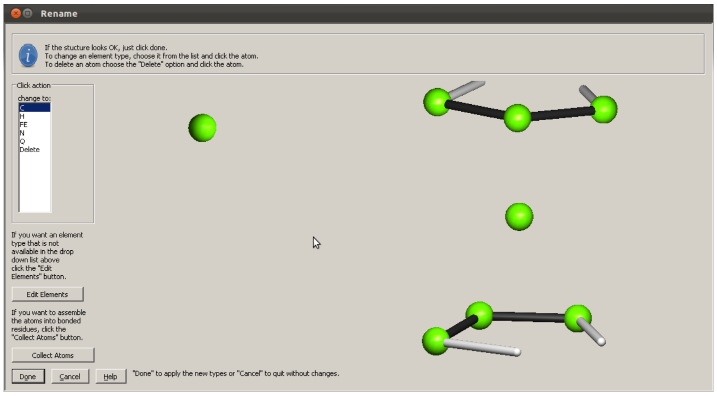


Figure 1: Crystal structure of Fc-C(CN)=C$(CN)_2$.

Structure solution by direct method implemented into SHELXS-86 revealed the ferrocene moiety to be on a symmetry element - a mirror plane (m) (Figure 2). All atoms were placed as carbons but lower sequence number corresponds to bigger electron density in Fourier map. Thus, the atom labeled as C(1) (located between two Cp rings) corresponds to the Iron element and should be renamed. Since only the ferrocene moiety was clear recognized, we can safety delete the other nonbonded atom (Figure 3).



If the stucture looks OK, just click done.
To change an element type, choose it from the list and click the atom.
To delete an atom choose the "Delete" option and click the atom.

If you want an element type that is not available in the drop down list above click the "Edit Elements" button.

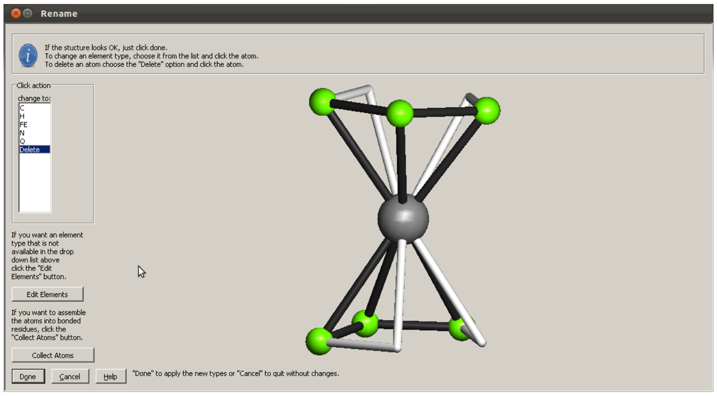
If you want to assemble the atoms into bonded residues, click the "Collect Atoms" button.

"Done" to apply the new types or "Cancel" to quit without changes.

Figure 2: Model after solution by SHELXS-86

After changing of the atom type we need renumber our model ***(Structure →Renumber atoms)*** and change order of atoms. Iron should go first and other carbons can be in the any order. Since we didn't find all (or almost all) atoms for our molecule, it useful to do Fourier analysis to reveal missing atoms. It should be noted we are not doing any refinement yet. All atomic parameters such as coordinates, displacement parameters are left without change. After Fourier analysis with default parameters we should get a model with electron density maxima as presented in Figure 4.

Tricyanoferrocenylethene doesn't have mirror symmetry, but the molecule in the crystal structure lies on the mirror symmetry plane. This means that the tricyanoethene part must be disordered over two positions with occupation 0.5 per each. After relocation of all peaks by symmetry (right button click on position where you want to bring your atom) and removing all other peaks around the ferrocene group, we should



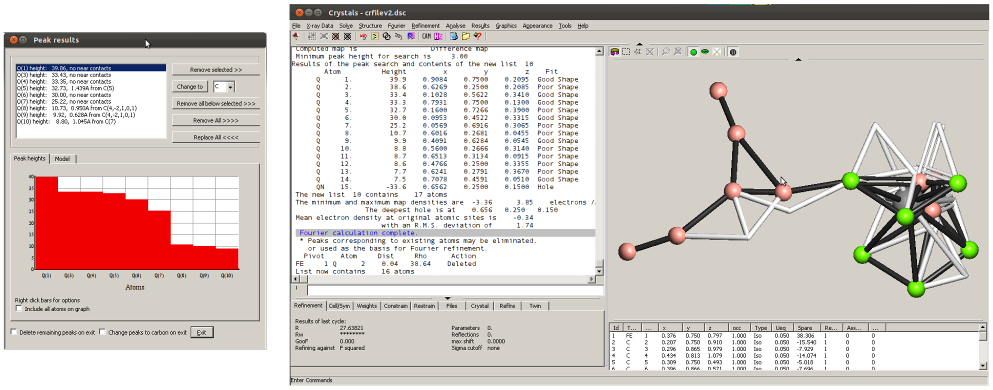
If the stucture looks OK, just click done.
To change an element type, choose it from the list and click the atom.
To delete an atom choose the "Delete" option and click the atom.

If you want an element type that is not available in the drop down list above click the "Edit Elements" button.

If you want to assemble the atoms into bonded residues, click the "Collect Atoms" button.

"Done" to apply the new types or "Cancel" to quit without changes.

Figure 3: Model after "cleaning"



```
Q(1) height:   39.86, no near contacts
Q(3) height:   33.43, no near contacts
Q(4) height:   33.35, no near contacts
Q(5) height:   32.73,  1.439A from C(5)
Q(6) height:   30.00, no near contacts
Q(7) height:   25.22, no near contacts
Q(8) height:   10.73,  0.950A from C(4,-2,1,0,1)
Q(9) height:    9.92,  0.628A from C(4,-2,1,0,1)
Q(10) height:   8.80,  1.045A from C(7)
```

Right click bars for options

☐ Include all atoms on graph

☐ Delete remaining peaks on exit ☐ Change peaks to carbon on exit

```
 Computed map is                 Difference map
 Minimum peak height for search is     3.00
Results of the peak search and contents of the new list  10
        Atom           Height        x         y         z    Fit
      Q      1.          39.9    0.9084    0.7500    0.2095  Good Shape
      Q      2.          38.6    0.6269    0.2500    0.2085  Poor Shape
      Q      3.          33.4    0.1028    0.5622    0.3410  Good Shape
      Q      4.          33.3    0.7931    0.7500    0.1300  Good Shape
      Q      5.          32.7    0.1600    0.7266    0.3900  Poor Shape
      Q      6.          30.0    0.0953    0.4522    0.3315  Good Shape
      Q      7.          25.2    0.0569    0.6916    0.3065  Poor Shape
      Q      8.          10.7    0.6016    0.2681    0.0455  Poor Shape
      Q      9.           9.9    0.4091    0.6284    0.0545  Good Shape
      Q     10.           8.8    0.5600    0.2666    0.3140  Poor Shape
      Q     11.           8.7    0.6513    0.3134    0.0915  Poor Shape
      Q     12.           8.6    0.4766    0.2500    0.3355  Poor Shape
      Q     13.           7.7    0.6241    0.2791    0.3670  Poor Shape
      Q     14.           7.5    0.7078    0.4591    0.0510  Good Shape
      QN    15.         -33.6    0.6562    0.2500    0.1500  Hole
 The new list  10 contains    17 atoms
 The minimum and maximum map densities are  -3.36      3.85    electrons /
                  The deepest hole is at    0.656   0.250   0.150
 Mean electron density at original atomic sites is    -0.34
                      with an R.M.S. deviation of      1.74
  Fourier calculation complete.
  * Peaks corresponding to existing atoms may be eliminated,
    or used as the basis for Fourier refinement.
   Pivot    Atom     Dist     Rho      Action
 FE     1 Q      2    0.04   38.64    Deleted
 List now contains    16 atoms
```

Results of last cycle:
R 27.63821
Rw ********
GooF 0.000
Refining against F squared
Parameters 0.
Reflections 0.
max shift 0.0000
Sigma cutoff none

Id	T...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	FE	1	0.376	0.750	0.797	1.000	Iso	0.050	38.306	1	0	0
2	C	2	0.207	0.750	0.910	1.000	Iso	0.050	-15.540	1	0	0
3	C	3	0.296	0.865	0.979	1.000	Iso	0.050	-7.929	1	0	0
4	C	4	0.434	0.813	1.079	1.000	Iso	0.050	-14.074	1	0	0
5	C	5	0.309	0.750	0.493	1.000	Iso	0.050	-5.018	1	0	0
6	C	6	0.396	0.866	0.571	1.000	Iso	0.050	-7.696	1	0	0

Figure 4: Electron maxima after Fourier analysis.

get model presented in Figure 5.

As we can see from Figure 6 one group of atoms (circled) lies on the mirror symmetry and is a subject for constraints. We need to rename all maxima of the electron density to correct atom types and renumber the atoms once again: the iron atom goes first, the carbons from the cyclopentadienyl ring and disordered part goes last. We should get model represented in Figure 7.

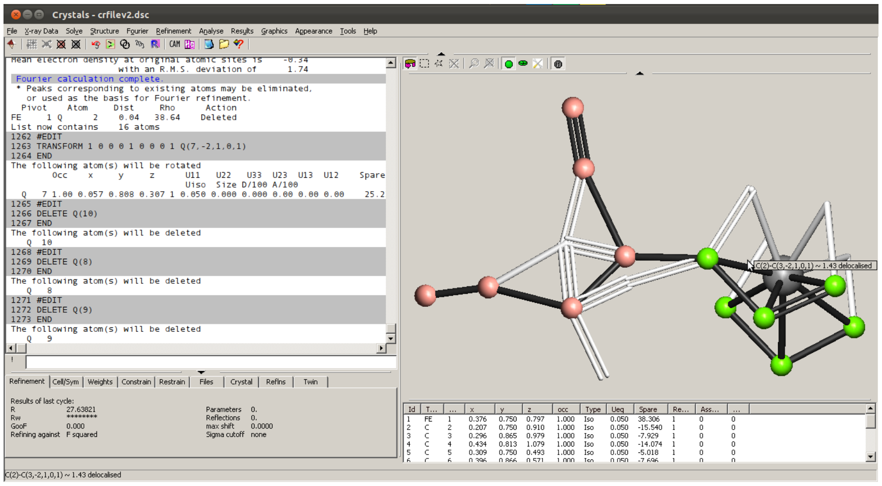
As we can see, one nitryl group lies on a mirror plane (red circle), while two carbons lie very close to it and related through it (blue circle). We need to change the occupation factor for all atoms of the disordered part to be 0.5. We can do this via GUI (Right click on ***atom*** →***Edit***) or by typing command:

```
\edit
change c(8,occ) until last 0.5
\end
```

CRYSTALS automatically constrains coordinates for atoms on or around special positions. The default threshold is 0.6 Å. This means, if the distance between two atoms related by symmetry element is less or equal to 0.6 Åthen that atom is the subject for the constraint. In our example the two atoms are on the symmetry element and one atom very close to it. We can type

```
\dist
end
```

and check the distance between C(8)'s atoms. In this example we have 0.464 Å. To avoid "merging" of



```
Mean electron density at original atomic sites is    -0.34
                      with an R.M.S. deviation of      1.74
 Fourier calculation complete.
 * Peaks corresponding to existing atoms may be eliminated,
   or used as the basis for Fourier refinement.
  Pivot    Atom     Dist     Rho      Action
FE     1 Q      2    0.04   38.64    Deleted
List now contains    16 atoms
1262 #EDIT
1263 TRANSFORM 1 0 0 0 1 0 0 0 1 Q(7,-2,1,0,1)
1264 END
The following atom(s) will be rotated
        Occ    x     y     z      U11   U22   U33  U23  U13  U12    Spare
                                  Uiso  Size D/100 A/100
  Q   7 1.00 0.057 0.808 0.307 1 0.050 0.000 0.000 0.00 0.00 0.00    25.2
1265 #EDIT
1266 DELETE Q(10)
1267 END
The following atom(s) will be deleted
   Q  10
1268 #EDIT
1269 DELETE Q(8)
1270 END
The following atom(s) will be deleted
   Q   8
1271 #EDIT
1272 DELETE Q(9)
1273 END
The following atom(s) will be deleted
   Q   9
```

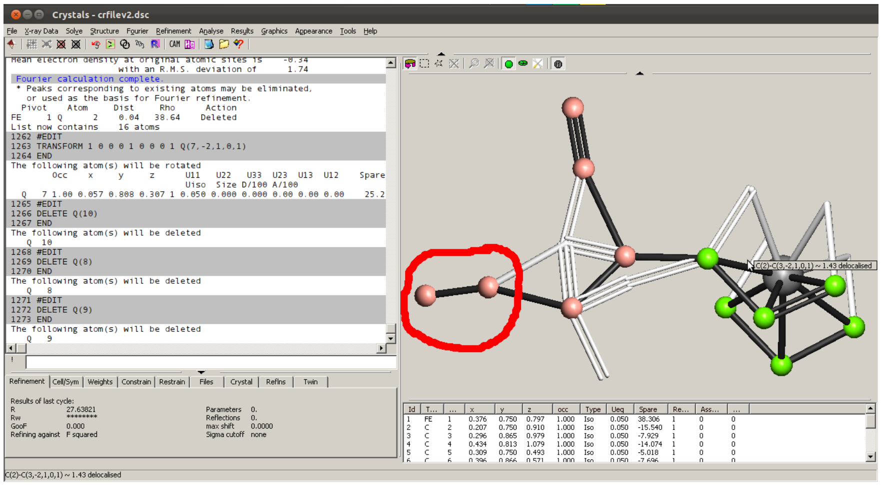
Results of last cycle:

R	27.63821	Parameters	0.
Rw	********	Reflections	0.
GooF	0.000	max shift	0.0000
Refining against	F squared	Sigma cutoff	none

Id	T...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	FE	1	0.376	0.750	0.797	1.000	Iso	0.050	38.306	1	0	0
2	C	2	0.207	0.750	0.910	1.000	Iso	0.050	-15.540	1	0	0
3	C	3	0.296	0.865	0.979	1.000	Iso	0.050	-7.929	1	0	0
4	C	4	0.434	0.813	1.079	1.000	Iso	0.050	-14.074	1	0	0
5	C	5	0.309	0.750	0.493	1.000	Iso	0.050	-5.018	1	0	0
6	C	6	0.396	0.866	0.571	1.000	Iso	0.050	-7.696	1	0	0

C(2)-C(3,-2,1,0,1) ~ 1.43 delocalised

Figure 5: Relocated by symmetry maxima of the electron density. Peaks around ferrocene were removed.



```
Mean electron density at original atomic sites is    -0.34
                      with an R.M.S. deviation of      1.74
 Fourier calculation complete.
 * Peaks corresponding to existing atoms may be eliminated,
   or used as the basis for Fourier refinement.
  Pivot    Atom     Dist     Rho      Action
FE     1 Q      2    0.04   38.64    Deleted
List now contains    16 atoms
1262 #EDIT
1263 TRANSFORM 1 0 0 0 1 0 0 0 1 Q(7,-2,1,0,1)
1264 END
The following atom(s) will be rotated
        Occ    x     y     z      U11   U22   U33  U23  U13  U12    Spare
                                  Uiso  Size D/100 A/100
  Q   7 1.00 0.057 0.808 0.307 1 0.050 0.000 0.000 0.00 0.00 0.00    25.2
1265 #EDIT
1266 DELETE Q(10)
1267 END
The following atom(s) will be deleted
   Q  10
1268 #EDIT
1269 DELETE Q(8)
1270 END
The following atom(s) will be deleted
   Q   8
1271 #EDIT
1272 DELETE Q(9)
1273 END
The following atom(s) will be deleted
   Q   9
```

Results of last cycle:

R	27.63821	Parameters	0.
Rw	********	Reflections	0.
GooF	0.000	max shift	0.0000
Refining against	F squared	Sigma cutoff	none

Id	T...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	FE	1	0.376	0.750	0.797	1.000	Iso	0.050	38.306	1	0	0
2	C	2	0.207	0.750	0.910	1.000	Iso	0.050	-15.540	1	0	0
3	C	3	0.296	0.865	0.979	1.000	Iso	0.050	-7.929	1	0	0
4	C	4	0.434	0.813	1.079	1.000	Iso	0.050	-14.074	1	0	0
5	C	5	0.309	0.750	0.493	1.000	Iso	0.050	-5.018	1	0	0
6	C	6	0.396	0.866	0.571	1.000	Iso	0.050	-7.696	1	0	0

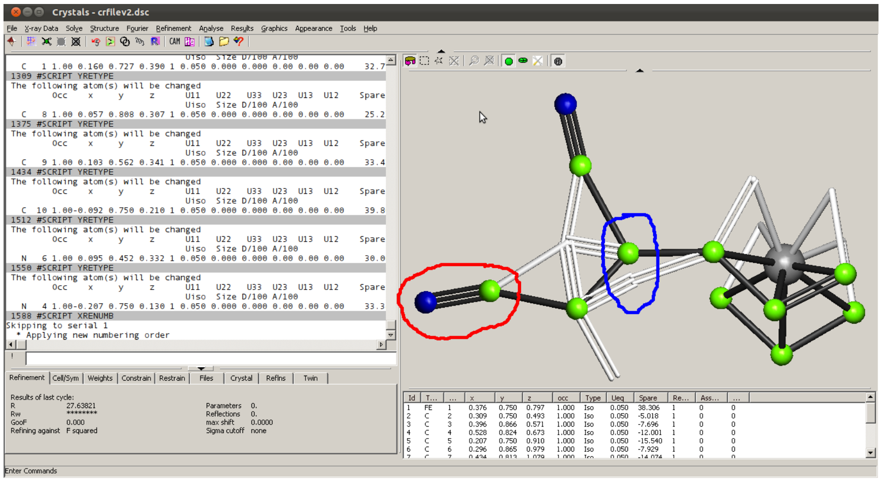
C(2)-C(3,-2,1,0,1) ~ 1.43 delocalised

Figure 6: Two maxima lie on symmetry element.

the atoms into one we need decrease that threshold to say 0.1 Å. Go to ***Refinement* →*F or Fsq and advanced option*** and change value in "Snap onto position if within:" from 0.6 to 0.1. Now we can refine our molecule in the isotropic approximation to make sure our C(8) atoms will not merge into the one on a special position. We can use GUI or command:

```
\list 12
block scale Fe(1,x's, u[iso]) until last
end
\sfls
refine
refine
refine
end
```

After refinement R = 18.84, Rw = 41.94, maxshift = 1.548, GooF = 3.62. Now we need to check the coordinates for our nitryl group (C(11) and N(13)).



```
                                  Uiso  Size D/100 A/100
   C   1 1.00 0.160 0.727 0.390 1 0.050 0.000 0.000 0.00 0.00 0.00     32.7
 1309 #SCRIPT YRETYPE
 The following atom(s) will be changed
        Occ     x      y      z       U11    U22    U33   U23   U13   U12     Spare
                                  Uiso  Size D/100 A/100
   C   8 1.00 0.057 0.808 0.307 1 0.050 0.000 0.000 0.00 0.00 0.00     25.2
 1375 #SCRIPT YRETYPE
 The following atom(s) will be changed
        Occ     x      y      z       U11    U22    U33   U23   U13   U12     Spare
                                  Uiso  Size D/100 A/100
   C   9 1.00 0.103 0.562 0.341 1 0.050 0.000 0.000 0.00 0.00 0.00     33.4
 1434 #SCRIPT YRETYPE
 The following atom(s) will be changed
        Occ     x      y      z       U11    U22    U33   U23   U13   U12     Spare
                                  Uiso  Size D/100 A/100
   C  10 1.00-0.092 0.750 0.210 1 0.050 0.000 0.000 0.00 0.00 0.00     39.8
 1512 #SCRIPT YRETYPE
 The following atom(s) will be changed
        Occ     x      y      z       U11    U22    U33   U23   U13   U12     Spare
                                  Uiso  Size D/100 A/100
   N   6 1.00 0.095 0.452 0.332 1 0.050 0.000 0.000 0.00 0.00 0.00     30.0
 1550 #SCRIPT YRETYPE
 The following atom(s) will be changed
        Occ     x      y      z       U11    U22    U33   U23   U13   U12     Spare
                                  Uiso  Size D/100 A/100
   N   4 1.00-0.207 0.750 0.130 1 0.050 0.000 0.000 0.00 0.00 0.00     33.3
 1588 #SCRIPT XRENUMB
Skipping to serial 1
  * Applying new numbering order
```

Results of last cycle:

R	27.63821	Parameters	0.
Rw	********	Reflections	0.
GooF	0.000	max shift	0.0000
Refining against	F squared	Sigma cutoff	none

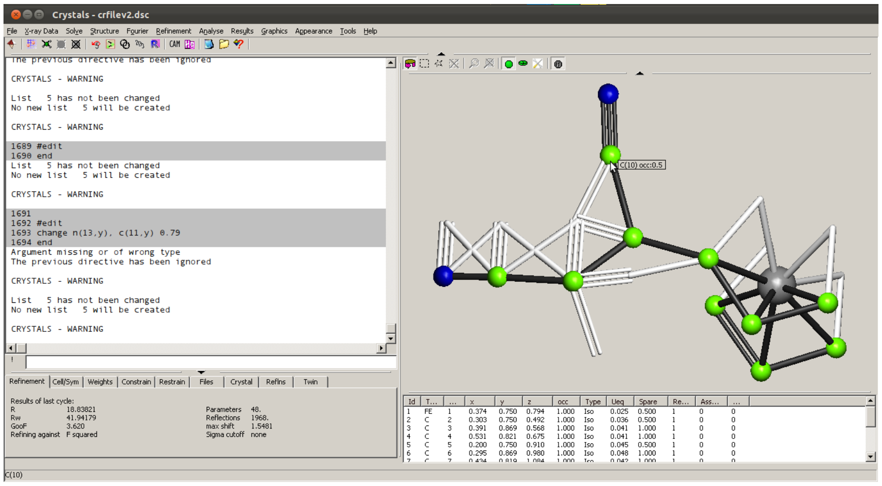
Id	T...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	FE	1	0.376	0.750	0.797	1.000	Iso	0.050	38.306	1	0	0
2	C	2	0.309	0.750	0.493	1.000	Iso	0.050	-5.018	1	0	0
3	C	3	0.396	0.866	0.571	1.000	Iso	0.050	-7.696	1	0	0
4	C	4	0.528	0.824	0.673	1.000	Iso	0.050	-12.001	1	0	0
5	C	5	0.207	0.750	0.910	1.000	Iso	0.050	-15.540	1	0	0
6	C	6	0.296	0.865	0.979	1.000	Iso	0.050	-7.929	1	0	0

Figure 7: Two groups of the atoms are target for merging during refinement. Red circle - C(11) and N(13); Blue circle - C(8) and C(8,-2,1,0,1)

```
\summary list 5
end
```

In the printed information we find that the Y coordinate for C(11) and N(13) is constrained to be exactly 0.75. That corresponds to position of the atoms on mirror symmetry. We need manually change that coordinate say to 0.8.

```
\edit
change c(11,y) 0.8
change n(13,y) 0.8
end
```



```
The previous directive has been ignored

CRYSTALS - WARNING

List   5 has not been changed
No new list   5 will be created

CRYSTALS - WARNING

1689 #edit
1690 end
List   5 has not been changed
No new list   5 will be created

CRYSTALS - WARNING

1691
1692 #edit
1693 change n(13,y), c(11,y) 0.79
1694 end
Argument missing or of wrong type
The previous directive has been ignored

CRYSTALS - WARNING

List   5 has not been changed
No new list   5 will be created

CRYSTALS - WARNING
```

Results of last cycle:

R	18.83821	Parameters	48.
Rw	41.94179	Reflections	1968.
GooF	3.620	max shift	1.5481
Refining against	F squared	Sigma cutoff	none

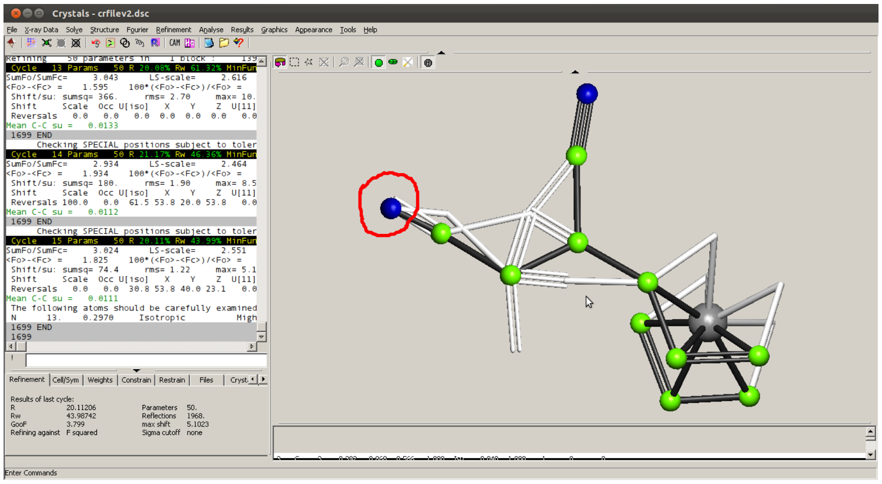
Id	T...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	FE	1	0.374	0.750	0.794	1.000	Iso	0.025	0.500	1	0	0
2	C	2	0.303	0.750	0.492	1.000	Iso	0.036	0.500	1	0	0
3	C	3	0.391	0.869	0.568	1.000	Iso	0.041	1.000	1	0	0
4	C	4	0.531	0.821	0.675	1.000	Iso	0.041	1.000	1	0	0
5	C	5	0.200	0.750	0.910	1.000	Iso	0.045	0.500	1	0	0
6	C	6	0.295	0.869	0.980	1.000	Iso	0.048	1.000	1	0	0

Figure 8: Model after coordinate manipulation.

The model should look as presented in Figure 8. After these coordinates manipulations, we need to repeat a couple cycles of refinement.

```
\sfls
refine
refine
refine
end
```

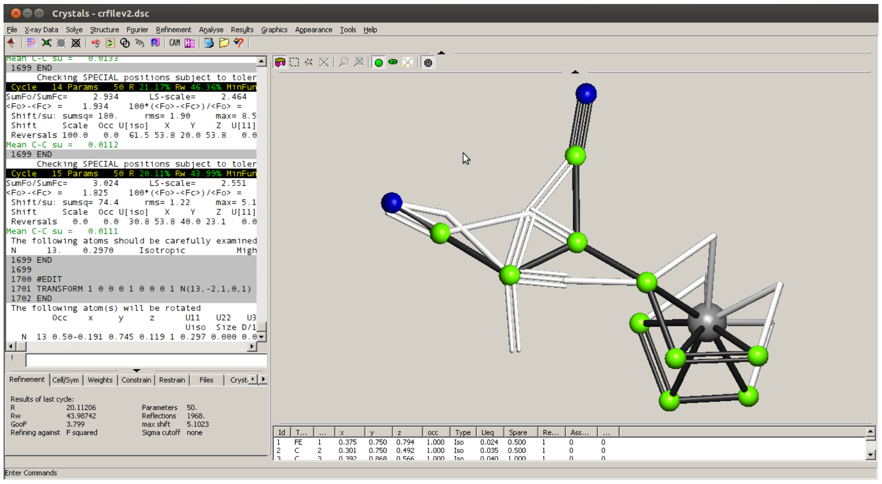
The model after refinement presented in Figure 9. We can also see nitrogen atom doesn't correspond to the first disordered part and needs to be relocated by a symmetry operation (right click on symmetry related position where we expect new atom should be) (Figure 10).



```
Refining    50 parameters in    1 block :     139
 Cycle   13 Params    50 R 20.08% Rw 61.32% MinFun
SumFo/SumFc=     3.043      LS-scale=     2.616
<Fo>-<Fc> =    1.595    100*(<Fo>-<Fc>)/<Fo> =
 Shift/su: sumsq= 366.      rms= 2.70     max= 10.
 Shift      Scale  Occ U[iso]   X     Y     Z  U[11]
 Reversals   0.0    0.0   0.0  0.0  0.0  0.0   0.0
Mean C-C su =   0.0133
 1699 END
      Checking SPECIAL positions subject to toler
 Cycle   14 Params    50 R 21.17% Rw 46.36% MinFun
SumFo/SumFc=     2.934      LS-scale=     2.464
<Fo>-<Fc> =    1.934    100*(<Fo>-<Fc>)/<Fo> =
 Shift/su: sumsq= 180.      rms= 1.90     max= 8.5
 Shift      Scale  Occ U[iso]   X     Y     Z  U[11]
 Reversals 100.0    0.0  61.5 53.8 20.0 53.8   0.0
Mean C-C su =   0.0112
 1699 END
      Checking SPECIAL positions subject to toler
 Cycle   15 Params    50 R 20.11% Rw 43.99% MinFun
SumFo/SumFc=     3.024      LS-scale=     2.551
<Fo>-<Fc> =    1.825    100*(<Fo>-<Fc>)/<Fo> =
 Shift/su: sumsq= 74.4      rms= 1.22     max= 5.1
 Shift      Scale  Occ U[iso]   X     Y     Z  U[11]
 Reversals   0.0    0.0  30.8 53.8 40.0 23.1   0.0
Mean C-C su =   0.0111
 The following atoms should be carefully examined
 N      13.    0.2970     Isotropic          Migh
 1699 END
 1699
```

```
Results of last cycle:
R                  20.11206          Parameters    50.
Rw                 43.98742          Reflections   1968.
GooF               3.799             max shift     5.1023
Refining against   F squared         Sigma cutoff  none
```

Figure 9: Model after Least-squares refinement. The red circled nitrogen atoms should be relocated.



```
Mean C-C su =   0.0133
 1699 END
      Checking SPECIAL positions subject to toler
 Cycle   14 Params    50 R 21.17% Rw 46.36% MinFun
SumFo/SumFc=     2.934      LS-scale=     2.464
<Fo>-<Fc> =    1.934    100*(<Fo>-<Fc>)/<Fo> =
 Shift/su: sumsq= 180.      rms= 1.90     max= 8.5
 Shift      Scale  Occ U[iso]   X     Y     Z  U[11]
 Reversals 100.0    0.0  61.5 53.8 20.0 53.8   0.0
Mean C-C su =   0.0112
 1699 END
      Checking SPECIAL positions subject to toler
 Cycle   15 Params    50 R 20.11% Rw 43.99% MinFun
SumFo/SumFc=     3.024      LS-scale=     2.551
<Fo>-<Fc> =    1.825    100*(<Fo>-<Fc>)/<Fo> =
 Shift/su: sumsq= 74.4      rms= 1.22     max= 5.1
 Shift      Scale  Occ U[iso]   X     Y     Z  U[11]
 Reversals   0.0    0.0  30.8 53.8 40.0 23.1   0.0
Mean C-C su =   0.0111
 The following atoms should be carefully examined
 N      13.    0.2970     Isotropic          Migh
 1699 END
 1699
 1700 #EDIT
 1701 TRANSFORM 1 0 0 0 1 0 0 0 1 N(13,-2,1,0,1)
 1702 END
 The following atom(s) will be rotated
        Occ     x      y      z       U11   U22   U3
                                      Uiso  Size D/1
   N  13 0.50-0.191 0.745 0.119 1 0.297 0.000 0.0
```

```
Results of last cycle:
R                  20.11206          Parameters    50.
Rw                 43.98742          Reflections   1968.
GooF               3.799             max shift     5.1023
Refining against   F squared         Sigma cutoff  none
```

Id	T...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	FE	1	0.375	0.750	0.794	1.000	Iso	0.024	0.500	1	0	0
2	C	2	0.301	0.750	0.492	1.000	Iso	0.035	0.500	1	0	0
3	C	3	0.392	0.868	0.566	1.000	Iso	0.040	1.000	1	0	0

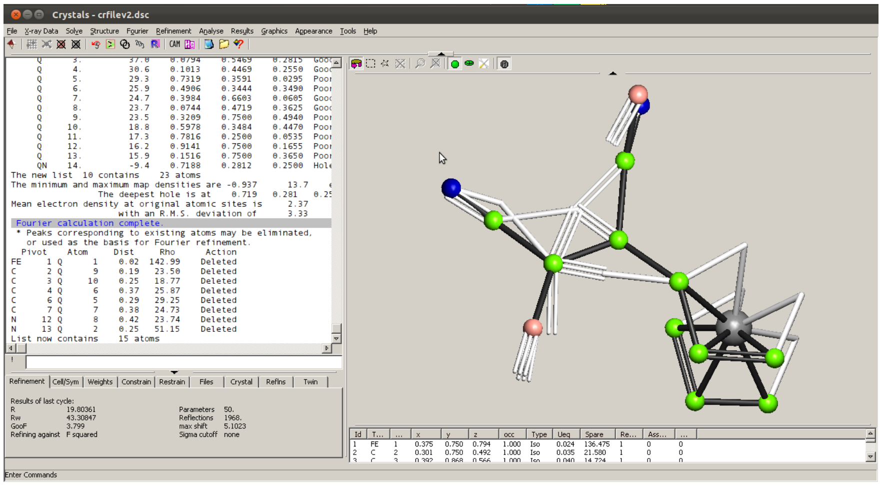
Figure 10: Model after moving nitrogen atoms through symmetry element.

The Fourier analysis with default parameters reveals two maxima of the electron density (Figure 11).

We also need to reorganize (relocate) these peaks. As we can see the third nitryl group has emerged. We need to change the atom type for the maxima of the electron density and renumber the atoms once again. The final model presented in Figure 12.

The atoms from C(8) to N(14) belong to disordered tricyanothene fragment. We need to change the occupancy of all the atoms to be 0.5:

```
\edit
```

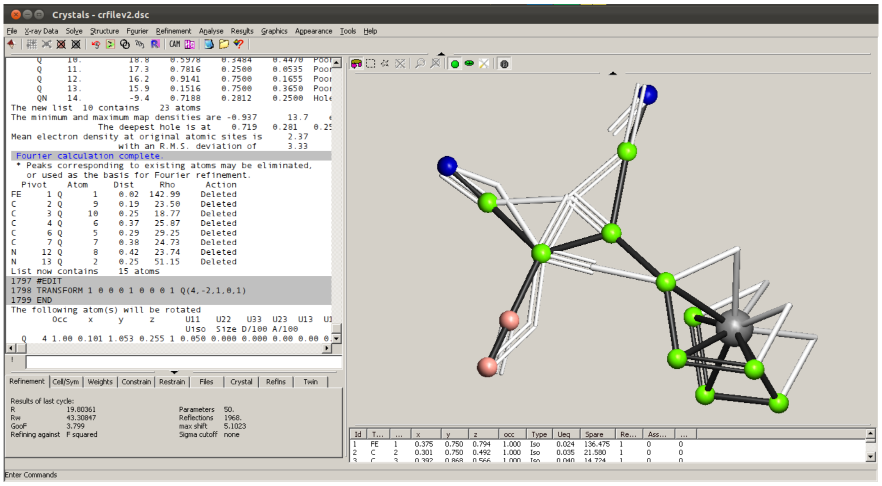


```
     Q       3.          37.0    0.0794    0.5469    0.2815  Goo
     Q       4.          30.6    0.1013    0.4469    0.2550  Goo
     Q       5.          29.3    0.7319    0.3591    0.0295  Poor
     Q       6.          25.9    0.4906    0.3444    0.3490  Poor
     Q       7.          24.7    0.3984    0.6603    0.0605  Goo
     Q       8.          23.7    0.0744    0.4719    0.3625  Goo
     Q       9.          23.5    0.3209    0.7500    0.4940  Poor
     Q      10.          18.8    0.5978    0.3484    0.4470  Poor
     Q      11.          17.3    0.7816    0.2500    0.0535  Poor
     Q      12.          16.2    0.9141    0.7500    0.1655  Poor
     Q      13.          15.9    0.1516    0.7500    0.3650  Poor
     QN     14.          -9.4    0.7188    0.2812    0.2500  Hole
The new list  10 contains    23 atoms
The minimum and maximum map densities are -0.937      13.7     e
                 The deepest hole is at    0.719   0.281   0.25
Mean electron density at original atomic sites is     2.37
                     with an R.M.S. deviation of      3.33
 Fourier calculation complete.
 * Peaks corresponding to existing atoms may be eliminated,
   or used as the basis for Fourier refinement.
  Pivot    Atom     Dist     Rho      Action
FE     1 Q      1    0.02  142.99    Deleted
C      2 Q      9    0.19   23.50    Deleted
C      3 Q     10    0.25   18.77    Deleted
C      4 Q      6    0.37   25.87    Deleted
C      6 Q      5    0.29   29.25    Deleted
C      7 Q      7    0.38   24.73    Deleted
N     12 Q      8    0.42   23.74    Deleted
N     13 Q      2    0.25   51.15    Deleted
List now contains    15 atoms
```

```
Results of last cycle:
R                  19.80361          Parameters     50.
Rw                 43.30847          Reflections    1968.
GooF               3.799             max shift      5.1023
Refining against   F squared         Sigma cutoff   none
```

Id	T...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	FE	1	0.375	0.750	0.794	1.000	Iso	0.024	136.475	1	0	0
2	C	2	0.301	0.750	0.492	1.000	Iso	0.035	21.580	1	0	0
3	C	3	0.392	0.868	0.566	1.000	Iso	0.040	14.724	1	0	0

Figure 11: Model after Fourier analysis.



```
     Q      10.          18.8    0.5978    0.3484    0.4470  Poor
     Q      11.          17.3    0.7816    0.2500    0.0535  Poor
     Q      12.          16.2    0.9141    0.7500    0.1655  Poor
     Q      13.          15.9    0.1516    0.7500    0.3650  Poor
     QN     14.          -9.4    0.7188    0.2812    0.2500  Hole
The new list  10 contains    23 atoms
The minimum and maximum map densities are -0.937      13.7     e
                 The deepest hole is at    0.719   0.281   0.25
Mean electron density at original atomic sites is     2.37
                     with an R.M.S. deviation of      3.33
 Fourier calculation complete.
 * Peaks corresponding to existing atoms may be eliminated,
   or used as the basis for Fourier refinement.
  Pivot    Atom     Dist     Rho      Action
FE     1 Q      1    0.02  142.99    Deleted
C      2 Q      9    0.19   23.50    Deleted
C      3 Q     10    0.25   18.77    Deleted
C      4 Q      6    0.37   25.87    Deleted
C      6 Q      5    0.29   29.25    Deleted
C      7 Q      7    0.38   24.73    Deleted
N     12 Q      8    0.42   23.74    Deleted
N     13 Q      2    0.25   51.15    Deleted
List now contains    15 atoms
1797 #EDIT
1798 TRANSFORM 1 0 0 0 1 0 0 0 1 Q(4,-2,1,0,1)
1799 END
The following atom(s) will be rotated
        Occ    x      y      z       U11    U22    U33   U23  U13   U1
                                     Uiso  Size D/100 A/100
  Q    4 1.00 0.101 1.053 0.255 1 0.050 0.000 0.000 0.00 0.00 0.
```

```
Results of last cycle:
R                  19.80361          Parameters     50.
Rw                 43.30847          Reflections    1968.
GooF               3.799             max shift      5.1023
Refining against   F squared         Sigma cutoff   none
```

Id	T...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	FE	1	0.375	0.750	0.794	1.000	Iso	0.024	136.475	1	0	0
2	C	2	0.301	0.750	0.492	1.000	Iso	0.035	21.580	1	0	0
3	C	3	0.392	0.868	0.566	1.000	Iso	0.040	14.724	1	0	0

Figure 12: Relocated maxima of the electron density.

```
change c(8,occ) until last 0.5
end
```

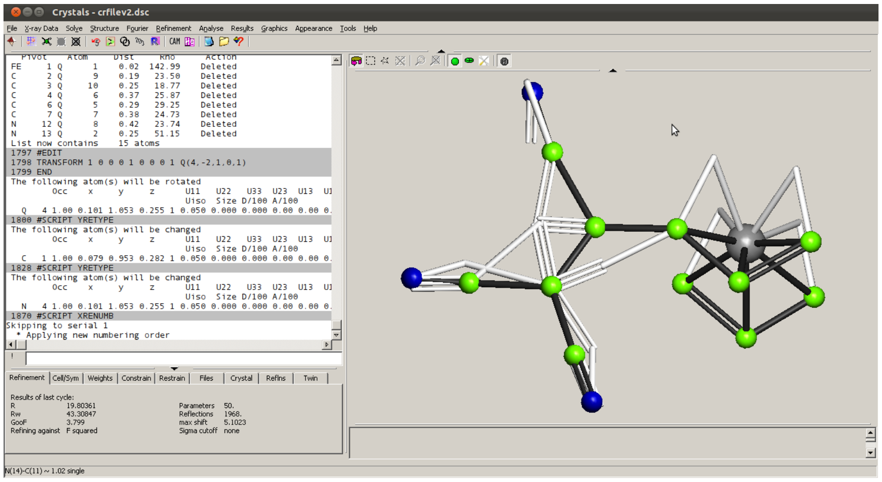
Actually, we need to change occupation factors only for new added atoms. Since we renumbered atoms it is quicker to do this in the way shown above. Now we are ready to refine our model in isotropic approximation:

```
\sfls
refine
refine
refine
end
```

After refinement R = 9.52, Rw = 28.86, maxshift = 12.88, GooF = 2.50 and the final model is presented in Figure 14. The circled nitrogen atoms need to be symmetry relocated.

We can refine iron atom (Fe(1)) and all the carbon atoms from ferrocene (C(2)-C(7)) in the anisotropic approximation but the disordered part should be refined in the isotropic approximation:

```
\list 12
```

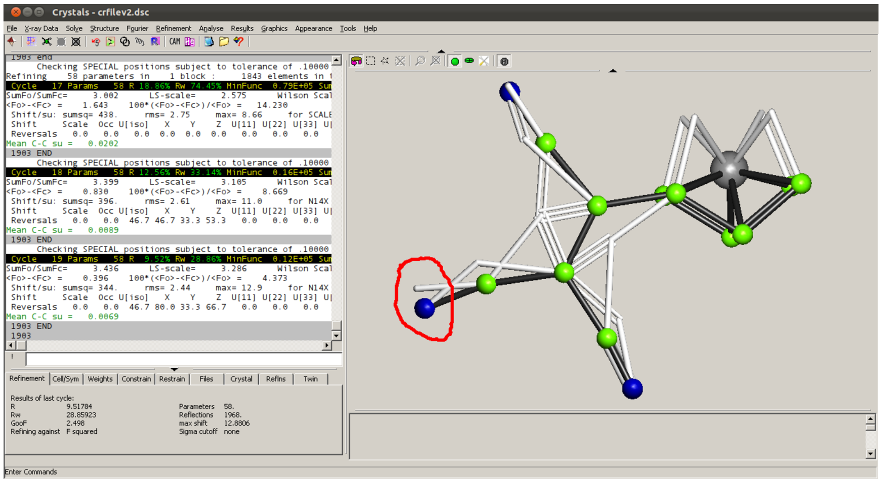


```
  Pivot    Atom     Dist     Rho      Action
FE     1 Q      1    0.02  142.99    Deleted
C      2 Q      9    0.19   23.50    Deleted
C      3 Q     10    0.25   18.77    Deleted
C      4 Q      6    0.37   25.87    Deleted
C      6 Q      5    0.29   29.25    Deleted
C      7 Q      7    0.38   24.73    Deleted
N     12 Q      8    0.42   23.74    Deleted
N     13 Q      2    0.25   51.15    Deleted
List now contains    15 atoms
1797 #EDIT
1798 TRANSFORM 1 0 0 0 1 0 0 0 1 Q(4,-2,1,0,1)
1799 END
The following atom(s) will be rotated
        Occ    x     y     z      U11   U22   U33  U23  U13  U1
                                  Uiso  Size D/100 A/100
  Q   4 1.00 0.101 1.053 0.255 1 0.050 0.000 0.000 0.00 0.00 0.
1800 #SCRIPT YRETYPE
The following atom(s) will be changed
        Occ    x     y     z      U11   U22   U33  U23  U13  U1
                                  Uiso  Size D/100 A/100
  C   1 1.00 0.079 0.953 0.282 1 0.050 0.000 0.000 0.00 0.00 0.
1828 #SCRIPT YRETYPE
The following atom(s) will be changed
        Occ    x     y     z      U11   U22   U33  U23  U13  U1
                                  Uiso  Size D/100 A/100
  N   4 1.00 0.101 1.053 0.255 1 0.050 0.000 0.000 0.00 0.00 0.
1870 #SCRIPT XRENUMB
Skipping to serial 1
  * Applying new numbering order
```

```
Results of last cycle:
R                  19.80361          Parameters    50.
Rw                 43.30847          Reflections   1968.
GooF               3.799             max shift     5.1023
Refining against   F squared         Sigma cutoff  none
```

N(14)-C(11) ~ 1.02 single

Figure 13: Final model after all maxima of the electron density were renamed.



```
 1903 end
      Checking SPECIAL positions subject to tolerance of .10000
Refining    58 parameters in    1 block :     1843 elements in t
 Cycle   17 Params    58 R 18.86% Rw 74.45% MinFunc  0.79E+05 Sum
SumFo/SumFc=     3.002      LS-scale=     2.575      Wilson Scal
<Fo>-<Fc> =    1.643    100*(<Fo>-<Fc>)/<Fo> =   14.230
 Shift/su: sumsq= 438.      rms= 2.75      max= 8.66      for SCALE
 Shift     Scale  Occ U[iso]   X    Y    Z  U[11] U[22] U[33] U[
 Reversals   0.0   0.0   0.0  0.0  0.0  0.0   0.0   0.0   0.0
Mean C-C su =   0.0202
 1903 END
      Checking SPECIAL positions subject to tolerance of .10000
 Cycle   18 Params    58 R 12.56% Rw 33.14% MinFunc  0.16E+05 Sum
SumFo/SumFc=     3.399      LS-scale=     3.105      Wilson Scal
<Fo>-<Fc> =    0.830    100*(<Fo>-<Fc>)/<Fo> =    8.669
 Shift/su: sumsq= 396.      rms= 2.61      max= 11.0      for N14X
 Shift     Scale  Occ U[iso]   X    Y    Z  U[11] U[22] U[33] U[
 Reversals   0.0   0.0  46.7 46.7 33.3 53.3   0.0   0.0   0.0
Mean C-C su =   0.0089
 1903 END
      Checking SPECIAL positions subject to tolerance of .10000
 Cycle   19 Params    58 R  9.52% Rw 28.86% MinFunc  0.12E+05 Sum
SumFo/SumFc=     3.436      LS-scale=     3.286      Wilson Scal
<Fo>-<Fc> =    0.396    100*(<Fo>-<Fc>)/<Fo> =    4.373
 Shift/su: sumsq= 344.      rms= 2.44      max= 12.9      for N14X
 Shift     Scale  Occ U[iso]   X    Y    Z  U[11] U[22] U[33] U[
 Reversals   0.0   0.0  46.7 80.0 33.3 66.7   0.0   0.0   0.0
Mean C-C su =   0.0069
 1903 END
 1903
```

```
Results of last cycle:
R                  9.51784           Parameters    58.
Rw                 28.85923          Reflections   1968.
GooF               2.498             max shift     12.8806
Refining against   F squared         Sigma cutoff  none
```

Enter Commands

Figure 14: Final model after Least-square refinement. Red circled atoms need to be symmetry relocated.

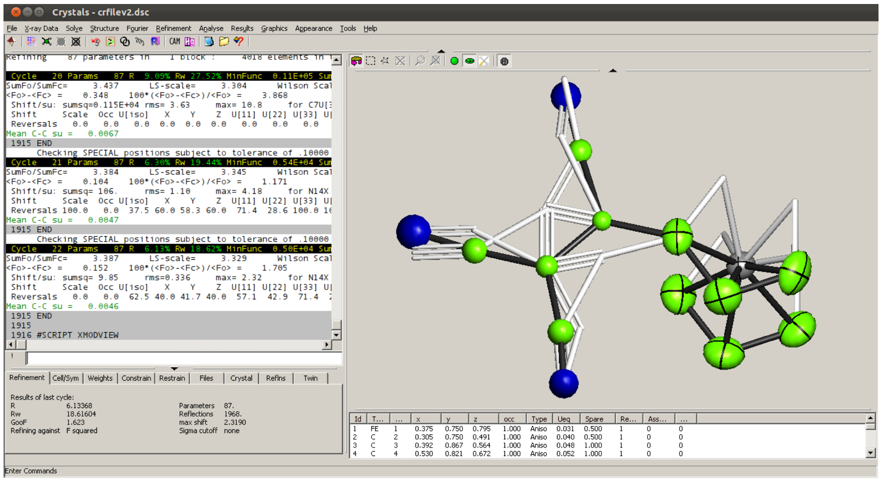
```
block scale Fe(1,x's,u's) until c(7)
cont c(8,x's,u[iso]) unitl last
end
\sfls
refine
refine
refine
end
```

The final model after refinement presented in Figure 15. After refinement R = 6.13, Rw = 18.61, maxshift = 2.32, GooF = 1.623. As we can see, all ADP's (anisotropic and isotropic) are reasonable.

We can also check numeric values for atomic parameters:

```
\summary list 5
end
```

or if we need more detail analysis of refined parameters we can punch our LIST 5 and analyze it:

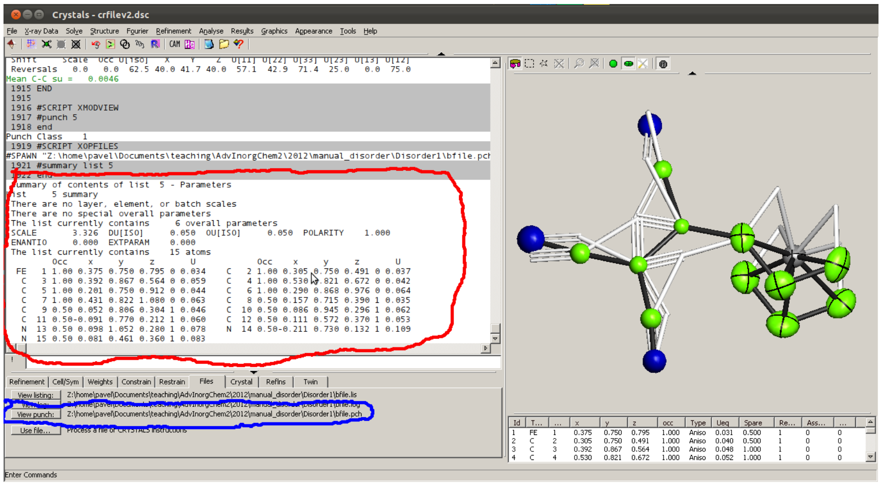


```
Cycle   20 Params   87 R  9.09% Rw 27.52% MinFunc  0.11E+05 Sum
SumFo/SumFc=     3.437      LS-scale=     3.304      Wilson Scal
<Fo>-<Fc> =    0.348    100*(<Fo>-<Fc>)/<Fo> =    3.868
 Shift/su: sumsq=0.115E+04 rms= 3.63     max= 10.8      for C7U[3
 Shift     Scale  Occ U[iso]   X     Y     Z  U[11] U[22] U[33] U[
 Reversals   0.0    0.0   0.0  0.0  0.0  0.0   0.0   0.0   0.0
Mean C-C su =   0.0067
 1915 END
      Checking SPECIAL positions subject to tolerance of .10000
 Cycle   21 Params   87 R  6.30% Rw 19.44% MinFunc  0.54E+04 Sum
SumFo/SumFc=     3.384      LS-scale=     3.345      Wilson Scal
<Fo>-<Fc> =    0.104    100*(<Fo>-<Fc>)/<Fo> =    1.171
 Shift/su: sumsq= 106.     rms= 1.10     max= 4.18      for N14X
 Shift     Scale  Occ U[iso]   X     Y     Z  U[11] U[22] U[33] U[
 Reversals 100.0   0.0  37.5 60.0 58.3 60.0  71.4  28.6 100.0 10
Mean C-C su =   0.0047
 1915 END
      Checking SPECIAL positions subject to tolerance of .10000
 Cycle   22 Params   87 R  6.13% Rw 18.62% MinFunc  0.50E+04 Sum
SumFo/SumFc=     3.387      LS-scale=     3.329      Wilson Scal
<Fo>-<Fc> =    0.152    100*(<Fo>-<Fc>)/<Fo> =    1.705
 Shift/su: sumsq= 9.85     rms=0.336     max= 2.32      for N14X
 Shift     Scale  Occ U[iso]   X     Y     Z  U[11] U[22] U[33] U[
 Reversals   0.0    0.0  62.5 40.0 41.7 40.0  57.1  42.9  71.4  2
Mean C-C su =   0.0046
 1915 END
 1915
 1916 #SCRIPT XMODVIEW
```

```
Results of last cycle:
R                   6.13368          Parameters    87.
Rw                  18.61604         Reflections   1968.
GooF                1.623            max shift     2.3190
Refining against    F squared        Sigma cutoff  none
```

Id	T...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	FE	1	0.375	0.750	0.795	1.000	Aniso	0.031	0.500	1	0	0
2	C	2	0.305	0.750	0.491	1.000	Aniso	0.040	0.500	1	0	0
3	C	3	0.392	0.867	0.564	1.000	Aniso	0.048	1.000	1	0	0
4	C	4	0.530	0.821	0.672	1.000	Aniso	0.052	1.000	1	0	0

Figure 15: Model after refinement. Ferrocene unit refined in anisotropic approximation.



```
 Shift     Scale  Occ U[iso]   X     Y     Z  U[11] U[22] U[33] U[23] U[13] U[12]
 Reversals   0.0    0.0  62.5 40.0 41.7 40.0  57.1  42.9  71.4  25.0   0.0  75.0
Mean C-C su =   0.0046
 1915 END
 1915
 1916 #SCRIPT XMODVIEW
 1917 #punch 5
 1918 end
Punch Class    1
 1919 #SCRIPT XOPFILES
#SPAWN "Z:\home\pavel\Documents\teaching\AdvInorgChem2\2012\manual_disorder\Disorder1\bfile.pch
 1921 #summary list 5
 1922 end
 Summary of contents of list  5 - Parameters
 List     5 summary
 There are no layer, element, or batch scales
 There are no special overall parameters
 The list currently contains     6 overall parameters
 SCALE        3.326  DU[ISO]      0.050  OU[ISO]      0.050  POLARITY    1.000
 ENANTIO      0.000  EXTPARAM     0.000
 The list currently contains    15 atoms
         Occ    x     y     z      U            Occ    x     y     z      U
  FE   1 1.00 0.375 0.750 0.795 0 0.034    C    2 1.00 0.305 0.750 0.491 0 0.037
   C   3 1.00 0.392 0.867 0.564 0 0.059    C    4 1.00 0.530 0.821 0.672 0 0.042
   C   5 1.00 0.201 0.750 0.912 0 0.044    C    6 1.00 0.290 0.868 0.976 0 0.064
   C   7 1.00 0.431 0.822 1.080 0 0.063    C    8 0.50 0.157 0.715 0.390 1 0.035
   C   9 0.50 0.052 0.806 0.304 1 0.046    C   10 0.50 0.086 0.945 0.296 1 0.062
   C  11 0.50-0.091 0.770 0.212 1 0.060    C   12 0.50 0.111 0.572 0.370 1 0.053
   N  13 0.50 0.098 1.052 0.280 1 0.078    N   14 0.50-0.211 0.730 0.132 1 0.109
   N  15 0.50 0.081 0.461 0.360 1 0.083
```

```
View listing:  Z:\home\pavel\Documents\teaching\AdvInorgChem2\2012\manual_disorder\Disorder1\bfile.lis
View log:      Z:\home\pavel\Documents\teaching\AdvInorgChem2\2012\manual_disorder\Disorder1\bfile.log
View punch:    Z:\home\pavel\Documents\teaching\AdvInorgChem2\2012\manual_disorder\Disorder1\bfile.pch
Use file...    Process a file of CRYSTALS instructions
```

Id	T...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	FE	1	0.375	0.750	0.795	1.000	Aniso	0.031	0.500	1	0	0
2	C	2	0.305	0.750	0.491	1.000	Aniso	0.040	0.500	1	0	0
3	C	3	0.392	0.867	0.564	1.000	Aniso	0.048	1.000	1	0	0
4	C	4	0.530	0.821	0.672	1.000	Aniso	0.052	1.000	1	0	0

Figure 16: Summary information of LIST 5 (Red circled).

```
\summary list 5 high
end
```

or

```
\punch 5
end
```

If we use the "*punch*" command, we put information into the punch file *bfile.pch*. To check that file go to "Files" tab or go to the project folder and open it with any text editor (Figure 16). Outgoing information from the *SUMMARY* command will be stored in the *bfileXX.lis* file. It is also useful to run a difference Fourier analysis to make sure we didn't miss some atoms. We can use the GUI or command:

```
\fourier
map type=diff
end
```

The minimum and maximum map densities are -0.892 and 1.16 e$^-$/Å^3. Taking into account the values of our R factors and that fact we don't have hydrogen atoms yet we can say there is no electron density left for atoms such as carbon. Since we don't have any problem with refinement we can refine all atoms in anisotropic approximation. We can use the GUI (***Refinement →and refine***) or the command line.

```
\list 12
block scale x's, u's
end
\sfls
refine
refine
refine
end
```

If needed we can do extra 5 cycles of refinement:

```
\sfls
refine
refine
refine
refine
refine
end
```

Table 1: Final parameters after refinement

Formula	$C_{15}H_9FeN_3$		
Crystal Class	Monoclinic	Space Group	P21/m
a, Å	9.688(2)	alpha,°	90
b, Å	9.907(3)	beta,°	106.35(2)
c, Å	6.989(2)	gamma,°	90
Volume, Å^3	643.7(3)	Z	2
Radiation type	Mo-Kα	Wavelength, Å	0.710730
Dx, g/cm^3	1.48	Mr, g/mol	143.55
μ, mm^3	1.158	Temp. (K)	293
Reflections measured	1974	Independent reflections	1974
R-factor	0.035	Weighted R-factor	0.083
		Max shift/su	0.0008
Delta Rho min	-0.34	Delta Rho max	0.62
Reflections used	1968	sigma(I) limit	-10.00
Number of parameters	128	Goodness of fit	1.048

After refinement R = 4.42, Rw = 13.29, maxshift = 0.048, GooF = 0.972. The minimum and maximum map densities after Fourier analysis are -0.46 and 0.617 e$^-$/Å^3. It is time to add hydrogens. The best way to place hydrogens is to use the GUI (***Structure →Add hydrogen geometrically***). Afterwards, we can refine our model together with hydrogens ("riding mode") ***Refinement →Setup and refine*** and setup "Ride H atoms" in "Hydrogen" section. To optimize weight scheme go to ***Refinement →Choose weights*** and accept the proposed "Auto-statistical" scheme type. Repeat refinement once again. If the GooF drops significantly below or above 1.0 we need re-optimize the weight scheme once again. Make sure we also included anomalous dispersion correction: ***Refinement →F or Fsq and advanced options*** and check "Anomalous scattering". Repeat refinement and reoptimize weights if needed. It is also very useful to check the consistency of our calculated and observed F values: ***Analysis →Fo vs Fc graph*** (omit reflections that deviate significantly from straight line by right-clicking on them and repeat refinement if needed). Go to ***Analysis →Publication check →Local Acta Checks*** to finish the validation process. Generate a *publish.cif*. Final parameters after refinement presented in Table 1.

Disorder of the butyl group

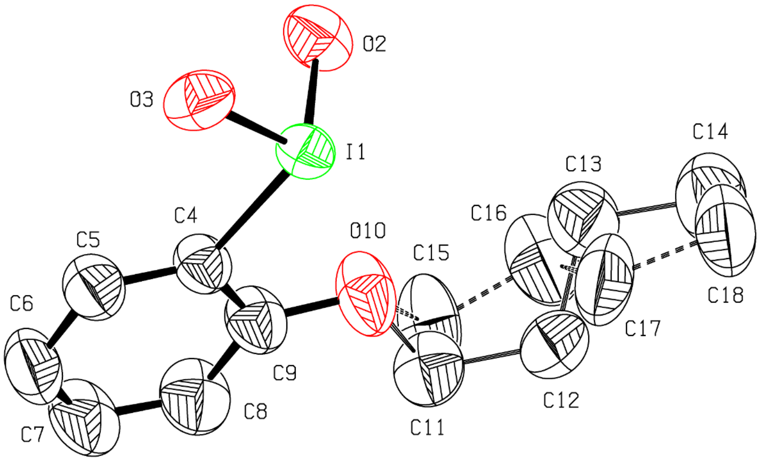
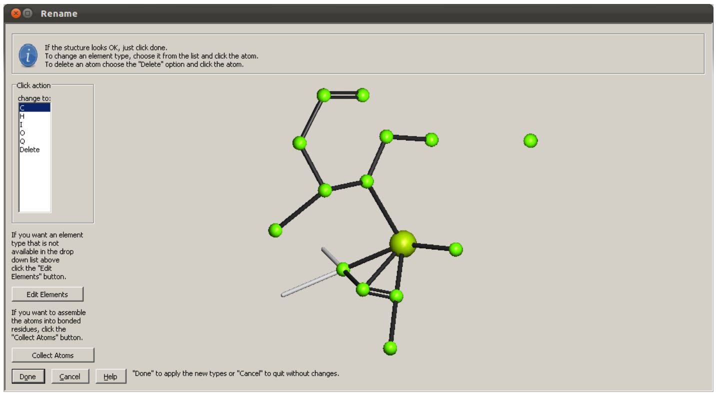


Figure 17: Example of the disordered n-butyl chain.

Another example of disorder will be discussed based on example published by Viktor V. Zhdankin and Victor V. Nemykin (J. Org. Chem., **2006**, 71 (22), 8452?8458) and kindly provided by Victor V. Nemykin (Figure 17). The compound crystallizes in monoclinic symmetry (P2_1/c) with four molecules per unit cell. The experimental data was integrated in space group P2_1/n. To convert the hkl data from space group P2_1/c to P2_1/n, the transformation matrix 0 0 1 0 1 0 -1 0 -1 should be provided in "Advanced" tab during reading the refection file. The structure was solved by the Patterson method implemented in SHELXS-86 and the results of the solution presented in figure 18.



If the stucture looks OK, just click done.
To change an element type, choose it from the list and click the atom.
To delete an atom choose the "Delete" option and click the atom.

If you want an element type that is not available in the drop down list above click the "Edit Elements" button.

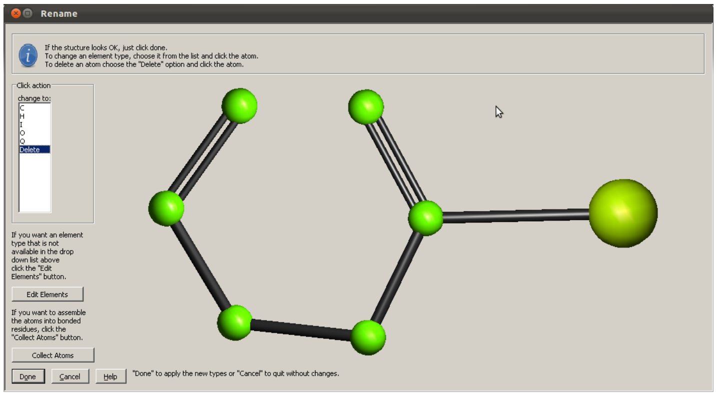
If you want to assemble the atoms into bonded residues, click the "Collect Atoms" button.

"Done" to apply the new types or "Cancel" to quit without changes.

Figure 18: Crystal structure solution by Patterson method using SHELXS-86 program.

As we can see, the structure solution reveals the positions of the iodine atom and carbon atoms of the benzene ring. The positions of others are not clear for now. After cleaning, the model it looks as presented in Figure 19.

We need to renumber all atoms starting from iodine. Since iodine is only one heavy element being present in the crystal structure we can start refinement in the isotropic approximation or leave all coordinates without refinement and run Fourier analysis. Let us try to do Fourier analysis without refinement. Go to ***Fourier***



If the stucture looks OK, just click done.
To change an element type, choose it from the list and click the atom.
To delete an atom choose the "Delete" option and click the atom.

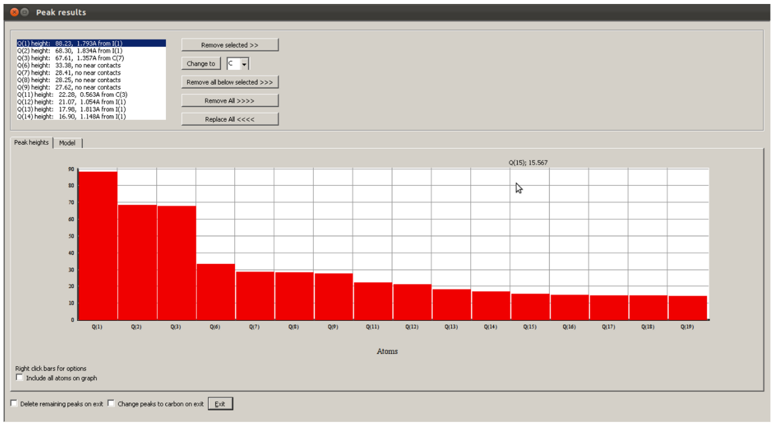
If you want an element type that is not available in the drop down list above click the "Edit Elements" button.

If you want to assemble the atoms into bonded residues, click the "Collect Atoms" button.

"Done" to apply the new types or "Cancel" to quit without changes.

Figure 19: Model after "cleaning"

→***Difference*** and accept default parameters. Transfer all peaks to our model (just press "Transfer" button in the pop-up dialog). We should get a "Peak Results" window as pointed out in Figure 20. Three most intense maxima of the electron density have emerged. We can delete all peaks from Q(6) and up to end. Now, switch to the "Model" tab and check the position of the peaks in the model. As we can see they are oxygen atoms bonded to I(1) (Q(1) and Q(2)) and oxygen bonded to the phenyl (Q(3)) ring near C(7). We can rename all peaks to oxygen atoms by pressing "Change to" button and press exit.



```
Q(1) height:   88.23,  1.793A from I(1)
Q(2) height:   68.30,  1.834A from I(1)
Q(3) height:   67.61,  1.357A from C(7)
Q(6) height:   33.38, no near contacts
Q(7) height:   28.41, no near contacts
Q(8) height:   28.25, no near contacts
Q(9) height:   27.62, no near contacts
Q(11) height:   22.28,  0.563A from C(3)
Q(12) height:   21.07,  1.054A from I(1)
Q(13) height:   17.98,  1.813A from I(1)
Q(14) height:   16.90,  1.148A from I(1)
```

Right click bars for options
☐ Include all atoms on graph

☐ Delete remaining peaks on exit ☐ Change peaks to carbon on exit

Figure 20: Information window for the Fourier analysis.

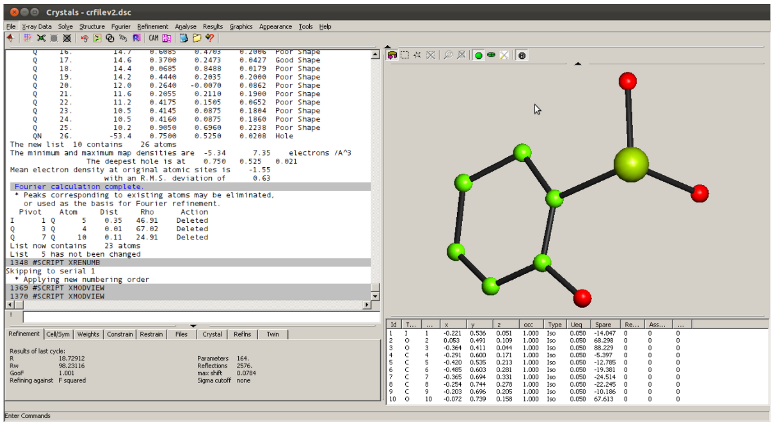
Now we also need to rename our atoms: iodine will be first then two oxygens bonded to iodine, the benzene ring and lastly oxygen. The final model presented in Figure 21.

Since we already found all the sharpest maxima of electron density from Fourier map, it is a time to improve our model by Least-square refinement in isotropic approximation. We need to setup parameters for refinement (LIST 12):

```
\list 12
full i(1,x's,u[iso]) until last
end
```

For list 12 "full" is a synonym for "block scale". Since all parameters will be refined in one block, it is also called the Full-matrix least-square method. To start refinement (3 cycles) type

```
\sfls
ref
```



```
      Q     16.          14.7   0.6085   0.4703   0.2006  Poor Shape
      Q     17.          14.6   0.3700   0.2473   0.0427  Good Shape
      Q     18.          14.4   0.0685   0.8488   0.0179  Poor Shape
      Q     19.          14.2   0.4440   0.2035   0.2000  Poor Shape
      Q     20.          12.0   0.2640  -0.0070   0.0862  Poor Shape
      Q     21.          11.6   0.2055   0.2110   0.1900  Poor Shape
      Q     22.          11.2   0.4175   0.1505   0.0652  Poor Shape
      Q     23.          10.5   0.4145   0.0875   0.1804  Poor Shape
      Q     24.          10.5   0.4160   0.0875   0.1860  Poor Shape
      Q     25.          10.2   0.9050   0.6960   0.2238  Poor Shape
      QN    26.         -53.4   0.7500   0.5250   0.0208  Hole
 The new list  10 contains    26 atoms
 The minimum and maximum map densities are  -5.34      7.35    electrons /A^3
                    The deepest hole is at    0.750   0.525   0.021
 Mean electron density at original atomic sites is    -1.55
                        with an R.M.S. deviation of      0.63
  Fourier calculation complete.
  * Peaks corresponding to existing atoms may be eliminated,
    or used as the basis for Fourier refinement.
   Pivot    Atom     Dist     Rho      Action
 I      1 Q      5    0.35   46.91    Deleted
 Q      3 Q      4    0.01   67.02    Deleted
 Q      7 Q     10    0.11   24.91    Deleted
 List now contains    23 atoms
 List   5 has not been changed
 1348 #SCRIPT XRENUMB
Skipping to serial 1
  * Applying new numbering order
 1369 #SCRIPT XMODVIEW
 1370 #SCRIPT XMODVIEW
```

Results of last cycle:
R 18.72912
Rw 98.23116
GooF 1.001
Refining against F squared
Parameters 164.
Reflections 2576.
max shift 0.0784
Sigma cutoff none

Id	T...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	I	1	-0.221	0.536	0.051	1.000	Iso	0.050	-14.047	0	0	0
2	O	2	0.053	0.491	0.109	1.000	Iso	0.050	68.298	0	0	0
3	O	3	-0.364	0.411	0.044	1.000	Iso	0.050	88.229	0	0	0
4	C	4	-0.291	0.600	0.171	1.000	Iso	0.050	-5.397	0	0	0
5	C	5	-0.420	0.535	0.213	1.000	Iso	0.050	-12.785	0	0	0
6	C	6	-0.485	0.603	0.281	1.000	Iso	0.050	-19.381	0	0	0
7	C	7	-0.365	0.694	0.331	1.000	Iso	0.050	-24.514	0	0	0
8	C	8	-0.254	0.744	0.278	1.000	Iso	0.050	-22.245	0	0	0
9	C	9	-0.203	0.696	0.205	1.000	Iso	0.050	-10.186	0	0	0
10	O	10	-0.072	0.739	0.158	1.000	Iso	0.050	67.613	0	0	0

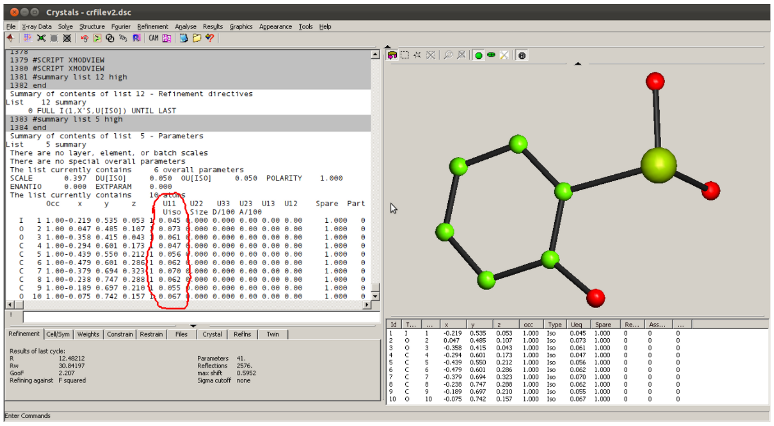
Figure 21: The model after location of the oxygen atoms.

```
ref
ref
end
```

After refinement R = 12.48, Rw = 30.84, maxshift = 0.595, GooF = 2.207. To check the isotropic parameters after refinement type

```
\summary list 5 high
end
```

An example of list 5 summary is shown in Figure 22.



```
 1378
 1379 #SCRIPT XMODVIEW
 1380 #SCRIPT XMODVIEW
 1381 #summary list 12 high
 1382 end
 Summary of contents of list 12 - Refinement directives
List    12 summary
     0 FULL I(1,X'S,U[ISO]) UNTIL LAST
 1383 #summary list 5 high
 1384 end
 Summary of contents of list  5 - Parameters
List     5 summary
 There are no layer, element, or batch scales
 There are no special overall parameters
 The list currently contains     6 overall parameters
 SCALE       0.397  DU[ISO]     0.050  OU[ISO]     0.050  POLARITY    1.000
 ENANTIO     0.000  EXTPARAM    0.000
 The list currently contains    10 atoms
        Occ     x      y      z      U11   U22   U33  U23  U13  U12     Spare  Part
                                     Uiso  Size D/100 A/100
   I   1 1.00-0.219 0.535 0.053 1 0.045 0.000 0.000 0.00 0.00 0.00      1.000   0
   O   2 1.00 0.047 0.485 0.107 1 0.073 0.000 0.000 0.00 0.00 0.00      1.000   0
   O   3 1.00-0.358 0.415 0.043 1 0.061 0.000 0.000 0.00 0.00 0.00      1.000   0
   C   4 1.00-0.294 0.601 0.173 1 0.047 0.000 0.000 0.00 0.00 0.00      1.000   0
   C   5 1.00-0.439 0.550 0.212 1 0.056 0.000 0.000 0.00 0.00 0.00      1.000   0
   C   6 1.00-0.479 0.601 0.286 1 0.062 0.000 0.000 0.00 0.00 0.00      1.000   0
   C   7 1.00-0.379 0.694 0.323 1 0.070 0.000 0.000 0.00 0.00 0.00      1.000   0
   C   8 1.00-0.238 0.747 0.288 1 0.062 0.000 0.000 0.00 0.00 0.00      1.000   0
   C   9 1.00-0.189 0.697 0.210 1 0.055 0.000 0.000 0.00 0.00 0.00      1.000   0
   O  10 1.00-0.075 0.742 0.157 1 0.067 0.000 0.000 0.00 0.00 0.00      1.000   0
```

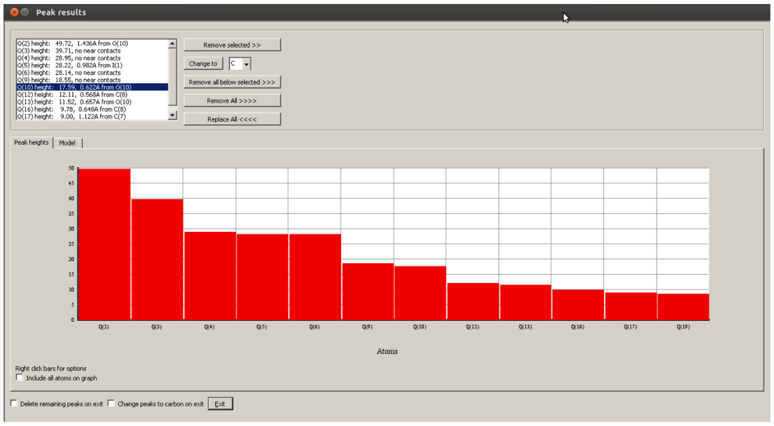
Results of last cycle:
R 12.48212
Rw 30.84197
GooF 2.207
Refining against F squared
Parameters 41.
Reflections 2576.
max shift 0.5952
Sigma cutoff none

Id	T...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	I	1	-0.219	0.535	0.053	1.000	Iso	0.045	1.000	0	0	0
2	O	2	0.047	0.485	0.107	1.000	Iso	0.073	1.000	0	0	0
3	O	3	-0.358	0.415	0.043	1.000	Iso	0.061	1.000	0	0	0
4	C	4	-0.294	0.601	0.173	1.000	Iso	0.047	1.000	0	0	0
5	C	5	-0.439	0.550	0.212	1.000	Iso	0.056	1.000	0	0	0
6	C	6	-0.479	0.601	0.286	1.000	Iso	0.062	1.000	0	0	0
7	C	7	-0.379	0.694	0.323	1.000	Iso	0.070	1.000	0	0	0
8	C	8	-0.238	0.747	0.288	1.000	Iso	0.062	1.000	0	0	0
9	C	9	-0.189	0.697	0.210	1.000	Iso	0.055	1.000	0	0	0
10	O	10	-0.075	0.742	0.157	1.000	Iso	0.067	1.000	0	0	0

Figure 22: Example of the LIST 5 summary output.

All isotropic ADP's are reasonable and of the same magnitude. The Difference Fourier synthesis revealed all maxima corresponding to the butyl group. Results of the Fourier analysis are presented in Figure 23. All peaks starting from Q(9) can be safety deleted. Peak Q(5) located on distance 0.98 Åfrom iodine and doesn't correspond to any atom. We can also delete it. The remained peaks correspond to a butyl group as we can see in "Model" tab. We need to rename them to carbons and exit from the dialog. After renumbering, the model (C(11)-C(14) assigned to butyl chain) should look as shown in Figure 24. Since we used "last" parameter in LIST 12 we don't need to edit LIST 12 file and can start refinement.

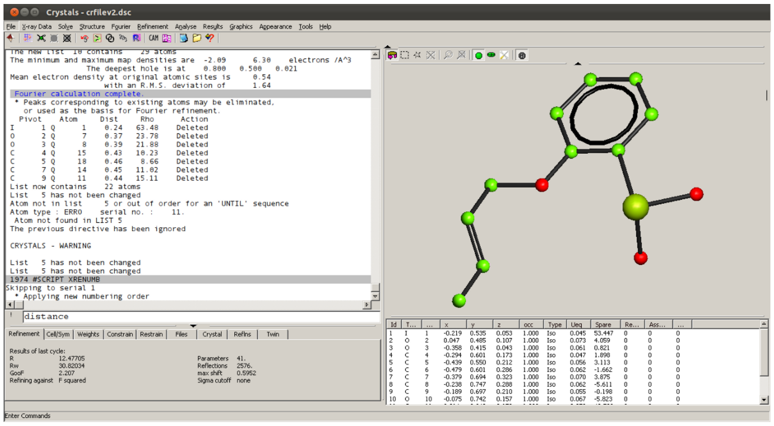
```
\sfls
ref
```



```
Q(2) height:   49.72,  1.436A from O(10)
Q(3) height:   39.71, no near contacts
Q(4) height:   28.95, no near contacts
Q(5) height:   28.22,  0.982A from I(1)
Q(6) height:   28.14, no near contacts
Q(9) height:   18.55, no near contacts
Q(10) height:   17.59,  0.622A from O(10)
Q(12) height:   12.11,  0.568A from C(8)
Q(13) height:   11.52,  0.657A from O(10)
Q(16) height:    9.78,  0.648A from C(8)
Q(17) height:    9.00,  1.122A from C(7)
```

Figure 23: Results of the Fourier analysis.

```
ref
ref
end
```



```
The new list  10 contains    29 atoms
The minimum and maximum map densities are  -2.09      6.30    electrons /A^3
                   The deepest hole is at    0.800   0.500   0.021
Mean electron density at original atomic sites is      0.54
                     with an R.M.S. deviation of      1.64
 Fourier calculation complete.
 * Peaks corresponding to existing atoms may be eliminated,
   or used as the basis for Fourier refinement.
  Pivot    Atom     Dist     Rho      Action
I      1 Q      1    0.24   63.48    Deleted
O      2 Q      7    0.37   23.78    Deleted
O      3 Q      8    0.39   21.88    Deleted
C      4 Q     15    0.43   10.23    Deleted
C      5 Q     18    0.46    8.66    Deleted
C      7 Q     14    0.45   11.02    Deleted
C      9 Q     11    0.44   15.11    Deleted
List now contains    22 atoms
List   5 has not been changed
Atom not in list     5 or out of order for an 'UNTIL' sequence
Atom type : ERRO    serial no. :    11.
 Atom not found in LIST 5
The previous directive has been ignored

CRYSTALS - WARNING

List   5 has not been changed
List   5 has not been changed
1974 #SCRIPT XRENUMB
Skipping to serial 1
 * Applying new numbering order
!   distance
```

Results of last cycle:

R	12.47705	Parameters	41.
Rw	30.82034	Reflections	2576.
GooF	2.207	max shift	0.5952
Refining against	F squared	Sigma cutoff	none

Id	T...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	I	1	-0.219	0.535	0.053	1.000	Iso	0.045	53.447	0	0	0
2	O	2	0.047	0.485	0.107	1.000	Iso	0.073	4.059	0	0	0
3	O	3	-0.358	0.415	0.043	1.000	Iso	0.061	0.821	0	0	0
4	C	4	-0.294	0.601	0.173	1.000	Iso	0.047	1.898	0	0	0
5	C	5	-0.439	0.550	0.212	1.000	Iso	0.056	3.113	0	0	0
6	C	6	-0.479	0.601	0.286	1.000	Iso	0.062	-1.662	0	0	0
7	C	7	-0.379	0.694	0.323	1.000	Iso	0.070	3.875	0	0	0
8	C	8	-0.238	0.747	0.288	1.000	Iso	0.062	-5.611	0	0	0
9	C	9	-0.189	0.697	0.210	1.000	Iso	0.055	-0.198	0	0	0
10	O	10	-0.075	0.742	0.157	1.000	Iso	0.067	-5.823	0	0	0

Figure 24: Model after renaming all peaks into carbons of the butyl tail.

Aliphatic chains are often found to be disordered in crystal structures. We need to very carefully check the bond distances and ADP's for the butyl chain after refinement. To print the connectivity table (LIST 41) type:

```
\summary list 41
end
```

To print information about atomic parameters type

```
\summary list 5 high
end
```

As we can see from Table 2, the C-C distances for the butyl group don't correspond to the correct values for sp^3 hybridized carbon atoms. We need to restrain these distances to be 1.54 within e.s.d. 0.01. All restraints are located in LIST 16 file. Afterwards, we need to make some cycles of least-squares refinement.

Table 2: Distances

O(10)-C(11) = 1.451 Å
C(11)-C(12) = 1.644 Å
C(12)-C(13) = 1.286 Å
C(13)-C(14) = 1.771 Å

Table 3: Analysis of the ADP's

	O(10)	C(11)	C(12)	C(13)	C(14)
U_{iso}	0.077	0.095	0.148	0.120	0.175

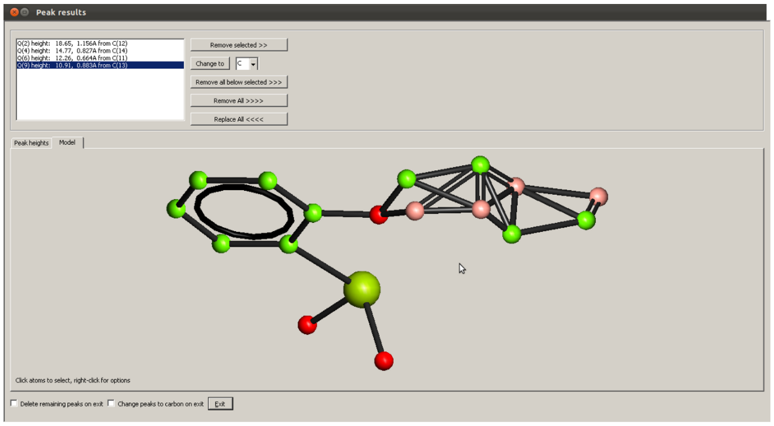
```
\list 16
dist 1.54,0.01 = c(11) to c(12)
dist 1.54,0.01 = c(12) to c(13)
dist 1.54,0.01 = c(13) to c(14)
end
\sfls
ref
ref
ref
end
```

Displacement parameters for the butyl chain are also higher compared to other atoms. The iodine, oxygen and carbon atoms of the benzene ring have reasonable displacement parameters and there are no problems with bond distances. We can refine those atoms in the anisotropic approximation.

```
\list 12
full i(1,x's,u's) until o(10)
cont c(11,x's,u[iso]) until c(14)
end
\sfls
ref
ref
ref
end
```

A difference Fourier analysis revealed a set of maxima of the electron density around the butyl chain (Figure 25). There is a second component of the disordered butyl group. We need to rename all new peaks into carbons and renumber the atoms. The old butyl chain retains its numbering, while the new ones will be C(15)-C(18). The C(11)-C(14) is the first component, C(15)-C(18) is the second component. As soon as you have two components of a disordered group it is very convenient to assign unique PART number for the each disordered component. Go to ***Structure →allocate part nos*** (Figure 26) and create a new group. All atoms are in group #0. We need to create two groups #1 and #2 and put the disordered component C(11)-C(14) into group #1, and the component C(15)-C(18) into group #2. Create a new group and select atoms from model to put them into the current group. Atoms from different group can't be bonded to each other. It is especially useful for hydrogen placement. When we are done press "close". Now we have two parts: part(1) containing atoms C(11)-C(14) and part(2) containing atoms C(15)-C(18) (Figure 27).

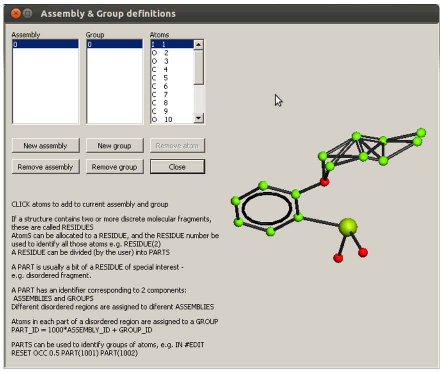
We need to bind the occupation of the second component (1-x) to the occupation of the first component



```
Q(2) height:   18.65,  1.156A from C(12)
Q(4) height:   14.77,  0.827A from C(14)
Q(6) height:   12.26,  0.664A from C(11)
Q(9) height:   10.91,  0.883A from C(13)
```

Click atoms to select, right-click for options

Figure 25: Extra electron density around butyl substituent.



CLICK atoms to add to current assembly and group

If a structure contains two or more discrete molecular fragments,
these are called RESIDUES
AtomS can be allocated to a RESIDUE, and the RESIDUE number be
used to identify all those atoms e.g. RESIDUE(2)
A RESIDUE can be divided (by the user) into PARTS

A PART is usually a bit of a RESIDUE of special interest -
e.g. disordered fragment.

A PART has an identifier corresponding to 2 components:
ASSEMBLIES and GROUPS
Different disordered regions are assigned to diferent ASSEMBLIES

Atoms in each part of a disordered region are assigned to a GROUP
PART_ID = 1000*ASSEMBLY_ID + GROUP_ID

PARTS can be used to identify groups of atoms, e.g. IN #EDIT
RESET OCC 0.5 PART(1001) PART(1002)

Figure 26: Pop-up window to create new group for disordered fragment.

(x), while total contribution from two components should be 1. The refinement of the atoms I(1)-O(10) will be performed in the anisotropic approximation, while the disordered carbon atoms will be refined in the isotropic approximation. We also need to change the occupation factors for the disordered atoms to be 0.5 and add restrains for bond distances for the two parts. To change the occupation factors type

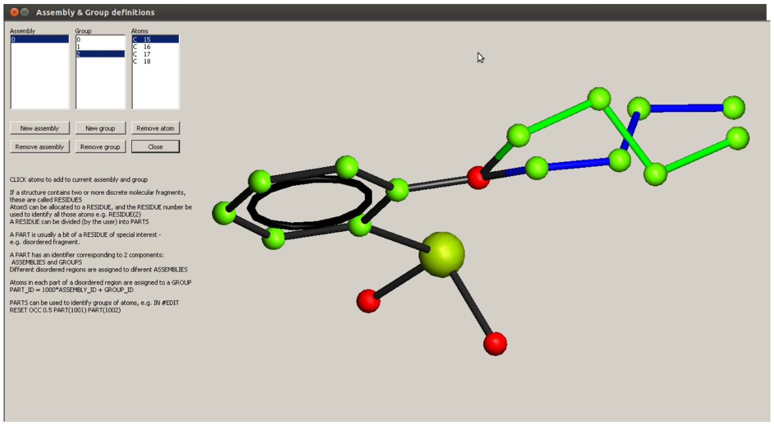
```
\edit
reset occ 0.5 part(1) part(2)
end
```

Bind the two component of the disorder in least-square matrix

```
\list 12
full i(1,x's,u's) until o(10)
cont c(11,x's,u[iso]) until c(18)
equiv part(1,occ) part(2,occ)
weight -1 part(1,occ)
end
```

Add bond restrains for the butyl chain

```
\list 16
```



CLICK atoms to add to current assembly and group

If a structure contains two or more discrete molecular fragments, these are called RESIDUES
AtomS can be allocated to a RESIDUE, and the RESIDUE number be used to identify all those atoms e.g. RESIDUE(2)
A RESIDUE can be divided (by the user) into PARTS

A PART is usually a bit of a RESIDUE of special interest - e.g. disordered fragment.

A PART has an identifier corresponding to 2 components: ASSEMBLIES and GROUPS
Different disordered regions are assigned to diferent ASSEMBLIES

Atoms in each part of a disordered region are assigned to a GROUP
PART_ID = 1000*ASSEMBLY_ID + GROUP_ID

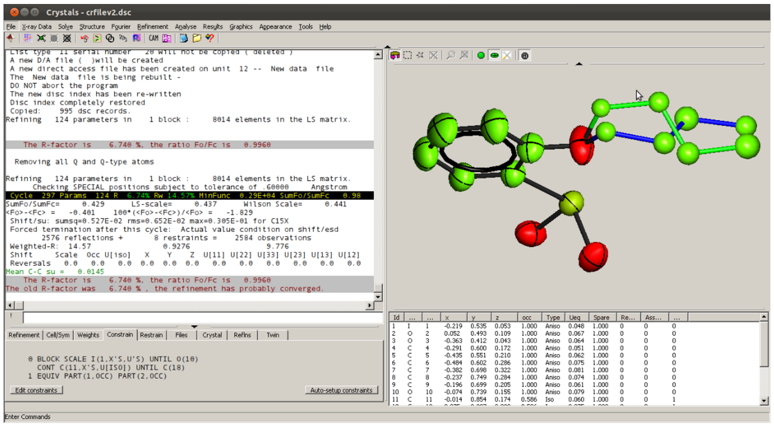
PARTS can be used to identify groups of atoms, e.g. IN #EDIT
RESET OCC 0.5 PART(1001) PART(1002)

Figure 27: Two parts selected by different colors.

```
dist 1.54,0.01 = c(11) to c(12)
dist 1.54,0.01 = c(12) to c(13)
dist 1.54,0.01 = c(13) to c(14)
dist 1.54,0.01 = c(15) to c(16)
dist 1.54,0.01 = c(16) to c(17)
dist 1.54,0.01 = c(17) to c(18)
end
```

Refine model.

```
sfls
ref
ref
ref
ref
end
```



```
 List type  11 serial number   20 will not be copied ( deleted )
 A new D/A file (  )will be created
 A new direct access file has been created on unit  12 --  New data  file
 The  New data  file is being rebuilt -
 DO NOT abort the program
 The new disc index has been re-written
 Disc index completely restored
 Copied:    995 dsc records.
Refining   124 parameters in    1 block :     8014 elements in the LS matrix.


   The R-factor is    6.740 %, the ratio Fo/Fc is   0.9960


  Removing all Q and Q-type atoms

Refining   124 parameters in    1 block :     8014 elements in the LS matrix.
      Checking SPECIAL positions subject to tolerance of .60000     Angstrom
 Cycle  297 Params  124 R  6.74% Rw 14.57% MinFunc  0.29E+04 SumFo/SumFc   0.98
SumFo/SumFc=     0.429      LS-scale=     0.437      Wilson Scale=     0.441
<Fo>-<Fc> =   -0.401    100*(<Fo>-<Fc>)/<Fo> =   -1.829
 Shift/su: sumsq=0.527E-02 rms=0.652E-02 max=0.305E-01 for C15X
 Forced termination after this cycle:  Actual value condition on shift/esd
       2576 reflections +       8 restraints =    2584 observations
 Weighted-R:  14.57                 0.9276                  9.776
 Shift     Scale  Occ U[iso]   X    Y    Z  U[11] U[22] U[33] U[23] U[13] U[12]
 Reversals   0.0   0.0   0.0  0.0  0.0  0.0   0.0   0.0   0.0   0.0   0.0   0.0
Mean C-C su =   0.0145
   The R-factor is    6.740 %, the ratio Fo/Fc is   0.9960
The old R-factor was   6.740 % , the refinement has probably converged.
```

```
    0 BLOCK SCALE I(1,X'S,U'S) UNTIL O(10)
      CONT C(11,X'S,U[ISO]) UNTIL C(18)
    1 EQUIV PART(1,OCC) PART(2,OCC)
```

Id	...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
1	I	1	-0.219	0.535	0.053	1.000	Aniso	0.048	1.000	0	0	0
2	O	2	0.052	0.493	0.109	1.000	Aniso	0.067	1.000	0	0	0
3	O	3	-0.363	0.412	0.043	1.000	Aniso	0.064	1.000	0	0	0
4	C	4	-0.291	0.600	0.172	1.000	Aniso	0.051	1.000	0	0	0
5	C	5	-0.435	0.551	0.210	1.000	Aniso	0.062	1.000	0	0	0
6	C	6	-0.484	0.602	0.286	1.000	Aniso	0.075	1.000	0	0	0
7	C	7	-0.382	0.698	0.322	1.000	Aniso	0.081	1.000	0	0	0
8	C	8	-0.237	0.749	0.284	1.000	Aniso	0.074	1.000	0	0	0
9	C	9	-0.196	0.699	0.205	1.000	Aniso	0.061	1.000	0	0	0
10	O	10	-0.074	0.739	0.155	1.000	Aniso	0.079	1.000	0	0	0
11	C	11	-0.014	0.854	0.174	0.586	Iso	0.060	1.000	0	0	1

Figure 28: Model after refinement of the disordered butyl group.

After refinement, two disordered components have occupation 0.41 and 0.59, respectively. All displacement parameters also smaller. Since the isotropic refinement is stable we can finish refinement of all atoms in the anisotropic approximation.

```
\list 12
full i(1,x's,u's) until c(18)
equiv part(1,occ) part(2,occ)
weight -1 part(1,occ)
end
```

It is also advisable to add restrains to the ADP's for C(11) to C(18). The ADP's of all pairs of bonded atoms in each component should be restrained to be equal in the direction of the bond (DELU command).

```
\list 16
dist 1.54,0.01 = c(11) to c(12)
dist 1.54,0.01 = c(12) to c(13)
dist 1.54,0.01 = c(13) to c(14)
dist 1.54,0.01 = c(15) to c(16)
dist 1.54,0.01 = c(16) to c(17)
dist 1.54,0.01 = c(17) to c(18)
delu 0.01 c(11) until c(14)
delu 0.01 c(15) until c(18)
end
```

Now we can make some cycles of refinement.

```
sfls
ref
ref
ref
end
```

After refinement it is always useful to check all restrains being used for refinement:

```
\check high
end
```

Brief information will be printed on the screen, but more detailed information could be found in the file *bfile##.lis*. An example of the "\CHECK" command from file *bfile##.lis* has been shown below. From analysis of that table we can conclude there are not any problems with our restrains. **Mean delta** is always less than 2*e.s.d. for our restraints.

```
Restraints checking  -
 restraints that produce no contributions are marked with a ’?’

  0. Restrain these distances to be    1.540 Angstrom,
               with an E.S.D. of   0.010

           Atom  1    S(I) L TX TY TZ       Atom  2    S(I) L TX TY TZ   distances    Delta

          C      11     1  1  0  0  0      C      12     1  1  0  0  0      1.550    -0.010
     Mean value =   1.5495  Mean delta =  -0.0095  r.m.s. delta =   0.0095

  1. Restrain these distances to be    1.540 Angstrom,
```

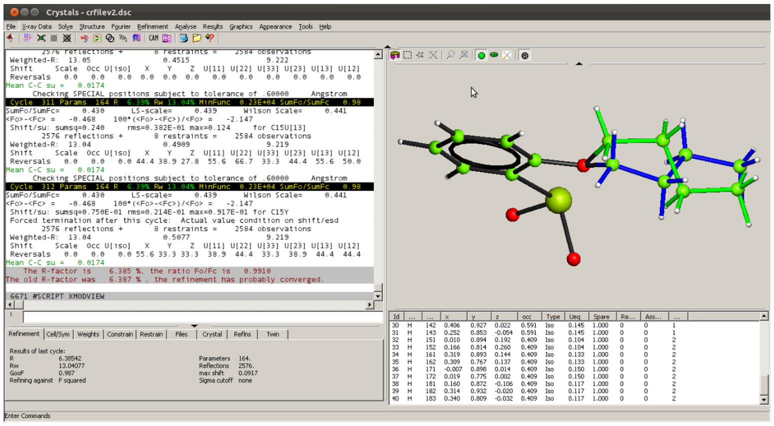
```
          with an E.S.D. of   0.010

      Atom  1    S(I) L TX TY TZ       Atom  2    S(I) L TX TY TZ   distances    Delta

     C      12     1  1  0  0  0      C      13     1  1  0  0  0      1.532     0.008
 Mean value =   1.5318  Mean delta =   0.0082  r.m.s. delta =   0.0082

2. Restrain these distances to be    1.540 Angstrom,
          with an E.S.D. of   0.010

      Atom  1    S(I) L TX TY TZ       Atom  2    S(I) L TX TY TZ   distances    Delta

     C      13     1  1  0  0  0      C      14     1  1  0  0  0      1.559    -0.019
 Mean value =   1.5588  Mean delta =  -0.0188  r.m.s. delta =   0.0188

3. Restrain these distances to be    1.540 Angstrom,
          with an E.S.D. of   0.010

      Atom  1    S(I) L TX TY TZ       Atom  2    S(I) L TX TY TZ   distances    Delta

     C      15     1  1  0  0  0      C      16     1  1  0  0  0      1.554    -0.014
 Mean value =   1.5545  Mean delta =  -0.0145  r.m.s. delta =   0.0145

4. Restrain these distances to be    1.540 Angstrom,
          with an E.S.D. of   0.010

      Atom  1    S(I) L TX TY TZ       Atom  2    S(I) L TX TY TZ   distances    Delta

     C      16     1  1  0  0  0      C      17     1  1  0  0  0      1.538     0.002
 Mean value =   1.5379  Mean delta =   0.0021  r.m.s. delta =   0.0021

5. Restrain these distances to be    1.540 Angstrom,
          with an E.S.D. of   0.010

      Atom  1    S(I) L TX TY TZ       Atom  2    S(I) L TX TY TZ   distances    Delta

     C      17     1  1  0  0  0      C      18     1  1  0  0  0      1.555    -0.015
 Mean value =   1.5546  Mean delta =  -0.0146  r.m.s. delta =   0.0146

6.DELU - Restrain the difference in the M.S.D.'s along a bond to be
     0.00000  angstrom squared, with an E.S.D. of  0.01000

      Atom  1    S(I) L TX TY TZ    M.S.D.'s         Atom  2    S(I) L TX TY TZ    M.S.D.'s    Delta

     C      11     1  1  0  0  0     0.05530         C      12     1  1  0  0  0     0.06646   0.01116
 Mean value =   0.0609  Mean delta =   0.0112  r.m.s. delta =   0.0112

7.DELU - Restrain the difference in the M.S.D.'s along a bond to be
     0.00000  angstrom squared, with an E.S.D. of  0.01000

      Atom  1    S(I) L TX TY TZ    M.S.D.'s         Atom  2    S(I) L TX TY TZ    M.S.D.'s    Delta

     C      15     1  1  0  0  0     0.05466         C      16     1  1  0  0  0     0.04650  -0.00816
 Mean value =   0.0506  Mean delta =  -0.0082  r.m.s. delta =   0.0082
```

The next step of the refinement is to place hydrogens. If you assigned different parts for your disordered fragments it more convenient to do this via GUI (***Structure →Add hydrogens geometrically***). Also, we are going to refine all hydrogen atoms in a riding mode so we need to add appropriate commands into the LIST 12 file. Also, all non-hydrogen atoms will be refined in anisotropic approximation, therefore, it is more easer to create new a LIST 12 via the GUI (***Refinement →Setup and refine***) and select "Ride H atoms" and press "OK". Old LIST 12 file will be overwritten. Afterwards, we need to manually correct this LIST 12 file to include refinement of the occupation positions for our disordered fragments. All hydrogens will be automatically in the appropriate part. The final LIST 12 file should look as presented below:

```
\list 12
```

```
full i(1,x's,u's) until c(18)
equiv part(1,occ) part(2,occ)
weight -1 part(1,occ)
ride c(5,x's) h(51,x's)
ride c(6,x's) h(61,x's)
ride c(7,x's) h(71,x's)
ride c(8,x's) h(81,x's)
ride c(11,x's) h(111,x's) h(112,x's)
ride c(12,x's) h(121,x's) h(122,x's)
ride c(13,x's) h(131,x's) h(132,x's)
ride c(14,x's) h(141,x's) h(142,x's) h(143,x's)
ride c(15,x's) h(151,x's) h(152,x's)
ride c(16,x's) h(161,x's) h(162,x's)
ride c(17,x's) h(171,x's) h(172,x's)
ride c(18,x's) h(181,x's) h(182,x's) h(183,x's)
end
```

The final model after some cycles of the refinement presented in Figure 29.



```
        2576 reflections +        8 restraints =     2584 observations
 Weighted-R:  13.05                 0.4515                  9.222
 Shift      Scale  Occ U[iso]   X     Y     Z  U[11] U[22] U[33] U[23] U[13] U[12]
 Reversals   0.0    0.0    0.0  0.0  0.0  0.0   0.0   0.0   0.0   0.0   0.0   0.0
Mean C-C su =   0.0174
      Checking SPECIAL positions subject to tolerance of .60000     Angstrom
 Cycle  311 Params  164 R  6.39% Rw 13.04% MinFunc  0.23E+04 SumFo/SumFc   0.98
SumFo/SumFc=     0.430      LS-scale=     0.439      Wilson Scale=     0.441
<Fo>-<Fc> =   -0.468    100*(<Fo>-<Fc>)/<Fo> =   -2.147
 Shift/su: sumsq=0.240     rms=0.382E-01 max=0.124     for C15U[13]
        2576 reflections +        8 restraints =     2584 observations
 Weighted-R:  13.04                 0.4909                  9.219
 Shift      Scale  Occ U[iso]   X     Y     Z  U[11] U[22] U[33] U[23] U[13] U[12]
 Reversals   0.0    0.0    0.0 44.4 38.9 27.8  55.6  66.7  33.3  44.4  55.6  50.0
Mean C-C su =   0.0174
      Checking SPECIAL positions subject to tolerance of .60000     Angstrom
 Cycle  312 Params  164 R  6.39% Rw 13.04% MinFunc  0.23E+04 SumFo/SumFc   0.98
SumFo/SumFc=     0.430      LS-scale=     0.439      Wilson Scale=     0.441
<Fo>-<Fc> =   -0.468    100*(<Fo>-<Fc>)/<Fo> =   -2.147
 Shift/su: sumsq=0.750E-01 rms=0.214E-01 max=0.917E-01 for C15Y
 Forced termination after this cycle:  Actual value condition on shift/esd
        2576 reflections +        8 restraints =     2584 observations
 Weighted-R:  13.04                 0.5077                  9.219
 Shift      Scale  Occ U[iso]   X     Y     Z  U[11] U[22] U[33] U[23] U[13] U[12]
 Reversals   0.0    0.0    0.0 55.6 33.3 33.3  38.9  44.4  33.3  38.9  44.4  44.4
Mean C-C su =   0.0174
    The R-factor is     6.385 %, the ratio Fo/Fc is   0.9910
The old R-factor was   6.387 % , the refinement has probably converged.

 6671 #SCRIPT XMODVIEW
```

Results of last cycle:

R	6.38542	Parameters	164.
Rw	13.04077	Reflections	2576.
GooF	0.987	max shift	0.0917
Refining against	F squared	Sigma cutoff	none

Id	...	...	x	y	z	occ	Type	Ueq	Spare	Re...	Ass...	...
30	H	142	0.406	0.927	0.022	0.591	Iso	0.145	1.000	0	0	1
31	H	143	0.252	0.853	-0.054	0.591	Iso	0.145	1.000	0	0	1
32	H	151	0.010	0.894	0.192	0.409	Iso	0.104	1.000	0	0	2
33	H	152	0.166	0.814	0.260	0.409	Iso	0.104	1.000	0	0	2
34	H	161	0.319	0.893	0.144	0.409	Iso	0.133	1.000	0	0	2
35	H	162	0.309	0.767	0.137	0.409	Iso	0.133	1.000	0	0	2
36	H	171	-0.007	0.898	0.014	0.409	Iso	0.150	1.000	0	0	2
37	H	172	0.019	0.775	0.002	0.409	Iso	0.150	1.000	0	0	2
38	H	181	0.160	0.872	-0.106	0.409	Iso	0.117	1.000	0	0	2
39	H	182	0.314	0.932	-0.020	0.409	Iso	0.117	1.000	0	0	2
40	H	183	0.340	0.809	-0.032	0.409	Iso	0.117	1.000	0	0	2

Figure 29: Final model after refinement with hydrogens ("riding mode")

The difference electron density maximum is 1.84 $e^{-}/Å^{3}$ and located at a distance 1.090 Åfrom the iodine. That peak doesn't correspond to any atom and is probably diffraction ripple and can be ignored.

To optimize the weighting scheme go to ***Refinement →Choose weights*** and accept the proposed "Auto-statistical" scheme type. Repeat refinement once again. If GooF drops significantly below or above 1.0 we need to re-optimize the weighting scheme once again. Make sure anomalous dispersion correction is included: ***Refinement →F or Fsq and advanced options*** and check "Anomalous scattering". Repeat refinement and re-optimize the weights if needed. It is also useful to check agreement between observed and calculated F values. Go to ***Analysis →Fo vs Fc graph*** (omit reflections that deviate significantly from straight line and repeat refinement). Go to ***Analysis →Publication check →Local Acta Checks*** to finish validation test. Final parameters after refinement presented in Table 4.

Table 4: Final parameters after refinement

Formula	$C_{10}H_{13}IO_3$		
Crystal Class	Monoclinic	Space Group	$P2_1/c$
a, Å	6.582(5)	alpha,°	90
b, Å	12.342(3)	beta,°	107.59(4)
c, Å	14.635(7)	gamma,°	90
Volume, $Å^3$	1133.3(11)	Z	4
Radiation type	Mo-Kα	Wavelength, Å	0.710730
Dx, g/cm^3	1.81	Mr, g/mol	308.12
μ, mm^3	2.806	Temp. (K)	293
Reflections measured	2586	Independent reflections	2586
R-factor	0.064	Weighted R-factor	0.130
		Max shift/su	0.0005
Delta Rho min	-1.49	Delta Rho max	1.84
Reflections used	2576	sigma(I) limit	-10.00
Number of parameters	164	Goodness of fit	0.987