Symmetry and Structure
Readable Group Theory for Chemists
Third Edition

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Preface to Third Edition

Although this third edition of ‘Symmetry and Structure’ has much in common with previous editions, there are major differences too. Most important is a new emphasis on the fact that irreducible representations characterize particular nodal patterns (or vice versa!). It is possible to draw pictures of these nodal patterns and so to give pictorial illustrations of irreducible representations. This is particularly useful for the simpler groups, where much of the group theory may be done pictorially. To obtain the maximum benefit from this approach, Chapters 2–4 contain a basic but reasonably complete overview of the application of group theory to chemistry (or, more accurately, the water molecule!). The major omission, of course, is that of degeneracy. The nodal pattern approach applies not only to the simple groups. Its use has enabled the inclusion of a chapter on electron spin, double groups and spin-orbit coupling. The inclusion of these has been facilitated by the addition of a chapter which includes the spherical group. Hopefully, the treatment of double groups is both readable and accurate. In general, the mathematical content of the book has been reduced, both in the text and in the Appendices. Although clearly there are limits, I have tried to make each chapter as independent as possible. This has led to some duplication of material – which may be no bad thing. By providing cross-references, the student can obtain a, somewhat, different approach to a difficult point, should the need arise. Above all, I have borne in mind the sub-title of the book, that the content should be readable, and with no loss of accuracy. If at some points the reader finds it fun too, that would be a bonus.

I am particularly grateful to Professors K. Gatterer (Graz) and E. Diana (Turin) for providing material which I have used and also for their comments on the text itself. All deficiencies which remain are, of course, my responsibility.

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1 Theories in conflict

1.1 Introduction
As its title says, this book is concerned with the symmetry and structure of molecules. Of these, the latter – both in the sense of the geometric and of the electronic structure of molecules – has long been of concern to chemists. We shall be interested in both these aspects and will adopt the viewpoint that the geometric structure of a molecule tells us something about its electronic structure. The connection between the two will be provided by the molecular symmetry, or rather its expression in what is called group theory. Ultimately, however, this book is concerned with the chemical consequences of molecular symmetry, the application of group theory to molecules, and these extend far beyond the problems of chemical bonding. Rather, the problem of chemical bonding will be used as a particularly convenient – and important – way of introducing the concepts of symmetry. The concepts revealed in this way can then be extended to other areas of chemistry. In an introductory text such as this there will be no attempt to cover all of the uses of symmetry in chemistry – an objective which it would be difficult to achieve in any text. Rather, the more important aspects will be detailed, but sometimes with more than a hint of the advanced. The aim will be to provide a cover of the basics of the subject sufficient to enable the reader to apply them in other areas. Further, this will be done in a readable, almost entirely non-mathematical manner. The take-home message is that the use of symmetry in chemistry is all about phase patterns: that is, about nodal planes akin to those that distinguish different atomic orbitals. But this is to come; in the present chapter we cover material that, hopefully, is familiar to the reader – explanations of why molecules have the shapes that are observed. The examples covered are chosen to be simple and mostly well known. But the final conclusions are surprising and lead us to query the validity of the simple models that we discuss. Rather than exploring these uncertainties, we will find more value in reversing the argument – and this reversal will be a recurrent theme throughout the book. It has already been mentioned. Start with the observed structure and use this to obtain information about the bonding. But first, the more traditional approach.

1.2 The ammonia molecule
The ammonia molecule provides a convenient starting point for our study and it will be used to see the problem of chemical bonding in a rather unusual perspective, one that leads to the approach indicated above – the attempt to infer molecular bonding from molecular
The ammonia molecule; the models in the text seek to explain the experimental bond angle geometry (in contrast to the more common procedure of explaining molecular geometry in terms of chemical bonding). Several approaches to the bonding in the ammonia molecule will first be reviewed, approaches which have been in the chemical literature for many years. The reader may well not be familiar with all of them but he or she should not feel that they have to spend much time trying to master any new ones – our concern is with generalities, not details. However, references are given to enable the reader to explore any of the approaches in more detail, if they so wish.

1.2.1 The atomic orbital model

This model has an historic importance – it is the only description to be found in many pre-1955 texts. Before looking at it, the facts. The ammonia molecule is pyramidal in shape; all three hydrogen atoms are equivalent, the HNH bond angle being 107° (Figure 1.1). Note the restriction that has implicitly been made: we will not attempt to explain bond lengths, only angles. The simplest, and oldest, explanation of the (angular) shape follows from the recognition that the ground state electronic configuration of an isolated nitrogen atom is $$(1s)^2 (2s)^2 (2p)^3$$, each of the 2p electrons occupying a different p orbital. Each of these 2p electrons may be paired with the electron present in the 1s orbital of a hydrogen atom by placing one hydrogen atom at one end of each 2p orbital so that each nitrogen 2p orbital overlaps with a hydrogen 1s orbital, giving a localized N-H bond. The result is an ammonia molecule which has the correct, pyramidal shape and which has all of three hydrogen atoms equivalently bonded to the nitrogen (Figure 1.2). However, the angle between any pair of 2p orbitals is 90° so that a bond angle of 90° is predicted by this model. Agreement with an experimental value of 107° is obtained by postulating the existence of electrostatic repulsion forces between the hydrogen atoms, each of which, it is assumed, carries a small residual charge. These repulsions cause the H atoms to move further apart – and so the bond angles increase. If, as seems probable, each N-H bond is slightly polar with each hydrogen carrying a small positive charge, this repulsion is nuclear–nuclear in origin. The consequent modification of the original bonding scheme as a result of this distortion of the bond angle from 90° is not usually considered.

1 See, for example, p. 65 of Inorganic Chemistry, by E. de Barry-Barnett and C.L. Wilson, Longman Green, London, 1953.
2 The reader who wishes to perform this correction should make a note to do it after they have read Chapter 7, when they will be adequately equipped.
THE AMMONIA MOLECULE

Figure 1.2 N—H bonding in NH₃ envisaged as resulting from the overlap of 2p orbitals of the nitrogen with 1s orbitals of the hydrogens. Because the three nitrogen 2p orbitals have their maximum amplitudes at 90° to each other, bond angles of this value are predicted. The overlap regions are shown shaded.

1.2.2 The hybrid orbital model

This is detailed in many post-1955 texts.³ In this model an alternative description of the bonding in the ammonia molecule is obtained by hybridizing the valence shell orbitals of an isolated nitrogen atom, 2s, 2px, 2py, and 2pz, to give four, equivalent, sp³ hybrid orbitals pointing towards the corners of a regular tetrahedron. Because there are five electrons in the valence shell of the nitrogen atom, three of these hybrid orbitals may be regarded as containing one electron whilst the fourth is occupied by two electrons. As in the previous model, 1s electrons from three hydrogen atoms pair with the unpaired electrons on the nitrogen, now in hybrid orbitals, to give three localized bonds and a pyramidal ammonia molecule (Figure 1.3). Again, the three hydrogen atoms are equivalent but the bond angle is predicted to be 109.5°, the angle between the axes of a pair of sp³ hybrid orbitals. This value is in closer agreement with experiment than that given by the previous model but again some correction is needed if the experimental value is to be reproduced. This time, the predicted bond angle is too big so a different source has to be found for the correction. It is usually made by invoking the effects of electron–electron repulsion. It is this electron–electron repulsion which forms the basis of a third model for ammonia and so the way that the ‘hybrid orbital’ model is modified to give agreement with experiment is contained in the description of

³ See, for example, p. 159 of Valency and Molecular Structure by E. Cartmell and G.W.A. Fowles, Butterworth, London, 1956.