Introduction to single crystal X-ray analysis
VII. Refinement of disordered structure

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1. Introduction

A single crystal of target material is necessary to conduct single crystal X-ray structure analysis, but in an ideal single crystal, atoms and molecules have an ordered, three-dimensional repetitive structure. That is, the ideal single crystal is one in which all molecules comprising the single crystal have the same steric structure, and the geometrical arrangement of molecules within a unit cell is the same viewing from any direction. However, it is frequently the case that actual single crystals are not ideal, and there may be irregularities such as more than one molecules in an asymmetric unit, multiple crystal domains (twinning), or the disordered structure which is the topic here (disorder).

This paper starts by describing what disordered structure is, and then introduces how to determine disordered structure, and methods of refinement using the SHELX-97 structure refinement program. The author will be happy if, when the reader encounters a situation which must be analyzed as disordered structure, he or she can take their time and handle the problem, rather than giving up simply because it is a disordered structure.

2. What is disordered structure?

In reality this would not happen, but imagine a group of people who are lifting weights together at the same time. If they are regularly aligned and all of them lift and lower their barbells together, then they are an ordered, ideal group. This state corresponds to an ideal single crystal.

However, in actual problems this does not happen, and every group will have some people who are not lifting. Let us assume that, under normal conditions where everyone must lift their barbells at the same time, 20% of the people are resting with their weights down. That is the situation in Fig. 1. If those with their barbells up and those with their barbells down are lined up alternately, then there will be order, but the point to notice here is that they are lined up in a disordered way. In single crystal X-ray structure analysis, we look at the average spatial image of all molecules (atoms) present in the crystal. Therefore, as a group the state is a mixture of people with their barbells lifted and lowered, and that is how the average for the group as a whole appears (Fig. 2). This is a disordered structure.

In actual crystals, analysis is done using the average structure, even if there are molecules with somewhat different structure. Figure 3 shows an example of a disordered structure of ethyl groups. When there is a

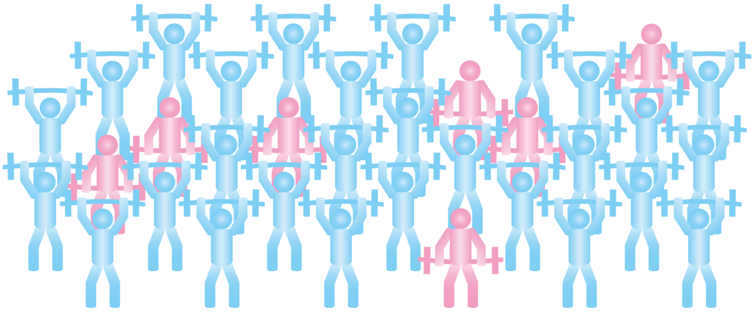

Fig. 1. A “disordered” group exercising with barbells.

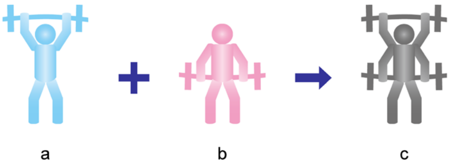

Fig. 2. Person with barbell lifted (a), person with barbell lowered (b), and their average (c).

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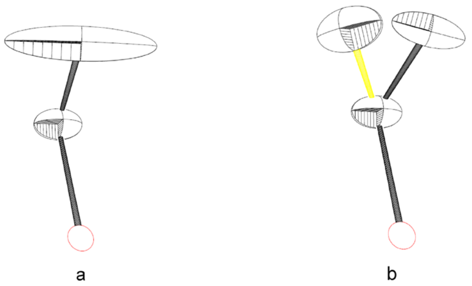


Fig. 3. Disordered structure of ethyl group.
An ethyl group for which marked anisotropy is seen in temperature factors (a) is analyzed as the sum of two steric structures with different positions of the end carbon atom (b).

disordered structure, there may be marked anisotropy if the structure is expressed with thermal ellipsoids.

3. Types of disordered structure

In brief, disordered structures are divided into three basic categories.

The first is the case where atoms of different types are present at the same site of two or more unit cells. This is called substitutional disorder. The second is called positional disorder. This is the case where one atom is present at two or more sites, i.e., where a single molecule assumes multiple steric structures. Structures with positional disorder are further divided into discrete (or static) disordered structures and continuous (or dynamic) disordered structures. The third category is comprised of a special case not belonging to the substitutional or positional type.

3.1. Substitutional disorder

Disordered structure of the substitutional type is generally seen in minerals and organic materials. One example would be substitution of Al (aluminum) and Si (silicon) in zeolite. This is also seen in coordination complexes and organic materials, such as substitutions between the central metals Pt (platinum) and Pd (palladium) in organometallic complexes, and between Cl (chlorine) and Br (bromine) in organic halogen compounds.

Key points for ascertaining substitutional disordered structure are temperature factors and residual electron density. If abnormalities are apparent, such as anisotropic or isotropic temperature factors which are too small or too large, there is a possibility of a substitutional disordered structure. However, if the temperature factor is too large, careful examination is necessary because partial occupation is also a possibility. For noncoordinating solvents too, it is possible to determine a substitutional disordered structure based on temperature factor abnormalities, but the temperature factor of a noncoordinating solvent tends to be large, and thus caution is necessary. In addition, if the residual electron density at or near the position of an atom is negative, then the actual occupancy may be smaller than 1.

3.2. Positional disorder

The probability of encountering a positional disordered structure is perhaps higher than that of encountering a substitutional disordered structure. A static disordered structure arises due to apparent motion in the crystal as a whole. This is because the average structure appears to be moving if there are molecules with different steric configurations. Phrased in terms of the above example of people lifting weights, this is the situation where some people have lowered their barbells and are resting, even though they should be stationary with their barbells lifted.

A dynamic disordered structure, on the other hand, is due to intramolecular vibrations in the unit cells. Unlike a static disordered structure, the molecules are actually moving. A tert-butyl group has no steric hindrance and can assume any rotation angle, and thus a dynamic disordered structure is frequently seen. When a dynamic disordered structure is seen, and it is difficult to carry out structure analysis taking into account intramolecular vibration, then creative approaches are needed to minimize the effects such as treating the sample as a disordered structure, or carrying out measurement at low temperature.

This is a bit off the current topic of disordered structure refinement, but one effect of low-temperature measurement is suppression of disordered structure. This is because setting to a low temperature limits the movement of molecules in the crystal. In addition, measurement at a low temperature may convert a dynamic disordered structure into a static disordered structure. Even with the same positional disordered structure, it is much easier to analyze a static disordered structure. Also, although this is not an effect of low-temperature measurement, if a crystal has two or more types of unit cells, i.e., if it has a modulated structure, then there is no temperature dependence in measurement, but apparently there are cases where, by growing crystals at low temperature, a marked relative difference in energy arises between structures with highly similar steric configurations, and only the dominant structure appears.

3.3. Special case

The third type is the case (bulk solvent) where solvent molecules are present in a disordered fashion in the voids of a crystal. During data collection, bulk solvent can be regarded as solvent frozen in an amorphous state. This is frequently seen with solvents in protein crystals, but it is also sometimes seen in small molecule crystals.

If the situation is such that a structural model cannot be assembled, then correction may sometimes be done with formulas using the SWAT instruction of SHELXL. Refinement while excluding the effects of solvent is also frequently done by using the SQUEEZE program of PLATON.

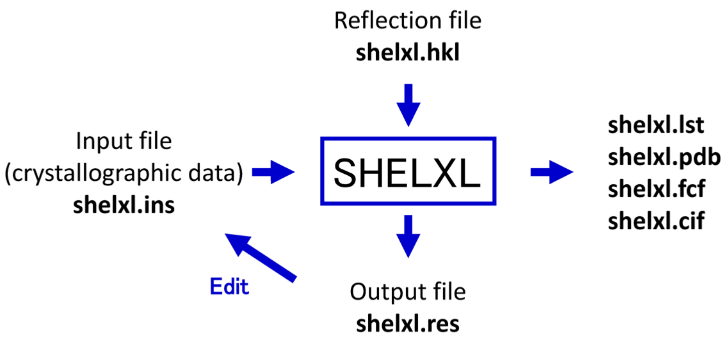


Fig. 4. Composition of output files from refinement using SHELXL.

4. Refinement of disordered structures

In refinement of disordered structures, it is sufficient in many cases to determine the position of atoms which have disordered structure, i.e., to refine atom coordinates. The meaning of "sufficient" here comes from the fact that for most programs, it is impossible to execute refinement beyond that point.

However, properly speaking, refinement of a disordered structure requires finding the position (coordinates) and population (occupancy) for each atom. If the SHELXL program is used, then by using the PART instruction it is possible to divide the atoms and atom groups comprising the disordered structure into two or more groups, and using the FVAR instruction it is possible to refine each occupancy. This approach is effective for structure analysis of crystals with a disordered structure.

4.1. SHELX-97 program package

SHELX is a program package for phase determination and refinement. It consists primarily of SHELXS and SHELXL. SHELXS is a program for phase determination using direct methods and Patterson methods, so the details will be omitted. SHELXL (SHELXH) is a program for refinement.

SHELXL executes refinement based on the information in two files: a reflection file shelxl.hkl and a refinement input file shelxl.ins. The results are output as a shelxl.res file. In addition, in order to correct the obtained structure, the shelxl.res file is edited and used again as an input file shelxl.ins. Also, after execution of refinement, shelx1.lst and a number of other files are output as results (Fig. 4).

4.2. Using SHELXL with CrystalStructure

In order to use SHELXL with Rigaku's CrystalStructure structure analysis program package, SHELXL must first be installed. If SHELXL is installed, the user can select from [Refinement tools] on the [Tools] menu whether to use [CRYSTALS] or [SHELXL] as the refinement program (Fig. 5).

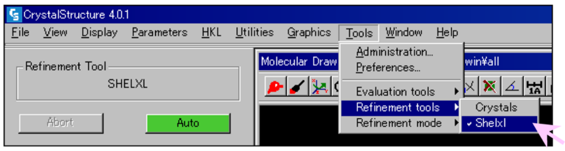
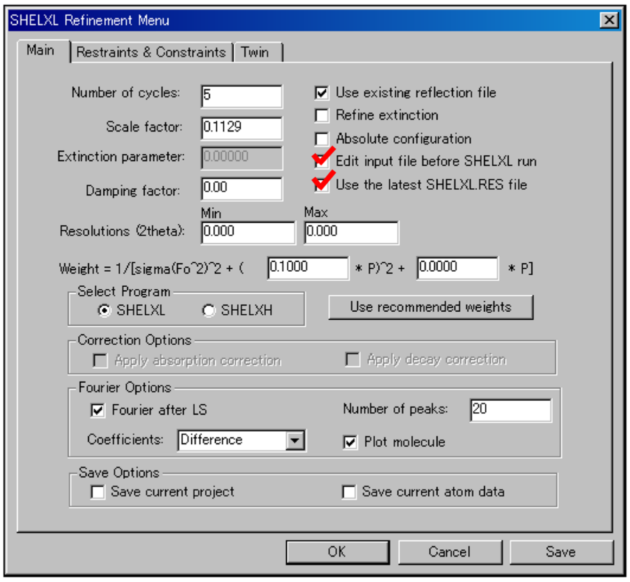


Fig. 5. Selection of SHELXL refinement program in CrystalStructure.


SHELXL Refinement Menu

Main | Restraints & Constraints | Twin

Number of cycles: 5

Scale factor: 0.1129

Extinction parameter: 0.00000

Damping factor: 0.00

Resolutions (2theta): Min 0.000 Max 0.000

☑ Use existing reflection file

☐ Refine extinction

☐ Absolute configuration

☑ Edit input file before SHELXL run

☑ Use the latest SHELXL.RES file

Weight = 1/[sigma(Fo^2)^2 + (0.1000 * P)^2 + 0.0000 * P]

Select Program: ● SHELXL ○ SHELXH

Correction Options: ☐ Apply absorption correction ☐ Apply decay correction

Fourier Options: ☑ Fourier after LS; Number of peaks: 20; Coefficients: Difference; ☑ Plot molecule

Save Options: ☐ Save current project ☐ Save current atom data

Fig. 6. SHELXL dialog box.

If [SHELXL] is selected here, a dialog box for SHELXL is displayed when executing refinement (Fig. 6). Also, if the [Edit input file before SHELXL run] checkbox is turned on, the shelxl.ins input file for SHELXL is opened in a text editor prior to refinement execution, and can be freely edited. To access the results of a previous refinement, turn on the [Use the latest SHELXL.RES file] checkbox. When analyzing a complex disordered structure, turn on these two checkboxes, and edit the input file as appropriate.

4.3. Refinement of disordered structure using SHELXL instructions

4.3.1. Grouping (PART)

If a disordered structure is evident, it is necessary to first perform grouping using the PART instruction. "PART n" means that the atom below the instruction belongs to the nth disordered structure. The instruction terminates with n=0, without creating a bond with an atom belonging to another PART number. If there are atoms on a symmetrical element, negative numbers such

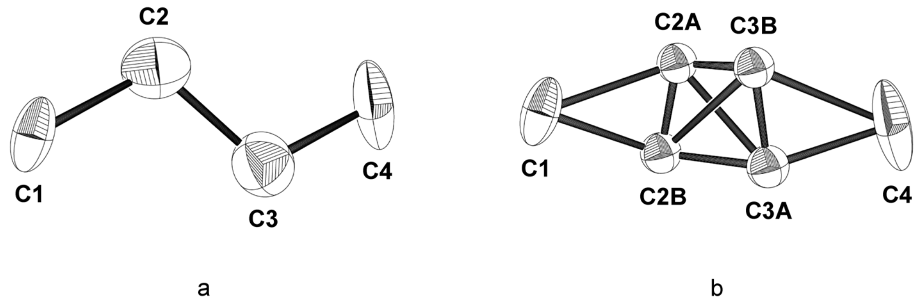
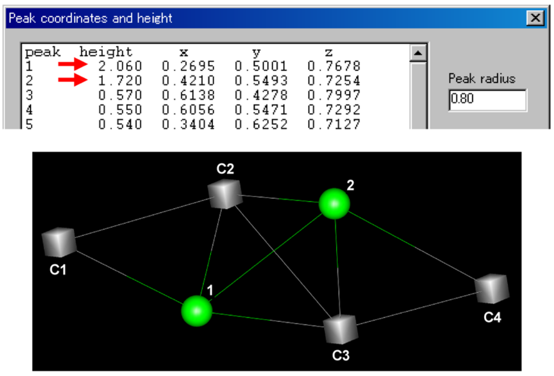


Fig. 7. Refinement of disordered structure.

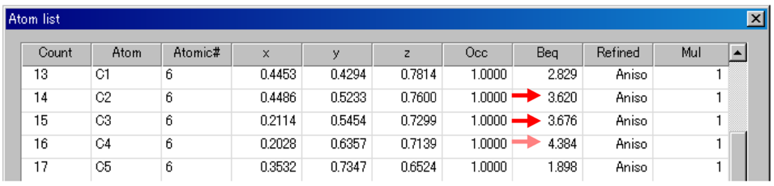


Peak coordinates and height

```
peak   height      x       y       z
1        2.060  0.2695  0.5001  0.7678
2        1.720  0.4210  0.5493  0.7254
3        0.570  0.6138  0.4278  0.7997
4        0.550  0.6056  0.5471  0.7292
5        0.540  0.3404  0.6252  0.7127
```

Peak radius: 0.80

Fig. 8. Determination of positional disordered structure (residual electron density).



Atom list

Count	Atom	Atomic#	x	y	z	Occ	Beq	Refined	Mul
13	C1	6	0.4453	0.4294	0.7814	1.0000	2.829	Aniso	1
14	C2	6	0.4486	0.5233	0.7600	1.0000	3.620	Aniso	1
15	C3	6	0.2114	0.5454	0.7299	1.0000	3.676	Aniso	1
16	C4	6	0.2028	0.6357	0.7139	1.0000	4.384	Aniso	1
17	C5	6	0.3532	0.7347	0.6524	1.0000	1.898	Aniso	1

Fig. 9. Determination of positional disordered structure (temperature factors).

as −1 and −2 are assigned to n. If n is set to a negative number, then bonds are excluded with atoms that arise in symmetrical operations, and with atoms belonging to other PART numbers.

Now, let us look at an example of a case where the carbon chain from C1 to C4 shown in Fig. 7(a) assumes a disordered structure like that shown in Fig. 7(b).

The possibility of a positional disordered structure is determined first from the residual electron density. If [List Peaks] is selected under the [Utilities] menu, the [Peak coordinates and height] dialog box is displayed (Fig. 8). It is evident that the two electron density peaks shown by the red arrows are extremely large compared to the others. Also, if [List atoms] is selected under the [Utilities] menu, then the [Atom list] dialog box is displayed (Fig. 9). Looking at the temperature factor B_{eq}, it can be seen that the temperature factors of the C2 and C3 carbon atoms are large compared to the surrounding atoms. Therefore, there seems to be a need for analysis assuming that C2 and C3 have a disordered structure.

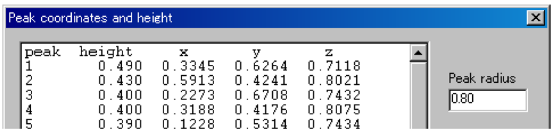
Figure 10 shows an example of input of PART instructions in an actual shelxl.ins file. In the example, the names of C2 and C3 are changed, respectively, to C2A and C3A, and those are taken to be the PART 1 group. The electron density peaks Q1 and Q2 are taken to be, respectively, C2B and C3B, and those are assumed to be the PART 2 group. C2A and C3A directly under the PART 1 instruction, and C2B and C3B directly under the PART 2 instruction, belong to the same group, and PART 0 means that the grouping ends.

In addition, occupancy is designated in the sixth column from the left, which is called the site of occupancy (sof). In the ordinary case where an atom is not at a special location, the sof value is “11.0,” but in the case of a disordered structure, 11.0 is changed to 10.5. The occupancy value can be changed from the GUI of CrystalStructure. The “1.0” of 11.0 indicates occupancy1, and the “0.5” of 10.5 indicates an occupancy of half or 0.5.

When refinement was executed while taking into account the disordered structure by using the PART instruction, the extremely large electron density disappeared (Fig. 11). However, since the difference of the temperature factors of the atoms in PART 1 and PART 2 is large, it appears to not be the case that they

```
(・・・)
C1    1    0.443763    0.429210    0.781702    11.00000    0.05127    0.02933 =
           0.02096    -0.00479    -0.00985    0.01810
PART 1
C2A   1    0.448646    0.523293    0.760039    10.50000    0.00634
C3A   1    0.211417    0.545348    0.729897    10.50000    0.00896
PART 2
C2B   1    0.2695      0.5001      0.7678      10.50000    0.04580
C3B   1    0.4210      0.5493      0.7254      10.50000    0.04436
PART 0
C4    1    0.204090    0.635347    0.714014    11.00000    0.12055    0.02533 =
           0.02431     0.01054    -0.01068    -0.00434
(・・・)
```

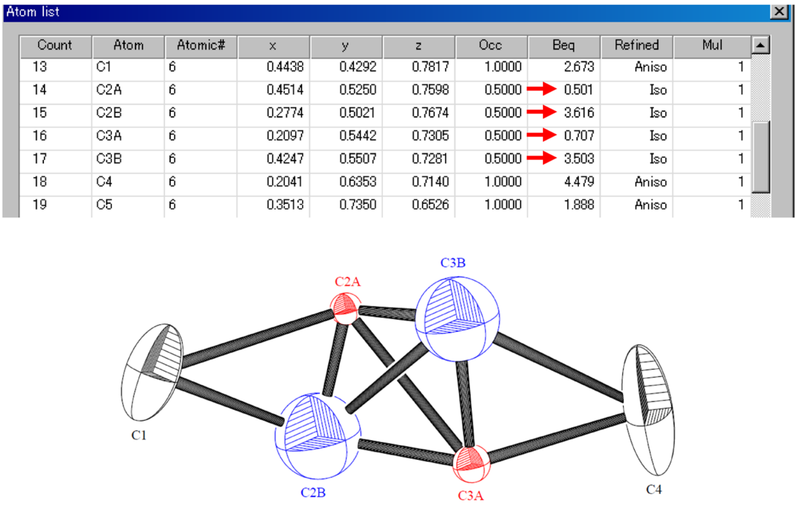
Fig. 10. Example of inputting PART instructions into shelxl.ins file.



```
peak  height    x       y       z
1        0.490  0.3345  0.6264  0.7118
2        0.430  0.5913  0.4241  0.8021
3        0.400  0.2273  0.6708  0.7432
4        0.400  0.3188  0.4176  0.8075
5        0.390  0.1228  0.5314  0.7434
```

Peak radius: 0.80

Fig. 11. Result of grouping using PART instructions (residual electron density).



Count	Atom	Atomic#	x	y	z	Occ	Beq	Refined	Mul
13	C1	6	0.4438	0.4292	0.7817	1.0000	2.673	Aniso	1
14	C2A	6	0.4514	0.5250	0.7598	0.5000	0.501	Iso	1
15	C2B	6	0.2774	0.5021	0.7674	0.5000	3.616	Iso	1
16	C3A	6	0.2097	0.5442	0.7305	0.5000	0.707	Iso	1
17	C3B	6	0.4247	0.5507	0.7281	0.5000	3.503	Iso	1
18	C4	6	0.2041	0.6353	0.7140	1.0000	4.479	Aniso	1
19	C5	6	0.3513	0.7350	0.6526	1.0000	1.888	Aniso	1

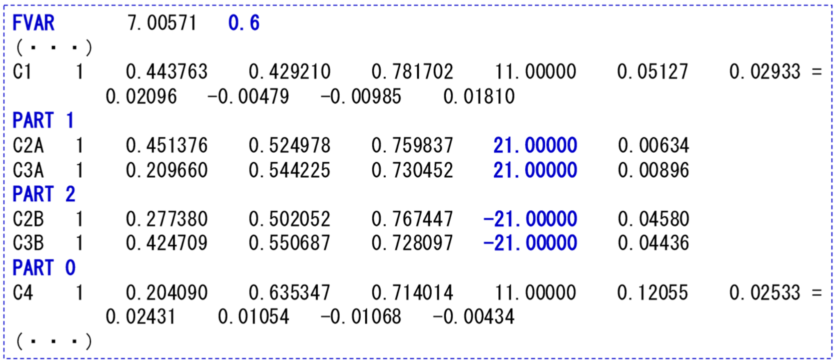
Fig. 12. Result of grouping using PART instructions (temperature factors).

are present with occupancy of one half each (Fig. 12). In this case, one method is to execute refinement while appropriately changing the occupancy, and set so the occupancy is just right while looking at the obtained temperature factors. However, if the SHELXL program is used, occupancy can also be refined.

4.3.2. Free variables (FVAR)

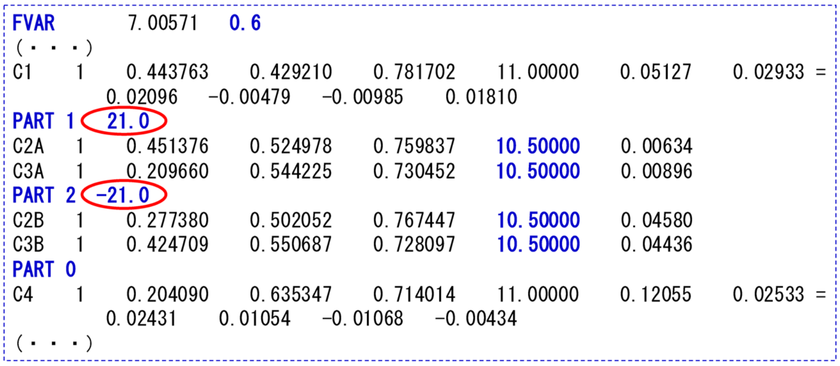
Free variables (FVAR) are used for refinement of occupancy. The first parameter of an FVAR instruction is always an overall scale factor, and thus the second and subsequent positions can be used as occupancy parameters. At this time, the initial value is designated in the interval from 0 to 1. This value is refined as the occupancy of the atoms belonging to the designated PART number. The occupancy of the counterpart atoms becomes [1−(value of designated free variable)]. If the occupancy of a minor domain is roughly 15% or less, then there is almost no contribution to electron density, and thus there is no need to take into account disordered structure. However, in some cases the contribution to electron density is large, even at about 15%, such as when metal atoms with a high atomic number are involved, and analysis taking into consideration disordered structure may sometimes be necessary.

Figure 13 shows an input example. The overall scale factor is input at the first parameter in the line where FVAR is written. A value of about 0.6 is input as the initial value of occupancy for the second FVAR parameter. Next, the sof of the atom belonging to PART 1 is changed from 11.0 or 10.5 to 21.0. The sof of the atom belonging to PART 2 is changed to −21.0. In the sof "21.0" in PART 1, the 10s place digit indicates the position among free variable numbers, and the 1s place indicates the weight. In other words, this indicates an occupancy of 1x the value "0.6" of the second free variable. In addition, the sof "−21.0" in PART 2 indicates [1−(value of the second free variable)], i.e., the



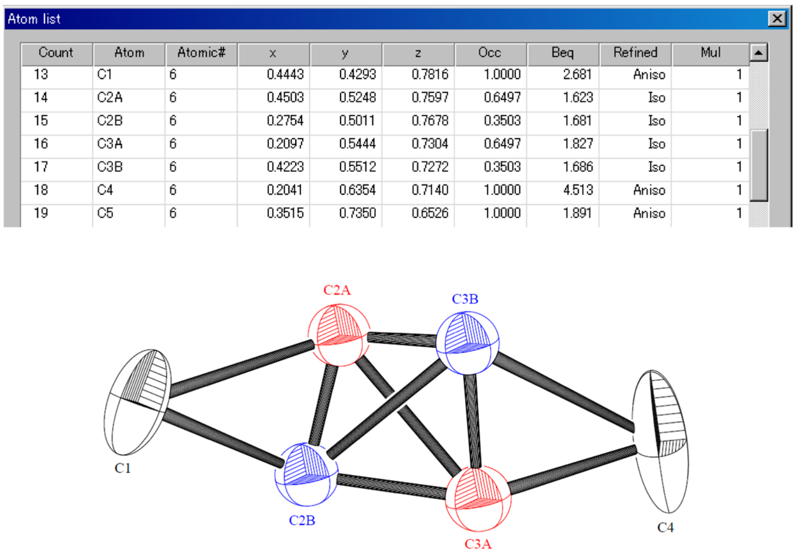
```
FVAR        7.00571   0.6
(・・・)
C1     1    0.443763    0.429210    0.781702    11.00000    0.05127    0.02933 =
          0.02096   -0.00479   -0.00985    0.01810
PART 1
C2A    1    0.451376    0.524978    0.759837    21.00000    0.00634
C3A    1    0.209660    0.544225    0.730452    21.00000    0.00896
PART 2
C2B    1    0.277380    0.502052    0.767447   -21.00000    0.04580
C3B    1    0.424709    0.550687    0.728097   -21.00000    0.04436
PART 0
C4     1    0.204090    0.635347    0.714014    11.00000    0.12055    0.02533 =
          0.02431    0.01054   -0.01068   -0.00434
(・・・)
```

Fig. 13. Example of inputting FVAR instructions into shelxl.ins file (1).



```
FVAR        7.00571   0.6
(・・・)
C1     1    0.443763    0.429210    0.781702    11.00000    0.05127    0.02933 =
          0.02096   -0.00479   -0.00985    0.01810
PART 1  21.0
C2A    1    0.451376    0.524978    0.759837    10.50000    0.00634
C3A    1    0.209660    0.544225    0.730452    10.50000    0.00896
PART 2 -21.0
C2B    1    0.277380    0.502052    0.767447    10.50000    0.04580
C3B    1    0.424709    0.550687    0.728097    10.50000    0.04436
PART 0
C4     1    0.204090    0.635347    0.714014    11.00000    0.12055    0.02533 =
          0.02431    0.01054   -0.01068   -0.00434
(・・・)
```

Fig. 14. Example of inputting FVAR instructions into shelxl.ins file (2).



Atom list

Count	Atom	Atomic#	x	y	z	Occ	Beq	Refined	Mul
13	C1	6	0.4443	0.4293	0.7816	1.0000	2.681	Aniso	1
14	C2A	6	0.4503	0.5248	0.7597	0.6497	1.623	Iso	1
15	C2B	6	0.2754	0.5011	0.7678	0.3503	1.681	Iso	1
16	C3A	6	0.2097	0.5444	0.7304	0.6497	1.827	Iso	1
17	C3B	6	0.4223	0.5512	0.7272	0.3503	1.686	Iso	1
18	C4	6	0.2041	0.6354	0.7140	1.0000	4.513	Aniso	1
19	C5	6	0.3515	0.7350	0.6526	1.0000	1.891	Aniso	1

Fig. 15. Result of refinement as disordered structure.

initial value is an occupancy of 1x the value 1−0.6=0.4. When refinement is executed, the free variable is refined so that the sum of the occupancy of PART 1 and PART 2 becomes "1".

In this example, the atom is present at a general position, and thus the value was set to 21.0 or −21.0, but in the case of an atom at a special position, for example if it is located on a two-fold rotation axis or at a center of symmetry, then the occupancy will be 0.5, and it will be 0.25 if the atom is located on a four-fold rotation axis. Therefore, in this case, it is necessary to change the sof values, respectively, to 20.5 or 20.25.

The sof value is used with priority, even if it is placed after the PART instruction, and the sof of the atom belonging to the PART is automatically rewritten (Fig. 14).

The results of refining occupancy are as shown in Fig. 15. The occupancy of the PART 1 group is about 0.65, and the occupancy of the PART 2 groups is about 0.35. The marked difference in temperature factors has disappeared.

```
(・・・)
0.0568  0.0366  0.0223  C14
0.5526  0.0468  0.0288  C15  may be split into  0.1299 0.0969 0.5045 and 0.1043 0.0616 0.5033
0.0454  0.0301  0.0226  C16
(・・・)
```

Fig. 16. Example of shelx1.lst file output when marked anisotropy is found in an anisotropic temperature factor parameter.

5. Discovery of disordered structure

Now, what is the best approach for discovering positional disordered structure? The ideal is for two electron density peaks to be evident in the difference Fourier map, but in reality that is frequently not the case.

With the SHELXL program, if marked anisotropy is evident in the anisotropic temperature factor parameters, then two site candidates are output to the shelxl.lst file (Fig. 16). However, if the two sites are separated, and it is not possible to express the anisotropic temperature factors of the two domains with a single thermal vibration parameter, then the message “may be split into” is not output. With CrystalStructure, it is possible to automatically divide the atom into two by using the “Split atom” function displayed by right clicking on an atom.

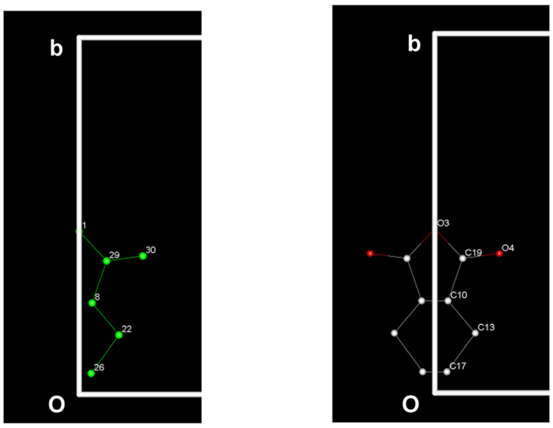
In some cases, it may be necessary to decrease occupancy, but if an atom is placed in one domain of the disordered structure, then an electron density peak corresponding to the other domain may appear. In this case, the best approach is to check the size of Q in the shelxl.res file, or the peak list in CrystalStructure. When a rigid model is considered, the form of a molecule of that type may appear.

6. Disordered structure at special positions

Next is the case where a molecule is present at a special position. If a molecule is present at a special position in a space group with a symmetric element of at least the symmetry assumable by molecules, then it is changed to a space group with lower symmetry which does not have this symmetry element. Or it may be handled as a disordered structure. In general, the latter approach is recommended. In this case the negative PART instruction is used.

As an example, let us look at benzoic acid on a two-fold rotation axis (Fig. 17(a)). If these sort of electron density peaks are evident, and atoms are placed as is at the electron density peaks near the two-fold rotation axis, then when the atoms to be related with the symmetry operation are displayed, the resulting structure will be chemically abnormal (Fig. 17(b)).

In the case of this example, it is necessary to analyze as two benzoic acid molecules (light blue and pink) as shown in Fig. 18. The SHELXL input file is like that in Fig. 19. The PART number is set to “–1” and the sof to “10.5”. If the molecule is on a three-fold rotation axis or four-fold rotation axis, then the sof is changed to, respectively, “10.333” or “10.25”.



a b

Fig. 17. Benzoic acid on a two-fold rotational axis. Electron density peaks (a) and results of displaying atoms related with symmetry operation (b).

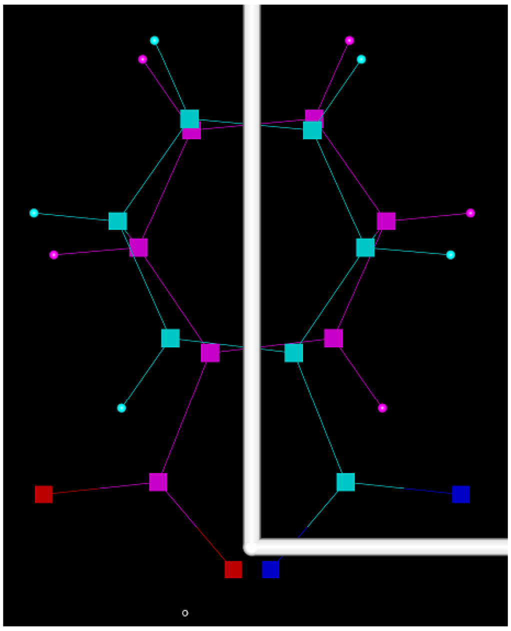


Fig. 18. Analysis of benzoic acid on a two-fold rotational axis.

7. Disordered structure seen at multiple sites

We have looked at examples of ordinary positional disordered structure, but in some cases, crystals are encountered in which disordered structure is present at multiple sites. In that case, the first step is to assign a single free variable to each disordered structure site. That is, the sof values will be 21.0 and −21.0, 31.0 and −31.0, and 41.0 and −41.0. Next, at each of the disordered structure sites, grouping is done as PART

1 and PART 2. If possible, it is best to avoid handling multiple disordered structures, but up to a maximum of 99 free variables can be set, and thus with SHELXL it is possible to handle disordered structure at 98 points.

8. Restraints and constraints

When handling a disordered structure, there is a marked increase in the number of parameters to be refined, and thus in some cases it becomes necessary to use restrictions to prevent an increase in the ratio between the number of reflections and parameters. Soft restrictions are called restraints, and they place limitations on the structure based on chemical and physical knowledge. For example, since it is known that an aromatic ring has a flat structure, or that the three methyl groups of tert-butyl are the same, restrictions are placed on the structure for cases where the structure might break down.

With restraints, the number of parameters does not decrease, but it is possible to add correct information regarding structure, and this indirectly affects the ratio between the number of reflections and parameters. With constraints, the number of parameters to be refined is reduced.

8.1. Restraints on structure

DFIX and DANG are restrictions on bond distance. Distance is designated with an arbitrary value. For example, if "DFIX 1.54 0.02 C1 C2" is input, this means that the bond distance between C1 and C2 is restricted to 1.54 Å with $\sigma=0.02$. The weight becomes $1/\sigma^2$, and the weight and effect of the restraint increase as the value of σ is decreased.

SADI is also a restriction on bond distance. It makes the bond distance between designated atoms the same. If "SADI C1 C2 C3 C4" is input, this means the bond distances will be made equal between C1 and C2, and between C3 and C4.

FLAT is a restriction which places atoms in the same plane. In cases like that shown in Fig. 20, the tendency is to designate in the order C1, C2, C3, but apparently the effect of the restriction is enhanced by designating the atoms in an alternating order, as in "FLAT C1 C3 C5 C2 C4 C6".

SAME is a restriction on bond distance just like SADI. This is used when there are molecules or sites with the same chemical structure, and a SADI instruction for the 1,2- and 1,3- bond distances is automatically generated between the two domains. Figure 21 shows an example of input when THF

```
(・・・)
PART -1
O1    4   -0.089341    0.046171    0.011297   10.50000    0.08714
O2    4   -0.009078   -0.020421    0.002352   10.50000    0.14423
C7    1   -0.039769    0.057042    0.005475   10.50000    0.08811
C1    1   -0.017741    0.170276    0.002502   10.50000    0.12856
C2    1   -0.050917    0.260096    0.004182   10.50000    0.15350
C3    1   -0.029728    0.365710    0.000699   10.50000    0.09516
C4    1    0.022853    0.378377   -0.005421   10.50000    0.10471
C5    1    0.056396    0.291310   -0.008301   10.50000    0.15669
C6    1    0.035165    0.185819   -0.005368   10.50000    0.14498
PART 0
(・・・)
```

Fig. 19. Example of input for a shelxl.ins file in analysis of benzoic acid on a two-fold rotational axis.

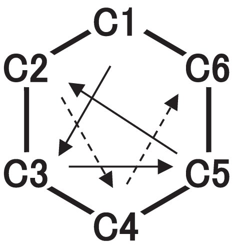


Fig. 20. FLAT instruction for aromatic ring.

```
FVAR .... 0.6
(・・・)
PART 1
SAME O1B C1B C2B C3B C4B
SAME O1A C4A C3A C2A C1A
O1A   4   .... .... ....    21.000
C1A   1   .... .... ....    21.000
C2A   1   .... .... ....    21.000
C3A   1   .... .... ....    21.000
C4A   1   .... .... ....    21.000
PART 2
O1B   4   .... .... ....   -21.000
C1B   1   .... .... ....   -21.000
C2B   1   .... .... ....   -21.000
C3B   1   .... .... ....   -21.000
C4B   1   .... .... ....   -21.000
PART 0
```

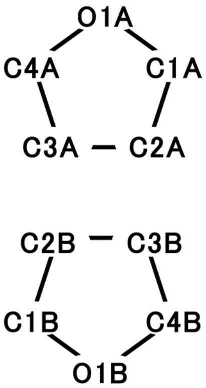


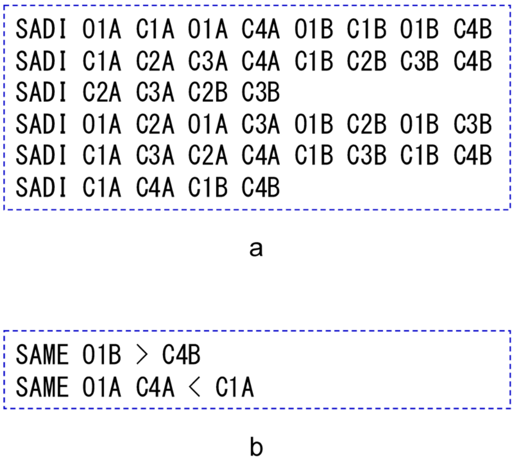
Fig. 21. Example of inputting SAME instructions in shelxl.ins file.

from O1A to C4A and from O1B to C4B assumes a disordered structure.

SAME can be rewritten as SADI, but an extremely large number of instructions have to be input if the SAME instructions in Fig. 21 are changed to SADI instructions (Fig. 22(a)). The atoms in the atom list can be indicated with a greater than (>) or less than (<) symbol instead of inputting all of the atom names (Fig. 22(b)).

8.2. Restraints on temperature factors

DELU, SIMU and ISOR are restraints on temperature factors. DELU regards bonds as rigid, and restricts so that temperature factors of bond direction components are the same. SIMU provides restriction so that anisotropic temperature factors of atoms whose inter-atom distance is at or below a designated value are kept similar. SIMU is frequently used with the DELU instruction. ISOR provides restriction so that temperature factors are roughly isotropic. It is also effective in cases where the temperature factor is non-positive definite (NPD).



```
SADI O1A C1A O1A C4A O1B C1B O1B C4B
SADI C1A C2A C3A C4A C1B C2B C3B C4B
SADI C2A C3A C2B C3B
SADI O1A C2A O1A C3A O1B C2B O1B C3B
SADI C1A C3A C2A C4A C1B C3B C1B C4B
SADI C1A C4A C1B C4B
```

a

```
SAME O1B > C4B
SAME O1A C4A < C1A
```

b

Fig. 22. Example of inputting SADI instructions (a) and example of inputting SAME instructions using symbols (b).

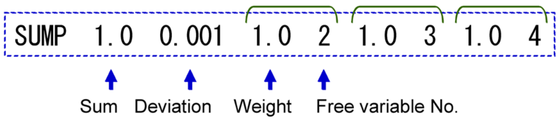
8.3. Other restraints

SUMP is another restraint. SUMP is used to restrict the total value of free variables to an arbitrary value. For example, in the case of a disordered structure made up of 3 or more domains, the sum of the occupancies must ordinarily come out to be 1. In terms of the procedure, each domain is divided into PART 1, PART 2 and PART 3, and free variables are allocated to the respective domains. The sof values of atoms belonging to each group are changed to 21.0, 31.0 and 41.0, and, as shown in Fig. 23, and restricted with the SUMP instruction so that their sum is 1, as indicated in Fig. 23. The items following SUMP are the sum of occupancies, σ, the weight, and the free variable number.

8.4. Constraints

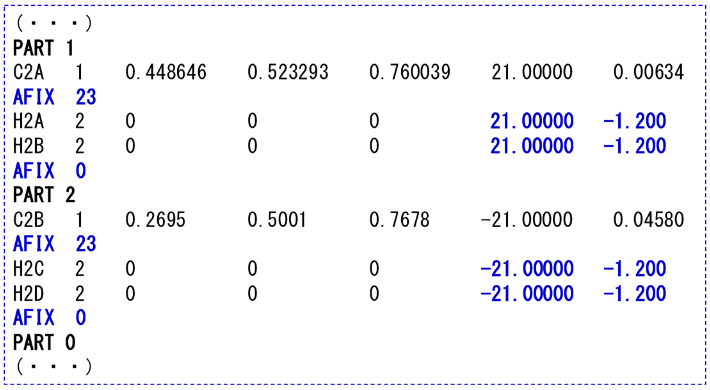
Finally, there are constraints. EXYZ is a restriction which makes atom coordinates equal, and it is used for substitutional disordered structure. EADP restricts so that atom temperature factors are equal. It is frequently used together with EXYZ.

AFIX is a restriction relating to rigid models. AFIX 66 creates a rigid model of a six-membered ring with 6 non-hydrogen atoms after the instruction, and AFIX 56 creates a rigid model of a five-membered ring with 5 non-hydrogen atoms after the instruction. The AFIX instruction is also used to generate hydrogen atoms at geometrical positions in calculation. The AFIX 23 instruction generates $-CH_2$ hydrogen atoms, and the AFIX 33 instruction generates $-CH_3$ hydrogen atoms. AFIX 137 generates $-CH_3$ hydrogen atoms just like AFIX 33, but the hydrogen atoms are made to rotate around the carbon atom, and the coordinates of the $-CH_3$ are determined to be the position which best fits the electron density.



```
SUMP 1.0 0.001 1.0 2 1.0 3 1.0 4
```

Fig. 23. Example of input of SUMP instruction in shelxl.ins file.



```
(・・・)
PART 1
C2A    1    0.448646    0.523293    0.760039    21.00000    0.00634
AFIX  23
H2A    2    0           0           0           21.00000   -1.200
H2B    2    0           0           0           21.00000   -1.200
AFIX  0
PART 2
C2B    1    0.2695      0.5001      0.7678     -21.00000    0.04580
AFIX  23
H2C    2    0           0           0          -21.00000   -1.200
H2D    2    0           0           0          -21.00000   -1.200
AFIX  0
PART 0
(・・・)
```

Fig. 24. Example of inputting SUMP instructions into shelxl.ins file.

Figure 24 shows an example of input to a shelxl.ins file when generating $-CH_2$ hydrogen atoms using AFIX 23 instructions at C2A and C2B, which have a disordered structure. The final column for each atom is the parameter relating to temperature factor, but the temperature factor "−1.2" of the hydrogen atoms means that the factor becomes 1.2 times the temperature factor of the parent atom the hydrogen is bound to.

9. Conclusion

By using SHELXL instructions, it is possible to execute refinement while taking into account disordered structure. Therefore, before giving up because the R value will not decrease, try looking closely at the analysis results. Hints to the solution may be hidden in the residual electron density and temperature factor information. However, marked anisotropy in temperature factors, or residual electron density, is not always due to disordered structure. When conducting analysis as disordered structure, do not forget the need for a chemically valid explanation.

References

(1) P. Müller: *Crystal Structure Refinement: A Crystallographer's Guide to SHELXL*, Oxford University Press, (2006).