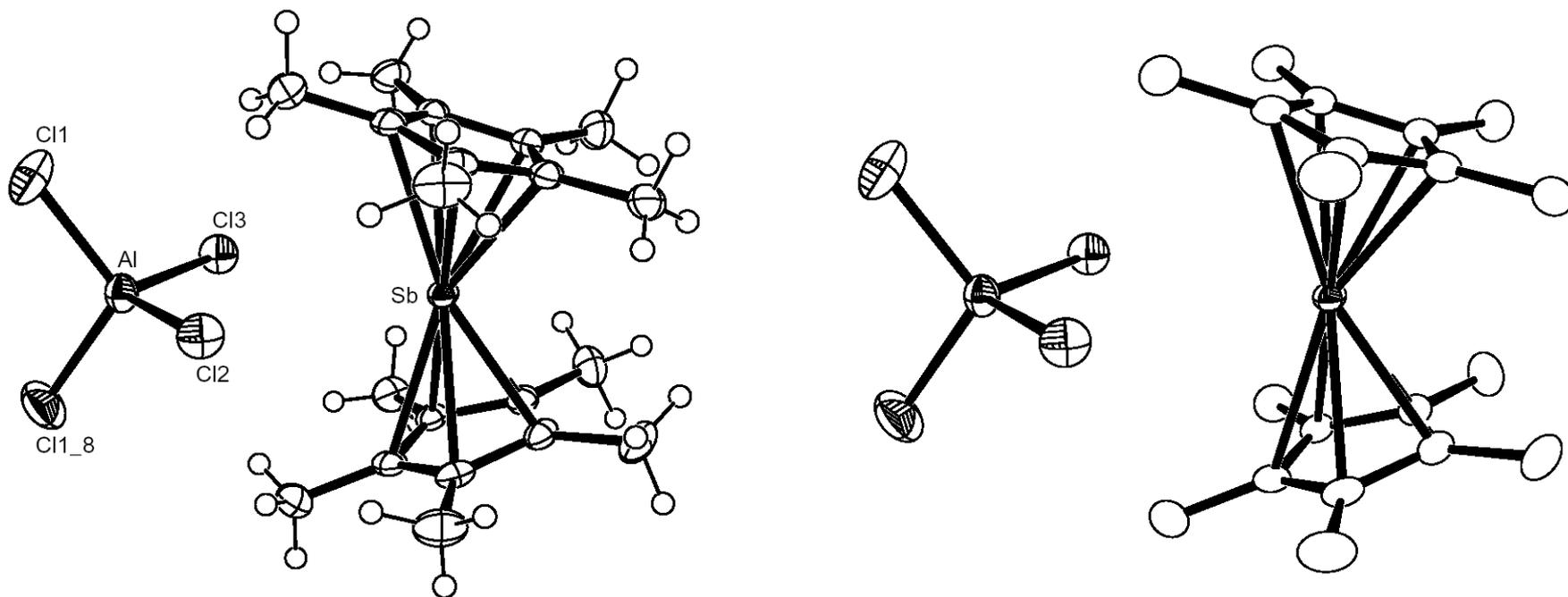
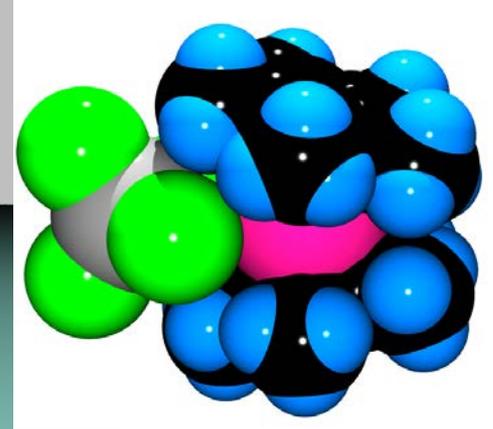
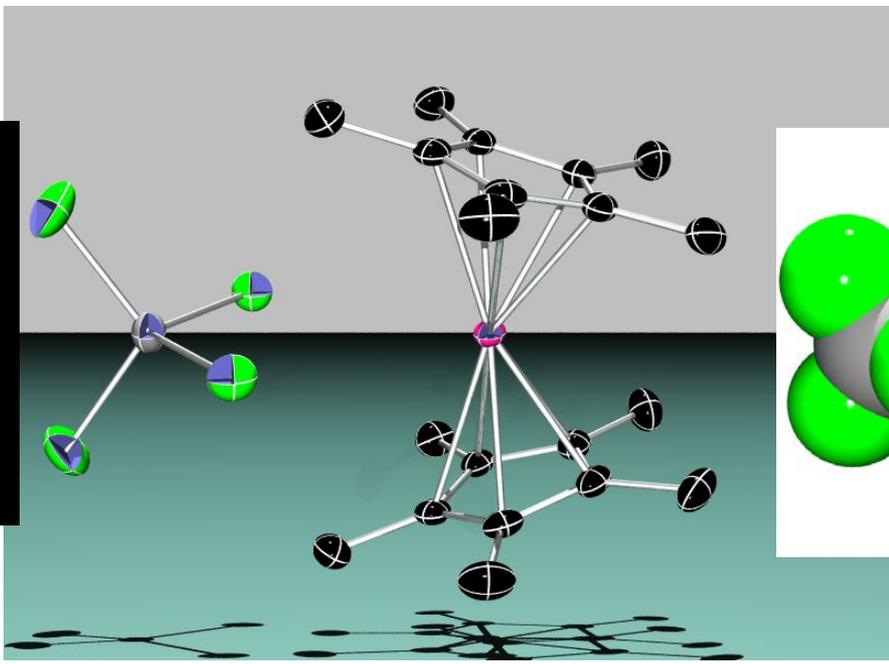
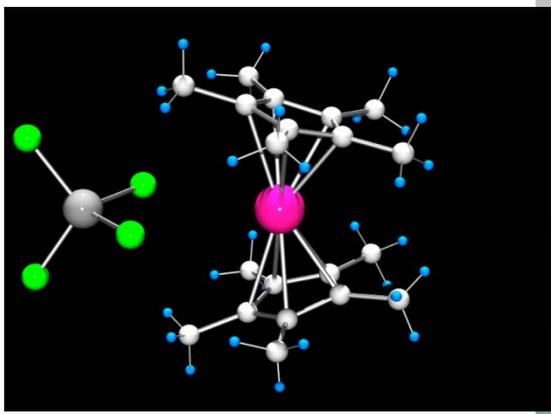
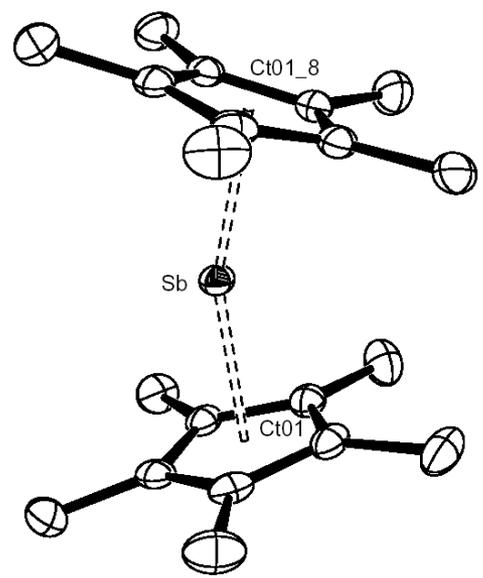
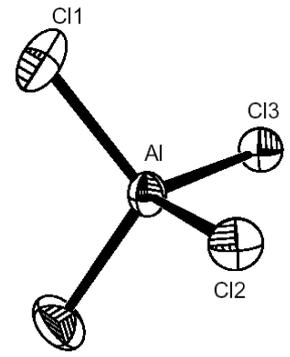
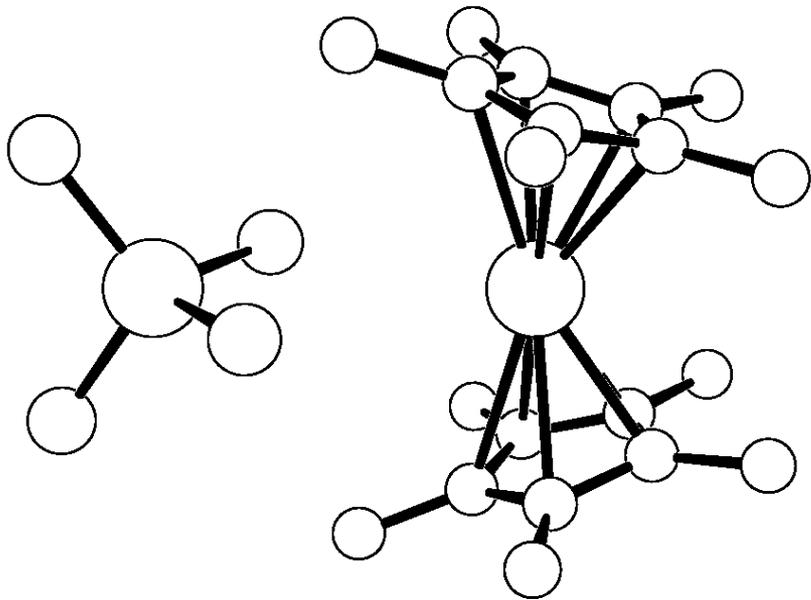


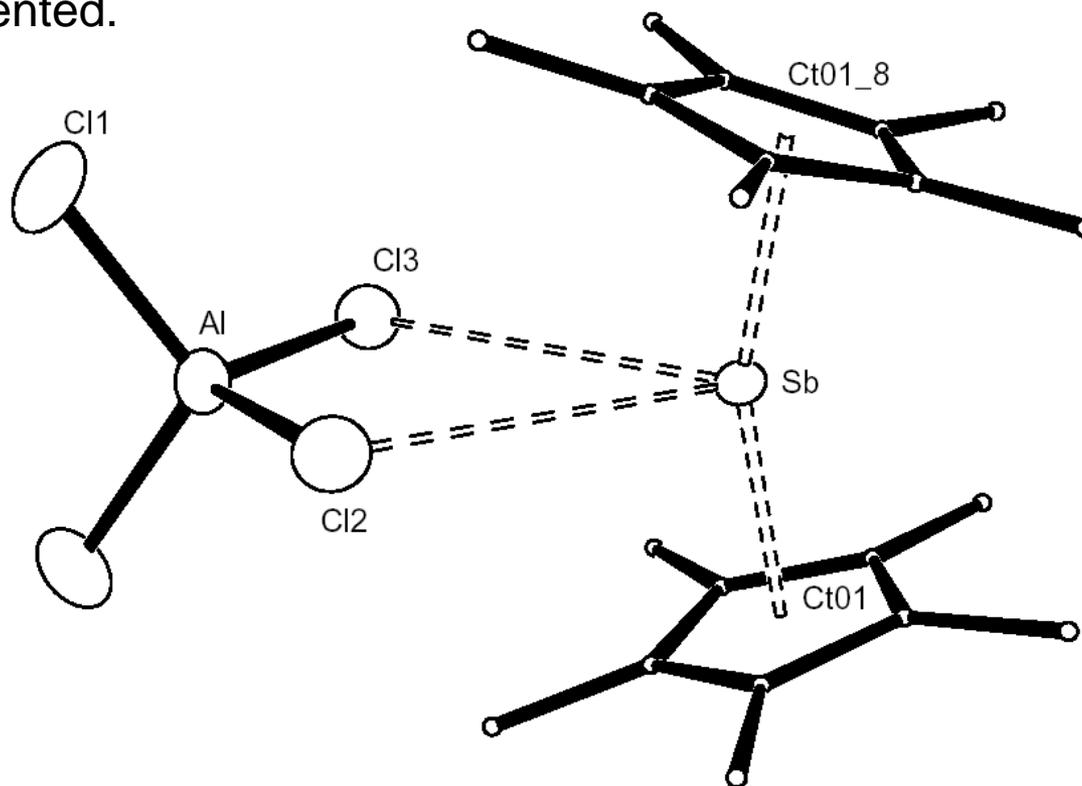
One of the most important aspects of the data reporting process (i.e. publication or presentation) is the graphical presentation of your results. There are numerous software packages that may be used to generate informative and attractive drawings of your molecules including: ORTEP-3 (sometimes in combination with POV-ray), SHELXP (XP), Diamond, and many others. I suggest that you examine a few different applications and become comfortable with at least a few of them.





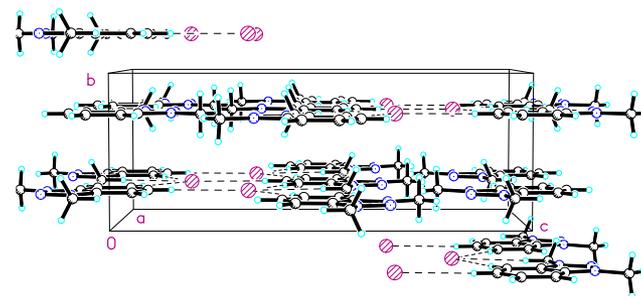
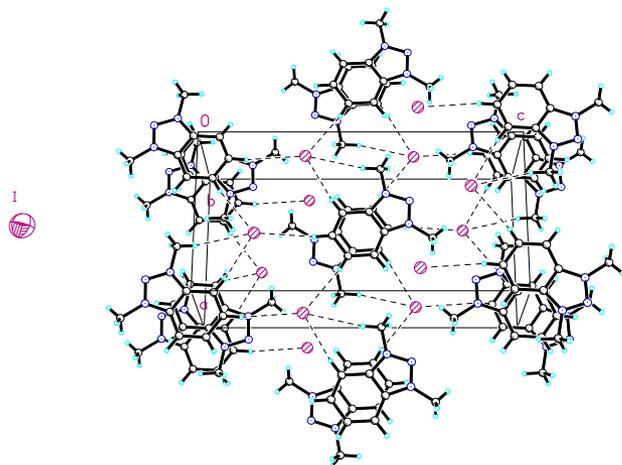
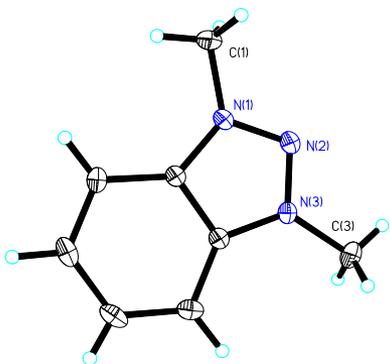
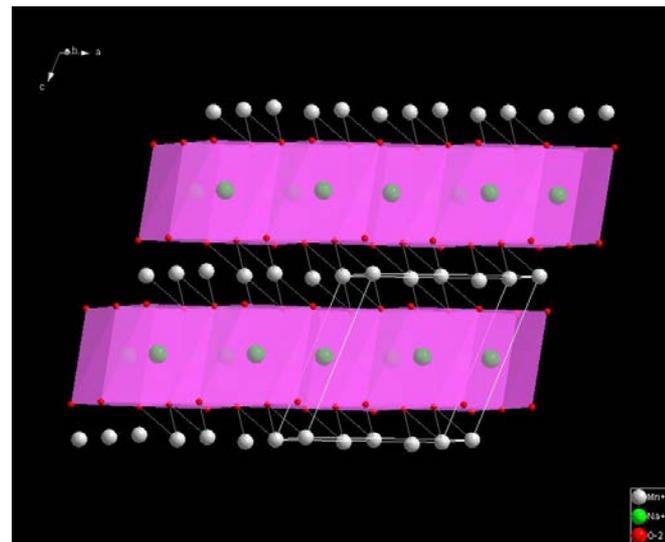
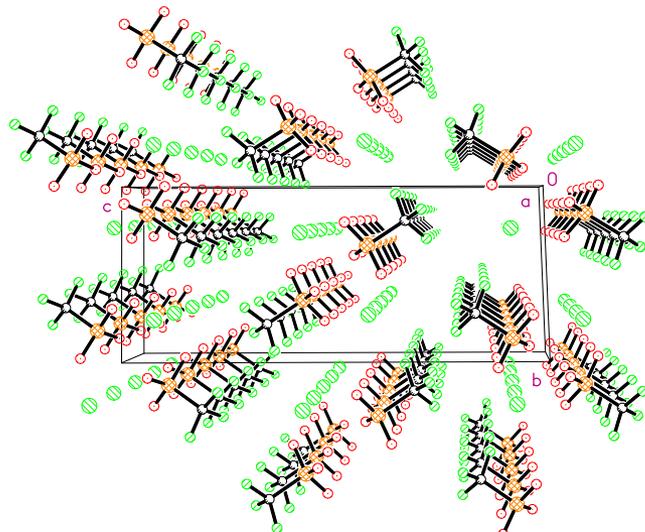
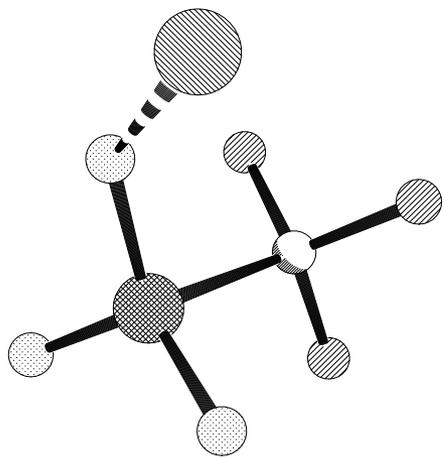


Regardless of the type of picture you want to make, remember that the primary goal is to convey some sort of information! In this light, it is often wise to change the representations of atoms or bonds that are unnecessary so as to offer a clear view of the important features of the structure. You know the chemistry your structure is helping to explain so you are the best judge of how the information should be presented.



Remember that sometimes key information is provided by the packing and other interactions are important so you should always look at extended views of the structure.

Packing diagrams can provide information about the overall crystal structure, the intermolecular interactions, hydrogen bonding etc.



One of the most common “problems” you may encounter during the refinement of a crystal structure is disorder. In general, “disorder” implies that the arrangement (or identity) of the atoms is not the same for every unit cell in the crystal. **Remember that since each structure factor is determined by the entire contents of the unit cell, disorder in any part of the model affects the quality of the entire model!**

Disorder can be considered in two major (sometimes related) types:

Positional disorder – the arrangement of groups of atoms in the model are different (as illustrated at right).

Occupational disorder – the atoms, ions, or molecules are not the same in every unit cell. This is common in minerals where e.g. a site can be occupied by various types of cations.

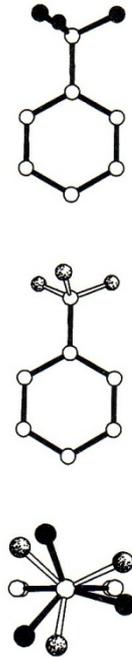


Fig. 4.1 A disordered trifluoromethyl group attached to a benzene ring: top and centre, the two observed disorder components; bottom, the combined disorder model seen in projection along the bond between the CF₃ group (in front) and the ring (behind).

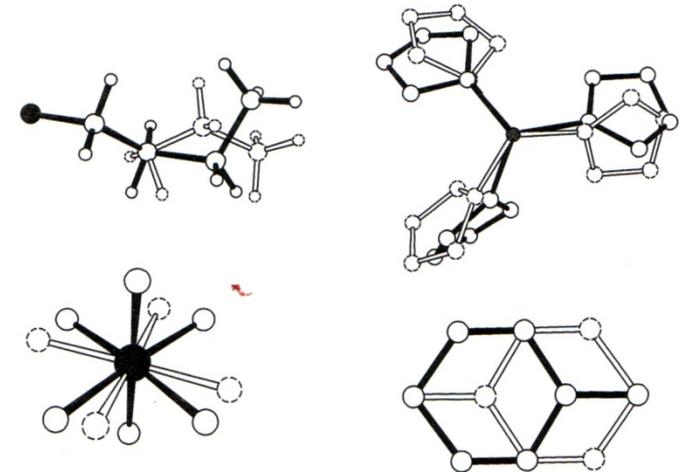


Fig. 4.2 Some examples of disorder: top left, an *n*-butyl chain in which the last two carbon atoms (with their hydrogen atoms) adopt two alternative positions; top right, three disordered thf ligands coordinated to a metal atom; bottom left, an AsF₆⁻ anion with two orientations related by rotation about one of the linear FAsF units; bottom right, a toluene solvent molecule disordered over an inversion centre (hydrogen atoms not located!).

Most disorder is easily handled during the refinement by refining both of the disordered components separately with the requirement that the sum of the individual components is 1. E.g. if you model a disordered ^tBu group with two parts, the total contribution from each part must add up to unity (there must be a total of one ^tBu group).

Such models are accomplished using the free variables and PART commands in SHELX. Sometimes you will also want to use the EADP command to constrain the thermal ellipsoids to be equal for the equivalent atoms in both models.

```
EADP C11 C21
EADP C12 C22
EADP C13 C23
....
FVAR .... 0.75
```

Free variable 2 (FV 2) with a starting value of 0.75

```
....
PART 1
C11 1 ..... 21.000 ...
C12 1 ..... 21.000 ...
C13 1 ..... 21.000 ...
```

With this value for FV 2, this position is modeled as 75% occupied.

```
PART 2
C21 1 ..... -21.000 ...
C22 1 ..... -21.000 ...
C23 1 ..... -21.000 ...
```

The “-2” implies (1-FV 2) so this arrangement will be treated as 25% occupied.

```
PART 0
....
```

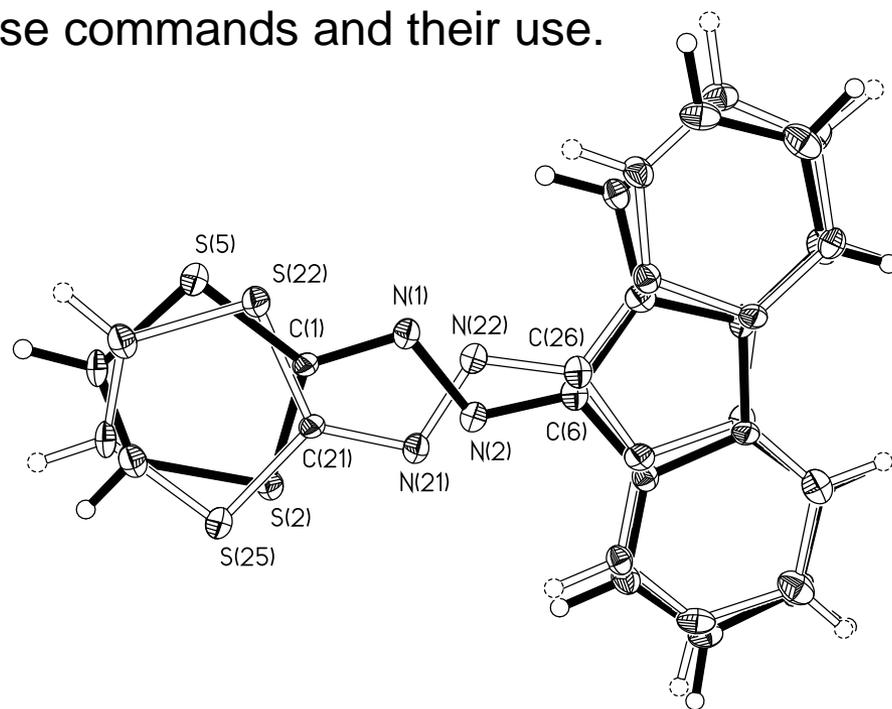
The PART instructions tell the software not to connect the atoms from the different parts.



Fig. 4.1 A disordered trifluoromethyl group attached to a benzene ring; top and centre, the two observed disorder components; bottom, the combined disorder model seen in projection along the bond between the CF₃ group (in front) and the ring (behind).



Sometimes an entire molecule can pack itself effectively in more than one way. This can be considered as a form of occupational disorder. The more commonly found occupational disorder occurs because different simple cations (e.g. Na or K) can occupy the same type of site in many types of crystals. Such disorder can also be modeled using free variables with appropriate PART, EADP, EXYZ (equivalent xyz positions) and other commands. See the online SHELX manual for more complete descriptions of these commands and their use.



In this structure, the molecule can sit in two different orientations and still occupy the same volume and roughly the same shape of space in the lattice. In this case, the major component (drawn with dark lines) is found around 75% of the time: FVAR 0.25983 **0.75266**

Another common problem you may encounter is known as twinning, which occurs when two (or more) lattices grow together in an oriented manner. Macroscopic twinning is generally observable when the crystals are examined under a microscope, especially if it is equipped with polarizers. Examples of obviously twinned crystals are shown below. This is called “non-merohedral” twinning and can be solved with CELLNOW or, sometimes, a decent single crystal can be obtained by cutting away the twin.

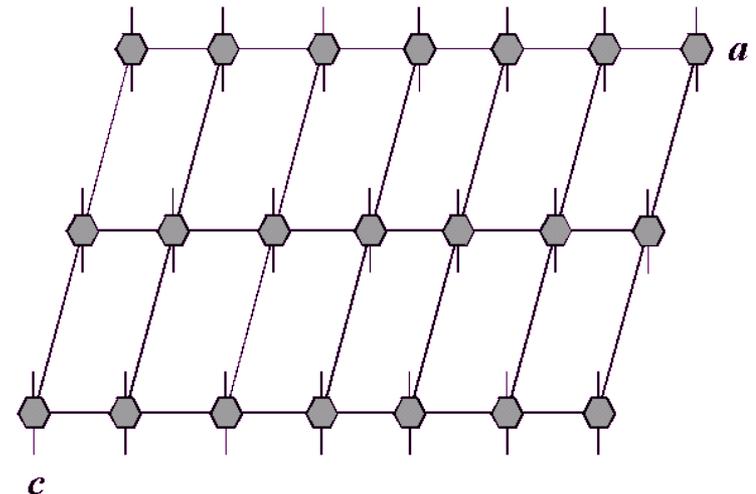
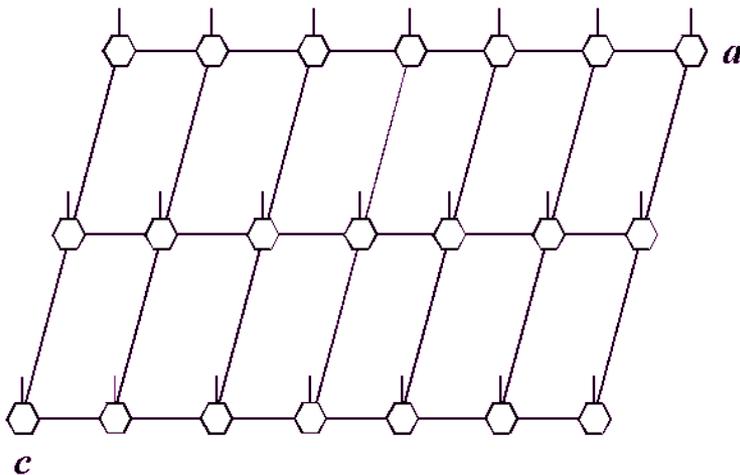


More problematic forms of twinning are often not observable by optical methods but become apparent in the solution or refinement of the structure. Such twins are “generated” by the presence of symmetry elements that are not part of the true space group – in reality the crystals grow the way they want to and we classify them based on the relationship between the lattices. These types of twinning include merohedral twinning, pseudo-merohedral twinning, reticular twinning, pseudo-reticular twinning and, again, non-merohedral twinning. Each of these types of twinning are described at the web site: <http://www.lcm3b.uhp-nancy.fr/mathcryst/twins.htm> (from which I obtained the diagrams on the following pages) and some methods that are used to solve such problems are found at: <http://shelx.uni-ac.gwdg.de/~rherbst/twin.html>. “Merohedral” indicates the presence of symmetry that is not that of the lattice.

In merohedral twins, the real and reciprocal lattices of both components are coincident. This type of twinning is easily handled by SHELX.

Projection along $[010]$ of a monoclinic Pm structure (lattice point symmetry $2/m$) with an object with point symmetry $2mm$ at the origin. The symmetry of the motif is only m

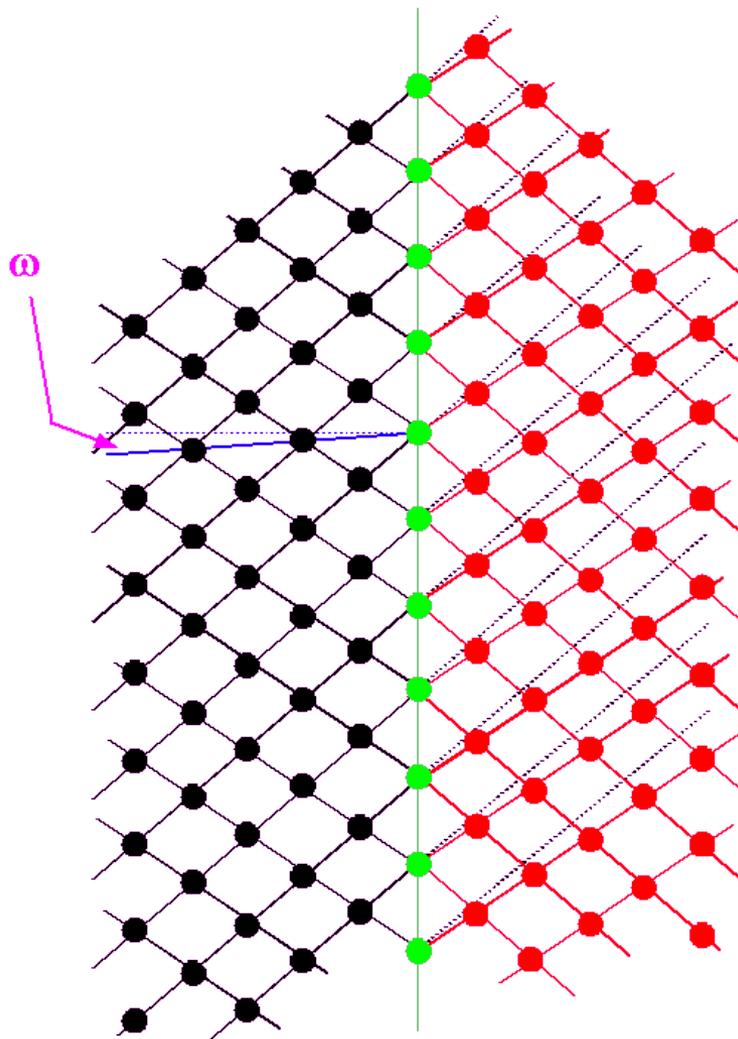
Effect of the axis $2_{[010]}$ as twin element: the motif is repeated in the same positions but with a different, non-equivalent orientation (two rotated copies of the same motif are shown superposed in the projection).



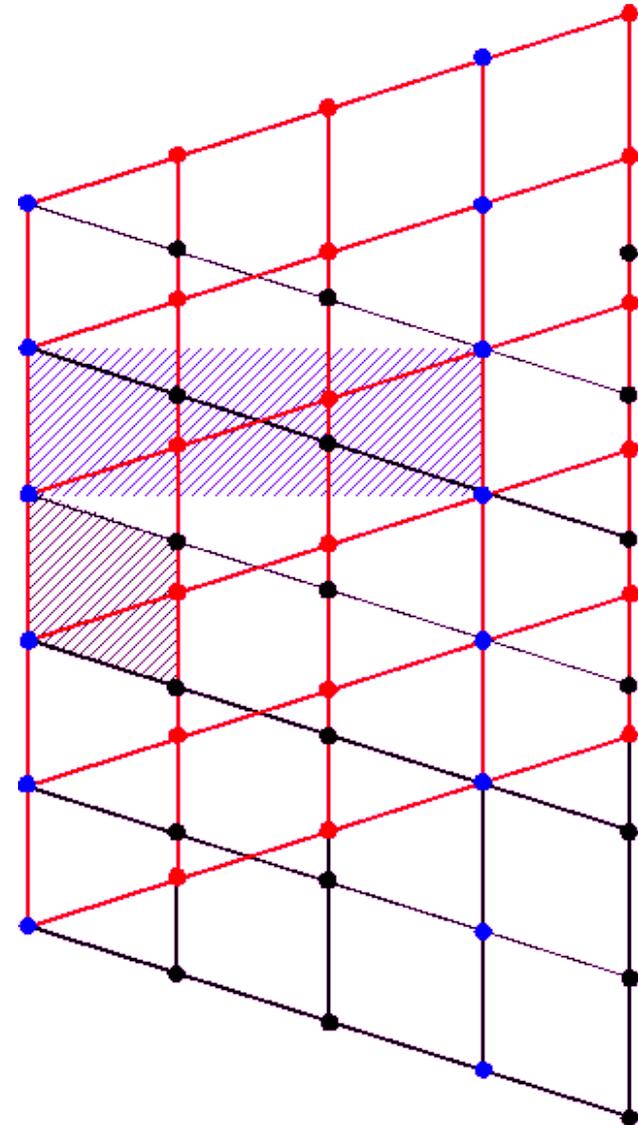


Pseudo-merohedral generally occurs when the metrical parameters of a lower symmetry unit cell are similar to those of a higher symmetry cell. E.g. if a monoclinic cell has $\beta \approx 90^\circ$ it can emulate an orthorhombic cell, if it has $\beta \approx 120^\circ$ it can emulate a trigonal cell.

In this picture the angle β is not drawn close to 90° to highlight the difference between the orientation of the black lattice and the red lattice. If the angles are close to 90° , the two lattices would nearly coincide. This type of twinning is easily handled in SHELX.



In this type of twinning, the two different lattices (red and black) are arranged such that some of the lattice points (shown in blue) end up being common to both of the component lattices. This situation ends up producing a “supercell” shown in blue. Note that, **in this case**, since every third lattice point ends up being common the overall structure is described as having a twin index of 3. Such indices are only used for this type of twinning.

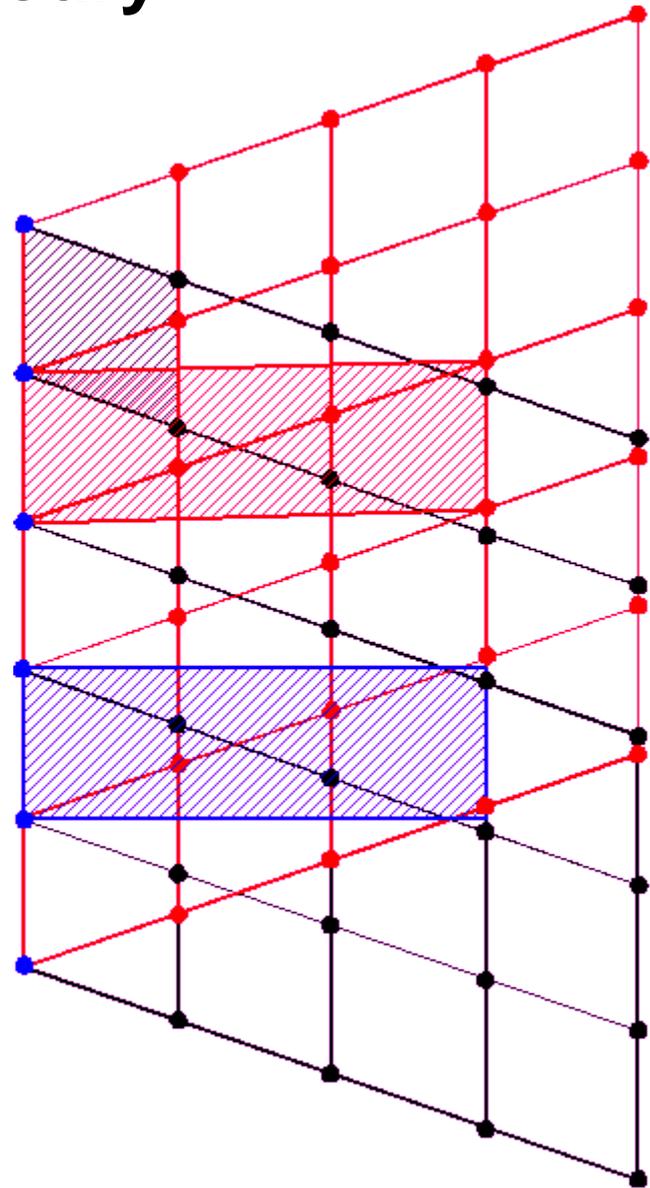


Twinning by Reticular Pseudo-Merohedry

Twinning by reticular pseudo-merohedry is similar to a combination of the second and third types outlined on the previous pages.

In this type of twinning, the two different lattices (red and black) are arranged such that some of the lattice points (shown in blue) end up being ALMOST common to both of the component lattices. This situation ends up producing a “supercell” shown in blue.

Overall, you should be aware that twinning may problems with the solution, refinement and interpretation of your data. Consult the handout for some of the possible indications of twinning.

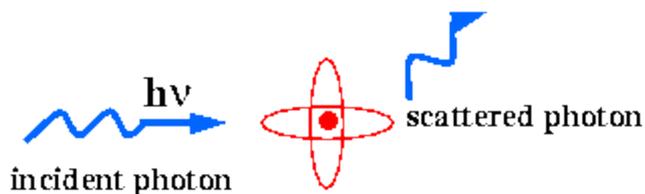




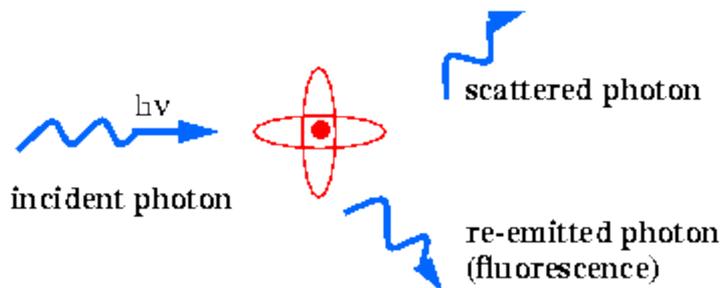
Anomalous Scattering and Absolute Configuration

X-ray crystallography can be used to determine the absolute configuration of chiral molecules when they crystallize in non-centrosymmetric space groups. To understand how this is done, we must look at the effect of “anomalous scattering” on the structure factors.

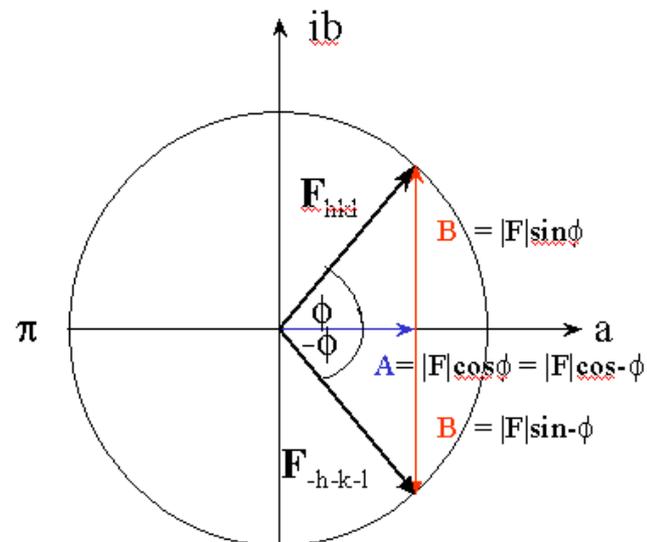
The scattering that we have considered to date is “normal” elastic scattering.



“Anomalous” scattering refers to elastic scattering events that are **delayed** because of absorption by the atoms.



While this effect is not observable in centro-symmetric system (where \mathbf{F}_{hkl} is only on the real axis), it has an effect on non-centric systems.



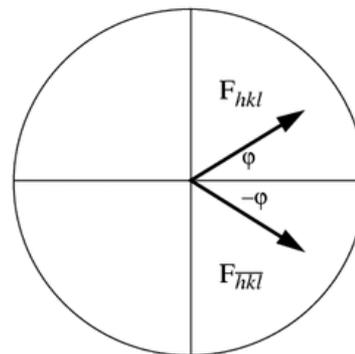


Anomalous Scattering and Absolute Configuration

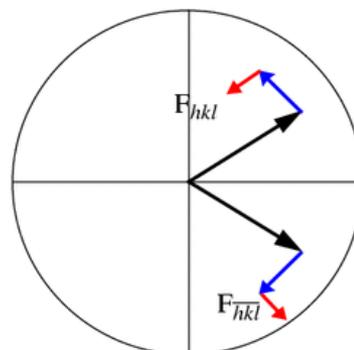
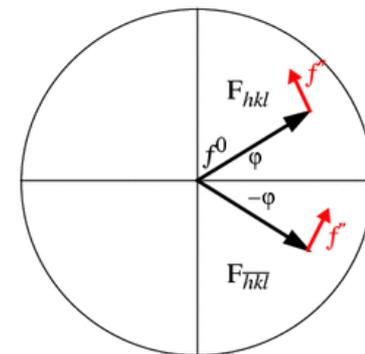
While this effect is not observable in centro-symmetric system (where F_{hkl} is only on the real axis), it has an effect on non-centric systems: Friedel's Law is no longer valid. Since the anomalous scattering involves a delay, one can consider that the phase shift associated with this (shown with the red vectors) event will be in the same "direction" (the angle between the scattering vector and the anomalous scattering vector is the same).

Modern detectors are able to measure the difference in intensities between the reflections that would have been equal if Friedel's law held. Note that in the past, anomalous scattering required the presence of heavy atoms, which are not required for most small molecules using the current technology.

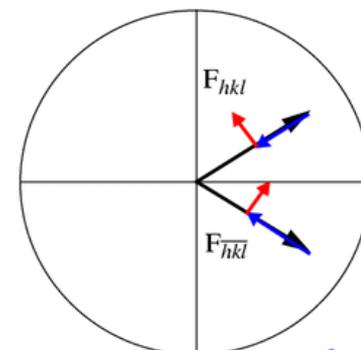
Using the Hamilton R factor approach, you would solve the structure (xyz) and solve the "inverted" structure (-x-y-z) and compare the R values for the solution. This approach is not particularly dependable and is not generally used at present.



*Equal atom case:
all atoms have the same
scattering behaviour*

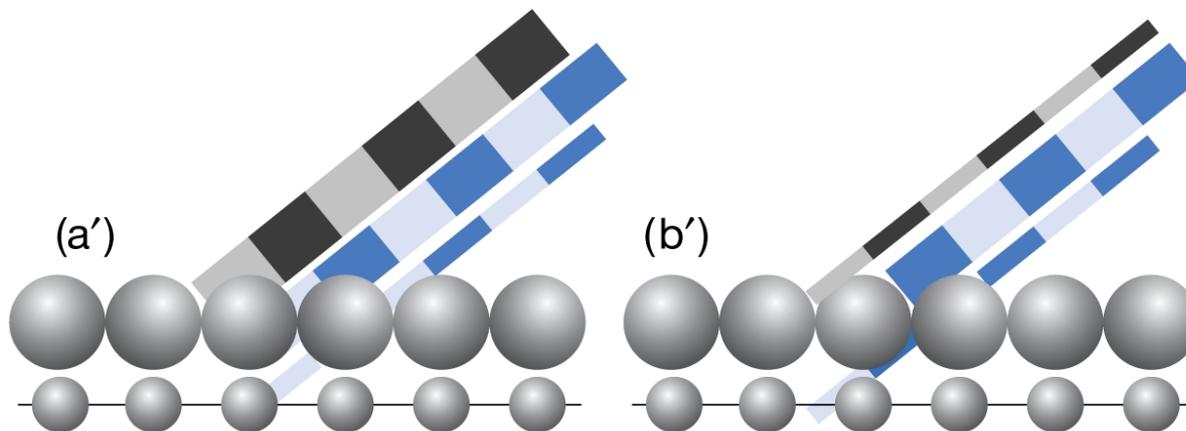
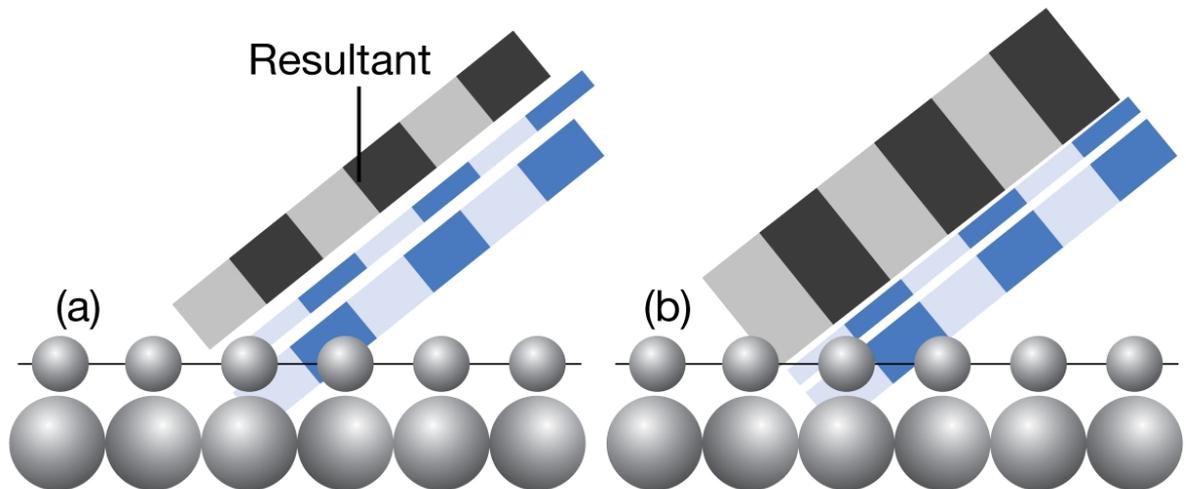


ΔF is largest when the contribution f^0 from the anomalous scattering atoms is $\pi/2$ out of phase with that of the non-anomalous atoms



ΔF is smallest (zero) when the f^0 contribution is in phase with that of the non-anomalous atoms

Anomalous Scattering and Absolute Configuration



No anomalous scattering thus the intensities of the resultant structure factor are equivalent.

Anomalous scattering alters the intensities of the resultant structure factors.



Anomalous Scattering and Absolute Configuration

Since Friedel's law no longer holds, there will be differences in the intensities of reflections that would have been related. These are known as Bijvoet pairs.

$$|F^+| \equiv |F_{hkl}| = |F_{\bar{h}\bar{k}\bar{l}}| \quad |F^-| \equiv |F_{\bar{h}kl}| = |F_{h\bar{k}l}| \quad \Delta F = |F^+| - |F^-|$$

For non-centrosymmetric space groups one can thus compare $F(hkl)$ and $F(-h-k-l)$ to determine absolute configuration.

This can be accomplished by calculating $F(hkl)$ and $F(-h-k-l)$ for your model and the inverted model and comparing the calculated magnitudes to those of the observed data.

F(obs)	xyz model-calc	-x-y-z-model-calc
F(hkl) 200	160	190
F(-h-k-l) 180	150	170

repeat for several hundred reflections to confirm handedness of molecule

In practice, SHELX calculates a Flack parameter from these data. If the Flack parameter is 0, your structure has the correct configuration. If it is 1, your model is the inverted configuration. If the Flack parameter is 0.5, you might have racemic twinning. Other methods (e.g. Hooft, Parsons) have recently been developed: see www.absolutestructure.com)