
The CIF file, refinement details and validation of the structure

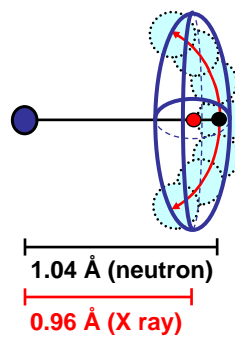
CCCW 2011

Artefacts *versus* errors

Artefacts in crystallography: An error which cannot be avoided, since it is inherent in the method.

Examples of artefacts:

- Shortened bond distances to light atoms due to **libration**



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Examples of artefacts:

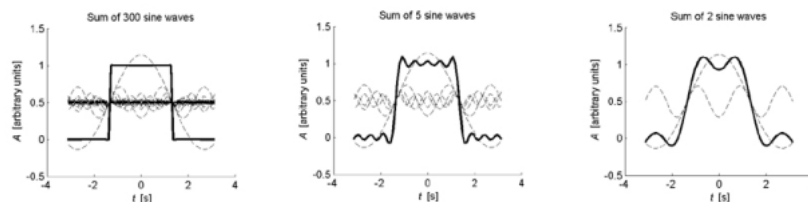
- Shortened bond distances due to libration.
- Shortened bond distances for triple bonds C≡C ou C≡N (electron density in the bond)
- Wrong hydrogen positions
- Residual electron density **around special positions** or **close to heavy atoms** because of **Fourier truncation errors**, also called **Fourier truncation ripples**.

Fourier truncation errors

The electron density, obtained from the Fourier transformation, is an (infinite) sum of sinus functions.

$$\rho(x, y, z) = \frac{1}{V} \sum_{hkl} |F_{hkl}| \cdot e^{i\alpha_{hkl}} \cdot e^{-2\pi i(hx+ky+lz)}$$

If some of the elements of this sum is missing (finite sum), because we cannot measure reflections up to very high angles or because some reflections are not accessible, we observe “ripples” in the obtained electron density.



<http://www.theses.ulaval.ca/2005/23016/apd.html>

The errors

An artefact is an error which is unavoidable.

Thus, what are the avoidable errors? (P. Müller, *Crystal Structure Refinement*, 2006)

- Wrong unit cell
- Twin refined as a disorder
- Wrong atom assignment
- Wrong space group
- Interpretation of Fourier truncation ripples as hydrogen atoms and *vice versa*

And there are the “really avoidable errors” (Roland Boese, 1999):

- Typographic errors in the unit cell
- Errors in the refinement
- Wrong data collection strategy
- Data collection at room temperature

Documentation and validation

1. Documentation of an X-ray diffraction study

2. The CIF file

3. Values to judge the quality of a structure

4. Aids for structure verification

Documentation of an X-ray diffraction study

As every scientific experience, an X-ray diffraction study has to be documented according to good scientific principles.

- 1. Lab book:** Use a dedicated lab book for the determination of structures. The lab book should contain information not included in the electronic data (such as crystal size, color etc.) as well as your choices made during refinement.
- 2. Report:** The results have to include:
 - **Crystallisation details** (solvent, temperature, how did you obtain the crystal)
 - **Details of the data collection** (instrument, number of reflections, crystal size)
 - **Details of the solution/refinement** (confidence factors, hydrogen treatment)
 - **Details of the structure** (atom positions, thermal parameters, bond distances and angles)
 - **A figure showing the atom numeration**
 - **A figure showing the thermal ellipsoid (ORTEP)** (could be combined)
- 3. Archiving:** **You** are responsible to archive reliably (min. 5 years)
 - experimental results (images etc)
 - solution/refinement results (files .res, .hkl, .cif, .lst)

(A reliable archiving includes that one can find the relevant data after several years, even in your absence!)

Documentation and validation

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- 2. The CIF file**
- 3. Values to judge the quality of a structure**
- 4. Aids for structure verification**

The CIF file

CIF (Crystallographic Information File):

- S. R. Hall, F. H. Allen, I. D. Brown *Acta Cryst.* 1991, *A47*, 655-685
- Contains nearly all the information regarding an X-ray diffraction study structure
- Nearly all journals require a CIF file as supporting information
- CIFs are used directly for publication in *Acta Cryst.*
- Automated validation of a diffraction study
- Automated report generation

The CIF file

```
data_recp1
_audit_creation_method SHELXL
_chemical_formula_motif
"C35 H40 N6 O, C H Cl3"
_chemical_formula_sum
'C36 H41 Cl3 N6 O'

_refine_special_details
;
Refinement on F2 for ALL
reflections except for 0 with
very negative F2
;
loop_
  _geom_bond_atom_site_label_1
  _geom_bond_atom_site_label_2
  _geom_bond_distance
  _geom_bond_site_symmetry_2
  _geom_bond_publ_flag
N1 C1 1.346(3) ?
N1 C5 1.349(3) . ?
N2 N3 1.375(3) . ?

_refine_diff_density_max 0.452
_refine_diff_density_min -0.616
```

Text file: only 80 characters per line, only simple ASCII code.

Each data bloc starts with *data_nom*. Several data blocs can be combined in the same file.

A variable has the format *_nom*.

The value of a variable can appear after the variable separated by a space (or spaces) or on the next line.

If a value contains spaces, it has to be included in single or double quotation marks. If a value contains several lines of text, it has to be separated by semicolons.

A list of values can be initiated with the command *loop_*. The list ends with the next variable name.

Generation of the CIF file

1. A first version of *name.cif* is generated with the command ACTA in **SHELXTL (XL)**
2. You can use **XCIF** (or other software) to replace unknown values in *name.cif* with values included in another file, such as *name.pcf* (generated by XPREP). Attention: XCIF does not update values, it only replaces unknown ones (i. e. question marks).
3. Inspection and manual manipulation of the CIF file (using values from other files, your lab book etc.)
4. **If you add another refinement cycle, you have to repeat steps 2 + 3.**

If you need to modify your CIF, use a simple text editor (Notepad, Wordpad). **Do not use a text editing software, such as Word!** Such software might introduce formatting codes on saving, which are not included in the CIF format.

Meaning of variables in the CIF

What does a variable stands for? Which values are allowed?

Information can be found:

- Chapter 4.1 of *International Tables for Crystallography Volume G, First edition (2005)*
- http://www.iucr.org/iucr-top/cif/cif_core/index.html

```
exemple.cif:
...
_refine_ls_hydrogen_treatment    ?
```



```
exemple.cif:
...
_refine_ls_hydrogen_treatment    constr
```

_refine_ls_hydrogen_treatment

Definition: Treatment of hydrogen atoms in the least-squares refinement.

The data value must be one of the following:

refall	refined all H-atom parameters
refxyz	refined H-atom coordinates only
refU	refined H-atom U's only
noref	no refinement of H-atom parameters
constr	H-atom parameters constrained
mixed	some constrained, some independent
undef	H-atom parameters not defined

Documentation and validation

1. Documentation of an X-ray diffraction study

2. The CIF file

3. Values to judge the quality of a structure

- R_{sigma} , R_{int} , $wR2$, $R1$, GoF
- Residual electron density
- Correlation matrix elements

4. Aids for structure verification

The refinement – step by step

1. Reading of the .hkl file containing the reflection intensities

```
example.ins:  
...  
HKLF 4  
END
```

In contrast to the res/ins/cif files, the file *.hkl has a **precise format!**

Thus each space matters. But there is no reason at all, why you should edit a hkl-file anyway.

```
example.hkl:  
0 0 1 14.04 2.27 1  
0 0 220748.33 212.60 1  
0 0 3 3.91 4.31 1  
0 0 4 8452.21 96.84 1  
0 0 5 15.19 9.36 1  
0 -1 -690345.18 728.10 1  
0 0 7 11.09 8.55 1  
0 0 8 2957.52 45.64 1  
...  
0 0 0 End of file
```

Miller indices h k l	Intensity I	Standard deviation of the intensity $\sigma(I)$	batch number (see BASF in the SHELX manual)
0 0 1	14.04	2.27	1
0 0 2	220748.33	212.60	1
0 0 3	3.91	4.31	1
0 0 4	8452.21	96.84	1
0 0 5	15.19	9.36	1
0 -1	-690345.18	728.10	1
0 0 7	11.09	8.55	1
0 0 8	2957.52	45.64	1

The refinement – step by step

1. Reading of the .hkl file containing the reflection intensities

```

exemple.lst:
h k l Fo^2 Sigma Why rejected
0 0 1 104.55 5.29 observed but should be systematically absent
2 0 1 74.15 6.04 observed but should be systematically absent
etc.
20975 Reflections read, of which 685 rejected
-10 <= h <= 10, -13 <= k <= 13, -18 <= l <= 18, Max. 2-theta = 137.96
23 Systematic absence violations

Inconsistent equivalents etc.
h k l Fo^2 Sigma(Fo^2) N Esd of mean(Fo^2)
2 0 0 127128.20 518.46 4 3194.33
0 2 0 65677.31 243.31 6 1223.07
etc.
14 Inconsistent equivalents
2847 Unique reflections, of which 0 suppressed

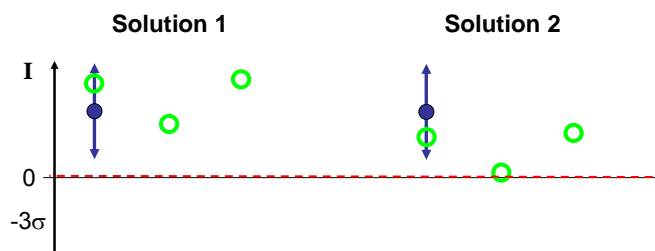
R(int) = 0.0275 R(sigma) = 0.0111 Friedel opposites merged
    
```

- Rejected reflections:
- Systematic absences
 - Inconsistent equivalents
 - Reflections with $I < -3 \cdot \sigma(I)$

Why use reflections with negative intensities?

- During the integration of the reflections (peaks), the intensities are determined by $I = I_{\text{reflection}} - I_{\text{background}}$
- For weak reflections the result can be negative.

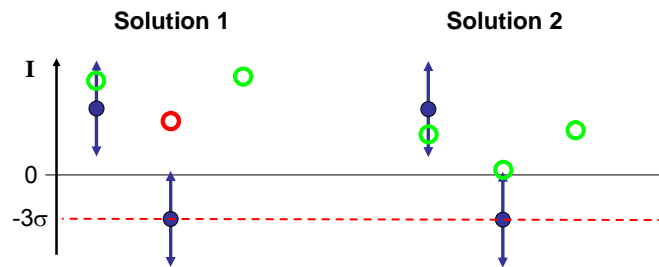
If we consider only reflections with $I > 0$ both solutions 1 and 2 are equally probable.



Why use reflections with negative intensities?

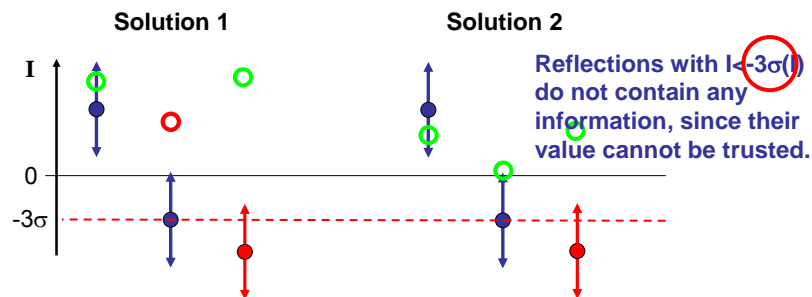
- During the integration of the reflections (peaks), the intensities are determined by $I = I_{\text{reflection}} - I_{\text{background}}$
- For weak reflections the result can be negative.
- Reflections with $0 < I < -3\sigma(I)$ contain useful information. ($I = 0$ is in the margin of errors for these reflections.)

Solution 2 is more probable



Why use reflections with negative intensities?

- During the integration of the reflections (peaks), the intensities are determined by $I = I_{\text{reflection}} - I_{\text{background}}$
- For weak reflections the result can be negative.
- Reflections with $0 > I > -3\sigma(I)$ contain useful information. ($I = 0$ is in the margin of errors for these reflections.)
- Reflections with $I < -3\sigma(I)$ are physically impossible, indicate problems in the determination and are thus omitted.

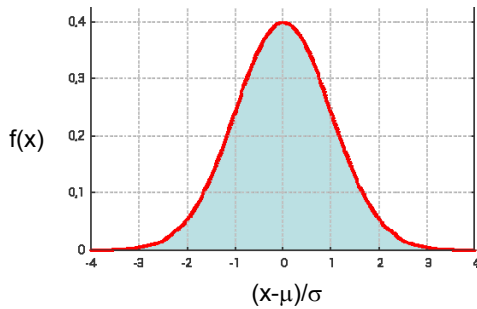


3 σ : What connects the standard deviation with the confidence interval ?

A random distribution of errors should follow a Gaussian distribution

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

μ : correct value
 σ : standard deviation



$$\int_{\mu-\sigma}^{\mu+\sigma} f(x) = 0.68 = 68\%$$

$$\int_{\mu-2\sigma}^{\mu+2\sigma} f(x) = 0.96 = 96\%$$

$$\int_{\mu-3\sigma}^{\mu+3\sigma} f(x) = 0.99 = 99\%$$

99.7% probability that x is in the interval $\mu \pm 3\sigma$

$$a=1.234; \sigma=0.005: a = 1.234(5) \rightarrow a = 1.234 \pm 0.015$$

The refinement – Merging of reflections

1. Reading of the .hkl file containing the reflection intensities

```

exemple.lst:
20975 Reflections read, of which 685 rejected
-10 =< h =< 10, -13 =< k =< 13, -18 =< l =< 18, Max. 2-theta = 137.96
23 Systematic absence violations

Inconsistent equivalents etc.
h k l Fo^2 Sigma(Fo^2) N Esd of mean(Fo^2)
2 0 0 127128.20 518.46 4 3194.33
0 2 0 65677.31 243.31 6 1223.07
etc.
14 Inconsistent equivalents
2847 Unique reflections, of which 0 suppressed
R(int) = 0.0275 R(sigma) = 0.0111 Friedel opposites merged
    
```

Number of reflections measured

Number of independent reflections measured (not repeated, not related by symmetry)

Governed by the command MERG in the ins-file (see SHELXTL manual). We touch at this command only in special cases.

The refinement – Error of merging

1. Reading of the .hkl file containing the reflection intensities

```

exemple.lst:
20975 Reflections read, of which 685 rejected
...
2847 Unique reflections, of which 0 suppressed
R(int) = 0.0275 R(sigma) = 0.0111 Friedel opposites merged
  
```

R_{int} is indicated by a blue arrow pointing to the value 0.0275 in the output.

$$R_{int} = \frac{\sum |F_o^2 - F_o^2(\text{mean})|}{\sum F_o^2}$$

- R_{int} : Merging error (measure of the precision/reproducibility)
- **Possible error sources (high R_{int} value):**
 - Incorrect Laue group
 - Bad or missing adsorption correction
 - Crystal decomposition
 - Twinning
 - Goniometer problems (covered reflections, misalignment)

The refinement – Error of merging

1. Reading of the .hkl file containing the reflection intensities

```

exemple.lst:
20975 Reflections read, of which 685 rejected
...
2847 Unique reflections, of which 0 suppressed
R(int) = 0.0275 R(sigma) = 0.0111 Friedel opposites merged
  
```

R_{sigma} is indicated by a blue arrow pointing to the value 0.0111 in the output.

$$R_{sigma} = \frac{\sum \sigma(F_o^2)}{\sum F_o^2}$$

- Measure of the signal-to-noise ratio
- In rough approximation, the structure confidence factor R1 cannot be much better than R_{sigma}
- If $R_{int} \gg R_{sigma}$, i. e. more than 2-3 times, there is a problem

Confidence factors

Optimised value:
$$M = \sum w(F_o^2 - F_c^2)^2$$

(The lower M, the better is the agreement of our model with the experimental data.)

But: M increases with the number of reflections and with their intensity. It is thus structure dependent, with well diffracting structures with high redundancy giving the highest M values. We thus need a structure independent value.

Confidence factor, Residual, R-factor:

R2 →
$$wR_2 = R_w(F^2) = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$$

For statistical reasons, refinement against F^2 gives R-factors approximately twice as high than those for refinement against F . To facilitate comparison (and to increase acceptance of the new method) SHELXTL calculates also the R-factor based on F .

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad \leftarrow R1$$

Goodness of Fit

The GoF or GooF is another value which describes the quality of our model:

$$GooF = S = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{N_{Ref.} - N_{Par.}}}$$

$N_{Ref.}$: number of independent reflections, $N_{Par.}$: number of parameters

In contrast to the R-factor, which also depends on the signal-to-noise ratio, S is relatively independent from the noise.

S should be around 1.

S > 1: bad model or bad data/parameter ratio

S < 1: model is better than the data: problems with the absorption correction, space group problems

Criteria for a good structure

SHELXL calculates 4 confidence values:

- **wR2 (all data)**
 - **wR2 (observed data, $I > 2\sigma(I)$)**
 - **R1 (all data)**
 - **R1 (observed data, $I > 2\sigma(I)$)**
- Refinement against F^2 requires a correct weighing scheme
- The weighing schemes optimised for refinement against F^2 cannot be used for the calculation of R1.

The important values are **wR2 (all data)** (since we do the refinement with all data) and **R1 (observed data)**, for comparison with the old method.

	Good	Acceptable	Problematic	Really problematic
R1	< 5%	< 7%	>10%	>15%
wR2	< 12%	< 20%	>25% (ou > 2*R1)	>35%
S	0.9-1.2	0.8-1.5	<0.8 ou >2	<0.6 ou >4

Residual electron density

If our model is good, we should have described all electrons in our structure. Thus the remaining electron density should be zero.

Acceptable values for residual electron density:

- For light atom structures (H – F) : < **0.5 e⁻/Å³**
- For heavy atom structures : 10% of the electrons of the heavy atom per Å³ in a distance smaller 1.2 Å from the heavy atom. (Fourier truncation errors)
- Accumulation of electron density on special positions

Sources of errors:

- Bad absorption correction
- Disorder

XP: info Q1

How to find the residual electron density?

```
test.cif:
_refine_diff_density_max 0.425
_refine_diff_density_min -0.560
```

```
test.lst:
Electron density synthesis with coefficients Fo-Fc
Highest peak 0.42 at 0.2140 0.0398 0.5135 [ 0.40 A from C2 ]
Deepest hole -0.56 at 0.1424 0.4014 0.6865 [ 0.53 A from F3 ]
```

Correlation matrix elements

test.lst:		
Largest correlation matrix elements		
0.853 U11 Fe1 / OSF	0.728 U11 S2 / U11 Fe1	0.524 U11 S1 / U11 Fe1
0.771 U11 S2 / OSF	0.588 U11 S1 / OSF	0.543 U12 S1 / U23 S1

Values > 0.5 for the correlation matrix elements indicate that some parameters in the refinement are dependent from each other.

Some dependences are acceptable, such as f. e. between the thermal parameters of the heavy atom and the overall scale factor or between the U_{xy} of the same atom.

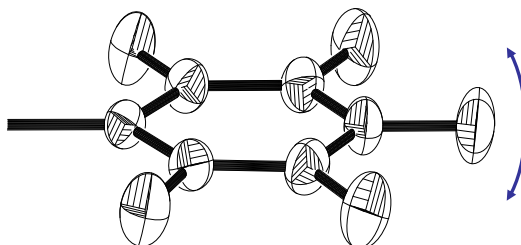
Attention: A high number of dependences > 0.5 between multiple atoms might indicate a missed symmetry! (wrong space group)

Manual inspection : Thermal parameters

With the exception of a wrong space group, most other problems of a structure are more visible in the thermal parameters than in the atom positions. For bad structures, thermal parameters serve as the garbage bin of the refinement.

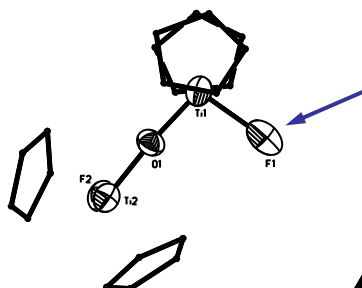
In general:

- Values of the thermal displacement should be comparable for comparable atoms.
- The displacement should be in agreement with the thermal vibration of lowest energy.



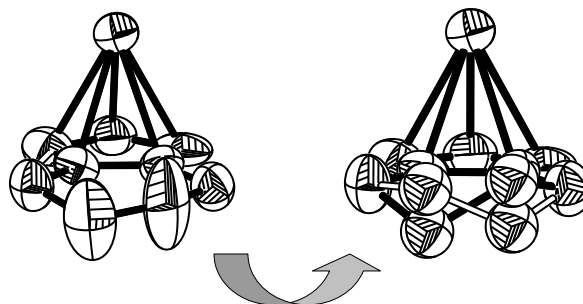
Manual inspection : Thermal parameters

Disorder



Displacement parallel to a bond greater than perpendicular displacement
⇒ disorder, two atoms with different bond lengths sharing the same position, here F et Cl.

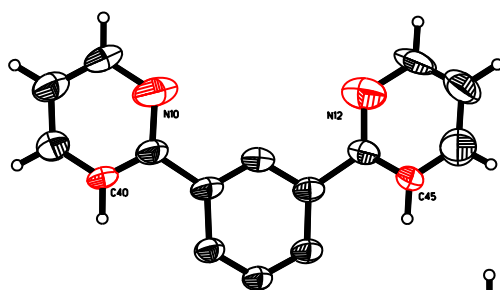
CHECKCIF: Violation of the “Hirshfeld test”



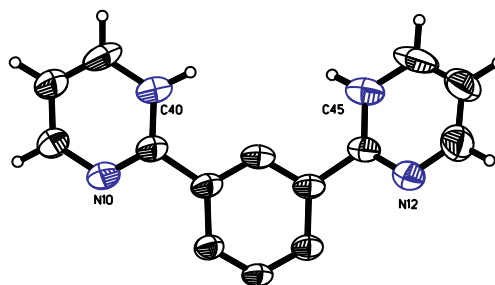
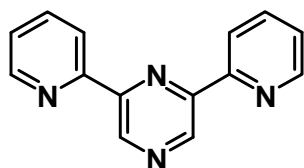
```
*.lst:  
Principal mean square atomic displacements U  
[...]  
0.3098 0.0893 0.0464 C4 may be split into 0.6218 0.2673 0.2408 and 0.6118 0.2471 0.2666  
0.3100 0.0924 0.0392 C5 may be split into 0.5976 0.3191 0.3424 and 0.5834 0.3017 0.3597
```

Manual inspection : Thermal parameters

Wrong atom assignments



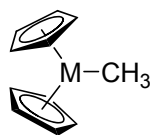
CHECKCIF: Violation of the “Hirshfeld test”



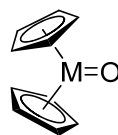
Bond Distances

Verify if the obtained geometry is reasonable

For example, M-CH₃ versus M=O:



synthesized



crystallized

Sources for bond distances and angles values:

- Cambridge data base
- A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, R. Taylor, *J. Chem. Soc. Dalton Trans.* **1989**, S1-S83.
- F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. II* **1987**, S1-S19.

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Aids to verify your structure

The CIF file enables an automated verification of your structure

- Using PLATON (<http://www.cryst.chem.uu.nl/platon>)
- **Better, at: <http://journals.iucr.org/services/cif/checkcif.html>**

Verifications:

- Missed symmetry (wrong space group)
- Holes/voids in the structure
- Thermal parameters (Hirshfeld test)
- Bond distances and angles
- Atom assignment
- Other details of the refinement and the data collection

**There are absolutely no reasons, nor excuses,
not to verify a structure with CHECKCIF!**

The Checkcif report

The automated report contains three types of alerts:

ALERT level A = In general: serious problem

ALERT level B = Potentially serious problem

ALERT level C = Check and explain

It is impossible to explain all possible CHECKCIF errors here. If you use the checkcif routine on the site www.iucr.org, you can click on the alert to obtain more information. Or ask other crystallographers. Or me. But there is no excuse for ignorance.

If you ignore or comment an error, which you do not understand, you are not an expert, but a scientific failure!

Try to eliminate all problems. If not, comment on the error, explaining where this alert is coming from and why we can ignore it or cannot do anything about it.

Example of a checkcif report

The following ALERTS were generated.

Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.


Click on the hyperlinks for more details of the test.

Alert level A

PLAT761_ALERT_1_A CIF Contains no X-H Bonds ?

PLAT762_ALERT_1_A CIF Contains no X-Y-H or H-Y-H Angles ?

Redo the refinement
with BOND \$H instead
of BOND



Alert level B

PLAT230_ALERT_2_B Hirshfeld Test Diff for C24 - C25 .. 7.36 su

Alert level C


CRYSC01_ALERT_1_C The word below has not been recognised as a standard identifier. : plates

CRYSC01_ALERT_1_C No recognised colour has been given for crystal colour.

PLAT222_ALERT_3_C Large Non-Solvent H Ueq(max)/Ueq(min) ... 3.08 Ratio

PLAT230_ALERT_2_C Hirshfeld Test Diff for C25 - C26 .. 5.93 su

Correct manually
in the CIF file



.cif:

_exptl_crystal_description

red

_exptl_crystal_colour

plates

Correcting the CIF file

It is often your job to manually correct wrong entries in the CIF.

But: You do have to know which values you are allowed to change and have a good reason for changing them. **Do not change the CIF or alter your refinement just to make CHECKCIF alerts vanish!**

If you are not sure: Ask!

Example of a checkcif report

The following ALERTS were generated.

Each ALERT has the format [test-name_ALERT_alert-type_alert-level](#).

Click on the hyperlinks for more details of the test.

Alert level A

Alert level B

PLAT230_ALERT_2_B **Hirshfeld Test** Diff for C24 - C25 .. 7.36 su

Alert level C

PLAT222_ALERT_3_C Large Non-Solvent H Ueq(max)/Ueq(min) ... 3.08 Ratio

PLAT230_ALERT_2_C Hirshfeld Test Diff for C25 - C26 .. 5.93 su

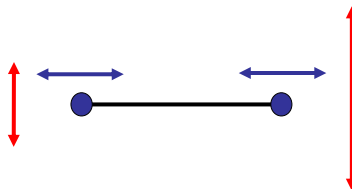
Short detour: Hirshfeld rigid-bond test

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).”

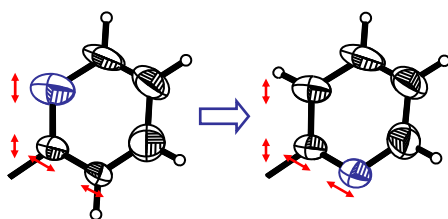
Hirshfeld, F. L. (1976). *Acta Cryst.* A32, 239–244.

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

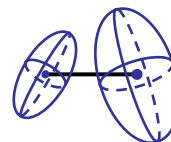


Hirshfeld test violations

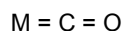
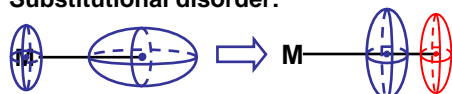
Wrong atom assignment:



Bad description of thermal ellipsoids
(data quality problem, disorder etc.)



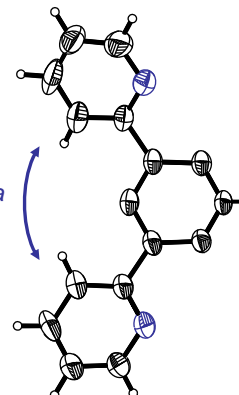
Substitutional disorder:



Linear distribution of electrons in bonds

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

but:
Vibration of a
whole group



Example of a checkcif report

Alert level B

PLAT230_ALERT_2_B Hirshfeld Test Diff for C24 - C25 .. 7.36 su

=> *caused by vibration of a complete phenyl substituent*

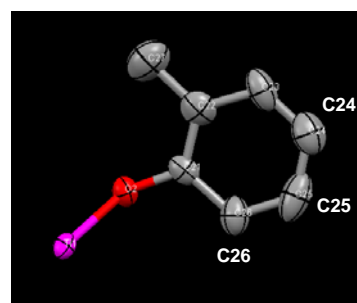
Alert level C

PLAT222_ALERT_3_C Large Non-Solvent H Ueq(max)/Ueq(min) ... 3.08 Ratio

=> *presence of strongly vibrating terminal phenyl groups and strongly bound Cp-groups*

PLAT230_ALERT_2_C Hirshfeld Test Diff for C25 - C26 .. 5.93 su

=> *caused by vibration of a complete phenyl substituent*



The Checkcif report

Why should you comment on CHECKCIF errors:

- You have to do it anyway, if you want to publish a structure.
- It shows the reader that, despite the errors, the structure is of good quality.
- When you write up your thesis or a publication, sometimes years later, you might not recall what caused the alert and what you have already tried to resolve it. Even worse, if you are gone and your supervisor tries to publish your results.
- **Finish all structures to the point, where they are immediately publishable.**

How to comment on remaining CHECKCIF errors:

1. Copy the report in a Word or equivalent software, add your comments and archive it together with the CIF. **Not the best choice, since the information is not in the CIF.**

The Checkcif report

How to comment on remaining CHECKCIF errors:

2. **Write your comments in the CIF file. For example, under the variable `_refine_special_details` :**

```
_refine_special_details
;
Refinement of F^2^ against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on F^2^, conventional R-factors R are based
on F, with F set to zero for negative F^2^. The threshold expression of
F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on F^2^ are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.

Comments on remaining CHECKCIF errors:

Hirshfield test violations for atoms C24, C25 and C26 are caused by a
strong vibration of a complete phenyl substituent.

The large difference between Ueq(max)/Ueq(min) is caused by the presence
of strongly vibrating phenyl groups and strongly bound Cp atoms in the
structure.
;
```

Advantage: already present in CIF. **Disadvantage:** Easily missed by reviewers.

The Checkcif report

How to comment on remaining CHECKCIF errors:

3. Add your comments using the “Virtual reply form” :

Checkcif report:

```
Alert level B
PLAT230_ALERT_2_B Hirshfeld Test Diff for C24 - C25 .. 7.36 su
Alert level C
PLAT222_ALERT_3_C Large Non-Solvent H Ueq(max)/Ueq(min) ... 3.08 Ratio
```

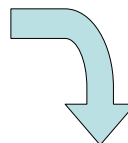
CIF file:

```
data_example1
_vrf_PLAT230_example1
;
RESPONSE:
Caused by vibration of a complete phenyl substituent
;
_vrf_PLAT222_example1
;
RESPONSE:
Presence of strongly vibrating terminal phenyl groups and
strongly bound Cp-groups.
;
```

The Checkcif report

Disadvantage: A bit more effort, the format must be followed exactly!

```
_vrf_error code_data code
;
RESPONSE:
Your reply
Your reply
Your reply
;
```



Datablock: shap30

The following ALERTS were generated. Each ALERT has the format [test-name_ALERT_alert-type_alert-level](#). Click on the hyperlinks for more details of the test.

- **Alert level B** [PLAT230_ALERT_2_B](#) Hirshfeld Test Diff for C24 - C25 .. 7.36 su

Author Response: [Caused by vibration of a complete phenyl substituent](#)

- **Alert level C** [PLAT222_ALERT_3_C](#) Large Non-Solvent H Ueq(max)/Ueq(min) ... 3.08 Ratio

Author Response: [Presence of strongly vibrating terminal phenyl groups and strongly bound Cp-groups.](#)

Advantage: Your comments will be visible if anybody submits the CIF file to the CHECKCIF routine

PLAT154_ALERT_1_G The su's on the Cell Angles are Equal 0.00200 Deg.
Author's response: Provided data is correct. Unrounded su's show slight differences.

CIF:

_cell_angle_alpha 92.702(2)
_cell_angle_beta 93.216(2)
_cell_angle_gamma 98.523(2)

	A	B	C	Alpha	Beta	Gamma	Vol
	9.40774	9.44160	21.46292	92.7024	93.2165	98.5227	1879.43
	0.00006	0.00006	0.00015	0.0002	0.0003	0.0002	0.03
Corrected for goodness of fit:							
	0.00057	0.00058	0.00135	0.0023	0.0025	0.0021	0.23

PLAT761_ALERT_1_A CIF Contains no X-H Bonds ?

PLAT762_ALERT_1_A CIF Contains no X-Y-H or H-Y-H Angles ?

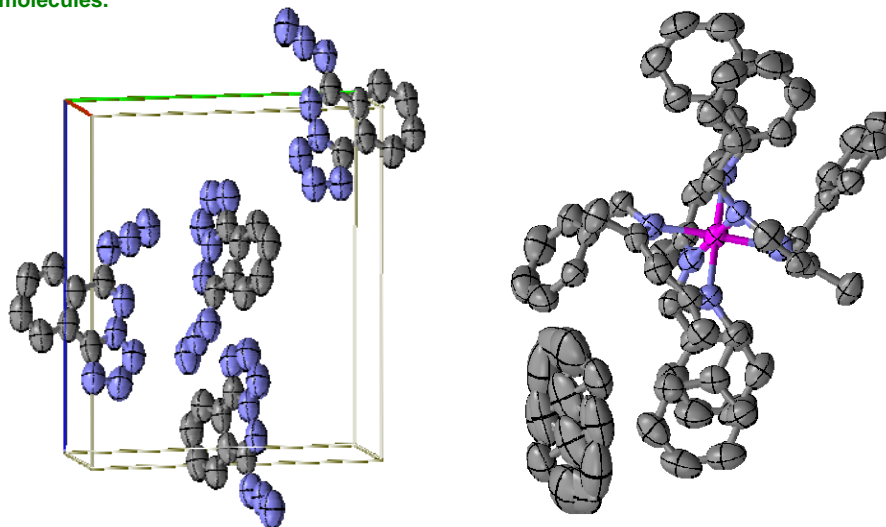
Add a BOND \$H command to the INS file. Repeat the refinement.

PLAT093_ALERT_1_B No su's on H-atoms, but refinement reported as . Mixed

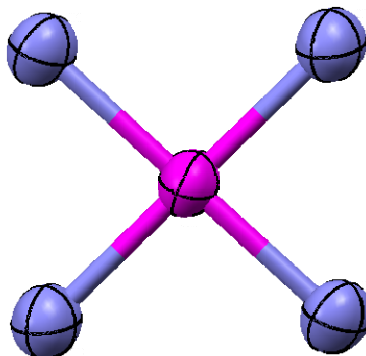
Enter the correct value, most likely constr

PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor 3.5

Author Response: Manual inspection of the thermal ellipsoids does not indicate any preferred orientation. The increased U3/U1 ratio is most probably caused by the toluene solvent disordered around the inversion center, which has increased thermal ellipsoids parallel to the line connecting the centers of gravity of the disordered molecules.



PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Cr1 -- N1 .. 6.0 su
Author Response: Manual inspection of the thermal ellipsoids does not indicate any problems. The alert might be caused by the low sd of the heavy atom position.

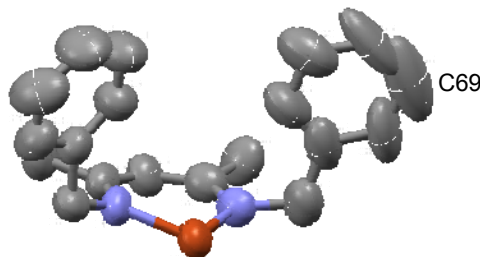


Since the Hirshfeld test is performed relative to the esd of the thermal parameters, heavy atoms with very low esds show sometimes “invisible” Hirshfeld test violations.

PLAT072_ALERT_2 SHELXL First Parameter in WGHT Unusually Large. 0.12
Author Response: PLATON TWINROTMAT did not indicate any evidence for twinning.

PLAT366_ALERT_2_C Short? C(sp²)-C(sp²) Bond C26 - C27 ... 1.38 Ang.
Author Response: Styrene olefinic bond. For discussion, see text.

PLAT241_ALERT_2_A Check High Ueq as Compared to Neighbors for C69
Author Response: We observed deviations of expected thermal parameters which are in agreement with a slight rotational disorder of the benzyl groups. (ADPs decrease from para to ipso). The disorder is present in all benzyl groups and affects the molecule as a whole. Resolution of the disorder was possible using very strong geometric restraints, but even upon application of strong restraints on the thermal parameters, anisotropic refinement of the solved disorder was not possible. The isotropic, disordered model did not improve the structural quality (as judged from variances of chemically equivalent bond lengths) and the structure was refined anisotropically with the disorder unresolved to provide the uncertainties of atom positions in ORTEP plots and bond precision. No indication of twinning was observed during integration or in post-refinement checks (TWINROTMAT etc.)



Checklist

- $wR2 < 12\%$
- $R1 < 5\%$
- $R_{\text{int}} < 3 \times R_{\text{sigma}}$
- $0.9 < \text{GoF} < 1.2$
- Residual electron density $< 0.5 \text{ e}/\text{\AA}^3$
- No correlation matrix elements > 0.5
- Thermal ellipsoids are acceptable
- Checkcif, checkcif report and explications

- Figure showing thermal ellipsoids (50% probability level) and the numeration of atoms

- Printed version of the structural details, bond distances and angles

- Archiving: 1 x with the X-ray service, 1 x for you, 1 x for the synthetic chemist, 1 x for your supervisor

The end