
Entropy rules!

Disorder

Squeeze

CCCW 2011

- 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**.

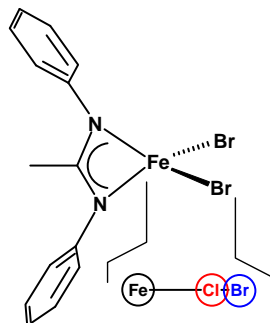
The obtained structure is an overlay, an average of all asymmetric units.

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 zeolites 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.



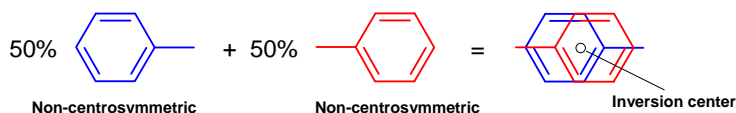
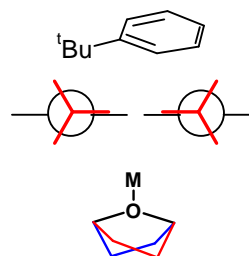
Types of disorder

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 rotamers. 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.

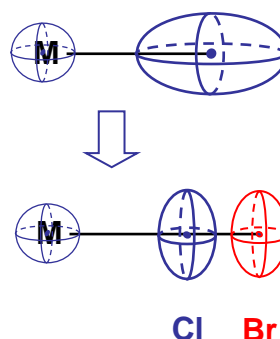
Static and dynamic disorders are treated identically during refinement.

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

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



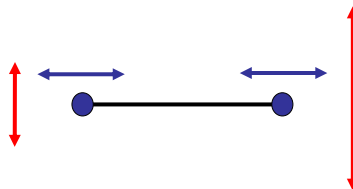
Hirshfeld rigid-bond test

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.

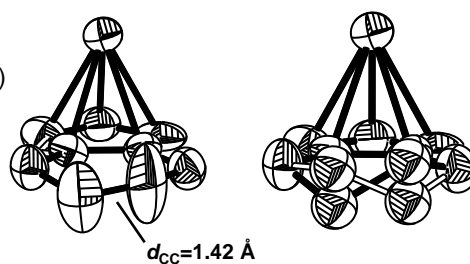
Braga, D. & Koetzle, T. F. (1988). *Acta Cryst.* B44, 151–156.



Warning signs of disorder

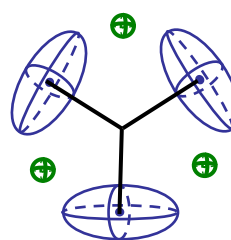
2. Pseudorotational disorder

- Increase (compared to neighbours) thermal ellipsoids
- Shortened C-C distances
- Flattened saturated carbocycles



3. Rotational disorder

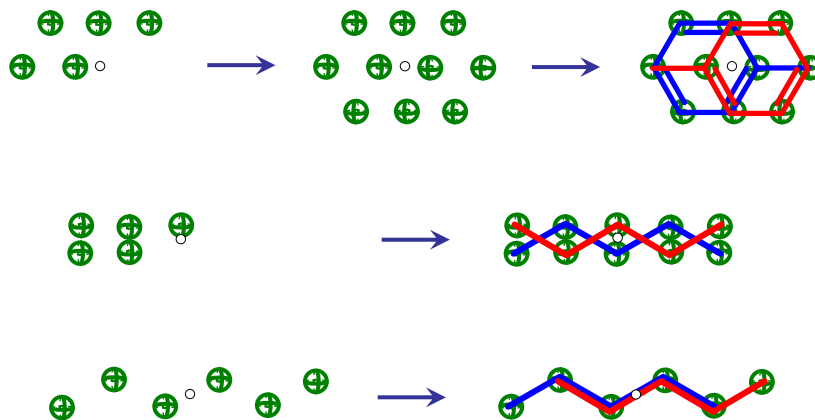
- Increased thermal ellipsoids
- Electron density present between the refined atom positions



Warning signs of disorder

4. Whole molecule disorder of solvent

- Symmetric distribution of electron density around a symmetry element



Treating disorder

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>

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. 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.

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.

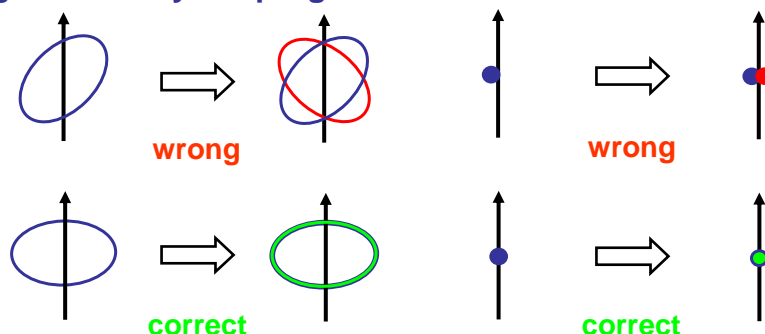
$$M = \sum w_x (F_o^2 - F_c^2)^2 + \sum w_r (T_{\text{target}} - T_c)^2$$

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

Types of constraints used in the SHELX program package

- **Special positions** (generated automatically)

These constraints, which are necessary for atoms positioned on symmetry elements, are automatically generated by the program.



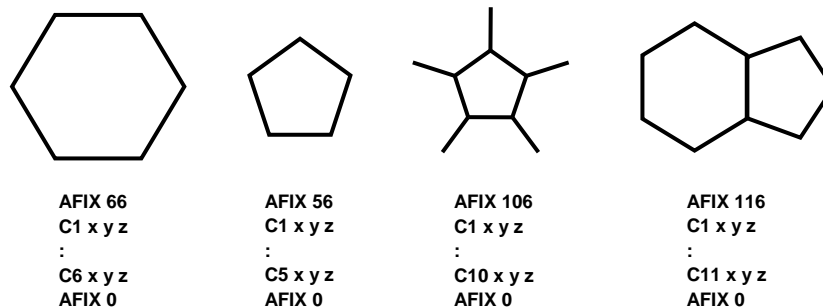
```
File *.lst:
Special position constraints for Zr1
x = 0.0000    z = 0.2500    U23 = 0    U12 = 0    sof = 0.50000
```

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 x6**: completely rigid group; **AFIX x9**: group can grow and shrink keeping its relative geometry.

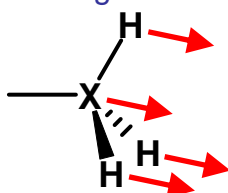


Types of constraints used in the SHELX program package

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

$$\begin{aligned}x_H &= x_C + \Delta x \\y_H &= y_C + \Delta y \\z_H &= z_C + \Delta z \\U_H &= 1.2 \cdot U_x\end{aligned}$$

No additional parameters are refined for the hydrogen atoms, if they are treated by a riding model!



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.

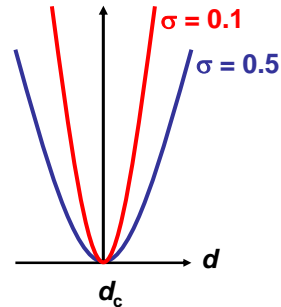
Normally occupation factors are not refined.

```
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  11.00000  0.03871  0.02965 =
    0.03073  0.00631  0.00674  -0.00625
```

(The program adds automatically the constraints for atoms on special positions.)

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 $\sigma = 0$ yields a constraint.



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

Restraints in SHELX

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

DELU, SIMU, ISOR: thermal motion parameters

FLAT, CHIV, BUMP, NCSY, SUMP

Free variables

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

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

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

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

C1	1	0.31357	0.46194	0.73087	11.00000	0.03221
C2	1	0.17696	0.39844	0.65307	11.00000	10.035
C3	1	0.13022	0.26106	0.57225	11.00000	10.035
CL1	2	0.25000	0.17682	0.50000	10.50000	0.05684
Br1	3	0.25000	0.19763	0.50000	10.50000	0.05110

Annotations: Values fixed at 1.0000 (pointing to the first three rows), Values fixed at 0.035 (pointing to the last two rows), Values fixed at 0.5000 (pointing to the last two rows).

- We can exclude any value from refinement by adding 10.
- For atoms on special positions, the program does this automatically without our intervention.

C1	1	0.31357	0.46194	0.73087	11.00000	0.03221
C2	1	0.17696	0.39844	0.65307	11.00000	10.035
C3	1	0.13022	0.26106	0.57225	11.00000	10.035
CL1	2	10.25000	0.17682	10.50000	10.50000	0.05684
Br1	3	10.25000	0.19763	10.50000	10.50000	0.05110

Free variables

In SHELXL, each value is provided in the form of $x = 10m + p$.
 p : value, which is refined; m : refinement mode

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

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

$m > 1$: $x = p \cdot$ "free variable no. m "

$m < -1$: $x = p \cdot (1 -$ "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:

$$31.000 + -31.0000 = 1$$

$$30.500 + -30.5000 = 0.5$$

$$(10m)p + (-10m)p = p$$

Free variable no. m , targetvalue p

Free variables

In SHELXL, each value is provided in the form of $x = 10m + p$.
 p : value, which is refined; m : refinement mode

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

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

$m > 1$: $x = p \cdot$ "free variable no. m "

$m < -1$: $x = p \cdot (1 -$ "free variable no. m " $)$

FVAR 0.73503 0.0239 0.2365

- There is no "free variable no. 1", since adding 10 is used to exclude values from refinement.
- The first position of the FVAR command is thus occupied by the "overall scale factor" (OSF).
- The OSF scales our (arbitrary) intensities, which depends on crystal size, detector sensitivity etc., to the theoretical diffraction by a single unit cell.

Free variables

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

$m < -1$: $x = p(1 - \text{"free variable no. } m\text{"})$

FVAR		0.73503	0.6439	0.2365			
C1	1	0.31357	0.46194	0.73087	11.00000	0.03221	
C2	1	0.17696	0.39844	0.65307	21.00000	10.035	Value fixed at 1.0000
C3	1	0.13022	0.26106	0.57225	-21.00000	10.035	Value fixed at 0.035
CL1	2	0.25000	0.17682	0.50000	30.50000	0.05684	
Br1	3	0.25000	0.19763	0.50000	-30.50000	0.05110	

Value fixed at: 0.50000 x var. #3 = 0.1183
 Value fixed at: 0.50000 x (1-var. #3) = 0.3817

Value fixed at: 1.0000 x var. #2 = 0.6439
 Value fixed at: 1.0000 x (1-var. #2) = 0.2561

Constraints for special positions are automatically generated by the program.

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).

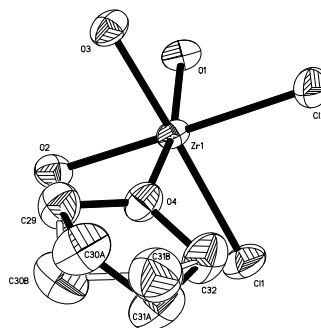
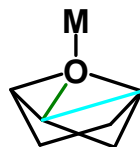
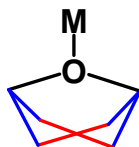
The SAME command allows us to generate a multitude of SADI instructions with a single line.

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

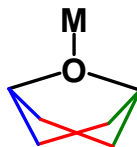
SAME O4 C32 C31B C30B C29

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	[...]

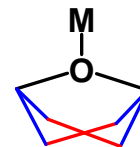
It is very important to have the atoms in the required order!

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

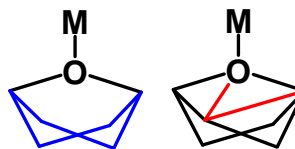


SADI ...continued

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

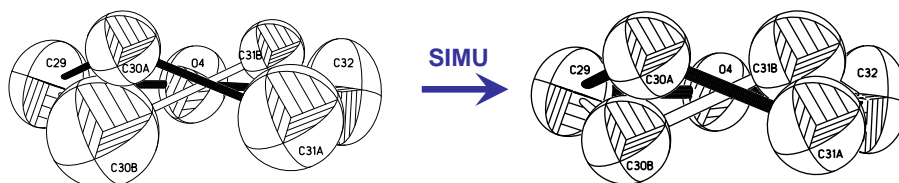
This starts to violate chemical knowledge about equivalent bond and should only be done exceptionally.



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 thermal 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 < 0.8 Å) have identical thermal parameters and enables the refinement of their occupation.



SIMU and DELU

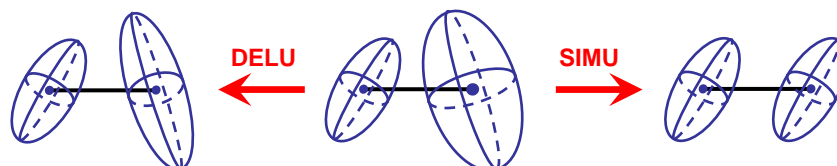
Anisotropic refinement: SIMU restraints for superimposed atoms can be accompanied by restraints DELU and/or SIMU for **neighbouring atoms**.

```
SIMU C29 C30A C30B C31A C31B C32
  DELU C30A C31A
  DELU C30B C31B
```

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.

SIMU: Equivalence of all thermal factors

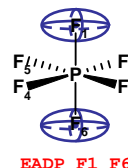
DELU: Equivalence of the thermal factors parallel to a bond (c. f. Hirshfeld test)



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 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

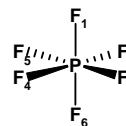
- Forces the anisotropic parameters to become more isotropic
- Last resort for **non-positive defined** atoms

Non-positive defined: An atom is called “non-positive defined”, if at least one of its radii refined to an negative value (which of course does not make any physical sense). Non-positive defined 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.

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	[...]					

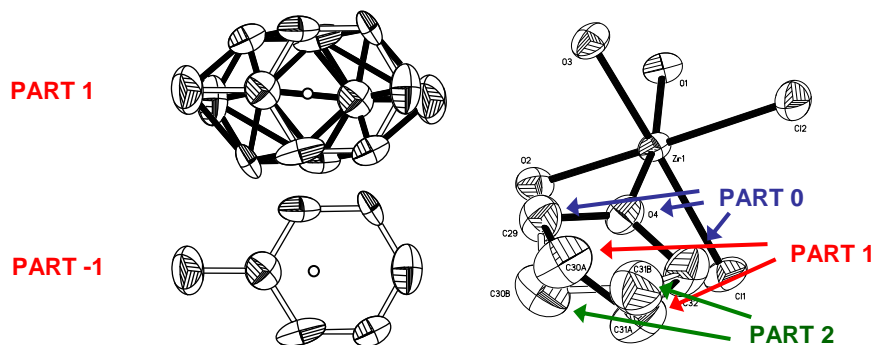


Often several SADI commands might be replaced by one SAME command

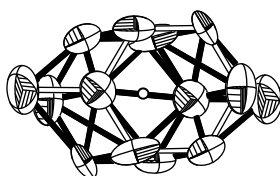
PART

PART n

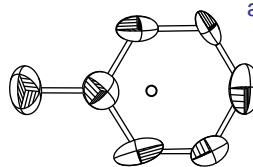
- Not a restraint
- No influence on the refinement
- Influence on the [connectivity list](#)
- $n > 1$: Atoms with this part number can be bonded to all other atoms with PART number n and all atoms with n=0.
- $n < 0$: Atoms can be bonded to all atoms with PART 0 and PART n, but not to those generated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



Occupation factor



PART 1



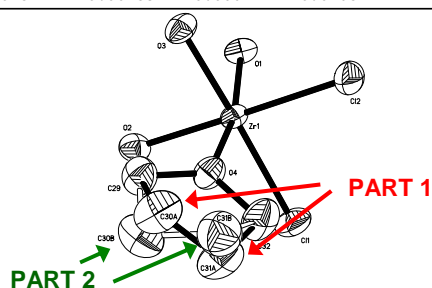
PART -1

Thermal parameters need attention!

PART		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	Disordered THF				
[...]							
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							= 1.000* FVAR #2 = 0.58208
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							= 1-1.000* FVAR #2 = 0.41792
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		



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
```

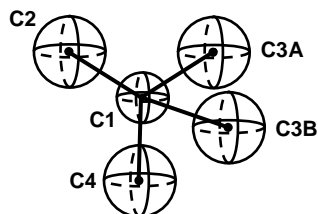
```
*.ins:
FVAR 0.293 0.4
[...]
PART 1
C4A 1 0.6218 0.2673 0.2408 21.00000 0.04
C5A 1 0.5834 0.3017 0.3597 21.00000 0.04
PART 2
C4B 1 0.6118 0.2471 0.2666 -21.00000 0.04
C5B 1 0.5976 0.3191 0.3424 -21.00000 0.04
PART 0
```



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
```

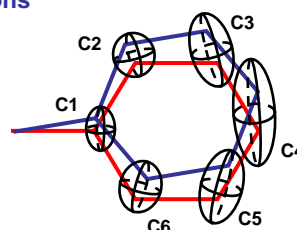
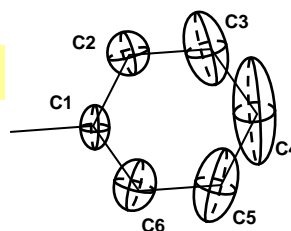
```
C1B 1 0.519760 0.310792 -0.089059 11.00000 0.06836
C2B 1 0.545505 0.299615 0.052950 11.00000 0.05727
C3B 1 0.587307 0.232816 0.100964 11.00000 0.06729
C4B 1 0.621837 0.265112 0.234704 11.00000 0.08464
C5B 1 0.587307 0.232816 0.100964 11.00000 0.06729
C6B 1 0.582099 0.301674 0.361645 11.00000 0.08794
```

```
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

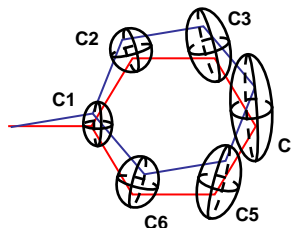
C6B 1 0 0 0 11.00000 0.05

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

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						

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

Stepwise refinement of disorder

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

3. Freeing 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						

Stepwise refinement of disorder

```
[...]  
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
```

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!

- Check bond lengths -> decrease sigma for restraints if necessary
- Check thermal parameters -> decrease sigma for SIMU, introduce additional SIMU with a distance of 1.6, introduce DELU. If necessary, return to isotropic

Disorder solving strategy

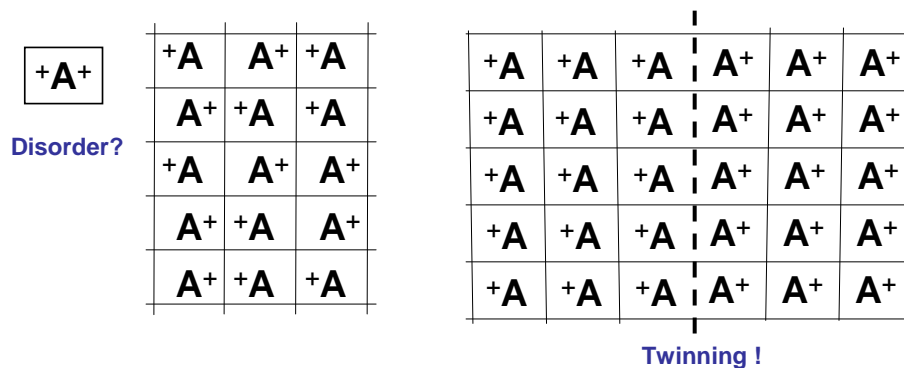
1. Identify the disorder (does it make sense ?)
2. Find the positions
3. Refine with the necessary constraints and restraints
4. Refine anisotropic
5. Apply restraints/constraints for the anisotropic refinement if necessary. (SIMU 0.02 0.04 0.8 is always present!)
6. Decide to return to isotropic refinement 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”.

Twinning 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.

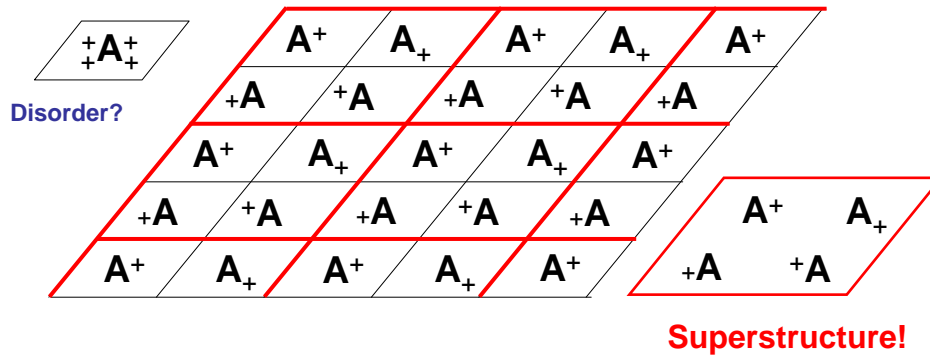


Superstructures and disorder

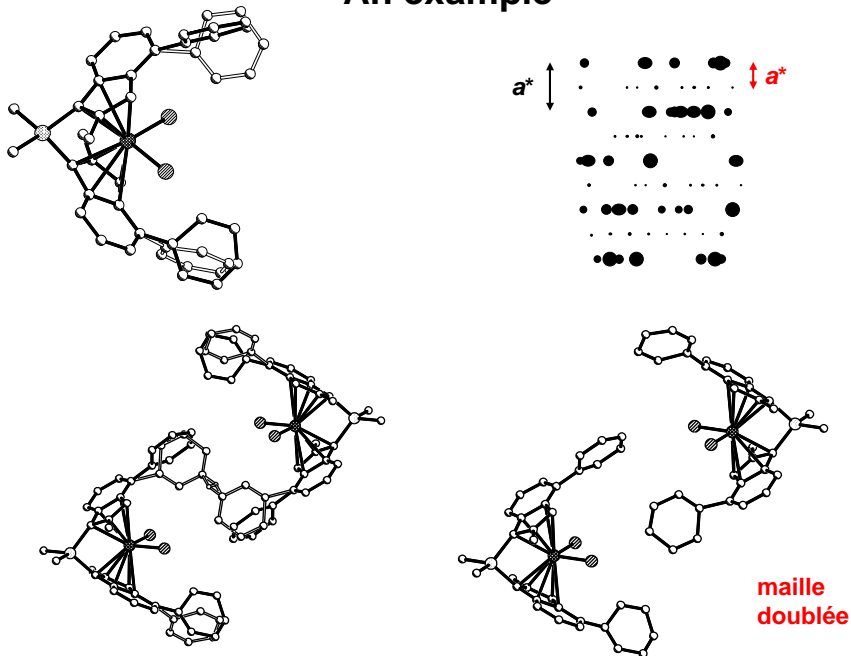
A disorder, which is not a disorder but hidden order:

- Twinning
- Superstructures

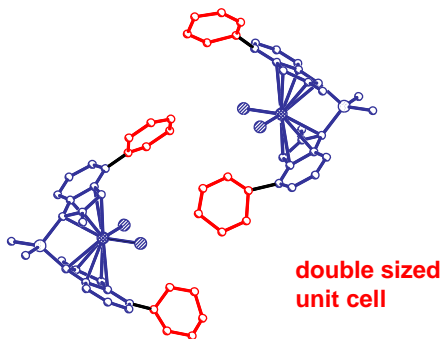
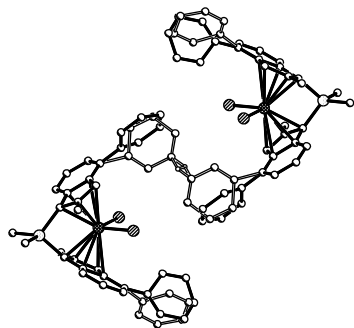
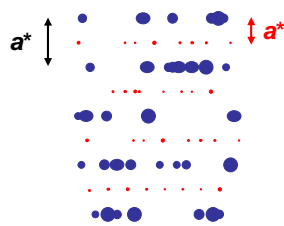
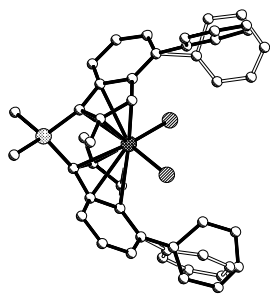
Superstructure: A disorder which is not random, but follows a certain order with a periodicity which is bigger than that of the unit cell.



An example



An example



Fin