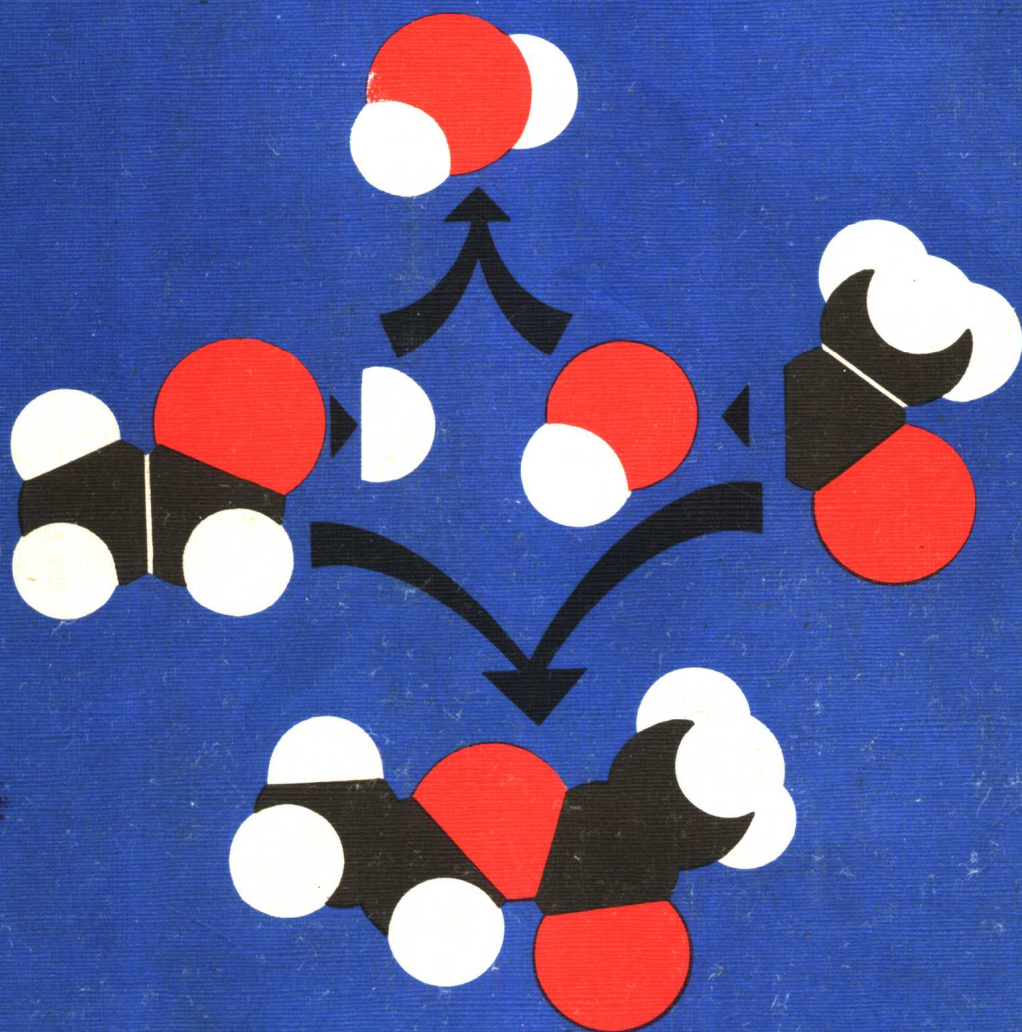# Principles of Organic Chemistry
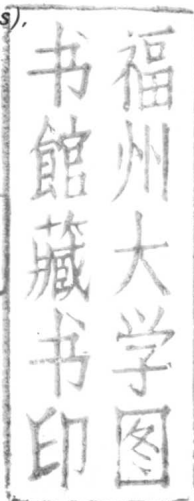
SECOND EDITION

Peter R.S. Murray

Principles of Organic Chemistry

A Modern and Comprehensive Text for Schools and Colleges

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Second Edition

Heinemann Educational Books
London

Preface

Preface to the First Edition

My objective has been to provide a textbook suitable for both teachers and students which comprehensively covers the modern approach to Advanced and Scholarship organic chemistry. The work has been extended considerably to make it suitable for other courses of similar academic level and should provide a useful and interesting background to First Year University students as well as those in Colleges of Education and other higher educational establishments. It more than adequately deals with the theoretical aspects of the more industrially biased O.N.C. and O.N.D. courses and should provide interest and stimulation to students for H.N.C., H.N.D., L.R.I.C. and Grad. R.I.C. (Part I) examinations.

The book has been developed in two sections, the first of which deals with the fundamental theoretical principles essential for introducing mechanistic organic chemistry. There is also included in this section a sizeable chapter on methods of isolating and identifying compounds, including the principles and mechanics of modern spectroscopic and chromatographic techniques. In Part II, which provides the much greater part of the text by volume, these principles are applied to each of the different homologous series of compounds. In addition, there are chapters on Polymers, Carbohydrates, and Amino Acids, Proteins and Polypeptides. The arrangement of material in two sections in this way allows some flexibility for the teacher to choose his preferred sequence, integrating the ideas introduced in Part I with the more specific reactions in Part II.

I wish to convey my gratitude to Mr P. R. Dawson, Mr J. H. Deakin, Dr K. Mullen and Mr J. J. Wharton for their invaluable criticisms and suggestions during the early stages of preparation, and to my wife, Jean, for her unfailing patience in undertaking what was probably the most tedious task of all, namely that of typing the original manuscript. Finally, I should like to express my appreciation to Heinemann Educational Books, and especially to Mr H. MacGibbon and his advisers, for their advice and assistance during the development of the text.

1972   P.R.S.M.

Preface to Second Edition

In this second edition nomenclature has been modified in order to bring it into line with the recommendations made by the Association for Science Education in their publication, *Chemical Nomenclature, Symbols and Terminology*. In cases where the compound is widely known by an alternative, but often less systematic, name, both the A.S.E. recommended name and the alternative name are used in conjunction. In this way it is hoped that unnecessary confusion will be avoided for those students and teachers who are more familiar with the more traditional

nomenclature. Where there is no ambiguity about oxidation states, especially in compounds of the elements of Groups I and II, reference to the oxidation state is omitted.

In other respects, this edition is not appreciably different from the first, although reprinting has provided an opportunity to include some additional information and make a few amendments.

1977   P.R.S.M.

Contents

1 Introduction

Chemistry is a study of the elements and of how they react together to form compounds. ORGANIC CHEMISTRY relates solely to the chemistry of the compounds of carbon, which in the majority of cases also contain hydrogen. At first, it is difficult to realize the vast extent of this field of study until one appreciates that the number of compounds containing carbon and hydrogen is many times greater than the sum total of all the compounds of all the other elements and is increasing every year.

The term 'organic chemistry' is rather misleading in as much as it is a relic of days when chemical compounds were categorized into only two classes, organic and inorganic, depending largely upon their source of origin. Organic compounds were derived from living organisms such as vegetables and animal matter, whereas inorganic compounds were obtained from mineral sources.

Organic substances were known to man in prehistoric times and although nothing was known about them, other than their function and source of origin, they were utilized in a variety of ways. Sugar in fruit was used for sweetening purposes and for making simple wines. Oils and fats from vegetables and animal matter were employed for making soap, and vegetable pigments, such as indigo and alizarin, were used for dyeing fabrics.

It was not until the sixteenth and seventeenth centuries that any really significant progress in isolating new organic substances was made. During this period, compounds such as methanol, propanone (acetone) and ethanoic (acetic) acid were extracted from pyroligneous acid, which was obtained from the dry distillation of wood. Towards the end of the eighteenth century, with the wide application of solvent extraction to plant and animal matter, numerous new compounds were added to the list of those already known. It was during this era that a Swedish chemist, Scheele, succeeded in extracting 2-hydroxypropane-1,2,3-tricarboxylic (citric) acid from lemons, and later others isolated 2,3-dihydroxybutanedioic (tartaric) acid from grapes, 2-hydroxybutanedioic (malic) acid from apples, 2-hydroxypropanoic (lactic) acid from sour milk, uric acid from urine, 3,4,5-trihydroxybenzenecarboxylic (gallic) acid from nut galls and ethanedioic (oxalic) acid from wood sorrels. Between 1772 and 1777, Lavoisier conducted a series of experiments on combustion, and it was during these experiments that he identified the presence of carbon and hydrogen in organic compounds, since they yielded carbon dioxide and water respectively as the products of combustion. Furthermore, he was able to determine the amount of carbon dioxide evolved by dissolving it in a solution of potassium hydroxide.

Gradually the presence of other elements such as oxygen, nitrogen and sulphur, was found to be common to large groups of organic substances, and for the first time something was known about their chemical nature.

During the early nineteenth century, as more and more elements were being discovered, it became apparent that those elements associated with compounds derived from living organisms were limited to only a few and also that they tended to be readily combustible.

In 1828 the German chemist, Wohler, became the first person deliberately to

synthesize an organic substance in the laboratory. After a chance observation that an aqueous solution of ammonium cyanate (NH_4CNO) evaporated, producing carbamide (urea), NH_2CONH_2, he then repeated the experiment several times to confirm his conclusion.

Nowadays preparative techniques and principles have become so lucid that organic compounds can be prepared with almost as much ease as most inorganic.

The Unique Nature of Carbon

The ability of an atom to attract the electrons in a chemical bond towards itself when combined with different atoms in a compound is termed the ELECTRONEGATIVITY of the atom. Small atoms tend to have higher electronegativity values than large ones, especially those with nearly filled shells of electrons. On traversing the periodic table, the electronegativity values of the elements increase on moving from Group I across to Group VII. The values within a group tend to increase on ascending it.

This means that carbon, being the first element in Group IV, has an electronegativity value which is not sufficiently different from those of most other elements with which it combines to enable it to form wholly ionic (electrovalent) compounds. In chemical combination it therefore forms bonds which, although possessing various degrees of polarity, are essentially covalent in character.

Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca					Br
0.8	1.0					2.8
						I
						2.5

Hydrogen has an electronegativity value of 2.1.

The above table illustrates Pauling's electronegativity values for some of the most commonly encountered elements. Those elements with which carbon combines by forming covalent bonds are enclosed in the box and are principally in Groups V, VI and VII. This means that in bonds in which an electronegativity difference does occur between carbon and elements bonded to it, carbon tends to be the less electronegative atom, except when bonded to hydrogen or phosphorus.

The carbon atom possesses the unique ability to form multiple bonds between itself and other carbon atoms, $>C=C<$ and $-C\equiv C-$, and also with the atoms of certain other elements such as oxygen, $>C=O$, sulphur, $>C=S$, and nitrogen, $-C\equiv N$.
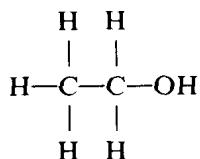
It is also one of the few elements for which CATENATION (the ability to form chains of identical atoms) is an essential feature of its chemistry. These chains may exist as short or long open systems, where several modes of branching are possible (as will be seen later), or alternatively as closed ring systems. Each different arrangement corresponds to a different compound with its own distinctive properties. In order to be able to catenate, an element must have a valency of at least two and be able to form fairly strong covalent bonds with itself. Carbon has a valency of four, permitting the existence of multiple bonds in chains of carbon atoms in certain compounds.

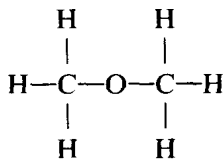## Characteristic Properties of Organic Compounds

Organic compounds are generally gases, volatile liquids or low melting-point solids, they tend to be insoluble in water unless they contain polar groups, such as —OH, —COOH, —SO$_3$H etc., but are usually soluble in organic, non-polar solvents, such as tetrachloromethane (carbon tetrachloride), ethoxyethane (diethyl ether), benzene etc. On burning in excess oxygen they yield carbon dioxide and water (except when the compound contains no hydrogen, which is comparatively rare), and the complete combustion of hydrocarbons (i.e. compounds containing only carbon and hydrogen) yields these as the only products.

Organic reactions are generally slow in comparison with many inorganic reactions and often require energy, usually in the form of heat. The reactions seldom proceed to completion, and consequently careful purification is necessary in order to isolate the desired product in a high state or purity. This contrasts quite markedly with many inorganic reactions which often proceed to completion instantaneously, especially those that take place in polar media.

The phenomenon known as isomerism is commonplace in organic chemistry. Isomerism is the ability of certain compounds, possessing the same molecular formula, to exist in different forms on account of their having different structural arrangements of atoms. For example, the formula C$_2$H$_6$O applies to two entirely different compounds, ethanol and methoxymethane, which possess distinctly different properties.

```
      H  H                        H        H
      |  |                        |        |
  H—C—C—OH                 H—C—O—C—H
      |  |                        |        |
      H  H                        H        H

     Ethanol           Methoxymethane (dimethyl ether)
```

In this field of study, we can concentrate on a relatively small group of commonly encountered elements: carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, and the halogens.

In order to understand and appreciate just how the molecules of compounds are formed from their constituent elements, it is essential to have at least a qualitative knowledge of the structure of the atoms of these elements, and then to consider the type of bonding involved in joining these atoms together.

QUESTIONS

1. In which one of the following predominantly covalent molecules is the departure from equal sharing of the bonding electrons greatest?

   A H_2
   B CH_4
   C CH_3CH_3
   D NH_3
   E H_2O
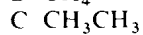
2. In what way is the chemistry of carbon a reflection of its position in the periodic table?

The Nature of the Atom

The Fundamental Particles

All atoms consist of a central nucleus of extremely high density surrounded by one or more orbital electrons. The number of protons determines the atomic number of an element and also gives the element its identity. As the chemist is concerned primarily with electrons and electronic theory, it is generally convenient for him to consider the nucleus in a simplified form, comprising protons and neutrons.

With the exception of the normal hydrogen atom, whose nucleus consists of a single proton, the nucleus invariably contains neutrons which, together with the protons, make up most of the mass of the atom, i.e. the mass number. The number of neutrons present is generally similar to the number of protons, although in the larger atoms the number of neutrons exceeds the number of protons. This can, in certain cases, cause instability of the nucleus, resulting in radioactive emission.

The protons and neutrons are particles of approximately the same mass, but whereas each proton carries a unit positive charge, the neutron is electrically neutral. The number of protons in the nucleus is always equal to the number of orbital electrons, each of which possesses a unit negative charge, so that an overall neutral atom results.

The mass of an electron is only approximately $1/1840$ of the mass of either a proton or a neutron. Since these electrons occupy a vast volume of space relative to the volume of the nucleus, the electron density is negligible compared with the density of the nucleus, thus allowing their mass to be justifiably ignored when considering atomic mass.

| Particle	Relative mass	Relative charge
Proton	1	$+1$
Neutron	1	0
Electron	1/1840	-1

All known elements are built up from these three fundamental particles. The simplest atom is hydrogen, the next simplest is helium.

The structures of all other elements can be built up by a series of successive additions of one proton and consequently one electron to the basic hydrogen structure, until the heaviest atom,* lawrencium, is arrived at. This is made up of 103 protons and 103 electrons. The increase in the number of neutrons does not follow such a regular pattern.

The Rutherford–Bohr theory of atomic structure portrays electrons in certain well-defined orbits or shells about a central nucleus with a limited number of electrons in each shell, the actual number being determined by energy considerations. Each shell of electrons represents a particular energy level, and the

*Elements of higher atomic number than lawrencium have been synthetically made and detected, but their half-life is so minute that they are of little practical significance and are seldom included in periodic table charts.
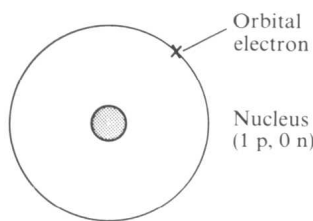
Fig. 2.1 Hydrogen atom: atomic number 1
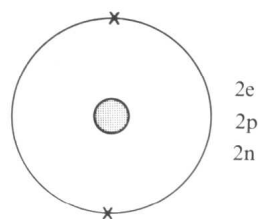
Fig. 2.2 Helium atom: atomic number 2

number of electrons in any one shell is limited accordingly. The innermost shell is defined by the PRINCIPAL QUANTUM NUMBER, $n = 1$, (sometimes referred to as the 'K-Shell'), and contains a maximum of two electrons. The second shell is defined by the principal quantum number, $n = 2$, ('L-Shell') and contains a maximum of eight electrons. The third shell, $n = 3$, ('M-Shell') has a maximum of eighteen electrons, and so on, with the maximum number of electrons in further shells becoming progressively greater.

Shell	K	L	M	N
Principal quantum number, n	1	2	3	4
Maximum number of electrons	2	8	18	32
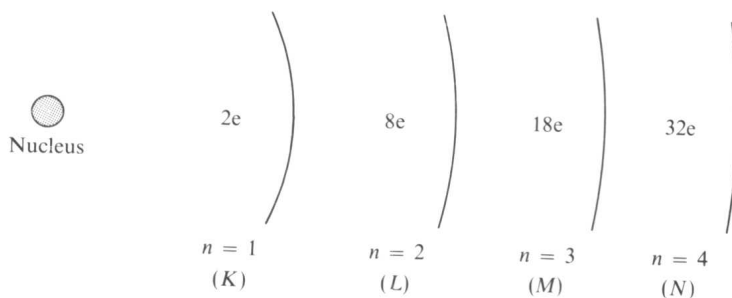
Fig. 2.3

The negatively-charged orbital electrons are attracted towards the positively-charged nuclear protons, those electrons nearest to the nucleus being firmly held by strong attractive forces whereas those further away are less firmly held by weaker attractive forces. The more firmly held electrons have a low potential energy while those less firmly held have a higher potential energy. Therefore, on moving further away from the nucleus, each shell represents electrons of progressively higher energy.

Quantum Theory

The quantum theory states that orbital electrons can only exist in certain definite energy levels and cannot have all possible energy values. Thus, whenever an electron is transferred from one energy level to another, a definite integral amount of energy, a QUANTUM corresponding to a particular frequency of radiation, is absorbed or emitted. The essence of this is that the energy of a body can only change in definite whole-number multiples of this unit of energy known

as a quantum, and that this energy is only emitted or absorbed when an electron undergoes a transition from one energy level to another.

$$\text{Energy change} = n \times \text{Quantum},$$

where n is a whole number.

The energy emitted by an electron in undergoing a transition between two energy states, E_1 and E_2, is given by the Einstein–Planck equation:

$$E_1 - E_2 = hv$$

where h represents Planck's constant and v the frequency of the radiation.

Modern Concepts of the Atom

The theories of Rutherford and Bohr and the interpretation of atomic spectra by Sommerfeld were satisfactory as far as they went, but they provided no means of accounting for the binding forces between atoms or for the shapes of molecules. The inadequacies of these theories are a result of considering the electron as a discrete particle. Modern science requires the atom to be interpreted more as a mathematical concept, rather than to be visualized pictorially as it was by Bohr.

De Broglie (1924) postulated the *dual nature of electrons*. He suggested that just as light waves can behave as particles, so electrons might be capable of behaving as waves of radiation. Further, Heisenberg (1927), in his UNCERTAINTY PRINCIPLE, stated that *it is impossible to know both the energy and position of any particle such as an electron at the same time.*

Utilizing these concepts, Schrödinger devised a WAVE EQUATION which provided the basis for a mathematical image of the atom. The significance of the wave equation is that *the solution of it provides a means of measuring the probability of finding an electron in a particular volume of space.* However, as the number of electrons in an atom increases beyond three or four, the mathematical complexity of the problem requires the introduction of simplifying approximations. These approximations are of no real significance here, but the solutions of the calculations, treated qualitatively, provide a considerable insight into the study of molecular formulae, the nature and strength of chemical bonds, and also the shapes of molecules.

Atomic Orbitals

Since the classical concept of electrons orbiting the nucleus in certain well-defined circular orbits is no longer valid, it is necessary to introduce an entirely different principle for locating electrons. Instead, *the volume of space where there is a high probability of finding a particular electron* is considered. This volume of space is called an ORBITAL, the actual shape of which has been deduced from wave-mechanical calculations. Moreover, each of these atomic orbitals can accommodate no more than two electrons.

Electron Spins

In the same way as the earth rotates about its own axis as it orbits the sun, an electron can be thought to spin on its own axis as it orbits the nucleus. In any one orbital, the spins of the two electrons must be in opposite directions, i.e. the spins are said, to be OPPOSED or PAIRED.
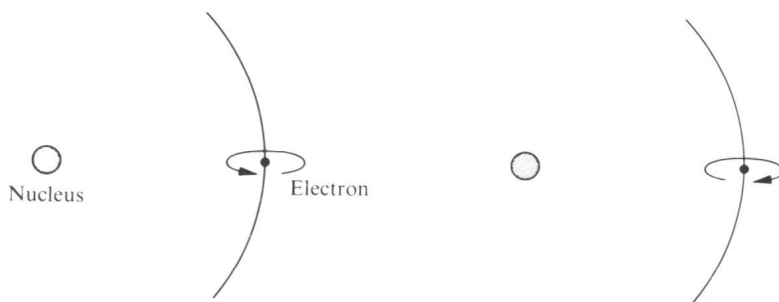
Nucleus   Electron

Fig. 2.4 Opposed or paired spins

Spectral Studies

As already stated, each shell represents a particular energy level and is described by a principal quantum number, n. The study of the frequency of atomic spectral lines has enabled the energy levels available to electrons in atoms to be depicted, and has also shown that the main levels, defined by a principal quantum number, are further divided into sub-levels of slightly different energy. These levels are defined by a secondary quantum number called the AZIMUTHAL QUANTUM NUMBER, l, having values 0, 1, 2, ..., $n-1$.

s, p, d and f Orbitals

When $l = 0$, the orbital is spherical about the nucleus and is called an s ORBITAL. When $l = 1$, the orbital is dumb-bell shaped and is called a p ORBITAL. When $l = 2$, the orbital is double dumb-bell shaped and is called a d ORBITAL, and when $l = 3$, the orbital is even more complicated and is called an f ORBITAL.
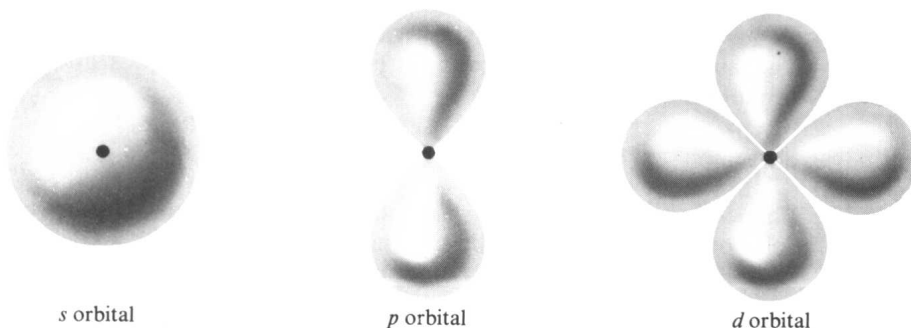

s orbital p orbital d orbital

Fig. 2.5

For orbitals defined by the same principal quantum number, the s orbital is the one of lowest energy. This is followed by the p, d and f orbitals respectively, which are of progressively higher energy.

There are two further sub-levels in addition to the one defined by the azimuthal quantum number. These are given by the magnetic quantum number, m_l, and the spin quantum number, m_s. The magnetic quantum number is determined by

observing the way in which an applied magnetic field splits the spectral lines, and the spin quantum number simply denotes the opposed spins of the electrons in any one orbital. This means that no two electrons in any one atom can be defined by the same four quantum numbers. This principle is known as the PAULI EXCLUSION PRINCIPLE.

In organic chemistry we are primarily concerned with electrons in *s* and *p* orbitals since the atoms of most of the elements with which we are concerned, i.e. carbon, hydrogen, oxygen, sulphur, nitrogen, fluorine, chlorine, do not possess electrons in *d* and *f* orbitals. Where we do encounter atoms that do contain electrons in these orbitals, e.g. bromine and iodine, they are not valence electrons, i.e. they do not affect the valency or oxidation state of the atom, and therefore do not directly affect the type of reactions and the properties that these elements exhibit.

The letters *s*, *p*, *d* and *f* are derived from the spectroscopic terms; sharp, principal, diffuse and fundamental, which are used to define certain spectral lines in atomic spectra.

Orientation of Atomic Orbitals in Space

Since *s* orbitals are spherical about the nucleus, the chance of finding one of the orbital electrons is the same in all directions.
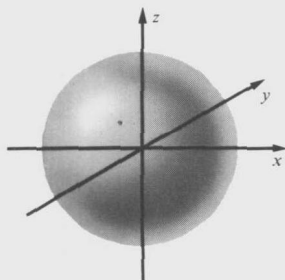

Fig. 2.6

There are three exactly similar *p* orbitals in any one energy level, and as each one can contain a maximum of only two electrons, there are, at the most, six *p* electrons in any one level. These are divided between three dumb-bell shaped orbitals which are arranged mutually at right angles to each other, pointing along *x*, *y* and *z* axes. These orbitals are called p_x, p_y and p_z respectively.

Fig. 2.7

p_x orbital p_y orbital p_z orbital
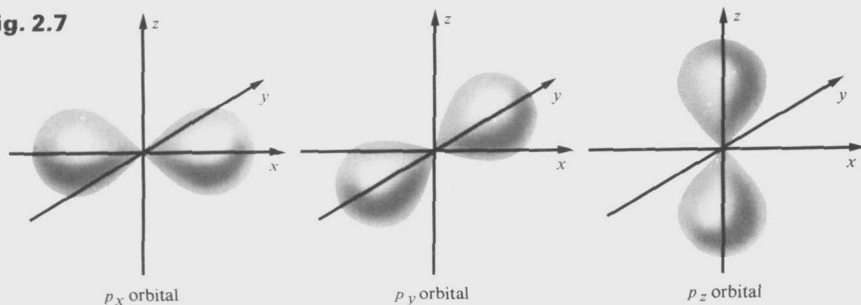
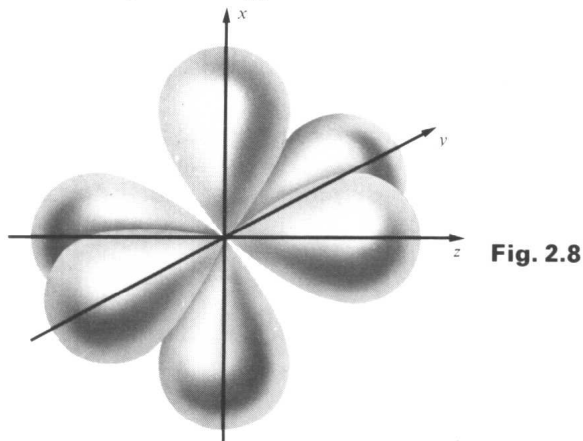Combining the *p* orbitals of any one energy level:

Fig. 2.8

All three *p* orbitals are of equvalent energy, and are of slightly higher energy than the *s* orbital governed by the same principal quantum number.

Between spherical *s* orbitals of different energy, there is a region in which the probability of finding an *s* electron becomes negligible and approaches zero. This volume of space is called a NODAL SURFACE.
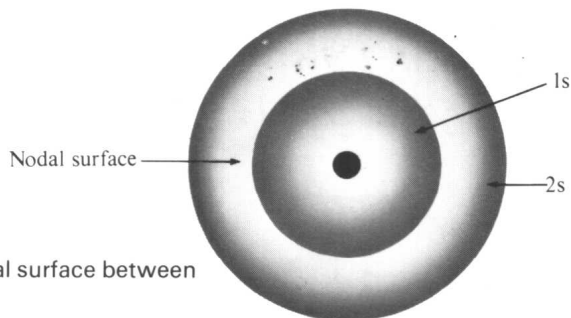

Fig. 2.9 The nodal surface between 1*s* and 2*s* orbitals

Similarly, there is a volume of space within the *p* orbitals where the likelihood of finding the electrons approaches zero. This region is called the NODAL PLANE, and lies at right angles to the *x*, *y* and *z* axes.
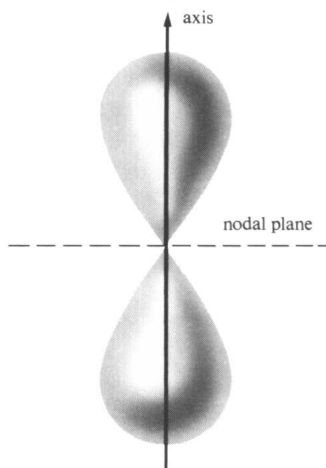

Fig. 2.10

The boundary surface of an atomic orbital is drawn so that the chance of finding a particular electron within this region is about 95 per cent.

Electronic Build-up and Hund's Rule

The first orbitals to be filled with electrons are those of lowest energy. Therefore, when considering electrons all governed by the same principal quantum number, the first two electrons fill the *s* orbital, the next three enter each of the *p* orbitals in turn (which, remember are all of equivalent energy), and then the following three electrons form pairs of electrons in these same orbitals.
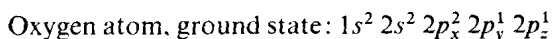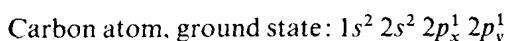
Pairing takes place only after each of the equivalent *p* orbitals has obtained one electron, since a certain amount of extra energy is required for pairing electrons within an orbital. This is in accordance with HUND'S RULE, which states that *in a given energy level (i.e. within the s level, or p level etc.) the number of unpaired electrons should be a maximum.*

A convenient way of representing the electronic structure of an atom is to use the letters *s*, *p*, *d* and *f* to describe the orbitals, prefixed by the principal quantum number denoting the energy level. A superscript to the letter is used to specify the number of electrons in each orbital.

For example, consider the electronic structure of the carbon atom (six electrons) and the oxygen atom (eight electrons) in their GROUND STATE (i.e. lowest energy state). In each case, the first two electrons enter the 1*s* orbital and the next two the 2*s* orbital. The remaining two carbon and four oxygen electrons enter the 2*p* orbitals.

$$\text{Carbon}: 1s^2\, 2s^2\, 2p^2$$

$$\text{Oxygen}: 1s^2\, 2s^2\, 2p^4$$
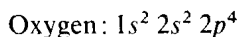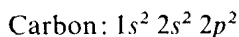
The *p* orbitals can be further divided into the p_x, p_y and p_z orbitals and represented as:

$$\text{Carbon atom, ground state}: 1s^2\, 2s^2\, 2p_x^1\, 2p_y^1$$

$$\text{Oxygen atom, ground state}: 1s^2\, 2s^2\, 2p_x^2\, 2p_y^1\, 2p_z^1$$

This may be shown diagrammatically, using arrows for electrons and boxes for energy levels.

Carbon atom, ground state:

1*s* 2*s* 2*p* (p_x p_y p_z)

Paired electrons   Unpaired electrons

Oxygen atom, ground state:

1*s* 2*s* 2*p* (p_x p_y p_z)

Paired electrons   Unpaired electrons