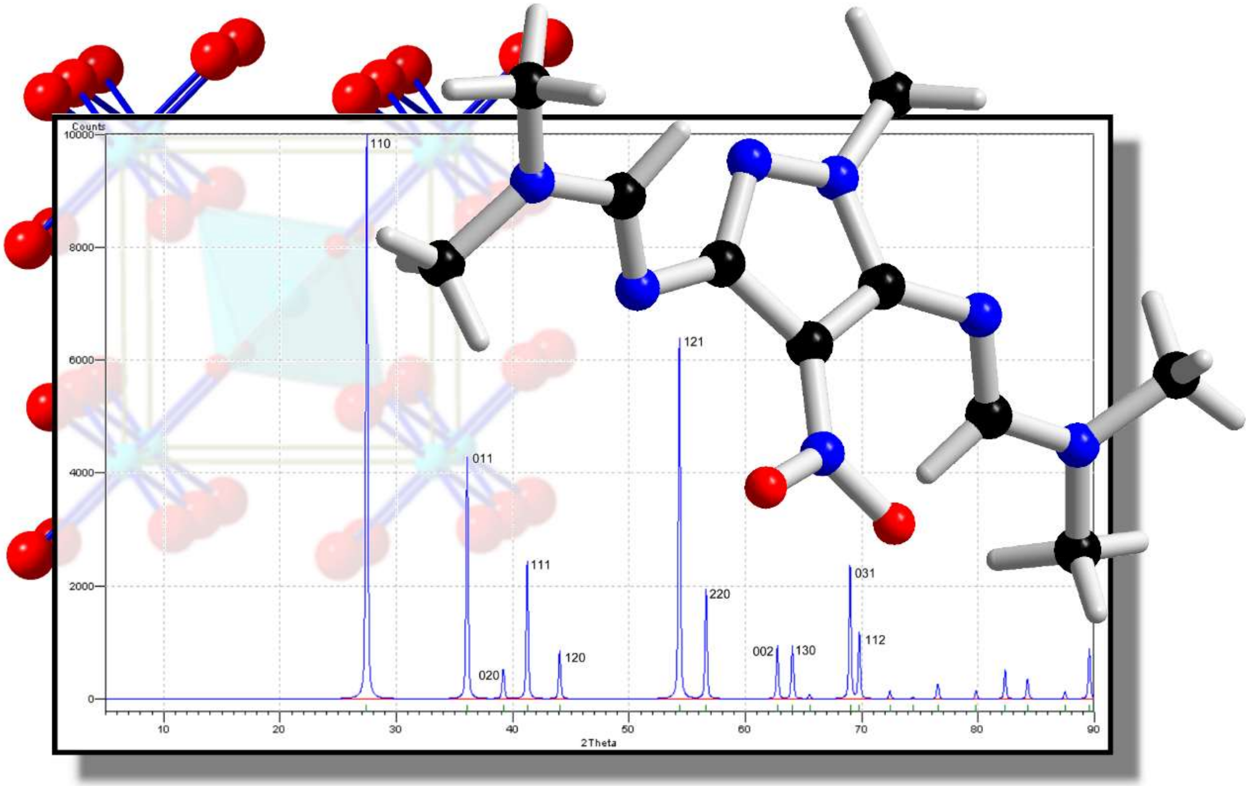
ENDEAVOUR

Structure Solution from Powder Diffraction



Tutorial Handbook

CRYSTAL IMPACT

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Version 1.8

(Revised version dated February 19, 2021)

CRYSTAL
IMPACT

Endeavour – Structure Solution from Powder Diffraction – Version 1.8 (revised version Febr. 19, 2021)

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Citation of Endeavour

If you want to publish a crystal structure which you have solved using Endeavour, you should use the following citations in your paper: "...structure solved using Endeavour [1,2] ..."

[1] H. Putz, J.C. Schön, M. Jansen, "Combined Method for 'Ab Initio' Structure Solution from Powder Diffraction Data", J. Appl. Cryst. **32**, 864-870 (1999).
[2] Crystal Impact GbR, Endeavour, Internet: https://www.crystalimpact.de/endeavour, E-mail: info@crystalimpact.de, Bonn, Germany.

Please include also the references for the symmetry checking facility ("Symmetry Finder", SFND/RGS), as it is used by Endeavour:

[3] A. Hannemann, R. Hundt, J.C. Schön, M. Jansen, "A New Algorithm for Space-Group Determination", J. Appl. Cryst. **31**, 922-928 (1998).
[4] R. Hundt, J.C. Schön, A. Hannemann, M. Jansen, "Determination of Symmetries and Idealized Cell Parameters for Simulated Structures", J. Appl. Cryst. **32**, 413-416 (1999).

Contents

Welcome!

ENDEAVOUR is a powerful tool for solving crystal structures from powder (or single crystal) diffraction data. Based on nearly 20 years of experience, the software is capable of solving many small to medium sized structures.

To get started, please install Endeavour on your computer now (if you have not already done so), following the guidelines in the software maintenance chapter starting on p. 54.

Afterwards, follow the next chapter "Quick start" on p. 8 to learn how to enter your data and get things running. Once you have learnt about the basics (and probably have already tried to solve one or the other own structure), we strongly recommend to also have a closer look at the rest of this manual:

- If you would like to get an overview about what Endeavour actually does, you should read the chapter "Endeavour at a glance" on p. 8.

- The chapter "Structure solution tutorial" (p. 18) will demonstrate various features that could not be covered yet in the "Quick start", like the usage of space group information directly in the calculation, the handling of molecule structures, what you can do if you have low-quality diffraction data, etc. These hints will certainly be helpful when you start solving your own crystal structures.

- If you are interested in advanced options, would like to learn some more details about structure solution from powder in general or the algorithms that are implemented in Endeavour, you should have a look at the chapter "Endeavour in detail" (p. 18).

- If you would like to learn how you can visualize your crystal structure according to your special requirements, you can do so in the chapter "Structure visualization" starting on p. 54.

- If Endeavour cannot find a reasonable structural model from your data, please have a look at p. 62, where you will get a lot of tips and hints on what you could do.

- If you need help or are in doubt how to perform a certain operation, the first place to look at is the online help. There is just one basic keyboard shortcut you should always keep in mind in this context: **<F1>** will open the online help at the index page, so that you can easily search for information about a given keyword/issue.
  If you need more help, please refer to page 76 where you will get contact information.

Endeavour at a glance

Endeavour[1] is a program designed for structure solution from diffraction data, using the so-called "direct-space approach": Moving the atoms through the unit cell at random, it applies a combined global optimization of the difference between calculated and measured diffraction pattern and of the potential energy of the system ("Pareto optimization"). Details about the underlying concepts and methods implemented in Endeavour have been published in the literature[1]; an overview can be found on p. 72.

The program uses diffraction data either in the form of a simple peak list (Bragg positions vs. integrated intensities; I(2θ)) or as a list of |F(hkl)| or I(hkl) values. For both, knowledge of the unit cell parameters is mandatory. The structure solution calculation may be performed in space group P1 or in any other space group. In any case, a symmetry finder can detect a higher space group in the resulting structural model.

Endeavour itself is not able to process (raw) (step-)scan data/profile data. Thus, to get the input diffraction parameters, peak search and raw data processing procedures must have been performed before its application. Besides this, the diffraction data must have been indexed, i.e. the unit cell parameters must have been determined. Both tasks can be accomplished e.g. using our software package "Match!" (in combination with indexing packages like Treor or Dicvol).

In a similar manor, Endeavour is not able to perform a Rietveld refinement. This can also be performed using our Match! software in combination with the well-known FullProf package for Rietveld refinement.

With Endeavour, the crystal structure of the results as well as the intermediate steps of the structure solution calculation can be visualized using an Auto Build function that automatically generates the contents of the unit cell, e.g., creates bonds between selected atom types, builds polyhedra, etc.

Endeavour can import refined crystal structures and visualize anisotropic displacement parameters as well as deal with standard deviations for cell and atomic parameters. However, since these data can generally not be determined from conventional laboratory powder but rather from single crystal diffraction data, the current version does not support the direct calculation of these parameters.

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[1] H. Putz, J.C. Schön, M. Jansen, "Combined Method for 'Ab Initio' Structure Solution from Powder Diffraction Data", J. Appl. Cryst. **32**, 864 (1999).

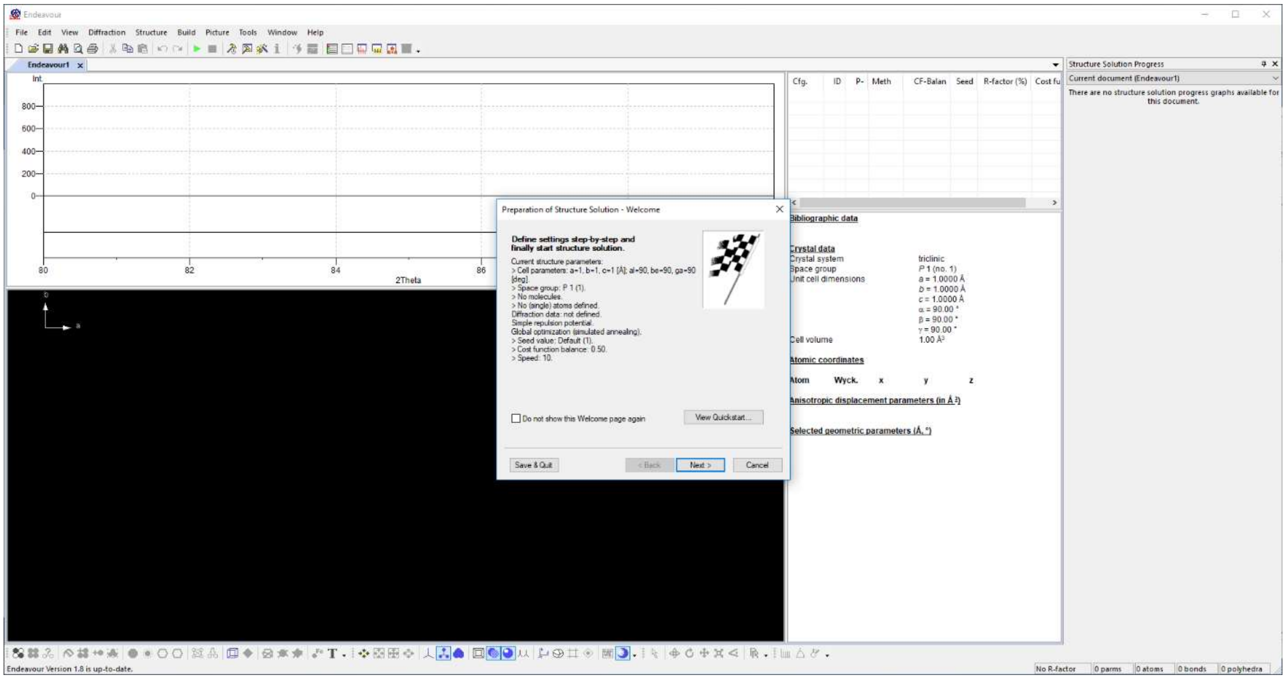
Quick start

In this session you will "solve" the crystal structure of RuS_2 and learn the basics:
- How to enter the data required for the structure solution,
- how to run a structure solution calculation incl. space group analysis,
- and finally how to use/export of the resulting structural model.

Let's start with a very simple example so that you can draw your attention to the usage and work flow of Endeavour rather than to the actual structure solution problem:

Suppose that you have made a new compound; X-ray fluorescence measurements show that its formula sum is RuS_2. The X-ray powder diffraction pattern shows a few sharp lines; indexation and cell parameter refinement result in a cubic unit cell with a = 5.6095 Å. With regard to the many overlapping reflections you decide not to commit yourself to a certain space group at this early stage. Supposing that you would not be able to generate a structural model from scratch, you decide to use Endeavour.

Please start Endeavour by double-clicking on the corresponding icon on your desktop, or by selecting "Endeavour" from the "Start-Programs-Endeavour" Windows menu. After a few seconds, Endeavour's main window will appear, and the so-called "Structure Solution Wizard" will be displayed[2] (Fig. 1). This wizard[3] step-by-step asks for all data required for the structure solution.



There are no structure solution progress graphs available for this document.

Define settings step-by-step and finally start structure solution.

Current structure parameters:
> Cell parameters: a=1, b=1, c=1 [Å]; al=90, be=90, ga=90 [deg].
> Space group: P 1 (1).
> No molecules.
> No (single) atoms defined.
Diffraction data: not defined.
Simple repulsion potential.
Global optimization (simulated annealing).
> Seed value: Default (1).
> Cost function balance: 0.50.
> Speed: 10.

Bibliographic data

Crystal data
Crystal system triclinic
Space group P 1 (no. 1)
Unit cell dimensions a = 1.0000 Å
b = 1.0000 Å
c = 1.0000 Å
α = 90.00 °
β = 90.00 °
γ = 90.00 °
Cell volume 1.00 Å³

Atomic coordinates

Atom Wyck. x y z

Anisotropic displacement parameters (in Å²)

Selected geometric parameters (Å, °)

Endeavour Version 1.8 is up-to-date.

No R-factor | 0 parms | 0 atoms | 0 bonds | 0 polyhedra

Fig. 1: By default, Endeavour displays the "Structure Solution Wizard" (here showing the 'Welcome' page) after it has been started, so that you can start entering your data right away.

First, the wizard displays a "welcome page", on which a summary of any structural data that might already be present is given. Up to now, there are no corresponding data present yet, so simply press "Next" to advance to the next page. Here, you have to provide the result of the indexation of the diffraction pattern, i.e. the unit cell parameters and eventually the space group. Please enter 5.6095 in the fields "a", "b" and "c" as well as 90 in the fields "alpha", "beta" and "gamma". In this example, we assume that it was not possible to determine the space group from the

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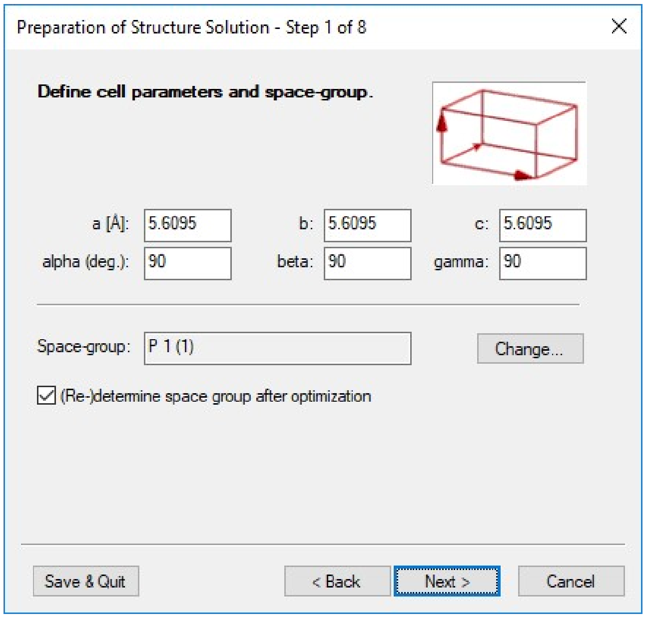
[2] You can disable the opening of the structure solution wizard at program start in the "Options" dialog which can be opened from the "Tools" menu.

[3] To open the structure solution wizard if it is not displayed automatically, select "Start Solution..." from the "Structure" menu, or press the corresponding button (the green arrow to the right) in the toolbar.

diffraction data. Hence, we will have to perform the structure solution in P1. This is the default space group, so just leave it as it is (Fig. 2).



Preparation of Structure Solution - Step 1 of 8

Define cell parameters and space-group.

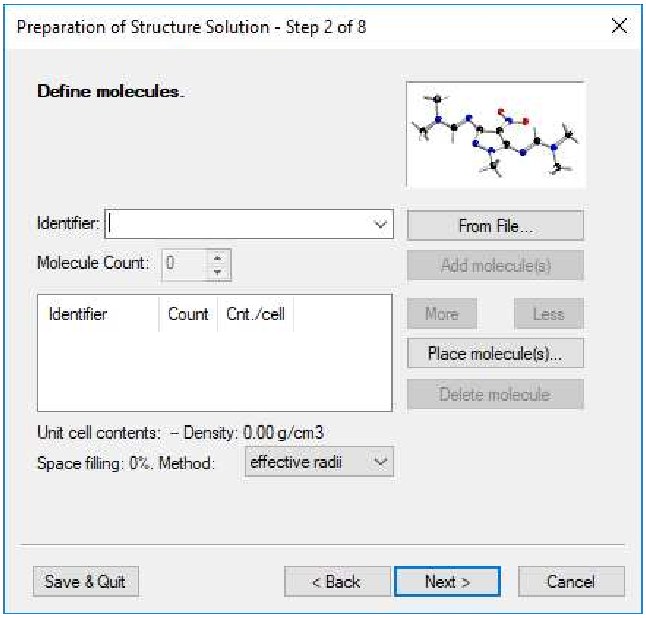
a [Å]: 5.6095 b: 5.6095 c: 5.6095
alpha (deg.): 90 beta: 90 gamma: 90

Space-group: P 1 (1)

☑ (Re-)determine space group after optimization

Fig. 2: Structure Solution Wizard p. 1: Unit cell parameters entered

Proceed to the next wizard page by clicking “Next”. Page 2 of the wizard is dedicated to the input of molecules (Fig. 3). Since you assume that your compound consists of individual atoms or ions, respectively, you can skip this page by pressing “Next” again. Page 3 of the structure solution wizard appears (Fig. 4).



Preparation of Structure Solution - Step 2 of 8

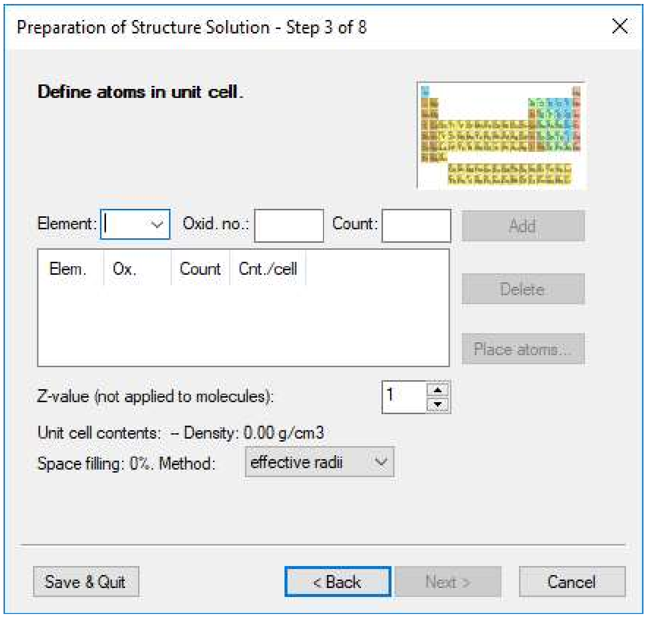
Define molecules.

Identifier:
Molecule Count: 0

Identifier	Count	Cnt./cell

Unit cell contents: -- Density: 0.00 g/cm3
Space filling: 0%. Method: effective radii

Fig. 3: Structure Solution Wizard p. 2: Declaration of molecules



Preparation of Structure Solution - Step 3 of 8

Define atoms in unit cell.

Element: Oxid. no.: Count:

Elem.	Ox.	Count	Cnt./cell

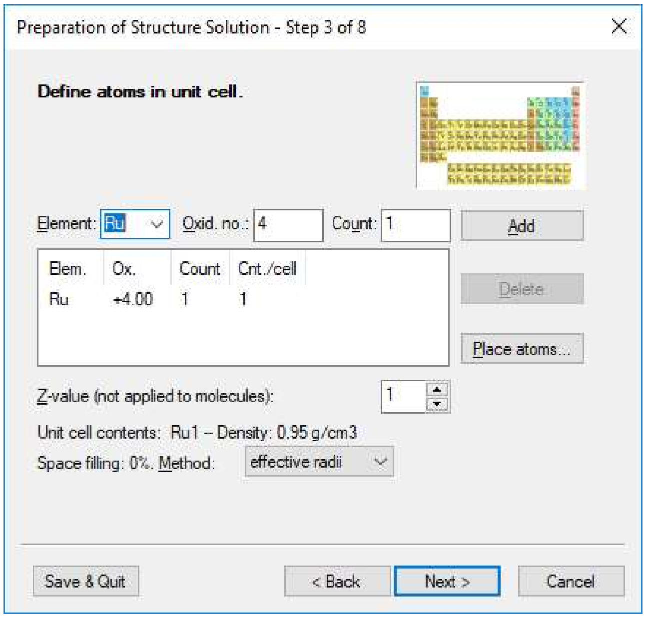
Z-value (not applied to molecules): 1

Unit cell contents: – Density: 0.00 g/cm3

Space filling: 0%. Method: effective radii

Fig. 4: Structure Solution Wizard p. 3: Definition of unit cell contents

On page 3 you have to enter the unit cell contents, i.e. the formula sum (in case of single atoms as in this example) and the number of formula units per unit cell Z. The formula sum is entered atom by atom. Since the formula of your compound is “RuS_2”, write “Ru” in the input field next to “Element:”, then press <tab> to advance to the next field “Oxid. no.:”. Assuming that RuS_2 is a compound basically consisting of ions, you give the oxidation state of Ru (4 in this case). Press <tab> again to advance to “Count:”. The composition is 1*Ru, 2*S, so please enter a 1. Afterwards, click on “Add” to add the newly created atom type to the list (Fig. 5).



Preparation of Structure Solution - Step 3 of 8

Define atoms in unit cell.

Element: Ru Oxid. no.: 4 Count: 1

Elem.	Ox.	Count	Cnt./cell
Ru	+4.00	1	1

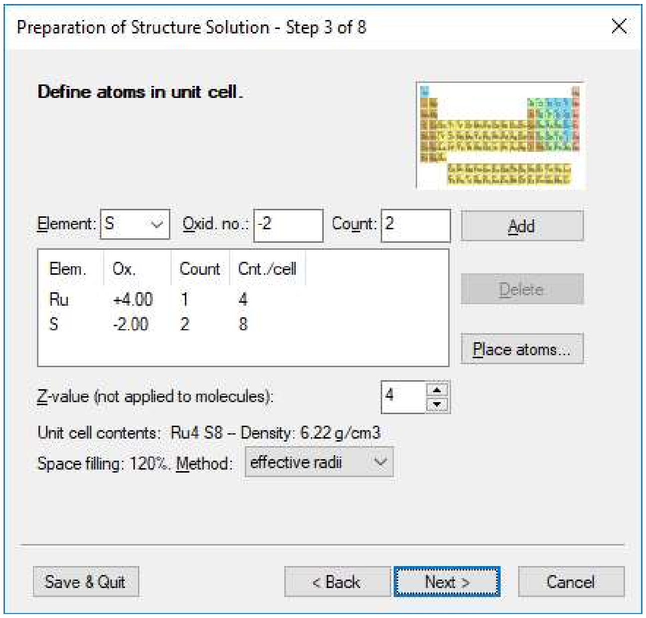
Z-value (not applied to molecules): 1

Unit cell contents: Ru1 – Density: 0.95 g/cm3

Space filling: 0%. Method: effective radii

Fig. 5: One Ru^{4+} -ion is present in the formula unit.

Now proceed by entering the data for S (S,-2,2). Finally, you have to give the number of formula units per unit cell Z. Endeavour offers a variety of options to calculate guidelines for the selection of Z, like the density or the space filling. In this first simple example, however, we simply assume the correct value of 4, so please enter this value in the appropriate field below the atom list. The wizard page should now look like Fig. 6. Please press "Next" to advance to page 4 of the wizard (Fig. 7).



Preparation of Structure Solution - Step 3 of 8

Define atoms in unit cell.

Element: S Oxid. no.: -2 Count: 2

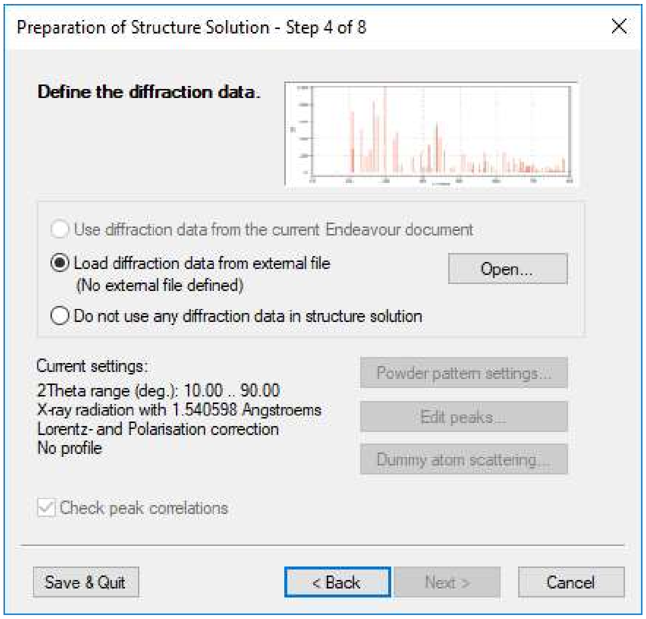
Elem.	Ox.	Count	Cnt./cell
Ru	+4.00	1	4
S	-2.00	2	8

Z-value (not applied to molecules): 4

Unit cell contents: Ru4 S8 – Density: 6.22 g/cm3

Space filling: 120%. Method: effective radii

Fig. 6: One Ru 4+ and two S 2- -ions in the formula unit; 4 formula units in the unit cell



Preparation of Structure Solution - Step 4 of 8

Define the diffraction data.

○ Use diffraction data from the current Endeavour document

● Load diffraction data from external file
(No external file defined)

○ Do not use any diffraction data in structure solution

Current settings:
2Theta range (deg.): 10.00 .. 90.00
X-ray radiation with 1.540598 Angstroems
Lorentz- and Polarisation correction
No profile

☑ Check peak correlations

Fig. 7: Wizard page 4: Diffraction pattern settings

Page 4 is dedicated to the input of the diffraction data. The first thing you now have to do is prepare the file that contains the diffraction data:

Endeavour imports the powder diffraction data as integrated intensity values at the Bragg peak positions (not the profile or step/scan data)[4]. These data are typically provided by your diffractometer software after you have performed the raw data processing. Export and reformat the corresponding file such that each line contains one peak, first the 2θ, then the intensity value.

We have prepared this file (rus2.dif[5]) in the "Examples\RuS2" directory which is present in your Endeavour program directory (e.g. "C:\Program Files\Endeavour")[6].

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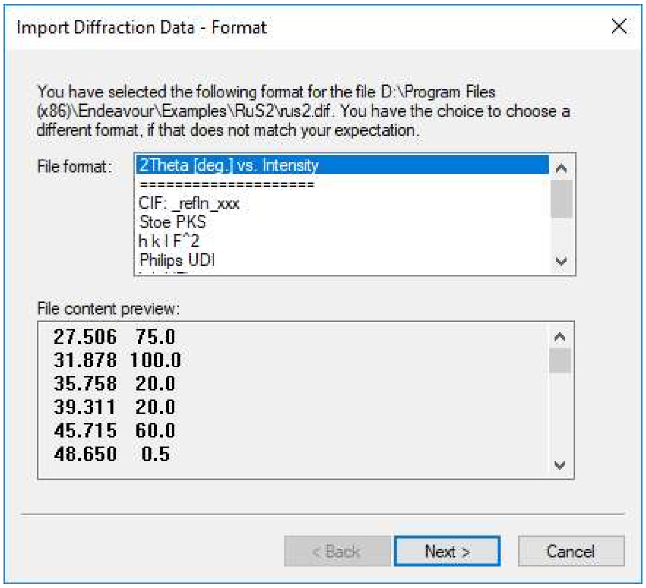
[4] You can obtain these data from raw (profile) powder diffraction data e.g. using our software package "Match!" for phase identification from powder diffraction data (https://www.crystalimpact.de/match).

[5] Sutarno et al., Can. J. Chem. **45**, 1391 (1967).

[6] If you want to have a look at the diffraction data file format, you can open the file using any conventional ASCII text editor (e.g. the Windows program "Notepad").

Now you should instruct Endeavour to open the prepared file mentioned above containing the diffraction data as a list of 2θ and corresponding intensity values: Press “Open...”. A conventional Windows file dialog box appears with the file type set to “*.dif” which is the default file extension for this kind of diffraction data representation. Select “rus2.dif” from the “Examples\RuS2” directory in your Endeavour program directory, then press “Open”.


Import Diffraction Data - Format

You have selected the following format for the file D:\Program Files (x86)\Endeavour\Examples\RuS2\rus2.dif. You have the choice to choose a different format, if that does not match your expectation.

File format: 2Theta [deg.] vs. Intensity

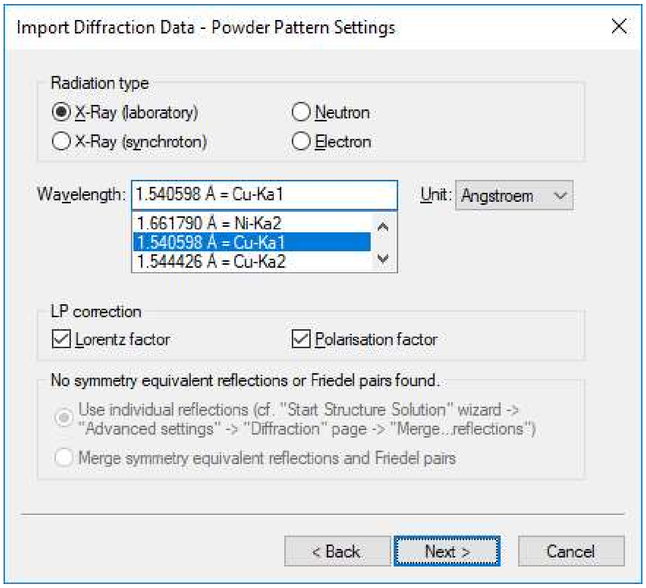
File content preview:

```
27.506  75.0
31.878 100.0
35.758  20.0
39.311  20.0
45.715  60.0
48.650   0.5
```

Fig. 8: Selection of dif-file format: Intensity vs. 2theta or d-value ?

Afterwards, a dialog box appears asking for a confirmation or more detailed specification of your diffraction data file format (Fig. 8). Please make sure that “2Theta (deg.) vs. intensity” is selected, then press the “Next” button at the bottom.

On the next page of the dialog, you have to specify the experimental conditions, especially the radiation type and the wavelength used in the diffraction experiment. Please select/mark “X-Ray (laboratory)”, wavelength “Cu Ka1” and both “Lorentz factor” and “Polarization factor” for “LP correction” (Fig. 9). Afterwards, please “Next”.


Import Diffraction Data - Powder Pattern Settings

Radiation type

● X-Ray (laboratory)　○ Neutron

○ X-Ray (synchroton)　○ Electron

Wavelength: 1.540598 Å = Cu-Ka1　Unit: Angstroem

LP correction

☑ Lorentz factor　☑ Polarisation factor

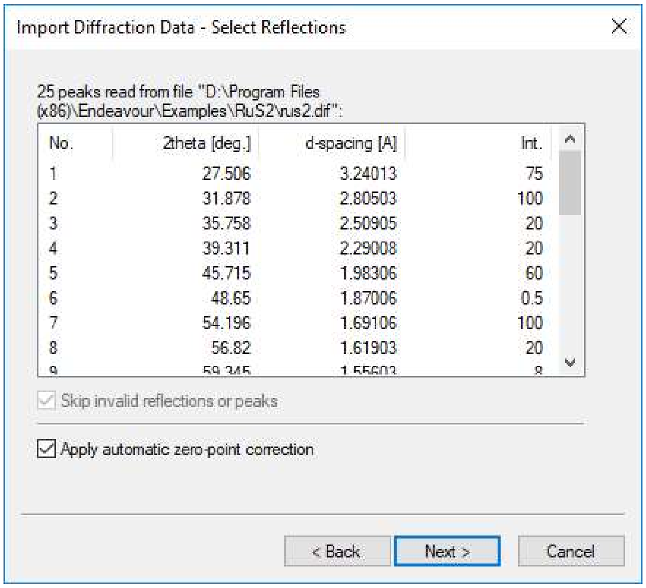
No symmetry equivalent reflections or Friedel pairs found.

○ Use individual reflections (cf. "Start Structure Solution" wizard -> "Advanced settings" -> "Diffraction" page -> "Merge...reflections")

○ Merge symmetry equivalent reflections and Friedel pairs

Fig. 9: Setting of the experimental conditions: An X-ray laboratory diffractometer has been used for collecting the data, the wavelength of the radiation was 1.540598Å (Cu Kα1), and Lorentz- and polarization correction are applied for the calculated pattern.

In the next step (Fig. 10), a list of all imported diffraction peaks will be presented (so that you can check your data), and you will have the option to let Endeavour perform an automatic check/correction of a potential shift of the zero point (2theta shift) in the diffraction pattern. Normally, you should use/activate this option (as in Fig. 10), so please click on “Next” now in order to proceed.



Import Diffraction Data - Select Reflections

25 peaks read from file "D:\Program Files (x86)\Endeavour\Examples\RuS2\rus2.dif":

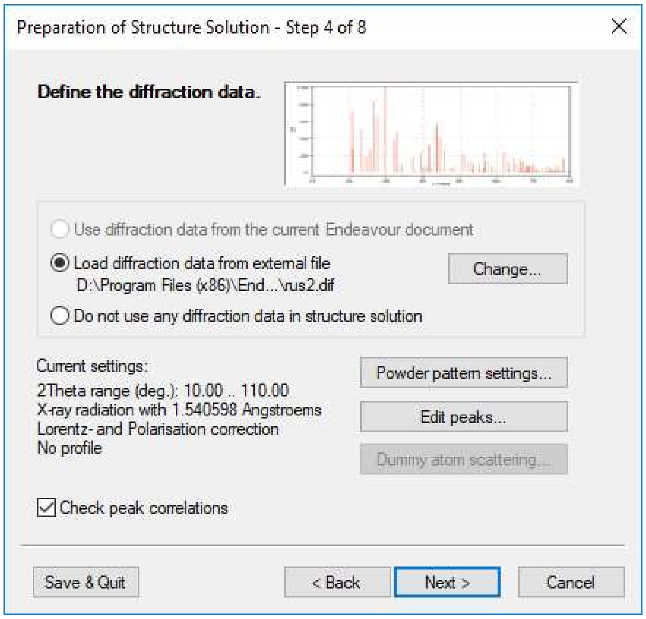
No.	2theta [deg.]	d-spacing [A]	Int.
1	27.506	3.24013	75
2	31.878	2.80503	100
3	35.758	2.50905	20
4	39.311	2.29008	20
5	45.715	1.98306	60
6	48.65	1.87006	0.5
7	54.196	1.69106	100
8	56.82	1.61903	20
9	59.345	1.55603	8

☑ Skip invalid reflections or peaks

☑ Apply automatic zero-point correction

Fig. 10: A list of all diffraction peak data that were imported from the selected file is displayed, along with the option to run an automatic correction of the zero shift.

You will be informed about the result of the zero point correction; afterwards, please press “Finish” to return to the 4th wizard page; the file name you just selected appears in the line after “Load diffraction data from external file” (Fig. 11).



Preparation of Structure Solution - Step 4 of 8

Define the diffraction data.

○ Use diffraction data from the current Endeavour document

● Load diffraction data from external file
D:\Program Files (x86)\End...\rus2.dif

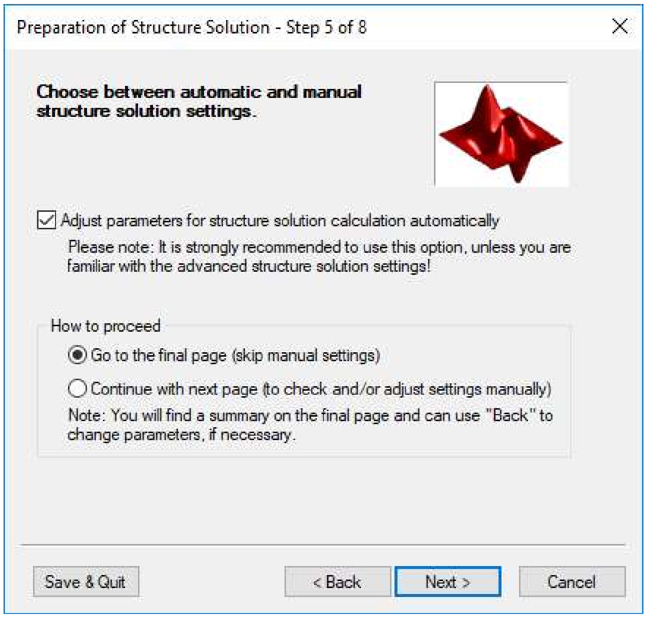
○ Do not use any diffraction data in structure solution

Current settings:
2Theta range (deg.): 10.00 .. 110.00
X-ray radiation with 1.540598 Angstroems
Lorentz- and Polarisation correction
No profile

☑ Check peak correlations

Fig. 11: The file containing the diffraction pattern has been selected.

This wizard page also offers a variety of options to enter additional information concerning your diffraction data, however, don't care about them at the moment; just press “Next” at the bottom of the wizard to proceed to step 5 (Fig. 12).



Preparation of Structure Solution - Step 5 of 8

Choose between automatic and manual structure solution settings.

☑ Adjust parameters for structure solution calculation automatically

Please note: It is strongly recommended to use this option, unless you are familiar with the advanced structure solution settings!

How to proceed

● Go to the final page (skip manual settings)

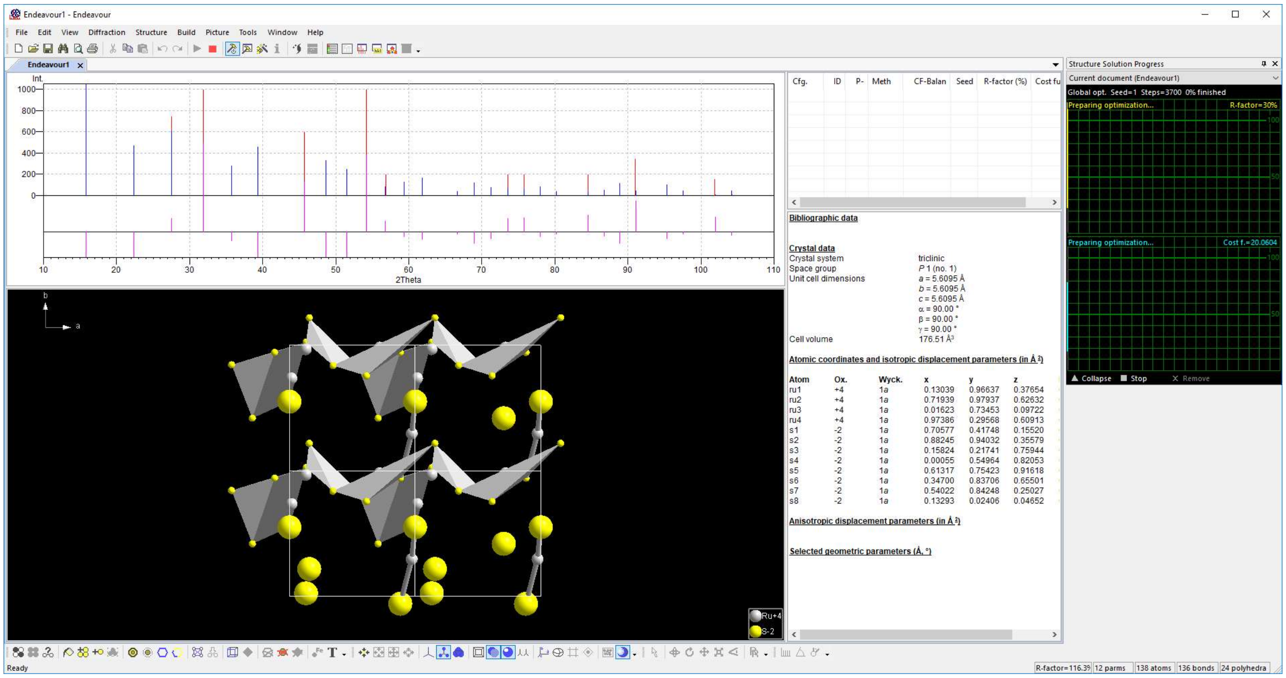
○ Continue with next page (to check and/or adjust settings manually)

Note: You will find a summary on the final page and can use "Back" to change parameters, if necessary.

Fig. 12: Wizard page 5: Shall Endeavour adjust all structure solution calculation parameters automatically?

Here, you can select if you would like Endeavour to adjust all structure solution calculation parameters automatically (which is the default), or if you would like to do so on your own. Besides this, you can instruct the structure solution wizard to skip all following pages (the ones that are dedicated to the adjustment of the calculation parameters) and directly go to the final page.

For beginners, it is recommended to leave all settings according to their default values, and to advance to the final page right away. Please compare your dialog to fig. \ref{emptywizp5}, then press "Next" to go to the final page. Here, simply press the “Start” button to finish the data input and start the calculation. The structure solution wizard vanishes, and the “structure solution progress viewer” is displayed on the right-hand side of the window. The screen should look similar to Fig. 13.



Global opt. Seed=1 Steps=3700 0% finished

Preparing optimization... R-factor=30%

Preparing optimization... Cost f.=20.0604

Bibliographic data

Crystal data

Crystal system	triclinic
Space group	*P* 1 (no. 1)
Unit cell dimensions	*a* = 5.6095 Å *b* = 5.6095 Å *c* = 5.6095 Å α = 90.00 ° β = 90.00 ° γ = 90.00 °
Cell volume	176.51 Å³

Atomic coordinates and isotropic displacement parameters (in Å²)

Atom	Ox.	Wyck.	x	y	z
ru1	+4	1*a*	0.13039	0.96637	0.37654
ru2	+4	1*a*	0.71939	0.97937	0.62632
ru3	+4	1*a*	0.01623	0.73453	0.09722
ru4	+4	1*a*	0.97386	0.29568	0.60913
s1	-2	1*a*	0.70577	0.41748	0.15520
s2	-2	1*a*	0.88245	0.94032	0.35579
s3	-2	1*a*	0.15824	0.21741	0.75944
s4	-2	1*a*	0.00055	0.54964	0.82053
s5	-2	1*a*	0.61317	0.75423	0.91618
s6	-2	1*a*	0.34700	0.83706	0.65501
s7	-2	1*a*	0.54022	0.84248	0.25027
s8	-2	1*a*	0.13293	0.02406	0.04652

Anisotropic displacement parameters (in Å²)

Selected geometric parameters (Å, °)

R-factor=116.39 | 12 parms | 138 atoms | 136 bonds | 24 polyhedra

Fig. 13: The structure solution calculation for RuS_2 has just been started.

The overall calculation will take approx. 5 minutes, so you now have a little bit of time to examine the layout of the Endeavour window:

As you see, it is by default divided into five parts (so-called “panes”): In the upper left area, the powder pattern is shown. The current crystal structure is displayed in the lower left area. In the column to its right, the so-called “configuration list”[7] is displayed in the upper area, while in the lower pane textual output in various forms can be displayed (default is the data sheet, giving the current crystal structure data).

The textual pane on the right-hand side has the so-called “configuration list” (the list of calculation results) at the top. Below, it can have the peak list, the results report, the data sheet of the compound or several tables for atomic parameters, the atoms of the structure picture, distances and/or angles etc. Panes are divided by so-called “splitters”, which can be shifted by dragging with the mouse, e.g. like the splitter between the tree view (left part) and the list view in the Windows Explorer. You can activate a pane by clicking into it with the mouse or by using the hotkey F6 which is common to Windows application using different panes.

The configuration list is the central part in Endeavour. It provides an overview over the structural models that are available in the current document. In many cases, these structural models are the result of structure solution calculations with different seed-values, but they may also result from local optimizations (“refinements”), “find symmetry” operations etc. You can switch between these structural models by clicking on the corresponding line in the configuration list, whereupon the structure picture, diffraction pattern and the remaining panes will be updated accordingly.

In the right-most column, the progress of the current calculation is monitored. Both the R-factor as well as the overall cost function are drawn graphically as a function of the calculation progress. Once you got used to it, you will find this pretty handy in order to estimate the success probability of the current calculation, as well as to “design” the hypersurface of the cost function (e.g. by adapting the cost function balance parameter).

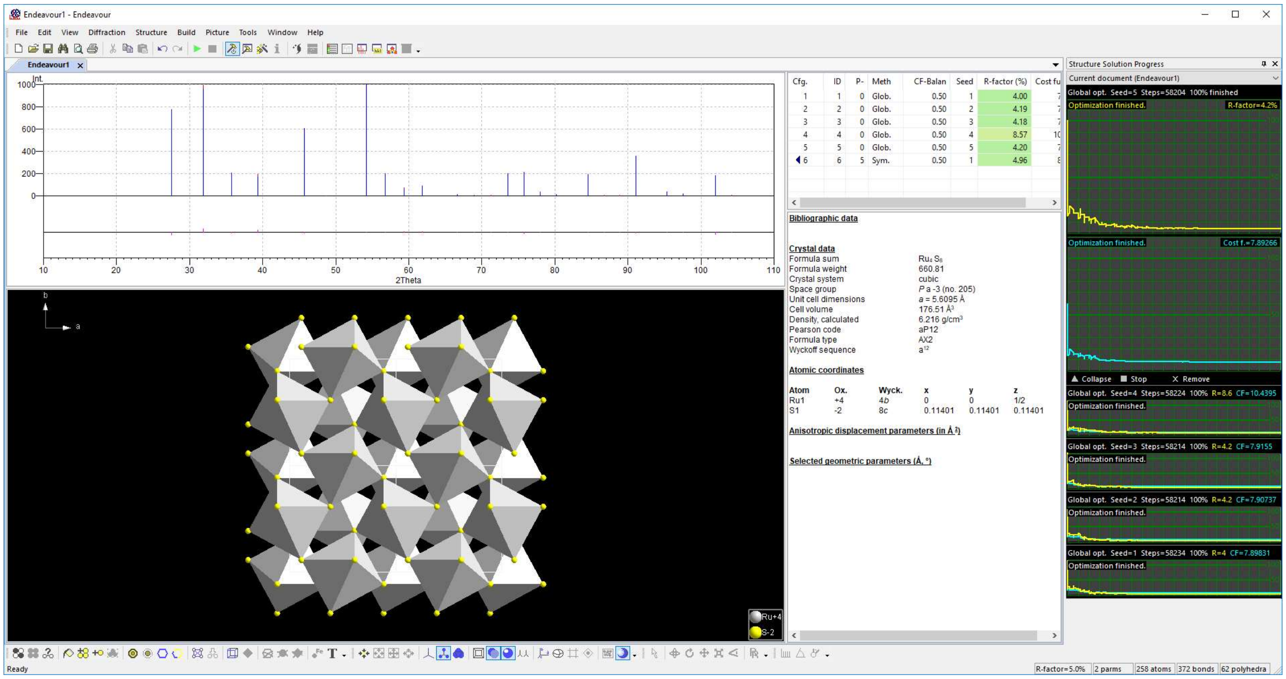
Sit back, relax and watch the atoms move around in the unit cell while the program tries to find the global optimum of the cost function. If you look carefully you can see that the Ru-atoms reach their final cubic arrangement way before the S-atoms due to their larger number of electrons and hence their larger X-ray scattering power. In the progress viewer on the right-hand side you can watch the R-factor decrease and finally reach a limit of around 4.2\% at the end of most calculations.

You will also note that Endeavour does not only perform a single but rather five calculations, each of them starting with different random initial atom positions. This is due to the global optimization method applied by Endeavour, which is called “simulated annealing”. In practice, the result obtained by this optimization method depends on the random number sequence applied, so Endeavour by default performs five different calculations with different initial starting values of the random number simulator (also called “seed”).

When the five calculations have been finished, Endeavour will automatically select the resulting structure with the lowest cost function value. For this structure, it will then try to determine the space group automatically. If this is successful (as in our example), it will create a new corresponding line/structure in the configuration list, select it, and finally display the resulting crystal structure data in the so-called “data sheet” in the textual pane on the right-hand side (Fig. 14).

---

[7] The configuration list provides an overview over all structural data sets of the current document. Each line in the configuration list represents the result of one structure solution calculation. The corresponding structure, diffraction pattern etc. can be displayed simply by clicking on the corresponding line.



Cfg.	ID	P-	Meth	CF-Balan	Seed	R-factor (%)	Cost fu
1	1	0	Glob.	0.50	1	4.00	7
2	2	0	Glob.	0.50	2	4.19	7
3	3	0	Glob.	0.50	3	4.18	7
4	4	0	Glob.	0.50	4	8.57	10
5	5	0	Glob.	0.50	5	4.20	7
◀ 6	6	5	Sym.	0.50	1	4.96	8

Bibliographic data

Crystal data

Formula sum	$Ru_4 S_8$
Formula weight	660.81
Crystal system	cubic
Space group	*P* a -3 (no. 205)
Unit cell dimensions	*a* = 5.6095 Å
Cell volume	176.51 Å^3
Density, calculated	6.216 g/cm^3
Pearson code	aP12
Formula type	AX2
Wyckoff sequence	a^{12}

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Ru1	+4	4*b*	0	0	1/2
S1	-2	8*c*	0.11401	0.11401	0.11401

Anisotropic displacement parameters (in Å^2)

Selected geometric parameters (Å, °)

Global opt. Seed=5 Steps=58204 100% finished
Optimization finished. R-factor=4.2%
Optimization finished. Cost f.=7.89266
Global opt. Seed=4 Steps=58224 100% R=8.6 CF=10.4395
Optimization finished.
Global opt. Seed=3 Steps=58214 100% R=4.2 CF=7.9155
Optimization finished.
Global opt. Seed=2 Steps=58214 100% R=4.2 CF=7.90737
Optimization finished.
Global opt. Seed=1 Steps=58234 100% R=4 CF=7.89831
Optimization finished.

R-factor=5.0% | 2 parms | 258 atoms | 372 bonds | 62 polyhedra

Fig. 14: The crystal structure of RuS_2 has been solved.

At this stage, the structure solution is complete; all crystal structure data necessary for the Rietveld refinement have been determined. You may now export your crystal structure data (or the structure picture) in a variety of common formats (e.g. CIF, BMP), by selecting the “Save as...” command from the “File” menu. In addition, you might also want to save or print the data sheet, by right-clicking into the data sheet on the right-hand side and selecting the corresponding command from the context menu which opens.

Before you finish the “Quick start”, please note:

The example you have just processed (like most of the remaining examples) is rather artificial, and certainly most “real world’s” structure solution tasks are not so easy to solve. Please take a look at the chapter “Structure solution in practice” (p. 20) in order to get an impression how a structure solution using Endeavour normally works in practice.

Endeavour in detail

Now that you have solved your first crystal structure using Endeavour and have seen how it works, you might be eager to learn a bit more about the task, the method and the program itself.

Some basics on structure solution from powder diffraction data

In the past, the atomic structure of crystalline solids was typically determined using single crystal X-ray diffraction: A single crystal measuring about 0.1 mm in diameter is mounted on a machine called “four circle diffractometer” which determines the diffracted intensity for each single reflection I(hkl). Nevertheless, though a large amount of data is collected this way, it is not possible to calculate the atomic arrangement directly. The problem is that the measured intensity is proportional only to the square of the structure factor F^2(hkl), hence it remains unknown whether F(hkl) is positive or negative.

This so-called “phase problem” prohibits any analytical calculation of the direct space atomic positions from the reciprocal space I(hkl) data. Nevertheless, it may be overcome by numerical methods, e.g. by so-called “Direct Methods”. The application of these methods to single crystal diffraction data is quite routine nowadays, so that structure solution from single crystals generally does not pose serious problems anymore.

However, the matter is completely different if no single crystals may be obtained for the compound under investigation, so that the crystal structure has to be determined from a microcrystalline powder. Here, the X-ray (or neutron) beam is diffracted by a large amount of randomly orientated microcrystals at the same time. Hence, instead of single reflections the well-known Debye-Scherrer-rings are observed, or in other words: The originally three-dimensional diffraction information is projected into just one dimension (at least on the macroscopic level). It is evident that this projection may lead to some sort of loss of information.

Today, the powder diffraction data are generally not used in this Debye-Scherrer ring form but as a sort of cross section through these rings. This leads to a intensity (I) versus diffraction angle 2θ (or Miller plane distance d) plot called “powder diffraction pattern”.

The loss of information mentioned above becomes evident if two or more reflections (hkl) have the same or at least nearly the same d-spacing of the corresponding Miller planes, due to symmetry or even by accident. Thus, the intensities belonging to these reflections appear at the same position (2θ or d) in the diffraction pattern, so that only the sum of the intensities may be observed. Hence, it may be very difficult to determine the intensities of these so-called “overlapping” reflections with sufficient accuracy to apply conventional direct methods which are based on the knowledge of I(hkl).

In the chapter “Scientific Background” on page 72, a method developed since appr. the 1990’s is described which is called “direct-space method”. This method avoids the often-ambiguous extraction of intensities I(hkl) by proposing a structural model without using the diffraction data. Endeavour implements an improved version of this method to solve crystal structures ab initio from powder diffraction data. If you are interested in any more details, you should read chapter on p. 72 and/or the corresponding article[1] in the literature.

We now will have a closer look at the way crystal structures are determined from powder diffraction data, with special emphasis on the usage of Endeavour.

General workflow

Starting with the **raw (profile) diffraction data** as it has been obtained from the diffractometer, the first task is to locate the peaks and to extract their intensities and maybe FWHM[8] values as a function of the diffraction angle 2θ (the so-called “peak list”). Besides this, the zero-point correction may be calculated from the peak positions. These tasks are called “**raw data processing**”.

---

[8] FWHM means “**F**ull **W**idth at **H**alf **M**aximum” of the peaks.

Afterwards, you should identify all known phases that may be present in the sample and eliminate the corresponding peaks from the peak list. The result is a peak list file ("dif-file") which contains the peak list as 2θ versus intensity[9].

Afterwards, this peak list is submitted to an indexing program (e.g. Treor[10] or Dicvol[11] to obtain the unit cell parameters. The number of formula units per unit cell is then calculated from measured density (or atom size and space filling) considerations. All these tasks (starting with raw data processing) can be performed using our software package "Match!"[12], for example.

Another important piece of information is the composition of the compound for which the crystal structure shall be determined, and (if possible) its density. These data must be obtained separately, e.g. by X-ray fluorescence spectroscopy (XRF) and/or chemical analysis.

Once you have collected the required data (peak data, unit cell parameters, space group (if available), composition and maybe density) you can run Endeavour[13].

Typically, not only one but a multitude of structure solution calculations is performed based on these data. This is especially true if more than a single unit cell and/or space group are considered. The actual structure solution (optimization) calculations may take between a few seconds for simple small structures like rutile to a couple of days or even weeks for larger and more complex problems.

Once a reasonable structural model has been found, the symmetries and the space group of the output structural model can be determined (or verified) in Endeavour, using the programs SFND[Fehler! Textmarke nicht definiert.] and RGS[Fehler! Textmarke nicht definiert.]. Finally, once the calculations have finished and a promising structural model has been found, you can export the resulting crystal structure from Endeavour to a cif-file.

The crystal structure has been solved at this point (a suitable model has been obtained). However, even though the solution from an Endeavour calculation may look promising, chemically reasonable and "correct", it is nevertheless absolutely necessary to perform a subsequent Rietveld refinement, in order to finish the crystal structure determination. The final proof that a structure solution is correct is the convergence of a Rietveld refinement at low R-factors, starting from the structural model resulting from the Endeavour calculation[14].

Our experience has shown, that certain basic requirements must be fulfilled for a successive application of Endeavour:

- The quality of the powder pattern has to be high enough so that enough accurate peak positions are available to allow a reliable indexation resulting in the correct unit cell.

- The peaks should not be too broad, in order to allow the extraction of fairly accurate intensities at the peak positions.

- The contents of the unit cell should be known accurately.

- The approximate description of the structure of the compound under investigation must be possible using a simple empirically parametrized potential, i.e. the desired structure should exhibit a low potential energy, preferably constituting a deep minimum of the energy landscape.

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[9] In some rare cases it may be necessary to smooth the data (to reduce the "noise") and subtract the background before determining the peak data.

[10] P.E. Werner, L. Eriksson, M. Westdahl, J. Appl. Cryst. **18**, 367 (1985).

[11] A. Boultif, D. Louër, J. Appl. Cryst. **24**, 987 (1991).

[12] Match! - Phase Identification from Powder Diffraction, Crystal Impact - Dr. H. Putz & Dr. K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany, https://www.crystalimpact.de/match

[13] If you have used Match! for the raw data processing, you can forward the diffraction data to Endeavour and run it from within Match!.

[14] Again, if you are using Match!, you can re-import this cif-file into a so-called "manual entry" and run Rietveld refinement (using FullProf[14]) from within Match!.

Structure solution in practice

Most tutorial examples in this manual (p. 21) seem to work straight away and look pretty easy. However, please understand that this is not the normal situation in the daily work with Endeavour: The tutorial examples have been basically selected to demonstrate certain functions and procedures and are no "real world" structure solutions tasks (at least not nowadays).

Hence, we feel it could be helpful to provide you with some information how solving a crystal structure with Endeavour works and feels like in practice:

The typical starting point is one (or even more) powder diffraction patterns of a compound that you assume to consist only of a single phase. Many of our customers use Match! to process these raw diffraction data (e.g. extract the peak data, 2θ and intensity values), check for additional phases etc. Afterwards, Treor and/or Dicvol are used (probably also from within Match!) to determine one (sometimes more) promising unit cell parameter sets and maybe also space group suggestion(s).

Another important piece of information for a successful crystal structure solution using "direct-space" programs like Endeavour is the composition (i.e. formula sum) of the compound under investigation. Typically, it is obtained from X-ray fluorescence spectroscopy (XRF), chemical analysis or similar. In addition, it is rather helpful to determine the bulk density of the compound (if possible), in order to learn about the number of formula units in the unit cell (Z) and hence to define the unit cell contents (elements and their counts in the unit cell).

Starting from this basic information (diffraction pattern peak list, unit cell parameter set(s), space group suggestion(s) and composition), most "real world" crystal structure solutions work step-wise: In the beginning, you run structure solution calculations without any knowledge of the structure, just trying to verify unit cell parameters, space group and (arbitrary) composition. After some (maybe dozen) calculations you realize that some combinations of unit cell parameters, space group and composition give lower R-factors and look more reasonable (at least in parts) from a chemical/physical point of view than others.

Focusing on these combinations one looks for certain structural motives that are observed in a similar manner in different calculations. For example, it happens quite often that "heavy" atoms (elements with large number of electrons) are observed close to certain positions in the unit cell, while the rest of the structure still seems to be unclear.

In these cases, the next step is to set (and fix) these atoms at the corresponding positions right from the beginning of the calculations, so that they can serve as anchor points around which the rest of the structure is build. Sometimes not only atoms, but whole building blocks (molecules, e.g. SiO_4 tetrahedra) can be placed, so that the remaining part of the structure that still needs to be determined is getting smaller.

It is quite normal that each of these steps takes several days or even weeks. In addition, it happens rather frequently that "arbitrary" solutions are obtained that do not provide the complete structure in a single model. In these cases, we have made good experiences with collecting these solutions in a single document of "Diamond", our software for crystal and molecular structure visualization[15]. Diamond can read the currently selected structure from an Endeavour document file; you can then copy these structures (along with their structure pictures) into a single document. Reviewing these collections can be quite helpful in developing an idea of how the structure may look like, and which kind of work may still be required for the solution of the structure.

Solving crystal structures from powder using the "direct space method" (like in Endeavour) typically takes a lot of computer time. The structure solution calculations demonstrated in this "Structure solution tutorial" (p. 21) are rather simple examples that are solved relatively fast. Normal structure solutions using Endeavour typically take several hours or even days. Don't be afraid, no user interaction is required during the calculations, so you can run your calculations at night or during the weekend. Once you are used to it, you will enjoy entering your office on Monday and have a look at the screen to check if the structure has been solved during the weekend.

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[15] Diamond - Crystal and Molecular Structure Visualization, Crystal Impact - H. Putz & K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany, https://www.crystalimpact.de/diamond

Structure solution tutorial

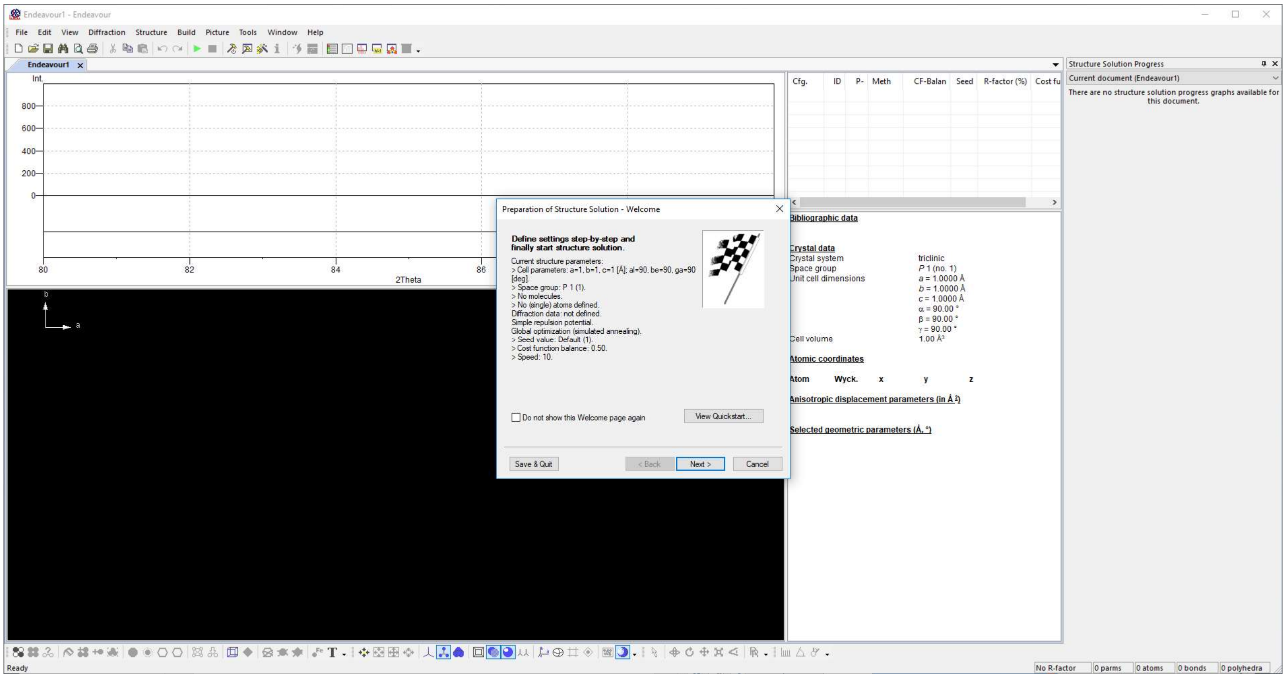
Solving your first real crystal structure ($BaMoCl_6$)

In this session you will learn:
- How to use space group information.
- How to solve the problem of assigning peaks to calculated positions.

We would like to begin our series of tutorial sessions with a relatively simple but nevertheless real case example: Solve the crystal structure[16] of $BaMoCl_6$. The data required for structure solution are:

- unit cell parameters: a=9.7132 Å, b=8.6483 Å, c=10.564 Å, β=92.19°
- space group[17]: C 1 2/c 1
- composition (elements and numbers of atoms in the unit cell): $BaMoCl_6$, Z=4
- powder diffraction pattern (peak list): given in file “BaMoCl6.dif”

Please start Endeavour by double-clicking on the corresponding icon on your desktop, or by selecting “Endeavour” from the “Start-Programs-Endeavour” Windows menu. After a few seconds, Endeavour’s main window will appear, and the so-called “structure solution wizard” will be displayed[18] (Fig. 15). This wizard[19] step-by-step asks for all data required for the structure solution.



There are no structure solution progress graphs available for this document.

Preparation of Structure Solution - Welcome

Define settings step-by-step and finally start structure solution.

Current structure parameters:
> Cell parameters: a=1, b=1, c=1 [Å]; al=90, be=90, ga=90 [deg].
> Space group: P 1 (1).
> No molecules.
> No (single) atoms defined.
Diffraction data: not defined.
Simple repulsion potential.
Global optimization (simulated annealing).
> Seed value: Default (1).
> Cost function balance: 0.50.
> Speed: 10.

☐ Do not show this Welcome page again

Bibliographic data

Crystal data

Crystal system	triclinic
Space group	*P* 1 (no. 1)
Unit cell dimensions	*a* = 1.0000 Å *b* = 1.0000 Å *c* = 1.0000 Å α = 90.00 ° β = 90.00 ° γ = 90.00 °
Cell volume	1.00 Å³

Atomic coordinates

Atom	Wyck.	x	y	z

Anisotropic displacement parameters (in Å²)

Selected geometric parameters (Å, °)

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[16] U. Keßler, University of Bonn, private communication, Bonn 2008.

[17] If you are not sure about the space group, it is also perfectly possible to use a common subgroup of all possible space groups (or even P1), and determine the correct space group from the structural model later on (menu ”Structure/Find symmetry…”).

[18] You can disable the opening of the structure solution wizard at program start in the “Options” dialog which can be opened from the “Tools” menu.

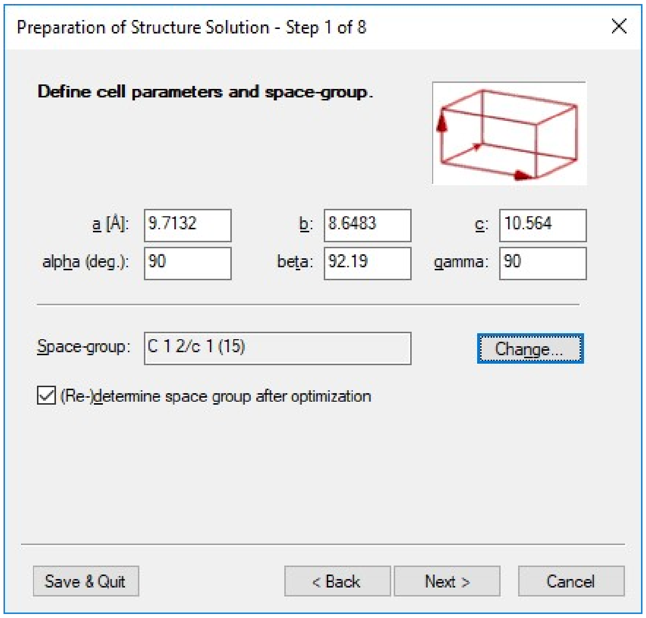
[19] To open the structure solution wizard if it is not displayed automatically, select “Start Solution…” from the “Structure” menu, or press the corresponding button ▶ in the toolbar.

Fig. 15: By default, Endeavour displays the “Structure Solution Wizard” after it has been started, so that you can start entering your data right away

The first page of the structure solution wizard provides an overview over the current crystal structure data. If no data are present yet (as in this example), the corresponding default values are displayed. Similar to the “Quick start”, simply skip this page by pressing “Next”.

Now you have to provide the unit cell parameters (i.e. the result of the indexing[20] of the powder diffraction pattern) and eventually the space group. Please enter **9.7132** in the field “a”, **8.6483** in the field “b”, **10.564** for “c”, and finally **92.19** for “beta”.

Afterwards, you can provide the space group (if known/available as in this example): Please click “Change...” to open the space group selection box. Enter the Hermann-Mauguin-symbol “C12/c1” in the upper left field, or scroll down the list and select space group no. 15. Finally, press “OK”. The dialog should now look like Fig. 16.



Preparation of Structure Solution - Step 1 of 8

Define cell parameters and space-group.

a [Å]: 9.7132
b: 8.6483
c: 10.564
alpha (deg.): 90
beta: 92.19
gamma: 90

Space-group: C 1 2/c 1 (15)

☑ (Re-)determine space group after optimization

Fig. 16: Structure solution wizard p. 1: Unit cell parameters and space group have been entered.

Proceed to the next wizard page by clicking “Next”. Page 2 of the wizard is dedicated to the input of molecules (Fig. 17). Although it would be possible to use $MoCl_6$- octahedra as rigid bodies (“molecules”) with regard to the formula sum, you decide to use individual atoms at this stage, in order to keep the structure solution process more flexible. Hence, you can skip this page by pressing “Next” again. Page 3 of the structure solution wizard appears (Fig. 18).

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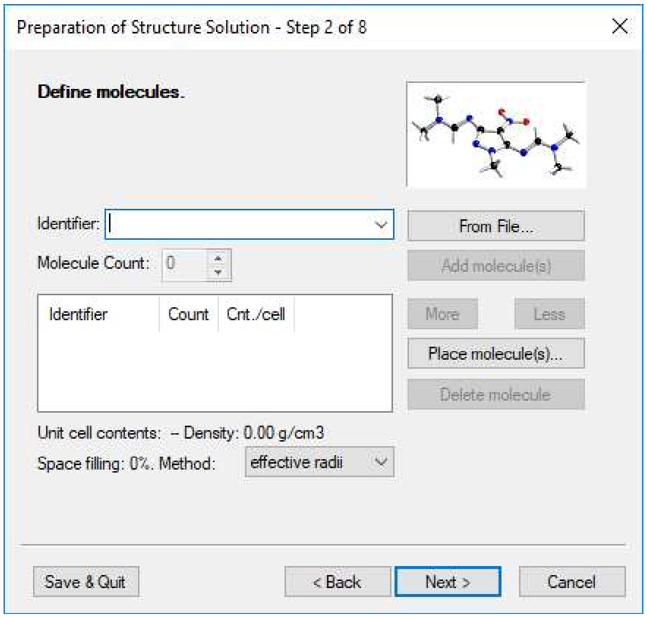
[20] Endeavour does not provide any means for the indexing of diffraction patterns. For this task, you can e.g. use our software package “Match!” (https://www.crystalimpact.de/match) in combination with the well-known “Treor” and “Dicvol” programs.



Preparation of Structure Solution - Step 2 of 8

Define molecules.

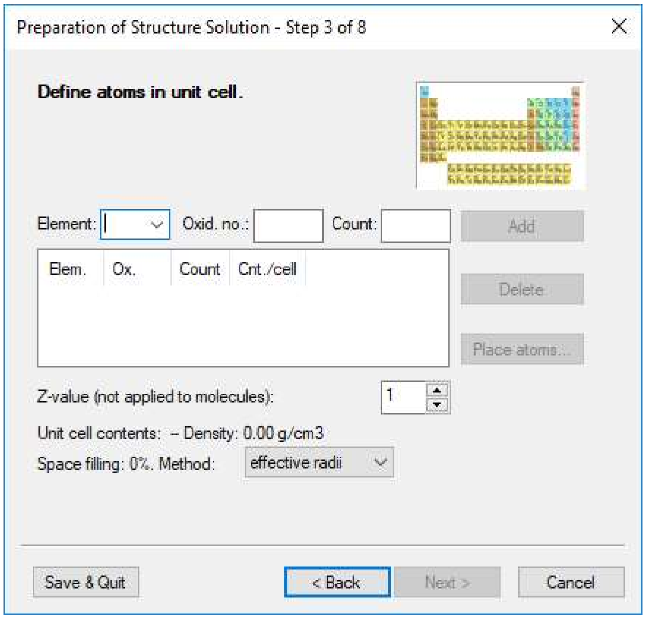
Identifier:

Molecule Count: 0

Unit cell contents: – Density: 0.00 g/cm3

Space filling: 0%. Method: effective radii

Fig. 17: Structure solution wizard p. 2: Declaration of molecules (not used in this session)



Preparation of Structure Solution - Step 3 of 8

Define atoms in unit cell.

Element:

Oxid. no.:

Count:

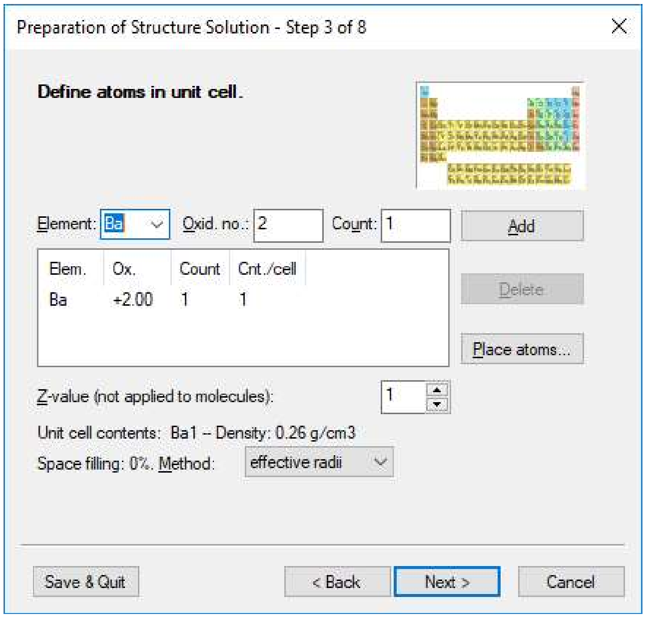
Z-value (not applied to molecules): 1

Unit cell contents: – Density: 0.00 g/cm3

Space filling: 0%. Method: effective radii

Fig. 18: Structure solution wizard p. 3: Definition of unit cell contents

On page 3 you have to enter the single atoms in the unit cell, and the number of formula units per unit cell Z . The formula sum is entered atom by atom. Since the formula of your compound is “$BaMoCl_6$”, write “Ba” in the input field next to “Element:”, then press <tab> to advance to the next field “Oxid. no.:”. Assuming that $BaMoCl_6$ is a compound basically consisting of ions, you give the oxidation state of Ba (2 in this case). Press <tab> again to advance to “Count:”. The composition is 1*Ba, 1*Mo, 6*Cl, so please enter a 1. Afterwards, click on “Add” to add the newly created atom type to the list (Fig. 19).



Preparation of Structure Solution - Step 3 of 8

Define atoms in unit cell.

Element: Ba Oxid. no.: 2 Count: 1

Elem.	Ox.	Count	Cnt./cell
Ba	+2.00	1	1

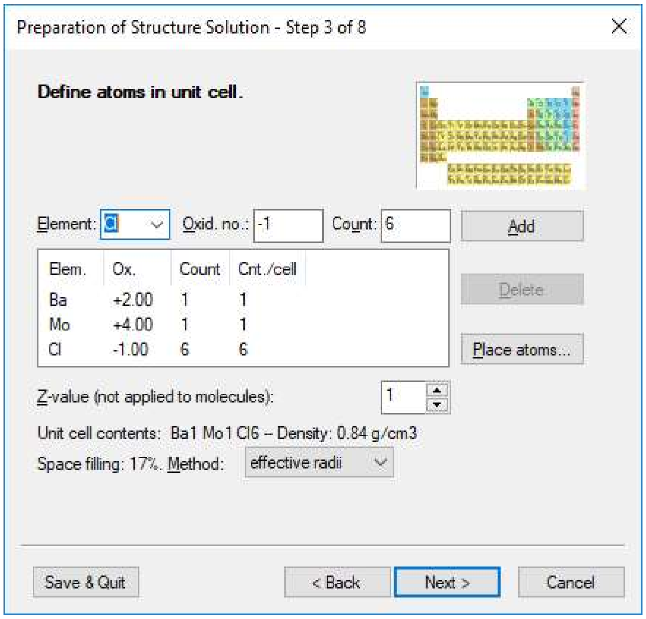
Z-value (not applied to molecules): 1

Unit cell contents: Ba1 -- Density: 0.26 g/cm3

Space filling: 0%. Method: effective radii

Fig. 19: One Ba^{2+} -ion is present in the formula unit

Now proceed by entering the data for Mo (Mo,4,1) and Cl (Cl,-1,6) in a similar manner. Finally, you have to give the number of formula units per unit cell Z. Endeavour offers a variety of aids to estimate this value, however, in this example we simply assume the correct value of 4, so please enter this value in the appropriate field below the atom list. The wizard page should now look as Fig. 20. Please press "Next" to advance to page 4 of the wizard (Fig. 21).



Preparation of Structure Solution - Step 3 of 8

Define atoms in unit cell.

Element: Cl Oxid. no.: -1 Count: 6

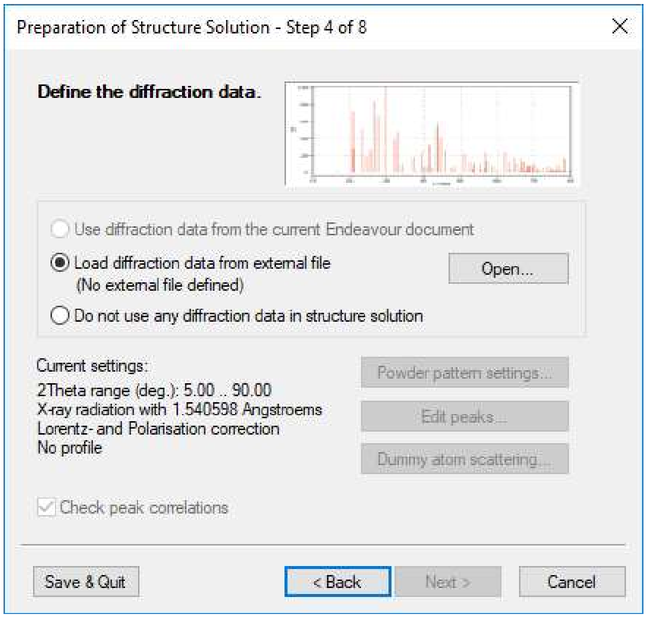
Elem.	Ox.	Count	Cnt./cell
Ba	+2.00	1	1
Mo	+4.00	1	1
Cl	-1.00	6	6

Z-value (not applied to molecules): 1

Unit cell contents: Ba1 Mo1 Cl6 -- Density: 0.84 g/cm3

Space filling: 17%. Method: effective radii

Fig. 20: One Ba 2+, one Mo 4+ and six Cl 1- -ions in the formula unit; 4 formula units in the unit cell



Preparation of Structure Solution - Step 4 of 8

Define the diffraction data.

○ Use diffraction data from the current Endeavour document

● Load diffraction data from external file
(No external file defined)

○ Do not use any diffraction data in structure solution

Current settings:
2Theta range (deg.): 5.00 .. 90.00
X-ray radiation with 1.540598 Angstroems
Lorentz- and Polarisation correction
No profile

☑ Check peak correlations

Fig. 21: Wizard page 4: Diffraction pattern settings

Page 4 is dedicated to the input of the diffraction data, so the next thing you have to do is prepare the file that contains the diffraction data: Endeavour imports the integrated intensity values at the Bragg peak positions. If you have profile or step/scan data, you first have to process these raw data, in order to obtain the peak list data required by Endeavour. You can e.g. use our Match! software (https://www.crystalimpact.de/match) or any other suitable software package (e.g. your diffractometer software) for this purpose. Export and reformat the corresponding peak list file such that each line contains one peak, first the 2θ, then the intensity value.

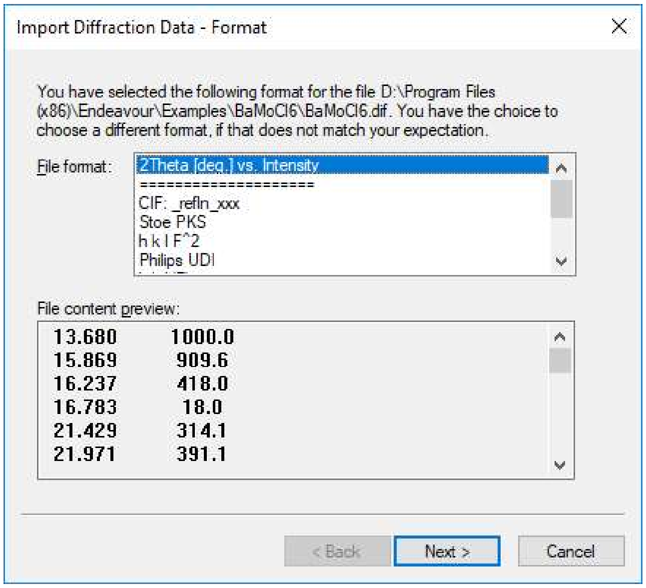
We have already prepared this file (BaMoCl6.dif) in the "Examples\BaMoCl6" directory which is present in your Endeavour program directory (e.g. "C:\Program Files\Endeavour")[21].

Please open the prepared file mentioned above containing the diffraction data as a list of 2θ and corresponding intensity values: Press "Open...". A conventional Windows file dialog box appears with the file type set to "*.dif" which is the default file extension for this kind of diffraction data representation. Select "BaMoCl6.dif" from the "Examples\BaMoCl6" directory in your Endeavour program directory.

Once you have pressed the "Open" button, a new dialog appears asking for a confirmation or more detailed specification of your diffraction data file format (Fig. 22). Please make sure that "2Theta (deg.) vs. intensity" is selected, then press the "Next" button at the bottom. On the next page of the dialog, you have to specify the experimental conditions, especially the radiation type and the wavelength used in the diffraction experiment. Verify that your settings correspond to Fig. 23, then press "Next".

---

[21] If you want to have a look at the diffraction data file format, you can open the file using any conventional ASCII text editor (e.g. the Windows program "Notepad").



Import Diffraction Data - Format

You have selected the following format for the file D:\Program Files (x86)\Endeavour\Examples\BaMoCl6\BaMoCl6.dif. You have the choice to choose a different format, if that does not match your expectation.

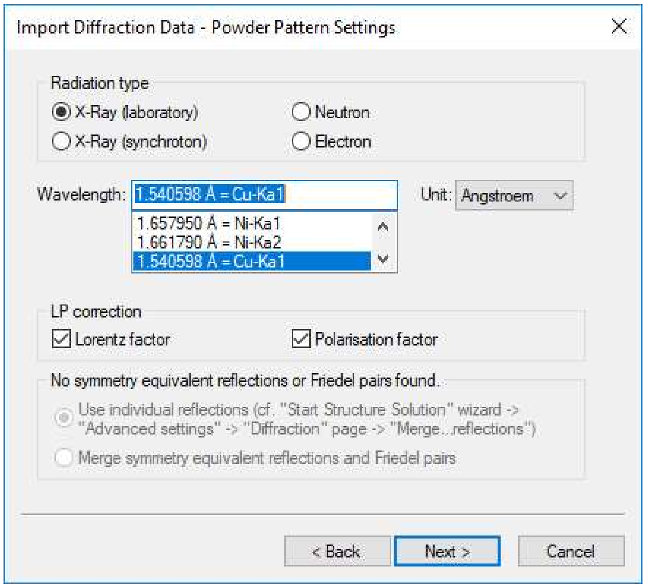
File format:

- 2Theta [deg.] vs. Intensity
- ====================
- CIF: _refln_xxx
- Stoe PKS
- h k l F^2
- Philips UDI

File content preview:

```
13.680      1000.0
15.869       909.6
16.237       418.0
16.783        18.0
21.429       314.1
21.971       391.1
```

Fig. 22: Selection of diffraction data file format



Import Diffraction Data - Powder Pattern Settings

Radiation type

● X-Ray (laboratory) ○ Neutron

○ X-Ray (synchroton) ○ Electron

Wavelength: 1.540598 Å = Cu-Ka1 Unit: Angstroem

- 1.657950 Å = Ni-Ka1
- 1.661790 Å = Ni-Ka2
- 1.540598 Å = Cu-Ka1

LP correction

☑ Lorentz factor ☑ Polarisation factor

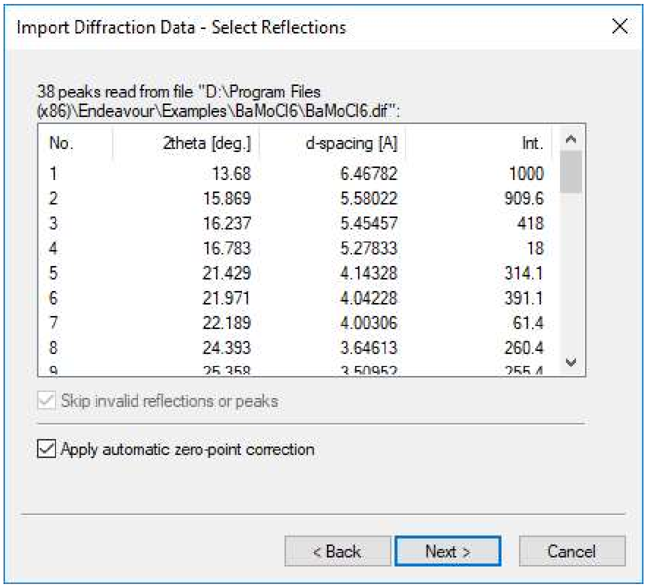
No symmetry equivalent reflections or Friedel pairs found.

○ Use individual reflections (cf. "Start Structure Solution" wizard -> "Advanced settings" -> "Diffraction" page -> "Merge...reflections")

○ Merge symmetry equivalent reflections and Friedel pairs

Fig. 23: Setting of the experimental conditions: An X-ray laboratory diffractometer has been used for collecting the data, the wavelength of the radiation was 1.540598 Å (Cu Kalpha1), and Lorentz- and polarization correction are applied for the calculated pattern.

In the next step (Fig. 24), a list of all imported diffraction peaks will be presented (so that you can check your data), and you will have the option to let Endeavour perform an automatic check/correction of a potential shift of the zero point (2θ shift) in the diffraction pattern. Normally, you should use/activate this option (as in Fig. 24), so please click on “Next” now in order to proceed.



Import Diffraction Data - Select Reflections

38 peaks read from file "D:\Program Files (x86)\Endeavour\Examples\BaMoCl6\BaMoCl6.dif":

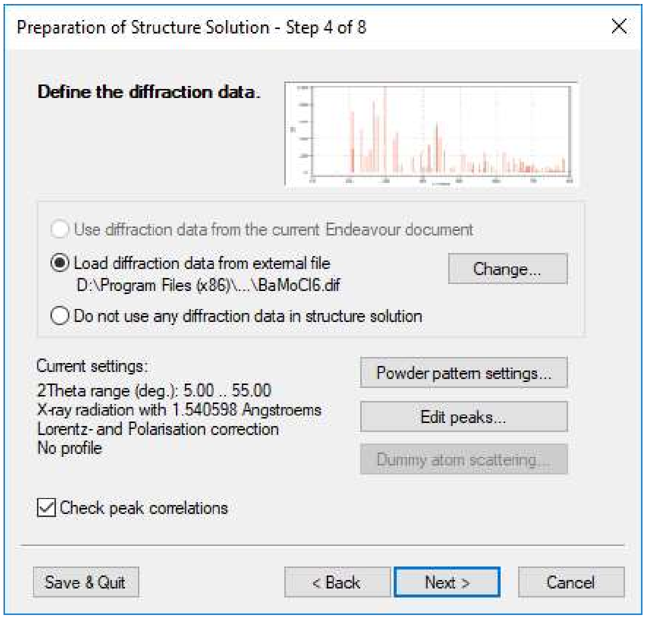
No.	2theta [deg.]	d-spacing [A]	Int.
1	13.68	6.46782	1000
2	15.869	5.58022	909.6
3	16.237	5.45457	418
4	16.783	5.27833	18
5	21.429	4.14328	314.1
6	21.971	4.04228	391.1
7	22.189	4.00306	61.4
8	24.393	3.64613	260.4

☑ Skip invalid reflections or peaks

☑ Apply automatic zero-point correction

Fig. 24: A list of all diffraction peak data that were imported from the selected file is displayed, along with the option to run an automatic correction of the zero shift.

You will be informed about the result of the zero point correction; afterwards, please press "Finish" to return to the 4th wizard page; the file name you just selected appears in the line after "Load diffraction data from external file" (Fig. 25).



Preparation of Structure Solution - Step 4 of 8

Define the diffraction data.

○ Use diffraction data from the current Endeavour document

● Load diffraction data from external file
D:\Program Files (x86)\...\BaMoCl6.dif

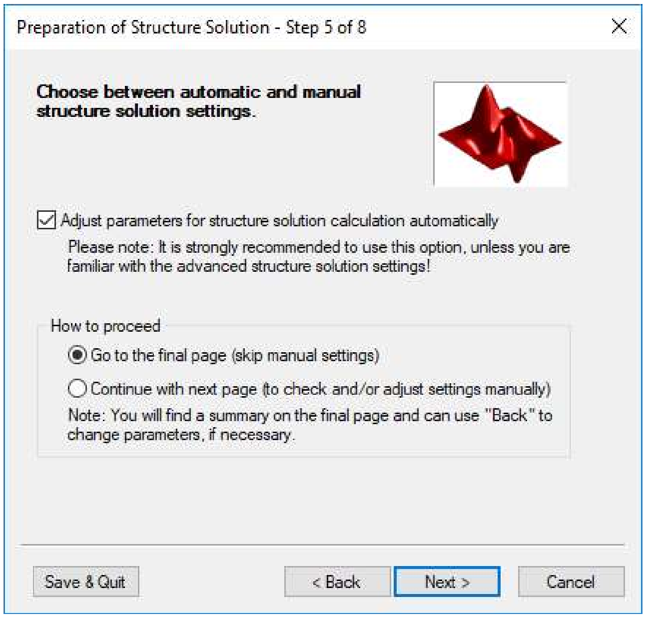
○ Do not use any diffraction data in structure solution

Current settings:
2Theta range (deg.): 5.00 .. 55.00
X-ray radiation with 1.540598 Angstroems
Lorentz- and Polarisation correction
No profile

☑ Check peak correlations

Fig. 25: The file containing the diffraction pattern has been selected.

Now that you have provided the file name of the diffraction data, please press "Next" at the bottom of the wizard to proceed to step 5 (Fig. 26).



Preparation of Structure Solution - Step 5 of 8

Choose between automatic and manual structure solution settings.

☑ Adjust parameters for structure solution calculation automatically

Please note: It is strongly recommended to use this option, unless you are familiar with the advanced structure solution settings!

How to proceed

● Go to the final page (skip manual settings)

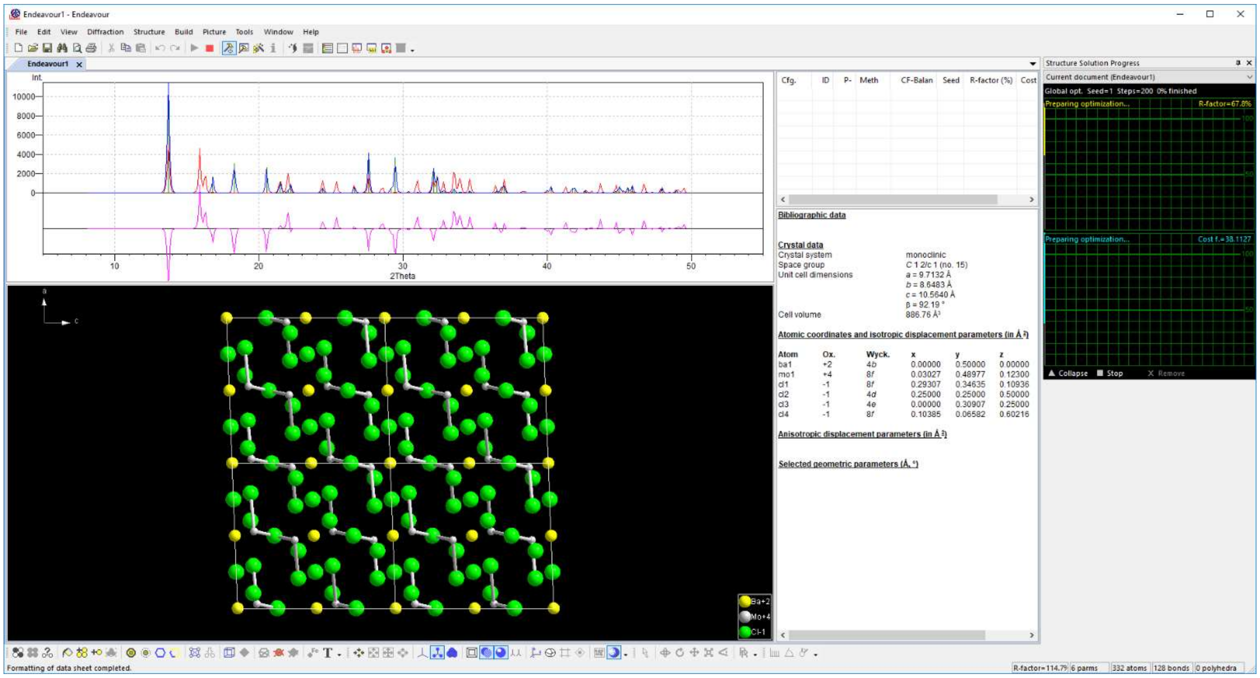
○ Continue with next page (to check and/or adjust settings manually)

Note: You will find a summary on the final page and can use "Back" to change parameters, if necessary.

Fig. 26: Wizard p. 5: We would like Endeavour to adjust all structure solution calculation parameters automatically.

Here, you can select if you would like Endeavour to adjust all structure solution calculation parameters automatically (which is the default), or if you would like to do so on your own. Besides this, you can instruct the structure solution wizard to skip all following pages (the ones that are dedicated to the adjustment of the calculation parameters) and directly go to the final page.

For beginners, we recommend to leave all settings according to their default values, and to advance to the final page right away. Please compare your dialog to Fig. 26, then press "Next" to go to the final page. Here, simply press the "Start" button to finish the data input and start the calculation. The structure solution wizard vanishes, and the so-called "structure solution progress viewer" is displayed on the right-hand side of the window. Your screen should now look similar to Fig. 27.



Global opt. Seed=1 Steps=200 0% finished

Preparing optimization... R-factor=67.8%

Preparing optimization... Cost f.=38.1127

Bibliographic data

Crystal data

Crystal system	monoclinic
Space group	C 1 2/c 1 (no. 15)
Unit cell dimensions	*a* = 9.7132 Å *b* = 8.6483 Å *c* = 10.5640 Å β = 92.19 °
Cell volume	886.76 Å³

Atomic coordinates and isotropic displacement parameters (in Å²)

Atom	Ox.	Wyck.	x	y	z
ba1	+2	4*b*	0.00000	0.50000	0.00000
mo1	+4	8*f*	0.03027	0.48977	0.12300
cl1	-1	8*f*	0.29307	0.34635	0.10936
cl2	-1	4*d*	0.25000	0.25000	0.50000
cl3	-1	4*e*	0.00000	0.30907	0.25000
cl4	-1	8*f*	0.10385	0.06582	0.60216

Anisotropic displacement parameters (in Å²)

Selected geometric parameters (Å, °)

Formatting of data sheet completed.

R-factor=114.79 | 6 parms | 332 atoms | 128 bonds | 0 polyhedra

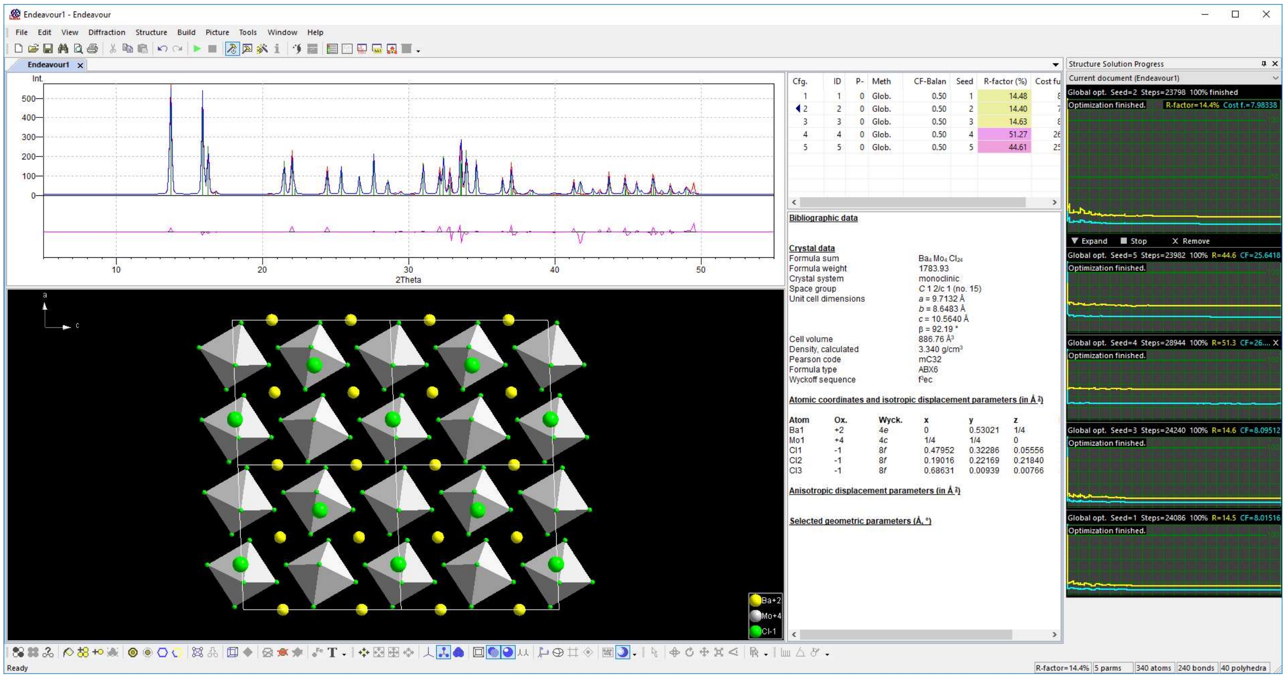
Fig. 27: The structure solution calculation for $BaMoCl_6$ has just been started.

In contrast to the "Quick start" example, this calculation will take significantly longer (about 45 minutes). One main reason for this can instantly be seen in the diffraction pattern pane: Endeavour has converted your peak list data into a diffraction profile. During the structure solution calculation, Endeavour now tries to match the profile calculated for each trial crystal structure to this "experimental" profile. Of course, the calculation of the trial structure profiles as well as their comparison to the “experimental” profile takes significantly longer than the simple comparison of a few peak's intensities in the “Quick start”.

> Why did Endeavour decide to use the slow "profile" calculation now, whereas it used the much faster peak calculation in the “Quick start” example? The background is the density of peaks in the current diffraction pattern which is much higher than the one in the “Quick start” example, caused by the monoclinic unit cell (while it was cubic in the “Quick start” example).
> Endeavour checks if it is possible to assign the calculated peaks to the experimental peaks without any doubt. Typically, this is the case when high-symmetry structures are investigated, due to the low number of peaks observed in the diffraction pattern. If at least one peak assignment is ambiguous, Endeavour uses the “profile matching” algorithm instead, since it cannot decide which calculated peak position shall be assigned to the experimental one. Due to the profile, the intensities of both (or even more) calculated peaks are compared to the experimental peak.

Another reason why the calculation takes so long is that Endeavour is a little bit too “conservative” in this example when it adjusts the parameters of the structure solution calculation automatically. However, this is necessary for the general case to ensure that enough trial structures are investigated, so that small-medium sized structures are solved with high probability. From our own experience we know that normal structure solution calculations using Endeavour typically take between a few hours to a couple of days, depending on the size of the structure. We recommend to let your PC do the work at night time or during the week-end.

Once the five calculations using different seed values has finished, Endeavour will automatically select the configuration (“solution”) with the lowest cost function value[22]. For this structure, the data sheet is displayed (Fig. 28).



Cfg.	ID	P-	Meth	CF-Balan	Seed	R-factor (%)	Cost fu
1	1	0	Glob.	0.50	1	14.48	8
◀ 2	2	0	Glob.	0.50	2	14.40	7
3	3	0	Glob.	0.50	3	14.63	8
4	4	0	Glob.	0.50	4	51.27	26
5	5	0	Glob.	0.50	5	44.61	25

Bibliographic data

Crystal data

Formula sum	$Ba_4 Mo_4 Cl_{24}$
Formula weight	1783.93
Crystal system	monoclinic
Space group	*C* 1 2/*c* 1 (no. 15)
Unit cell dimensions	*a* = 9.7132 Å *b* = 8.6483 Å *c* = 10.5640 Å β = 92.19 °
Cell volume	886.76 $Å^3$
Density, calculated	3.340 g/cm^3
Pearson code	mC32
Formula type	ABX6
Wyckoff sequence	f^3ec

Atomic coordinates and isotropic displacement parameters (in $Å^2$)

Atom	Ox.	Wyck.	x	y	z
Ba1	+2	*4e*	0	0.53021	1/4
Mo1	+4	*4c*	1/4	1/4	0
Cl1	-1	*8f*	0.47952	0.32286	0.05556
Cl2	-1	*8f*	0.19016	0.22169	0.21840
Cl3	-1	*8f*	0.68631	0.00939	0.00766

Anisotropic displacement parameters (in $Å^2$)

Selected geometric parameters (Å, °)

Global opt. Seed=2 Steps=23798 100% finished
Optimization finished. R-factor=14.4% Cost f.=7.98338

Global opt. Seed=5 Steps=23982 100% R=44.6 CF=25.6418
Optimization finished.

Global opt. Seed=4 Steps=28944 100% R=51.3 CF=26....
Optimization finished.

Global opt. Seed=3 Steps=24240 100% R=14.6 CF=8.09512
Optimization finished.

Global opt. Seed=1 Steps=24086 100% R=14.5 CF=8.01516
Optimization finished.

R-factor=14.4% | 5 parms | 340 atoms | 240 bonds | 40 polyhedra

Fig. 28: The structure of $BaMoCl_6$ has been solved.

At this stage, the structure solution is complete; all crystal structure data required for the Rietveld refinement have been determined. You may now export your crystal structure in a variety of common formats (e.g. CIF, CRYSTIN, CSD, PDB, SHELX) by selecting the “File/Save as...” command. In addition, you might also want to save and/or print the data sheet or the structure picture.

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[22] In fact, Endeavour also performs an analysis of the space group symmetry (like the “Quick start”), in order to check if additional symmetry elements are present in the final structure. However, this is not the case in our example, so in fact there are no changes.

Structure solution from electron diffraction data I(hkl) ($BaSO_4$)

In this session you will learn:
- How **single crystal diffraction data** (I(hkl), |F(hkl)| or F^2(hkl)) can be used for structure solution with Endeavour.
- How to **solve a crystal structure from electron diffraction data**.

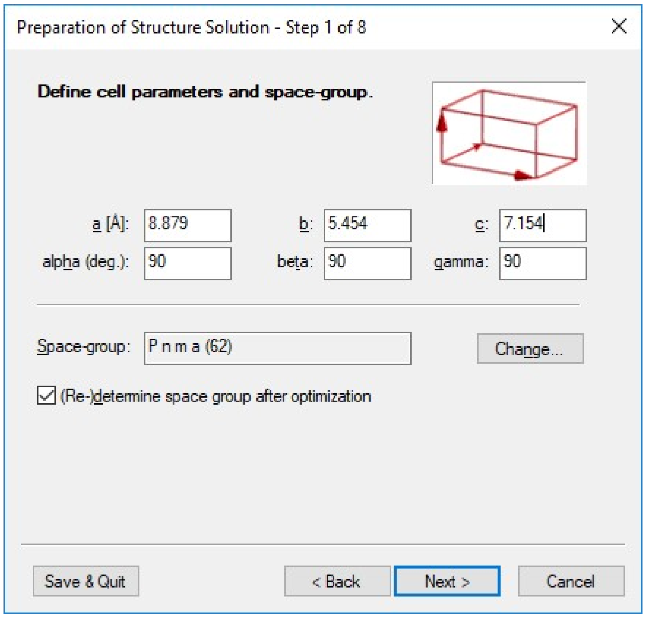
This example is pretty like the previous one, with a single exception: This time, we do not want to solve a crystal structure ($BaSO_4$) from powder diffraction data, but rather from single crystal diffraction data obtained by electron diffraction[23]. In other words, the diffraction data are not intensities at various Bragg peak positions 2θ (like in the previous examples), but intensities of distinct reflections I(hkl).

The data required for structure solution are:

- unit cell parameters: a=8.879 Å, b=5.454 Å, c=7.154 Å
- space group: P n m a
- composition (elements and numbers of atoms in the unit cell): $BaSO_4$, Z=4
- diffraction data I(hkl) obtained by electron diffraction (300 kV) (given in file 'BaSO4.hkl')

In order to solve the structure of $BaSO_4$, please run Endeavour as usual. Once the structure solution wizard is displayed[24], advance to page 2 (skip the overview page).

Provide the unit cell parameters (**a = 8.879 Å, b = 5.454 Å, c = 7.154 Å**). Afterwards, please select the space group by pressing the "Change..." button, entering the Hermann-Mauguin-symbol "**Pnma**" in the upper left field in the "Symmetry" dialog, pressing <tab>, and finally pressing "OK". Your dialog window should now look like Fig. 29:


Preparation of Structure Solution - Step 1 of 8

Define cell parameters and space-group.

a [Å]: 8.879
b: 5.454
c: 7.154
alpha (deg.): 90
beta: 90
gamma: 90

Space-group: P n m a (62)

☑ (Re-)determine space group after optimization

Fig. 29: Structure solution wizard p. 1: Unit cell parameters and space group have been entered.

Skip page 2 of the wizard (input of molecule structures) and advance directly to page 3 by pressing "Next" two times.

As usual, you have to enter the single atoms in the unit cell on this page, as well as the number of formula units per unit cell Z. The formula of your compound is "$BaSO_4$", so please write "Ba" in the input field next to "Element:",

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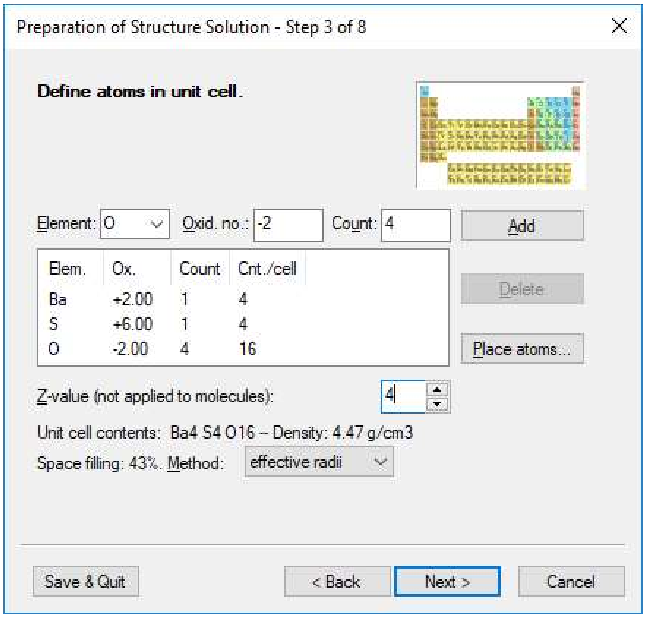
[23] E. Mugnaioli, T. Gorelik and U. Kolb, in print (2009).

[24] If the structure solution wizard is not displayed automatically, please select "Start Solution..." from the "Structure" menu, or press the corresponding button ▶ in the toolbar.

then press <tab> to advance to the next field "Oxid. no.:". Assuming that $BaSO_4$ is a compound basically consisting of ions, you give the oxidation state of Ba (2 in this case). Press <tab> again to advance to "Count:".

The composition is 1*Ba, 1*S, 4*O, so please enter a 1. Afterwards, click on "Add" to add the newly created atom type to the list.

Proceed in a similar manner by entering the data for S (S,6,1) and O (O,-2,4). Finally, you have to give the number of formula units per unit cell Z. Endeavour offers a variety of aids to estimate this value, for example the density. Please adjust Z so that an experimental density of 4.45 g/cm^3 is matched as closely as possible (if you are not sure about it: Z=4 is correct). Please make sure that your dialog looks similar to Fig. 30, then proceed to wizard step 4 afterwards.



Define atoms in unit cell.

Element: O Oxid. no.: -2 Count: 4

Elem.	Ox.	Count	Cnt./cell
Ba	+2.00	1	4
S	+6.00	1	4
O	-2.00	4	16

Z-value (not applied to molecules): 4

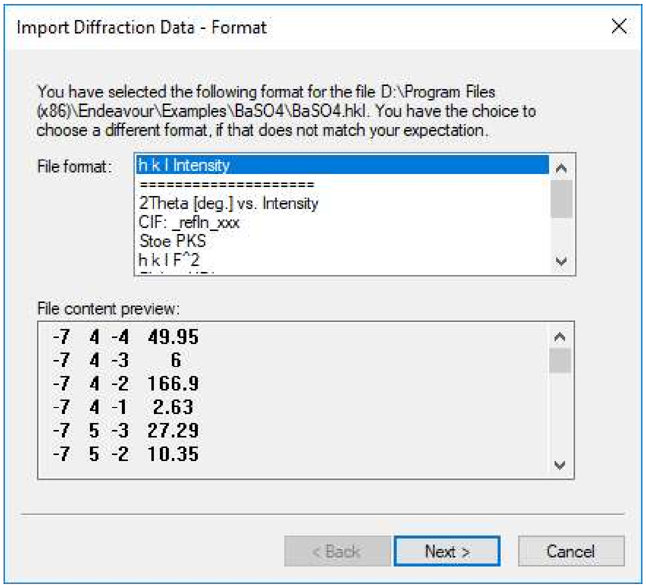
Unit cell contents: Ba4 S4 O16 – Density: 4.47 g/cm3

Space filling: 43%. Method: effective radii

Fig. 30: One Ba^{2+}, one S^{6+} and four O^{2-} -ions in the formula unit, with 4 formula units in the unit cell.

The next thing you have to do is to import the diffraction data, in this case the file containing I(hkl) values obtained by electron diffraction (300 kV). Please open the prepared file by pressing the "Open..." button on wizard page 4. A conventional Windows file dialog box appears. In the "Type of file" box at the bottom of the dialog you can select various diffraction data file formats. In this example, the data file contains intensities of various reflections (hkl), so please select "h k l Intensity (*.hkl)" in the "Type of file" box, then select the file "BaSO4.hkl" from the "Examples\BaSO4" directory in your Endeavour program directory.

Once you have pressed the "Open" button, a new dialog appears asking for a confirmation or more detailed specification of your diffraction data file format (Fig. 31). Please make sure that "'h k l Intensity"' is selected, then press the "Next" button at the bottom.



Import Diffraction Data - Format

You have selected the following format for the file D:\Program Files (x86)\Endeavour\Examples\BaSO4\BaSO4.hkl. You have the choice to choose a different format, if that does not match your expectation.

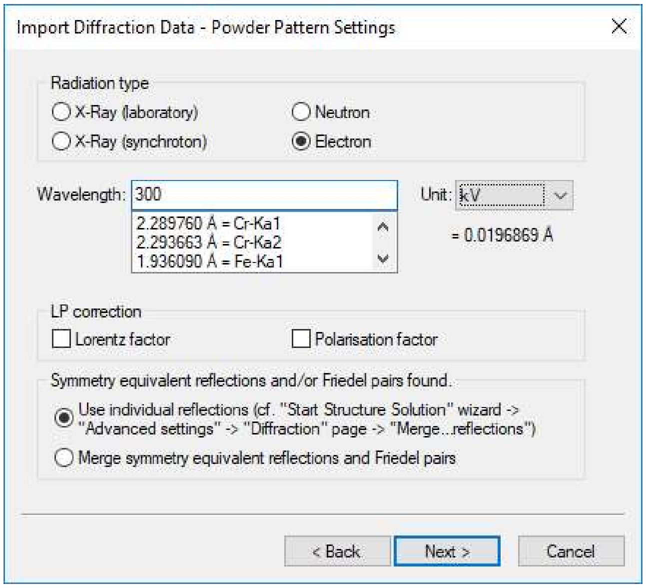
File format:
h k l Intensity
====================
2Theta [deg.] vs. Intensity
CIF: _refln_xxx
Stoe PKS
h k l F^2

File content preview:

```
-7  4 -4  49.95
-7  4 -3    6
-7  4 -2  166.9
-7  4 -1   2.63
-7  5 -3  27.29
-7  5 -2  10.35
```

Fig. 31: In this dialog, you can precisely define the contents of the diffraction data file. As a rough guide, the contents of the file is displayed.

On the next page of the dialog, you have to specify the experimental conditions, especially the radiation type and the wavelength used in the diffraction experiment. In our case, the diffraction data were collected by electron diffraction at 300kV, so please make the corresponding selections: Mark “Electron” as “Radiation type”, then select “kV” from the “Unit” combo box on the right-hand side. Finally, please enter “300” in the “Wavelength” box.



Import Diffraction Data - Powder Pattern Settings

Radiation type
○ X-Ray (laboratory) ○ Neutron
○ X-Ray (synchroton) ● Electron

Wavelength: 300
2.289760 Å = Cr-Ka1
2.293663 Å = Cr-Ka2
1.936090 Å = Fe-Ka1

Unit: kV
= 0.0196869 Å

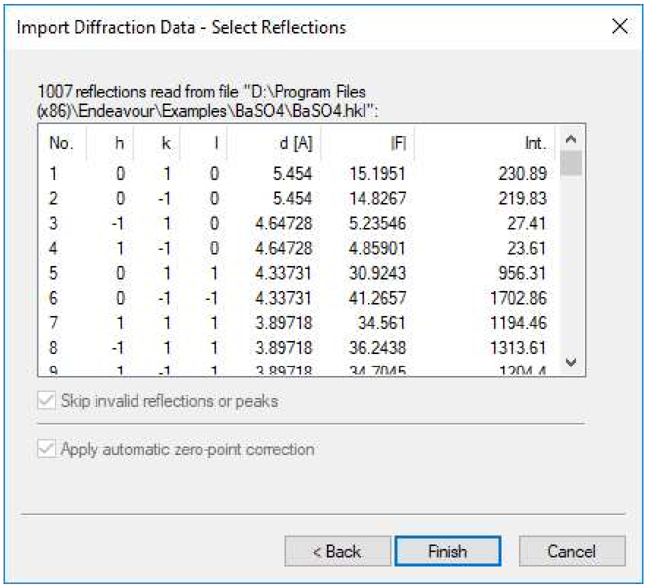
LP correction
☐ Lorentz factor ☐ Polarisation factor

Symmetry equivalent reflections and/or Friedel pairs found.
● Use individual reflections (cf. "Start Structure Solution" wizard -> "Advanced settings" -> "Diffraction" page -> "Merge...reflections")
○ Merge symmetry equivalent reflections and Friedel pairs

Fig. 32: The diffraction data originate from electron diffraction at 300kV.

In the lower part of the "Powder Pattern Settings" dialog you may have noticed the option "Symmetry equivalent reflections found". Here, you can select what you would like Endeavour to do if the diffraction data file contains reflections that are correlated by the space group symmetry (so that in theory they should have the same intensity/structure factor values) and/or Friedel reflection pairs (I(hkl); I(-h-k-l)).
You can either use the data of the individual reflections in the structure solution calculation, or let Endeavour use the average value of the correlated reflections. It is also possible to precisely define which kind of reflections you would like to merge (symmetry correlated or Friedel) on the “Diffraction” page of the “Advanced settings” dialog (section “Merge reflections”).

Verify that your settings correspond to Fig. 32, then press “Next”. You will be presented a list of all reflections that were imported from the selected file for checking purposes (Fig. 33).



Import Diffraction Data - Select Reflections

1007 reflections read from file "D:\Program Files (x86)\Endeavour\Examples\BaSO4\BaSO4.hkl":

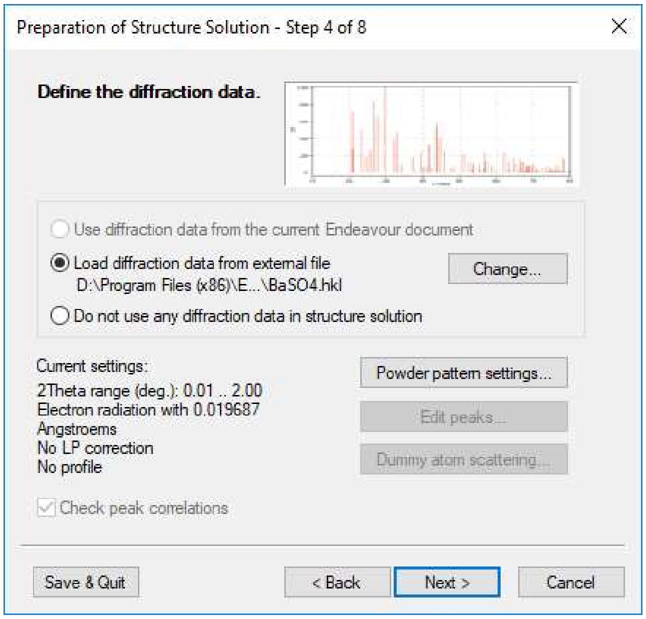
No.	h	k	l	d [A]	|F|	Int.
1	0	1	0	5.454	15.1951	230.89
2	0	-1	0	5.454	14.8267	219.83
3	-1	1	0	4.64728	5.23546	27.41
4	1	-1	0	4.64728	4.85901	23.61
5	0	1	1	4.33731	30.9243	956.31
6	0	-1	-1	4.33731	41.2657	1702.86
7	1	1	1	3.89718	34.561	1194.46
8	-1	1	1	3.89718	36.2438	1313.61
9	1	-1	1	3.89718	34.7045	1204.4

☑ Skip invalid reflections or peaks

☑ Apply automatic zero-point correction

Fig. 33: This is the list of all reflections that have been imported from the selected file.

Afterwards, please press "Finish" in order to return to the 4th wizard page. The file name you have just selected appears in the line after "Load diffraction data from external file"; besides this, the experimental conditions are displayed below (Fig. 34).



Preparation of Structure Solution - Step 4 of 8

Define the diffraction data.

○ Use diffraction data from the current Endeavour document

● Load diffraction data from external file
D:\Program Files (x86)\E...\BaSO4.hkl

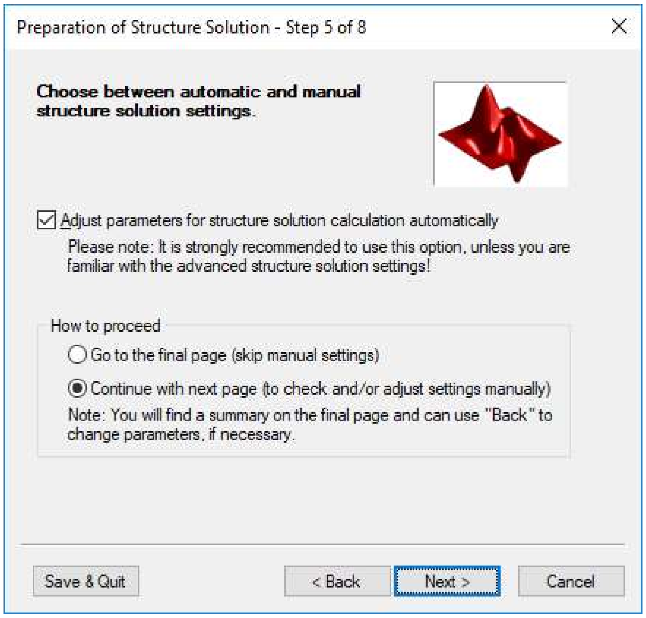
○ Do not use any diffraction data in structure solution

Current settings:
2Theta range (deg.): 0.01 .. 2.00
Electron radiation with 0.019687 Angstroems
No LP correction
No profile

☑ Check peak correlations

Fig. 34: The file containing the diffraction pattern as well as the experimental conditions (electron diffraction) have been selected.

Now that you have provided the diffraction data, please press "Next" at the bottom of the wizard to proceed to step 5 (Fig. 35).



Preparation of Structure Solution - Step 5 of 8

Choose between automatic and manual structure solution settings.

☑ Adjust parameters for structure solution calculation automatically

Please note: It is strongly recommended to use this option, unless you are familiar with the advanced structure solution settings!

How to proceed

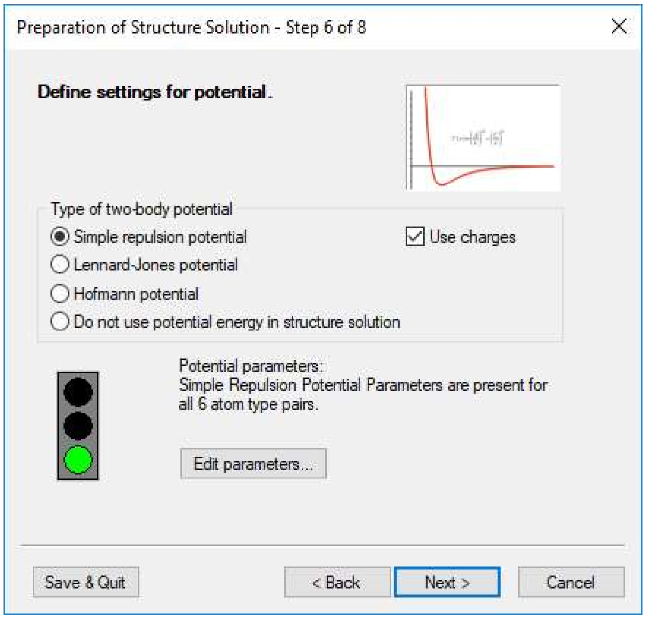
○ Go to the final page (skip manual settings)

● Continue with next page (to check and/or adjust settings manually)

Note: You will find a summary on the final page and can use "Back" to change parameters, if necessary.

Fig. 35: Wizard p. 5: We would like Endeavour to adjust all structure solution calculation parameters automatically.

Similar in the previous examples, we would like Endeavour to adjust all structure solution calculation parameters automatically. However, we would like to apply one modification regarding the cost function balance, so please mark “Continue with next page” in the “How to proceed” section, compare your dialog to Fig. 35, then press “Next” to go to the next page (which is dedicated to the parameters required for the calculation of the potential energy (Fig. 36).



Preparation of Structure Solution - Step 6 of 8

Define settings for potential.

Type of two-body potential

● Simple repulsion potential

○ Lennard-Jones potential

○ Hofmann potential

○ Do not use potential energy in structure solution

☑ Use charges

Potential parameters:
Simple Repulsion Potential Parameters are present for all 6 atom type pairs.

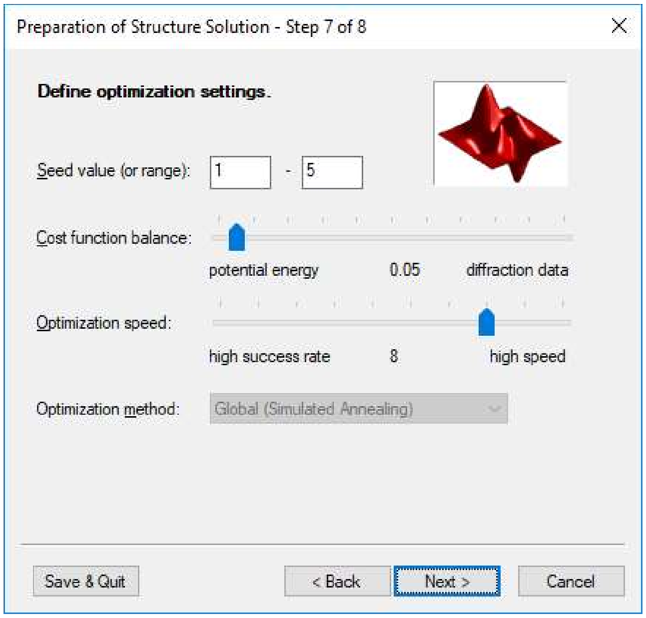
Fig. 36: On this page of the structure solution wizard, you can select how the potential energy shall be calculated.

For the current, we won’t modify anything here, so please press “Next” to advance to wizard step 7. Here you can select options regarding the cost function optimization, i.e. the calculation that Endeavour uses to solve the crystal structure.

We will modify a single setting only: As you may remember, Endeavour uses two contributions in the cost function to be optimized: The R-factor (agreement between calculated and experimental diffraction pattern) and the potential energy. Because of this, you can adjust the contribution of these two compounds to the overall cost function, using the setting “Cost function balance”. By default, this value is 0.5, so that both R-factor and potential energy contribute equally to the overall cost function.

However, in this case, we would like to give more weight to the potential energy than to the R-factor. The reason is that the reflection intensities are not too accurate in many cases if determined with electron diffraction due to various reasons (e.g. dynamic diffraction). On the other hand, a potential function that treats the atoms as ions (like the one used by default in Endeavour) seems to approximate the bonding in the compound BaSO4 quite will.

Hence, we will put more weight on the potential energy (and less on the diffraction data), by moving the "Cost function balance" slider to 0.05. Compare your dialog to Fig. 37, then press "Next" to advance to step 8.



Preparation of Structure Solution - Step 7 of 8

Define optimization settings.

Seed value (or range): 1 - 5

Cost function balance: 0.05 (potential energy – diffraction data)

Optimization speed: 8 (high success rate – high speed)

Optimization method: Global (Simulated Annealing)

Fig. 37: In wizard step 7 you can define parameters regarding the optimization of the cost function. We here use an increased contribution of the potential energy by adjust the "Cost function balance" slider to 0.05.

In step 8, you can define how the intermediate crystal structure pictures that are shown during the calculation shall look like. We will get back to this later on and leave all settings at their default values for now.

Please press "Next" again to advance to the wizard "Summary". Here, simply press the "Start" button to finish the data input and run the calculation. It will take about 10 minutes.

Once the calculation using five different seed values has finished, Endeavour will automatically select the configuration ("solution") with the lowest cost function value[25]. For this structure, the data sheet is displayed (Fig. 38).

At this stage, the structure solution of $BaSO_4$ from electron diffraction data is complete. Like in the previous tutorial sessions, you can now export your crystal structure in a variety of common formats (e.g. CIF, CRYSTIN, CSD, PDB, SHELX) by selecting the "File/Save as..." command. In addition, you might also want to save and/or print the data sheet or the structure picture.

Please note:

- In a similar manner, you can also **solve crystal structures from single crystal X-ray diffraction data**, simply by making the corresponding selection in the "Powder Pattern Settings" dialog. This may be useful if the data set is rather small (few reflections have been measured), so that conventional direct methods may run into problems.
- If the intensity (or structure factor) values are rather bad, you could activate the option "Reduce influence of |F(hkl)| differences, if |F(hkl)| > 0" (in the "Advanced settings" dialog[26], page "Diffraction", section "Smooth intensity differences"). If this parameter is active (=1), Endeavour will reduce the negative impact

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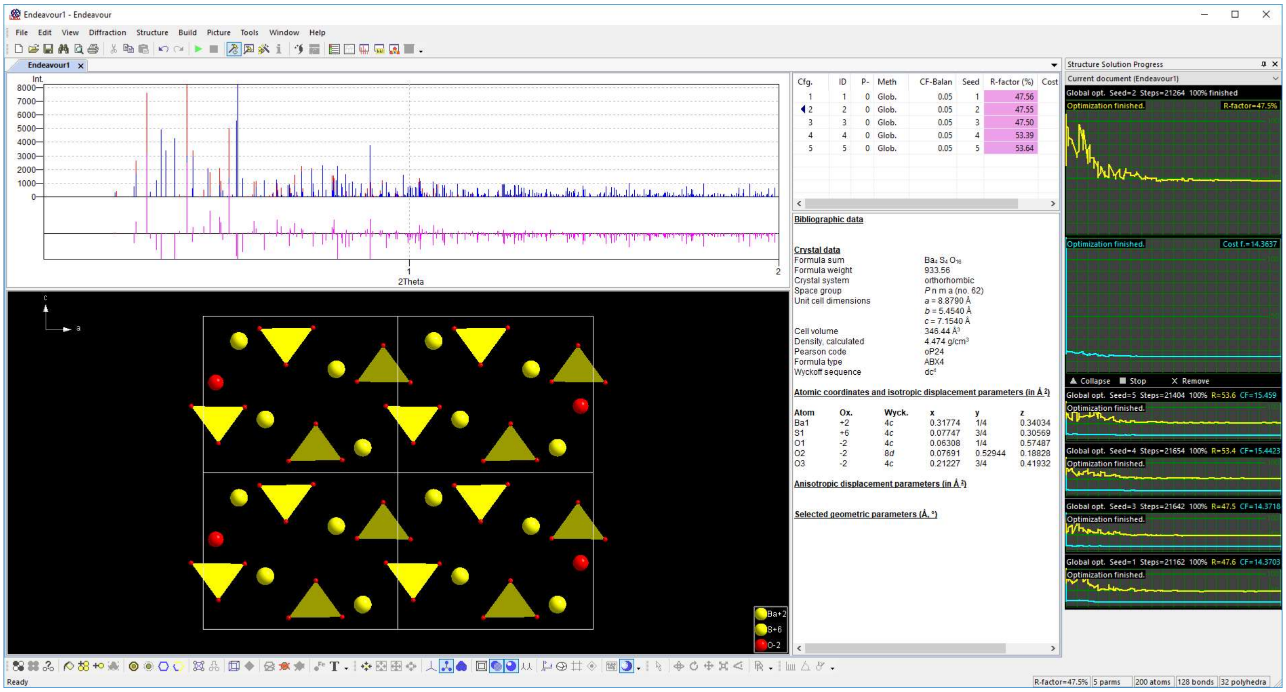
[25] Like in the previous example, Endeavour in fact also performs an analysis of the space group symmetry, in order to check if additional symmetry elements are present in the final structure. However, this is not the case in our example, so in fact there are no changes.

[26] The "Advanced settings" dialog can be opened from the final ("Summary") page of the structure solution wizard.

of reflection intensity differences for all reflections with an intensity/structure factor greater than 0.0. In other words, if an experimental reflection intensity is equal to 0.0, the full difference to the calculated reflection intensity is taken into account (so that the effect of systematically absent reflections is visible). Otherwise, only the logarithm of the intensity difference is used in the calculation.

- If you know that there is **no intensity for a certain reflection (hkl)**, it is important and extremely helpful for the calculation to include this information in the diffraction data file!



Cfg.	ID	P-	Meth	CF-Balan	Seed	R-factor (%)	Cost
1	1	0	Glob.	0.05	1	47.56	
◀ 2	2	0	Glob.	0.05	2	47.55	
3	3	0	Glob.	0.05	3	47.50	
4	4	0	Glob.	0.05	4	53.39	
5	5	0	Glob.	0.05	5	53.64	

Bibliographic data

Crystal data

Formula sum	$Ba_4 S_4 O_{16}$
Formula weight	933.56
Crystal system	orthorhombic
Space group	*P* n m a (no. 62)
Unit cell dimensions	*a* = 8.8790 Å *b* = 5.4540 Å *c* = 7.1540 Å
Cell volume	346.44 Å^3
Density, calculated	4.474 g/cm^3
Pearson code	oP24
Formula type	ABX4
Wyckoff sequence	dc^4

Atomic coordinates and isotropic displacement parameters (in Å^2)

Atom	Ox.	Wyck.	x	y	z
Ba1	+2	4*c*	0.31774	1/4	0.34034
S1	+6	4*c*	0.07747	3/4	0.30569
O1	-2	4*c*	0.06308	1/4	0.57487
O2	-2	8*d*	0.07691	0.52944	0.18828
O3	-2	4*c*	0.21227	3/4	0.41932

Anisotropic displacement parameters (in Å^2)

Selected geometric parameters (Å, °)

```
Global opt.  Seed=2  Steps=21264  100% finished
Optimization finished.                 R-factor=47.5%
Optimization finished.                 Cost f.=14.3637
Global opt.  Seed=5  Steps=21404  100%  R=53.6  CF=15.459
Optimization finished.
Global opt.  Seed=4  Steps=21654  100%  R=53.4  CF=15.4423
Optimization finished.
Global opt.  Seed=3  Steps=21642  100%  R=47.5  CF=14.3718
Optimization finished.
Global opt.  Seed=1  Steps=21162  100%  R=47.6  CF=14.3703
Optimization finished.
```

R-factor=47.5% | 5 parms | 200 atoms | 128 bonds | 32 polyhedra

Fig. 38: The structure of $BaSO_4$ has been solved from electron diffraction data.

Solution of molecular structure (2,4,6-Tri-isopropylbenzenesulfonamide)

In this session you will learn:
- How to solve a "real-case" molecular structure starting with a drawing of the molecule and the diffraction data.
- How to use the software package “ACD ChemSketch” (Freeware version) to sketch a molecule and transform it into a 3-dimensional structure.
- How rotatable bonds are dealt with.

This tutorial demonstrates a typical solution of a molecular crystal structure: The diffraction data are experimental (taken from the literature[27]), the molecule contains four bonds around which parts of it may be rotated, and the only thing which is provided concerning the structure of the molecule is a typical 2-dimensional drawing.

The example we will use is 2,4,6-Tri-isopropylbenzenesulfonamide (“Triiso”, Fig. 39), the structure of which has been solved by M. Tremayne and co-workers[27] several years ago by a Monte Carlo method.

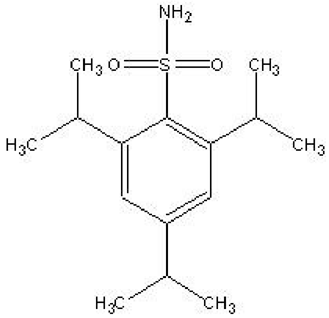


Fig. 39: Constitution of 2,4,6-Tri-isopropylbenzenesulfonamide

The first thing you should do is convert the (2-dimensional) drawing of the molecule into a file containing the 3-dimensional structure of the molecule in an appropriate file format (“emo-file”, i.e. “**E**ndeavour **MO**lecule file”), just from the sketch of the molecule’s constitution in Fig. 39. You will first have to draw this molecule on your computer screen and afterwards transform this into a 3-dimensional structure[28]. You can use your own program for performing this task if you like, if it is able to export the 3-dimensional structure of the molecule in one of Endeavour’s molecule input formats[29].

If you would like to create the 3-dimensional molecule structure file using your own software, you should do this now and proceed on p. 39 starting Endeavour. Otherwise, you should check whether ACD ChemSketch is installed on your computer. If not, please download and install it now from

https://www.acdlabs.com/resources/freeware/chemsketch/

Afterwards, please start ChemSketch, e.g. by selecting “ChemSketch” from the “Start-ACDLabs Freeware 20xx”

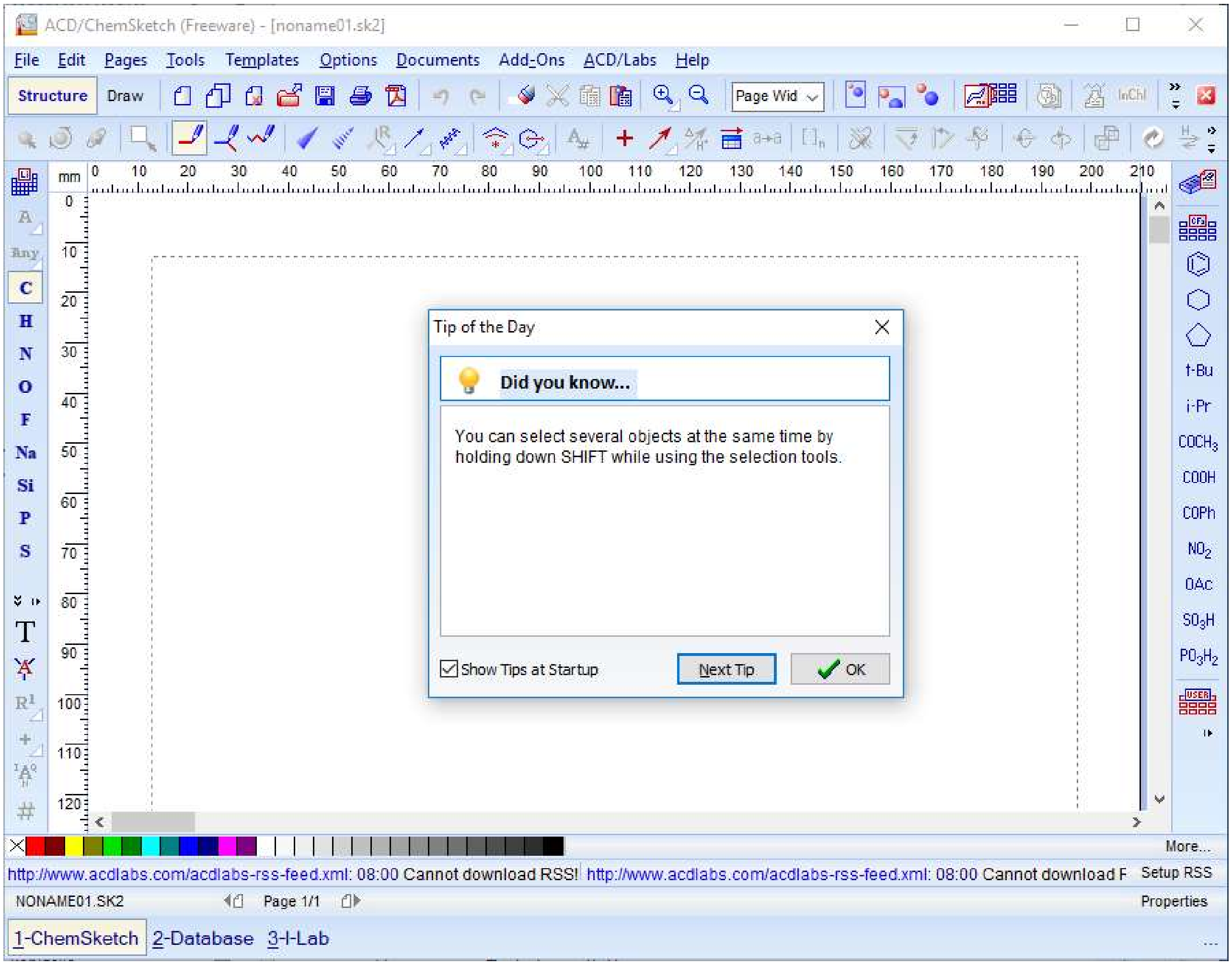
Windows menu (Fig. 40).

---

[27] M. Tremayne, E.J. MacLean, C.C. Tang, C. Glidewell, Acta Cryst. B**55**, 1068-1074 (1999).

[28] You can skip this step if you like, by using the mol-file “triiso.mol” which is present in the “Examples\Triiso” directory. In this case, please continue reading on p. 36 starting Endeavour.

[29] The following molecular file formats can be read by Endeavour: Endeavour (*.edf,*.emo), Diamond (*.dsf), Cambridge CSD-FDAT (*.dat, *.fdat, *.csd), MDL Molfile/SDFile (e.g. from ACD ChemSketch) (*.mol,*.mdl,*.sd), Cerius2 CSSR (*.cssr, *.dat), Sybyl MOL/MOL2 (*.mol, *.mol2), CIF (*.cif).



Tip of the Day

Did you know...

You can select several objects at the same time by holding down SHIFT while using the selection tools.

☑ Show Tips at Startup

Next Tip ✓ OK

http://www.acdlabs.com/acdlabs-rss-feed.xml: 08:00 Cannot download RSS! http://www.acdlabs.com/acdlabs-rss-feed.xml: 08:00 Cannot download F

Fig. 40: The ACDLabs ChemSketch software has been started.

We will start by drawing the central Benzene ring: Please open the “Table of Radicals” by pressing the corresponding button in the toolbar on the right-hand side, select the Benzene ring (section “Cycles”), and place it somewhere in the middle of the white sheet, by clicking the left mouse button at the appropriate position. Afterwards, press the C-atom button **C** on the left-hand side of the screen.

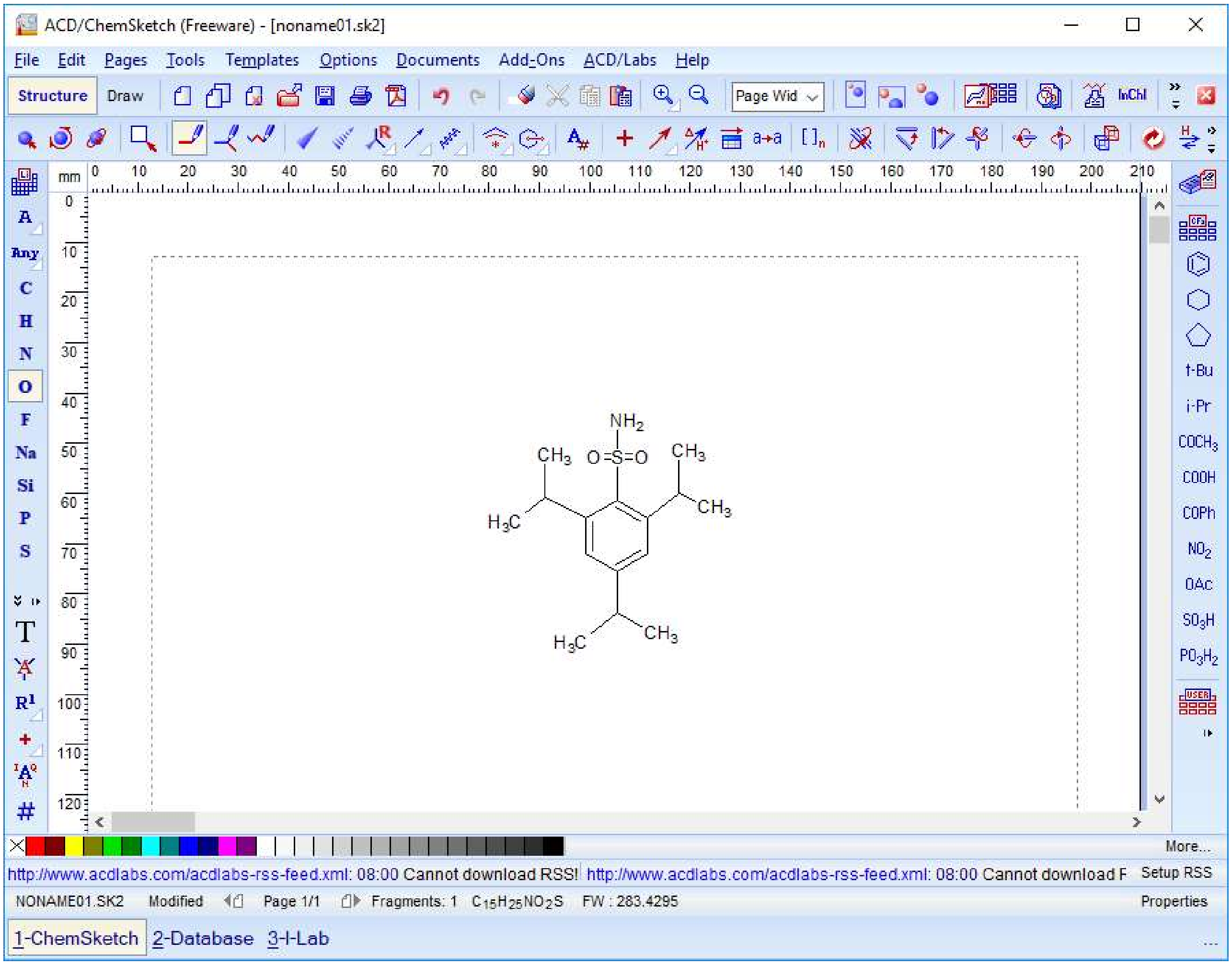
Now, draw three iso-propyl-groups, starting from the appropriate atoms of the benzene ring according to Fig. 39 (p. 37): Move the mouse over the benzene ring atom, press the left button and draw the bond. As soon as you release the button, a CH_3-group has been added to the molecule[30]. Don't worry about appropriate bond lengths and angles at the moment; ChemSketch has a “Clean Structure” option which can “tidy up the molecule” when you have finished drawing the molecule.

Start again drawing from the newly created CH_3-group and add two new CH_3-groups to it in the same manner as above. Three iso-propyl groups in meta-position to each other have to be drawn this way (ref. to Fig. 39 if you are not sure where to place the atoms!).

Finally, add the sulfonamide-group somewhere between two iso-propyl groups, by selecting the appropriate elements from the toolbar on the left-hand side and mounting them to the molecule. The double-bonds between S and the O-atoms can be introduced by single-clicking on the appropriate bond with your left mouse button. Your molecule should now look similar to Fig. 41.

---

[30] Note that the H-atoms are added automatically by ChemSketch.



http://www.acdlabs.com/acdlabs-rss-feed.xml: 08:00 Cannot download RSS! http://www.acdlabs.com/acdlabs-rss-feed.xml: 08:00 Cannot download F

NONAME01.SK2 Modified Page 1/1 Fragments: 1 $C_{15}H_{25}NO_2S$ FW : 283.4295

Fig. 41: The molecule has been drawn with arbitrary bond lengths and angles.

To tidy up the molecule, please press the “Clean Structure” button to the top of the drawing area. Afterwards, the structure looks much better with “normal” bond lengths and angles. However, it is still a 2-dimensional drawing; you still have to transform it into a 3-dimensional form.

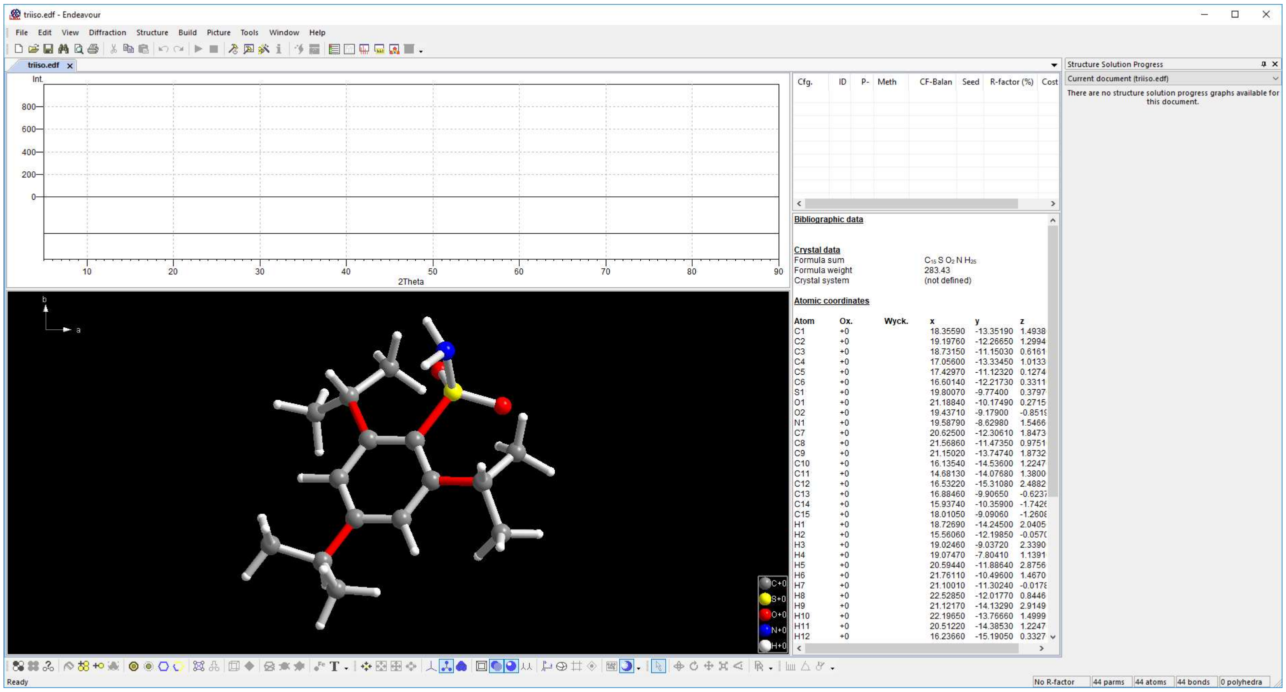
Please press the “3D Optimization” button (it may be hidden in the “More buttons” menu to the right of the “clean structure” button). At a first glance, only minor changes have occurred, however, once you "grab" an atom of the molecule using the left mouse button, you can rotate the molecule with your mouse as long as you keep the left mouse button pressed.

The only thing which is left to do in ChemSketch is to export it to a file format which can be read by Endeavour. Please select “Export...” from the “File” menu. The default MDL mol format suggested by ChemSketch is just fine, so simply select an appropriate directory where you would like to store the molecule structure file, enter the filename and press “Save”. Afterwards, you can close the ChemSketch program (there is generally no need to save any changes in ChemSketch's own format).

Now you can start working with Endeavour. If Endeavour is not already running on your computer, please double-click the corresponding icon on your desktop. Before you start the input for the actual structure solution, you have to define the rotatable bonds in the molecule you just have sketched, and save the molecule in Endeavour's own format[31].

Please open the mol-file you have exported from ChemSketch: Select "File/Open" (or press the corresponding toolbar button 📂), then adjust the "Type of file" at the bottom of the "Open" dialog to "MDF Molfile (*.MOL,*.MDL)". Finally, select the molecule file you have created in the previous step, and press "Open". Endeavour realizes that a molecular structure (no translational symmetry) has been loaded and displays the molecule automatically.

Right-click on the bond between the S- and the C-atom and select "Rotatable Bond" from the context-menu. The color of the bond changes to red in order to indicate that parts of the molecule shall/can be rotated around this bond during the structure solution calculation[32]. Please mark the remaining three bonds between the three iso-propyl groups and the benzene ring in the same manner. Your screen should now look similar to Fig. 42.



There are no structure solution progress graphs available for this document.

Bibliographic data

Crystal data

Formula sum	$C_{15}\,S\,O_2\,N\,H_{25}$
Formula weight	283.43
Crystal system	(not defined)

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
C1	+0		18.35590	-13.35190	1.4938
C2	+0		19.19760	-12.26650	1.2994
C3	+0		18.73150	-11.15030	0.6161
C4	+0		17.05600	-13.33450	1.0133
C5	+0		17.42970	-11.12320	0.1274
C6	+0		16.60140	-12.21730	0.3311
S1	+0		19.80070	-9.77400	0.3797
O1	+0		21.18840	-10.17490	0.2715
O2	+0		19.43710	-9.17900	-0.851
N1	+0		19.58790	-8.62980	1.5466
C7	+0		20.62500	-12.30610	1.8473
C8	+0		21.56860	-11.47350	0.9751
C9	+0		21.15020	-13.74740	1.8732
C10	+0		16.13540	-14.53600	1.2247
C11	+0		14.68130	-14.07680	1.3800
C12	+0		16.53220	-15.31080	2.4882
C13	+0		16.88460	-9.90650	-0.623
C14	+0		15.93740	-10.35900	-1.742
C15	+0		18.01050	-9.09060	-1.260
H1	+0		18.72690	-14.24500	2.0405
H2	+0		15.56060	-12.19850	-0.057
H3	+0		19.02460	-9.03720	2.3390
H4	+0		19.07470	-7.80410	1.1391
H5	+0		20.59440	-11.88640	2.8756
H6	+0		21.76110	-10.49600	1.4670
H7	+0		21.10010	-11.30240	-0.017
H8	+0		22.52850	-12.01770	0.8446
H9	+0		21.12170	-14.13290	2.9149
H10	+0		22.19650	-13.76660	1.4999
H11	+0		20.51220	-14.38530	1.2247
H12	+0		16.23660	-15.19050	0.3327

No R-factor | 44 parms | 44 atoms | 44 bonds | 0 polyhedra

Fig. 42: There are four rotatable bonds (marked in red) in the "Triiso" molecule.

Finally, save the molecule structure to the Endeavour-proprietary "*.emo"-format. This by achieved by right-clicking on one of the molecule's atoms and selecting "Save-Save Molecule as…" from the context menu, e.g. using the filename "triiso.emo". Afterwards, close the molecule structure document.

Now that the molecule structure file has been prepared, we can start the actual structure solution calculation. Please open a new Endeavour document by selecting "New" from the "File" menu (or simply click on the corresponding toolbar button 🗋. Depending on your settings in "Tools/Options", this will also bring up the structure solution wizard right away[33].

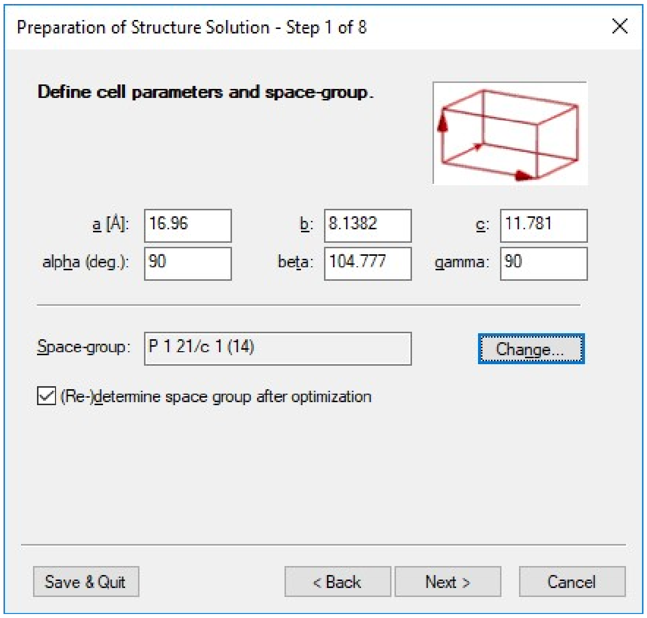
The unit cell parameters (monoclinic cell) are **a = 16.96Å, b = 8.1382 Å, c = 11.781 Å and β = 104.777**°; the space group is P 1 21/c 1 (International Tables no. 14). Please enter these data and compare your screen to Fig. 43.

---

[31] You can also skip this step and use the prepared Endeavour molecule file "triiso.emo" which is present in the "Examples\Triiso" directory. In this case, please continue reading at the beginning of the structure solution calculation below.

[32] Please note that rotatable bonds are only visible in the molecule-mode of Endeavour as well as during structure solution calculations, but not in the "normal" crystal structure viewing mode.

[33] To open the structure solution wizard if it is not displayed automatically, select "Start Solution…" from the "Structure" menu, or press the corresponding button ▶ in the toolbar.


Preparation of Structure Solution - Step 1 of 8

Define cell parameters and space-group.

a [Å]: 16.96 b: 8.1382 c: 11.781

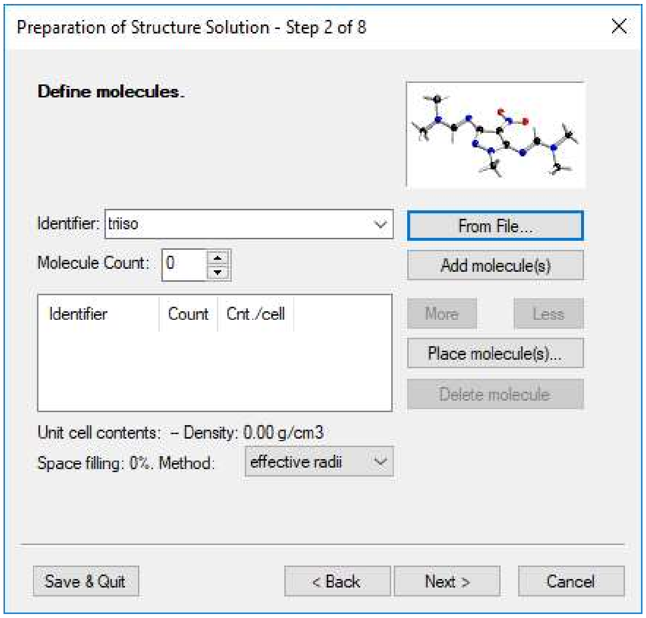
alpha (deg.): 90 beta: 104.777 gamma: 90

Space-group: P 1 21/c 1 (14)

☑ (Re-)determine space group after optimization

Fig. 43: Setting of unit cell parameters and space group for "Triiso"

Afterwards, advance to step 2 of the wizard. You now have to load the 3-dimensional molecule structure data file (triiso.emo) you have just prepared: Please select "From file..." which will bring up a conventional Windows file open dialog. Select the emo-file you have just created (the one in which you have marked the rotatable bonds; e.g. "triiso.emo"), then press "Open". The file dialog vanishes, and the name of the molecule is displayed in the field "Identifier" (Fig. 44).


Preparation of Structure Solution - Step 2 of 8

Define molecules.

Identifier: triiso

Molecule Count: 0

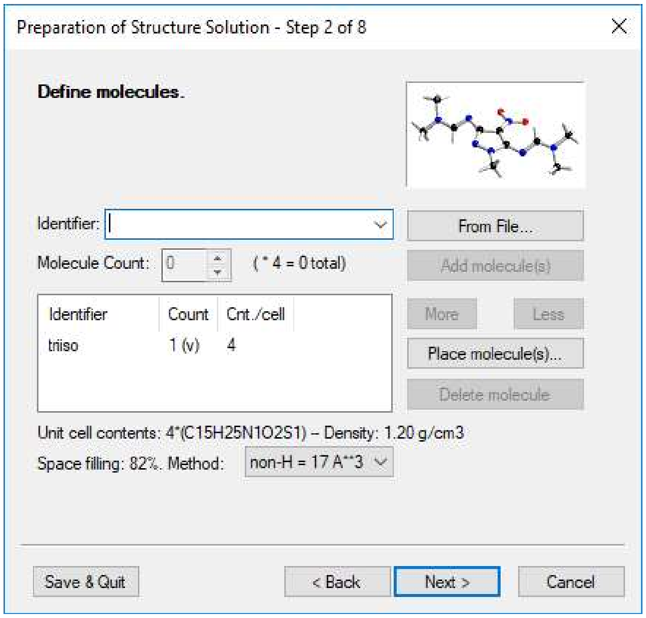
Identifier	Count	Cnt./cell

Unit cell contents: – Density: 0.00 g/cm3

Space filling: 0%. Method: effective radii

Fig. 44: The 3-dimensional structure of the "Triiso" molecule has been loaded.

Increase the "Molecule Count" value to 1 and check that "(*4 = 4 total)" is displayed to the right of the "Molecule Count" entry field. Similar to session 4, the multiplicity of the general position of the space group used is 4, so placing one molecule on the general position leads to 4 molecules in the unit cell. Finally, press "Add molecule(s)". The molecule identifier together with the number in the unit cell will be displayed in the table (Fig. 45).


Preparation of Structure Solution - Step 2 of 8

Define molecules.

Identifier:

Molecule Count: 0 (* 4 = 0 total)

Identifier	Count	Cnt./cell
triiso	1 (v)	4

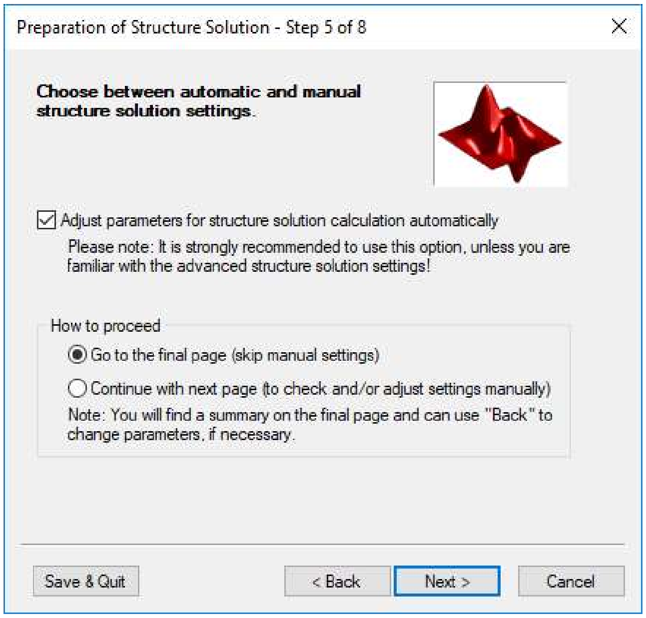
Unit cell contents: 4*(C15H25N1O2S1) – Density: 1.20 g/cm3

Space filling: 82%. Method: non-H = 17 A**3

Fig. 45: A total of 4 "Triiso" molecules are present in the unit cell.

Afterwards, press "Next" to advance to wizard page 3. This time, there are no single atoms in the structure, thus you can skip this page and advance right away to wizard page 4.

On page 4, please load the diffraction data from the file "triiso.dif" which is present in the "Examples\Triiso" directory of your Endeavour installation and check/adjust the following settings: file format "2Theta vs. Intensity", radiation: X-ray-laboratory, wavelength Cu Kα1 (1.540598 Å). Afterwards, please advance to step 5.


Preparation of Structure Solution - Step 5 of 8

Choose between automatic and manual structure solution settings.

☑ Adjust parameters for structure solution calculation automatically

Please note: It is strongly recommended to use this option, unless you are familiar with the advanced structure solution settings!

How to proceed

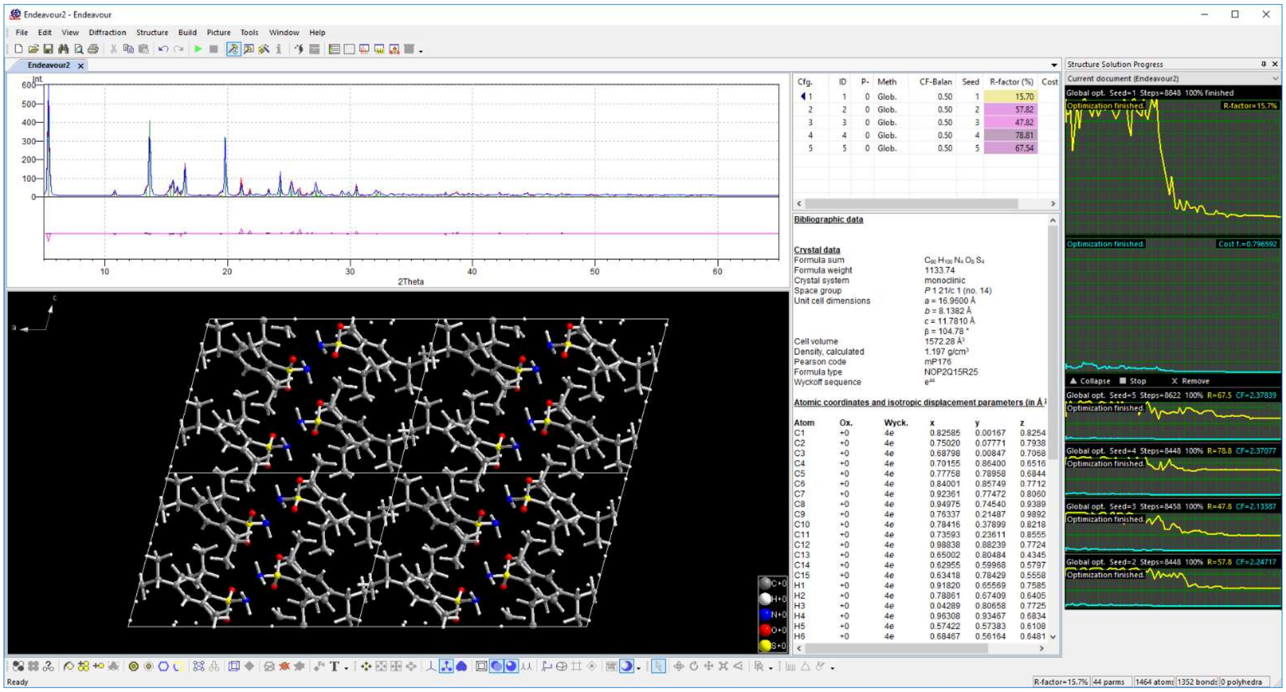
● Go to the final page (skip manual settings)

○ Continue with next page (to check and/or adjust settings manually)

Note: You will find a summary on the final page and can use "Back" to change parameters, if necessary.

Fig. 46: Wizard p. 5: We would like Endeavour to adjust all structure solution calculation parameters automatically.

Similar to the previous sessions, you should let Endeavour adjust all structure solution calculation parameters automatically (which is the default), skip all following pages (the ones that are dedicated to the adjustment of the calculation parameters), and directly go to the final page: In order to do so, please compare your dialog to Fig. 46, then press "Next" to go to the final page. Here, simply press the "Start" button to finish the data input and start the calculation.



Cfg.	ID	P-	Meth	CF-Balan	Seed	R-factor (%)	Cost
1	1	0	Glob.	0.50	1	15.70	
2	2	0	Glob.	0.50	2	57.82	
3	3	0	Glob.	0.50	3	47.82	
4	4	0	Glob.	0.50	4	78.81	
5	5	0	Glob.	0.50	5	67.54	

Bibliographic data

Crystal data

Formula sum	$C_{60} H_{100} N_4 O_8 S_4$
Formula weight	1133.74
Crystal system	monoclinic
Space group	*P* 1 21/c 1 (no. 14)
Unit cell dimensions	*a* = 16.9600 Å *b* = 8.1382 Å c = 11.7810 Å β = 104.78 °
Cell volume	1572.28 Å³
Density, calculated	1.197 g/cm³
Pearson code	mP176
Formula type	NOP2Q15R25
Wyckoff sequence	e^{44}

Atomic coordinates and isotropic displacement parameters (in Å

Atom	Ox.	Wyck.	x	y	z
C1	+0	4e	0.82585	0.00167	0.8254
C2	+0	4e	0.75020	0.07771	0.7938
C3	+0	4e	0.68798	0.00847	0.7068
C4	+0	4e	0.70155	0.86400	0.6516
C5	+0	4e	0.77758	0.78958	0.6844
C6	+0	4e	0.84001	0.85749	0.7712
C7	+0	4e	0.92361	0.77472	0.8060
C8	+0	4e	0.94975	0.74540	0.9389
C9	+0	4e	0.76337	0.21487	0.9892
C10	+0	4e	0.78416	0.37899	0.8218
C11	+0	4e	0.73593	0.23611	0.8555
C12	+0	4e	0.98838	0.88239	0.7724
C13	+0	4e	0.65002	0.80484	0.4345
C14	+0	4e	0.62955	0.59968	0.5797
C15	+0	4e	0.63418	0.78429	0.5558
H1	+0	4e	0.91820	0.65569	0.7585
H2	+0	4e	0.78861	0.67409	0.6405
H3	+0	4e	0.04289	0.80658	0.7725
H4	+0	4e	0.96308	0.93467	0.6834
H5	+0	4e	0.57422	0.57383	0.6108
H6	+0	4e	0.68467	0.56164	0.6481

Global opt. Seed=1 Steps=8848 100% finished
Optimization finished. R-factor=15.7%
Optimization finished. Cost f.=0.796592
Global opt. Seed=5 Steps=8622 100% R=67.5 CF=2.37839
Optimization finished.
Global opt. Seed=4 Steps=8448 100% R=78.8 CF=2.37077
Optimization finished.
Global opt. Seed=3 Steps=8458 100% R=47.8 CF=2.13387
Optimization finished.
Global opt. Seed=2 Steps=8448 100% R=57.8 CF=2.24717
Optimization finished.

R-factor=15.7% | 44 parms | 1464 atoms | 1352 bonds | 0 polyhedra

Fig. 47: This structural model for 2,4,6-Tri-isopropylbenzenesulfonamide has the lowest cost function value.

Once the five calculations using different seed values have finished, Endeavour will automatically select the configuration ("solution") with the lowest cost function value. For this structure, the data sheet is displayed then (Fig. 47). At this stage, the structure solution is complete; all crystal structure data required for the Rietveld refinement have been determined.

Balancing of low quality neutron diffraction data by potential energy (Li_2CuO_2)

In this session you will learn:
- How to solve a crystal structure from **neutron diffraction data**
- How to **balance** a relatively raw diffraction pattern by **simultaneous potential energy optimization**
- How to **obtain parameters** for the **Lennard-Jones potential**
- How to **"fine-tune" the optimization parameters** with regard to the **specific optimization problem**
- How to **adapt the Auto-build function** to visualize intermediate structures during the structure solution calculation according to your requirements

Although the automatic structure solution calculations in the previous tutorial sessions were successful, there may of course also be cases in which using the automatic adjustment of all parameters of the structure solution calculation is not applicable. This is especially the case if there are uncertainties regarding the composition and/or the quality of the diffraction data.

The crystal structure in this tutorial session is not overly complicated; however, you won't be able to solve it using the default simple repulsion potential (without using charges). There are two basic reasons for this:

- The space-filling is rather low for a single atom structure.
- The intensities of the diffraction pattern are somewhat inaccurate.

These two facts allow a wide range of atomic arrangements to reveal an R-factor equally to or even below the one of the correct crystal structure with still reasonable interatomic distances. Therefore, the default (uncharged) simple repulsion potential doesn't help much in this case.

In this session, we will show you a possibility to overcome similar problems: Fit a Lennard-Jones potential to similar structures[34]. We will discuss this point later on when we come to structure solution wizard page 5 dealing with the calculation of the potential energy.

In Endeavour, the cost function is normally calculated as a weighted sum of the R-factor and of the potential energy of the trial structure. It is this combined cost function value that is optimized during the structure solution calculation.
The potential energy is normally calculated using a so-called "simple repulsion potential" which keeps the atoms at appropriate distances, along with the Coulomb energy if charged atoms (ions) are present). Appropriate minimum interatomic distances for all element pair combinations are implemented in Endeavour; they have been derived manually from distance statistics of a large crystallographic database called "Pearson's Crystal Data".

Let's get the structure solution running like in the previous sessions: Start Endeavour (if you haven't done so yet), open a new crystal structure document by pressing the corresponding button in the toolbar. Once the structure solution is displayed, please skip its "Welcome" page by pressing "Next". Afterwards, please enter the following unit cell parameters: **a = 3.654 Å, b = 2.859 Å, c = 9.374Å, α = β = γ = 90°**. Assuming that you were not able to determine the space group from the diffraction data, leave the space group setting to P1 (Fig. 48). Afterwards, advance to wizard step 3 (skip step 2 since no molecules are present in the compound).

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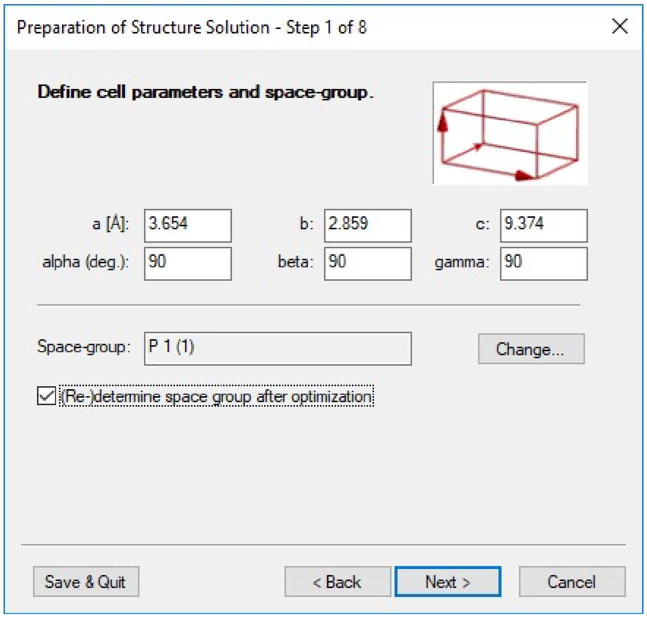
[34] The Hofmann potential which is also available in wizard step 5 is dedicated basically to organic molecules and does quite often (as in this case) not contain potential parameters for inorganic compounds.



Preparation of Structure Solution - Step 1 of 8

Define cell parameters and space-group.

a [Å]: 3.654 b: 2.859 c: 9.374

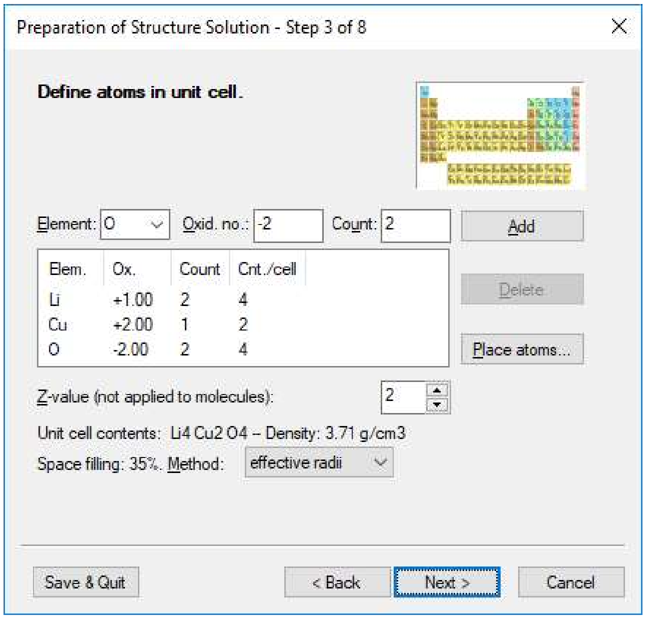
alpha (deg.): 90 beta: 90 gamma: 90

Space-group: P 1 (1)

☑ (Re-)determine space group after optimization

Fig. 48: Setting of unit cell parameters for Li_2CuO_2; the space group is unknown

Please enter the composition (2 Li^{1+}, 1 Cu^{2+}, 2 O^{2-}) and adjust Z so that an experimental density of 3.6 g/cm^3 is matched as close as possible (if you are not sure about it: Z=2 is correct). Please make sure that your dialog looks similar to Fig. \ref{li2cuo2_filledwizp3} and proceed to wizard step 4 afterwards.



Preparation of Structure Solution - Step 3 of 8

Define atoms in unit cell.

Element: O Oxid. no.: -2 Count: 2

Elem.	Ox.	Count	Cnt./cell
Li	+1.00	2	4
Cu	+2.00	1	2
O	-2.00	2	4

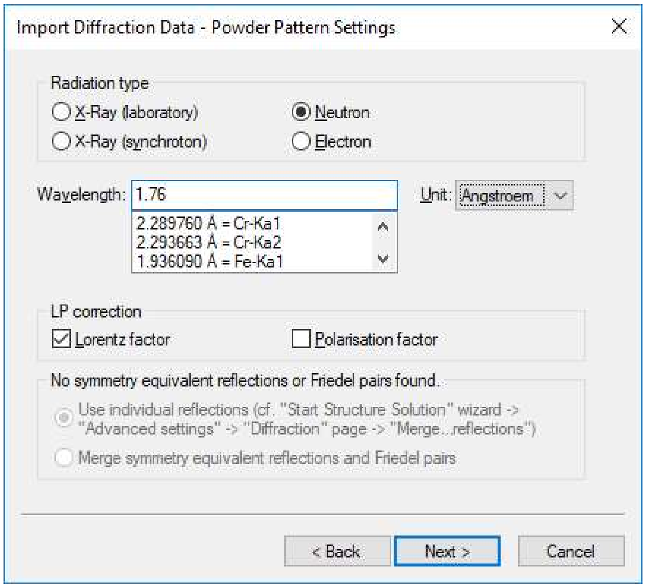
Z-value (not applied to molecules): 2

Unit cell contents: Li4 Cu2 O4 – Density: 3.71 g/cm3

Space filling: 35%. Method: effective radii

Fig. 49: Unit cell contents of Li_2CuO_2

Now, load the diffraction data for Li_2CuO_2 (li2cuo2.dif) from the directory "Examples$\Li2CuO2" in your Endeavour program directory. The data are 2θ versus intensity as usual, however, neutron radiation of wavelength 1.76 Å has been used in the diffraction experiment this time, so please make the appropriate settings in the "Powder Pattern Settings" dialog (Fig. 50).



Import Diffraction Data - Powder Pattern Settings

Radiation type
○ X-Ray (laboratory) ● Neutron
○ X-Ray (synchroton) ○ Electron

Wavelength: 1.76 Unit: Angstroem

2.289760 Å = Cr-Ka1
2.293663 Å = Cr-Ka2
1.936090 Å = Fe-Ka1

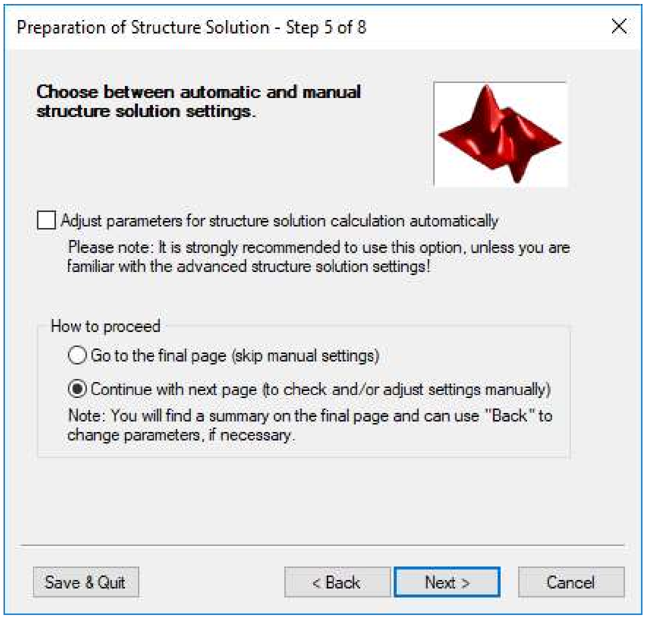
LP correction
☑ Lorentz factor ☐ Polarisation factor

No symmetry equivalent reflections or Friedel pairs found.
● Use individual reflections (cf. "Start Structure Solution" wizard -> "Advanced settings" -> "Diffraction" page -> "Merge...reflections")
○ Merge symmetry equivalent reflections and Friedel pairs

Fig. 50: Powder pattern settings for Li_2CuO_2: Neutron radiation of wavelength 1.76 Å has been used in the experiment.

If everything is correct, please press “Next”. Make sure that “Apply automatic zero-point correction”" is marked on the next page, then press “Next” again. Accept the automatic zero-point correction by clicking “OK”, then press “Finish”. Finally, please advance to step 5 by pressing “Next”.

In contrast to all previous examples, we will not use the “automatic adjustment of optimization parameters” option, due to the fact that we would like to apply a special fine-tuned Lennard-Jones potential, so please deactivate the option “Adjust parameters for structure solution automatically”. Afterwards, mark the option “Continue with next page” under “How to proceed”, and verify that your dialog looks like Fig. 51fig. 54, then advance to wizard step 6 by pressing “Next”.



Preparation of Structure Solution - Step 5 of 8

Choose between automatic and manual structure solution settings.

☐ Adjust parameters for structure solution calculation automatically

Please note: It is strongly recommended to use this option, unless you are familiar with the advanced structure solution settings!

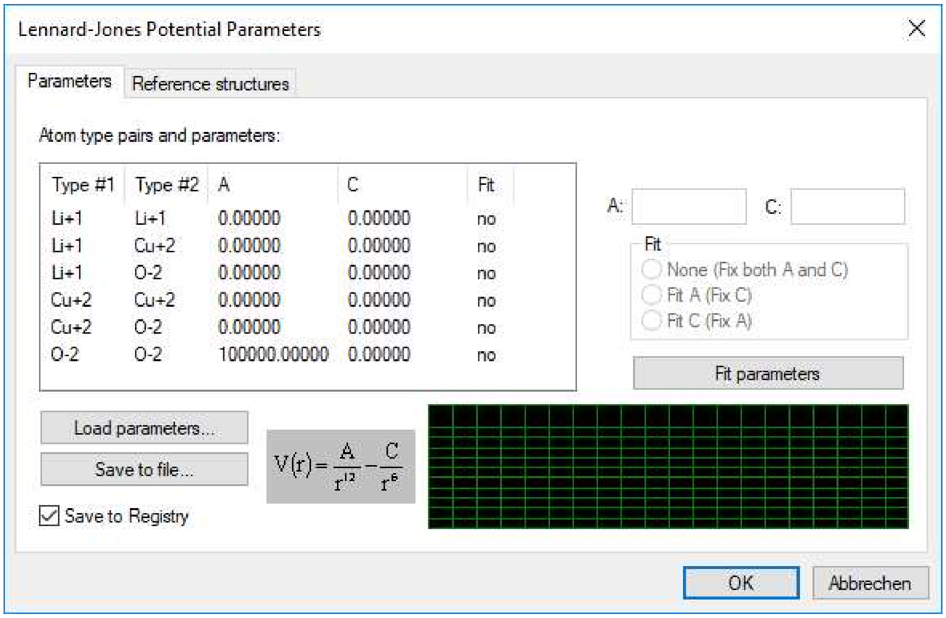
How to proceed
○ Go to the final page (skip manual settings)
● Continue with next page (to check and/or adjust settings manually)

Note: You will find a summary on the final page and can use "Back" to change parameters, if necessary.

Fig. 51: In contrast to all previous sessions, we do not want Endeavour to adjust all optimization parameters automatically.

As has been mentioned, we would like to use the Lennard-Jones potential. This potential uses some parameters that can be used to “fine-tune” the numerical description of the interatomic interactions, so that the potential energy is typically more accurate compared to the simple repulsion potential. The drawback is that you have to “fit” appropriate parameters to similar structures. This is a little bit more complicated than using the charged simple repulsion potential, however, the Lennard-Jones potential may be more accurate in certain cases, so it is good to know how to use it if you run into problems solving your own crystal structures later.

Please select “Lennard-Jones potential” on wizard step 6. The “traffic light” may be now be green or red, depending on if someone performed this calculation earlier on your computer (and so the appropriate parameters are already present in the program's database) or not. In any case, we will perform the parameter fit, so please select “Edit parameters...” which will bring up the Lennard-Jones potential parameters dialog (Fig. 52).



Atom type pairs and parameters:

Type #1	Type #2	A	C	Fit
Li+1	Li+1	0.00000	0.00000	no
Li+1	Cu+2	0.00000	0.00000	no
Li+1	O-2	0.00000	0.00000	no
Cu+2	Cu+2	0.00000	0.00000	no
Cu+2	O-2	0.00000	0.00000	no
O-2	O-2	100000.00000	0.00000	no

☑ Save to Registry

Fig. 52: The Lennard-Jones potential parameters fitting dialog

Before we can describe the further steps, it is necessary to have a little bit of background knowledge:

The Lennard-Jones potential (which in fact is used together with the Coulomb potential for charged atoms) needs 2 parameters for each possible atom-type pair (A and C). You can guess their influence from the formula of the potential:

$$V(r) = \frac{A}{r^{12}} - \frac{C}{r^6} \tag{1}$$

The larger the parameter A, the larger the value of the potential V (assuming that the distance between the two atoms r is unchanged). Thus, the parameter A describes how fast the value of the potential V should increase with decreasing interatomic distance r, or, in other words, A parametrizes the repulsion between two atoms. From similar considerations it can be deduced that C, on the other hand, is dedicated to the attractive interaction between two atoms (which in fact is the dispersion interaction due to induced dipole -induced dipole interactions of the atom's electrons).

In order to obtain values for these parameters A and C for each possible two-body interaction in the compound, you have to modify them in a way so that the Lennard-Jones potential which uses them reproduces the properties of known compounds as good as possible. This procedure is generally called “fitting of (potential) parameters”.

The fitting of parameters is generally a very difficult task, if you want to obtain a really good potential. A good potential should reproduce a compound's physical properties as realistic as possible, i.e. not only the static properties like crystal structure(s) and polymorphs, but also dynamic properties like vibrational spectra, phonon dispersion etc.

However, if one is not interested in dynamic properties, this task becomes much easier. In this case, it is generally sufficient to fit the potential's parameters such that the crystal structure of a compound is well reproduced. If the structure of the compound is not known as in our case, it is possible (within certain limits) to fit parameters to similar structures and use them in the calculation of the unknown crystal structure of the compound under investigation.

In our case, we will fit the parameters to the known crystal structures of $MgCu_2O_3$ and to the binary compounds Li_2O and MgO, since we assume that the structure of Li_2CuO_2 is not known up to now.

Nevertheless, there are still some important considerations concerning the fit of these parameters A and C:

- It is generally not appropriate to fit both parameters A and C for a selected atom-type pair at the same time. The reason is that these parameters to a certain degree work opposite to each other, since A parametrizes the repulsion and C the attraction. Hence, the system may e.g. increase both parameters at the same time without any significant result.

- Furthermore, all parameters A and C concerning the interaction between two cations are generally set to zero, the only interaction left being the repulsion due to the Coulomb force.

- The fit of parameters for the interaction between two anions (e.g. between O(-2) and O(-2)) is rather difficult; there may be dramatic fluctuations in the values without any reasonable influence on the structure. Hence, these parameters are generally fitted to a large amount of different structures at the same time (e.g. in case of O(-2) to Al_2O_3, MgO, SiO_2, Li_2O...). Afterwards, these values are taken as fixed in further parameter fits.

How does all this apply to our example? Have a look at the Lennard-Jones potential parameters dialog on your screen: The table shows a row for each possible two-body interaction in your compound. In each row, two parameters (A and C) and a “Fit flag” is shown which indicates which of the two parameters (A or C) (if any) should be fitted during the next fitting calculation. If a “?” is displayed in a parameter value field, this parameter has not yet been set up to now, i.e. no appropriate value is present in Endeavour's database.

In agreement to what has been said above, we will use A and C parameters with value 0.0 for all interactions between two cations (Li-Li, Li-Cu and Cu-Cu). Please check all these values and enter 0.0 values wherever necessary.

On the other hand, values of A = 100000.0 and C = 0.0 are shown for the interaction between two O(-2) atoms. These values have shown to be quite reasonable for a large variety of crystal structures and should generally not be changed.

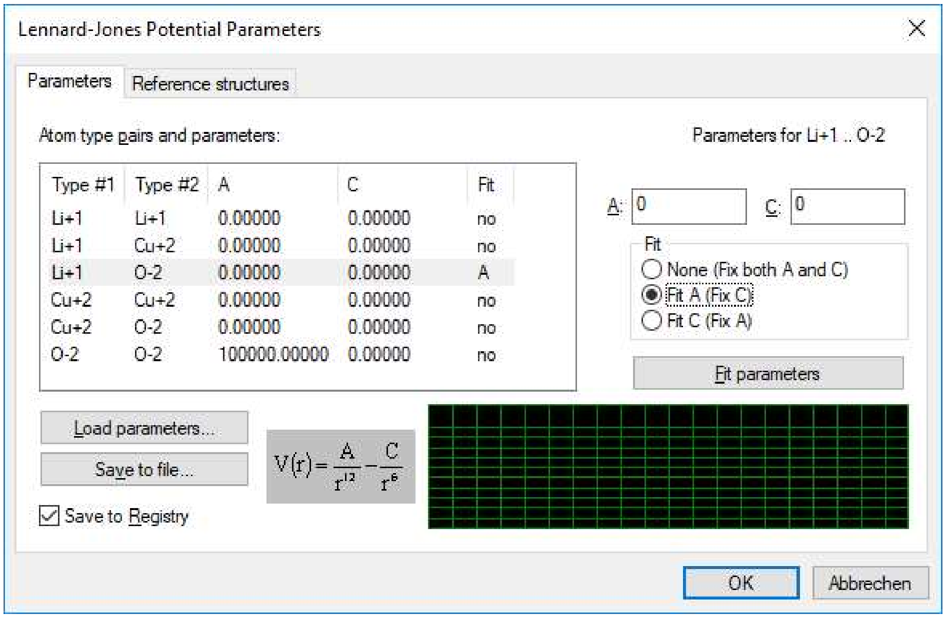
The remaining interactions for which parameters have to be defined are Li+1 - O-2 and Cu+2 - O-2. Since the Coulomb interaction is already attractive in both cases, we will fix the attractive parameters C to 0.0. Thus, at the end, two parameters (A(Li+1 - O-2) and A(Cu+2 - O-2)) have to be fitted to known crystal structures of similar compounds. In our case, we will fit the A(Li-O) parameter to the structure of Li_2O and A(Cu-O) to $MgCu_2O_3$. In the latter case, we also have to provide a parameter for A(Mg+2 - O-2) in order to be able to fit the A(Cu+2 - O-2) parameter in this compound. Hence, we will have to fit A(Mg+2 - O-2) also, which will be done using the crystal structure of the binary phase MgO.

Two important notes must be added before we can actually start the fit:

- You cannot fit parameters to reference structures in space groups other than P1. This is because only the true forces between the atoms (which shall be described by the potential parameters) are important in parameter fitting, not some limitations in space group symmetry which could prohibit distortions of the structure which would possibly occur in P1. Hence, all reference structures must be transformed to P1 for being used in the Lennard-Jones parameters fit. Fortunately, you don't have to worry about this fact using Endeavour, since the program does this automatically for you.

- You cannot fit parameters to very high-symmetric reference structures like Li_2O or MgO. To understand this point, think of the structure of MgO being NaCl type. Every atom is surrounded by six oppositely charged atoms in a perfect octahedron. No matter which parameter values you choose, the interaction to one neighboring atom is always balanced by the one on the opposite side. Mathematically spoken, the first derivation of the potential energy with regard to the central atom's coordinates is zero independent from the parameter values. Or, in other words, you can take any parameter value you like; there is no influence on the reference structure. These parameters have no practical value: If they are used in a less symmetric environment, they will most probably give a completely wrong structure. To deal with this problem, you should first transform the high-symmetric structure to P1 by loading the reference structure as a new document in Endeavour and executing the “Transform to P1” command from the “Structure” menu. Afterwards, you have to perform small changes on the atomic coordinates (which can be accessed in the dialog called by the “Atomic parameters” command in the “Structure” menu, too). If an atom's coordinates are e.g. (0.5,0.5,0.5), you should change them to something like (0.49,0.46,0.53). Once you have done this for all atoms in the unit cell, save the “distorted” reference structure using a new filename. In general, you have to think about these things, however, for this tutorial, you don't have to care about it. We have already prepared the corresponding distorted reference structures for you.

Now that you have some theoretical background we can actually get things running. Let's start with A(Li-O): Mark the corresponding line in the parameter table and select "Fit A (Fix C)" in the "Fit" box to the right of the table. Besides this, enter a starting value of 0.0 for "A", replacing any prior value which might be present. For "C", you should enter 0.0 according to what has been said. Your dialog should now look like Fig. 53.



Atom type pairs and parameters:

Type #1	Type #2	A	C	Fit
Li+1	Li+1	0.00000	0.00000	no
Li+1	Cu+2	0.00000	0.00000	no
Li+1	O-2	0.00000	0.00000	A
Cu+2	Cu+2	0.00000	0.00000	no
Cu+2	O-2	0.00000	0.00000	no
O-2	O-2	100000.00000	0.00000	no

Parameters for Li+1 .. O-2

A: 0 C: 0

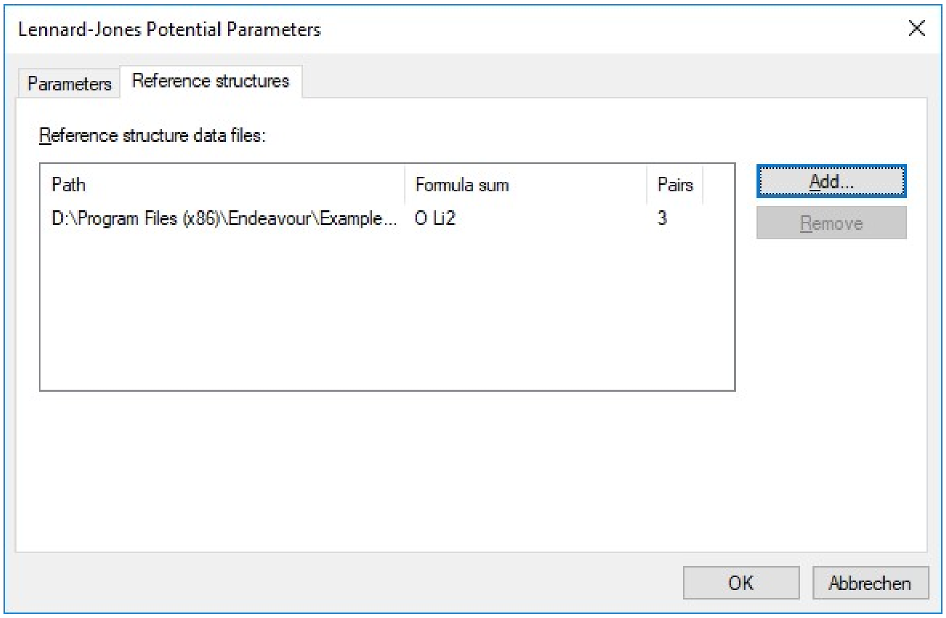
Fit
○ None (Fix both A and C)
● Fit A (Fix C)
○ Fit C (Fix A)

☑ Save to Registry

$$V(r) = \frac{A}{r^{12}} - \frac{C}{r^6}$$

Fig. 53: LJ-parameter fitting dialog: The repulsion parameter (A) between Li and O shall be fitted.

Before you can start the actual fit, you have to provide the (distorted!) crystal structure of Li_2O in an appropriate file format. In our case, the structure is given in the file "li2o_p1_distorted.cif" in the "Examples\Li2CuO2" directory of your Endeavour installation. Please select the register card "Reference structure" in the background of the dialog, press "Add..." and select the file mentioned above in the file dialog. (Be sure that "CIF (*.CIF)" or "All files (*.*)" is selected for file type). Please check that your dialog corresponds to Fig. 54.

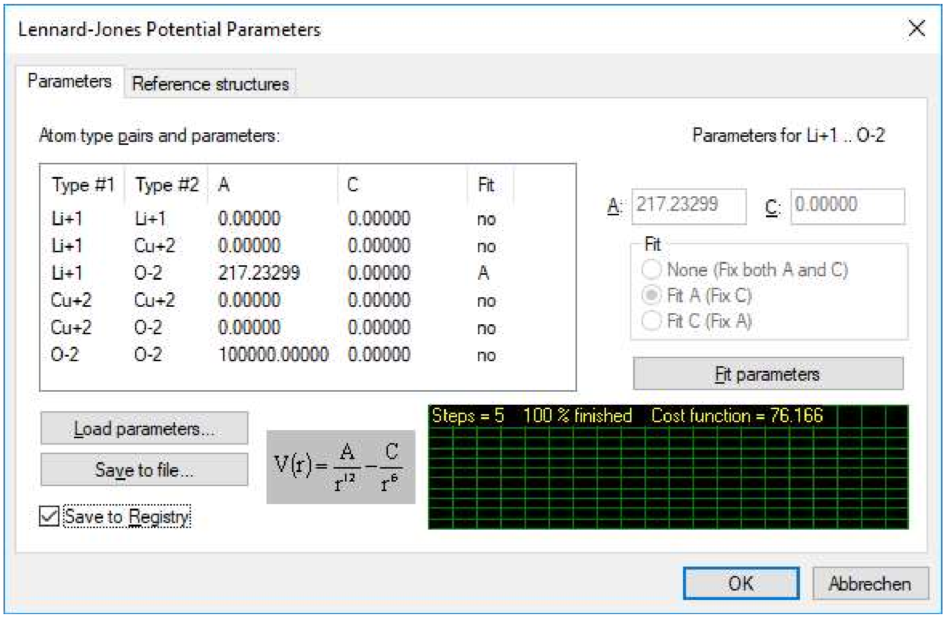


Reference structure data files:

Path	Formula sum	Pairs
D:\Program Files (x86)\Endeavour\Example...	O Li2	3

Fig. 54: The selected parameters shall be fitted with regard to the crystal structure of Li_2O.

Return to the "Parameters" register of the dialog, then start the actual parameter fit by clicking "Fit parameters" to the right of the parameter table. During the calculation, the progress of the cost function (which describes the agreement between the correct crystal structure and the one calculated using the current parameter values) is displayed in the corresponding box to the right of your dialog (Fig. 55).



Atom type pairs and parameters:

Type #1	Type #2	A	C	Fit
Li+1	Li+1	0.00000	0.00000	no
Li+1	Cu+2	0.00000	0.00000	no
Li+1	O-2	217.23299	0.00000	A
Cu+2	Cu+2	0.00000	0.00000	no
Cu+2	O-2	0.00000	0.00000	no
O-2	O-2	100000.00000	0.00000	no

Parameters for Li+1 .. O-2

A: 217.23299 C: 0.00000

Fit
○ None (Fix both A and C)
● Fit A (Fix C)
○ Fit C (Fix A)

$$V(r) = \frac{A}{r^{12}} - \frac{C}{r^{6}}$$

Steps = 5 100 % finished Cost function = 76.166

☑ Save to Registry

Fig. 55: The fitting of the LJ repulsion parameter for Li-O has been started.

After a few seconds, the calculation has finished. The value of the parameter A for the Li-O interaction has changed to a value like 217.0.

Finally, mark the Li-O parameter line and select “None” from the “Fit” box to the right, indicating that this parameter should not be fitted in the next calculation. Then, switch to the “Reference Structures” page and delete the Li_2O structure, by selecting the line and pressing “Remove” to the right of the dialog.

Afterwards, you have to perform the same steps as for A(Li+1 - O-2) for the parameter A(Cu+2 - O-2). However, in this case the reference structure $MgCu_2O_3$ contains an additional cation-anion interaction for which a parameter A(Mg+2 - O-2) must be known. Hence, we first have to find a suitable parameter for this interaction before we can proceed with the A(Cu+2 - O-2) parameter fit.

On the “Reference Structures” page, please load the distorted MgO structure from the file “mgo_p1_distorted.cif” from the same directory as the distorted Li_2O structure. Afterwards, switch to the “Parameters” page of the dialog, select the line “Mg+2 - O-2”, and set the corresponding parameter A to 0.0. Select “Fit A (Fix C)”, then press the “Fit parameters” button. The parameter A(Mg+2 - O-2) in the table will have changed to about 1756.0.

Once this parameter value has been calculated, you have to tidy up again: Select “None” for the current atom type pair “Mg+2 - O-2” in the “Fit” group box to the right of the dialog, then switch to the “Reference Structures” page and delete the distorted MgO-structure from the list as has been described above.

Now you can finally fit the A(Cu+2 - O-2) parameter to the structure of $MgCu_2O_3$: Load the file “mgcu2o3.cif” on the “Reference Structures” page, then switch back to the “Parameters” page and select the line “Cu+2 - O-2”. Afterwards, set the A(Cu+2 - O-2) parameter to 0.0, select “Fit A (Fix C)” from the “Fit” group box and start the fitting by pressing the “Fit parameters” button. Once the fitting calculation has finished, the A(Cu+2 - O-2) parameter will have changed to about 2420.0.

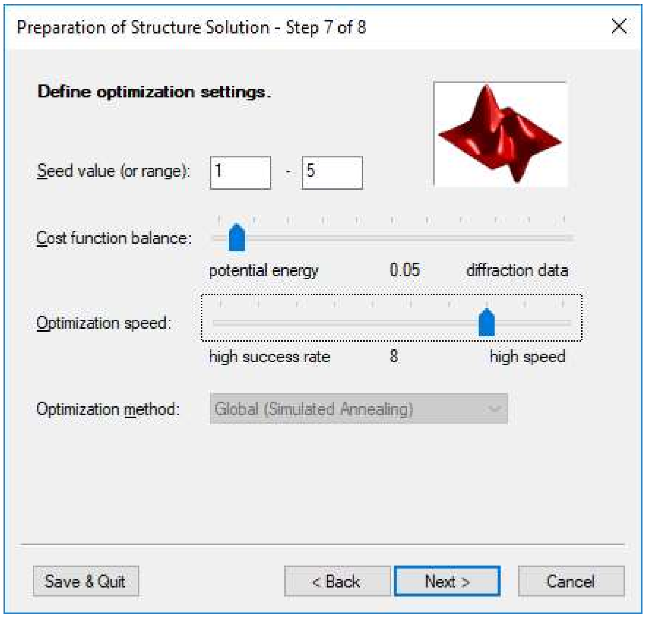
At this stage, all parameters necessary for the structure solution of Li_2CuO_2 are present. Tidy up as above, make sure that “Save to Registry” is checked on the lower left hand side of the dialog (in order to store the newly fitted parameters in Endeavour's internal database) and press “OK” to return to wizard step 6. Afterwards, advance to step 7 by pressing “Next”.

Like in the electron diffraction example, we will now change some optimization parameters to best match our structure solution problem: First, please enter the seed values “1” to “5” in the corresponding fields to the right of “Seed value (or range)”, in order to perform 5 structure solution calculations with different random number sequences.

As has already been mentioned, the intensities of the diffraction data are not overly good, so it might be a good idea to balance the relatively low-quality diffraction data by a good potential (the charged simple repulsion or Lennard-

Jones potential) with a larger influence on the overall cost function than the diffraction data. Hence, please pull the "Cost function balance" slider to the left (to the side in favor of the potential energy), and adjust it to a value of 0.05.

Besides this, the optimization should not be run at highest speed, so please reduce the optimization speed a little bit, by adjusting the "Optimization speed" slider to a value of 8. Your wizard page should now look similar to Fig. 56.



Preparation of Structure Solution - Step 7 of 8

Define optimization settings.

Seed value (or range): 1 - 5

Cost function balance: 0.05

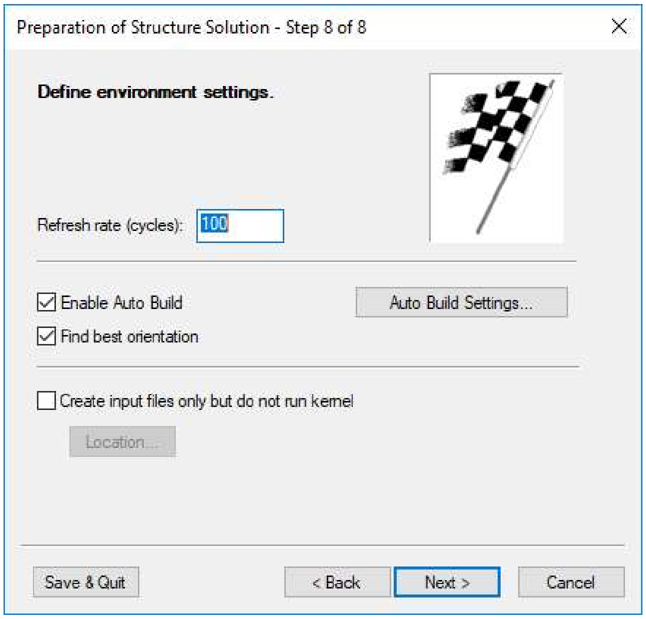
Optimization speed: 8

Optimization method: Global (Simulated Annealing)

Fig. 56: The cost function balance has been reduced to increase the contribution of the potential energy in the overall cost function. Besides this, the calculation speed has been reduced a little bit to perform a gentler and more cautious optimization.

Afterwards, proceed to step 8. While we started the structure solution calculations right away in the previous sessions, without taking care of how the intermediate crystal structures are displayed, we now want to adapt the called "Auto Builder" in order to display the structure the way we like (in this case to avoid the displaying of polyhedra).

Please make sure that "Enable Auto Build" is checked on the left hand side of the dialog (Fig. 57), then press "Auto Build Settings..." which will bring up the Auto Builder dialog



Preparation of Structure Solution - Step 8 of 8

Define environment settings.

Refresh rate (cycles): 100

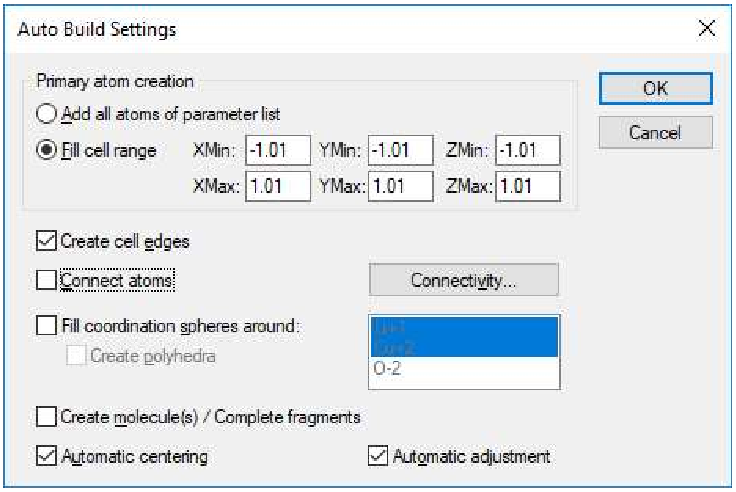
☑ Enable Auto Build

☑ Find best orientation

☐ Create input files only but do not run kernel

Fig. 57: Please verify that "Enable Auto Build" is checked on step 8 of the structure solution wizard.

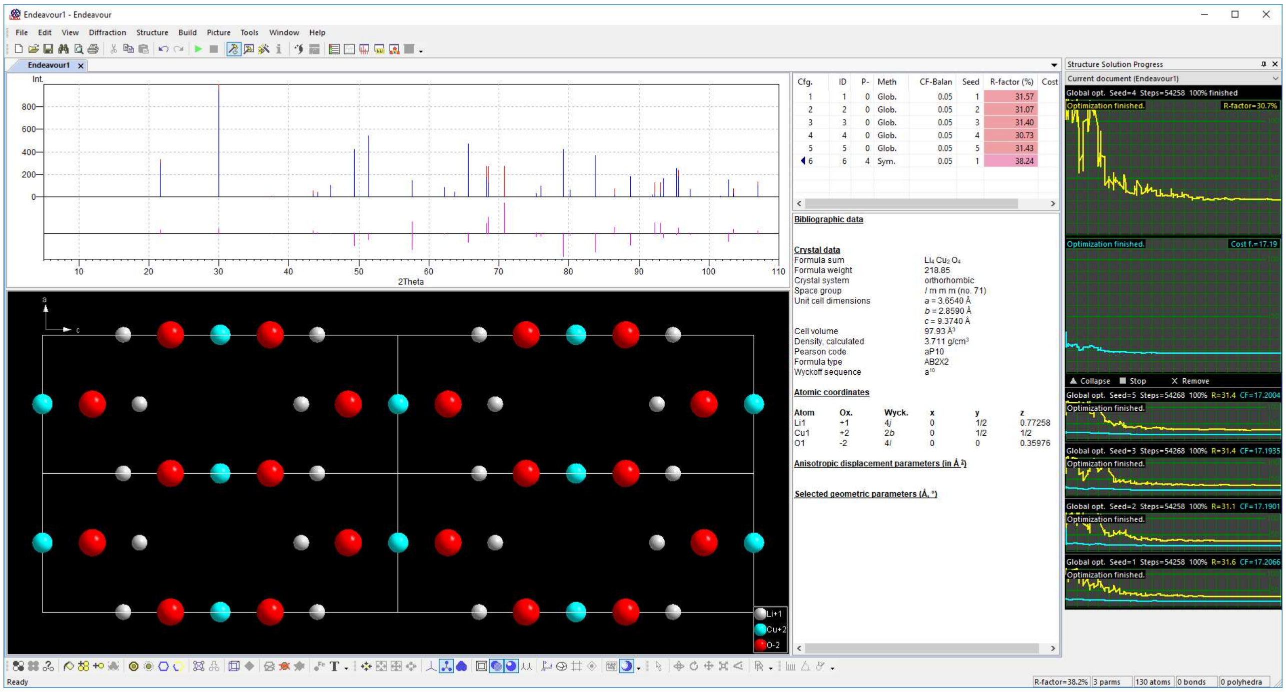
In this dialog you see a variety of options which you might already have used for a conventional display of a crystal structure (e.g. using **Diamond**). In our case, we want to fill two unit cells in each direction which is the default setting (check the “Primary atom creation” field at the top of the dialog where “Fill cell range” should be selected with appropriate values for Xmin, Xmax,...). Besides this, we do not want to fill any coordination spheres or draw polyhedra, so please disable (remove the hook) for “Fill coordination spheres around”. Check that all Auto Build settings are adjusted according to Fig. 58, then press “OK”.



Primary atom creation
○ Add all atoms of parameter list
● Fill cell range XMin: -1.01 YMin: -1.01 ZMin: -1.01
XMax: 1.01 YMax: 1.01 ZMax: 1.01
☑ Create cell edges
☐ Connect atoms
☐ Fill coordination spheres around: Li+1, Cu+2, O-2
☐ Create polyhedra
☐ Create molecule(s) / Complete fragments
☑ Automatic centering
☑ Automatic adjustment

Fig. 58: Auto Builder: Only single atoms shall be drawn.

Once you have returned to wizard page 8, please press “Next” to advance to the final page (on which the summary is displayed), then start the calculation (click “Start”). The result will look similar to Fig. 59.



Cfg.	ID	P-	Meth	CF-Balan	Seed	R-factor (%)	Cost
1	1	0	Glob.	0.05	1	31.57	
2	2	0	Glob.	0.05	2	31.07	
3	3	0	Glob.	0.05	3	31.40	
4	4	0	Glob.	0.05	4	30.73	
5	5	0	Glob.	0.05	5	31.43	
6	6	4	Sym.	0.05	1	38.24	

Bibliographic data

Crystal data

Formula sum	$Li_4 Cu_2 O_4$
Formula weight	218.85
Crystal system	orthorhombic
Space group	*I* m m m (no. 71)
Unit cell dimensions	*a* = 3.6540 Å *b* = 2.8590 Å *c* = 9.3740 Å
Cell volume	97.93 Å^3
Density, calculated	3.711 g/cm^3
Pearson code	aP10
Formula type	AB2X2
Wyckoff sequence	a^{10}

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Li1	+1	4*j*	0	1/2	0.77258
Cu1	+2	2*b*	0	1/2	1/2
O1	-2	4*i*	0	0	0.35976

Anisotropic displacement parameters (in Å^2)

Selected geometric parameters (Å, °)

Global opt. Seed=4 Steps=54258 100% finished
Optimization finished. R-factor=30.7%
Optimization finished. Cost f.=17.19
Global opt. Seed=5 Steps=54268 100% R=31.4 CF=17.2004
Optimization finished.
Global opt. Seed=3 Steps=54268 100% R=31.4 CF=17.1935
Optimization finished.
Global opt. Seed=2 Steps=54258 100% R=31.1 CF=17.1901
Optimization finished.
Global opt. Seed=1 Steps=54258 100% R=31.6 CF=17.2066
Optimization finished.

R-factor=38.2% | 3 parms | 130 atoms | 0 bonds | 0 polyhedra

Fig. 59: The structure solution calculation for Li_2CuO_2 has been finished.

As you see in the data sheet to the right of the structure picture, the space group Immm has been determined automatically from the triclinic structural model resulting from the structure solution calculation; there are only 3 atoms left in the asymmetric unit.

Note that the R-factor of the structure in the correct space group Immm is about 38-39% (displayed e.g. in the status line at the bottom of Fig. 59), while the R-factor of the preceding structure solution in P1 was about 31%. The R-factor of the distorted structure in P1 is smaller than the one of the perfect structure in space group Immm, a clear hint (apart from the absolute height of the R-factors) that the intensities of the diffraction data are not too good (as has already been mentioned at the beginning of this tutorial session).

If you are interested in more details concerning the structure solution calculation, you should take a look at the so-called "Results Report". As you might know, Endeavour consists of a graphical Windows user interface and a calculation kernel which basically performs the actual structure solution calculation. The output of this calculation kernel is displayed as the "Results Report".

Please click on the appropriate button ▤ in the toolbar or select "Results Report" from the "View" menu. The output will be displayed in the textual part to the right of the structure picture.

If you have followed the instructions above, the results report will display the result of the cost function calculation after the space group has been transformed to Immm. In order to view the result of a global optimization calculation, simply mark one of the configurations 1-5 in the "Configuration list" at the top. Afterwards, scroll down the results report and examine what has been written by the Endeavour kernel. Most of the output are just diffraction data or parameter settings; the actual calculation protocol are the lines after "`Global Optimization`".

Structure visualization

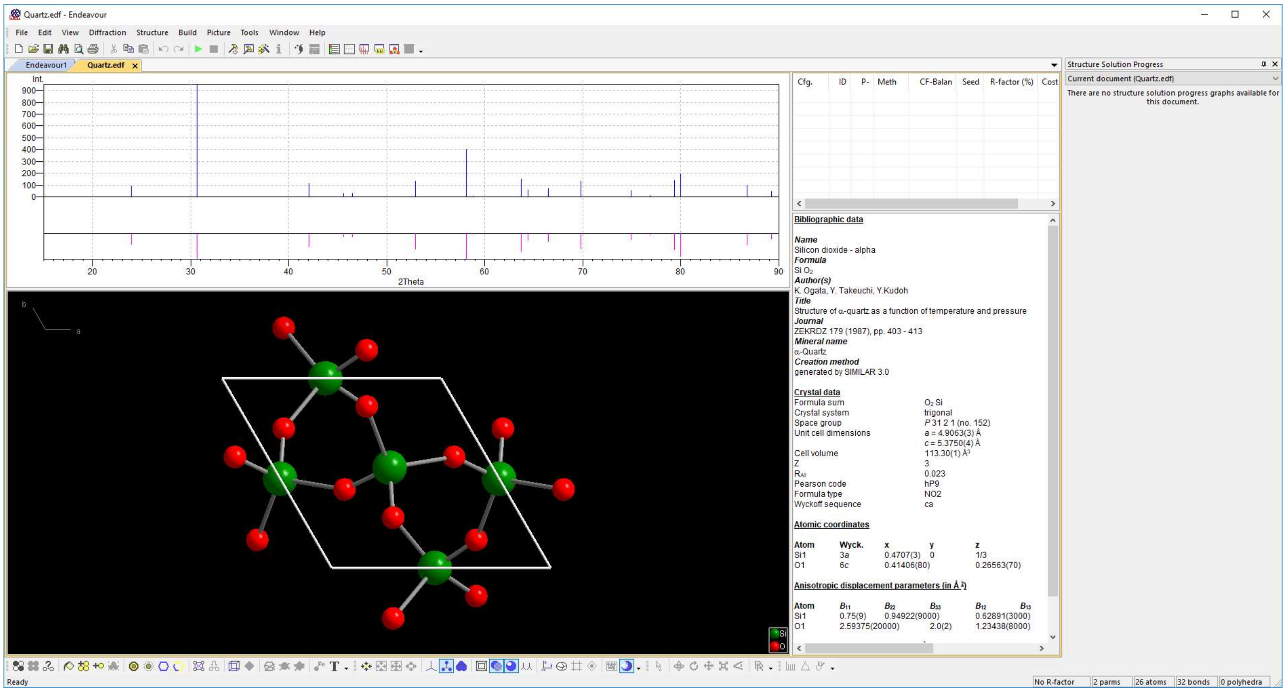
In addition to its structure solution capabilities, Endeavour also provides some basic functionality for crystal structure visualization. This can be used both for viewing the intermediate structures during the structure solution calculation ("Auto Builder") as well as for investigating and checking the resulting crystal structures.

In this session you will learn:
- How to **read structure files** which have been edited by Endeavour.
- How the contents of the **structure window** is arranged and where to find which information about the structure.
- How to **change the orientation** of the structure model.
- Which **variations of representations** Endeavour can use to display a structure.

In the **first step** you will learn the basics of handling with the help of a prepared structure file. You will be told how to bring the expected structural part into the right position. In the **second step** you will get to know Endeavour's several potentialities to represent a structure.

Open file

Click on the "Open" button in the standard toolbar. Choose the directory "Examples\Tutorial" in the directory where you have installed Endeavour, and then double-click on the file with name "Quartz.edf" (Fig. 60).



Structure Solution Progress

Current document (Quartz.edf)

There are no structure solution progress graphs available for this document.

Bibliographic data

Name
Silicon dioxide - alpha
Formula
Si O_2
Author(s)
K. Ogata, Y. Takeuchi, Y.Kudoh
Title
Structure of α-quartz as a function of temperature and pressure
Journal
ZEKRDZ 179 (1987), pp. 403 - 413
Mineral name
α-Quartz
Creation method
generated by SIMILAR 3.0

Crystal data

Formula sum	O_2 Si
Crystal system	trigonal
Space group	*P* 31 2 1 (no. 152)
Unit cell dimensions	*a* = 4.9063(3) Å *c* = 5.3750(4) Å
Cell volume	113.30(1) Å^3
Z	3
R_{All}	0.023
Pearson code	hP9
Formula type	NO2
Wyckoff sequence	ca

Atomic coordinates

Atom	Wyck.	x	y	z
Si1	3*a*	0.4707(3)	0	1/3
O1	6*c*	0.41406(80)		0.26563(70)

Anisotropic displacement parameters (in Å^2)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}
Si1	0.75(9)	0.94922(9000)		0.62891(3000)	
O1	2.59375(20000)		2.0(2)	1.23438(8000)	

Ready | No R-factor | 2 parms | 26 atoms | 32 bonds | 0 polyhedra

Fig. 60: The sample file Quartz.edf has been loaded.

In the upper left area of the window, you will find the powder diffraction pattern (which has automatically been calculated from the crystal structure data); the structure picture is by default displayed on the lower left hand side, whereas textual information is provided in the right area. This is by default the so-called data sheet where the crystal structure data can be viewed, but there may also be a table of atoms, bonds, or other objects instead. You can shift the borders (the so-called "splitters") between these areas with the mouse.

Rotating and shifting the structure

- Click on the "Rotation X/Y" button ✥. The mouse cursor will change its standard arrow symbol. If you now press down the left mouse button and move the mouse with left button down, the structure will rotate corresponding to the movement along x- and y-axis. (Both axes are located in the screen area. The x-axis points toward right, the y-axis up.)

- Click on the “Rotation Z” button . Like for the rotation along x- and y-axis, you can now rotate the structure along the z-axis. (The z-axis is perpendicular to the screen and points towards you.)

- Click on the “Shift” button . Now you can shift the structure within the window, while the left mouse button is pressed down.

- Now click again on the “Rotation X/Y” button. You will notice that the structure does not rotate along the center of picture but along its center of gravity.

- Click on the “End Tracking Mode” button to return to the normal mode. Instead you can press the <Escape> key on your keyboard.

Moving the center of rotation

- Select the uppermost Si atom by clicking on it with the mouse. Then click on the “Center of rotation” button Endeavour will move the center of rotation to the position of the selected atom.

- Click on the “Rotation X/Y” button . Now the structure can be rotated along the new center of rotation.

- Click on the “End tracking mode” button to return to the normal mode.

- Now select two neighboring Si atoms, by clicking on the atoms one after the other with the <Shift> key pressed down. Then click on the “Center of rotation” button . Endeavour puts the center of rotation into the center of both selected atoms.

- Now click again on the “Rotation X/Y” button . The structure can now be rotated along the new center of rotation.

Changing enlargement factor

Click on the “Enlargement factor” button . Again, the mouse cursor will change its symbol. With left mouse button pressed down, the enlargement factor can now be varied by moving the mouse.

If you want to enlarge a **detail** of the structure picture, click on the “**Zoom**” button , and then, with left mouse button pressed down, draw up a frame around the detail of interest. After you have released the left mouse button, Endeavour enlarges the detail to fill out the entire structure window.

You can use the “Center+Adjust” button to adjust the enlargement factor so that the entire structure picture fits into the structure window. This function also moves the center of rotation into the center of the structure. This function can also be called using the <F9> key.

Models for structure visualization

To visualize a three-dimensional chemical structure, various models have proved successful:

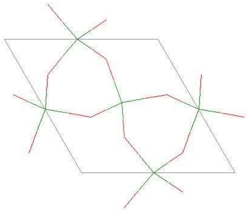
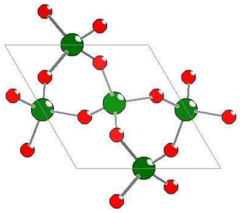
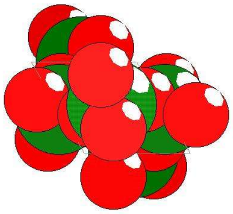
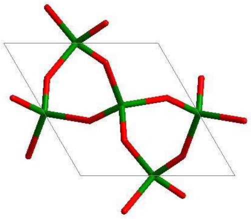
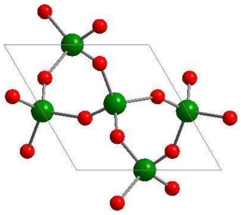
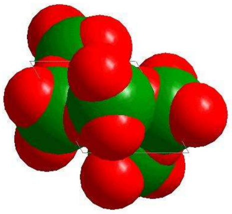
The **wire model** displays only the bonds that are defined in the structure, while the atoms are represented by the terminal points of the bonds. This model requires defined bonds, a condition that is often not fulfilled, especially in inorganic compounds. It allows a very good overview on the bonding geometry and is the method of choice for molecular structures, but the space filling of a structure cannot be represented.

In the **ball-and-stick model** atoms are represented as spheres, and bonds are drawn as sticks or lines. This is the standard model of Endeavour. By variation of the atomic radii an optimal overview on geometric relationships can be adjusted as well as on space filling aspects.

The **space-filling model** does not show any bonds but atoms only, where van-der-Waals radii are used so that the spheres touch or interpenetrate. This model allows a good impression of the space filling aspects of the structure, whereas constitutions and coordination relationships are difficult to recognize.

All mentioned models can be displayed either **flat** or **rendered**. The rendered mode offers a more realistic representation, while the flat mode works significantly faster, especially when rotating the structure.

Table 1: Quartz structure in wire, ball-and-stick and space-filling model, each in flat (above) and rendered mode (below).

	Wireframe model	Ball-and-stick model	Space filling model
			
☽			

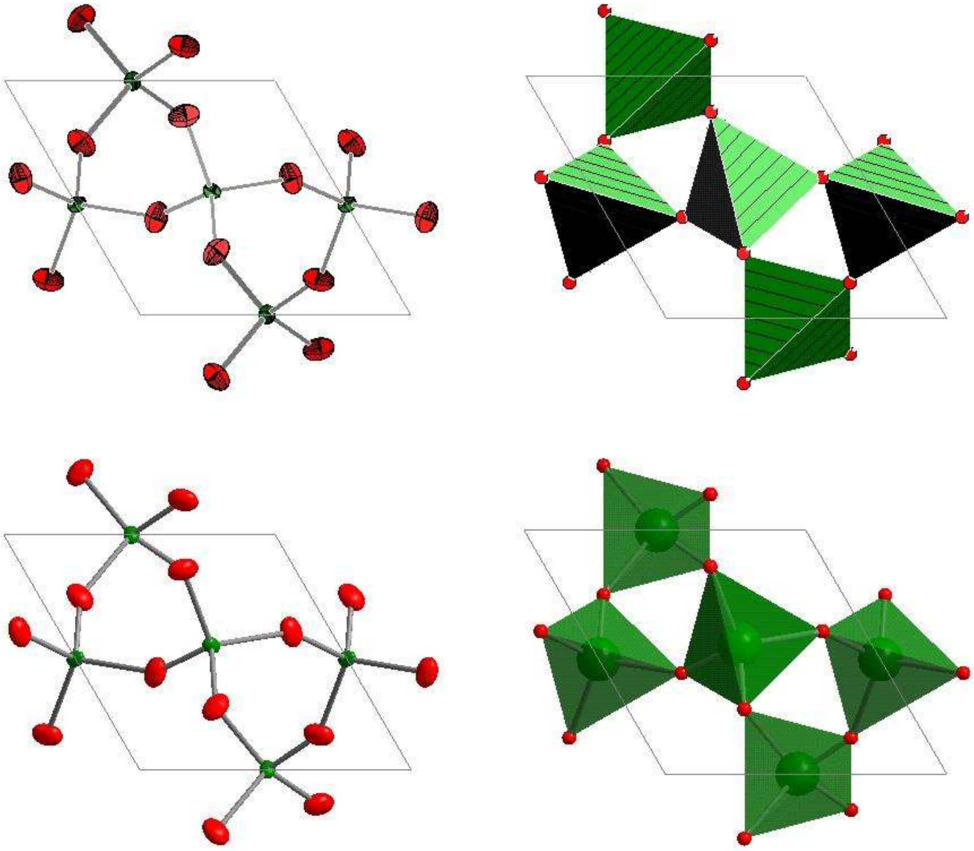
Thermal ellipsoids and Coordination Polyhedra

A special variant of the ball-and-stick model are the so-called **thermal ellipsoids**. They represent the displacement of the atoms caused by thermal vibrations. Therefore, information from the so-called ***anisotropic displacement parameters*** are needed which can generally only be derived from single crystal diffraction data.

Coordination polyhedra can be used to characterize the atoms' neighborhood. Therefore, local coordination} is symbolized by geometric polyhedra, whose orientation to each other may represent higher coordination. Like for thermal ellipsoids, coordination polyhedra are a variation of the ball-and-stick model in Endeavour. To select coordination polyhedra, select the corresponding central atom, and then click on the "Add polyhedra" button.

Table 2: Quartz structure with thermal ellipsoids and polyhedra, both in flat and rendered mode.

	Thermal ellipsoids	Polyhedra



Perspective

Normally Endeavour displays structures using the so-called **parallel projection**. That means looking at the structure from infinite distance and can be compared with observing a faraway object using binoculars. Thus, parallel projection leads to a parallel display of parallel lines.

But in fact, nobody does permanently observe his environment with a binocular. The natural way means a “real” distance from the observed object and is better described with the so-called **central projection**. This projection leads to a non-parallel display of parallel lines, which makes it difficult to understand the geometrical relationships.

Endeavour supports both ways of projection and allows a comfortable switching between them using the shown button ▣.

Stereoscopic projection

A real 3-dimensional impression is obtained by a **stereoscopic projection**. Therefore, the structure is drawn twice side-by-side, where each is rotated before around the y-axis of the view

coordinate system for the **stereo angle** (the left picture in positive direction, the right picture in negative direction) (Fig. 61).

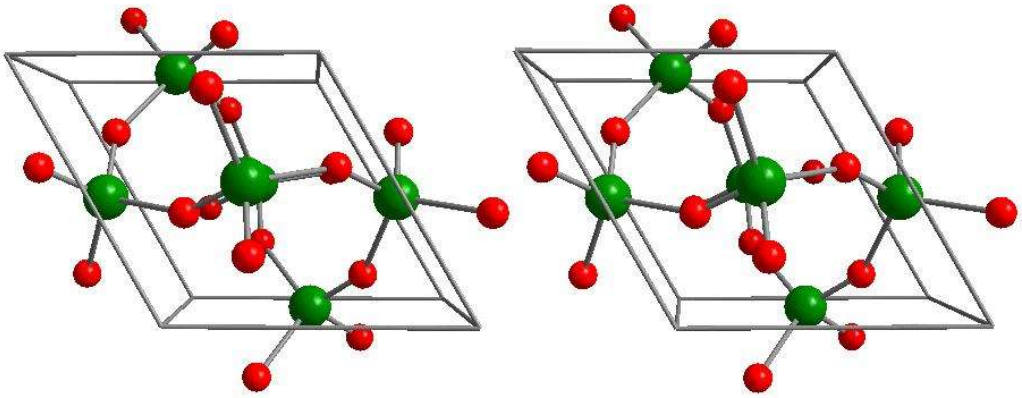


Fig. 61: Stereoscopic projection of the quartz structure

Some principles on building of structure pictures

Automatic vs. manual building

When you create ("build up") a structure picture from structural parameters, Endeavour offers two different strategies, the first one being called "automatic building", the second one "manual building".

Automatic building is a kind of script or template that automatically creates a picture from a set of structural parameters (cell, space group and atomic positions), e.g.

Generate all atoms with crystal coordinates between xmin=.... and zmax=...: Then generate all O atoms around Si atoms within a coordination sphere of rmax=... Angstroems and create polyhedra.

The great advantage of this kind of building is that it can be easily applied to heavily changing structural parameters, e.g. during a structure solution process, where the atoms are hurled violently by the area.

Manual building means a kind of creating a model from a basic set of structural parameters. You can choose from a variety of tools to generate atoms, bonds, polyhedra, labels, etc., which may be rather raw like the above-mentioned generation of atoms within a parallelepiped but may also be highly individual, e.g. by clicking on one of thousands of atoms in a structure picture you can change color, pattern or you can delete it. The disadvantage of that kind of building is that it relies on fixed structural parameters. If you have manually created a structure picture with several bonds, coordination polyhedra, individual colors, etc. and then change the coordinates of one atom of the parameter list, this causes distortions within the structure picture. The symmetry-equivalent atoms are shifted and bonds with these atoms as origin are stretched or tossed; the same is for coordination polyhedra.

You can find commands for both automatic and manual building in the "Build" menu. The settings for automatic building are comprised in the dialog box that is opened from the "Settings..." command of the "Auto Build" submenu of the "Build" menu. Automatic building is switched on or off with the "Active" command in the same submenu. Switching off automatic building means activation of manual building and vice versa. The commands in the "Build" menu below the "Auto Build" submenu do all apply to manual building.

Table 3 compares how functions differ in automatic and manual building (commands refer to the "Build" menu).

Table 3: Automatic vs. manual building

Function	Automatic building	Manual building
Filling of a cell range	by definition of a parallelepiped with boundaries in crystal coordinates (xmin, ymin,...,zmax)	by definition of a parallelepiped with boundaries in crystal or cartesian coordinates. Also available: definition of boxes or spheres around selected atoms of the parameter list; user-defined rectangle with given depth (in Å) within the current structure picture.

Function	Automatic building	Manual building
		(See commands in the "Fill" submenu.).
Direct generation of atoms of the parameter list	All atoms of the parameter list can be created directly without application of symmetry operations	All or selected atoms of the parameter list can be created, with or without application of symmetry operations. (See commands "Add All Atoms" and "Add Atoms...", rsp.)
Creation of cell edges	Can be created automatically, if using the "fill cell range" option. The edges belong to the unit cell or a bigger "super cell", depending on the boundaries of the cell range.	Can be created automatically during one of the "Fill" functions or built individually using the "Add Cell Edges..." command.
Definition of connectivity (which means: which atom types are to be connected and how are the bonding spheres?)	Bonds are automatically deleted or added, if the connectivity changes.	Bonds are not automatically added or deleted, if connectivity changes. This gives you the possibility to build up a rather complicated structure by variation of bonding spheres. (See command "Connectivity...".
Connecting atoms with bonds	by activating an option. The atoms to be connected as well as the bonding spheres are derived from the connectivity.	All or selected atoms are connected (as far as allowed by the current connectivity settings), using the "Connect Atoms" command. In addition, selected atoms of the structure picture can be connected, ignoring the current connectivity settings. (See "Insert Bonds" command.)
Generation of atoms within spheres	by defining the atom types of the atoms that shall serve as central atoms. The size of the coordination spheres is derived from the connectivity.	There are two kinds of spheres: "fixed" and "coordination" spheres. The first type uses fixed values rmin and rmax. The second type derives sizes from the connectivity. Spheres can be built around atoms of selected types or around atoms in the structure picture that have been selected by the user. These operations can be performed with more than one cycle. The created atoms may be hidden to simulate so-called "broken-off" bonds.
Generation of polyhedra	by activating an option, which is only available, if coordination spheres are to be created. Uses default design for the polyhedron faces and edges, which can be changed using the "Polyhedron Designs..." command from the "Picture" menu.	Polyhedra can be created around atoms of selected types with atoms of selected types in the coordination spheres, or around selected atoms in the current structure picture. The size of the polyhedron may be fixed or depend from the current connectivity settings. Polyhedra can also be constructed by collecting the atoms from the structure picture

Function	Automatic building	Manual building
		without pre-definition of a central atom. (See "Add Polyhedra..." command.)
Generation of molecules from "scratch" or by completion of fragments	by activating an option. Bonding spheres are derived from the connectivity settings. If a cell range has been filled, the fragments are automatically completed to molecules. Otherwise molecules are generated from "scratch".	Molecules are generated from scratch, which means: by generating atoms from parameter list and recursively completing their coordination spheres until a molecule is complete. (See command "Molecules".). To complete existing fragments to molecules, use the "Complete Fragments" command, instead. There is a "Cage..." command where you may define boundaries to prevent excrescences in polymeric structures.
Destroying parts of structure picture	Not applied, since every structure picture is built up from scratch when automatic building is performed.	There are several commands to destroy the entire structure picture or only parts of the picture. (See commands in the "Destroy" submenu.)

Selecting objects in a structure picture

This section describes how objects of the Endeavour structure picture (that means, atoms, labels, etc.) can be selected.

In Table 4 you can see how different object types of the structure picture can be selected. The table lists how an object is selected by clicking into an object-dependent 2D range within the structure picture.

Table 4: Selection of objects in structure picture

Atom	Click into the rectangle that surrounds the atom. In standard representation using no ellipsoids, this is a square with the radius of the atom. In ellipsoid representation, it is the rectangle which surrounds the ellipsoid projection completely.
Polyhedron	A polyhedron is selected by its corresponding central atom.
Bond	Click on the bond. The marker of the bond is the rectangle surrounding the 2D projection of the bond completely.
Atom or bond label	Click into the surrounding rectangle of the label.
Text	Click into the surrounding rectangle of the user-defined text.
Coordinate system	Click into the rectangle that surrounds the coordinate system which symbolizes the current orientation.
Legend	Click into the rectangle of the legend of atom types.

Standard selection

The most common way to select an object is to move the mouse cursor to a suitable position of the object (see Table 4 above) and then click the left mouse button. The selection is reflected by a rectangle which surrounds the selected object. All other selections will be restored in that moment.

Extended selection

If you hold down the **<Shift>** key when you click on an object, the selection of that object will be inverted independent from the selection state of all other objects in the structure picture. Usually the auxiliary Shift key is used to select multiple objects that cannot be "catched" with a rectangle (see below). That means, object at different positions may be clicked and selected one after the other.

Rectangle selection

If you press down the left mouse button **outside** of an object, then pull up a rectangle by moving the mouse cursor with left mouse button down, and then release the button, you will select all objects that lie completely inside that rectangle. You can press the Shift key in addition to invert the selection of all objects in the rectangle (combination of extended and rectangle selection).

Temporarily hiding of objects}

You can hide objects of selected types temporarily for a better access to other objects. For example, it is easy to select atoms that are covered by labels or to access polyhedra by their associated central atoms when the polyhedron faces are closed. To hide objects temporarily, choose the "Hide..." command from the "View" menu. Please note that the objects will not be discarded, and the hiding is not stored in the document.

Indirect selection with auxiliary object lists

You can select objects of the structure picture by selecting the corresponding items in the lists that can be displayed in the data pane. To open a list in the data pane, choose the corresponding command from the submenu which opens when you choose the "List" command from the "View" menu.

If the list of created atoms is displayed in the text pane, the selection of each atom in the structure picture is reflected in the atom list. On the other hand, you can change the selection of the atoms in the picture by changing the selection of the corresponding items of the atom list. That means, by sorting the atom list in a suitable way, you have varied possibilities to select a very special portion of the atoms in the picture.

Like atoms, bonds can be selected from the bond list. For example, if you sort the bonds in the list for bond lengths, you can select all bonds with lengths within that given range.

Polyhedra (that means, the corresponding central atoms) can be selected with the help of the polyhedra list.

The lists of atomic parameters, atom types, and bond types offer enhanced features to select atoms and bonds. For example, if you want to select all atoms that have been created from a special atom of the parameter list (e.g. all symmetry-equivalent atoms of "Fe 3"), first select the atom in the parameter list, and then choose the "Select atom(s)" command from the context menu of the atomic parameter list. The atom type list and the bond type list can be used to select all atoms and bonds that belong to the selected atom type(s) and bond type(s).

Commands for selection

To select a complete molecule, select an atom of the molecule, and choose the "Select molecule" command from the context menu.

To select **all** objects of the structure picture, choose the "Select All" command from the "Edit" menu, or simply use the "hotkey" **<Ctrl+A>**.

To invert the current selection, choose the "Invert Selection" command from the "Edit" menu, or simply use the "hotkey" **<Ctrl+I>**. This command can be used to select all but one molecule, for example.

Tips & Tricks

General hints

We have no doubt that you will find Endeavour a really good and useful program, however, it is not perfect. There is no guarantee that it will solve your crystal structure, though we do our best to permanently improve the program. Hence, it is a good idea to frequently visit our webpage (https://www.crystalimpact.de/endeavour) and look for updates which will be provided for free within version 1.x of the program.

Here are some tricks what to do if your calculation yielded no reasonable result:

- Is your compound suitable for Endeavour calculations? Currently, Endeavour does not support the solution of structures containing mixed sites or vacancies.
- Be sure that your diffraction data are okay:
    - Does your sample contain more than one phase? Have all reflections belonging to other phases been eliminated from the peak list?
    - Is the unit cell correct? Did you get a reasonable figure-of-merit? Have all reflections been indexed?
    - Do the 2θ-values in your diffraction pattern fit to the unit cell parameters? Use the 2θ-values calculated for the unit cell instead of the experimental ones, e.g. using the peak editor (button "Edit peaks...") on page 4 of the structure solution wizard).
    - Are the intensity values accurate enough? Strong anisotropic shape of the crystals (texture effects), very broad lines or a significant background that has not been eliminated are possible reasons for weak intensity accuracy. You may combine several peaks which are rather close to each other to a single peak (sum of individual intensities) using the peak editor on wizard page 4 (button "Edit peaks...").
    - Especially the high-angle part of a diffraction pattern may reveal significant errors both in 2θ- and intensity values. Hence, try to use only the low-angle part of your diffraction pattern, i.e. only the reflections below 40°-60°, especially if the quality of the data seems to be not so good. This can be achieved by setting the "2Theta max." parameter in the Peak editor (button "Edit Peaks...") on page 4 of the structure solution wizard to an appropriate value.
- If the peak density in your diffraction pattern is rather high, and/or you have not used the automatic parameter setting option (page 5 of the structure solution wizard), you definitely should activate the "profile calculation" option in the "Advanced Settings" dialog which can be opened from the final page of the wizard.
  The background is that Endeavour normally calculates the R-factor by first assigning each experimental peak to the closest calculated peak position, and then calculating the intensity difference between these two peaks (which is of course repeated for all peaks). However, if the peak density is rather high (e.g. caused by low symmetry, and/or at high 2θ values), or if a certain 2θ error is present, the experimental peaks may be assigned to the **wrong** calculated peak positions, resulting in an intensity comparison of non-equivalent peaks. Of course, this may lead to R-factor errors and can prevent a whole crystal structure from being solved.
  In order to account for this potential problem, you can let Endeavour calculate diffraction profiles both from the experimental and from the calculated diffraction peaks first, and then compare the profile intensities (i.e. calculate R_P instead of R_B) (set "Advanced settings" parameter "Use profile instead of peaks..." to 1). By doing so, the R-factor calculation is much less sensitive to 2θ errors and wrong peak assignments. You can define both the "Profile step size" as well as the "full width at half maximum" (FWHM) value to be used in the calculation of the profiles.
  The drawback is that a calculation using profile comparison takes much longer than a calculation using the intensity differences between assigned peaks, especially if peaks at large 2θ values are present in the experimental diffraction pattern.

- If your optimization problem is very "rigid" (e.g. caused by one or more large, inflexible molecules in the structure), it may be reasonable to activate **"Automatically determine the starting temperature for the simulated annealing"** to avoid being trapped in some local minimum right from the beginning. The corresponding option can be activated on the "Optimization" page of the "Advanced Settings" dialog. You can adjust the "minimum percentage of accepted moves" that need to be observed before the actual simulated annealing temperature program is started.

- If you are dealing with **large inflexible molecules**, or if you have selected a **space group with several special positions**, the benefit from a large modification of the structure (e.g. rotation of the molecule or moving of one atom to a certain position) may not directly become visible in the cost function calculation. Instead, it can be necessary to perform a short local optimization ("quench") after the move, right before the actual cost function value is calculated. This can be achieved by activating the option "**Intermediate local optimizations**" on the "Optimization" page of the "Advanced Settings" dialog. You can define a "minimum number of intermediate quench steps" before the actual cost function value is calculated **Note that activating this option is generally appropriate if you are using individual atoms in combination with predefining a space group!**

- If your crystal structure contains some **"heavy" atoms**, the positions of which you already know (e.g. from difference Fourier calculations), you should fix these atoms to their positions. This is favorable, since otherwise small shifts of these heavy atoms may cause large changes in the calculated diffraction pattern, which may "cover" the effects of the changes in positions of "light" atoms.
You can set atoms to special positions and fix them by clicking on the "Place atoms..." button on page 3 ("Define atoms in unit cell") of the structure solution wizard. It is possible to only fix the Wyckoff position (so that free parameters of the position may still be varied), or to fix all parameters.
Note that it is also possible to place molecules at a certain position in the unit cell, leaving their rotation as a free parameter.

- Try to use a potential as good as possible. If you employ the default simple repulsion potential, you may improve its quality by using charges (selection on wizard page 5) and/or minimum distance values as close as possible to the compound under investigation. These values may be derived from similar compounds or modifications. The small effort to retrieve these values from similar structures and set these values in the potential parameters dialog is definitely worth while!

- If the structural model resulting from an Endeavour calculation looks p**romising but still "distorted"** (so that e.g. the automatic space group finder is not able to detect all symmetry elements that can be "seen" in the structure), you might want to try a **local optimization** using a cost function with large contribution of the potential energy.
In order to do so, please open the "Structure solution wizard" (press "F7") when the "distorted" structure is displayed. Walk through the pages of the wizard until you come to page 5 ("Choose between automatic and manual structure solution settings"), then remove the hook in the checkbox "Adjust parameters for structure solution automatically". In addition, make sure that "Continue with next page" is selected for "How to proceed". Finally, press "Next".
You can skip page 6 of the wizard ("Define settings for potential") by pressing "Next". On page 7 ("Define optimization settings"), you should adjust the slider "Cost function balance" to the left (towards "potential energy", e.g. to a value of 0.05 or 0.1). Besides this, select "Local (Refinement)" in the combo box "Optimization method". Afterwards, please press "Next" to advance to page 8. Please press "Next" again (page "Summary"), then click "Start" to run the local optimization calculation.
The structure resulting from this calculation has been optimized to a large part with regard to the potential energy. Since the potential energy is calculated using a two-body potential, the structure should be more "regular" compared to the original structure.

- Is your space group correct? Try calculating in a subgroup or in P1!

- You should always keep in mind that diffraction data of poor quality may be balanced to a large degree by a good potential and vice versa! Try some more calculations using a higher value for the cost function balance (recommended value: 0.8-0.9), i.e. increase the influence of the diffraction data on the structure solution process. In most cases, the optimization of the potential energy is just used as a hint to in which region of the hypersurface of the cost function physically reasonable structures may be found.

- The Endeavour kernel has been optimized concerning the success rate and optimization speed. Nevertheless, Endeavour uses a Monte Carlo global optimization procedure called "simulated annealing". An intrinsic feature of this method is that the result may depend on the random numbers generated, and hence on the start value of the random number simulator ("seed"): The shorter the optimization, the stronger the dependence (and vice versa). If the result of your calculation is not to your satisfaction though you are employing good quality diffraction and/or potential parameter data, there are two possible strategies:
    - Try as many short (set the parameter "optimization speed" close to 10) calculations as possible using a broad range of different values for "seed".
    - Alternatively, if you have a fast PC, try to decrease the "optimization speed" parameter. This is especially appropriate if you are using space group symmetry or if there are more than 12-16 atoms in the unit cell. You should keep in mind that the more atoms are in the unit cell, the slower the optimization must be in order to yield the same success rate!

Molecule crystal structures

In typical crystal structures consisting of neutral molecules, there are little to no long-range interactions of the potential energy that could help to "drive" the structure solution calculation in a reasonable direction at an early stage. As a result, many different crystal structures with quite similar cost function values are be obtained (polymorphism).

A potential solution could be to increase the "pressure" within the unit cell, so that neighboring molecules "feel" each other a lot more than in the normal calculation. There are basically two options for this:

- Increase the minimum interatomic distances for relevant atom type (element) pairs.
- Use small to medium charges on the molecule atoms of the same sign, i.e. all atoms are positive or all negative. Due to the long range of the Coulomb forces, this can build up a significant "pressure" in the cell even if the molecules are not close to each other.

Molecules/rigid bodies on special positions of the space group

If a space group other than P1 is used, Endeavour can vary the placement of single atoms on special positions during the calculation. Thus, it is not necessary that the user makes a-priori assumptions on the special positions being occupied by certain atoms (though this can be done, too).

In contrast to the single atoms just mentioned, molecules (and rigid bodies) always had to be placed on the general position of the space group in earlier versions of Endeavour. If at least one of the molecule's atoms had to be placed on a special position in the target structure, it could not be solved with Endeavour in a space group other than P1.

In version 1.8, we have started to remove this limitation: There is a new option "Allow molecule atoms to be placed on special positions" on top of the "Molecules" tab of the "Advanced settings dialog. If this option is active (which is the default state), Endeavour tolerates effects that become evident if an atom belonging to a molecule (rigid body) is moved or placed close to (or even on) a special position of the space group.

Typically, this causes the creation of multiple copies of the molecule (or at least some of its atoms) at rather close distances, which normally would be rejected due to the corresponding dramatic increase of potential energy and / or scattering power (→ R-factor!). With the new option, Endeavour now adapts the site occupation factors of the corresponding atoms according to the situation, in order to reduce the effects just mentioned.

If the new option is active, molecules can now move freely through the unit cell without avoiding special positions. It is also possible to manually place molecule atoms (e.g. S in SO_4^{2-}) on certain positions and let the molecule rotate around this atom.

If you are using this option (i.e. if you do not deactivate it explicitly), you should also make sure to activate the option "(Re-)determine space group after optimization" on page 1 of the structure solution wizard. If this option is active, Endeavour will run SFND/RGS to redetermine the space group at the end of the calculation[35]. A useful side effect is

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[35] If you do not use the "(Re-)determine space group" option, you can use the "Structure/Find symmetry…" command to reduce the atomic parameters using SFND/RGS.

that these programs also perform a reduction of the atomic parameters, i.e. it collects several atoms that may be placed close to (but not on) a special position in one atom that is placed directly on the special position, summing up the corresponding site occupation factors as well. You may regard this as some kind of "idealization" of the structure.

Cost function balancing

The idea of a combined cost function implemented in Endeavour (consisting of potential energy and R-factor) works best if the numerical values of the two cost function parts are of approximately the same size. This can be achieved by adjusting the "cost function balance" parameter to a reasonable value. You can check this e.g. by watching the R-factor and the overall cost function graph in the progress viewer on the right-hand side.

Calculation drops into minimum close to starting point

The idea of "simulated annealing", the global optimization method used in Endeavour, is to walk around on the hypersurface of the cost function, controlled by an algorithm which does not only walk "downhill" but also accepts modifications that cause in increase of the cost function with a certain probability (controlled by the so-called "temperature").

At the beginning of the optimization (structure solution calculation), the value of the "temperature" (i.e. the control parameter) is rather high, so that the probability that "bad" modifications are accepted is large and the system can walk around and visit large parts of the hypersurface of the cost function. When the calculation progresses, the "temperature" is reduced more and more, so that "bad" modifications are accepted with reduced probability. As a consequence, the system will most probably be getting trapped in the largest minimum (with regard to the number of states), which is supposed to be coincident with the deepest (hopefully global) minimum of the hypersurface.

If the system is stuck in a certain minimum right from the beginning of the calculation, this is a clear indicator that the default initial value of the control parameter "temperature" is too low, so that the system cannot visit large parts of the hypersurface. In these cases, you should modify the value of "Initial control parameter value" on the "Optimization" tab (section "Simulated Annealing") of the "Advanced settings" dialog.

The default value of this parameter is 0.5, so using a value of 3.0 to 5.0 is a good starting point in these cases.

No more progress in the second half of the calculation

It may happen that quite a lot of optimization is done in the first half of the structure solution calculation (as e.g. indicated by the "cost function" line in the progress viewer on the right-hand side moving vividly up and down), while there is little to no progress anymore (flat cost function line) in the second part of the calculation.

This is a clear indicator that the "target temperature" (please take a look at the section "" above) is too low. The effect may lead to a significant waste of calculation time.

To fix this, you can increase the value "Simulated annealing stops when t reaches t-limit" on the "Optimization" tab (section "Simulated Annealing") of the "Advanced settings" dialog. The default value of this parameter is 0.001, so using an increased value of 0.1 generally works quite well in these cases.

Collection of best structural models in Diamond

It happens quite frequently that promising solutions are obtained that nevertheless do not provide the complete structure in a single model. In these cases, we have made good experiences with collecting these solutions in a single document of "Diamond", our software for crystal and molecular structure visualization[36]. Diamond can read the currently selected structure from an Endeavour document file; you can then copy these structures (along with their structure pictures) into a single document. Reviewing these collections can be quite helpful in developing an idea of how the structure may look like, and which kind of work may still be required for the solution of the structure.

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[36] Diamond - Crystal and Molecular Structure Visualization, Crystal Impact - H. Putz & K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany, https://www.crystalimpact.de/diamond

Software maintenance (installation and updates)

Before you install and run Endeavour, you should check the following system requirements:

- Personal Computer with Microsoft Windows XP, Vista, Windows 7, Windows 8/8.1 or Windows 10 operating system
- 1 GB of RAM
- Hard disk with minimum 50 MB of free disk space
- Graphics resolution of 1024 x 768 pixels (1280 x 800 pixels or more recommended)

Installing from installation DVD-R

Please insert the installation disk (DVD) into your drive; an installation selection program will start automatically. Please click on the button next to "Install Endeavour".

If the selection program does not start automatically, please run “autostart.exe” in the main directory of the DVD.

The installation program will lead you through the setup process. Please note the terms of the "End User License Agreement", which will appear in the second dialog.

Installing from download package

The first thing you have to do is to download and install the Endeavour demonstration version. Afterwards, download the Endeavour demonstration version from

https://www.crystalimpact.de/endeavour/download.htm

Install it by double-clicking on the file you have downloaded. The setup program will start and lead you through the installation procedure. When the installation procedure has been finished, execute Endeavour to see if the installation was successful.

At this point you have a working demo version but still need to install your license file, in order to transform Endeavour to the full version:

Close all Endeavour windows, then extract (“unzip”) the file “license_Endeavour.zip” you have obtained (e.g. by e-mail) to some temporary directory on your local hard disk. Afterwards, please move the extracted file “yourlicense.lic” into your Endeavour program directory (e.g. “C:\Program Files\Endeavour”).

Finally, restart Endeavour. A message window will be displayed indicating that the demonstration version has been transformed into the full version. Your license data should now be displayed both in the “splash screen” at program startup as well as in the “About Endeavour” window which can be opened by selecting the “About Endeavour” command in the “Help” menu.

If this is not the case, please verify that the file “yourlicense.lic” is present in your Endeavour program directory!

Documentation available after installation

Once you have installed the Endeavour software on your PC, both a comprehensive online help (which can be accessed through the “Help” menu) as well as a manual are available as documentation.

In the manual, a “Quick start” chapter is available, in which the basic usage of Endeavour is demonstrated in short.

In addition, detailed tutorials are also included, demonstrating the most important functionality of Endeavour for solving crystal structures from various kinds of diffraction data. We strongly recommend working through these tutorials in order to learn about Endeavour's most prominent features, so that can get the most of it later on when you work on your own data.

You can access the manual either from the menu ("Help-Manual-Tutorial"), or directly by double-clicking in the Windows Explorer on the "tutorial.pdf" file in Endeavour's program directory. Alternatively, you can also access it from the Windows Start menu: "Start/Programs/Endeavour/Tutorial".

In addition to the manual, there is one basic keyboard shortcut you should always keep in mind: Pressing **F1** on your keyboard will open a context sensitive help window in which detailed information about your current options and situation will be given.

Furthermore, Endeavour provides a comprehensive online help system, covering all aspects of Endeavour and its use. To access the online help when Endeavour is running, choose the “Help Topics” command from the Help menu.

Online update

Endeavour is able to automatically download and install a new version once it has become available. It connects to the Crystal Impact webserver and compares the version of the most recent update available there to the version which is currently installed on your PC. To achieve this, a working connection to the internet is required, of course. If you are not connected to the internet, Endeavour will ask you to do so before continuing.

If a more recent version is found on the webserver, a list of changes and improved features in the new version will be displayed, and you will be asked if you would like to download the corresponding update. Once you have acknowledged and the corresponding files have been downloaded, you will be asked to close all open Endeavour windows so that the update program can replace the program executable. After the update has been completed, Endeavour will be restarted so that you can check if the update was successful. This can e.g. be achieved by selecting the “About Endeavour..”" command in the “Help” menu and checking the version number and date in the dialog which is displayed.

By default, Endeavour checks the Crystal Impact webserver for a new version automatically each time it is executed. If you would like to disable this feature (e.g. if you are not permanently connected to the internet), you can do so on the “Desktop” page of the “Tools/Options” dialog, simply by removing the hook in front of “Check for available updates when starting” at the bottom of the dialog.

Even if you have disabled the “Automatic update checking” option, you can update your software online by selecting the “Online update” command from the “Help” menu. The procedure will be the same as the one described above for the automatic update.

Appendix

Endeavour user interface

Desktop

This chapter will give you an overview of the arrangement of window types, the different panes, and the meaning of main menu and context-sensitive menus as well as of toolbars.

Endeavour uses the Multiple Document Interface (MDI), which means that you can open a second, third, etc. document window without closing the first one. Opening and closing of single Endeavour documents works independent from other documents. An Endeavour document contains diffraction data, crystal or molecular structure data, results of structure solution calculations (optimizations) etc.

Menus

Endeavour uses the following pulldown menus:

File	Commands to create a new document, to open an existing one (including "import"), to save a document, to print or to make a print preview, or to exit the application.
Edit	Standard commands like in most other Windows application, such as "Undo", "Redo", "Copy", "Select All", etc.
View	Commands to switch between the several panes of an Endeavour document.
Diffraction	Commands to open a peak, I(hkl) or |F(hkl)| file or to change powder pattern settings.
Structure	Commands to edit structural parameters (cell, space group, atomic positions), to start or stop the structure solution as well as to transform to other space group.
Build	Commands to create a structure picture from structural parameters.
Picture	Commands to change the appearance and orientation of the structure picture.
Tools	Several commands: Info mode, interactive measuring of distances and angles. Calculation of potential parameters.
Window	Standard commands like in most other Windows application to switch between Endeavour document windows or to arrange them.
Help	Commands to open the Endeavour Application Help or to navigate to the Endeavour Support Page on the Internet or to get information about the current version.

Toolbars

A toolbar is a control bar which contains a row of button images, often called "icons". These buttons represent a lot of functions which are also available via menu commands, such as "New", "Open", or "Save". Additionally, they contain buttons for commands that you else would reach only indirectly (e.g. via dialog boxes).

Toolbars are usually aligned to the top of the Endeavour application window, that means below the menu bar. However, the toolbars used in Endeavour can be "docked" to any side (or sides) of the Endeavour application window. They can also be made "floating" in draggable" mini-frame windows", and you can now resize floating toolbars.

Endeavour provides five different toolbars:

Standard	Standard commands such as "New", "Open", "Copy" etc. as well as specific commands to start or stop a structure solution etc.

Picture display Most common commands for the representation of the structure picture.

Build	Commands for adding structural parts to the structure picture, like atoms, molecules or polyhedra.
Tracking	Commands to switch between tracking modes, like shift, rotate, end tracking mode etc.
Measure	Interactive measuring of distances or angles.

You can shift, dock or "undock" a toolbar by dragging the corresponding toolbar with the left mouse button. You can also switch between docked and floating state by double-clicking into the interior of the toolbar (but outside the buttons on the toolbar). You can hide and re-display toolbars via the *Toolbars and Docking Windows* command of the *View* menu.

Status bar

The status bar is a control bar with a row of text output panes, or "indicators", at the bottom of the Endeavour application window. The main part (beginning at the left) displays either result messages or brief help for the menu or toolbar command where the mouse cursor is just pointing to.

During lengthy processes, such as filling of larger cell ranges or displaying a rendered picture with some hundreds of atoms, the progress of the operation will be displayed.

At the right end of the status bar, five panes, called "indicators", show the current R-factor as well as the actual contents of the structure picture:

- R-factor (calculated from the calculated and the experimental diffraction pattern if present)
- number of atoms in the parameter list,
- number of created atoms,
- number of bonds between created atoms,
- and number of coordination polyhedra.

Whenever a progress bar is displayed in the status bar, the corresponding operation (e.g. filling a cell range or creating an enhanced picture) can be cancelled by pressing the <Ctrl+Break> key combination.

Context-sensitive help

This paragraph describes where and how context-sensitive help is available for the several working situations in your Endeavour session.

Pressing F1 key: If neither a dialog box is open nor a menu item is highlighted, pressing of the <F1> key opens the "Endeavour Help Index", a general page with an introduction to the Endeavour Help Library.

If a menu item is highlighted, help for that menu item (usually command) will be displayed. The menu item may be highlighted using the mouse or with the cursor keys.

If a dialog box is open, <F1> will show specific help for the usage of that dialog and the meaning of the controls in the dialog box.

Entering Help Mode: A special mode, the "Help mode", is activated by pressing the <Shift+F1> key combination. This is a more versatile method of getting context-sensitive help. After this mode has been activated, the mouse cursor changes to a symbol consisting of standard arrow and question mark. In this mode, you will get context-sensitive help, if you click on a menu item or a symbol in a toolbar or on special parts of the Endeavour application window, such as the status bar, system menu etc.

The Help mode can be cancelled by pressing the <Esc> key. The previous mouse cursor will be restored. The Help mode ends automatically, when you get help for a clicked item.

Info Mode: Whereas the previously described Help mode is common to many other Windows application, a special mode offering information about objects of the Endeavour structure picture is available by pressing the **i** button in the standard toolbar, or by choosing the Info mode command from the *Tools* menu.

When this mode is activated, the mouse cursor changes to an arrow with an "i" letter. This mode can be cancelled by pressing the <Esc> key or by pressing the button again or by choosing the Info mode again from the *Tools* menu. The previous mouse cursor will be restored.

Undo and redo

Endeavour has a multiple-step Undo function, which means that each time document data may change, the previous state is saved temporarily. The Undo buffer works with the "Last in – First out" principle. You can call the Undo function and restore previous states of the document stepwise until the bottom of the Undo buffer is reached. The bottom is the state where the document has been created (new document) or has been loaded or imported from an existing file. The action that will be restored is described in brief after the *Undo* command in the *Edit* menu, for example "Undo: Fill unit cell Ctrl+Z".

The restoring of a previous state may be restored in the same way, using the "Redo" function. In that case, you work to the top of the Undo buffer. Like for Undo, the action that will be "re-restored" is described in brief after the *Redo* command in the *Edit* menu.

Endeavour offers several possibilities to work with the Undo/Redo buffer:

Undo:

- Choose the Undo command from the Edit menu.
- Or click on the ↶ button in the standard toolbar.
- Or press the <Ctrl+Z> key combination.

Redo:

- Choose the Redo command from the Edit menu.
- Or click on the ↷ button in the standard toolbar.
- Or press the <Ctrl+Y> key combination.

Remarks: The "Undo" and "Redo" functions refer to the document in the currently active window only! Example: If you first change document A and then focus the structure picture or diffraction diagram or a table of document B, the "Undo" or "Redo" function applies to document B! That means you cannot restore any changes of document A as long as document B is focused and not until document A is activated again.

You cannot restore any changes to a document after its corresponding window has been closed. Neither closing nor saving of document data can be restored. But you may undo the last operations and then save the restored state.

Introduction to Advanced Settings

You may already have noticed the button “Advanced Settings” on the final page of the structure solution wizard. If you press it, a dialog window opens containing an awful number of parameters and settings regarding the structure solution calculation. What are all these values for?

If you do not get a reasonable result using the automatic approach, we recommend getting a nice hot cup of tea, and work through the remaining structure solution tutorial sessions step by step.

First, don't worry, you don't need to adjust all these parameters for every structure solution calculation! In the following, we will discuss the most important parameters and their application. You will find information for all parameters in the Endeavour online help.

Molecule Settings

Flexibility

Normally, molecules are taken as rigid bodies, the only exception being rotatable bonds. With this parameter (group) it is possible to make the whole molecule flexible, in the sense that not only torsion angles but also bond lengths and angles may be varied during the structure solution calculation. This may be useful if it is difficult to select an exact molecular geometry (e.g. if some bond lengths depend on neighboring atoms).

If you decide to use **flexible molecules**, you can define a parameter using which deviations from the “ideal” (=initial) geometry are “punished” (“flexibility parameter”), so that the molecules my either become more rigid or more flexible. Besides this, you can define the influence of the “molecule distortion energy” on the overall cost function (“weighting factor for molecule distortion energy”).

Max. shift/rotation

Using these parameters, you can define the maximum step size of molecule displacements and rotations during different phases of the structure solution calculation. Note that it may be useful to have large steps in the beginning, in order to investigate the hypersurface of the cost function as completely as possible, while it is normally appropriate to use smaller steps in later phases of the optimization.

Single Atom Settings

Using these parameters, you can define the maximum step size of atom displacements during different phases of the structure solution calculation. Note that it may be useful to have large steps in the beginning, in order to investigate the hypersurface of the cost function as completely as possible, while it is normally appropriate to use smaller steps in later phases of the optimization.

Diffraction Settings

Smooth intensity differences

It is possible to make the R-factor hypersurface (which is normally very “rugged”) “smoother” and hence much more suitable for global optimizations. You can define the degree of smoothing using the parameter “Exponent coefficient”. Smoothing is approximately proportional to the logarithm of the smooth parameter. A value of 0.0 is equivalent to “no smoothing”.

However, please note that while smoothing this function also eliminates details of the R-factor hypersurface, so may lose valuable information if your smoothing is too efficient!

Temperature factor}

Normally, Endeavour optimizes the temperature facture used in the calculation of the diffraction pattern from the current crystal structure data in every R-factor calculation, in order to obtain the best possible agreement between calculated and experimental diffraction pattern. If you define a value for “Overall temperature factor”, Endeavour will use this value instead of the automatic optimization. This will make the calculation somewhat faster, but the drawback is that you should be sure about the arbitrary value of B0.

Check of peak positions

Using this option, you can let Endeavour compare the 2θ positions of the experimental diffraction peaks to the ones of the correlated calculated positions. If the deviation is too strong (depending on the parameter "Maximum average deviation"), a warning message is displayed. Potential reasons for a too strong deviation are:

- Error in unit cell parameters
- Wavelength does not correspond to diffraction experiment
- 2θ error (e.g. zero-point shift, specimen displacement)
- Diffraction pattern contains more than a single phase

If this warning is displayed and you are not able to find/eliminate the reason, you should consider using a profile comparison of calculated and experimental diffraction pattern, as described below.

R-factor calculation

Normally, Endeavour calculates the R-factor by first assigning each experimental peak to the closest calculated peak position and then comparing the intensities between these two peaks. However, if the peak density is rather high (e.g. caused by low symmetry, and/or at high 2θ values), or if a certain 2θ error is present, the experimental peaks may be assigned to the wrong calculated peak positions, resulting in an intensity comparison of non-equivalent peaks. Of course, this may lead to R-factor errors and can prevent a whole crystal structure from being solved.

In order to account for this potential problem, you can let Endeavour calculate diffraction profiles both from the experimental and from the calculated diffraction peaks first, and then compare the profile intensities (i.e. calculate R_P instead of R_B) (set parameter "Use profile instead of peaks..." to 1). By doing so, the R-factor calculation is much less sensitive to 2θ errors and wrong peak assignments. You can define both the "Profile step size" as well as the "full width at half maximum" (FWHM) value to be used in the calculation of the profiles.

The drawback is that a calculation using profile comparison takes much longer than a calculation using the intensity differences between assigned peaks, especially if peaks at large 2θ values are present in the experimental diffraction pattern.

It is also possible to **"Increase the R-factor contribution of peaks at large 2theta values"**, in order to add more weight to peaks above the "Angle above which intensity difference contribution is increased" in the R-factor calculation. This is appropriate if a diffraction pattern contains one (or few) strong peaks and a lot of small peaks which in fact contain most of the structural information. You can adjust a "Weighting factor" for the high-angle part.

Optimization

If your optimization problem is very "rigid" (e.g. caused by one or more large, inflexible molecules in the structure), it may be reasonable to **"Automatically determine the starting temperature for the simulated annealing"**, in order to avoid being trapped in some local minimum right from the beginning. You can adjust the "minimum percentage of accepted moves" that need to be observed before the actual simulated annealing temperature program is started.

If you are dealing with **large inflexible molecules**, or if you have selected a **space group with several special positions**, the benefit from a large modification of the structure (e.g. rotation of the molecule or moving of one atom to a certain position) may not directly become visible in the cost function calculation. Instead, it can be necessary to perform a short local optimization ("quench") after the move, right before the actual cost function value is calculated. This can be achieved by activating the option **"Intermediate local optimizations"**. You can define a "minimum number of intermediate quench steps" before the actual cost function value is calculated. **Note that activating this option is generally appropriate if you are using individual atoms in combination with predefining a space group and special positions!**

Scientific Background

Today the determination of the atomic structure of crystalline solids has become more or less a routine process using single crystal X-ray diffraction. Nevertheless, even nowadays this task quickly becomes difficult if the compound under investigation can only be prepared as a microcrystalline powder. One of the first methods for determining crystal structures from powder diffraction data was developed by Hugo Rietveld[37] and co-workers in the late sixties. This approach has become an integral part of nearly any crystal structure determination, though it actually addresses only the last step in the structure determination process consisting of six steps:

1. Determination of peak positions
2. Indexing and calculation of lattice parameters
3. Determination of crystal symmetry and space group (if possible)
4. Extraction of intensities
5. Structure solution (creation of a structural model with approximate atomic positions)
6. Structure refinement (of the atomic positions)

The steps no. 1, 3, 4 and 6 are almost routine nowadays, with a number of computer programs available; however, indexing (step no. 2) still remains a challenging task[38]. Nevertheless, routines that extract information from diffraction data (steps 1-4) are included in many operating software packages for diffractometry. The Rietveld refinement has also been implemented in a variety of programs (e.g. GSAS, FullProf, DBWS). They can generally be used in a routine fashion[39].

However, one of the main problems associated with Rietveld's method is its implicit use of local optimization of the atomic positions. Thus, it depends on the availability of a structural model, i.e. an approximate idea of what the atomic arrangement should be. Providing such a model from a powder diffraction pattern (step no. 5 in the list above) remains a difficult task in general. In some cases, the analogy to existing compounds and their structures allows a relatively simple construction of a model, but in many other cases this is not possible.

Several approaches which address this problem have been developed since publication of the Rietveld method in 1969; very good reviews and more information can be found at [40,41,42]. Usually they generate a structural model "ab initio" (i.e. without any previous knowledge concerning the structure) from a powder diffraction pattern that is subsequently submitted to a Rietveld refinement.

Most of these methods (especially the "classical" direct methods[43], Patterson method[44], method of maximum entropy and likelihood[45], but also some more recent approaches, e.g. FOCUS[46] consider intensity values for each reflection (hkl), more or less in analogy to single crystal methods. Unfortunately, the extraction of the intensities I(hkl) from the experimental diffraction pattern $I(2\theta)$ as a function of the scattering angle 2θ quite frequently poses serious problems because of the ambiguity arising from the overlap of different reflections (hkl) at the same value of 2θ. Though a variety of sophisticated techniques[47,48] has been developed for the extraction of I(hkl) from overlapping reflections, it may be difficult to determine these intensity values with sufficient accuracy for the "classical" methods to be applicable.

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The so-called "direct-space methods" avoid this problem by proposing a structural model independent of the powder diffraction diagram[49,50,51,52,53,54,55,1]. The models are subsequently validated by comparing the calculated and the experimental powder pattern concerning I(2θ). These values are readily obtained from experimental powder diffraction data of sufficient quality.

In general, direct-space methods work as follows: Beginning with some arbitrarily chosen starting configuration, the difference between the calculated and the measured diffraction pattern (cost function) is minimized through repeated change of the atomic arrangement, while the unit cell is kept fixed. If no other constraints are introduced, this straightforward prescription (also known as the "Reverse Monte Carlo"-method[56,57]) is in practice limited by the fact that for most crystalline solids the system is quickly getting trapped in some minimum that does not correspond to a physically reasonable atomic arrangement. The reason for this lies in the landscape of the cost function which includes numerous deep local minima[57].

In order to avoid these traps, Endeavour[1] solves crystal structures from powder patterns by a **combined global optimization** of the difference between the calculated and the measured diffraction pattern (**R-factor**) and of the **potential energy** of the system ("Pareto-optimization"). Each cost function, potential energy and pattern difference, depends on all atomic coordinates, thus setting up a high dimensional hypersurface. "Merging" both hypersurfaces weakens or even eliminates the minima that belong to only one of the two surfaces and strengthens those which belong to both of them. Therefore, a sufficiently long global optimization run should sooner or later reach the global minimum of the system corresponding to the correct crystal structure.

Endeavour uses the Monte Carlo (MC) based global optimization method "simulated annealing"[58] in order to find the global minimum concerning a weighted sum of both cost functions. The weight of either cost function may be chosen as to the quality of the available data:

If only a very approximate potential is available, this can be compensated for to a large degree by a high precision powder diffraction diagram. One might then use the potential only for ensuring reasonable distances between the various atom types, thus enforcing the optimization according to the difference in powder diffraction patterns.

If, on the other hand, only few and not very reliable diffraction data are available for the compound under investigation, a high-quality potential can nevertheless lead to a reasonable structure. Here, the effect of the pattern difference cost function lies in the enhancement of one of the many structures that constitute local minima of the potential energy.

Of course, if both an accurate potential function and a high-quality powder diffraction pattern are available, the optimization may be very fast and yields the correct crystal structure with high probability.

In general, there is no need to provide any space group information in the input of the calculation. In this case, all atomic positions in the unit cell are variables of the optimization, i.e. the calculation is performed in triclinic crystal symmetry (space group P1). Once a promising crystal structure candidate has been found in P1, the nearly fully automated application of the built-in programs SFND**Fehler! Textmarke nicht definiert.** and RGS**Fehler! Textmarke nicht definiert.** will yield the full space group.

However, if the space group can be deduced from systematic absences of reflections in the diffraction pattern, it is perfectly possible to use the full space group symmetry. Of course, it is also possible to perform the calculation in a subgroup of the "correct" space group if only a subset of the symmetry elements can be found in the diffraction

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pattern. Again, the application of SFND and RGS will determine the correct space group once a reasonable structure solution is obtained.

In principle any method for the calculation of the potential energy can be used, but the global optimization usually makes ab initio energy calculations not feasible. Fortunately, we found that simple empirically parametrized two-body potentials are generally sufficient:

- A **simple repulsion potential** punishing (but not prohibiting) interatomic distances below a certain atom-pair specific minimum value is the easiest potential that can be used. Endeavour guides the user in the selection of reasonable minimum interatomic distance values by displaying a histogram of corresponding observed distance values from an early version of the ICSD.

- If at least some of the atoms in the model have charges (i.e. are ions), the calculation of the corresponding **Coulomb forces** (Ewald sum) can be included in the potential energy calculation. Using ions can also help to direct the structural model in a certain direction.

- In case of structures of inorganic solid-state compounds, a Lennard-Jones potential with parameters fitted to similar structures can help to balance low-quality diffraction data (chapter "Balancing of low quality neutron diffraction data by potential energy (Li_2CuO_2)" starting on 44).

- In some special cases, the Hofmann intermolecular potential[59,60]$can also be used. Please note though that the Hofmann potential may not be available for all atom type pairs in your compound, in which case using the simple repulsion potential based on minimum interatomic distances could be used.

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[60] D.W.M. Hofmann, L.N. Kuleshova, Crystallography Reports 50(2), 372-374 (2005).

Endeavour Kernel Scripts

Endeavour is generally employed like many other conventional Windows programs, the user interacting with the program by mouse, keyboard and a graphical user interface. If the user wants the program to do something, he/she selects a command from a menu or clicks on a toolbar icon.

However, Endeavour is not a monolithic block containing everything in one big program. Instead, it consists of a Windows based graphical user interface and a separate executable called "the kernel" that actually performs the calculations. The latter can be copied to any other directory (or even PC) in order to use it independent of the graphical user interface.

The executable file "enkernel.exe" that is present in your Endeavour program directory is the **Windows** version of the kernel. Kernel versions for **macOS** and **Linux** are available for download from the Endeavour download web page:

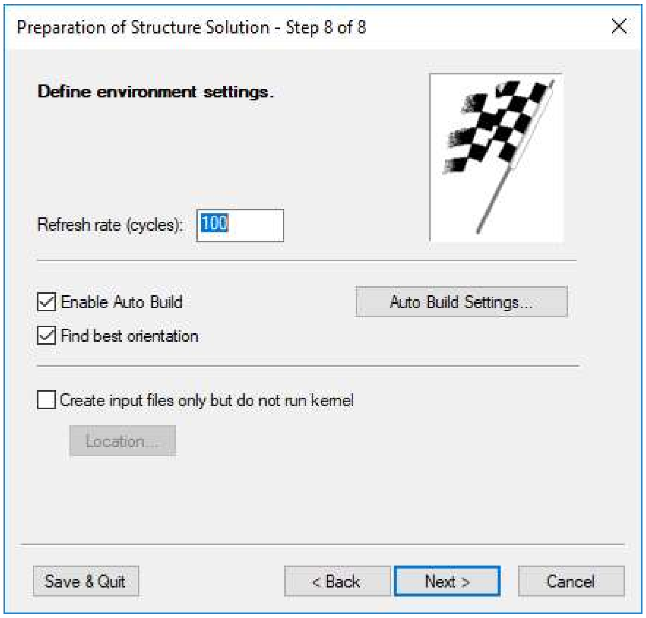
https://www.crystalimpact.de/endeavour/download.htm#kernel

The kernel itself provides no user interface. It is controlled by a text file containing the so-called "script". This script consists of a list of commands (one per line) which are worked through from the beginning to the end by the kernel. The script file is normally created by the Endeavour Windows interface mentioned above.

The kernel may be used for structure solution calculations directly without the graphical user interface, if the corresponding script is provided. This is especially useful if a whole series of calculations shall be performed without an attending user, i.e., if Endeavour shall be used in a "batch-like" manner. It can also be useful if you would like to run Endeavour calculations on macOS or Linux.

Script generation using the structure solution wizard

The script may be generated in two different ways. The first (and more convenient) way is to use the structure solution wizard of the Windows user interface. It is used just like in any other Endeavour calculation until you reach the final wizard page 8 (Fig. 62).



Preparation of Structure Solution - Step 8 of 8

Define environment settings.

Refresh rate (cycles): 100

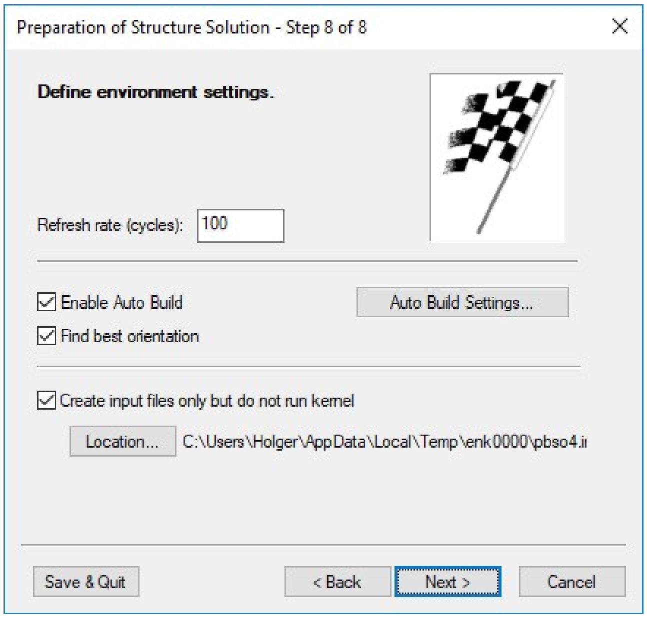
☑ Enable Auto Build

☑ Find best orientation

☐ Create input files only but do not run kernel

Fig. 62: Default settings on structure solution wizard page 8

In order to let Endeavour create script files for the kernel (instead of running the calculation straight away), please mark the option "Create input files only but do not run kernel" on this page. Afterwards, you should give the directory in which you want the script and the other files needed for the kernel-only calculation shall be stored. If you do not change the default setting (which can be achieved by clicking "Location..."), these files will be stored in a directory called "enk0000" in your temporary directory, as in Fig. 63.



Preparation of Structure Solution - Step 8 of 8

Define environment settings.

Refresh rate (cycles): 100

☑ Enable Auto Build

☑ Find best orientation

☑ Create input files only but do not run kernel

Location... C:\Users\Holger\AppData\Local\Temp\enk0000\pbso4.i

Fig. 63: The option for creating script and input files for the Endeavour kernel has been marked.

Once you press "Next" (advancing to the "Summary" page of the wizard) and "Start", the files together with the kernel executable for Windows will be copied to the given directory, however, the calculation itself will not be started.

You may then copy the contents of this directory to the machine where the calculation shall actually be performed. The calculation may then be invoked from the command line interface of this computer as described below. Alternatively, you can open the script file (file extension ".inp") from the Endeavour user interface, and start the calculation as usual by invoking the structure solution wizard afterwards. All input data will be already present in the corresponding wizard pages.

Script generation from scratch using a text editor

A second way to obtain the kernel script and the other necessary files is to generate or modify them using any conventional text (ASCII) editor, e.g. the Windows program "Notepad" or "vi" on macOS or Linux.

Let´s work through a simple example so that you can see how everything works:

Suppose you have made a new compound[61]. Elementary analysis shows that its composition is RuS_2. Unfortunately, you always yield a microcrystalline powder; no single crystals may be grown. Thus, you decide to solve the crystal structure from powder diffraction data.

Indexation of the experimental diffraction pattern yields a cubic unit cell with a = 5.6095 Å. With regard to the ionic radii it is evident that there is room for 4 formula units in the unit cell.

The first thing you have to care about is the diffraction pattern. It must be given as a peak list file, sorted from low to higher 2θ values. Each line contains a 2θ value and the corresponding intensity of one observed peak. These values should be given by most of the standard software packages provided with the diffractometers. In our example, the peak list file is named "rus2.dif" and contains the following lines:

```
27.506   75.0
31.878  100.0
35.758   20.0
39.311   20.0
45.715   60.0
48.650    0.5
54.196  100.0
56.820   20.0
```

---

[61] The example we are using here for demonstrating the kernel scripting is identical to the one used in the chapter "Quick start" on p. 7.

```
    59.345    8.0
```

Since Endeavour works by a simultaneous optimization of pattern difference and potential energy, you have to give certain parameters for the empirically parametrized two-body potential. The easiest way to do this (and the default method) is to supply minimum distances between any pair of atom types. In our case, we provide the potential parameters in the file "rus2.pdt"[62]. This file must at least contain the following lines (providing minimum interatomic distances for the default simple repulsion potential):

```
<repulsion>
ru   4.0  ru   4.0       2.50
ru   4.0  s   -2.0       2.00
s   -2.0  s   -2.0       2.75
```

In the next step you have to generate the script ("instruction") file for the Endeavour kernel which tells the kernel what to do. Using your favorite text editor, you create a new file named "rus2.inp".

Give the full set of unit cell parameters (a, b, c, α, β, γ) obtained from the indexation in the first line:

```
set(cell,5.6095,5.6095,5.6095,90.0,90.0,90.0)
```

If you could already determine the space group from systematic absences, this would now be the right time to provide it. However, in this example we assume that the space group is unknown at the current stage, thus the calculation has to be performed in P1. If you use P1, there is no need to give any space group information or file.

Afterwards, you have to generate the atoms which should be placed at random positions. You generate the atoms for each type (Ru, S) separately using the command "newatoms" providing the oxidation states as charges and the formula indices. The formula unit is RuS_2, and the oxidation states are Ru(4+) and S(2-). The number of formula units per unit cell is Z=4, which means that there are 4 Ru^{4+} and 8 S^{2-} ions in the unit cell. As a result, the next three lines of the script file are

```
newatoms(ru,4.0,4)
newatoms(s,-2.0,8)
```

With regard to the calculation of the potential energy, we would like to use the simple repulsion potential (pottype=3) in addition to Coulomb forces (i.e. using charges). Hence, we add

```
set(pottype,3)
set(simpreppot_uses_charges,1)
```

We then load the file containing the potential parameters (in our case the minimum interatomic distances):

```
loadpotdat(pot.pdt)
```

Before we load the powder diffraction data (peak list), we specify the radiation type (radiation=0: X-rays, laboratory) and wave length (1.540598 Å, Cu Kα1):

```
set(radiation,0)
set(lambda,1.540598)
```

Subsequently you give the name of the peak list file mentioned above to be loaded:

```
loadpdiffexp(rus2.dif)
```

---

[62] A sample file "pot.pdt" which already contains some potential parameters is present in the main Endeavour program directory.

We will use the default equal size weighting of the two cost function parts “potential energy” and “R-factor” (diffraction pattern difference):

```
set(cfweight,0.5)
```

The speed of the calculation is controlled by a parameter “optspeed” that could take any integer value from 1 to 10. optspeed=10 means highest optimization speed, however, because of the underlying simulated annealing optimization method, also lowest success probability. The more degrees of freedom are present, the lower the recommended value for optspeed. In our example, we have 12 independent atoms (i.e. $3 \cdot N = 36$ degrees of freedom), so it seems reasonable to employ a slightly decreased value for optspeed, say

```
set(optspeed,8)
```

In the final line of the script file the actual calculation (optimization) is started:

```
optimize
```

In summary your script file "rus2.inp" should contain the following lines:

```
set(cell,5.6095,5.6095,5.6095,90.0,90.0,90.0)
newatoms(ru,4.0,4)
newatoms(s,-2.0,8)
set(pottype,3)
set(simpreppot_uses_charges,1)
loadpotdat(rus2.pdt)
set(radiation,0)
set(lambda,1.540598)
loadpdiffexp(rus2.dif)
set(cfweight,0.5)
set(optspeed,8)
optimize
```

In addition to the calculation specific files just mentioned (“rus2.inp”, “rus2.dif” and “rus2.pdt”), you will need the Endeavour kernel program itself (file “enkernel.exe” or “Enkernel”), as well as your license file which will be checked by the kernel (file “yourlicense.lic”). Both files may be copied from your Endeavour program directory depending on your installation (e.g. “C:\Program Files\Endeavour”).

Now all files needed for the calculation should be present in the current working directory:

- Endeavour kernel executable (“enkernel.exe” or “Enkernel”)
- Your personal license file (“yourlicense.lic”)
- File containing the experimental diffraction pattern as a peak list (“rus2.dif”)
- File containing the potential parameter data to be used in the calculation (“rus2.pdt”)
- Finally the script file itself (“rus2.inp”)

The calculation is run from the command line (on Windows you can use “cmd.exe”), simply by giving the executable name of the Endeavour kernel (“enkernel.exe” or “Enkernel”) followed by the name of the script file, e.g.

```
enkernel rus2.inp <Return>
```

During the calculation, some additional files containing the intermediate status of the optimization are frequently written to the current directory. These files are named “inter.*extension*”, where *extension* may be “cfg”, “cif”, “rgs”, "dif", "emo" or "dat". You can watch the proceeding of the calculation by the contents of these files. For example, the file "inter.dat" contains the step number and the current values of cost function and control parameter.

When the calculation has finished, the final structural model is written to a file "end*scriptname*.cfg", where *scriptname* is the name of the script file. In our example, the final configuration can be found in "endrus2.cfg".

The "results report" (the protocol) of the calculation will be saved in "rus2.pro". You should read it carefully after the calculation.

Some other files with similar names are generally provided, too. With regard to our example, "endrus2.cif" contains the final configuration in CIF-format which can directly be used for visualization by the Endeavour windows interface (alternatively by most other visualization programs, e.g. Diamond). The file "endrus2.rgs" is the input file for the symmetry finder SFND/RGS which will provide the full space group of the calculation result. These data may then be used as an input to the Rietveld refinement.

Handling of space group data

If a "kernel only" calculation shall be performed in a space group other than P1 without the aid of the structure solution wizard, a so-called "symmetry-data-file" (sdt-file must be provided, since the kernel itself does not contain space group information. Hence, this sdt-file contains the complete information on space group symmetry and Wyckoff positions.

The easiest way to create this file is to copy the data from the corresponding dialog-box in Endeavour.

In order to generate a new sdt-file, run Endeavour, then select "File/New structure solution…" to generate a (temporary) new document. Cancel the structure solution wizard if it is displayed automatically. Afterwards, select "Structure/Space-group..." to open the space group dialog box. Search your desired space group and setting by scrolling the list on the left-hand side. Mark your selection so that you can see the data available for this space group in the right-hand part of the window. The first line contains Endeavour's internal space group number.

Create a new document in your favorite text editor (e.g. "Notepad"). Type Endeavour's internal space group number in the very first line, followed by the Hermann-Mauguin-symbol in braces, as in

```
1400 (P 1 21/c 1)
```

Afterwards, mark all lines in the Endeavour dialog window starting from the one beginning with "Centering" to the end using the mouse and press <Ctrl-C>. Paste these lines in the second line in your text editor. The text editor should now contain the following lines:

```
1400 (P 1 21/c 1)
Centering: Primitive (P)
Monoclinic axis: b
Monoclinic Cell Choice: 1
Monoclinic Setting: abc
Symmetry Matrices:
(1) x, y, z
(2) -x, 0.5+y, 0.5-z
(3) -x, -y, -z
(4) x, 0.5-y, 0.5+z
Positions:
4e 1 x,y,z
2d -1 0.5, 0, 0.5
2c -1 0, 0, 0.5
2b -1 0.5, 0, 0
2a -1 0, 0, 0
```

You may now close the Endeavour dialog and exit the program. If a monoclinic space group is chosen (as in this example), all lines beginning with "Monoclinic" have now to be removed. This step is not necessary in all other crystal systems.

Finally save the text editor document to the filename "p121c1.sdt". This file should now contain the following:

```
1400 (P 1 21/c 1)
Centering: Primitive (P)
Symmetry Matrices:
(1) x, y, z
(2) -x, 0.5+y, 0.5-z
(3) -x, -y, -z
(4) x, 0.5-y, 0.5+z
Positions:
4e 1 x,y,z
2d -1 0.5, 0, 0.5
2c -1 0, 0, 0.5
2b -1 0.5, 0, 0
2a -1 0, 0, 0
```

That's it! You should copy this file to a separate directory for future usage. This space group may now be employed in the calculation by inserting the line

```
spacegroup(p121c1.sdt)
```

right after the line

```
set(cell,...)
```

in the script file (*.inp).

One final remark: The sdt-files must not contain any tab-characters! Make sure that your text editor converts them to spaces automatically or remove them manually.

Commands to load or save the current configuration

loadcfg(*filename*)

Load an atomic configuration from the file *filename* in the current directory (file extension is **cfg**).

Example:

```
loadcfg(rutile.cfg)
```

The file is an ASCII text file. The first line contains the name of the corresponding space group symmetry file (*.sdt). If the space group is P1, the corresponding symmetry file "p1.sdt" does not need to be present; however, in general this file must be present in order to be able to use the configuration file!

The second line contains Endeavour's internal space group number and the Hermann-Mauguin-symbol. In the next (third) line, the unit cell data (a, b, c, α, β, γ) and the overall temperature factor are given. The remaining lines contain the atomic data (one per line), with the element, charge, Wyckoff symbol, atom coordinates (x, y, z), a parameter which tells whether the corresponding atom is fixed to its position or coordinates (ref. to Table 5), and a number giving the number of the rigid body this atom belongs to (0 means single atom).

Example: $MgCu_2$

```
fd-3m
22700 (F d -3 m)
7.0340 7.0340 7.0340 90.00 90.00 90.00 1.30
mg 0.0 8b 0.50000 0.50000 0.50000 0 0
cu 0.0 16c 0.12500 0.12500 0.12500 0 0
```

The fixing parameter may take the values listed in Table 5.

Table 5: Possible values for the fixing parameter in Endeavour

Value	**Meaning**
0	No fixing
1	Atom is fixed to its current Wyckoff position; free parameters may still be varied during the calculation.
2	x-parameter (fraction of unit cell axis a) is kept fix.
3	Wyckoff-position and x-parameter (fraction of unit cell axis a) are kept fix.
4	y-parameter (fraction of unit cell axis b) is kept fix.
5	Wyckoff position and y-parameter (fraction of unit cell axis b) are kept fix.
6	x-parameter (fraction of unit cell axis a) and y-parameter (fraction of unit cell axis b) are kept fix.
7	Wyckoff position, x-parameter (fraction of unit cell axis a) and y-parameter (fraction of unit cell axis b) are kept fix.
8	z-parameter (fraction of unit cell axis c) is kept fix.

Value	Meaning
9	Wyckoff position and z-parameter (fraction of unit cell axis c) are kept fix.
10	x-parameter (fraction of unit cell axis a) and z-parameter (fraction of unit cell axis c) are kept fix.
11	Wyckoff position, x-parameter (fraction of unit cell axis a) and z-parameter (fraction of unit cell axis c) are kept fix.
12	y-parameter (fraction of unit cell axis b) and z-parameter (fraction of unit cell axis c) are kept fix.
13	Wyckoff position, y-parameter (fraction of unit cell axis b) and z-parameter (fraction of unit cell axis c) are kept fix.
14	x-parameter (fraction of unit cell axis a), y-parameter (fraction of unit cell axis b) and z-parameter (fraction of unit cell axis c) are kept fix.
15	The atom is completely fixed to its current position and coordinates.

savecfg(*filename*)

Save the current configuration in text file *filename* (file extension is **cfg**). File format is the same as in **loadcfg**.

savecifcfg(*filename*)

Save the current configuration in file *filename* using the **CIF-format** (file extension is **cif**). This file is generally used as input for visualization programs like Endeavour or Diamond.

savergscfg(*filename*)

Save the current configuration in text file *filename* (file extension is **rgs**). This file may directly be used as input for the space group detection programs SFND/RGS.

Commands to generate a new configuration

set(cell,a,b,c,alpha,beta,gamma)

Set unit cell parameters.

spacegroup(filename)

Use the space group information in file *filename* (file extension is **sdt**). The generation of this file is described in chapter “Script generation from scratch using a text editor” on p. 77.

Example:

```
spacegroup(fm-3m)
```

newatoms(e, q, n)

The formula unit contains n atoms of element e with charge q.

Example:

```
newatoms(li,1.0,3)
```

The sum formula contains 3 Li^{1+}-ions, as in Li_3RuO_4.

placeatom(e, q, wy, x, y, z, fixed)

Place an atom with element e and charge q at the Wyckoff position wy with coordinates (x,y,z), and eventually fix its position (possible values for *fixed* are listed in Table 5 on p. 82).

Example:

```
placeatom(na,1.0,2b,0.5,0.5,0.5,0)
```

places a new Na^{1+} ion in the middle of the unit cell (if this is compatible with position 2b in the current space group, of course).

newrigid(filename,n)

Loads a molecule described in the emo-file *filename*, determines a random rotation angle and places the rotated molecule at a point chosen at random in the unit cell. This operation is performed n times, so that n molecules are actually placed in the unit cell if the space group is P1.

Note:

Please be aware that **(n * multiplicity of the general position) is the number of molecules in the unit cell, if you employ a space group other than P1 !**

If you have rigid molecules AND single atoms in your calculation, you must use the following order:

```
...
spacegroup(...)
set(z,...)
newrigid(...)
newatoms(...)
...
```

i.e., first select the space group, then give the number of formula units per unit cell Z (if necessary), afterwards create the rigid bodies, and finally create all the single atoms in your compound.}

Example:

```
newrigid(so4.emo,4)
```

generates 4 new SO_4^{2-} molecules described in file “so4.emo”.

The emo-file format is as follows:

The file has three parts: In the first part (first line), an identifier for the molecule (e.g. its trivial name) is given. In the second part (starting with the second line) atoms (element and charge) and positions (given as cartesian coordinates) are given. The third part contains the list of the bonds between the atoms. Each bond is given as the number of the first atom in part one, the number of the second atom, and a bond order number that is currently only used to distinguish between fixed (-1.0) and rotatable (1.0) bonds.

For example, this may be the contents of the file "so4.emo":

```
Sulfate
S 6.0 4.79160 1.34938 5.68411
O -2.0 3.45273 1.34938 6.30277
O -2.0 5.87100 1.34938 6.65072
O -2.0 4.92896 2.54816 4.80728
O -2.0 4.92896 0.15059 4.80728
1 2 -1.0
1 3 -1.0
1 4 -1.0
1 5 -1.0
```

The creation of emo-files is described in detail in the chapter "Solution of molecular structure (2,4,6-Tri-isopropylbenzenesulfonamide)" starting on p. 37.

placerigid(filename, 1, na, x, y, z, fix, allow_rotation)

Loads a molecule described in the emo-file *filename* and places the molecule with atom no. *na* at point (*x*, *y*, *z*) in the unit cell. If *fix* is set to 1 (default value: 0), the molecule is fixed at this position. If *allow_rotation* is set to 1 (default value: 0) in addition to *fix*=1, the molecule is allowed to rotate around atom no. *na*, the position of which is kept fix.

Example:

```
placerigid(triiso.emo,1,0.74252,0.72595,0.97666,0,0)
```

Normally (i.e. when using the user interface), you can **place and/or fix molecules** by pressing the "Place molecule(s)..." button on page 2 of the structure solution wizard.

Commands to load or save powder diffraction data

loadpdiffexp(*filename*)

Load an experimental powder diffraction pattern that is provided in a simple "intensity vs. 2θ" format from the file *filename* in the current directory (file extension is **dif**). The 2θ-values given in this file are adjusted to the nearest peak position in the pattern calculated from the unit cell. Hence, the **unit cell parameters have to be set before execution of this command!**

Example: X-ray powder diffraction pattern of Na_3OBr (Cu Kα1 radiation, λ = 1.540598 Å):

```
19.7189  25.9
27.8637  87.3
34.2050 100.0
39.6483  90.4
44.6710   8.7
49.1801  20.6
57.3520  38.3
61.1547   7.0
```

```
  64.8108  12.9
68.3557  37.4
71.7964  14.2
75.2016   5.5
78.5329  16.0
```

loadfhklexp(*filename*, *type_of_values*)

Load experimental diffraction data that are provided either as structure factor values |F(hkl)| (**type_of_values = 0**), square of structure factor values F^2(hkl) (**type_of_values = 1**), or intensity values I(hkl) (**type_of_values = 2**) for some selected (or all) Bragg reflections (given as hkl) from the file **filename** in the current directory (file extension is **hkl**). The file contains one factor per line, in the order h k l value(|F|, F^2 or I).

Example: Selected structure factors |F(hkl)| (triclinic) taken from the $PbSO_4$*-example of Le Bail's program "Espoir":*

```
1  0  0   0.000
0  0  1   0.000
0  1  0   0.000
1  0 -1  13.010
1  0  1  13.010
1 -1  0   0.000
1  1  0   0.000
0  1 -1  94.999
0  1  1  94.999
2  0  0  83.841
```

Please note: If you would like to use the information that some reflections are systematically absent, you should give these reflections with 0.0 intensity or structure factor values, e.g.

```
1  0  0   0.000
```

savepdiffexp(*filename*)

Save the experimental powder diffraction pattern in memory in "intensity vs. 2θ" format to the file *filename* in the current directory (file extension is **dif**).

savepdiffcalc(*filename*)

Save the powder diffraction pattern calculated for the current configuration in "intensity vs. 2θ" format to the file *filename* in the current directory (file extension is **dif**).

savehklcalc(*filename*)

Save the powder diffraction pattern calculated for the current configuration as |F(hkl)| (structure factor for each Bragg reflection between 2thetamin and 2thetamax) to the file *filename* in the current directory (file extension is **hkl**).

savepdifference(*filename*)

Save the difference of the experimental and the calculated powder diffraction pattern to the file *filename* in the current directory (file extension is **dff**). A special output format is used if only selected Bragg reflections were loaded (*loadhklexp*).

Commands to influence the curse of the program

loopstart

This command marks the beginning of a loop. The loop counter is the seed value of the random number simulator. Its current value is the starting point. The end of the loop is marked by *loopend*.

loopend(n)

This command marks the end of the loop. If the current seed value is lower than n, the program will enlarge seed by 1, close the current protocol file, open a new one, and proceed with the command following loopstart.

Please note: Only one loop construction per script is permitted!

Example: Loop from seed=6 to seed=10 (5 runs) for the example Li_3RuO_4*:*

```
set(seed,6)
loopstart
set(cell,5.1059,5.8540,5.1056,90.0,110.0,90.0)
set(z,2)
newatoms(li,1.0,3)
newatoms(ru,5.0,1)
newatoms(o,-2.0,4)
loadpdiffexp(rus2.dif)
optimize
loopend(10)
```

exit

Save the current configuration in a variety of formats, close the output (protocol) file and stop. There is no need to give an *exit* command at the end of the script file!

Commands that affect the calculation of the potential energy

tempfactfit

Fit the overall temperature factor during every cost function evaluation so that the difference between the calculated and the experimental diffraction pattern reaches a minimum. This is the default setting.

no_tempfactfit

Do not fit the overall temperature factor; use the predefined value *tempfact* instead.

set(dumscatter, radiation,a1,b1,a2,b2,a3,b3,a4,b4,c)

Set the scattering power of the dummy atoms (element "du") for the radiation type "radiation" (given as a number, e.g. 0 for X-rays). The parameters a1..c are compatible to those given in the International Tables. Default is no scattering.

Commands that affect the optimization process

optimize

Start the actual structure solution calculation (i.e. simulated annealing optimization).

refine

Performs a local Monte Carlo-based optimization until convergence is reached. Convergence is defined by the "optspeed" parameter: The lower its value, the longer the calculation.

Commands for the setting/printing of parameter values

set(*variable,value(s)*)

Set the variable variable equal value. See the list of variables below. If there are more than one value, the values are separated by comma.

Example:

```
set(seed,5)
```

restarts the random number simulator with the start value 5.

printparameters

Print the values of all parameters and variables to the protocol file. This is done automatically before an optimization is started.

Other commands

#

Sign for **comment**. It has to be the first sign in the line. Any other text in this line will be ignored.

printcost

Prints the current value of the cost function to the protocol file. This is done automatically at the beginning and at the end of every optimization run.

List of Variables (to be set with "set(varname,value)"

Table 6: Variables that affect the calculation of the pattern difference

Name	Type	Min.	Max.	Default	Comment
cfweight	float	0.0	1.0	0.5	Weighting factor for the two cost function parts pattern difference and potential energy. The larger the value, the larger the contribution of the pattern difference (R-factor). cfweight = 0 indicates that no comparison of the calculated and the experimental pattern shall be performed, cfweight = 1.0 means no use of potential energy.
radiation	integer	0	2	0	Type of radiation combined with Lorentz-(L) and polarization (P) correction. radiation = 0: X-rays (L+P) = 1: neutron (L+P) = 2: electron (L+P) =10: X-rays (L) =11: neutron (L) =12: electron (L) =20: X-rays (P) =21: neutron (P) =22: electron (P) =30: X-rays (-) =31: neutron (-) =32: electron (-) lambda is set to the corresponding default value (X-ray: 1.540598 Å, neutron: 1.76 Å, electron: 0.111 Å (12 kV)) **Notes concerning neutron radiation:**} Hydrogen (H) is assumed to be Deuterium (D). The imaginary part in scattering lengths of B, Cd, In, Sm, Eu, Gd, Dy is neglected. **Notes concerning electron radiation:** Only kinematic model, no calculation of dynamic scattering!
lambda	float	0.01	5.0	1.540598 Å (Cu Kα1)	Wavelength of the X-ray, neutron or electron radiation in Å.

Name	Type	Min.	Max.	Default	Comment
geometry	integer	0	1	0	Geometry of the powder diffractometer: geometry=0 is Debye-Scherrer, geometry=1 is Guinier.
guinangle	float	2.0	180.0	30.0	Only for Guinier geometry: Angle between the normal to the specimen and the direction of the incident beam.
guind	float	0.5	10.0	3.343	Only for Guinier geometry: Diffraction angle of monochromator.
precession_angle_alpha	float	0.0	90.0	0.0	Precession angle alpha.
background	float	0.0	100.0	0.1	Intensity of the background radiation. Intensities lower than this value will be ignored in the comparison of the pattern difference.
tempfact	float	0.0	100.0	1.3	Overall temperature factor B_0. If this value is not set, Endeavour automatically optimizes the temperature factor before each R-factor calculation.
2thetamin	float	2.0	2thetamax	2.0	Minimum 2θ-value from which the powder pattern is calculated. May be used to exclude low angle diffraction data from the calculation. You have to set this value after the loadpdiffexp command.
2thetamax	float	2thetamin	180.0	180.0	Maximum 2θ-value up to which the powder pattern is calculated. This value is set automatically if a new experimental diffraction pattern is read in. If you want to exclude high angle diffraction data from the calculation, you have to set this value after the loadpdiffexp command.
smooth_rfactors	integer	0	1	0	Smoothing of R-factor hypersurface. Smoothing is appr. proportional to log(smooth_parameter).
smooth_parameter	float	0.0	100.0	3.0	Coefficient of R-factor smoothing function. A value of 0.0 is equivalent to “no smoothing”.
smooth_Fhkl_comparison	integer	0	1	0	Smoothing of structure factor F(hkl) or intensity I(hkl) comparison if F(hkl) or I(hkl) > 0.0.
merge_reflections_Fhkl	integer	0	3	0	= 0: Use individual reflections (do not merge); =1: Use average for Friedel reflections, do not merge symmetry equivalent refl.;

Name	Type	Min.	Max.	Default	Comment
					=2: Use average for symmetry equivalent reflections, do not merge Friedel refl.; =3: Use average for Friedel and symmetry equivalent reflections.
check_peak_positions	integer	0	1	1	Check agreement of experimental and calculated peak positions in order to verify the unit cell parameters.
max_average_peak_dev	float	0.0	1.0	0.05	Maximum average deviation of exp. peak positions from calculated values.
peak_triangles	integer	0	1	0	Use profile function instead of peaks for R-factor calculation, in order to reduce/avoid problems in assignment experimental ↔ calc. peak (position).
step_size	float	0.01	1.0	0.1	Step size 2θ for profile calculations
triangle_base_width	float	0.01	1.0	0.15	Full width at half maximum (FWHM) for profile calculation
increase_large_2theta_ contribution	integer	0	1	0	Increase R-factor contribution of peaks at large 2θ values.
point_of_inflection	float	5.0	120.0	25.0	2θ angle above which the intensity difference contribution to the R-factor is increased
max_weight	float	1.0	100.0	10.0	Maximum weighting factor for high-angle contributions to the R-factor

Table 7: Variables that affect the calculation of the potential energy

Name	Type	Min.	Max.	Default	Comment
pottype	integer	2	3	3	Type of two-body potential: =2: Lennard-Jones potential =3: Simple repulsion potential =4: Hofmann potential
simpreppot_uses_charges	integer	0	1	0	Defines whether the simple repulsion potential shall use charges (i.e. perform an Ewald sum) (=1) or not (=0)
molecule_stiffness	float	0.0	5000.0	400.0	Flexibility parameter for the “flexible molecules” option
molecule_distortion_ weight	float	0.0	10.0	1.0	Weighting factor for “molecule distortion energy” (for “flexible molecules” option)

Table 8: Variables that control the generation of the first configuration

Name	Type	Min.	Max.	Default	Comment
Cell	6*float	3*1.0 3*10.0	3*1000.0 3*180.0	-	Unit cell parameters given in the order a, b, c, α, β, γ
Z	integer	1	INT_MAX	1	Number of formula units per unit cell

Table 9: Variables that control the generation of every subsequent configuration

Name	Type	Min.	Max.	Default	Comment
molecules_flexible	integer	0	1	0	If activated (=1), atoms in molecules may move independent from the rest of the molecule. Molecules are no longer rigid bodies. Flexibility is controlled by parameters "molecule_stiffness" and "molecule_distortion_weight" (see potential energy calculation variables).
allow_molecules_on_special_pos	integer	0	1	1	This is a new option introduced in Endeavour version 1.8. If it is active, Endeavour tolerates effects that become evident if an atom belonging to a molecule (rigid body) is moved or placed close to (or even on) a special position of the space group. Typically, this causes the creation of multiple copies of the molecule (or at least some of its atoms) at rather close distances, which normally would be rejected due to the corresponding dramatic increase of potential energy and / or scattering power (→ R-factor!).
atom_move_max_0	float	0.01	10.0	1.5	Max. shift of atoms [Å] in initialization phase (phase 0)
atom_move_max_1	float	0.01	10.0	0.9	Max. shift of atoms [Å] in first optimization phase (phase 1)
atom_move_max_2	float	0.01	10.0	0.5	Max. shift of atoms [Å] in middle optimization phase (phase 2)
atom_move_max_3	float	0.01	10.0	0.3	Max. shift of atoms [Å] in final optimization phase (phase 3)
at_move_max_ref_1	float	0.01	10.0	2.7	Max. shift of atoms [Å] during first part of local opt. ("refinement")
at_move_max_ref_2	float	0.01	10.0	0.8	Max. shift of atoms [Å] during second part of local opt. ("refinement")
mol_move_max_0	float	0.01	10.0	3.0	Max. shift of molecules [Å] in initialization phase (phase 0)

Name	Type	Min.	Max.	Default	Comment
mol_move_max_1	float	0.01	10.0	3.0	Max. shift of molecules [Å] in first optimization phase (phase 1)
mol_move_max_2	float	0.01	10.0	3.0	Max. shift of molecules [Å] in middle optimization phase (phase 2)
mol_move_max_3	float	0.01	10.0	0.5	Max. shift of molecules [Å] in final optimization phase (phase 3)
mol_rot_max_0	float	0.1	360.0	270.0	Max. rotation of molecules [°] in initialization phase (phase 0)
mol_rot_max_1	float	0.1	360.0	180.0	Max. rotation of molecules [°] in first optimization phase (phase 1)
mol_rot_max_2	float	0.1	360.0	90.0	Max. rotation of molecules [°] in second optimization phase (phase 2)
mol_rot_max_3	float	0.1	360.0	25.0	Max. rotation of molecules [°] in final optimization phase (phase 3)
mol_part_rot_max	float	0.1	360.0	270.0	Max. rotation of molecule part [°] around rotatable bond
mol_move_max_quench	float	0.01	10.0	3.0	Max. shift of molecules [Å] during intermediate local optimizations
mol_rot_max_quench	float	0.1	360.0	90.0	Max. rotation of molecules [°] during intermediate local optimizations
mol_part_rot_max_quench	float	0.1	360.0	90.0	Max. rotation of molecule part [°] around rotatable bond during intermediate local optimizations
mol_move_max_ref_1	float	0.01	10.0	0.1	Max. shift of molecules [Å] during first part of local optimization (“refinement”)
mol_move_max_ref_2	float	0.01	10.0	0.1	Max. shift of molecules [Å] during second part of local optimization (“refinement”)
mol_rot_max_ref_1	float	0.1	360.0	0.5	Max. rotation of molecules [°] during first part of local optimization (“refinement”)
mol_rot_max_ref_2	float	0.1	360.0	0.5	Max. rotation of molecules [°] during second part of local optimization (“refinement”)
mol_part_rot_max_ref_1	float	0.1	360.0	270.0	Max. rotation of molecule part [°] (around rotatable bond) during **first** part of local optimization (“refinement”)
mol_part_rot_max_ref_2	float	0.1	360.0	270.0	Max. rotation of molecule part [°] (around rotatable bond) during **second** part of local optimization (“refinement”)

Table 10: Options and parameters which control the global optimization (simulated annealing)

Name	Type	Min.	Max.	Default	Comment
tinit	float	1.0E-70	10000.0	0.5	Initial control parameter (“temperature”) value for the simulated annealing.
find_tinit_automatically	integer	0	1	0	Automatically determine the starting “temperature”, by increasing the control parameter “temperature” until a certain minimum acceptance rate regarding the moves (“min_start_acc_rate “) is exceeded
min_start_acc_rate	integer	1	99	75	Minimum percentage of accepted “moves” (changes) for the starting of the “annealing” (cooling)
max_start_temperature	float	1.0	10000.0	10000.0	Maximum search “temperature” above which the annealing is started in any case, independent if the “required minimum percentage of accepted moves” has been reached or not.
equilsteps	integer	1	10000	300	“Equilibration” steps per degree-of-freedom in initialization phase (phase 0) of the global optimization
intermediate_quenches	integer	0	1	0	Perform a short local optimization (“quench”) after each extensive structure modification (e.g. exchange of atoms, rotation of molecule etc.)
min_num_relaxsteps	integer	1	1000	10	Minimum number of intermediate quench steps
t_ref_phase_1	float	1.0E-7	0.1	0.0001	Control parameter (“temperature”) for the **first** part of a local optimization (“refinement”)
t_ref_phase_2	float	1.0E-7	0.1	0.0001	Control parameter (“temperature”) for the **second** part of a local optimization (“refinement”)
min_num_tsteps_0	integer	1	10000	10	Minimum number of Monte-Carlo steps (“moves”) per “temperature” step during **initialization** phase of global optimization (phase 0)
min_num_tsteps_1	integer	1	10000	10	Minimum number of Monte-Carlo steps (“moves”) per “temperature” step during **first** optimization phase of global optimization (phase 1)
min_num_tsteps_2	integer	1	10000	10	Minimum number of Monte-Carlo steps (“moves”) per “temperature” step during **middle** optimization phase of global optimization (phase 2)
min_num_tsteps_3	integer	1	10000	10	Minimum number of Monte-Carlo steps (“moves”) per “temperature” step during **final** optimization phase of global optimization (phase 3)

Name	Type	Min.	Max.	Default	Comment
tparam	float	0.1	0.999	0.9	Reduction factor for control parameter ("temperature"): $T_{n+1} = T_n \cdot tparam$
tlimit	float	1.0E-7	0.1	0.001	Simulated annealing (global optimization) stops when the control parameter "temperature" has fallen below this value.
maxnumsteps	integer	0	1E9	1E9	Simulated annealing (global optimization) stops when this maximum number of steps has been reached.

Table 11: Other variables

Name	Type	Min.	Max.	Default	Comment
cfweight	float	0.0	1.0	0.5	Pareto parameter to adjust the cost function balance. The higher the value, the larger is the contribution of the R-factor (pattern difference) to the overall cost function. cfweight = 0.0 allows an optimization based on potential energy only (no diffraction data needed); cfweight = 1.0 uses ONLY diffraction data and no potential energy is calculated.
seed	integer	1	INT_MAX	1	Start value for the random number simulator. Identical values of seed cause an identical sequence of random numbers that are generated.
writestep	integer	0	INT_MAX	1	Every *writestep* steps the current configuration is saved in the "intermediate" files inter.*
optspeed	integer	1	10	10	Optimization speed. The higher this value, the faster the optimization, but the less is the probability that the global minimum (assumed to be equivalent with the correct crystal structure model) is found (and vice versa).

Structure data file formats

Native format (EDF)

The native structure file format used by Endeavour is the “Endeavour Document File” format (EDF). This format is binary, which means that it cannot be read by a text processor (in contrast to e.g. files in CIF format).

Please note: The EDF format is the only file format that can store all kinds of data entered or changed in an Endeavour session, whereas the other file formats supported by Endeavour usually store structural parameters or diffraction data and some textual data only.

Files with the extension “EDF” are treated automatically as Endeavour Document Files, since Endeavour has registered this file type on your Windows operating system. Thus, Windows recognizes an EDF file as “Endeavour Document” and starts Endeavour automatically when you double-click on an EDF file, e.g. in the Windows Explorer.

Foreign files are opened in principally the same way as native Endeavour document files. That means, there is no separate “Import” command like in some other competitive applications. Moreover, Endeavour recognizes the format automatically and creates a temporary EDF file (as copy) from the original file, where it reads data from later. This applies to crystal or molecular structure files as well as to diffraction data files (containing a peak list or |F(hkl)| values).

In the following, we refer to crystal structure files only.

If the file contains one structure description only, a structure window will be created for that structure automatically. If there are multiple structure descriptions, a list of all entries in the file will be displayed, where you can select one or more structures from.

If the file contains one structure description only, a structure window will be created for that structure automatically. If there are multiple structure descriptions, a list of all entries in the file will be displayed, where you can select one or more structures from.

Foreign file formats supported by Endeavour and how they are recognized

The following file formats can be recognized and read by the current version of Endeavour:

Diamond 2.x	This format (DSF 2) is fully compatible with the Endeavour 1.x format.
Diamond 1.x	This format is binary like EDF (or DSF 2), but uses a quite different format than Diamond 2, and is thus treated as a “foreign” format like the other formats below.
Crystallographic Information File (CIF)	This free text format is recognized by a line beginning with “data_”, e.g. “data_global” or “data_cstio3”.
CRYSTIN Download	This text format is created by the retrieval system called “Retrieve” belonging to the Inorganic Crystal Structure Database (ICSD) release 2002 (or earlier); it is recognized by a line beginning with “0000”, which signs the beginning of the first or the next entry.
Cambridge Structural Database (CSD) FDAT	This text format is created by the retrieval system of the Cambridge Structural Database (CSD) with the “SAVE 3” command and is recognized by a line beginning with “#” followed by the CSD Reference Code, which signs the beginning of the first or the next entry.
Brookhaven Protein Data Bank (PDB)	This text format may be created from the browser of the Protein Data Bank (PDB) and is recognized by the “HEADER” statement signing the beginning of the PDB entry.
Philips X'Pert Plus (IDF)	This text format is normally created by the program X'Pert Plus (crystallography and Rietveld analysis) from PANalytical and is recognized by the “[ANZAHLATOME]” keyword. Each phase no. n in this file starts with a “[PHASE n]” record.
SHELX-93	To recognize this text format, Endeavour searches for a line beginning with “CELL”, which indicates wave length and the cell parameters a, b, c, alpha, beta, and gamma.

XYZ	This text format is recognized as XYZ format, if the first line contains a number and the third line consists of element symbol plus three floating point numbers.

Data items read from a Crystallographic Information File (CIF)

You can get all information about the Crystallographic Information File (CIF) format[63] from the web page of the International Union of Crystallography (IUCr):

https://www.iucr.org/resources/cif

The following CIF data items are evaluated by the current version of Endeavour:

CIF data item	**Comment**
_atom_site_aniso_label	This symbol is used to identify an atom in the parameter list.
_atom_site_aniso_U_11, etc.	The anisotropic displacement parameters of type U, given in Å².
_atom_site_aniso_B_11	dito for type B.
_atom_site_attached_hydrogens	The number of hydrogen atoms attached to the atom at this site excluding any H atoms for which coordinates (measured or calculated) are given.
_atom_site_calc_flag	"d": this site has been determined from diffraction measurements; "calc": this site has been calculated from molecular geometry; "dum": dummy site with meaningless coordinates.
_atom_site_fract_x, _atom_site_fract_y, _atom_site_fract_z	The coordinates of the atom site as fractional coordinates x/a, y/b, and z/c, that means relative to the axes of the unit cell.
_atom_site_label	The label (that means identifier) of the atom site.
_atom_site_occupancy	The fraction of the atom present at this site.
_atom_site_symmetry_multiplicity	The multiplicity of the site.
_atom_site_thermal_displace_type	A standard code used to describe the type of atomic displacement parameters used for this site. Endeavour accepts the following codes: "Bani" for anisotropic displacement parameters of type B, "Uani" for anisotropic displacement parameters of type U, "Biso" for an isotropic or equivalent displacement parameter of type B, "Uiso" for an isotropic or equivalent displacement parameter of type U.
_atom_site_type_symbol	The symbol of the corresponding atom type. This symbol must occur in the atom type loop.
_atom_site_U_iso_or_equiv	The isotropic displacement parameter, or the equivalent displacement parameter calculated from anisotropic displacement parameters, with units in Å².
_atom_site_Wyckoff_symbol	The Wyckoff letter of the site.

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[63] The original paper describing the CIF standard has been published in Acta Cryst. A**47**, 655-685 (1991).

CIF data item	**Comment**
_atom_type_oxidation_number	The formal oxidation state or charge of the corresponding atom type, which has usually been defined previously in the atom type loop.
_atom_type_radius_bond	The effective radius of the corresponding atom type.
_atom_type_symbol	The symbol of an atom type. This symbol may be used in the atom site loop to reference the atom type from the atomic parameter list.
_audit_creation_date	A date that the CIF is created, with format yy-mm-dd.
_audit_creation_method	A description of how data was entered into the CIF. This is treated as simple text.
_audit_update_record	A record of any changes to the CIF. Only the date (format yy-mm-dd) will be read by Endeavour, but not the description of changes, which may follow the date.
_cell_angle_alpha, _cell_angle_beta, _cell_angle_gamma	The unit cell angles alpha, beta, and gamma in degrees. Standard uncertainties will be accepted by Endeavour.
_cell_formula_units_Z	The number of formula units in the cell. This value is treated as integer number.
_cell_length_a, _cell_length_b, _cell_length_c	The lengths of the unit cell axes a, b, and c in Å (Angstroems).
_cell_volume	The volume of the unit cell in Å^3. This value will be overwritten, since Endeavour calculates the cell volume from the cell parameters.
_chemical_compound_source	The source of the compound, which will be treated as simple text.
_chemical_formula_analytical	The analytical formula which may contain traces of elements not mentioned in the atomic parameter list. This kind of formula is treated as text and not evaluated by Endeavour and not compared with the atomic parameter list.
_chemical_formula_structural	The structural formula, which is treated as text and not evaluated by Endeavour and not compared with the atomic parameter list.
_chemical_formula_sum	The formula sum, which should agree with the atomic parameter list. This data will be read by Endeavour, but overwritten there by the calculated formula sum.
_chemical_formula_weight	The formula mass in Daltons.
_chemical_formula_weight_meas	The formula mass in Daltons measured by a non-diffraction experiment.
_chemical_melting_point	The melting point of the crystal in Kelvin.
_chemical_name_mineral	The mineral name.
_chemical_name_structure_type	The name of the structure type (prototype).

CIF data item	Comment
_chemical_name_systematic	The IUPAC or Chemical Abstracts full name of the compound.
_database_code_CAS	The Chemical Abstracts Code.
_database_code_CSD	The "Reference Code" of the Cambridge Structural Database (CSD).
_database_code_ICSD	The "Collection Code" of the entry in the Inorganic Crystal Structure Database (ICSD).
_database_code_MDF	The reference code of the "CRYSTMET" Metals Data File.
_exptl_crystal_density_meas	Density value measured using standard chemical and physical methods, in g/cm^3.
_geom_angle	An angle in degrees bounded by the corresponding site labels. The apex of the angle is at site label #2.
_geom_angle_atom_site_label_1, _geom_angle_atom_site_label_2, _geom_angle_atom_site_label_3	The atom site labels of the three atoms which define the angle specified by "_geom_angle", where "_geom_angle_atom_site_label_2" specifies the atom at the apex of the angle.
_geom_angle_publ_flag	This code signals if the angle is referred to in a publication of should be placed in a table of significant angles ("yes" or "no").
_geom_angle_site_symmetry_1, _geom_angle_site_symmetry_2, _geom_angle_site_symmetry_3	The symmetry code of the atom #1, #2, and #3 that define the angle.
_geom_bond_atom_site_label_1, _geom_bond_atom_site_label_2	The atom site labels of the two atoms that form a bond.
_geom_bond_distance	The bond length in Å (Angstroems).
_geom_bond_publ_flag	This code signals if the bond distance is referred to in a publication of should be placed in a list of special bond distances ("yes" or "no").
_geom_bond_site_symmetry_1, _geom_bond_site_symmetry_2	The symmetry code of the atom #1 and #2 that define the bond distance.
_geom_contact_atom_site_label_1, etc.	Endeavour treats the items beginning with "_geom_contact..." like bonds, that means like the corresponding items beginning with "_geom_bond...".
_geom_torsion	The torsion angle in degrees bounded by the corresponding four atom sites. The torsion angle definition should be that of W. Klyne, V. Prelof, Experientia **16**, 521-528 (1960).
_geom_torsion_atom_site_label_1, _geom_torsion_atom_site_label_2, _geom_torsion_atom_site_label_3, _geom_torsion_atom_site_label_4	The atom site labels of the four atoms that define the torsion angle. The vector direction from atom #2 to #3 is the viewing direction, and the torsion angle is the angle of twist required to superimpose the projection of the vector site 2 - site 1 onto the projection of the vector site 3 - site 4. Clockwise torsions are positive, counterclockwise torsions are negative.

CIF data item	Comment
_geom_torsion_publ_flag	This code signals if the torsion angle is referred to in a publication of should be placed in a list of special torsion angles (“yes” or “no”).
_geom_torsion_site_symmetry_1, _geom_torsion_site_symmetry_2, _geom_torsion_site_symmetry_3, _geom_torsion_site_symmetry_4	The symmetry code of the atom #1, #2, #3, and #4 that define the torsion angle.
_journal_coden_ASTM	The ASTM journal coden of the publication.
_journal_page_first, _journal_page_last	The first and last page of the publication. These values are treated as text instead of numbers, since they may contain extensions like “255A”.
_journal_volume	The volume of the publication, treated as text.
_journal_year	The year of the publication. If it is less than 100, 1900 will be added.
_publ_author_name	The name of the author or the name of one of the authors.
_publ_section_comment	A comment which usually consists of multiple lines.
_publ_section_title	The title of the publication.
_refine_ls_R_factor_all	Residual factor for all reflection data.
_refine_ls_R_factor_obs	Residual factor for reflection data classified as “observed”.
_symmetry_cell_setting	The cell settings for the space group symmetry of the entry, which is used to supplement missing cell parameters. This can be one of the symbols “triclinic”, “monoclinic”, “orthorhombic”, “tetragonal”, “rhombohedral”, “trigonal”, “hexagonal”, and “cubic”.
_symmetry_equiv_pos_as_xyz	A symmetry matrix in the “x,y,z” format, including those for lattice centering and center-symmetry, if present.
_symmetry_int_tables_number	The space group number from the International Tables for Crystallography, Vol. A.
_symmetry_space_group_name_Hall	The Hall space group symbol (compare S.R. Hall, Acta Cryst. A**37**, 517-525 (1981).).
_symmetry_space_group_name_H-M	The Hermann-Mauguin space group symbol.

Data read from the CRYSTIN Download format

A “CRYSTIN download file” can contain multiple structure descriptions, usually of entries of the Inorganic Crystal Structure Database (ICSD). Endeavour reads the following data from each entry of the file. (This information is taken from the ICSD-CRYSTIN user's manual, by G.Bergerhoff, B.Kilger, C.Witthauer, R.Hundt, R.Sievers, Institut fuer Anorganische Chemie der Universitaet Bonn, 1986):

```
1st record of every entry:

 Byte
 1- 8  ' 0000   ' Record label
```

9-14	Collection code
15	free
16-21	Relative entry number
22-80	free

This record is followed by other records with various formats, according to the selected categories.

Categories with unstructured text:

Byte	
1	free
2- 3	figures according to the categories: 1 - NAME (N) Compound name 2 - RFCD (V) Refcode (only in CCDF) 3 - MINR (M) Mineral name 4 - FORM (F) Chemical formula 5 - TITL (T) Title of publication 7 - AUT (A) Author's name 9 - SGR (R) Space group symbol after Hermann-Mauguin 16 - REM (Z) Additional remarks 19 - PICT (K) Information to produce a drawing in optimized view
4	0
5	Number of continuation records. 0 if the text contains less than 73 characters.
6- 8	free
9-80	Text. After each 72 characters a continuation record is used.

Category REF (Q):

Byte	
1- 8	' 600 ' Record label
9-10	Year of publication
11-15	CODEN
16-22	Volume
23-29	First page
30-36	Last page (in CCDF: repetition of first page)
37	free
38	Character (if the page numbers consist of figures with a preceding alphabetic character); otherwise free
39-42	Issue, if necessary. Otherwise 0.

Category CELL (E). Missing fields are indicated by -1.0. Standard deviations are given in an absolute scale.

Byte	
1- 3	' 800 ' Record label
9-17	a (A)
18-25	Sigma(a)
26-34	b (A)
35-42	Sigma(b)
43-51	c (A)
52-59	Sigma(c)
60-66	Alpha (degrees)
67-74	Sigma(alpha)
75-80	free

Byte	
1- 3	' 810 ' Record label
9-15	Beta (degrees)
16-23	Sigma(beta)
24-30	Gamma (degrees)
31-38	Sigma(gamma)
39-41	Number of formula units
42-47	Measured density
48-55	Sigma(density)
56-66	Unit cell volume (A**3)
67-80	free

Category SYM (S):

Byte	
1- 8	' 100 ' Record label
9-16	1st line of symmetry matrix
17-24	2nd line
25-32	3rd line
33-80	free

Category PARM (P):

Byte	
1- 8	' 1200 ' Record label
9-10	Atomic symbol
11-13	Number
14-19	Oxidation state
20-22	Number of positions. In CCDF: Multiplicity of the general position.
23	Wyckoff symbol
24-31	x
32-39	Sigma(x)
40-47	y
48-55	Sigma(y)
56-63	z
64-71	Sigma(z)
72-80	free

Byte	
1- 8	' 1210 ' Record label
9	Type of temperature factor (B, U, A or L)
10-20	Isotropic temperature factor if byte 9 is B oder U
21-29	Standard deviation of isotropic temperature factor
30-36	Site occupation, related to the multiplicity of the special position
37-44	Standard deviation of the site occupation
45	Number of non-located hydrogen atoms (H or D) bonded to the atom
46	H or D, if byte 45 is not 0
47-80	free

Categories BETA (B), BIJ (C) or UIJ (D):

Byte	
1- 8	' 1300 ' = Temperature factor type "Beta(i,j)" ' 1400 ' = Type "B(i,j)" ' 1500 ' = Type "U(i,j)"
9-10	Atomic symbol
11-13	Number
14-24	Factor (1,1)
25-33	Sigma

```
34-44  Factor (2,2)
45-53  Sigma
54-64  Factor (3,3)
65-73  Sigma
74-80  free

 Byte
 1- 8  ' 1310   ' = Temperature factor type "Beta(i,j)"
       ' 1410   ' = Type "B(i,j)"
       ' 1510   ' = Type "U(i,j)"
 9-19  Factor (1,2)
20-28  Sigma
29-39  Factor (1,3)
40-48  Sigma
49-59  Factor (2,3)
60-68  Sigma
69-80  free


Category RVAL (I):

 Byte
 1- 8  ' 1800   ' Record label
 9-17  R value
18-80  free


Category TEST (Y):

 Byte
 1- 8  ' 2000   ' Record label
 9-10, 11-12, 13-14 etc.: Code figures


Category SMAT:

 Byte
 1- 4  ' 240' Record label
 5- 6  Number of SMAT Records which follow immediately
 7- 8  free
 9     Keys for the Bravais translations:
       0 = P     3 = B     7 = R (obverse)
       1 = F     4 = C     8 = R (reverse)
       2 = A     5 = I    (7 or 8 only for space
                           groups in hexagonal setting)
10     free
11-18  t1
19-22  r12
23-26  r13
27-30  r14
31-38  t2
39-42  r21
43-46  r22
47-50  r23
51-58  t3
59-62  r31
63-66  r32
67-70  r33
71-73  Space group number (Int. Tables) or 0
```

Data read from a Philips X'Pert Plus IDF file

Endeavour recognizes the IDF format by the keyword “[ANZAHLATOME]”. Since an IDF file may contain multiple (N) phases, it extracts N sets of structural parameters. If N is greater than one, the “Load” dialog is displayed after you have opened an IDF file, where you can select one or more crystal structure descriptions from. This behavior is comparable with the CIF/Crystin Import Structures dialog in X'Pert Plus. If N is one, a new structure window is opened automatically without further request.

Endeavour uses the keyword "[PHASE n]" keyword in the IDF file as beginning of the n-th structural description. For every structure, Endeavour extracts data from the following sections (keywords given in brackets) into the mentioned Endeavour data fields:

[AUDCREATDATE]	Date of creation of the structure/phase
[AUDCREATMETH]	Creation method
[DATACODEICSD]	ICSD Collection Code if the structure has been imported from the Inorganic Crystal Structure Database
[CHEMNAMESYST]	The systematical chemical name
[CHEMNAMEMIN]	The mineral name
[CHEMCOMPSOUR]	The source of the compound
[CHEMFORMSTRU]	The structural chemical formula
[CHEMFORMSUM]	The formula sum
[PUBLSECTTITL]	The title of the publication (not the title of the phase)
[PUBLSECTCOMMENT]	Comments
[PUBLAUTHNAME]	The name(s) of the author(s) of the publication
[JOURCODEASTM]	The ASTM Journal Coden of the publication
[JOURVOLUME], [JOURYEAR], [JOURPAGEFIRS], [JOURPAGELAST]	Volume, year, first and last page of the publication
[TITEL]	The title used to identify the structure/phase
[ANZAHLATOME]	Number of atoms in the parameter list
[CELLA], [CELLB], [CELLC], [CELLALPHA], [CELLBETA], [CELLGAMMA]	The cell parameters in Å (Angstroems) and ° (degrees) (Standard uncertainties are read if given.)
[DSFNO]	The internal space group number used by both X'Pert Plus and Endeavour
[NAME]	The symbols for the <ANZAHLATOME> atoms in the parameter list
[ELEMENT]	The element symbols for the atoms in the parameter list
[X], [Y], [Z]	The fractional coordinates x/a, y/b, z/c and their standard uncertainties of the atoms in the parameter list
[B]	The isotropic displacement parameters of type B (plus standard uncertainties) for the atoms in the parameter list
[F]	The site occupation factors (plus standard uncertainties) for the atoms in the parameter list

[B11], [B22], [B33], [B12], [B13], [B23]	The anisotropic displacement parameters of type Bij (plus standard uncertainties) of the atoms in the parameter list
[MULT]	The multiplicities of the atoms in the parameter list
[WYKSEQ]	The Wyckoff letters plus multiplicities of the atoms in the parameter list
[OXSTATE]	The oxidation numbers of the atoms in the parameter list

Data read from a SHELX file

The following data are read from a SHELX file:

TITL	The title for the structure (maximum 76 characters)
CELL	The first parameter is the wavelength and is overridden; the following six parameters are the cell parameters a, b, c, alpha, beta, and gamma in Angstroems and degrees
ZERR	The standard uncertainties of the values given in “CELL”. Only the standard uncertainties of the cell parameters are read by Endeavour.
LATT	The absolute value of the LATT parameter defines the lattice centering, the sign the presence (+) or absence (-) of centrosymmetry.
SYMM	The symmetry matrices. A space group symbol is not given in a SHELX file. Endeavour evaluates the space group of the compound from the symmetry matrices and the LATT parameter.
SFAC	These parameter(s) are used to assign the atoms of the parameter list to atom types (elements).
END	Defines the end of the structure description.

Other data items, such as UNIT, AXIS, etc. are not read by Endeavour. If the first four character of a line do not represent a SHELX keyword, this line will be interpreted as atom description, whereas four blanks define a comment.

Atomic parameters

Endeavour reads at least four parameters following the atom symbol. The first parameter is used to derive the element symbol from the previous SFAC definitions. The following parameters are the x, y, and z value of the atomic position in fractional coordinates. These parameters may be followed by the site occupation factor, the isotropic or equivalent displacement parameter of type U, or the six values of the anisotropic displacement parameters of type U.

Data read from CSD FDAT format

A file in the FDAT format of the Cambridge Structural Database (CSD) may contain multiple entries. The '#' character followed by a maximum of eight characters or digits at the beginning of a line defines the entry point of the first or a following structure description.

The characters #2 through #9 are taken as CSD Reference Code (the first character of a line has number #1). The following information of the first line of an entry will be read:

- The recording date of the entry, which has the format “yymmdd”.
- The year of the publication of the entry, which has two digits only.

The following line, which is not mandatory in CSD FDAT format, contains the cell parameters and space group information:

- The cell parameters a, b, c, alpha, beta, and gamma in Angstroms and degrees,

- The standard uncertainties of the cell parameters.
- The measured density in grams per cubic centimeter.
- The space group number according to International Tables for Crystallography, Vol. A.
- The Hermann-Mauguin space group symbol.
- The number of formula units per unit cell.

The following line(s) define several numeric and text fields:

- The R value.
- Remarks including “Disorder field” and “Error field”.

The next lines contain the coded symmetry matrices, if symmetry information is given.

If radii are given in the CSD FDAT file, these values will be read from the following line. These definitions consist of pairs of element symbol and radii in picometers. These values will be used as effective radii for the atom type definitions in Endeavour.

For each atom in the parameter list only element symbol and the coordinates x, y, and z are given. These coordinates are fractional, unless no cell parameters have been defined.

Bond distances will be ignored.

Bibliographic data

When converting a CSD FDAT file, Endeavour searches for a file with the same name of the FDAT file but with the extension JNL, to retrieve additional bibliographic data:

- The name of the compound.
- The structural formula.
- The name(s) of the author(s).
- The citation.

Data read from a PDB file

The first line of a Protein Data Bank (PDB) file begins with “HEADER”. From the first line, also the recording date of the PDB entry as well as the database code are read.

The following table lists the keywords that are interpreted by Endeavour when reading from a PDB file:

TITLE	The title of the compound or of the publication.
COMPND	This will be used as common name.
SOURCE	The source of the compound.
REVDAT	The revision date will be used as last update of the database entry.
JRNL	Retrieves data that specify a publication of the database entry. The sub-keywords “TITL”, “AUTH”, “REFN”, and “REF” are used to specify the title, the authors' names, and the citation.

CRYST1	Defines the cell parameters a, b, c, alpha, beta, and gamma in Å (Angstroms) and ° (degrees)
SCALE1, SCALE2, SCALE3	Define the three rows of a transformation matrix, which transforms the coordinates of the atomic parameters from cartesian back to fractional coordinates.
ATOM, HETATM	Define an atom. Endeavour does not distinguish between "normal" atom and hetero atom. From an ATOM or HETATM record, Endeavour extracts the atom symbol (which contains the element symbol), the coordinates x, y, and z, which are given as cartesian coordinates (in Angstrom units) and are transformed to fractional coordinates, the site occupation factor and the isotropic or equivalent displacement parameter of type U. Newer entries may have the oxidation number defined in one of the last columns of an atom record.
SIGATM	The standard uncertainties of the corresponding fields of an atom or hetero atom record.
ANISOU, SIGUIJ	The six anisotropic displacement parameters of type U and their standard uncertainties.
END	Signals the end of the database entry.

Data read from the XYZ format

The XYZ format is rather simple. The contents of the second line is treated as title. The following lines are atomic parameters containing element symbol and cartesian coordinates x, y, and z.

Support

In case of trouble when using Endeavour, please pay attention to the following hints:

- If you do not know how to operate in a dialog window, carefully read all information in the window. Make sure that you understand the meaning of the buttons, input fields, lists, etc. Look at the way several functions are grouped into frames and read the frame titles, too.

- Press the <F1> key in order to open the online help and examine the context sensitive help text. Especially read the items mentioned under Note: and See also:

- Look for appropriate keywords in the Help index and use the free-text search facility of the online help.

- If you do not find a command, use the Help index (*Index* tab on the Endeavour application Help window) to get an alphabetic list of search items.

- Visit the Endeavour web page at:

  https://www.crystalimpact.de/endeavour/update.htm

  This page offers the latest versions of online help files, sample files, and software patches for the executables.

- If this page does not give you an answer, or if the trouble is caused by an error in the software (a ”bug”), send an e-mail to support@crystalimpact.com

  Or – if you are not connected to the internet – send a fax to: ++49-228-9813644

  or write to:

  Crystal Impact GbR
  Kreuzherrenstr. 102
  D-53227 Bonn
  Germany

  Please describe how the bug can be reproduced as detailed as possible, and attach possibly required files (e.g. diffraction data)!

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