Structure analysis program package CrystalStructure[™] 4.1



1. Introduction

CrystalStructure is a small molecule structure analysis software package which provides every procedure necessary in a single crystal X-ray structure analysis from determining the space group through creating CIF files.

In CrystalStructure, a "Menu bar" and a "Toolbar" (Fig. 1) are available on the main window. Necessary commands can be executed by pulling down a menu or clicking on an icon. The most distinctive feature is the "Flowbar", which the necessary steps in a structure analysis are arranged in the sequence that you would perform them. The final result can be obtained by just running the steps in order starting at the top.

This document describes the new functions added to Crystal Structure 4.1 in its release on June 9, 2014.



Fig. 1. CrystalStructure main window.

2. Additional functions

2.1. Space group determination program "XPlain"

In "Process", the space group determination program featured in the previous version of CrystalStructure, the space group was determined automatically by judging the centricity and systematic absences based on a predetermined threshold.

However, the judgement status of systematic absences and the process of space group determination based on this judgment was able to be checked only by viewing the output text file (Fig. 2).



Fig. 2. Result of process.

In "XPlain", the new space group determination program added to CrystalStructure 4.1, the space group determination can be performed step by step (Fig. 3). The displayed results of each step are ranked in descending order of probability. The effectiveness of XPlain is the point that other candidates are displayed as well as the one with the highest probability. For example, if a single space group had to be selected out of multiple space group, the analysis can proceed while keeping in mind that the analysis may not reach the final structure due to the wrong space group. When the analysis is not successful, the structure analysis can be tried by selecting the space group ranked in second place. Each of the steps are described below in order.

In the step to select a lattice, if there is no conflict with forbidden reflections, it is indicated in green. If it is clearly in conflict, it is indicated in red. If it is on the borderline of the two, it is indicated in yellow. The adequate selection is visually clear as well. In Fig. 3, only the primitive lattice is shown in green for each item, and other lattice types are low in probability.



Fig. 3. XPlain dialog box.

In Fig. 4, the step to select a Patterson symmetry (diffraction symmetry including lattice) is shown. All point groups possible from the metric symmetry are displayed together with R_{meas} which indicates the degree of match of equivalent reflection. Normally, R_{meas} will be less than 10%. In the example below, all diffraction symmetries are similar in R_{meas} . *Pmmm* which has the highest symmetricity is selected as default.



Fig. 4. Results of Patterson symmetry.

In the step of selecting a space group, the lattice is displayed on the top area of the dialog window (Fig. 5). The lattice is automatically converted to a standard setting according to the selected space group. Since the original lattice is diaplayed as well, how the lattice was converted can be confirmed as well by a glance.

The value of " $|E^2-1|$ " is listed below the unit cell. This value is used to judge the centricity and is also useful as a benchmark to judge the potential of a merohedral twin. The theoretical values of $|E^2-1|$ for centric and acentric structures are 0.968 and 0.736 respectively. However, if there is a merohedral twin, the intensity is averaged and

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the variation in intensity is suppressed due to overlapped reflections, resulting in $|E^2-1|$ being smaller. Therefore, if $|E^2-1|$ is significantly smaller than the theoretical value, it is suspected that there is a merohedral twin. Thus, by using XPlain, it can be judged to some extent whether there is a merohedral twin or not at a early stage of analysis during space group determination.

In the window displaying the final result, checkboxes for "show only acentric space groups (Must be chiral)" or for "show all" are available. The user can select whether to limit the possible space group or broaden the alternatives according to the situation.



Fig. 5. Final result window.

3. Initial phase determination

In CrystalStructure, multiple programs such as direct methods, Patterson methods, and the charge-flipping method are included in the standard configuration. In CrystalStructure 4.1, SIR2011 has been incorporated as a new standard program. Other than the standard programs, numerous interfaces for direct method programs are avaialable. These interfaces can be used by acquiring a particular program and storing it in a specific directory. Figure 6 indicates the direct method programs which CrystalStructure supports through interfaces. The optional programs SHELXS/SHELX 2013 are compatible as well. Basically, the newer the program is, the more improved the calculation engines are, and phase determination of complex structure which was difficult to analyze in the past has become possible to analyze. Note that each program has its distinctive features; the more programs you have available, the probability that the initial structure determination will succeed will improve.



Fig. 6. List of phase determination programs supported by CrystalStructure.

4. Compatibility with SHELX 2013

For refinement, interfaces supporting SHELX 2013 are newly added. In SHELX 2013, new commands that were not available in SHELX 97 are added. Additional new features are as follows:

- 1) Improved evaluation of absolute structure
- 2) Usability of neutron diffraction data
- Improved refinement speed through use of multiprocessors.

CIF notations are in compliance with those recommended by the IUCr. In recent years, more journals are requiring the inclusion in the CIF file, the contents of .res file and .fcf file output from. SHELX 2013 has been improved so that the content of these files are automatically inserted in the CIF file after refinement. In CrystalStructure 4.1, additional information that is required (such as crystal information, space group, and equipment information) isoutput a CIF that is suited to be used in papers for publication.

5. Enhanced access to crystallographic PLATON

The accessibility to PLATON¹, the crystallographic program package frequently used for analysis, has been enhanced. In PLATON, a wide variety of calculation modules are available, as well as various functions from space group determination to CIF output are available. In CrystalStructure 4.1, the two modules of PLATON described below can be directly launched.

SQUEEZE²⁾, is a function to suppress the residual electron density resulting from disordered solvent molecules which which are difficult to model or cannot be assigned or localized. This function is recommended when there are clear reasons to use it, such as a solvent molecule that cannot be refined since there is a large void within the crystal structure or the disorder is severe.

TwinRotMat, judges whether there is merohedral twinning and calculates the Twin law. In a crystal structure with merohedral twinning, it is based on the fact that the measured diffraction intensity I_{obs} is larger than the intensity calculated from model I_{calc} for a significant number of reflections. Therefore the required input is an Fo-Fc file such as shelxl.fcf or a diffraction intensity file as well as a coordinate file such as the .ins file.

Examples of each program being used are shown below.

5.1. Example of using the program SQUEEZE

In the crystal structure shown in Fig. 7(a), the analysis of the host molecule is mostly completed, but a relatively high residual electron density can be observed in the area indicated by the red circle. From the crystallization condition, it is assumed that the ethanol molecule of the solvent is disordered, but a logical model is unable to be constructed. In this case, select SQUEEZE from PLATON in the Tools menu and execute SQUEEZE. By performing a refinement on the reflection file output from SQUEEZE, the electron density observed in Fig. 7(a) is suppressed as shown in

Fig. 7(b). SQUEEZE is used frequently especially for MOF (Metal Organic Framework) crystals which easily clathrate solvents.



Fig. 7. Before using SQUEEZE program (a) and refinement result after using it (b).

5.2. Example of using TwinRotMat program

In TwinRotMat, if a merohedral Twin is detected, the Twin law (matrix which prescribes the relationship between different domains) is displayed. If it is not detected, "No Twin Law Detected" is displayed (Fig. 8). If a Twin law is found, you then perform refinement by entering the matrix in the refinement program and see if there is improvement in the R value.



Fig. 8. Result of TwinRotMat.

An example of using TwinRotMat is shown below. Figure 9 is at the stage where a partial structure of the heavy atom and its peripheral atoms are obtained by direct methods³⁾. To search for the remaining partial structure, the differential Fourier synthesis was performed but electron density peaks suited to construct a logical structrure were not obtained. By confirming the value of $|E^2-1|$ in the output file of XPlain and direct method SIR2004, the value of $|E^2-1|$ of this structure was 0.527, which was significantly smaller than the theoretical value of acentric which is 0.736 (Fig. 10). Therefore, by executing TwinRotMat, the existence of a merohedral



Fig. 9. Normal differential Fourier synthesis result.

| mod(E) E**2 | all data 0.940 1.000 | acentric 0.886 1.000 | centric 0.798 1.000 | hypercentric 0.718 1.000 | * |
|----------------|----------------------------|----------------------------|---------------------------|--------------------------------|---|
| mod(E**2-1) | 0.527 | 7 0.736 | 0.968 | 3 1.145 | * |

Fig. 10. Result of SIR2004.out file.

Twin was indicated, and the Twin law was output.

Figure 11 shows the results of before and after applying the Twin law to the crystal structure in Fig. 8. The R1 before applying Twin law was about 25%, and further structure expansion was impossible. After applying Twin law, the distinctive six-membered ring structure of phenyl groups of ligand PPh₃ can be clearly seen. R1 improved to about 15% as well. It also became clear that the assignment of Cl atom was mistaken, and the final structure was elucidated after the appropriate assignment.



Fig. 11. Comparison of result before and after Twin process.

6. Conclusion

In CrystalStructure 4.1, the new space group determination program XPlain, interface for phase determination program SIR2011, and interface for refinement program SHLELXL 2013 have been incorporated. The interfaces to the SQUEEZE and TwinRotMat modules of PLATON have been enhanced as well. These programs are all extremely effective for difficult structure analysis. By implementing CrystalStructure 4.1, crystal structures impossible to analyze in the past have a higher possibility of being analyzed.

References

- (1) A. L. Spek: J. Appl. Cryst., 36 (2003), 7–13.
- (2) P. v.d. Sluis and A. L. Spek: Acta Cryst., A46 (1990), 194-201.
- (3) R. Herbst-Irmer and G. M. Sheldrick: *Acta Cryst.*, **B54** (1998), 443–449.