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Chemical structure

As organic chemists, we are primarily interested in the covalent bonds formed by the elements in the first row of the periodic table, in particular those of carbon. The study of organic chemistry is about the making and breaking of these bonds. However, before we consider the mechanisms by which these processes take place, it is worth spending a little time to look at the structures of organic molecules and the nature of the bonds which hold them together.

In this chapter we will look at the behaviour of electrons in atomic orbitals and the way these atomic orbitals can combine to form bonds. We will look at the movement of electrons in reactions, and how we can write this down so that we can see clearly what is happening. We will pay particular attention to those orbitals that take part directly in reactions, namely the frontier orbitals.

1.1 Chemical bonds

1.1.1 Atomic orbitals

Chemical bonds are formed when the atomic orbitals on one atom interact with those on another to form molecular orbitals. The electrons that each of the atoms brings to the bond are shared between them, occupying the resulting molecular orbital. Let us first look at the atomic orbitals that contribute to these bonds.

The behaviour of electrons in atoms is governed by the Schrödinger equation. Solving this equation¹ gives an infinite number of wavefunctions, each of which is a mathematical description of the energy of the electron and the probability of finding it in a certain place, and is defined by a set of four quantum numbers. Fortunately, although the number of mathematically possible wavefunctions is infinite, we need

¹ The Schrödinger equation may be solved exactly only for the hydrogen atom, and must be solved by numerical methods for more complicated atoms or molecules.

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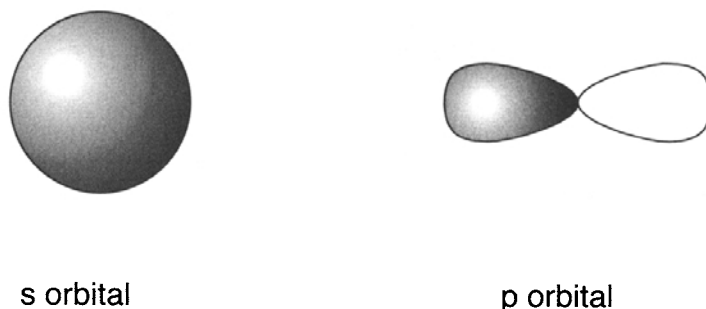


Figure 1.1

consider only a small number of them, as all the others are of too high energy (i.e. energetically unfavourable) to be chemically relevant. Wavefunctions are part of the language of the theoretical chemist, but they correspond to orbitals, which are an organic chemist's way of looking at the same thing.

The principal quantum number, n , may have any positive integer value from 1 upwards. This corresponds to the shell that the electrons occupy around the nucleus, thus an orbital with $n=1$ is in the closest shell to the nucleus (and the only occupied shell in a hydrogen or helium atom), $n=2$ describes the next shell outwards, and so on. Organic chemists are seldom interested in any orbitals with n greater than 3; $n=3$ corresponds to the outer orbitals of a second-row element. The higher the value of n , the greater is the average distance of the electron from the nucleus, and consequently the higher the energy.

The angular momentum quantum number, l , is perhaps of more interest to the organic chemist, as it specifies the shape of the orbital. Possible values of l range from 0 to $(n-1)$, thus when $n=1$, l must be 0, when $n=2$, l may be either 0 or 1, and so on. When $l=0$, the resulting orbital is spherically symmetric, and is called an s orbital. When $l=1$, this gives rise to a p orbital, which is dumbbell-shaped. These are the shapes of orbitals that are most relevant to organic chemistry, and are shown in Figure 1.1. Note that the two lobes of the p orbital have opposite numerical signs (the change in sign is shown by shading); the significance of this will become clear when we look at bonding in Section 1.1.2. The signs of wavefunctions are particularly important in pericyclic reactions, as we shall see in Section 6.5. Sometimes we may also be interested in d orbitals, for which $l=2$, but extremely rarely in any higher values of l .

The magnetic quantum number, m , may take any integer value between l and $-l$. This represents the spatial orientation of the orbital. Thus for a p orbital there are three possible values of m , and hence three possible orientations of the orbital. These are at right angles to each other, and are known as the p_x , p_y , and p_z orbitals.²

² The p_x , p_y , and p_z orbitals are not in fact those orbitals with m values of 1, 0, and -1 . You need not, however, be concerned with this. The important point is that there are three possible values of m , and three differently oriented p orbitals. There are many good theoretical chemistry textbooks that go into this in more detail for those who are interested.

1.1 CHEMICAL BONDS

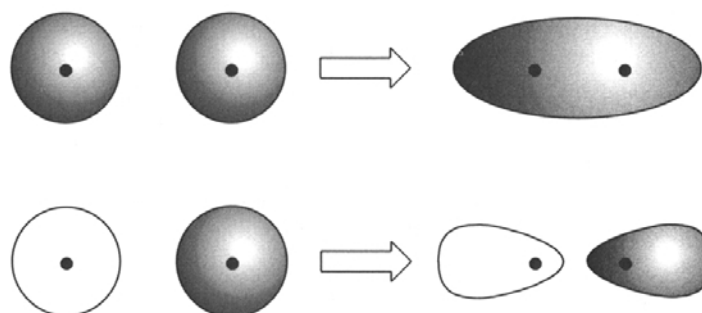


Figure 1.2 The bonding (top) and antibonding (bottom) orbitals of the hydrogen molecule.

The spin quantum number, s , has no effect on the size, shape, or orientation of the orbital, but refers to the electron. It may take the values $+1/2$ or $-1/2$, irrespective of the nature of the orbital. Electron spin is a purely quantum mechanical phenomenon, which has no counterpart in the macroscopic world, and cannot be described other than in mathematical terms. From the organic chemist's point of view, its consequence is this. The Pauli exclusion principle states that no two electrons in any atom or molecule may have the same set of quantum numbers. If two electrons occupy the same orbital, then they must have different values of s , as their other quantum numbers will be the same. As there are only two values of s allowed for the electron, it is not possible to have more than two electrons in any orbital.

Although these orbitals may be given an accurate mathematical specification only for the hydrogen atom, the above description applies just as well to other atoms in qualitative terms. Organic chemists are not interested in a precise mathematical description of orbitals, only in their approximate sizes and shapes, and hence how they influence chemical reactivity.

1.1.2 Simple bonds

We will begin by considering the simplest stable molecule of all: the hydrogen molecule. Each isolated hydrogen atom has one electron, contained in a $1s$ orbital. As the two atoms are brought together, their $1s$ orbitals interact, which they may do in two ways, either in phase or out of phase (Figure 1.2). When they are in phase, they add together to produce a wavefunction with a higher value between the nuclei. When they are out of phase, they will tend to cancel each other out, so that there is a nodal plane (a plane in which there is zero probability of finding the electron) halfway between the two nuclei. Thus we started with two atomic orbitals, and we now have two molecular orbitals. This is a general phenomenon – whenever there are a total of n atomic orbitals combining, the resultant molecule will always have n molecular orbitals.

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What exactly do we mean by atomic orbitals adding in phase or out of phase? The wavefunction for an electron at a particular point has a sign, in other words it may be positive or negative. This has no physical meaning by itself, because electron density is proportional to the square of the wavefunction. If, however, we imagine both atomic orbitals to have the same sign, then they will add in phase. Conversely, they will add out of phase if they have opposite signs. The signs of wavefunctions become more important as we consider p orbitals, as these have different signs on the two lobes.

It is obvious that the molecular orbitals from these two types of combination are not the same. The orbital resulting from the in-phase combination of atomic orbitals has a region of relatively high electron density between the two nuclei. This electron density attracts the positively charged nuclei and keeps them together. For this reason, this orbital is known as the bonding orbital. The other orbital has decreased electron density between the nuclei. This means that the two positive charges are not shielded from each other, and so they experience a repulsive force. This orbital is therefore known as the antibonding orbital, and is of higher energy (i.e. less stable) than the bonding orbital.

In the hydrogen molecule there are only two electrons, and these may both be accommodated in the bonding orbital, the antibonding orbital remaining empty. This gives rise to a stable bond, as we would expect. If we imagine a hypothetical helium molecule, He_2 , we have essentially the same orbitals, but now four electrons. The bonding orbital can accommodate only two electrons, so the other two must occupy the antibonding orbital. These two electrons in the antibonding orbital cancel out the effect of the two in the bonding orbital, so there is no net bonding interaction.³ This is why the helium molecule does not exist.

Combining atomic orbitals in this way is a mathematical convenience rather than a real physical process. An alternative way of arriving at the above molecular orbitals would be to solve the Schrödinger equation for the hydrogen molecule. Were we to do this (impossible to do exactly, although excellent approximations can be made), we would find the same two molecular orbitals, one bonding and one antibonding. (We would also find an infinite number of higher-energy orbitals, as indeed we would if we were to combine the higher-energy atomic orbitals in the way we have done for the 1s orbitals, but we can cheerfully ignore these because they contain no electrons.) Although it is mathematically more correct to think of molecular orbitals as being solutions to the Schrödinger equation for a whole molecule, it is usually more convenient to think of them as combinations of atomic orbitals, as we have done for hydrogen.

In principle, we can solve the Schrödinger equation for any molecule, and the wavefunctions that we obtain will describe the distribution of electrons, and hence

³ There is in fact a small net antibonding interaction, as the antibonding effect of an antibonding orbital is slightly greater than the bonding effect of a bonding orbital.

1.1 CHEMICAL BONDS

the bonding in the molecule. In practice, however, we will usually consider bonding in molecules as combinations of atomic orbitals, as we have done here. A precise mathematical description of electrons is not important in organic chemistry; we are more interested in how they take part in reactions. It is easier to predict this from a consideration of the properties of atoms and functional groups than from mathematical equations.

1.1.3 More complicated bonding and hybridization

The above description gives a good idea of what a chemical bond is at its simplest level, but as organic chemists we are not much concerned with hydrogen molecules. We are more interested in organic molecules, in other words those containing carbon. Carbon is in the first main row of the periodic table, so its 1s orbital is full, and we may ignore it. We are safe in doing this because orbitals interact significantly with other orbitals only if they are of similar energy. A filled inner orbital is much lower in energy than a valence orbital (the outer orbital of the atom, which takes part in reactions), and so the interaction between the carbon 1s orbital and the valence orbital of any atom with which carbon is bonding will be negligible. Of course, if the other atom also has a filled inner orbital, this may well be of a similar energy to the carbon 1s orbital, but we can still ignore the interaction, because the interaction of two filled orbitals leads to a bonding orbital and an antibonding orbital, which cancel each other out.

Carbon's valence shell consists of the 2s and three 2p orbitals. Carbon has six electrons, two of which occupy the 1s orbital, leaving four for the valence shell. As there are four orbitals and four electrons in the valence shell, we would expect carbon to be able to form four covalent bonds (each orbital has only one electron and so must gain a further electron from a covalent bond with another atom), and indeed we know that most carbon atoms in organic molecules are tetravalent.

Before we consider tetravalent carbons, however, let us first consider the simpler example of the methyl cation, CH_3^+ . Although this is extremely reactive and cannot be isolated, it does nonetheless have three stable bonds to hydrogen atoms and can be detected spectroscopically. Its reactivity arises from its vacant 2p orbital, perpendicular to the plane of the paper in Figure 1.3. The two remaining 2p orbitals and the 2s orbital are used in bonding to the hydrogens. If we consider the symmetry properties of the orbitals (this is really a job for theoretical chemists, so do not worry if this seems alien to you) we arrive at three combinations of atomic orbitals leading to bonding molecular orbitals. There are, of course, also three antibonding orbitals. Each of the three bonding orbitals contains two electrons, and so three bonds are formed.

This has already become much more complicated than the hydrogen molecule, and we still have only four atoms. Clearly, it would be advantageous to have some way of simplifying the problem, or we are going to run into great difficulties when

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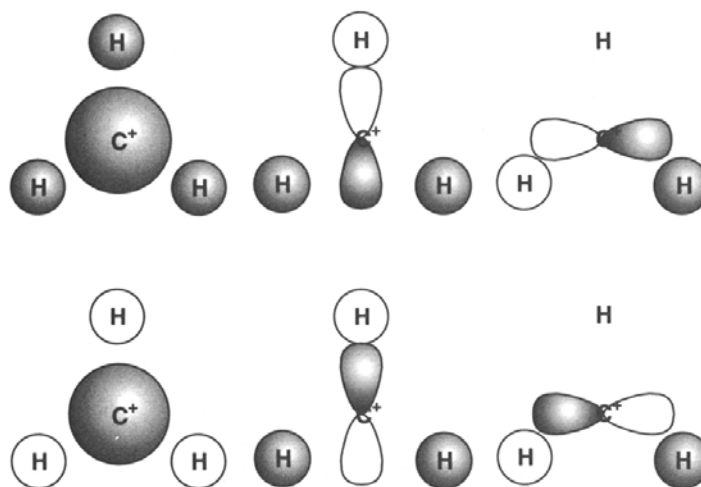


Figure 1.3 The three bonding (top) and three antibonding (bottom) orbitals of the methyl cation.

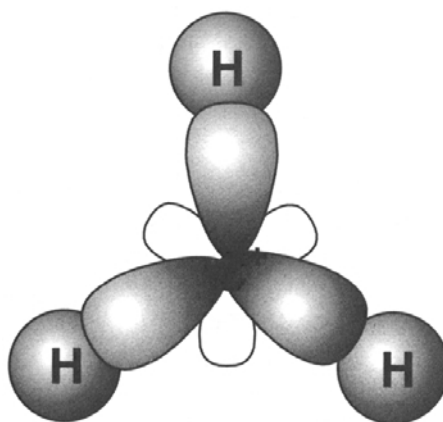


Figure 1.4

considering more grown-up organic molecules. Fortunately, such a trick is available. This is known as hybridization. Instead of considering the orbitals on the carbon atom in the way we have done above, we may think of the orbitals involved in the bonding as being equivalent. In this example, the resulting orbitals will be called sp_2 hybrids, because they are made up of one s orbital and two p orbitals. Each orbital has one third of the character of an s orbital, and two thirds that of a p orbital. They are arranged at 120° to each other, with each one pointing to a hydrogen atom (Figure 1.4). It is now much easier to see how three bonds are formed. Each of these bonds can be thought of as being localized and separate from the other two, and can hold two electrons. As before, we have six electrons taking part in bonding.

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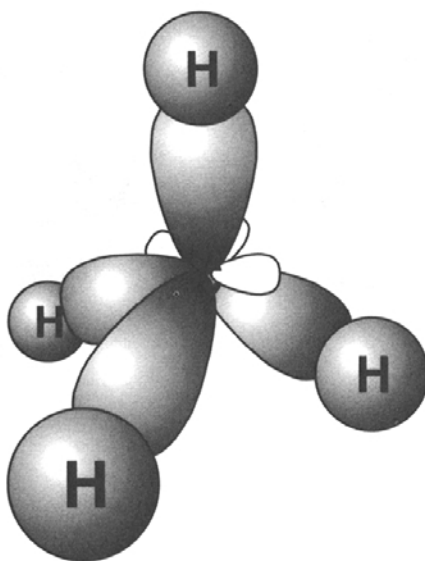


Figure 1.5

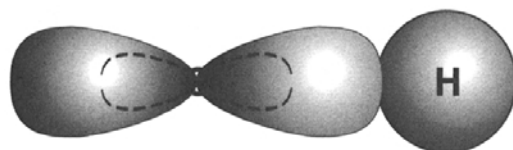


Figure 1.6

We should remember that hybridization of orbitals is just a mathematical trick; hybrid orbitals do not really exist. However, the molecular orbitals arrived at by considering hybrid orbitals have the same electron distribution as those derived from combinations of real atomic orbitals, or for that matter, from solving the Schrödinger equation for the whole molecule. It is obviously much more convenient to think of bonds in terms of the appropriate hybrid orbitals.

We may apply the same technique to methane, in which carbon is bonded to four hydrogen atoms at the vertices of a regular tetrahedron (Figure 1.5). All four orbitals participate in bonding, so we now use sp_3 hybrids, derived from one s orbital and three p orbitals. These are arranged tetrahedrally, with each one forming a bond to a hydrogen atom. We therefore have four localized bonds, as we would expect.

The third commonly used possibility is an sp hybrid, as found in acetylene. We shall ignore the bonding between the two carbon atoms in acetylene for the moment; this is explained in Section 1.1.4. The carbon–hydrogen bond is formed from an sp hybrid orbital on the carbon atom, which is at 180° to the carbon–carbon bond (Figure 1.6). This gives the molecule a linear shape.

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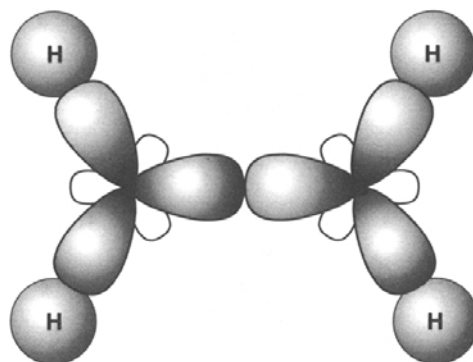


Figure 1.7

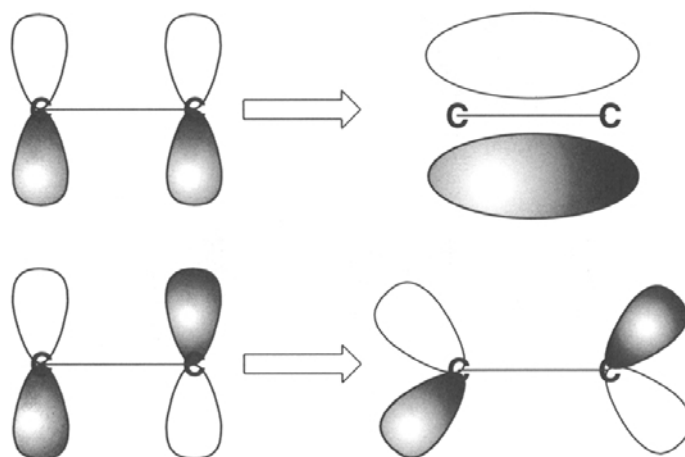


Figure 1.8 The bonding (top) and antibonding (bottom) π orbitals of ethylene.

1.1.4 Multiple bonds

Let us now consider the bonding in ethylene, one of the simplest molecules to have a multiple bond. It is easiest to think of the carbon atoms being sp_2 hybridized. We may thus draw the molecule as shown in Figure 1.7, with two of the sp_2 hybrid orbitals pointing towards the hydrogen atoms, and the third towards the other carbon.

This leaves us with a spare p orbital on each carbon atom. The p orbitals are perpendicular to the plane of the molecule. If we look at the molecule edge on (Figure 1.8) we see that there are two ways in which they may interact. This is exactly analogous to the overlap of s orbitals; in-phase overlap leads to a bonding orbital, out-of-phase overlap results in an antibonding orbital.

It is obvious that this is a different type of bond to those we have considered

1.2 RESONANCE STRUCTURES

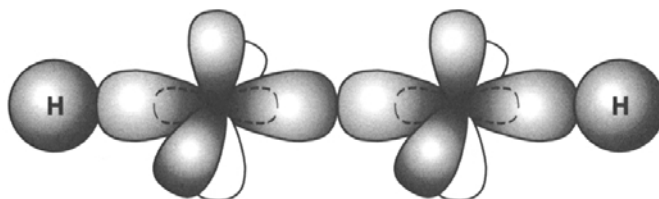


Figure 1.9

hitherto. Previously, we have looked at bonds in which the bonding overlap occurs along the axis joining the two nuclei. Such interactions are known as σ (sigma) bonds. In this new bond, there is no overlap of orbitals along the internuclear axis. The overlap occurs instead above and below it. This is called a π (pi) bond. Ethylene has one σ bond and one π bond joining the two carbon atoms; in other words there are two bonds, which is why ethylene is commonly written with a double bond.

A π bond is not as strong as a σ bond, because the orbitals are overlapping sideways, rather than head on. Consequently, although a double bond is stronger (and shorter) than a single bond, it is less than twice as strong. This is worth remembering, as there are many reactions in which σ bonds are formed at the expense of π bonds, for example the Diels–Alder reaction (Section 6.5.3).

An important feature of π bonds is that because there is no electron density between the two nuclei, it is all concentrated into electron clouds above and below the plane of the bond. These electron clouds readily take part in reactions, as they are held less tightly by the nuclei than electrons in σ bonds. This explains the tendency of olefins (compounds with carbon–carbon double bonds, otherwise known as alkenes) to react with electrophilic reagents, for example bromine (Section 6.1.3).

We can now return to acetylene. The σ framework consists of the sp hybrid orbitals from carbon and the s orbitals from hydrogen. This leaves two p orbitals on each carbon, which are perpendicular to the σ bonds and to each other. These form π bonds in just the same way that the π bond in ethylene is formed, but there are now two such bonds, one above and below the molecule, and one to either side of it (Figure 1.9). Thus the triple bond of acetylene is composed of one σ bond and two π bonds.

1.2 Resonance structures

The types of molecules we have discussed so far can be adequately described by a single structural formula. This simple state of affairs is not always so. Let us consider nitromethane. This may be written as shown in Figure 1.10a. According to this formula, one of the oxygen atoms is joined to the nitrogen with a double bond, and is electrically neutral, while the other is joined by a single bond and carries a negative charge.

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Figure 1.10

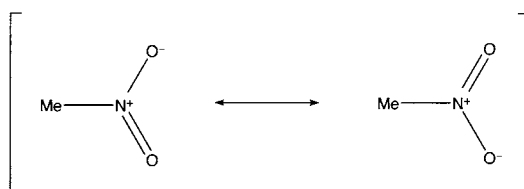


Figure 1.11

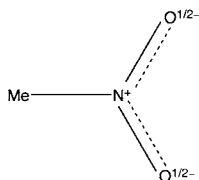


Figure 1.12

If we were to believe this formula, we would think that the two oxygen atoms are different. It is known, however, that the two oxygen atoms of the nitro group are equivalent. Each of the two bonds between oxygen and nitrogen is intermediate in length and strength between a single and a double bond. We could also write the structure of nitromethane as shown in Figure 1.10b. Here, the bonding of the two oxygens is written the other way round. We may think of the real bonding as being intermediate between the two ways of writing the structure.

Neither of these two formulae on their own is sufficient to describe the structure accurately. We may, however, write the structure of nitromethane as being composed of both structures, as in Figure 1.11. These are known as resonance structures. The double-headed arrow is the conventional way of showing that two structures are resonance forms of the same thing. Note also that it is common for resonance structures to be written within square brackets. It is important to realise that although we write the structure as these two separate forms, the real structure is in between the two. A common mistake is to think that the molecule spends some time as one of these structures as drawn, then the electrons rearrange themselves into the other form, and so on. This is not so. The molecule spends its entire time in an intermediate state. It would be more accurate to draw the molecule as in Figure 1.12, with half