

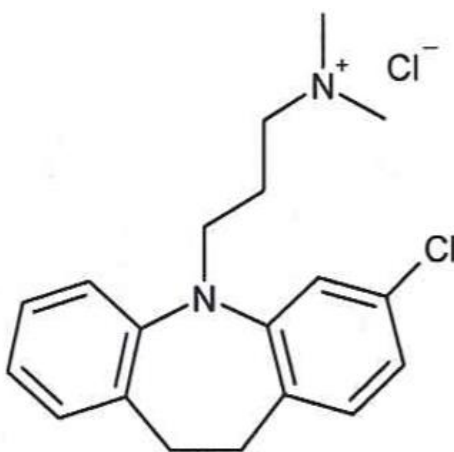
TUTORIAL EXPO: INDEXING

The **Indexing** folder contains:

- **DEFAULT** folder
- **NO_DEFAULT** folder

- **DEFAULT** folder

It contains: **clomipra.exp** [the input file for the default indexing run of EXPO in case of Clomipramine hydrochloride ($C_{19}H_{24}ClN_2 \cdot Cl$)]; **pd_0023.pow** (the file containing the experimental profile counts); **clomipra.fra** (the file of the fractional coordinates and isotropic thermal factors of the true model, hydrogen atoms excluded), **clomipra.pdf** (the file containing the structure information published in **paper.pdf**).



The input file 'clomipra.exp' consists of the following lines:

```
%Structure clomipra
%Job Clomipramine hydrochloride (C19H24ClN2Cl)
%Data
Pattern      pd_0023.pow
Wavelength 1.54056
%ntreor
%continue
```

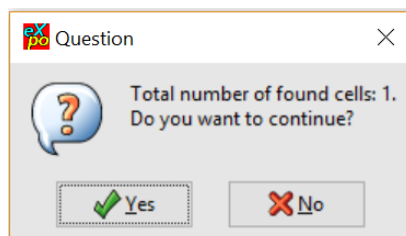
To run EXPO on **clomipra**, in order to index the powder pattern in default way by N-TREOR09:

- Click on EXPO icon
- **File** in the upper Menu
- **Load and Go**
- Use 'clomipra.exp' as Input File and give the Output Filename you like (clomipra.out is the default output file name)
- **Go**
The powder diffraction pattern is visualized.
- Click on **Next**

The peak-search step is automatically carried out. The peak positions are marked by vertical red bars.

- Click on **Next**

The two-theta values $\{2\theta_p\}$ of the located peaks are automatically refined by EXPO and the corresponding interplanar distances $\{d_p\}$ are supplied to the indexing program N-TREOR09. At the end of the first indexing run, based on the $\{d_p\}$ values, the following window will appear



enabling the user to stop the automatic indexing procedure, by clicking on '**No**'. The dialog window will appear each time new additional cell(s) will be found.

The default choice of EXPO is '**Yes**', consequently, if no user intervention will occur to change this choice, EXPO will automatically continue to search for the most plausible cell *via* additional indexing attempts that exploit new sets of d values obtained, for each new indexing run, by applying positive or negative two-theta shifts to the initial $\{2\theta_p\}$ values. EXPO will stop the indexing procedure as soon as it will recognize that the best cell has been found.

In case of **clomipra**, at the end of the automatic default indexing procedure the following window will appear:

| Nr. | Prog. | a | b | c | alpha | beta | gamma | Vol. | M20 | FOMnew | Mc20 | shift | NIX | Symmetry Info |
|-----|-------|----------|---------|----------|--------|--------|--------|--------|-------|--------|------|--------|-----|---------------|
| 1 | N | 15.51508 | 8.61221 | 14.03808 | 90.000 | 96.909 | 90.000 | 1862.1 | 34.00 | 2.370 | - | 0.000 | 0 | P 1 21/c 1 |
| 2 | N | 15.49584 | 8.59605 | 14.01586 | 90.000 | 96.918 | 90.000 | 1853.4 | 20.00 | 1.868 | - | -0.040 | 0 | P 1 21/c 1 |
| 3 | N | 15.53739 | 8.62310 | 14.06291 | 90.000 | 96.902 | 90.000 | 1870.5 | 13.00 | 1.452 | - | 0.040 | 0 | P 1 21/c 1 |

The window supplies a set of plausible cells, listed in function of decreasing value of the figure of merit FOMnew. The indexing process is successful and the information on the unit cell enables EXPO to solve the crystal structure; it can be easily verified by the following steps:

- Click on **OK** to select the first ranked cell;
- Provide the Cell Content '(C19H24ClN2Cl)4';
- Click on **OK**;
- Click on **Next** button to go on continuously until the space group determination process is carried out;
- Click on **OK** to select the Space Group 'P 21/c' first ranked in the list (the file 'clomipra1.exp' is created);
- Click on **OK**;

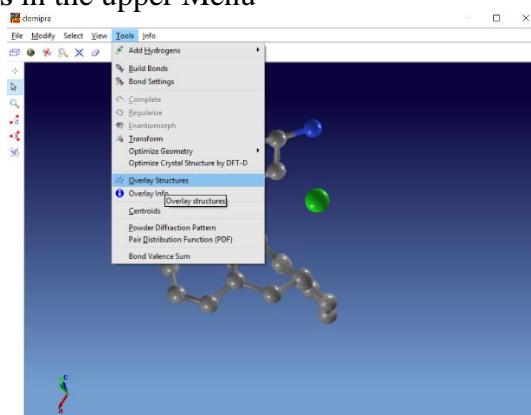
- Click on **Next** button to go on continuously until the end of the run.

The structure model obtained at the end of Direct Methods (DM) procedure, executed on the first set of phases (default choice), is partially correct, it could be improved by the Structure model optimization tools of EXPO (*e.g.*, via the COVMAP procedure, for more details see the 'Readme structure model optimization.docx' file available at the 'Structure model optimization' folder); the solution could be searched also by exploring the rest of the stored sets of phases (for more details, see the 'Readme solution by Direct Methods.docx' file available at the 'Solution by Direct Methods' folder); in this last case:

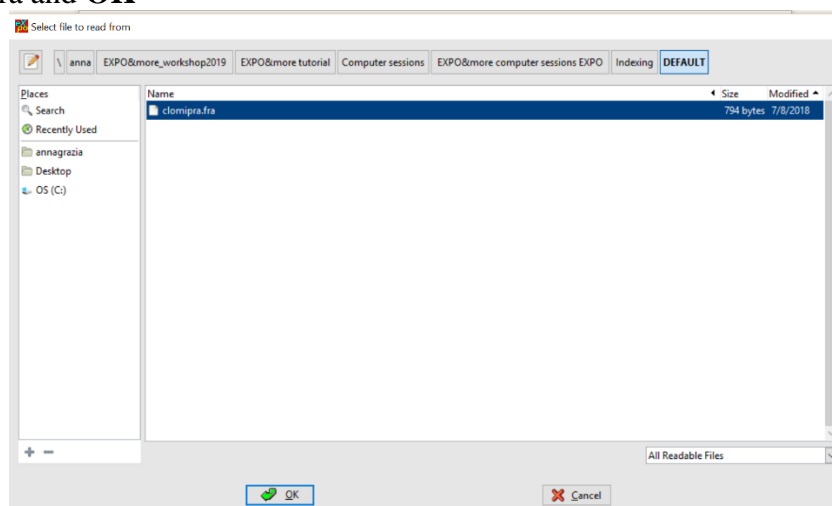
- Select **Solve > Explore Trials** in the main Menu;
- Select by check button the option '**Explore trials not processed yet**'

At the end of the procedure the twenty available structure models are ranked according to increasing RF values and the first ranked model, except for some labelling errors, is the correct one; it can be verified by comparing the structure model with the published one stored in the **clomipra.fra** file, *via* the graphic interface, by choosing:

Tools > Overlay structures in the upper Menu

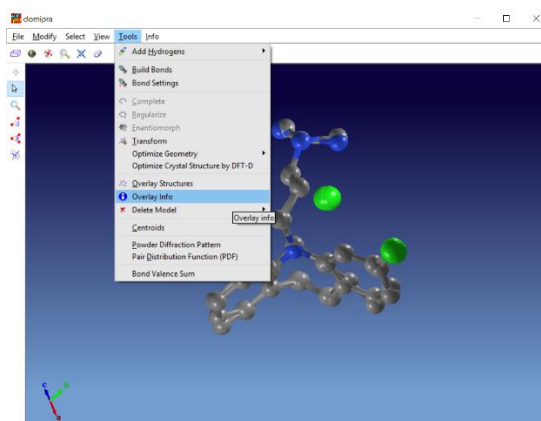


select **clomipra.fra** and **OK**



The two structure models are overlaid and the comparison results can be visualized by selecting

Tools > Overlay Info in the upper Menu



EXPO opens the following window:

Overlay Info

| Matches | | | | | | |
|---------|-------------|--------|-------|----------|------|----------------------|
| Atom | Coordinates | | | Distance | Atom | x,y,z (clomipra.fra) |
| Cl1 | 0.551 | 0.232 | 0.353 | 0.127 | Cl1 | 0.547 0.220 0.353 |
| Cl2 | 1.024 | 0.385 | 0.695 | 0.086 | Cl2 | 1.029 0.388 0.693 |
| N1 | 0.597 | 0.415 | 0.612 | 0.223 | C19 | 0.584 0.423 0.610 |
| N2 | 0.460 | 0.210 | 0.592 | 0.234 | C18 | 0.465 0.236 0.593 |
| C1 | 0.779 | -0.004 | 0.584 | 0.166 | N1 | 0.788 -0.013 0.581 |
| C2 | 0.742 | -0.083 | 0.388 | 0.104 | C6 | 0.746 -0.074 0.386 |
| C3 | 0.760 | -0.359 | 0.420 | 0.105 | C7 | 0.761 -0.361 0.427 |
| C4 | 0.793 | -0.452 | 0.576 | 0.257 | C9 | 0.806 -0.444 0.587 |
| C5 | 0.871 | 0.124 | 0.452 | 0.266 | C13 | 0.876 0.096 0.460 |
| C6 | 0.959 | 0.174 | 0.435 | 0.312 | C4 | 0.944 0.192 0.443 |
| C7 | 0.823 | 0.002 | 0.377 | 0.152 | C5 | 0.829 0.014 0.373 |
| C8 | 0.980 | 0.284 | 0.592 | 0.267 | C2 | 0.968 0.273 0.603 |

Distance limit: 0.600 Select model: clomipra.fra

Results

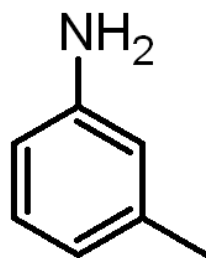
Atoms in clomipra: 23
Atoms in clomipra.fra: 23
Matches found: 23
Mean Phase Error: 21.032 using 659 reflections
<Dist>: 0.177
RMSD: 0.042

Cancel

All the 23 atoms in the asymmetric unit are rightly positioned, some labelling errors occur and they can be corrected by graphic interface.

- **NO_DEFAULT** folder

It contains: **lefebvre.exp** [the input file for a non-default indexing run of *N-TREOR09* in case of 3-methylbenzenamine (*m*-Toluidine) - (C_7H_9N)]; the non-default directive 'nix=3' has been introduced]; **lefebvre.pow** (the file containing the experimental profile counts); **lefebvre.fra** (the file of the fractional coordinates of the true model, hydrogen atoms excluded); **lefebvre.pdf** (the article in which the structure is cited).



The input file 'lefebvre.exp' consists of the following lines:

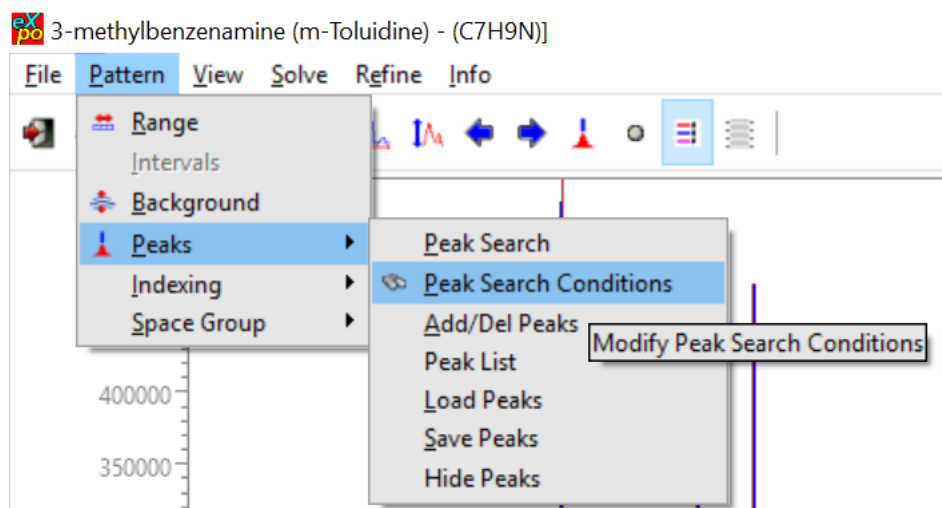
```
%Structure lefebvre
%Job 3-methylbenzenamine (m-Toluidine) - (C7H9N)
%Data
Pattern lefebvre.pow
Wavelength 1.54056
%Ntreor
nix=3,
%Continue
```

By a default indexing run (*i.e.*, if the directive 'nix=3' is removed in the 'lefebvre.exp' input file), it can be verified that *EXPO* is not able to find the correct monoclinic cell (published cell parameters: $a = 24.8727 \text{ \AA}$, $b = 5.8073 \text{ \AA}$, $c = 8.7615 \text{ \AA}$, $\beta = 100.062^\circ$).

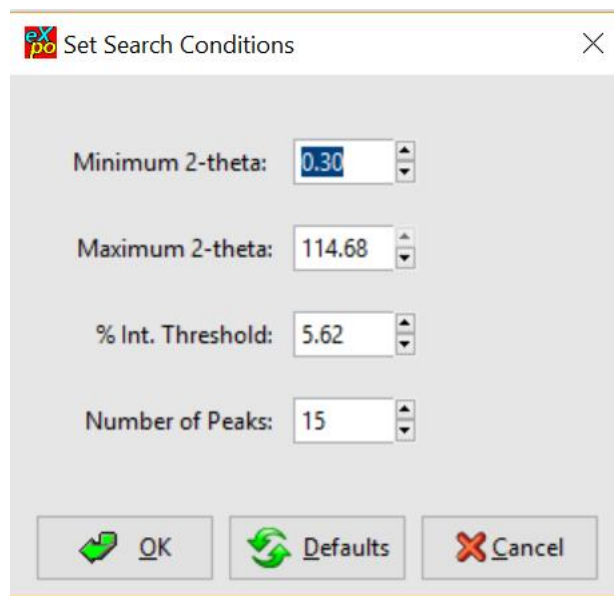
One of the possible reasons of an indexing failure is the presence of peaks due to an impurity and belonging to the set of peaks automatically located by *EXPO* for the unit cell determination.

In case of **lefebvre**, the authors assumed the presence of a minority phase and succeeded in indexing the powder pattern by selecting only 15 largest intensity peaks among the experimental ones.

A default indexing process (*i.e.*, the directive 'nix=3' is not introduced in the input file) can be tried by *EXPO* by exploiting a similar not default peak selection, *i.e.*, by changing *via* graphical interface the peak-search conditions, selecting **Pattern > Peaks > Peak Search Conditions** in the upper Menu



and modifying the 'Number of Peaks' to be located (*i.e.*, 15)



If this non-default peak search is tried, EXPO will be able to find the correct cell by a default indexing procedure.

Alternatively, in case of indexing failure due to the presence of a minority phase, it can be tried a non-default indexing approach, without changing the default peak-search conditions, by introducing in the EXPO input file the directive '`nix=n`' of the '`%ntreor`' command, to increase the allowed number of unindexed lines (`nix`) from 1 (*i.e.*, the default value for N-TREOR09) to n ($n > 1$).

In case of **lefebvre**, the introduction of the directive '`nix=3`' in the EXPO input file enables to find the correct cell.

To run EXPO on **lefebvre**, in order to index the powder pattern by a non-default run of N-TREOR09:

- Click on EXPO icon
 - **File** in the upper Menu
 - **Load and Go**
 - Use '`lefebvre.exp`' as Input File and give the Output Filename you like (`lefebvre.out` is the default output file name)
 - **Go**
The powder diffraction pattern is visualized.
 - Click on **Next**
The peak-search step is automatically carried out. The peak positions are marked by vertical red bars.
- At the end of the indexing procedure the following window will appear:

Plausible cell parameters

Select cell

| Nr. | Prog. | a | b | c | alpha | beta | gamma | Vol. | M20 | FOMnew | Mc20 | shift | NIX | Symmetry Info |
|-----|-------|----------|----------|----------|--------|---------|--------|--------|-------|--------|------|--------|-----|---------------|
| 1 | N | 24.83338 | 5.80944 | 8.74583 | 90.000 | 100.104 | 90.000 | 1242.2 | 12.00 | 0.687 | - | 0.000 | | 2 P 1 21/c 1 |
| 2 | N | 10.71777 | 24.48799 | 5.99604 | 90.000 | 101.835 | 90.000 | 1540.2 | 11.00 | 0.473 | - | 0.040 | | 2 P 1 21 1 |
| 3 | N | 32.45689 | 6.08640 | 12.53210 | 90.000 | 95.843 | 90.000 | 2462.8 | 11.00 | 0.310 | - | -0.040 | | 3 P 1 _ 1 |

OK Cancel Export

The first ranked cell is the correct one and, if it is selected (default choice), EXPO will be able to solve the crystal structure.

To verify it, the following steps should be carried out:

- Click on **OK**;
- Provide the unit cell content '(C₇H₉N)₈';
- Click on **OK**;
- Click on **Next** button to go on continuously until the space group determination process is carried out;
- Click on **OK** to select the Space Group 'P 21/c' first ranked in the list (the file 'lefebvre1.exp' is created);
- Click on **OK**;
- Click on **Next** button to go on continuously until the end of the run.

The structure model obtained at the end of Direct Methods procedure, executed on the first set of phases (default choice), is not interpretable, the rest of stored sets of phases can be explored in order to find the correct structure model (for more details, see the 'Readme solution by Direct Methods.docx' file available at the 'Solution by Direct Methods' folder):

- Select **Solve > Explore Trials** in the main Menu;
- Select by check button the option '**Explore trials not processed yet**'.

At the end of the procedure the twenty available structure models are ranked according to increasing RF values; the first ranked structure model is partially correct, the second and third ranked models, except for some labelling errors, are correct (it can be verified by comparing, by graphic interface, the structure models with the published one stored in the **lefebvre.fra** file).