1 Determining Structures – How and Why

1.1 Structural chemistry – where did it come from?

Structure is so fundamental to our way of thinking about chemistry that it is easy to take it for granted, and forget how important it is. The foundations were laid in the 19th century by scientists using simple analytical methods and a lot of intuition. In 1857, August von Kekulé proposed that certain elements, in particular carbon, could be assigned a particular number of chemical bonds, a property we know as 'valency'. His representation of acetic acid (ethanoic acid), shown in Figure 1.1(a), shows that he had some concept of structure. The following year, however, Archibald Scott Couper gave us the first diagrams that we might recognize as molecular structures, using lines to represent bonds between atoms for the first time (Figure 1.1(b)). The first use of the word 'structure' in this context is attributed to Aleksandr M. Butlerov (Figure 1.2), who in 1861 presented a paper entitled "Einiges über die chemische Struktur der Körper", meaning "something about the chemical structure of compounds". Butlerov's big contribution was recognizing that compounds were not random clusters of atoms but had regular structures that conformed to the laws of valency of the constituent atoms.

By 1864, Alexander Crum Brown (Figure 1.3) was able to propose a structure for ethanoic acid (Figure 1.1(c)) that is remarkably close to what we accept today, with circles to denote the atoms and lines between atomic symbols to indicate the bonds, and even with a carbon-oxygen double bond. He is also attributed with what we believe to be the oldest existing three-dimensional structural model, made from balls of wool and knitting needles (Figure 1.3(b)). The structure, of the crystal lattice of NaCl, is instantly recognizable to all chemists, and is quite an accomplishment by Crum Brown when we remember that even the simplest crystal structures had not yet been determined.

By the beginning of the 20th century a lot was known about structure, but almost none of what we now call structural methods were available to allow scientists direct access to structural information. The exception was visible spectroscopy. This provided the insight into atomic structure on which the revolutionary developments in physics of the 1920s were founded. And on those foundations rest the spectroscopic methods that we use today, as well as computational methods.

The importance of structural methods has been repeatedly demonstrated by awards of Nobel Prizes. We mention a few of those in Physics and in Chemistry for the development of some of the methods we describe in this book, but there have been many, many more, even some in Medicine, for applications of the methods. After the discovery of X-rays by Wilhelm Röntgen in 1895 they were soon put to good use, and Nobel Prizes were awarded to Max von Laue (Figure 1.4(a)) in 1914 for his observation of interference patterns, and in 1915 to William Bragg and his son, also called William, for crystal structure analysis (Figure 1.4(b)). In 1936, Peter Debye received a Nobel Prize for his work on dipole moments and diffraction of X-rays by solids and gases, although by that time electrons were used for diffraction studies of gases. But all these experiments were extremely time consuming (the first determination of the structure of $CuSO_4 \cdot 5H_2O$ (Figure 1.4(c)) took

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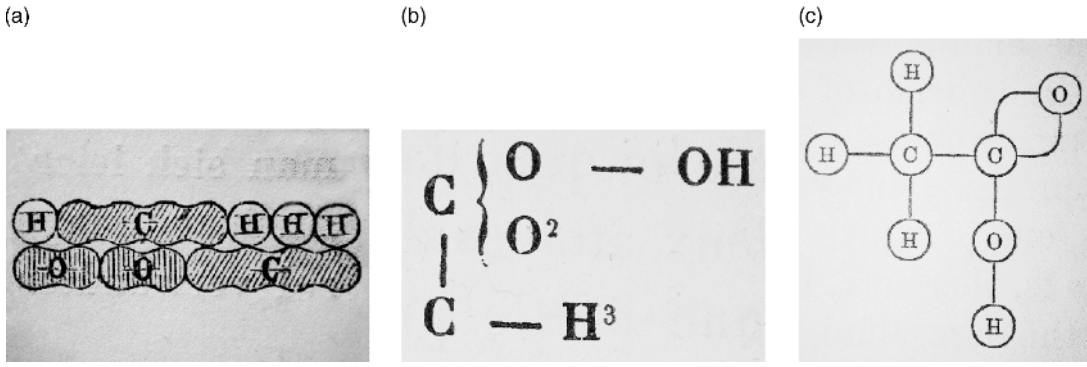
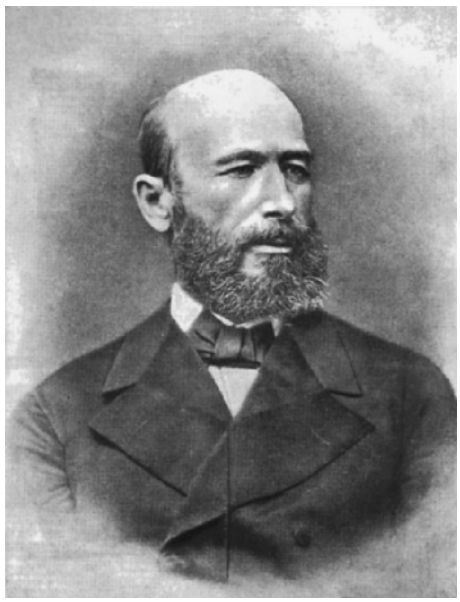


Figure 1.1
Early representations of the structure of ethanoic acid according to (a) Kekulé, (b) Scott Couper and (c) Crum Brown.

several years!) until the process of data analysis was greatly simplified by the development of direct methods in crystallography by Herbert Hauptmann and Jerome Karle, who received a Nobel Prize in 1985. The Chemistry Nobel Prize that was awarded during the writing of this book went to Dan Shechtman (2011) for his work on quasicrystals, a form of matter that was for a long time denied to exist by others.

The other structural technique that predated the rise of spectroscopic methods was mass spectrometry. The deflection of beams of ions was studied as early as 1886, but it was Francis Aston, a graduate student of J. J. Thomson, who constructed the first functioning mass spectrometer, leading to the award of a Nobel Prize in 1922.

By the end of the 1920s much of what we now understand about quantum mechanics had been worked out. It was an astonishingly fruitful period. Almost every part of the electromagnetic spectrum has since then



"I don't want to introduce anything new, just to express ideas proposed by many chemists. I must say that the views and formulae of Couper, which I originally rejected, were based on similar ideas, but they were not thought through clearly enough. All I want to say now is that it is time to use the ideas of atomicity and chemical structure whenever we think about the constitution of a chemical. This will provide a solution to the difficulties currently facing the study of chemistry."

Figure 1.2
Aleksandr Butlerov, with part of his presentation to the 36th congress of German physicians and scientists in 1861, paraphrased from the German original.

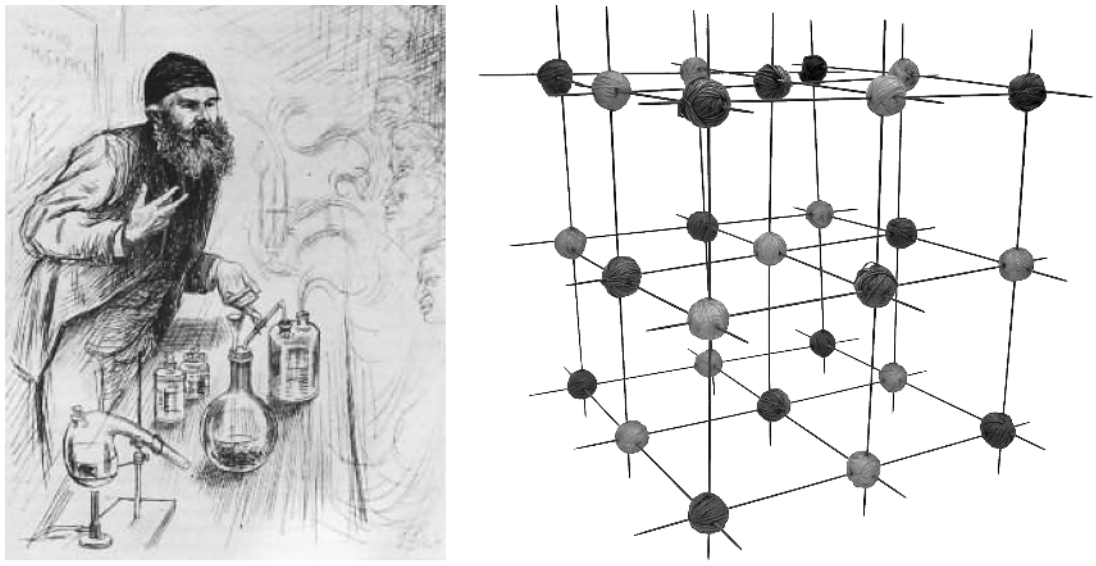


Figure 1.3
(a) Alexander Crum Brown. Published by Edinburgh University Press in 1884, and (b) his model of the crystal structure of NaCl, built in 1883 from balls of wool and knitting needles.

been put to use in structural chemistry, and over the next 50 years all of the remaining experimental structural methods that we use today were developed. Nobel Prizes were awarded to Chandrasekhara Raman in 1930 for his discovery of the Raman Effect, and to Rudolph Mössbauer in 1961 for his work on the absorption of gamma rays by nuclei, which is applied in Mössbauer spectroscopy. In both these cases it was the subsequent applications of the basic physics that are of primary interest to the structural chemistry community. The same can be said for nuclear magnetic resonance (NMR) spectroscopy, the fundamentals of which were studied by

Figure 1.4
Pioneers of X-ray diffraction: (a) Max von Laue (Deutsches Bundesarchiv (German Federal Archive), Bild 183-U0205-502); (b) son and father, William L. Bragg and William H. Bragg. (c) The first X-ray interference pattern of $CuSO_4 \cdot H_2O$. Photograph (c) Copyright Deutsches Museum.

Felix Bloch and Edward Purcell, who jointly received the Physics Nobel Prize in 1952. The development of complex NMR methods has had enormous impact on the development of chemistry, and the technique has become a universal tool for organic, inorganic and biochemists alike. Of particular relevance to inorganic chemists are multi-pulse techniques and two-dimensional spectroscopy, for which Richard Ernst was awarded a Nobel Prize in 1991.

By the 1970s all the spectroscopic methods that form the basis of this book existed. But the advances since then have probably had even more impact than those that went before. These exciting developments have been driven by the electronics revolution. Detectors have allowed vast quantities of data to be collected in real time, and ever-faster computers have been able to process the data. This in turn has made it possible to study reactions with ever-shorter timescales. Gerhard Herzberg, who was awarded a Nobel Prize in 1971, included short-lived intermediates and radicals in his studies, but he would have been delighted to know that less than 30 years later a Nobel Prize would be awarded, to Ahmed Zewail, for time-resolved studies of reactions on the femtosecond (10^{-15} s) timescale.

In parallel with these advances in experimental techniques, the rapid and so far unending rise in computer power has led to the emergence of computational methods. The mathematical basis for quantum mechanics was laid out by Erwin Schrödinger and Paul Dirac in 1926, leading to their joint award of a Nobel Prize in 1933, but it was the prize awarded to John Pople and Walter Kohn in 1998 that at last recognized their roles in the development of the indispensable modern-day *ab initio* molecular orbital and density functional theories.

Structural chemistry has therefore enjoyed more than a century of quite breathtaking development. Modern inorganic chemists now have at their disposal a broad range of physical chemistry tools to inform them about sample purity, composition, identity of functional groups, molecular geometry, electronic structure, and much else besides. A robust study will often involve a combination of a number of techniques. The techniques themselves continue to improve and advance. The great success of chemistry is based on relating chemical structures to the properties of matter. So the better we understand structure, the better we can understand such properties. Then we can make predictions about new compounds that will have the properties we desire. Structural chemistry, therefore, lies at the very heart of chemistry.

This book focuses on the problem of identifying suitable techniques for a structural study out of the many possibilities now available to us, or on making use of combinations of techniques. On the whole we teach using simple molecules, but the methods can generally be applied to complex systems as well.

1.2 Asking questions about structure

The purpose of this book is to lay the foundations for understanding the principles behind these techniques and how to apply them. But before we can make a start, we have to ask: what *is* structure?

The questions we might try to ask depend on the system we are studying, upon the progress of separation and isolation, and on the level of detail we need to know about the product. If we are dealing with reactions that lead to products that have not been made before, we need to ask a series of questions, in order of increasing subtlety. To start with, we need to ask:

1. Does the material consist of or contain any known compound that we can identify?
2. Is it a pure single compound or a mixture?

Once we have isolated a single compound we can then ask more questions, such as:

3. What is its molecular weight and elemental composition?
4. What functional groups does it contain?
5. How are the functional groups or the atoms linked together, i.e. what is the pattern of connectivity?
6. What is its three-dimensional shape?

7. What is its molecular symmetry (which determines the possibility of chirality)?
8. What is its geometrical structure, i.e. the bond lengths and angles, or the nuclear positions, from which the bond lengths and angles can be deduced?
9. What is its electronic structure, how are the electrons distributed over the molecular orbitals, and which of the orbitals are occupied or vacant?
10. How is the electron density (charge) distributed in space?

The techniques we can use to try to answer some or all of these questions will depend on the kind of material we are working with. In this introductory chapter, we begin the process of providing some general answers to these questions; they will often require a combination of methods. More in-depth responses will be found in the specialized chapters that follow.

1.3 Answering questions about structure

So, first of all, does a synthesis yield a material that contains any known compound that we can identify? The key to answering this question is to recognize that complicated spectra, although difficult to interpret, are more useful for this purpose than simple spectra; they contain more information. A complex spectrum can be thought of as a molecular 'fingerprint', and positive identification can be obtained through pattern matching using chemical databases, a point we return to in Section 2.11.4. In many cases, NMR spectroscopy, mass spectrometry and X-ray diffraction techniques are good for general compound identification, because they are high-resolution methods that give many sharp lines or diffraction patterns; vibrational spectroscopy is also quick to do and gives information about functional groups. UV/vis and Mössbauer spectroscopy, which generally result in spectra with a small number of broad absorption lines, are examples of techniques that provide more restricted information.

The second question we asked was whether our product was a single, pure compound. The key factors to recognize here are that, first, we should use techniques that give clear distinct peaks. This again brings NMR and vibrational spectroscopy, and possibly mass spectrometry, into focus, and powder X-ray diffraction can tell us how many crystalline phases are present. Second, if possible, we would like to use the peak intensities for quantitative analysis. We pursue this point in Section 2.9, but here we can note that if our compound has been characterized before, any peaks that are present in the new spectrum, but were not recorded for the original sample, may be assigned to impurities. But it is, of course, important to ensure that reference and sample spectra are recorded under the same conditions of phase, temperature, concentration and instrument resolution, so that the comparison can be as detailed and reliable as possible.

Similarly, the weakening of spectroscopic signals due to impurities is an invaluable indicator of the progress of purification. Here, though, we must be careful. Impurities do not necessarily give signals that can be resolved from those of the products we are trying to purify. If we are certain that by using a particular technique we can detect the impurity that we are trying to remove, we have no problems; but there is no spectroscopic technique that can be relied on as a general test for purity. ^{31}P NMR spectroscopy, for instance, will not tell us if a sample of $P(OCH_3)_3$ contains 90% CH_3OH, as it sees ^{31}P nuclei only and is blind for C, H and O, and ^{1}H NMR won't tell us if it contains some PCl_3, for similar reasons. Or if a desired product and a reagent or impurity differ in only some minor respect, their vibrational spectra may be very similar. The best we can do is to use more than one method and to make sure that each type of spectrum contains no bands other than those due to the pure product.

When we come to more detailed questions about molecular composition, functional groups present, molecular weight and molecular geometry, the methods we choose will depend on the phase and type of sample we are investigating. There are now reliable ways of doing quantitative analysis for every element, and the results are both reliable and precise. Typical chemical analysis of the elements C, H, N and S is based on combustion followed by separation of the resulting gases and weighing them in absorbed form or

measuring their concentration. Other methods of elemental analysis include hydrolysis (and measuring resulting gases), wet chemical analysis followed by titration or detection of metal complexes by UV/vis spectroscopy, and physical techniques such as atomic absorption spectroscopy and X-ray fluorescence for more-or-less direct measurement of element contents.

To determine the molecular weight of a volatile compound we can use mass spectrometry. The different methods of ionization available make it possible to obtain mass spectra from virtually all molecular compounds, whether volatile in the conventional sense or not. The molecular ion is particularly important, as it gives the molecular weight of the compound directly; this can be done so accurately that the atomic composition can be deduced by matching the sum of exact atomic weights. This can even be done for the individual components of mixtures. Molecular weights in solution can also be determined using colligative properties, particularly osmotic pressure. Such traditional methods should not be ignored; although they may not be very precise, they are quick and very cheap to do, and can be most useful in helping to decide whether a compound is associated or dissociated in solution, particularly through the use of several different solvents. It is very important to recall that elemental analysis and measurement of colligative properties are based on completely different principles to those that apply to the rest of the methods described in this book, and this makes them particularly important because they provide us with independent observations that allow us to check whether our conclusions from spectroscopic or diffraction methods are correct.

We can usually obtain a good idea of the identity of functional groups in a compound using vibrational spectroscopy. The correlation patterns that have been drawn up for organic functional groups can be extended to organometallic systems, and there are similar correlations for purely inorganic species. Where a compound contains heavy atoms, it may be necessary to rely on low-frequency vibrations. We may then find that absorption bands are sometimes weak and frequency patterns are less well-defined, but it is still almost always possible to learn something useful. The way in which these groups are linked is part of the connectivity of the molecule, and if the compound contains suitable nuclei or unpaired electrons, we may be able to discover a great deal from NMR or electron paramagnetic resonance (EPR) spectra, and less easily using vibrational spectra. We may even be able to determine stereochemical relationships between groups using these techniques.

Next, if we want more specific information about molecular symmetry (and therefore three-dimensional shape), we might succeed using vibrational spectroscopy, provided we record both infrared and Raman spectra. The two techniques have different symmetry-dependent selection rules, so comparing the spectra could allow the symmetry of a species to be identified. If we want precise measurements of bond lengths and angles, from which we might also infer symmetry and three-dimensional shape as well as connectivity, our choice of method is more limited. The structures of many simple molecules in the gas phase can be determined very accurately by microwave spectroscopy or electron diffraction, and modeled using computational chemistry. Even complicated molecules of low symmetry can be tackled by these experimental techniques, but the interpretation of the data obtained might then require support from computational methods. Before endeavouring to undertake a study of this kind we must usually know what it is we are studying (i.e. the molecular connectivity). If, however, a material is suitable for single-crystal X-ray diffraction, these limitations no longer hold. Using this technique, we can answer all questions about connectivity, symmetry and geometry in one go. In such cases, the most serious uncertainty could be whether or not the crystal studied is typical of the sample as a whole, or turn out to be a product of decomposition, oxidation or hydrolysis, or a minor impurity created during the compound synthesis. To make completely sure that the crystal chosen for structure determination is a true representation of the whole sample the (sometimes hard-earned) crystals can be finely ground so that structural data from many small crystallites can be sampled simultaneously in a powder diffraction analysis.

For selected elements, the electronic situation of atoms, typically characterized as formal oxidation states, can often be determined directly by several methods, including Mössbauer spectroscopy. Relative energies of orbitals, occupied or vacant, and ionization energies, can be measured by methods such as UV/visible spectroscopy, photo-electron spectroscopy (including X-ray methods for core orbitals) and X-ray absorption

near edge structure, and other techniques, notably EPR spectroscopy, depend critically on orbital occupancy. Orbital energies are also readily estimated by quantum mechanical methods. But even when we know about the energies and occupancies of orbitals, we may want answers to questions about the structure of the electron density. There are several techniques at our disposal. We can use EPR spectroscopy to identify spin couplings between the electron and the atomic nuclei, from which we can deduce the nature of the orbitals in which unpaired electrons are located. We can also use X-ray diffraction to produce maps of the electron density distribution in crystals and we can use quantum mechanics to calculate them for molecules and even solids. And once we have the three-dimensional electron charge distribution in hand, we can analyze its topological features.

But when we begin to look in detail at the information we obtain from any of the methods mentioned, we find that much of it is limited. Crystallography seems to answer all our questions, but it provides a restricted view, and only for species in very specific situations. It gives us a frozen snapshot of a molecule or ion in the form it adopts under the influence of the forces exerted by its neighbours. In solids, many molecules take up different conformations or even have structures that are completely different from those existing in solution or in the freedom of the gas phase. Microwave spectroscopy gives us information about the rotation of molecules in a gas in whichever vibrational states are populated at the temperature of the experiment; we see separate sets of lines for each. In contrast, gas electron diffraction tells us about the distances between pairs of atoms in molecules averaged over all population states. While these distances lead in principle to a complete structure, they are obviously affected by vibrations, and so we need to know something about the vibrations of the molecule before we can interpret the data reliably. The internuclear distances we obtain from these and other methods do not represent exactly the same physical parameters (we will discuss this further in Section 2.7), and so they have different physical significances. These differences emphasize that molecules are not static and rigid like the molecular models we build from plastic kits. We may think of molecules in this way, but it is quite misleading to do so. They are dynamic. They twist and they turn, they vibrate, rotate and translate; they might exchange electrons, single atoms, or even groups of atoms with other molecules, and groups within a single molecule might change partners. If we are to understand the structure of a particular molecule, we must study it by as wide a range of methods and over as wide a range of conditions as we possibly can.

1.4 Plan of the book

This introductory chapter has set the scene, and the next one discusses general tools and concepts that are widely relevant to the chapters that follow. The next nine chapters all deal with particular techniques or groups of related methods. When using a technique, it might not be essential to know in detail how a particular instrument or some computational method works, though such understanding may well help in collecting the best or most useful data. But what is absolutely vital is for chemists to be able to interpret the structural information they obtain. In this book, we have therefore put the major emphasis on such interpretation. As far as we can, we present spectra or other experimental information to illustrate the points we make.

Each chapter is also supported by a series of review questions for you to test your own understanding, and a series of discussion problems, which we hope will be a valuable resource for tutors (and, of course, their students). The answers to the review questions and some notes on the discussion problems can also be found on the book's website (see Section 1.5).

The last chapter differs from the rest of the book. Here we present a collection of 'case histories', in which we discuss examples from the chemistry research literature on what has been learned about chemical structures using all appropriate physical and computational methods. It draws on what has been derived and explained in Chapters 2–11, but from the point of view of the chemist who has a compound and wants to know as much as possible about it rather than that of someone with a particular instrument or simulation software

who wants to find a use for it. Some of these are updated versions of stories from the earlier incarnation of this book, and it is interesting to see how unexpected results have now been explained – but by no means in every case. Most are completely new. They all show how the application of a range of structural techniques can solve problems that would otherwise be too difficult to crack.

Inside the front cover of the book is a periodic table, which includes some useful data relevant to structural methods. Inside the back cover there is a molecular symmetry point-group decision tree, refined over many years of teaching undergraduate students. It refers to the symmetry species most often encountered in molecular inorganic chemistry. Character tables are available in the on-line supplementary material for Chapter 2.

Inorganic chemists have many different questions to ask about different types of system, and it is not possible to explain how to answer all of them in a single text. This book is written from the point of view of the chemist who has to deal with well-defined chemical species, although a good deal of what is described would also be useful to a solid-state scientist. The principles of structure determination apply equally to organic compounds too, although the relative importance of the techniques might be different.

We hope that readers of this book will understand the principles of using chemical information given by the methods we document, and will see how to apply them to their own problems.

1.5 Supplementary information

In the method chapters of this book (2–11) we explain the physical principles of each technique, but we have tried to avoid going into the theory in great detail. For the avid follower there is extension material for all chapters available on the book's website (http://www.wiley.com/go/rankin/structural), dealing with topics that are more advanced or less widely applicable than the core subjects that we present here. There is a reference to each supplementary section at the appropriate place in the printed text, as well as an index at the book's home page. We hope that this facility will also slow down the ageing process of this book, since we will endeavour to update the on-line resource with information about relevant new instrumentation or developments in methodology. At the end of each chapter we also provide references to other more formal and rigorous treatments. There are also some worked examples on the website; these are also referenced in the text.

Finally, the last chapter of case histories could be extended indefinitely. It is our intention that there should be more, and we hope that those of you who have an interesting story to tell will tell it. Let us know if you have one, and then we can ensure that these accounts of structural research become an ever more valuable and up-to-date resource.