Chapter 2: X-ray crystallography in practice

Exercise 2.1

Which steps in the flowchart of Fig. 2.1 have become generally faster as a result of improved computer hardware and software, and which have been largely unaffected by these developments?

All the computer-related steps 2–7 have become generally faster; so has step 8 (interpretation), though it has also become more extensive with the help of many new tools for investigating the structural features and therefore often yields more information and does not necessarily take less time! Step 1 is unaffected, particularly methods of growing suitable crystals.

Exercise 2.2

Why must a crystal be rotated in the X-ray beam during data collection (a) in order to obtain the complete diffraction pattern; (b) even in the measurement of a single reflection with a serial diffractometer?

a) The Bragg equation and related diffraction conditions are very severe, so few reflections would be observed for a crystal held in one particular orientation.

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b) For a crystal with mosaic spread, the slight misalignment of individual crystal grains means that slightly different orientations are required to satisfy the Bragg condition for all of them.

Exercise 2.3

What advantages are there in measuring the complete diffraction pattern (with a full range of negative and positive values for all 3 indices, as would be necessary for a non-centrosymmetric triclinic structure in space group *P*1) rather than only the unique portion without symmetry-equivalent measurements?

Advantages include the following.

a) Symmetry-equivalent reflections can be averaged to give more reliable intensities, reducing some systematic errors.

b) Individual poor measurements (due to instrument factors, systematic errors, etc.) can be recognised as outliers and either re-measured, corrected if possible, or eliminated from the data set.

c) Sets of symmetry-equivalent reflections, which should have equal intensity, can be used as a basis for some kinds of absorption corrections.

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Exercise 2.4

List the types of information that are available (a) in direct space and (b) in reciprocal space at the stage when X-ray diffraction data have been measured and 'reduced' (corrected) and the next step is to solve the structure.

a) The unit cell geometry; the crystal system and space group (or a small number of possible candidates); possibly some indications of molecular symmetry and unit cell contents.

b) A set of reflection intensities together with their standard uncertainties and the reflection indices.

Exercise 2.5

If possible, obtain a copy of the Excel spreadsheet described in Section 2.7 and a copy of the publication describing its use, and work through the stages outlined for the solution of the 1D structure.

No answer provided.

Exercise 2.6

Why do Fig. 2.17(c) and (d) show only two of the six F atoms of the $[AsF_6]^-$ anion? Why are H atoms not found until all the other atoms have been located and refined?

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Fig. 2.17 shows planar sections through 3D electron density maps. The atoms shown here lie in the plane. The other 4 F atoms lie above and below this plane, related to each other in pairs by mirror symmetry; the plane shown is a crystallographic mirror plane.

H atoms have very little electron density and so make only small contributions to the diffraction pattern. They can be found usually only when other atoms have been located and refined, so that the phases calculated from the model structure are close to the correct (unknown) values, giving a reliable electron density via the reverse Fourier transform.

Exercise 2.7

Give two reasons why crystallographic *R* factors never decrease to a value of zero, even with good quality data and the best available refinement software.

a) Even the best experimental data are subject to random and (possibly) systematic errors and therefore cannot exactly match the diffraction pattern calculated from a model structure.

b) The model used for a crystal structure, with individual atoms having a particular mathematical form for anisotropic displacements, is always an approximation to the true electron density.

Exercise 2.8

Which of the following solvent molecules must be disordered, and which could be ordered?

- THF on a twofold rotation axis

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- THF on a mirror plane
- *n*-pentane on an inversion centre
- *n*-hexane on an inversion centre

- THF can be ordered on a twofold axis, if this passes through the O atom and the midpoint of the opposite C–C bond. Note that the ring of THF is not planar, as this would give an eclipsed arrangement of adjacent CH_2 groups. An ordered non-planar ring is compatible with the twofold axis as described: the O atoms and the two C atoms bonded to it define a plane, and the other two C atoms are one above and one below this plane.
- THF cannot be ordered on a mirror plane, as this would impose an eclipsed arrangement for adjacent CH_2 groups, whether the mirror plane contains all five non-H atoms or whether the mirror plane contains only the O atom and bisects the opposite C–C bond.
- *n*-Pentane cannot be ordered on an inversion centre: the molecule has an odd number of C atoms, so the central one would have to lie on the inversion centre, which is incompatible with the tetrahedral arrangement of bonds found for C atoms of alkanes.
- *n*-Hexane can be ordered on an inversion centre, this symmetry element being the midpoint of the central C–C bond. Three of the C atoms (and their H atoms) are related by inversion symmetry to the other three. The central C–C bond must have an *anti* configuration in this case, but there is no symmetry restriction on the other C–C bond configurations except that they must be in inversion-related pairs.

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Exercise 2.9

Why are copper-target X-rays often used in preference to molybdenum-target X-rays for the study of natural products containing only C, H, N, O and F atoms?

There are two possible reasons, and either or both may apply.

a) Diffraction intensities measured with Cu-target X-rays are considerably higher than those with Mo-target X-rays, using the same sample crystal, if there is no strong absorption (which is the case here with no atoms heavier than F); diffraction intensities have a dependence on λ^3. This is an advantage if crystals are small, which may often be the case for low-yield natural products.

b) Resonant scattering effects are much greater for these atoms with Cu-target X-rays than with Mo-target X-rays (for which the imaginary contributions are almost zero). This is important if the absolute configuration is to be determined, often an objective in natural product structural chemistry.

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