Chapter 6.1.3

SHELXL-97

Examples

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3. Examples of Small Molecule Refinements with SHELXL

Two test structures supplied with the SHELXL-97 are intended to provide a good illustration of routine small moiety structure refinement. The output discussed here should not differ significantly from that of the test jobs, except that it has been abbreviated and there may be differences in the last decimal place caused by rounding errors.

3.1 First example (ags4)
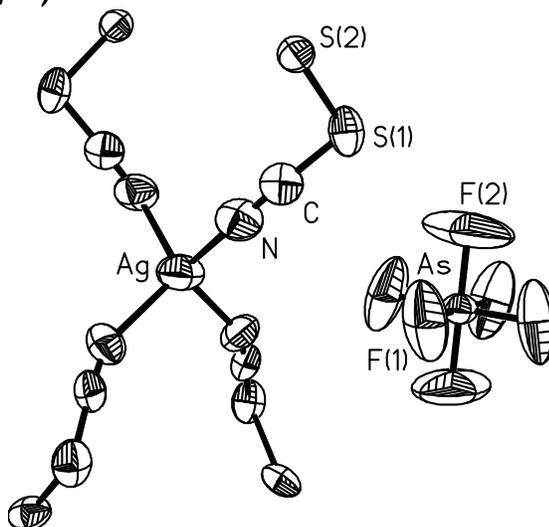
The first example (provided as the files *ags4.ins* and *ags4.hkl*) is the final refinement job for the polymeric inorganic structure $Ag(NCSSSSCN)_2$ AsF_6, determined by Roesky, Gries, Schimkowiak & Jones (1986). Each ligand bridges two Ag^+ ions so each silver is tetrahedrally coordinated by four nitrogen atoms. The silver, arsenic and one of the fluorine atoms lie on special positions. Normally the four unique heavy atoms (from Patterson interpretation using SHELXS) would have been refined isotropically first and the remaining atoms found in a difference synthesis, and possibly an intermediate job would have been performed with the heavy atoms anisotropic and the light atoms isotropic. For test purposes we shall simply input the atomic coordinates which assumes isotropic U's of 0.05 for all atoms. In this job all atoms are to be made anisotropic (ANIS). We shall further assume that a previous job has recommended the weighting scheme used here (WGHT) and shown that one reflection is to be suppressed in the refinement because it is clearly erroneous (OMIT).

The first 9 instructions (TITL...UNIT) are the same for any SHELXS and SHELXL job for this structure and define the cell dimensions, symmetry and contents. The SHELXTL program XPREP can be used to generate these instructions automatically

for any space group etc. SHELXL knows the scattering factors for the first 94 neutral atoms in the Periodic Table. Ten least-squares cycles are to be performed, and the ACTA instruction ensures that the CIF files *ags4.cif* and *ags4.fcf* will be written for archiving and publication purposes. ACTA also sets up the calculation of bond lengths and angles (BOND) and a final difference electron density synthesis (FMAP 2) with peak search (PLAN 20). The HKLF 4 instruction terminates the file and initiates the reading of the *ags4.hkl* intensity data file.

It is possible to set up special position constraints on the x,y,z-coordinates, occupation factors, and U_{ij} components by hand. However this is totally unnecessary because the program will do this automatically for any special position in any space group, conventional or otherwise. Similarly the program recognizes polar space groups ($P\bar{4}$ is non-polar) and applies appropriate restraints (Flack & Schwarzenbach, 1988), so it is no longer necessary to worry about fixing one or more coordinates to prevent the structure drifting along polar axes. It is not necessary to set the overall scale factor using an FVAR instruction for this initial job, because the program will itself estimate a suitable starting value. Comments may be included in the *.ins* file either as REM instructions or as the rest of a line following '!'; this latter facility has been used to annotate this example.

```
TITL AGS4 in P-4                        ! title of up to 76 characters
CELL 0.71073 8.381 8.381 6.661 90 90 90  ! wavelength and unit-cell
ZERR 1 .002 .002 .001 0 0 0              ! Z (formula-units/cell), cell
esd's
LATT -1                                 ! non-centrosymmetric primitive
lattice
SYMM -X, -Y, Z
SYMM Y, -X, -Z               ! symmetry operators (x,y,z must be left out)
SYMM -Y, X, -Z
SFAC C AG AS F N S           ! define scattering factor numbers
UNIT 4 1 1 6 4 8             ! unit cell contents in same order
L.S. 10                      ! 10 cycles full-matrix least-squares
ACTA                         ! CIF-output, bonds, Fourier, peak search
OMIT -2 3 1                  ! suppress bad reflection
ANIS                         ! convert all (non-H) atoms to anisotropic
WGHT 0.037 0.31              ! weighting scheme
AG  2  .000  .000  .000
AS  3  .500  .500  .000
S1  6  .368  .206  .517      ! atom name, SFAC number, x, y, z (usually
S2  6  .386  .034  .736      ! followed by sof and U(iso) or Uij); the
C   1  .278  .095  .337      ! program automatically generates special
N   5  .211  .030  .214      ! position constraints
F1  4  .596  .325 -.007
F2  4  .500  .500  .246
HKLF 4                       ! read h,k,l,Fo^2,sigma(Fo^2) from 'ags4.hkl'
```

The *.lst* listing file starts with a header followed by an echo of the above *.ins* file. After reading TITL...UNIT the program calculates the cell volume, F(000), absorption coefficient, cell weight and density. If the density is unreasonable, perhaps the unit-cell contents have been given incorrectly. The next items in the

.lst file are the connectivity table and the symmetry operations used to include a shell of symmetry equivalent atoms (so that all unique bond lengths and angles can be found):

```
Covalent radii and connectivity table for AGS4 in P-4

C    0.770
AG   1.440
AS   1.210
F    0.640
N    0.700
S    1.030


Ag - N N_$3 N_$4 N_$2
As - F2 F2_$6 F1_$7 F1_$6 F1_$5 F1
S1 - C S2
S2 - S2_$1 S1
C - N S1
N - C Ag
F1 - As
F2 - As


Operators for generating equivalent atoms:

$1    -x+1, -y+1, z
$2    -x, -y, z
$3    y, -x, -z
$4    -y, x, -z
$5    -x+1, -y+1, z
$6    y, -x+1, -z
$7    -y+1, x, -z
```

Note that in addition to symmetry operations generated by the program, one can also define operations with the EQIV instruction and then refer to the corresponding atoms with _$n in the same way. Thus:

```
EQIV $1 1-x, -y, z
CONF S1 S2 S2_$1 S1_$1
```

could have been included in *ags4.ins* to calculate the S-S-S-S torsion angle. If EQIV instructions are used, the program renumbers the other symmetry operators accordingly.

The next part of the output is concerned with the data reduction:

```
 1475  Reflections read, of which     1  rejected

0 =< h =< 10,      -9 =< k =< 10,       0 =< l =<  8,    Max. 2-theta =
55.00

    0  Systematic absence violations


Inconsistent equivalents etc.
```

```
h   k   l        Fo^2     Sigma(Fo^2)   Esd of mean(Fo^2)

3   4   0      387.25        8.54          47.78

      1   Inconsistent equivalents
    903   Unique reflections, of which      0   suppressed

R(int) = 0.0165     R(sigma) = 0.0202      Friedel opposites not merged
```

Special position constraints are then generated and the statistics from the first least-squares cycle are listed (the output has been compacted to fit the page). The maximum vector length refers to the number of reflections processed simultaneously in the rate-determining calculations; usually the program utilizes all available memory to make this as large as possible, subject to a maximum of 511. This maximum may be reduced (but not increased) by means of the fourth parameter on the L.S. (or CGLS) instruction; this may be required to prevent unnecessary disk transfers when large structures are refined on virtual memory systems with limited physical memory. The number of parameters refined in the current cycle is followed by the total number of refinable parameters (here both are 55).

```
Special position constraints for Ag
x =  0.0000        y =  0.0000        z =  0.0000        U22 = 1.0 * U11
U23 = 0            U13 = 0            U12 = 0            sof = 0.25000

Special position constraints for As
x =  0.5000        y =  0.5000        z =  0.0000        U22 = 1.0 * U11
U23 = 0            U13 = 0            U12 = 0            sof = 0.25000

Special position constraints for F2
x =  0.5000        y =  0.5000        U23 = 0            U13 = 0
sof = 0.50000


Least-squares   cycle   1          Maximum   vector   length=511       Memory
required=1092/82899


wR2 =  0.5042 before cycle   1 for    903 data and   55 /   55 parameters


GooF = S =  8.127;     Restrained GooF =     8.127   for      0 restraints


Weight        =         1/[sigma^2(Fo^2)+(0.0370*P)^2+0.31*P]           where
P=(Max(Fo^2,0)+2*Fc^2)/3


** Shifts scaled down to reduce maximum shift/esd from    17.64   to    15.00
**

  N      value       esd       shift/esd   parameter

  1     2.31065     0.04324     9.042       OSF
  2     0.07314     0.00206    11.250       U11 Ag
 11     0.07309     0.00669     3.453       U33 S1
```

```
 47      0.11304      0.01391      4.533      U33 F1

Mean shift/esd =   1.238    Maximum =  11.250 for  OSF

Max. shift = 0.045 A for C      Max. dU = 0.033 for F2
```

Only the largest shift/esd's are printed. More output could have been obtained using 'MORE 2' or 'MORE 3'. The largest correlation matrix elements are printed after the last cycle, in which the mean and maximum shift/esd have been reduced to 0.003 and 0.017 respectively. This is followed by the full table of refined coordinates and U_{ij}'s with esd's (too large to include here, but similar to the corresponding table in SHELX-76 except that U_{eq} and its esd are also printed) and by a final structure factor calculation:

```
Final Structure Factor Calculation for  AGS4 in P-4

Total number of l.s. parameters = 55  Maximum vector length = 511
wR2 =  0.0780 before cycle  11 for    903 data and   2 /   55 parameters

GooF = S =       1.063;      Restrained GooF =       1.063   for       0
restraints
Weight       =        1/[sigma^2(Fo^2)+(0.0370*P)^2+0.31*P]       where
P=(Max(Fo^2,0)+2*Fc^2)/3
R1 =  0.0322 for    818 Fo > 4.sigma(Fo)  and  0.0367 for all    903 data
wR2 =  0.0780,  GooF = S =   1.063,  Restrained GooF =    1.063   for all
data

Flack x parameter = 0.0224   with esd  0.0260   (expected values are 0
(within 3 esd's) for correct and +1 for inverted absolute structure)
```

There are some important points to note here. The weighted *R*-index based on F_o^2 is (for compelling statistical reasons) much higher than the conventional *R*-index based on F_o with a threshold of say $F_o > 4\sigma(F_o)$. For comparison with structures refined against *F* the latter is therefore printed as well (as *R*1). Despite the fact that *wR*2 and not *R*1 is the quantity minimized, *R*1 has the advantage that it is relatively insensitive to the weighting scheme, and so is more difficult to manipulate.

Since the structure is non-centrosymmetric, the program has automatically estimated the Flack absolute structure parameter x in the final structure factor summation. In this example x is within one esd of zero, and its esd is also relatively small. This provides strong evidence that the absolute structure has been assigned correctly, so that no further action is required. The program would have printed a warning here if it would have been necessary to 'invert' the structure or to refine it as a racemic twin.

This is followed by a list of principal mean square displacements U for all anisotropic atoms. It will be seen that none of the smallest components (in the third column) are in danger of going negative [which would make the atom 'non

positive definite' (NPD)] but that the motion of the two unique fluorine atoms is highly anisotropic (not unusual for an AsF_6 anion). The program suggests that the fluorine motion is so extended in one direction that it would be possible to represent each of the two fluorine atoms as disordered over two sites, for which x, y and z coordinates are given; this may safely be ignored here (although there may well be some truth in it). The two suggested new positions for each 'split' atom are placed equidistant from the current position along the direction (and reverse direction) corresponding to the largest eigenvalue of the anisotropic displacement tensor.

This list is followed by the analysis of variance (reproduced here in squashed form), recommended weighting scheme (to give a flat analysis of variance in terms of $F_c{}^2$), and a list of the most disagreeable reflections. For a discussion of the analysis of variance see the second example.

```
Principal mean square atomic displacements U

    0.1067    0.1067    0.0561    Ag
    0.0577    0.0577    0.0386    As
    0.1038    0.0659    0.0440    S1
    0.0986    0.0515    0.0391    S2
    0.0779    0.0729    0.0391    C
    0.1004    0.0852    0.0474    N
    0.3029    0.0954    0.0473    F1
  may be split into  0.5965  0.3173  0.0288  and 0.5946  0.3324 -0.0369
    0.4778    0.1671    0.0457    F2
  may be split into  0.5320  0.5089  0.2462  and 0.4680  0.4911  0.2462


Analysis of variance for reflections employed in refinement
K = Mean[Fo^2] / Mean[Fc^2]   for group

Fc/Fc(max)      0.000 0.026 0.039 0.051 0.063 0.082 0.103 0.147 0.202 0.306
1.0
Number in group     94.   89.   90.   91.   89.   91.   89.   91.   88.
91.
GooF         1.096 1.101 0.997 1.078 1.187 1.069 1.173 0.922 1.019 0.966
K            1.560 1.053 1.010 1.004 1.007 1.021 1.026 1.002 0.997 0.984

Resolution(A)   0.77   0.81   0.85   0.90   0.95   1.02   1.10   1.22   1.40   1.74
inf
Number in group     97.   84.   92.   91.   89.   90.   89.   90.   93.
88.
GooF         1.067 0.959 0.935 0.895 1.035 1.040 1.115 1.149 1.161 1.228
K            1.047 1.010 1.009 0.991 1.004 0.996 0.989 1.012 0.997 0.982
R1           0.166 0.100 0.069 0.059 0.051 0.036 0.033 0.027 0.020 0.020

Recommended weighting scheme:  WGHT    0.0314 0.3674


Most Disagreeable Reflections (* if suppressed or used for Rfree)
```

```
   h    k    l          Fo^2        Fc^2       Delta(F^2)/esd   Fc/F(max)
Resolution(A)
   4    4    4        18.32       33.30         3.62            0.062       1.11
  -4    1    3        15.79        4.17         3.50            0.022       1.50
   0    2    2        41.60       57.32          3.26            0.082          2.61
etc.
```

After the table of bond lengths and angles (BOND was implied by the ACTA instruction), the data are merged (again) for the Fourier calculation after correcting for dispersion (because the electron density is real). In contrast to the initial data reduction, Friedel's law is assumed here; the aim is to set up a unique reflection list so that the (difference) electron density can be calculated on an absolute scale.

The algorithm for generating the 'asymmetric unit' for the Fourier calculations is general for all space groups, in conventional settings or otherwise. The rms electron density (averaged over all grid points) is printed as well as the maximum and minimum values so that the significance of the latter can be assessed. Since PLAN 20 was assumed, only a peak list is printed (and written to the *.res* file), followed by a list of shortest distances between peaks (not shown below); PLAN -20 would have produced a more detailed analysis with 'printer plots' of the structure. The last 40 peaks and some of the interatomic distances have been deleted here to save space. In this table, 'distances to nearest atoms' takes symmetry equivalents into account.

```
Bond lengths and angles         [severely squashed to fit page!]

Ag – Distance      Angles
N    2.2788(0.0058)
N_$2 2.2788(0.0058) 113.08(0.15)
N_$4 2.2788(0.0058) 113.08(0.15) 102.47(0.29)
N_$3 2.2788(0.0058) 102.47(0.29) 113.08(0.15) 113.08(0.15)
     Ag –           N           N_$3          N_$4

As – Distance      Angles
F2   1.6399(0.007)
F2_$6 1.6399(0.007)180.00(0.00)
F1_$7 1.6724(0.0037) 89.08(0.41)  90.92(0.41)
F1_$6 1.6724(0.0037) 89.08(0.41)  90.92(0.41)178.15(0.82)
F1_$5 1.6724(0.0037) 90.92(0.41)  89.08(0.41) 90.01(0.01) 90.01(0.01)
F1               1.6724(0.0037)    90.92(0.41)    89.08(0.41)    90.01(0.01)
90.01(0.01)178.15(0.82)
     As –          F2         F2_$6         F1_$7         F1_$6         F1_$5

S1 – Distance      Angles
C    1.6819(0.0069)
S2   2.0633(0.0025)  98.61(0.20)
        S1 –          C

S2 – Distance  Angles
S2_$1 2.0114(0.0028)
S1   2.0633(0.0025) 105.37(0.07)
```

```
        S2 -         S2_$1
```

```
C -  Distance  Angles
N   1.1472(0.0074)
S1  1.6819(0.0069) 175.67(0.49)
      C -          N
```

```
N -  Distance  Angles
C   1.1472(0.0074)
Ag  2.2788(0.0058) 152.38(0.45)
      N -          C
F1 - Distance  Angles
As  1.6724(0.0037)
      F1 -
```

```
F2 - Distance  Angles
As  1.6399(0.0075)
      F2 -
```

FMAP and GRID set by program

```
FMAP 2   3  18
GRID  -3.333  -2  -1      3.333   2   1
```

R1 = 0.0370 for 590 unique reflections after merging for Fourier

Electron density synthesis with coefficients Fo-Fc

```
Highest peak   0.32  at  0.0000  0.0000  0.5000  [2.60 A from N]
Deepest hole  -0.36  at  0.5000  0.5000  0.1863  [0.40 A from F2]
Mean = 0.00,  Rms deviation from mean = 0.07 e/A^3 Highest memory used
1133/13851
```

Fourier peaks appended to .res file

```
          x       y       z       sof      U    Peak  Dist to nearest atoms
Q1  1  0.0000  0.0000  0.5000  0.25000  0.05  0.32  2.60 N  2.69 C  3.33 AG
Q2  1  0.5690  0.3728  0.1623  1.00000  0.05  0.27  1.20 F1 1.34 F2 1.62 AS
Q3  1  0.5685  0.3851 -0.1621  1.00000  0.05  0.24  1.19 F1 1.25 F2 1.56 AS
Q4  1  0.4075  0.4717  0.2378  1.00000  0.05  0.23  0.81 F2 1.78 AS 1.79 F1
Q5  1  0.5848  0.2667  0.0312  1.00000  0.05  0.23  0.55 F1 2.09 AS 2.47 F1
Q6  1  0.5495  0.3425 -0.1122  1.00000  0.05  0.21  0.83 F1 1.57 AS 1.65 F2
Q7  1  0.2617 -0.1441  0.1446  1.00000  0.05  0.20  1.59 N  2.17 F1 2.40 C
Q8  1  0.7221  0.1898  0.0030  1.00000  0.05  0.20  1.55 F1 2.39 N  2.54 N
Q9  1  0.1997  0.0293  0.1024  1.00000  0.05  0.19  0.75 N  1.79 C  1.82 AG
Q10 1  0.4606 -0.0113  0.8165  1.00000  0.05  0.19  0.91 S2 1.41 S2 2.82 S1
```

3.2 Second example (sigi)
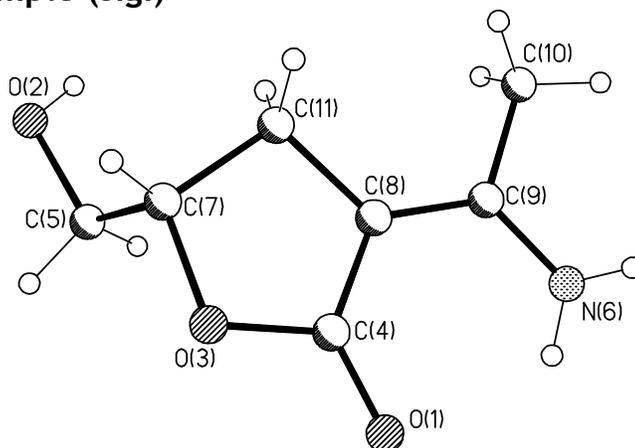
In the second example (provided as the files *sigi.ins* and *sigi.hkl*) a small organic structure is refined in the space group $P\bar{1}$. Only the features that are different from the ags4 refinement will be discussed in detail. The structure consists of a five-membered lactone [-C7-C11-C8-C4(O1)-O3-] with a -CH_2-OH group [-C5-O2] attached to C7 and a =C(CH_3)(NH_2) unit [=C9(C10)N6] double-bonded to C8.

Of particular interest here is the placing and refinement of the 11 hydrogen atoms via HFIX instructions. The two -CH_2- groups (C5 and C11) and one tertiary CH (C7) can be placed geometrically by standard methods; the algorithms have been improved relative to those used in SHELX-76, and the hydrogen atoms are now idealized before each refinement cycle (and after the last). Since N6 is attached to a conjugated system, it is reasonable to assume that the -NH_2 group is coplanar with the C8=C9(C10)-N6 unit, which enables these two hydrogens to be placed as ethylenic hydrogens, requiring HFIX (or AFIX) 9n; the program takes into account that they are bonded to nitrogen in setting the default bond lengths. All these hydrogens are to be refined using a 'riding model' (HFIX or AFIX m3) for x, y and z.

The -OH and -CH_3 groups are trickier, in the latter case because C9 is sp^2-hybridized, so the potential barrier to rotation is low and there is no fully staggered conformation available as the obvious choice. Since the data are reasonable, the initial torsion angles for these two groups can be found by means of difference electron density syntheses calculated around the circles which represent the loci of all possible hydrogen atom positions. The torsion angles are then refined during the least-squares refinement. Note that in subsequent cycles (and jobs) these groups will be re-idealized geometrically with retention of the current torsion angle; the circular Fourier calculation is performed only once. Two 'free variables' (2 and 3 yes, they still exist!) have been assigned to refine common isotropic displacement parameters for the 'rigid' and 'rotating' hydrogens respectively. If these had not been specified, the default action would have been

to hold the hydrogen U values at 1.2 times the equivalent isotropic U of the atoms to which they are attached (1.5 for the -OH and methyl groups).

The *sigi.ins* file (which is provided as a test job) is as follows. Note that for instructions with both numerical parameters and atom names such as HFIX and MPLA, it does not matter whether numbers or atoms come first, but the order of the numerical parameters themselves (and in some cases the order of the atoms) is important.

```
TITL SIGI in P-1
CELL 0.71073 6.652 7.758 8.147 73.09 75.99 68.40
ZERR 2 .002 .002 .002 .03 .03 .03
SFAC C H N O
UNIT 14 22 2 6           ! no LATT and SYMM needed for space group P-1

L.S. 4
EXTI 0.001              ! refine an isotropic extinction parameter
WGHT .060 0.15          ! (suggested by program in last job);  WGHT
OMIT 2 8 0              ! and OMIT are also based on previous output
BOND $H                 ! include H in bond lengths / angles table
CONF                    ! all torsion angles except involving hydrogen
HTAB                    ! analyse all hydrogen bonds
FMAP 2                  ! Fo-Fc Fourier
PLAN -20                ! printer plots and full analysis of peak list

HFIX 147 31 O2          ! initial location of -OH and -CH3 hydrogens from
HFIX 137 31 C10         ! circular Fourier, then refine torsion, U(H)=fv(3)

HFIX 93 21 N6           ! -NH2 in plane, xyz ride on N, U(H)=fv(2)
HFIX 23 21 C5 C11       ! two -CH2- groups, xyz ride on C, U(H)=fv(2)
HFIX 13 21 C7           ! tertiary CH, xyz ride on C, U(H)=fv(2)

EQIV $1 X-1, Y, Z       ! define symmetry operations for H-bonds
EQIV $2 X+1, Y, Z-1
HTAB N6 O1              ! outputs H-bonds D-H...A with esds
HTAB O2 O1_$1           ! _$1 and _$2 refer to symmetry equivalents
HTAB N6 O2_$2
                                ! l.s. planes through 5-ring and
through
MPLA 5 C7 C11 C8 C4 O3 O1 N6 C9 C10 ! CNC=CCC moiety, then find deviations
MPLA 6 C10 N6 C9 C8 C11 C4 O1 O3 C7 ! of last 4 and 3 named atoms resp. too

FVAR 1 .06 .07                          ! overall scale and free variables for
U(H)

REM name sfac# x y z sof(+10 to fix it) U11 U22 U33 U23 U13 U12 follow

O1  4   0.30280   0.17175   0.68006   11.00000   0.02309   0.04802 =
     0.02540  -0.00301  -0.00597  -0.01547
O2  4  -0.56871   0.23631   0.96089   11.00000   0.02632   0.04923 =
     0.02191  -0.00958  0.00050  -0.02065
O3  4  -0.02274   0.28312 0.83591 11.00000 0.02678 0.04990 =
     0.01752  -0.00941  -0.00047  -0.02109
C4  1   0.10358   0.23458 0.68664 11.00000 0.02228 0.02952 =
     0.01954  -0.00265  -0.00173  -0.01474
C5  1  -0.33881   0.18268 0.94464 11.00000 0.02618 0.03480 =
     0.01926  -0.00311  -0.00414  -0.01624
N6  3  0.26405   0.17085 0.33925 11.00000 0.03003 0.04232 =
     0.02620  -0.01312  0.00048  -0.01086
```

```
C7  1  -0.25299    0.33872 0.82228 11.00000 0.02437 0.03111 =
      0.01918  -0.00828  -0.00051  -0.01299
C8  1  -0.03073    0.27219 0.55976 11.00000 0.02166 0.02647 =
      0.01918  -0.00365  -0.00321  -0.01184
C9  1   0.05119    0.24371 0.39501 11.00000 0.02616 0.02399 =
      0.02250  -0.00536  -0.00311  -0.01185
C10 1  -0.10011    0.29447 0.26687 11.00000 0.03877 0.04903 =
      0.02076  -0.01022  -0.00611  -0.01800
C11 1  -0.26553    0.36133 0.63125 11.00000 0.02313 0.03520 =
      0.01862  -0.00372  -0.00330  -0.01185

HKLF 4   ! read intensity data from 'sigi.hkl'; terminates '.ins' file
END
```

The data reduction reports 1904 reflections read (one of which was rejected by OMIT) with indices $-7 \le h \le 7$, $-8 \le k \le 9$ and $-9 \le l \le 9$. Note that these are the limiting index values; in fact only about 1.5 times the unique volume of reciprocal space was measured. The maximum 2θ was 50.00, and there were no systematic absence violations, 34 (not seriously) inconsistent equivalents, and 1296 unique data. R(int) was 0.0196 and R(sigma) 0.0151.

The program uses different default distances to hydrogen for different bonding situations; these may be overridden by the user if desired. These defaults depend on the temperature (set using TEMP) in order to allow for librational effects. The list of default X-H distances is followed by the (squashed) circular difference electron density syntheses to determine the C-OH and C-CH$_3$ initial torsion angles:

```
Default effective X-H distances for T =    20.0 C

AFIX m =    1    2    3    4   4[N]  3[N]  15[B]  8[O]   9   9[N]   16
d(X-H) = 0.98 0.97 0.96  0.93  0.86  0.89  1.10  0.82  0.93  0.86  0.93

Difference electron density (eA^-3x100) at 15 degree intervals for AFIX 147
group attached to O2. The center of the range is eclipsed (cis) to C7 and
rotation is clockwise looking down C5 to O2
  2 -2 -6 -9 -8 -5 -1  0  0  0  1  0 -2 -2  0  9 23 39 48 42 29 16  9  5

Difference electron density (eA^-3x100) at 15 degree intervals for AFIX 137
group attached to C10. The center of the range is eclipsed (cis) to N6 and
rotation is clockwise looking down C9 to C10
  50 47 39 28 19 15 20 30 38 41 39 37 34 29 25 27 33 35 29 19 12 15 29 43

After local symmetry averaging:   40  41  36  28  21  20  24  33
```

It will be seen that the hydroxyl hydrogen is very clearly defined, but that the methyl group is rotating fairly freely (low potential barrier). After three-fold averaging, however, there is a single difference electron density maximum. The (squashed) least-squares refinement output follows:

```
Least-squares    cycle    1            Maximum    vector    length=511        Memory
required=1836/136080


wR2 =  0.1130 before cycle   1 for    1296 data and  105 /   105 parameters


GooF = S =        1.140;        Restrained GooF =        1.140    for        0
restraints


Weight        =        1/[sigma^2(Fo^2)+(0.0600*P)^2+0.15*P]        where
P=(Max(Fo^2,0)+2*Fc^2)/3


   N      value        esd        shift/esd   parameter


   1     0.97891     0.00384     -10.702      OSF
   2     0.04044     0.00261      -7.494      FVAR  2
   3     0.07317     0.00394       0.805      FVAR  3
   4     0.01781     0.00946       1.777      EXTI


Mean shift/esd =   0.747    Maximum = -10.702 for FVAR  2


Max. shift = 0.028 A for H10A      Max. dU =-0.020 for H5A


  .......... etc (cycles 2 and 3 omitted) .........


Least-squares   cycle  4    Maximum   vector   length  =  511  Memory  required
=1836/136080


wR2 =  0.1035 before cycle   4 for    1296 data and  105 /   105 parameters


GooF = S =        1.016;        Restrained GooF =        1.016    for        0
restraints


Weight        =        1/[sigma^2(Fo^2)+(0.0600*P)^2+0.15*P]        where
P=(Max(Fo^2,0)+2*Fc^2)/3


   N      value        esd        shift/esd   parameter
   1     0.97902     0.00358      -0.003       OSF
   2     0.03605     0.00176       0.012      FVAR  2
   3     0.07345     0.00376      -0.031      FVAR  3
   4     0.02502     0.01081      -0.010      EXTI


Mean shift/esd =   0.008    Maximum =  -0.244 for tors H10A


Max. shift = 0.004 A for H10A       Max. dU = 0.000 for H2



Largest correlation matrix elements

 0.509 U12 O2 / U22 O2     0.507 U12 O3 / U11 O3
 0.509 U12 O2 / U11 O2     0.500 U12 O3 / U22 O3



Idealized hydrogen atom generation before cycle   5

Name      x        y        z      AFIX   d(X-H)   shift   Bonded    Conformation
                                                            to       determined by
H2    -0.6017  0.2095  0.8832   147    0.820    0.000   O2          C5   H2
```

```
H5A  -0.2721  0.0676  0.9001   23   0.970   0.000   C5       O2  C7
H5B  -0.2964  0.1554  1.0576   23   0.970   0.000   C5       O2  C7
H6A   0.3572  0.1389  0.4085   93   0.860   0.000   N6       C9  C8
H6B   0.3073  0.1559  0.2347   93   0.860   0.000   N6       C9  C8
H7   -0.3331  0.4598  0.8575   13   0.980   0.000   C7       O3  C5  C11
H10A -0.0176  0.2947  0.1525  137   0.960   0.000   C10      C9  H10A
H10B -0.2042  0.4192  0.2692  137   0.960   0.000   C10      C9  H10A
H10C -0.1764  0.2036  0.2964  137   0.960   0.000   C10      C9  H10A
H11A -0.3575  0.2948  0.6198   23   0.970   0.000   C11      C8  C7
H11B -0.3198  0.4943  0.5737   23   0.970   0.000   C11      C8  C7
```

The final structure factor calculation, analysis of variance etc. produces the following edited output:

```
Final Structure Factor Calculation for  SIGI in P-1
Total number of l.s. parameters = 105    Maximum vector length =  511

wR2 =  0.1035 before cycle 5 for 1296 data and    0 /  105 parameters

GooF = S =   1.016;     Restrained GooF =       1.016  for    0 restraints

Weight          =          1/[sigma^2(Fo^2)+(0.0600*P)^2+0.15*P]          where
P=(Max(Fo^2,0)+2*Fc^2)/3
R1 = 0.0364 for   1189 Fo > 4.sigma(Fo)  and  0.0397 for all   1296 data
wR2 =  0.1035,  GooF = S = 1.016,  Restrained GooF =    1.016  for all data

Occupancy sum of asymmetric unit = 11.00 for non-hydrogen and 11.00 for
hydrogen atoms.


Principal mean square atomic displacements U

   0.0504   0.0254   0.0188   O1
   0.0492   0.0229   0.0189   O2
   0.0513   0.0194   0.0165   O3
   0.0326   0.0208   0.0159   C4
   0.0376   0.0204   0.0190   C5
   0.0439   0.0319   0.0214   N6
   0.0329   0.0201   0.0185   C7
   0.0276   0.0190   0.0181   C8
   0.0289   0.0220   0.0191   C9
   0.0493   0.0352   0.0181   C10
   0.0353   0.0215   0.0183   C11

Analysis of variance for reflections employed in refinement
K = Mean[Fo^2] / Mean[Fc^2]  for group


Fc/Fc(max)    0.000 0.009 0.017 0.027 0.038 0.049 0.065 0.084 0.110 0.156 1.0


Number in group   135.  125.  131.  139.  119.  132.  131.  128.  131.  126.


       GooF  1.034 1.000 1.085 1.046 1.093 0.999 0.937 0.995 1.027 0.931
```

```
       K     1.567 1.127 0.964 1.023 1.008 0.992 0.997 0.998 1.008 1.010


Resolution(A)  0.84  0.88  0.90  0.95  0.99  1.06 1.14  1.25  1.44  1.79  inf

Number in group   136.  127.  128.  128.  136.  124.  128.  130.  130.  129.

       GooF  0.978 0.881 0.854 0.850 0.850 0.921 0.874 1.088 1.242 1.434

       K     1.024 1.013 1.017 0.990 0.991 0.989 1.013 0.995 1.037 1.004

       R1    0.061 0.049 0.050 0.046 0.034 0.034 0.031 0.039 0.038 0.037

Recommended weighting scheme:  WGHT   0.0545   0.1549
```

The analysis of variance should be examined carefully for indications of systematic errors. If the *Goodness of Fit* (GooF) is significantly higher than unity and the scale factor K is appreciably lower than unity in the extreme right columns in terms of both *F* and resolution, then an extinction parameter should be refined (the program prints a warning in such a case). This does not show here because an extinction parameter is already being refined. The scale factor is a little high for the weakest reflections in this example; this may well be a statistical artifact and may be ignored (selecting the groups on F_c will tend to make F_o^2 greater than F_c^2 for this range). The increase in the GooF at low resolution (the 1.79 to infinity range) is caused in part by systematic errors in the model such as the use of scattering factors based on spherical atoms which ignore bonding effects, and is normal for purely light-atom structures (this interpretation is confirmed by the fact that difference electron density peaks are found in the middle of bonds). In extreme cases the lowest or highest resolution ranges can be conveniently suppressed by means of the SHEL instruction; this is normal practice in macromolecular refinements, but refining a diffuse solvent model with SWAT may be better, inadequate solvent modeling for macromolecules produces similar symptoms to lack of extinction refinement for small molecules.

The weighting scheme suggested by the program is designed to produce a flat analysis of variance in terms of F_c, but makes no attempt to fit the resolution dependence of the GooF. It is also written to the end of the *.res* file, so that it is easy to update it before the next job. In the early stages of refinement it is better to retain the default scheme of WGHT 0.1; the updated parameters should not be incorporated in the next *.ins* file until all atoms have been found and at least the heavier atoms refined anisotropically.

The list of most disagreeable reflections and tables of bond lengths and angles (BOND $H - omitted here) and torsion angles (CONF) are followed by the HTAB (hydrogen bonds) and MPLA (least-squares planes) tables:

```
 Selected torsion angles

  -175.08 ( 0.12)  C7 - O3 - C4 - O1
```

```
    5.73 ( 0.15)   C7 - O3 - C4 - C8
  109.69 ( 0.12)   C4 - O3 - C7 - C5
  -11.65 ( 0.15)   C4 - O3 - C7 - C11
  171.12 ( 0.10)   O2 - C5 - C7 - O3
  -72.04 ( 0.15)   O2 - C5 - C7 - C11
   -1.46 ( 0.24)   O1 - C4 - C8 - C9
  177.61 ( 0.12)   O3 - C4 - C8 - C9
 -176.27 ( 0.14)   O1 - C4 - C8 - C11
    2.80 ( 0.16)   O3 - C4 - C8 - C11
    3.08 ( 0.22)   C4 - C8 - C9 - N6
  176.93 ( 0.13)   C11 - C8 - C9 - N6
 -177.23 ( 0.13)   C4 - C8 - C9 - C10
   -3.39 ( 0.22)   C11 - C8 - C9 - C10
  176.05 ( 0.13)   C9 - C8 - C11 - C7
   -9.39 ( 0.14)   C4 - C8 - C11 - C7
   12.37 ( 0.14)   O3 - C7 - C11 - C8
 -104.74 ( 0.13)   C5 - C7 - C11 - C8
```

Specified hydrogen bonds (with esds except fixed and riding H)

```
 D-H         H...A        D...A          <(DHA)
 0.86        2.23         2.8486(18)     129.3          N6-H6A...O1
 0.82        2.04         2.8578(16)     174.0          O2-H2...O1_$1
 0.86        2.17         2.9741(19)     155.1          N6-H6B...O2_$2
```

Least-squares planes (x,y,z in crystal coordinates) and deviations from them
 (* indicates atom used to define plane)

  2.3443 (0.0044) x + 7.4105 (0.0042) y - 0.0155 (0.0053) z = 1.9777 (0.0044)

```
 *   -0.0743 (0.0008)   C7
 *    0.0684 (0.0008)   C11
 *   -0.0418 (0.0009)   C8
 *   -0.0062 (0.0008)   C4
 *    0.0538 (0.0008)   O3
     -0.0061 (0.0020)   O1
     -0.0980 (0.0028)   N6
     -0.0562 (0.0023)   C9
     -0.0314 (0.0030)   C10
```

 Rms deviation of fitted atoms =   0.0546

  2.5438 (0.0040) x + 7.3488 (0.0040) y - 0.1657 (0.0042) z = 1.8626 (0.0026)

 Angle to previous plane (with approximate esd) = 2.45 (0.07)

```
 *    0.0054 (0.0008)   C10
 *    0.0082 (0.0008)   N6
 *   -0.0052 (0.0012)   C9
 *   -0.0337 (0.0012)   C8
 *    0.0135 (0.0008)   C11
 *    0.0118 (0.0009)   C4
      0.0568 (0.0019)   O1
      0.0214 (0.0018)   O3
     -0.1542 (0.0020)   C7
```

```
Rms deviation of fitted atoms =   0.0162


Hydrogen bonds with  H..A < r(A) + 2.000 Angstroms  and  <DHA > 110 deg.

D-H            d(D-H)   d(H..A)   <DHA    d(D..A)    A
O2-H2          0.820    2.041    174.05   2.858     O1 [ x-1, y, z ]
N6-H6A         0.860    2.225    129.29   2.849     O1
N6-H6B         0.860    2.172    155.06   2.974     O2 [ x+1, y, z-1 ]
```

All esds printed by the program are calculated rigorously from the full covariance matrix, except for the esd in the angle between two least-squares planes, which involves some approximations. The contributions to the esds in bond lengths, angles and torsion angles also take the errors in the unit-cell parameters (as input on the ZERR instruction) rigorously into account; an approximate treatment is used to obtain the (rather small) contributions of the cell errors to the esds involving least-squares planes.

There follows the difference electron density synthesis and line printer 'plot' of the structure and peaks. The highest and lowest features are 0.27 and -0.17 eA^{-3} respectively, and the rms difference electron density is 0.04. These values confirm that the treatment of the hydrogen atoms was adequate, and are indeed typical for routine structure analysis of small organic molecules. This output is too voluminous to give here, and indeed users of the Siemens SHELXTL molecular graphics program XP will almost always suppress it by use of the default option of a positive number on the PLAN instruction, and employ interactive graphics instead for analysis of the peak list.