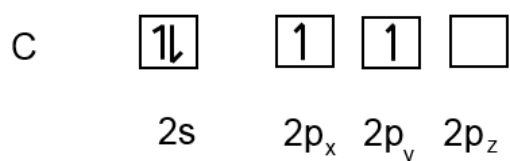
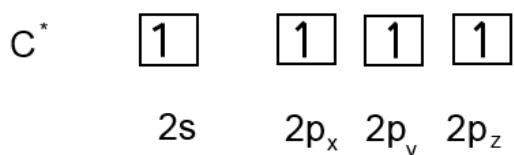


## A BRIEF REVIEW OF CHEMICAL BONDING IN ORGANIC COMPOUNDS

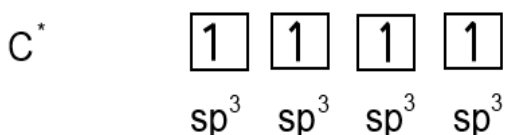
The elements most commonly encountered in organic compounds are carbon, nitrogen, hydrogen and oxygen. In the ground state of these elements there are varying numbers of outer shell or valence electrons which participate in covalent chemical bonds. A bond is formed when two atoms share one or more pairs of electrons. Each element forms these bonds in characteristic patterns, and these patterns can be explained by the theories of hybridisation of atomic orbitals and VSEPR (Valence Shell Electron Pair Repulsion). Beginning with carbon, which has the electronic configuration in the ground state  $1s^2 2s^2 2p^2$ , there are four outer shell electrons with which bond formation may occur. (The inner shell of  $1s^2$  electrons can be ignored as these do not take part in bonding) However, two of these are paired in the  $2s$  orbital, and two are unpaired in the  $2p_x$  and  $2p_y$  orbitals, as shown in this diagram :



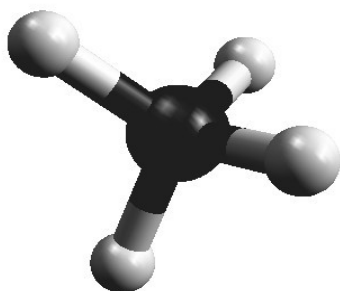
It is predicted by theory that paired electrons require energy input to become unpaired before they can form a bond, hence one  $2s$  electron must be promoted to the empty  $2p_z$  orbital



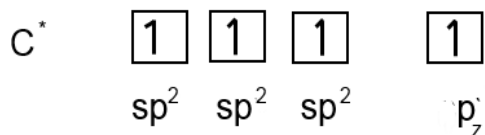
There are now 4 unpaired electrons available for bonding, but because the original  $p$  orbital lobes are arranged orthogonally, while the  $s$  orbital is spherical, this would lead to repulsion between the  $p$  orbital electron pairs in the completed bonds. Hybridisation theory predicts that four new orbitals will be formed having lower overall energy than the above arrangement. These are the  $sp^3$  hybrid orbitals.



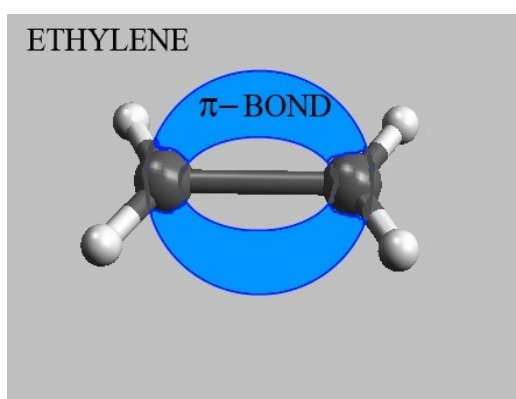
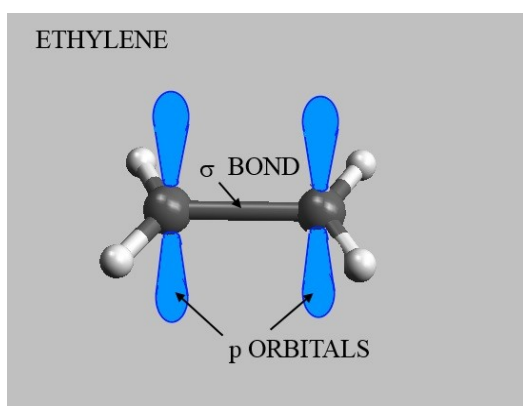
These four orbitals are arranged pointing toward the vertices of a tetrahedron, so that repulsive interactions between them are minimised, and it is these hybridised orbitals that participate in bond formation. For example, if bonds are formed with four hydrogen atoms, the resulting compound is methane  $\text{CH}_4$ , which is known to have tetrahedral geometry from experiments.



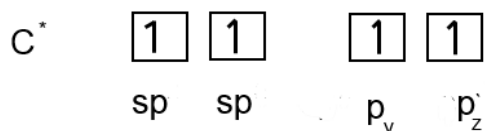
As well as forming four  $sp^3$  hybrids, Carbon can also hybridise in two other geometries, identified as  $sp^2$  and  $sp$ . To form  $sp^2$  hybrids, two  $s$  orbital electrons and one  $p$  orbital electron combine resulting in three  $sp^2$  hybrid orbitals arranged in trigonal planar geometry. The remaining electron is left in a standard  $p$  orbital, which is located orthogonal to the trigonal plane of the  $sp^2$  hybrids.



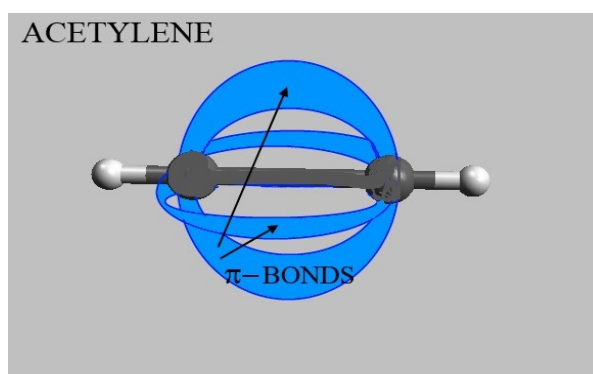
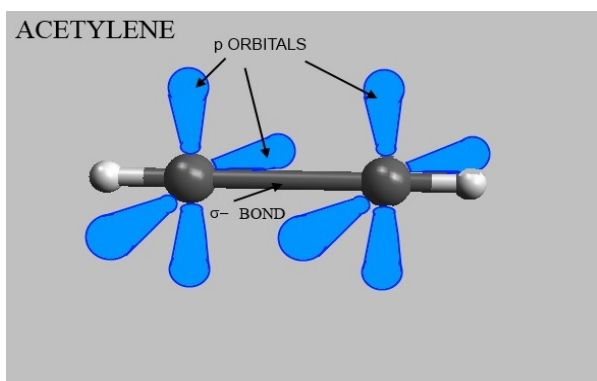
These  $sp^2$  hybrids are involved in the formation of what is known as a double bond, such as occurs in ethylene,  $\text{C}_2\text{H}_4$ , propylene,  $\text{C}_3\text{H}_6$  and other olefinic compounds. Double bonds are conventionally shown in Lewis structures as two identical bonds, ie  $\text{C}=\text{C}$ , but in fact they consist of one  $\sigma$  (sigma) bond, formed by end-on overlap of two  $sp^2$  orbitals, plus one  $\pi$  (pi) bond formed by side-to-side overlap of two  $p$  orbitals. The  $\pi$  bond is not as strong as the  $\sigma$  bond due to the smaller overlap volume, but the combination of both is stronger than a single  $\sigma$  bond.



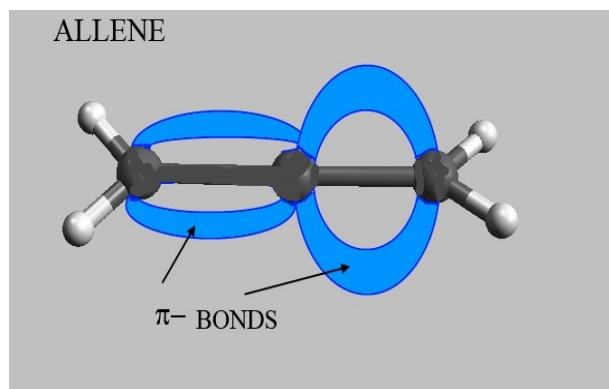
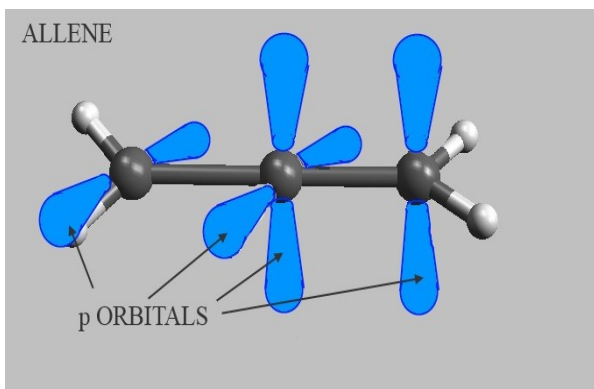
In the acetylenic series of compounds Carbon exhibits  $sp$  hybridisation. Here there are two hybrid orbitals formed from the two  $s$  orbital electrons, with two electrons remaining in  $p$  orbitals.



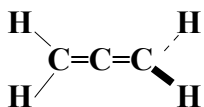
Here the  $sp$  orbitals are co-linear, with the two  $p$  orbitals located orthogonally. These hybrids are involved in two types of bonding, either a conventional triple bond, or an allenic bond in which two double bonds are formed on the same Carbon atom.



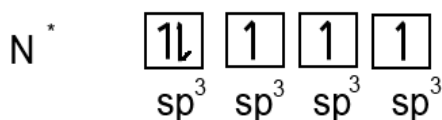
ACETYLINIC TRIPLE BOND  $\text{H}-\text{C}\equiv\text{C}-\text{H}$



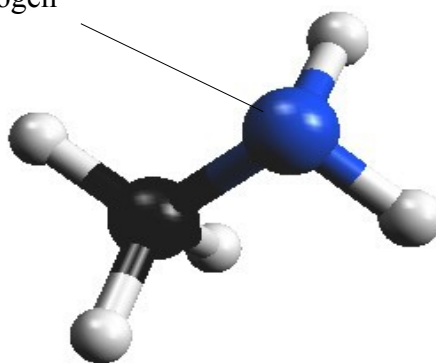
### ALLENIC DOUBLE BONDS



Hybridisation also occurs with other atoms, in particular Nitrogen and Oxygen. Nitrogen has 5 outer shell electrons in the configuration  $2s^2 2p^3$ . It can form four  $sp^3$  hybrid orbitals in which one orbital has a pair of electrons and the other three contain one electron each. This is the type of hybridisation which is involved in compounds such as methylamine,  $\text{CH}_3\text{NH}_2$ . This has tetrahedral geometry.

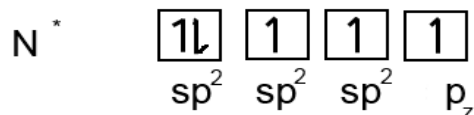


$sp^3$  nitrogen

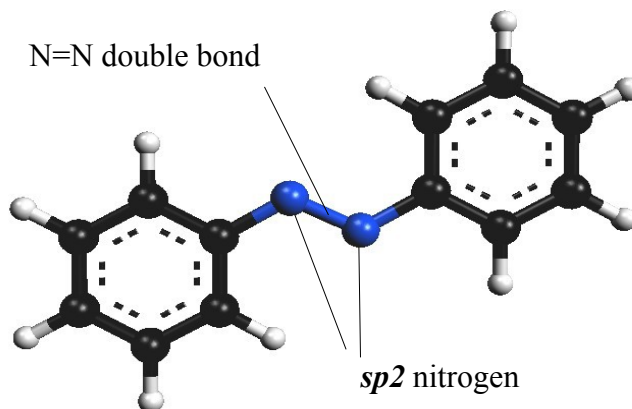


The paired electrons are normally not available for bonding without extra energy input, and are referred to as a lone pair or non-bonding pair. ( They can be involved in bonding in some molecules )

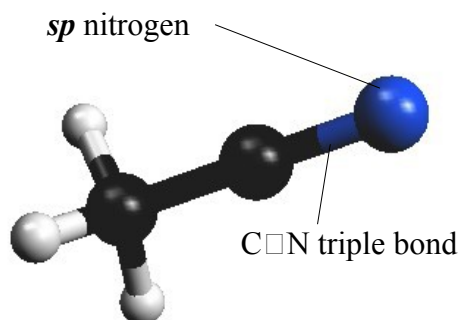
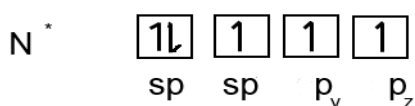
In  $sp^2$  hybridised Nitrogen there are three trigonal  $sp^2$  orbitals, one containing the lone pair and two with a single electron, plus one  $p$  orbital located orthogonally. This hybridisation occurs in double-bonded Nitrogen compounds like azobenzene,  $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5$



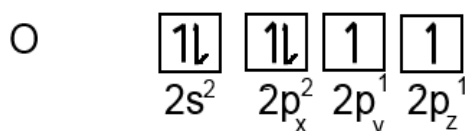
N=N double bond



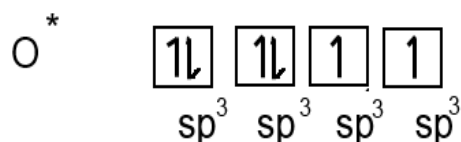
Nitrogen with  $sp$  hybridisation is found in molecules such as acetonitrile,  $\text{CH}_3\text{C}\equiv\text{N}$ . These compounds are linearly arranged about the triple bond.



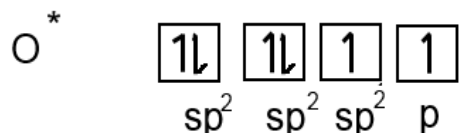
Oxygen has 6 outer electrons in the configuration  $2s^2 2p^4$ . In the ground state, the  $2s$  electrons and two of the  $2p$  electrons are spin-paired.



The hybridisation patterns for Oxygen are :



$sp^3$  hybridisation : Two bonding electrons and two lone pairs in (approximate \*) tetrahedral geometry



$sp^2$  hybridisation : One bonding electron and two lone pairs in (approximate \*) trigonal geometry, plus one  $p$  electron

Oxygen does not form  $sp$  hybrids, because it can only accept up to 2 electrons from other atoms in its outer shell before its orbitals are completely filled.

- \* The proximity of the lone electron pairs in Nitrogen and Oxygen hybrid orbitals causes repulsion of the other orbitals so that the geometric angles between the resulting bonds depart slightly from their values in completely symmetrical molecules like methane and ethylene.
- This brief summary of hybridisation and VSEPR theories is sufficient to allow models of most organic compounds to be accurately constructed. To understand reaction mechanisms in organic chemistry and to construct models of transition states, especially those involving frontier orbital interactions, some knowledge of molecular orbital theory is also necessary. Suitable text books should be consulted for this purpose.