

# EXPO2014

## Table of contents

---

General Information .....	3
EXPO2014 installation .....	4
Tutorials .....	7
Preparing input file .....	14
Indexing by N-TREOR09 .....	16
Space group determination .....	24
Structure solution by Direct Methods .....	28
All steps of structure solution procedure .....	38
Extraction of the integrated intensities .....	38
Normalization of the integrated intensities .....	44
Estimate of structure invariants .....	46
Application of the tangent formula .....	49
Crystal structure completion and refinement .....	53
Structure solution by Direct Space methods .....	60
Direct Methods combined with Simulated Annealing .....	71
Rietveld Refinement .....	75
Commands of EXPO2014 and their use .....	78
Description of EXPO2014 commands .....	81
Preparation of data .....	86
Examples .....	91
Crystal Structure Visualization .....	101
How to .....	102
File .....	102
Modify .....	105
Select .....	105
View .....	106
Tools .....	108
Info .....	109

## General Information

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# EXPO2014

The program EXPO2014 (Altomare *et al.*, 2013) is the evolution of EXPO2009 (Altomare *et al.*, 2009). EXPO2014 performs all the steps of the *ab-initio* structure solution by powder data: indexing, space group determination, estimation of the reflection integrated intensities, structure solution by Direct/Patterson methods or/and by direct space/hybrid approaches, model refinement by Rietveld technique.

The program has been designed to:

- require a minimal information as [input](#)
- work automatically
- reduce the user intervention and facilitate the interaction by means of a user-friendly graphic interface.

### Program specification

X-ray, synchrotron or neutron diffraction data can be used. There are no limits on the number of counts in the pattern. The maximum number of reflections is 3000.

### The background of system

EXPO2014, the updated version of EXPO2009 is able to solve crystal structures from unindexed powder diffraction pattern. Its main steps are (select the topic for more details):

#### [Indexing](#)

An automatic peak search routine generates a list of "d" values corresponding to the experimental peaks. The values are processed for providing the cell parameters.

#### [Space Group Determination](#)

A statistical analysis is performed by using the experimental diffraction intensities compatible with the identified crystal system. The procedure is able to provide a list of all the possible extinction symbols ranked according to their probability value. For each of them, the corresponding list of compatible space groups is supplied *via* graphic interface.

#### [Structure Solution](#)

Structure solution can be carried out by the two alternative following methods:

- Direct Methods for phasing the reflections. The electron density map is calculated and then optimized.
- Direct Space Methods for generating trial structure models (compatible with the expected molecular geometry) and selecting that one providing the best agreement with the experimental data.

## Rietveld Refinement

The structure model is refined by [Rietveld method](#).

## Files generated by EXPO2014

- EXPO2014 creates the following files (in the work directory):
- a direct access file to preserve data and results (name.bin);
  - an ascii file containing the Miller indices (hkl) and integrated intensities of the generated reflections (name.hkl);
  - an ascii file to store peak positions if the indexing process has been carried out (name.pea);
  - output file containing information about all the steps of structure determination (name.out).

### Authors

A. Altomare<sup>(\*)</sup>, C. Cuocci<sup>(\*)</sup>, C. Giacovazzo<sup>(\*)</sup>, A. Moliterni<sup>(\*)</sup>, R. Rizzi<sup>(\*)</sup>.

<sup>(\*)</sup> Institute of Crystallography CNR, (Bari) - Italy

### Support

[sirmail@ic.cnr.it](mailto:sirmail@ic.cnr.it)  
<http://www.ic.cnr.it/>

### Acknowledgements

The authors are indebted to Giovanni Luca Cascarano and Mariarosaria Mallamo for their help in the development of the graphic environment.

### Main References

Altomare, A., Camalli, M., Cuocci, C., Giacovazzo, C., Moliterni, A. & Rizzi, R. (2009). *J. Appl. Cryst.* **42**, 1197-1202.  
 Altomare, A., Cuocci, C., Giacovazzo, C., Moliterni, A., Rizzi, R., Corriero, N. & Falcicchio, A. (2013). *J. Appl. Cryst.*, Submitted.

## EXPO2014 installation

### Hardware and software environment

EXPO2014 is built utilizing OpenGL for three-dimensional molecular visualization and the GTK for the graphic user interface. All binary packages are pre-compiled by using the Intel Fortran Composer XE 2013 and the GNU C++ compiler. Expo2014 runs on the most popular operating systems: Windows, Apple's Mac OS and some Linux distributions.

### On Windows platforms



Both 32- and 64-bit versions of EXPO2014 are available for Windows. They were tested on Windows 7, Vista, and XP.

To get the 32-bit or 64-bit version of EXPO2014 for Windows, download the file expo-020513\_install.exe or expo-020513-x64\_install.exe from

<http://www.ba.ic.cnr.it/content/expo2013>

Note that the 32-bit version of EXPO2014 can also be used on 64-bit Windows. To install the software, double click on the downloaded file and follow the instructions.

The program can be launched by double click on the icon of EXPO2014



## Mac OS X

The Mac OS X version of EXPO2014 runs on Mac OS X 10.5 (Leopard), Mac OS X (Snow Leopard), Mac OS X 10.7 (Lion), OS X 10.8 (Mountain Lion). The program was not tested on on Mac OS X 10.4 (Tiger) or older.

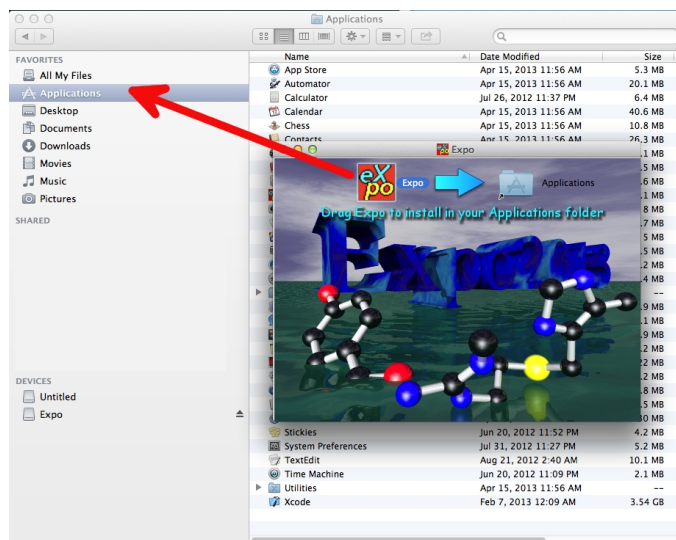
The Mac OS X version is contained in a file .dmg with a disc image format.

1. Download the file .dmg from

<http://www.ba.ic.cnr.it/content/expo2013>

2. Double-click the .dmg file to mount it. A new Finder window containing the EXPO2014's icon should appear.

3. Open a new Finder window and then drag the program EXPO2014 over the "Applications" in the left side of window.



To do cleaning:

- Close any Finder Windows
- Eject the disk image (not the .dmg file).
- Delete the .dmg file by dragging it to the trash.

In order to add EXPO2014 to the dock, follow these steps:

- Open up a new Finder window
- Click on "Applications".
- Locate the EXPO2014's icon.

- Drag the icon to your Dock, and drop it wherever you like.

EXPO2014 can be launched by Double click on the icon of EXPO2014.

### On Linux platforms

#### Installing from binary package

Debian and Red Hat RPM packages are available via the download page.

- Install the .deb package typing from the terminal

```
sudo dpkg -i expo_1.13.05_ubuntu12.10_amd64.deb
```

- To install RPM package, enter the command:

```
rpm -i expo-1.13.05.fc18.x86_64.rpm
```

EXPO2014 can be launched by

1. Double click the icon of the EXPO2014 icon
2. Type a command in a command line:

```
expo file.exp file.out
```

This command will start EXPO2014 running the input `file.exp` and generating the output file `file.out`.

The output file may be omitted:

```
expo file.exp
```

or simply

```
expo
```

In addition, Expo2014 can read crystal structures from different types of file (e.g. \*.cif). You can supply the name of the crystal structure file on the command line, and Expo2014 will open the file when it starts, e.g.

```
expo paracetamol_best1.cif
```

To run EXPO2014 simply typing `expo`, the environmental variable `PATH` must be set to include absolute path of the directory where EXPO2014 is placed.

#### Compiling from source

- Install build tools

Most Linux distributions come with the core set of development tools already installed but if not, you will need to install the following packages *via* the appropriate package manager.

**Autoconf** Program which writes configure scripts

**automake** Program which writes Makefiles

**libtool** Generic library support script

**g++** C++ compiler from the GNU compiler collection

**Fortran compiler** compliant with Fortran 95 standard: EXPO has been written and tested using the Intel Fortran Compilers (IFORT) but if the IFORT is not available, GNU Fortran (Gfortran) could be also used.

- Install graphic development packages  
Expo requires development files for gtk+ library, Mesa OpenGL utility library. The name of the libraries could be slightly different depending on your GNU/Linux distribution. The names of the packages is reported for some tested distribution.
  - Debian distributions: libgtk2.0-dev, libgl1-mesa-dev, libglu1-mesa-dev, libcurl4-gnutls-dev
  - RedHat distributions: gtk2-devel-....., mesa-libGL-devel-....., mesa-libGLU-devel-....., libcurl-devel-....
  - Mandriva: libgtk+2.0-devel, libmesag11-devel, libmesaglu1-devel, libcurl-devel
  - Suse: gtk2-devel, mesa-devel, libcurl-devel
- Download the file **expo\_1.13.05.tar.gz**  
Install "expo" using the following commands

```
tar xvfz expo_1.13.05.tar.gz
cd expo_1.13.05
sh ./autogen.sh
./configure      --prefix=destination_directory      --
srcdir=expo_source_directory
make clean
make install
```

Executable files will be stored in

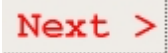
destination\_directory/bin

Be sure that the destination\_directory/bin is in the PATH

For more information read the file INSTALL in the expo directory.

### Running the program

Test structures can be found in the folder `examples`. On Windows platform this folder is typically located in `C:\Users\username\share\expo\examples`. To run the program select the test structures by means of the menu **File > Load Examples**

Click on  on the toolbar to perform the steps of structure solution.

Three test structures are supplied and described in the section [Tutorials](#).

### Contact

If you are having trouble during the installation contact [corrado.cuocci@ic.cnr.it](mailto:corrado.cuocci@ic.cnr.it)

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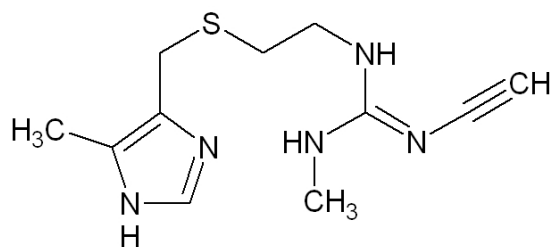
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## Tutorials

## Tutorial 1 - Crystal structure determination of Cimetidine compound

The first tutorial is supplied for carrying out the full pathway of the ab-initio structure solution process (from indexing up to the structure solution) in case of cimetidine.



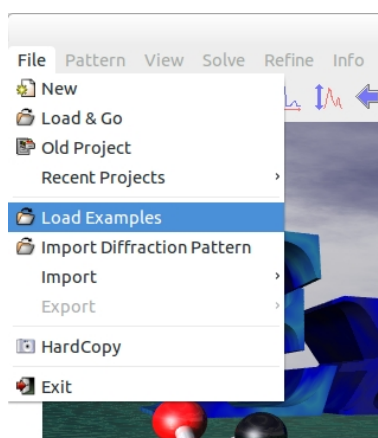
The only required information by EXPO2014 is the diffraction data and the chemical formula ( $C_{10}H_{16}N_6S_4$ ).

The *examples* directory contains the necessary files:

- *cime.exp*: input file for EXPO2014
- *cime.pow*: a synchrotron X-ray diffraction data file containing the initial 2-theta, the 2-theta step and the final 2-theta values (in the first line) and the experimental counts (in the rest of lines).

To access to *examples* directory:

- Open EXPO2014 by double clicking on Expo2014 icon.
- Click on **File > Load Examples**

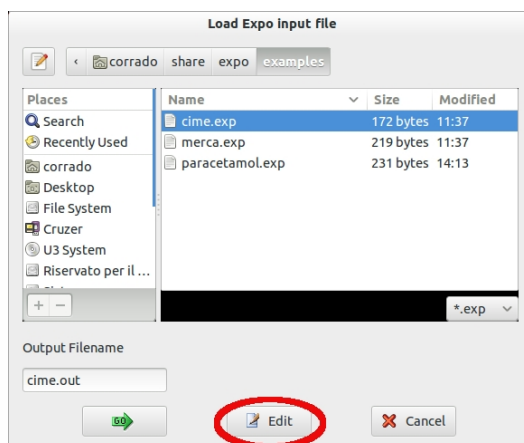


and select the file *cime.exp*.

The content of file *cime.exp* is here reported

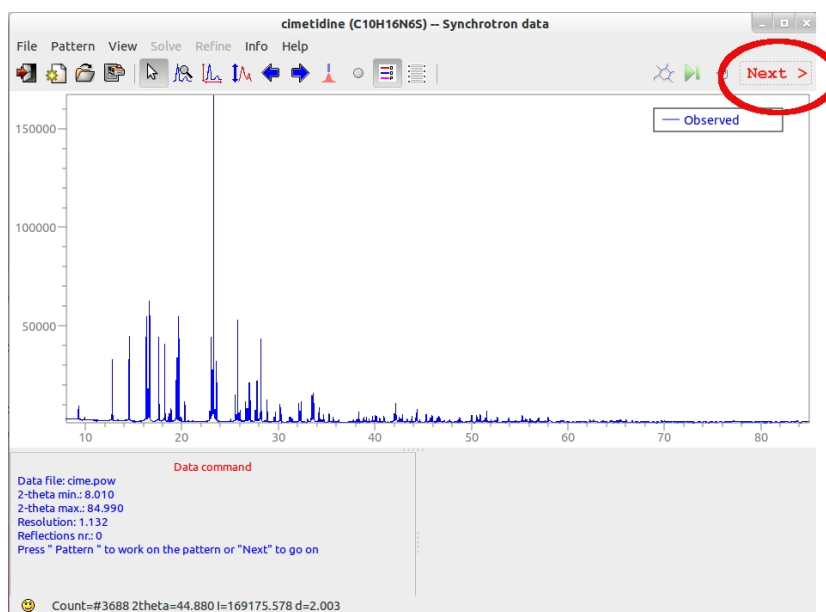
```
%structure cime
%job cimetidine (C10H16N6S) -- Synchrotron data
%initialize
%data
pattern cime.pow
wavelength 1.52904
synchrotron
%ntreor
%continue
```

It contains the minimal required information (name of data file, wavelength and type of radiation used to collect the data if different from X-rays) and commands for the ab-initio structure solution. This file can be visualized and eventually modified by the 'Edit' button.



More information about the creation of input file can be found in the section [Preparing input file](#).

Clicking on **OK** the powder diffraction data will be displayed.





Selecting **Next**, an automatic peak search procedure will be applied and the  $d$ -values corresponding to the selected experimental peaks will be automatically supplied to the [indexing procedure](#). At the end of this process EXPO2014 will provide the indexing results by graphic interface:

Plausible cell parameters

Select cell

Nr.	a	b	c	alpha	beta	gamma	Vol.	FOMnew	M20	shift	NIX	Extinction	Group
1	10.39360	18.81587	6.82411	90.00000	106.43857	90.00000	1280.0	1.00000	112	0.000	0	P 1 21/a 1	

 OK

 Cancel

Click on **OK** to accept the selected plausible cell parameters and to move to the next step: the space group determination.

The space group determination step, as well as Direct Methods, requires the unit cell content information. It can be easily derived by taking into account the structure formula and the cell volume ( $V_{\text{cell}}$ ) provided by the window above or by the output file of EXPO2014.

The cell content is given by  $Z$  multiplied by the structure formula. You can calculate  $Z$  as the ratio between  $V_{\text{cell}}$  and the molecular volume ( $V_{\text{mol}}$ ):  $Z = V_{\text{cell}}/V_{\text{mol}}$ .

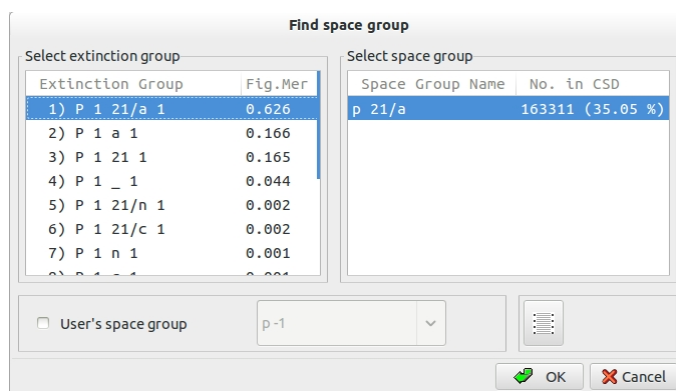
$V_{\text{mol}}$  can be calculated by one of the two following alternative ways:

1. Using the 18 Å<sup>3</sup> rule: counting all the non-hydrogen atoms in the chemical formula and multiplying this number by 18 Å<sup>3</sup>;
2. Using the following approximate atomic volumes: 14 Å<sup>3</sup> for C, 12 Å<sup>3</sup> for N, 11 Å<sup>3</sup> for O, 5 Å<sup>3</sup> for H, 26 Å<sup>3</sup> for Cl, 25 Å<sup>3</sup> for S.

In case of cimetidine compound, the chemical formula is C<sub>10</sub>H<sub>16</sub>N<sub>6</sub>S<sub>4</sub> and the cell volume is 1280 Å<sup>3</sup>. If the first criterion is applied, the molecular volume is given by:  $V_{\text{mol}} = 20 \times 18 = 360$  Å<sup>3</sup>.

The corresponding  $Z$  value is:  $Z = V_{\text{cell}}/V_{\text{mol}} = 1280/360 = 3.55$ , that can be approximated to 4. So 4 molecules of cimetidine are in the unit cell and the unit cell content to be supplied to EXPO2014 by graphic interface is (C<sub>10</sub>H<sub>16</sub>N<sub>6</sub>S)<sub>4</sub> or C<sub>40</sub>H<sub>64</sub>N<sub>24</sub>S<sub>4</sub>

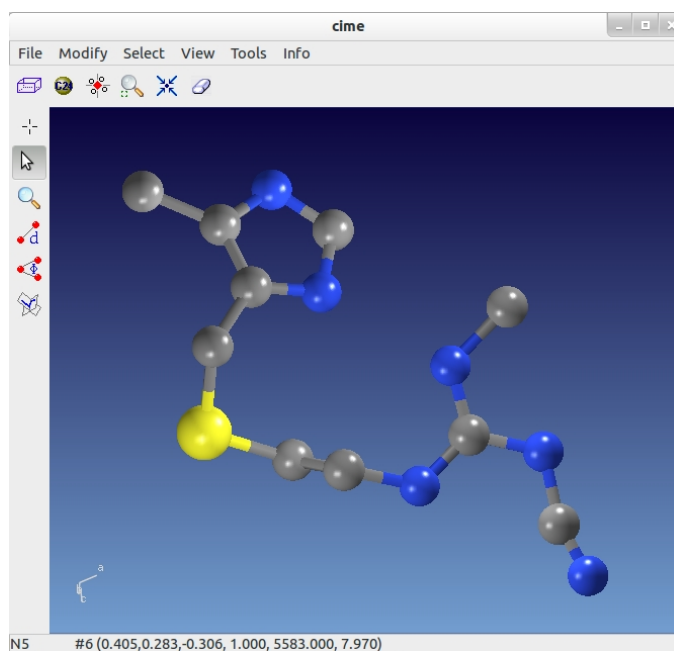
Click on **OK** in order to perform the space group determination and then on **Next** button to go on continuously. At the end of the procedure a list of the Extinction Groups, compatible with the lattice symmetry and ranked according to a probability value, is given:



the most plausible Extinction Group *P 1 21/a 1* is automatically selected and by clicking on **OK** the space group *P 21/a*, corresponding to this extinction group, will be chosen.

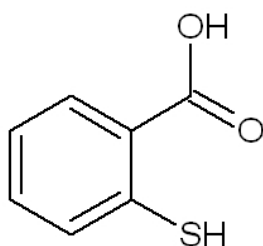
After the determination of the space group, EXPO2014 starts with the extraction step which is carried out in the selected space group. Click on **Next** button continuously. At the end of the process a list of integrated intensity values, extracted from the experimental powder pattern, is obtained and automatically supplied to Direct Methods for structure solution.

The final result will be visualized on JAV Molecular Viewer.



Some errors in the assignment of carbon or nitrogen atomic species can be easily recognized and corrected by using the option 'Modify' from JAV menu.

## Tutorial 2 - Crystal structure solution of 2-Mercaptobenzoic acid compound



The aim of this example is to guide the user in case of failure of a default run of EXPO2014.

Open EXPO2014 by double click on Expo2014 icon.

Click on **File > Load Examples**

Select the input file 'merca.exp'.

```
%Structure merca
%Initialize
%Job 2-Mercaptobenzoic acid
%Data
Cell          7.885   5.976   14.949   90.0   100.48   90
SpaceGroup p 21/c
Content       C 28 O 8 S 4 H 24
Pattern       merca.xy
Wavelength    1.54056
%continue
```

In this example it is assumed that the cell and space group have been already determined and the unit cell content corresponds to 4 molecule of  $C_7H_6O_2S$ .

Click on **Next** button to go on continuously.

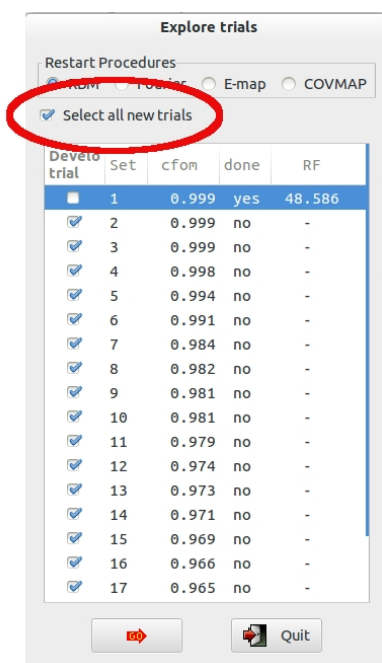
The final structure model provided by EXPO2014 could not correspond to the correct crystal structure of 2-Mercaptobenzoic acid. This can occur when the most plausible set of phases, provided by Direct Methods, is unreliable.

In a default run of EXPO2014, Direct Methods generate several phasing trials; 20 of them are stored and ranked according to decreasing values of a suitable combined figure of merit (CFOM). The largest CFOM set of phases is automatically selected for structure solution. In case of failure, all the rest of stored phasing trials should be explored in order to find the solution.

This can be automatically performed by graphic interface:

- Selecting from the top-level menu **Solve** and then **Explore Trials**
- Clicking on the **Select all new trials** button





c) Clicking on **GO**

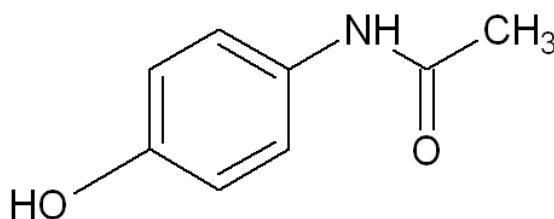
At the end of the procedure, EXPO2014 will rank the phasing trials (and the corresponding structure models) according to the increasing  $R_F$  agreement factor values.

The best solution (corresponding to the lowest  $R_F$  value) will be selected and displayed.

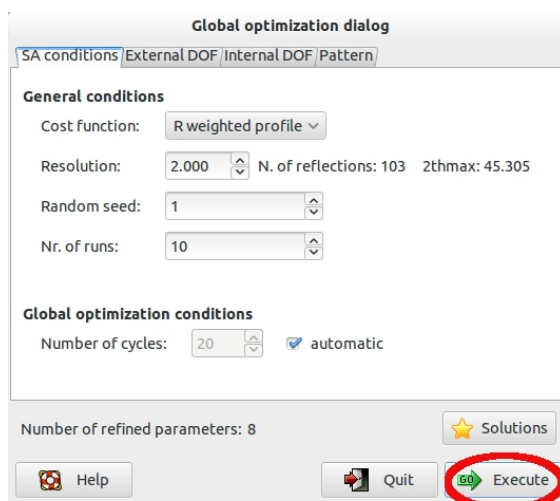
More information about the strategies to apply when Direct Methods fail are described in the [next section](#) of this manual.

### Tutorial 3 - Crystal structure solution of paracetamol compound by direct space methods

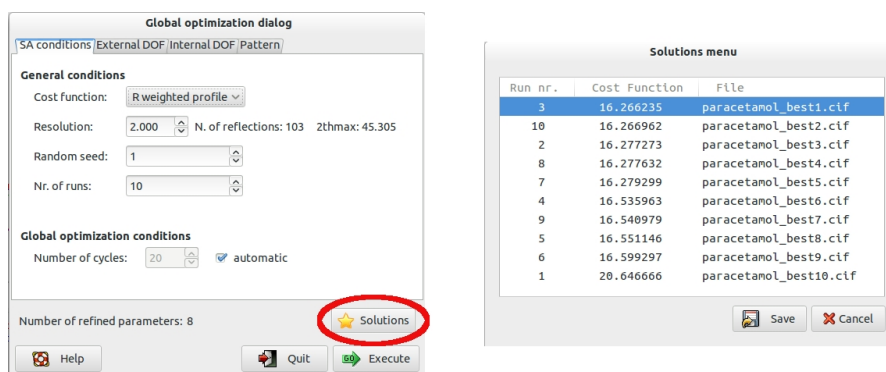
The purpose of this tutorial is to guide the user through the crystal structure solution by [direct space methods](#) of paracetamol (form I polymorph) compound.



Open EXPO2014, select **Load Examples** and load the input file 'paracetamol.exp'. Clicking on **Next** button, the file paracetamol.mol, containing a 3D molecular description of paracetamol, will be loaded and displayed and the following window will appear:



Select **Execute**; the Simulated Annealing procedure will be applied performing 10 runs whose corresponding final structure models can be explored by the button **Solutions**



## References

**Cimetidine** - Cernik, R.J., Cheetham, A.K., Prout, C.K., Watkin, D.J., Wilkinson, A.P., Willis, B.T.M. (1991). *J. Appl. Cryst.* **24**, 222-226.

**2-Mercaptobenzoic acid** - Florence, A. J., Shankland, N., Shankland, K., David, W. I. F, Pidcock, E., Xu, X., Johnston, A., Kennedy, A. R., Cox, P. J., Evans, J. S. O., Steele, G., Cosgrove, S. D. & Frampton, C. S. (2005). *J. Appl. Cryst.* **38**, 249-259.

**Paracetamol (form I polymorph)** - Florence, A. J., Shankland, N., Shankland, K., David, W. I. F, Pidcock, E., Xu, X., Johnston, A., Kennedy, A. R., Cox, P. J., Evans, J. S. O., Steele, G., Cosgrove, S. D. & Frampton, C. S. (2005). *J. Appl. Cryst.* **38**, 249-259.

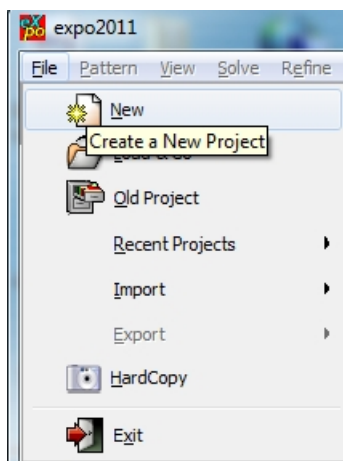
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## Preparing input file

### Preparing input file in EXPO2014

To run EXPO2014 you need of an input file (\*.exp). Two possibilities are available: 1) to create a new input file; 2) to use an already existing input file.  
Possibility n.1): creation of an input file by selecting, *via* graphic interface, the creation of a

new project by the menu "File">"New".



 A screenshot of the 'New Project: cime' dialog box. The dialog contains several fields and options, each annotated with a red number:
 

- 1**: Points to the 'Structure Name' field, which contains 'cime'.
- 2**: Points to the 'Profile Counts filename' field, which contains 'cime.pow'.
- 3**: Points to the 'Range' section, which includes a 'Modify range' checkbox and fields for '2theta min' (8.010) and '2theta max' (84.990).
- 4**: Points to the 'Source' section, which includes radio buttons for 'X rays', 'Neutron', and 'Synchrotron' (selected), and a 'Wavelength' field (1.52904).
- 5**: Points to the 'Space Group' section, which includes a checked 'Find Space Group' checkbox and a 'Space Group Symbol' dropdown.
- 6**: Points to the 'Cell Determination by N-TREOR' checkbox, which is checked.
- 7**: Points to the 'Cell Content' text input field.
- 8**: Points to the 'Structure Solution' section, which includes radio buttons for 'Direct Methods' (selected) and 'Simulated Annealing'.
- 9**: Points to the 'Save' button.
- 10**: Points to the 'Open' button.

 Other fields include 'a:', 'b:', 'c:', 'alpha:', 'beta:', and 'gamma:' for cell parameters, and 'Volume:' and 'Volume per Atom:' for volume calculations.

The required information are here listed.

1. You must specify the structure name. This name will be used to create the name of output file.
2. Load the profile counts file. The following powder diffraction data file can be imported: ASCII XY files (\*.xy), CIF powder files (\*.rtv, \*.cif), GSAS files (\*.qda), CCDC Mercury xye (\*.xye). Use the extension \*.pow to indicate an ASCII xy file or an ASCII file with 2theta min, 2theta step, 2theta max in the first row and counts in free format in the subsequent lines.
3. Select the 'Range' button if you want to change the 2theta min and/or the 2theta max.
4. Input the wavelength and the type of radiation source (X rays source is the default choice).
5. To carry out the space group determination it is necessary to activate the check button 'Find Space Group'.
6. For indexing, it is necessary to click on button 'Cell Determination by N-TREOR'.
7. You must provide the content of unit cell. This information is important for the space group determination and for the structure solution by Direct Methods. A valid molecular

formula for the cell content must meet the following criteria:

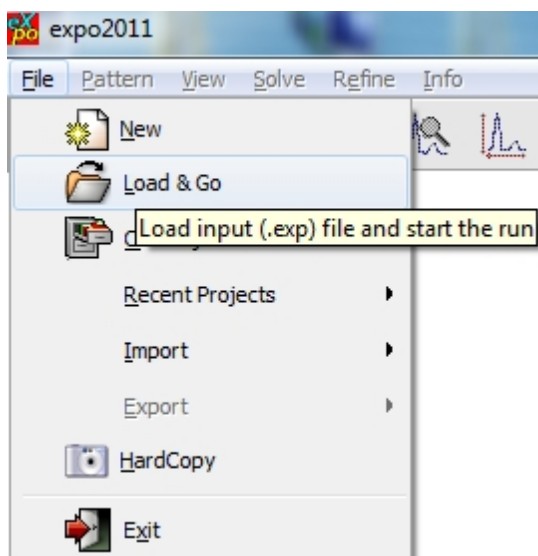
- Elements are represented by valid atomic symbols (IUPAC-nomenclature) each optionally followed by a number.
- It is possible to write the formula in lower-case or upper-case but please note that 'Sb' will be interpreted as one antimony but 'SB' will be one antimony and one boron. Spaces are also permitted (eg. 'S B', one antimony and one boron). We suggest to write the two-letter elements with the second letter in lower-case.
- Valid operators are: **()[]{}**

Examples of valid formula:  $[C_3H_5(OH)_3]_4$ ,  $C_{28}O_8S_4h_{24}$

If your formula doesn't follow the required criteria, the input string will appear written in red.

When you press the button 'Save' (9) an EXPO input file (\*.exp) will be created in the same folder of powder data file and automatically loaded by the program for the indexing. The button 'Open' (10) is used to open (and possibly modify with a text editor) an already existing input file.

An already existing \*.exp input file can be loaded from menu 'File' > 'Load & Go'.




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## Indexing by N-TREOR09

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### Indexing by N-TREOR09 in EXPO2014

In powder diffraction the first necessary step for solving crystal structure is the indexing, i.e. finding the unit cell parameters and reconstructing the three dimensional lattice from the one-dimensional information of the powder diffraction pattern. The indexing is performed by EXPO2014 via the program N-TREOR09 (Altomare *et al.*, 2009), the evolution of the N-TREOR software (Altomare *et al.*, 2000).

[Preparing input file for indexing in EXPO2014](#)

[Indexing by N-TREOR09 in EXPO2014](#)

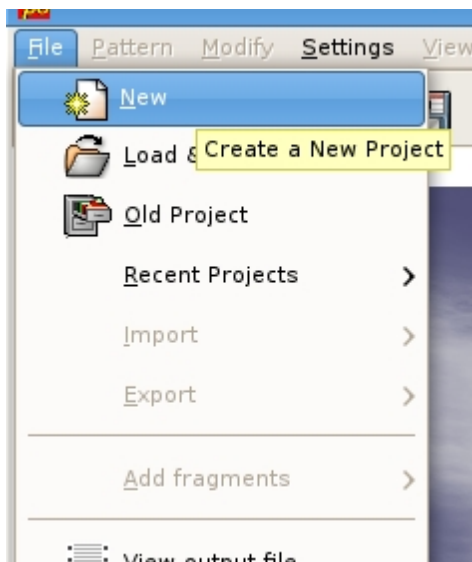
[Output of indexing](#)

[The indexing directives](#)

[Contact and References](#)

### Preparing input file for indexing in EXPO2013


To run EXPO2014 for indexing you need to create an input file (\*.exp). It is possible by graphic interface, creating a new project by the menu "File" > "New".



You must specify the structure name, the profile counts filename and its format, the wavelength and the type of radiation source. Click on button 'Cell Determination by N-TREOR09' and press 'Save'. In addition you can activate the check buttons 'Find Space Group' and 'Structure Solution' if you intend to continue the crystal structure determination process by performing the space group determination and the structure solution steps. The following picture is an example of creation of the input file for crystal structure determination of the cimetidine from the unindexed pattern. All the 2theta range is used even if it is suggested to remove the region at high 2theta values when the noise could be very high and the overlapping of reflections very severe. Alternatively use the button 'Open' to import an existing input exp file.

**New Project: cime**

Structure Name:

Profile Counts filename:  


**Range**

☐ Modify range    2theta min     2theta max

**Source**

☐ X rays    ☐ Neutron    ☒ Synchrotron    Wavelength     ☐ K Alpha2 Correction

**Space Group**

☒ Find Space Group    Space Group Symbol:  

**Cell Parameters**

☒ Cell Determination by N-TREOR

a:  b:  c:   $\alpha$ :   $\beta$ :   $\gamma$ :





Volume:

Cell Content:

Content Volume:     Volume per Atom:

**Structure Solution**

☒ Direct Methods    ☐ Simulated Annealing

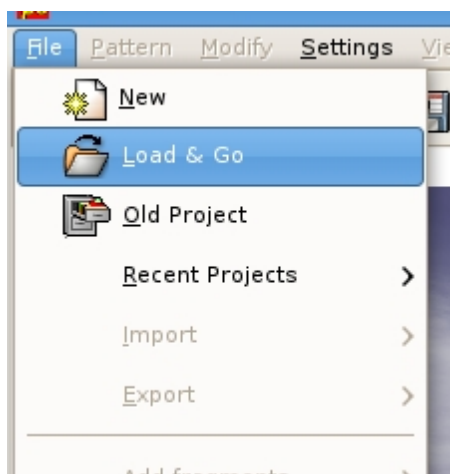
When you press the button 'Save' an input file cime.exp will be created in the same folder of powder data file and automatically loaded by the program for the indexing. Its content is the following one:

```
%structure cime
%job structure cime
%init
%data
    pattern cime.pow
    filetype counts
    synchr
    wave 1.52904
%ntreor
%continue
```

The command that has to be introduced in the input file for coming out the indexing process by N-TREOR09 is %ntreor. It must be added after command %data. Add %continue if you want to continue the crystal structure determination. You can read the meaning of the rest of instructions of the input file in the chapter "command and their use" of this manual.

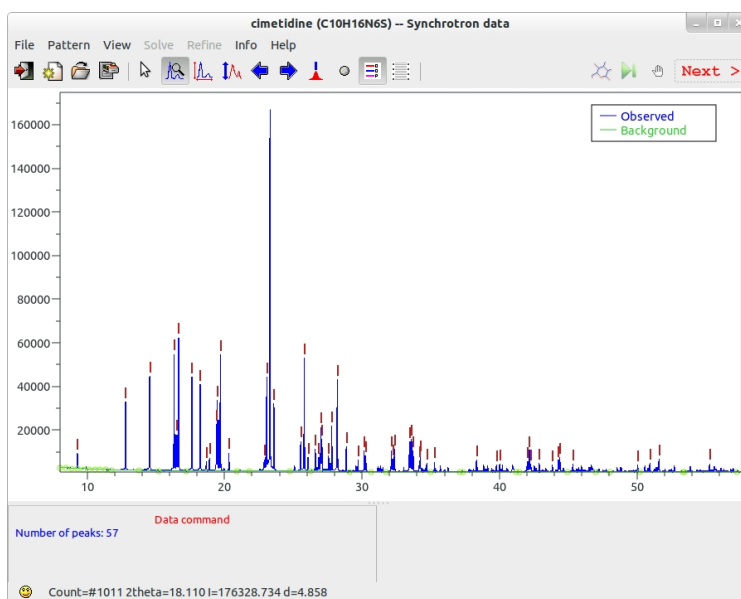
Alternatively you can edit a new input file or modify an exiting input file with a text editor and save it with the extension '.exp'. Once a time the input file has been created, load the exp input file from the menu 'File' > 'Load & Go'.


More details about preparation of data are reported [here](#).


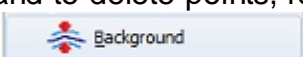



### Main steps for Indexing by N-TREOR09 in EXPO2014

First of all, use the button **Next >** to carry out to the next steps. Firstly an automatic peak-search will be performed.



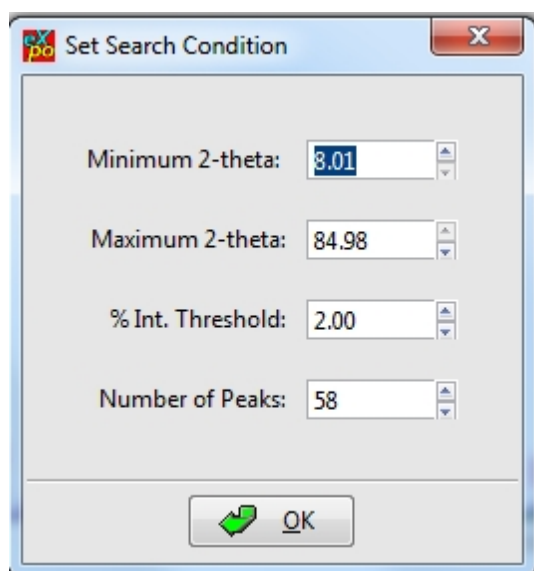
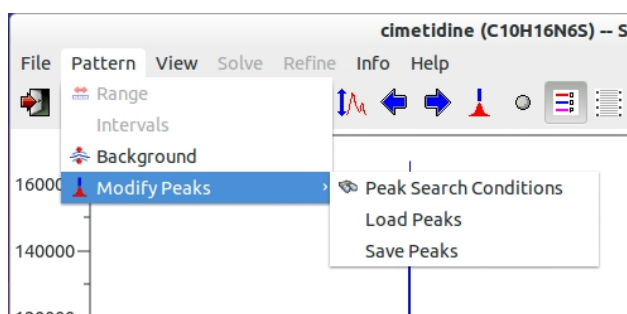
Accurate peak search is a fundamental stage for a correct powder pattern indexing; computing and graphical tools are provided to improve it. In order to check the reliability of the automatic peak search results, use the buttons  to explore the pattern. If the automatic peak search outcome is not reliable, you can modify the peak search options *via different ways*:

1) by changing the curve describing the background. This is possible adding or removing background points by clicking on the button  and using left mouse click or/and right mouse click to add or/and to delete points, respectively. Background function can be also modified by the button  of the 'Pattern' option. When background is changed, the peak positions are automatically updated;

2) by choosing the tool bar button  to add or remove peaks by left click and right click of mouse, respectively;

3) by the menu 'Pattern' > 'Modify Peaks'. The button 'Peak search conditions' opens the following window that enables to modify the main search conditions.

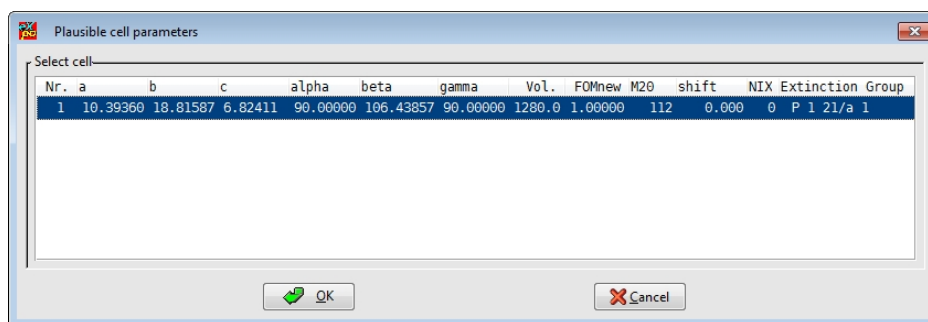
4) use 'Pattern' > 'Modify Peaks' > 'Load Peaks' / 'Save peaks' to load or save peaks as 2theta or d values.



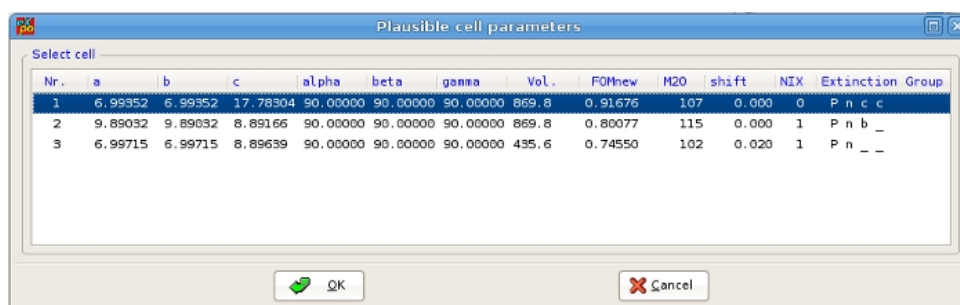
During the peak search remember that the number of peaks must be not too high and N-TREOR09 can generally solve the indexing problem with the 25 first peaks (even very weak peaks included). Peaks at low angle not clearly resolved and with an appreciable peak width should be not included in case they appear strongly uncertain.

The next step is the automatic refinement of peak positions and profile parameters (a Pearson VII function is used). At the end of the peak search a file named *structure\_name.pea*, containing the refined d values associated to the selected peaks, is automatically created by the program. This file can be used in the future for jumping the peak search procedure (see the directive [extefile](#)) if a new indexing process is performed. At the end of the indexing procedure the cell parameters and the cell volume, the figure of merit FOMnew (Altomare *et al.*, 2009), the classical figure of merit M20 (De Wolff, 1968), the applied zero-shift, the number of unindexed lines and the most probable Extinction group, are supplied by the following window.



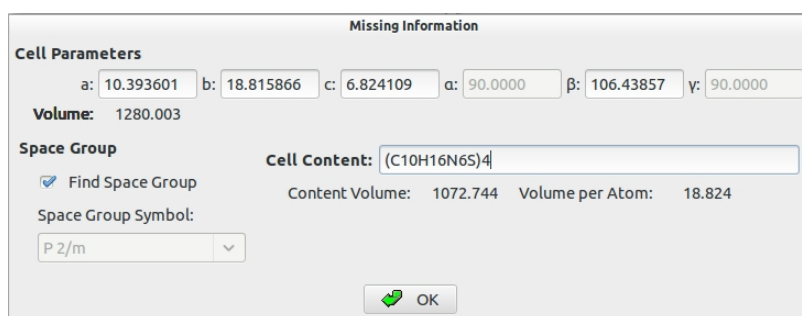


Sometimes more plausible cells are suggested by N-TREOR09, ranked according to a new figure of merit (Altomare *et al.*, 2009), FOMnew in figure.



Clicking on each suggested cell of the list, the tick marks at the bottom of the experimental pattern indicating the calculated positions of the Bragg reflections, will be displayed. The tick marks must correspond to peaks in the pattern. When no experimental peaks are associated to the tick mark, the corresponding reflection is probably systematically absent. On the other side, if a diffraction peak in the pattern is not associated to any tick, the peak can be referred to an impurity phase or the determined cell might be wrong.


Once the cell parameters calculation step has been carried out, you may perform the space group determination step by selecting the cell parameters and by clicking on the OK button. The following dialog window will appear.

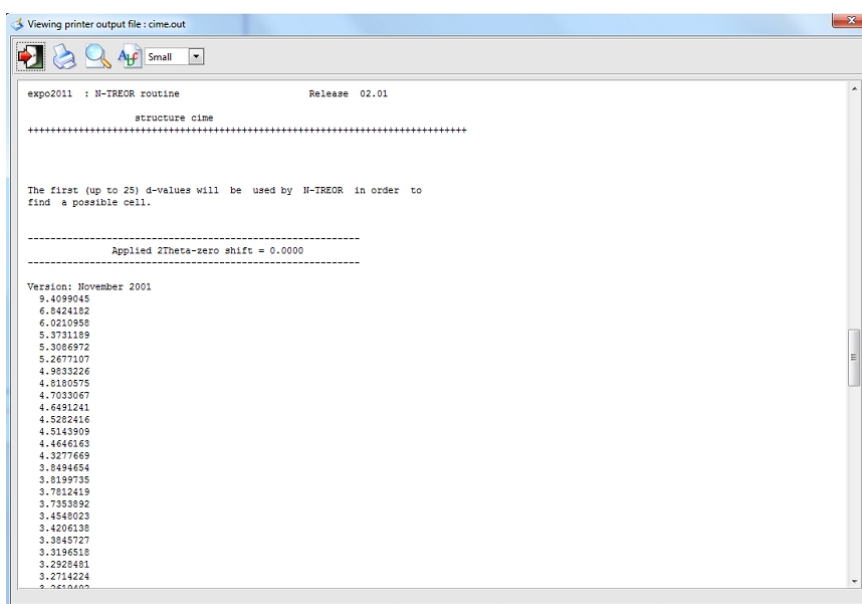


Before clicking OK, in this window you must specify the unit cell content. In the case of the cimetidine structure the cell volume suggests that the cell can accommodate 4 molecules ( $Z=4$ ). During the editing of the cell content, the program calculates and displays a rough estimate of the *Content Volume* and of the *Volume per Atom*. *Content Volume* is an approximate value of the cell volume calculated using the Van der Waals radius and the covalent radius associated to the supplied atoms, *Volume per Atom* is simply the ratio between the cell volume and number of non-hydrogen atoms. To check the correctness of

the cell content consider that the expected *Content Volume* must be not very different from the cell volume and the *Volume per Atom* usually has a value between 15-25. Significantly deviation from the expected value, can be observed in the *Content Volume* or in the *Volume per Atom*, due to the presence of H-bonding or large void space (e.g. zeolites) in the crystal structure.

## Output of indexing

The output file contains details about indexing. Use 'Info' > 'View output file' to access to the output file or open the file *structure\_name.out* with a text editor or click on the button  from the main menu.



## The indexing directives

### Directives in data command

The following directives must be added after the command '%data' in the input file to activate some specific features of the indexing procedure

**EXTEFILE** *file\_name*

This directive is used to supply an external file containing 'd' or '2theta' values of peak positions. In the latter case the additional '2-THETA' directive has to be used. An example of the use of the directive *extefile* for the indexing of the pattern of structure cime:

```
%structure cime
%job structure cime
%init
%data
    pattern cime.pow
    filetype counts
    synchr
    wave 1.52904
    extefile cime.pea
%ntreor
```

```
%continue
```

'cime.pea' is an ASCII file containing the observed 'd' values associated to the selected peaks.

## 2-THETA

This directive is used combined with the EXTEFILE directive to supply to the indexing program N-TREOR09 an external file containing 2theta values of the peak positions.

### Directives in ntreor command

**The N-TREOR09 directives must be added after the command '%ntreor' in the input file to enable some specific features of the indexing procedure**

All the directives of the indexing program TREOR (Werner, Eriksson & Westdahl, 1985) are still valid for the "%ntreor" command and have to be used with the same syntax (see the [N-TREOR manual](#) for the details).

The default choices can be changed *via* suitable directives.

N-TREOR09 directives:

### CEM n

```
%structure diltia
%initialize
%data
    pattern pd_0029.pow
    wavelength 1.54056
    filetype xy
    extefile diltia.pea
%ntreor
    CEM = 50,
```

If a set of d (or 2theta) values is already available, the peak search procedure is skipped.

'diltia.pea' is an ASCII file containing the d peak positions.

In a default indexing run, N-TREOR09 searches for cells with a maximum cell volume of 4000 Å<sup>3</sup> and a maximum cell axis of 35 Å. Due to this limits the correct cell is not found in a default indexing run for compounds having larger cell axis values. This is the case of Diltiazem hydrochloride for which one of the maximum axis value is 42.190 Å. The directive 'CEM = 50' activates N-TREOR09 for a search for a cell having a maximum axis value of 50 Å.

### Contact

For suggestions and bugs contact [annagrazia.moliterni@ic.cnr.it](mailto:annagrazia.moliterni@ic.cnr.it).

### References

Altomare, A., Campi, G., Cuocci, C., Eriksson, L., Giacobazzo, C., Moliterni, A., Rizzi, R. & Werner, P.-E. (2009). *Advances in powder diffraction pattern indexing: N-TREOR09*. *J. Appl. Cryst.* **42**, 768-775.

Altomare, A., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Rizzi, R. & Werner, P.-E. (2000). *New techniques for indexing: N-TREOR in EXPO*. *J. Appl. Cryst.* **33**, 1180-1186.

De Wolff, P. M. (1968). *A simplified criterion for the reliability of a powder pattern indexing*. *J. Appl. Cryst.* **1**, 108-113

Werner, P.-E., Eriksson, L., & Westdahl, M. (1985). *TREOR, a semi-exhaustive trial-and-error powder indexing program for all symmetries*. *J. Appl. Cryst.* **18**, 367-370.

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## Space group determination

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### Space group determination by EXPO2014

In the crystal structure solution process the determination of the space group usually follows the indexing step. This task is carried out by a careful investigation of the experimental intensities, aimed at finding the correct extinction group. Because of the collapse of the experimental data into the Bragg angle one-dimension space, the experimental pattern suffers by peak overlap and uncertain background definition. As a consequence, the judge about the 'presence' or 'absence' of the reflections may provide ambiguous results. A new probabilistic procedure aiming at recognizing the extinction symbol has been implemented in EXPO2014. It uses the statistics of the normalized  $z$  intensities (as extracted by the Le Bail method) to calculate the probability of each extinction symbol compatible with the crystal system suggested by N-TREOR09. A suitable weight  $w$  is associated to the intensity of each reflection, depending on the expected reliability of its estimate. The algorithm provides a probability for each extinction symbol of the considered crystal system. It has been tested on a large number of test structures and on all the crystal systems, providing good results (Altomare *et al.*, 2004; Altomare *et al.*, 2005; Altomare *et al.*, 2007).

[Preparing input file for space group determination by EXPO2014](#)

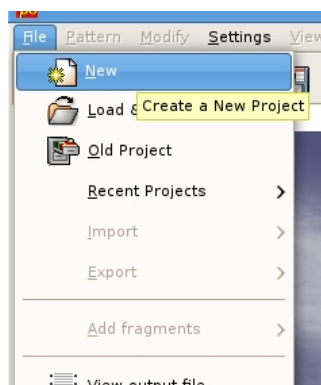
[Space group determination by EXPO2013](#)

[Output of space group determination](#)

[Contact and References](#)

#### Preparing input file for space group determination in EXPO2014

To run EXPO2014 for space group determination you need to create an input file (\*.exp). You can create an input file for space group determination by graphic interface by the menu "File" > "New".



You must specify the structure name, the profile counts filename and its format, the type of radiation source. Click on button 'Find Space Group', fill the frame 'Cell Parameters' and 'Cell Content'. The following picture is an example of input file for the crystal structure determination in case of cimetidine structure from the indexed pattern.

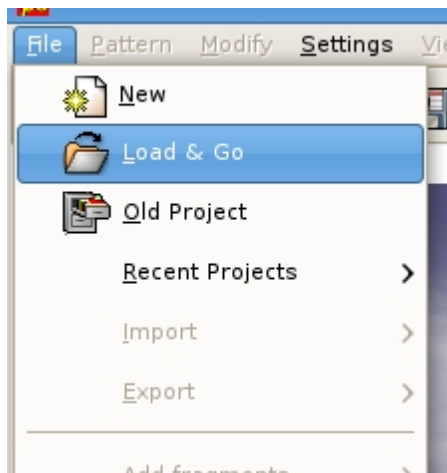
Once the button 'Save' has been selected, an input file cime.exp will be created and automatically loaded by the program for the space group determination.

```
%structure cime
%job structure cime
%init
%data
    pattern cime.pow
    filetype counts
    wave 1.52904
    findspace
    cell 10.69808 18.81786 6.82267 90.00000 111.28911
    90.00000
    cont h 64 c 40 n 24 s 4
%continue
```

The directive `findspace` enables the space group determination procedure. It is a

directive of the command %data. The unit cell is assumed to be determined by indexing of the experimental pattern. To know the meaning of the other lines of the input file, see the chapter "command and their use" of this manual.

Alternatively you can edit a new input file or modify an exiting input file by a text editor and save it with extension '.exp'. Once a time the input file has been created, load the exp input file from menu 'File' > 'Load & Go'.



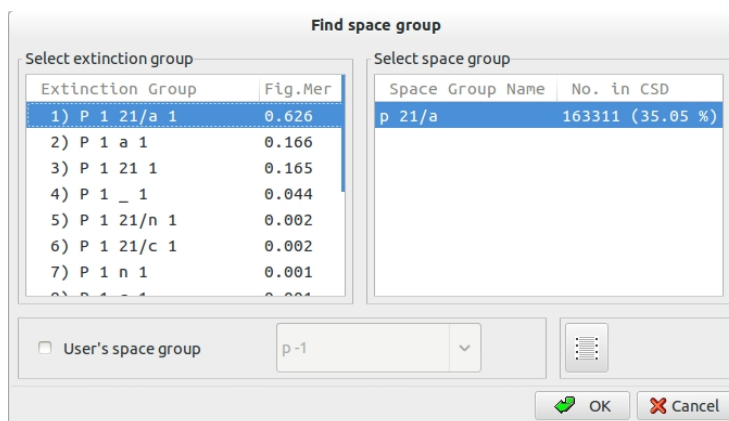
### Space group determination by EXPO2013

The different steps of the algorithm are here schematized.


- 1) The full pattern decomposition is performed, according to the Le Bail algorithm, in the space group having the largest Laue symmetry and no extinction conditions (e.g.,  $P\ 1\ 2/m\ 1$  in the monoclinic system,  $P\ 2/m\ 2/m\ 2/m$  for the orthorhombic,  $P\ 4/m\ mm$  for the tetragonal,  $P\ 6/m\ mm$  for the trigonal-hexagonal,  $Pm\text{-}3m$  for the cubic systems).
- 2) The extracted intensities are then normalized, according to the classical Wilson method, by using the space group mentioned at the point 1).
- 3) The z statistic is used to define the probability of the extinction symbol.
- 4) For each crystal system the probability of the different possible extinction symbols is calculated.

Use the button **Next >** on the toolbar to carry out to next steps.

At the end of the procedure the following window will be displayed.



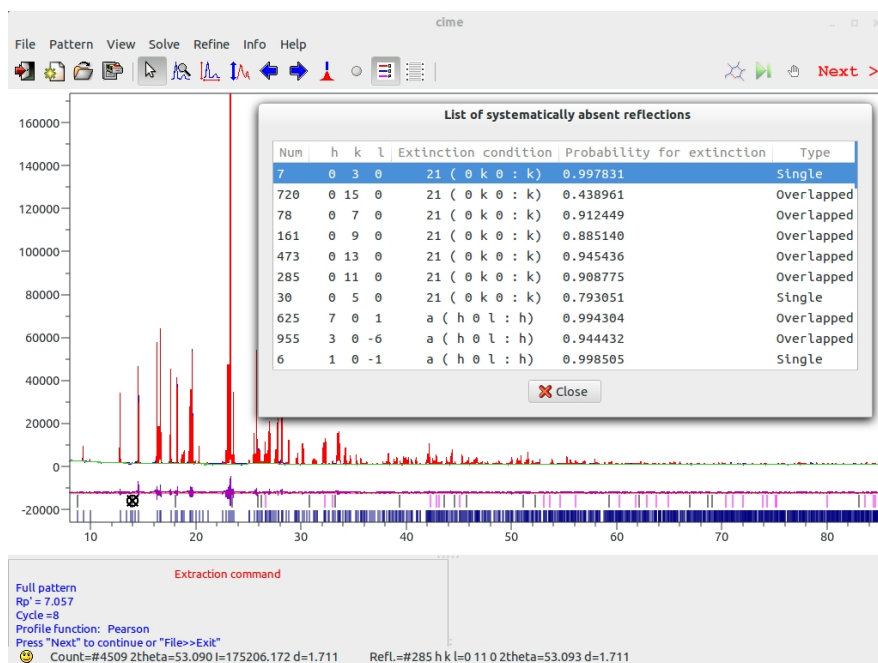
The window contains the extinction symbols ranked according to their calculated probability. When the user clicks on one of them, the corresponding list of compatible space groups is supplied. The frequency of the selected space group in the Cambridge Structural Database (CSD) is reported in terms of number of occurrences in the CSD and percentage. This information can be useful when different space groups are associated to an extinction group.

Press the button  to access to a list of reflections that, according to the selected extinction symbol, should be systematically absent. For each reflection the following specifications are given: the order number of reflection, the Miller index, the symmetry operator responsible for the extinction and the corresponding extinction condition, the probability for the extinction, the type of reflection (single or in overlap).

By default the reflections are ordered according to the extinction condition but you can change the order selecting a different ordering criterion by clicking on the title column. The selected reflection on a list will be marked on the pattern.

The reflections that are expected to be absent according to the selected extinction symbol are marked by a vertical bars situated below the observed pattern, just above the set of bars defining the reflection positions. They have different colors depending on whether the reflection is single (or belongs to a whole extinct cluster) or in overlapping. By default, a black vertical bar marks single systematically absent reflections, while the rest of the absent reflections (those in overlap) are marked with a purple bar. This graphical support helps the user to discard unreliable extinction symbols even if estimated with large probability.

Press the 'OK' button to accept the selected space group and continue with the structure solution process.



### Output of space group determination

The output file contains details about the space group determination procedure. Use 'Info' > 'View output file' to access to the output file or open the file *structure\_name.out* with a text editor. At the end of the procedure the new input file, called

*structure\_name1.exp* (e.g. *cime1.exp*) will be created. This file contains the selected space group and can be loaded for skip the space group determination and to perform the structure solution with Direct Methods.

### Contact

For suggestions and bugs contact [angela.altomare@ic.cnr.it](mailto:angela.altomare@ic.cnr.it), [annagrazia.moliterni@ic.cnr.it](mailto:annagrazia.moliterni@ic.cnr.it), [rosanna.rizzi@ic.cnr.it](mailto:rosanna.rizzi@ic.cnr.it), [corrado.cuocci@ic.cnr.it](mailto:corrado.cuocci@ic.cnr.it).

### References

Altomare, A., Caliendo, R., Camalli, M., Cuocci, C., da Silva, I., Giacovazzo, C., Moliterni, A. G. G. & Spagna, R. (2004). *Space-group determination from powder diffraction data: a probabilistic approach*. *J. Appl. Cryst.* **37**, 957-966.

Altomare, A., Camalli, M., Cuocci, C., da Silva, I. Giacovazzo, C., Moliterni, A. G. G & Rizzi, R. (2005). *Space group determination: improvements in EXPO2004*. *J. Appl. Cryst.* **38**, 760-767.

Altomare, A., Camalli, M., Cuocci, C., Giacovazzo, C., Moliterni, A. G. G. and Rizzi, R. (2007). *Advances in space-group determination from powder diffraction data*. *J. Appl. Cryst.* **40**, 743-748.

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## Structure solution by Direct Methods

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### Structure Solution in EXPO2014 program

Typical X-ray diffraction experiments provide structure factor moduli, while the relative phases are lost. Recovery of the phase information is crucial for crystal structure solution and is referred in crystallography as the *phase problem*. In EXPO2014 program, the default strategy used to solve this problem is based on the application of the Direct Methods (DM) theory (Giacovazzo, 1998). DM are able to estimate phases directly from the structure factor amplitudes. The application of DM to powder data requires the previous decomposition of the full pattern to extract single diffraction intensities for each reflection in the measured 2theta range. Owing to the peak overlap the estimates of the diffraction moduli will be affected by unavoidable errors: this weakens the efficiency of DM (naively, wrong moduli will produce wrong phases), and still today makes crystal structure solution from powder data a challenge.

[Load input file for Structure Solution by Direct Methods](#)

[When default EXPO2014 fails: strategies](#)

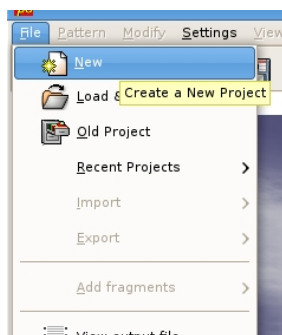
[Suggestions](#)

[Contact and References](#)

### Load input file for Structure Solution with Direct Methods

To run EXPO2014 for structure solution you need to create an input file (\*.exp). You can create an input file accessing by graphic interface by the menu "File" > "New".





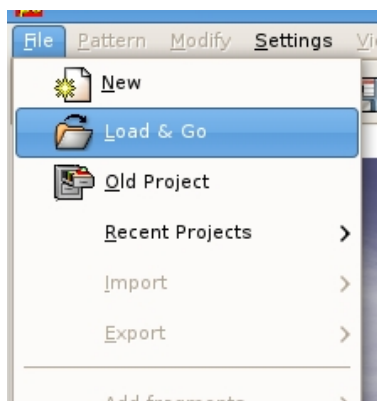
You must specify the structure name, the profile count filename and its format, the type of radiation source. It is supposed that the cell parameters and the space group have been determined before so fill the frame 'Cell Parameters' and 'Space Group'. Activate the check button 'Structure Solution' if you intend to perform the crystal structure solution process with Direct Methods. Otherwise use the button 'Open' to import an existing input exp, for example you could load the file `cime.exp` already existing in the directory 'examples'. The following picture is an example of the input file for crystal structure determination of the cimetidine compound.

When you press the button 'Save' an input file `cime.exp` will be created and automatically loaded by the program for the structure solution process by DM.

```
%structure cime
%job structure cime
%init
%data
pattern cime.pow
content s 4 c 40 n 24 h 64
wave 1.52904
cell 10.6986 18.8181 6.8246 90.000 111.284 90.000
space p 21/n
sync
filetype counts
%continue
```

You can know the meaning of lines of the input file by looking at the chapter "command and their use" of this manual.

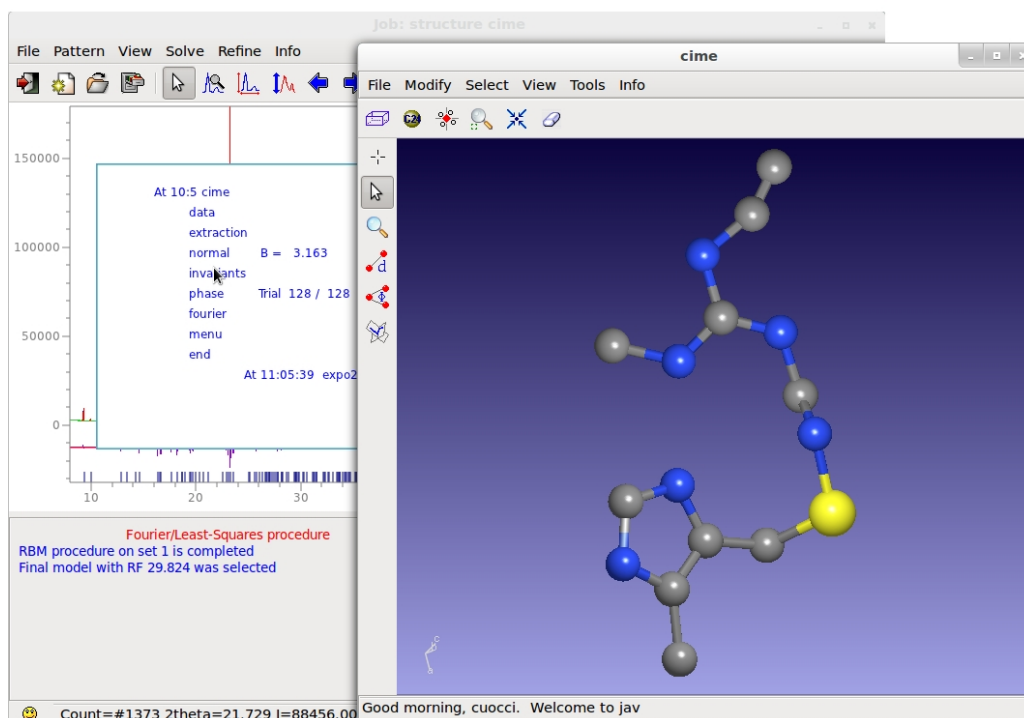
Alternatively you can edit a new input file or modify an exiting input file with a text editor and save it with extension '.exp'. Once a time the input file has been created, load the exp input file from menu 'File' > 'Load & Go'.



Press the button **Next >** in the toolbar and the following steps of the structure solution process will be automatically performed:

- 1) Extraction of the integrated intensities from the powder diffraction pattern;
- 2) The integrated intensities are normalized *via* Wilson method (Wilson,1942);
- 3) Triplet invariants are calculated and their phases are estimated *via*  $P_{10}$  formula (Cascarano *et al.*, 1984);
- 4) Phasing process: more plausible sets of phases are generated whose reliability is assessed *via* the CFOM figure of merit (Cascarano *et al.*, 1992);
- 5) Twenty sets of phases with the largest CFOM values are stored and ranked in decreasing CFOM order. The first set of phases is automatically selected and used for computing an electron density map *via* an E-Fourier synthesis (E-map): the most intense peaks in the E-map are located and chemically interpreted. The obtained structure model is optimized and completed *via* the automatic structure model optimization.

More information about the structure solution process by Direct Methods are in the chapter ['The steps of structure solution procedure'](#).

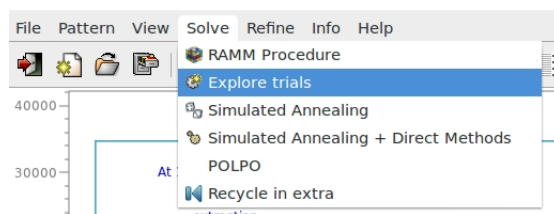


### When default EXPO2014 fails: strategies

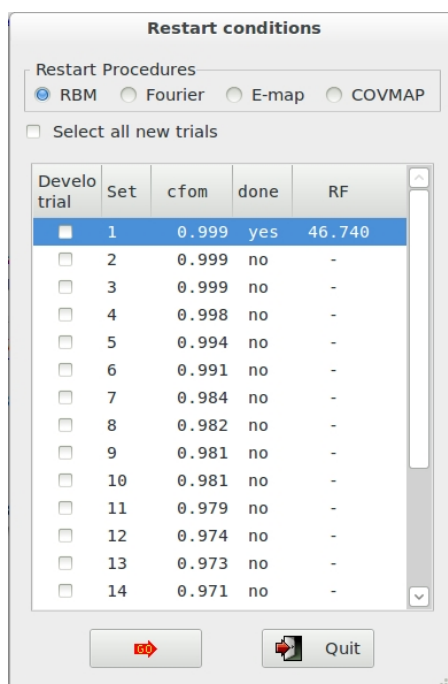
A lot of crystal structures are solved by EXPO2014 by default settings in few minutes and in completely automatic way. Unfortunately not always you can obtain the correct structure solution in default. In this situation two different strategies are suggested and can be applied at the end of the default run.

#### Explore trials


In a typical Direct Methods procedure more sets of phases (*trials*) are generated and ranked according to the combined CFOM figure of merit (estimating the quality of the trial) and only the best trial is used to calculate a Fourier map. Because of the unavoidable errors on the phases, the figure of merit can fail to evaluate the best trial, so it is strictly suggested to develop the other trials by menu 'Solve' > 'Explore trials'.



The following window will be opened (the procedure has been applied to 2-Mercaptobenzoic acid compound, whose input file is in the directory 'examples').



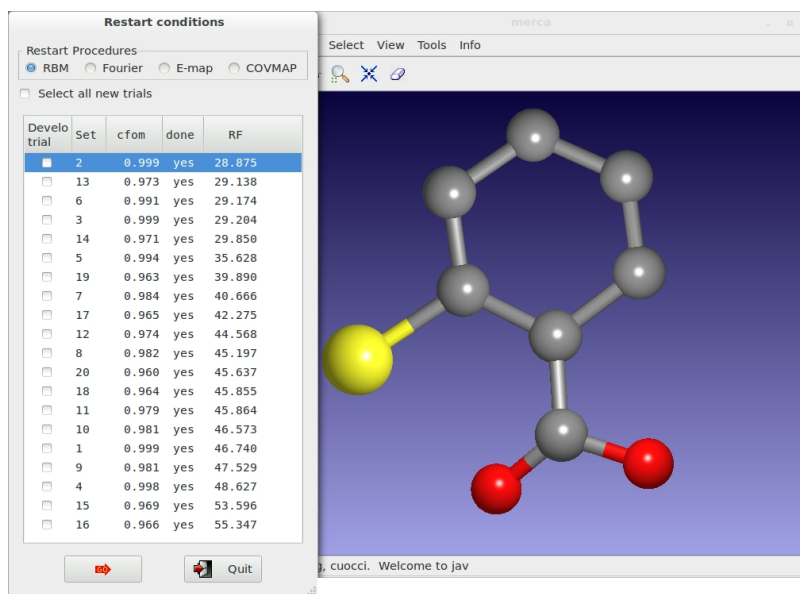
and the the CFOM value can be read. The highest CFOM value could not correspond to the correct solution while subsequent different trials may be successful. This is particularly true when several nearly equivalent CFOM's are available for different trials as in the picture. If the trial has been already developed (done='yes'), you can read the  $R_F$  figure of merit value that quantifies the agreement between the structure factors extracted from the experimental pattern and calculated by the model.

Check the button in the first column to decide which trial will be developed and press the button  If you check the button 'Select all new trials', all the trial not already explored will be automatically selected and developed.

You can choose three different actions for the structure model optimization (see later):

- 1)RBM: Resolution Bias Modification is the default action for organic and metal organic compounds.
- 2)Fourier: classical Fourier refinement, default choice for inorganic compounds.
- 3)E-map: the first electron density map calculated directly after the phasing process by Direct Methods.
- 4)COVMAP: the covariance principle based completion.

At the end of the procedure, all the trials will appear ordered according to the  $R_F$  and the user can also view the model corresponding to each trial by mouse selection.



Alternatively to the graphical option, the use of the command `%alltrials` in the input file automatically activate the 'Explore trials' approach. An example of input file is here reported:

```
%Structure merca
%Initialize
%Job merca
%Data
  Cell      7.885  5.976  14.949  90.0  100.48  90
  SpaceGroup p 21/c
  Content   c 28 O 8 S 4 h 24
  Pattern   pd_0002.xy
  Wavelength 1.54056
%extra
%normal
%invar
%phase
%alltrials
```

### Structure model optimization

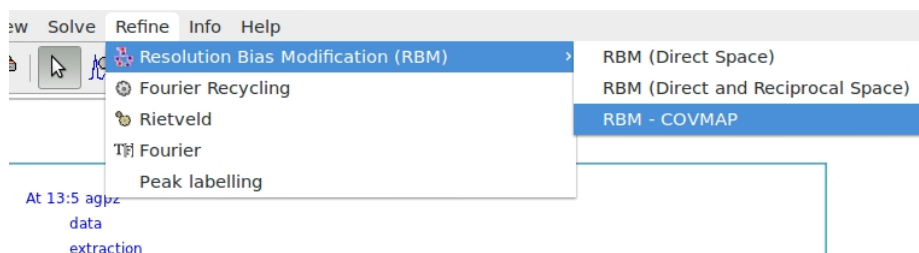
The structure model obtained at the end of the default strategy, generally is a partially correct representation of the true model: some atoms are in correct positions but other are incorrectly positioned or completely false. In this situation the user can try to improve the quality of the Fourier map, as obtained at the end of Direct Methods, by using different optimization strategies implemented in the EXPO2014 program:

1. suitably weighted least squares ( $wLSQ$ ) (Altomare *et al.*, 2006), able to compensate the low accuracy of the intensities of strongly overlapped reflections. The procedure is automatically applied in case of inorganic compounds.
2. the resolution bias correction algorithm (RBM) (Altomare *et al.*, 2008a, 2008b; 2009, 2010a, 2010b) for reducing, in the electron density map, the errors caused by the limited experimental resolution: peak broadening, peak shift, intensity distortion.

The correction has been developed in direct space (it represents the default choice in case of organic and metal organic compounds), in reciprocal space and in both direct and reciprocal space;

- the procedure of electron density modification based on the concept of covariance between points of the map (COVMAP) (Altomare *et al.*, 2012) The procedure executes the following strategy: the structural model provided by the RBM procedure is submitted to COVMAP approach which suitably modifies the electron density map and successively submits the improved model to *wLSQ* analysis. The resulting new model is again modified by COVMAP and cyclically processed in the other two steps. The number of cycles depends on the structure complexity. The structure model obtained at the end of the default strategy can be partly correct with some atoms in correct position but other atoms are incorrectly positioned or completely false. In this situation the user can try to optimize the model by using different optimization strategies.

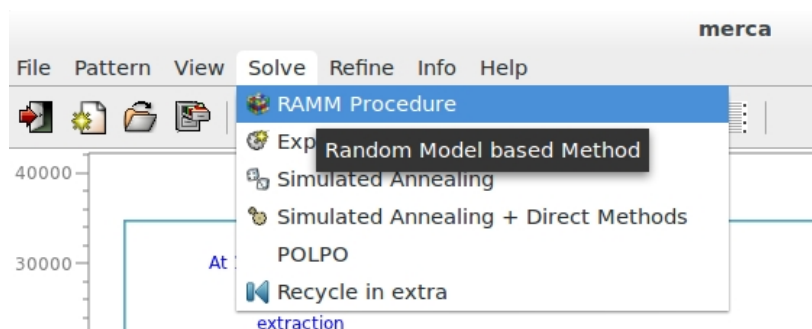
It is possible to graphically choose different RBM procedures for model optimization by the menu 'Resolution Bias Modification (RBM)', via 'Refine' button from the upper EXPO2014 menu.



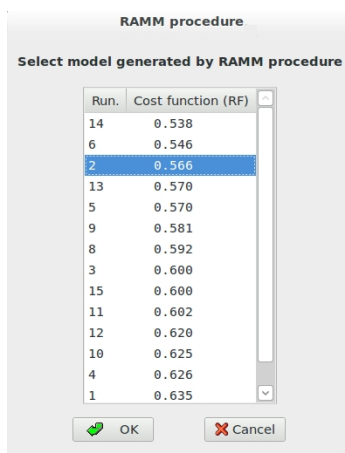
### Apply the RAMM (RAndom Model based Method) procedure

The new method RAMM (Altomare *et al.*, 2013) has been developed and implemented in the EXPO2014 computing program for improving the *ab initio* crystal structure solution process. When the available information consists of only the experimental powder diffraction pattern and the chemical formula of the compound under study, the structure solution classical approach follows two main steps: 1) phasing by Direct Methods (or by Patterson methods) in order to obtain a structure model (this last is usually uncompleted and/or approximate); 2) improving the model by structure optimization techniques. The alternative RAMM approach skips step 1) and supplies a fully random model to step 2). Such model is then submitted to important structure optimization tools present in EXPO: *wLSQ*, *RBM* and *COVMAP* which are able to lead to correct structure. RAMM is based on a cyclic process generating several random models which are then optimized. The process stops automatically when recognizes the correct structure.

Click 'RAMM' on the menu 'Solve' to activate this alternative strategy for structure solution at the end of the default run of EXPO2014. The following pictures are related to 2-Mercaptobenzoic acid whose input file is in the directory 'examples'.



The procedure can take from some minutes to several hours depending on the complexity of problem (number of atoms, quality of data, data resolution). If more than one plausible solution is found they will be ordered according to the R-structure factor in an interactive list.



The selected model will be visualized on the molecular viewer. Press 'OK' to accept the selected model.

When Direct Methods procedure fails, the RAMM approach can be a very useful tool to find the correct solution.

The use of the command `%randomsolve` in the input file automatically activate the 'Explore trials' approach. An example of input file is here reported:

```
%Structure merca
%Initialize
%Job merca
%Data
  Cell      7.885  5.976  14.949  90.0  100.48  90
  SpaceGroup p 21/c
  Content   c 28 O 8 S 4 h 24
  Pattern   pd_0002.xy
  Wavelength 1.54056
%randomsolve
```

## Suggestions

The number of options in the program is quite large. The optional strategies regard the improvement of both the decomposition process for carrying out more reliable reflection intensities and the Direct Methods performances. We give some other secondary

strategies.

### About the improvement of the decomposition process

- It is important to provide good quality diffraction pattern. For example, it is recommended to reduce the pattern range in case of high noise signal at large 2theta values. Use the directive `range` in the command `%data` to select a portion of pattern or select 'Pattern' > 'Range' by the graphical interface.
- If a partial structure fragment has been located by the default run, it may be recycled in the extraction process (a graphic option must be selected). Click on 'Restart' > 'Recycle in extra'.
- The use of the 'RANDOM' directive in the EXTRACTION module activates the procedure for overcoming the Le Bail method tendency to equipartition the intensity of a group of strongly overlapped reflections. Based on a Monte Carlo approach, it may provide a set of more statistically meaningful intensities.
- If the default run has revealed pseudo symmetry effects and, in particular, if the percentage of electron density affected by pseudo is large, it may be very useful to exploit that information in the extraction process (a graphic option activates the procedure).

### About the optimization of Direct Methods procedure

- Magic integers procedure is an effective and simple way for starting a multi-solution process.  
A random approach may be alternatively chosen in the phasing process (directive 'RANDOM' in the PHASE module).
- Second representation formula for triplet invariants proved much more powerful than first representation formula therefore it is used as a default for estimating triplets. In case of failure, the user can choose P3 formula (directive 'COCHRAN' in the INVARIANT module) and/or conveniently increase the number of symbols in the phasing step (directive 'SYMBOLS' followed by the number of symbols to be used in the 'PHASE' module).
- A check for possible pseudotranslational symmetry is always made by EXPO2014: if PSEUDO keyword is not activated the information is given but not used in the normalization routine and in the phasing process. The user can decide to use it (directive 'PSEUDO' in the NORMAL module).
- the value of NREF (number of reflections actively used in the phasing process) is fixed by EXPO2014. For some special structures the ratio "number of active triplets/NREF" is too small (less than 10). Larger values of NREF may improve the phasing procedure (directive 'NREFLECTIONS' followed by the number of reflections in the NORMAL module).
- High (or low) resolution reflections may occasionally play a too important role in the first steps of convergence and divergence process. Fixing a thermal factor lower (or larger) than that automatically provided by the normalization routine may successfully change convergence and divergence process (directive 'BFACTOR' followed by the



isotropic thermal factor in the NORMAL module).

- An alternative space group should be carefully considered (directive 'SPACEGROUP' in the DATA module).
- Sometimes the structure model is partial. Successive combined Fourier map calculations ( $F_o - F_c$ ,  $2F_o - F_c$  or  $F_o$ ) and Rietveld refinements may be conveniently selected by graphical options.

### Contact

For suggestions and bugs contact:

[angela.altomare@ic.cnr.it](mailto:angela.altomare@ic.cnr.it)

[annagrazia.moliterni@ic.cnr.it](mailto:annagrazia.moliterni@ic.cnr.it)

[rosanna.rizzi@ic.cnr.it](mailto:rosanna.rizzi@ic.cnr.it)

[corrado.cuocci@ic.cnr.it](mailto:corrado.cuocci@ic.cnr.it)

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## All steps of structure solution procedure

### The steps of structure solution procedure

Using the command `%continue`, the program runs in default conditions carrying out the commands

```
%extraction
%normal
%invar
%phase
%fourier
%menu
%end
```

and each command corresponds to a step in the structure solution with Direct Methods. All the following steps are described.

- 1) [Extraction of the integrated intensities](#) (`%extraction` command)
- 2) [Normalization of the integrated intensities](#) (`%normal` command)
- 3) [Estimate of structure invariants](#) (`%invariants` command)
- 4) [Application of the tangent formula](#) (`%phase` command)
- 5) [Crystal structure completion and refinement](#) (`%fourier` command)

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## Extraction of the integrated intensities

### Extraction of the integrated intensities ('extraction' command)

To calculate the integrated intensities, the program uses the Le Bail algorithm (Le Bail *et al.*, 1988) and combines it with a least squares procedure minimizing the quantity:

$$\sum_i w_i (y_{oi} - y_{ci})^2 \quad (1)$$

The summation in (1) goes over all the data points,

$$w_i = 1/y_i^2$$

$y_{oi}$  = observed intensity at the i-th step

$y_{ci}$  = calculated intensity at the i-th step

$$y_{ci} = s \sum_h L P_h m_h |F_h|^2 P(2\theta_i - 2\theta_h) A(2\theta_i - 2\theta_h) + y_{bi} \quad \left( \frac{1}{2} \right)$$

)

The summation over  $\mathbf{h}$  includes neighbouring Bragg  $\mathbf{h}$  reflections,

$s$  = scale factor

$LP_h$  = Lorentz - polarization factor

$m_h$  = reflection multiplicity

$F_h$  = structure factor

$P$  = profile function

$A$  = asymmetry function

$y_{bi}$  = background intensity at the  $i$ -th step.

The background in (2) is automatically estimated and is described by the polynomial function (Young, 1993)

$$y_{bi} = \sum_{m=0}^N b_m \left[ \frac{2\theta_i}{2\theta_M} - 1 \right]^m$$

$N$ , the polynomial degree, is automatically defined by the program as the number which provides the best fit of the background interpolation points.

$2\theta_M$  is the  $2\theta$  associated to the minimum intensity in the range in which the background is estimated.

From the pattern a standard peak is automatically selected. The standard peak fitting is performed to provide the starting values of the variables to refine in the least squares procedure.

The full pattern is automatically divided into intervals. The refined parameters derived by the fitting of each interval will be taken into account for the final full pattern fitting.

The following profile shape functions are available for user choice:

$$\frac{\Gamma(\beta_h)}{\Gamma(\beta_h - 0.5)} \left( \frac{C_2}{M} \right)^{1/2} \frac{2}{H_h} \left( 1 + 4C_2 X_{ih}^2 \right)^{-\beta_h} \quad \text{Pearson VII}$$

$$\frac{C_0^{1/2}}{\sqrt{\pi H_h}} \exp(-C_0 X_{ih}^2) \quad \text{Gaussian}$$

$$\frac{C_1^{1/2}}{\pi H'_h} (1 + C_1 X_{ih}^2)^{-1}$$

*Lorentzian*

$$\eta \frac{C_1^{1/2}}{\pi H_h} (1 + C_1 X_{ih}^2)^{-1} + (1 - \eta_h) \frac{C_0^{1/2}}{\pi^{1/2} H_h} \exp(-C_0 X_{ih}^2)$$

$$\text{with } 0 \leq \eta \leq 1$$

*P  
s  
e  
u  
d  
o  
-  
V  
o  
i  
g  
t*

where

$$C_0 = 4 \ln 2 \quad C_1 = 4$$

$$X_{ih} = (\Delta\theta_{ih}/H_h)$$

$$H_h = [w + v \cdot \operatorname{tg} \theta_h + u \cdot \operatorname{tg}^2 \theta_h]^{1/2} \quad H'_h = Z \cdot \operatorname{tg} \theta_h + T/\cos \theta$$

$$\eta_h = \eta_0 + \eta_1 \cdot \operatorname{tg} \theta_h + \eta_2 \cdot \operatorname{tg}^2 \theta_h$$

$$\beta_h = \beta_0 + \frac{\beta_1}{2\theta_h} + \frac{\beta_2}{(2\theta_h)^2}$$

The default is the Pearson VII function. In this case

$$A (2\theta_i - 2\theta_h) = \frac{\alpha \cdot (2\theta_i - 2\theta_h)^3}{\left(\frac{H_h^2}{C_{2h}} + (2\theta_i - 2\theta_h)^2\right)^{3/2}} + 1$$

otherwise

$$C = \frac{2 \cdot |E_h \cdot E_k \cdot E_{h-k}|}{\sqrt{N}}$$

The peak shape, the asymmetry, the cell and the background parameters are all refined by the program. To overcome the tendency of the Le Bail algorithm to equipartition the intensities of strongly overlapping reflections, a new approach was introduced. It is based on the random variation of the reflection intensities belonging to a given cluster and on the subsequent selection of the good fit feasible trials.

After a first default run of EXTRA, it is possible to run it again starting from the refined variables in the previous run. In this case the preliminary standard peak procedure and the interval by interval extraction procedure are skipped. The related command is % RECYCLE.

### Directives in extraction command

**The following directives must be added after the command '%extraction' in the input file to activate some specific features of the procedure**

#### ALL

To activate the procedure of selection of the profile function type (among Pearson VII, Gaussian, Lorentzian, Pseudo-Voigt) from the best fit of each interval.

#### DAMPING *x*

*x* is the damping factor used in the least squares routine (default value 0.1). (It is convenient to use a small *x* value).

#### FAST

This directive is used if the graphic interface has been requested by the "window" command. In this case, the user graphic interaction in a default run is avoided.

#### FIRST

To activate the procedure of selection of the profile function type (among Pearson VII, Gaussian, Lorentzian, Pseudo-Voigt) from the best fit of the first interval .

#### FRECYCLE *filename.ext*

If the "filename" is available from a previous run of EXPO2014 (or EXTRA), or from any source containing hkl and the corresponding F-squared values, Le Bail algorithm is started again for obtaining new estimates.

#### GAUSSIAN

To use only if the gaussian function is preferred.

#### INTERVAL *n*

*n* is the number of intervals in which the powder pattern is divided (max 8). *n* is only given if the user wants to change the automatic division of the pattern.

#### LORENTZIAN

To use only if the lorentzian function is preferred.

### **LOWB**

To reduce the background by a constant factor equal to the minimum value observed count.

### **NCYCLE $n$**

$n$  is the number of cycles for each interval (default value is 60).

### **NOBA**

To not refined the background

### **NOCELL**

To skip the cell refinement.

### **NOSINGLE**

This directive is used if the preliminary fitting of the standard peak (automatically selected by the program) is omitted. In this case a preliminary fitting of the first interval is carried out.

### **OPTI**

To continue the refinement procedure for each interval.

### **POLYNOMIAL $k$**

$k$  is the background polynomial degree (max 10).  $k$  is given if the user wants to use a fixed degree in each interval and not the degree automatically selected by the program.

### **PVOIGT**

To use only if the Pseudo-Voigt function is preferred.

### **RANDOM $p$**

To activate the random procedure in the integrated intensity extraction step.  $p$  is the coefficient for the reflection overlapping definition. Default value = 0.5

### **SMOO**

To activate the procedure for calculating the background by following (Brückner, 2000). In this case the background is not refined.

### **STANDARD**

To activate the procedure of selection of the profile function type (among Pearson VII, Gaussian, Lorentzian, Pseudo-Voigt) from the best fit of the standard peak.

### **SLOW**

This directive can be used if the graphic interface has been requested by the "window" command. In this case the program stands by after some relevant calculations and waits for the user graphic interaction to go on.

## VERBOSE

This directive is used to have a more detailed print in the output file. In this case, the Rp and Rwp values and the values of the refined variables are printed interval by interval.

## WIDTH *x*

*x* is the factor which, multiplied by the FWHM of each peak, gives the total peak width. (In this case the automatic calculation of *x* is not taken into account).

## ZEROPROFILE *x*

*x* is the 2 $\theta$  shift value supplied by the user (to be subtracted from the 2 $\theta$  observed positions). In this case the automatic calculation of the 2 $\theta$  shift using the preliminary fitting of the standard peak is skipped by the program).

## EXAMPLES

### Example 1

A Pseudo-Voigt function will be used and the background in each interval will be described by a constant. The counts file format is not the default one and the graphic window is suppressed.

```
%structure mes
%job MES - data from home diffractometer
%initialize
%data
  pattern mes.pow
  cell 8.588 9.931 11.105 90.0 93.754 90.0
  content C 24 N 4 O 20 S 4 H 52
  spacegroup p 21/c
  wavelength 1.5406
  filetype double
%extraction
  pvoigt
  polynomial 0
%end
```

### Example 2

The starting values of the integrated intensities in the extraction step are supplied by the user in the file "yono.ext" and the number of least-square cycles is set to 40.

```
%structure yono
%job YONO - Synchrotron data
%initialize
%data
  pattern yono.pow
  cell 9.385 16.394 3.627 90.000 101.067 90.000
  content Y 8 O 26 N 2 H 18
  spacegroup p 21
  wavelength 1.2323
  synchrotron
%extraction
  fstarting yono.ext
  ncycle 40
%end
```

Example 3

The preliminary fitting of the standard peak is skipped and the starting 2 $\theta$  shift value is supplied by the user (the program refines it).

```
%window
%structure agpz
%job AGPZ - data from home diffractometer
%init
%data
    pattern agpz.pow
    cell 6.526 20.059 6.464 90.000 90.000 90.000
    spacegroup p b c a
    content Ag 8 N 16 C 24 H 24
    wavelength 1.54056
%extraction
    nosing
    zeroprof 0.02
%continue
```

Example 4

Neutron data and a deuterium atom in the cell content are used. Fast graphic interaction for the integrated intensities extraction process is activated.

```
%structure baco
%job BACO - Neutron data
%initialize
%data
    neutron
    isotope H 0.67
    pattern baco.pow
    cell 10.0632 7.9330 6.8487 90.0 122.3423 90.0
    spacegroup C 2/m
    content Ba 4 C 8 O 20 H 8
    wavelength 1.909
%extraction
    fast
%continue
```

## References

Le Bail, A., Duroy, H., Fourquet, J.L. (1988). *Ab-initio structure determination of LiSbWO<sub>6</sub> by X-ray powder diffraction. Math. Res. Bull.* **23**, 447-452.

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## Normalization of the integrated intensities

### Normalization of the integrated intensities ('%normal' command)

In this module diffraction intensities are normalized using the Wilson method. Statistical analysis of the intensities is made in order to suggest the presence or absence of the inversion center, to identify the possible presence and type of pseudotranslational symmetry (Cascarano *et al.* 1988 a,b; Fan, Yao *et al.* 1988) and to detect preferred orientation effects (Altomare *et al.* 1994; Altomare *et al.* 1996). Possible deviations (of displacive type) from ideal pseudotranslational symmetry are also detected. All the above



information is used as prior information in the integrated intensities extraction process, unless the directive NOPSEUDO is given to the program.

When some additional prior information, besides positivity and atomicity of electron density, is available, then a suitable renormalization of structure factors is made.

### Directives in normal command

The following directives must be added after the command '%normal' in the input file to activate some specific features of the procedure

#### BFACTOR *x*

Temperature factor if the user wants to supply it. (The scale factor is assumed equal to 1).

#### NOPREFERRED

If this directive is given the program does not apply the correction for preferred orientation.

#### NOPSEUDO

If this directive is given the program does not recycle the PSEUDO information in a new extraction process.

#### NREFLECTIONS *n*

Number of active reflections with largest E-values subject to a minimum value of E(obs) = 1.0.

Default = 4 \* number of independent atoms + 50 if centrosymmetric + 50 if triclinic + 150 to a maximum of 499. If PSEUDO directive is on, the program tries to use all the E's down to 1.0.

#### NZRO *n*

Number of smallest E-values (maximum E-value 0.3) to calculate psi-zero triplets. The default (and the maximum) is 1/3 of the strong reflections. (The directive allows to decrease that number).

#### NPLA *n*

*n* is the number of candidate planes for preferred orientation analysis (default 10; maximum 30)

The number includes the equivalent planes which will not be considered.

#### PLANE *h k l G*

Preferred orientation direction supplied by the user; G is the correction factor.

#### PSEUDOTRANSlation *n(1,1) n(2,1) n(3,1) n(4,1) n(1,2) . . . n(4,3)*

If parameters are equal to zero, or omitted, the normalization routine performs statistics for the pseudotraslation effects and renormalizes the reflections on assuming the most probable pseudotranslation as prior information.

If user wants to supply a specific pseudotranslational symmetry, and this corresponds to a class given in Table 1 the *n(1,1)* can be set to the class number and the other values must be omitted.

If the pseudotranslation is more complex, it should be specified by up to 3 sets of 4 values *n(i,j)* so that

$$(n(1,j)*h + n(2,j)*k + n(3,j)*l = n(4,j)*m) \quad j=1,...,3$$

where *m* is an integer number.

**THRP x**

Threshold value of the mean fractionary scattering power (M.F.S.P.) to recycle the pseudo-translational symmetry information in a new extraction process.

**EXAMPLE****Example 1**

Use of the pseudotranslational symmetry (if it is present) as prior information for a new extraction process is inhibited.

```
%structure agpz
%job AGPZ - data from home diffractometer
%initialize
%data
  pattern agpz.pow
  cell 6.526 20.059 6.464 90.000 90.000 90.000
  spacegroup p b c a
  content Ag 8 N 16 C 24 H 24
  wavelength 1.54056
  filetype xy
%extraction
%normal
  nopseudo
%continue
```

**References**

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**Estimate of structure invariants****Estimate of structure invariants ('%invariants' command)**

Up to 10000 triplets relating reflections with normalized E values greater than a given threshold (strong triplets) are stored for active use in the phasing process. Also triplets (PSI-ZERO triplets) relating two reflections with large E and one with E close to zero are generated: they are used to define a special figure of merit (PSCOMB). Special types of triplets (PSI-E triplets) based on two strong and one intermediate reflections (just below the threshold of strong reflections) are calculated and used in the FOURIER/LEAST-SQUARES module in order to extend phase information (Altomare *et al.* 1991).

Negative quartets are generated by combining the psi-zero triplets in pairs, and those with cross-magnitudes smaller than a given threshold are estimated by means of their first representation, as described by Giacovazzo (1976). These quartets are used to provide an important contribution to the CPHASE FOM.

Active triplets may be estimated according to Cochran's (1955) P3 distribution: the concentration parameter of the von Mises distribution is then:

$$C = \frac{2 \cdot |E_h \cdot E_k \cdot E_{h-k}|}{\sqrt{N}} \quad (3)$$

Triplets can also be estimated according to their second representation (i.e. P10 formula, as described by Cascarano *et al.*, 1984). The concentration parameter of the new von Mises distribution is given by

$$G = C (1 + q) \quad (4)$$

where  $q$  is a function (positive or negative) of all the magnitudes in the second representation of the triplet. The  $G$  values are rescaled on the  $C$  values and the triplets are ranked in decreasing order of  $G$ . The top relationships represent a better selection of triplets with phase value close to zero than that obtained when ranking according to  $C$ . These triplets will be actively used in the phase determination process.

Triplets characterized by a negative  $G$  represent a sufficiently good selection of relationships close to 180 degrees, to be used for the calculation of a powerful FOM (CPHASE). Triplets with  $G$  close to zero are expected to have values widely dispersed around 90 or 270 degrees and are used to compute an enantiomorph sensitive FOM. A similar FOM is also computed using quartets estimated with a very small concentration parameter.

As a default, triplets are estimated according to P10 formula.

The parameter  $C$  of the Cochran distribution (say P3) is suitably modified when the pseudo information in the section 'NORMAL module' is available. Then triplet phases are no longer expected to be around zero (see quoted references) and may lie anywhere between 0 and  $2\pi$ .

The method of the joint probability distribution functions (Cascarano *et al.*, 1991; Carrozzini *et al.*, 1997) can be applied to obtain an estimate of normalized structure factors, that will be used as a source of supplementary prior information in the extraction process (if directive ESTIMATION is used).

### Directives in invariants command

**The following directives must be added after the command '%invariants' in the input file to activate some specific features of the procedure**

#### **GMIN $x$**

Positive triplets with  $G < x$  are not actively used.

Default value  $x=0.6$  (in any case  $0.2 < x \leq 1.0$  is accepted range of value).

#### **COCHRAN**

To use the P3 formula. (By default P10 formula is used).

#### **CORRECTION $x$**

If a PSEUDOTRANSFORMATION procedure is on, a correction factor depending on  $x$  is applied to the probabilistic argument of weak-weak-weak triplets when they are present. The default value is calculated by program.

$x = -1$  eliminates weak-weak-weak triplets,

$x = 1$  corresponds to the largest confidence in them.

#### **EMAX $x$**

Maximum value of  $E$  for the weak reflections for the psi-zero search (up to a maximum of

NRPSIZEZERO reflections).  $x > 0.3$  not accepted.

Minimum value for the normalized structure factors in the sigma2 search.  $x < 1.0$  not accepted.

Default = minimum value of E for the strongest reflections selected by normalization routine.

## ESTIMATION

To run the procedure which estimates the  $|E|$ 's for all the reflections and use them as a prior information in a new extraction process.

The procedure will not be applied if PSEUDOTRANSLATIONAL information has been recycled.

## NPSIO

To not calculate PSI-0 triplets (Default uses them).

## NRPSIZEZERO *n*

The number of weakest reflections for the psi-zero search.

Default = number computed by normalization routine.

The value will substitute the default one in the direct access file.

## NRTRIPLETS *n*

The number of strongest reflections for the sigma2 search. ( Up to  $E_{min} = 1.0$  )

Default = number computed by normalization routine (nstrong).

The value will substitute the default one in the direct access file.

Value less than  $nstrong/2$  is not accepted.

## NLARGE *n*

To supply the number of largest reflections for the psi-zero search ( default = number of strongest reflections used for sigma2 search).

$nlarge > nrtriplets$  is not accepted.

## NQUARTETS

To not calculate negative quartets (Default uses them).

## NUMK *n*

The number of free-vectors used by P10 formula.

Default value is provided by EXPO according to the structural complexity:

$n = \min ( n_{atom} / m_{sym} + 30, 70 )$

where  $n_{atom}$  is the number of atoms in the cell and  $m_{sym}$  is the number of symmetry operators of the space group.

## YPSIE

To calculate PSI-E triplets (Default doesn't use them).

## EXAMPLE

### Example 1

Use of the triplets estimation as prior information for a new extraction process.

```
%structure mes
%job MES - data from home diffractometer
%initialize
%data
```

```

pattern mes.pow
cell 8.588 9.931 11.105 90.0 93.754 90.0
content C 24 N 4 O 20 S 4 H 52
spacegroup p 21/c
wavelength 1.5406
filetype double
%extraction
%normal
  nopseudo
%invariants
  estimation
%continue

```

## References

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## Application of the tangent formula

### Application of the tangent formula ('%phase' command)

In the EXPO2014 program the most reliable one-phase s.s. are treated as known phases. Besides triplets, also the most reliable negative quartets and two-phase s.s. may be actively used.

Each relationship is used with its proper weight: the concentration parameter of the first representation for quartets and two-phase s.s., and C or G for triplets.

#### - CONVERGENCE/DIVERGENCE PROCEDURE -

The convergence procedure (Germain *et al.* 1970) is a convenient way of defining an optimum starting set of phases to be expanded by the tangent formula or by any other algorithm.

When the P10 formula is used, as a default, a special convergence process is devised which chooses the starting set according to

$$\langle \alpha_h \rangle = \sum_j \left[ G_j \cdot D_1(G_j) \cdot D_1(\langle \alpha_k \rangle) \right] \cdot D_1(\langle \alpha_{h-k} \rangle) \left( \frac{5}{5} \right)$$

as suggested by Giacovazzo (1979-a,b) and by Burla *et al.* (1987), with

$$D_1(G_j) = \frac{I_1(G_j)}{I_0(G_j)} \quad \left( \begin{matrix} 6 \\ 6 \end{matrix} \right)$$

$I_1$  and  $I_0$  represent modified Bessel functions of order one and zero respectively. The summation in (5) is over all relationships defining the reflection  $h$ . If P3 formula is used the default choice is

$$\langle \alpha_h \rangle = \sum_j [C_j \cdot D_1(G_j)] \quad (7)$$

Once the starting set has been defined, a good pathway for phase expansion is determined by a divergence procedure. In the divergence map, starting from the reflections in the starting set, each new reflection is linked to the preceding ones with the highest value of  $\langle \alpha \rangle$ .

#### - PHASE EXTENSION AND REFINEMENT -

The starting set defined by the preceding step is usually formed by the origin (and enantiomorph) fixing reflections, a few one phase s.s. and a number of other phases which may be obtained:

a) by magic integer permutation (White *et al.* 1975; Main, 1978),

b) by a random approach (Baggio *et al.* 1978; Burla *et al.* 1992).

The option a) is the default, b) runs if the directive RANDOM is used. In this last case a large number (depending on the available computer time) of trials can be requested.

Directives SYMBOLS, SPECIALS, MAXTRIAL may be used to change default values.

Phase expansion and refinement are carried out by means of a tangent formula using triplets, negative quartets, psi-zero triplets and the most reliable two-phase structure seminvariants. In the weighting scheme the experimental distributions of the alpha parameters are forced to match with the theoretical ones (Burla *et al.* 1987).

For each phase set, several FOM's are computed using all invariants and seminvariants estimated by means of the representation method. Their meaning and an optimized way of combining all the computed FOM's to give a highly selective combined figure of merit (CFOM) is described in the papers by Cascarano *et al.* (1987, 1992).

All FOM's, as well as the combined CFOM, are expected to be equal to 1.0 for correct solutions. CFOM larger than 0.5 can be considered encouraging.

If pseudotranslational symmetry is present then CFOM > 0.3 may characterize the correct solution.

#### Directives in phase command

**The following directives must be added after the command '%phase' in the input file to activate some specific features of the procedure**

##### ENANTIOMORPH $n$

Code of the reflection chosen by the user to fix the enantiomorph (by default the enantiomorph is chosen by the program).

##### LIST $n$

The number of reflections at the top of the divergence map for which a list of the map is obtained. Default = no printout of the map.

### **MAXTRIALS *n***

Maximum number of trials when random approach is used. (Default 100). Only if RANDOM directive is on.

### **MINFOM *x n***

*x*: the program automatically stops when a solution is found with CFOM > *x*. Default value = 1.00.

*n*: is the maximum number of phase sets (with the largest combined figure of merit - CFOM) to retain (default value = 10).

### **NOREJECT**

Used to retain equivalent sets of phases.

### **ORIGIN *n(i) phi(i)***

Codes and phases of the reflections chosen by the user to fix the origin. The total number of reflections (max 3) needed to fix the origin must be given (by default the origin is chosen by the program).

### **PERMUTE *n(i)***

Codes of the permuted reflections chosen by the user (i.e. included in the number of required symbols, max 12).

### **PHASE *n(i) phi(i) wt(i)***

Codes, phases and weights of reflections with known phase (max 200).

If one card is not sufficient, the directive PHASE must be repeated in the other card(s).

### **RANDOM *n***

To use random phases starting sets.

*n*: is the number of random phases. If *n* is omitted, it is equal to one half of the strong reflections (*nstrong*).

Maximum value allowed for *n* = *nstrong* - 4

Minimum value allowed for *n* = *nstrong* / 4

Default value for random generation seed is 67543.

(Not consistent with SYMBOLS directive)

### **SEED *n***

Random generation seed. *n* must be an integer large value and must be odd.

### **SPECIALS *n***

The number of reflections with restricted phase to be permuted (i.e. included in the number of required symbols, max 12).

### **SYMBOLS $n$**

The number of permuted phases (max 12). Default = 5.

(Not consistent with RANDOM directive)

### **TABLE**

To print the table of alpha values (at the beginning of PHASE procedure).

### **TEST**

To restart the random number generator using the default seed. Only if RANDOM directive is on.

### **TRIAL $n$**

To print the final phases for the specified trial  $n$ .

### **YNEG**

To actively use negative triplets in the phasing process. (Default does not use them).

### **YNGQ**

To actively use negative quartets in the phasing process. (Default does not use them).

## **EXAMPLE**

### Example 1

The program restarts from the PHASE procedure.

A random approach is used and the best 100 sets of phases, over 250 trials, are retained in the direct access file. No Fourier is required.

```
%structure nizr
```

```
%job nizr structure
```

```
%init
```

```
%data
```

```
pattern nizr.pow
```

```
cell 12.388 8.9269 8.8449 90.0 90.550 90.0
```

```
cont zr 8 p 12 o 48 ni 4
```

```
space p 21/n
```

```
wave 1.0302
```

```
filetype double
```

```
synch
```

```
%extraction
```

```
%normal
```



```
%invar
%phase
  random
  maxtrials 250
  minfom 1.0 100
%end
```

### References

- Baggio R., Woolfson M.M., Declercq J.P. & Germain G. (1978). *Acta Cryst.* **A34**, 883-892.  
 Burla M.C., Cascarano G., Giacovazzo C., Nunzi A. & Polidori G. (1987). *Acta Cryst.* **A43**, 370-374.  
 Burla M.C., Cascarano G. & Giacovazzo C. (1992). *Acta Cryst.* **A48**, 906-912.  
 Cascarano G., Giacovazzo C. & Viterbo D. (1987). *Acta Cryst.* **A43**, 22-29.  
 Cascarano G., Giacovazzo C. & Guagliardi A. (1992). *Acta Cryst.* **A48**, 859-865.  
 Germain G., Main P. & Woolfson M.M. (1970). *Acta Cryst.* **B26**, 274-285.  
 Main P. (1978). *Acta Cryst.* **A34**, 31-38.  
 White P.S. & Woolfson M.M. (1975). *Acta Cryst.* **A31**, 53-56.

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### Crystal structure completion and refinement

#### Crystal structure completion and refinement ('%fourier' command)

The sets of phases generated by the tangent routine are first expanded through psi-E relationships and then passed to the fast fourier transform routine written by L.F. Ten Eick (1977) and subsequently modified by the MULTAN team (Main, 1978; Main *et al.* 1980).

Several additional features have been introduced in the present version:

- From the solution with the highest CFOM value a Fourier map may be calculated by involving a supplemental number of reflections which are phased through the so-called psi-E triplets (Altomare *et al.* 1991)
- Special positions are handled, peaks very close to symmetry elements are moved onto symmetry elements, the site symmetry is defined and the atomic occupancy factor is calculated; key numbers for designating free, coupled or fixed positional parameters for least-squares subroutines are also calculated together with symmetry conditions on the thermal ellipsoid.
- Cycles of structure factor calculation -least squares- (2Fo -Fc) Fourier synthesis are automatically performed in order to provide a more complete and refined crystal structure. Due to reflection overlapping the results of the refinement must carefully be considered by the user who will take always into account the ratio 'number of parameters to refine/number of independent observations'.

The program provides the following R-factors which can be used as reliability parameters:

$$R(f) = \frac{\sum |F_o - F_c|}{\sum |F_o|} \quad (8)$$

$$R_w(f) = \frac{\sum |F_o - F_c| \cdot F_o^2}{\sum |F_o| \cdot F_o^2} \quad (9)$$

$$R(f^2) = \frac{\sum |F_o^2 - F_c^2|}{\sum |F_o^2|} \quad (10)$$

An alternative approach, based on real space techniques (Altomare *et al.* 2002) originally used for phase extension and refinement of proteins (Giacovazzo & Siliqi, 1997; Burla *et al.* 2000), has been introduced in EXPO and modified to improve the phasing process from powder data. It combines an Electron Density Modification procedure with Fourier map calculations.

### Directives in fourier command

**The following directives must be added after the command '%fourier' in the input file to activate some specific features of the procedure**

#### **COORDINATION *El dmin dmax n***

The minimum and maximum value of the bond distance are assigned to element El. n is the coordination type.

Allowed values for bond angles are:

n = 1    55 - 180 Degrees

n = 2    85 - 145 Degrees

#### **EDMO**

This directive is used to enable a direct space procedure consisting of an Electron Density Modification (EDM) process followed by successive Fourier maps using (2Fobs -Fcalc) coefficients. Except for the Fourier directive 'set', all the rest of Fourier recycling directives are not valid for EDM procedure.

#### **2EOEC**

This directive enables to use (2Eobs-Ecalc) as Fourier coefficients in the Fourier step (if EDM procedure is applied).

#### **EOBS**

This directive enables to use the observed normalised structure factors (Eobs) as Fourier coefficient in the Fourier step (if EDM procedure is applied).

#### **FRAGMENT *string***

Used to supply a known fragment to be completed. String is the name of the file in which, for each atom, are stored: Element X, Y, Z, isotropic thermal factor.

#### **FWHM *D***

This directive is used in order to change the value of  $D$  that is the parameter for the condition  $2q_1 - 2q_2 < D \cdot \text{FWHM}$ .

Default value is approximately 0.9 depending on the ratio between the number of observations and the number of parameters to refine.

### **GRID $x$**

The grid on which the Fourier-map is evaluated will have a spacing of approximately  $x$  angstroms. The default spacing is computed by the program ( $1/3 \text{ \AA}$ ).

### **INTEGRATION $x n$**

$x$  is the radius of integration in the peak search routine. (Default value 0.5).  $n$  may be 1 to use the gaussian fitting of the fourier peak in the map or 2 to use the peak average density. (Default value 2).

### **LAYX**

This directive can be used only if MAP directive is given. The Fourier-map will be printed in section of constant  $x$ .

### **LAYY**

This directive can be used only if MAP directive is given. The Fourier-map will be printed in section of constant  $y$ .

### **LAYZ**

This directive can be used only if MAP directive is given. The Fourier-map will be printed in section of constant  $z$ .

### **LEVEL $n$**

All numerical values in the E-map greater than  $n$  will be underlined with \*\*\*\* in the lineprinter output to facilitate contouring.

The default is 100. The map is automatically scaled between  $\pm 999$  (approximately) at the grid points at which it is calculated.

Note, however, that it is printed between  $\pm 99$ . (This directive can be used only if associated to MAP directive).

### **LIMITS $x_1 x_2 x_3$**

The E-map will be printed from 0 to  $x_1$  along  $x$ , from 0 to  $x_2$  along  $y$ , from 0 to  $x_3$  along  $z$ . (This directive can be used only if associated to MAP directive).

### **MAP**

If MAP is specified, the E-map will be printed on the lineprinter. The printing of the E-map is rarely used.

The output is in sections of constant  $y$  with  $x$  across the page and  $z$  running down it on a grid of about three points per angstrom.

The maximum number of grid points across the page is 36 ( i.e. about 12 angstroms in

length). If more are needed, a new page is started.

### **PEAKS *n***

The number of peaks to be searched for in the map. The default is the number of peaks which

$$\text{a}(\text{occ}(i)*m) = 1.3 * n$$

where occ is the crystallographic site occupancy factor, m is the number of symmetry operators, n is the number of non-hydrogen atoms in the unit cell.

### **PSE**

To actively use PSI-E triplets in these procedures (Default doesn't use them). (This directive can be used only if associated to YPSIE directive of INVARIANTS routine).

### **RADIUS *E/x***

The value x of the radius used to compute the connectivity is assigned to element E.

### **RECYCLE *n***

Used to stop the recycling procedure after cycle number n. If n is equal to zero only the E-map will be calculated.

### **SET *n***

The serial number of the set from which to calculate the E-map. If 'SET n' is not specified, the set with the highest combined figure of merit will be used, and then if FOURIER routine is re-run, the set with the next highest combined FOM will be used.

### **SOGF *x***

The percentage of the largest |F| value reflections actively used in the Fourier recycling routine.

The reflections with the smallest |F| values corresponding to the rejected percentage have a zero weight value in the refinement process. (Default value 100.0).

### **SOGI *x***

The percentage of the most intense groups of overlapping reflections actively used in the Fourier recycling routine. (Default value 91.0).

### **STOPF *x***

This directive enables to stop the Fourier step at the cycle number x (if EDM procedure is applied). The default value of x is 10 (the maximum allowed value).

### **THRE *x***

x is the threshold for the E value of the reflections actively used in the Electron Density Modification step. The default value is 0.8.

### **THRM *x***

x is the fraction of the Fourier map points actively used in the Electron Density Modification step. The default value is 0.025.

### **THRW x**

x is the threshold of the Bessel weight of the reflections actively used in the Fourier step (if EDM procedure is applied). The default value is 0.5.

## **EXAMPLES**

### Example 1

Only the E-map corresponding to the set number 7 and the complete FOURIER/LEAST-SQUARES procedure for set number 10 are requested by the user. The binary file "vfi.bin" must exist.

```
%structure nbpo
```

```
%fourier
```

```
set 7
```

```
recyc 0
```

```
%fourier
```

```
set 10
```

```
%continue
```

## **Directives in label command**

Direct methods applied to powder diffraction data often provide electron density maps of which the quality is usually affected by systematic and/or random phase errors, by amplitude truncation effects in the series representation of the electron density, etc. The frequent incorrect labelling of the peaks can strongly affect the efficiency of the procedures used for crystal structure refinement. An algorithm has been introduced in EXPO aiming at using the crystal chemical information that is usually available *a priori* to improve the peak labelling (Altomare *et al.*, 2001)

**The following directives must be added after the command '%label' in the input file to activate some specific features.**

### **DLIGHT d tol**

d is the expected heavy atom to light atom distance;

tol is the tolerance around the ideal distances. Default value = 0.5.

The program uses only one value of 'd' for all types of light atoms.

### **DWEIGHT d tol**

d is the expected heavy atom to heavy atom distance;

tol defines the tolerance around the ideal distances. Default value = 0.5.

The program uses only one value of 'd' for all types of heavy atoms.

**LABEL *n1 El1 n2 El2***

*n* is the number of peaks to relabel using *El* element;

*El* is the atomic species to assign to the peaks.

Only two combination (*n*, *El*) can be used.

**COORD *xi***

*x* specifies the expected number of heavy atoms surrounding each *i*-th heavy atom (the coordination type) (*i* = 1,2).

**EXAMPLE**Example 1

Use of the label change procedure to relabel the peaks of an electron density map obtained by applying the FOURIER procedure. The binary file "vfi.bin" must exist.

```
% window
% structure vfi
% job VFI - Synchrotron data
% changelab
  label 3 al 3 p
  coord 4 4
  dwei 3.1 0.5
  dlig 1.9 0.5
% continue
```

**Directives in polyhedra command**

The following directives must be added after the command '%polyhedra' in the input file to activate some specific features of the polyhedra procedure

**MISSING *n1 n2 El tetrahedron (octahedron) d tol1 tol2***

*n1* and *n2* are the two order numbers (taken from an external file or from a Fourier map) of the cations between which the missing cation must be located;

*El* is the missing cation label tetrahedron (octahedron): the type of coordination of the missing cation. (The procedure can only handle octahedron and tetrahedron);

*d* is the expected cation-anion distance;

tol1, tol2 are the tolerance parameters for the distance and the tetrahedron (octahedron) angle respectively. Default values are 0.3.

### **OCTAHEDRON *El d tol1 tol2***

d is the expected octahedral coordination distance around the El element;  
tol1 and tol2 are the tolerance parameters for distances and angles respectively.

### **TETRAHEDRON *El d tol1 tol2***

d is the expected tetrahedral coordination distance around the El element;  
tol1 and tol2 are the tolerance parameters for the distances and angles respectively.

## **EXAMPLES**

### Example 1

The POLPO1 procedure is applied to locate the light atoms around each specified heavy atoms. The crox.fra file contains the cations coordinates.

The binary file 'crox.bin' must exist.

```
% window
%structure crox
%job CROX - home diffractometer data
%polyhedra
    fragment crox.fra
    octahedron 1 1.92 0.2 0.2
    tetrahedron 2 1.75 0.2 0.2
    tetrahedron 3 1.75 0.2 0.2
    tetrahedron 4 1.75 0.2 0.2
%continue
```

### Example 2

The POLPO2 procedure is applied to locate one or more missing cations and surrounding anions. The sapo.fra file contains the located cations coordinates.

The binary file 'sapo.bin' must exist.

```
% window
%structure sapo
%job SAPO - data from home diffractometer
%polyhedra
    fragment sapo.fra
    tetrahedron Si 1 1.6 0.2 0.2
    tetrahedron Si 2 1.6 0.2 0.2
    missing 1 2 Si tetrahedron 1.6 0.2 0.2
    missing 1 2 Si tetrahedron 1.6 0.2 0.2
%continue
```

## **Directives in Patterson command**

The following directives must be added after the command '%patterson' in the input file to activate some specific features of the patterson procedure.

### **E\*\*2 (or E\*E)**

Coefficients to be used in the Patterson synthesis. This is the default.

### **E\*F (or F\*E)**

Coefficients to be used in the Patterson synthesis.

### **F\*\*2 (or F\*F)**

Coefficients to be used in the Patterson synthesis.

### **INVERSE**

To activate the procedure of calculating the  $|F|$  values from an inverted suitably modified Patterson map to use as starting point for the Le Bail algorithm in the extraction routine.

**MAP, LAYX, LAYY, LAYZ, PEAKS, LIMIT, GRID:** See FOURIER directives.

### **NPAT *n***

The number of cycles of successive inversions of the Patterson map.( Default values: 6 for X-ray data, 5 for neutron data

### **References**

- Altomare A., Cascarano G., Giacovazzo C. & Viterbo D. (1991). *Acta Cryst.* **A47**, 744-748.
- Main P. (1978). *Acta Cryst.* **A34**, 31-38.
- Main P., Fiske S.J., Hull S.E., Lessinger L., Germain G., Declercq J.P. & Woolfson M.M. (1980) - *MULTAN80, a system of computer programs for the automatic solution of crystal structures from x-ray diffraction data* - Univ. of York, England.
- Ten Eick L.F. (1977). *Acta Cryst.* **A33**, 977-979.

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## Structure solution by Direct Space methods

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## **Direct Space algorithms in EXPO2014**

Direct space methods for crystal structure determination from powder diffraction data have become widely available and popular in recent years and have successfully been applied to solve the structures of organic, inorganic and organometallic materials. Different but similar procedures can be realized: grid search, Monte Carlo, Simulated Annealing (SA), parallel tempering, genetic algorithm. Each method involves the generation of a random sequence of trial structures starting from an appropriate 3D model



and moving it until a good match between the calculated and the observed pattern is found. The information about chemical knowledge of molecules is actively used to reduce the number of parameters to be varied: bond distances and angles are usually known and kept fixed while only the torsion angles are varied during the procedure.

Two Direct Space algorithms are now available in the EXPO2014 program, for crystal structure solution.

They are:

- 1) a classical Simulated Annealing (SA) approach;
- 2) the Hybrid Big Bang Big Crunch (HBB-BC) algorithm (Altomare *et al.*, 2013). It results from an appropriate combination of BB-BC approach with SA and relies on one of the evolutionary theory of the universe consisting of two successive phases: 1) the Big Bang, corresponding to an energy dissipation procedure for creating a completely random initial population; 2) the Big Crunch, corresponding to a contraction procedure for converging to a global optimum point.

The procedure is supported by the same graphic interface of Simulated Annealing and is automatically applied by the program for compounds described by less than 6 internal degrees of freedom (torsion angles) and constituted by less than 3 fragments. In all other cases the classical SA approach is used.

[Preparing Input file](#)

[Graphic Interface of Simulated Annealing](#)

[Output file](#)

[When Direct Space approach fails](#)

[The directives in Simulated Annealing](#)


[Contact and References](#)

### Preparing Input file

To run EXPO2014 for structure solution by Direct Space approaches, first you need to create the input file. It is supposed that the cell parameters and the space group have been determined before so, fill the frame 'Cell Parameters' and 'Space Group'. Activate the check button 'Structure Solution', select 'Simulated Annealing' and import the starting model from 'fragment filename'. The following picture is an example for the crystal structure determination of the paracetamol molecule. The profile counts file (paracetamol.xy) is in the directory 'examples'.

**New Project: paracetamol**

Structure Name:

Profile Counts filename:  


**Range**

☐ Modify range    2theta min:     2theta max:

**Source**

☒ X rays    ☐ Neutron    ☐ Synchrotron    Wavelength:     ☐ K Alpha2 Correction

**Space Group**

☐ Find Space Group    Space Group Symbol:  

**Cell Parameters**

☐ Cell Determination by N-TREOR

a:     b:     c:      $\alpha$ :      $\beta$ :      $\gamma$ :


Volume:

Cell Content:

Content Volume:    Volume per Atom:

**Structure Solution**

☐ Direct Methods    ☒ Simulated Annealing

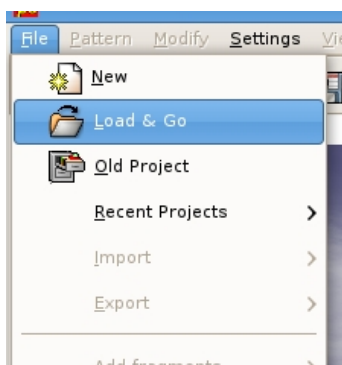
Fragment filename:  

When you press the button 'Save' an input file paracetamol.exp (shown below) will be created and automatically loaded by the program for the structure solution process by Simulated Annealing.

```
%Structure paracetamol
%Initialize
%Job paracetamol
%Data
    Cell 7.100 9.380 11.708 90.0 97.42 90.0
    SpaceGroup p 21/n
    Pattern paracetamol.xy
    Wavelength 1.54056
%fragment paracetamol.mol
%sannel
```

Otherwise you can import an existing input file by the button 'Open' on the 'New Project' dialog window or selecting 'File' > 'Load & GO' in the main menu. For example you could load the file paracetamol.exp already existing in the example folder.



%sannel is a command to access to the Simulated Annealing graphic interface.

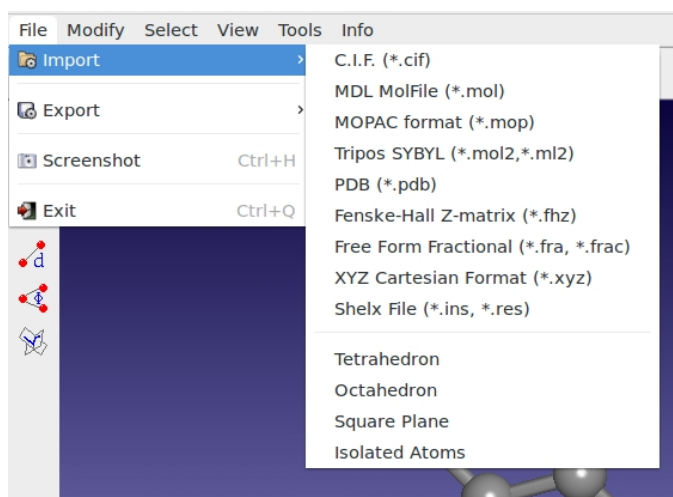
"%fragment paracetamol.mol" is the command to import the starting structural model

for Simulated Annealing in [MDL Molfile](#) format (\*.mol). This command can be repeated several times to import more than one fragment. Some other file types can be imported in the same way: MOPAC file (\*.mop), Tripos Sybyl file (\*.mol2, \*.ml2), [C.I.F.](#) file (\*.cif), Protein Data Bank file (\*.pdb), Fenske-Hall Z-matrix (\*.zmt), EXPO fragment or Free Fractional Format (\*.frac), XYZ format (\*.xyz), Tripos SYBYL (\*.mol2, \*.ml2), Shelx File (\*.ins).

Refer to [openbabel](#) wiki or <http://www.ch.ic.ac.uk/chemime> for informations about common molecular file formats.

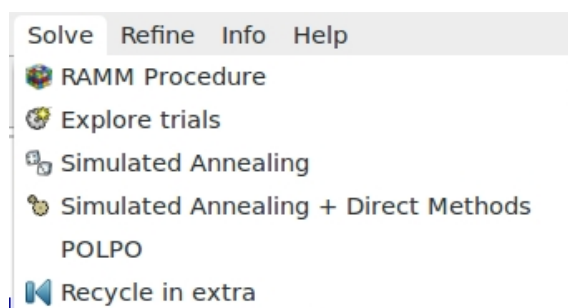
Refer to [http://en.wikipedia.org/wiki/Molecule\\_editor](http://en.wikipedia.org/wiki/Molecule_editor) and [http://www.ccp14.ac.uk/solution/2d\\_3d\\_model\\_builders/index.html](http://www.ccp14.ac.uk/solution/2d_3d_model_builders/index.html) for an exhaustive list of programs for building 3D starting models. Suggested free available programs for building 3D models are [ACD/ChemSketch](#) (Windows), [Avogadro](#) (all platforms), [Marvin](#) (all platforms), [Gchemical](#) (Linux). [NIST Chemistry WebBook](#) and [Drugbank](#) are useful links to look up fragments.

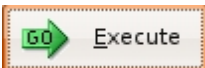
Instead of command "%fragment *name\_starting\_model.ext*", with ext=mol, frac, cif etc, you can import the starting structural model directly from the graphic interface from menu 'File'>'Import'.



'Modify'>'Add fragments' to add fragment to an existing partial structural model.

Instead of command %sannel, you can access directly to the graphic interface from menu "Solve" > "Simulated Annealing".



Press the button  in the dialog window to run the Simulated Annealing procedure.

## Graphic Interface of Simulated Annealing

The dialog window of Direct Space algorithms in EXPO2014 is composed by 4 pages.

The first page contains the general settings of:

Simulated Annealing algorithm:

The screenshot shows the 'Global optimization dialog' window with the 'SA conditions' tab selected. The 'General conditions' section includes:
 

- Cost function: R weighted profile (dropdown)
- Resolution: 2.000 (spinbox) | N. of reflections: 103 | 2thmax: 45.305
- Random seed: 1 (spinbox)
- Nr. of runs: 10 (spinbox)

 The 'Simulated annealing options' section includes:
 

- Starting temperature: 10.000 (spinbox) | ☒ automatic
- Number of moves: 60 (spinbox) | ☒ automatic
- Temperature reduction factor: 0.900 (spinbox)

 At the bottom, it shows 'Number of refined parameters: 8', a 'Solutions' button with a star icon, and 'Help', 'Quit', and 'Execute' buttons.

or *HBB-BC* algorithm:

The screenshot shows the 'Global optimization dialog' window with the 'SA conditions' tab selected. The 'General conditions' section is identical to the previous window. The 'Global optimization conditions' section includes:
 

- Number of cycles: 20 (spinbox) | ☒ automatic

 The bottom section is also identical, showing 'Number of refined parameters: 8', a 'Solutions' button, and 'Help', 'Quit', and 'Execute' buttons.

**Cost function:** 2 cost functions can be selected: R weighted profile (default cost function), R-Bragg intensities.

**Resolution:** defines the maximum resolution used by Simulated Annealing procedure.

**Random seed:** selects the value determining the sequence of random numbers used from the algorithm. When is set to 0 the random seed will be calculated by the system clock.

**Nr. of runs:** select the number of Simulated Annealing runs. At the beginning of each run a new value of random seed is calculated.

**Starting temperature:** selects the starting temperature. Check on 'automatic' and the program automatically will find the starting temperature at the beginning of the procedure.

**Number of moves:** the number of moves for each step of temperature is  $N_p \cdot N \cdot 20$  where  $N_p$  is the number of refined parameters and  $N$  is a number set by the user in the entry box.

Choosing 'automatic' the program automatically will determine the value of  $N$  by taking into account the external and internal DOFs and the flexibility of the molecule.

**Temperature reduction factor:** the reduction factor applied to the temperature at each step in the annealing schedule. The default value is 0.90. Increasing this value, the chance to find the global minimum can be improved even if a longer execution time will be taken by the procedure.

**Solutions:** browse the best solutions saved at the end of each run.

The second page **External DOF** contains information about the external degrees of freedom (DOFs):

	Refine	Lower	Upper
X Translation	<input checked="" type="checkbox"/>	0.000	1.000
Y Translation	<input checked="" type="checkbox"/>	0.000	1.000
Z Translation	<input checked="" type="checkbox"/>	0.000	1.000
Rotation	<input checked="" type="checkbox"/>	0.000	1.000

**Select fragment:** selects the fragment and visualizes the corresponding structure information.

**Atoms:** list of the atoms in the selected fragment.

**Parameter for fragment:** list of the external DOFs for the selected fragment. Check the parameters to refine, enter the lower and upper bounds of the parameters.

The third page **Internal DOF** contains information about the internal degrees of freedom (DOFs):

**Global optimization dialog**

SA conditions External DOF **Internal DOF** Pattern

Internal DOFs

Torsion	Refine	Value	Lower	Upper
C3:C2:N1:C7	<input checked="" type="checkbox"/>	0.00	-180.00	180.00
C2:N1:C7:C8	<input checked="" type="checkbox"/>	-59.43	-180.00	180.00

☐ Dynamical Occupancy Correction Atomic Parameters

Number of refined parameters: 8 Solutions

Help Quit Execute

**Internal DOFs:** list of the torsions associated to each refinable internal DOF. Check the parameters to refine, enter the lower and upper bounds of parameters.

**Dynamical Occupancy Correction:** automatic detection of atoms in special position and atoms that share the same position. If this option is not active all refined atoms are considered in general position (default).

Press the button '**Atomic parameters**' to access to the following dialog window:

**Atomic parameters refinement**

Atom	x	y	z	B[iso]	
O1	-0.481837	0.048326	0.914179	<input type="checkbox"/>	<input type="checkbox"/>
C1	-0.281583	0.049542	0.928819	<input type="checkbox"/>	<input type="checkbox"/>
C2	0.112122	0.051940	0.959652	<input type="checkbox"/>	<input type="checkbox"/>
C3	0.015070	-0.076620	0.952052	<input type="checkbox"/>	<input type="checkbox"/>
C4	0.012315	0.179307	0.951836	<input type="checkbox"/>	<input type="checkbox"/>
N1	0.317490	0.053188	0.974668	<input type="checkbox"/>	<input type="checkbox"/>
C5	-0.181775	-0.077814	0.936636	<input type="checkbox"/>	<input type="checkbox"/>
C6	-0.184545	0.178102	0.936419	<input type="checkbox"/>	<input type="checkbox"/>
C7	0.421601	-0.079680	0.981754	<input type="checkbox"/>	<input type="checkbox"/>

Maximum shift on position 0.001

Cancel OK

**X Y Z:** check the buttons on column 'X Y Z' to refine the atom positions, in this case the fragment is not rigid but the atom positions are shifted respect to the barycentre. Click on label 'X Y Z' to select all checks in the column. The positions refinement (x,y,z) is generally discouraged because can considerably increase the time to reach the global minimum.


**Thermal parameters:** check the buttons on column 'B[iso]' to refine the thermal parameters of atoms. Click on label 'B[iso]' to select all checks in the column. If the

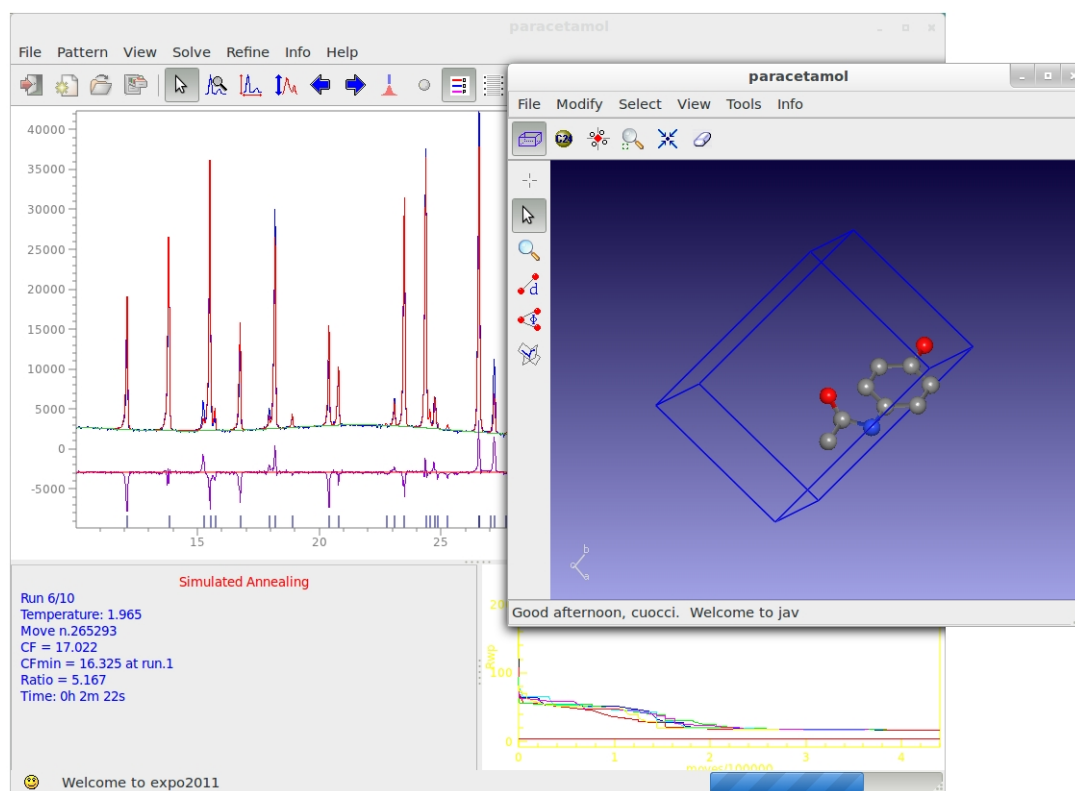
thermal parameters are not indicated in the imported fragment file, the program assigns the default values of  $B=3.0$  for non-hydrogen atoms and  $B=6.0$  for hydrogen atoms. These default values can be changed editing the new values in the column. The refinement of the thermal parameters is discouraged because usually doesn't improve the results.

**Maximum shift on position:** enter the value of the maximum shift of the atomic positions. 0.020 is the suggested value. Increasing this value the explored parameter space becomes wider so increasing the probability of falling into a local minimum.

**Pattern:** Enter the direction of the preferred orientation and check 'G Factor'. The *March-Dollase* correction will be applied and the magnitude of the preferred orientation will be optimized.

A visual match between observed and calculated powder pattern is plotted when Simulated Annealing is running, the progress of structure solution is monitored and the user can examine:

- 1) the graph of the minimum values of the cost function (CF) vs. the number of moves;
- 3) the crystal packing by using the button  on the JAV viewer.



During the Direct Space runs, three buttons are active on the toolbar of the main window:



opens the JAV viewer for crystal structure visualization.



skips the current run.



stops the procedure.

### Output file

The output file generated from the procedure, contains information on:

- 1) the starting structure
- 2) the volume per atom

- 2) the connectivity
- 3) the internal and external DOFs
- 4) the refined parameters by SA
- 5) each SA or *HBB-BC* run
- 6) the summary of all the SA or *HBB-BC* runs
- 7) the selected final structure

At the end of each run the structure coordinates are saved in CIF file with name created by project name with suffix `_best1`, `_best2`, ... (e.g. `paracetamol_best1.cif` is the best solution, `paracetamol_best2.cif` is the second best solution, etc.). The order number in the name represents the position in the list of structures ordered according to the cost function.

### When Direct Space approach fails

When Direct Space approaches fail:

- 1) The quality of data is not good and the diffraction pattern is not suitable for the extraction of integrated intensities. In this case can be convenient to perform the optimization by using the cost function *R* weighted profile.
- 2) The starting model is incorrect: bond distances and angles are not entirely accurate, the number of building blocks is wrong. Improve your model with Cambridge Structural Database (CSD) or building packages (Avogadro, ChemSketch, ChemDraw, ...), check for atom in the output file (about 15-20 Å/atom).
- 3) The assumption about thermal factors is invalid. Check thermal factors from similar structures.
- 4) Space group and cell parameters are not correct. Additionally, in many cases it may be necessary to carry out a series of independent calculations to test different potential space groups and/or unit cell choices.
- 5) The default conditions, for complex structure, cannot be appropriate. Increase the number of moves and/or runs, try with slower temperature reduction.

### The directives in Simulated Annealing

Usually you don't need to read this paragraph unless you are interested to run Simulated Annealing without interaction with graphic interface. In this case use the command `%sannel` to run Simulated Annealing from the input file (\*.exp). Use command `%automatic` to skip the interaction with the graphical interface and the program will perform the Simulated Annealing using the default values. An example of input file with command `%automatic` and `%sannel` is the following:

```
%automatic
%Structure paracetamol
%Initialize
%Job paracetamol
%Data
    Cell    7.100   9.380   11.708   90.0   97.42   90.0
    SpaceGroup p 21/n
    Pattern  paracetamol.xy
    Wavelength 1.54056
%fragment paracetamol.mol
```



```
%sannel
%continue
```

To modify the default values of SA, some directives can be used after the command %sannel.

An example of application of directive **NRUN**

```
%automatic
%Structure paracetamol
%Initialize
%Job paracetamol
%Data
    Cell 7.100 9.380 11.708 90.0 97.42 90.0
    SpaceGroup p 21/n
    Pattern paracetamol.xy
    Wavelength 1.54056
%fragment paracetamol.mol
%sannel
    nrun 20
%continue
```

**The following directives must be added after the command %sannel in the input file to activate some specific features of the Simulated Annealing procedure**

Abbreviations for directives name at least 4 character are permissible, i.e. "cost 2" instead of "cost\_function 2".

**nrnrun n**

To modify the number of Simulated Annealing runs. The default is 10.

**niter n**

To modify the number of moves for each temperature step. In a default run the number of moves is automatically calculated.

**resmax val**

To define the maximum resolution used by Simulated Annealing. The default value is 2.0 Å.

**temper temp**

To modify the initial temperature. In a default run the initial temperature is automatically calculated.

**tfactor val**

Determines the temperature reduction factor. val ranges between 0 and 1 and its default value is 0.90.

**rotate Ax1 Ax2 At1 At2 At3 ...**

or

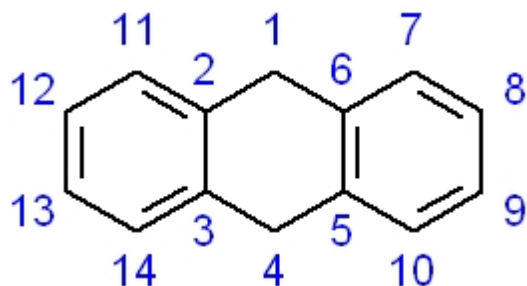
**rotate Ax1 Ax2 At1 At2 At3 ... theta**

Rotate atoms At1, At2, At3, ... around a rotation axis defined by atoms Ax1 and Ax2.

**theta** is an optional value (degrees) used to specify the limits of rotation angle from -theta to +theta.

When rotate directive is used the specified rotation will be included in the panel 'Internal DOF' of the graphical interface.

E.g.



```
rotate C1 C4 C5 C6 C7 C8 C9 C10
```

the phenyl ring C5-C6-C7-C8-C9-C10 will be rigidly rotated around the axis C1-C4

#### bump

Automatic generation of anti-bumping restraints extended to all C, N, O and S atoms

```
res atom1 atom2 target_dist tol weight
```

Apply restraints between 2 atoms. atom1 and atom2 are the labels of atoms. The other parameters are optional and can be omitted.

target\_dist is the ideal distance between the pair of atoms, when omitted the distance is automatically deduced by using an internal table of distances.

tol is a permitted tolerance, when omitted the default value is 0.2

weight is a user supplied weight. A default weight is specified as 100.

```
fixrotation atom1 atom2
```

To fix the internal DOF. atom1 and atom2 are the 2 atoms defining the rotation axis. This directive is useful when, relying on the prior chemical knowledge of the structure, some internal DOFs, can be fixed. For example, double bonds in conjugated acyclic systems, triple bonds, nitrilic triple bonds, etc.

```
fftranslation atom1 atom2 ....
```

To fix the translation of fragments containing atom1, atom2, ... It is enough to specify at least one of atom belonging to the molecular fragment.

E.g.

```
fftranslation Ag1 Ag2
```

If Ag1 and Ag2 are in 2 different fragment, the translation of fragment containing Ag1 will be fixed and the translation of other one will be fixed.

```
ffrotation atom1 atom2 ...
```

To fix the rotation of fragments containing atom1, atom2, ... It is enough to specify at least one of atom belonging to the molecular fragment.

```
refinetf
```

To refine the thermal parameters.

```
shift_atom val
```

or

**shift\_atom** atom1 atom2 atom3 ... val

To optimize the atomic parameters by applying shifts (up to val) on the atoms with respect to the centre of gravity of the fragment. The default val is 0.5. Add atom1, atom2, atom3, ... to refine only some specific atoms.

**cost\_function** n

To choose the cost function: 1 for Rw-profile, 2 for RF, 3 for RI. The default choice is 1.

**randomize** n

To randomize the internal and external DOFs and the atomic parameters (if refined). n is an optional parameters used as seed of random generator.

**rotat** n1 n2

To specify the internal DOF using the input file.

**doc**

Activate the dynamical occupancy correction

**po** H K L

Activate the *March-Dollase* preferred orientation correction. H K L are three integer numbers necessary to specify the direction of the preferred orientation

### Contact

For suggestions and bugs contact [corrado.cuocci@ic.cnr.it](mailto:corrado.cuocci@ic.cnr.it).

### References

Altomare, A., Corriero, N., Cuocci, C., Moliterni, A., Rizzi, R. (2013). *J. Appl. Cryst.*, **46**, 779-787.

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## Direct Methods combined with Simulated Annealing

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# Direct Methods combined with Simulated Annealing in the EXPO2014 program

The information contained in the electron density maps provided by Direct Methods has been combined with the Simulated Annealing technique in order to solve organic crystal structures from powder diffraction data. In this procedure each peak of the Fourier map is in turn associated to all the atoms of the imported model (Altomare *et al.*, 2008). For each association (the atom of the structural model is moved on the peak) the position of the model is fixed, while its orientation and internal conformation have to be found by SA runs.

[Run of Direct Methods combined with Simulated Annealing](#)

[Graphic Interface of Direct Methods combined with Simulated Annealing](#)

[Output of Direct Methods combined with Simulated Annealing](#)

[The Directives in Direct Methods combined with Simulated Annealing](#)

[About the construction of the models](#)

[Contact and References](#)

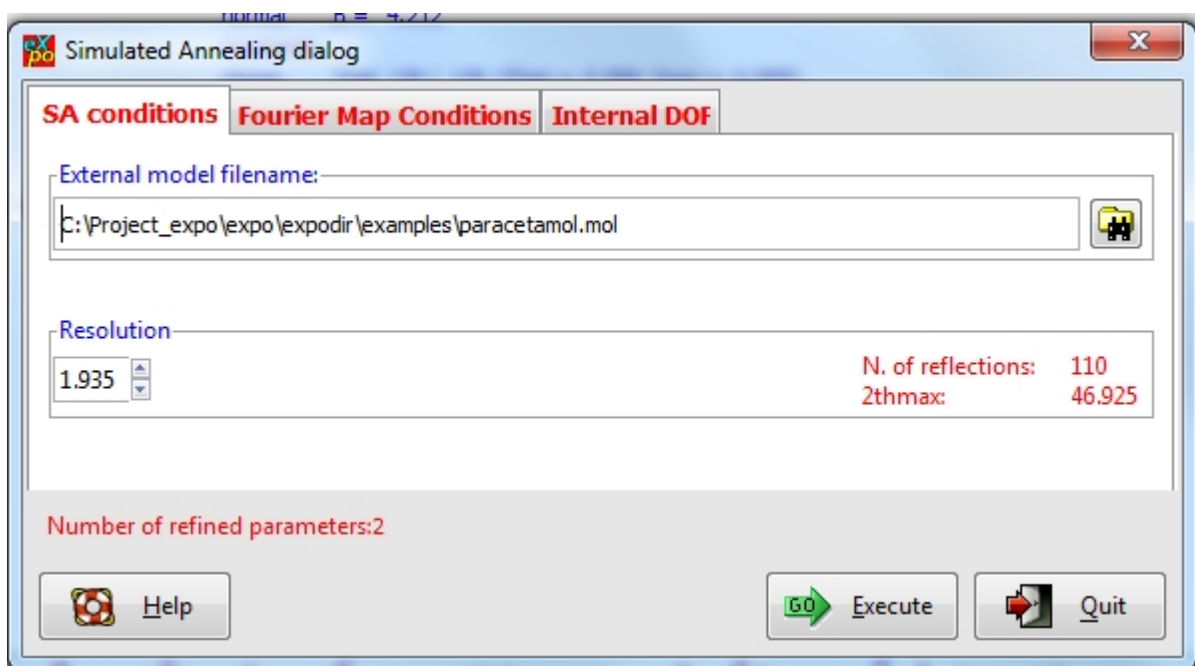
### Run of Direct Methods combined with Simulated Annealing

After a run of EXPO2014, the procedure can be graphically activated by 'Simulated Annealing+Direct Methods' option of 'Solve' button in the upper menu of the EXPO2014 window.

### Graphic Interface of Direct Methods combined with Simulated Annealing

The dialog window of Direct Methods combined with Simulated Annealing procedure in EXPO2014 is composed by 3 pages containing the general settings of the procedure.

The first page '**SA conditions**' contains the general settings of the algorithm:



**External model filename:** the name of the imported starting structural model must be specified. Some file types can be imported: C.I.F. file (\*.cif), Expo fragment or Free Fractional Format (\*.fra), XYZ format (\*.xyz), MOPAC file (\*.mop), MDL MolFile (\*.mol), Protein Data Bank file (\*.pdb), Tripos SYBYL (\*.mol2, \*.ml2), Fenske-Hall Z-Matrix (\*.zmt)

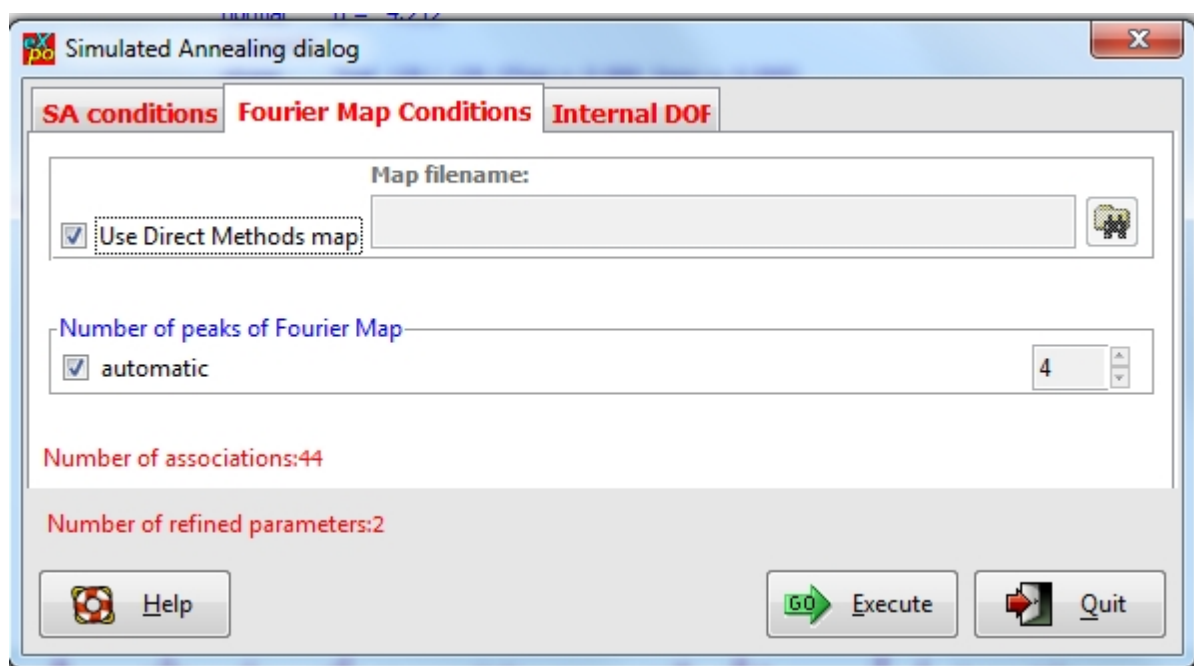
and Shelx File (\*.ins).

Refer to [openbabel](http://openbabel.org/wiki/Molecular_file_formats) wiki or <http://www.ch.ic.ac.uk/chemime> for informations about common molecular file formats.

Refer to [http://en.wikipedia.org/wiki/Molecule\\_editor](http://en.wikipedia.org/wiki/Molecule_editor) and [http://www.ccp14.ac.uk/solution/2d\\_3d\\_model\\_builders/index.html](http://www.ccp14.ac.uk/solution/2d_3d_model_builders/index.html) for an exhaustive list of programs for building 3D starting models. Suggested free available programs for building 3D models are [ACD/ChemSketch](#) (Windows), [Avogadro](#) (all platforms), [Marvin](#) (all platforms), [Ghemical](#) (Linux). [NIST Chemistry WebBook](#) and [Drugbank](#) are useful links to look up fragments.

**Resolution:** defines the maximum resolution used by Simulated Annealing + Direct Methods procedure.

The second page '**Fourier map condition**' contains the information about the Fourier map at which the imported starting model will be associated:



**Use Direct Methods map:** if selected, the program will use the atomic positions of the Fourier map obtained at the end of the current run of EXPO2014.

**Map filename:** it is activated only if 'Use Direct Methods map' is de-selected. The filename of the external Fourier map (in term of atomic positions) must be supply. Some file types can be imported: C.I.F. file (\*.cif), Expo fragment or Free Fractional Format (\*.fra), etc.

**Number of peaks of Fourier Map:** the number of atomic positions selected from the map. If 'automatic' is selected, the program will use the 40% of the electron density peaks (those with the largest intensity) to associate in turn to each model atom. This number can

be reduced by the user if 'automatic' is de-selected.

The third page '**Internal DOF**' contains the information about the internal degrees of freedom (DOFs):

**Torsion**: List of torsions associated to each refinable internal DOF. The order number of each atom involved in the torsion angle to vary are also shown. The internal DOFs can be or not refined (check Refine).


**Lower-Upper**: range of variation of the torsion angle. 180 means that the allowed range is  $(x-180, x+180)$ , where  $x$  is the value of the torsion angle in the initial model.

A visual match between the observed and calculated powder diffraction pattern is plotted when the procedure is running. When Direct Methods combined with Simulated Annealing procedure are running the progress of structure solution is monitored and the user can examine:

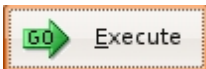
- 1) the graph of the minimum value of the cost function (CF) vs. the number of moves;
- 2) the match between the observed and calculated pattern.

Use the buttons  to zoom on graph.

During the Direct Methods combined with Simulated Annealing procedure runs two buttons on the toolbar are activated:

 opens the JAV viewer for crystal structure visualization.

 stops the procedure.

Press the button  to run the Simulated Annealing+Direct Methods procedure.

### Output of Direct Methods combined with Simulated Annealing

The output file contains information on:

- 1) the selected peaks of the Fourier Map imported or obtained at the end of a run of EXPO2014;
- 2) the imported starting structural model;
- 3) the table of connectivity;
- 4) the list of internal degree of freedoms (DOFs) to be varied;
- 6) the information about each association: peak of the map-atom of the model;
- 7) the summary of the ten best associations which are refined in sequence;

8) the selected best final structure.

### About the construction of the models

Refer to [openbabel](http://openbabel.org/wiki/Main_Page) wiki or <http://www.ch.ic.ac.uk/chemime> for information about common molecular file formats.

Refer to [http://en.wikipedia.org/wiki/Molecule\\_editor](http://en.wikipedia.org/wiki/Molecule_editor) and [http://www.ccp14.ac.uk/solution/2d\\_3d\\_model\\_builders/index.html](http://www.ccp14.ac.uk/solution/2d_3d_model_builders/index.html) for an exhaustive list of programs for building 3d molecules. Suggested free available programs for building 3D molecules are [ACD/ChemSketch](http://www.acd/chemsketch/) (windows), [Avogadro](http://www.avogadro.cc/) (linux), [Marvin](http://www.marvin.biochem.ucl.ac.uk/) (all platforms), [Ghemical](http://www.chemical.scripps.edu/) (linux) [NIST Chemistry webbook](http://www.nist.gov/) and [Drugbank](http://www.drugbank.ca/).

### Contact

For suggestions and bugs please contact [rosanna.rizzi@ic.cnr.it](mailto:rosanna.rizzi@ic.cnr.it).

### References

A. Altomare, R. Caliendo, C. Cuocci, C. Giacovazzo, A. G. G. Moliterni, R. Rizzi and C. Platteau. 'Direct methods and simulated annealing: a hybrid approach for powder diffraction data'. *J. Appl. Cryst.* (2008). **41**, 56-61.

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## Rietveld Refinement

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### Rietveld Refinement in EXPO2014

Structure refinement by Rietveld method (Rietveld, 1969) is available in EXPO2014. Graphical and computing tools are available in the program in order to attain a successful automatic or user-defined Rietveld refinement.

The refined variables include peak shape parameters, unit cell dimensions, coordinates of atoms in the structure model, background coefficients, scale factor, isotropic displacement parameters. Atomic displacement parameters can be refined individually or in a group of atoms with the same atomic type or the same environment. Correction for the preferred orientation can be achieved by the March-Dollase approach. The background is described using empirical functions: classical polynomial function, Chebyshev polynomial function, cosine Fourier series. The background can also modeled by mouse-click selection of pattern points. The available peak shape functions are: Pseudo-Voigt, Pearson VII, Thompson-Cox-Hastings pseudo-Voigt.

The non-linear least squares are carried out by employing the damped Gauss-Newton

method. The refinement convergence condition is reached when the increments on parameters become smaller with respect to their standard deviations or when the relative gradient of  $\chi^2$  minimized function is less than a tolerance value. Tolerance value and the maximum number of cycles could be suitably modified by the user.

The Le Bail technique can be adopted to perform a full pattern decomposition prior to Rietveld refinement in order to determine starting values of parameters (background, peak shape, zero shift and unit cell dimensions) to refine. This strategy is suggested especially if the available structure model is not completed (McCusker *et al.*, 1999) or when the starting model is too different from the target model.

The refinement can be carried out by following two alternative approaches: 1) the user can decide the refinement strategy *via* graphic interface; 2) an automatic refinement schedule can be applied. In the automatic mode, groups of parameters are refined according to a fixed sequence as established in the Rietveld guidelines (Young, 1995). In the last step of refinement all parameters are refined simultaneously.

The knowledge of molecular geometry can be exploited in the refinement in form of restraints on bond distances, angles and planes. To simplify the setting of restraints, the program is able to extract from the connectivity of the initial model the possible restraints providing a list of current and target values. The user can select the restraints to be included in the refinement procedure and eventually modify the target value.

Some figures of merit are available in order to follow the progress and evaluate the quality of refinement: the weighted profile R-factor and the unweighted profile R-factor calculated for the full pattern ( $R_{wp}$ ,  $R_p$ ); the corresponding figures background-subtracted ( $R'_{wp}$ ,  $R'_p$ ); the statistically expected R value ( $R_{exp}$ ); the goodness-of-fit ( $R_{wp}/R_{exp}$ ); the Durbin-Watson  $d$ -statistic. R values similar to those used in case of single crystal data are also available:  $R_F$  and the Bragg-intensity R ( $R_b$ ) which use the structure factor moduli extracted from the experimental profile. In addition, graphical tools are available for visualizing: 1) the observed, calculated and difference pattern and the cumulative  $\chi^2$  value; 2) the evolution of the structure model during the refinement in real time.

$$R_p = \frac{\sum_i^N |y_i - y_{ci}|}{\sum_i^N y_i}$$

$$R_{pw} = \left[ \frac{\sum_i^N w_i (y_i - y_{ci})^2}{\sum_i^N w_i y_i^2} \right]^{1/2}$$

$$R'_p = \frac{\sum_i^N |y_i - y_{ci}|}{\sum_i^N (y_i - y_{bi})}$$

$$R'_{pw} = \left[ \frac{\sum_i^N w_i (y_i - y_{ci})^2}{\sum_i^N w_i (y_i - y_{bi})^2} \right]^{1/2}$$



$$R_p = \frac{\sum_i^{N_p} |y_i - y_{ci}|}{\sum_i^{N_p} (y_i - y_{bi})}$$

$$R_{pw} = \left[ \frac{\sum_i^{N_p} w_i (y_i - y_{ci})^2}{\sum_i^{N_p} w_i (y_i - y_{bi})^2} \right]^{1/2}$$

$$R_{\text{exp}} = \left[ \frac{(N - P)}{\sum_i^N w_i y_i^2} \right]^{1/2}$$

$$R'_{\text{exp}} = \left[ \frac{(N - P)}{\sum_i^N w_i (y_i - y_{bi})^2} \right]^{1/2}$$

where:

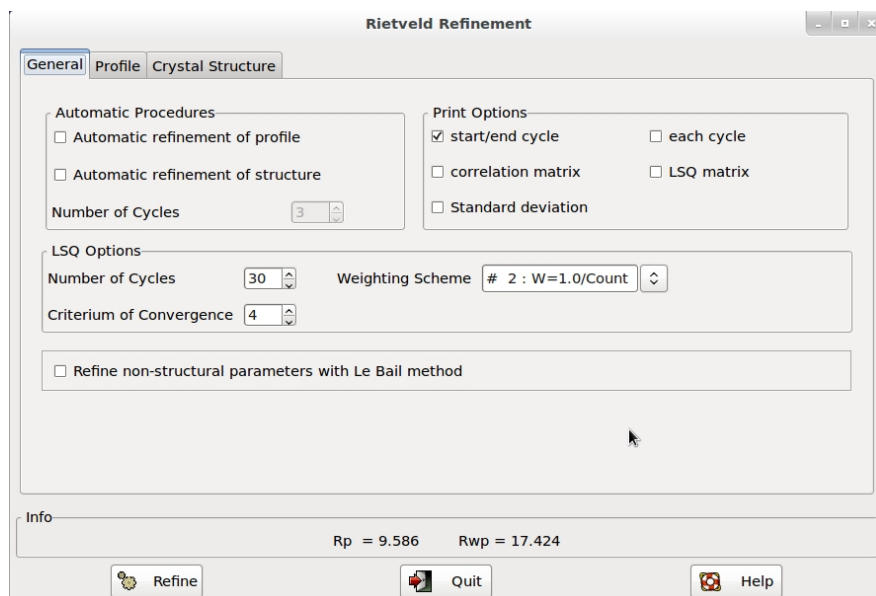
N is the total number of counts in the pattern and P is the number of refined parameters.

### Preparing Input file for Rietveld Refinement

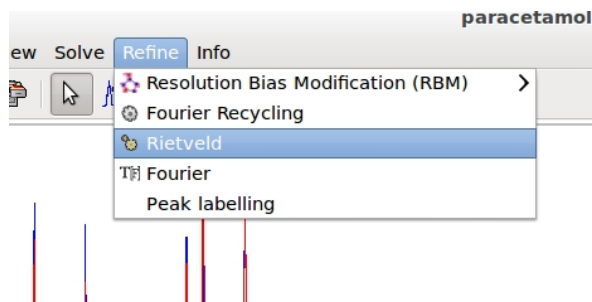
To run EXPO2014 for Rietveld refinement, first you need to create the input file. This is an example of the typical input file:

```
%Structure paracetamol
%Initialize
%Job paracetamol
%Data
    Cell 7.100 9.380 11.708 90.0 97.42 90.0
    SpaceGroup p 21/n
    Pattern paracetamol.xy
    Wavelength 1.54056
%fragment paracetamol.cif
%rietveld
```

It is supposed that the cell parameters and the space group have been determined before and a structure model is available and imported by using the command `%fragment` followed by the file name containing the structure. `%rietveld` is a command to access to the Rietveld Refinement graphical interface.



Alternatively, when a structure model is available, you can access directly to the graphic interface from menu "Refine" > "Rietveld"



## Contact

For suggestions and bugs contact:

[angela.altomare@ic.cnr.it](mailto:angela.altomare@ic.cnr.it)

[annagrazia.moliterni@ic.cnr.it](mailto:annagrazia.moliterni@ic.cnr.it)

[rosanna.rizzi@ic.cnr.it](mailto:rosanna.rizzi@ic.cnr.it)

[corrado.cuocci@ic.cnr.it](mailto:corrado.cuocci@ic.cnr.it)

## References

Rietveld, H.M.: A profile refinement method for nuclear and magnetic structures. *J. Appl. Cryst.* **2** (1969) 65–71.

McCusker, L.B.; Von Dreele, R.B.; Cox, D.E.; Louër, D.; Scardi, P.: Rietveld refinement guidelines. *J. Appl. Cryst.* (1999). **32**, 36-50

The Rietveld Method. Edited by R. A. Young, Oxford University Press, Oxford (1995)

## Commands of EXPO2014 and their use

The input file name for EXPO2014 is constituted by the name of the structure to analyze followed by the suffix **.exp**, i.e.

***name.exp***

The input consists of a sequence of commands, directives and comments. The commands are headed by '%' character and directives must follow the related command.

For the default run see [Example 1](#).

EXPO recognizes the following commands:

%WINDOW	Graphic window is required
%NOWINDOW	Graphic window is suppressed
%STRUCTURE string	This command is used to specify the name of the structure to investigate. The program creates the name of the files adding the appropriate extension to the structure name. The file names are: string.bin -> binary file string.out -> output file If this command is not used the default string "STRUCT" (instead of the name of the structure) is used to create file names
%JOB caption	A caption is printed in the output
%INITIALIZE	Initialize the direct access file (to override previous results and data)
<a href="#">%DATA</a>	Data input routine
<a href="#">%NTREOR</a>	Indexing routine
<a href="#">%EXTRACTION</a>	Integrated intensities extraction routine
<a href="#">%NORMAL</a>	Normalization routine
<a href="#">%INVARIANTS</a>	Invariants routine
<a href="#">%PHASE</a>	Converge-tangent routine
<a href="#">%FOURIER</a>	Fourier/Least-Squares routine
%MENU	
%END	End of the input file
%CONTINUE	The program runs in default conditions from the last given command up to the end
<a href="#">%PATTERSON</a>	Patterson map calculation routine
%REFINE	Fourier/Least-Squares restart routine
%RECYCLE	Extraction recycle routine
<a href="#">%SANNEL</a>	direct space routines
<a href="#">%SDIRECT</a>	Direct Methods combined with direct space routine
<a href="#">%EXPORT filename.xxx</a>	Export files (xxx=hkl,cif,xyz,frac)

Directives are described below, in the sections dedicated to the various routines. All commands and directives are in free format (between columns 1-80) and are cases independent. Only the first four characters are significant. The keywords can start in any position. If the first non-blank character is ">", then the record is interpreted as a comment. EXPO2014 preserves intermediate results in the file named ***name.bin*** (*binary file or project file*). For example, if invariant estimates have been already obtained during a previous run of EXPO2014, in a new run the command %INVARIANTS can be omitted.

Commands can be given in any order, under the following conditions:

- first routine used must be DATA, if it has not been used in a previous run;
- EXTRACTION routine must be used to extract integrated intensities from the diffraction pattern, if a reflections file is not supplied by the user;
- NORMAL must be used if reflections file has been supplied or EXTRACTION step has been performed;
- INVARIANT routine has no meaning if diffraction moduli are not normalized;
- PHASE routine has no meaning if no triplets have been calculated;
- FOURIER routine cannot run before PHASE routine (unless a fragment information is supplied by the user; in this case only DATA, EXTRACTION and FOURIER commands are needed).

The minimal information needed by EXPO2014 for a full run (from indexing to structure solution) is constituted by (see Example 1):

- cell parameters (not necessary if N-TREOR program is used)
- space group symbol (not necessary if the Space Group Determination procedure is applied by using "findspace" directive)
- cell content
- diffraction pattern (or reflections if an external reflection file is provided by any profile fitting program)
- wavelength
- type of radiation (if neutron or synchrotron data have been used; home diffractometer data is the default).

EXPO2014 prints results in a file named ***name.out***.

Add '%EXPORT filename.xxx' in the input file to export files. Filename is the name of file to export and xxx define the type of file. Use xxx=cif, xyz, frac to export structure model respectively in cif file, xyz cartesian coordinates, fractional coordinates; use xxx=hkl to export file with hkl, extracted structure factors, calculated structure factors, phases from the obtained model.

In the following example, the command export before '%data' is used to export hkl and cif file and it will be processed only at the end of structure solution process with Direct Methods.

```
%structure cime
%job structure cime
%init
%export cime.hkl
%export cime.cif
%data
pattern cime.pow
cont s 4 c 40 n 24 h 64
wave 1.52904
cell 10.6986 18.8181 6.8246 90.000 111.284 90.000
space p 21/n
sync
%continue
```

An other example in case of structure solution with Simulated Annealing

```
%Structure paracetamol
%Job paracetamol
%Initialize%Initialize
%export paracetamol.hkl
%export paracetamol.cif
%Data
Cell 7.100 9.380 11.708 90.0 97.42 90.0
SpaceGroup p 21/n
Content c 32 o 8 n 4 h 36
Pattern paracetamol.pow
Wavelength 1.54056
%extraction
%normal
%fragment paracetamol.mol
%sannel
%continue
```

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## Description of EXPO2014 commands

### Description of EXPO2014 commands

The main modules of the program are:

EXPO, LIST, DATA, NTREOR, EXTRACTION, NORMAL, INVARIANTS, PHASE, FOURIER/LEAST-SQUARES, DIRECT, PATTERSON.

### EXPO module

It interprets commands and calls desired routines.

### LIST module

It is the software interface between EXPO2013 and the direct access file on which data and results are stored.

### DATA module

This routine reads the basic crystallographic informations like cell parameters, space group symbol (it may be also found by the program, using "findspace" directive), wavelength, unit cell content and the counts (or reflections). It includes a modified version of the subroutine SYMM Burzlaff & Houtas (1982). Symmetry operators are directly derived from the space group symbol.

An external file (containing counts or reflections) is supplied by the user. If an external reflection file is supplied (avoiding the extraction step), diffraction data are checked in order to find out equivalent reflections or systematically absent reflections (which are then excluded from the data set).

### N-TREOR module

This routine performs the indexing step (a peak search procedure is automatically carried out by the program before the indexing step). If available, an external peak positions file can be supplied to the program and the automatic peak search procedure will be skipped by EXPO2014. The indexing procedure retains the basic search algorithm of TREOR90, (Werner *et al.*, 1985) and has been strengthened in the last version of N-TREOR09 (Altomare *et al.*, 2009).

### EXTRACTION module

In this module diffraction integrated intensities are extracted from the powder diffraction pattern.

To calculate the integrated intensities, the program uses the Le Bail algorithm (Le Bail, Duroy & Fourquet, 1988) and combines it with a least squares procedure minimizing the quantity:

$$\sum w_i (y_{oi} - y_{ci})^2 \quad (1)$$

### **NORMAL module**

In this module diffraction intensities are normalized using the Wilson method (Wilson, 1942). Statistical analysis of the intensities is made in order to suggest the presence or absence of the inversion centre, to identify the possible presence and type of pseudotranslational symmetry (Cascarano *et al.*, 1988 a,b; Fan, Yao & Qian, 1988) and to detect preferred orientation effects (Altomare *et al.*, 1994; Altomare *et al.*, 1996). Possible deviations (of displacive type) from ideal pseudotranslational symmetry are also detected. All the above information is used as prior information in the integrated intensities extraction process, unless the directive NOPSEUDO is given to the program. When some additional prior information, besides positivity and atomicity of electron density, is available, then a suitable renormalization of structure factors is made.

### **INVARIANTS module**

Up to 10000 triplets relating reflections with normalized E values greater than a given threshold (strong triplets) are stored for active use in the phasing process. Also triplets (PSI-ZERO triplets) relating two reflections with large E and one with E close to zero are generated: they are used to define a special figure of merit (PSCOMB). Special types of triplets (PSI-E triplets) based on two strong and one intermediate reflections (just below the threshold of strong reflections) are calculated and used in the FOURIER/LEAST-SQUARES module in order to extend phase information (Altomare *et al.*, 1991). Negative quartets are generated by combining the psi-zero triplets in pairs, and those with cross-magnitudes smaller than a given threshold are estimated by means of their first representation, as described by Giacovazzo (1976). These quartets are used to provide an important contribution to the CPHASE FOM.

### **PHASE module**

In the EXPO2014 program the most reliable one-phase s.s. are treated as known phases. Besides triplets, also the most reliable negative quartets and two-phase s.s. may be actively used.

Each relationship is used with its proper weight: the concentration parameter of the first representation for quartets and two-phase s.s., and C or G for triplets.

- CONVERGENCE/DIVERGENCE PROCEDURE -

The convergence procedure (Germain *et al.*, 1970) is a convenient way of defining an optimum starting set of phases to be expanded by the tangent formula or by any other algorithm.

When the P10 formula is used, as a default, a special convergence process is devised which chooses the starting set.

Once the starting set has been defined, a good pathway for phase expansion is determined by a divergence procedure. In the divergence map, starting from the reflections in the starting set, each new reflection is linked to the preceding ones with the highest value of  $\langle a \rangle$ .

#### - PHASE EXTENSION AND REFINEMENT -

The starting set defined by the preceding step is usually formed by the origin (and enantiomorph) fixing reflections, a few one phase s.s. and a number of other phases which may be obtained:

- a) by magic integer permutation (White & Woolfson, 1975; Main, 1978),
- b) by a random approach (Baggio *et al.*, 1978; Burla *et al.*, 1992).

The option a) is the default, b) runs if the directive RANDOM is used. In this last case a large number (depending on the available computer time) of trials can be requested.

#### [FOURIER/LEAST-SQUARES module](#)

The sets of phases generated by the tangent routine are first expanded through psi-E relationships and then passed to the fast fourier transform routine written by L.F.Ten Eick (1977) and subsequently modified by the MULTAN team (Main *et al.*, 1980).

#### [DIRECT module](#)

In this module some "direct-space" approaches for solving crystal structures from powder diffraction data, can be used. The basic idea is to actively use structural and geometrical information, available *a priori*, during the structure solution process.

#### [LABELLING procedure](#)

The atomic species assigned to the peaks of an electron density map obtained at the end of a direct method procedure, can be modified using chemical information about the structure. The procedure (Altomare *et al.*, 2002) requires: 1) the prior information on the number and coordination of the heavy atoms (the procedure can only handle tetrahedral and octohedral coordinations); 2) the range of the typical distances between heavy atoms;



3) the range of the typical distances between heavy and light atoms.

### **POLPO procedure**

Using the "%polyhedra" command, two procedures can be activated. Both of them use a Monte Carlo approach and exploit the experimental information about the heavy - atom connectivity. The first one (POLPO1) (Altomare *et al.*, 2000) is suggested when all the heavy atoms are rightly positioned and labelled. It is able to correctly locate the light atoms. The second one (POLPO2) (Giacovazzo *et al.*, 2002) is able to position one or more missing cations and surrounding anions.

### **PATTERSON module**

In the EXPO2014 program it is possible to compute a PATTERSON map using various coefficients.

By using a special directive (INVERSION) it is possible to exploit the positivity of the electron density (in the direct space) in the extraction routine. The so-modified Patterson map is inverted providing a set of structure factor values to use in a new extraction process.

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## Preparation of data

### Preparation of data for the DATA routine

This routine reads the basic crystallographic information like cell parameters, space group symbol (it may be also found by the program, using "findspace" directive), wavelength, unit cell content and the counts (or reflections). It includes a modified version of the subroutine SYMM Burzlaff & Houtas (1982). Symmetry operators are directly derived from the space group symbol.

An external file (containing counts or reflections) is supplied by the user. If an external reflection file is supplied (avoiding the extraction step), diffraction data are checked in order to find out equivalent reflections or systematically absent reflections (which are then excluded from the data set).

### ALPHA

It is used to start the alpha2 stripping.

**CELL** *a b c a b g*

cell dimensions a, b, and c are in angstroms, a, b and g in degrees.

**CONTENTS** *El1 n1 El2 n2 El3 n3 .....*

Unit cell contents. Eli is the chemical symbol of atomic species i, ni is the corresponding number of atoms in the unit cell (to a maximum of 8 atomic species). For each chemical element up to Cf (Z=98) X-ray scattering factor constants are stored, together with information on the atomic number and weight, covalent and Van-der-Waals radii, etc. in a file (see notes on implementation). Neutron scattering factors are coded in the program for elements up to Pu (Z=94).

## EQUIPORTION

If this directive is given the overall intensity of a group of overlapping reflections is equiportioned among the reflections in the group (equal E-values are obtained).

## EXTEFILE *string*

This directive is used to supply an external file containing 'd' or '2q' values of peak positions. In the latter case the additional '2-THETA' directive has to be used.

If this directive is used the program will skip the automatic "*peaksearch*" procedure.

## FILETYPE *string*

This directive is used to specify the format of input file containing the diffraction data. *string* defines the type of file and can be 'counts', 'xy', 'double', 'gsas'.

If the directive FILETYPE *string* is absent or *string* is 'counts' the first three number at the beginning of the counts file must be the 2theta minimum, 2theta step and 2theta maximum. The following lines must be counts. The number of counts for row or the format of counts can vary.

#Example 1: use, in the input file, the directive '**FILETYPE counts**' or nothing

7.00 0.020 100.00

3017	2925	3056	2983	3008	2953	2875	2976	2886	2928
2973	2831	2960	2821	2854	2900	2857	2798	2876	2798
2819	2865	2830	2735	2771	2813	2806	2704	2823	2878
2793	2795	2756	2722	2705	2736	2802	2657	2811	2736
2753	2722	2780	2734	2795	2741	2812	2808	2713	2746
2696	2747	2799	2876	2741	2921	2776	2966	3017	3082
3058	3193	3147	3309	3319	3404	3490	3554	3684	3845
4015	4069	4293	4450	4657	4905	5201	5587	5796	6172
6646	7225	7834	8918	9767	10641	11891	13411	15091	17902

.....

#Example 2: use, in the input file, directive '**FILETYPE counts**' or nothing

6 0.01 55.98

412.98

404.51

412.40

405.57

403.30  
 405.94  
 404.89  
 389.39  
 396.55  
 408.00  
 403.24  
 385.44  
 396.46  
 393.20  
 390.52  
 401.58

.....

If *string* is 'xy' the counts file contains 2theta in the first column and the intensities in the second one. The format of counts can vary.

#The use of directive '**FILETYPE xy**'

4.700	4769.000	69.05795
4.714	4860.000	69.71370
4.729	4794.000	69.23872
4.743	4857.000	69.69218
4.758	4837.000	69.54855
4.772	4891.000	69.93568
4.787	4788.000	69.19537
4.801	4886.000	69.89993
4.816	4720.000	68.70226
4.830	4688.000	68.46897
4.845	4690.000	68.48357
4.859	4867.000	69.76389
4.874	4800.000	69.28204
4.888	4863.000	69.73521

.....

If *string* is 'double' the first line in the counts file contains 2theta minimum, 2theta step, 2theta maximum. The rest of file contains intensities and standard deviations on separated lines.

#The use of directive '**FILETYPE double**'

3.000 0.005 41.600

```

3567.2 3405.3 3370.1 3432.4 3476.2 3526.9 3354.7 3596.6 3476.8 3676.7
67.27 65.44 65.16 65.78 66.12 66.55 64.64 67.14 66.08 67.88
3623.0 3703.6 3555.1 3500.3 3558.6 3584.8 3606.2 3556.8 3710.3 3704.8
67.46 68.33 66.89 66.12 66.77 67.00 67.75 66.77 68.73 68.03
3721.0 3670.7 3775.1 3796.4 3820.9 3880.8 3809.1 3922.7 3963.5 3919.6
68.76 67.82 68.60 69.04 69.28 70.05 69.39 69.91 70.44 70.11
4062.6 4104.5 4148.8 4219.5 4221.6 4376.3 4294.3 4439.1 4349.1 4500.5
71.69 71.85 71.87 72.61 72.61 73.94 73.66 74.44 74.18 75.39
4449.2 4704.1 4833.7 4851.3 4892.2 5105.9 5143.3 5161.8 5272.0 5418.5
74.34 77.34 78.13 78.37 78.02 79.82 80.53 80.55 81.09 81.93
5543.3 5635.8 5918.0 6007.9 6406.6 6395.2 6515.0 6753.3 7255.9 7464.6
83.36 84.18 86.37 86.95 89.58 89.58 90.60 91.99 95.62 96.94
7811.5 8415.6 8597.6 9251.3 9995.7 10714.5 11097.2 11067.4 10678.3 9864.0
98.89 102.81 103.75 107.71 111.43 115.71 117.76 117.40 115.54 110.72

```

.....

In the previous cases comment records can appear at the beginning of data file if the first character is '#' or '!' or '>'. Examples in directory examples.

'FILETYPE gsas' can be used to read counts files in GSAS standard format with keyword TYPE='STD' and TYPE='ESD'.

## **FINDSPACE**

This directive is used in order to find a possible space group when the cell parameters are known.

## **FWHM *x***

This directive supplies the value of *x* for the overlapping calculation. Two reflections are assumed to be in overlapping if  $2q_1 - 2q_2 < x * \text{FWHM}$ . Default is  $x = 0.1$ .

## **HISTOGRAM *n***

*n* is the number of bars in the histogram for the alpha2 stripping procedure (only if ALPHA directive is used).

## **ISOTOPE *El sf***

To modify the value of the neutron scattering factor for element *El* using the value *sf*. (It must be used if NEUTRON directive is given).

## **MOREPEAKS**

This directive is used together with the peaksearch directive in order to add more low intensity peaks to the set of peaks already detected via the peaksearch directive.

## **NEUTRON**

This directive is used to specify that neutron radiation has been used.

## **NOREFINE**

This directive is used to skip the cluster refinement step in the peak search procedure.

## **PATTERN *filename***

Filename is the name of the profile counts file (up to 40 characters). It is used to change the default. [Default is name.pow where name is defined using the command %STRUCTURE].

## **RANGE *thmin thmax***

Only intensities included in the range thmin-thmax will be considered; thmin and thmax are the minimum and maximum 2 $\theta$  value of the powder pattern respectively.

## **REF2 *string***

This directive is used to supply an external reflection file. EXPO reads directly the output provided by any profile fitting program. HKL, FWHM and F<sup>2</sup> must be supplied [default format is (3i4,2f15.4)]. If a comment line is at the beginning of the reflection file, the first character must be '>'. If this directive is used, the directives 'pattern' and 'range' must not be introduced.

## **SHIFT *sx sy sz***

Origin shift components if desired by the user. They must be integral multiples of 1/24.

## **SPACEGROUP *string***

String is the symbol of the space group, according to International Tables (1974). Blanks are necessary among the terms constituting the space group symbol (see examples at the end of this manual).

## **SYNCHROTRON**

This directive is used to specify that synchrotron radiation has been used.

## **STEP *step\_value***

You can use this directive to specify that your data were collected at fixed step. This

directive is activated when the data file contains two columns (2theta values and intensities) and you are using the directive 'FILETYPE xy'. If you use the directive STEP, the first column is ignored and the program automatically recreates the 2theta values by using *step\_value* for the step and the first 2theta value in the data file.

### THCORR *x*

*x* is the  $D_{q_0}$  value that is used to correct by zeropoint shift the set of 2q peak positions.

The shift value will be equal to  $2(n-1)D_{q_0}$ , where *n* is the sequential number of the N-TREOR trial.

If this directive is not introduced the  $D_{q_0}$  default value is the experimental 2q step.

### 2-THETA

This directive is used combined with the EXTEFILE directive to supply to the indexing program N-TREOR09 an external file containing 2q values of peak positions.

### WAVELENGTH *w*

*w* is the wavelength (in Angstrom) used to collect the powder pattern.

## References

Burzlaff H. & Hountas A. (1982). *J. Appl. Cryst.* **15**, 464-467.

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## Examples

# Examples of input for EXPO2014

### Example 1

The following example shows the default use of EXPO2014 in case of indexed pattern. Most of the structures can be solved in this way. Diffraction data are in the file *crox.pow*. The content of the file *crox.exp* is

```
%structure crox
%job CROX- data from home diffractometer
%initialize
%data
  pattern crox.pow
  cell 5.447 6.5576 12.1147 106.382 95.715 77.970
  content Cr 8 O 21
```

```
wavelength 1.3922
spacegroup p -1
%continue
```

Default "profile counts file" name: crox.pow

crox.pow content:

```
6.0000 0.02 100.0
1166. 1179. 1224. 1172. 1221. 1159. 1204. 1347.
1295. 1146.
1353. 1188. 1214. 1250. 1253. 1240. 1285. 1344.
1314. 1324.
1438. 1444. 1463. 1522. 1664. 1548. 1836. 1865.
1913. 2160.
2367. 2412. 2856. 3186. 3681. 4280. 4941. 5883.
7298. 8978.
11248. 14375. 20187. 25377. 23771. 15690. 8496. 6385.
5553. 5022.
4643. 4371. 4202. 3840. 3684. 3296. 3199. 3047.
2833. 2710.
2567. 2334. 2412. 2156. 2163. 2134. 1981. 1981.
2033. 1901.
1849. 1768. 1761. 1709. 1654. 1616. 1580. 1629.
1561. 1609.
1658. 1609. 1493. 1334. 1298. 1331. 1305. 1289.
1292. 1214.
1149. 1182. 1081. 1146. 1094. 1065. 1030. 1055.
981. 1020.
1046. 981. 971. 1049. 975. 965. 900. 929.
861. 858.
874. 929. 835. 793. 839. 787. 907. 858.
822. 826.
```



## Example 2

The Ka2 stripping with a 3 bars histogram is requested.

```
%structure dada
%job DADA- data from home diffractometer
%initialize
%data
    spacegroup p 21 21 21
    cell 7.13115 9.9077 12.9256 90.0 90.0 90.0
    content Si 12 Ti 4 K 8 O 40
    wavelength 1.540562
    pattern dada.pow
    alpha2
    histogram 3
%continue
```

dada.pow content is:

```
10.00 0.02 95.00
    457.0
    437.0
    421.0
    475.0
    469.0
    425.0
    465.0
    405.0
    447.0
    461.0
    433.0
    433.0
    433.0
    415.0
    453.0
    451.0
    429.0
    453.0
    427.0
```

## Example 3

Data are from neutron source.

```
%structure cfcl
%job CFCL - data from neutron source
%initialize
%data
    pattern cfcl.pow
    cell 10.168 14.964 5.100 90.000 90.000 90.000
    content C 8 F 16 Cl 16
    spacegroup f d d 2
```

```
wavelength 1.595
neutron
%continue
```

#### Example 4

A Pseudo-Voigt function will be used and the background in each interval will be described by a constant. The counts file format is not the default one and the graphic window is suppressed.

```
%structure mes
%job MES - data from home diffractometer
%initialize
%data
    pattern mes.pow
    cell 8.588 9.931 11.105 90.0 93.754 90.0
    content C 24 N 4 O 20 S 4 H 52
    spacegroup p 21/c
    wavelength 1.5406
%extraction
    pvoigt
    polynomial 0
%end
```

#### Example 5

The starting values of the integrated intensities in the extraction step are supplied by the user in the file "yono.ext" and the number of least-square cycles is set to 40.

```
%structure yono
%job YONO - Synchrotron data
%initialize
%data
    pattern yono.pow
    cell 9.385 16.394 3.627 90.000 101.067 90.000
    content Y 8 O 26 N 2 H 18
```

```

spacegroup p 21
wavelength 1.2323
synchrotron
%extraction
  freecycle yono.ext
  ncycle 40
%end

```

### Example 6

The preliminary fitting of the standard peak is skipped and the starting 2 $\theta$  shift value is supplied by the user (the program refines it).

```

%structure agpz
%job AGPZ - data from home diffractometer
%init
%data
  pattern agpz.pow
  cell 6.526 20.059 6.464 90.000 90.000 90.000
  spacegroup p b c a
  content Ag 8 N 16 C 24 H 24
  wavelength 1.54056
%extraction
  nosing
  zeroprof 0.02
%continue

```

### Example 7

Neutron data and a deuterium atom in the cell content are used. Fast graphic interaction for the integrated intensities extraction process is activated.

```

%structure baco
%job BACO - Neutron data
%initialize
%data
  neutron
  isotope H 0.67
  pattern baco.pow
  cell 10.0632 7.9330 6.8487 90.0 122.3423 90.0

```

```

spacegroup C 2/m
content Ba 4 C 8 O 20 H 8
wavelength 1.909
%extraction
fast
%continue

```

### Example 8

The program restarts from the PHASE procedure.

A random approach is used and the best 100 sets of phases, over 250 trials, are retained in the direct access file. No Fourier is required.

```

%structure nizr
%phase
random
maxtrials 250
minfom 1.0 100
%end

```

### Example 9

The program restarts from the FOURIER procedure.

Only the E-map corresponding to the set number 7 and the complete FOURIER/LEAST-SQUARES procedure for set number 10 are requested by the user.

```

%structure nbpo
%fourier
set 7
recyc 0
%fourier
set 10
%continue

```

### Example 10

To view only the structure previously produced by FOURIER routine.

```

>window
%structure crox
%menu
%end

```

### Example 11

Use of the pseudotranslational symmetry (if it is present) as prior information for a new extraction process is inhibited. Use of nopse directive after command %normal.

```
%structure agpz
%job AGPZ - data from home diffractometer
%initialize
%data
    pattern agpz.pow
    cell 6.526 20.059 6.464 90.000 90.000 90.000
    spacegroup p b c a
    content Ag 8 N 16 C 24 H 24
    wavelength 1.54056
%extraction
%normal
    nopseudo
%continue
```

### Example 12

Use of the triplets estimation as prior information for a new extraction process.

```
%structure mes
%job MES - data from home diffractometer
%initialize
%data
    pattern mes.pow
    cell 8.588 9.931 11.105 90.0 93.754 90.0
    content C 24 N 4 O 20 S 4 H 52
    spacegroup p 21/c
    wavelength 1.5406
%extraction
%normal
    nopseudo
%invariants
    estimation
%continue
```

### Example 13

Use of the Patterson map inversion as prior information for a new extraction process.

```
%structure lasi
%job lasi - Neutron data
%initialize
%data
    pattern lasi.pow
    cell 5.4059 8.7934 14.2754 90.000 112.731 90.00
    content La 8 Si 8 O 8
    spacegroup p 21/c
    wavelength 2.3400
    neutron
%extraction
```

```
%normal
    nopse
%patterson
    inverse
%continue
```

### Example 14

A known fragment is used to complete the structure by applying the FOURIER/LEAST-SQUARES procedure. The binary file "sapo.bin" must exist.

```
%structure sapo
%fourier
    fragment SAPO.FRA
%continue
```

Coordinates are in the file "SAPO.FRA" which contains

Si .00000 .00000 .00000

### Example 15

The indexing process is performed.

```
%structure gapo
%job GAPO - Synchrotron data
%initialize
%data
    wave 1.24012
    pattern gapo.pow
    synchrotron
%ntreor
%end
```

### Example 16

If a set of d (or 2 q) values is already available, the automatic peak search procedure is skipped:

```
%structure mes
%job MES - data from home diffractometer
%initialize
%data
    pattern mes.pow
    wavelength 1.5406
    2-theta
    extefile mes.pea
%ntreor
```

```
VOL = 6000, CEM = 40,
%end
```

'mes.pea' is an ASCII file containing the 2q peak positions.

The N-TREOR09 directives 'VOL = 6000' and 'CEM = 40' activate a search for a cell having a maximum volume of 6000 Å<sup>3</sup> and maximum axis value of 40 Å.

### Example 17

Use of the change label procedure to relabel the peaks of an electron density map obtained by applying the FOURIER procedure. The binary file "vfi.bin" must exist.

```
%structure vfi
%job VFI - Synchrotron data
%changelab
    label 3 al 3 p
    coord 4 4
    dwei 3.1 0.5
    dlig 1.9 0.5
%continue
```

### Example 18

The POLPO1 procedure is applied to locate the light atoms around each specified heavy atoms. The crox.fra file contains the cations coordinates. The binary file 'crox.bin' must exist.

```
%structure crox
%job CROX - home diffractometer data
%polyhedra
    fragment crox.fra
    octahedron 1 1.92 0.2 0.2
    tetrahedron 2 1.75 0.2 0.2
    tetrahedron 3 1.75 0.2 0.2
    tetrahedron 4 1.75 0.2 0.2
%continue
```

### Example 19

The POLPO2 procedure is applied to locate one or more missing cations and surrounding anions. The sapo.fra file contains the located cations coordinates. The binary file 'sapo.bin' must exist.

```
%structure sapo
%job SAPO - data from home diffractometer
%polyhedra
    fragment sapo.fra
    tetrahedron Si 1 1.6 0.2 0.2
    tetrahedron Si 2 1.6 0.2 0.2
    missing 1 2 Si tetrahedron 1.6 0.2 0.2
```

```
missing 1 2 Si tetrahedron 1.6 0.2 0.2
%continue
```

## Example 20

To find the space group.

```
%structure cf3br
%job CF3BR - Neutron data
%init
%data
    pattern cf3br.pow
    cell 8.146 5.85 7.962 90. 111.722 90.
    cont c 4 br 4 f 12
    wave 1.911
    neutro
    findspace
%continue
```

**Table 1**

Classes of reflections corresponding to the low index pseudo-translational symmetry.

1) $h+k+l = 1n$	2) $h = 2n$	3) $k = 2n$
4) $l = 2n$	5) $h+k+l = 2n$	6) $h+k = 2n$
7) $h+l = 2n$	8) $k+l = 2n$	9) $h = 3n$
10) $k = 3n$	11) $l = 3n$	12) $h+k = 3n$
13) $h+l = 3n$	14) $k+l = 3n$	15) $h+k+l = 3n$
16) $h+k+2l = 3n$	17) $h+2k+l = 3n$	18) $2h+k+l = 3n$
19) $h+2k = 3n$	20) $h+2l = 3n$	21) $k+2l = 3n$
22) $l = 4n$	23) $k = 4n$	24) $h = 4n$
25) $h+k = 4n$	26) $h+l = 4n$	27) $k+l = 4n$
28) $h+k+l = 4n$	29) $2h+2k+l = 4n$	30) $2h+k+2l = 4n$
31) $h+2k+2l = 4n$	32) $2h+k+l = 4n$	33) $h+2k+l = 4n$
34) $h+k+2l = 4n$	35) $h+2k = 4n$	36) $h+2l = 4n$
37) $k+2l = 4n$	38) $2h+k = 4n$	39) $2h+l = 4n$
40) $2k+l = 4n$	41) $3h+3k+l = 4n$	42) $3h+k+3l = 4n$
43) $h+3k+3l = 4n$	44) $h+2k+3l = 4n$	45) $h+3k+2l = 4n$
46) $3h+k+2l = 4n$	47) $h+3k = 4n$	48) $h+3l = 4n$
49) $k+3l = 4n$	50) $3k+2l = 6n$	51) $2k+3l = 6n$
52) $2h+3k = 6n$	53) $3h+2k = 6n$	54) $3h+2l = 6n$
55) $2h+3l = 6n$	56) $2h+2k+3l = 6n$	57) $3h+2k+3l = 6n$
58) $3h+3k+2l = 6n$	59) $4k+3l = 12n$	60) $4h+3l = 12n$
61) $4h+3k = 12n$	62) $3k+4l = 12n$	63) $3h+4k = 12n$
64) $3h+4l = 12n$	65) $h = 2n \text{ \& } k = 2n$	66) $h = 2n \text{ \& } l = 2n$
67) $k = 2n \text{ \& } l = 2n$	68) $h = 2n \text{ \& } k+l = 2n$	69) $k = 2n \text{ \& } h+l = 2n$



70)  $l = 2n \text{ \& } h+k = 2n$

71)  $h+k = 2n \text{ \& } h+l = 2n$

72)  $h = 2n \text{ \& } k = 2n \text{ \& } l = 2n$

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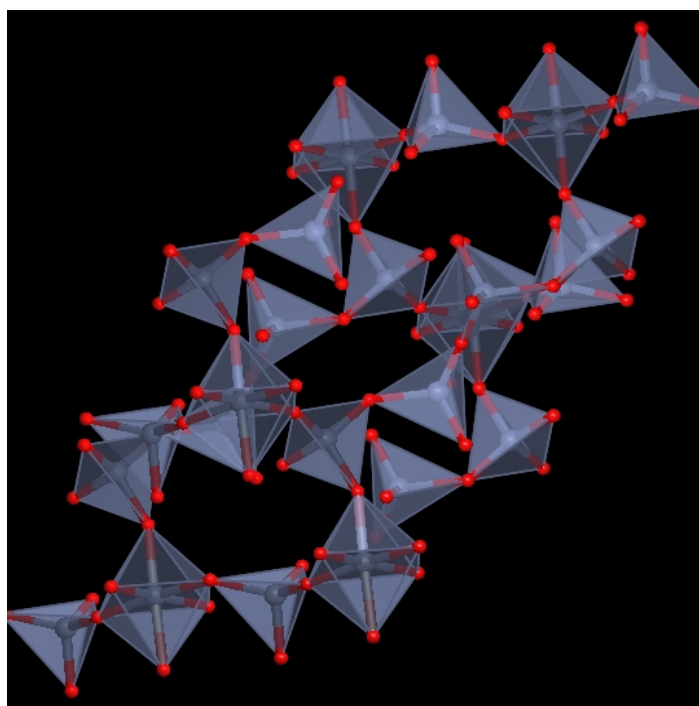
## Crystal Structure Visualization

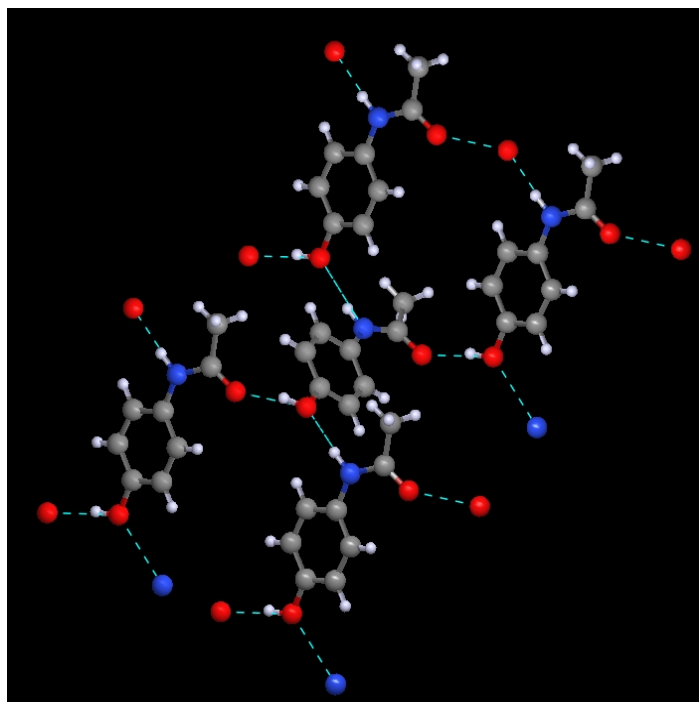
---

# Crystal Structure Visualization

EXPO2014 includes a viewer for 3D crystal structure visualization. This viewer is a modified version of **Jav** (**J**ust **A**nother **V**iewer), program to visualize structural models and electron density maps.

The program uses GTK Cairo and OpenGL libraries which are distributed under the GPL (GNU General Public License).





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## How to

Many possibilities are available to interact with the program: through the toolbar, the menu and using [keyboard/mouse](#).

The menu items follow:

- [File](#)
- [Modify](#)
- [Select](#)
- [View](#)
- [Tools](#)
- [Info](#)

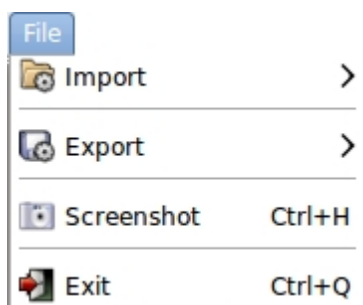
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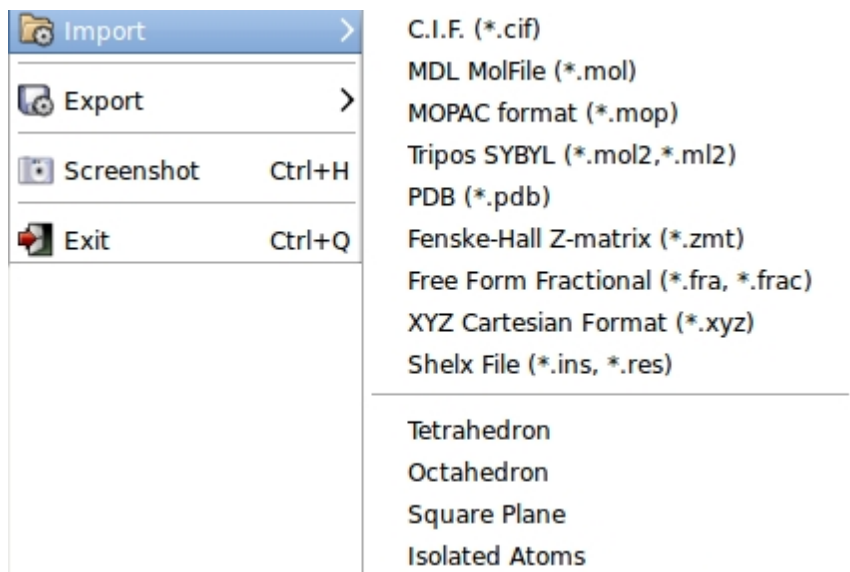
## File

The sub-menu File is shown on the left. It allows:



- Import Opens a coordinate file
- Export Saves a coordinate file
- Screenshot Produces an image file of Jav screen
- Exit Closes the viewer

## Import



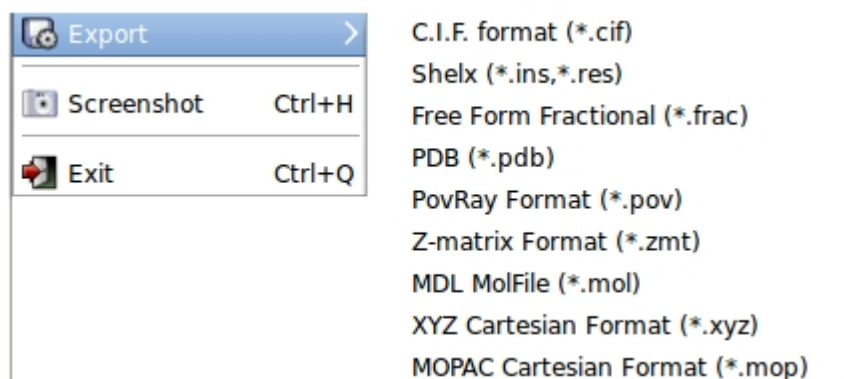
It is possible to read crystal structure from the following types of file:

- Crystallographic Information File (\*.cif) <http://www.iucr.org/resources/cif>
- MDL Molfile (\*.mol) <http://accelrys.com/products/informatics/cheminformatics/ctfile-formats/no-fee.php>
- MOPAC File Formats. It can handle data structure in Cartesian coordinates or in internal coordinates. <http://openmopac.net/manual/index.html>
- Tripos SYBYL Mol2 File (\*.mol2, \*.ml2) <http://tripos.com/data/support/mol2.pdf>
- Protein Data Bank (\*.pdb) <http://www.wwpdb.org/>
- Fenske-Hall Z-matrix (\*.zmt), Z-matrix file created by [Open Babel](#)
- Free Form Fractional (\*.fra, \*.frac) [http://openbabel.org/wiki/Free\\_Form\\_Fractional](http://openbabel.org/wiki/Free_Form_Fractional)
- XYZ Cartesian Format (\*.xyz) [http://en.wikipedia.org/wiki/XYZ\\_file\\_format](http://en.wikipedia.org/wiki/XYZ_file_format)
- Input/Output files of SHELXL (\*.ins, \*.res) <http://shelx.uni-ac.gwdg.de/SHELX/>

Isolated atoms and some common chemical geometries (tetrahedron, octahedron, square plane) can also be imported. They are useful building blocks in structure solution by global

optimization.

## Export



Information about the currently displayed crystal structure can be in following text files:

- Crystallographic Information File (\*.cif) <http://www.iucr.org/resources/cif>
- Input/Output files of SHELXL (\*.ins, \*.res) <http://shelx.uni-ac.gwdg.de/SHELX/>
- Free Form Fractional (\*.fra, \*.frac) [http://openbabel.org/wiki/Free\\_Form\\_Fractional](http://openbabel.org/wiki/Free_Form_Fractional)
- Protein Data Bank (\*.pdb) <http://www.wwpdb.org/>
- POV-Ray input file (\*.pov) input file for the freeware program POV-Ray. <http://www.povray.org/download/>
- MDL Molfile (\*.mol) <http://accelrys.com/products/informatics/cheminformatics/ctfile-formats/no-fee.php>
- Fenske-Hall Z-matrix (\*.zmt), Z-matrix file created by [Open Babel](#)
- MDL Molfile (\*.mol) <http://accelrys.com/products/informatics/cheminformatics/ctfile-formats/no-fee.php>
- XYZ Cartesian Format (\*.xyz) [http://en.wikipedia.org/wiki/XYZ\\_file\\_format](http://en.wikipedia.org/wiki/XYZ_file_format)
- MOPAC File Formats with cartesian coordinates. <http://openmopac.net/manual/index.html>

## Screenshot

Images of crystal structure displayed in the graphic area can be saved in files of different following formats:

- Bitmap File (\*.bmp)
- ICO file (\*.ico)
- jpeg file (\*.jpg)
- Portable Network Graphics file (\*.png)

- Tagged Image File (\*.tif)

## Exit

This is used to exit the program.













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## Modify

The sub-menu Modify is shown on the left. It allows:

<b>Modify</b>		
 Undo import	Ctrl+Z	<a href="#">Undo/Redo</a>
 Redo	Ctrl+Y	<a href="#">Delete Selection</a>
<hr/>		
 Delete Selection		<a href="#">Delete Bonds</a>
 Delete Bonds		<a href="#">Delete All Type ...</a>
 Delete All Type ...	>	<a href="#">Delete All Type</a>
<hr/>		
 Change Species	>	<a href="#">Change Species</a>
 Rename		<a href="#">Rename</a>
 Renumber		<a href="#">Renumber</a>
 Sort by Species		<a href="#">Sort by Species</a>
 Add Bonds		<a href="#">Add Bonds</a>
<hr/>		
 Edit structure		<a href="#">Edit structure</a>
<hr/>		
 Add fragments	>	<a href="#">Add fragments</a>

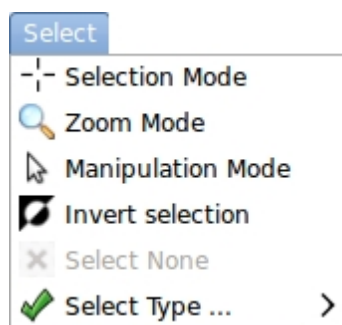
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## Select

The sub-menu Select is shown on the left. It allows:



[Selection Mode](#)

[Zoom Mode](#)

[Manipulation Mode](#)

[Invert selection](#)

[Select none](#)

[Select Type](#)

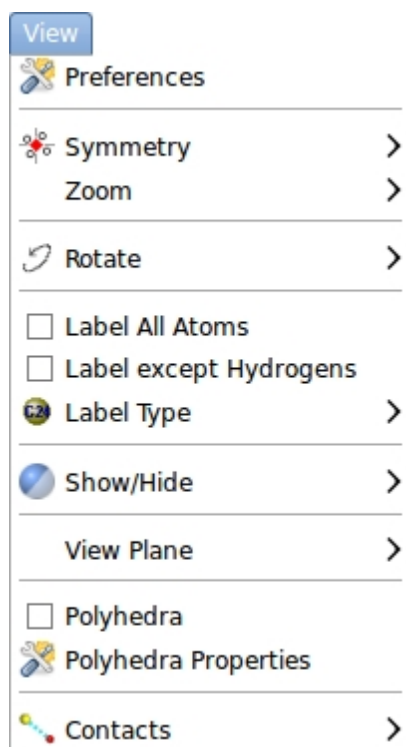
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## View

The sub-menu View is shown on the left. It allows:



[Preferences](#)

[Symmetry](#)

[Zoom](#)

[Rotate](#)

[Label All Atoms](#)

[Label except  
Hydrogens](#)

[Label Type](#)

[Show/Hide](#)

[View Plane](#)

[Polyhedra](#)

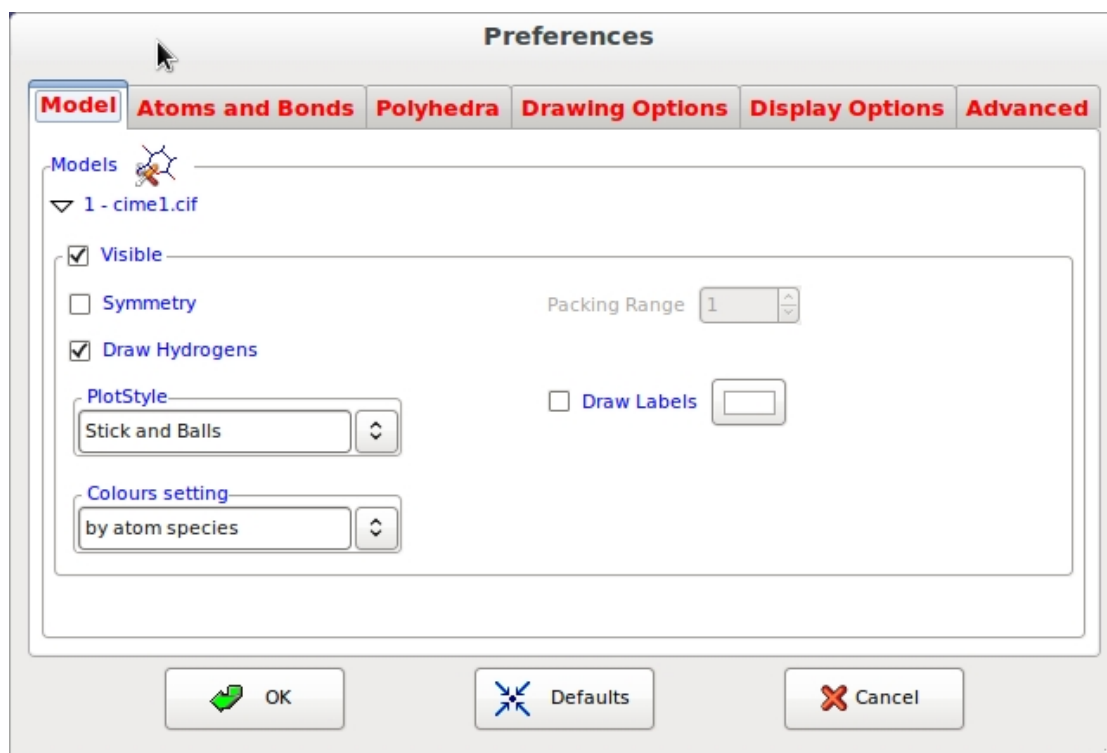
[Polyhedra  
Properties](#)

[Contacts](#)

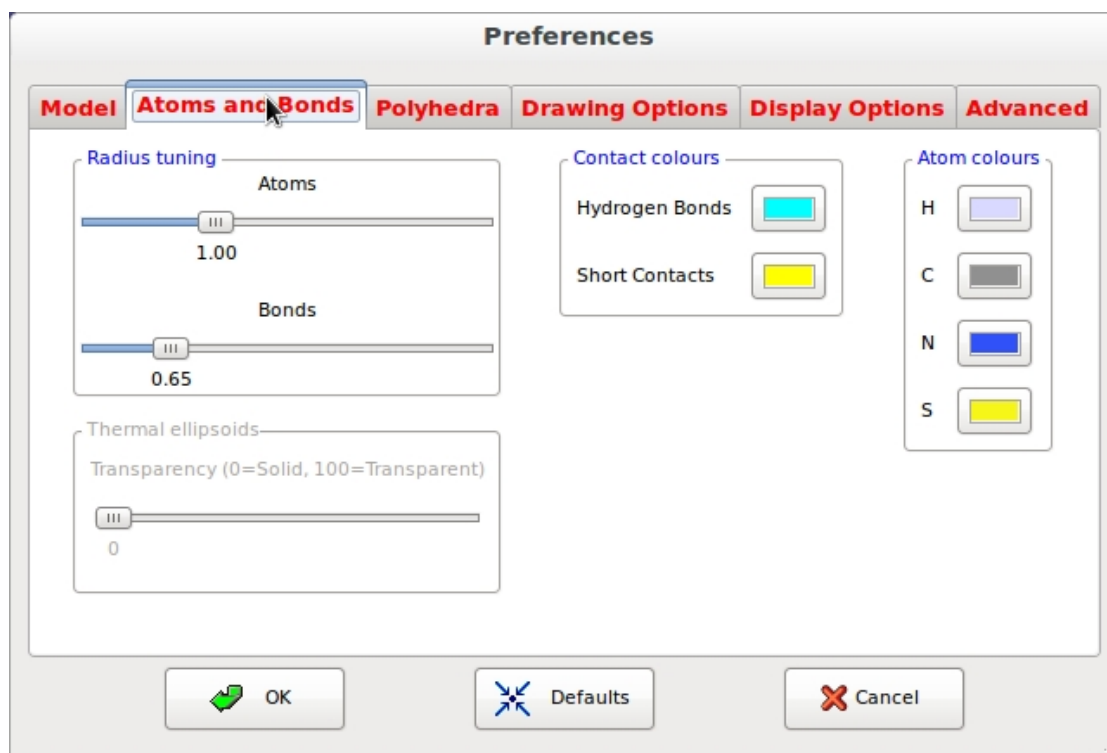
## Preferences

Some details about models are reported.

The following window shows what modifications can be applied to the model.

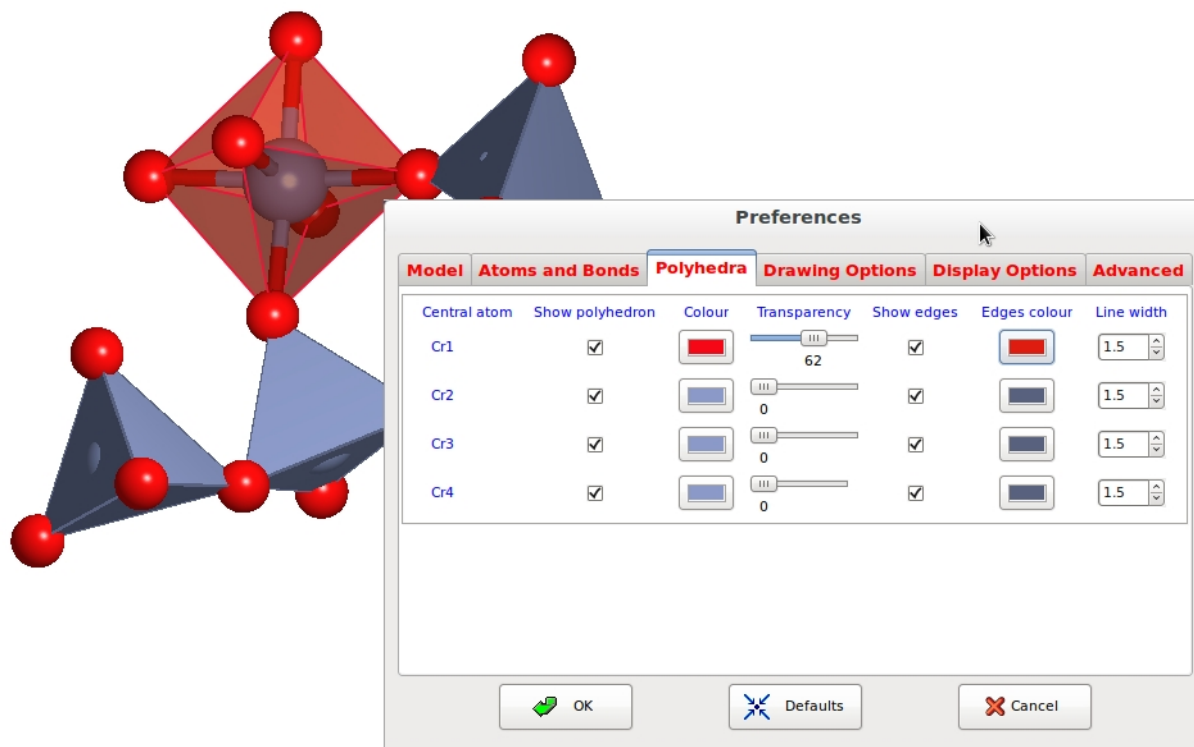


In order to get a better view of a model it is possible to tune the radius of the spheres representing the atoms and the radius of the cylinders representing the bonds. The atom colors can be modified.



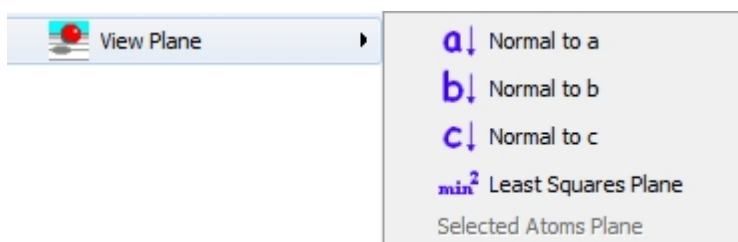
## Polyhedra Properties

This window provides some tools to set the properties of the polyhedra; it is possible to visualize or to hide some of them, it is possible to change the colors and the transparency, to show or to hide the edges etc.



## View plane

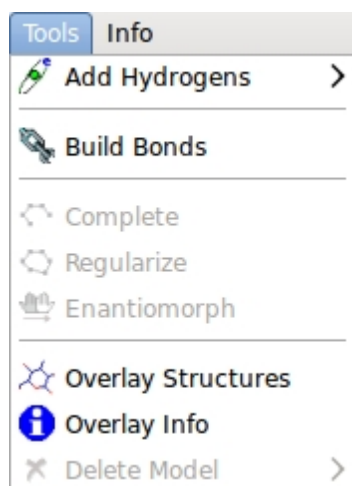
Set the preferred view plane.



## Tools

The sub-menu Tools is shown on the left. It allows:





[Add Hydrogens](#)

[Build Bonds](#)

[Complete](#)

[Regularize](#)

[Enantiomorph](#)

[Overlay Structures](#)

[Overlay Info](#)

[Delete Info](#)

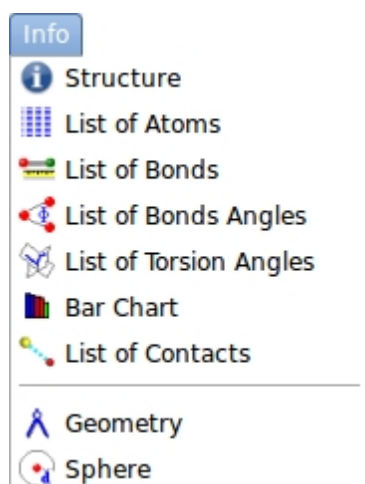
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## Info

The sub-menu Info is shown on the left. It allows:



[Structure](#)

[List of Atoms](#)

[List of Bonds](#)

[List of Bond Angles](#)

[List of Torsion Angles](#)

[Bar Chart](#)

[List of Contacts](#)

[Geometry](#)

[Sphere](#)

Info on the structure.

List of Atoms.

List of Bond Distances.

List of Bond Angles.

List of Torsion Angles.

Histogram of the peak intensities.

Some geometric calculations can be performed.

list of atoms around a selected atom

## Structure

In the following tabs detailed information of the model are reported.

**cimetidine**

**Structure** Atoms Bonds Angles Torsion Angles Bar Chart Contacts

Name cimetidine

Cell Lengths a 10.699 b 18.818 c 6.825

Cell Angles alpha 90.000 beta 111.284 gamma 90.000

Space Group P 21/n (centrosymmetric)

Symmetry operations  
 1) x,y,z  
 2) 1/2-x,1/2+y,1/2-z  
 3) -x,-y,-z  
 4) 1/2+x,1/2-y,1/2+z



Cell Volume 1280.230

Cell Content  
 H 64  
 C 40  
 N 24  
 S 4

Volume per atom 18.827

R-Factor 28.393

Atoms in model 17

 Save  Close



## List of Atoms

The second tab contains the information related to the atoms.

**cimetidine**

**Structure** **Atoms** Bonds Angles Torsion Angles Bar Chart Contacts

Number	Label	Type	Intensity	Xfrac	Yfrac	Zfrac	B	s.o.f.	Symm.Op
1	S1	S	16719.00000	0.48185	0.41469	0.19725	4.51421	1.00000	x,y,z
2	N1	N	6562.00000	0.62974	0.23371	0.72680	3.36343	1.00000	x,y,z
3	N2	N	6279.00000	0.95063	0.37542	0.54685	3.40571	1.00000	x,y,z
4	N3	N	6153.00000	0.87073	0.44743	0.24875	4.44055	1.00000	x,y,z
5	N4	N	5543.00000	1.09869	0.40861	0.39000	3.95594	1.00000	x,y,z
6	N5	N	5413.00000	1.16586	0.48553	0.15358	5.43250	1.00000	x,y,z
7	N6	N	5401.00000	0.71092	0.31939	0.58086	4.04593	1.00000	x,y,z
8	C1	C	5332.00000	0.63725	0.39924	0.15331	4.48181	1.00000	x,y,z
9	C2	C	5078.00000	0.53363	0.28805	0.66299	4.04910	1.00000	x,y,z
10	C3	C	4986.00000	0.40380	0.28380	0.70951	4.72578	1.00000	x,y,z
11	C4	C	4944.00000	0.73520	0.25285	0.67636	4.39471	1.00000	x,y,z
12	C5	C	4923.00000	0.97095	0.40969	0.39064	2.77809	1.00000	x,y,z
13	C6	C	4871.00000	1.12231	0.45105	0.25634	3.85322	1.00000	x,y,z
14	C7	C	4615.00000	0.58344	0.33910	0.57113	5.01616	1.00000	x,y,z
15	C8	C	4447.00000	0.73739	0.46058	0.26631	3.08464	1.00000	x,y,z
16	C9	C	4369.00000	0.52202	0.41038	0.47842	4.07738	1.00000	x,y,z
17	C10	C	3997.00000	1.06300	0.34428	0.72908	4.82915	1.00000	x,y,z

 Save  Close



## List of Bonds

The third tab contains the list of the bond distances.

**cimetidine**

**Structure Atoms Bonds Angles Torsion Angles Bar Chart Contacts**

Number	Atom 1	Atom 2	Distance	Symm.Op1	Symm.Op2
1	S1	C1	1.81675	x, y, z	x, y, z
2	S1	C9	1.80959	x, y, z	x, y, z
3	N1	C2	1.40276	x, y, z	x, y, z
4	N1	C4	1.34281	x, y, z	x, y, z
5	N2	C5	1.32952	x, y, z	x, y, z
6	N2	C10	1.50002	x, y, z	x, y, z
7	N3	C5	1.35573	x, y, z	x, y, z
8	N3	C8	1.49493	x, y, z	x, y, z
9	N4	C5	1.36840	x, y, z	x, y, z
10	N4	C6	1.30425	x, y, z	x, y, z
11	N5	C6	1.16922	x, y, z	x, y, z
12	N6	C4	1.39193	x, y, z	x, y, z
13	N6	C7	1.39146	x, y, z	x, y, z
14	C1	C8	1.57330	x, y, z	x, y, z
15	C2	C3	1.53509	x, y, z	x, y, z
16	C2	C7	1.35730	x, y, z	x, y, z
17	C7	C9	1.52636	x, y, z	x, y, z

 Save
  Close



### List of Bond Angles

The fourth tab contains the list of the bond angles.

**cimetidine**

**Structure Atoms Bonds Angles Torsion Angles Bar Chart Contacts**

Number	Atom 1	Atom 2	Atom 3	Angle
1	C1	S1	C9	106.77
2	S1	C1	C8	107.63
3	S1	C9	C7	112.31
4	C2	N1	C4	108.32
5	N1	C2	C3	120.94
6	N1	C2	C7	107.03
7	N1	C4	N6	109.27
8	C5	N2	C10	122.63
9	N2	C5	N3	120.64
10	N2	C5	N4	116.71
11	C5	N3	C8	124.04
12	N3	C5	N4	122.50
13	N3	C8	C1	109.82
14	C5	N4	C6	116.13
15	N4	C6	N5	168.47
16	C4	N6	C7	105.97
17	N6	C7	C2	109.37
18	N6	C7	C9	121.40
19	C2	C3	C7	121.07



 Save
  Close

## List of Torsion Angles

The fifth tab contains the list of the torsion angles.

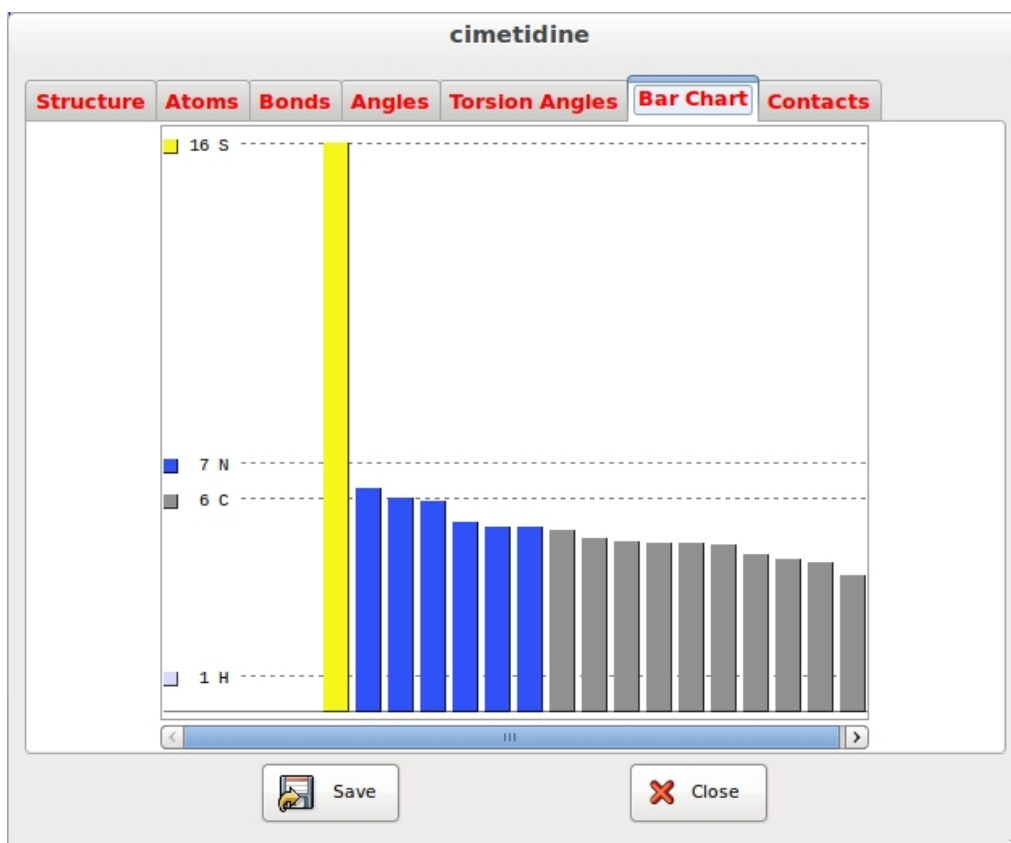
**cimetidine**

Structure	Atoms	Bonds	Angles	<b>Torsion Angles</b>	Bar Chart	Contacts
Number	Atom 1	Atom 2	Atom 3	Atom4	Angle	
1	C9	S1	C1	C8	-61.77	
2	C1	S1	C9	C7	-58.42	
3	C4	N1	C2	C3	-176.71	
4	C4	N1	C2	C7	0.91	
5	C2	N1	C4	N6	0.33	
6	C10	N2	C5	N3	-168.53	
7	C10	N2	C5	N4	7.24	
8	C8	N3	C5	N2	6.88	
9	C8	N3	C5	N4	-168.63	
10	C5	N3	C8	C1	-89.79	
11	C6	N4	C5	N2	-169.82	
12	C6	N4	C5	N3	5.86	
13	C5	N4	C6	N5	172.94	
14	C7	N6	C4	N1	-1.41	
15	C4	N6	C7	C2	1.99	
16	C4	N6	C7	C9	179.00	
17	S1	C1	C8	N3	175.76	
18	N1	C2	C7	N6	-1.80	
19	N1	C2	C7	C9	170.51	

 Save
  Close

## Bar Chart

The tab Bar Chart contains the histograms of the fourier intensities of the atoms.



## List of Contacts

The tab Contacts contains a list of non bonded contacts.

**cimetidine**

Structure Atoms Bonds Angles Torsion Angles Bar Chart **Contacts**

Number	Atom 1	Atom 2	Distance	Symm.Op1	Symm.Op2
1	N4	N1	2.96500	x, y, z	1/2+x, 1/2-y, 1/2+z
2	N5	N3	2.91607	x, y, z	-x, -y, -z
3	N1	N4	2.96500	x, y, z	1/2+x, 1/2-y, 1/2+z
4	N3	N5	2.91607	x, y, z	-x, -y, -z
5	N2	N6	2.85911	x, y, z	x, y, z

Save Close

## Geometry

The value of the distances, angles and torsion angles among the atoms can be calculated.

