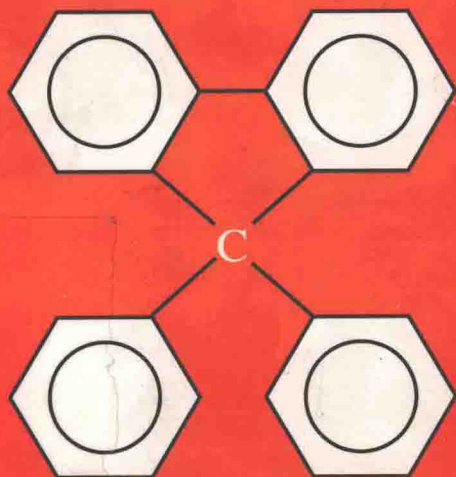


A GUIDEBOOK TO  
MECHANISM  
IN ORGANIC  
CHEMISTRY

SIXTH EDITION  
有机化学机理导论  
第6版

PETER SYKES



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# A guidebook to mechanism in organic chemistry

**Peter Sykes** M.Sc., Ph.D., F.R.S.C., C.Chem.

*Fellow of Christ's College, Cambridge*



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# Foreword

Fifty years ago the student taking up organic chemistry—and I speak from experience—was almost certain to be referred to one or other of a few textbooks generally known by the name of their authors—e.g. Holleman, Bernthsen, Schmidt, Karrer and Gattermann. On these texts successive generations of chemists were nurtured, and not in one country alone, for they were translated into several languages. These, the household names of fifty years ago, have for the most part gone. In past times of course the total number of books available was rather small and it is only in the last quarter of a century that we have seen a veritable flood of organic chemical textbooks pouring into booksellers' lists. The increase in the number of texts may be in part due to the rise in student numbers but the primary reason for it is the revolutionary impact of mechanistic studies on our approach to organic chemistry at the elementary level. With the plethora of books available, however, it is now much more difficult for an author to become a household name wherever the subject is taught. Yet this has indeed happened to Dr. Peter Sykes through his *Guidebook to Mechanism in Organic Chemistry*.

In the Foreword which I was privileged to write for the First Edition in 1961 I described not only my own view of what was happening in organic chemistry but also the type of approach to teaching it which was favoured by Dr. Sykes. Having known and watched him over many years first as student, then as colleague, and always as friend, I was confident that he had written an excellent book which, in my view at least, would add new interest to the study of organic chemistry. But its success has far exceeded even my high expectations and in its later editions it has been revised and refined without ever losing the cutting edge of the original.

The present volume continues the tradition. Once again the recent literature has been combed for new examples the better to exemplify principles of reactions. Of particular interest is an admirable chapter dealing with reactions controlled by orbital symmetry. Until I read it I was not convinced that this very important new development in the theory of organic reactions could be simply yet usefully communicated to students at an elementary level. To have succeeded in doing so only underlines further Dr. Sykes' gifts as a teacher and writer and I am sure that this new edition of the *Guidebook* will more than equal the success of its predecessors.

## Preface to sixth edition

It is now twenty-five years since this Guidebook first appeared and, hardly surprisingly, the current version is vastly different in both content and physical appearance from that first offering of so long ago. Over the years a real endeavour has been made to incorporate new, and to delete old, material not to reflect current trends and fashions, but to encompass significant changes in our fundamental understanding of organic chemistry; more particularly, to decide how these changes can best be conveyed to a largely undergraduate audience. At the same time care has been taken to retain the underlying framework and structure of the book for the excellent, pragmatic reason that this has been found to work well in practice.

The current version incorporates no new chapter but a number of new topics have been introduced, e.g. *ipso* aromatic substitution; the mechanistic borderline in nucleophilic substitution; more use of activation parameters, particularly in ester hydrolysis; Dimroth's  $E_T$  parameter; correlation of spectroscopic data with Hammett's  $\sigma_x$ ;  $^{13}\text{C}$  n.m.r. in biogenesis, etc. The now outmoded term 'carbonium ion' has been replaced throughout by 'carbocation', which has the advantage of being the natural antithesis to carbanion, and avoids the rather dubious alternative of carbenium ion. Apart from these more obvious changes, the whole text has been gone through, line by line, in an effort to remove ambiguities, to provide clearer, more cogent explanations, and more telling examples. The overall result, in garage parlance, has been a very thorough overhaul and extensive re-tune!

It has always been my feeling that many textbooks fall short of their full potential because the author has never entirely made up his or her mind whether the subject matter is addressed wholly to students or, in part at least, to their mentors; and the requirements of the two are, after all, different. This new edition is directed, as were its predecessors, unequivocally at the student; I trust therefore that it will continue to prove helpful to chemistry students in general, irrespective of the particular institution in which they happen to be studying.

As always I am greatly indebted to many correspondents who have pointed out errors, infelicities, and made suggestions for improvements; wherever feasible these have been incorporated in this revision. I should greatly appreciate similar kind assistance from readers in the future.

Finally, acknowledgement is made to the copyright holders for permission to reprint diagrams as follows: the American Chemical Society for Fig. 13.1 (Hammett, L. P. and Pfluger, H. L., *J. Amer. Chem. Soc.*, 1933, **55**, 4083), Fig. 13.2 (Hammett, L. P. and Pfluger H. L., *J. Amer. Chem. Soc.*, 1933, **55**, 4086), Fig. 13.3 (Hammett, L. P., *Chem. Rev.*, 1935, **17**, 131), Fig. 13.4 (Taft, R. W. and Lewis, I. C., *J. Amer. Chem. Soc.*, 1958, **80**, 2437), Fig. 13.5 (Brown, H. C. and Okamoto, Y., *J. Amer. Chem. Soc.*, 1957, **79**, 1915), Fig. 13.6 (Brown, H. C., Schleyer, P. von R. *et al.*, *J. Amer. Chem. Soc.*, 1970, **92**, 5244), Fig. 13.8 (Hart, H. and Sedor, F. A., *J. Amer. Chem. Soc.*, 1967, **89**, 2344); the Chemical Society and Professor J. A. Leisten for Fig. 13.7 (Leisten, J. A. and Kershaw, D. N., *Proc. Chem. Soc.*, 1960, 84).

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PETER SYKES

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# 1

## Structure, reactivity, and mechanism

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The chief advantage of a mechanistic approach, to the vast array of disparate information that makes up organic chemistry, is the way in which a relatively small number of guiding principles can be used, not only to explain and interrelate existing facts, but to forecast the outcome of changing the conditions under which already known reactions are carried out, and to foretell the products that may be expected from new ones. It is the business of this chapter to outline some of these guiding principles, and to show how they work. As it is the compounds of carbon with which we shall be dealing, something must be said about the way in which carbon atoms can form bonds with other atoms, especially with other carbon atoms.

### 1.1 ATOMIC ORBITALS

The carbon atom has, outside its nucleus, six electrons which, on the Bohr theory of atomic structure, were believed to be arranged in orbits at increasing distance from the nucleus. These orbits corres-



pounded to gradually increasing levels of energy, that of lowest energy, the 1s, accommodating two electrons, the next, the 2s, also accommodating two electrons, and the remaining two electrons of the carbon atom going into the 2p level, which is actually capable of accommodating a total of six electrons.

The Heisenberg indeterminacy principle, and the wave-mechanical view of the electron, have made it necessary to do away with anything so precisely defined as actual orbits. Instead the wave-like electrons are now symbolised by *wave functions*,  $\psi$ , and the precise, classical orbits of Bohr are superseded by three-dimensional *atomic orbitals* of differing energy level. The size, shape and orientation of these atomic orbitals—regions in which there is the greatest probability of finding an electron corresponding to a particular, quantised energy level—are each delineated by a wave function,  $\psi_A$ ,  $\psi_B$ ,  $\psi_C$ , etc. The orbitals are indeed rather like three-dimensional electronic contour maps, in which  $\psi^2$  determines the relative probability of finding an electron at a particular point in the orbital.

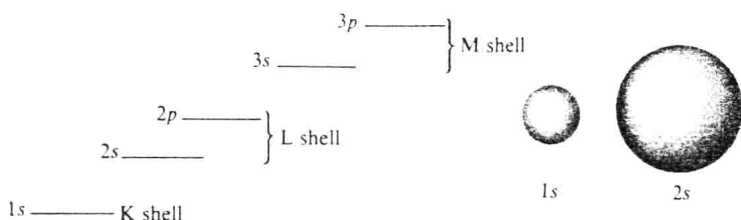
The relative *size* of atomic orbitals, which is found to increase as their energy level rises, is defined by the principal quantum number,  $n$ , their *shape* and *spatial orientation* (with respect to the nucleus and each other) by the subsidiary quantum numbers,  $l$  and  $m$ , respectively.\* Electrons in orbitals also have a further designation in terms of the *spin* quantum number, which can have the values  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . One limitation that theory imposes on such orbitals is that each may accommodate not more than two electrons, these electrons being distinguished from each other by having opposed (*paired*) spins.† This follows from the Pauli exclusion principle, which states that no two electrons in any atom may have exactly the same set of quantum numbers.

It can be shown, from wave-mechanical calculations, that the 1s orbital (quantum numbers  $n = 1$ ,  $l = 0$ ,  $m = 0$ , corresponding to the classical K shell) is spherically symmetrical about the nucleus of the atom, and that the 2s orbital (quantum numbers  $n = 2$ ,  $l = 0$ ,  $m = 0$ ) is similarly spherically symmetrical, but at a greater distance from the nucleus; there is a region between the two latter orbitals where the probability of finding an electron approaches zero (a *spherical nodal surface*).

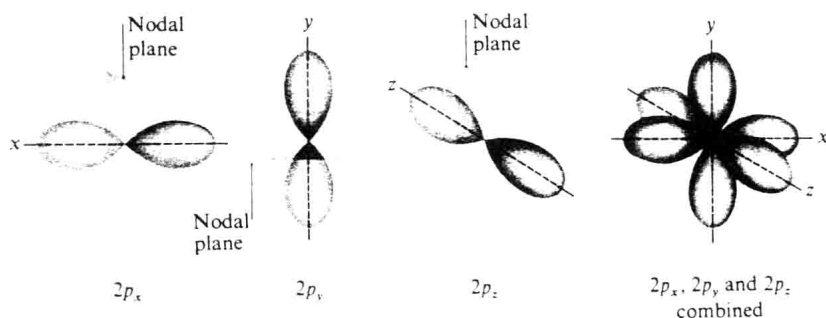
As yet, this marks no radical departure from the classical picture of orbits, but with the 2p level (the continuation of the L shell) a difference becomes apparent. Theory now requires the existence of *three* 2p orbitals (quantum numbers  $n = 2$ ,  $l = 1$ , with  $m = +1, 0$ , and

\*  $n$  can have values of 1, 2, 3, ...,  $l$  values of 0, 1, 2, ...,  $n - 1$ , and  $m$  values of 0,  $\pm 1$ ,  $\pm 2$ , ...,  $\pm l$ . We shall normally be concerned only with  $l$  values of 0 and 1, the corresponding orbitals being referred to (from spectroscopic terminology) as *s* and *p* orbitals, respectively, e.g. 1s, 2s, 2p orbitals, etc.

† One electron with spin quantum number  $+\frac{1}{2}$ , the other  $-\frac{1}{2}$ .



–1, respectively), all of the same shape and energy level (orbitals having the same energy level are described as *degenerate*), but differing from each other in their spatial orientation. They are in fact arranged mutually at right-angles along notional  $x$ ,  $y$  and  $z$  axes and, therefore, designated as  $2p_x$ ,  $2p_y$  and  $2p_z$ , respectively. Further, these three  $2p$  orbitals are found not to be spherically symmetrical, like the  $1s$  and  $2s$ , but 'dumb-bell' shaped with a plane, in which there is zero probability of finding an electron (*nodal plane*), passing through the nucleus (at right-angles to the  $x$ ,  $y$  and  $z$  axes, respectively), and so separating the two halves of each dumb-bell:



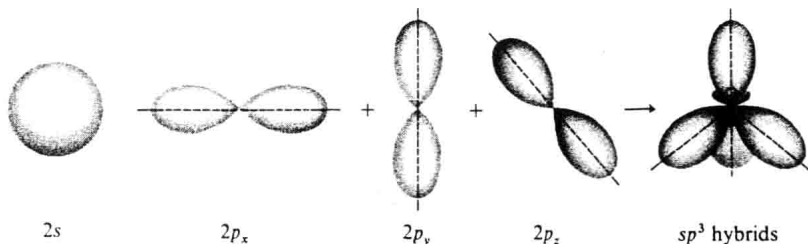
The six electrons of the carbon atom are then accommodated in atomic orbitals of increasing energy level until all are assigned (the *aufbau*, or build-up, principle). Thus two electrons, with paired spins, will go into the  $1s$  orbital, a further two into the  $2s$  orbital, but at the  $2p$  level the remaining two electrons could be accommodated either in the same, e.g.  $2p_x$ , or different, e.g.  $2p_x$  and  $2p_y$ , orbitals. Hund's rule, which states that two electrons will avoid occupying the same orbital so long as there are other energetically equivalent, i.e. degenerate, orbitals still empty, will apply, and the *electron configuration* of carbon will thus be  $1s^2 2s^2 2p_x^1 2p_y^1$ , with the  $2p_z$  orbital remaining unoccupied. This represents the *ground state* of the free carbon atom in which only two unpaired electrons (in the  $2p_x$  and  $2p_y$  orbitals) are available

for the formation of bonds with other atoms, i.e. at first sight carbon might appear to be only divalent.

This, however, is contrary to experience, for though compounds are known in which carbon is singly bonded to only two other atoms, e.g.  $\text{CCl}_2$  (p. 267), these are highly unstable; in the enormous majority of its compounds carbon exhibits quadrivalency, e.g.  $\text{CH}_4$ . This can be achieved by uncoupling the  $2s^2$  electron pair, and promoting one of them to the vacant  $2p_z$  orbital. The carbon atom is then in a higher energy (*excited*) state,  $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$ , but as it now has *four* unpaired electrons it is able to form *four*, rather than only *two*, bonds with other atoms or groups. The large amount of energy produced by forming these two extra bonds considerably outweighs that required [ $\approx 406 \text{ kJ (97 kcal) mol}^{-1}$ ] for the initial  $2s^2$  uncoupling, and  $2s \rightarrow 2p_z$  promotion.

## 1.2 HYBRIDISATION

A carbon atom combining with four other atoms clearly does not use the one  $2s$  and the three  $2p$  atomic orbitals that would now be available, for this would lead to the formation of three directed bonds, mutually at right angles (with the three  $2p$  orbitals), and one different, non-directed bond (with the spherical  $2s$  orbital). Whereas in fact, the four C—H bonds in, for example, methane are known to be identical and symmetrically (tetrahedrally) disposed at an angle of  $109^\circ 28'$  to each other. This may be accounted for on the basis of redeploying the  $2s$  and the three  $2p$  atomic orbitals so as to yield four new (identical) orbitals, which are capable of forming stronger bonds (*cf.* p. 5). These new orbitals are known as  $sp^3$  hybrid atomic orbitals, and the process by which they are obtained as *hybridisation*:



It should, however, be emphasised, despite the diagram above, that hybridisation is an operation carried out not actually on orbitals themselves but on the mathematical functions that define them.

Similar, but different, redeployment is envisaged when a carbon atom combines with three other atoms, e.g. in ethene (ethylene) (p. 8): three  $sp^2$  hybrid atomic orbitals disposed at  $120^\circ$  to each other in the same plane (*plane trigonal hybridisation*) are then employed. Finally, when carbon combines with two other atoms, e.g. in ethyne (acetylene) (p. 9): two  $sp^1$  hybrid atomic orbitals disposed at  $180^\circ$  to each other (*digonal hybridisation*) are employed. In each case the  $s$  orbital is always involved as it is the one of lowest energy level.

These are all valid ways of deploying one  $2s$  and three  $2p$  atomic orbitals—in the case of  $sp^2$  hybridisation there will be one unhybridised  $p$  orbital also available (p. 8), and in the case of  $sp^1$  hybridisation there will be two (p. 10). Other, equally valid, modes of hybridisation are also possible in which the hybrid orbitals are not necessarily identical with each other, e.g. those used in  $\text{CH}_2\text{Cl}_2$  compared with the ones used in  $\text{CCl}_4$  and  $\text{CH}_4$ . Hybridisation takes place so that the atom concerned can form as strong bonds as possible, and so that the other atoms thus bonded (and the electron pairs constituting the bonds) are as far apart from each other as possible, i.e. so that the total intrinsic energy of the resultant compound is at a minimum.

### 1.3 BONDING IN CARBON COMPOUNDS

Bond formation between two atoms is then envisaged as the progressive overlapping of an atomic orbital from each of the participating atoms, the greater the overlap achieved (the *overlap integral*), the stronger the bond so formed. The relative overlapping powers of atomic orbitals have been calculated as follows:

$$\begin{aligned}s &= 1.00 \\ p &= 1.72 \\ sp^1 &= 1.93 \\ sp^2 &= 1.99 \\ sp^3 &= 2.00\end{aligned}$$

It will thus be apparent why the use of hybrid orbitals, e.g.  $sp^3$  hybrid orbitals in the combination of one carbon and four hydrogen atoms to form methane, results in the formation of stronger bonds.

When the atoms have come sufficiently close together, it can be shown that their two atomic orbitals are replaced by two *molecular orbitals*, one being at a lower, and the other at a higher, energy level than the two original atomic orbitals. These two new molecular orbitals spread over both atoms and either may contain the two electrons (Fig. 1.1):

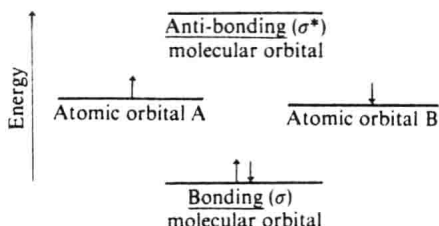


Fig. 1.1

The molecular orbital of lower energy is called the *bonding orbital*, and its occupancy results in the formation of a stable bond between the two atoms. In the above case, the pair of electrons constituting the bond tend to be concentrated between the two positively charged atomic nuclei, which can thus be thought of as being held together by the negative charge between them. The molecular orbital of higher energy is called the *anti-bonding orbital*; this corresponds to a state in which the internuclear space remains largely empty of electrons, and thus results in repulsion between the two positively charged atomic nuclei. The anti-bonding orbital remains empty in the ground state of the molecule, and need not here be further considered in the formation of stable bonds between atoms.

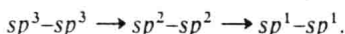
If overlap of the two atomic orbitals has taken place along their major axes, the resultant bonding molecular orbital is referred to as a  $\sigma$  orbital,\* and the bond formed as a  $\sigma$  bond. The  $\sigma$  molecular orbital, and the electrons occupying it, are found to be *localised* symmetrically about the internuclear axis of the atoms that are bonded to each other. Thus on combining with hydrogen, the four hybrid  $sp^3$  atomic orbitals of carbon overlap with the  $1s$  atomic orbitals of four hydrogen atoms to form four identical, strong  $\sigma$  bonds, making angles of  $109^\circ 28'$  with each other (the regular tetrahedral angle), in methane. A similar, exactly regular, tetrahedral structure will result with, for example,  $\text{CCl}_4$ , but where the atoms bonded to carbon are not all the same, e.g.  $\text{CH}_2\text{Cl}_2$ , the spatial arrangement may depart slightly from the exactly symmetrical while remaining essentially tetrahedral (*cf.* p. 5).

### 1.3.1 Carbon-carbon single bonds

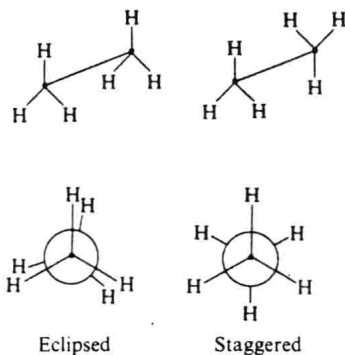
The combination of two carbon atoms, for example in ethane, results from the axial overlap of two  $sp^3$  atomic orbitals, one from each

\* The anti-bonding molecular orbital is referred to as a  $\sigma^*$  orbital.

carbon atom, to form a strong  $\sigma$  bond between them. The carbon-carbon bond length in saturated compounds is found to be pretty constant—0.154 nm (1.54 Å). This refers, however, to a carbon-carbon single bond between  $sp^3$  hybridised carbons. A similar single bond between two  $sp^2$  hybridised carbons,  $=CH-CH=$ , is found on average to be about 0.147 nm (1.47 Å) in length, and one between two  $sp$  hybridised carbons,  $\equiv C-C\equiv$ , about 0.138 nm (1.38 Å). This is not really surprising, for an  $s$  orbital and any electrons in it are held closer to, and more tightly by, the nucleus than is a  $p$  orbital and any electrons in it. The same effect will be observed with hybrid orbitals as their  $s$  component increases, and for two carbon atoms bonded to each other the nuclei are drawn inexorably closer together on going from



We have not, however, defined a unique structure for ethane: the  $\sigma$  bond joining the two carbon atoms is symmetrical about a line joining the two nuclei, and, theoretically, an infinite variety of different structures is still possible, defined by the position of the hydrogens on one carbon atom relative to the position of those on the other. The two extremes, of all the possible species, are known as the *eclipsed* and *staggered* forms:



The above quasi three-dimensional representations are known as 'sawhorse' and Newman projections, respectively. The eclipsed and staggered forms, and the infinite variety of possible structures lying between them as extremes, are known as *conformations* of the ethane molecule: conformations being defined as different arrangements of the same group of atoms that can be converted into one another without the breaking of any bonds.

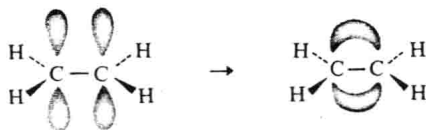
The staggered conformation is likely to be the more stable of the two as hydrogen atoms on one carbon are then as far away from those on the other as they can get (0.310 nm; 3.1 Å), and any so-called 'non-bonded' interaction between them is thus at a

minimum; whereas in the eclipsed conformation they are suffering the maximum of crowding [ $0.230\text{ nm}$  ( $2.3\text{ \AA}$ ), slightly less than the sum of their van der Waals radii]. The long cherished principle of free rotation about a carbon-carbon single bond is not contravened, however, as it has been shown that the eclipsed and staggered conformations differ by only  $\approx 12\text{ kJ}$  ( $3\text{ kcal}$ )  $\text{mol}^{-1}$  in energy content at  $25^\circ$ , and this is small enough to allow their ready interconversion through the agency of ordinary thermal motions at room temperature—the rotation frequency at  $25^\circ$  being  $\approx 10^{12}\text{ sec}^{-1}$ . That such crowding *can* lead to a real restriction of rotation about a carbon-carbon single bond has been confirmed by the isolation of two forms of  $\text{CHBr}_2\text{CHBr}_2$ , though admittedly only at low temperatures where collisions between molecules do not provide enough energy to effect the interconversion.

### 1.3.2 Carbon-carbon double bonds

In ethene each carbon atom is bonded to only *three* other atoms, two hydrogens and one carbon. Strong  $\sigma$  bonds are formed with these three atoms by the use of *three* orbitals derived by hybridising the  $2s$  and, this time, *two* only of the carbon atom's  $2p$  atomic orbitals—an atom will normally only mobilise as many hybrid orbitals as it has atoms or groups to form strong  $\sigma$  bonds with. The resultant  $sp^2$  hybrid orbitals all lie in the same plane, and are inclined at  $120^\circ$  to each other (*plane trigonal orbitals*). In forming the molecule of ethene, two of the  $sp^2$  orbitals of each carbon atom are seen as overlapping with the  $1s$  orbitals of two hydrogen atoms to form two strong  $\sigma\text{ C-H}$  bonds, while the third  $sp^2$  orbital of each carbon atom overlap axially to form a strong  $\sigma\text{ C-C}$  bond between them. It is found experimentally that the  $\text{H-C-H}$  and  $\text{H-C-C}$  bond angles are in fact  $116.7^\circ$  and  $121.6^\circ$ , respectively. The departure from  $120^\circ$  is hardly surprising seeing that different trios of atoms are involved.

This then leaves, on each carbon atom, *one unhybridised  $2p$  atomic orbital* at right angles to the plane containing the carbon and hydrogen atoms. When these two  $2p$  orbitals become parallel to each other they can themselves overlap, resulting in the formation of a bonding molecular orbital spreading over both carbon atoms and situated above and below the plane (i.e. it has a node in the plane of the molecule) containing the two carbon and four hydrogen atoms (' $\backslash$ ' indicates bonds to atoms lying *behind* the plane of the paper, and ' $\wedge$ ' bonds to those lying in *front* of it):



This new bonding molecular orbital is known as a  $\pi$  orbital,\* and the electrons that occupy it as  $\pi$  electrons. The new  $\pi$  bond that is thus formed has the effect of drawing the carbon atoms closer together, and the C=C distance in ethene is found to be 0.133 nm (1.33 Å), compared with a C—C distance of 0.154 nm (1.54 Å) in ethane. The *lateral* overlap of the  $p$  atomic orbitals that occurs in forming a  $\pi$  bond is less effective than the axial overlap that occurs in forming a  $\sigma$  bond, and the former is thus weaker than the latter. This is reflected in the fact that the energy of a carbon-carbon double bond, though more than that of a single bond is, indeed, less than twice as much. Thus the C—C bond energy in ethane is 347 kJ (83 kcal) mol<sup>-1</sup>, while that of C=C in ethene is only 598 kJ (143 kcal) mol<sup>-1</sup>.

The lateral overlap of the two  $2p$  atomic orbitals, and hence the strength of the  $\pi$  bond, will clearly be at a maximum when the two carbon and four hydrogen atoms are exactly coplanar, for it is only in this position that the  $p$  atomic orbitals are exactly parallel to each other, and will thus be capable of maximum overlap. Any disturbance of this coplanar state, by twisting about the  $\sigma$  bond joining the two carbon atoms, would lead to reduction in  $\pi$  overlapping, and hence a decrease in the strength of the  $\pi$  bond: it will thus be resisted. A theoretical justification is thus provided for the long observed resistance to rotation about a carbon-carbon double bond. The distribution of the  $\pi$  electrons in two lobes, above and below the plane of the molecule, and extending beyond the carbon-carbon bond axis, means that a region of negative charge is effectively waiting there to welcome any electron-seeking reagents (e.g. oxidising agents); so that it comes as no surprise to realise that the characteristic reactions of a carbon-carbon double bond are predominantly with such reagents (*cf.* p. 178). Here the classical picture of a double bond has been replaced by an alternative, in which the two bonds joining the carbon atoms, far from being identical, are considered to be different in nature, strength and position.

### 1.3.3 Carbon-carbon triple bonds

In ethyne each carbon atom is bonded to only *two* other atoms, one hydrogen and one carbon. Strong  $\sigma$  bonds are formed with these two atoms by the use of *two* hybrid orbitals derived by hybridising the  $2s$  and, this time, *one* only of the carbon atom's  $2p$  atomic orbitals. The resultant *digonal*  $sp^1$  hybrid orbitals are co-linear. Thus, in forming the molecule of ethyne, these hybrid orbitals are used to form strong  $\sigma$  bonds between each carbon atom and one hydrogen atom, and between the two carbon atoms themselves, resulting in a linear molecule

\* An anti-bonding,  $\pi^*$ , molecular orbital is also formed (*cf.* p. 12).



having *two* unhybridised  $2p$  atomic orbitals, at right angles to each other, on each of the two carbon atoms. The atomic orbitals on one carbon atom are parallel to those on the other, and can thus overlap with each other resulting in the formation of *two*  $\pi$  bonds in planes at right angles to each other:



The ethyne molecule is thus effectively sheathed in a cylinder of negative charge. The  $\text{C}\equiv\text{C}$  bond energy is  $812 \text{ kJ (194 kcal) mol}^{-1}$ , so that the increment due to the third bond is less than that occurring on going from a single to a double bond. The  $\text{C}\equiv\text{C}$  bond distance is  $0.120 \text{ nm (1.20 \AA)}$  so that the carbon atoms have been drawn still further together, but here again the decrement on going  $\text{C}=\text{C} \rightarrow \text{C}\equiv\text{C}$  is smaller than that on going  $\text{C}-\text{C} \rightarrow \text{C}=\text{C}$ .

### 1.3.4 Carbon-oxygen and carbon-nitrogen bonds

An oxygen atom has the electron configuration  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ , and it too, on combining with other atoms, can be looked upon as utilising hybrid orbitals so as to form the strongest possible bonds. Thus on combining with the carbon atoms of two methyl groups, to form methoxymethane (dimethyl ether),  $\text{CH}_3-\ddot{\text{O}}-\text{CH}_3$ , the oxygen atom could use four  $sp^3$  hybrid orbitals: two to form  $\sigma$  bonds by overlap with an  $sp^3$  orbital of each of the two carbon atoms, and the other two to accommodate its two lone pairs of electrons. The  $\text{C}-\text{O}-\text{C}$  bond angle is found to be  $110^\circ$ , the  $\text{C}-\text{O}$  bond length,  $0.142 \text{ nm (1.42 \AA)}$ , and the bond energy,  $360 \text{ kJ (86 kcal) mol}^{-1}$ .

An oxygen atom can also form a double bond to carbon; thus in propanone (acetone),  $\text{Me}_2\text{C}=\ddot{\text{O}}$ , the oxygen atom could use three  $sp^2$  hybrid orbitals: one to form a  $\sigma$  bond by overlap with an  $sp^2$  orbital of the carbon atom, and the other two to accommodate the two lone pairs of electrons. This leaves an unhybridised  $p$  orbital on both oxygen and carbon, and these can overlap with each other laterally (*cf.*  $\text{C}=\text{C}$ , p. 9) to form a  $\pi$  bond:

