Bonding in Organic Compounds
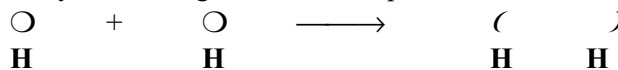
A covalent bond is formed by the sharing of an electron pair between two atoms, ex. H_2

$$\bigcirc \quad + \quad \bigcirc \quad \longrightarrow \quad (\quad\quad)$$

$$\textbf{H} \qquad\qquad \textbf{H} \qquad\qquad\qquad \textbf{H} \qquad \textbf{H}$$

The two single occupied 's' orbitals (containing unpaired electrons), on two hydrogen atoms combine to form one bonding molecular orbital extending over both nuclei, in H_2. The molecular orbital is occupied by two electrons with opposite spins.

Bonds like these, where two half-filled orbitals on neighbouring atoms combine, i.e. in which orbital overlap occurs along the line of the atomic nuclei, to give a bonding molecular orbital with high electron density between the two nuclei involved are called sigma or σ-**bonds**.
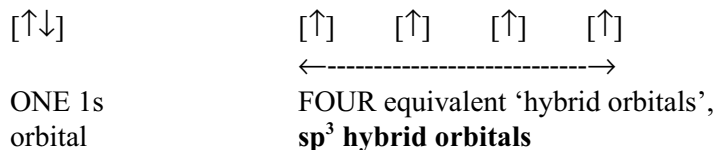
Making four single bonds to carbon

If a carbon atom remained in its ground state in a molecule it could form only two covalent bonds, using its two unpaired p-electrons, and it would have only six electrons in its outer shell:

C atom $\qquad\quad 1s^2 \qquad 2s^2 \qquad\qquad 2p^2$

$$\qquad\qquad\qquad ↑↓ \qquad ↑↓ \qquad [↑] \ [↑] \ [\ \ ]$$
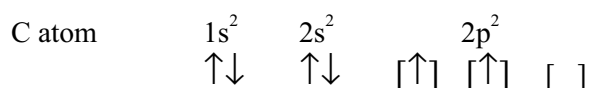
It is energetically more favourable to promote one of the 2s electrons into the vacant p-orbital. The four half-filled orbitals can then combine with half-filled orbitals on four other atoms (ex. H) to form *four equivalent covalent bonds*, **hybrid orbitals, sp^3**, **four σ-bonds**. The carbon atom makes four bonds and so will share eight electrons in its outer shell (two electrons per bond).

Carbon atom (after formation of four covalent bonds)

$$[↑↓] \qquad\qquad\qquad [↑] \quad\ [↑] \quad\ [↑] \quad\ [↑]$$

$$\qquad\qquad\qquad\qquad\qquad ←-----------------------→$$

ONE 1s $\qquad\qquad\qquad$ FOUR equivalent 'hybrid orbitals',

orbital $\qquad\qquad\qquad\qquad$ **sp^3 hybrid orbitals**

The energy for the promotion, about 400 kJ mol^{-1}, is more than repaid by the bond energy released from making four bonds instead of two.

Methane, CH_4: the four tetrahedral **sp^3** hybrid orbitals of the carbon atom in the molecule may be represented as:

Mutual repulsion of the electron pairs in these molecular orbitals or bonds leads to their pointing to the corners of a tetrahedron.
*(In general n atomic orbitals combine to form n molecular orbitals, of which n/2 are occupied and bonding).*

Making Multiple Bonds to Carbon: π - bonds

There are other ways in which the four half-filled orbitals of carbon can be combined, allowing carbon to make double or triple bonds to another atom.

Double Bonds

Three of the three half-filled orbitals are used to form *three equivalent 'hybrid' orbitals, called* sp^2, leaving one half-filled p orbital to form one other bond.

[↑↓]	[↑] [↑] [↑]	[↑]
	←------------------→	
ONE 1s	THREE equivalent	ONE p orbital
Orbital	**'hybrid' orbitals, sp^2**	
		'unhybridized'
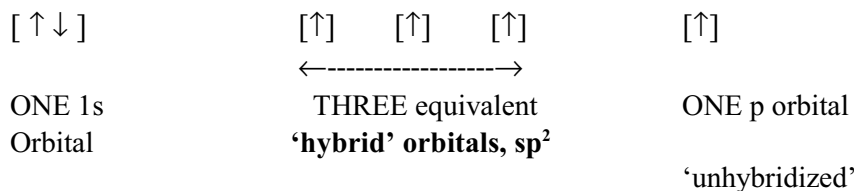
In the ethene molecule, C_2H_4, the two carbon atoms each make use of three equivalent sp_2 hybrid orbitals formed from the 2s and the 2p orbitals, to give three sigma bonds, **σ-bonds**., one to carbon and two to hydrogens…

The ethene molecule is planar with **H-C-H** bond angles of approximately 120^0 .

The remaining unhybridized 2p orbital of each carbon atom is at right angles to the plane of the carbon – carbon and the four carbon – hydrogen bonds. These half-filled p orbitals combine to form a new bonding orbital: a π-bond.
The π-bond is formed by the sideways overlap of the unhybridized 2p orbitals. The shared electron pair of the π-bond is most likely to be found in the two sausage-shaped lobes on either side of the line joining the two nuclei i.e. the p orbital is situated above and below the plane of the molecule…

The double bond between the two carbons then consists of an ordinary single, σ-bond, and a π-bond. Similar π-bonds occur in the carbonyl group, C = O, in aldehydes, ketones, esters, and so on. The geometry is again planar with bond angles of about 120^0. The π-bond results in **restricted** (hindered) rotation around the bond axis, thus resulting in **geometrical isomerism**.

The π-bond is considerably weaker than the σ-bond and the π-electrons are more readily accessible to a reagent than electrons in the σ-bond. Consider the bond dissociation energies…

C - C	348 kJ mol$_{-1}$	σ
C = C	612 kJ mol$_{-1}$	σ + π

[Recall: bond strength is defined as the enthalpy change of the process $X\text{-}Y_{(g)} \longrightarrow X_{(g)} + Y_{(g)}$]

The C = C double bond energy is less than twice the C - C single bond energy and it may,
be assumed that the second bond in the C = C double bond, (the p-bond) is weaker than the single, σ -bond by…

$$(2 \times 348) - 612 = 80 \text{ kJ mol}^{-1}.$$

Triple Bonds

Two of the half-filled orbitals on carbon form two equivalent 'hybrid' orbitals, called **sp**, leaving two half-filled p-orbitals to form two p-bonds…

Linear triple bonds in alkynes and nitriles, (bond angles 180^0), are the result of the formation of two π-bonds using two mutually perpendicular p-orbitals on each of the triple bonded atoms, with σ-bond in the middle as before. So, the two π-bonds of the triple bond are in planes at right angles to each other. The effect of this overlapping is the formation of a cylindrical sheath of high density round the
carbon – carbon axis…

Bonding Summary Table

Bond	Component bonds	Bond length (nm)	Bond Strength (kJ mol^{-1})	Hybridization	Bond Angles
C - C	σ	0.154	348	sp^3	109.5^0
C = C	$\sigma + \pi$	0.134	612	sp^2	120^0
C $\equiv$ C	$\sigma + \pi + \pi$	0.120	837	sp	180^0

As expected the p-bond effectively draws the carbon atoms closer together and the carbon – carbon bond length **decrease**s as the number of p-bonds increases from zero in ethane to two in ethyne.
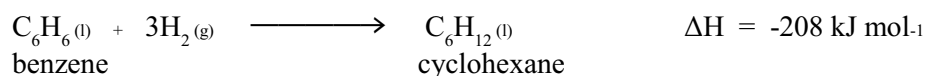
The structure of Benzene, C_6H_6

The benzene molecule is an example of a resonance hybrid which has more than two resonance forms. In the Kekule structures the six carbon atoms form a ring of alternate single and double bonds…

However, modern physical methods, such as X-ray and electron diffraction, show that the
1. benzene molecule is flat, with a regular hexagonal arrangement of the carbon atoms,
2. all six carbon - carbon bond lengths being identical (0.139 nm).
3. The carbon – carbon bond length is thus seen to be intermediate between the carbon – carbon single bond length (0.154 nm) and the carbon – carbon double bond length (0.134 nm).
4. Benzene does not behave chemically as a typical unsaturated compound and one of its most characteristic reaction is the replacement of one of its hydrogen atoms with another atom or group of atoms i.e. a substitution reaction (see later notes) : it is in general more stable than would be expected for a compound which could be accurately represented by a single Kekule structure.

This stability is reflected in the observed heat of hydrogenation of benzene:

$$C_6H_{6\,(l)} \;+\; 3H_{2\,(g)} \;\longrightarrow\; C_6H_{12\,(l)} \qquad\qquad \Delta H = -208 \text{ kJ mol}^{-1}$$
benzene   cyclohexane

which compares with a value of 360 kJ mol^{-1} calculated on the basis of a Kekule structure with its three carbon – carbon double bonds. The observed heat of hydrogenation of cyclohexene (one double bond only) is 120 kJ mol^{-1}…

$$C_6H_{10\,(l)} \;+\; H_{2\,(g)} \;\longrightarrow\; C_6H_{12\,(l)} \qquad\qquad \Delta H = -120 \text{ kJ mol}^{-1}$$
cyclohexene   cyclohexane
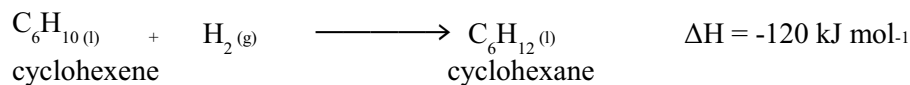
so that if benzene could be correctly represented by a Kekule structure (three alternate double bonds), its heat of hydrogenation for three carbon – carbon double bonds would be expected to be 3 x 120 = 360 kJ mol^{-1}

Thus benzene is 360 – 208 = 152 kJ mol^{-1} more stable than would be expected for a compound with a Kekule structure and this extra stability is known as the **resonance energy**.

The resonance energy is measured by the difference between the calculated and the observed heat of hydrogenation : the greater the resonance energy the more stable the compound.

The concept of resonance accounts satisfactorily for most of the observed properties of benzene, including its great stability, the six identical carbon – carbon bond lengths and the observed heat of hydrogenation.

The structure of the benzene molecule may be described in terms of molecular orbital theory. Each of the six atoms and makes use of three equivalent sp^2 hybrid orbitals to form three σ-bonds, two to carbon and one to hydrogen, at an angle of approximately 120^0 to each other as in ethene…

The remaining unhybridized 2p orbital of each atom is at right angles to the plane of the ring of six carbon atoms and sideways overlap of these orbital to form π-bonds can occur equally well between carbon atoms 1 and 2, 3 and 4, 5 and 6 or between 2 and 3, 4 and 5 and 1 and 6.

The p orbitals overlap to give two electron clouds above and below the plane of the ring. The six p -electrons are accommodated in three delocalised π-orbitals, each molecular orbital containing two electrons. These are usually summarized as a double ring doughnut of electron density…

This delocalization of the six p- electrons in benzene may be represented by means of a hexagon enclosing a circle…

Summary Table

Name of Molecule	Lewis Structure	Valence Bond Types	Valence Bond Diagram	VSEPR Shape Around The Carbon
Methane, CH_4		$4(sp^3)\sigma$		tetrahedral (sp^3)
Ethane, C_2H_6				tetrahedral (sp^3)
Ethene, C_2H_4				planar triangular (sp^2)
Ethyne, C_2H_2				linear (sp)
Benzene, C_6H_6				planar triangular (sp^2)
Methanal, HCHO				planar triangular (sp^2)