Entropy rules!

Disorder

Squeeze

- What is disorder
- Warning signs of disorder
- Constraints and restraints in SHELXL
- Using restraints to refine disorder
- How to find the positions of disordered atoms
- Disorder or no disorder?

Disorder

A disorder is a violation of the crystal symmetry and translation. The content of the asymmetric units is not identical, but it is identical on average.

The obtained structure is an overlay, an average of all asymmetric units.

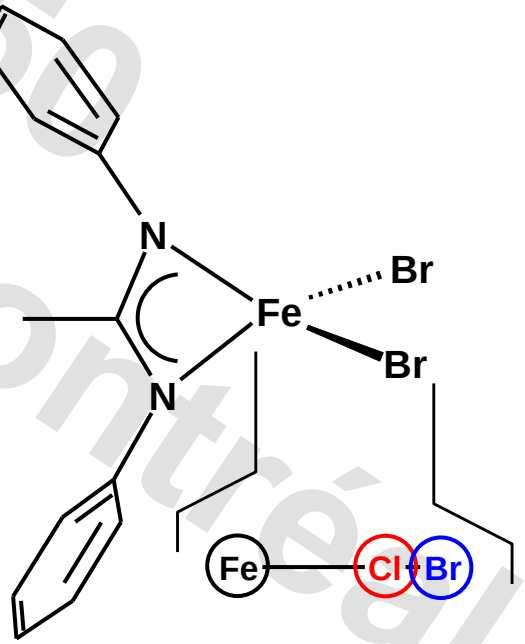
Types of disorder:

1. **Substitutional disorder**

   A crystallographic position is occupied by more than one type of atom. This situation might occur often in :

   - Compounds obtained by ion exchange
   - Minerals or ionic crystals (f. e. in zeolithes Si and Al share the same position)
   - Macromolecular compounds: Often water and sodium are found on the same position.

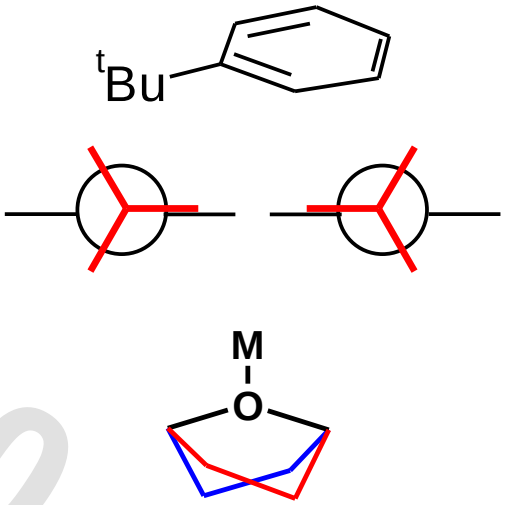
   The disordered atoms might be found exactly on the same position or slightly displaced from each other.



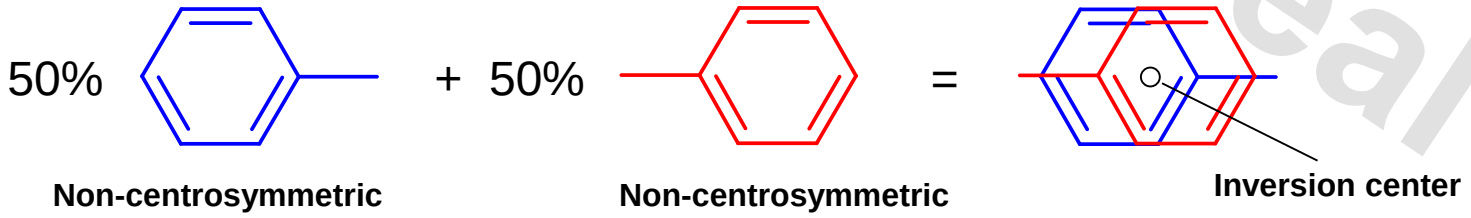
Types of disorder

2. Positional disorder

An atom might be found in more than one position.
Typical examples are:



- **Rotational disorder:** A group with rotational freedom might be found in two different rotatmers. A typical example is the *tert*-butyl group.
- **Pseudorotational disorder:** Saturated cycles might also be found in two conformations next to each other. THF is a typical example.
- **Whole molecule disorder:** Most often found for co-crystallised solvents, especially if they are found around a symmetry element. The disorder assures that the crystal symmetry is kept in average, even if the solvent molecule itself does not contain this symmetry. Whole molecule disorder of the complete structure is a controversial subject and might often be a result of another effect (twinning, wrong space group etc.)



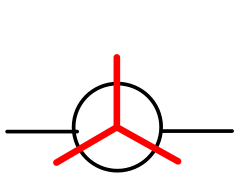
Types of disorder

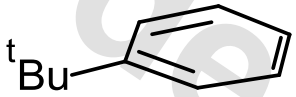
Static disorder: Atoms do not change their position during data collection (substitutional disorders are (normally) static disorders).

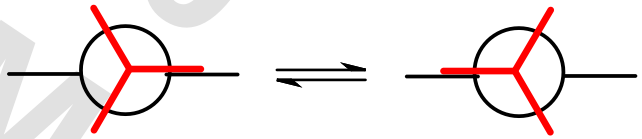
Dynamic disorder: During data collection the atoms migrate between their respective positions.

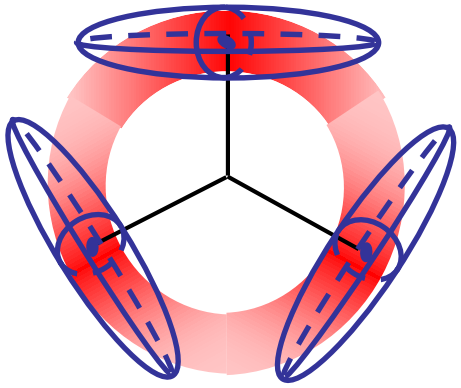
Static and dynamic disorders are treated identically during refinement.

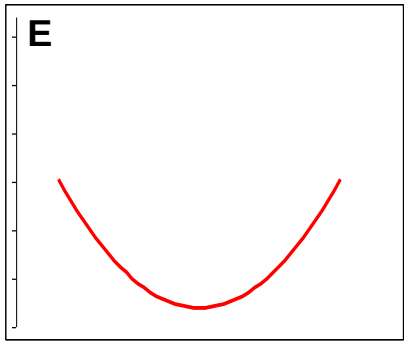
Strong thermal motion: Due to the limitations of the model, strong thermal motion is sometimes better treated as disorder, since this yields the better description.

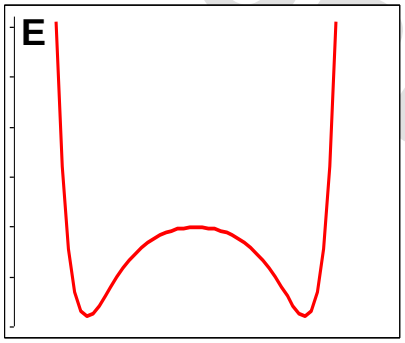


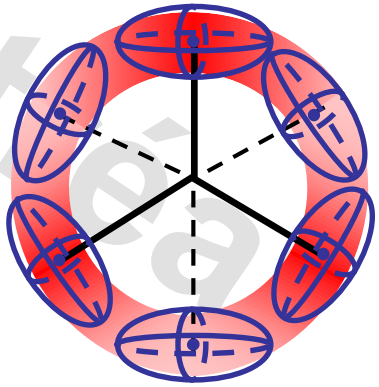








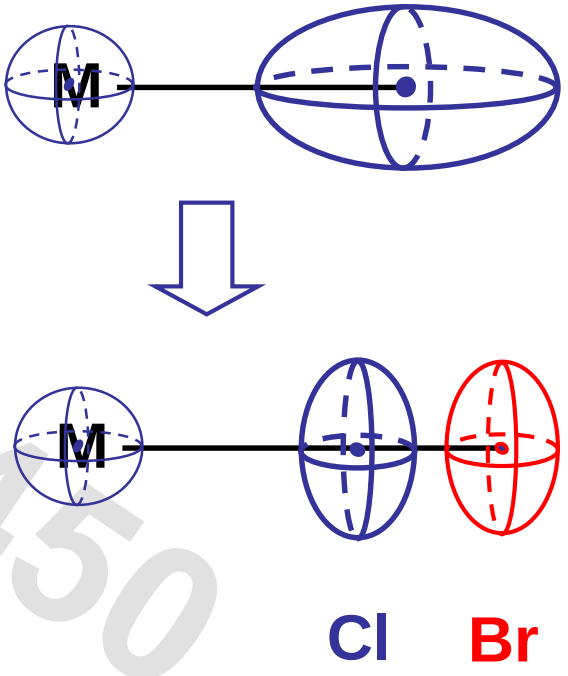




Warning signs of disorder

1. Substitutional disorder

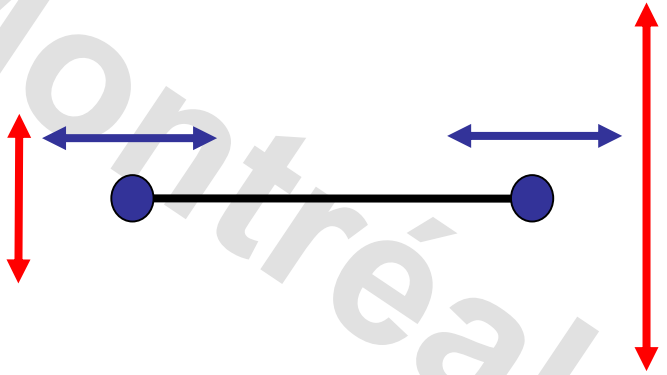
- a thermal factor too big or too small,
- orientation of the ellipsoid parallel to a bond, and/or
- an incorrect bond distance
- CHECKCIF: Hirshfeld test violation



Hirshfeld rigid-bond test

Anthony L. Spek (author of PLATON), Acta Cryst. (2009). D65, 148–155

"The Hirshfeld rigid-bond test (Hirshfeld, 1976) has proved to be very effective in revealing problems in a structure. It is assumed in this test that two bonded atoms vibrate along the bond with approximately equal amplitude. **Significant differences, i.e. those which deviate by more than a few standard uncertainties from zero, need close examination.** Notorious exceptions are metal-to-carbonyl bonds, which generally show much larger differences (Braga & Koetzle, 1988)."

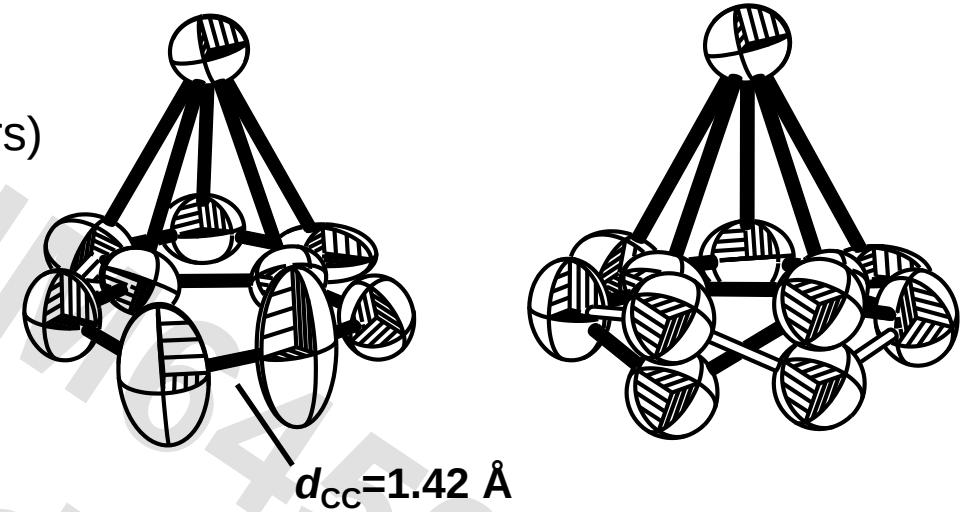


Hirshfeld, F. L. (1976). Acta Cryst. A32, 239–244.
Braga, D. & Koetzle, T. F. (1988). Acta Cryst. B44, 151.

Warning signs of disorder

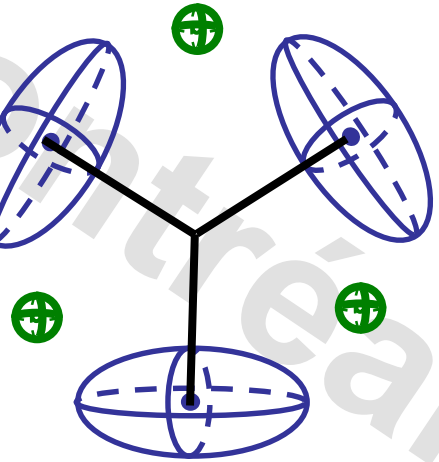
2. Pseudorotational disorder

- Increased (compared to neighbours) thermic ellipsoids
- Shortened C-C distances
- Flattened saturated carbocycles



3. Rotational disorder

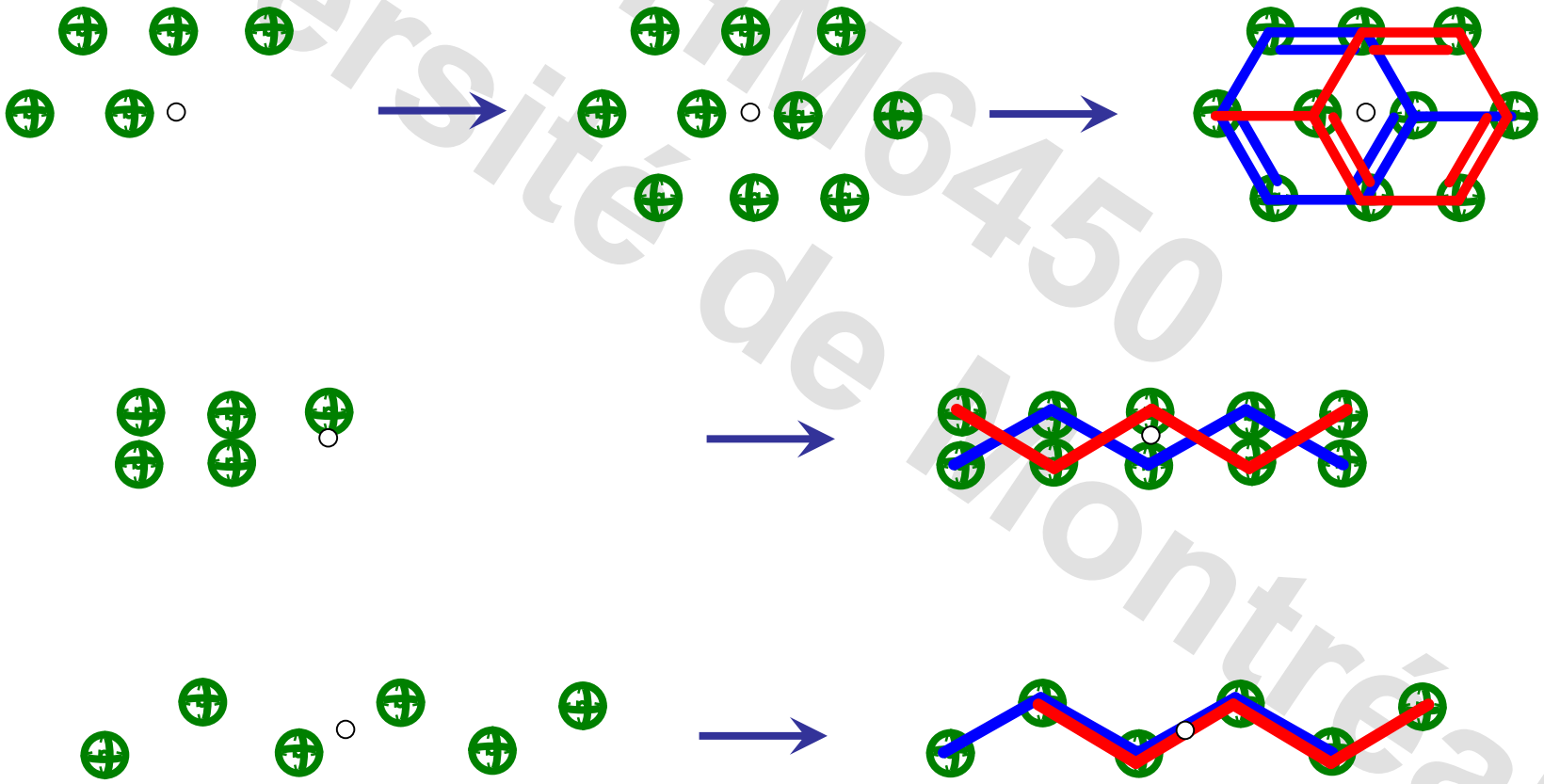
- Increased thermal ellipsoids
- Electron density present between the refined atom positions



Warning signs of disorder

4. Whole molecule disorder of solvent

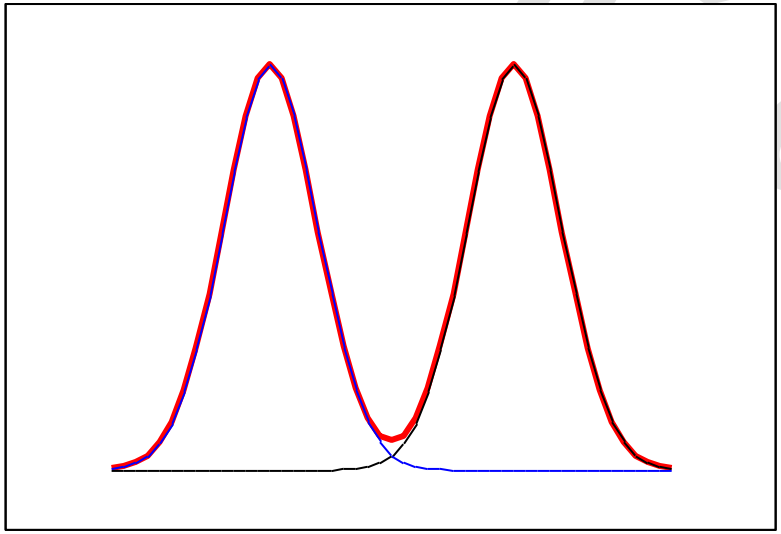
- Symmetric distribution of electron density around a symmetry element



Treating disorder

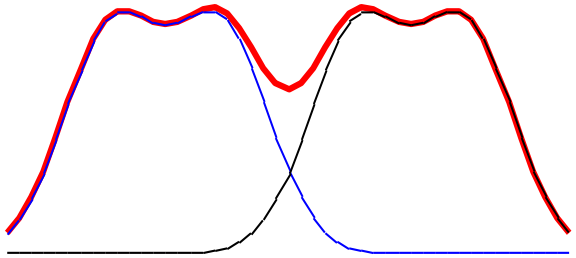
A disorder is a distribution of an atom over several positions or the sharing of a position by several atoms. In both cases, we are dealing with overlapping atoms of reduced electron density, which do not yield well defined maxima in the electron density map. Disorder refinement is thus always done using restraints.

We want to use the smallest number and weakest restraints possible, but do not hesitate to use them in big numbers to avoid obtaining dubious results.



Disorder:

- lower electron density per disordered atom
- smaller distances between atoms



Additional sources:

- Peter Müller, *Crystal Structure Refinement: A Crystallographer's Guide to SHELXL* Oxford University Press **2006**.
- Peter Müller's small disorder tutorial: http://shelx.uni-ac.gwdg.de/~peterm/tutorial/disord.htm

Constraints and restraints

Constraint: Exact mathematical condition, which results in a reduction of the number of parameters. A constraint cannot be violated. Example: rigid groups and “riding” hydrogen atoms.

Restraint: Additional observations/restraints which are added to the data during refinement. Restraints can be violated to a certain degree.

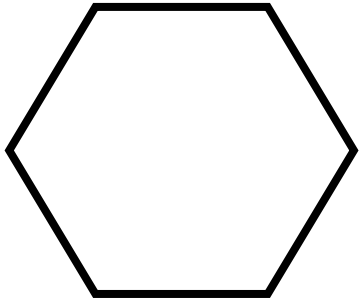
$$M = \sum w_x(F_o^2 - F_c^2)^2 + \sum w_r(T_{target} - T_c)^2$$

Both, constraints and restraints increase the data/parameter ratio.

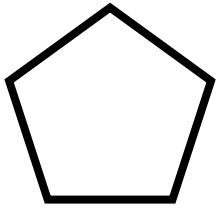
Types of constraints used in the SHELX program package

- **Special positions** (generated automatically)
- **Rigid groups (e. g. AFIX x6 … AFIX 0)**

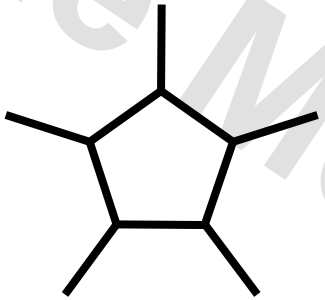
In rigid groups the parameters for all atomic positions (3 x n) are replaced by 3 rotations and 3 translations for the complete group. The idealized geometry of the group is fixed and the atoms cannot move independently. *AFIX x**6***: completely rigid group; *AFIX x**9***: group can grow and shrink keeping its relative geometry.



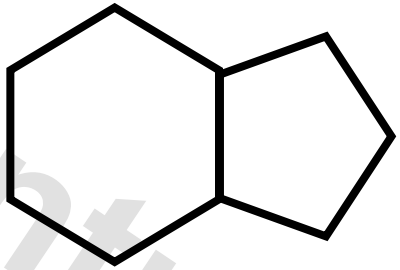
AFIX 66
C1 x y z
:
C6 x y z
AFIX 0



AFIX 56
C1 x y z
:
C5 x y z
AFIX 0



AFIX 106
C1 x y z
:
C10 x y z
AFIX 0



AFIX 116
C1 x y z
:
C11 x y z
AFIX 0

Types of constraints used in the SHELX program package

- **Special positions** (generated automatically)
- **Rigid groups (e. g. AFIX x6 … AFIX 0)**
- **“Riding model” for hydrogen atoms (AFIX mn)**
- **Fixed parameters**

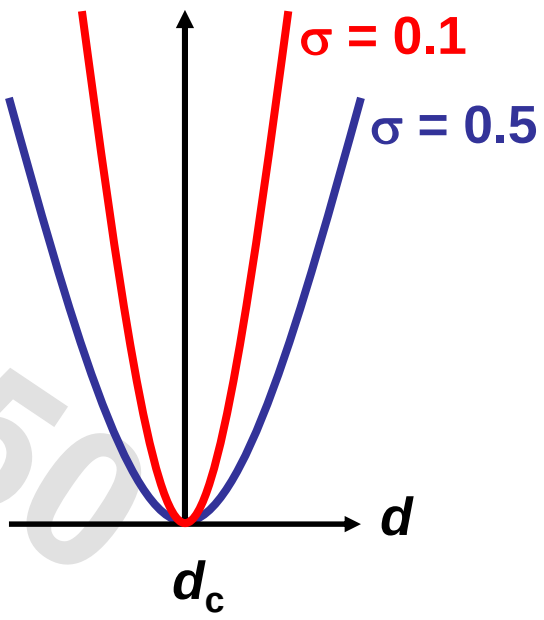
Addition of 10 excludes a value from the refinement.

Normally occupation factors are not refined.

```
C1    1   0.31357   0.46194   0.73087  11.00000   0.03221   0.02339 =
       0.02334   0.00728   0.00820   0.00568
C2    1   0.17696   0.50000   0.65307  10.50000   0.03174   0.02909 =
       0.02961   0.01051   0.00909   0.00550
C3    1   0.13022   0.26106   0.57225  10.50000   0.03871   10.025
```

Restraints

In contrast to constraints, which cannot be violated, restraints define only a target value for some parameters. They are associated with a standard deviation σ, which describes how much a violation of the target value is penalised. The smaller σ, the more the parameter is forced to be close to the targeted value d_c. A σ = 0 yields a constraint.



$$M = \Sigma\, w_x(F_o^2 - F_c^2)^2 + \Sigma\, 1/\sigma\,(d - d_c)^2$$

Restraints in SHELX

DFIX, DANG, SADI, SAME: distances and angles (1,3-distances)

DELU, SIMU, ISOR, RIGU: thermal motion parameters

FLAT, CHIV, BUMP, NCSY, SUMP

Free variables

In SHELXL, each value is provided in the form of ***x* = 10*m* + *p*.**

p: value, which is refined; *m*: refinement mode

m* = 0: normal refinement, *x* = *p

m* = 1: no refinement, *x* is fixed at *p

***m* > 1: *x* = *p* · "free variable no. *m*"**

***m* <-1: *x* = *p* · (1 - "free variable no. *m*")**

The same value is refined for all three atoms

```
FVAR          0.73503  0.0239   0.2365
C1     1    0.31357    0.46194    0.73087   11.00000    21.00000
C2     1    0.17696    0.39844    0.65307   11.00000    21.00000
C3     1    0.13022    0.26106    0.57225   11.00000    21.00000
CL1    2    0.25000    0.17682    0.50000   31.00000     0.05684
Br1    3    0.25000    0.19763    0.50000  -31.00000     0.05110
```

Using the m<-1 option, a ratio can be defined with a fixed sum of the two variables:

31.000 + -31.0000 = 1
30.500 + -30.5000 = 0.5

(10*m*)*p* + (-10*m*)*p* = *p*
Free variable no. *m*, targetvalue *p*

How to use restraints to refine disorder

1. Position restraints

Restraints are never directly on a position, but always on interatomic distances and thus molecule geometry.

SHELX does not offer angle restraints. Restraints on angles have thus to be effected by restraining the 1,3-distances of the atoms.

DFIX d sd <atome 1> <atome 2> <atome 3> <atome 4> …

Fixation of an interatomic distance between a pair (or pairs) of atoms to a specific value *d* with a standard deviation *sd* (default, if omitted).

I discourage the excessive use of DFIX restraints, since they impose a bias/preconception on the structure. There are, however, occasions where the use of DFIX restraints is appropriate.

Restraints in SHELXL

SADI sd <atome 1> <atome 2> <atome 3> <atome 4> …

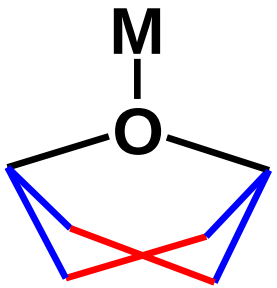
Interatomic distances between pairs of atoms are restraint (with standard deviation *sd*, which can be omitted) to be equal. The actual value of these distances is free to refine.

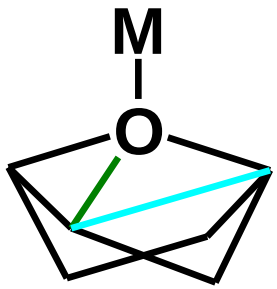
SADI is the most useful restraint for refining disorders. Without inflicting a preconception on the value of a distance, we can safely use our chemical/crystallographic knowledge to decide that two or more bonds should have identical values (in the margin of error of the provided standard deviation).

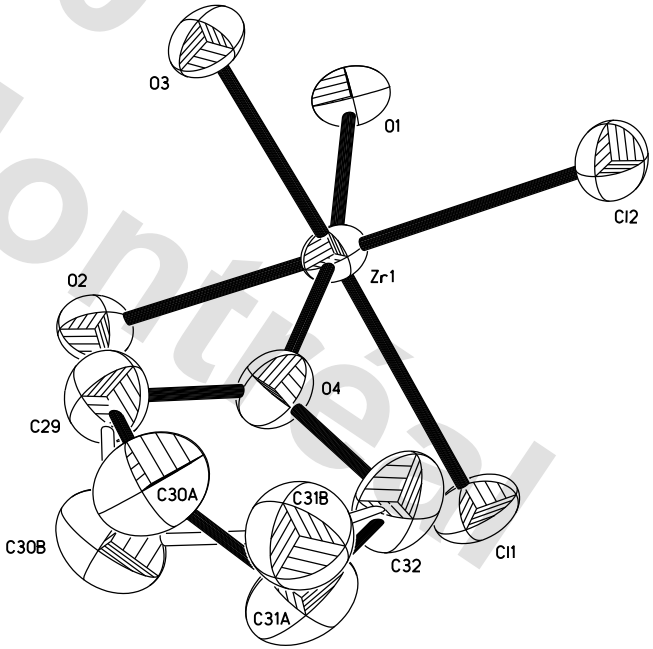
The SAME command allows us to generate a multitude of SADI instructions with a single line.

SADI C29 C30A C29 C30B C32 C31A C32 C31B
SADI C30A C31A C30B C31B

SADI O4 C30A O4 C30B O4 C31A O4 C31B
SADI C32 C30A C32 C30B C29 C31A C29 C31B







SAME command

SAME O4 C29 C30B C31B C32
SAME O4 C32 C31B C30B C29

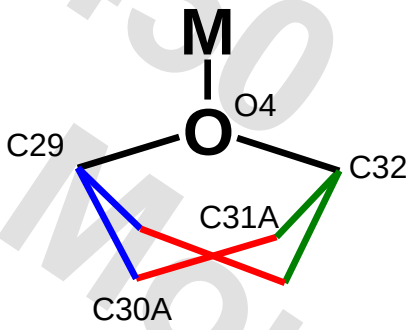
```
O4      3   0.30266   -0.00504   -0.11751   [...]
C29     1   0.19024   -0.06291   -0.13854   [...]
C30A    1   0.12758   -0.13129   -0.06586   [...]
C31A    1   0.27046   -0.15492   -0.01832   [...]
C32     1   0.34071   -0.05601   -0.04205   [...]
```

It is very important to have the atoms in the required order!

Typographic errors here are fatal!

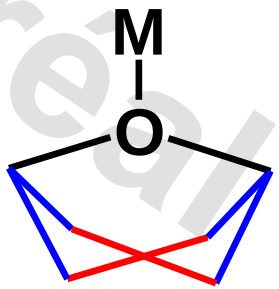
SADI C29 C30A C29 C30B
SADI C32 C31A C32 C31B
SADI C30A C31A C30B C31B

SADI O4 C30A O4 C30B
SADI O4 C31A O4 C31B
SADI C32 C30A C32 C30B
SADI C29 C31A C29 C31B



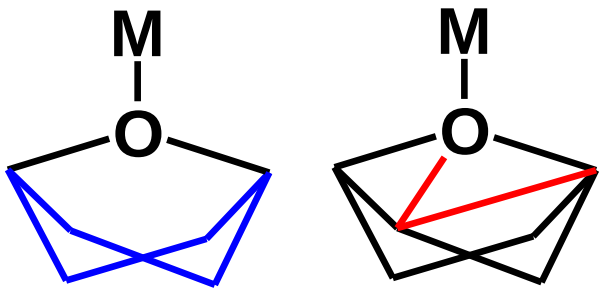
SADI C29 C30A C29 C30B C32 C31A C32 C31B
SADI C30A C31A C30B C31B

SADI O4 C30A O4 C30B O4 C31A O4 C31B
SADI C32 C30A C32 C30B C29 C31A C29 C31B



SADI …continued

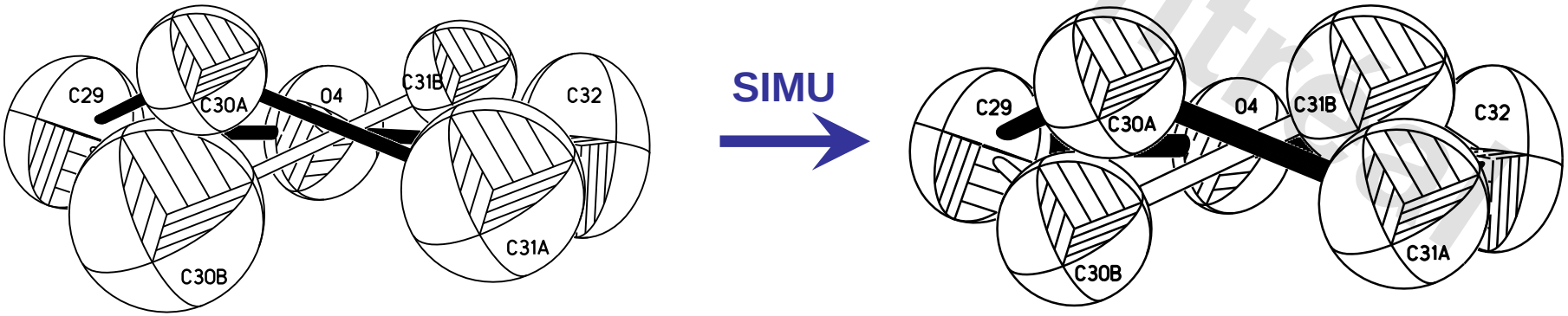
SADI C29 C30A C29 C30B C32 C31A C32 C31B =
C30A C31A C30B C31B
SADI O4 C30A O4 C30B O4 C31A O4 C31B =
C32 C30A C32 C30B C29 C31A C29 C31B



This starts to violate chemical knowledge about equivalent bonds and should only be done for bad data.

2. Thermal factor restraints

SIMU sd1 sd2 dmax[1.7] <atomlist, ***all atoms if omitted***>
Superimposed atoms share their electron density. There is thus a linear dependence between their thermic factors and their occupation factor. In cases of disorder, a command **SIMU 0.04 0.08 0.9** has to be **always present**. It ensures that superimposed atoms (distance < 0.9 Å) have identical thermal parameters and enables the refinement of their occupation.



SIMU and DELU

Anisotropic refinement: SIMU restraints for superimposed atoms can be accompanied by restraints DELU and/or SIMU for **neighbouring atoms**.

SIMU C29 C30A C30B C31A C31B C32

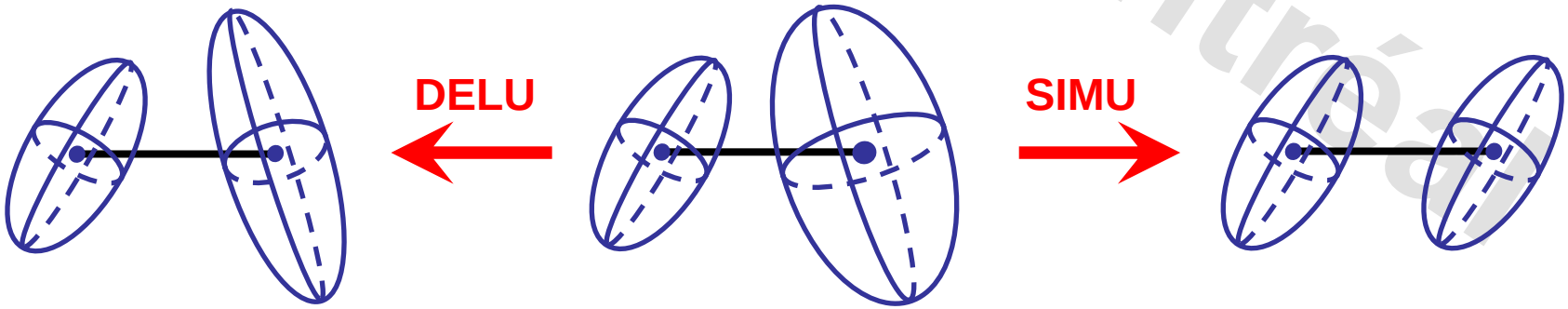
DELU C30A C31A
DELU C30B C31B

or

SIMU C30A C31A C30B C31B

SIMU (without further values specified) uses a default distance of 1.7 Å, below which restraints are applied. In contrast to SIMU 0.04 0.08 0.9, we thus have to specify the atoms to which we apply the restraint. Otherwise it is applied to the whole structure. You can also include neighbouring non-disorderd atom in a SIMU or DELU command as an “anchor” for the ellipsoid.

SIMU: Equivalence of all thermal factors
DELU: Equivalence of the thermal factors parallel to a bond (c. f. Hirshfeld test)

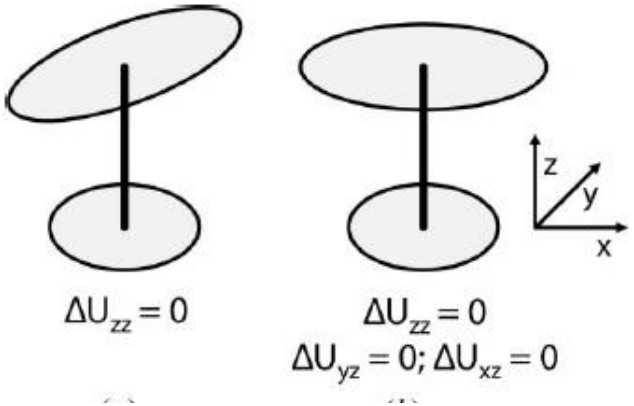


RIGU

RIGU is the newer version of the DELU restraint. RIGU can be applied to a whole group of atoms and will apply appropriate restraints on atoms in 1,2- and 1,3-distance.

The DELU restraint just enforces that the motion parallel to the bond is identical for both atoms. The RIGU restraint also enforces that the thermal motion is perpendicular to the bond.

DELU **RIGU**



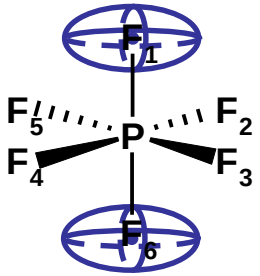
Thorn, Dittrich, Sheldrick, *Acta Cryst.* **2012**, *A68*, 448-451

Please do not apply DELU to every atom pair showing Hirshfeld test violation in CHECKCIF! As we have discussed, motions of a whole chemical group can cause seeming Hirshfeld test violations, but are nevertheless correct thermal motions.

EADP and ISOR

EADP <atoms>

- The same anisotropic parameters are used for all atoms
- Useful, par ex. for opposite fluorines in PF_6^- or disordered CF_3



EADP F1 F6

EADP is a powerful constraint but should be used only exceptionally. There is in most cases no good reason why two independent atoms should have the same anisotropic parameters.

ISOR

- Forces the anisotropic parameters to become more isotropic
- Last resort for **non-positive definite** atoms

Non-positive definite: An atom is called “non-positive definite”, if at least one of its radii refined to an negative value (which of course does not make any physical sense). Non-positive definite atoms indicate severe problems, very often wrong atom assignments or low data-parameter ratios. **These problems have to be addressed!** Use of an ISOR restraint is acceptable as a last resort **only**, when we can define the source of the problem and its not a structural one, other measures were unsuccessful (i. e. SIMU restraints) and we comment on this clearly in the manuscript text and the CIF.

XNPD

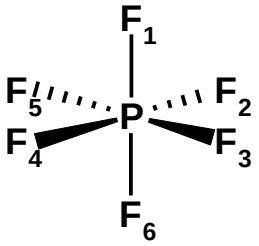
One problem of non-definite atoms is that they might cause the refinement to explode, thus preventing you from improving your solution and ultimately take care of the problem.

XNPD still allows the refinement of the thermal parameters to negative values, but limts them to -0.001. This allows the program to report an atom as non-positive definite, but it will not negatively influence the refinement by refining against large negative values.

Example for using restraints

Example PF_6^-: Due to their nearly spherical nature PF_6 anions are often found disordered or at least showing high thermal parameters indicating not well localized atoms. In these cases refinement with restraints is often necessary, when the geometry of the anions becomes unreasonable. (I. e. variations of more than 10% in P-F bond lengths.)

```
SADI P1 F1   P1 F2   P1 F3   P1 F4   P1 F5   P1 F6
SADI F1 F2   F1 F3   F1 F4   F1 F5   F2 F3   F2 F6  =
     F2 F5   F3 F6   F3 F4   F5 F6
SADI F1 F6   F2 F4   F3 F5
EADP F1 F6
EADP F2 F4
EADP F3 F5
```




```
P1    4     0.424356    -0.021611     0.009848    10.50000     0.06381     0.03516 [...]
F1    5     0.327987     0.417746     0.265512    11.00000     0.06119     0.06335 [...]
F2    5     0.385421     0.357821     0.166673    11.00000     0.05997     0.06456 [...]
F3    5     0.265277     0.346163     0.220067    11.00000     0.06713     0.07757 [...]
F4    5     0.519635     0.310843    -0.088822    11.00000     0.06978     0.07860 [...]
F5    5     0.545683     0.299782     0.052783    11.00000     0.05744     0.07086 [...]
F6    5     0.587478     0.232770     0.100987    11.00000     0.06598     0.07993 [...]
```

Often several SADI commands might be replaced by one SAME command. E. g. a **SAME P1 F2 F3 F6 F5 F1 F4** before P1 replaces all SADI commands. Feel free to use SAME, but do not overdo it with complicated examples, since this has a high risk of errors.

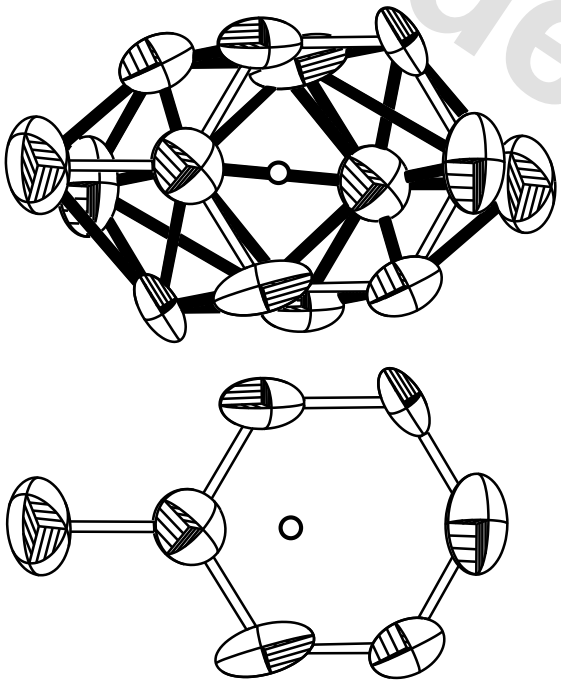
PART

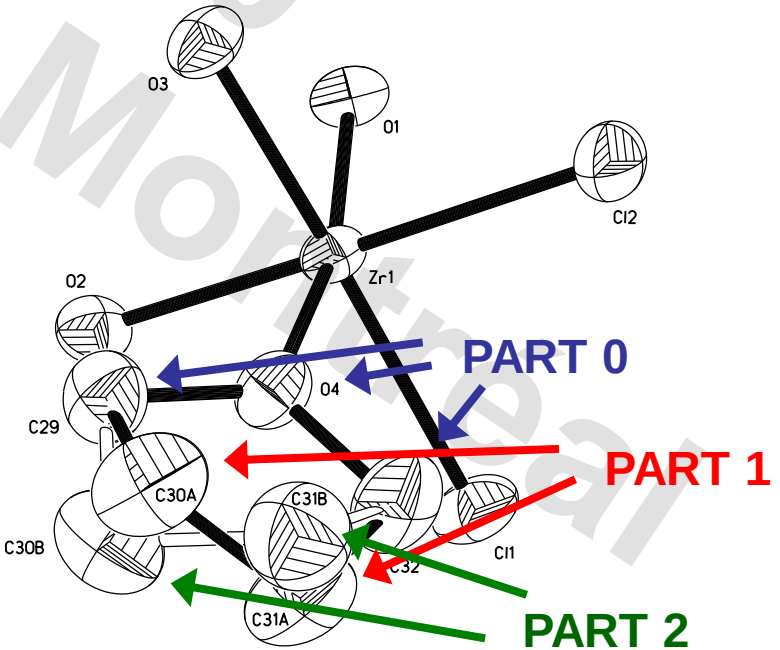
PART n

- Not a restraint
- No influence on the refinement
- Influence on the connectivity list
- **n > 1** : Atoms with this part number can be bonded to all other atoms with PART number n and all atoms with n=0.
- **n < 0** : Atoms can be bonded to all atoms with PART 0 and PART n, but not to those generated by a symmetry operation.
- Avoids unnecessary bonds in molecular drawings
- essential if AFIX is used for hydrogen atoms in disordered groups

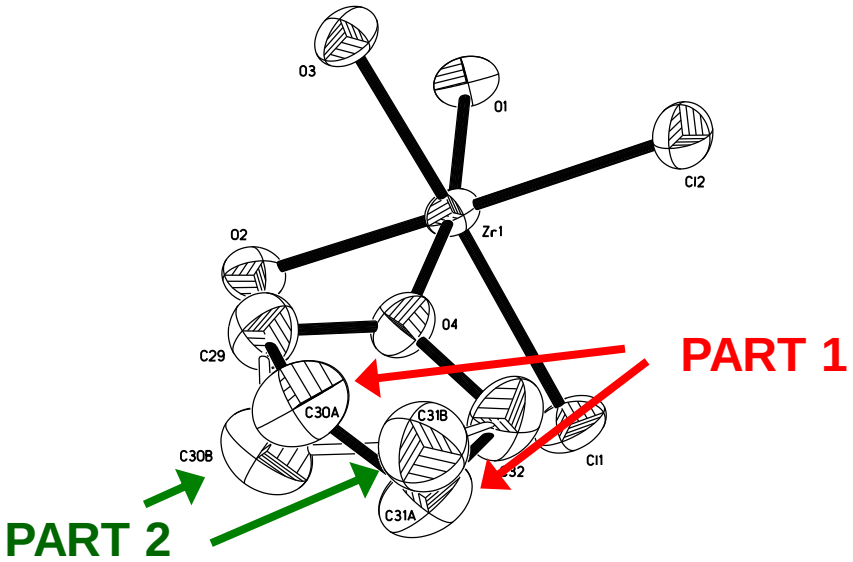
PART 1

PART -1





```
FVAR       0.42837   0.58208
[...]
O4    3    0.302705    -0.005024    -0.117529    11.00000    0.03588    0.04172 =
          0.02975    -0.00291    -0.00309    -0.01165
C29   1    0.190224    -0.062926    -0.138556    11.00000    0.04345    0.05179 =
          0.05469    -0.01254    -0.00430    -0.02030
PART 1
C30A  1    0.127840    -0.130979    -0.065373    21.00000    0.05283    0.06736 =
          0.07186     0.00717     0.00151    -0.02926
C31A  1    0.274211    -0.156883    -0.019306    21.00000    0.05632    0.05613 =
          0.05575    -0.00802    -0.00165    -0.01273
PART   2
C30B  1    0.191961    -0.163582    -0.084484   -21.00000    0.05715    0.05259 =
          0.07274    -0.01448     0.01353    -0.02752
C31B  1    0.208671    -0.126727    -0.015288   -21.00000    0.05579
PART   0
C32   1    0.340691    -0.056023    -0.042066    11.00000    0.07080    0.06487 =
          0.02841     0.00483    -0.00617    -0.02682
```



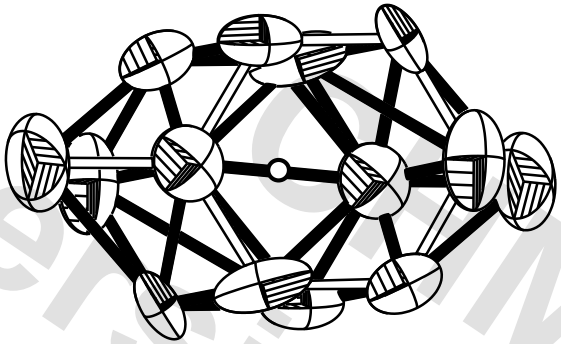
Error message: BAD AFIX connectivity. C29 bound to 3 atoms.

Make sure to use PART also for your AFIX commands on the atoms bound to disordered atoms:

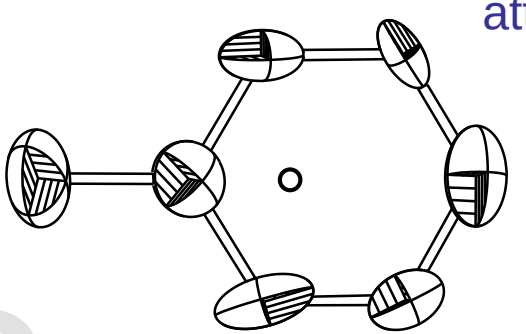
```
C29  ...
PART 1
AFIX 23
H29A 2 u v w 21.000 -1.2
H29B 2 u v w 21.000 -1.2
AFIX 0
PART 2
AFIX 23
H29C 2 u v w -21.000 -1.2
H29D 2 u v w -21.000 -1.2
AFIX 0
PART 0
```

Occupation factor

Thermal parameters need attention!



PART 1



PART -1

Disordered toluene

```
PART  -1
C20   1    0.424356   -0.021611    0.009848   10.50000    0.06381    0.03516 =
         0.05315   -0.00588    0.00671   -0.00304
C21   1    0.428540    0.011059   -0.068300   10.50000    0.06186    0.05445 =
         0.03609    0.00542   -0.01401    0.00890
[...]
C24   1    0.634868    0.025612    0.045748   10.50000    0.04323    0.05896 =
         0.04699   -0.00149   -0.01253    0.00164
C25   1    0.530284   -0.013916    0.066481   10.50000    0.05856    0.06452 =
         0.04128   -0.01875   -0.02223    0.02545
C26   1    0.312605   -0.062961    0.030505   10.50000    0.09882    0.09599 =
         0.07637   -0.00566    0.01279   -0.06335
PART 0
```

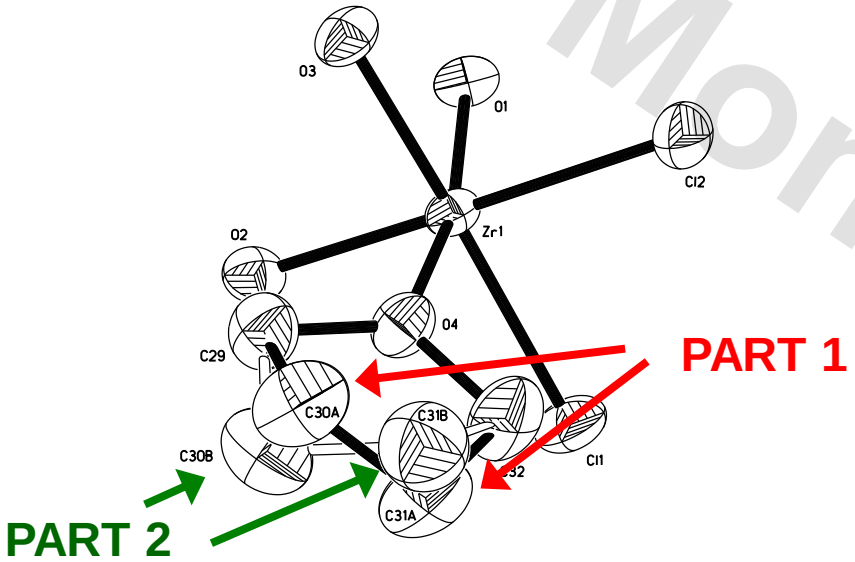
Occupation factor

```
FVAR       0.42837   0.58208
[...]
O4    3    0.302705   -0.005024   -0.117529    11.00000    0.03588    0.04172 =
          0.02975   -0.00291   -0.00309   -0.01165
C29   1    0.190224   -0.062926   -0.138556    11.00000    0.04345    0.05179 =
          0.05469   -0.01254   -0.00430   -0.02030
PART 1
C30A  1    0.127840   -0.130979   -0.065373    21.00000    0.05283    0.06736 =
          0.07186    0.00717    0.00151   -0.02926
C31A  1    0.274211   -0.156883   -0.019306    21.00000    0.05632    0.05613 =
          0.05575   -0.00802   -0.00165   -0.01273
PART   2
C30B  1    0.191961   -0.163582   -0.084484   -21.00000    0.05715    0.05259 =
          0.07274   -0.01448    0.01353   -0.02752
C31B  1    0.208671   -0.126727   -0.015288   -21.00000    0.05579
PART   0
C32   1    0.340691   -0.056023   -0.042066    11.00000    0.07080    0.06487 =
          0.02841    0.00483   -0.00617   -0.02682
```

Disordered THF

= 1.000* FVAR #2 = 0.58208

= 1.00*(1-FVAR #2) = 0.41792



How to find the positions of disordered atoms?

1. Warnings in the output file .lst

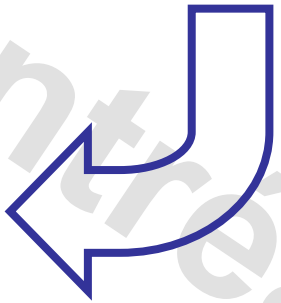
```
*.lst:
 Principal mean square atomic displacements U
[…]
   0.3098    0.0893    0.0464    C4     may be split into  0.6218  0.2673  0.2408  and  0.6118  0.2471  0.2666
   0.3100    0.0924    0.0392    C5     may be split into  0.5976  0.3191  0.3424  and  0.5834  0.3017  0.3597
```

*.res:

C4 1 0.620102 0.244385 0.267042 11.00000 0.03885 0.06703 =
0.03096 0.00488 -0.00631 -0.00106
C5 1 0.592263 0.310218 0.343259 11.00000 0.03679 0.05091 =
0.04370 0.01162 -0.00769 0.00426

*.ins:

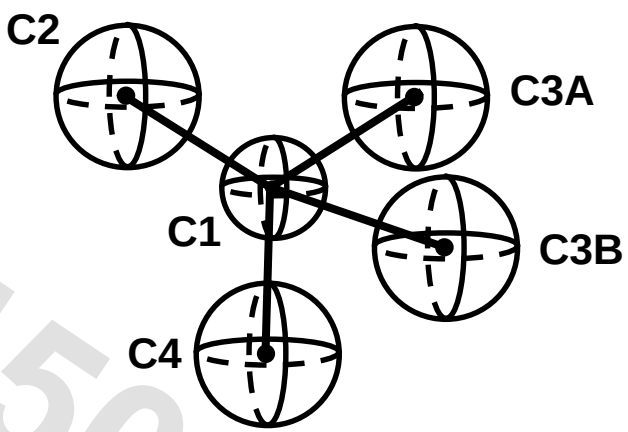
FVAR 0.293 **0.4**
[…]
PART 1
C4A 1 **0.6218 0.2673 0.2408 21.00000** 0.04
C5A 1 **0.5834 0.3017 0.3597 21.00000** 0.04
PART 2
C4B 1 **0.6118 0.2471 0.2666 -21.00000** 0.04
C5B 1 **0.5976 0.3191 0.3424 -21.00000** 0.04
PART 0



How to find the positions of disorderd atoms?

2. Inforce the refinement starting from the original positions using restraints

```
C1   1   0.519760   0.310792   -0.089059   11.00000   0.06836
C2   1   0.545505   0.299615    0.052950   11.00000   0.05727
C3A  1   0.587307   0.232816    0.100964   11.00000   0.06729
C4   1   0.621837   0.265112    0.234704   11.00000   0.08464
C3B  1   0.563423   0.245364    0.134634   11.00000   0.07693
C5   1   0.582099   0.301674    0.361645   11.00000   0.08794
```




```
SADI C1 C2A   C1 C3A   C1 C4A   C1 C2B   C1 C3B   C1 C4B
SADI C2A C3A   C3A C4A   C4A C2A   C2B C3B   C3B C4B   C4B C2B
FVAR 0.234 0.6
[…]
C1   1   0.519760   0.310792   -0.089059   11.00000   0.06836
PART 1
C2A  1   0.545505   0.299615    0.052950   21.00000   0.05727
C3A  1   0.587307   0.232816    0.100964   21.00000   0.06729
C4A  1   0.621837   0.265112    0.234704   21.00000   0.08464
PART 2
C2B  1   0.545505   0.299615    0.052950   -21.00000  0.05727
C3B  1   0.563423   0.245364    0.134634   -21.00000  0.07693
C4B  1   0.621837   0.265112    0.234704   -21.00000  0.08464
PART 0
C5   1   0.582099   0.301674    0.361645   11.00000   0.08794
```

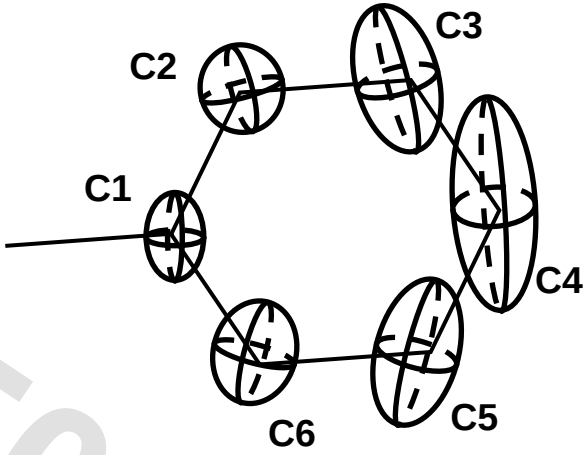
How to find the positions of disorderd atoms?

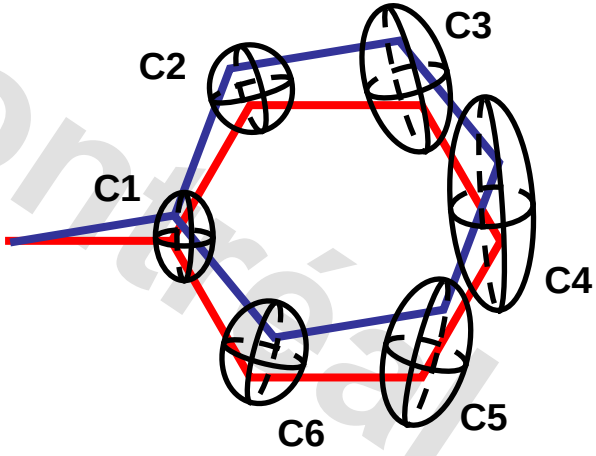
3. Using rigid groups (AFIX)

```
FVAR 0.234   0.4
[…]
PART 1   21.0000
AFIX 66
C1A  1  0.519760  0.310792  -0.089059  11.00000  0.06836
C2A  1  0.545505  0.299615   0.052950  11.00000  0.05727
C3A  1  0.587307  0.232816   0.100964  11.00000  0.06729
C4A  1  0.621837  0.265112   0.234704  11.00000  0.08464
C5A  1  0.587307  0.232816   0.100964  11.00000  0.06729
C6A  1  0.582099  0.301674   0.361645  11.00000  0.08794
AFIX 0
PART 2   -21.0000
AFIX 66
C1B  1  0.519760  0.310792  -0.089059  11.00000  0.06836
C2B  1  0.545505  0.299615   0.052950  11.00000  0.05727
C3B  1  0.587307  0.232816   0.100964  11.00000  0.06729
C4B  1  0.621837  0.265112   0.234704  11.00000  0.08464
C5B  1  0.587307  0.232816   0.100964  11.00000  0.06729
C6B  1  0.582099  0.301674   0.361645  11.00000  0.08794
AFIX 0
PART 0
```

All occupation factors are replaced by the second value of the PART command.

Copy/paste: Identical start positions



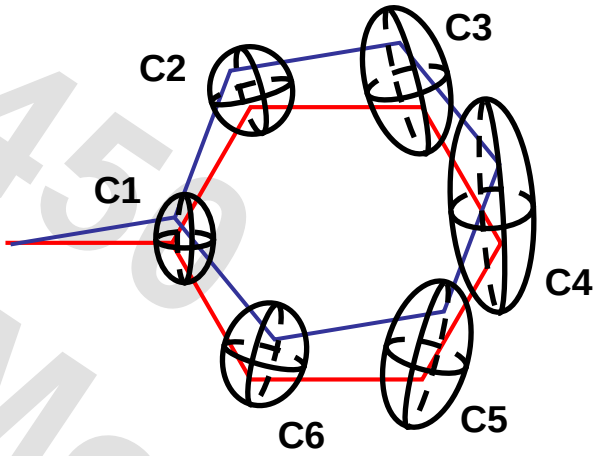


How to find the positions of disorderd atoms?

4. Using rigid groups II

```
*.lst:
 Principal mean square atomic displacements U
[…]
   0.2998    0.0292    0.0374    C3    may be split into  0.6433  0.2938  0.1109  and  0.6322  0.2673  0.1320
   0.3098    0.0893    0.0464    C4    may be split into  0.6218  0.2673  0.2408  and  0.6118  0.2471  0.2666
```

```
FVAR 0.234   0.4
[…]
PART 1   21.0000
AFIX 66
C3A   1 0.6433  0.2938  0.1109 11.00000   0.06836
C4A   1 0.6218  0.2673  0.2408 11.00000   0.05727
C5A   1 0.5976  0.3191  0.3424 11.00000   0.06729
C6A   1   0 0 0   11.00000   0.05
C1A   1   0 0 0   11.00000   0.05
C2A   1   0 0 0   11.00000   0.05
AFIX 0
PART 2   -21.0000
AFIX 66
C3B   1  0.6322  0.2673  0.1320 11.00000   0.06836
C4B   1  0.6118  0.2471  0.2666 11.00000   0.05727
C5B   1  0.5976  0.3191  0.3424 11.00000   0.06729
C6B   1   0 0 0   11.00000   0.05
C1B   1   0 0 0   11.00000   0.05
C2B   1   0 0 0   11.00000   0.05
AFIX 0
PART 0
```



With the three first positions defined, AFIX 66 can complete the cycle automatically.

Stepwise refinement of disorder

```
*.lst:
 Principal mean square atomic displacements U
[…]
   0.3098    0.0893    0.0464    C4     may be split into  0.6218  0.2673  0.2408  and  0.6118  0.2471  0.2666
   0.3100    0.0924    0.0392    C5     may be split into  0.5976  0.3191  0.3424  and  0.5834  0.3017  0.3597
```

1. Assigning initial positions

```
*.ins:
SADI C2 C4A   C2 C4B   C6 C5A   C6 C5B
SADI C4A  C4B   C5A C5B
SADI C2 C5A   C2 C5B   C6 C4A   C6 C4B
[…]
PART 1
C4A   1  0.6218  0.2673  0.2408  10.50000   10.03
C5A   1  0.5834  0.3017  0.3597  10.50000   10.03
PART 2
C4B   1  0.6118  0.2471  0.2666  10.50000   10.03
C5B   1  0.5976  0.3191  0.3424  10.50000   10.03
PART 0
```

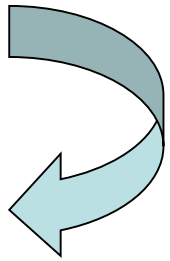
Check if atoms are assigned correctedly. If necessary switch atoms around.

Stepwise refinement of disorder

2. Refining the occupation factor

```
 FVAR 0.293  0.4
[…]
 PART 1
 C4A    1  0.6218  0.2673  0.2408   21.00000  10.03
 C5A    1  0.5834  0.3017  0.3597   21.00000  10.03
 PART 2
 C4B    1  0.6118  0.2471  0.2666  -21.00000  10.03
 C5B    1  0.5976  0.3191  0.3424  -21.00000  10.03
```

We do not need a SIMU command, since thermal parameters remain fixed.



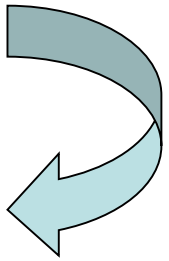
```
 FVAR 0.293   0.265
[…]
 PART 1
 C4A    1  0.6218  0.2673  0.2408   21.00000 10.03
 C5A    1  0.5834  0.3017  0.3597   21.00000 10.03
 PART 2
 C4B    1  0.6118  0.2471  0.2666  -21.00000 10.03
 C5B    1  0.5976  0.3191  0.3424  -21.00000 10.03
```

Stepwise refinement of disorder

3. Allowing isotropic refinement

```
SIMU 0.02 0.04 0.8
FVAR 0.293  0.265
[…]
 PART 1
 C4A    1  0.6218  0.2673  0.2408   21.00000   0.03
 C5A    1  0.5834  0.3017  0.3597   21.00000   0.03
 PART 2
 C4B    1  0.6118  0.2471  0.2666   -21.00000  0.03
 C5B    1  0.5976  0.3191  0.3424   -21.00000  0.03
 PART 0
```

Now we need the SIMU command.

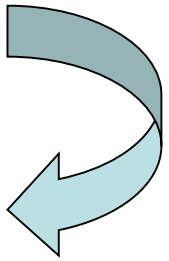


```
[…]
 PART 1
 C4A    1  0.6218  0.2673  0.2408   21.00000   0.04213
 C5A    1  0.5834  0.3017  0.3597   21.00000   0.03812
 PART 2
 C4B    1  0.6118  0.2471  0.2666   -21.00000  0.03932
 C5B    1  0.5976  0.3191  0.3424   -21.00000  0.04098
 PART 0
```

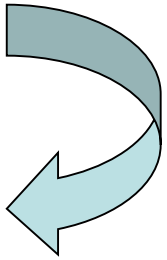
Stepwise refinement of disorder

4. Anisotropic refinement

```
[…]
 ANIS C4A C4B C5A C5B
 PART 1
 C4A    1  0.6218  0.2673  0.2408   21.00000   0.04213
 C5A    1  0.5834  0.3017  0.3597   21.00000   0.03812
 PART 2
 C4B    1  0.6118  0.2471  0.2666  -21.00000  0.03932
 C5B    1  0.5976  0.3191  0.3424  -21.00000  0.04098
 PART 0
```



Stepwise refinement of disorder



```
[…]
 PART 1
 C4A   1  0.6218  0.2673  0.2408   21.00000   0.03221 0.02339 =
     0.02334   0.00728   0.00820   0.00568
 C5A   1  0.5834  0.3017  0.3597   21.00000   0.03174 0.02909 =
     0.02961   0.01051   0.00909   0.00550
 PART 2
 C4B   1  0.6118  0.2471  0.2666  -21.00000   0.03871   0.02965 =
     0.03073   0.00631   0.00674  -0.00625
 C5B   1  0.5976  0.3191  0.3424  -21.00000   0.03221   0.02339 =
     0.02334   0.00728   0.00820   0.00568
 PART 0
```

5. Check the results!

- Verify bond lengths -> decrease sigma for restraints if necessary
- Check thermal parameters -> introduce RIGU, decrease sigma for SIMU, introduce addtional SIMU with a distance of 1.6. If necessary, return to isotropic refinement!

Disorder solving strategy

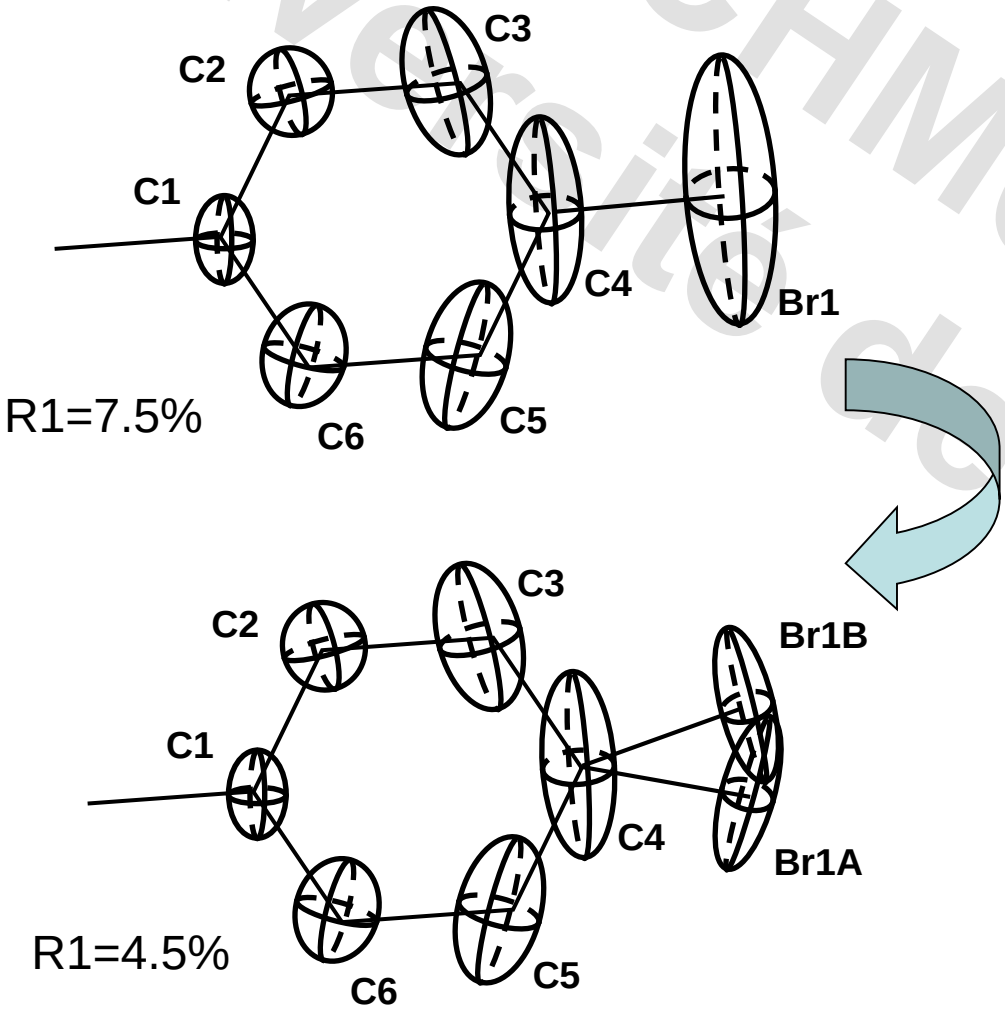
1. **Identify the disorder (does it make sense ?)**
2. **Find the positions**
3. **Refine with the necessary constraints and restraints**
4. **Refine anisotropic**
5. **Apply restraints/constraints for the anisotropic refinement if necessary.** (SIMU 0.02 0.04 0.8 is always present!)
6. **Decide to return to isotropic refinement or not**
7. **(Try to lighten or delete restraints/constraints)**
8. **Arrive at a solution which contains the least number of restraints/constraints, but is in reasonable agreement with "reality".**

Verification of your solution

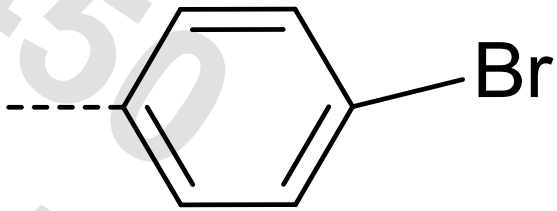
- In the end, you are proposing a structural model. If you refine disorder, **each disordered part in combination with the rest of the molecule should yield an acceptable geometry**, i. e. acceptable bond distances and angles. If not, either you need to tighten restraints or your refinement strategy is wrong.
- A very useful structural help is to compare chemically equivalent distances. If you have a disordered and a non-disorderd PF_6^- molecules, the P-F distances should be comparable in both of them.
- While you have more leeway with thermal parameters in disordered parts, they still have to make sense (shape and orientation). **There is no shame to switch back to isotropic refinement if necessary.** Overestimating data quality and to include too many parameters, however, is your error.

Unacceptable disorders

```
*.lst:
 Principal mean square atomic displacements U
[…]
   0.3098   0.0893   0.0464   Br1    may be split into  0.6218  0.2673  0.2408  and  0.6118  0.2471  0.2666
```

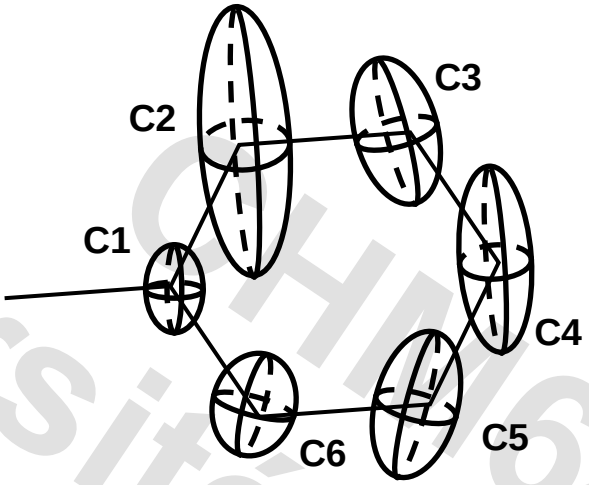


Acceptable ?



Only if you really believe that this is a minimum!

Unacceptable disorders



There is **no possible disorder**, which would yield reasonable geometries or would agree with excessive thermal motion. This is most likely a real problem in the structure.

In this example, the line

```
C2    1  0.6118   0.2471   0.2666   -21.00000   0.03871   0.02965 =
      0.03073   0.00631   0.00674  -0.00625
```

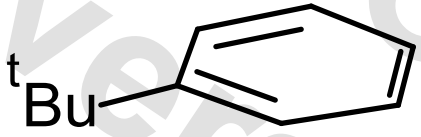
was accidentally changed to

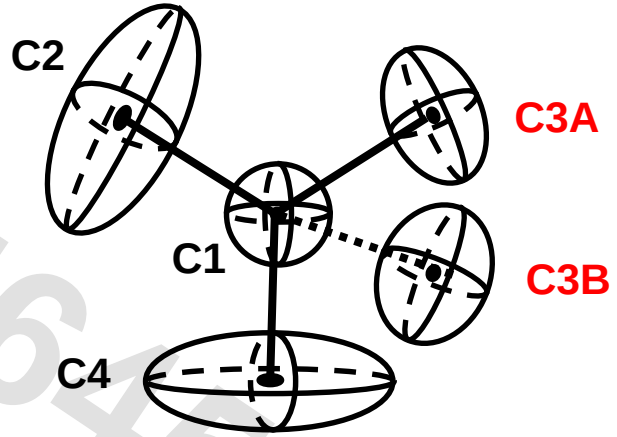
```
C2    4  0.6118   0.2471   0.2666   -21.00000   0.03871   0.02965 =
      0.03073   0.00631   0.00674  -0.00625
```

Thus C2 was (independent from its label) considered to be of atom type 4 in SFAC.

A good strategy for unexplainable errors: Delete the offending atoms, refine, assign from scratch, re-refine and see if the problem persists.

Unacceptable disorders



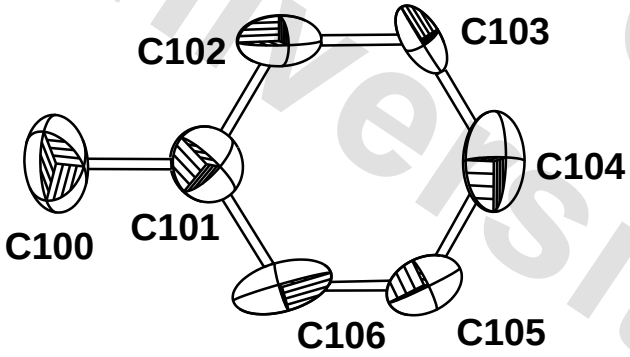


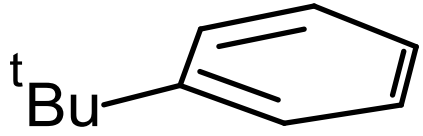
Acceptable ?

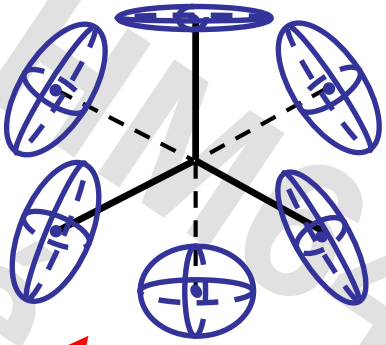
None of the disordered geometries represent a true geometry.

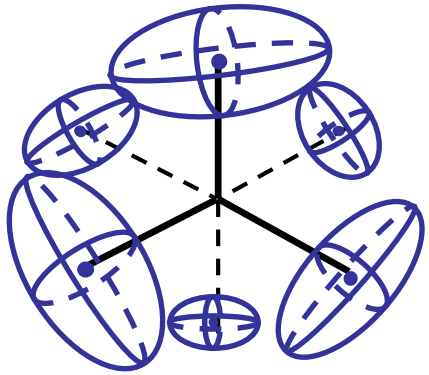
Unacceptable disorders

Toluene disordered around an inversion center:









Unreasonable ellipsoids

- Check for SIMU 0.02 0.04 0.8
- Include:
  RIGU **C100 > C107**
- Reduce to SIMU 0.005 0.01 0.8

Attention : you have to specify atoms if SIMU has a distance > 1 Å

- Refine isotropic, if nothing helps
- Avoid the use of ISOR

Size variation

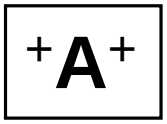
- Check occupation factor refinement
- Check for SIMU 0.02 0.04 0.8
- Introduce RIGU

Twinnig and disorder

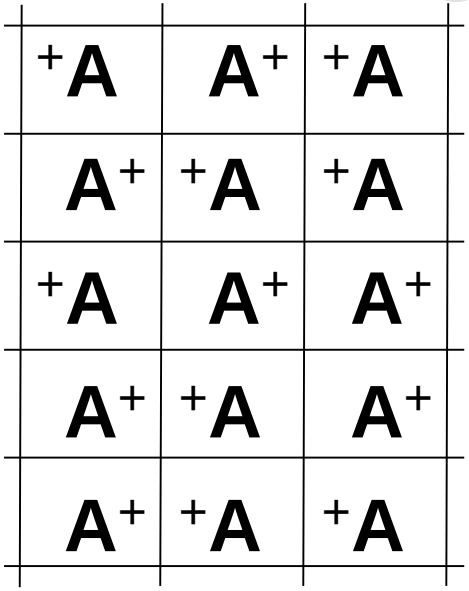
A disorder, which is not a disorder but hidden order:

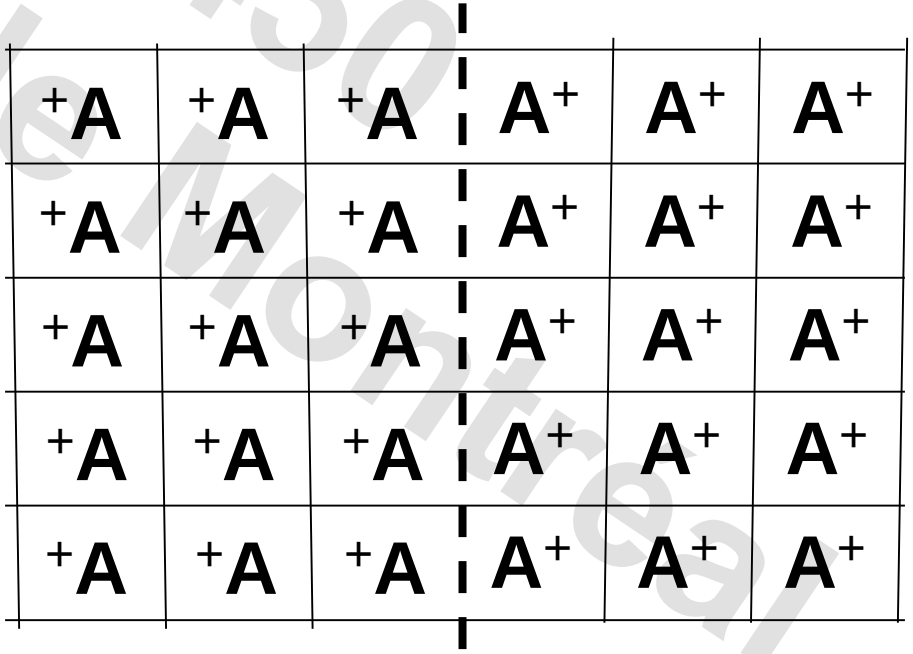
- **Twinning**
- **Superstructures**

Some twinned crystals might simulate the presence of a symmetry element and a higher space group symmetry of a disordered structure.



Disorder?





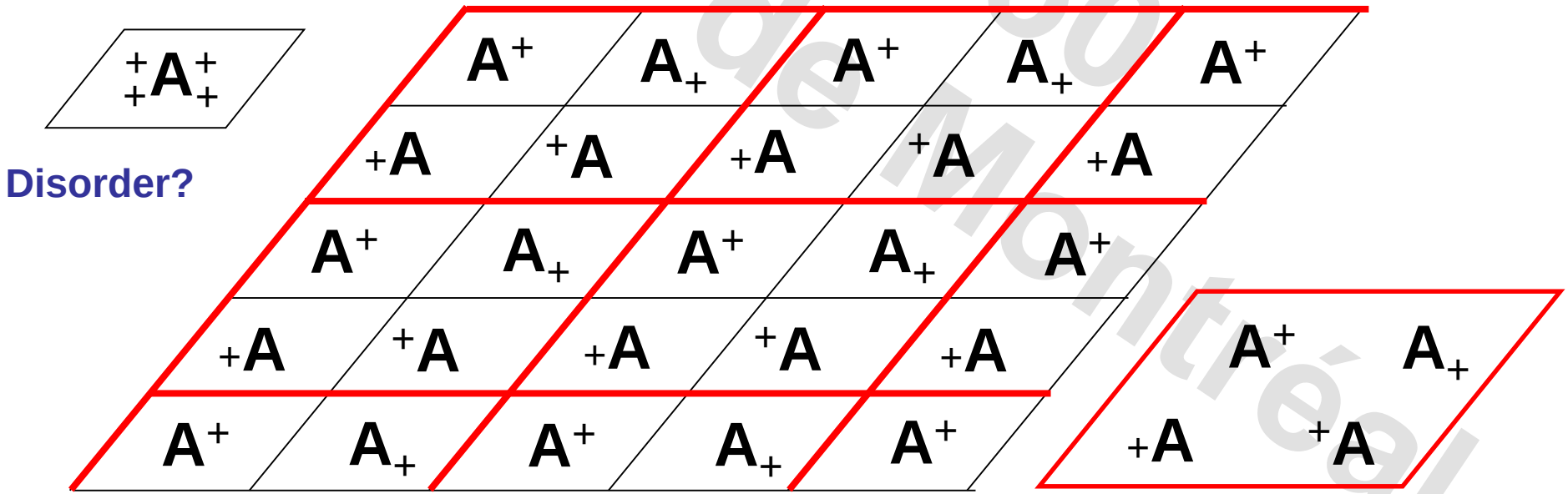
Twinning !

Superstructures and disorder

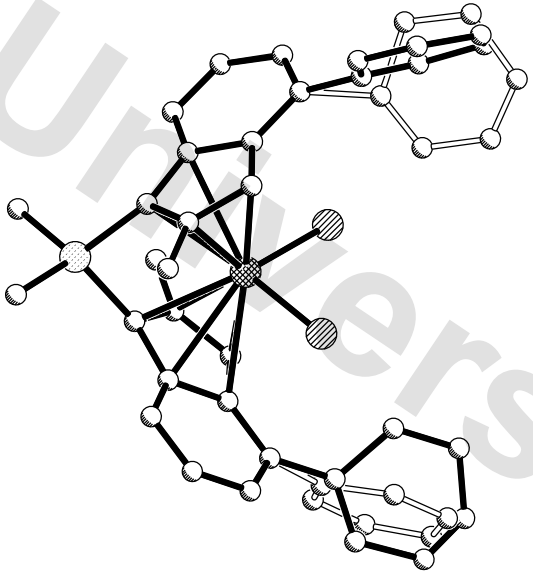
A disorder, which is not a disorder but hidden order:

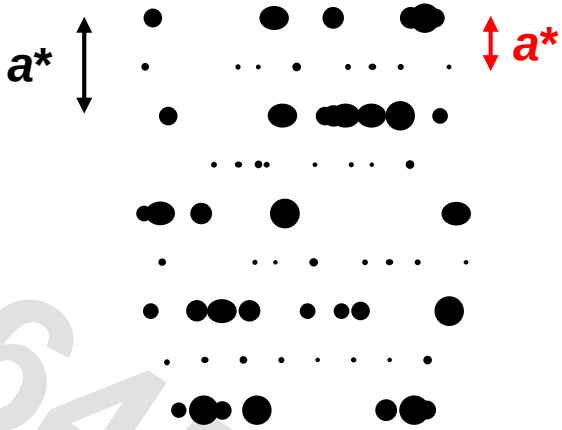
- **Twinning**
- **Superstructures**

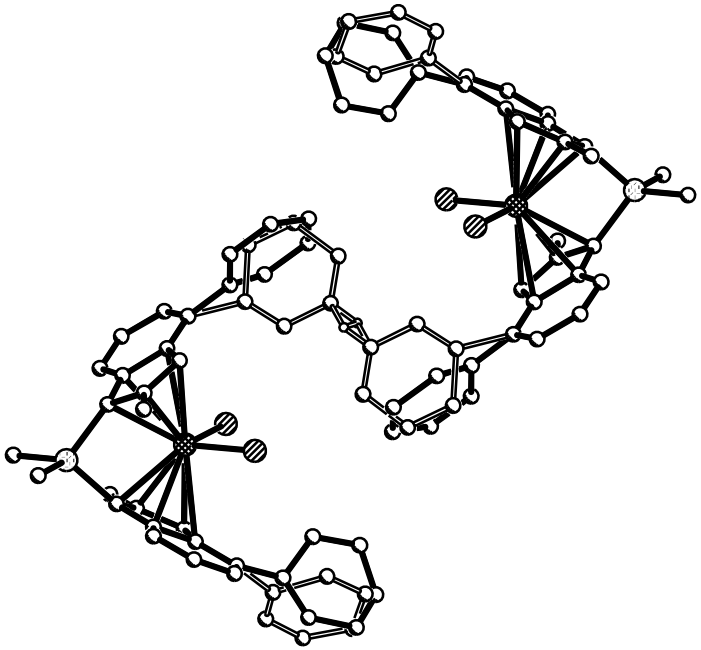
Superstructure: A disorder which is not random, but follows a certain order with a periodicity which is bigger than that of the unit cell.

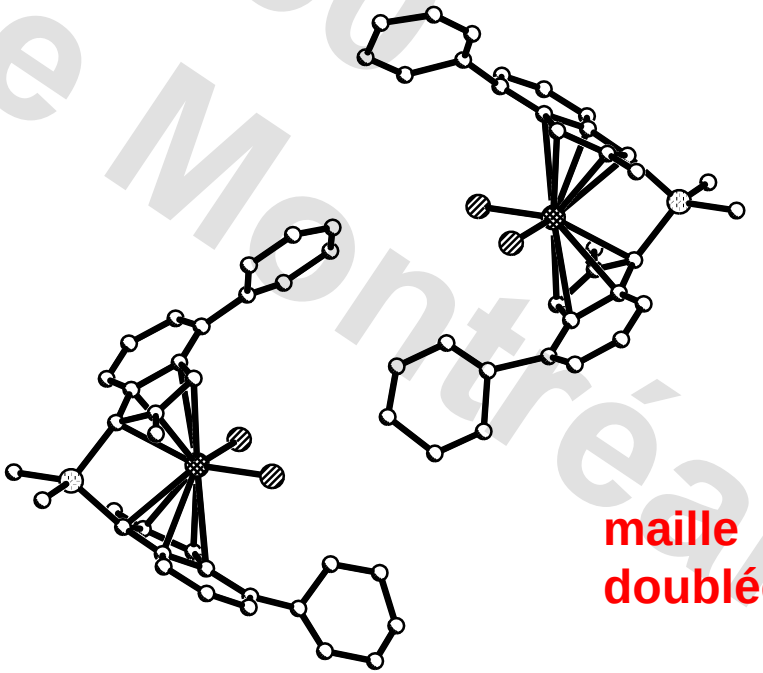


An example



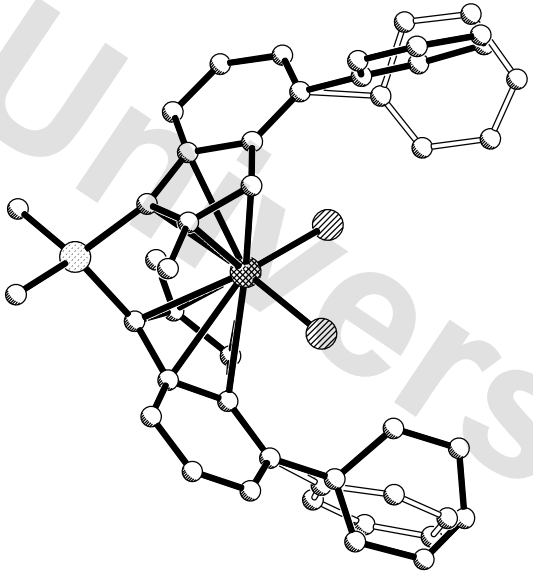


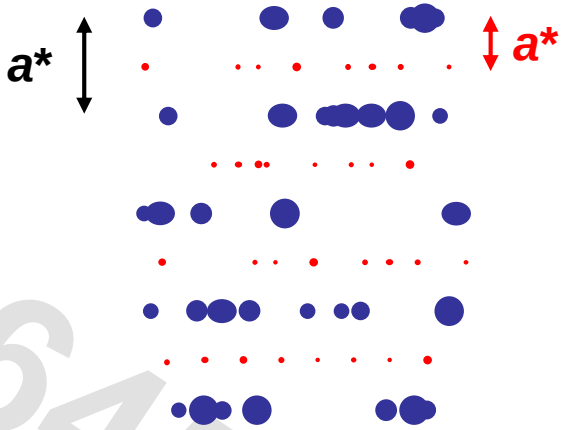


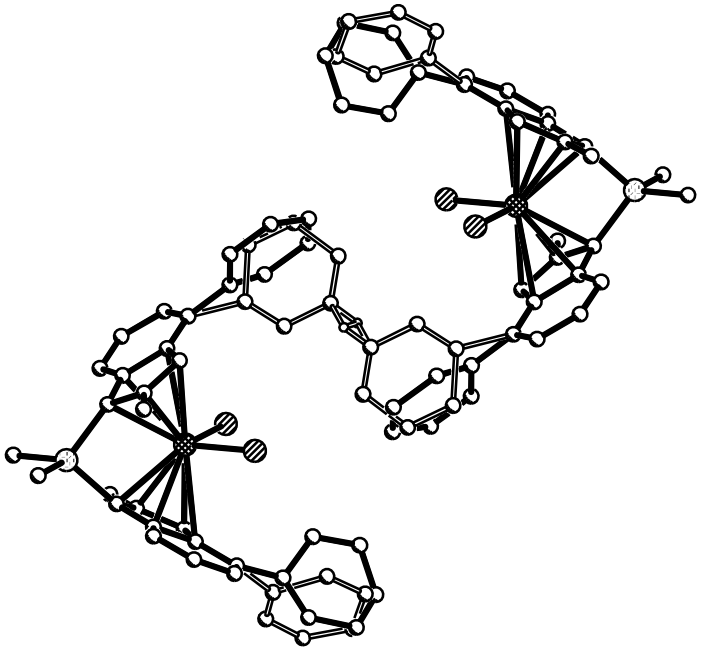


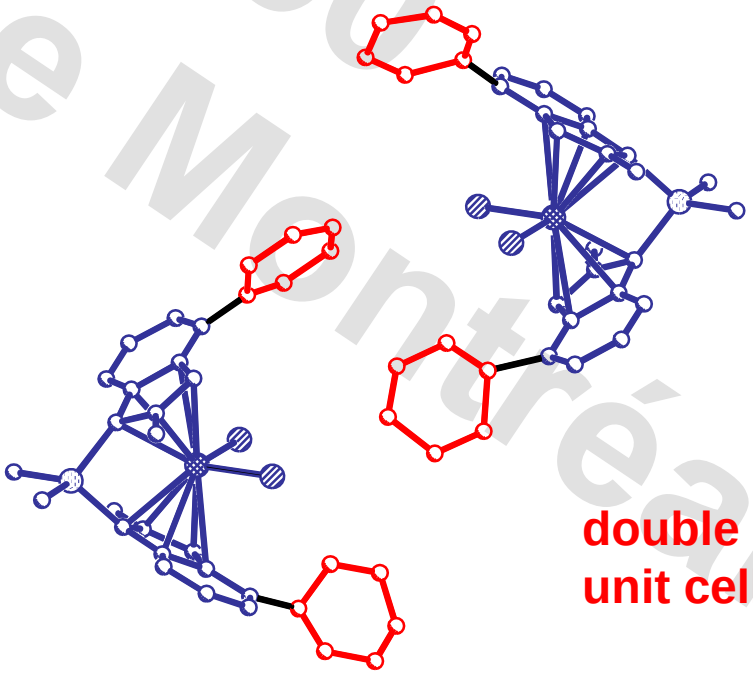
maille doublée

An example









double sized
unit cell

Warning signs of superstructures

- Occupation factors refine to 50:50
- Impossible packing diagrams
- Problems indexing
- Unindexed reflections at regular intervals, i. e. h = n+½

How to deal with it:

1. Investigate very carefully the reflection data (images) for unindexed reflections
2. Brute force approach: doube all unit cell dimensions, re-integrate the data, solve in P1 and check if disorder persists.