

Refinement of disordered solvent moleculesⁱ

Solvent molecules, especially when they are not coordinated to metal atoms, are quite often involved in disorders. They just fill voids in the crystal lattice and so can possess several positions in the same void, when these are energetically almost equivalent.

Relatively common too are solvent molecules on special positions that do not possess the appropriate symmetry for these positions. In the spatial average this leads to disorder.

As a matter of experience, molecules of some solvents are rarely involved in disorders (e.g. acetonitrile, which is linear and therefore has less opportunity to be disordered) while other solvents like chloroform seem to be disordered in almost every case.

THF

Tetrahydrofuran is a coordinating solvent and is indeed often found in crystal structures acting as an electronically neutral ligand coordinated to metal atoms. In such cases the oxygen atom is seldom disordered. However, rotation about the M-O-axis is still possible (and often observed for thf) and the thf ring itself, possessing an envelope conformation, may be disordered in several different ways.

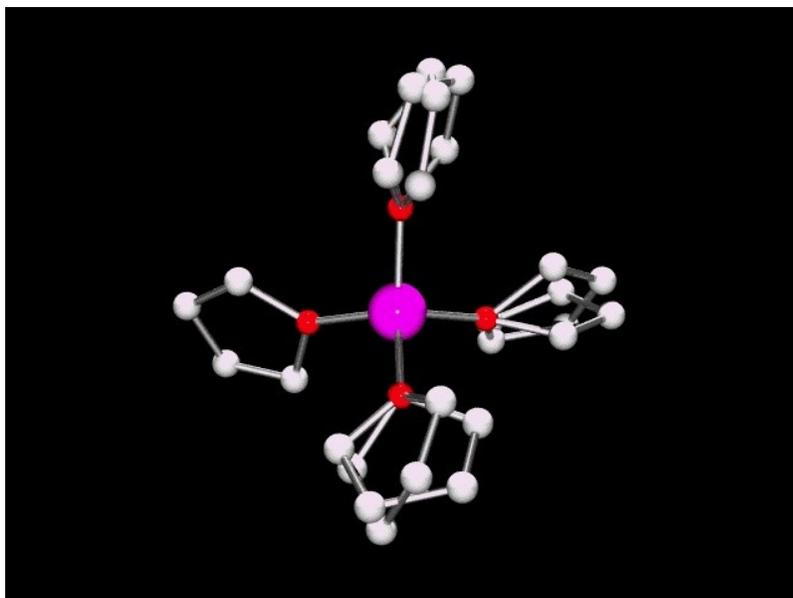


fig. 1: Four thf molecules, three of which are disordered, coordinated to a Li-Kation.

The SHELX manual (pages 5-5 *ff.*) gives an example for the refinement of thf disorders.

Chloroform

One is more likely to find a disordered chloroform molecule in a crystal than a well ordered one. When compared to other disordered solvent molecules, the disorder of chlorine-containing solvents has stronger (negative) influences on the structure because of the relatively high number of electrons that are disordered with the solvent. Therefore, where possible one should avoid using chloroform (or dichlormethane) as crystallization solvent.

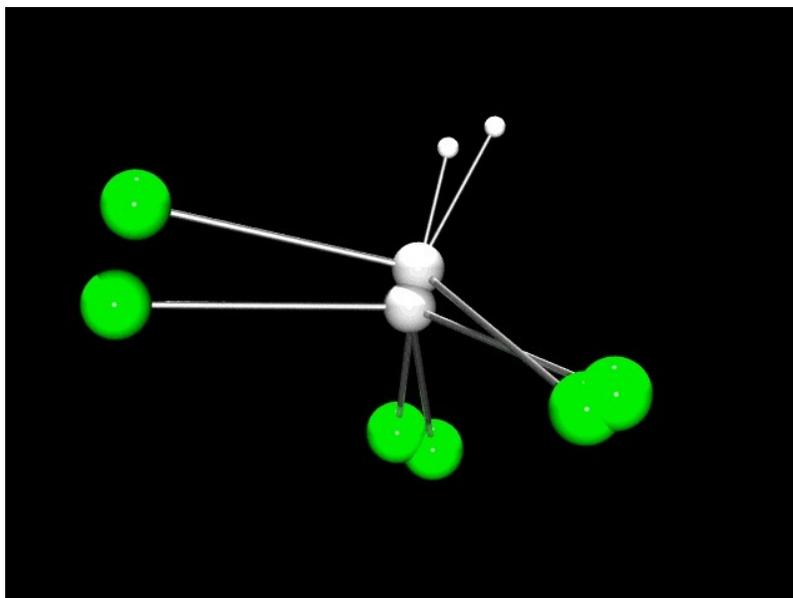


fig. 2: Typical disorder of a chloroform molecule.

The refinement of disordered chloroform is relatively easy. Therefore it is not necessary to explicitly discuss an example here.

Toluene

Because of the methyl group, toluene (point group C_{2v}) possesses a lower symmetry than benzene (point group D_{6h}). Nevertheless toluene loves occupying positions, that would be fine for benzene but not toluene, e.g. inversion centers or twofold axes perpendicular to the Ph-Me bond. This behavior causes disorder in the spatial average.

Besides that, toluene is often disordered even when it is not near a special position.

There are two typical cases of toluene disorder:

The first case shows two discrete positions, whereby the second position is twisted relative to the first one by about 180° . Thus, the methyl group of one component lies close to

the carbon atom C4 of the other component so that both components are more or less coplanar one to another (see **fig. 3**). In most such cases this type of toluene disorder involves a special positions but it can also be found for toluene molecules on general positions. An example is given below:

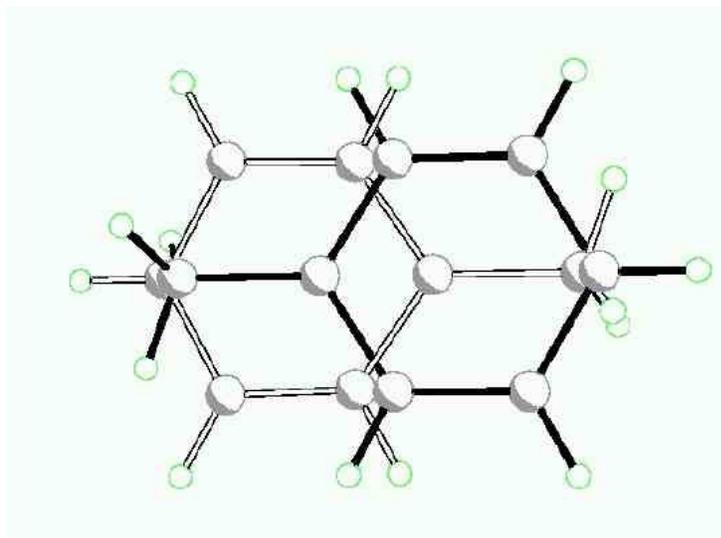


fig. 3: Typical disorder of a toluene molecule.

The second case is characterized by a particularly undetectable methyl group. The cause is a virtual rotation about the sixfold axis, which is part of the benzene molecule but not of the toluene. Thus, in the spatial average density the methyl group is distributed amongst six sites. This disorder is best refined by ignoring it; such a toluene molecule should be refined as a benzene molecule.

Typical disorder of a toluene molecule

You may wish to download some files you need to perform the refinements yourself:

[tol_1-01.ins](#) (input file for SHELXL)

[tol_1-01.hkl](#) (merged data)

Refinement with SHELXL generates the file [tol_1-01.res](#). It contains the complete anisotropic model with hydrogen atoms but not yet the solvent.

The seven highest residual electron density peaks Q(1) to Q(5), Q(8), and Q(9) (6.52, 6.10, 5.13, 5.10, 4.93, 2.10, and 1.82, respectively) are separated from the molecule and seem to be sort of solvent.

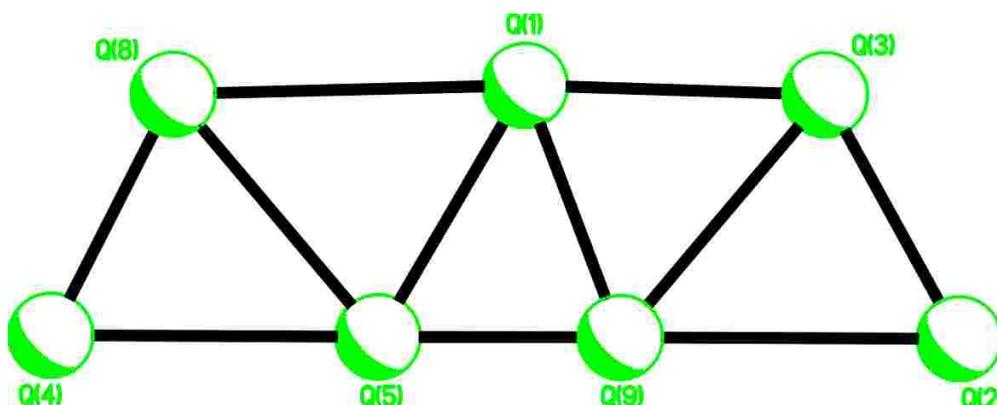


fig. 4: The seven highest residual electron density peaks. The crystallization conditions say *toluene*; the peaks Q(2), Q(4), Q(5), and Q(7) lie on the crystallographic mirror. After the generation of the symmetry equivalent atoms (e.g. using the GROW command in *XP*), one sees clearly the shape of two disordered toluene molecules, oriented in the way described above:

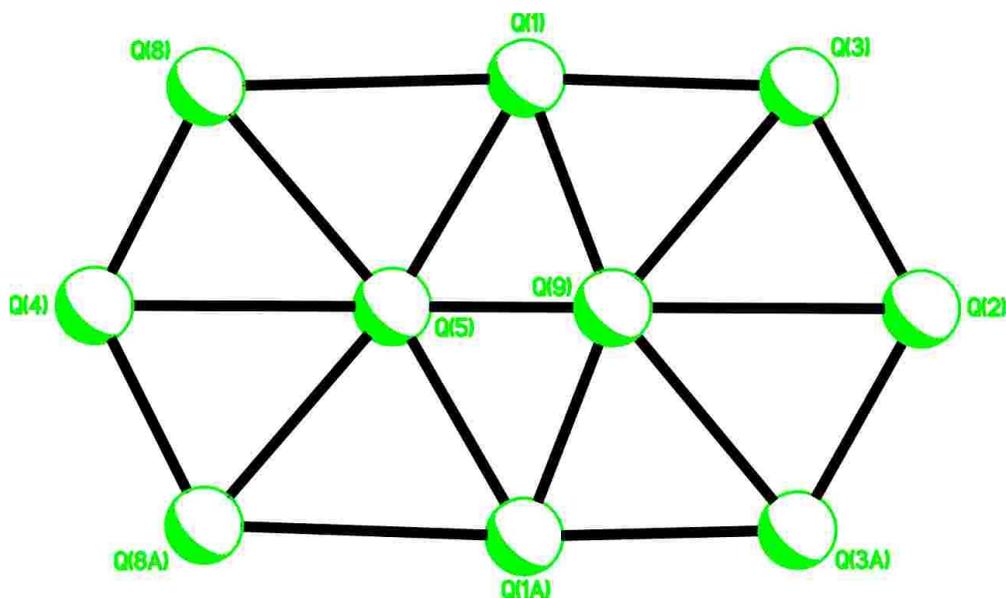
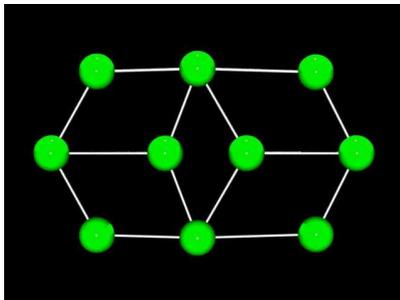


fig. 5: The same peaks after generating the symmetry equivalent atoms.

For an animated gif of the solution showing the two different toluene positions click on the image below:



For the next refinement step rename the crystallographically independent Qs:

Q(1) --> C(2A) **and** C(2B)

Q(2) --> C(4A) **and** C10B

Q(3) --> C(3A)

Q(4) --> C(C10A) **and** C(4B)

Q(5) --> C(1A)

Q(8) --> C(3B)

Q(9) --> C(1B)

Thereby A belongs to PART 1 and B to PART 2

Don't forget to change the site occupation factors and to set the second Free Variable as well as to give the similarity restraints (**SAME**) and **SIMU**, **DELU** and **FLAT** for the disordered atoms as it has been done in the file [tol_1-02.ins](#). Take into account the symmetry equivalents (use **EQIV**).

SHELXL produces the file [tol_1-02.res](#).

The second Free Variable refined to 0.75, which is a reasonable value and the *R* values are a lot better now. **Fig. 6** shows th two molecules.

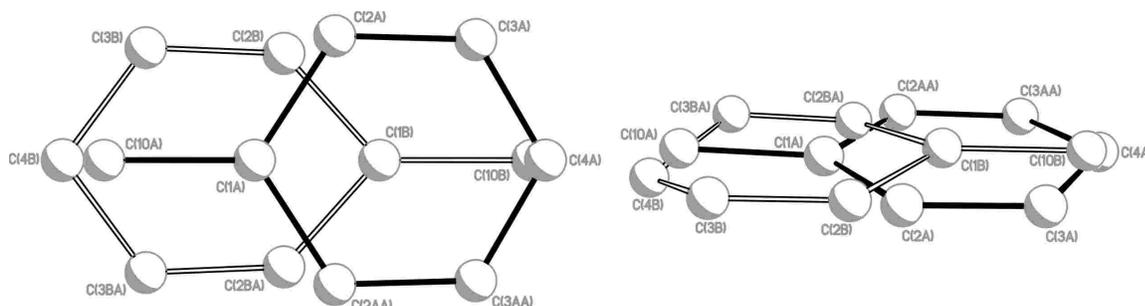


fig. 6: Two different views to the first refinement of the disordered toluene molecule.

In the next step one can allow the disordered atoms to be refined anisotropically (just add **ANIS**; see [tol_1-03.ins](#)). Now, in [tol_1-03.res](#), the two toluene molecules look rather fine as shown in **fig. 7**.

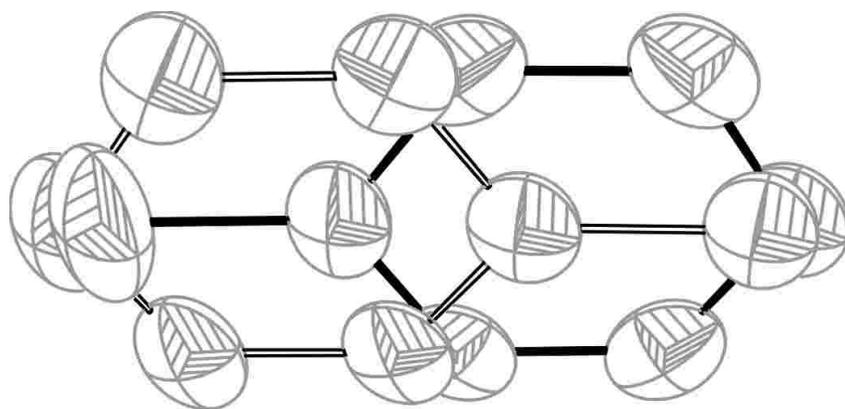


fig. 7: Reasonable model for the disordered toluene.

Next step (realized in [tol_1-04.ins](#)):

HFIX 43 for C(2A), C(2B), C3(A), C(3B), C(4A), and C(4B).

HFIX 33 for C(10A) and C(10B).

The refinement seems to be stable (results in [tol_1-04.res](#)).

All that has to be done now is to refine until the weighting scheme has converged as is the case in the file [tol_1-05.res](#).

i <http://shelx.uni-ac.gwdg.de/~peterm/tutorial/do-solv.htm>